BORON ISOTOPE GEOCHEMISTRY IN THE SEDIMENTARY ENVIRONMENT

Doctoral Dissertation

by

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The analytical data, interpretation and conclusions presented in this thesis are my own unless otherwise acknowledged in the text or acknowledgements.

Avner Vengosh

CONTENTS

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BORON ISOTOPE GEOCHEMISTRY IN THE SEDIMENTARY ENVIRONMENT

SUMMARY

This study is an attempt to apply the unique geochemical characteristics of boron isotope geochemistry to a variety of aspects of the sedimentary environment. Major emphasis has been made to evaluate the potential of boron isotope geochemistry as a tracer for the origin of natural solutions and the origin of modern and ancient evaporites. Samples selected for boron isotopic analyses were seawater; artificial evaporated seawater and co-precipitated salts; brines and groundwaters from salt lakes in Australia, the Qaidam Basin of China, and the Rift Valley, Israel (the Dead Sea); and subsurface brines from oilfields at the southern Coastal Plain of Israel. In addition, the boron isotopic compositions and boron contents of biogenic carbonate skeletons have been determined.

An analytical technique for the rapid and relatively precise determinations of the boron isotopic composition in geological materials has been developed. Boron isotopic analyses have been carried out by negative thermal ionization mass spectrometry, in which BO_2^- ions were detected in a reverse-polarity solid-source mass spectrometer. The high reactivity of boron (and chlorine) enables production of negative ions directly from untreated solutions, water-soluble salts and HCl-soluble minerals.

The study explores several aspects of boron isotope geochemistry as outlined below:

1) Boron isotope geochemistry has been investigated in brines, groundwaters and sediments from the modern Australian salt lakes of Victoria, South and Western Australia. The geochemical history of the brines has been reconstructed using $\delta^{11}B$, B/Cl, and Na/Cl ratios.

The Victorian lakes of southeastern Australia are located in volcanic craters and have water salinities of up to 60 g/L, Na/Cl ratios similar to the marine ratio (0.87), B/Cl ratios of 2.9×10^{-4} to 4.9×10^{-4} and $\delta^{11}B$ values of 54‰ to 59‰ (relative to NBS

951). The depletion of total B and the high positive $\delta^{11}B$ values relative to seawater (B/Cl ratio=7.9×10^{-4}; $\delta^{11}B$=39‰) are attributed to a marine (cyclic) salt origin together with adsorption processes in closed systems with low water/sediment (W/R) ratios. In contrast, salt lakes from South and Western Australia which are large shallow playas associated with halite, gypsum, and detrital clay minerals have interstitial and surface brines characterized by salinities of 80 to 280 g/L, Na/Cl ratios of 0.85 to 1, B/Cl of 4×10^{-6} to 4×10^{-4} and $\delta^{11}B$ values of 25‰ to 48‰. The $\delta^{11}B$ values of these brines are different from those of groundwaters from the Great Artesian Basin ($\delta^{11}B$ = -15.9‰ to 2.2‰), country rocks ($\delta^{11}B$ = -8.7‰ to 6.8‰), and modern detrital sediments present in these salt lakes ($\delta^{11}B$ = -3.2‰ to 12.3‰). The $\delta^{11}B$ values of these salt lakes overlap with those of surface and brackish waters ($\delta^{11}B$ = 28‰ to 35‰) and with the boron isotopic composition of seawater ($\delta^{11}B$ = 39‰). Both low Na/Cl (<1) and high $\delta^{11}B$ values suggest that the source of the bulk of the dissolved solids in the Australian brines is dominated by cyclic salts, derived from seawater, rather than from local rock weathering. While the low B/Cl ratios and high $\delta^{11}B$ values (> 39‰) of some brines indicate interaction of the brines with detrital sediments within the salt lake systems, $\delta^{11}B$ values < 39‰ suggest mixing of brines of marine origin from which B was partly removed by adsorption, with waters of terrestrial origin with low $\delta^{11}B$.

Na/Cl ratios are used as indicators of the origin of the salts as well as halite dissolution-precipitation. The $\delta^{11}B$ values and B/Cl ratios are sensitive to a marine or non-marine origin, adsorption of boron onto clays, and the effective water/sediment ratio. At low W/R ratios, the preferential removal of ^{10}B from the solution affects the bulk solution, whereas at high W/R ratios, the $\delta^{11}B$ value of a solution is not affected by adsorption. Although the $\delta^{11}B$ value of borate minerals may be a discriminant of marine or non-marine origin, boron isotopes are less distinctive in evaporative environments where boron is not an abundant component and where water/sediment interaction occurs.

2) Bromide, lithium and boron are considered in the literature as conservative elements which accumulate in the liquid phase during evaporation of seawater. The well defined isotopic composition of boron in seawater makes it a potential tracer for

identifying the origin of brines and salts. The variations of boron isotopes, elemental boron, bromide and lithium have been examined in brines and co-precipitated salts during fractional evaporation of Mediterranean seawater under laboratory-controlled conditions. Analyses of the brines show a deficiency of Br, Li and B relative to their expected concentrations from mass-balance calculations. The deficiency occurs beyond a degree of evaporation of about 30 and is associated with a gradual increase in the $\delta^{11}B$ value of the evaporated seawater from 39‰ to 54.7‰. The high $\delta^{11}B$ values of the brines, and the relatively lower $\delta^{11}B$ values of the coexisting precipitates (magnesium-sulfate and potassium-magnesium-sulfate salts; $\delta^{11}B$ =11.4‰ to 36.0‰) suggest selective uptake of ^{10}B by the salts. Coprecipitation of $B(OH)_4^-$ species with Mg-sulfate and K- and Mg-sulfate minerals and/or precipitation of Mg-borate minerals with a coordination number of four, are the proposed mechanisms for boron isotope fractionation during fractional evaporation of seawater.

The boron-isotope and the trace-metal variations observed in the evaporation experiment can be applied to the determination of the origin of brines as well as to clay adsorption and salt precipitation processes. The depletion of the salts in ^{11}B by 26±6‰ relative to their coexisting brines permits investigation of the origin (marine *versus* non-marine) of ancient salt deposits.

3) The general chemistry and boron isotope composition were investigated in freshwaters and hypersaline brines from the Qaidam Basin, northern Tibet, China. This basin is a large, tectonically active system, isolated from the ocean and composed of thick clastic and evaporite sediments. The modern playas are subject to intense evaporation and are characterized by hypersaline brines, and potash and borate evaporites. The chemical composition of the dissolved solutes in the modern brines and waters reveals three main sources: a) hot springs, distinguished by non-marine solute compositions enriched in sodium, sulfate and boron. Evaporation of these waters leads to a high Na/Cl ratio (>1), a Na-Cl-SO_4 brine and an evaporite mineral assemblage of halite-mirabilite-borate (Lake Xiaoqaidam) ; b) inflow surface waters which are modified by preferential dissolution of halite and potassium and magnesium salts characterized by a Na-(Mg)-Cl solute type with

low Na/Cl, Br/Cl, Li/Cl and B/Cl ratios; and c) Ca-chloridic subsurface brines which are controlled by both salt dissolution and dolomitization processes. Evaporation and salt crystallization of the latter two types leads to a "marine-like" brine (e.g. a Na-Mg-Cl type, Na/Cl ratio lower than unity) and mineral assemblages similar to that predicted for progressive evaporation of seawater (Qarhan playa: halite-sylvite-carnallite-bischofite).

The $\delta^{11}B$ values of the input waters to the Qaidam Basin (range of -0.7‰ to 10.9‰) and brines from salt lakes (0.5‰ to 15.0‰) are similar to those of associated granitic rocks ($\delta^{11}B$ = -2.3‰ to 3.7‰; n=3) and hence indicate the non-marine origin of these fluids. The highest $\delta^{11}B$ values are associated with low B/Li ratios, indicating selective removal of elemental boron and ^{10}B. The boron isotopic composition of the brines is thus not related to the internal dissolution-precipitation processes but is affected by boron adsorption onto clay minerals. The magnitude of ^{11}B enrichment due to adsorption is about 15‰, i.e. the boron-isotope signature remains "non-marine". It is proposed to use this unique geochemical characteristic of boron isotopes that is demonstrated in the terrestrial environment of the Qaidam Basin as a tracer for the origin of ancient evaporite environments.

4) A boron isotope study combined with analyses of elemental boron, lithium and chlorine are used to suggest that brines from the Dead Sea and on-shore hypersaline thermal springs (Hamme Yesha, Hamme Zohar and Hamme Mazor) are the products of interaction of evaporated seawater with detrital sediments. The high $\delta^{11}B$ values of the Dead Sea brines (55.7‰ to 57.4‰) and the hot springs (52.2‰ to 55.7‰), and low B/Li ratios (2.0 to 2.3 and 2.5 to 2.7, respectively), relative to seawater, indicate preferential removal of ^{10}B from the brines and hence boron adsorption onto clay minerals. The brackish 'En Feshcha springs and the freshwater 'En Dawid and Nahal Arugot springs yield lower B contents and $\delta^{11}B$ values (37.7‰ to 40.6‰ and 33.8‰ to 36.9‰, respectively). The $\delta^{11}B$ values and B contents of diluted Dead Sea brines lie on calculated mixing lines between the composition of the brackish and freshwater springs with the composition of the Dead Sea. The $\delta^{11}B$ values of the hot springs however, given their boron content, are significantly lower than those of the mixing lines. Thus,

waters from the hot springs cannot be a mixing product of the Dead Sea brine with freshwater. Instead, the Dead Sea brine has evolved from the brines of the hot springs through further isotopic fractionation and boron adsorption onto detrital sediments.

5) The negative thermal ionization mass spectrometry technique has also been employed for the determination of $\delta^{11}B$ values and elemental B in subsurface brines. Brines from the Heletz oilfield of the southern Coastal Plain of Israel have $\delta^{11}B$ values of 32.6‰ to 42.2‰, high B/Cl (molar) ratios of $2.9x10^{-3}$ to $4.2x10^{-3}$, Na/Cl ratios of 0.84 to 0.92 and SO4/Cl ratios of $1x10^{-5}$ to $5x10^{-3}$. The marine isotopic signature of boron in some brines is concordant with marine Na/Cl ratios of most of the brines while lower $\delta^{11}B$ values in others are associated with low-salinity water with high Na/Cl and SO4/Cl ratios. This indicates a dilution of the marine brines with freshwaters that have dissolved evaporites (halite, gypsum or anhydrite and borates). The B/Cl ratios show an enrichment in boron relative to modern seawater which also has been reported in oilfield brines from different locations and ages. The excess of boron is interpreted as: a) an enrichment of boron in the Messinian Sea, the proposed source of these brines; and/or b) interaction with oil or decomposed organic matter.

6) A boron isotope study has been carried out on groundwaters from the Rift Valley, Israel. The saline waters from Timna have $\delta^{11}B$ values of 14.4‰ to 26.7‰; the Hammat Gader thermal springs have $\delta^{11}B$ values of 20.9‰ to 41.9‰ and springs in the Sea of Galilee have $\delta^{11}B$ of 18.5‰ to 45‰. The relatively low, "terrestrial" $\delta^{11}B$ values of some of the investigated waters suggest that a large fraction of boron is derived from high-temperature water-rock interactions. In Hammat Gader the $\delta^{11}B$ values of the thermal springs are correlated with temperature, boron content, and salinity and decrease gradually from marine values (for dilute cold water) to 20.9‰ (for saline hot waters) indicating a mixing of meteoric boron with terrestrial boron. The high $\delta^{11}B$ value (45‰) and low B/Cl ratios of the saline Tiberias hot spring show that boron can be derived also from connate, trapped brines in the subsurface. A comparison of the boron-, oxygen-, and strontium isotopic compositions, shows that while oxygen-isotope compositions

reflect the meteoric origin of these waters, the Sr and B isotopic compositions of waters are much more sensitive to the composition of rock component in water-rock interactions.

7) The abundances and isotopic composition of boron have been examined by negative thermal-ionization mass spectrometry in modern, biogenic calcareous skeletons from the open ocean, Gulf of Elat, Israel, the Great Barrier Reef, Australia, and in modern deep-sea sediments. The selected species (Foraminifera, Pteropoda, corals, Gastropoda, and Pelecypoda) yield large variations in boron concentration that range from 1 ppm in gastropod shells to 80 ppm in corals. The boron content of the biogenic skeletons is independent of the mineralogical composition and is probably related to biological (vital) effects. The $\delta^{11}B$ values of the carbonates range from 14.2‰ to 32.2‰ and overlap with the $\delta^{11}B$ values of modern deep-sea carbonate sediments ($\delta^{11}B$= 8.9‰ to 26.2‰). The variations of $\delta^{11}B$ may be controlled by isotopic exchange of boron species in which ^{10}B is preferentially partitioned into the tetrahedral species, and coprecipitation of different proportions of trigonal and tetrahedral species in the calcium carbonates. Carbonates with low $\delta^{11}B$ values (~15‰) may indicate preferential incorporation of tetrahedral species, whereas the higher $\delta^{11}B$ values (~30‰) may indicate: a) uptake of both boron species assuming equilibrium with seawater; b) preferential incorporation of $B(OH)_4^-$ from *in-situ* high pH internal fluids of organisms; and/or c) isolation of the internal reservoir from seawater.

The B content and $\delta^{11}B$ values of deep-sea sediments, Foraminifera tests and corals are used to estimate the global oceanic sink of elemental boron by calcium carbonate deposition. As a result of enrichment of B in corals, a substantially higher biogenic sink of $6.4\pm0.9x10^{10}$ g/yr is calculated for carbonates. This is only slightly lower than the sink for desorbable B in marine sediments ($10x10^{10}$ g/yr) and approximetely half that of altered oceanic crust ($14x10^{10}$ g/yr). Thus carbonates are an important sink for B in the oceans being ~20% of the total sinks. The preferential incorporation of ^{10}B into calcium carbonate results in oceanic ^{11}B-enrichment, estimated as $1.2\pm0.3x10^{12}$ permil•g/yr.

The boron-isotope composition of authigenic, well preserved carbonate skeletons may provide a useful tool to record secular boron-isotope variations in seawater at various times in the geological record. In addition, boron isotopes may record variations of the alkalinity of seawater. The potential use of boron-isotope geochemistry in skeletons as a tracer for palaeoenvironments is demonstrated in Ostracoda and Foraminifera from the Gulf of Carpentaria, Australia. The $\delta^{11}B$ values of glacial-age, buried skeletons (4.0‰ and 4.9‰, respectively) are lower than that of their modern equivalents (13.3‰ and 17.6‰, respectively). This may reflect a "terrestrial" boron-isotope signature of the water in the Gulf during the Late Quaternary when it was isolated from the ocean.

In principle, the isotopic fractionation of boron in nature is controlled by the exchange reactions of boron species. ^{11}B is preferentially partitioned into the dissolved boron in a solution that is predominantly composed of the trigonal species, i.e. boric acid, while ^{10}B is preferentially fractionated into the tetrahedral species that is incorporated into the solid phase, i.e. clay, evaporite and carbonate minerals. The association of high $\delta^{11}B$ values and low B/Cl or B/Li ratios in solutions indicate the reactivity and the non-conservative behaviour of boron in nature.

The fractionation of boron isotopes during adsorption onto clay minerals, precipitation of Mg-sulfate and potash minerals, and precipitation of biogenic calcium carbonate must therefore be considered if boron-isotope systematics are to be successfully applied to the reconstruction and identification of the origins of ancient sedimentary environments, and in particular in attempts to distinguish between marine and non-marine origins.

INTRODUCTION

"In chemical compounds, boron (ionic radius 0.22Å) is always trivalent, and has properties analogous to those of carbon and silicon . Boron forms nonionic bonds with oxygen, resulting in two types of oxyanions, those in which boron has a coordination number of three (the trigonal $B(OH)_3^0$ - undissociated boric acid) and those with coordination number four..." (the tetrahedral $B(OH)_4^-$ - borate ion) (REYNOLDS, 1972). The borate ion tends to form complexes with cations that, in turn, form borate cations, e.g. $MgB(OH)_4^+$, (CHRIST and HARDER, 1978).

The reactivity of boron is particularly high with clay minerals (HARDER, 1970). It has been shown that in seawater boron is removed by rapid reversible adsorption processes onto the clay surface (SPIVACK, 1986), through a mechanism referred to as ligand exchange, where the adsorbed species displaces OH^- or H_2O from the surface and forms partly covalent bonds with the structural cations (KEREN and MEZUMAN, 1981). The fixation of boron into the clay structure is a slow process which occurs in the high-temperature diagenetic régime (PERRY, 1972).

Natural boron has two stable isotopes, ^{11}B (79.98%) and ^{10}B (20.02%). Ion-exchange separation experiments have shown that the fractionation of boron isotopes is controlled mainly by the exchange reaction of the boron species, between boric acid and the borate ion (KAKIHANA et al., 1977). Seawater is enriched by 40‰ with ^{11}B relative to crustal material due to isotopic fractionations that occur while boron in the form of $B(OH)_4^-$ is taken from seawater onto detrital clays, weathered basalts and authigenic clay minerals (SCHWARCZ et al., 1969; SPIVACK and EDMOND, 1987; SPIVACK et al., 1987).

Diagenetic effects, and the fact that the isotopic composition of 'fixed boron' in the clay structure overlaps the average terrestrial crustal composition (unaltered basalts and island arc volcanics), exclude the potential of using boron isotope geochemistry in sediments as a potential tracer for the identification of subducted marine sediments into magmatic zones beneath island arcs (SPIVACK and EDMOND, 1987).

The distinctive isotopic composition of seawater relative to that of the continental crust, however, may have a role in discriminating between marine and non-marine environments. The identification of the origin of evaporites by several geochemical techniques (e.g. Br/Cl ratios) has been carried out in the last few decades but recently some questions have been raised concerning the validity of these techniques (HARDIE, 1984). Therefore, the application of boron isotope geochemistry for tracing the origin of evaporites seems attractive.

DEVELOPMENT OF ANALYTICAL TECHNIQUES

Knowledge of the isotope geochemistry of boron is surprisingly lacking, mainly because of analytical difficulties in chemical extraction and isotopic analyses. The determination of boron isotopes has been carried out by ion-exchange separation, methyl borate distillation, and by converting boric acid to $Na_2B_4O_7$ or $Cs_2B_4O_7$ before loading into a solid-source mass spectrometer (McMULLEN et al., 1961; SPIVACK and EDMOND, 1986). One of the aims of this study was to simplify the analytical technique for boron isotope determinations. The **negative thermal ionization** technique has been adopted as a replacement for the traditional analytical methods. This method has been successfully tested in the MSZ and NUCLIDE mass spectrometers at the Research School of Earth Sciences by reversing the polarities (accelerating potential, magnetic field, and electrometer). The extraction of boron from waters was initially preformed using boron-specific resin (KISS, 1988). However, it was later found that both boron and chlorine isotopic ratios can be determined by loading natural water samples **directly** onto filaments for analysis using a reversed polarity solid-source mass spectrometer. The new method has been successfully applied to samples with a variety of water chemistries and salinities. The comparison of treated and untreated samples yielded the same isotopic composition (within the experimental error). The boron concentration of both natural waters and sediments was carried out by developing an isotope-dilution technique. The high precision and simplicity of the isotope-dilution method makes it the preferred method for the determination of boron concentrations relative to other commonly used techniques. Thus, the negative thermal-ionization technique may also have applications to other areas of Earth Sciences.

OUTLINE OF THE THESIS

The thesis is directed towards understanding the isotopic fractionation of boron in various sedimentary environments, by examining the following aspects:

1) The potential of boron isotope geochemistry as a tracer for the origin of natural fluids, i.e. surface and subsurface brines and groundwaters;

2) The mode of isotopic fractionation of boron during evaporation of seawater;

3) The potential of boron isotope geochemistry as a tracer for the origin of ancient marine and non-marine evaporitic environments;

4) The potential use of boron isotope analyses of marine carbonates as indicators of modern and ancient oceanographic régimes.

All the chapters in this thesis have also been prepared as separate papers for publication. Chapter 1 describes the analytical procedure developed and the potential application of boron (and chlorine) isotopes in geochemistry. The manuscript was published in *Chemical Geology (Isotope Geoscience Section),* 79, p. 333-343 (1989).

Chapter 2 presents the results of boron isotope analyses of brines from Australian salt lakes. The possible boron sources in the non-marine environments of Australia are examined with comparison to the general chemistry of the salt lakes. The reactivity of boron with detrital minerals is also investigated with implications for evaluation of water/sediment ratios. The manuscript was submitted to *Geochimica et Cosmochimica Acta.*

Chapter 3 examines the mode of isotopic fractionation of boron during fractional evaporation of seawater to its final stages.

Chapter 4 investigates the general chemistry and boron isotope composition of non-marine brines from the Qaidam Basin, Tibet, China. This study is directed towards understanding the processes of evaporite formation and the chemical and isotopic signatures of "typical" non-marine brines.

Chapter 5 describes a boron isotope study of the Dead Sea and associated springs from Israel. The study attempts to reconstruct the geochemical evolution of the Dead Sea and hot springs along its western coast. The manuscript was submitted to *Geochimica et Cosmochimica Acta.*

Chapter 6 introduces the possible application of boron isotopes for tracing the origin of subsurface brines associated with hydrocarbons. The study investigates the boron-isotope composition of oilfield brines from the southern Mediterranean coast of Israel.

Chapter 7 presents the results of boron isotopes in groundwaters from the Rift Valley, Israel. The possible boron sources in groundwaters and water-rock interactions are examined.

Finally, Chapter 8 examines the boron contents and isotopic composition of various biogenic carbonates from the modern marine environments of the open ocean, Gulf of Elat (Israel), and Great Barrier Reef (Australia). The study is directed towards understanding the coprecipitation and isotopic fractionation of boron with different biogenic phases.

Chapter 1

DIRECT DETERMINATION OF BORON AND CHLORINE ISOTOPIC COMPOSITIONS IN GEOLOGICAL MATERIALS BY NEGATIVE THERMAL-IONIZATION MASS SPECTROMETRY

1.1. INTRODUCTION

The large relative mass difference between ^{10}B (abundance 19.9%) and ^{11}B (80.1%) and the high geochemical reactivity of boron can produce large natural isotopic variations. The most distinctive geochemical reservoir is seawater, which is enriched by 40‰ in ^{11}B ($^{11}B/^{10}B$ ratios are normalized to SRM NBS 951) relative to crustal material (AGYEI and McMULLEN, 1968; SCHWARCZ et al., 1969; SPIVACK, 1986; SPIVACK and EDMOND, 1987). This enrichment is attributed to isotopic fractionation that occurs as boron is taken from seawater and adsorbed onto detrital clays (AGYEI and McMULLEN, 1968; SCHWARCZ et al., 1969; SPIVACK et al., 1987), and to weathered basalts and authigenic clay minerals by adsorption and fixation (SPIVACK and EDMOND, 1987). However, until recently, the development of boron isotope geochemistry has been limited, mainly by analytical difficulties associated with extraction of boron from natural samples and precise determination of its isotopic composition.

Chlorine is a major element in most surface fluids. The chlorine isotopes, ^{35}Cl (75.99%) and ^{37}Cl (24.01%) have previously been reported as having constant ratios in nature (OWEN and SCHAEFFER, 1955; HOERING and PARKER, 1961; SHIELDS et al., 1962; KAUFMANN et al., 1984). The only significant isotopic variations (3‰) reported to date have been found in slow-flowing groundwater where a diffusion mechanism was suggested as a cause for isotope partitioning of chlorine (DESAULNIERS et al., 1987).

The development of a new, rapid and simple procedure for the determination of boron and chlorine isotopic compositions in natural geologic materials, has enabled the investigation of isotopic patterns of boron and chlorine in various environments. Examples using ocean waters, and evaporative environments from Australia, China and Israel are presented to demonstrate the geochemical potential of boron and chlorine isotope geochemistry.

1.2. BACKGROUND OF ANALYTICAL TECHNIQUES

1.2.1. Boron

Although boron isotope geochemistry can potentially yield important geochemical information, this technique has not been extensively applied in the earth sciences . This is mainly due to analytical difficulties associated with quantitative extraction of boron from natural materials (GLADNEY and ROELANDTS, 1987) and in the determination of boron isotopic composition. The extraction and separation of boron has been carried out by ion-exchange resin (MARTIN and HAYES, 1952; AGYEI and McMULLEN, 1968; LERNER, 1970; KAKIHANA et al.,1977), boron-specific resin (PINON et al., 1968; DÉSON and ROSSET, 1968; BHATNAGAR and MARTHUR, 1977; KISS, 1988) and methyl borate distillation (McMULLEN et al., 1961; SHIMA, 1963; AGYEI and McMULLEN, 1968; EGNEUS and UPPSTROM, 1973; SPIVACK and EDMOND, 1986).

The determination of boron isotopes by gas mass spectrometry (INGHRAM, 1946; THODE et al., 1948) failed due to the memory effects of reactive BF_3 (BENTLEY, 1960). Subsequently, McMULLEN et al. (1961) developed a thermal ionization mass spectrometric technique, in which $Na_2BO_2^+$ ions were detected using a solid-source mass spectrometer. This technique was successfully applied in numerous chemical studies (DE BIÈVRE and DEBUS, 1969; REIN and ABERNATHY, 1972; KAKIHANA et al., 1977) and geochemical investigations (FINLEY et al., 1962; SHIMA, 1963; AGYEI and McMULLEN, 1968; KANZAKI et al., 1979; NOMURA et al., 1982; SWIHART et al., 1986). As suggested by REIN and ABERNATHEY (1972), RAMAKUMAR et al., (1985) and SPIVACK and EDMOND (1986) modified this technique by producing

$Cs_2BO_2^+$ ions. The substitution of ^{133}Cs for ^{23}Na increases the mass of the molecular ions and therefore reduces mass discrimination and any preferential volatilization effects in the mass spectrometer source. Their reported precision of 0.25 ‰ is better by a factor of 10 than the sodium tetraborate method.

The negative thermal ionization technique in which BO_2^- ions are measured in a solid-source mass spectrometer that has been converted for negative ions, is discussed in HEUMANN (1982). DUCHATEAU and DE BIÈVRE (1983), ZEININGER and HEUMANN (1983), HEUMANN and ZEININGER (1985), and DUCHATEAU et al. (1986) investigated this technique and found that it has several advantages compared with positive thermal ionization:

(1) The BO_2^- ion intensity is always higher by a factor of 100 -1000 compared with that of the positive ion; (2) in contrast to positive-ion spectrometry, emission of negative ions is largely independent of the chemical purity of the samples, as well as the mole ratios of the alkali ion and boric acid used to form the molecular complex; (3) with positive ions there is a possibility of impurities and interference with other ions, e.g. ^{88}Sr, that affects the positive ion emission whereas no interference has been identified in the mass range of the BO_2^- ions (42 - 43); and (4) it is possible to produce negative ions from ng and sub-ng size boron samples, whereas the positive thermal ionization technique requires larger amounts e.g. 13 -54 µg B (SPIVACK and EDMOND, 1986).

1.2.2. Chlorine

Measurements of chlorine isotope abundances have been made by several techniques in the past 30 years. Gaseous chlorine compounds have been introduced into gas-source mass spectrometers in the forms of HCl (HOERING and PARKER, 1961) and methyl chloride (CH_3Cl^+) (OWEN and SCHAEFFER, 1955; KAUFMANN et al., 1984). In addition, chlorine isotopes have been measured in gas- and solid-source mass spectrometers by negative ionization (SHIELDS et al., 1962; TAYLOR and GRIMSRUD, 1969; HEUMANN, 1982). The negative-ion technique has been used for total chlorine determination by isotope-dilution mass spectrometry (HEUMANN et al., 1980; HEUMANN and SEEWALD, 1987). In this method, chlorine was isolated from natural materials as silver chloride and was deposited on the filaments in the form of ammoniacal solutions.

Although the maximum yield obtained in the preparation of methyl chloride gas was only 35% (OWEN and SCHAEFFER, 1955), this technique was recently adopted by KAUFMANN et al. (1984) and DESAULNIERS et al. (1987). Their analytical procedure included quantitative precipitation of AgCl, reaction with excess methyl iodide for 2 days and separation of CH_3Cl by gas chromatography. High yields were obtained and the reported analytical precision was 0.24‰ (KAUFMANN et al., 1984), better by a factor of 10 than previous techniques.

1.3. ANALYTICAL PROCEDURE

The analyses of boron and chlorine isotopes were carried out in two single-collector, solid-source mass spectrometers, a 'NUCLIDE' type with 90^0 sector extended geometry, and the MSZ 60^0 sector, normal geometry instrument with retardation lens that was built at the Australian National University (CLEMENT and COMPSTON, 1972). The mass spectrometers were modified for negative ions by reversing the polarities of the accelerating potential, the magnetic field and the electrometer. Droplets of sample typically containing 50 -200 ng boron and 1 - 500 µg chlorine were deposited onto single Re filaments and evaporated to dryness in an oven at a constant temperature of about 50^0C. Each filament had to be loaded individually in the MSZ mass spectrometer; however, 15 filaments could be placed in a carousel and loaded simultaneously into the NUCLIDE mass spectrometer. The filaments were then pumped to vacuum of 10^{-8} - 10^{-7} Torr. In the early stages of this study some cross-contamination effects were identified. These effects were eliminated by careful cleaning of the sample holder between analyses and measurement of spiked samples on only one of the instruments (MSZ).

The magnetic field values for ^{35}Cl , ^{37}Cl, $^{10}B^{16}O^{16}O$ (mass 42) and $^{11}B^{16}O^{16}O$ (mass 43) were set and controlled by computer. Timing and operation conditions were strictly repeated in each sample as follows :

(1) 0 - 20 minutes, heating up procedure. Filament current was slowly increased over twenty minutes in fixed steps of 0.5A to 1.7 - 2.2A filament current.

(2) 20 - 30 minutes, signal optimization by focusing the ion beam and/or increasing the filament current in steps of 0.025A until $^{37}Cl^-$ ion intensity of 2 - 3 volts was achieved. The Cl^- beam was emitted at a slightly lower temperature than the BO_2^- beam and was therefore measured first.

(3) 30 - 45 minutes, chlorine data collection. Data were collected for chlorine by switching the magnetic fields between masses 37 and 35, twelve times per set with a 1-s integration time and a delay interval of 1 s. Before each set, the beam was automatically centred and the base-line measured at mass position 35.5. Normally each run contained 8 to 16 sets, i.e. 96 - 192 ratio measurements.

(4) 45 - 50 minutes, the filament current was increased until a $^{11}BO_2^-$ ion beam intensity of 1.0-1.5 volts was achieved.

(5) 50 - 70 minutes, boron data collection. Data were collected for boron at masses 43 ($^{11}BO_2^-$) and 42 ($^{10}BO_2^-$) with the baseline at mass 42.5.

1.4. RESULTS AND DISCUSSIONS

1.4.1. BORON

A stable ion beam with an intensity of 1.5 volt ($10^{11}\Omega$ input resistor) for 100ng boron sample on the filament could be maintained for several hours before exhaustion of the sample. The addition of $La(NO_3)_3$ to pure boric acid solutions (with mole ratios of 10:1 of boric acid to lanthanum nitrate) was found essential, as no ion beam was detected in samples without the $La(NO_3)_3$. However, in natural samples that were not processed through the boron-specific ion-exchange resin (i.e. groundwater, brines, dissolved salts), this addition was found to be **not necessary**. Lanthanum nitrate addition appears to result in a reduction of the electron work potential which produces a higher ion yield (ZEININGER and HEUMANN, 1983). The presence of natural salts in unprocessed samples also enhances the ion beam. For example, one drop of untreated seawater loaded directly onto the filament (70 ng boron) produces a BO_2^- ion beam intensity of several volts, which could be maintained for several hours. Analyses of seawater samples processed using a boron-specific resin (KISS, 1988) were compared to those without previous chemical treatment and the $^{11}B/^{10}B$ ratios were found to be identical within the experimental error. A similar comparison of treated and untreated groundwaters and hypersaline brines (Table 1.1) gave the same results. The possible interference of the species $^{10}B^{16}O^{17}O$ at mass 43 was corrected by subtracting 0.00076 from the absolute $^{11}B/^{10}B$ ratios (CATANZARO et al., 1970).

Both NBS SRM 951 and seawater samples were repeatedly analysed to determine the reproducibility of the boron negative-ion technique. The 1 σ standard deviation of 24 NBS 951 replicates was 2 ‰ and of 10 seawater replicates was 1.1 ‰ at the 95% confidence limit (Table 1.1). The reproducibility for the relatively small number of replicate analyses, listed in Table 1.3, was calculated using the techniques of DEAN and DIXON (1951), applicable to a small number of observations. The standard deviation was obtained from the range of observations multiplied by the deviation factor. The mean of the standard deviations calculated in this manner is 1.7‰ (see Table 1.3), which is consistent with the reproducibility obtained from a large number of analyses of the NBS SRM 951 standard. This precision is lower than the precision reported by SPIVACK and EDMOND (1986) of 0.24 ‰ but similar to the sodium tetraborate technique of 2 - 3 ‰ (e.g. SWIHART et al., 1986) and higher than the inductively coupled plasma-mass spectrometry (ICP-MS) technique with a precision of 7 ‰ recently reported by GREGOIRE (1987).

The average measured absolute, oxygen-corrected $^{11}B/^{10}B$ ratio of NBS SRM 951 was 4.010 ± 0.005 for the MSZ mass spectrometer and 3.996 ± 0.009 for the NUCLIDE . These results are similar to the values reported by ZEININGER and HEUMANN (1983) of 4.016. However, the certified values of NBS SRM 951 using positive thermal ionization is 4.0436 (CATANZARO et al., 1970). The difference may reflect varying degrees of fractionation during formation of positive and negative ions (ZEININGER and HEUMANN, 1983). Analysis of natural samples of SRM NBS 951standard were undertaken using the same conditions. No long-term variations in the apparent composition of the SRM NBS 951 standard were identified.

TABLE 1.1. Comparison of absolute $^{11}B/^{10}B$ ratios measured on water samples after chemical separation using boron-specific resin (KISS, 1988), and with direct measurements of natural materials in the Nuclide mass spectrometer without chemical pretreatment.

Samples	**$^{11}B/^{10}B$ ratios of samples after column chemistry**	**$^{11}B/^{10}B$ ratios of samples without chemical pretreatment**
seawater from Jervis Bay,	4.153	4.142
eastern Australia	4.153	4.152
	4.149	4.141
	4.141	4.154
		4.165
		4.139
Seawater - mean ($\pm 1\sigma$)	4.149±0.005	4.149±0.008
SA -22 brine, Lake Eyre, South Australia	4.159	4.152
WA-31 brine, 'the salt lake' Western Australia	4.172	4.184
GAB 93, groundwater from the Great Artesian Basin, Australia	3.955	3.983±0.012

1.4.2. Boron assay in natural samples by isotope dilution

Determination of boron concentration in natural materials has been carried out using isotope dilution with ^{10}B-enriched spike (SRM NBS 952, ^{11}B/^{10}B ratio = 0.0554 ± 0.0001). The ^{10}B spike was added to sample solutions of natural waters and $CaCO_3$ dissolved in HCl. The spiked solutions were analysed in the mass spectrometer, and boron concentrations were calculated using standard isotope-dilution equations. The precision of the isotope-dilution technique is dependent on the isotopic composition of the spike, natural sample and spiked mixtures as well as the spike concentration. The concentration of the spike was calibrated using standard solutions prepared from both the NBS SRM 951 as well as a Specpure boric acid. The isotope dilution results are presented in Table 1.2 together with boron data obtained by a modified spectrophotometric technique using the reagent Azomethine H (KISS, 1988). The results obtained by these two methods are in agreement in general although the isotope-dilution measurements have a substantially higher precision.

1.4.3. Geochemical application of boron isotopes

Boron isotope analyses (Table 1.3) of terrestrial waters and evaporites are expressed in this study in δ notation such that:

$$\delta^{11}B = \left[\frac{(^{11}B/^{10}B)_{sample}}{(^{11}B/^{10}B)_{NBS\ 951}} - 1 \right] \times 10^3$$

The samples were chosen from a variety of environments in order to assess the geochemical potential of boron isotope geochemistry, and the magnitude of isotopic variations, particularly in evaporites and terrestrial environments. The localities sampled include groundwaters from the Great Artesian Basin of Australia (HABERMEHL, 1980), salt lakes from inland Australia (BOWLER, 1976), salt lakes from the Qaidam Basin,Qinghai (northern Tibet), China (CHEN KEZAO and BOWLER, 1986) and the Dead Sea, Israel (NEEV and EMERY, 1967).

TABLE 1.2

Boron concentration data obtained by isotope-dilution mass spectrometry and spectrophotometric techniques (results are reported in ppm)

Sample	Description	Isotope-dilution mass-spectrometry (ppm)	Spectrophotometric determination (ppm)
Seawater	Jervis Bay, eastern Australia	4.69 ± 0.08	4.69 ± 0.09
D-*2*	brine from Dampier halite pond, Western Australia	58.47 ± 0.6	59.78 ± 0.6
SA-*22*	brine from Lake Eyre, South Australia	5.92 ± 0.08	6.13 ± 0.08
GAB-*93*	groundwater from the Great Artesian Basin, Australia	2.92 ± 0.08	1.4 ± 0.03
GAB-*92*	groundwater from the Great Artesian Basin, Australia	1.07 ± 0.08	1.02 ± 0.08
SA-*9*	brine from Lake Frome, South Australia	0.27 ± 0.08	0.41 ± 0.06
SA-*32*	brine from Lake Cadibarrawirracanna, South Australia	2.47 ± 0.08	2.59 ± 0.04
SA-*34*	brine from Lake Cadibarrawirracanna, South Australia	17.31 ± 0.08	15.39 ± 0.57
V-*7*	brine from Lake Tyrrell, Victoria, Australia	1.46 ± 0.08	1.56 ± 0.05
V-*8*	groundwater from Lake Tyrrell, Victoria, Australia	1.64 ± 0.08	1.77 ± 0.05
WA-*1*	brine from Lake Gilmore, Western Australia	4.03 ± 0.08	3.66 ± 0.01
WA-*3*	brine from Lake Hann, Western Australia	7.27 ± 0.08	6.91 ± 0.03
WA-*8*	brine from lake near Lake Biddy, Western Australia	3.04 ± 0.08	2.91 ± 0.13
WA-*31*	brine from "the salt lake" Tammin, Western Australia	2.17 ± 0.08	2.19 ± 0.08
WA-*37*	brine from Lake Brown, Western Australia	1.19 ± 0.08	1.22 ± 0.03
DS-*1*	Ein Gedy hot spring, Israel	20.38 ± 0.2	
DS-*2*	Dead Sea brine, Israel	37.76 ± 0.4	
Aragonite	modern coral dissolved in HCl	56.63 ± 0.6	
N.B.S. *88*	dolomite dissolved in HCl	14.6 ± 0.2	
N.B.S. *19*	calcite dissolved in HCl	17.98 ± 0.08	

TABLE 1.3

Boron and chlorine isotopic results for some evaporites and terrestrial waters

Sample	Location and description	δ^{11}B (‰)	Number of analyses	δ^{37}Cl (‰)	Number of analyses
Seawater	Jervis Bay, eastern Australia	+38.4±1.1	12	0±2.0	18
Australian salt lakes:					
SA-*22*	Lake Eyre, S.A., interstitial brine	+38.4±1.9	4		
SA-*9*	Lake Frome, S.A., interstitial brine	+41.3±2.0	1		
SA-*32*	Lake Cadibarrawirracanna, S.A., interstitial brine	+43.4±1.4	2		
GW-*23*	Lake Acraman, S.A., interstitial brine	+34.4±1.4	2		
V-1	Lake Bullenmeri, Victoria, surface brine	+53.4±2.0	1		
WA-*31*	"the salt lake", Tammin, W.A., surface brine	+47.0±2.0	1		
GW-*15*	Lake Moore, W.A., interstitial brine	+34.7±2.0	1		
V-*7*	Lake Tyrrell, Victoria, surface brine	+27.2±2.4	2		
Great Artesian Basin, Australia:					
GAB-*93*	groundwater	−6.8±2.1	3		
GAB-*92*	groundwater	−15.9±2.1	3		
GAB-*83*	groundwater	−14.7±1.4	2		
GAB-*81*	groundwater	−7.8±2.1	2		
Qaidam Basin, Qinghai, China:					
Q-*12*-A(b)[*1]	inlet brine to the artificial ponds	0.0±1.9	2	−3.5±1.4	2
Q-*12*-A(s)[*2]	halite in first artificial pond	+4.4±2.0	1	+2.7±1.4	2
Q-*12*-B(b)	brine of second pond			−7.2±1.4	2
Q-*12*-B(s)	halite in the second pond			+3.6±1.2	3
Q-*12*-C(b)	brine of third pond			−2.0±1.4	2
Q-*12*-C(s)	sylvite+carnallite in third pond			−4.9±1.2	3
Q-*12*-D(b)	brine of fourth pond			−0.6±1.4	2
Q-*12*-D(s)	carnallite in the fourth pond	+14.6±2.0	1	+24.7±2.9	2
Q-*42*	brine of the fifth pond			+9.1±1.9	2
Q-*41*	brine of bitterns final stage	+10.5±1.4	2	−4.1±2.5	2
Q-*13*	brine from Lake Dabuxan	+12.5±2.4	2		
Dead Sea, Israel:					
DS-*1*	Ein Gedy hot spring	+49.1±1.6	3	+0.5±1.2	3
DS-*2*	Dead Sea northern basin, surface brine	+54.5±1.4	2	−5.6±2.3	2
DS-V-*2*	Dead Sea southern basin, 3-m-deep brine	+53.0±1.4	2	−7.2±2.0	2

SA, WA, GAB refer to South Australia, Western Australia and the Great Artesian Basin, respectively. Errors are 1σ standard deviations, and are estimates of the external reproducibility. Errors are calculated from the range of repeat analyses times the deviation factor (see text) or the average standard deviation (2‰) divided by the square root of the number of repeat analyses, which ever is greater.

[*1] b = brine; [*2] s = salt.

The distinctive boron-isotope composition of seawater ($\delta^{11}B$ = 40‰) is generally attributed to the preferential incorporation of ^{10}B onto different solid phases in the oceanic environment (AGYEI and McMULLEN, 1968; SCHWARCZ et al., 1969; SPIVACK, 1986; SPIVACK and EDMOND, 1987). The large difference between the isotopic composition of boron in seawater and the continental crust gives boron-isotope geochemistry the potential use as a tracer for a distinguishing between marine and non-marine evaporites. SWIHART et al. (1986) have showed that some marine evaporite borates are enriched with ^{11}B ($\delta^{11}B$ = +18 to +31‰) relative to non-marine evaporite borates ($\delta^{11}B$ = -22 to 0 ‰).

Preliminary boron isotopic data presented in this study (Fig 1.1 and Table 1.3) indicate in some cases that boron in brines from non-marine locations has a "marine" isotopic composition. This is particularly apparent in the modern Australian inland salt lakes where the isotopic composition of interstitial brines in some lakes is similar to that of seawater (e.g. Lake Eyre, $\delta^{11}B$ = +38.4 ± 2.1‰). However, in the Chinese salt lakes ($\delta^{11}B$ = 0.0‰ to +14.6‰) and the Dead Sea brines ($\delta^{11}B$ = +49.1‰ to +54.5‰) the $^{11}B/^{10}B$ ratios are respectively lower and higher than that of seawater.

The boron isotopic composition of deeply buried groundwater from the Great Artesian Basin, Australia ($\delta^{11}B$ = -15.9‰ to -7‰) is obviously different from the surface hypersaline Australian salt-lakes brines ($\delta^{11}B$ =+27.2‰ to +47.0‰) . These differences could be the result of different sources of boron and processes. While in the Great Artesian Basin boron is probably derived from the argillaceous rocks of the intervening confining beds, the high $\delta^{11}B$-values in the Australian salt lakes may indicate that boron is derived from cyclic (marine) salts. The elevated $\delta^{11}B$ may also indicate a high degree of interaction with detrital sediments, e.g. isotopic fractionation during the adsorption of boron onto clay minerals.

In the Qaidam basin, Qinghai, China, where borate minerals are precipitating due to high concentrations of boron (ZIQIANG and ZHIQIANG, 1983), boron in the brines has a typically terrestrial isotopic composition (Table 1.3, Fig. 1.1). Any addition of high-$\delta^{11}B$ cyclic boron from precipitation in the extremely arid zones of northern Tibet would cause a negligible effect on the isotopic composition of the brines.

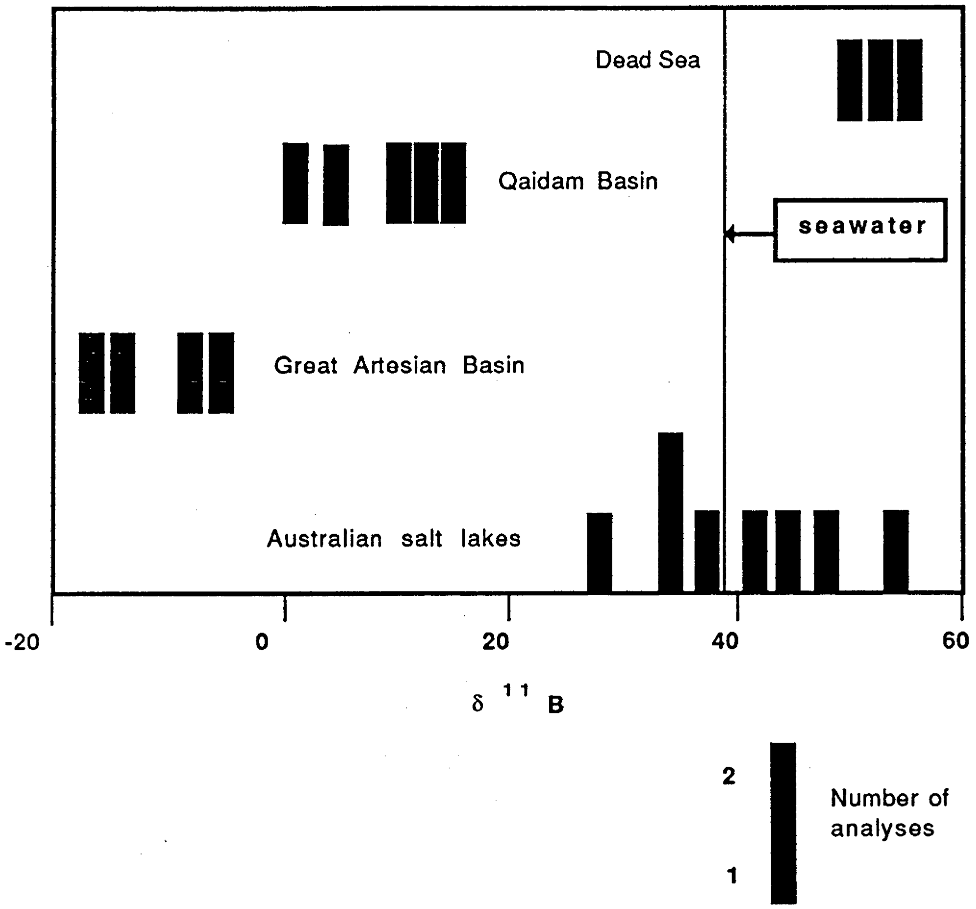


Figure 1.1 Histogram of δ^{11}B values of terrestrial waters from Australia, China, and Israel. Note the large variability of δ^{11}B values in the waters and the similarity in some cases as the inland Australian salt lakes, to seawater isotopic composition.

Pliocene Mediterranean seawater has also been modified to Ca-chloride brines in the modern Dead Sea (STARINSKY, 1974). Therefore, boron in ancient (Pliocene - Holocene) and modern Dead Sea brines has had a considerable time over which to interact with sediments at elevated salinities, leading to the observed 16‰ enrichment of ^{11}B relative to seawater. Thus, boron isotope geochemistry is a sensitive tracer of different sources (marine and non-marine) and the degree of interaction of fluids with sediments and rocks.

1.4.4. CHLORINE

For a directly loaded seawater sample, it was found that an ion beam intensity of 4 - 5 volts, for a typical 10 μg Cl sample on the filament, could be maintained stable for several hours. Seawater samples were repeatedly analysed and used as an external standard. The 1 sigma standard error of 18 seawater replicates was 2‰. The mean standard deviation calculated for the different samples using the DEAN and DIXON (1951) method is 1.5‰ which is consistent with the reproducibility obtained from a large number of standard analyses. The average measured absolute ^{37}Cl/^{35}Cl ratio of seawater was 0.3152 ±0.0006 for the MSZ and 0.3157 ±0.0006 for the NUCLIDE. Samples were loaded and analysed before and after the seawater standards in the same conditions. The normalization to the seawater isotopic ratios minimizes the importance of the absolute ^{37}Cl/^{35}Cl ratio. In order to test for possible matrix effects, Cl from both natural seawater and seawater enriched with MgSO4 were analysed. To 1 g of seawater 0.035 g $MgSO_4$ $\cdot 6H_2O$ was added which raised the Mg content from 1.3 to 4.8 mg g^{-1} and the SO_4 content from 2.7 to 16.9 mg g^{-1}. The ^{37}Cl/^{35}Cl ratio of the artificially enriched seawater is the same within analytical uncertainty as that of normal seawater. Addition of $NaHCO_3$ was unsuccessful due to attack and premature burn out of the Re filament. We have not excluded the possibility of apparent isotopic variations arising from solute compositions (e.g. carnallite) outside that of Na-Cl rich brines. Although not all the δ ^{37}Cl results reported in Table 1.3 used constant amounts of Cl on each filament, we have found it convenient and more precise to adopt a uniform procedure of using approximately constant amounts of Cl for each sample. We have chosen to dissolve salts or to dilute brines to seawater chlorinity and load each filament with similar amounts of solutions. Although the precision obtained using negative ions is lower than the precision reported in the most recent studies (0.24‰ using CH_3Cl gas mass spectrometry; KAUFMANN et al., 1984), the advantage of our approach is that it minimizes the chemical preparation required for chlorine prior to the analysis. In addition, direct measurements eliminate the possible bias introduced by chemical separation, e.g. high-chlorine blank (HEUMANN et al., 1980).

1.4.5. Geochemical application of chlorine isotopes

Chlorine isotope results from brines and salts from the Qaidam Basin, China and the Dead Sea, Israel are expressed in δ notation as:

$$\delta\,^{37}Cl = \left[\frac{(^{37}Cl/^{35}Cl)_{sample}}{(^{37}Cl/^{35}Cl)_{seawater}} - 1\right] \times 10^3$$

Chlorine isotope geochemistry has been investigated in recent papers, particularly in groundwater systems (KAUFMANN et al., 1984; DESAULNIERS et al., 1986). PHILLIPS and BENTLEY (1987) proposed that the fractionation of chlorine isotopes during flow of fluids through semi-permeable clay discs could be a result of differences in the ionic mobility of the two isotopes. The chlorine isotopes were not, however, studied in hypersaline environments where the brines are saturated with respect to chloride minerals. In such systems the removal of chlorine from the brines into solid phases may also affect the isotopic composition of the two phases.

Brines and salts from a series of artificial ponds in the Qaidam Basin have been analysed. In these ponds, brines are concentrated beyond halite saturation and a series of progressively more soluble chloride minerals, i.e. halite, carnallite, and bischofite, are precipitated.

The preliminary results (Table 1.3) indicate that $\delta^{37}Cl$ values in the salts are usually higher than in the coexisting brines. This indicates that ^{37}Cl preferentially enters the solid phase during the incorporation of dissolved chlorine into the chloride salts. The magnitude of this enrichment is different for the different salts. The largest apparent ^{37}Cl enrichment was observed in the carnallite pond where the salts are enriched by 24 ‰ relative to the coexisting brine. The brine of the bischofite ponds also has an apparently anomalous chlorine isotopic composition (δ^{37}Cl = -4.1‰ and +9.1‰). At present the possibility of experimental biasses due to the Mg-rich nature of the matrix cannot be excluded.

It may be possible to use the chlorine isotopes to identify the origin and nature of brines. Brines that are in equilibrium with precipitating salts should yield lower δ^{37}Cl values than brines that are forming from dissolution of an older salt crust . This is demonstrated in the Dead Sea system. The isotopic composition of the hot springs of Ein Gedy on the west shore of the Dead Sea is different (δ^{37}Cl = +0.5 ±1.0‰) to that of the Dead Sea brines themselves (δ^{37}Cl = -7.2‰ to -5.6‰). The relative enrichment in ^{37}Cl in the hot spring is probably a result of dissolution of salts in the Mt. Sdom Formation that underlies the present Dead Sea (MAGARITZ et al., 1986). In contrast, the precipitation of modern halite from the Dead Sea brines (NEEV and EMERY, 1967; STARINSKY, 1974) has depleted the residual brines in ^{37}Cl.

1.5. CONCLUSIONS

It has been demonstrated that it is possible to directly measure BO_2^- and Cl^- ions in a reverse polarity solid-source mass-spectrometer . The techniques are applicable to natural waters and salts where boron and chlorine are dissolved, and also to minerals that are dissolved by HCl (e.g. calcium carbonate). Both elements are two-isotope systems and isotopic discrimination in the mass spectrometer source will occur and consequently standardized procedures are required for isotopic analysis.

The main advantage of the negative thermal-ionization technique is that for waters or acid-soluble minerals **no chemistry is involved** prior to boron and chlorine isotope analysis and boron assay of certain geological materials. Seawater, groundwater, brines, salts and HCl-soluble minerals of differing chemistry or boron and chlorine concentrations can be loaded directly into the mass spectrometer and successfully analysed for boron and chlorine isotopes. The negative-ion method is simple, rapid, sensitive, reasonably precise (about ±2‰) and does not require a special instrument, as virtually any solid-source mass spectrometer can be converted for negative-ion production.

Boron isotope geochemistry can be used to trace the sources of fluids in terms of marine or non-marine origin, to estimate the degree of chemical interaction of waters with sediments and role of environmental conditions in these reactions. Chlorine isotope fractionation accompanies the precipitation of some chloride salts. It may be possible to use the $^{37}Cl/^{35}Cl$ ratios to discriminate between brines that are in equilibrium with precipitated salts and brines that have dissolved former salt crusts or buried evaporites.

Chapter 2

BORON ISOTOPE GEOCHEMISTRY OF AUSTRALIAN SALT LAKES

2.1. INTRODUCTION

The composition of brines and evaporites may provide important constraints on palaeoenvironments, particularly the distinction between marine and non-marine environments. A number of approaches have been utilised in attemptsto establish criteria for identifying the sources of evaporite minerals. Among them is the mineralogical analysis of ancient evaporites and comparisons with the evaporation products of modern seawater (SONNENFELD, 1985). In addition, the geochemical analysis of single elements or ratios of elements in evaporites such as Br/Cl has been proposed (HOLSER, 1966; HOLSER, 1979; HARDIE, 1984; SONNENFELD, 1985).

GOLDSCHMIDT and PETERS (1932), LANDERGREN (1945), and DEGENS et al., (1957) showed that boron was concentrated in marine argillaceous sediments due to adsorption by clay minerals. Hence they proposed that the boron content of clays might be used to discriminate between marine and non-marine environments. The validity of the use of boron abundances as indicators of palaeosalinity has however, been questioned as additional factors controlling boron incorporation into clays have been recognized. These factors include diagenesis, boron content in solution, salinity, temperature, grain size, mineralogical composition of the sediments, abundance of organic material, predepositional history and rate of deposition (FLEET, 1965; LERMAN, 1966; HARDER, 1970; PERRY, 1972).

An additional dimension to boron geochemistry was introduced by AGYEI and McMULLEN (1968) and SCHWARCZ et al. (1969). They showed that seawater is higher in $\delta^{11}B$ relative to terrestrial rocks by about 40‰, and suggested that this enrichment is due to isotopic fractionation during adsorption of boron onto clays. SPIVACK and EDMOND (1987) and SPIVACK et al. (1987) have demonstrated that the removal of boron from seawater into altered basalts also affects the boron isotopic composition of seawater. The large difference between the isotopic composition of boron in seawater and the continental crust suggests that boron isotope geochemistry may be applied as a potential tracer for distinguishing between marine and non-marine evaporites and brines. SWIHART et al. (1986) showed that marine evaporite borates are indeed enriched with ^{11}B ($\delta^{11}B$ = 18‰ to 31‰) relative to non-marine evaporite borates ($\delta^{11}B$ = -22‰ to 0 ‰).

This chapter examines the boron isotope geochemistry in the modern Australian terrestrial environment. The boron isotope systematics of seawater during evaporation are also discussed.

2.2. BORON ISOTOPIC SYSTEMATICS

Boron in the non-marine environment can be derived from subsurface, trapped brines, crustal rocks ($\delta^{11}B$ ~ 0‰) and the atmosphere. Boron in the atmosphere exists in gaseous and particulate forms, where the gaseous boron makes up 97% of total boron in the troposphere (FOGG and DUCE, 1985). The source of boron in the gas phase in the atmosphere has long been debated. GAST and THOMPSON (1959) and FOGG and DUCE (1985) have argued that the ocean is an ultimate source of boron, whereas NISHIMURA and TANAKA (1972) and NISHIMURA et al. (1973) suggested that seawater is a sink rather than a source for atmospheric boron. FOGG and DUCE (1985) estimated that 43% to 84% and 10%to 49% of the total gaseous boron is derived from fumarole gases and sea-salt degassing, respectively.

The residence time of boron in the atmosphere is approximately one month (FOGG and DUCE, 1985). Therefore large isotopic variations are expected in the atmosphere since the isotopic composition of the source materials is different: the ocean: $\delta^{11}B$=39‰, (SPIVACK, 1986), volcanic gases: $\delta^{11}B$ = 1.5 to 6.5‰ (KANZAKI et al., 1979), and clay particles: $\delta^{11}B$~0‰ (SCHWARCZ et al., 1969). This variability is reflected in the wide range of $\delta^{11}B$ values (0.8 to 35 ‰) reported by SPIVACK (1986) in 4 rainwater samples from the Pacific Ocean. These few analyses, however, are the only reported boron isotope data for rainwaters.

Boron adsorption. Boron is present in aqueous solutions as $B(OH)_4^-$ ion, undissociated boric acid $B(OH)_3^0$, polyborate ions and borates ($(Na\text{-}Ca\text{-}Mg)B(OH)_4^+$) (CHRIST and HARDER, 1978). The distribution of these species is controlled by the pH, ionic strength, and specific cation concentrations (BYRNE and KESTER, 1974; REARDON, 1976; KEREN and MEZUMAN, 1981; KEREN et al., 1981; MATTIGOD et al., 1985; HERSHEY et al., 1986; ROGERS and VAN DEN BERG, 1988).

The isotopic fractionation of boron is due to the differences in the interatomic boron/oxygen vibrational energy and the symmetry between the trigonal boron species (undissociated boric acid $B(OH)_3$) and the tetrahedral anions ($B(OH)_4^-$). The isotope exchange reaction in aqueous solutions is given by:

$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- = {}^{11}B(OH)_3 + {}^{10}B(OH)_4^- \qquad (1)$$

Various experiments have examined the isotopic fractionation of boron, particularly during the adsorption of boron from seawater onto marine clays (SHERGINA and KAMISKAYA, 1967; SCHWARCZ et al., 1969; SPIVACK et al., 1987; PALMER et al., 1987). These workers have found that the isotopic fractionation is dependent on the distribution of boron species, temperature, pH, and clay mineralogy. It was shown that during adsorption, ^{10}B is preferentially incorporated into the adsorbed phase, probably as the tetrahedral form. As clays have a stronger adsorption affinity for $B(OH)_4^-$, the conditions that are favoured for the dominance of $B(OH)_3$ species (e.g. low pH) would cause a relatively lower degree of boron adsorption but higher degree of isotopic fractionation. Thus, the isotopic fractionation of boron in the adsorption process is dependent on the distribution of boron species. The maximum boron isotopic shift produced during adsorption onto clay minerals, reported by PALMER et al. (1987), is 32 ‰.

Uptake of boron by clay minerals may occur in two steps. The first is a rapid and reversible adsorption onto the clay surface, referred to as "the adsorbed boron", the second is slow incorporation into the tetrahedral sites of the mica structure, referred to as "fixed boron" (HARDER, 1970). The adsorption process is controlled by a number of factors including pH, boron content in the parent solution, the type of clay mineral, wetting and drying cycles, ionic strength, the nature of the exchangeable cation, and the cation medium of adsorption. (HINGSTON, 1964; LERMAN, 1966; SIMS and BINGHAM, 1968; HARDER, 1970; KEREN and MEZUMAN, 1981; KEREN and GAST, 1981; KEREN and O'CONNOR, 1982; MATTIGOD et al., 1985). Consequently, in adsorption processes, ^{10}B would enter preferentially onto the adsorbed phase and the liquid phase would be depleted in total boron and enriched in ^{11}B relative to ^{10}B.

2.3. THE AUSTRALIAN SALT LAKES

The Australian salt lakes occur in the arid or semi-arid zone of the Australian continent (BOWLER, 1976; 1981). Based on geography, geology, and chemical composition, the salt lakes investigated in this study can be subdivided into five main groups (Table 2.1 and Fig. 2.1). These are: (1) maar lakes from western Victoria; (2) a playa lake from northern Victoria; (3) large playa lakes overlying the Great Artesian Basin in South Australia; (4) playas from the Gawler Ranges in South Australia; and (5) salt lakes from the Yilgarn Block, Western Australia.

The Australian basins are located mostly within stable shield areas with uniformly low relief. The evaporation and basin filling by rainwater and groundwater control the salinities of the brines, and consequently the formation of halite and gypsum in the basins (BOWLER 1986). The modern salt crusts are underlain by clastic sediments composed of kaolinite, illite, montmorillonite, and rarely chlorite (FÖRSTNER, 1977).

The chemical composition of the inland Australian salt lakes has been the subject of several studies. The dominance of Cl^- and Na^+ ions in the Australian inland brines (WILLIAMS, 1967; JOHNSON, 1980; MANN, 1983), and the uniform chemical and mineralogical composition of the salt lakes over large area of the weathered Australian continent is in conspicuous contrast the variety of chemical composition of hypersaline waters from more typical terrestrial environments in other continents, e.g. EUGSTER,(1980), HARDIE and EUGSTER (1970). The origin of the salts in the Australian inland basins has long been debated and various sources have been proposed. Among them are cyclic salts (i.e., marine derived aerosols), weathering of rocks in individual drainage basins, evaporated river waters, and relict seawater (see summary in

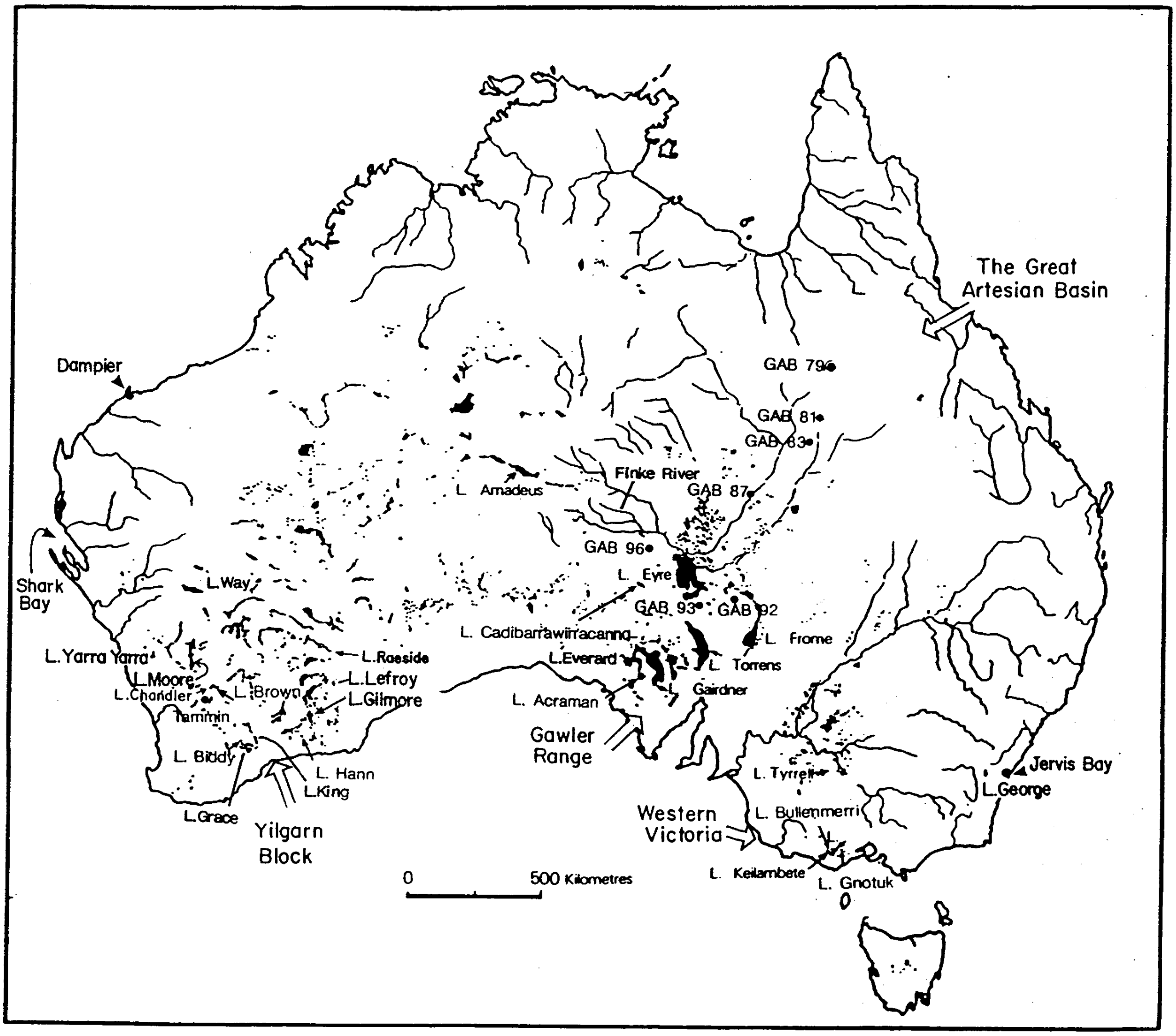


Figure 2.1. Map showing the location of the evaporated-seawater samples (Shark Bay and Dampier), Australian salt lakes, and groundwaters from the Great Artesian Basin used in this study.

TABLE 2.1. Location and geological environments of some Australian salt lakes

Lake, Basin and Location	Country rocks
Maar lakes from Western Victoria	
Lake Bullenmerri, Lake Gnotuk, Lake Keilambete	Small volcanic crater lakes (maars), internal drainage, Quaternary olivine basalts and tuffs overlying Tertiary marine limestones
Northern Victoria	
Lake Tyrrell, Murray Basin	Cainozoic fluviatile sediments
The Great Artesian Basin, South Australia	
Lake Eyre, Lake Frome Lake Cadibarrawirracanna	Cretaceous Bulldog Shale, Miocene lacustrine dolomites (Etadunna and Namba Formations)
Gawler Range, South Australia	
Lake Acraman	Centre of depressed impact structure in Proterozoic dacitic volcanics
Yilgarn Block, Western Australia	
Lake Gilmore, Lake Hann, unnamed lake near Lake Biddy, "the salt lake" near Tammin, Lake Brown , Lake Chandler, Lake Moore, Lake Raeside	Weathered profiles of kaolinized saprolites overlying Archaean intrusive granitoid and metamorphosed rocks (granite-greenstone belts)

JOHNSON, 1980). Using $^{87}Sr/^{86}Sr$, $^{40}Ca/^{42}Ca$, $^{34}S/^{32}S$ and ^{36}Cl isotopes, it has been shown that each element has its own budget, and different sources contribute varying proportions for each element (CHIVAS et al.,1988; 1990). For example, CHIVAS et al., (1988) and NELSON and McCULLOCH (1989) have shown that Sr- and Ca-isotope ratios in gypsum from the salt lakes are related to the isotopic composition of the country rocks, whereas $\delta^{34}S$ values (CHIVAS et al., 1990) indicate that much of the sulphur has a cyclic marine origin.

Na^+ and HCO_3^- are the major dissolved ions in most of the fresh groundwaters and rivers in Australia. The possibility of direct evaporation of these waters as the major source for the Australian salt-lakes has been ruled out by JOHNSON (1980) as soda pans are not present in the Australian environment. Modification of groundwater by preferential salt dissolution and base exchange reactions in the evolution of waters in the drainage basin was proposed by HERCZEG and LYONS (1990). MANN and DEUTSCHER (1978) have shown that precipitation of calcite, dolomite, sepiolite, and amorphous silica during the genesis of calcrete in drainage zones peripheral to salt lakes controls the removal of Ca^{2+}, Mg^{2+}, CO_3^{2-} and SiO_2 from the groundwaters. Calcium and sulphate depletion in the interstitial brines is attributed to gypsum precipitation.

Most of the subsurface playa brines are related to the modern hydrological systems. For example, in Lake Frome in South Australia, a large interstitial brine pool extends to 60 m below the playa floor and is inter-related with the modern surface system (BOWLER, 1986).

2.4. METHODS

2.4.1. Sampling

In July-August 1987 a series of samples from the Australian salt lakes were collected (Table 2.2). Some of the lakes contained water at the surface (depth of few cm to ~ 1 m, with the exception of the three Victorian maar lakes which contain a permanent water column of about 10 m) which is referred to as "surface brine". Other playas were dry with or without a halite crust. In order to obtain fluids from such systems, holes (10 cm to 60 cm) were excavated. The pore water which seeped into the holes is referred to as

TABLE 2.2. Location, description, pH and density of brines from salt works in Western Australia and from Australian salt lakes used in this study.

sample	location and description	date of collection	pH	density (g/cc)
Evaporated seawater (salt works)				
UL-1	evaporite pond, Useless Loop, Shark Bay	25/8/87	8.13	1.031
UL-4	evaporite pond, gypsum stage, Useless Loop	25/8/87	7.86	1.115
UL-5	evaporite pond, gypsum stage, Useless Loop	25/8/87	7.67	1.162
UL-6	evaporite pond, halite stage, Useless Loop	25/8/87	7.30	1.24
D-2	evaporite pond, halite stage, Dampier	28/8/87	7.01	1.238
Maar lakes from Victoria				
V-1	Lake Bullenmerri, surface brine	29/7/87	8.82	1.006
V-2	Lake Gnotuk, surface brine	29/7/87	8.64	1.041
V-3	Lake Keilambete, surface brine	29/7/87	9.00	1.046
"K"	K Spring, Lake Keilambete, groundwater	23/2/85		1.001
Northwestern Victoria				
V-7	Lake Tyrrell, surface brine	30/7/87	7.20	1.210
V-8	Lake Tyrrell, discharge groundwater	30/7/87	3.42	1.074
The Great Artesian Basin, South Australia				
SA-9	Lake Frome, interstitial brine	4/8/87	7.38	1.193
SA-10	Lake Frome, interstitial brine	4/8/87	7.20	1.198
SA-16	Lake Eyre North, interstitial brine	5/8/87	6.74	1.201
SA-22	Lake Eyre North, interstitial brine	5/8/87	7.35	1.214
SA-26	Lake Eyre South, interstitial brine	7/8/87	7.67	1.227
SA-32	Lake Cadibarrawirracanna, interstitial brine	8/8/87	6.89	1.131
SA-34	Lake Cadibarrawirracanna, surface brine in a natural channel on the edge of the lake	8/8/87	8.03	1.079
"F"	Finke River, freshwater			1.001
Gawler Block, South Australia				
SA-38	Lake Everard, interstitial brine	10/8/87	6.89	1.177
SA-43	Lake Gairdner, interstitial brine	10/8/87	7.02	1.206
SA-44	Lake Acraman, interstitial brine	11/8/87	7.20	1.167
SA-45	Lake Acraman, interstitial brine	11/8/87	7.10	1.177
SA-51	Acraman Bore, groundwater	11/8/87	7.98	1.006
Yilgarn Block, Western Australia				
WA-1	Lake Gilmore, interstitial brine	14/8/87	2.82	1.136
WA-3	Lake Hann, surface brine	14/8/87	3.20	1.089

TABLE 2.2. (continued)

sample	location and description	date of collection	pH	density (g/cc)
WA-8	unnamed lake near Lake Biddy, surface brine	15/8/87	3.13	1.201
WA-31	"the salt lake", near Tammin, surface brine	22/8/87	3.33	1.157
WA-33	Lake Chandler, interstitial brine	22/8/87	3.55	1.065
WA-34	Lake Brown (SE side), interstitial brine	23/8/87	4.74	1.110
WA-37	Lake Brown (NE side), surface brine	23/8/87	4.29	1.060
WA-38	Quibabbin Soak, groundwater (near Lake Brown)	23/8/87	6.84	1.001
WA-49	Lake Way, interstitial brine	31/8/87	7.58	1.138
WA-50	Lake Raeside, interstitial brine	1/9/87	7.94	1.066
GW-3	Lake Raeside, interstitial brine	30/10/86		1.083
GW-5	Lake Lefroy, interstitial brine	1/11/86		1.192
GW-15	Lake Moore (North), interstitial brine	7/11/86	6.5	1.146
GW-17	Lake Yarra Yarra, interstitial brine	11/11/86	6.6	1.171
GW-18	Lake Grace, interstitial brine	12/11/86	6.5	1.170
GW-19	Lake King, interstitial brine	13/11/86	6.2	1.170
GW-20	Lake Gilmore, interstitial brine	13/11/86	3.2	1.133

"interstitial brine". pH measurements and water filtration (<0.45μm) were performed at the collection sites.

2.4.2. Analytical procedure

The determination of boron isotope compositions was carried out by negative thermal-ionization mass-spectrometry (ZEININGER and HEUMANN, 1983; HEUMANN and ZEININGER, 1985; DUCHATEAU and DE BIÈVRE, 1983; DUCHATEAU et al., 1986; VENGOSH et al., 1989). The high reactivity of boron enables production of BO_2^- from untreated fluid samples which were loaded directly onto filaments in a reverse polarity mass spectrometer. Boron from silicate minerals (e.g. shales, granites) was separated by KCO_3 fusion and boron-specific resin (KISS, 1988). Droplets of samples typically containing 50-150 ng boron were deposited onto filaments and evaporated to dryness before loading into the mass spectrometer. The mode of filament loading, rate of heating and running conditions were strictly replicated for each sample in order to minimize the variability of mass-spectrometer-induced isotopic discrimination. Both NBS SRM 951 (boric acid power) and seawater samples were repeatedly analysed to determine reproducibility. The 2-sigma standard error of 24 NBS SRM 951 replicates was 1.9 ‰ and of 10 seawater replicates was 1.1‰ at the 95% confidence limit (VENGOSH et al., 1989). This precision is lower than that reported for the dicesium metaborate method by SPIVACK and EDMOND (1986) of 0.24 ‰, but is similar to that of the sodium tetraborate technique of 2-3 ‰ (e.g. SWIHART et al., 1986) and better than the ICP-MS technique with a precision of 7‰, reported by GREGOIRE (1987).

In order to evaluate the negative-ion method, known mixtures of NBS 951 and seawater were analysed. The calculated and analysed isotopic compositions of the mixtures are in good agreement within experimental error (Fig. 2.2) indicating the validity of the negative thermal ionization mass spectrometry procedure.

Boron concentrations from groundwaters and brines were determined by a modified spectrophotometric technique using the reagent Azomethine H (KISS, 1988) and by isotope dilution mass spectrometry. Boron concentrations in silicate rocks were determined by isotope-dilution mass spectrometry (VENGOSH *et al.*, in preparation).

Isotope ratios are reported as permil deviation ($\delta^{11}B$) in the $^{11}B/^{10}B$ ratios relative to the standard NBS SRM 951:

$$\delta^{11}B = [(^{11}B/^{10}B_{\text{sample}} \;/\; ^{11}B/^{10}B_{\text{NBS 951}}) - 1]\ 1000$$

The mean of the absolute $^{11}B/^{10}B$ ratios of the NBS SRM 951 replicates, determined by the negative-ion method is 3.996.

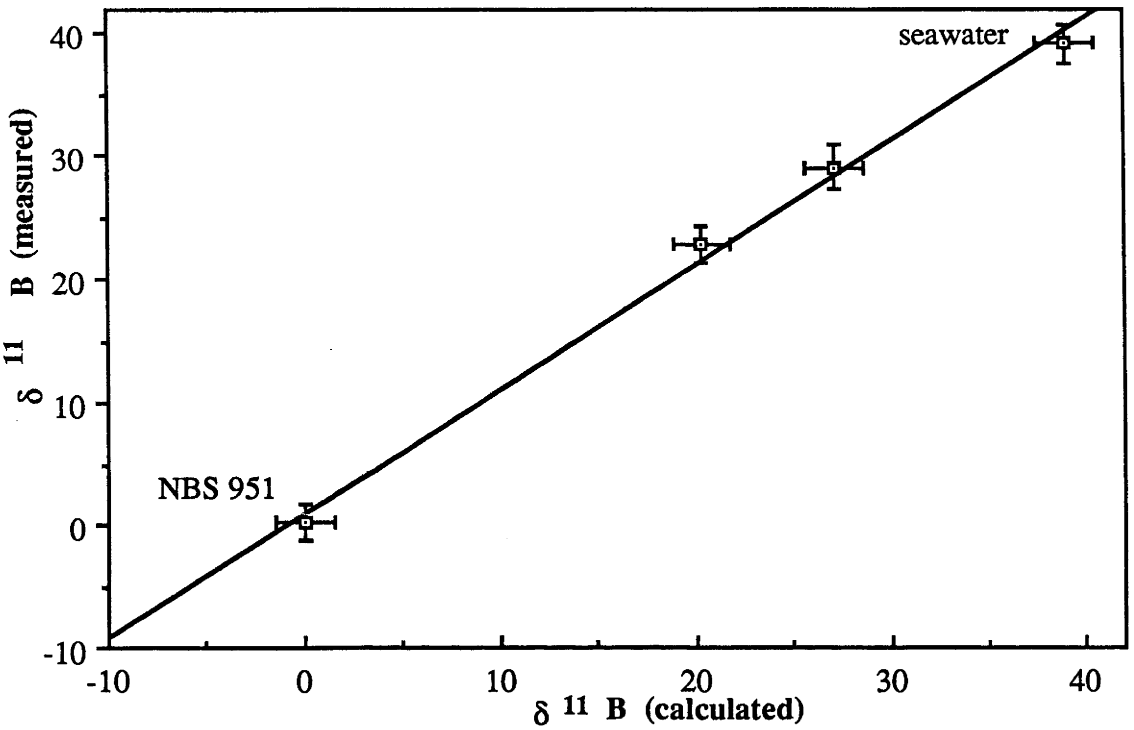


Figure 2.2. Comparison of the measured and calculated $\delta^{11}B$ values of NBS 951 and seawater and their mixtures.

2.5. RESULTS

Evaporation of seawater. The effects of evaporation of seawater on the boron-isotope composition of brines was examined by analysing evaporated seawater from successively evaporated artificial ponds. Results from brines from the salt works at Useless Loop in Shark Bay and at Dampier, Western Australia are presented in Table 2.3. The marine boron-isotope signature of the brines (an average of $\delta^{11}B = 38.6 \pm 1.8‰$) is maintained in the evaporation of seawater to the halite-saturation stage, i.e.degree of evaporation of about 10. The gradual increase of boron concentrations and the constant $\delta^{11}B$ values are consistent with the conservative behaviour of boron in evaporation processes up to a degree of evaporation of about 30 (ZHEREBTSOVA and VOLKOVA, 1966; VALYASHKO, 1970; see also Chapter 3).

Australian salt lakes. The boron isotope composition and the general chemistry of brines from some Australian modern playas is presented in Table 2.3, Fig. 2.3, and Fig. 2.4. Most of the Australian brines are Na-Cl type and their Na/Cl ratios are lower than unity. The $\delta^{11}B$ value for brine from Lake Eyre ($\delta^{11}B = 38.4 \pm 1.9$ ‰) overlaps with that of seawater but is significantly different from that of country rock at its shore (Bulldog Shale; $\delta^{11}B = -8.7‰$ to -6.7 ‰, Table 2.4). Salt lakes from other locations yield $\delta^{11}B$ values both lower and higher relative to seawater ($\delta^{11}B = 25.5‰$ to $59.2‰$, Fig. 2.3). Boron concentrations in the interstitial brines are in the range of 0.3 to 17.3 mg/l. The molar B/Cl values of the interstitial brines (4×10^{-6} to 4×10^{-4}) are generally lower than that of seawater (7.8×10^{-4}; Fig. 2.4). The only exception is a surface brine from a natural channel on the edge of Lake Cadibarrawirracanna. There is no obvious correlation of the $\delta^{11}B$ values of the salt lakes with their geographical position (e.g. distance from the sea), drainage area, or rock type.

Analyses of fresh and brackish waters from several locations in Australia yield boron concentrations in the range of 0.1 to 0.5 mg/l and $\delta^{11}B$ of 28.2‰ to 34.9‰ (Table 2.3, Fig. 2.3). In some cases the isotopic composition of the B in the brackish water is similar to that of the salt lake in the same location (e.g. Quibabbin Soak and Lake Brown;

TABLE 2.3. Boron isotopic and major-element analyses of brines from some Australian salt lakes, from some surface brackish and fresh waters, and from subsurface groundwaters from the Great Artesian Basin. The chemical data are reported in mg/l. The Na/Cl and B/Cl ratios are molar. The chemical data for the Maar lakes in Victoria and the groundwaters from the Great Artesian Basin are from CHIVAS et al. (1986) and HERCZEG et al. (in prep.), respectively. The seawater sample is from Jervis Bay, eastern Australia.

Sample and location	$\delta^{11}B$ (‰)	Na	K	Ca	Mg	Cl	Br	SO_4	B	Na/Cl	B/Cl ($x10^{-5}$)
seawater	38.4	10800	391	400	1280	19390	65	2649	4.7	0.86	78.0
Evaporated seawater											
UL-1 Shark B.	-	-	-	-	-	23200	-	-	5.5	-	78.0
UL-4 Shark B.	-	-	-	-	-	88000	-	-	20.7	-	77.1
UL-5 Shark B.	36.5	-	-	-	-	129700	-	-	31.1	-	78.6
UL-6 Shark B.	39.4	-	-	-	-	194000	-	-	57.7	-	97.5
D-2 Dampier	39.9	-	-	-	-	191500	-	-	59.8	-	102.4
Maar lakes from southwestern Victoria											
V-1 Bullenm.	54.6	-	-	-	-	-	-	-	0.9	-	-
V-2 Gnotuk	53.7	18455	511	125	2293	33430	-	-	0.9	0.85	28.9
V-3 Keilam.	59.2	22915	459	20	1193	39000	-	100	5.6	0.91	49.0
Salt lakes from northwestern Victoria											
V-7 Tyrrell	28.5	114807	685	514	6424	188097	348	10994	1.8	0.94	3.1
V-8 Tyrrell	30.6	-	-	-	-	-	-	-	1.7	-	-
Salt lakes from the Great Artesian Basin, South Australia											
SA-9 Frome	41.3	114291	88	624	497	171750	118	8992	0.5	1.03	0.9
SA-10 Frome	-	117124	102	677	567	177536	90	10343	-	1.02	-
SA-16 Eyre N.	-	110840	682	606	4051	178476	86	11235	-	0.96	-
SA-22 Eyre N.	38.4	115307	1260	432	5937	187926	112	14211	7.2	0.95	1.3
SA-26 Eyre S.	-	119372	1824	276	6301	182488	220	32410	-	1.01	-
SA-32 Cadib.	43.5	52311	599	716	10898	106876	145	13959	2.8	0.75	8.6
SA-34 Cadib.	48.7	-	-	-	-	-	-	-	18.7	-	-
Salt lakes from the Gawler Block, South Australia											
SA-38 Everard	-	83652	1279	748	10486	155819	96	10709	-	0.83	-
SA-43 Gairdner	-	111077	1004	1916	6148	192824	52	2161	-	0.88	-
SA-44 Acraman	34.4	86929	1475	2433	5060	153982	117	2954	0.2	0.87	0.4
SA-45 Acraman	-	88496	1711	2241	7210	164036	136	2941	-	0.83	-

TABLE 2.3. (continued)

Sample and location	$\delta^{11}B$ (‰)	Na	K	Ca	Mg	Cl	Br	SO_4	B	Na/Cl	B/Cl (x10^{-5})
Salt lakes from Yilgarn Block, Western Australia											
WA-1 Gilmore	44.2	63495	315	720	6242	114989	151	22103	4.5	0.85	13.1
WA-3 Hann	25.5	39621	524	346	5039	71383	175	8617	7.9	0.86	36.4
WA-8	30.3	114274	482	859	2435	187269	92	3322	3.7	0.94	6.4
WA-31 Tammin	47.0	91844	200	1013	1072	148389	51	2838	2.5	0.95	5.6
WA-33 Chandler	-	30976	323	1468	1595	53268	54	3690	5.1	0.89	31.0
WA-34 Brown	-	53064	963	2076	4019	95267	110	4917	-	0.86	-
WA-37 Brown	27.6	-	-	-	-	-	-	-	1.3	-	-
WA-49 Way	-	61292	6154	657	6300	101773	97	20510	-	0.93	-
WA-50 Raeside	-	31146	754	952	2828	50499	60	6315	-	0.95	-
GW-3 Raeside	41.9	39421	999	1201	4011	70099	101	9392	0.6	0.87	2.8
GW-15 Moore	34.7	75414	1676	896	7765	132885	73	12141	0.9	0.88	2.2
GW-17 Yarra	-	91895	2538	713	8145	160401	190	11228	3.4	0.88	6.9
GW-18 Grace	-	94336	909	697	6648	159614	120	10756	0.4	0.91	0.8
GW-19 King	-	81241	2494	442	14169	152177	282	21867	0.8	0.82	1.7
GW-20 Gilmore	-	71425	404	1022	4945	119140	64	10894	0.8	0.92	2.2
Surface brackish and freshwaters											
K Spring Keil	28.2	146	8	66	47	261	0.7	10	0.1	0.86	125
SA-51 Acraman	31.2	-	-	-	-	-	-	-	0.4	-	-
WA-38 Quib.	33.0	-	-	-	-	-	-	-	0.5	-	-
Finke River	34.9	-	-	-	-	-	-	-	0.2	-	-
Subsurface groundwaters from the Great Artesian Basin											
GAB-79	2.2	41	5	24	20.9	32	-	6.1	0.05	2.02	520
GAB-81	-7.8	126	5	8	0.2	31	-	2.7	0.17	6.25	1780
GAB-83	-14.7	336	3	2.8	0.1	208	-	1.9	0.66	2.49	1040
GAB-87	-	310	7	0.8	0.1	65	-	29.4	0.76	7.38	3840
GAB-92	-15.9	549	8	5.2	0.5	147	-	-	1.07	5.76	2380
GAB-93	-6.8	1214	17	15.6	13.1	851	-	51.4	2.91	2.20	1120
GAB-96	-1.6	1559	41	187	40.3	1925	-	589	0.71	1.25	120

Acraman bore and Lake Acraman). In another case, the $\delta^{11}B$ value of a spring in the drainage zone of Lake Keilambete is lower than that of the lake itself.

The boron content and isotopic composition of groundwaters from the lower Cretaceous-Jurassic aquifer of the Great Artesian Basin ($\delta^{11}B$ = -16‰ to 2.2 ‰) are given in Table 2.3 and Fig. 2.3. The $\delta^{11}B$ values are distinctively lower than those of seawater and the Australian salt lakes. Molar B/Cl ratios of the groundwaters (1.2×10^{-3} to 3.8×10^{-2}) are, however, higher than that of seawater and the Australian surface brines.

The Australian country rocks chosen for boron analysis (Table 2.4) are generally representative of the type of the exposed country rocks in the drainage of the selected salt-lake basins. These are the Cretaceous Bulldog Shale in South Australia (B = 37.3 to 63.9 ppm; $\delta^{11}B$ = -8.7‰ to -6.7 ‰) and late Archaean granites from the Yilgarn Block in Western Australia (B = 8.4 to 11.4 ppm; $\delta^{11}B$ = -3.2‰ to 6.8 ‰). Boron in sediment samples was extracted by KCO_3 fusion and boron-specific resin and hence represents the sum of "non-desorbable" or "fixed" boron in the clay structure and "desorbable" boron. The total boron concentrations of some modern sediments present in the Australian salt lakes (Table 2.4) are lower (45 to 96 ppm) than the total boron content in sediments from the ocean (60 to 160 ppm, SPIVACK et al., 1987; 120 to 250 ppm, HARDER, 1970). The $\delta^{11}B$ values of the total boron (-3.2‰ to 12.3‰) in sediments from the Australian salt lakes are generally in the range of the isotopic composition of sediments in the oceanic environment ($\delta^{11}B$= -6‰ to 3‰, SPIVACK et al., 1987).

Table 2.4. Boron isotope composition and concentrations of some country rocks from South Australia and Western Australia, and sediments from some Australian salt-lake basins.

Sample	Description and Location	B(ppm)	$\delta^{11}B$ (‰)
SA-28	Bulldog Shale, outcrop near the shore of Lake Eyre South, South Australia	37.28	-8.7±2.0
Toodla	Bulldog Shale (Toodla No.1 well, depth 243 m), 120 km north of Coober Pedy, South Australia	63.95	-6.7±1.8
86-306	Late Archaean coarse-grained biotite granite, Readymix quarry, 10 km northeast of Merredin, Western Australia	8.42	-3.2±1.0
86-307	Late Archaean coarse-grained biotite granite,quarry 2km west of Doodlakine, Western Australia	9.39	6.8±1.2
72-864	Late Archaean coarse-grained biotite granite, Wheeler Rocks, 10 km east of Lake Johnston, Western Australia	11.41	0.4±1.2
V-2-C	Black soft mud with high organic content Lake Gnotuk, Victoria	96.34	12.3±1.0
V-4-C	Black soft mud with high organic content Lake Keilambete, Victoria	69.69	11.5±1.2
SA-22-C	Grey-green mud, Lake Eyre North, South Australia	48.47	-3.2±0.9
SA-26-C	Black-green soft mud, high H_2S, Lake Eyre South, South Australia	63.99	-1.2±2.5
SA-32-C	Grey-brown mud, Lake Cadibarrawirracanna, South Australia	56.26	4.7±1.4
SA-44-C	Brown hard mud, Lake Acraman, South Australia	45.47	6.3±2.8

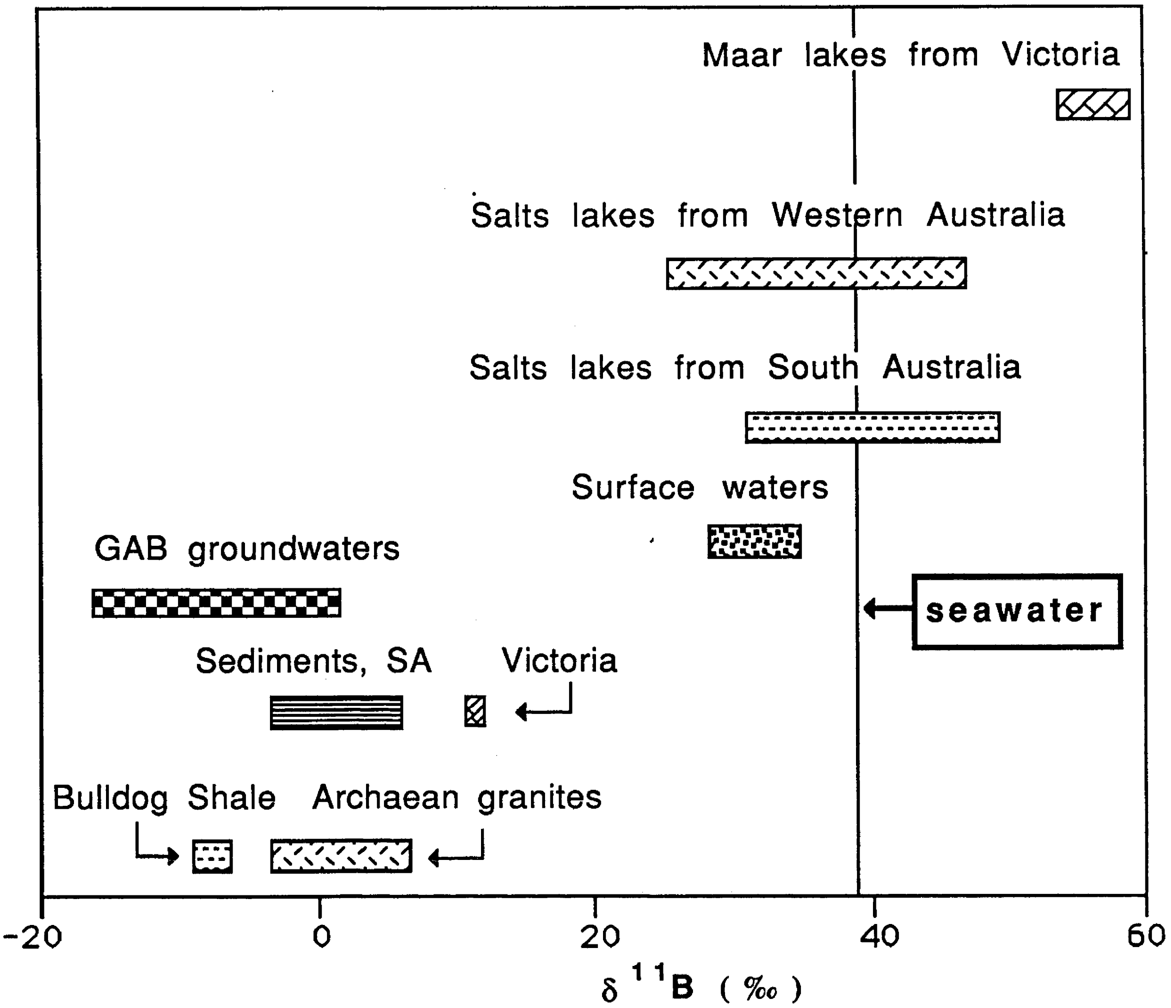


Figure 2.3.

Distribution of $\delta^{11}B$ values in some Australian brines, surface waters, groundwaters, sediments and country rocks. The seawater value is from SPIVACK et al., (1987) and this study. GAB = Great Artesian Basin.

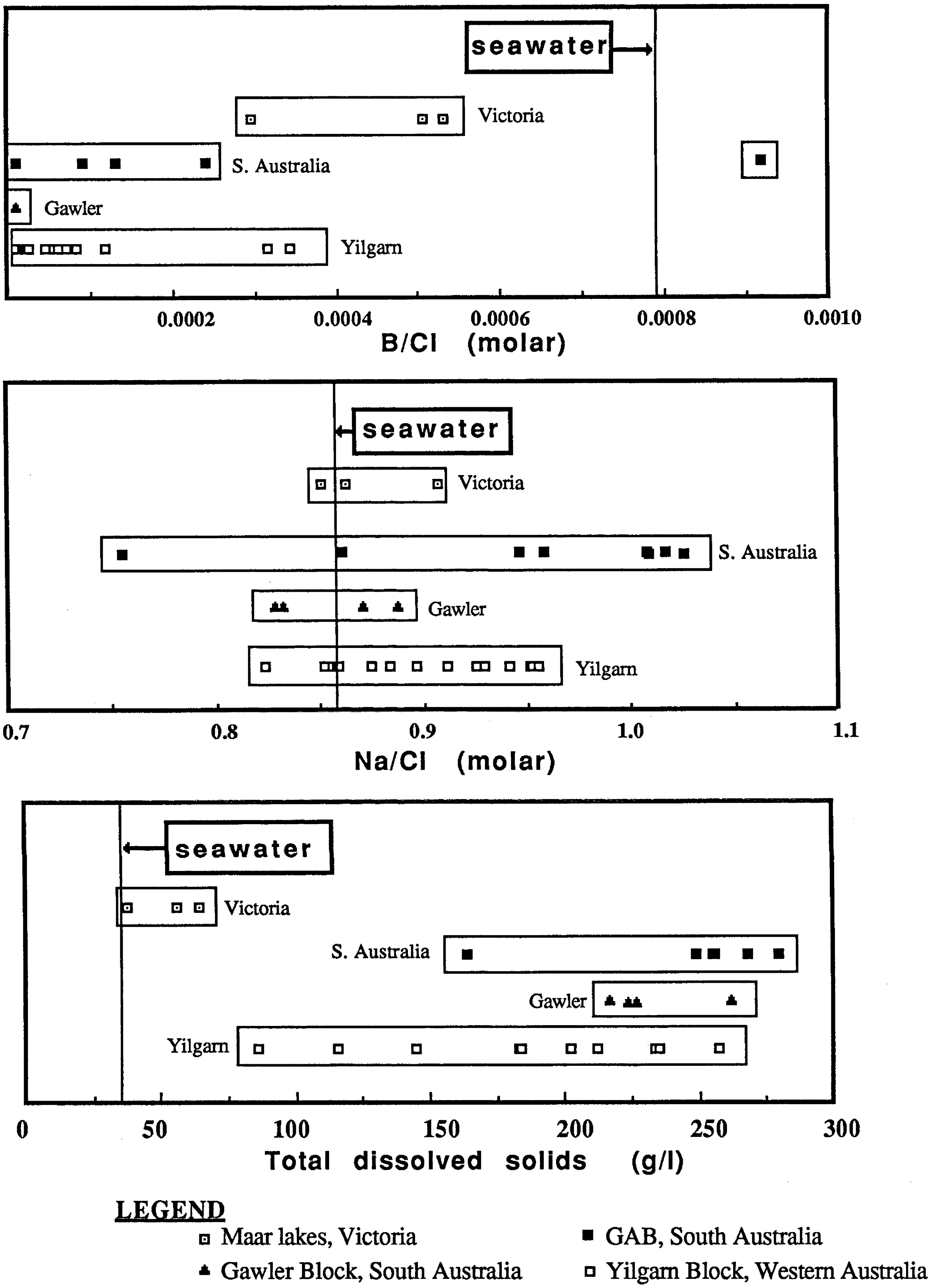


Figure 2.4. Total dissolved solids (TDS), Na/Cl and B/Cl ratios of brines from some Australian salt lakes

2.6. DISCUSSION

In the following section the environments of small, maar lakes in Victoria are contrasted with those of the large, hypersaline playas in South Australia (SA) and Western Australia (WA). Whereas the maar lakes are closed systems in small volcanic craters, the salt lakes from SA and WA are large and complex evaporative systems that are open to groundwater discharge.

2.6.1. The volcanic maar lakes from Victoria.

The volcanic maar lakes are located in volcanic craters in the western district of Victoria, 40 to 50 km north of the Southern Ocean coast (Fig. 2.1). The salinities of waters from the three sampled lakes (range from 10 g/L to 60 g/L) are lower than those of the other Australian salt lakes (Table 2.3; Fig. 2.4). Halite and gypsum are absent from the sedimentary records of these lakes (BOWLER, 1970). The high-pH waters (8.5 to 9.0) are depleted in Ca^{2+}, Mg^{2+}, CO_3^{2}, K^+, and SO_4^{2-} relative to the marine ratios, (as normalized to chlorine) (MADDOCKS, 1967; CHIVAS et al., 1986, Table III). The mean Na/Cl ratio of 13 maar lakes is 0.87±0.05, similar to seawater and therefore suggestive of a marine (cyclic) salt origin for Cl^- and Na^+ in these lakes (MADDOCKS, 1967).

The sediments of the maar lakes are composed of soft black calcareous muds and consolidated clays. A large proportion of the sediments is composed of authigenic calcite, high-Mg calcite, proto-dolomite, and dolomite (BOWLER, 1970). The carbonate minerals may be a sink for Ca^{2+} and Mg^{2+}, but the observed depletion of SO_4^{2-} cannot be explained by gypsum precipitation, as sulphate minerals are not recorded in the sedimentary profiles of the lakes (BOWLER and HAMADA, 1971). We suggest that bacterial sulphate reduction by organic matter has depleted the water in sulphate and increased the bicarbonate content of the interstitial brines, i.e. high pH. Consequently, aragonite precipitation has caused the removal of Ca^{2+} and the decrease of the Ca/Mg ratios of the lakes waters (9×10^{-3} to 3.2×10^{-2} relative to 1.8×10^{-1} in seawater). Elevated sulphide contents that are associated with low sulphate contents in the sediment-water interface at Lake Tyrrell, northwest Victoria (BOWLER and TELLER, 1986), are consistent with sulphate reduction .

Lake Keilambete occupies a volcanic crater that forms a closed basin, 1.8 km in diameter (BOWLER and HAMADA, 1971). The marine-like Na/Cl ratios suggest a cyclic (marine) origin for the salts. By integrating the area of the crater (2.5×10^6 m^2), the mean annual precipitation of 788 mm/yr and an estimated chlorine concentration of 7 mg/l Cl in rainwaters (data from HUTTON and LESLIE, 1958; HUTTON, 1976), an estimate of the chlorine input flux yields 1.4×10^4 g/yr. A chlorine inventory of the lake waters of 9.9×10^8 g Cl was calculated from the area, water depth (10m) and chloride concentration of 39,000 mg/L. Similar calculations for the other elements are summarised in Table 2.5. Estimates of the residence times [(mass x concentration)/(flux)] may indicate the "probabilities of removal" (BROECKER and PENG, 1982), or the reactivity of the different ions. The calculated residence times for chloride and sodium are 71,000 and 74,000 yr respectively, and are in fair agreement with the estimated age of formation of the crater lake (BOWLER 1970). Hence, chloride and sodium may have accumulated in the lake water since its formation. Shorter residence times (0.26 to 10 $\times 10^3$ years) are estimated for Ca^{2+}, K^+, SO_4^{2-} and boron (Table 2.5), that is consistent with their depletion with respect to chloride.

Table 2.5. Residence time estimates for several elements in Lake Keilambete, assuming all ions are initially derived from marine cyclic salts. Data from HUTTON and LESLIE (1958), HUTTON (1976) and CHIVAS et al. (1986).

Element	Conc. in coastal rain (mg/l)	Flux (g/yr)	Conc. in lake (mg/l)	Inventory (g)	Residence Time 10^3 years
Cl	7.0	1.4×10^4	39000	9.9×10^8	71
Na	3.9	7.8×10^3	23100	5.9×10^8	74
K	0.14	280	540	1.4×10^7	49
B	0.0016	3.4	5.6	1.4×10^5	42
Ca	0.15	300	20	5.1×10^5	1.7
SO_4	0.97	1.9×10^3	100	2.5×10^6	1.3

Both the $\delta^{11}B$ values (range of 53.7‰ to 59.2‰) and B/Cl ratios of brines (Table 2.3, Fig. 2.3) in the Victorian maar lakes are not marine. In Lake Keilambete $(B/Cl)_{lake}/(B/Cl)_{SW}=0.59$. The boron concentration and the $\delta^{11}B$ value of the lake water are 5.6 mg/l and 59.2‰, respectively. If boron had accumulated conservatively in these lakes, the boron concentration should be 9.4 mg/l. Consequently, the brines are depleted by 3.8 mg/l B and enriched in ^{11}B by 20.2‰ assuming a solely marine aerosol input. Similar calculations for Lake Gnotuk also yield a lower abundance of boron but an enrichment of ^{11}B (5.17 mg/l and 14.7 ‰, respectively).

Boron concentrations of 10 to 20 ng/g from rainwaters in marine sites were reported by FOGG and DUCE (1985). By using the estimated chlorine content in rainwaters of 7 mg/l at Lake Keilambete, and assuming a marine B/Cl ratio for such rainwater, a boron content of 1.6 ng/g for rainwater at Lake Keilambete is estimated. Consequently, the residence time of boron in Lake Keilambete waters is calculated to be 42,000 yr (Table 2.5). This estimate is consistent with the observation of relative boron depletion. In contrast to chlorine that has been accumulated progressively during the last 70,000 yr, the shorter residence time of boron indicates a removal of boron from the system.

If the source of boron to these lakes is also cyclic, originating from seawater, the initial $\delta^{11}B$ input into the lakes would be expected to have a marine isotopic signature ($\delta^{11}B$ = 39‰). Since $\delta^{11}B$ of the lakes falls in the range of 53.7 to 59.2‰ (Table 2.3, Fig. 2.3), and the B/Cl ratios are lower than that of seawater, additional processes are required in order to account for the ^{11}B enrichment and elemental B depletion. The removal of boron together with $\delta^{11}B$ enrichment in the maar lakes is probably the result of adsorption of $^{10}B(OH)_4^-$ onto the clay minerals in the sediments by the mechanism proposed by PALMER et al., (1987) and SPIVACK et al., (1987). Incorporation of $Ca^{10}B(OH)_4^+$ and $^{10}B(OH)_4^-$ species into the aragonite fraction, producing a further isotopic fractionation may also affect boron isotopes as high concentrations of boron in aragonite minerals are reported by ICHIKUNI and KIKUCHI, (1972); FURST et al. (1976); KITANO et al. (1978) and VENGOSH et al. (1989). The sediments from the Victorian maar lakes have $\delta^{11}B$ values of 11.5‰ and 12.3‰, higher than those of sediments from other salt lakes ($\delta^{11}B$ of -3.2‰ to 6.3‰; Table 2.4). This enrichment may be the result of the large carbonate fraction in the maar lake sediments (see Chapter 8) that is not present in the other Australian lakes.

The large ^{11}B enrichment in the maar lakes from Victoria indicate that these lakes are closed systems with respect to the local groundwaters implying that the mode of B input is atmospheric. Boron accumulation in these lakes has been limited only by removal to the sediments, but not by mixing with local low ^{11}B groundwaters. This is consistent with the hydrological model of Lake Keilambete of input received only by direct precipitation and water loss only by evaporation (BOWLER and HAMADA, 1971; CHIVAS et al., 1985).

The high $\delta^{11}B$ values recorded in the maar lakes are related to interaction of dissolved boron with the sediments. These interactions are probably controlled by the water/sediment ratios. In order to evaluate the water/sediment ratios in the maar lakes of Victoria, a series of mass-balance equations is derived. According to BOWLER and HAMADA (1971), water is lost from the maar lakes by evaporation alone as thick clay effectively prevents water loss through the lake floor. For a rainwater flux similar to that of the present-day (~800 mm yr^{-1}), a water column of about 10 metres (Lake Keilambete) would accumulate in tens of years. Thus, the water budget of the lakes reached a balance between evaporation and precipitation in the very early stages of the lake's history. Although the maar lakes experienced fluctuations in water level (and thus salinity) due to variations in the precipitation/evaporation ratio in the last 10,000 years (CHIVAS et al., 1985), chlorine has accumulated as a closed system within the lakes.

We can apply the simple mass-balance equation of

$$M_w{}^iC_w{}^i + M_pC_p = M_w{}^fC_w{}^f + M_s{}^fC_s{}^f \qquad (2)$$

where $M_w{}^i$ and $M_w{}^f$ are the initial and final masses of water

M_p and $M_s{}^f$ are the masses of precipitation and lake sediments, respectively; $C_w{}^i$ and $C_w{}^f$ are the initial and final concentrations of dissolved boron in the lake waters, C_p and $C_s{}^f$ are the boron concentrations in rainwaters and lake sediments, respectively. As it has been assumed that chlorine accumulates conservatively in the lake waters, the present chlorine content (Cl^f) is a result of net precipitation, Cl_p is the chlorine concentration in precipitation (rainwaters) and Cl^i is the initial Cl in water derived from the rocks, we have:

$$M_w^i Cl^i + M_p Cl_p = M_w^f Cl^f \quad (3)$$

Solving for M_p in equations (2) and (3), and assuming that the initial boron derived from the tuffaceous country rocks is negligible ($M_w^i C_w^i = 0$) yields

$$M_w^f Cl^f (B/Cl)_p = M_w^f C_w^f + M_s^f C_s^f \quad (4)$$

In the case of a homogeneous boron adsorption distribution coefficient (Kd), where the bulk sediments are in equilibrium with the whole solution, then $Kd = C_s^f/C_w^f$. Substituting C_s^f in Equation (4) ($C_s^f = C_w^f Kd$), dividing it by $M_w^f C_w^f$ and Kd, and rewriting gives:

$$M_s^f/M_w^f = 1/Kd\,[\,(Cl/B)^f (B/Cl)_p) - 1] \quad (5)$$

where $(Cl/B)^f$ and $(B/Cl)_p$ are the molar Cl/B and B/Cl ratios of the final solution in the lakes and of the precipitation, respectively. As M_s^f/M_w^f expresses the weight ratio of water to sediment (W/R), Equation 5 can be rewritten as:

$$W/R = Kd / [(Cl/B)^f (B/Cl)_p) - 1]. \quad (6)$$

By analogy to the elemental mass-balance (Equation 2), an isotopic mass balance equation can be derived:

$$M_w^i C_w^i R_w^i + M_p C_p R_p = M_w^f C_w^f R_w^f + M_s^f C_s{}^f R_s^f \quad (7)$$

where R_w^i, R_w^f, R_p and R_s^f are the $^{11}B/^{10}B$ ratios of initial and final boron in the lake, rainwaters and lake sediments, respectively. By a similar derivation we obtain the water/sediment (W/R) ratios of:

$$W/R = \alpha\, Kd / [(Cl/B)^f (B/Cl)_p (R_p/R_w^f) - 1]. \quad (8)$$

where the fractionation factor $\alpha = R_s{}^f/R_w^f$.

In order to solve the W/R ratio equations, B/Cl ratios of the precipitation must be estimated. By combining Equations (6) and (8), an expression for $(B/Cl)_p$ can be derived:

$$(B/Cl)_p = [\alpha - 1] / [\alpha (Cl/B)^f - (Cl/B)^f (R_p/R_w^f)]. \quad (9)$$

Applying the experimental Kd and α values from PALMER et al., (1987) for the Victorian high-pH maar lakes, several $(B/Cl)_p$ and W/R ratios values have been calculated

Table 2.6. Estimated water/sediment (W/R) ratios and B/Cl ratios of precipitation, $(B/Cl)_p$, using boron-isotope mass-balance equations for the Victorian maar lakes. The distribution coefficient (Kd) and isotopic fractionation factor (α) of boron adsorption is calculated from PALMER et al. (1987).

Lake	pH	Kd	α	$(Cl/B)^f$	R_w	$(B/Cl)_p$ ($x10^{-4}$)	W/R
Keilambete	9.0	4.18	0.9795	2113	4.23259	67.8	0.31
Gnotuk	8.6	3.59	0.9777	3460	4.21062	7.7	2.15
Bullenmerri	8.8	3.87	0.9786	2564	4.21421	12.6	1.73

(Table 2.6). Using these Equations the following is obtained: (1) B/Cl ratios of the precipitation in the Victorian lakes are in the range of 8×10^{-4} (marine values) to 6×10^{-3} (rainwater values: MARTENS and HARRIS, 1976; FOGG and DUCE, 1985); (2) if we apply, in these equations, R_p values ($^{11}B/^{10}B$ of precipitation) that are lower than that of the marine value, we obtain negative non-realistic $(B/Cl)_p$ values; and (3) the calculated W/R ratios are in the range of 0.31 to 2.15 (Table 2.6). Consequently, this model has further constrained the chemical and isotopic composition of the atmospheric input in the maar lakes, marine $\delta^{11}B$, and a range of high to marine B/Cl ratios.

In conclusion, the maximum effect of the isotopic fractionation during boron adsorption would take place in conditions of low W/R ratios. However the bulk of the solution would be less sensitive to boron adsorption as the W/R ratios increase.

2.6.2. The salt lakes of South and Western Australia.

The playas of Lake Eyre and Lake Frome (Fig. 2.1) are large closed basins within large catchment areas overlying the Great Artesian Basin (GAB), South Australia. Halite and gypsum crusts are underlain by thick clay sediments (5 to 10 m depth). The internal drainage system of Lake Eyre covers an area of 1.14 million km^2, receives 100-

150 mm annual rainfall, and is subject to evaporation rates exceeding 3000 mm yr^{-1} (KOTWICKI, 1988). The GAB, which underlies a large portion of the central and the northeastern Australian continent, was previously the site of lacustrine sedimentation at the end of the Cretaceous (JOHNS and LUDBROOK, 1963; JESSUP and NORRIS, 1971). The deep groundwaters in the basin were investigated by HABERMEHL (1980). The basin consists of a multi-layer confined aquifer system, with aquifers occurring in continental quartzose sandstones of Triassic, Jurassic and Cretaceous age. The intervening confining beds consist of siltstone and mudstone, and are overlain by a thick argillaceous sequence of Cretaceous marine sediments (HABERMEHL, 1980).

The playas from the Gawler Block in South Australia and the Yilgarn Block in Western Australia are located in Proterozoic dacitic volcanics and Archaean granites and greenstone, respectively. These salt lakes are also associated with halite, gypsum and clay minerals.

Although the salt lakes of the GAB, Gawler Block and Yilgarn Block are located in different geological environments, the major-element chemistry of these lakes is similar (Table 2.3): The salinities of the brines are in the range of 85 to 280 g/L, the brines are mainly composed of Na^+ and Cl^- and strongly depleted in Ca^{2+}, Mg^{2+}, CO_3^{2-}, K^+ and SO_4^{2-}-relative to the marine ratio (as normalized to chlorine). Na+Cl/TDS equivalent ratios in all the lakes, regardless of their locations, are in the range of 0.82 to 0.97. The chemical uniformity of the brines suggests that the sampling undertaken in this study is reasonably representative of the salt-lake systems.

Evaporation of a brine and halite precipitation from it removes equivalent molar amounts of Cl^- and Na^+ from the brine and the Na/Cl ratio of the brine residue is changed accordingly. Mass balance requires that if the Na/Cl ratio of the initial brine is lower than 1 (e.g. seawater, Na/Cl=0.86), the Na/Cl of the residual brine will be lowered for each mole of precipitated halite. Conversely, if Na/Cl in an initial solution is higher than 1, halite precipitation would increase the Na/Cl ratio of the residual brine.

Based on molar Na/Cl ratios, three main groups of waters can be identified in Australia:

(1) Brines with low Na/Cl ratios (<1). The interstitial brines from salt lakes on the Yilgarn Block, Gawler Craton, and the Great Artesian Basin have Na/Cl ratios ranges of 0.82-0.98, 0.82-0.87, and 0.75-1.03, respectively (Table 2.3; Fig. 2.4);

(2) Fresh groundwaters and rivers with distinctively higher Na/Cl ratios. Na/Cl ratios of groundwaters from the Cretaceous aquifer of the GAB are in the range of 1.71 to 9.57 (mean 6.05; n=17) in the east, and 1.11 to 2.20 (mean 1.37; n=5) in the west (HERCZEG et al., in prep.). The mean of Na/Cl ratios of rivers and freshwater lakes is 3.82 (range of 1.55 to 6.33, n= 16; JOHNSON, 1980);

(3) Rainwaters with marine Na/Cl ratios. As reported by HINGSTON and GAILITIS (1976), the mean of Na/Cl ratios in rainwaters from inland locations in Western Australia is 0.83 (n=45).

If the fresh groundwaters of the GAB, or the river waters with the high Na/Cl ratios, are the major sources of Cl^- and Na^+ in the Australian salt lakes, then even higher Na/Cl ratios are expected since the brines have precipitated halite. Instead, Na/Cl ratios in most of the Australian salt-lakes are lower than 1 (Fig. 2.4). Halite dissolution can reduce the high Na/Cl ratios in the brines. Even so, the Na/Cl ratios for any mixture between dissolved halite and brine residue with Na/Cl>1 should always be greater than 1. Therefore, the low Na/Cl ratios of the Australian salt lakes rule out the possibility of evolution of these brines by concentration of groundwaters with initally high Na/Cl ratios.

The only salt lakes with Na/Cl ratios higher than unity are those from the Great Artesian Basin in South Australia (Table 2.3; Fig.2.4). It seems that Lake Eyre and lake Frome are influenced by an input with Na/Cl ratio >1, i.e., discharge of the GAB groundwater. This source, however, cannot be the ultimate source for the salts budget of these lakes, as halite precipitation would increase the Na/Cl ratios to >>1. Another source or sources with Na/Cl<1 must also contribute salts to these lakes.

In order to obtain the Na/Cl ratios recorded in most of the Australian salt lakes (range of 0.82 to 1.03), another component with low Na/Cl ratios must be introduced, i.e. seawater (Na/Cl=0.86), or marine brines that have precipitated halite. However, the Australian salt lakes have probably not originated directly by evaporation of seawater as the sea has not penetrated inland during the Quaternary Period, and only limited transgressions have occurred during the Tertiary (JOHNSON, 1980). In addition, no trapped, subsurface, "basinal" brines are known to exist or to discharge to the modern hydrological systems of the Australian salt lakes. Consequently, the bulk of the salts i.e. Na^+ and Cl^-, in the Australian salt lakes must be derived from marine aerosol salts, originating from seawater.

The linear correlations of Na+Cl/TDS (equivalent) ratios with Na/Cl ratios (Fig. 2.5A), Na+Cl/TDS with Mg/Cl (molar) ratios (Fig. 2.5B), and Na/Cl with Br/Cl ratios (Fig. 2.5C) of brines from Western Australia suggest that the bulk of the solutes in these systems is controlled by halite dissolution, originating from marine salts. Most data points in Fig. 2.5A, 2.5B, and particularly in Fig. 2.5C lie below the theoretical mixing line between marine salts and pure NaCl solution . This may indicate mixing of NaCl solution with a brine having Na+Cl/TDS ratio higher and/or Na/Cl ratio lower than the marine value. During precipitation of gypsum from evaporated seawater, the Na+Cl/TDS ratios (in equivalents) will increase from the marine value of 0.84 to 0.86 due to the removal of Ca^{2+} and SO_4^{2-} (the "gypsum" arrow in Fig. 2.5A). By removal of all the sulphate and its balanced cation (in milliequivalents) from evaporated seawater, Na+Cl/TDS ratios would increase to 0.93 ("sulphate reduction" arrow in Fig. 2.5A). In some low-pH lakes, such as Lakes Hann and Gilmore, alunite precipitation (McARTHUR et al., 1989; BIRD et al., 1989) may be an alternative mechanism for sulphate removal. Therefore, the shift of the data points from the marine-NaCl mixing line may be the result of gypsum precipitation, sulphate reduction and/or alunite precipitation that has removed much of the sulphate and caused high Na+Cl/TDS ratios in the Western Australia brines. This is consistent with low SO_4/Cl ratios of some the brines from Western Australia (range 6×10^{-3} to 6.9×10^{-2}) that are lower than the SO_4/Cl ratios of seawater (5.0×10^{-2}).

Alternatively, the offset of the data points from the seawater-NaCl solution mixing lines can be the result removal of sodium, i.e., Na/Cl ratio lower than that of seawater (the "Na" arrow in Fig. 2.5A). This is apparent in Fig. 2.5C where the offset of the data points may be due to either depletion of bromide and/or sodium. Cation exchange reactions on clays can possibly remove Na^+ by replacement of Ca^{2+}, Mg^{2+} and K^+ and

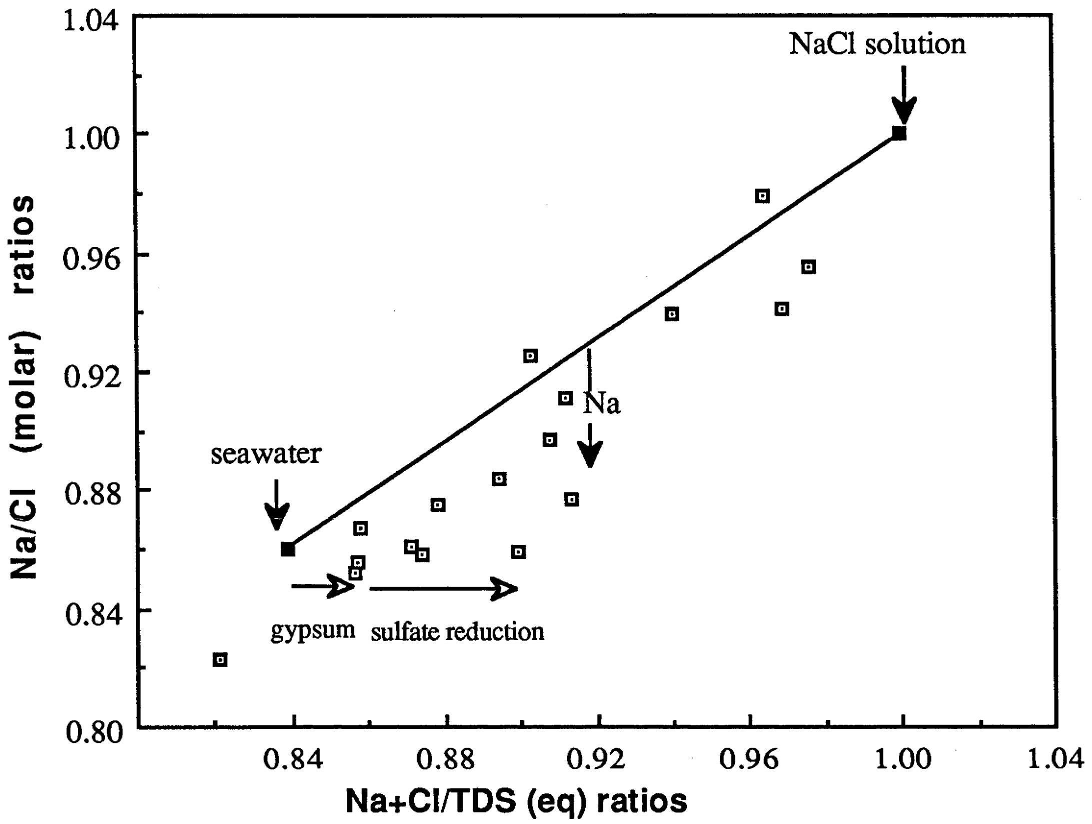


Figure 2.5. A. Na/Cl (molar) ratios *versus* Na+Cl/TDS ratios (in equivalents) in brines from Western Australia. Most data points plot below the mixing line of marine salts and NaCl solution (see text).

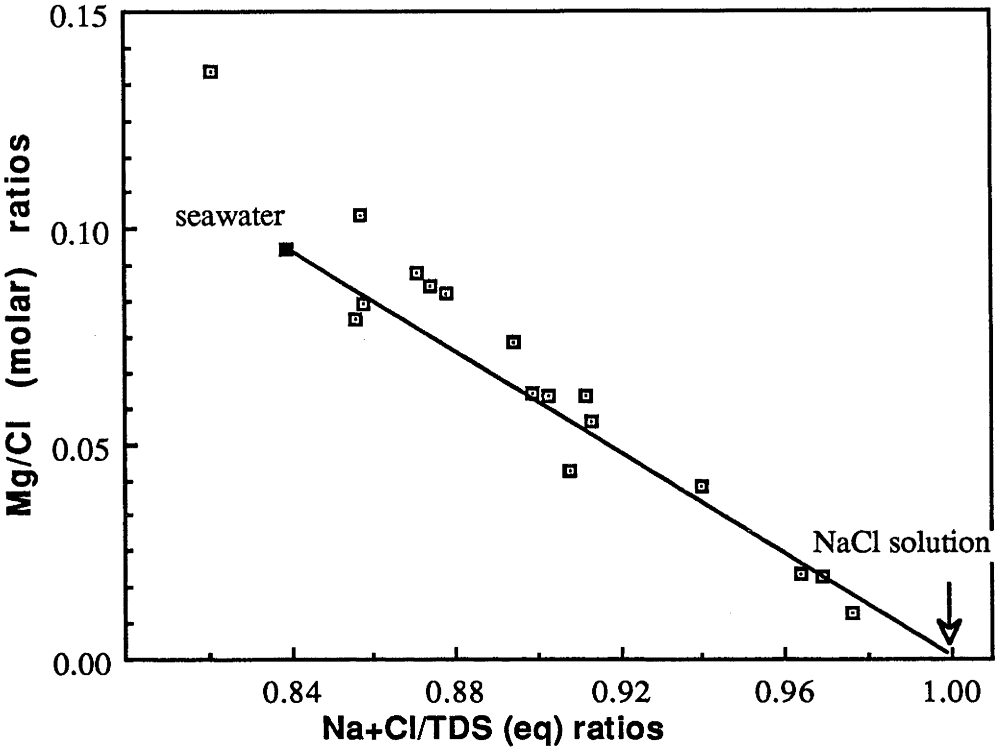


Figure 2.5. B. Mg/Cl (molar) ratios *versus* Na+Cl/TDS ratios (in equivalents) in brines from Western Australia.

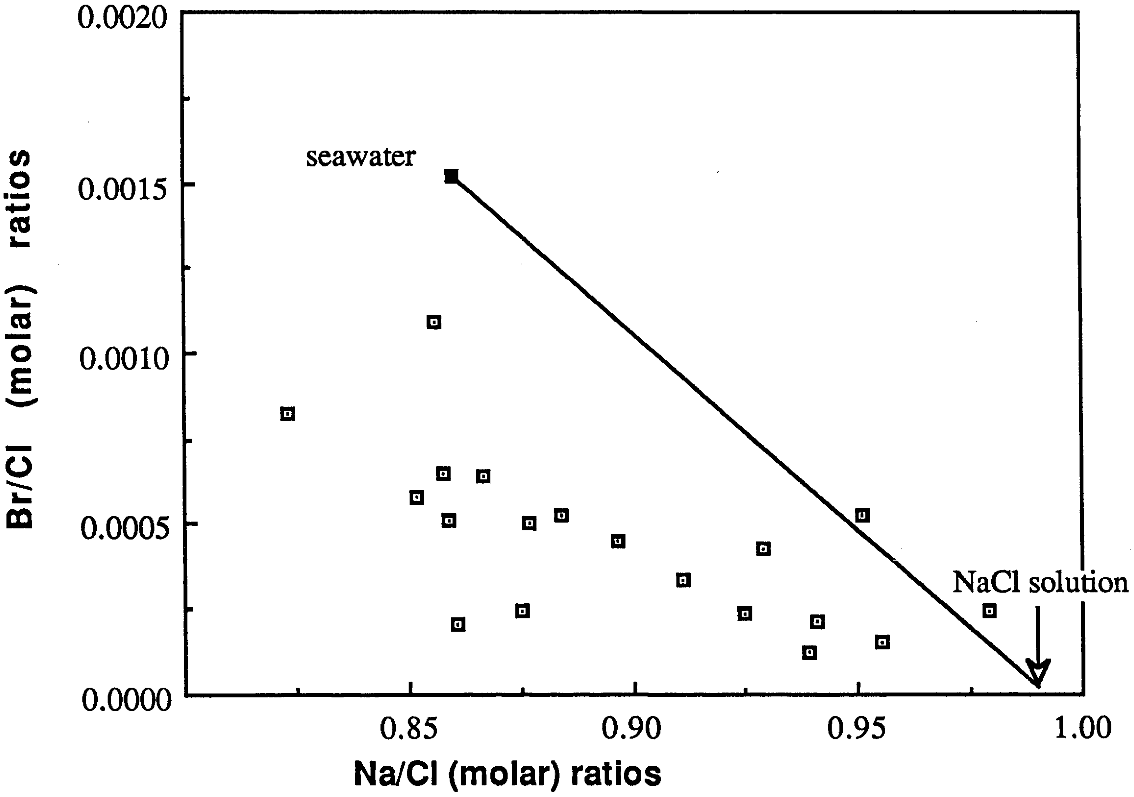


Figure 2.5. C. Br/Cl *versus* Na/Cl (molar) ratios in brines from Western Australia. Most data points plot below the mixing lines of marine salts and NaCl solution (see text).

hence reduce the Na/Cl ratio (CARPENTER, 1978). The brines from Australian salt lakes are not, however, Ca-chloridic as their Ca/SO4 ratios are always lower than 1 (in the range of 0.08 to 0.98). It seems that selective uptake of sodium by cation exchange has had only minor affects if any, on of the general chemistry of the brines.

Finally, based on the general chemical composition, it is suggested that the bulk of the salts of the Australian salt lakes have originated from marine aerosol salts. Additional processes such as halite dissolution, halite precipitation, gypsum precipitation, sulphate reduction, and alunite precipitation have modified the initial largely marine composition of the Western Australian brines. Apart from halite dissolution and halite precipitation, the chemical variations of the brines cannot distinguish between these processes. Other elements however, e.g. Ca^{2+}, Sr^{2+}, $CO_3{}^{2-}$ and K^+, and SiO_2 are partly controlled by rock weathering (CHIVAS et al., 1986; CHIVAS et al., 1988; NELSON and McCULLOCH 1989), precipitation of calcite, dolomite, sepiolite, and amorphous silica during the genesis of calcrete in the drainage zones (MANN and DEUTSCHER, 1978), and reactions with authigenic and detrital sediments within the salt lake basins.

The boron isotope composition of fresh and brackish waters from various locations in Australia may provide constraints on the sources of boron in the Australian salt lakes. This is mainly because the boron isotopic composition in these waters is not affected by some of the processes that occur within the salt-lake environment. Values of $\delta^{11}B$ of these surface waters (28.2‰ to 34.9‰, Table 2.3) overlap in part with those of the brines of the salt lakes but are distinct from the composition of groundwaters of the Great Artesian Basin ($\delta^{11}B$ = -16‰ to 2.2 ‰) (Fig. 2.3).

The relatively narrow range of $\delta^{11}B$ values recorded in the fresh and brackish surface waters from different locations in Australia, may indicate a similar source (or sources) of boron. The relatively high $\delta^{11}B$ values of these waters may indicate their origin by a mixture of a large fraction of cyclic boron, originating from seawater, with a subordinate amount of terrestrial boron with a low $\delta^{11}B$ value. In contrast, the lower $\delta^{11}B$ values (Fig. 2.3) and the high B/Cl ratios of the groundwaters from the Great

Artesian Basin indicate that boron in these waters is terrestrial, and is derived from leaching the aquifer rocks.

The $\delta^{11}B$ value of Quibabbin Soak (33.0‰) and Acraman Bore (31.2‰) in the drainages of Lake Brown ($\delta^{11}B$= 27.6‰) and Lake Acraman ($\delta^{11}B$= 34.4‰), respectively, show that there is no substantial difference between the boron isotopic composition of the brackish waters and the salt lakes. This may indicate that both the surface waters and the salt lakes have a common boron source or sources, i.e cyclic salts of marine origin. There are parallels with the marine-dominanted $\delta^{34}S$ values which are similar for salt-lake brines and the dissolved sulfate of regional groundwaters on the Yilgarn Block (CHIVAS et al., 1990) However, the $\delta^{11}B$ value of a freshwater spring in the drainage of Lake Keilambete, Victoria, (28.2‰) is lower than that of the lake ($\delta^{11}B$ = 59.2‰).

The Na/Cl ratios of salt lakes from South and Western Australia suggest marine (cyclic) input. If one assumes that boron in these lakes is also of largely marine origin, the variations of its isotopic composition ($\delta^{11}B$ = 25.5‰ to 48‰, Fig. 3) and the conspicuously low B/Cl ratios require special explanation. The processes that can decrease B/Cl ratios and affect the boron-isotope composition of the interstitial brines are: 1) boron adsorption onto clay minerals; and 2) mixing with a low-B and $\delta^{11}B$-value reservoir, e.g. groundwater. Dissolution of halite would reduce the B/Cl ratios but not the $\delta^{11}B$ values. As boron in the salt lakes from South and Western Australia is depleted even with respect to the mixing line between marine salt and NaCl solution (Fig. 2.6), it seems that boron has also been removed also by clay adsorption.

This study has shown that in evaporation of seawater to the degree of halite saturation, the boron concentration of evaporated brine increases conservatively and the boron isotope composition of the brine is not affected. The variations in the isotopic composition of boron in the Australian salt lakes is therefore not related to evaporation and halite precipitation or halite dissolution processes. In lakes where $\delta^{11}B$ is higher than that of seawater, adsorption processes appear to control the isotopic composition of boron in the brines. For such cases the water/sediment (W/R) ratio must have been low enough for sediment adsorption to effect the boron isotope composition of the bulk solution, e.g.,

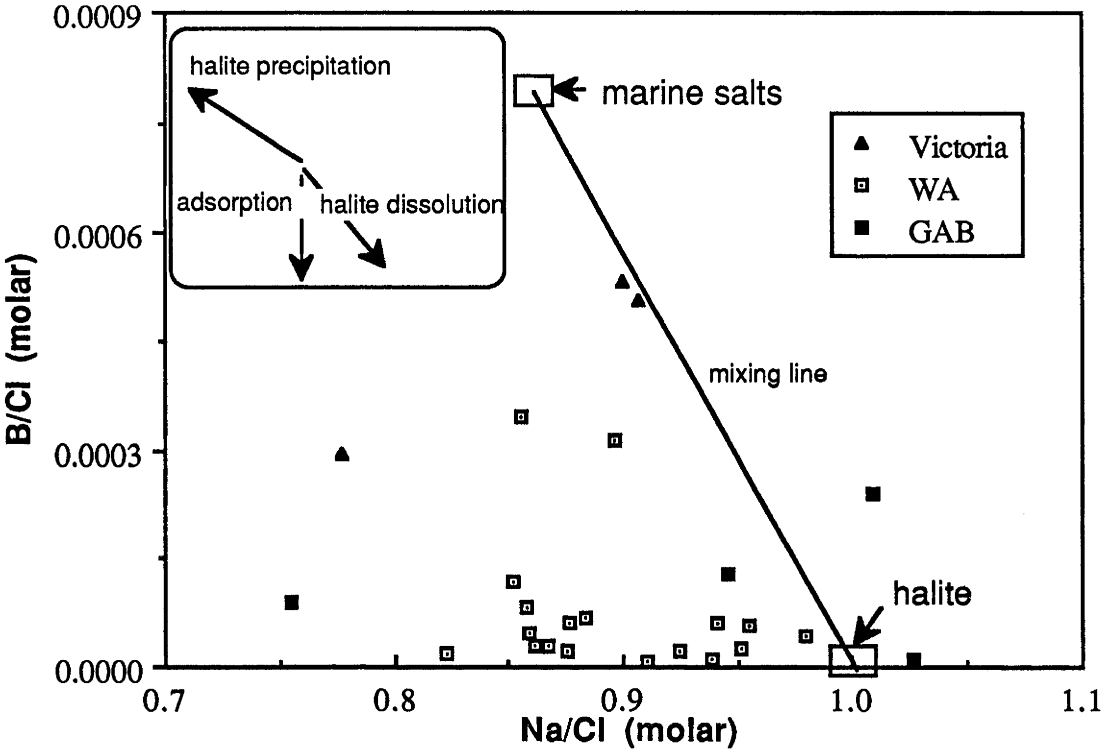


Figure 2.6. B/Cl *versus* Na/Cl ratios in Australian salt lakes. Most of the lakes are depleted in boron with respect to the mixing line between marine salts and halite. The vector rosette describes schematically the effects of adsorption, halite dissolution and precipitation processes. Note that the Western Australian ("WA") and Great Artesian Basin ("GAB") brines have lower B/Cl ratios than those of the Victorian maar lakes.

Lake Gilmore, "the salt lake" near Tammin, and Lake Raeside. In contrast, in lakes where the $\delta^{11}B$ value is lower than that of seawater, a component of groundwater with low $\delta^{11}B$ value may have mixed with the brines. For such cases we can not evaluate the W/R ratio as the system is not closed. Consequently, brines with $\delta^{11}B<39‰$ have a "terrestrial" component, i.e. boron that has been leached from the country rocks.

If the boron isotope signature is modified by clay adsorption, one might argue that the initial boron input into the salt lakes of Western and Southern Australia is solely terrestrial, leached from country rocks and modified by ^{11}B enrichment due to the reactions with clay minerals. We have shown that for the case of the Victorian maar lakes the initial $\delta^{11}B$ must be marine. Also the general chemistry and the Na/Cl ratios of most of the Australian salt-lakes (Na/Cl<1) suggest that both Cl^- and Na^+ cannot be derived entirely from the high Na/Cl groundwaters of the Australian continent.

SWIHART et al., (1986) have shown that ancient marine evaporite borates are isotopically heavier than their non-marine counterparts. The $\delta^{11}B$ results reported in this study demonstrate that in common evaporites such as the inland Australian salt-lakes, this is not the case. Therefore high $\delta^{11}B$ values do not necessarily indicate deposition in a marine environment although the salts themselves may have a marine origin.

The Australian salt lakes represent a terrestrial evaporitic environment in which the brine chemistry (Na/Cl ratios and $\delta^{11}B$) and the authigenic minerals (gypsum and halite) are similar to that of evaporated seawater. Australia has had a long history of surficial weathering. Some land surfaces and weathered profiles have been preserved on the surface since their formation in the late Palaeozoic, Cretaceous and Tertiary (BIRD and CHIVAS, 1988; 1989). A large input of marine cyclic salts to an exposed continental surface can result in the chemical composition of the terrestrial brines being similar to that of evaporated seawater. Any interpretation of ancient evaporite environments, e.g. HARDIE (1984), must therefore take this complexity into account as exemplified by the example of the Australian salt lakes.

The high $\delta^{11}B$ values of the inland Australian salt lakes is interpreted as reflecting a source largely derived from marine aerosols, internal (adsorption) processes within the basin, and mixing with terrestrial waters. This may imply that some terrestrial inputs to the ocean do not necessarily have a low $\delta^{11}B$ value. The possibility of high $\delta^{11}B$ values for some terrestrial inputs to the ocean need consideration in attempts to reconstruct the global mass-balance of boron in the oceans (McCULLOCH, in prep.).

2.7. CONCLUSIONS

1) The following geochemical criteria ($\delta^{11}B$, B/Cl and Na/Cl ratios) are proposed for the recognition of brine origins: A) high $\delta^{11}B$ (>39‰), low B/Cl, and Na/Cl<1 indicate a marine-origin brine and boron adsorption onto clay minerals; B) low $\delta^{11}B$ (<39‰) and Na/Cl<1 indicate a marine-origin brine and mixing with terrestrial (low $\delta^{11}B$) groundwaters; C) marine $\delta^{11}B$ values, high B/Cl and low Na/Cl (< 0.86) indicate evaporation and halite precipitation from seawater; D) low B/Cl and Na/Cl~1 indicate halite dissolution; and E) low $\delta^{11}B$ (~0‰), high B/Cl and Na/Cl>>1 indicate a terrestrial-origin brine. A partial exception to these proposed criteria are those brines where low Na/Cl ratios (< 1) are achieved in terrestrial solutions due to dissolution of K- and Mg chlorides. Such cases, although rare, have been identified (e.g. the Qaidam Basin, China; Chapter 4).

2) The Na/Cl ratios of a brine would not be affected by boron adsorption onto clay minerals and should reflect the original pre-adsorption values of the waters, the boron isotope composition is sensitive to adsorption but not to evaporation, halite precipitation, and dissolution. Therefore, by using both the Na/Cl ratios and $\delta^{11}B$ values it is possible to estimate the origin of a surficial fluid (marine *versus* non-marine), and identify processes of adsorption onto clay minerals, evaporation, halite precipitation and halite dissolution.

3) The general chemistry of the Australian salt lakes indicate that the bulk of the salts are cyclic, originating from seawater. Halite precipitation and dissolution, gypsum precipitation, sulphate reduction, and alunite precipitation are among the different processes that have altered the original marine signature of the Australian brines, although it can still be recognized.

4) The cyclic origin of the salts in the Australian salt lakes and surface inland waters is also supported by boron isotope geochemistry. The $\delta^{11}B$ of these solution is either similar to seawater boron isotopic composition, or its value can be accounted for by a combination of adsorption and mixing with a large fraction of terrestrial water.

5) Although boron is considered a conservative element in evaporitive environments, this study shows that it can be removed from the liquid phase by reacting with clay minerals. The $\delta^{11}B$ and B/Cl ratios in a solution reflect boron reactivity with clays. The depletion of elemental boron and enrichment of ^{11}B relative to seawater are recorded in some Australian lakes and indicate removal of B and associated isotopic fractionation.

6) Lake Eyre (~100 km x 80 km) is located within a large continental basin, near the centre of the Australian continent. The basin contains evaporitic sediments such as gypsum and halite, and its brine chemistry and boron isotope composition are similar to that of evaporated seawater. All these factors do not necessarily indicate deposition in a marine environment or connection to seawater. This may have a general implication in interpretations of ancient evaporite environments. The possibility of the creation of "seas within continents" must therefore be considered in attempts to interpret palaeoenvironments.

Chapter 3

BORON ISOTOPE SYSTEMATICS IN THE FRACTIONAL EVAPORATION OF SEAWATER

3.1. INTRODUCTION

One of the main problems in the identification of the origin of ancient evaporites is the discordance between the mineralogical composition of potash evaporites and the mineralogical sequences predicted by the evaporation of seawater (HARDIE, 1984; 1990; LOWENSTEIN and SPENCER, 1990). In particular, the absence of $MgSO_4$ salts in evaporites from the geological record is in conspicuous contrast to the predicted paragenesis of marine evaporite minerals where $MgSO_4$ is the dominant component (HARVIE et al., 1980; HARDIE, 1984; 1990). Several explanations have been postulated in an attempt to understand this phenomenon among them are syndepositional and post-depositional modification processes (see LOWENSTEIN and SPENCER 1990).

HARDIE (1984; 1990) suggested that the $MgSO_4$-poor potash evaporites originated from terrestrial solutions in non-marine environments where the Ca-chloridic signature of their associated brines is a result of high-temperature water-rock interactions.

The distinctive isotopic composition of boron in seawater makes it an attractive geochemical tracer for discriminating marine from non-marine evaporites. Natural boron has two stable isotopes, ^{11}B (80.1%%) and ^{10}B (19.9%). Seawater is largely enriched in ^{11}B relative to average terrestrial rocks due to isotopic fractionations which occur while boron is taken from seawater onto detrital clays and weathered basalts (SCHWARCZ et al., 1969; SPIVACK and EDMOND, 1987; SPIVACK et al., 1987). The selective removal of ^{10}B and elemental boron into solid phases depends on the distribution of boron species in the solution . The relative proportions of boric acid and borate ion species in the solution controls the distribution coefficient and isotopic fractionation of boron in the processes of clay adsorption and precipitation of borate minerals (KAKIHANA et al., 1977; SPIVACK, 1986; PALMER et al., 1987; OI et al., 1989).

In order to evaluate the potential of boron-isotope geochemistry as a tracer for the origin of ancient evaporites, i.e. to define the "rules of the game", we chose to study laboratory evaporation of seawater. Numerous investigations have examined the variations of brines and salts during evaporation of seawater, both in artificial and natural conditions (e.g. ZHEREBTSOVA and VOLKOVA, 1966; McCAFFREY et al., 1987 and references therein). In this study we examined in laboratory controlled conditions the variations of B, Br, Li concentrations and boron isotopes in brines and precipitates during fractional evaporation of seawater.

3.2. EXPERIMENTAL

Two sets (Y and R series) of 20 litres of Mediterranean seawater were evaporated in fume-hoods, under clean conditions where the air was filtered. At various stages of evaporation, measured fractions of residual brines and all the precipitated salts were separated from the main brine reservoir for chemical and isotopic analyses. In each stage the residual brine was not allowed to interact with brines and salts of previous stages. The brines were filtered several times after separation and the precipitates were rinsed with ethanol, dried at 60°C and crushed. Further details of the technical procedures of the fractional evaporation of seawater and the general chemistry results are reported in RAAB and SPIRO (in prep.).

Negative thermal-ionization mass spectrometry techniques (VENGOSH et al., 1989) were used to determine boron isotopic compositions. Brines and H_2O-dissolved salts at the various stages of evaporation were directly deposited onto Re filaments and evaporated to dryness before loading into a reverse-polarity, NUCLIDE-type, solid-source mass spectrometer. 15 sample solutions, including NBS SRM 951 standard solutions, were simultaneously loaded and analysed in the mass spectrometer over a day or two. The long term 2-sigma standard error of NBS SRM 951 replicates is 1.5‰ at the 95% confidence limit. Boron abundances were determined by isotope dilution mass spectrometry (VENGOSH et al., 1989) and lithium by inductively coupled plasma (ICP) spectrometry.

3.3. RESULTS and DISCUSSION

The experimental evaporation of [illegible] Mediterranean seawater yielded progressively concentrated brines and soluble salts that are predicted for fractional evaporation of seawater (ZHEREBTSOVA and VOLKOVA, 1966; HARVIE et al., 1980; McCAFFREY et al., 1987). Results of B, Li, Br, and boron-isotope analyses of brines and salts are presented in Table 3.1. In the artificial experimental evaporation of seawater where the volume, boron concentrations and hence the amount of total boron in each of the evaporation stages are known, mass-balance calculations can evaluate the expected concentration of boron (or other conservative element) and hence the theoretical "absolute" degree of evaporation at different stages. The degree of evaporation of a brine can be expressed as the the ratios of a conservative element to its concentration in the initial solution, i.e. seawater. An error may be introduced into the mass-balance estimates due to the aliquots of the separate fractions which were taken for chemical analyses and measured by volume. Assuming that an element accumulates conservatively in the solution, and considering the amounts which were removed during the experiment for chemical analyses, one can calculate the "absolute" degree of evaporation. The mass-balance calculations for boron ("ε (B)"), lithium ("ε (Li)"), bromide ("ε (Br)") and the "absolute" degree of evaporation ("ε calc") are summarized in Table 3.1.

Bromine, lithium, and boron are considered as conservative elements in evaporation processes and thus were used in the past as indicators of the degree of evaporation, e.g. ZHEREBTSOVA and VOLKOVA (1966) and McCAFFREY et al., (1987). The concentrations of these elements do indeed increase with evaporation (Fig. 3.1); however, when the actual (=volumetric) evaporation of boron, lithium and bromide is compared to the expected (calculated) degree of evaporation of the experiments ("ε calc"), a deficiency of these elements in the late stages of evaporation (Fig. 3.2) is demonstrated. The measured and expected values remain on a line with a slope of 1 up to a degree of evaporation of about 40. With further evaporation, the degrees of evaporation

TABLE 3.1. Concentrations (in mg/l) of boron, lithium, bromide, and $\delta^{11}B$ values (in permil) in brines, and boron abundances (in ppm) and $\delta^{11}B$ values in co-precipitated salts during fractional evaporation of seawater. The calculated degree of evaporation (" ε calc ") is estimated by mass-balance. ε(B), ε(Li) and ε(Br) are degrees of evaporation calculated for B, Li and Br, respectively. The abbreviations for the salts precipitated from each aliquot are: ha=halite; mg=Mg sulfates; k,mg=K and Mg sulfates.

sample and field	B	Li	Br	$\delta^{11}B$	B	$\delta^{11}B$	ε calc	ε(B)	ε(Li)	ε(Br)
	brines				salts					
seawater	5.33	0.24	75	39	-	-	1	1	1	1
R-5 (ha)	53.17	-	630	41.7	-	-	9.5	9.9	-	8.4
Y-11 (ha)	82.82	-	1261	-	-	-	18.6	15.5	-	16.8
Y-13 (ha)	130.85	-	1681	-	-	-	25.8	24.5	-	22.4
Y-14 (ha)	158.63	7.00	1978	43.4	-	13.2	32.9	29.8	29.4	26.4
R-15 (ha)	152.77	-	2169	42.9	-	-	34.7	28.7	-	28.9
R-16 (mg)	192.29	8.29	2534	46.1	2.5	14.0	42.3	36.1	34.8	33.8
Y-15 (mg)	222.62	-	2766	-	-	-	47.2	41.8	-	36.9
Y-16 (mg)	266.38	10.63	3254	44.1	8.5	11.4	54.8	49.9	44.7	43.4
Y-17 (mg)	369.11	14.41	4580	46.5	16.4	24.2	82.1	69.3	60.6	61.0
R-18 (k,mg)	603.50	23.69	7080	54.7	38.5	36.0	155.7	113.2	99.6	94.4

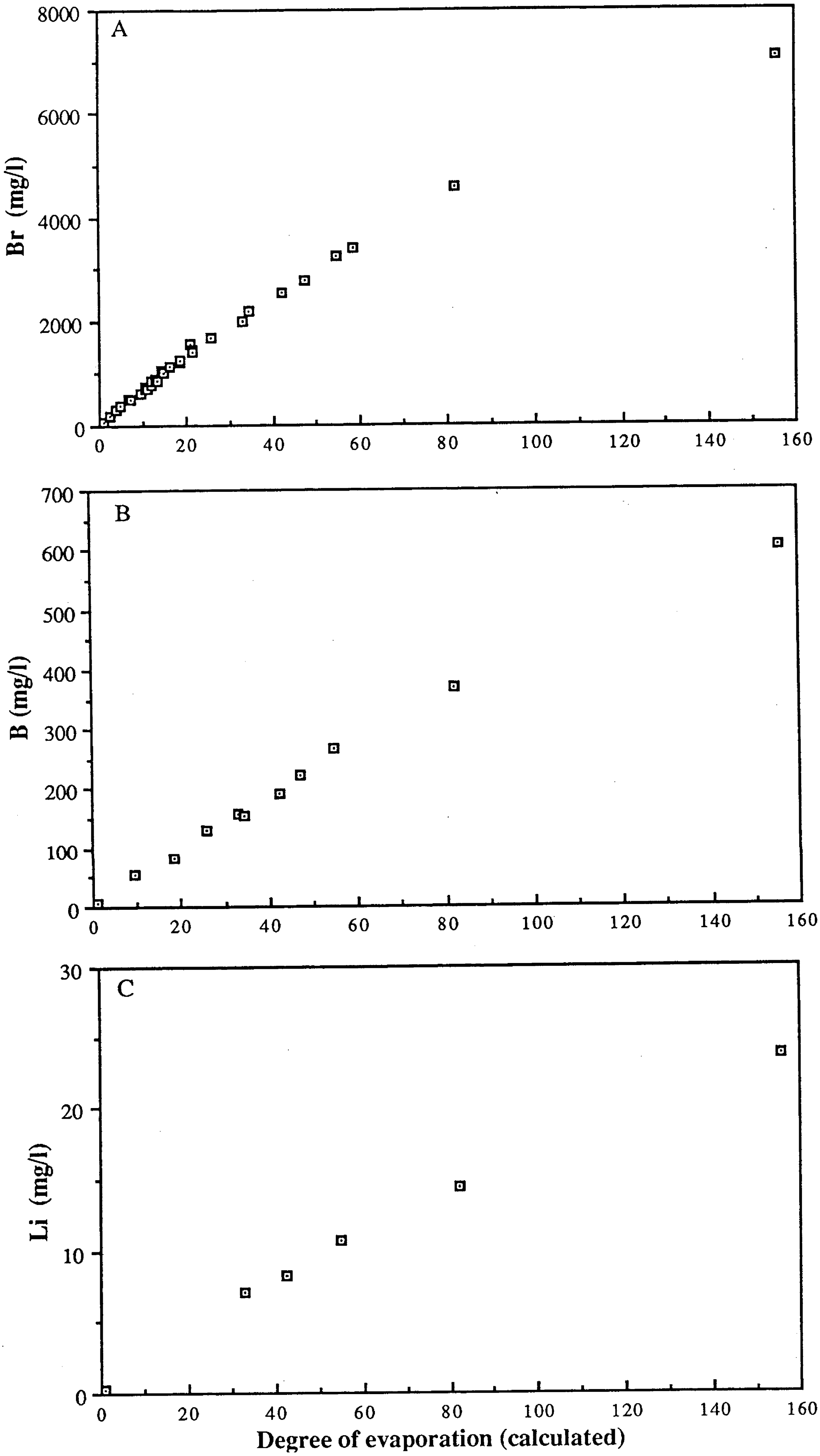


Figure 3.1. Concentrations of bromine (A), boron (B), and lithium (C) *versus* the calculated degree of evaporation during the fractional evaporation of seawater.

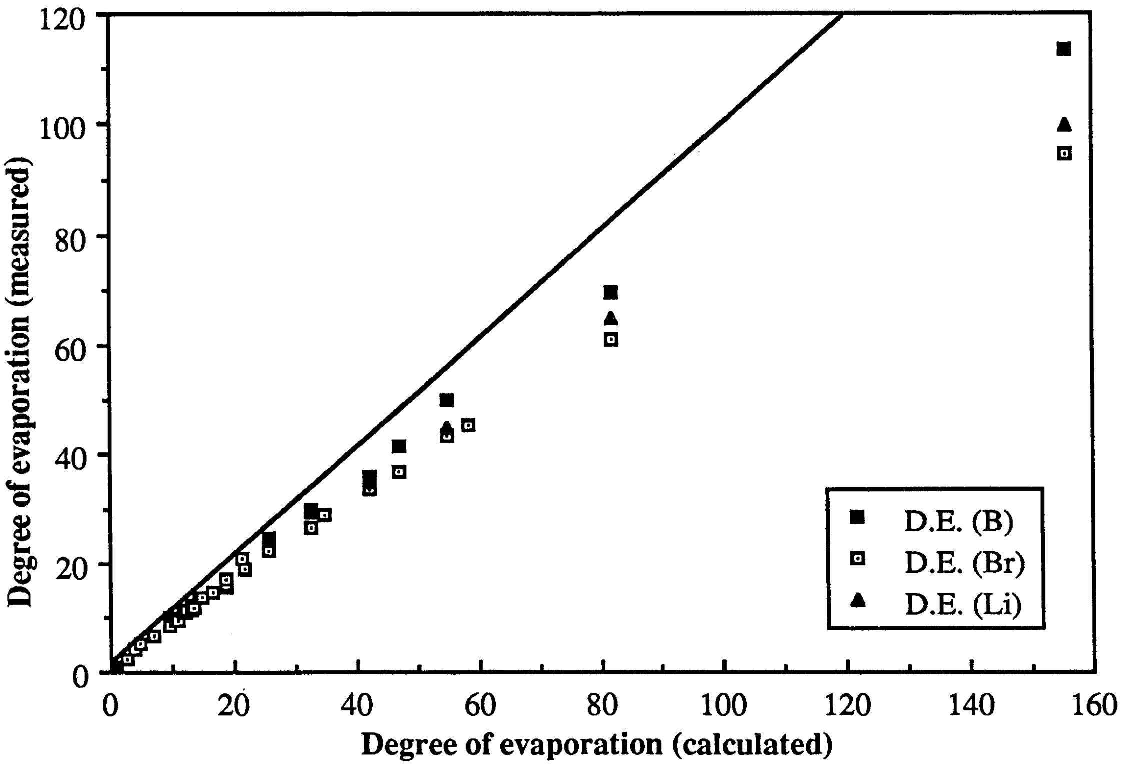


Figure 3.2. Measured *versus* calculated degree of evaporation (D.E.) of B, Br and Li in marine brines. The theoretical degree of evaporation was calculated by mass balance, assuming that the conservative elements in the evaporation experiment do not enter the solid phases. Note the depletion of B, Li and Br relative to the expected ("absolute") degree of evaporation in brines beyond a degree of evaporation of about 40.

as determined from the B, Li and Br abundances deviate negatively from that line. The three elements are thus not truly conservative - they do not accumulate solely in the liquid phase. In the late stages of evaporation, the measured apparent degree of evaporation of boron is higher than for lithium, which is, in turn, higher than for bromine (Fig. 3.2), yet considerable amounts of all these elements are lost to the solid phases.

The gradual increase of $\delta^{11}B$ values of the brines (up to 54.7‰), the relatively low $\delta^{11}B$ values of the coprecipitated salts ($\delta^{11}B$= 11.4 to 36.0‰; Fig. 3.3), the gradual increase of B content of the salts, and the relative depletion of B in the brines during the fractional evaporation of seawater suggest incorporation of some boron into the precipitates. An alternative mechanism for boron (and Br and Li) removal is trapping in fluid inclusions within the salts. Such mechanism, however, cannot affect the boron isotopic compositions of both the brines and the co-precipitated salts. Fractionation of boron isotopes during fractional evaporation of seawater can be described by using Rayleigh distillation terminology:

$$(\delta^{11}B_b+1000) = (\delta^{11}B_{sw}+1000)\ F^{\alpha-1} \qquad (1)$$

where $\delta^{11}B_b$ and $\delta^{11}B_{sw}$ are the $\delta^{11}B$ values of the brines at different stages of evaporation and the initial seawater, respectively; F is the fraction of boron remain in the solution and α is the "effective" isotopic fractionation that can be defined as

$$\alpha = (\delta^{11}B_s+1000) / (\delta^{11}B_b+1000) \qquad (2)$$

where $\delta^{11}B_s$ is the $\delta^{11}B$ of the precipitating salts .

Applying Equation (2), the empirical isotopic fractionation factor for the bulk of the precipitates during evaporation of seawater is estimated as 0.974±0.006 (n=5, Table 3.1).

The distribution of boron species, i.e. the ionization of boric acid and the formation of borate ion-pairs (e.g. $MgB(OH)_4^+$) is dependent on the pH, ionic strength and chemical composition of the solution (BRYNE and KESTER, 1974; REARDON, 1976; HARSHEY et al., 1986; ROGERS and VAN DEN BERG, 1988). HARSHEY et al. (1986) have shown that with increasing ionic strength (up to 6 molar) the pK* values of boric acid increase, i.e. the fraction of boric acid in the solution increases. As the pH

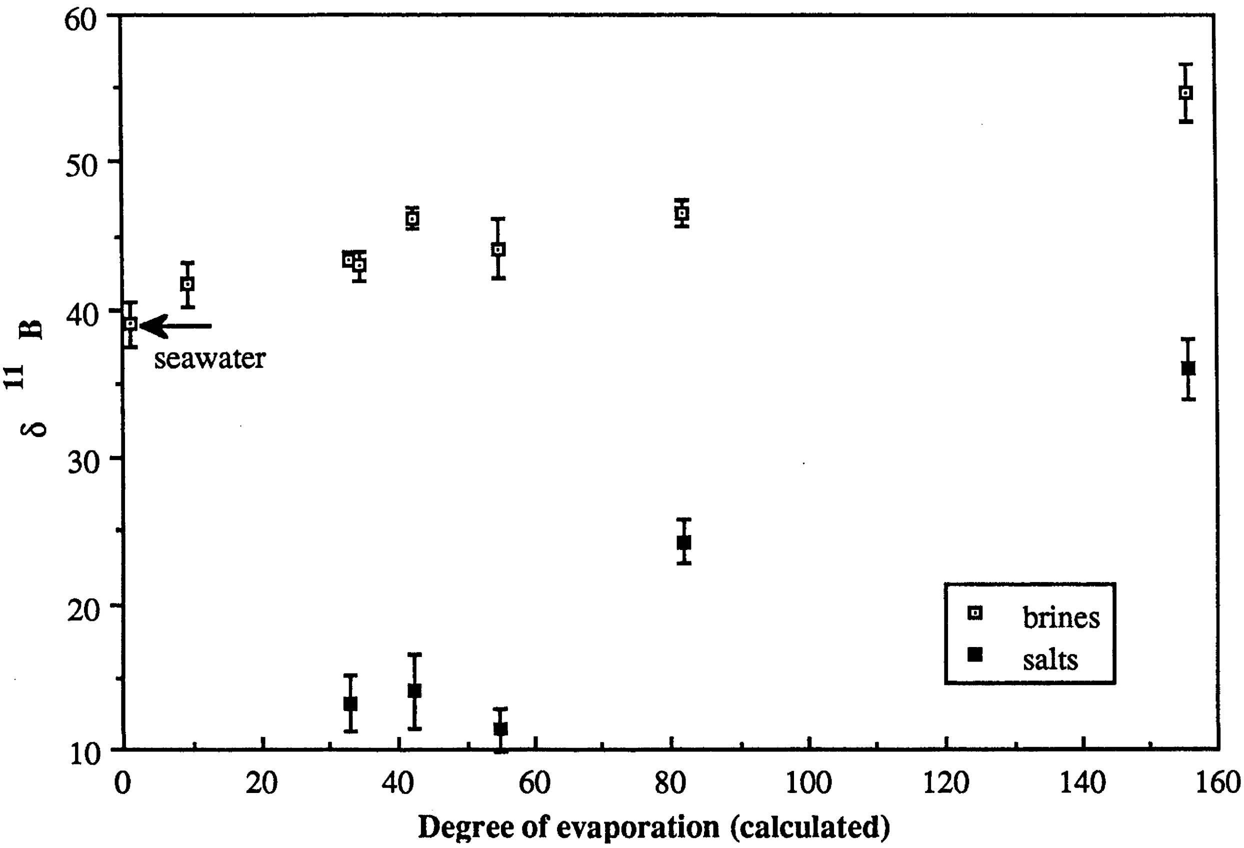


Figure 3.3. $\delta^{11}B$ values of evaporated seawater (open squares) and coexisting precipitated salts (filled squares) *versus* the degree of evaporation for the experimental fractional evaporation of seawater. Note the relative enrichment and depletion of ^{11}B of the brines and the salts for degrees of evaporation beyond 30.

of seawater decreases with evaporation (ZHEREBTSOVA and VOLKOVA, 1966; McCAFFREY et al., 1987), AKSENOVA et al. (1989) have demonstrated that during evaporation of seawater the predominant form of dissolved boron is boric acid (99.9%).

KAKIHANA et al. (1977) and OI et al. (1989) suggested that the distribution of boron isotopes between two chemical species depends on the isotopic reduced partition function ratios ("f*") of the species. The heavier isotope, ^{11}B is preferentially fractionated into the species with the larger f* values. The f values of $B(OH)_3$ and $B(OH)_4^-$ species have been calculated experimentally by KAKIHANA et al. (1977) as 1.2008 and 1.1780 respectively, at 25^0C, i.e., $B(OH)_3$ species would be enriched in ^{11}B relative to $B(OH)_4^-$.

The respective enrichment and depletion of ^{11}B in the brines and precipitates, during fractional evaporation of seawater (Fig. 3.3) may be related to the isotopic fractionation between boron species. While boron in the solution is mainly composed of boric acid and hence tends to be enriched in ^{11}B, it seems that the borate ion (together with ^{10}B) is preferentially removed from the solution and incorporated in the precipitated salts.

The calculated fractionation factor (α) for the isotopic exchange of $B(OH)_3$ and $B(OH)_4^-$ species at 25^0C is 0.981 (KAKIHANA et al., 1977), or 0.969, (PALMER et al., 1987). Applying Equation (1) and the fractionation factors suggested by KAKIHANA et al. (1977), PALMER et al. (1987), and determined by the brine-salt pairs (Equation 2), the fractions of boron remain in the solution (F) at different degrees of evaporation are solved and illustrated in Fig. 3.4. The fractionation factor obtain in this study (an average of 0.974 ± 0.006) is similar in sign and magnitude to that suggested by KAKIHANA et al. (1977) and PALMER et al. (1987). At a degree of evaporation of 155, about half the quantity of boron is removed by precipitating salts (Fig. 3.4).

VALYASHKO (1970; and references therein) has shown that during evaporation of seawater boron is precipitated mainly in the form of magnesium chloroborate which in diagenesis is converted to boracite ($Mg_3Cl[B_7O_{13}]$). In addition, AKSENOVA et al. (1989) have demonstrated that borate minerals can crystallize from evaporated seawater that has not yet reached the eutonic state. Evaporated seawater at the

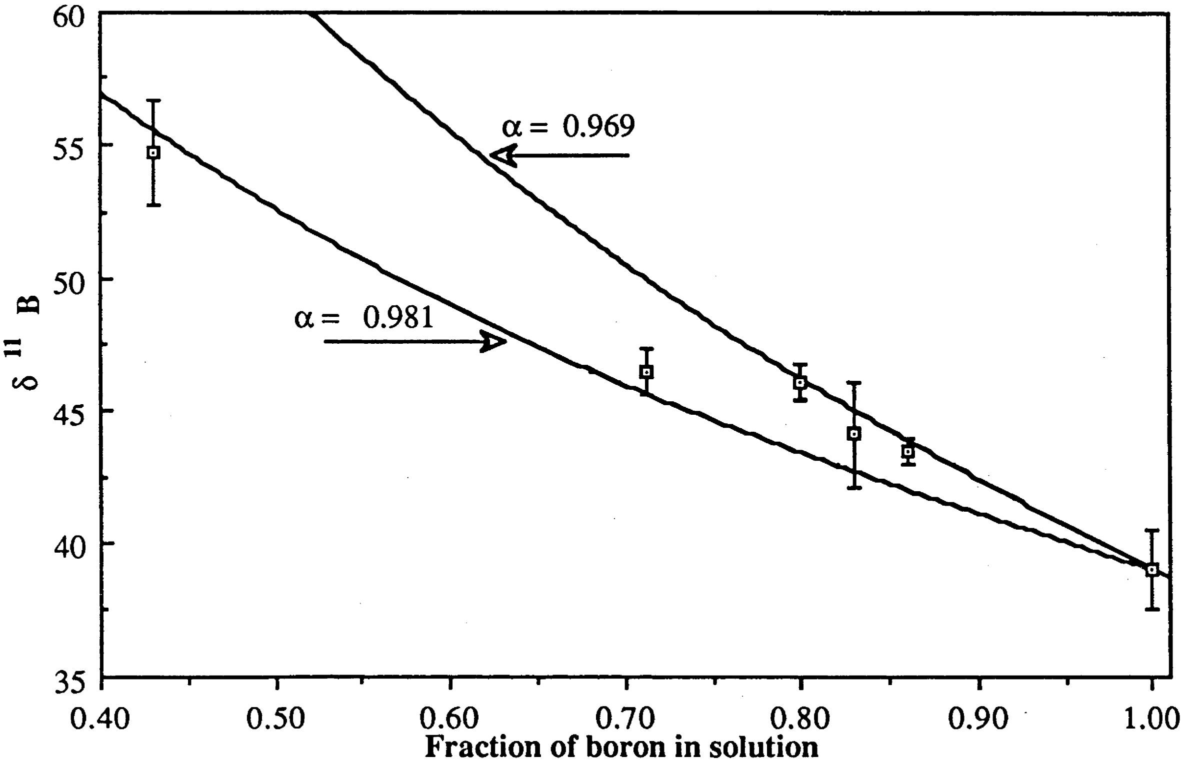


Figure 3.4. The $\delta^{11}B$ values of residual seawater *versus* the calculated fraction of boron remaining in solution during the fractional evaporation of seawater. The two lines were calculated using the fractionation factors suggested by KAKIHANA et al. (1977) (0.981) and PALMER et al. (1987) (0.969). The data points were calculated by the fractionation factor obtained from the salt-brine pairs.

stages where magnesium sulfate and potash salts are deposited, are close to saturation with respect to various Mg-borate minerals (ascharite, kaliborite, and pinnoite) (AKSENOVA et al., 1989). The mechanism of boron removal from the highly evaporated seawater may therefore be by direct precipitation of Mg-borate minerals and/or formation of a magnesium-borate ion pair ($MgB(OH)_4^+$) and coprecipitation with the salts. This is consistent with the coordination number of four of boracite (VALYASHKO, 1970) which allows the preferential removal of $B(OH)_4^-$ and hence ^{10}B. Other borate phases with atomic configurations which include both boron species (OI et al., 1989) cannot exclusively remove ^{10}B from the solution.

3.3.1. Applications for tracing the origin of evaporites

The large fractionation of boron isotopes during late stages of evaporation of seawater can place additional constraints on the geochemical application of this tracer. It has been shown that the high reactivity of boron and the preferential incorporation of ^{10}B into clay minerals would increase the $\delta^{11}B$ value of a solution where low water/sediment ratios pertain. Also brines with high $\delta^{11}B$ values in non-marine locations can be derived from marine-origin atmospheric salts, as demonstrated for some Australian salt lakes (Chapter 2).

The results reported in this study indicate that high $\delta^{11}B$ values in brines can also be the result of isotopic fractionation associated with the incorporation of boron into evaporite minerals. This constraint, however, is limited to evaporite systems with very high degrees of evaporation; so high , that they are relatively scarce in the geological record. In contrast, in evaporite environments where the brines have evolved only to the stage where halite is precipitated, the isotopic composition of boron is not controlled by evaporation processes (see Chapter 2)

The relationship between the "conservative" elements (B, Li, Br) and $\delta^{11}B$ can be used to infer the origin of brines. As shown in Fig. 3.2 the degree of conservation during evaporation of seawater is in the order of B>Li>Br, i.e., boron is the most conservative. One can reconstruct the history of a brine by using these parameters. Brines with high $\delta^{11}B$ values (higher than that of seawater) associated with marine or higher ratios of B/Li, must have evolved from seawater through evaporation and precipitation of potassium and magnesium salts (and/or borate minerals). In contrast, brines with high $\delta^{11}B$ values that are associated with low B/Li or B/Cl ratios indicate preferential removal of boron via isotopic fractionation and hence interaction with clay minerals. The latter case is demonstrated in the evolution of the Dead Sea, Israel. High $\delta^{11}B$ values in the range of 50‰ to 56‰, low B/Li and B/Cl, high Li/Cl and Br/Cl, marine Li/Br ratios, and marine $\delta^{7}Li$ values of the surface brine of the Dead Sea may indicate that (1) the salts in the Dead Sea were derived from seawater, probably the Pliocene Mediterranean; and (2) boron has been partially removed by adsorption onto clay minerals (Chapter 5).

During fractional evaporation of seawater, the salts are depleted in their $\delta^{11}B$ values by 26±6‰ (1000 ln α) relative to their coexisting brines. This difference can also be a useful tool in deducing the origin of evaporite deposits. The boron isotope composition of potassium- and magnesium chloride minerals should reflect therefore the isotopic composition of their parent brines. In the case of the Dead Sea, which is enriched in ^{11}B (Chapter 5), one would expect also precipitation of ^{11}B-enriched salts, with $\delta^{11}B$ values of 30±6‰. However, a carnallite sample from a core at Mt. Sdom, adjacent to the Dead Sea (see Fig. 5.1, Chapter 5), has a $\delta^{11}B$ value of 12.7±1.5‰. The $\delta^{11}B$ value of the carnallite suggests that it was precipitated from a brine with $\delta^{11}B$ value of 39‰, i.e. seawater, and confirms its marine origin, e.g. ZAK (1967). Consequently the boron isotopic composition of the investigated carnallite puts an additional constraint on the evolution of the Dead Sea. Assuming that the boron isotopic composition of the buried carnallite has maintained its original signature, i.e., has not been affected by recrystallization, the low $\delta^{11}B$ value may indicate that adsorption processes (that caused the high $\delta^{11}B$ values of the Dead Sea; Chapter 5) occurred largely after the deposition of potash salts in Mt. Sdom.

It is suggested that the isotopic fractionation of boron that is related to salt precipitation at the extreme stages of evaporation controls the boron isotope variations in evaporite environments. Halogenesis of seawater ($\delta^{11}B$ = 39‰) and terrestrially derived brine ($\delta^{11}B$ = 0±5‰), in a closed system would result an appreciable enrichment and depletion of the evaporated brines and precipitated salts in ^{11}B, respectively, relative to their parent solutions. Assuming an α of 0.974±0.006, the marine and non-marine brines would have $\delta^{11}B$ values in the ranges of 39‰ to 55‰, and 0‰ to 16‰, whereas the coexisting marine and terrestrial precipitates would have $\delta^{11}B$ values of 11‰ to 36‰ and -26‰ to 0‰, respectively. The predicted range of $\delta^{11}B$ values for marine and non-marine salts overlap respectively with those of marine and non-marine borate minerals, reported in SWIHART et al. (1987) and OI et al. (1989) (Fig 3.5).

OI et al. (1989) suggested that the boron isotopic composition of borate salts is related to their atomic configuration, i.e. the proportion of boron species in the mineral. Boron minerals can be composed of 100%-BO_4 (boracite), 66%-BO_4 (colemanite), 60%-BO_4 (ulexite), and 50%-BO_4 (borax), and hence always depleted in ^{11}B relative to their parent brines that are predominantly composed of boric acid, e.g. AKSENOVA et al. (1989). Consequently, $\delta^{11}B$ variations of borate salts in the geological record are related both to the boron isotopic composition of their parent brines and to the fractionation of boron isotopes (Fig. 3.5).

Selective uptake of ^{10}B by borate salts can also explain the conspicuously low $\delta^{11}B$ of non-marine borates ($\delta^{11}B$= -30‰ to 8‰; SWIHART et al., 1987) and of some tourmalines ($\delta^{11}B$ as low as -22.8‰; SLACK et al., 1989; PALMER and SLACK, 1989), relative to the $\delta^{11}B$ value of the continental crust ($\delta^{11}B$=-3±5‰; SPIVACK, 1986). If the ^{11}B-depleted tourmalines originated from non-marine borates (SLACK et al., 1989; PALMER and SLACK, 1989) their boron-isotope signature may reflect early, low-temperature, isotopic fractionation of boron.

In conclusion, by using the boron isotopic signature in potassium- and magnesium salts one can reconstruct the origin of ancient salt deposits and the nature (marine versus non-marine) of their parent brines.

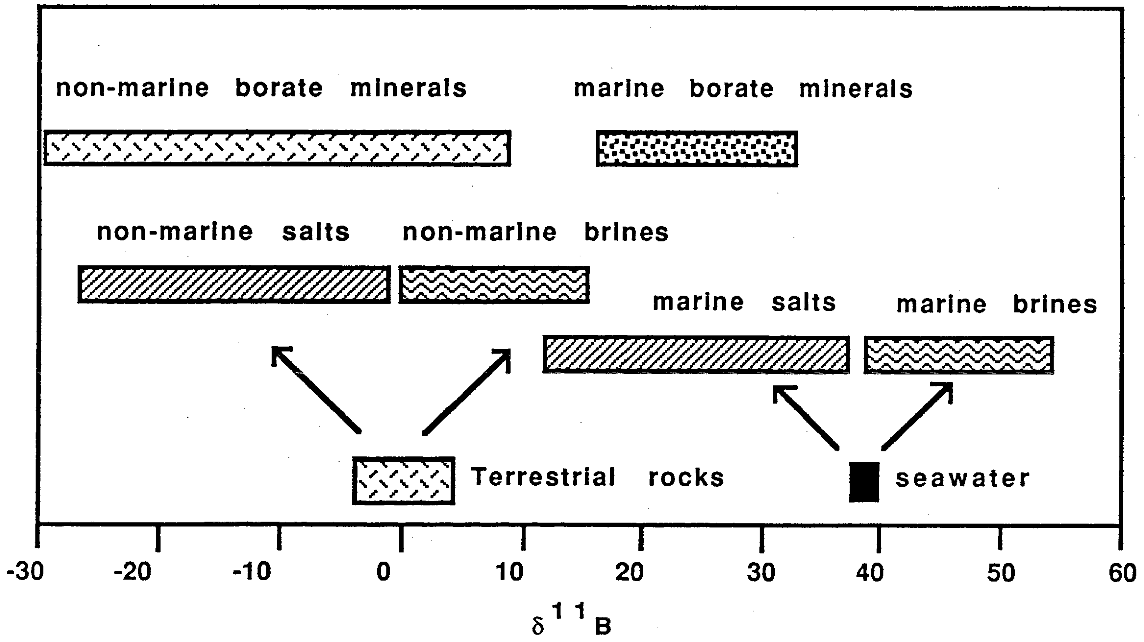


Fig. 3.5 Predicted $\delta^{11}B$ variations of marine brines, marine salts (magnesium- and potassium sulphate minerals), non-marine brines, and non-marine salts, assuming a fractionation factor for salt precipitation from brine of 0.974. The model considers evolution of marine and non-marine brines in closed systems, in a manner that is similar to the seawater-evaporation experiment. Boron in non-marine original solution is derived from the terrestrial crust ($\delta^{11}B$=-3±5‰; SPIVACK, 1986). Note the respective overlap of the predicted $\delta^{11}B$ values of the marine and non-marine salts with those of marine and non-marine borate minerals, reported in SWIHART et al. (1987) and OI et al. (1989).

Chapter 4

BORON ISOTOPE GEOCHEMISTRY OF NON-MARINE BRINES FROM THE QAIDAM BASIN (CHINA)

4.1. INTRODUCTION

Although salt lakes from terrestrial environments are not abundant in the geological record, the characterization of such deposits has important tectonic applications such as the identification of initial rift valley proto-oceans (HARDIE, 1984; KINSMAN, 1975; EVANS, 1978). The Eocene Green River Formation with its valuable trona and oil-shale deposits (BRADLEY, 1964; BRADLEY and EUGSTER, 1969; EUGSTER and HARDIE, 1973) and the Quaternary deposits from The Great Basin, Mojave Desert (HARDIE, 1968; JONES, 1966) are good examples of typical non-marine environments. Yet, the chemical composition of some non-marine brines and their associated minerals are not different from that of evaporated seawater and marine salts, giving additional uncertainties in distinguishing marine from non-marine evaporites (HARDIE, 1984).

The chemical and isotopic composition of brines in modern closed basins contain valuable information on the origin of the salts and evaporation processes. The interpretation of the depositional environment of ancient evaporites can therefore be based on their modern equivalents where the depositional conditions are known.

The large variations in $^{11}B/^{10}B$ ratios in nature and particularly the distinctive isotopic composition of boron in seawater relative to that of the terrestrial crust makes boron isotope geochemistry a potential candidate for tracing the origin of evaporites (SCHWARCZ et al., 1969; SWIHART et al., 1986). As part of a study of boron isotopes in modern non-marine environments, the general chemistry and boron isotope geochemistry of the Qaidam Basin have been investigated.

The Qaidam Basin located in the northern Qinghai-Xizang (Tibet) Plateau, China, is a typical 'terrestrial basin' that has evolved since the Jurassic (CHEN KEZAO and BOWLER, 1986). Brines from the basin are characterized by high salinity and extremely high potassium, boron and lithium contents, several orders of magnitude higher than those of evaporated seawater (QIAN ZIQIANG and XUAN ZHIQIANG, 1985).

Several early studies analysed the boron isotopic composition of modern or near-modern borate deposits from non-marine environments (PARWEL et al., 1956; FINLEY et al., 1962; McMULLEN et al., 1961). However, due to analytical difficulties contradictory results were reported. SWIHART et al., (1986) interpreted the origin of ancient borates according to their boron isotope composition. They distinguished ancient evaporite borates with high $\delta^{11}B$ values (18.2 ‰ to 31.7‰) and low $\delta^{11}B$ values (-21.9‰ to 0.3 ‰), and attributed the enrichment of ^{11}B in the borates to their marine origin.

This chapter attempts to monitor water composition from dilute inflows to concentrated brines in the Qaidam Basin. We analyse different geochemical tracers, including boron isotopes, in an attempt to use these parameters as geochemical tools to investigate the origin of salts.

4.2. THE QAIDAM BASIN

The Qaidam Basin is located in the northern margin of Tibet Plateau (Fig. 4.1) at an elevation of 2800 m. Surrounded by high mountains (up to 5000 m), the large basin is isolated from oceanic air masses and has a mean annual precipitation of 25 mm to evaporation of 3000 mm. Streams draining snow-capped mountains to the basin margin terminate in a series of saline lakes. The area lies within a region of strong northwesterly winds that transport large quantities of loess (BOWLER et al., 1986). The basin consists of clastic sediments, salt lakes and dry playas. The geological history of the basin is well reviewed in CHEN KEZAO and BOWLER (1986): the modern deposits in the Qaidam Basin are underlain by a thick pile of sediments. Continental sedimentation has continued since the earliest known deposits, dated as Jurassic, that are composed of coal units and clastic red beds. These deposits are unconformably overlain by fluviatile Lower Tertiary sediments. During the Neogene, Miocene and Pliocene, lacustrine environments are recorded and the accumulation of sediments in the basin was mainly controlled by

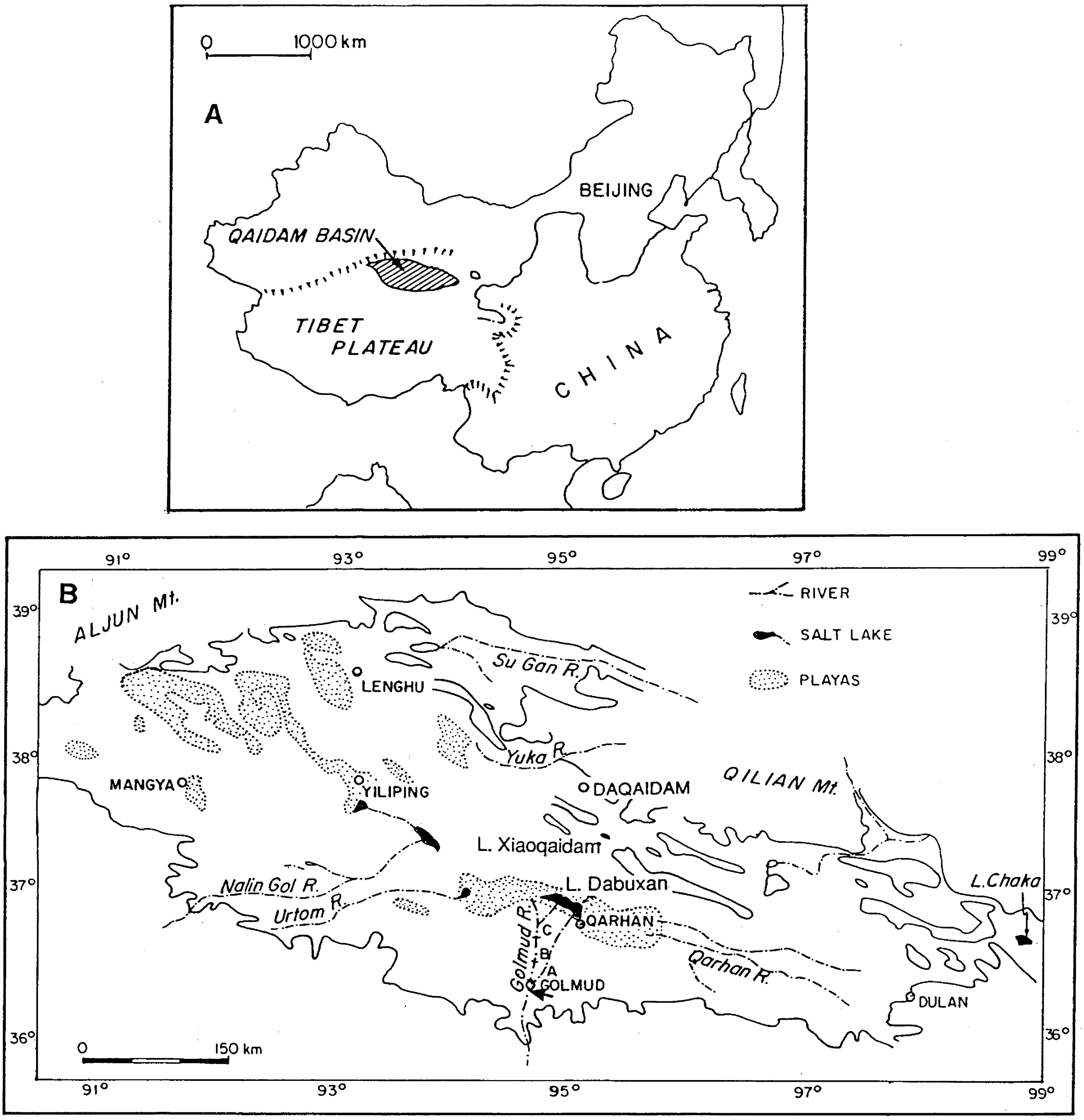


Figure 4.1. Location map of A) the Qaidam Basin on the northern margin of Qinghai-Xizang (Tibet) Plateau; B) salt lakes and rivers sampled from the Qaidam Basin. Note the location of samples Q-35, Q-37, and Q-38A marked respectively as A, B, and C in the Golmud River.

intensive tectonic activity, including the rapid rise of the Tibet Plateau. By the end of the Pliocene thick (1000 m) evaporitic sulphate and chloride deposits record the major shift in climate conditions. Late Pleistocene mudstone, sandstone and conglomerates mark the shorelines of an elongate mega-lake (500 km by 100 km) from which evolved the modern salt lakes (CHEN KEZAO and BOWLER, 1986).

In September 1987 a series of samples from the Qaidam Basin were collected by A. R. CHIVAS. The general data, description and locations of the samples are in Table 4.1 and Fig. 4.1. The samples can be subdivided into different groups: (1) granitic rocks from the mountains on the margin of the Qaidam Basin; (2) fresh, saline and hypersaline fluids associated with the Qaidam Basin, referred to as "input water". These are the Daqaidam hot spring in the north of the basin near Daqaidam town and the Golmud River sampled at several locations in the south of the basin, near and north of the town of Golmud (marked as A, B and C in Fig. 4.1). At site C the river transverses salt-laden soils and the river waters (sample Q-38A) are saline. The brine from the "karst pond" in the Qarhan playa represents also an input of deep subsurface brine that has risen to the surface along faults (LOWENSTEIN et al., 1989) and formed karst-like sink-holes in the massive halite crust; (3) natural brines from salt lakes in the Qaidam Basin. These are Lake Chaka, Lake Xiaoqaidam and Lake Dabuxan in the Qarhan playa (Fig. 4.1); and (4) brines from artificial ponds from the Qarhan Salt Works. In a series of industrial ponds, the brines are concentrated and precipitated as a series of progressively more soluble minerals (halite, carnallite and bischofite).

Lake Dabuxan, fed by waters of the Golmud River, lies within a large salt-flat known as the Qarhan salt crust in the centre of the Qaidam Basin (Fig. 4.1). This is the largest playa lake in China, extending 150 km in a NW-SE direction (BOWLER et al., 1986). The halite flat is underlain by up to 60 m of Holocene halite beds which in turn is underlain by thick lacustrine deposits that represent a freshwater and slightly saline environment formed under a relatively humid climate. The Holocene halite beds occur with interbedded clastic sediments, composed of quartz, micas, feldspar, illite and chlorite. A large fraction of the detrital sediment is composed of loessic deposits. The uppermost halite layer consists of potassium salts (sylvite and carnallite) in addition to

Table 4.1. Location, temperature, pH, and density of water samples from the Qaidam Basin.

sample	location and description	date of collection	T(^{o}C)	pH	density (g/cc)
input water					
Q-22	Daqaidam hot spring, north of Daqaidam town	23/9/87	29.2	7.32	1.001
Q-35	West Golmud River, south of Golmud town	24/9/87	9.5	8.46	1.001
Q-37	East Golmud River, at Xiaoqao, 23 km north of Golmud town	24/9/87	12.5	8.58	1.001
Q-38A	East Golmud River, 35 km north of Golmud town	25/9/87	-	7.93	1.027
Q-19	"Karst pond", 30 km north of Qarhan, brine from natural pond	22/9/87	15.9	6.46	1.217
Artificial ponds from Qarhan Salt Works					
Q12-A	inlet (natural) brine	21/9/87	14.0	6.31	1.236
Q12-B	brine from artificial "halite" pond	21/9/87	15.9	6.01	1.257
Q12-C	brine from artificial "carnallite" pond	21/9/87	11.2	5.82	1.281
Q12-D	waste brine from artificial "carnallite" pond	21/9/87	21.7	4.94	1.345
Q-42	brine from artificial "bischofite" pond	24/9/87		4.94	1.359
Q-41	final stage brine (bitterns)	24/9/87		4.79	1.357
Salt lakes					
Q-9	brine from Lake Chaka	20/9/87	12.2	6.92	1.253
Q-13	brine from Lake Dabuxan in Qarhan playa	21/9/87		5.58	1.301
Q-30	brine from Lake Xiaoqaidam	23/9/87		7.75	1.221

halite, gypsum (2-6%) and carbonate (2-8%) . The carbonate consists predominantly of low-magnesium calcite, dolomite and minor traces of aragonite and magnesite (CHEN KEZAO and BOWLER, 1986). The inlet brine at the Qarhan Salt Works (sample Q12-A) is a natural brine which seeps from channels cut in the Holocene Qarhan salt crust.

Lake Xiaoqaidam (sample Q-30) is a small lake on the northern basin margin (Fig. 4.1) fed by artesian springs and south-flowing streams. Sedimentary borate bodies, composed mainly of pinnoite and ulexite, associated with halite, gypsum and mirabilite ($NaSO_4 \cdot 10H_20$) occur at the bottom of and within the shoreline of the lake. A boron extraction industry is located at Lake Xiaoqaidam (BOWLER et al., 1986, QIAN ZIQIANG and XUAN ZHIQIANG, 1985).

Lake Chaka (sample Q-9) is located in an inter-montane sub-basin at the eastern margin of the Qaidam Basin (Fig. 4.1).

4.3. RESULTS

The general chemistry and the isotopic composition of boron of the solutions sampled from the Qaidam Basin are presented in Table 4.2. The charge balance (in equivalents) of the brines are in the range of of -3% to 3 %. The freshwater and saline samples have positive electrical imbalances that represent the HCO_3^- component which was not analysed in this study. For the less saline waters, approximate estimates of the HCO_3^- contents are given (Table 4.2) based on a restoration of charge balance. The implied high HCO_3^- contents are consistent with the values reported by LOWENSTEIN et al. (1989). The boron isotopic composition of granitic rocks from the margin of the Qaidam Basin are reported in Table 4.3. Several geochemical parameters of the different solutions are summarized in Table 4.4.

Input waters

The Daqaidam hot spring (Q-22) and Golmud River samples south and north of Golmud town (samples Q-35 and Q-37, respectively, marked as "A" and "B" in Fig. 4.1)

TABLE 4.2. Chemical and isotopic composition of waters and brines from the Qaidam Basin.

sample	$\delta^{11}B$ (‰)	Na	K	Ca	Mg	Cl	Br	SO_4	HCO_3*	B	Li	Sr	TDS**
						fresh and saline water (mg/kg)							
Input waters													
Q-22, Daqaidam Hot Spring	3.9	337.0	16.3	28.4	10.6	358.3	9.1	195.0	(229)	39.9	3.48	0.30	122
Q-35, Golmud River	0.2	69.6	3.0	36.6	31.5	95.1	3.7	67.0	(211)	0.8	0.04	0.44	520
Q-37, Golmud River	-0.7	185.0	8.3	28.6	66.8	256.2	4.2	143.0	(309)	1.3	0.09	0.54	990
Q-38, Golmud River	9.6	10546.0	191.1	702.0	1018.0	16668.0	40.1	4486.0	(1357)	11.9	1.28	35.7	35096
						brines (g/kg)							
Q-19, Karst Pond	10.9	55.17	1.96	13.06	19.60	168.47	0.057	0.44	-	0.033	0.005	0.317	244.4
Artificial ponds from the Qarhan Salt Works													
Q12-A, Inlet brine	15.0	28.98	15.33	0.65	42.88	182.89	0.046	3.38	-	0.080	0.023	0.016	274.3
Q12-B, Halite Pond	10.7	15.24	19.58	0.49	54.00	198.07	0.151	3.75	-	0.105	0.029	0.020	291.4
Q12-C, Carnallite Pond	10.7	6.79	12.70	0.21	66.69	216.24	0.065	4.32	-	0.140	0.035	0.016	307.2
Q12-D, Carnallite Pond	14.6	1.17	14.52	0.03	88.88	255.38	0.131	8.86	-	0.243	0.076	0.001	369.3
Q-42, Bischofite Pond	10.9	1.17	0.61	0.02	92.56	248.08	1.288	17.84	-	0.505	0.210	0.001	362.3
Q-41, Final Pond	10.5	1.14	0.59	0.02	92.59	251.16	1.256	16.56	-	0.536	0.233	0.001	364.1
salt lakes													
Q-9, Lake Chaka	7.1	36.53	8.29	0.12	42.59	153.97	0.099	42.35	-	0.064	0.014	0.008	284.0
Q-13, Lake Dabuxan	12.5	3.12	3.22	2.02	74.89	236.85	0.083	0.01	-	0.182	0.044	0.068	320.5
Q-30, Lake Xiaoqaidam	0.5	91.43	1.15	0.22	3.46	114.11	0.044	56.77	-	0.278	0.009	0.009	267.5

(*) HCO_3^- contents are estimates only, based on electrical balance;

(**) Total dissolved solids, including calculated HCO_3^-;

Table 4.3. Abundance and isotopic composition of boron from granitic rocks from the Qaidam Basin.

sample	Location and description	B content (ppm)	$\delta^{11}B$ (‰)
Q-25	near Daqaidam hot spring, coarse feldspathic granite	15.0	-2.4±1.9
Q-43	41 km east of Golmud town at altitude of 2960m	14.0	3.7±2.0
Q-44	276 km east of Golmud town (9km west of Xiang Ri De town)	14.6	3.6±2.3

are solutions with a very low TDS. The salinity of the Golmud River (Q-38A), sampled 35 km north of Golmud Town, towards Qarhan, is higher (TDS of 33.7 g/l; Fig. 4.2.A). The 'karst pond' that represents subsurface brine, is a hypersaline brine with TDS of 244 g/l. The chemical compositions of the freshwaters (Tables 4.2 and 4.4) are characterized by relatively high Na^+, Mg^{2+}, Ca^{2+}, K^+, SO_4^{2-}, HCO_3^-, Br^-, Li^+ and boron to chlorine ratios. The $\delta^{11}B$ values of the freshwaters from the Golmud River and the Daqaidam hot spring (-0.3±0.6‰ and 3.9‰, respectively) overlap with the $\delta^{11}B$ values of the granitic rocks associated with the Qaidam Basin ($\delta^{11}B$= -2.4‰ to 3.7‰, Table 4.3).

The progressive downstream increase in the salinity of the Golmud River is also accompanied by changes in the chemical composition of the river water (Table 4.4):

(1) The Na+Cl/TDS ratios (in equivalents) increase from 0.49 to 0.81 as the solution is modified to a Na-Cl type;

(2) The Na/Cl (molar) ratio decreases from 1.13 to 0.97 (Fig. 4.2.B);

(3) All ion/chlorine ratios (Mg/Cl, Ca/Cl, K/Cl, SO_4/Cl, HCO_3/Cl Br/Cl, Li/Cl, and B/Cl) decrease;

(4) The Ca/Mg and Ca/SO_4 ratios decrease;

(5) The Ca/HCO_3 ratio increases; and

(6) The B/Li ratio decreases and the $\delta^{11}B$ values increase from 0‰ to 9.6‰.

The brine from the karst pond is also of a Na-Cl type, characterized by a high Ca/SO_4 ratio and low Na/Cl, Br/Cl, Li/Cl and B/Cl ratios (Fig. 4.2).

TABLE 4.4. Ionic ratios of modern seawater and the investigated waters and brines from the Qaidam Basin. All ratios are molar, except the Na+Cl/TDS ratios that are in equivalents.

sample	Na+Cl / TDS	Na/Cl	Mg/Cl	K/Cl	Ca/Cl x10-3	SO_4/Cl x10-3	Br/Cl x10-3	B/Cl x10-3	Li/Cl x10-3	Ca/SO4	B/Li
seawater	0.84	0.86	0.10	0.02	19	52.0	1.5	0.8	0.05	0.36	14.4
input waters											
Q-22 d.h.s.	0.69	1.45	0.04	0.04	70	193.0	11.0	365	50.0	0.36	7.3
Q-35 river	0.49	1.13	0.48	0.03	341	250.0	17.0	28	2.3	1.36	12.1
Q-37 river	0.60	1.11	0.38	0.03	99	198.0	7.3	17	1.8	0.49	9.5
Q-38A river	0.81	0.97	0.09	0.01	37	95.0	1.1	2.3	0.4	0.39	5.9
Q-19 karst	0.79	0.52	0.17	0.01	11	0.09	0.15	0.7	0.2	11.37	4.2
Artificial ponds from Qarhan Salt Works											
Q12-A inlet	0.61	0.24	0.34	0.08	3.0	6.6	0.11	1.4	0.6	0.48	2.2
Q12-B halite	0.55	0.12	0.39	0.09	2.0	6.8	0.34	1.7	0.7	0.32	2.3
Q12-C carn.	0.52	0.05	0.54	0.05	0.8	7.1	0.13	2.1	0.8	0.11	2.5
Q12-D carn.	0.48	0.007	0.51	0.05	0.1	12.0	0.23	3.1	1.5	0.01	2.0
Q-42 bisch.	0.47	0.007	0.54	0.002	0.06	26.0	0.23	6.7	4.3	0.002	1.5
Q-41 final	0.41	0.007	0.54	0.002	0.07	24.0	0.22	6.9	4.7	0.003	1.5
Salt lakes											
Q-9 Chaka	0.56	0.37	0.40	0.05	0.7	98.0	0.29	1.4	0.4	0.007	2.9
Q-13 Dabuxan	0.52	0.02	0.46	0.01	7.0	0.01	0.15	2.5	0.9	471.9	2.7
Q-30 Xiaoq.	0.83	1.24	0.04	0.01	2.0	176.0	0.17	7.9	0.4	0.009	19.8

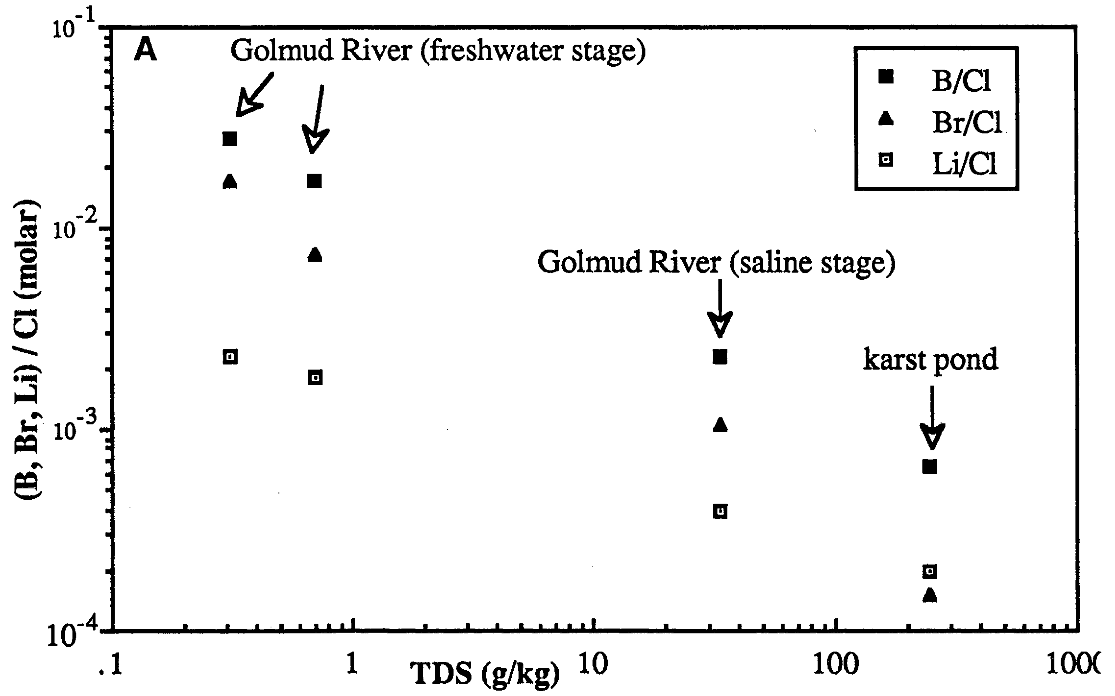


Figure 4.2.A. The evolution of solutes in the Qarhan playa is controlled by dissolution of evaporite minerals in the early stages and evaporation and salt-precipitation in later stages. The increase of the TDS of the Golmud River and the hypersaline brine of the karst pond are associated with gradual decrease in Na/Cl, Br/Cl, Li/Cl and B/Cl ratios.

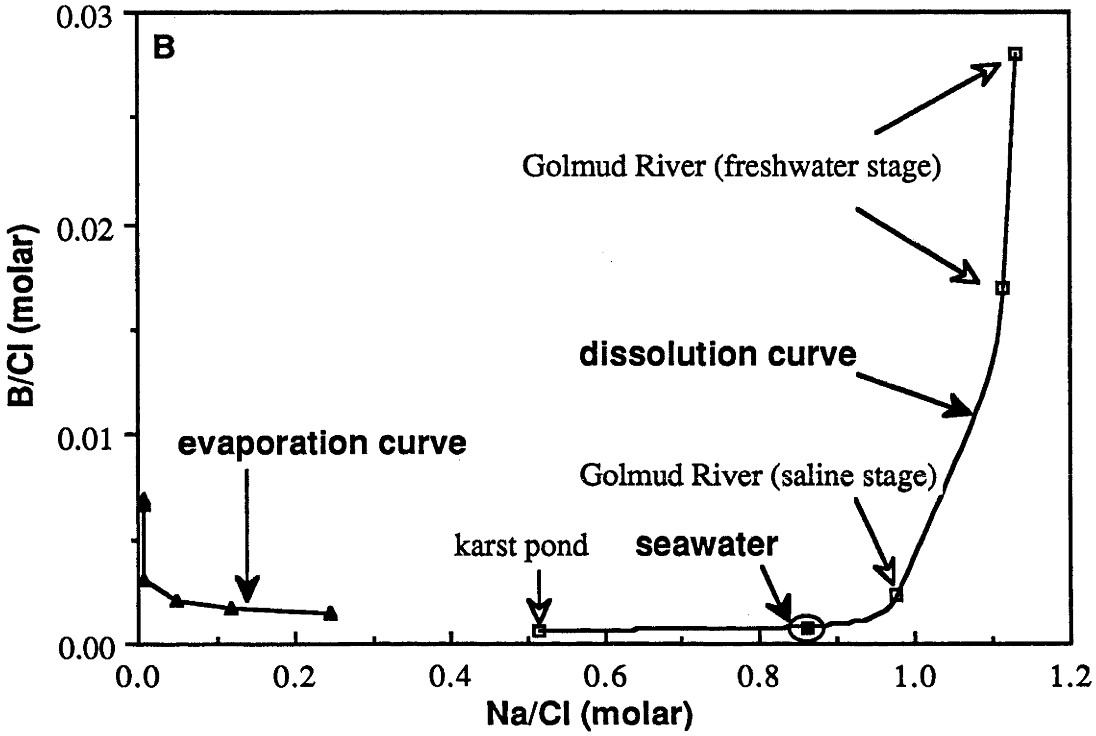


Figure 4.2.B. B/Cl *versus* Na/Cl ratios of waters from the Golmud River (3 locations), and of the karst pond brine, describe a "dissolution curve". For comparison, the ratios in seawater are plotted together with the compositions of brines (labelled "evaporation curve") during progressive crystallization in the artificial ponds.

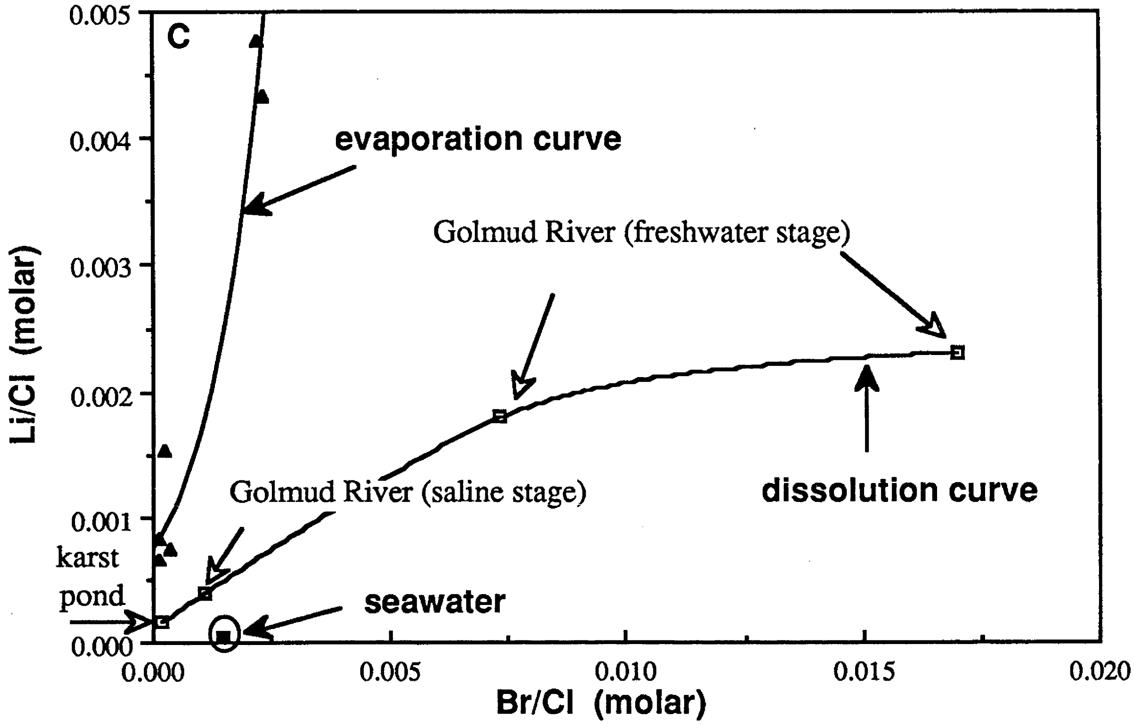


Figure 4.2.C. Li/Cl *versus* Br/Cl ratios of waters from the Golmud River (3 locations), the karst pond brine ("the dissolution curve"), seawater, and progressively evaporated brines from the artificial ponds (the "evaporation curve").

The Qarhan Salt Works

The evaporation of the brines is examined in a series of artificial ponds from the Qarhan Salt Works where halite, carnallite, and bischofite are precipitated. Several geochemical trends are identified in the brines from the artificial ponds as a function of progressive evaporation (Table 4.4; Figs 4.3):

(1) The Mg^{2+}, Li^+, Cl^-, SO_4^{2-}, Br^- and B concentrations increase;

(2) The Na^+, K^+ and Ca^{2+} contents decrease;

(3) The Na+Cl/TDS ratios (in equivalents) decrease from 0.61 to 0.47;

(4) The Na/Cl ratios decrease from 0.244 to 0.007;

(5) The Br/Cl, B/Cl, Mg/Cl, SO_4/Cl and Li/Cl ratios increase;

(6) The K/Cl, Ca/Cl, Ca/Mg and Ca/SO_4 ratios decrease;

(7) The pH values decrease; and

(8) The $\delta^{11}B$ values, which are in the range 10.5‰ to 15.0‰, are not related to the evaporation path.

Salt lakes

The sampled natural brines from salt lakes in the Qaidam Basin can be subdivided into two groups according to their geography and chemical composition (Table 4.4 and Fig 4.1): (1) Lake Dabuxan (sample Q-13) from the Qarhan playa in the southern areas of the basin which is characterized by a high Ca/SO_4 ratio (470), Na/Cl ratio<1 and a brine type of Mg-Cl, according to the brine classification scheme of EUGSTER and HARDIE (1978). The (natural) inlet brine (Q-12A) has similar chemical characteristics (Mg-Na-Cl type, and Na/Cl<1) yet its Ca/SO_4 ratio is less than 1;

(2) brines from Lake Xiaoqaidam (Q-30) and Lake Chaka (Q-9) at the northern and eastern margins, respectively, of the Qaidam Basin are characterized by low Ca/SO_4 ratios (<<1), Na/Cl>1 (only in Lake Xiaoqaidam) and are brines of Na-Cl-SO_4 type and Na-Mg-Cl-(SO_4) type, respectively.

4.4. DISCUSSION

The compositional history of closed-basin fluids can be separated into two phases. In the first, the solute composition of the dilute waters are the result of weathering-type reactions with the host country rocks . In the second phase the chemical composition of the fluids is controlled by evaporation and precipitation of evaporite minerals (JONES, 1966; GARRELS and McKENZIE, 1967; HARDIE, 1968; HARDIE and EUGSTER, 1970; EUGSTER, 1970; EUGSTER and HARDIE, 1978). In order to understand the chemical and isotopic composition of fluids from the Qaidam Basin, we first analyse the input fluids. Then we monitor evaporation trends by evaluating brines from evaporated artificial ponds from the Qarhan Salt Works. Once the chemical and isotopic composition of the inflows and the evaporation trends are considered, we analyse the natural brines from salt lakes in the basin.

4.4.1. Characterization of input salts

The Daqaidam hot spring and the Golmud River sampled near Golmud are enriched in Na^+, Mg^{2+}, Ca^{2+}, K^+, SO_4^{2-}, HCO_3^-, Br^-, Li^+ and boron, as normalized to chlorine, compared to the marine ratios (Table 4.4). This is a reflection of the relative deficiency of chlorine in the granitic country rocks and is consistent with the waters' non-marine origin.

The boron isotopic composition of the Daqaidam hot spring and the Golmud River also reflects a "terrestrial" source. The $\delta^{11}B$ values of these waters ($\delta^{11}B$= 3.9‰ and -0.3±0.6‰, respectively) overlaps with the $\delta^{11}B$ values of granitic rocks associated with the Qaidam Basin ($\delta^{11}B$= -2.4‰ to 3.7‰; Table 4.3).

It has been demonstrated by GARRELS and MACKENZIE (1967) that nearly all the chlorine and sulphate in the Ephemeral Springs in the granite area of the Sierra Nevada, California, have been derived from atmospheric precipitation. The Na^+, Ca^{2+}, Mg^{2+}, K^+ and HCO_3^- contents of the solutions are the results of reactions with silicate minerals in the host igneous country rocks, e.g. silicate hydrolysis (JONES, 1966). The relatively high Na/Cl, Ca/Cl, Mg/Cl ratios and the abundant calculated HCO_3^- content in the hot spring and freshwater river are the results of such processes in the drainage area of the Qaidam Basin.

As the freshwaters of the Golmud River flow within the Qarhan playa (Fig. 4.1), their salinity increases and their chemical composition is changed (Table 4.4). The high cation/chlorine ratios are progressively reduced. The Na/Cl ratio, for example, decreases from 1.13 to 0.97. The increase of TDS, Na+Cl/TDS ratios and the decrease of all cation/chlorine ratios (Table 4.4) accord with the observable dissolution of salts from the surface saline sands and salt crust in the Qaidam Basin. The gradual decrease of B/Cl, Li/Cl and Br/Cl ratios with progressive salinization of the Golmud River indicates dissolution of halite (see "dissolution curve" in Fig. 4.2) . However, in order to reduce the Na/Cl ratio of the river water, the assemblage of the dissolved minerals must also be composed of soluble salts, such as sylvite and carnallite that contribute chlorine but not sodium. This is consistent with the mineralogical composition of the uppermost halite layer of the Holocene salt crust in Qarhan where carnallite minerals are found (CHEN KEZAO and BOWLER, 1986; LOWENSTEIN et al., 1989). The more saline portion of the Golmud River is also characterized by high Ca/HCO_3 and low Ca/SO_4 ratios relative to the freshwater river, indicating precipitation of calcite or aragonite.

The karst pond is a hypersaline brine, yet its chemical characteristics are similar to that of the saline Golmud River. The Na/Cl ratio of the brine is 0.52. If the high TDS and the low Na/Cl ratio were the result of net evaporation and halite precipitation, we would expect high B/Cl, Li/Cl and Br/Cl ratios, as demonstrated in the artificial ponds (see "evaporation curves" in Fig. 4.2). In contrast, the low Li/Cl, B/Cl, Br/Cl ratios and the high Na+Cl/TDS ratio (0.8) of the karst-pond brine indicate dissolution of halite. We suggest that the low Na/Cl ratio also indicates dissolution of soluble K-chloride or Mg-chloride minerals. The high TDS of the karst pond is associated with lower values of Na/Cl, Li/Cl, B/Cl and Br/Cl ratios (Fig. 4.2), indicating further dissolution of the uppermost Qarhan salt crust and that the brine of the karst pond originated from a solution similar to that of the saline Golmud River.

The karst pond is also characterized by high Ca/SO_4 ratios (>1) (Table 4.4). LOWENSTEIN et al. (1989) recognized that the fluids from the karst zone in the northern margin of the Qarhan Playa are Ca-Cl springs and suggested a mechanism of formation via water-rock interaction. The modification to a Ca-Cl type brine can also be the result of dolomitization processes, e.g. the Dead Sea, Israel (STARINSKY, 1974). As the brine of the karst pond emerges at the surface along a linear fault zone (LOWENSTEIN et al., 1989), it may have been modified to a Ca-Cl type by dolomitization in the subsurface. In addition, the low SO_4/Cl ratios of the karst pond (Table 4.4) indicate removal of sulphate, i.e. precipitation of gypsum. As the Ca/SO_4 ratios of the subsurface brine become lower than 1 due to dolomitization processes, removal of an equivalent amount of calcium and sulphate would further increase these ratios. Alternatively, the low SO_4/Cl and high Ca/SO_4 ratios may also indicate removal of sulphate by sulphate reduction in the subsurface. Consequently, we interpret the chemical composition of the brine from the karst pond as reflecting a combination of subsurface processes of halite- and KMg-salt dissolution, dolomitization, gypsum precipitation and/or sulphate reduction.

The $\delta^{11}B$ values of the saline Golmud River are also modified from -0.3±0.6‰ to 9.6‰. This is accompanied by a decrease of the B/Li ratio from 10.8±1.8 to 5.9 (Table 4.4). The karst pond also has a similar $\delta^{11}B$ value (10.9‰) and a low B/Li ratio (4.2). As both lithium and boron are usually considered conservative elements, these variations may be the result of adsorption, i.e. selective removal of elemental B and ^{10}B from the solution. The ^{11}B enrichment cannot be a result of salt dissolution, as it has been shown (Chapter 3) that $\delta^{11}B$ values of K- and Mg-chloride minerals are lower that those of co-existing brines.

The magnitude of the shift in $\delta^{11}B$ values is only 10‰. While the bulk chemical composition of the diluted natural waters are largely affected by the dissolved minerals, the $\delta^{11}B$ value is not as much affected and its original terrestrial signature is maintained.

4.4.2. Evaporation processes in the Qarhan Salt Works

The evaporation systematics of the brines is examined in a series of artificial ponds from the Qarhan Salt Works. The initial inlet brine is a natural brine which seeps from the Holocene Qarhan salt crust. The chemical composition and the evaporation path of the subsequent brines are dependent on the initial brine composition.

Although Li^+ is considered conservative in evaporation processes (McCAFFREY et al., 1987), a parallel study shows that a fraction of lithium may be incorporated in salts at high degrees of evaporation (Chapter 3). Nevertheless, the lithium concentrations are used to determine the degrees of evaporation (calculated from $Li_{brine}/Li_{initial}$). Several geochemical trends can be identified (Table 4.4 and Fig. 4.3):

(1) The precipitation of halite during all the evaporation stages is reflected in the decrease in the absolute content of sodium, a decrease in Na+Cl/TDS ratios (in equivalent units) from 0.61 to 0.47, a decrease in Na/Cl ratios from 0.244 to 0.007, and the increase of Mg^{2+}, SO_4^{2-}, Br^-, Li^+ and boron ratios to chlorine (see "evaporation curve", Fig. 4.2). The gradual reduction in the Na/Cl ratios with progressive evaporation (Fig. 4.2) reflects the relatively low (<1) Na/Cl ratio of the inlet brine (Na/Cl=0.24). As the initial brine has a Na/Cl ratio lower than unity, halite precipitation removes equivalent amounts of chlorine and sodium, and further reduces this ratio in sequential brines.

(2) The precipitation of gypsum or anhydrite during all stages is reflected by the gradual decrease in the Ca/SO_4 and Ca/Mg ratios. As the initial Ca/SO_4 ratio in the inlet brine is lower than 1 (Ca/SO_4 in Q12-A = 0.48), removal of equivalent amounts of calcium and sulphate further reduces this ratio.

(3) The precipitation of sylvite and/or carnallite in the advanced stages of evaporation is shown by the decrease of the absolute content of potassium and a decrease in the K/Cl ratios.

(4) The precipitation of bischofite is reflected in the constant absolute contents of magnesium and chlorine and the slight decrease of Mg/Cl ratios.

4.4.3. The origin of the salt lakes from Qaidam Basin

The investigated salt lakes from the Qaidam Basin have a variety of chemical compositions. Lake Dabuxan (Q-13) from the Qarhan playa is a Ca-chloridic (Ca/SO_4=472), Mg-Cl type brine with low (<1) Na/Cl ratios. The inlet brine in the Qarhan playa (Q-12A) is a Mg-Na-Cl brine with low Na/Cl ratios. The brines from Lake Xiaoqaidam (Q-30) and Lake Chaka (Q-9) are sulphate-rich (Ca/SO_4 <<1) and are Na-Cl-SO_4 and Mg-Na-Cl-SO_4 types, respectively.

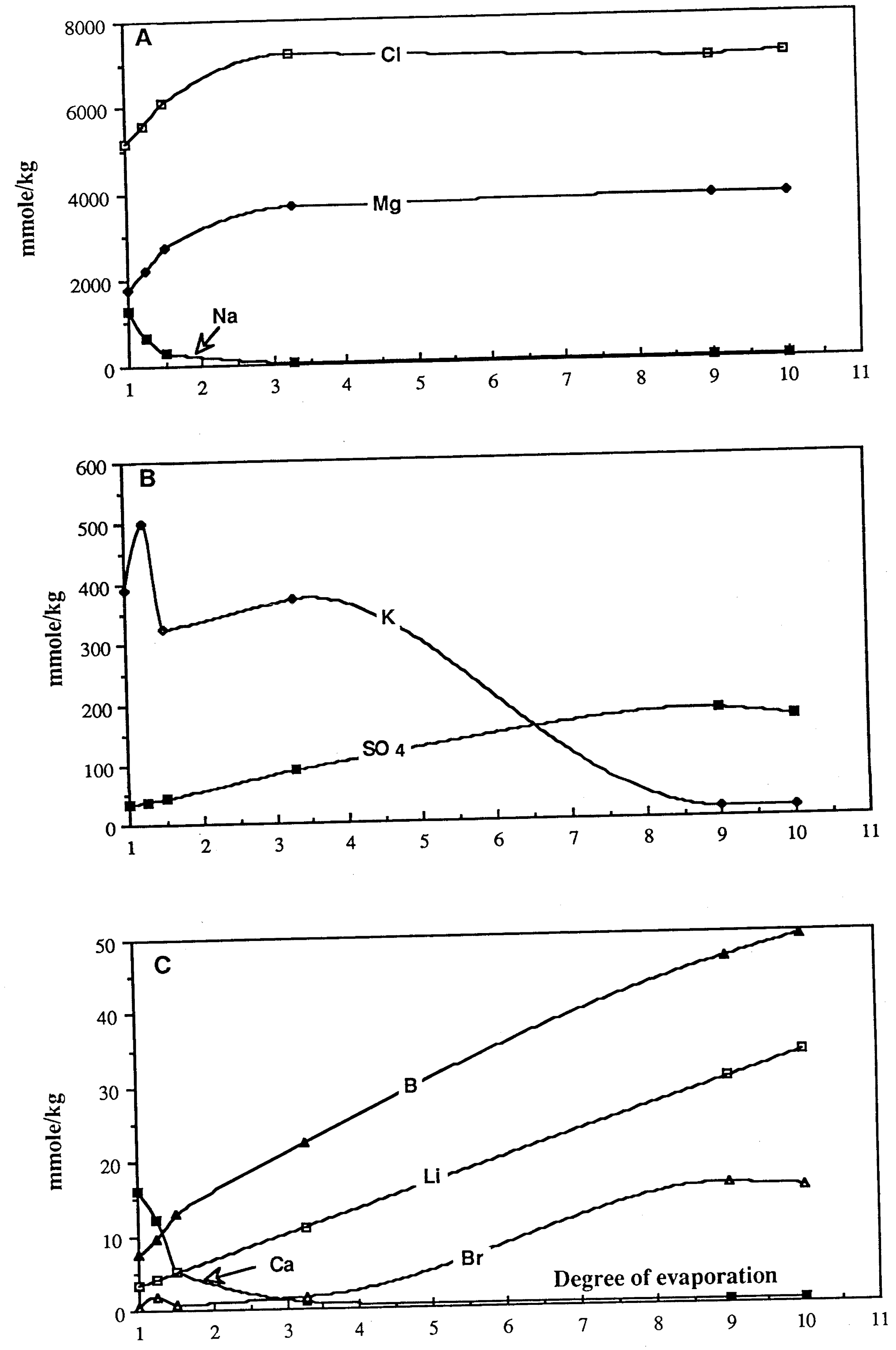


Figure 4.3. Concentrations of elements *versus* the degree of evaporation, expressed as ($Li_{sample}/Li_{initial}$) of progressively evaporated brines from artificial ponds in the Qarhan Salt Works.

The variety of chemical compositions of the salt lakes may indicate that they have originated from different parent solutions. The low Na/Cl ratios of Lake Dabuxan and the inlet brine indicate that they have originated from a solution with Na/Cl ratios lower than unity. During both evaporation and precipitation of halite, it is expected that a brine with initial Na/Cl>1 will evolve into one with Na/Cl>>1, as equivalent amounts of Cl and Na will be removed. In contrast, if the initial Na/Cl is lower than 1, such as in seawater (0.86), the evolved brine would have even lower Na/Cl ratios. Similar evolutionary patterns apply to Ca/SO_4 ratios during gypsum precipitation. Consequently the variations of Na/Cl or Ca/SO_4 ratios with respect to unity is virtually a "chemical divide" which controls the chemical composition of the brine with further evaporation.

The extremely high Ca/SO_4 ratios of the $CaSO_4$-saturated Lake Dabuxan (Table 4.4) indicate that this brine has evolved from a Ca-chloridic solution. The only identified input solution with these chemical signatures is the brine from the karst pond with Na/Cl and Ca/SO_4 ratios of 0.52 and 11.3, respectively. This is consistent with LOWENSTEIN et al. (1989) who suggested that Lake Dabuxan has originated from mixed proportions of Ca-Cl spring waters (from the karst zone) and water from the Golmud River.

The inlet brine (Q-12A) has originated from a brine with $Ca/SO_4<1$ and Na/Cl<1. As the karst pond is Ca-chloridic, the inlet brine must have evolved from a precursor that is similar to the saline stage of the Golmud River in which Ca/SO_4 is lower than 1.

The boron isotopic compositions of Lake Dabuxan (Q-13; $\delta^{11}B$ = 12.5‰) and the inlet brine (Q-12A; $\delta^{11}B$=15.0‰) are also similar to that of the saline Golmud River (Q-38A; $\delta^{11}B$ = 9.6‰) and to the karst pond (Q-19; $\delta^{11}B$=10.9‰) but not to the freshwater river with the low $\delta^{11}B$ of -0.7‰ to 0.2‰. Consequently, using a combination of three geochemical parameters (Na/Cl and Ca/SO_4 ratios and $\delta^{11}B$) we are able to trace the origin of salts in the salt lakes from the Qaidam Basin. Salts in these brines did not originate directly from the freshwater inflows but from saline waters and/or hypersaline brines that have been modified by salt dissolution, dolomitization and gypsum precipitation.

The chemical composition of the brine from Lake Xiaoqaidam (Q-30, Table 4.4) indicate that it has evolved from a parent solution with the chemical characteristics of: (1) Na/Cl ratio higher than 1; (2) Ca/SO_4 ratio lower than 1; (3) high B/Cl ratio; (4) low Mg/Cl ratio; and (5) low $\delta^{11}B$ value. These categories are in concordance with the chemical signature of the Daqaidam hot spring (sample Q-22; Table 4.4). We suggest that similar hot springs are the major source of salts for Lake Xiaoqaidam which supports the field observation of high boron content in hot springs that are located in that area (ZIQIANG and ZHIQIANG, 1985).

The brine from Lake Chaka (Q-9) is also sulphate-rich (low Ca/SO_4 ratio), yet its Na/Cl ratio is lower than 1, it has a relatively high magnesium content, and has a $\delta^{11}B$ value of 7.1‰. Therefore, we cannot identify a unique input to this lake which probably receives solutes from mixed sources.

4.4.4. Boron isotope variations and applications for tracing the origin of marine versus non-marine evaporites

The brines from the Qarhan playa are Mg-Cl types, and are associated with gypsum or anhydrite, halite, carnallite and bischofite minerals. The brine from Lake Xiaoqaidam is Na-Cl-SO_4-rich and the mineral assemblage at the bottom of Lake Xiaoqaidam consists of halite, mirabilite ($Na_2SO_4 \cdot 10H_2O$), Na-borate (borax) and Mg-borate (pinnoite) (ZIQIANG and ZHIQIANG, 1985; CHEN KEZAO and BOWLER, 1986).

Although the mineral paragenesis of the Qarhan playa is broadly similar to that predicted from progressively evaporated seawater, the evaporite minerals of Lake Xiaoqaidam are typically non-marine (e.g. HARDIE, 1984). This is also consistent with the chemical composition of both the proposed input waters and salt lakes. Lake Xiaoqaidam has evolved from a water similar to the typically non-marine Daqaidam hot spring whereas the brines in the Qarhan playa have evolved from non-marine solutions with a chemical composition similar to that of seawater. Both the saline Golmud River and the karst pond have low Na/Cl (<1), Br/Cl, Li/Cl and B/Cl ratios which are similar to those of seawater although the absolute values are different (Table 4.4, Fig. 4.2).

Consequently, based on the chemical signatures, particularly of the conservative trace elements (Li, B and Br), the Qarhan brines have chemical characteristics similar to those of evaporated seawater. The non-marine inflows become 'seawater-like' due to recycling processes, i.e. preferential dissolution of evaporite minerals.

In contrast, the data presented in this study indicate that the $\delta^{11}B$ values differ sharply from that of seawater and clearly reinforce a non-marine origin for the Qaidam brines. The $\delta^{11}B$ values of the investigated brines vary with both the B/Li (molar) ratios (Fig. 4.4) and the pH of the brines (Fig.4.5A). As boron is extractable with water that can leach over 50% of total B in granitic rocks (SAUERER et al., 1990), it seems that a terrestrial input of boron and lithium ($\delta^{11}B$ of 0±3‰, a relatively high B/Li ratio) has been modified by selective uptake of elemental boron and ^{10}B. Removal of elemental boron that has undergone isotopic fractionation can occur during adsorption processes (SCHWARCZ et al., 1969; SPIVACK et al., 1987; PALMER et al., 1987) or possibly by precipitation of borate minerals from borate-saturated brines (OI et al., 1989).

For the case of borate precipitation, one would expect that Lake Xiaoqaidam which has been saturated with borate minerals (QIAN ZIQIANG and XUAN ZHIQIANG, 1985) to have a high $\delta^{11}B$ value. In fact, Lake Xiaoqaidam has the lowest and highest $\delta^{11}B$ value and B/Li ratio (0.5‰ and 19.8, respectively), indicating that the observed enrichment of ^{11}B in the other salt lakes is a result of interaction with detrital sediments, rather than precipitation of borate minerals. In addition, in a parallel study (Chapter 3) it has been shown that the B/Li ratio increases during the extreme stages of evaporation and salt precipitation, i.e. lithium is also removed by salts.

The enrichment of ^{11}B in the brines is also associated with low pH (Fig.4.5A). PALMER et al., (1987) have demonstrated that the isotopic fractionation of boron is dependent on the distribution of boron species in the solution, which is, in turn, a function of the pH (Fig. 4.5B). During adsorption process, the borate ion and ^{10}B are preferentially adsorbed onto clay minerals. The magnitude of isotopic fractionation of boron is therefore increased with a larger fraction of boric acid in the solution, i.e. lower pH (PALMER et al., 1987). The association of higher $\delta^{11}B$ values with low-pH brines in the Qaidam Basin (Fig.4.5A) may be related to the larger isotopic fractionation of

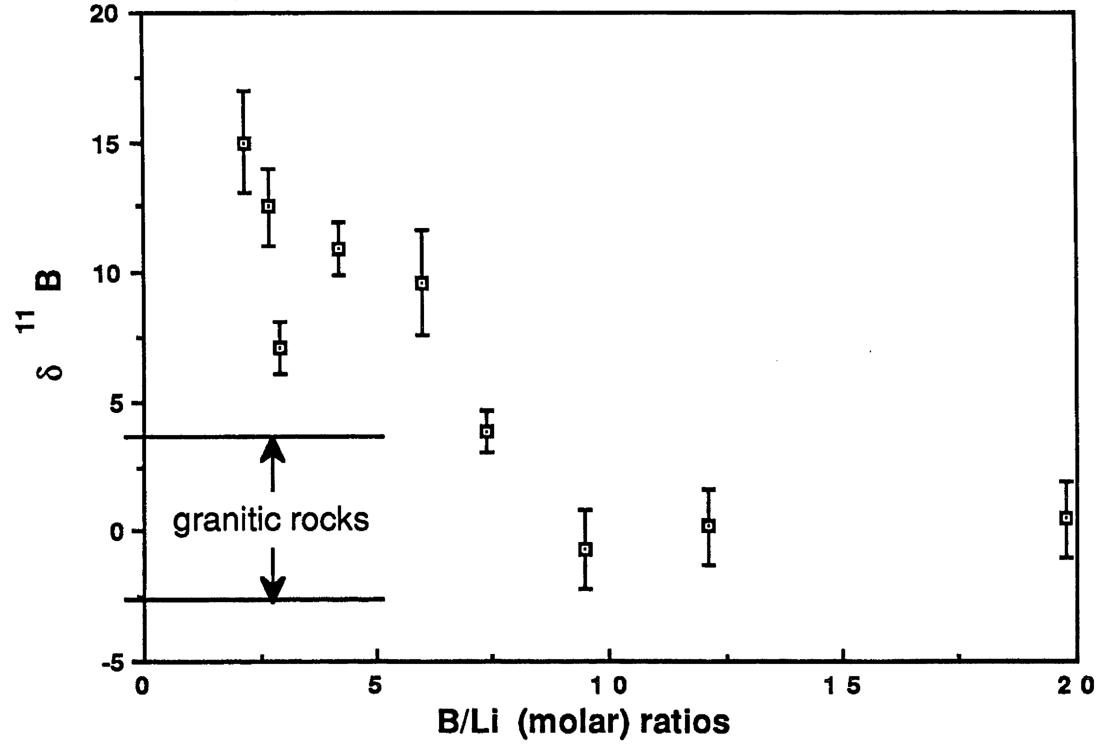
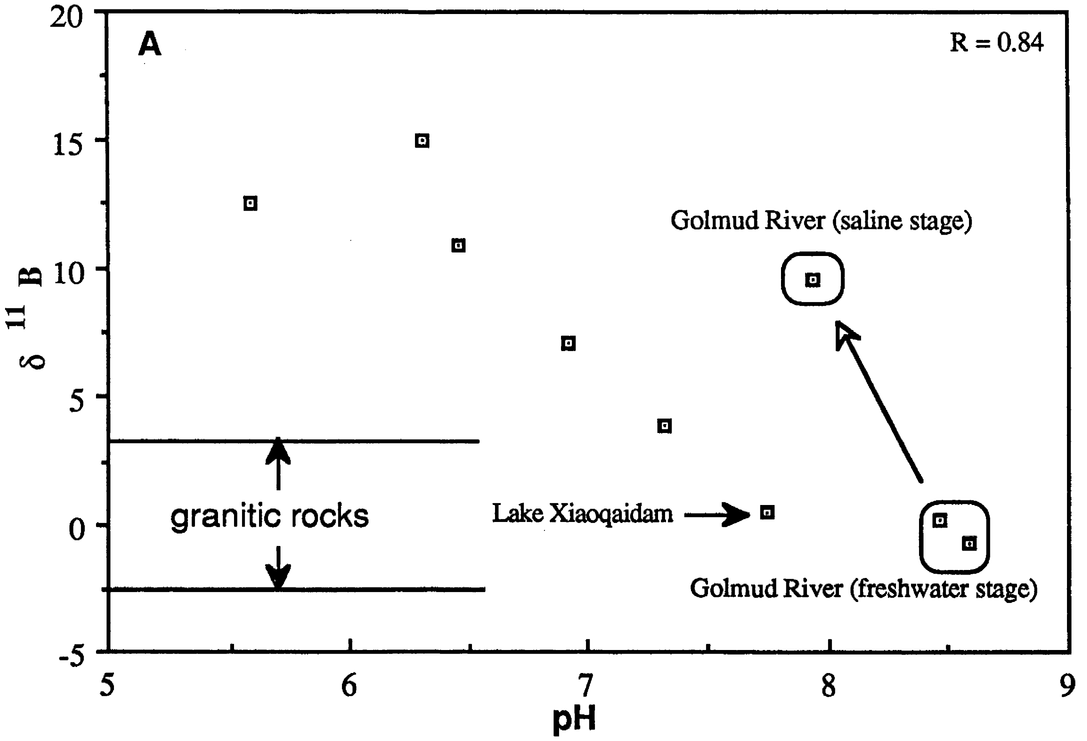


Figure 4.4. $\delta^{11}B$ values *versus* B/Li ratios of brines from the Qaidam Basin. The enrichment of ^{11}B in some brines relative to the terrestrial source ($\delta^{11}B$ = 0±3‰; e.g. granitic rocks) is associated with depletion of boron, normalized to lithium, and thus indicates selective removal of elemental boron and ^{10}B.



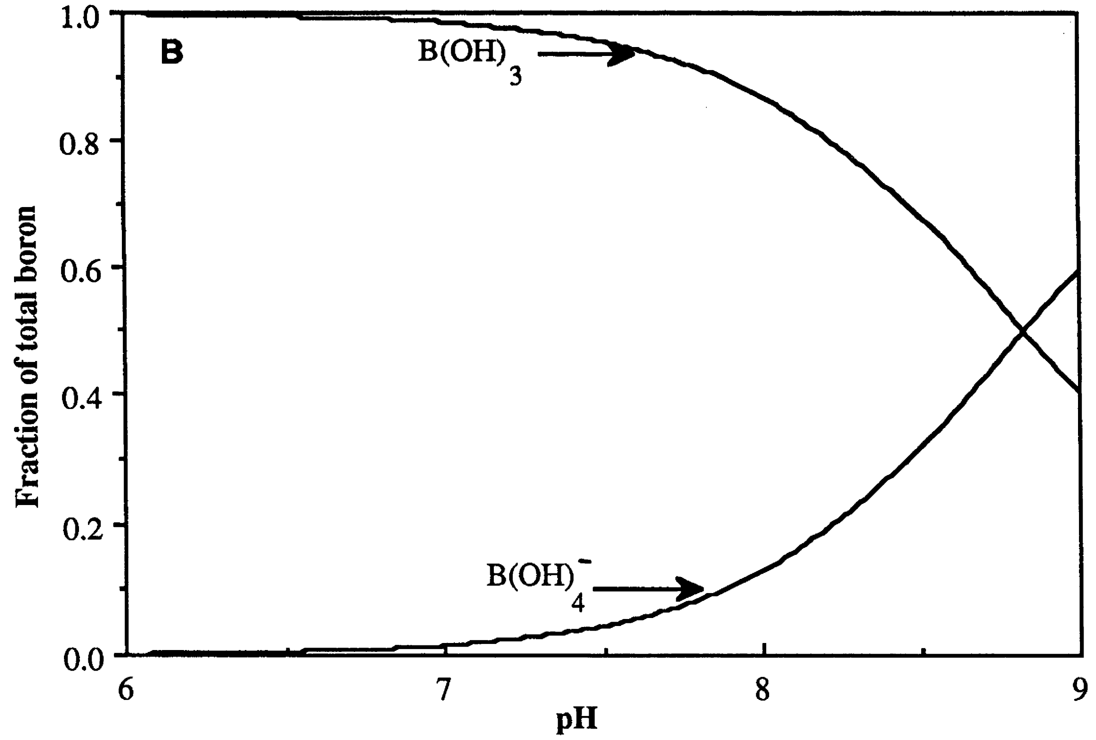


Figure 4.5.A. $\delta^{11}B$ values *versus* pH values of brines from the Qaidam Basin. **B**. Distribution of boron species in solution as a function of the pH (KAKIHANA et al., 1977; PALMER et al., 1987).

boron that is predicted for a solution in which the dissolved boron consists predominantly of boric acid.

Although the major-element composition of some of the brines of the Qarhan playa have been modified by dissolution of salts, dolomitization, and precipitation of calcium carbonate, $\delta^{11}B$ values are enriched by only 15‰ due to adsorption processess and the $\delta^{11}B$ signature remains non-marine. Similar magnitudes of ^{11}B enrichment have been shown in other environments such as the Australian salt lakes and the Dead Sea, Israel (VENGOSH et al., 1989; Chapters 2 and 5). Although boron is highly reactive with detrital sediments, the initial isotopic composition of the source fluids (terrestrial or marine) will determine the isotopic composition of the residual brines.

HARDIE (1984; 1990) and LOWENSTEIN et al., (1989) postulated that ancient evaporites with a "marine" mineralogical signature may have formed in non-marine environments. The chemical signatures of brines and the mineralogical sequence of precipitated salts in artificial ponds from the Qarhan are consistent with this observation.

We suggest that boron isotopic compositions can be used as geochemical tracers for the origin of brines and evaporites, and particularly in identifying marine and and non-marine evaporites. In evaporite systems such as the Qaidam Basin, boron accumulates to high concentrations. An input of atmospheric boron with a high (marine) $\delta^{11}B$ value in the extremely arid zones of northern Tibet would have a negligible effect on the isotopic composition of the boron-rich hypersaline brines, i.e. there is little scope for the possibility of derivation of boron from (marine) cyclic salts.

4.5. CONCLUSIONS

1) The salts in the salt lakes of the Qaidam Basin are derived from three main sources: (a) directly from 'terrestrial' inflows, such as the hot springs which are enriched in Na, SO_4, and B; (b) from surface solutions that are modified by preferential dissolution of halite and other soluble salts (e.g. the Golmud River contribution to the Qarhan playa); and (c) from subsurface brines (e.g. the karst pond in the Qarhan playa)

which are controlled by the combinations of preferential dissolution, dolomitization, gypsum precipitation and perhaps sulphate reduction processes.

2) The hot springs evolve into obviously non-marine brines and minerals (Lake Xaioqaidam), while surface and subsurface waters in the Qarhan playa evolve into marine-like brines and salts. The evolution of the Qarhan brines is controlled by dissolution of halite and other soluble minerals in early stages, dolomitization at the subsurface and evaporation and salt-precipitation (Fig. 4.2).

3) The boron isotopic composition of both the input waters and the salt lakes is typically non-marine (δ^{11}B of 0‰ to 15‰). The clear terrestrial signature of boron isotopes in the brines from the Qaidam Basin makes this method a potential tracer for identifying the origin of ancient evaporites, that is less prone to error than trace-element techniques.

Chapter 5

BORON ISOTOPE GEOCHEMISTRY AS A TRACER FOR THE EVOLUTION OF BRINES AND ASSOCIATED HOT SPRINGS FROM THE DEAD SEA, ISRAEL

5.1. INTRODUCTION

The Dead Sea is a terminal hypersaline lake, located in one of the rhomb-shaped grabens along the Jordan Rift Valley in Israel. Its brines are characterized by high salinity and are typically Ca-chloridic (STARINSKY, 1974). BENTOR (1961), ZAK (1967), NEEV and EMERY (1967) and STARINSKY (1974) suggested that the the Dead Sea salts are derived from subsurface brines, which originated from Pliocene seawater. The evolution of the Dead Sea started with a marine incursion in the Pliocene, followed by evaporative lagoon conditions where the salts of the Mount Sdom Formation were precipitated (ZAK, 1967). Using major-element ratios STARINSKY (1974) has postulated the sequence and mode of processes as follows: (1) precipitation of large halite bodies from seawater (resulting in a residual brine with low Na/Cl and high Br/Cl ratios); (2) bacterial sulfate reduction (SO_4^{2-} depletion, leading to high Ca/SO_4 ratios); (3) both early diagenetic and late epigenetic dolomitization (producing high Ca/Mg); and (4) contribution of terrestrial salts from inflows into the basin. In contrast, HARDIE (1990) recently suggested that the Ca-chloridic signature of the Dead Sea is a product of high-temperature water-rock interactions, and that virtually all the salts in the Dead Sea have a terrestrial origin.

The waters from hypersaline thermal springs along the western shore of the Dead Sea are also Ca-chloridic. GAT et al., (1969), MAZOR et al., (1969) and LERMAN (1970) suggested that these hot springs are mixture of freshwaters (e.g. Jordan River) with subsurface hypersaline brines. In contrast, STARINSKY (1974) considered these hot springs as sources for the modern Dead Sea, rather than products of its mixing.

Due to the unique geochemical characteristics of boron, its isotopes can be used to detect the sources of boron and hence the origin of brines and reactivity with clay

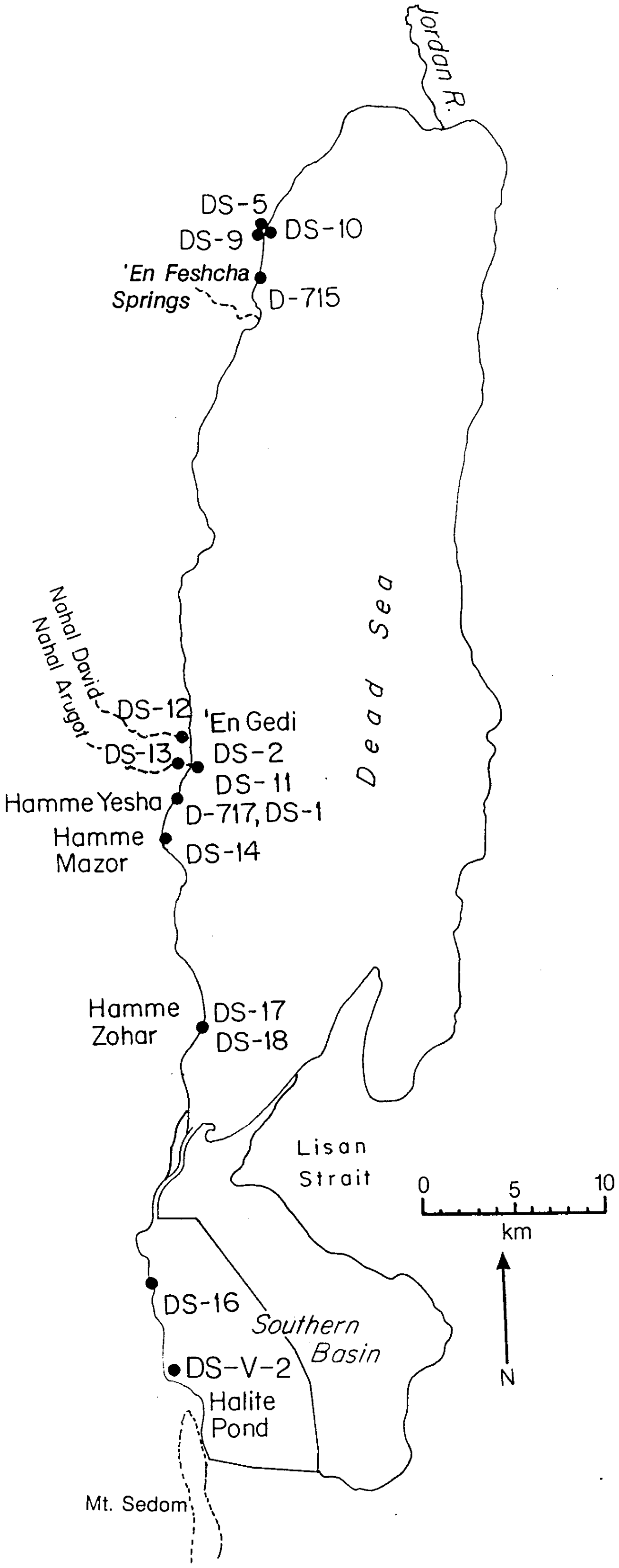


Figure 5.1. Location map of the investigated brines and waters. Note that what used to be the southern basin of the Dead Sea is now a huge evaporation pond.

TABLE 5.1. General description of samples analysed in this study.

sample	description	location
Dead Sea, northern Basin		
DS-2	Dead Sea surface brine	'En Gedi beach (April 1988)
DS-11	Dead Sea surface brine	'En Gedi beach (November 1988)
Dead Sea, southern Basin (artificial evaporation ponds)		
DS-V-2	Dead Sea, brine (from depth of 3m)	halite pool
DS-16	Dead Sea surface brine	halite pool, 1 km north of Moria beach
Diluted Dead Sea		
DS-10	Dead Sea surface brine	northern basin, 'En Feshcha beach
D-715	hypersaline spring	northern basin, seepage in conglomerates, 2.5 km north of Nahal Kidron
Hot springs		
DS-1	hot spring	Hamme Yesha, 'En Gedi Spa, 3 km south of 'En Gedi
DS-14	hot spring	Hamme Mazor, 100m west of the lake, 1 km south of 'En Gedi Spa
DS-17	hot spring	Hamme Zohar, "Hamme Zohar drilling" in the upper part of Zohar Spa
DS-18	hot spring	Hamme Zohar, lower spring in the beach of Zohar Spa
D-717	hot spring	Hamme Yesha, 1 km north of 'En Gedi
'En Feshcha brackish waters		
DS-5	spring	'En Feshcha spring, the northern spring in 'En Feshcha Reserve (Enot Zukim)
DS-9	spring	'En Feshcha southern spring, in 'En Feshcha Reserve (Enot Zukim)
Freshwater springs		
DS-12	freshwater spring	'En Dawid, Nahal Dawid, 1 km northwest of 'En Gedi
DS-13	freshwater spring	Nahal Arugot, 2 km west of 'En Gedi

minerals (SCHWARCZ et al., 1969; SWIHART et al., 1986; SPIVACK et al., 1987; VENGOSH et al., 1989). In an attempt to reconstruct the geochemical evolution of the Dead Sea brines and hot springs along its western coast, we analysed boron isotopes, and abundances of elemental boron, chlorine, and lithium in these brines. Samples were taken from the Dead Sea, hypersaline thermal springs along the western coast of the Dead Sea, brackish springs at 'En Feshcha and freshwaters from 'En Dawid and Nahal Arugot (Fig. 5.1 and Table 5.1). The chemical characteristics of the waters investigated in this study are summarized in Table 5.2.

5.2. RESULTS

The isotopic and chemical results are summarized in Table 5.3. Several groups of waters are recognized:

1) Surface brines from the Dead Sea are characterized by high $\delta^{11}B$ values (55.7‰ to 57.4‰; cf seawater with $\delta^{11}B$ of 39‰), high contents of boron (37.8 to 43.1 mg/kg), lithium (12.2 mg/kg), and chlorine (172,700 mg/kg). The B/Cl ratios are marine but the B/Li ratios (2.26) are lower than that of seawater (14.5). In the southern basin, which presently is an artificial evaporite pond of the Dead Sea Works Ltd, the concentrations of boron (54.69 mg/kg) and chlorine (191,760 mg/kg) are higher. The lithium content in the halite pond is also higher than that of the northern basin, in the range of 16.0 to 17.8 mg/kg (GANOR and KATZ, 1989). The $\delta^{11}B$ value however, is similar in the northern and southern basins of the Dead Sea.

2) The brines, sampled at 'En Feshcha beach (DS-10) and at seepage in conglomerates, 2.5 km north of Nahal Kidron (D-715) are diluted Dead Sea brines, i.e. mixtures of the Dead Sea surface brine with freshwaters. Their $\delta^{11}B$ values (55.7‰ to 57.4‰) are not distinguishable from those of the other Dead Sea samples, but their B, Li and Cl contents are lower. In the case of samples from 'En Feshcha beach, these elements are relatively depleted by a factor of ~0.4.

3) Hot springs from the western coast of the Dead Sea have $\delta^{11}B$ values in the range 51.7‰ to 54.9‰, B contents of 20.38 to 30.94 mg/kg, Li of 5.45 to 7.62 mg/kg and Cl of 97,474 to 162,092 mg/kg. B/Li ratios are in the range of 2.5 to 2.7.

TABLE 5.2. Average chemical composition of seawater, the Dead Sea, associated hot springs, and less saline springs at 'En Feshcha, 'En Dawid, and Nahal Arugot. Chemical data from STARINSKY (1974), GANOR and KATZ (1989), GAVRIELI et al. (1989), MAZOR et al. (1969), and MAZOR and MOLCHO (1972).

sample	t (°C)	TDS (g/l)	Na/Cl	Br/Cl (x10^{-3})	Ca/SO_4
				(molar ratios)	
seawater		35	0.86	1.5	0.35
Dead Sea	15-25	319-335	0.28-0.30	10.4-10.8	67.7-98.1
Hamme Zohar	15-32	52-130	0.31-0.40	4.9-9.9	10.2-23.6
Hamme Yesha	39*	159-201	0.32-0.39	2.3-8.3	18.7-41.1
'En Feshcha springs	26-30	3 - 7	0.38-0.45	7.4-19.2	10.0-12.1
'En Dawid and Nahal Arugot	15-20	0.5-0.8	0.81-0.91	-	1.5-3.9

* at a depth of 30m

TABLE 5.3. Boron isotopic and chemical composition of the investigated brines and freshwaters from the Dead Sea region. Boron, lithium and chloride concentrations are in mg/kg; B/Cl and B/Li ratios are molar.

Sample	$\delta^{11}B$ (‰)	B	Li	Cl	B/Li	B/Cl ($x10^{-4}$)	density (g/cc)
seawater	39.0	4.7	0.2	19000	15.1	8.1	1.023
Dead Sea, northern basin							
DS-11, Dead Sea (north)	57.3±1.0	43.08	12.22	172745	2.26	8.1	1.224
DS-2, Dead Sea (north)	57.2±1.6	37.76	na	na	-	-	-
Dead Sea, southern basin (artificial evaporite pond)							
DS-16, Dead Sea (south)	56.4±1.5	54.69	na	191760	-	9.4	1.243
DS-Y-2, Dead Sea (south)	55.7±1.0	na	na	na	-	-	-
Diluted Dead Sea							
DS-10, 'En Feshcha beach	57.4±1.5	16.99	5.40	71124	2.02	7.8	1.083
D-715, saline spring	55.7±1.5	8.57	2.74	38462	2.01	7.3	1.040
Hot Springs							
D-717, Hamme Yesha	52.2±1.5	22.05	na	98478	-	7.3	1.117
DS-1, Hamme Yesha	51.7±1.6	20.38	na	na	-	-	-
DS-14, Hamme Mazor	54.9±1.0	21.13	5.45	97474	2.49	7.1	1.108
DS-17, Hamme Zohar	52.9±1.5	22.69	5.32	56621	2.73	13.1	1.065
DS-18, Hamme Zohar	52.9±1.5	30.94	7.62	123884	2.60	8.2	1.144
'En Feshcha brackish springs							
DS-5, 'En Feshcha	40.6±1.0	0.44	na	1170	-	12.3	1.001
DS-9, 'En Feshcha	37.7±1.0	0.69	na	1824	-	12.4	1.002
Freshwater springs							
DS-12, 'En Dawid	33.8±1.1	0.25	na	84	-	97.5	1.000
DS-13, Nahal Arrugot	36.9±1.2	0.13	na	116	-	36.8	1.000

4) The brackish springs from 'En Feshcha have $\delta^{11}B$ values of 37.7‰ and 40.6‰, B contents of 0.44 and 0.69 mg/kg.

5) The $\delta^{11}B$ values of meteoric freshwater springs from 'En Dawid and Nahal Arugot are 33.8‰ and 36.9‰, and B contents are 0.13 and 0.25 mg/kg. The B/Cl ratios (9.75×10^{-3} and 3.68×10^{-3}) are higher than that of the Dead Sea and seawater (Table 5.3).

5.3. DISCUSSION

5.3.1. The origin of boron in the Dead Sea brine

Boron, lithium and bromine are usually considered as conservative elements, that is they remain in the solution during evaporation and are not removed into precipitated salts. In contrast, chlorine in halite-saturated brines is not conservative (ZHEREBTSOVA and VOLKOVA, 1966; STARINSKY, 1974, McCAFFREY et al., 1987).

The degree of evaporation of the Dead Sea brine determined by bromine, that is $Br_{Dead\ Sea}/Br_{seawater}$ ratio, in similar to that of lithium ($Li_{Dead\ Sea}/Li_{seawater}$ ratio). Both elements indicate a similar degree of evaporation of seawater of about 80 . In contrast, the degree of evaporation determined by boron is only 11.5. The B/Li ratios (range of 2.0 to 2.3) of the Dead Sea are also lower than that of seawater (14.5) and indicate a relative depletion of elemental boron in the Dead Sea by a factor of 7. This is a minimum estimate, as some Br was coprecipitaed in the formation of halite in the Mount Sdom Formation (ZAK, 1967).

The marine B/Cl ratios of the Dead Sea brines and the hot springs (Table 5.3) do not indicate conservative behavior of both boron and chlorine in the Dead Sea system. In a plot of Na/Cl versus B/Cl ratios (Fig. 5.2) one can see the variations of these parameters during progressive evaporation of seawater: Na/Cl ratios decrease while B/Cl ratios increase (Chapter 3). For the Na/Cl ratios of the Dead Sea (0.28) and hot springs (0.31 to 0.40) (STARINSKY, 1974), we would expect much higher B/Cl ratios (Fig. 5.2). Consequently, the "marine" B/Cl ratios indicate a depletion of boron. This is consistent with the low B/Li ratios.

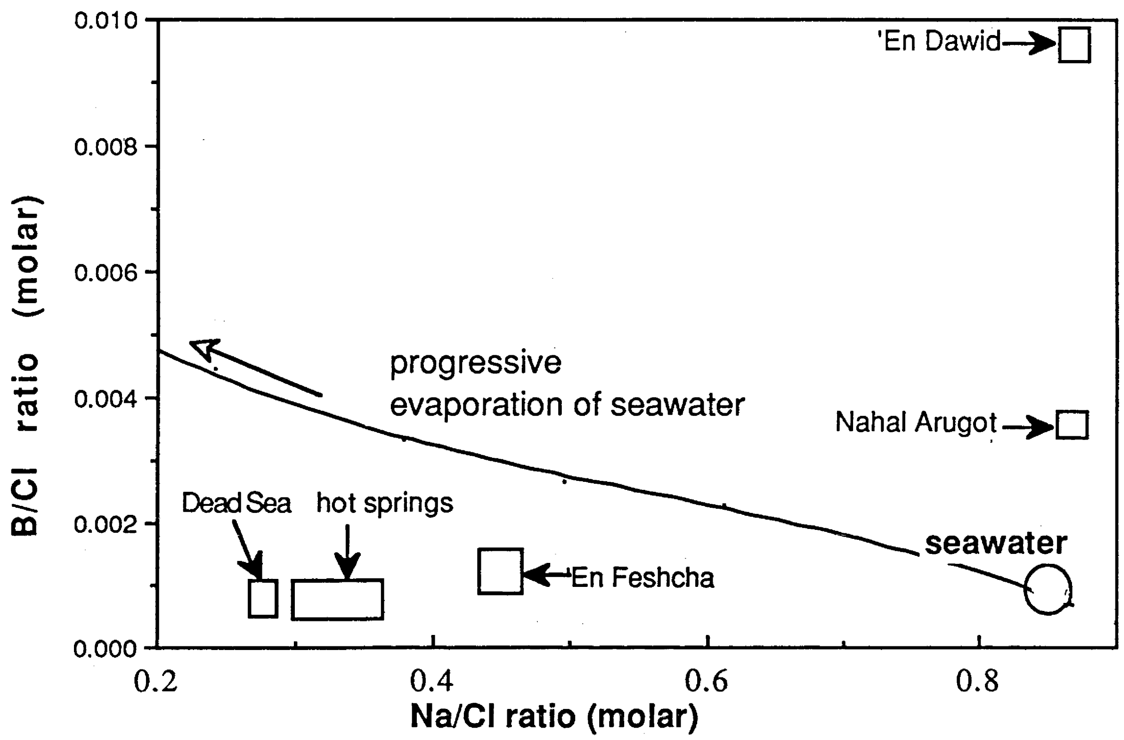


Figure 5.2. B/Cl *versus* Na/Cl ratios of evaporated seawater, Dead Sea, hot springs, 'En Feshcha, 'En Dawid and Nahal Arugot. The curve for progressive evaporation of seawater is from Chapter 3. The B/Cl ratios of the Dead Sea and hot springs are typically marine, but are lower than that of the evaporation curve, as normalized to their Na/Cl ratios. The B/Cl ratios of the freshwater ('En Dawid and Nahal Arugot) are higher than that of seawater.

In addition to depletion of elemental boron, the brines from the Dead Sea system are enriched with ^{11}B (δ^{11}B= 51.7‰ to 57.4‰) relative to seawater (δ^{11}B= 39‰), indicating that ^{10}B was preferentially removed from the liquid phase. The depletion of elemental boron and ^{10}B in the Dead Sea can be the result of: (1) adsorption of boron onto clay minerals (SCHWARCZ et al., 1969) and (2) coprecipitation of boron into soluble minerals during the late stages of evaporation of the original seawater. In a parallel study (Chapter 3) it is shown, however, that during evaporation of seawater to its final stages both the δ^{11}B values and B/Li ratios increase. The low B/Li ratios in the Dead Sea therefore rule out the latter possibility and hence the depletion of boron is interpreted as being due to adsorption onto clay minerals. The possible sinks for boron are the detrital sediments in the bottom of the modern Dead Sea and/or its precursor, Lisan Lake (KATZ and KOLODNY, 1989).

Assuming that (1) the original seawater had B/Li and δ^{11}B values similar to that of the present ocean; (2) the boron contribution from terrestrial inflows and rocks is negligible; and (3) the effective water/sediment ratio is close to 0, we use the measured B/Li and δ^{11}B in the modern Dead Sea to detect the empirical boron-isotope fractionation factor (α) between dissolved and adsorbed boron in the Dead Sea.

If the interaction of the brines with clay minerals is completely reversible and the adsorbed boron is in isotopic exchange equilibrium with the dissolved boron, the magnitude of the fractionation factor is:

$$\alpha = 1/(\delta^{11}B_{DS}+1000)\left[\frac{(\delta^{11}B_{sw}+1000)-X\,(\delta^{11}B_{DS}+1000)}{1-X}\right] \qquad (1)$$

where $\delta^{11}B_{sw}$ and $\delta^{11}B_{DS}$ represent seawater and Dead Sea brines, respectively; X is the fraction of boron which remains in the solution, normalized to lithium: $X = (B/Li)_{DS}/\,(B/Li)_{sw}$. α is the boron-isotope fractionation factor between dissolved and adsorbed boron. The calculated X and α for the Dead Sea are 0.14 and 0.980, respectively .

The normalization of boron to lithium in the Dead Sea is made because of the conservative behavior of lithium, as reflected in its isotopic composition. Seawater is enriched with ^{7}Li relative to submarine hydrothermal solutions, its principal Li source. This enrichment has been attributed by CHAN and EDMOND (1988) to isotopic fractionation associated with low-temperature alteration of basalt and incorporation in authigenic sediments. The preferential removal of ^{6}Li from seawater is grossly similar to the processes of depletion of seawater by ^{10}B (SPIVACK and EDMOND, 1987; SPIVACK et al., 1987). The ^{6}Li/^{7}Li ratios of the Dead Sea brine are similar to that of modern seawater (CHAN and EDMOND, 1988), indicating that the original marine Li has accumulated in the brine residues without isotopic exchange. In contrast to lithium, the high δ^{11}B values of the Dead Sea indicate the non-conservative behavior of boron.

The unique chemical matrix of the Dead Sea (STARINSKY 1974; GAVRIELI et al., 1989) may affect the distribution of boron species in the Dead Sea and hence the isotopic fractionation. The ion-pair formation of $B(OH)_4^-$ with major cations presented in seawater has been shown in several studies (BRYNE and KESTER, 1974; REARDON, 1976; HARSHEY et al., 1986; ROGERS and VAN DEN BERG, 1988). The formation of of an ion-pair can be described as:

$$M^{n+} + B(OH)_4^- = MB(OH)_4^{n-1} \qquad (2)$$

where M^{n+} is the metal cation and n is its charge. The ionization of boric acid and the formation of borate ion-pairs are depend on the chemistry of the solution, its ionic strength, the cation concentrations and the stability constants (HARSHEY et al., 1986; ROGERS and VAN DEN BERG, 1988). For the conditions of the Dead Sea of ionic strength=9.5M, Ca= 0.51M, Mg=1.98 M (GAVRIELI et al., 1989) and total B of 0.0049M, we would expect a large fraction of the boron to be present as $MgB(OH)_4^+$ and $CaB(OH)_4^+$.

The dissociation of boric acid and the formation of borate ion-pairs can reduce the pH of the system. REARDON (1976) has shown that in a high-pH dilute $Na_2B_4O_7.10H_2O$ solution an addition of $MgCl_2$ will cause a pH drop due to ion-pairing of Mg^{2+} with $B(OH)_4^-$ that enhances the dissociation of $B(OH)_3$. Thus, it may be that the borate ion-pair formation has been one of the factors that cause the low pH of 5.95 to 6.56 in the Dead Sea (NEEV and EMERY, 1967; NISSENBAUM, 1969; AMIT and BENTOR, 1971; SASS and BEN-YAAKOV, 1977).

In addition, the total alkalinity in the Dead Sea brine has been measured by conventional titration that includes all the charged species, including boron species. However, analyses of total dissolved CO_2 by NEEV and EMERY (1967) and NISSENBAUM and KAPLAN (1976) yield only one-third to one-fourth of the amount obtained by titrimetry. One may suggest that the fraction of the charged borate species are relatively important constituents in the Dead Sea. This can be determined only by careful measuring of the apparent dissociation constants of boric acid and borate ion-pairs in the unique chemical matrix of the Dead Sea.

5.3.2. The origin of boron in the hot springs

Upon mixing two solutions (*a,b*) with different boron-isotope compositions, the mixed solution (*mix*) will have a $\delta^{11}B$ value and an elemental boron content of:

$$\delta^{11}B_{mix} = \frac{B_a*\delta^{11}B_a*F}{B_{mix}} + \frac{B_b*\delta^{11}B_b*(1-F)}{B_{mix}} \quad ; \text{ and} \qquad (3)$$

$$B_{mix} = B_a*F + B_b*(1-F) \qquad (4)$$

where B_a, B_b and B_{mix} are boron concentrations, and $\delta^{11}B_a$, $\delta^{11}B_b$ and $\delta^{11}B_{mix}$ are the $\delta^{11}B$ values of the component a, b, and mixtures, respectively. F is the fraction of component a.

In a mixture of the Dead Sea brine ($\delta^{11}B$=57.4‰, B=43 mg/kg) with 'En Feshcha springs ($\delta^{11}B$=39.2, B=0.6 mg/kg) and meteoric freshwater ('En Dawid and Nahal Arugot, $\delta^{11}B$=35.4‰, B=0.2 mg/kg) mixing trends are apparent in a plot of elemental boron *versus* $\delta^{11}B$ values (Fig. 5.3). The $\delta^{11}B$ values and B contents of diluted Dead Sea that were sampled at 'En Feshcha Beach (DS-10) and the Dead Sea coast (D-715) lie on the mixing lines (Fig. 5.3) and illustrate the sensitivity of the $\delta^{11}B$ values to the mixing processes.

In contrast, the data points of the hot springs are not on the mixing lines (Fig. 5.3). The relative low $\delta^{11}B$ values of the hot springs, as expected from their B contents, indicates that these springs are not mixing products of the Dead Sea with brackish or freshwater, as suggested by GAT et al. (1969), MAZOR et al. (1969) and LERMAN

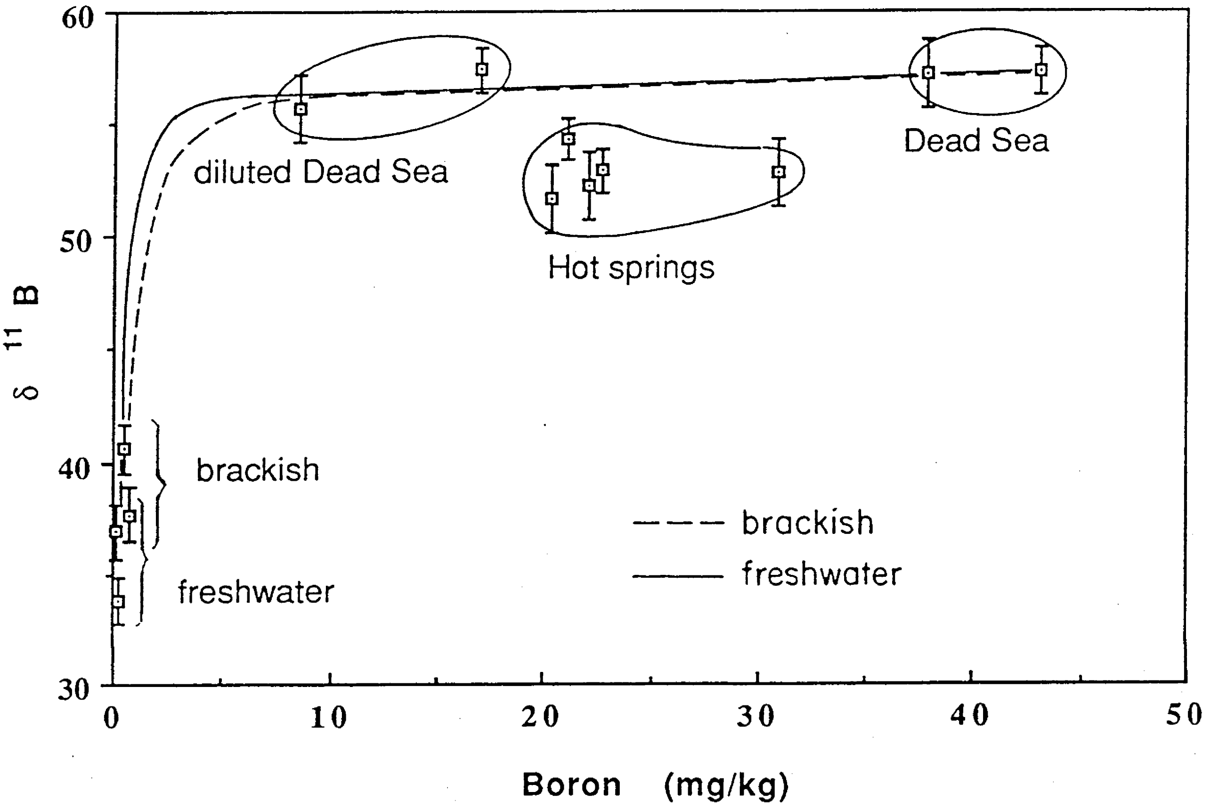


Figure 5.3. δ^{11}B values *versus* boron contents of the Dead Sea brines, diluted Dead Sea, hot springs, brackish water ('En Feshcha) and freshwaters in the Dead Sea system. The mixing lines were calculated from mixing equations of the Dead Sea brine with 'En Feshcha springs and with freshwater.

(1970).

The lower $\delta^{11}B$ values and higher B/Li ratios of the hot springs, relative to those of the Dead Sea (Fig. 5.4), suggest that the hot springs are the sources of the Dead Sea. The data points in Fig. 5.4 indicate that the hot springs have lost less elemental boron and ^{10}B. This could be the result of (1) higher water/sediment ratios in the hot springs; or (2) a higher degree of "maturation" of the Dead Sea, i.e. more adsorption. It is difficult to accept the first possibility, as one would expect much lower water/sediment ratios in a subsurface brine relative to the surface brine of the Dead Sea.

It is more probable that the relatively lower $\delta^{11}B$ values and higher B/Li ratios in the hot springs preserve the early stages of boron evolution in the Dead Sea system. Assuming that the $\delta^{11}B$ values and B/Li ratios in the original seawater were similar to that of the modern ocean (Table 5.3), the $\delta^{11}B$ values and B/Li ratios of the hot springs represent an early stage of the evolution of the Rift Valley brines. The adsorption of boron onto clay minerals caused the shifts in the $\delta^{11}B$ values from 39‰ to 52.9±1.2‰ and in B/Li ratios from 15.1 to 2.61±0.12, as represented by the hot springs (Fig. 5.4). During the evolution of the modern Dead Sea from its parent brines, further isotopic fractionation and boron adsorption onto detrital sediments have increased the $\delta^{11}B$ values of the hot springs to 57.0±0.7‰ and decreased the B/Li ratios to 2.1±0.1 (Fig. 5.4). Although the Dead Sea brine has lost more boron due to adsorption, the boron concentration in the lake is higher than that of the hot springs due to net evaporation processes. In addition, it may be that the boron content in the hot springs was higher than that of the Dead Sea, but dilution with freshwater has decreased their B concentrations but has not changed their relative higher B/Li ratios or their $\delta^{11}B$ values.

This interpretation is consistent with the concept that the Dead Sea brine is the product of evaporation of the hypersaline thermal springs as suggested by STARINSKY (1974). The hot springs therefore contain important information on the early phases of the Dead Sea and provide a link to the original seawater composition. This conclusion contradicts however, the "terrestrial" source for salts in the Dead Sea as argued by HARDIE (1990). If the Ca-chloridic signature of the Dead Sea and the thermal springs were a product of high-temperature water-rock interaction, one would expect low $\delta^{11}B$

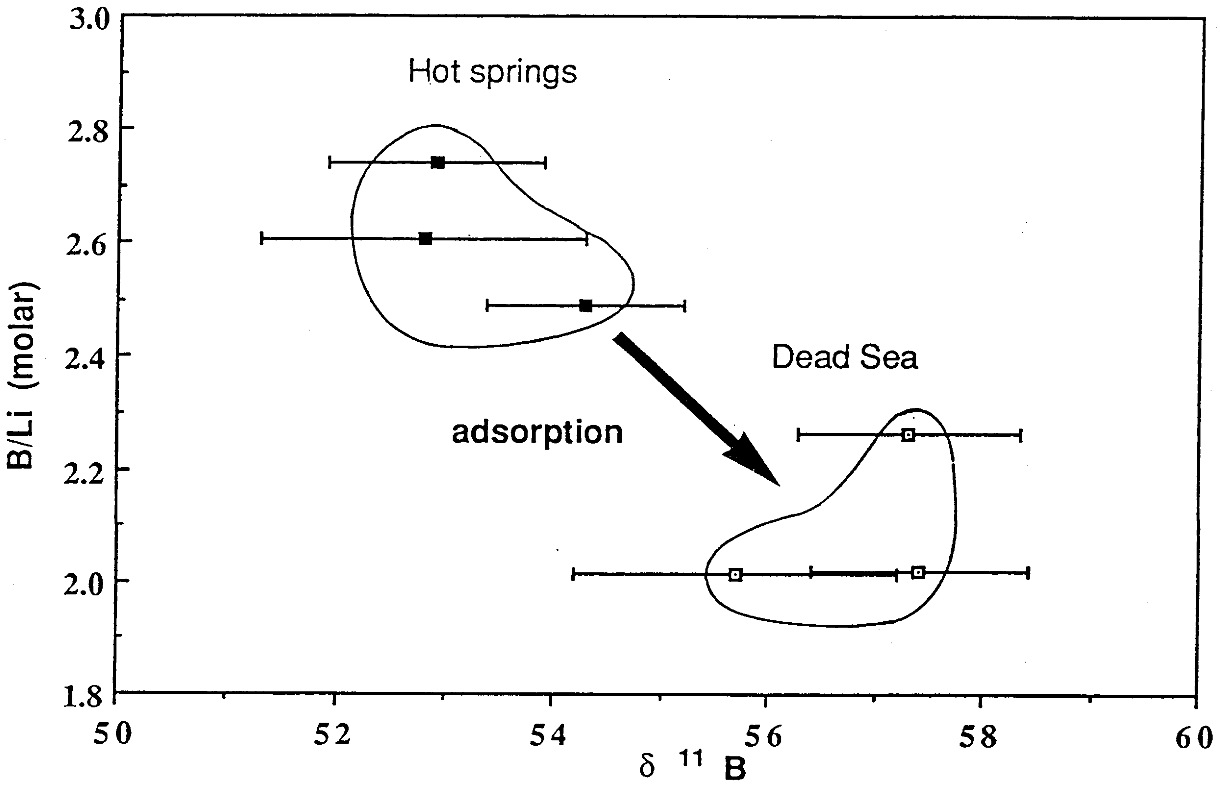


Figure 5.4. B/Li ratios *versus* δ^{11}B values of Dead Sea brines (squares) and hot springs (filled squares). The trend of adsorption is suggested by the lower B/Li ratios and higher δ^{11}B values of the Dead Sea brines relative to the hot springs.

values for the brines. SPIVACK and EDMOND (1987) have shown that the boron from marine hydrothermal vents ($\delta^{11}B$ values in the range 30.0‰ to 36.6‰) is a mixture of original seawater boron with boron that was extracted from the basaltic rocks. The high $\delta^{11}B$ values, particularly of the subsurface thermal springs rule out such a mechanism for the origin of salts in the Dead Sea.

5.3.3. The origin of boron in the brackish waters and freshwaters

The low B contents and $\delta^{11}B$ values in the freshwater springs from 'En Dawid and Nahal Arugot (Table 5.2) indicate that that boron in these waters is not derived from the Dead Sea brine by internal cyclic processes within the Rift Valley. This is consistent with the Na/Cl ratios of these waters (a range of 0.81 to 0.91) that are higher than that of the Dead Sea of 0.28 (Table 5.2).

Boron in the freshwater springs could be derived from (1) country rocks with $\delta^{11}B$ ~0‰ (SCHWARCZ et al., 1969); or (2) atmospheric cyclic salts that originated from seawater and have marine $\delta^{11}B$ values (SPIVACK, 1986; see also Chapter 2). Most of the country rocks in the eastern Judea Desert are composed of Cenomanian and Turonian carbonate rocks. Therefore an additional boron reservoir could be the carbonate fraction in these rocks. At this stage, we do not know the isotopic composition of boron in these rocks. Preliminary results of modern biogenic marine carbonates show that B concentrations in carbonates are in the range of 10 to 20 ppm (FURST et al., 1976) with $\delta^{11}B$ values of 20‰ to 30‰ (Chapter 8).

The $\delta^{11}B$ value of the freshwater (33.8‰ to 36.9‰), high B/Cl ratios (higher than that of seawater and the Dead Sea) and the marine Na/Cl ratios (Fig. 5.2) suggest that boron in these groundwaters is the product of mixing of meteoric boron, derived from marine cyclic salts ($\delta^{11}B$ =39‰, $B/Cl=8x10^{-4}$, Na/Cl = 0.86), with terrestrial boron, derived from clays ($\delta^{11}B$ ~0‰) and carbonates ($\delta^{11}B$ ~20‰ to 30‰). It seems that boron isotopes in the freshwaters are sensitive to rock leaching whereas Na/Cl ratios are not. The terrestrial end-member would have high B/Cl ratios and low $\delta^{11}B$ values.

The 'En Feshcha springs have higher $\delta^{11}B$ values and elemental boron contents, and lower B/Cl ratios relative to the freshwaters (Table 5.3, Fig. 5.2). In addition, their Na/Cl ratios are low (0.38-0.45, Table 5.2). This can be the result of mixing of the Dead Sea brines or the hot springs with groundwaters, such as those of 'En Dawid and Nahal Arugot (Fig. 5.3). In any combination, the fraction of the freshwater component is high. For mixing with the Dead Sea and with the hot springs the calculated freshwater fractions are 0.99 and 0.98, respectively.

5.4. CONCLUSIONS

1) The concordance of high $\delta^{11}B$ values and low B/Li ratios in a brine indicates adsorption of boron onto clay minerals, and hence interaction of brines with sediments. In a system that is saturated with halite, or has been saturated during its history, the B/Cl ratios should be normalized to the Na/Cl ratios.

2) The combinations of high $\delta^{11}B$ values, low B/Li, low Na/Cl and high Br/Cl ratios a of a brine indicates that it has originated from seawater ($\delta^{11}B$=39‰, Na/Cl=0.86) through evaporation, precipitation of salts, and interaction with clay minerals, i.e. adsorption. This is the interpretation that is suggested for the evolution of brines from the Dead Sea system.

3) An addition of boron derived from the country rocks in the Dead Sea basin, with a low $\delta^{11}B$ signature, may affect the isotopic composition of brackish and freshwaters. However, due to its relatively larger boron content, the main boron reservoir (the Dead Sea and hot-spring brines) is not isotopically affected by processes that contribute boron from rock leaching.

Chapter 6

BORON ISOTOPE SYSTEMATICS OF OILFIELD BRINES FROM THE COASTAL PLAIN OF ISRAEL

6.1. INTRODUCTION

The origin of deep subsurface brines, referred to as "oilfield brines" or "formation waters" has been investigated by means of their chemical composition (DEGENS et al., 1964; CARPENTER, 1978; EGEBERG and AAGAAD, 1989), oxygen- and hydrogen-isotope compositions (CLAYTON et al., 1966; FLEISCHER et al., 1977), and Sr isotopes (VEIZER and DEMOVIC, 1974; STARINSKY et al., 1983). Various models, often controversial, have been postulated in attempts to elucidate the origin and history of these waters (EGEBERG and AAGAAD, 1989). The various possible sources (seawater, meteoric water), as well as complex modification processes, such as interaction with the confining rocks (STARINSKY, 1974), make this task difficult.

The distinctive isotopic composition of boron in seawater makes it an attractive geochemical tracer for identifying the sources of boron in formation waters. Seawater is largely enriched in ^{11}B ($\delta^{11}B$=39‰) relative to terrestrial rocks ($\delta^{11}B$~0‰) due to isotopic fractionation that occurs as boron is adsorbed onto detrital clays and altered basalts (SCHWARCZ et al.,1969; SPIVACK et al., 1987). High $\delta^{11}B$ values and depletion of elemental boron (as normalized to chlorine or lithium) in brines may indicate adsorption onto clays. Such processes are demonstrated for instance in some Australian salt lakes and in the Dead Sea in Israel (VENGOSH et al., 1989; Chapters 2 and 5).

In order to evaluate the potential application of boron isotopes to the study of oilfield brines, well studied brines from the oilfield of the southern coastal plain of Israel have been investigated (Fig. 6.1). The brines were sampled from the Lower Cretaceous Heletz Formation (STARINSKY, 1974; FLEISCHER et al., 1977; STARINSKY et al.,

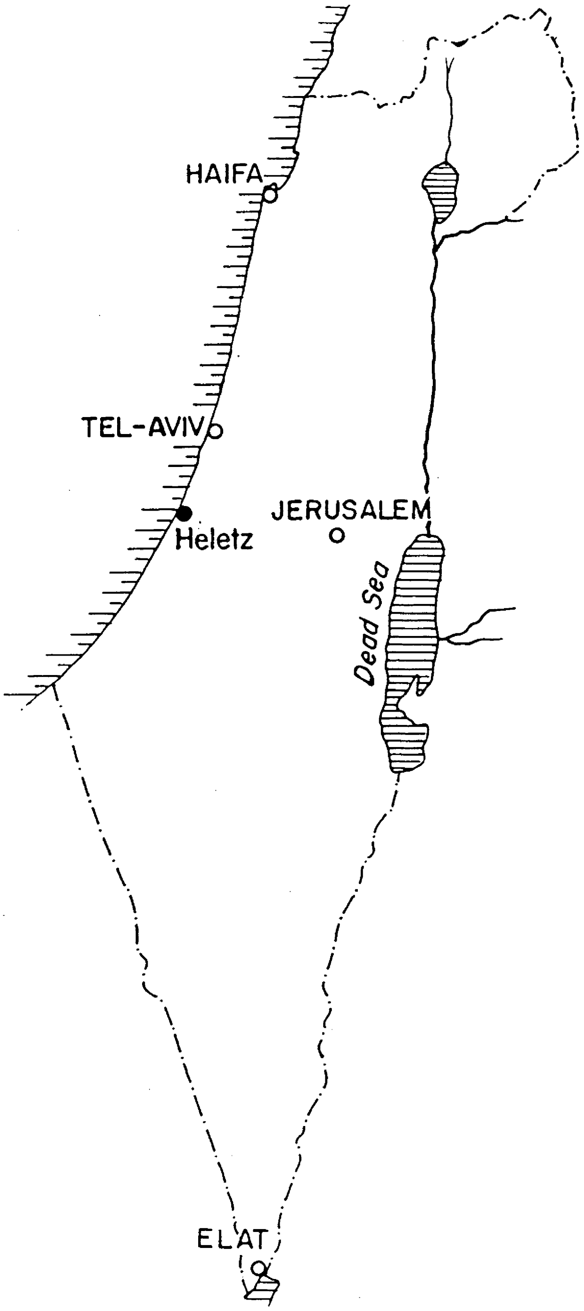


Figure 6.1. Location map of Heletz in the southern coastal plain of Israel.

1983). The rocks of this formation are carbonate-cemented sandstones with dolomitic lenses that have yielded about 16 million barrels of oil over the last 35 years. The brines were sampled in actively pumped wells and were originally mixed with oil.

6.2. RESULTS AND DISCUSSION

Subsurface brines that are associated with oil from the Heletz field were analysed for Na^+, Cl^-, SO_4^{2-}, B content and boron isotopic composition (Table 6.1). These brines are Ca-chloridic, and characterized by TDS contents of 28 to 93 g/l and low SO_4^{2-} contents (STARINSKY, 1974). The brines have $\delta^{11}B$ values of 32.6‰ to 42.2‰, high B/Cl ratios of 2.9×10^{-3} to 4.2×10^{-3} , Na/Cl ratios of 0.84 to 0.92, and low SO_4/Cl ratios of 1×10^{-5} to 5×10^{-3} (Table 6.1).

The relatively high $\delta^{11}B$ values of the subsurface brines from Heletz indicate a major contribution of marine boron with $\delta^{11}B$=39‰, or it may reflect adsorption processes similar to those of the Australian salt lakes and the Dead Sea, Israel (see Chapters 2 and 5). Brines with high $\delta^{11}B$ values which are solely the result of adsorption processes should be, however, associated with low B/Cl or B/Li ratios (see Chapters 2 and 3). This is obviously not the case in the investigated oilfield brines where the B/Cl ratios are high. A plot of B/Cl ratios *versus* $\delta^{11}B$ values (Fig. 6.2) shows an enrichment of boron relative to seawater, as normalized to chlorine. The $\delta^{11}B$ values of most of the brines overlap however, with the $\delta^{11}B$ values of modern seawater. The marine signature of boron is in concordance with the Sr isotopic composition of these brines (STARINSKY et al., 1983).

The enrichment of boron relative to modern seawater can be defined as $(B/Cl)_{brine}/(B/Cl)_{SW}$. In the investigated brines the magnitude of this enrichment is in the range 3.7 to 4.9.

TABLE 6.1. Chemical and boron isotopic results of subsurface brines from Heletz.

sample No.	well	depth (m)	sampling date	B (mg/l)	Cl (mg/l)	$\delta^{11}B$ (‰)	B/Cl ($x10^{-3}$)	Na/Cl	SO_4/Cl ($x10^{-4}$)
								molar	
seawater				4.7	19000	39.0	0.81	0.87	507.1
D-719	Heletz 5	1520	7/1/1980	34.5	35720	36.9±1.8	3.17		0.1
D-706	Kohav 3	1561	22/3/1979	17.5	16900	32.6±1.1	3.39	0.92	277.3
D-707	Heletz 35	1522	22/3/1979	40.4	33168	35.5±1.5	3.99	0.87	1.8
D-705	Kohav 14	1545	22/3/1979	36.8	27710	33.9±1.6	4.35	0.90	524.8
D-704	Heletz 11	1503	22/3/1979	39.2	33716	35.5±1.6	3.82	0.89	111.7
D-708	Heletz 22	1526	22/3/1979	40.1	37250	36.7±0.5	3.53	0.87	-
D-702	Heletz 5	1518	22/3/1979	38.5	36060	42.2±1.6	3.50	0.87	1.0
D-710	Heletz 3	1511	22/3/1979	37.1	38900	37.6±1.8	3.13	0.87	1.8
D-703	Heletz 31	1492	22/3/1979	34.0	36700	40.4±1.7	3.04	0.84	1.0

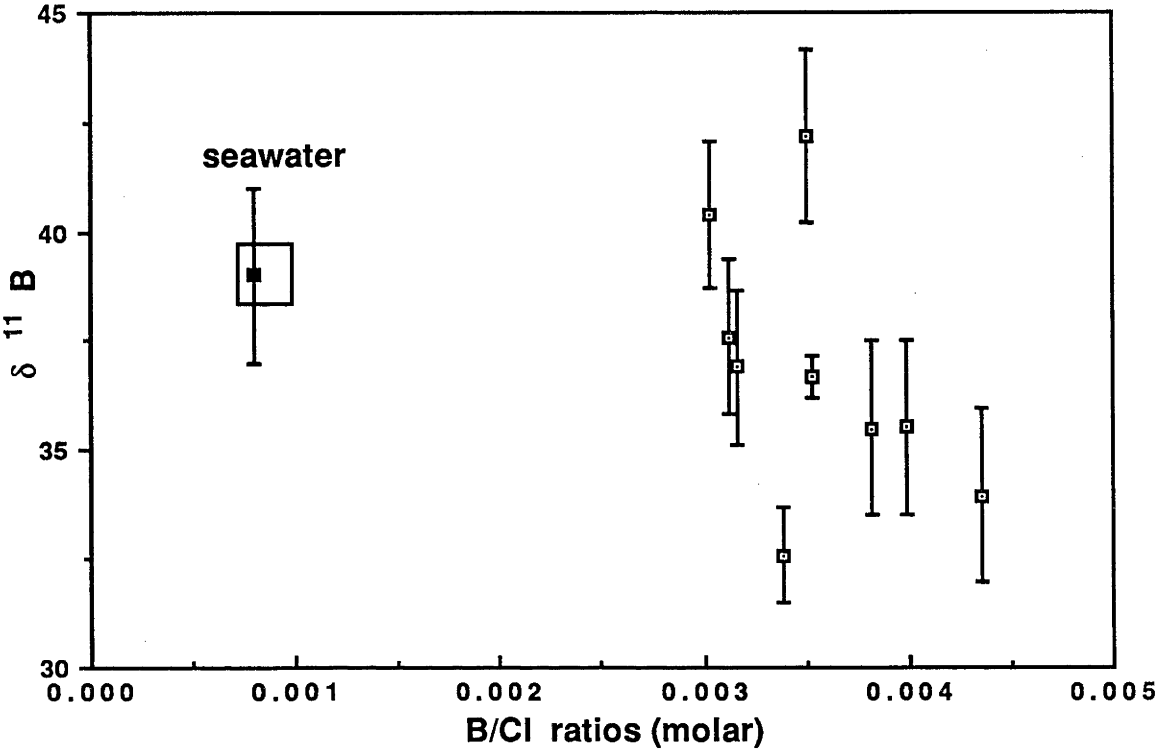


Figure 6.2. $\delta^{11}B$ values *versus* B/Cl ratios of brines from Heletz relative to modern seawater. Note the relative enrichment of elemental boron in the oilfield brines although their $\delta^{11}B$ values are broadly similar to the marine value.

The enrichment of boron could be the result of several processes:

(1) Evaporation and halite precipitation. The Na/Cl ratios of the investigated brines (Table 6.1, Fig. 6.3) indicate that halite has never been precipitated from these brines (STARINSKY, 1974; STARINSKY et al., 1983). Hence this argument is not valid for the case of the Heletz brines.

(2) Contribution of boron from the country rocks. The Sr isotopic composition and Sr/Ca ratios of these brines indicate exchange reactions of the marine brines with Cretaceous carbonate rocks (STARINSKY et al., 1983). Carbonate rocks contain only about 10-20 ppm boron (FURST et al., 1976; VENGOSH et al., 1989) and thus are not a major source of boron. However, boron is enriched in clay minerals (up to 150 ppm in marine sediments, HARDER, 1970; SPIVACK et al., 1987), thus leaching of clays can possibly contribute boron to the brines. Such boron would, however, have a different isotopic signature. The $\delta^{11}B$ values of desorbable and non-desorbable boron of modern marine sediments were estimated as 13.9‰ to 15.8‰ and -4.3‰ to 2.8‰, respectively (SPIVACK et al., 1987). If the enrichment of boron in the subsurface brines of Heletz was the result of leaching of clays we would expect much lower $\delta^{11}B$ values for the brines.

(3) High B/Cl in the original Messinian seawater. As the content of boron in the ocean through geological time has not been determined it is difficult to asses this argument;

(4) The observation that many oilfield brines from other locations and ages also have high B/Cl ratios (GULYAYEVA et al., 1966; COLLINS, 1975) may suggest that boron is also derived from organic matter. Most of the oilfield brines worldwide are characterized by high boron contents (up to 100 mg/l) and B/Cl ratios higher than that of the normal evaporation curve of seawater. The few examples of oilfield brines where the B/Cl ratio is not high are related to large fractions of dissolved halite in the brines (COLLINS, 1975).

The chemical properties of boron are analogous to those of carbon and silicon. Therefore boron is largely enriched in algae (up to 1500 ppm, NICHOLLS et al., 1959; FURST et al., 1981), coal (BROWN and SWAINE, 1964) and oil (range of 71 to 1043 ppm, GULYAYEVA et al., 1966). In oil, boron is concentrated in the wax fraction mainly in complexes with acid components, carbonic acids and phenols. Some of these components are soluble in water and hence boron in petroleum may pass to brines in close contact (GULYAYEVA et al., 1966).

The enrichment of boron in the oilfields of Heletz is also associated with an excess of bromine (STARINSKY, 1974). The $(Br/Cl)_{brine}/(Br/Cl)_{seawater}$ ratios are about 1.2, i.e. a bromine enrichment of 20%. An enrichment of bromine (and iodine) in fluids is generally attributed to derivation from decomposition of organic matter in the sediment (CAMPBELL and EDMOND, 1989; MACPHERSON and LAND, 1989). Consequently we suggest that the enrichment of boron in the investigated brines that are associated with oil may be the result of interaction with oil.

Although the bulk of the oilfield brines from Heletz have a marine signature (Na/Cl ratios and $\delta^{11}B$ values), small but significant additional variations can be identified: low-salinity (TDS) brines are associated with higher Na/Cl ratios (Fig. 6.3A), lower $\delta^{11}B$ values (Fig. 6.3B) and higher SO_4/Cl ratios (Fig. 6.3C). We distinguish between "normal marine" brines (with Na/Cl ratios of the range of 0.84 to 0.88 and $\delta^{11}B$ values of 36.7‰ to 42‰) and brines with "non-marine" values. The latter are also associated with an enrichment of sulphate (Fig. 6.3C). It is suggested that these associations indicate that the marine oilfield brines from Heletz have been diluted with water with a distinctive chemical signature. The more dilute component has a signal indicative of dissolution of rock salt (Na/Cl=1), anhydrite or gypsum (a source for sulphate) and borate minerals with low $\delta^{11}B$ values. In order to decrease the $\delta^{11}B$ value of the oilfield brines from 39‰ to 32.6‰, a relatively large quantity of boron with low $\delta^{11}B$ value is required. It has been shown that the $\delta^{11}B$ values of marine evaporite borates is 25±4‰ (SWIHART et al., 1987). In addition, a parallel study of boron isotope variations in evaporated seawater (Chapter 3), has indicated that some fraction of boron is taken into salts in late stages of evaporation. The removal of boron is associated with isotopic fractionation where the salts tend to be enriched in ^{10}B (Chapter 3). The bulk of the boron in the oilfield brines however, could not have been derived from borate

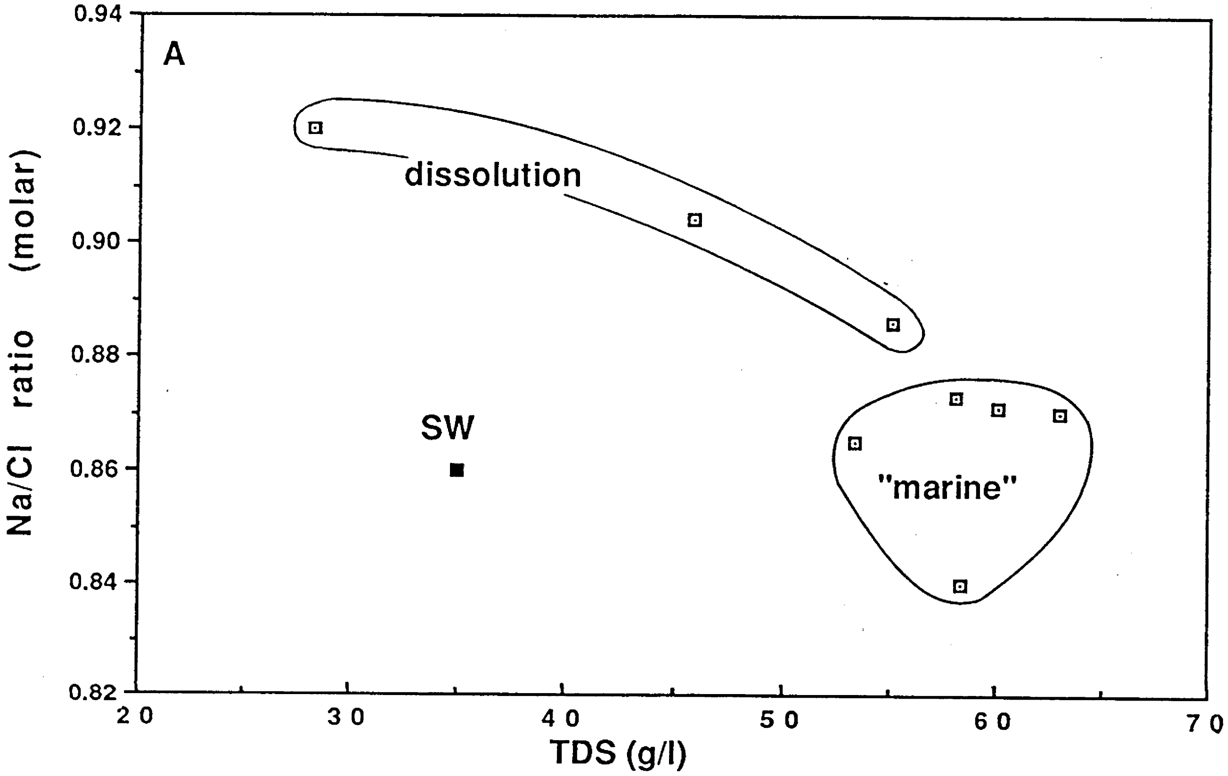


Figure 6.3.A. Na/Cl ratios *versus* TDS (g/l) of brines from Heletz. A distinction is made between brines that have a marine signature and brines that are characterized by lower TDS and higher Na/Cl ratios. The latter is interpreted as involving dissolution of Messinian evaporites.

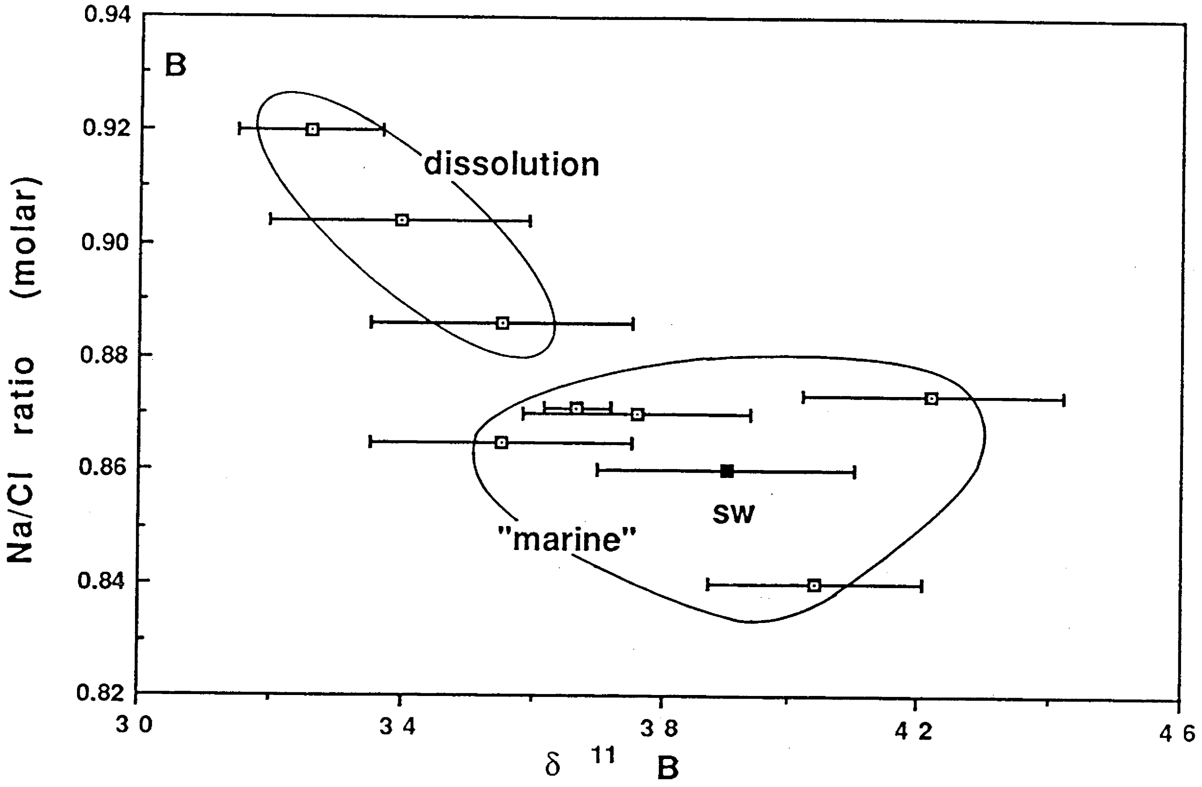


Figure 6.3.B. Na/Cl ratios *versus* $\delta^{11}B$ values of brines from Heletz. A distinction is made between brines that have a marine signature and brines that are characterized by lower $\delta^{11}B$ values and higher Na/Cl ratios. The latter is interpreted as involving dissolution of Messinian evaporites composed of rock-salt and borate minerals with lower $\delta^{11}B$ (<39‰) values.

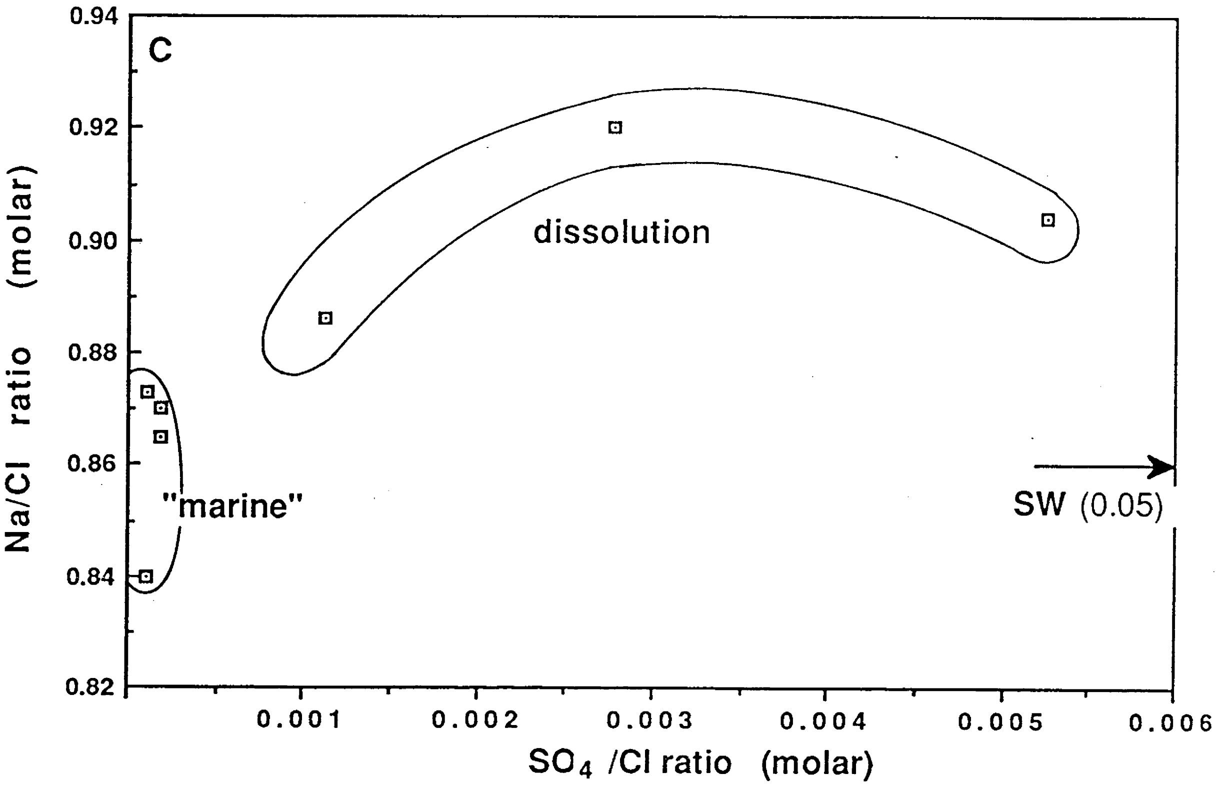


Figure 6.3.C. Na/Cl ratios *versus* SO_4/Cl ratios of brines from Heletz. A distinction is made between brines that have a marine signature and brines that are characterized by higher Na/Cl ratios and SO_4/Cl ratios. The latter is interpreted as involving dissolution of Messinian evaporites composed of rock-salt and anhydrite or gypsum.

minerals, or these brines would not have retained a largely marine $\delta^{11}B$ value. Only the more dilute brines have this "evaporite-dissolution" signature. Consequently, dissolution of Messinian (?) evaporite borates would contribute a large boron reservoir with low $\delta^{11}B$ values, high Na/Cl ratios and high sulphate contents.

Assuming that the oilfield brines have mixed with a freshwater end-member that has a Na/Cl ratio of 1, by mass-balance calculations, the concentrations and boron isotopic composition of the freshwater are estimated as: 1) Na and Cl of 625 mmoles; 2) SO_4^{2-} of 45 mmoles (SO_4/Cl ratio of 0.072); 3) $\delta^{11}B$ value of 21‰.

6.3. CONCLUSIONS

We suggest that the subsurface brines from Heletz have evolved in the following stages:

1) evaporation of Mediterranean seawater during the Messinian followed by sulphate reduction and dolomitization processes, i.e. modification into Ca-chloridic brines (STARINSKY, 1974; SASS and STARINSKY, 1979; STARINSKY et al., 1983).

2) interaction with oil and/or decomposed organic matter that has enriched the brines in boron but has not modified their $\delta^{11}B$ values, which remain marine;

3) dilution with water with a distinctive chemical and isotopic signature derived from the dissolution of Messinian evaporites.

The elemental boron and boron isotope data presented in this study have potential applications for both the reconstruction of the origin of oilfield brines and tracing their interaction with organic matter. The simplicity of the negative thermal-ionization mass spectrometry technique (VENGOSH et al., 1989) makes boron isotope analysis of oilfield brines a rapid and practical geochemical tool that assists in the identification of the sources of salts, diagenetic history and migration of fluids associated with oil.

Chapter 7

BORON ISOTOPE GEOCHEMISTRY OF GROUNDWATERS FROM THE RIFT VALLEY (ISRAEL)

7.1. INTRODUCTION

The sources of dissolved salts and the interaction of groundwaters with host rocks are usually studied by analysing the chemical and isotopic compositions of the water. In this chapter an investigation of the isotopic composition of boron in groundwaters is presented, in an attempt to apply boron isotope geochemistry as a tracer for the origin of groundwaters. The main advantages of the boron isotope method are the the conspicuous isotopic signature of seawater relative to that of terrestrial rocks (SCHWARCZ et al., 1969) and the large isotopic fractionation associated with adsorption of boron onto clay minerals (SCHWARCZ et al., 1969; SPIVACK et al., 1987, PALMER et al., 1987). These characteristics have been investigated in salt lakes from Australia and China (the Qaidam Basin) and in the Dead Sea, Israel (see Chapters 2, 4, and 5).

In this study, analyses of boron isotopes have been performed on several types of groundwaters that include a large range of salinities, different chemistries and different types of country rocks.

7.2. GEOLOGICAL AND GEOCHEMICAL SETTING

The Jordan-Arava Rift Valley (Fig. 7.1) is a transform fault, a branch of the Red Sea Rift extending from East Africa to Turkey. Waters in the rift range in salinities from snow in Mount Hermon at the north to the terminal, hypersaline Dead Sea, located about 400 m below sea level. The Ca-chloridic brines of the Dead Sea system evolved from a marine trangression in the Pliocene, through evaporite formation and interactions with sediments and country rocks (BENTOR, 1961; NEEV and EMERY, 1967; ZAK 1967; STARINSKY, 1974).

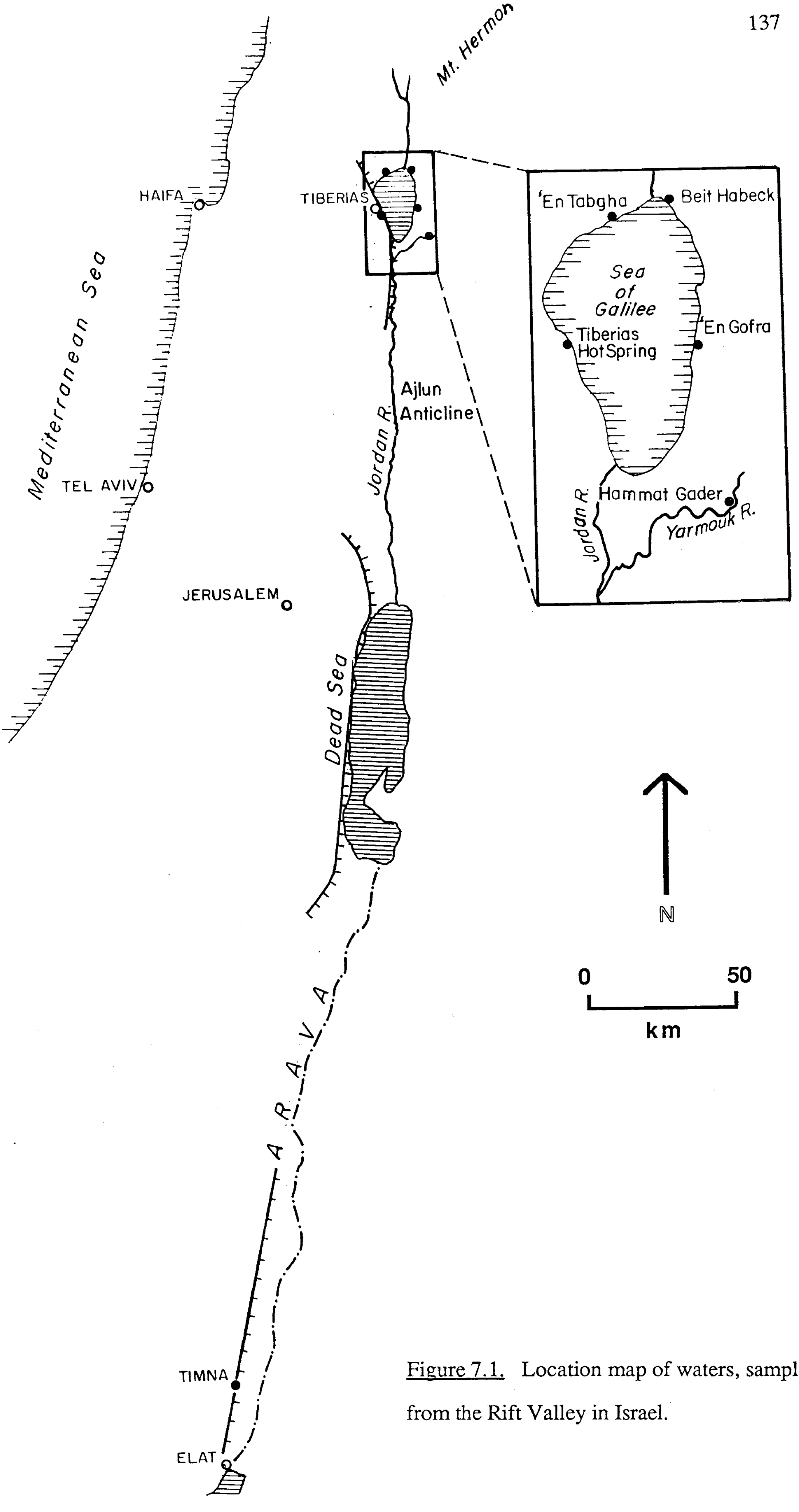


Figure 7.1. Location map of waters, sampled from the Rift Valley in Israel.

The sampling sites for this study (Table 7.1) are briefly described below.

1) Timna . The ancient copper mine of Timna is located in the the southern Arava Valley, 25 km north of Elat (Fig. 7.1). The investigated waters were collected from seepages in an open pit and underground copper mine. The chemical and isotopic characteristics (temperatures of 16^{o}C to 32^{o}C, TDS of 6000 mg/l to 16000 mg/l, Ca-chloridic type, high Ca/Mg ratios and the low ^{87}Sr/^{86}Sr ratios (in the range of 0.7058 to 0.7065; Table 7.2) of Timna waters are the result of interaction of ancient Ca-chloridic Rift Valley brines with basaltic rocks and dilution with meteoric water (STARINSKY et al., in prep.). The δ^{18}O (-8.4‰ to -6.4‰) and δD values of these waters are low and are interpreted as representing glacial-age palaeowaters (GAT and GALAI, 1982).

2) The Hammat Gader (El-Hamma) . The Hammat Gader hot springs discharge at the Yarmouk Valley, a major tributary of the Jordan River, 7 km east of the Sea of Galilee (Fig. 7.1). Five large springs with temperatures from 25 to 50^{o}C emerge from Eocene chalks at the northern margin of the Ajlun anticline. The content of the dissolved salts increases with increasing temperature. MAZOR et al., (1973) proposed a mixing model of a hot saline end-member with cold freshwaters. The δ^{18}O and δD values decrease with increasing temperature and salinity and were interpreted as mixing of ancient and recent meteoric waters (MAZOR et al., 1980). In contrast, STARINSKY et al., (1979) explained the chemical composition of the springs by the mixing of an ancient Ca-chloridic brine with modern meteoric waters. ARAD and BEIN (1986) suggested that the higher temperature low-δ^{18}O component is derived from recharge areas in the northern Golan Hights.

3) *The Sea of Galilee (Lake Kinnereth)*. The Sea of Galilee is sorrounded by brackish and saline springs which contribute salts to the lake. The investigated springs in this study are the *Roman Tiberias Hot Springs* and *'En Tabgha* on the western shore; *Biet Habeck* on the north-eastern shore, and *'En Gofra* on the western shore of the Sea of Galilee (Fig. 7.1). Although MAZOR and MERO (1969) suggested that seawater was the source for the salts in these springs, STARINSKY (1974) postulated a model of migration and dilution of ancient Ca-chloridic subsurface brines.

TABLE 7.1. Temperatures and sources of investigated groundwaters from the Rift Valley.

Sample	T (C^0)	Source
Timna		
D-682	22	spring
D-686	29	spring
D-735	27	spring
D-742	30	spring
Sea of Galilee and springs		
D-25, 'En Gofra	31	spring
D-26, Sea of Galilee	25	lake
D-27, 'En Tabgha	25	spring
D-654, Beit Habeck	-	drill hole
DS- 40, Tiberias Hot Spring	60	spring
Hammat Gader		
D-641	25	spring
D-642, 'En Saina	28	spring
D-643, 'En Reach	26	spring
D-644, 'En Balsam	42	spring
D-645, 'En Makle	50	spring

7.3. RESULTS

Timna saline waters

The four saline samples from Timna yield almost identical boron contents of 0.97 to 1.19 mg/l in spite of large differences in salinity, i.e. chlorine contents of 3323 to 8670 mg/l (Table 7.2). The $\delta^{11}B$ values range from 14.4‰ to 26.7‰ and B/Cl (molar) ratios are from $4.4x10^{-4}$ to $1.1x10^{-3}$. Samples with high $\delta^{11}B$ values are associated with higher TDS (Fig. 7.2A) and low B/Cl ratios (Fig. 7.2B).

Sea of Galilee

The Sea of Galilee has a boron content of 0.11 mg/l, a $\delta^{11}B$ value of 24.0±2‰ and a B/Cl ratio of $1.8x10^{-3}$. The springs in the area of the Sea of Galilee have boron concentrations of 0.03 to 3.92 mg/l, $\delta^{11}B$ values of 18.5‰ to 44.0‰ and B/Cl (molar) ratios of $1.8x10^{-4}$ to 1.84 $x10^{-3}$ (Table 7.2).

Hammat Gader

The five springs of Hammat Gader have boron contents of 0.09 to 0.34 mg/l and $\delta^{11}B$ values of 20.9‰ to 41.9‰ (Table 7.2). The boron content increases with increasing salinity (Fig. 7.3A) and temperature. The $\delta^{11}B$ values decrease progressively with increasing boron content (Fig. 7.3B.), TDS and temperature (Fig. 7.3C). The B/Cl (molar) ratios are in the range of $2.24x10^{-3}$ to $3.96x10^{-3}$ and are inversely correlated with TDS (Fig 7.3D), boron content and temperature.

7.4. DISCUSSION

7.4.1. *Characteristics of boron isotopes in groundwaters*

Boron in groundwaters may be derived from country rocks, meteoric waters and connate (ancient) subsurface brines. Each of these reservoirs has a distinct boron isotopic composition. Granites, fresh oceanic basalts, and non-desorbable ("fixed") boron in marine sediments have $\delta^{11}B$ values of about 0 ‰; altered oceanic basalts and desorbable boron in sediments have $\delta^{11}B$ values of 0‰ to 9‰ and 15‰, respectively (SCHWARCZ et al., 1969; SPIVACK and EDMOND, 1987; SPIVACK et al., 1987). Marine connate brines have high $\delta^{11}B$ values whereas non-marine brines, such as those

TABLE 7.2. Boron isotopic data for some groundwaters from the Rift Valley, Israel. The B/Cl ratios are molar.

sample No.	location	Cl (mg/l)	B (mg/l)	B/Cl ($x10^{-3}$)	$\delta^{11}B$ (‰)	$^{87}Sr/^{86}Sr$ *
Timna						
D-682		8180	1.19	0.48	23.3	0.70603
D-686		3450	1.18	1.12	16.2	0.70642
D-735		8670	1.15	0.44	26.7	0.70579
D-742		3323	0.97	0.96	14.4	0.70649
Sea of Galilee and springs						
DS-25	'En Gofra	2700	1.52	1.84	31.6	-
DS-26	Sea of Galilee	200	0.11	1.80	24.0	-
DS-27	'En Tabgha	1240	0.32	0.85	31.8	-
D-654	Beit Habeck	11078	0.62	0.18	18.5	0.70586
DS-40	Tiberias	18000	3.92	0.71	44.0	0.70770
Hammat Gader						
D-641		91	0.11	3.96	39.4	0.70773
D-642	'En Saina	74	0.09	3.99	41.9	-
D-643	'En Reach	210	0.19	2.97	28.2	-
D-644	'En Balsam	303	0.23	2.49	25.4	-
D-645	'En Makle	497	0.34	2.24	20.9	0.70773

* data from A. Starinsky (personal communication)

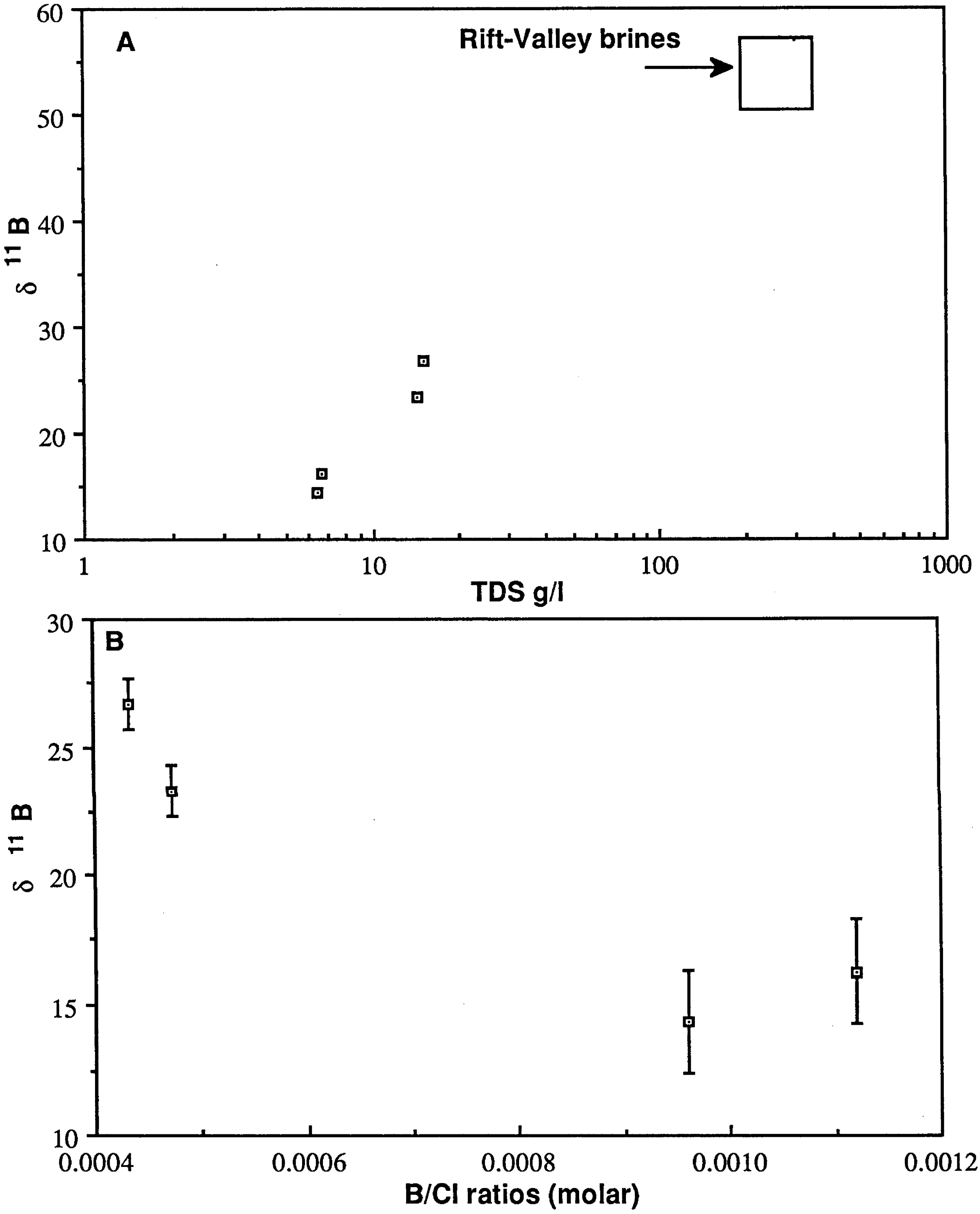


Figure 7.2.A $\delta^{11}B$ values *versus* total dissolved solids (TDS in g/l). **B.** $\delta^{11}B$ values *versus* B/Cl ratios of the saline waters from Timna. Note that the saline waters have higher $\delta^{11}B$ values.

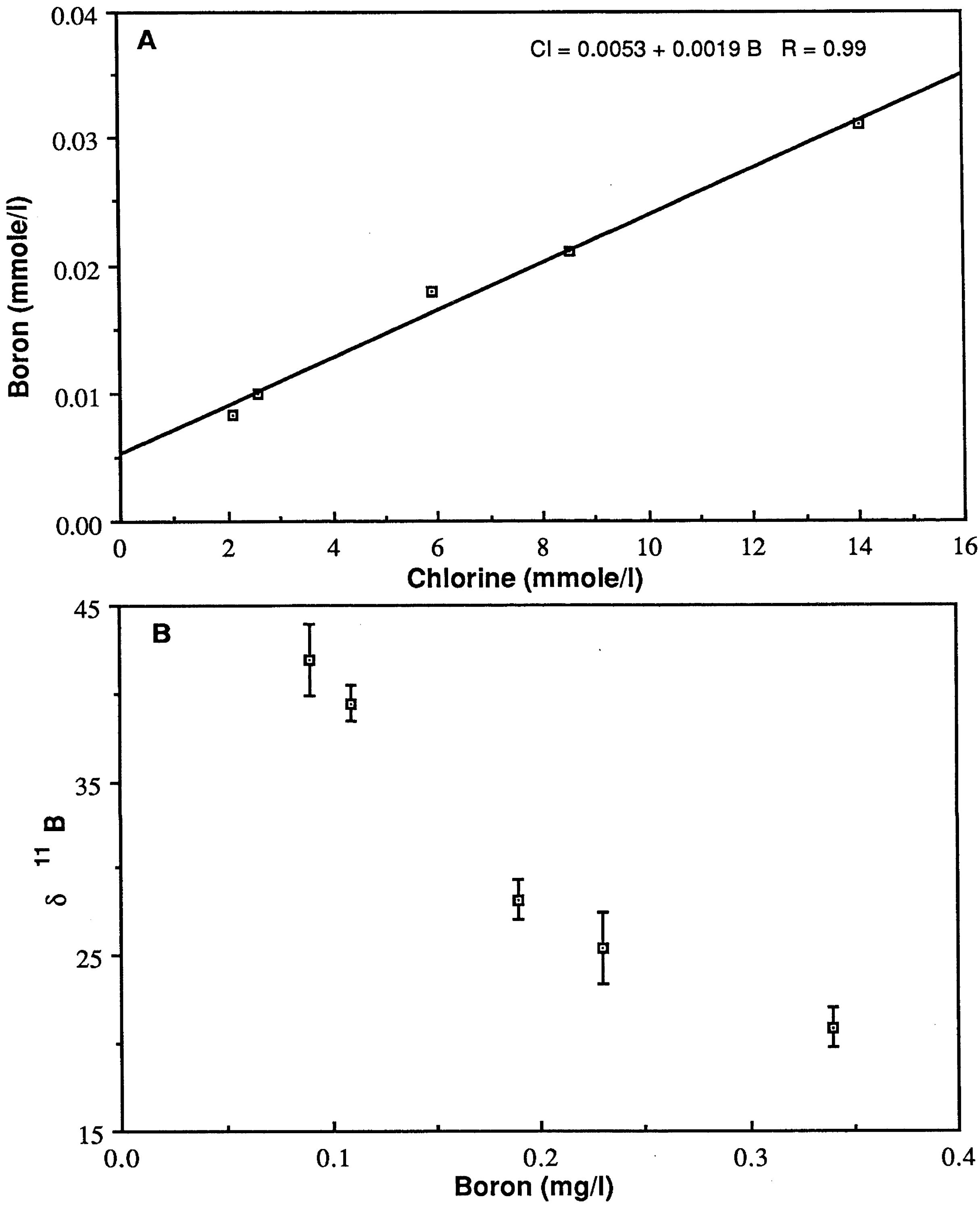


Figure 7.3.A . Boron *versus* chlorine (in mmole/l); **B**. $\delta^{11}B$ values *versus* boron content (in mg/l) of the thermal springs of Hammat Gader.

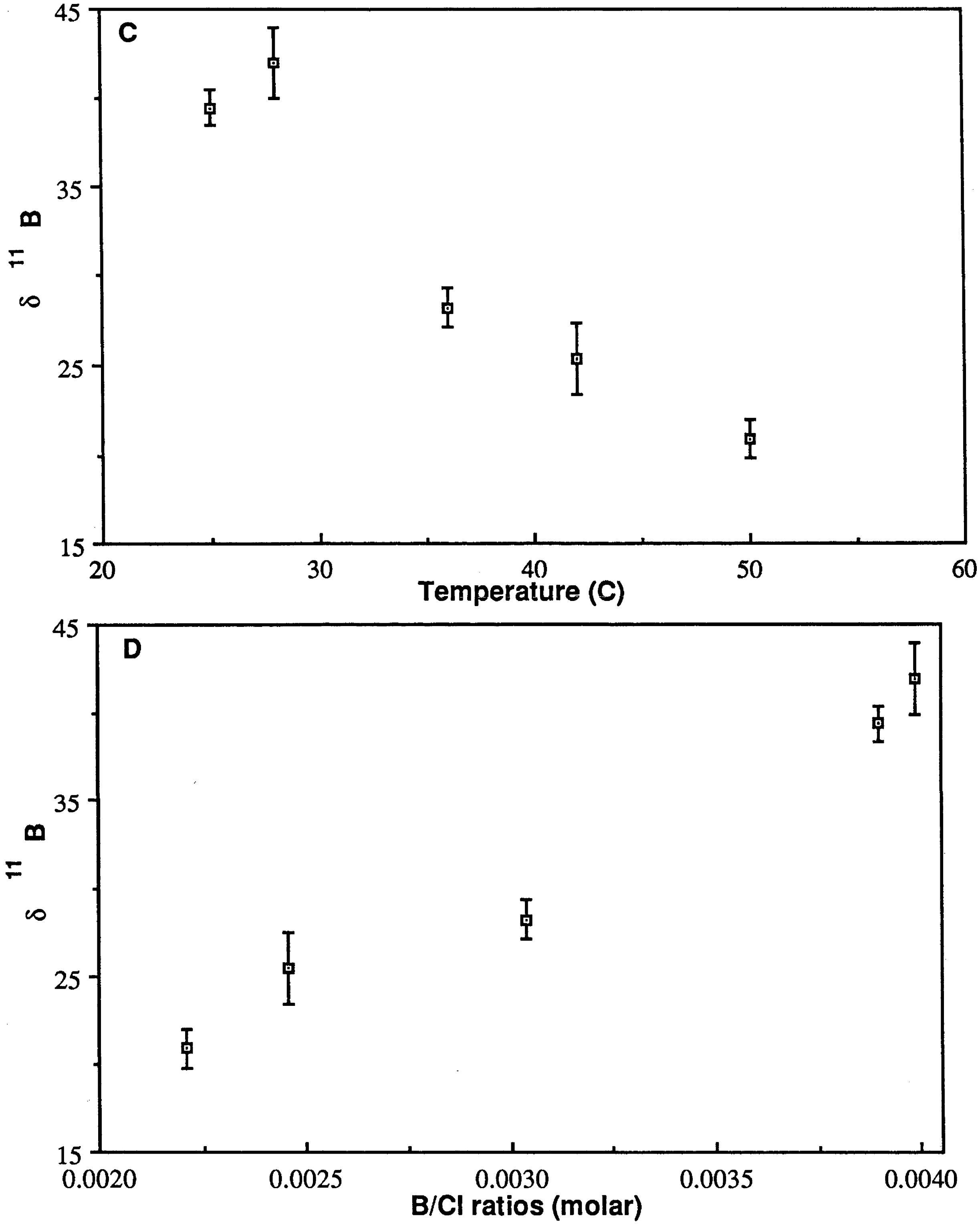


Figure 7.3.C . δ^{11}B values *versus* temperature (°C); **D.** δ^{11}B values *versus* B/Cl ratios of the thermal springs of Hammat Gader.

from the Qaidam Basin, China, have low, "terrestrial" $\delta^{11}B$ values (Chapter 4). In the case of the Rift Valley in Israel, STARINSKY (1974) and STARINSKY et al., (1979) have proposed that ancient saline brines have been trapped deep in the subsurface and contribute salts to the hydrological systems along the Rift Valley. Such brines would be characterized by low Na/Cl and B/Cl ratios, high Ca/SO_4 ratios and high $\delta^{11}B$ values (>39‰) (STARINSKY, 1974; see Chapter 5).

The few available analyses of rainwater and river water suggest that meteoric boron is derived from marine cyclic salts (SPIVACK, 1986). In the case of Australia, it has been shown that cyclic boron with a high (marine) $\delta^{11}B$ value is one of the sources of boron in Australian salt lakes (Chapter 5).

It has been shown that during low-temperature interaction of natural solutions with basalts or detrital sediments on the sea floor, boron is removed from solution. This removal is associated with isotopic fractionation in which ^{10}B is incorporated preferentially into the solid phase while the residual solution is enriched in ^{11}B, (SPIVACK and EDMOND,1987; SPIVACK et al., 1987; PALMER et al., 1987). In contrast, at higher temperatures (~ 380^0C) boron is extracted from oceanic basalts with no resolvable isotopic fractionation and the boron isotopic composition of the fluids is determined by $\delta^{11}B$ value of the rocks (SPIVACK and EDMOND, 1987).

Consequently, high $\delta^{11}B$ values and low B/Cl ratios in groundwaters may indicate that boron is removed from solution whereas low $\delta^{11}B$ values and high B/Cl ratios reflect extraction of boron from the rocks. The B/Cl (molar) ratios of igneous and sedimentary rocks range from 0.066 to 0.417 (data compiled from CHRIST and HARDER, 1978 and BREHLER and FUGE, 1974) and are significantly higher than that of seawater ($8x10^{-4}$). Both boron and chlorine are extractable with water that can leach over 50% of total Cl and B from igneous and sedimentary rocks (ELLIS and MAHON, 1967; SAUERER et al., 1990).

7.4.2. The origin of boron in the saline waters of Timna

According to STARINSKY (1974) the subsurface brines of the Rift Valley along the Dead Sea originated from ancient (Pliocene?) seawater, which evaporated and was responsible for the deposition of salts of the Sdom Formation. Thus such brines should have common chemical and isotopic fingerprints. In the case of boron, we would expect for these waters high $\delta^{11}B$ values (>39‰; Chapter 5). Low-temperature interactions of Rift-Valley brines with igneous rocks, which are abundant in the area of Timna, would also result in the brines maintaining high $\delta^{11}B$ values. The boron isotopic composition in Timna waters, (Table 7.2) ranging from $\delta^{11}B$ values of 14.4‰ to 26.7‰, suggest that these two sources cannot contribute significant boron to the waters from Timna.

Instead, high-temperature interactions with igneous rocks with low $\delta^{11}B$ values would reduce the $\delta^{11}B$ value of the brines. Similarly, interactions of seawater with basalts at elevated temperatures reduce the $\delta^{11}B$ values of the hydrothermal solution to a range of 30‰ to 34.9‰ (SPIVACK and EDMOND, 1987).

The association of high $\delta^{11}B$ values with brines with high salinity (Fig. 7.2A) and low B/Cl ratios (Fig. 7.2B) may reflect mixing of a Rift Valley brine with freshwater having a low $\delta^{11}B$ value (close to 0‰) . The low $\delta^{11}B$ values, high B/Cl ratios and low salinity end-member may be related to a solution that has interacted with country rocks. Thus, the boron isotopic composition of the saline waters from Timna suggest that boron has been derived from two sources: the Rift Valley brine with high $\delta^{11}B$ values, and the country rocks.

In spite of the large differences in salinity, the boron content in the waters from Timna (Table 7.2) is constant. This indicates that the extraction of boron from the rocks took place after the dilution of the ancient Rift Valley brine. Consequently, the suggested geochemical history of Timna waters is: (1) dilution of the ancient Ca-chloridic brines; followed by (2) interaction with igneous rocks.

The low Na/Cl and $^{87}Sr/^{86}Sr$ ratios of the waters from Timna (Table 7.2) suggest that these waters have originated from interaction of ancient Ca-chloridic Rift brines with mantle-derived materials, i.e. basalts or gabbro (STARINSKY et al., in prep.; BEYTH et al.,1984) and in agreement with the mechanism that is proposed based upon the boron isotopic results.

7.4.3. The origin of boron in the Sea of Galilee and surrounding springs

The chlorinity of the springs on the shore of the Sea of Galilee varies from 200 mg/l to 18000 mg/l. On the basis of chlorinity, the waters may be considered in two groups:

Two samples of saline springs around the Sea of Galilee yield different $\delta^{11}B$ values and $^{87}Sr/^{86}Sr$ ratios (Table 7.2) : (1) water from the drillhole at Beit Habeck has a low $\delta^{11}B$ value of 18.5‰ and a $^{87}Sr/^{86}Sr$ ratio of 0.70586; (2) the Tiberias Hot Spring has a high $\delta^{11}B$ value of 44 ‰ and a $^{87}Sr/^{86}Sr$ ratio of 0.7077. However, both springs have low Na/Cl ratios (of about 0.4). The low $\delta^{11}B$ values, $^{87}Sr/^{86}Sr$ and Na/Cl ratios of Beit Habeck may indicate a high-temperature interaction of an ancient Ca-chloridic brine with basaltic rocks that reduced the $\delta^{11}B$ value to 18.5‰ and the $^{87}Sr/^{86}Sr$ ratio to 0.70586. This suggested "basaltic" imprint is derived from Post-Pliocene basalts on the north-east of the Sea of Galilee (Fig. 7.1). The low Na/Cl ratios, the high $\delta^{11}B$ value and $^{87}Sr/^{86}Sr$ ratios of the Tiberias Hot Spring may reflect the original composition of the ancient Ca-chloridic brine.

The brackish springs of 'En Gofra and 'En Tabgha (Table 7.2) have $\delta^{11}B$ values of about 31.7‰. It is suggested that boron in these springs is a mixture of a high-$\delta^{11}B$ value component (connate brine) with a low $\delta^{11}B$ end-member, i.e. country rocks.

The boron isotopic composition of the Sea of Galilee itself is relatively low ($\delta^{11}B$=24.0±2‰). This may indicate that boron in the lake is derived from several possible sources: (1) The Jordan and associated small rivers that have catchments within basaltic and carbonate terrains; and (2) saline springs with $\delta^{11}B$ values in the range of 18‰ to 44‰.

7.4.4. The origin of boron in the thermal springs of Hammat Gader

According to STARINSKY et al., (1979) the thermal springs of Hammat Gader have originated from mixing an ancient, Ca-chloridic rift brine with present-day meteoric waters. If this were the case, we would expect that the deep, hot waters would have the signature of a rift brine, i.e. high $\delta^{11}B$ values. Instead, the $\delta^{11}B$ values of the waters from Hammat Gader decrease with increasing boron content (Fig. 7.3B.), salinity and temperature (Fig. 7.3C.). Sample D-641 which is the sample with the lowest salinity and temperature (Table 7.2) and the ^{14}C youngest age (MAZOR et al., 1973; MAZOR et al., 1980) has, on the other hand, a marine $\delta^{11}B$ signature.

The hyperbolic relationship between boron contents and $\delta^{11}B$ values (Fig. 7.3B) and the linear correlation of reciprocal boron with $\delta^{11}B$ values (Fig. 7.4) suggest mixing between a low-B, high-$\delta^{11}B$ component (freshwater; sample D-641) and a high-B, low-$\delta^{11}B$ end-member (hot, saline, deep water; sample D-645). In addition, the low-$\delta^{11}B$ end-member has low B/Cl ratios whereas the high-$\delta^{11}B$ and low-B component has much higher B/Cl ratios (Fig. 7.3D.). The B/Cl ratios of all of the springs from Hammat Gader (2.24×10^{-3} to 3.96×10^{-3}) are higher than that of seawater, or the Dead Sea (8×10^{-4}).

The boron isotope data suggest that boron in the thermal springs of Hammat Gader is derived from a reservoir with a $\delta^{11}B$ value lower than 20.9‰. Two possible modes of formation are considered:

(1) The relationship between $\delta^{11}B$ values and temperature (Fig. 7.3C) may indicate *in situ* leaching of the rocks. At high temperatures boron with a low $\delta^{11}B$ value is leached from the aquifer rocks and mixed with meteoric water with a low boron content and a high $\delta^{11}B$ value. According to this model, the budget of boron would not necessarily be related to that of the other dissolved components in the springs.

(2) It has been shown that the $^{87}Sr/^{86}Sr$ ratios of Pliocene $CaSO_4$ minerals in the northern Jordan Valley are low (M. RAAB, personal communication). The low $^{87}Sr/^{86}Sr$ ratio (0.70587) and low $\delta^{11}B$ value (18.5‰) in the subsurface saline waters from Beit Habeck may well be related to the low $^{87}Sr/^{86}Sr$ ratios of the Pliocene $CaSO_4$ minerals and suggest that an ancient Rift Valley brine had interacted with basaltic rocks. By a similar mechanism, which is described for the waters from Timna, the isotopic compositions of B and Sr were modified by the basalts at early stages in the history of this brine. Other parameters such as the Na/Cl ratios were not affected and maintained their Ca-chloridic inheritance. The interactions with basalts have modified the Ca-chloridic brine into a low-$\delta^{11}B$ brine.

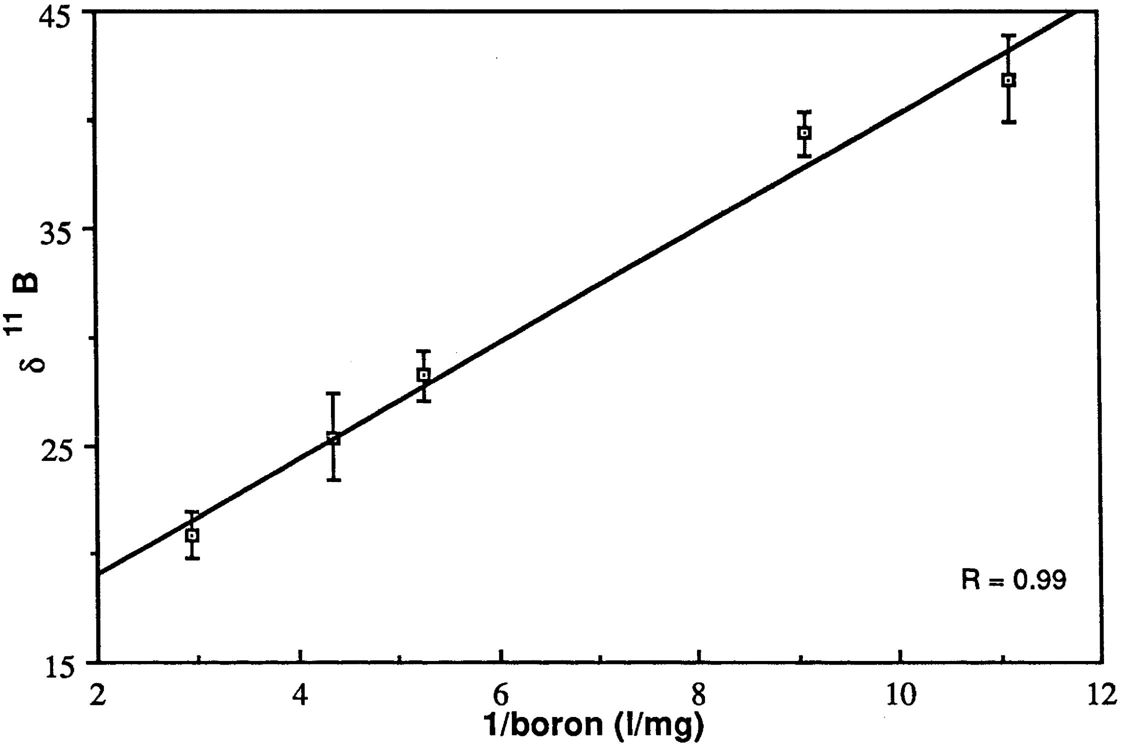


Figure 7.4. $\delta^{11}B$ value *versus* reciprocal boron content (l/mg) of water samples from the thermal springs of Hammat Gader.

The behaviour of boron is therefore a result of mixing of a low-$\delta^{11}B$ modified brine with a high-$\delta^{11}B$ end-member. The high-$\delta^{11}B$ component could be meteoric boron which has a marine isotopic composition or could be a brine similar to that of the Tiberias Hot Spring. This would also explain the observed decrease of B/Cl ratios with increasing TDS and $\delta^{11}B$ values (Fig. 7.3D) and would relate the dissolved boron content to the other major dissolved constituents in the Hammat Gader springs.

7.4.5. Sensitivity of boron to water-rock interactions

The rate of isotopic exchange between minerals and water depends upon the temperature of the system, the chemical composition, and grain-size and structure of the mineral involved. For oxygen isotopic exchange, quartz is the most resistant mineral, while the oxygen of clay minerals is more easily exchanged. Waters in deep sedimentary basins are commonly enriched in ^{18}O due to oxygen isotopic exchange at elevated temperatures with carbonates and silicates. In addition to the controls exerted by temperature and mineralogy, the magnitude of this enrichment depends on the amount of oxygen in the rock and in the fluid (HITCHON and FRIEDMAN, 1969).

The data presented in this study suggest that boron dissolved in groundwater contains a terrestrial isotopic signature, and hence was derived from the aquifer rocks. In contrast, the $\delta^{18}O$ of all the investigated groundwaters indicate little oxygen exchange with the aquifer rocks and no "oxygen isotopic shift" has been seen recognized (GAT and GALAI, 1982; ARAD and BEIN, 1986). In Timna, the Sr isotopic compositions of the waters are also dominated by rock compositions. The observed relationships are consistent with the expected behaviour given the relative concentrations of the different elements in water and rock.

This notion is considered further using, as examples, the relative abundances of a given element in a volume of water, say a litre, to its abundance in a gram of rock. In the case of Timna, where waters interact with basaltic rocks, the ratio of the amount of boron in a litre water (1 mg/l, i.e. 1000 mg) to that in a gram of basaltic rock (3 ppm, CHRIST and HARDER, 1978) is about 300. For the range of 20 to 70 mg/l Sr in these waters (STARINSKY et al., in prep.) the ratio of strontium in a litre of water to that in a gram rock (2000 ppm) is in the range of 10 to 35. In contrast, the ratio of oxygen in the water relative to that in the rock is about 1600.

These abundance-ratio figures are consistent with the measured isotopic compositions of boron, strontium and oxygen of the waters from Timna (Table 7.2; GAT and GALAI, 1982). Whereas the boron and strontium isotopic values of the waters reflect the interaction with the country rocks, the oxygen isotopic signature remains meteoric. Hence, whereas the isotopic composition of oxygen in water in an aquifer will be water (meteoric) dominated, that of Sr and boron will be influenced by rock composition.

7.5. CONCLUSIONS

1) The variations of $\delta^{11}B$ values in groundwaters may be used to trace the sources of dissolved boron (meteoric, connate, country rocks) and hence the origin of the dissolved salts in the water.

2) The large difference in the isotopic compositions of the boron reservoirs that contribute boron to the groundwaters, e.g. marine salts ($\delta^{11}B$=39‰), igneous rocks ($\delta^{11}B$=0‰), makes boron isotope compositions in groundwater sensitive indicators of water-rock interaction.

Chapter 8

COPRECIPITATION AND ISOTOPIC FRACTIONATION OF BORON IN MODERN BIOGENIC CARBONATES

8.1. INTRODUCTION

In spite of the high content of boron in clay minerals, boron concentrations in sediments are poor candidates for the determination of palaeosalinity (FLEET, 1965; LERMAN, 1966; HARDER, 1970; PERRY, 1972). SPIVACK et al., (1987) have shown that the bulk of boron in clays, that is fixed or "non-desorbable boron", is not in an isotopic equilibrium with modern seawater, while "adsorbed boron" (only ~10% of the bulk boron in clays) is governed by the boron isotopic composition of seawater. Hence the isotopic composition of bulk boron in clay minerals cannot indicate their depositional environment. In contrast, authigenic phases that are precipitated directly from seawater may monitor the nature of the parent solution and are worthy of investigation as a palaeoenvironmental tracers.

The best candidates for palaeoenvironmental indicators in the marine environment are the biogenic skeletal components. A few studies of boron geochemistry in carbonate materials have revealed boron enrichment in aragonite (15 ppm) relative to that in calcite (9 ppm) and that boron is concentrated in the non-organic parts of the shell matrices of bivalved molluscs. The boron content in the shells is related to the boron concentration in the host waters as well as the salinity (FURST et al., 1976). KITANO et al. (1978) have also demonstrated that inorganic coprecipitation of boron in calcium carbonate is proportional to both the concentration of boron in the parent solution and the mineralogical composition.

This chapter is directed towards understanding the mechanisms for coprecipitation and isotopic fractionation of boron in several skeletal components. In addition, an examination is made of the potential of boron isotope geochemistry for tracing palaeoenvironments and evaluation of the boron budgets of biogenic calcareous sediments being deposited in the oceans.

8.2. ANALYTICAL TECHNIQUES

Boron concentrations in calcium carbonate minerals have been previously determined by α-track counting (FURST et al.,1976) and spectrophotometry (ICHIKUNI and KIKUCHI, 1972; KITANO et al., 1978) techniques. In this study, $CaCO_3$ is dissolved in HCl and loaded directly into a reverse-polarity solid-source mass spectrometer (VENGOSH et al., 1989); thus both the isotopic composition and elemental concentration of boron are determined in small amounts of carbonate materials.

Carbonate minerals were freed of organic matter by hypochlorite solution or hydrogen peroxide and cleaned in distilled water with ultrasonic agitation. Analyses of aliquots of a sample cleaned only in distilled water, or H_2O_2 solution, or hypochlorite solution, yielded similar boron concentrations within the experimental error. Weighed amounts of powdered $CaCO_3$ were mixed with a ^{10}B-enriched spike (NBS 952, $^{11}B/^{10}B = 0.0554$) and dissolved in 1M HCl. The spiked solution was analysed in the mass spectrometer. Duplicate analyses of boron concentrations indicate a precision of 0.25% to 4% for the carbonate samples, with the main uncertainty being weighing errors.

Boron isotopic compositions were determined by dissolution of the powdered carbonate in 1M HCl, filtration, then addition of ultra clean $La(NO_3)_3$ or $MgCl_2$ solutions prior to loading onto filaments for mass spectrometry. The $^{11}B/^{10}B$ ratios were determined by analysing the BO_2^- ions and are reported as permil deviations ($\delta^{11}B$) relative to the standard NBS SRM 951 :

$$\delta^{11}B = [(^{11}B/^{10}B_{sample}/\ ^{11}B/^{10}B_{NBS\ 951}) - 1]\ 1000$$

The NBS SRM 951 and HCl-dissolved carbonate solutions were simultaneously loaded and analysed in a reverse-polarity, NUCLIDE-type, solid-source mass spectrometer. The addition of $La(NO_3)_3$ or $MgCl_2$ solutions enhanced the intensity of the ion beam. Both the carbonate samples and NBS SRM 951 solutions were modified for the same runs by $La(NO_3)_3$ or $MgCl_2$ matrix. The precision of the isotopic analysis by negative thermal-ionization is about 1.5‰. Analyses of direct-loaded HCl-dissolved calcium carbonate and samples in which B was separated through XE-243 columns yield similar isotopic compositions within the experimental error (H. BAADSGAARD, personal communication), and validate use of the direct loading technique.

8.3. RESULTS

Biogenic skeletons. A variety of calcareous biogenic skeletons was sampled from the Atlantic Ocean; Gulf of Elat, Israel; and the Great Barrier Reef, Australia (Table 8.1). The concentrations and boron isotopic compositions of the investigated biogenic carbonates are summarized in Table 8.1, Fig. 8.1 and Fig. 8.2. For comparison, the boron concentrations of particular species or species from the same groups previously compiled by MILLIMAN (1974) are also included in Fig 8. 2. The boron concentrations of aragonitic corals are conspicuously higher (51.4 to 79.7 ppm) than those of other biogenic skeletons. Aragonitic gastropod shells on the other hand have the lowest boron concentrations (2.1 to 3.3 ppm).

The coral *Platygira* sp. from several locations in the Gulf of Elat has similar boron concentrations, whereas a variety of coral genera (*Platygira* sp., *Fungia* sp. and *Stylofora pistilata*) from the same location yielded a range of boron concentrations from 64.3 ppm to 79.7 ppm. *Porites* sp. coral from Lady Elliot Island from the Great Barrier Reef, Australia, has a higher boron concentration (58.7 ppm) than that of *Porites* sp. from Palm Island (53.3 ppm), also located in the Great Barrier Reef.

The $\delta^{11}B$ results of the biogenic carbonate skeletons are in the range of 14.2‰ to 32.2‰, and in all cases are lower than that of seawater ($\delta^{11}B$=39‰, measured both in the Gulf of Elat and off-shore eastern Australia, Fig 8.1). Calcitic planktonic Foraminifera have the lowest $\delta^{11}B$ values of 14.2‰ to 19.8‰ whereas the aragonitic corals have the highest $\delta^{11}B$ values (and boron concentrations) among the carbonates (26.7 ‰ to 31.9‰; Fig. 8.1). The large variations in boron concentrations of the different coral species from the Gulf of Elat and the Great Barrier Reef (range of 28.3 ppm) is not reflected in their minor $\delta^{11}B$ variations (range of 5.2‰).

TABLE 8. 1. Abundances and isotopic composition of boron in selected biogenic carbonate skeletons (Cal = calcite; Arg = aragonite). Square brackets [] are A.N.U. sample numbers.

Sample	Group	Name	Mineral	B content (ppm)	δ^{11}B (‰)
Equatorial Atlantic (6°46.7'S 12°47.0'W)					
C-71	Foraminifera (plankton)	*Globigerinoides ruber*	Cal	17.9	14.2
C-72	Foraminifera (plankton)	*Globigerinoides sacculifer*	Cal	16.6	19.8
C-73	Foraminifera (plankton)	*Globorotalia menardii*	Cal	9.0	15.5
C-74	Foraminifera (plankton)	*Orbulina universa*	Cal	22.4	18.0
Gulf of Elat					
C-1	Foraminifera (plankton)	*Globigerinoides sacculifer*	Cal	14.2	14.7
C-2	Foraminifera (plankton)	*Globigerinoides ruber*	Cal	12.4	-
C-3	Foraminifera (benthos)	*Amphisorus hemprichii*	Cal	14.2	32.2
C-4	Foraminifera (benthos)	*Amphistegina* spp.	Cal	54.0	20.3
C-5	Pteropoda	*Clio convexa*	Arg	18.5	18.5
C-6	Pteropoda	*Creseis acicula*	Arg	-	18.0
C-7	Pteropoda	*Limacina inflata*	Arg	-	30.7
C-8	Coral (Taba)	*Platygira* sp.	Arg	64.1	29.6
C-9	Coral (Japanese Gardens)	*Platygira* sp.	Arg	64.4	31.5
C-10	Coral	*Fungia* sp.	Arg	77.6	30.2
C-11	Coral	*Stylofora pistilata*	Arg	79.7	31.9
C-12	Gastropoda	*Tectum virgatum*	Arg	2.1	31.5
C-16	Gastropoda	*Fusus polygamoides*	Arg	3.3	19.8
C-36	Pelecypoda	*Tridacna* sp.	Arg	15.0	20.1
Lady Elliot Island, The Great Barrier Reef					
C-49	Coral [LE-59]	*Porites* sp.	Arg	58.7	26.7
C-50	Pelecypoda [LE-60]	*Tridacna* sp.	Arg	11.0	25.3
C-51	Pelecypoda [LE-7] (age 6.5 ka)	*Tridacna* sp.	Arg	9.7	23.8
Palm Island, The Great Barrier Reef					
C-53	Coral [PI-3]	*Porites* sp.	Arg	53.3	27.4
C-54	Coral [PI-LONG]	*Porites* sp.	Arg	51.4	27.9
Gulf of Carpentaria					
C-42	Ostracoda	Bairdiids (modern)	Cal	-	17.6
C-43	Foraminifera (benthos)	Miliolids (modern)	Cal	-	13.3
C-46	Ostracoda (97.5 cm. deep in core)	*Cyprideis* sp.	Cal	-	4.0
C-47	Foraminifera (benthos) (97.5 cm. deep in core)	*Ammonia beccarii*	Cal	-	4.9

Surficial deep-sea sediments. Carbonate sediments (carbonate contents are estimated as 85% to 97%; P. MILLS, personal communication) from the core top or near the core top from the Atlantic and Pacific Oceans have boron concentrations of 9.9 ppm to 17.1 ppm and $\delta^{11}B$ values of 8.9‰ to 26.2‰ (Table 8.2). The boron concentrations and $\delta^{11}B$ values of the surficial sediments overlap with those of planktonic Foraminifera (Fig. 8.1 and 8.2).

Gulf of Carpentaria. Ostracoda and benthic Foraminifera were sampled from the sea floor and from a core in the centre of the Gulf of Carpentaria, northern Australia at a sediment depth of 97.5 cm (Table 8.1). The $\delta^{11}B$ values of the buried, ancient Ostracoda and Foraminifera shells ($\delta^{11}B$ of 4·0 ‰ and 4·9‰) are lower than that of their modern equivalents (17·6‰ and 13·3‰).

Cretaceous carbonate rocks. Analyses of carbonate rocks (limestones and dolomites) of Lower Cenomanian to Turonian age from outcrops in the Judea Mountains, Israel yielded boron concentrations of 1.5 ppm to 17.9 ppm and $\delta^{11}B$ values of 1.5‰ to 8.4‰ (Table 8.3). The $\delta^{11}B$ values of the limestone and dolomite rocks are significantly lower than that of modern carbonate sediments and biogenic calcareous skeletons.

TABLE 8.2 Abundance and isotopic composition of boron in surficial carbonate sediments from the Atlantic and the Pacific Oceans.

sample	ship	cruise-leg	core#	depth (cm)	latitude	longitude	B content (ppm)	$\delta^{11}B$ (‰)
Subtropical Atlantic								
C-63	AII	107-9	104 GC	0	31°15.8'S	35°54.9'W	11.6	26.2
C-64	AII	107-9	119 GGC	1	30°52.8'S	38°25.6'W	14.7	14.3
Equatorial Atlantic								
C-66	CHAIN	99-3	16PC	7	6°46.7'S	12°47.0'W	9.9	24.5
C-66B	CHAIN	99-3	16PC	7	6°46.7'S	12°47.0'W	9.9	25.9
C-66C	CHAIN	99-3	16PC	7	6°46.7'S	12°47.0'W	14.6	19.4
Equatorial Pacific								
C-68	AII	54-2	4PG	0	9°59.0'S	91°13.0'W	17.1	20.5
C-68B	AII	54-2	4PG	0	9°59.0'S	91°13.0'W	11.2	10.3
C-69	AII	52-2	17PG	0	5°30.6'S	102°43.2'W	16.7	17.3
C-70	CHAIN	100-10	83CC	0	7°15.7'S	168°27.6W	17.1	8.9

B - fraction > 64 µm

C- fraction < 64 µm

TABLE 8.3 Abundance and isotopic composition of boron in carbonate rocks from the Judea Mountains, Israel.

Sample	Formation and age	description	B content (ppm)	$\delta^{11}B$ (‰)
C-82	Bi'na, Turonian	bio-micritic limestone, rich fauna	1.5	1.5
C-83	Weradim,Cenomanian	micritic grey dolomite, no fauna	6.0	4.1
C-84	Kefar Sha'ul, Cenomanian	bio-micritic limestone	2.3	5.3
C-85	Soreq,Cenomanian	micritic grey-yellow dolomite, no fauna	6.3	2.5
C-86	Soreq,Cenomanian	micritic yellow marl-dolomite, no fauna	17.9	8.4

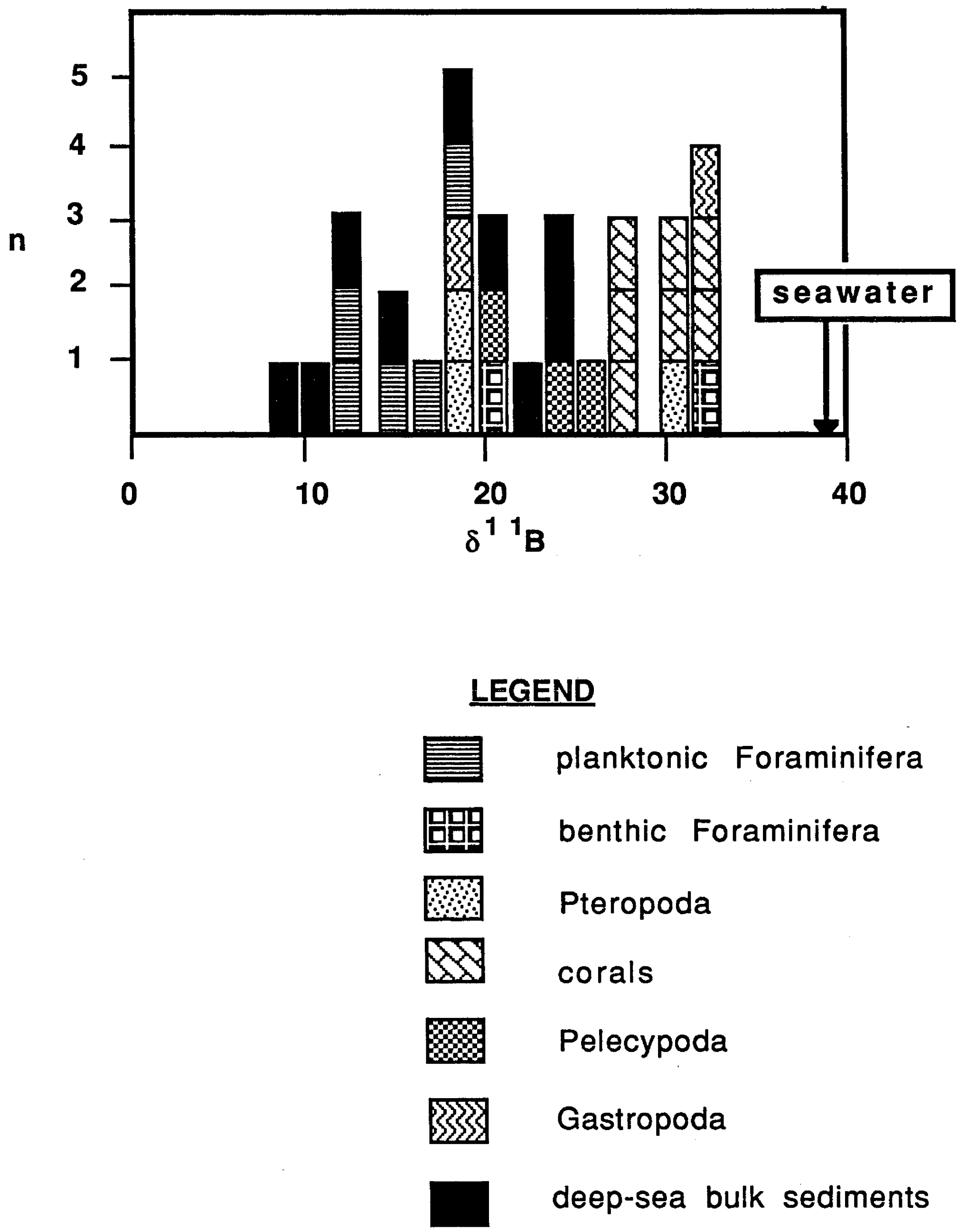
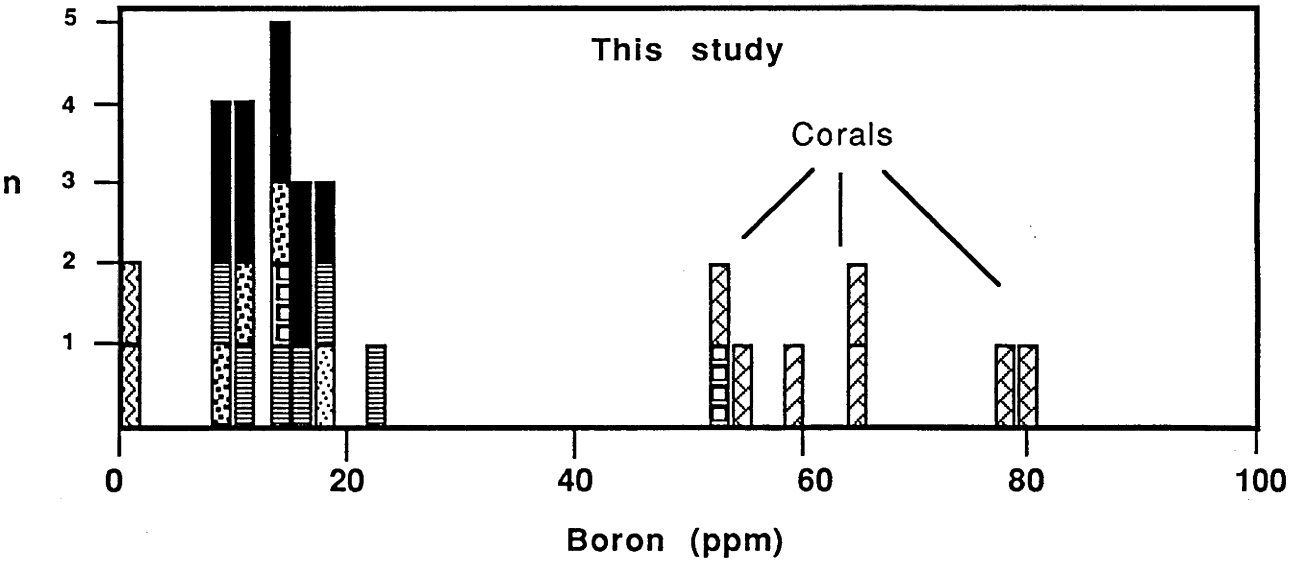


Figure 8.1

Histogram of $\delta^{11}B$ values from biogenic skeletons and deep-sea carbonate sediments. Note that all the carbonates have δ^{11} B values that are lower than that of seawater.



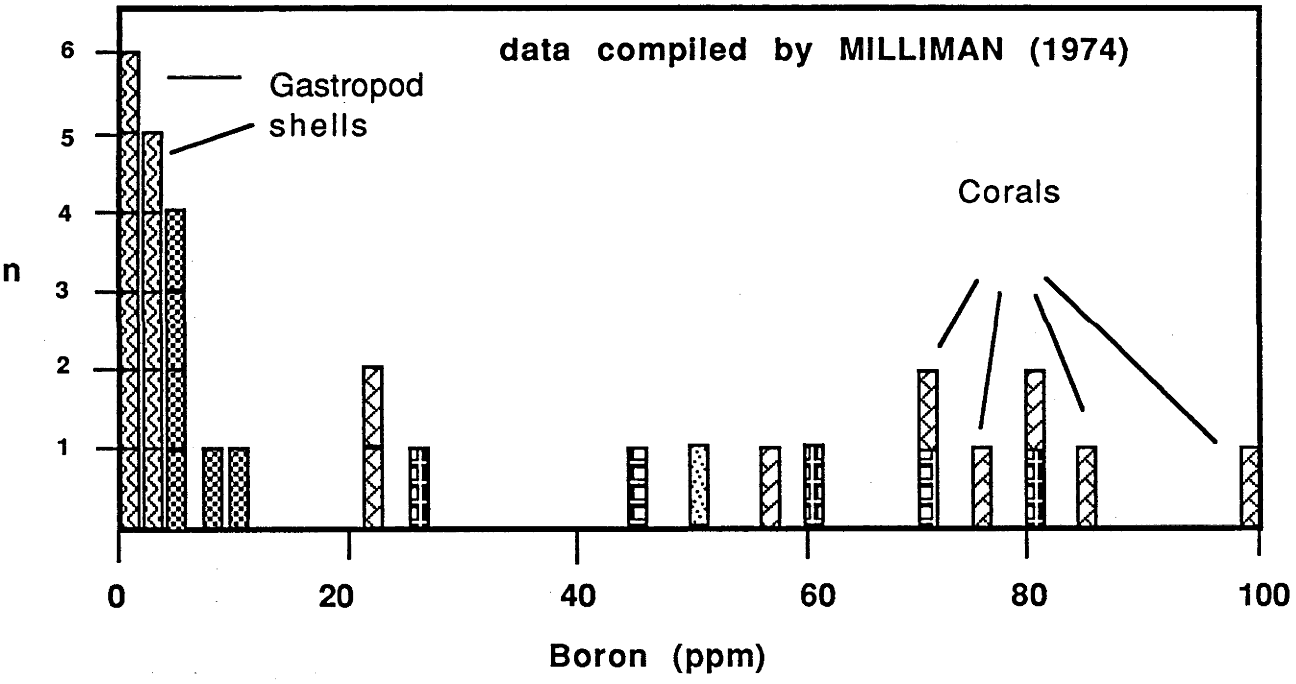


Figure 8.2

Histograms of boron concentrations of biogenic skeletons and deep-sea carbonate sediments analysed in this study and in various sources compiled by MILLIMAN (1974). Note the relative boron enrichment in corals. Symbols are the same as those used in Fig. 8.1.

8.4. DISCUSSION

8.4.1. Mode of boron uptake by biogenic calcium carbonate

The mechanism of inorganic boron coprecipitation in calcium carbonate has been investigated by ICHIKUNI and KIKUCHI (1972) and KITANO et al. (1978). These studies have shown that the amount of boron coprecipitated with aragonite is larger than that with calcite. ICHIKUNI and KIKUCHI (1972) proposed that boron concentrations of hot-spring travertines from Japan is controlled by adsorption processes. They suggested that boron incorporated into carbonate through two different stages: interaction of $B(OH)_4^-$ species with positive charge sites on $CaCO_3$ and formation of hydrogen bonds between $B(OH)_3$ and CO_3^{2-} of calcium carbonate (ICHIKUNI and KIKUCHI, 1972).

KITANO et al. (1978) suggested boron coprecipitation is dependent also on the distribution of boron species in the parent solution. They showed that the amount of coprecipitated boron in aragonite and calcite decreases and increases, respectively, with increasing salinity, and proposed that coprecipitation of $B(OH)_4^-$ is dominant for aragonite and $B(OH)_3$ for calcite (KITANO et al., 1978).

By extrapolation of the experimental data, KITANO et al. (1978) concluded that the boron content of calcium carbonate precipitated from seawater with a boron content of 4.7 mg/l, would be about 5 ppm for aragonite and 3.5 ppm for calcite.

A comparison of boron data presented in this study and from MILLIMAN (1974) (Fig 8.2), shows that the boron content of various marine calcareous skeletons is both lower and higher than the experimentally anticipated "inorganic" boron content and is not simply related to the mineralogical composition. Aragonitic corals, for example, contain large amounts of boron (up to 100 ppm) whereas aragonitic gastropod shells contain only 1 to 3 ppm (Fig. 8.2).

Consequently, it seems that biogenic ("vital") affects control the relative preferential incorporation (in the case of corals) or exclusion (e.g. gastropods) of boron. In molluscs the carbonate shell is precipitated from the extrapallial fluid which is isolated by the mantle membrane from the external solution, i.e. seawater (WILBUR and SALEUDDIN, 1983). The biological fractionation of ions between the extrapallial fluid and the ambient seawater (CRENSHAW, 1972) may control the exclusion mechanism of gastropods against boron uptake.

The dependence of boron coprecipitation on the distribution of boron species should be reflected in the boron isotope composition of the carbonates. It has been shown by KAKIHANA et al. (1977) and OI et al. (1989) that the distribution of boron isotopes between two chemical species depends on the isotopic reduced partition function ratios ("f*") of the species. The heavier isotope, ^{11}B is preferentially fractionated into the species with the larger f* values. The f* values of $B(OH)_3$ and $B(OH)_4^-$ species have been calculated experimentally by KAKIHANA et al. (1977) as 1.2008 and 1.1780 respectively, at 25^0C. Consequently, the $B(OH)_3$ species would be enriched in ^{11}B relative to the $B(OH)_4^-$ species.

OI et al. (1989) suggested that the isotopic composition of boron minerals is related to the proportions of $B(OH)_3$ and $B(OH)_4^-$ in the mineral. A $B(OH)_3$-rich mineral is enriched in ^{11}B whereas a coexisting borate mineral with a higher $B(OH)_4^-$ fraction would have a lower $\delta^{11}B$ value. We adopt this concept in evaluating the boron speciation in carbonates.

By mass balance, the $^{11}B/^{10}B$ ratio of seawater, that is R_{SW} is:

$$R_{SW} = R_3\ F + R_4\ (1-F) \tag{1}$$

where R_3 and R_4 are the $^{11}B/^{10}B$ ratios of $B(OH)_3$ and $B(OH)_4^-$ species respectively, F is the mole fraction of $B(OH)_3$.

The fractionation factor, is $\alpha = R_4/R_3$, therefore

$$R_4 = \alpha\ R_3 \tag{2}$$

Substitution of Equation 2 into Equation 1 produces

$$R_3 = R_{SW} / (F + \alpha - \alpha F) \tag{3}$$

The ionization constant of boric acid, that is

$$K^* = [B(OH)_4^-]\,[H^+] / [B(OH)_3] \tag{4}$$

has been determined experimentally by HARSHEY et al. (1986) at various ionic strengths. At salinity and pH of seawater ($pK^*=8.83$; $pH=8.2$) the mole fractions of $B(OH)_3$ ("F") and $B(OH)_4^-$ species are 0.81 and 0.19, respectively.

The calculated fractionation factor (α) for the isotopic exchange of $B(OH)_3$ and $B(OH)_4^-$ species at 25^{0}C is 0.981 (1000 lnα=-19.2‰, KAKIHANA et al., 1977), or 0.969, (1000 lnα=-31.5‰) according to PALMER et al. (1987). Calculating these values in Equation 3, the $^{11}B/^{10}B$ ratios of $B(OH)_3$ and $B(OH)_4^-$ species are 4.157 ($\delta^{11}B$=42.9‰) and 4.078 ($\delta^{11}B$=23.1‰), respectively for the α proposed by KAKIHANA et al. (1977) and 4.167 (45.3‰) and 4.037 (12.9‰) for the α proposed by PALMER et al., (1987).

Consequently, if the $B(OH)_4^-$ species is preferentially incorporated from seawater into calcium carbonate we would expect that its $\delta^{11}B$ would be 23.1‰ (KAKIHANA et al., 1977) or 12.9‰ (PALMER et al., 1987). Low $\delta^{11}B$ values such as in calcitic planktonic Foraminifera ($\delta^{11}B$= 14.2‰ to 19.8‰, Table 8.1) may indicate preferential coprecipitation of the $B(OH)_4^-$ species. The low $\delta^{11}B$ values also indicate that a large fractionation factor pertains that is not compatible with the value suggested by KAKIHANA et al., (1977) and hence in further discussion we will use the larger α suggested by PALMER et al. (1987).

Coprecipitation of both boron species would yield an isotopic composition that is proportional to the fraction of each species. The $\delta^{11}B$ value of calcium carbonate would increase with higher fractions of $B(OH)_3$ in the mineral (Fig 8.3). The $\delta^{11}B$ results reported in this study (Fig 8.1) may indicate a fraction of 80% of $B(OH)_4^-$ species in $CaCO_3$ for $\delta^{11}B$ of 20‰, and 50% for $\delta^{11}B$ of 30‰. The enrichment of corals with both elemental boron and ^{11}B ($\delta^{11}B$= 26.7‰ to 31.9‰; Fig 8.1 and 8.2), may be related to the relative abundance of $B(OH)_3$ species in seawater (81%). Hence, coprecipitation of a large quantity of boron would be associated with the abundant, ^{11}B-enriched $B(OH)_3$.

In the calculations of the dependence of $\delta^{11}B$ on the proportions of boron species in the skeletons we assumed that boron is extracted from the ambient environment, i.e. seawater. As mentioned earlier however, in molluscs the carbonate shell is precipitated directly from the extrapallial fluid and not from seawater (WILBUR and SALEUDDIN, 1983). In addition, KUILE and EREZ (1987) and KUILE et al. (1989) have shown that some benthic Foraminifera perforate species (*Amphistegina*

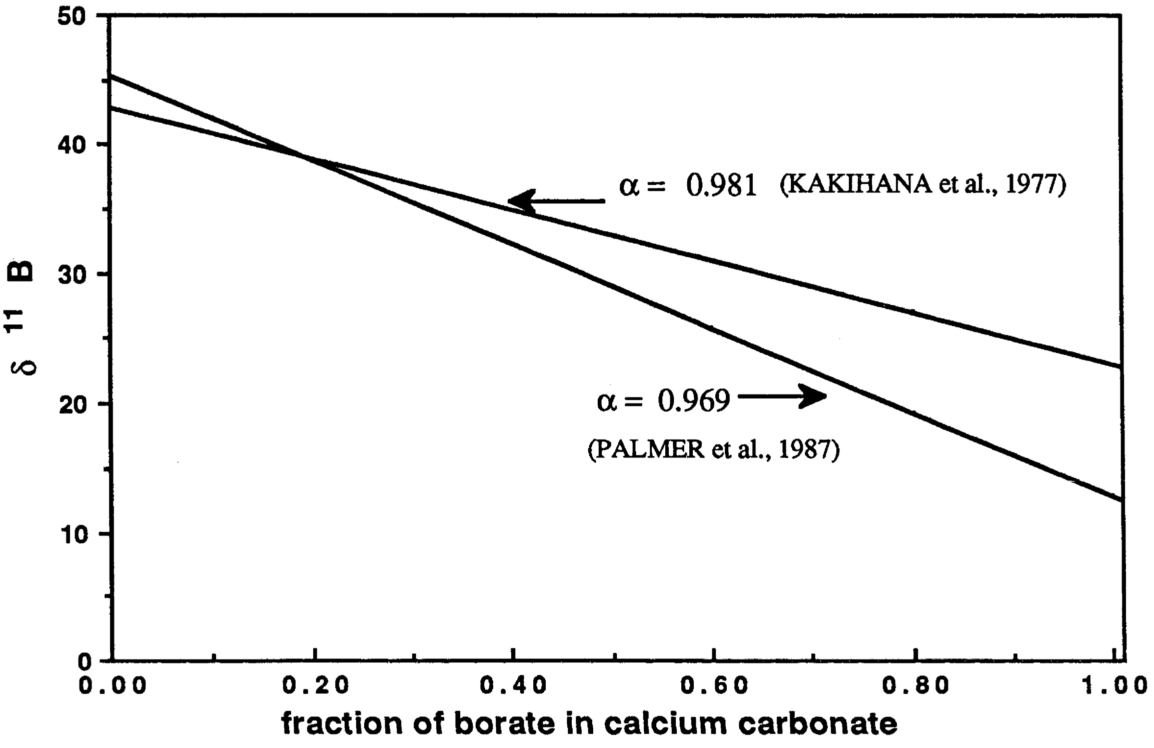


Figure 8.3. Possible $\delta^{11}B$ variations of carbonates as a function of the proportion of $B(OH)_4^-$ species in the mineral. The positions of the two lines were calculated using the fractionation factors of 0.981 and 0.969, determined by KAKIHANA et al. (1977) and PALMER et al. (1987), respectively.

lobifera) seem to have a large internal inorganic carbon pool which serves for calcification. In contrast, imperforate species (*Amphisorus hemprichii*) take up carbon and calcium directly from seawater.

The mechanism of boron coprecipitation can be therefore related to the chemistry and the characteristics of the internal reservoir. Two modes are considered:

1) If the pH in the internal fluid is different to that of the ambient seawater the distribution of boron species (F) and hence their isotopic compositions (Equation 3) would be also different. Variations in the pH of the internal fluids would change the isotopic composition of boron species and hence the $\delta^{11}B$ of biogenic skeletons. The $\delta^{11}B$ values of both boron species would increase with the pH, as illustrated in Fig 8.4. Hence the $\delta^{11}B$ results may indicate preferential coprecipitation of the charged $B(OH)_4^-$ species in relative high pH conditions. As shown in Fig 8.4, $\delta^{11}B$ values of 20‰ and 30‰ would indicate a pH of 8.7 and 9.2, respectively .

Using pH microelectrodes, JORGENSEN et al. (1985) have showed that in light, the pH value within the planktonic foraminifer *G. sacculifer* increases to 8.62. In addition, microelectrode measurements in corals detect pH values of up to 9.5 (Y.COHEN, personal communication). Consequently, precipitation of $CaCO_3$ from a high-pH microenvironment, where the isotopic exchange between boron species reaches an equilibrium, can be related to the relatively high $\delta^{11}B$ in some skeletons.

2) If the internal reservoir is a closed system with respect to the ambient seawater, selective uptake of the ^{11}B-depleted $B(OH)_4^-$ species would progressively enrich the internal fluid residue and consequently the skeleton with ^{11}B. On the other hand, an open system would produce low $\delta^{11}B$ values. The $\delta^{11}B$ variations can therefore be related to the isolation of the internal fluid from seawater where the higher $\delta^{11}B$ values indicate uptake of boron, as $B(OH)_4^-$, from an internal reservoir. As the system is reopened, the $B(OH)_4^-$ supply would lower the $\delta^{11}B$ in the skeleton.

In conclusion, assuming that the fractionation of boron isotopes is related only to its chemical speciation, the $\delta^{11}B$ data of the investigated carbonates (Table 8.1) indicates that the ^{11}B-enriched boric acid could not coprecipitate exclusively into the carbonates. Instead, high $\delta^{11}B$ values (corals) may indicate uptake of both boron species where the

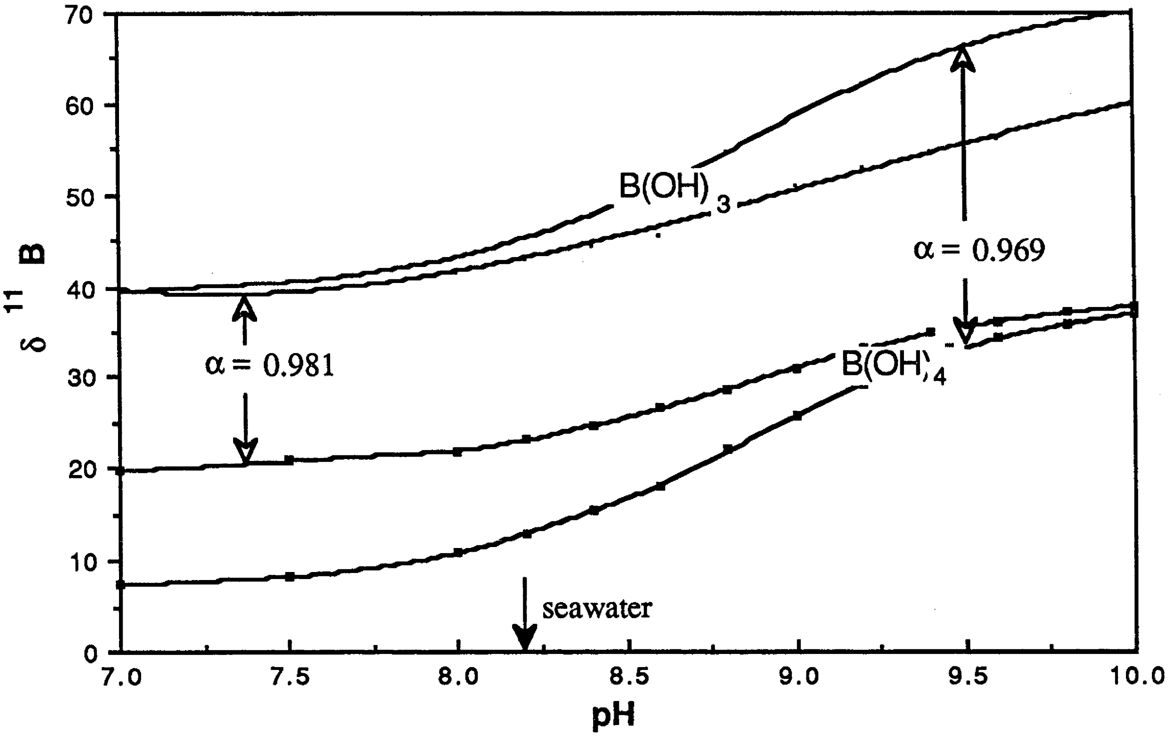


Figure 8.4 Possible variations of $\delta^{11}B$ values of $B(OH)_3$ and $B(OH)_4^-$ species as a function of the pH at the site of calcification. The two sets of lines were calculated using the fractionation factors of 0.981 and 0.969, determined by KAKIHANA et al. (1977) and PALMER et al. (1987), respectively. Note the progressive ^{11}B enrichment in both species as a function of increasing pH.

fraction of boric acid in the mineral is about 50% (Fig 8.3). Alternatively, it may indicate preferential coprecipitation of $B(OH)_4^-$ in a microenvironment of high pH (Fig 8. 4) and/or uptake of $B(OH)_4^-$ from an internal reservoir that is isolated from the ambient seawater.

8.4.2. The carbonate sink for boron in the oceans

In order to constrain the global boron sink by calcium carbonate we use the $\delta^{11}B$ values and boron concentration results of both planktonic Foraminifera and deep-sea sediments (Tables 8.1 and 8.2). As these sediments consist mainly of biogenic calcareous skeletons, both their boron abundances and isotopic compositions overlap with those of planktonic Foraminifera (Fig. 8.1 and 8.2).

Among the major recognized sinks for boron in the ocean are low-temperature basalt alteration and adsorption on detrital clay sediments (HARRISS, 1969; SEYFRIED et al., 1984; SPIVACK, 1986; SPIVACK et al., 1987). The magnitude of these processes is debated. HARRISS (1969) and SEYFRIED et al. (1984) estimated that basalt alteration and clay mineral adsorption remove about $18x10^{10}$ g B/yr and $33x10^{10}$ g B/yr, respectively; whereas SPIVACK et al. (1987) estimated these fluxes as $14x10^{10}$ g B/yr and $9.7x10^{10}$ g B/yr, respectively. The estimates of HARRISS (1969) and SEYFRIED et al. (1984) were based on the difference in boron concentrations between marine and freshwater sediments. On the other hand, the lower flux of boron removal by adsorption was calculated by SPIVACK et al. (1987) using adsorption experiments.

The boron sinks estimated by HARRISS (1969) and SEYFRIED et al. (1984) are balanced by continental runoff (~$50x10^{10}$ g B/yr) and hydrothermal springs (oceanic volcanism, $13x10^{10}$ g B/yr). SPIVACK and EDMOND (1987) estimated a lower input flux by hot springs of $0.9x10^{10}$ g B/yr. SPIVACK (1986) suggested that fluviative boron is dominated by cyclic, atmospherically derived boron. The various proposed elemental and isotopic fluxes of boron are summarized in Table 8.4.

The delivery of Ca to the world's oceans via rivers is estimated as $13.2x10^{14}$ g Ca/yr (WILKINSON and ALGEO, 1989; and references therein). In addition, alteration of basalts and hydrothermal Ca-Mg exchange, groundwater seepage and submarine

TABLE 8.4 Elemental and isotopic mass-balance of boron in the modern oceanic system. The processes and boron flux estimates are discussed in the text. $\Delta\delta^{11}$B is the difference in δ^{11}B of the fluxes relative to seawater.

Process	elemental B flux (x10^{10} g/yr)	$\Delta\delta^{11}$B (‰)	^{11}B contribution to the ocean (x10^{12} permil·g/yr)
Continental runoff	~50[a]		
	~30[c]	-25[c]	-7.5[c]
Hydrothermal flux	0.9[b]	-42±5[b]	-0.4±0.1
Oceanic crust alteration	14[b]	31±4[b]	4.3±0.5
Adsorption on detrital sediments	10[b]	25±1[b]	2.4±0.1
Coprecipitation with calcium carbonates	6.4±0.9[c]	19±5[c]	1.2±0.3[c]

a SEYFRIED et al. (1984)

b SPIVACK and EDMOND (1987)

c this study

dissolution also contribute to the global calcium flux. According to mass-age data for global sediments, WILKINSON and ALGEO (1989) suggested that the present calcium flux to carbonates is 23.7×10^{12} mole Ca/yr, i.e. 23.7×10^{14} g $CaCO_3$/yr. Similarly, the accumulation of calcium carbonates in the oceans was estimated by MILLIMAN (1974) as 18.9×10^{14} g $CaCO_3$/yr.

Both SMITH (1978) and MILLIMAN (1974, Table 64) suggested that coral reefs precipitate about 6×10^{14} g $CaCO_3$/yr. That means that reef production precipitates about 25% of the global $CaCO_3$ flux. Assuming that the investigated corals (B content =64±11 ppm, $\delta^{11}B$=29±2‰) represent the reef environments and the carbonate sediments and planktonic Foraminifera from the ocean floor (B content =15± 4ppm, $\delta^{11}B$=17±5‰) represent the deep sea, by mass-balance we suggest that the global boron sink due to oceanic $CaCO_3$ precipitation is 27±4 ppm with a mean $\delta^{11}B$ value of 20±5‰.

Consequently we estimate the global boron removal by calcium carbonate as 6.4×10^{10} g B/yr. This value is substantially higher than previously estimates, e.g. $(0.5\text{-}1.3) \times 10^{10}$ g/yr (SPIVACK et al., 1987) , and suggest that carbonates are an important sink for B in the oceans being ~20% of the total sinks.

Assuming that boron in seawater is in steady state, i.e. the input fluxes are balanced by the output fluxes , the true boron input to the ocean can be calculated by the sum of the boron sinks. Adopting the more recent evaluations of fluxes by SPIVACK (1986) and adding the calcium carbonate flux (Table 8.4) we suggest that the total boron sink in the ocean is 30.4×10^{10} g B/yr. Consequently it seems that only ~60% of the observed flux (fluviatile and hydrothermal; ~50×10^{10} g B/yr) is the true boron input, i.e. terrestrial input, to the ocean.

The flux of ^{11}B to and from the ocean ($\Delta^{11}B$) can be estimated by

$$\Delta^{11}B = FB \, \Delta\delta^{11}B \qquad (5)$$

where FB is annual input or output of elemental boron and $\Delta\delta^{11}B$ is the difference in $\delta^{11}B$ of the fluxes relative to seawater. Considering that the mean $\delta^{11}B$ of calcium carbonate in the ocean is 20‰ ($\Delta\delta^{11}B$=19‰) we estimate that the global sink of ^{11}B in $CaCO_3$ skeletons is 1.2×10^{12} permil·g/yr (Table 8.4). Including the calcium carbonate flux, the total ^{11}B sink in the ocean is about $7.9x10^{12}$ permil·g/yr. Extracting the hot-spring input ($0.4\ x10^{12}$ permil·g/yr, Table 8.4) we estimate that in steady state, $7.5x10^{12}$ permil·g/yr of ^{11}B enters the ocean via fluviatile runoff. As the true continental runoff is now estimated to be $30.1x10^{10}$g B/yr, we suggest that $\Delta\delta^{11}B$ (Equation 5) is -25 ‰. Hence the $\delta^{11}B$ value of continental runoff is about 14‰. This calculated $\delta^{11}B$ value is consistent with the measured $\delta^{11}B$ value in some major rivers (Amazon, Orinoco, Fraser and others, with a $\delta^{11}B$ range of 9.2‰ to 14‰; SPIVACK, 1986).

As the $\delta^{11}B$ value of the bulk Earth, including the terrestrial crust is -2±3 (SPIVACK, 1986) one would expect that this value would be reflected in the isotopic composition of fluviatile boron, as is the case for the Sr isotopic composition of rivers (PALMER and EDMOND, 1989). The estimated high $\delta^{11}B$ value of fluviatile boron (~14‰) probably integrates desorbable boron with a higher $\delta^{11}B$ value that is easily removed from terrestrial sediments and cycled boron within the continental crust.

In addition, it has been shown in Chapter 2 that adsorption processes within modern Australian continental sediments increase the $\delta^{11}B$ value of the residual solution up to 60‰. Therefore internal processes in the upper continental crust can modify its boron isotopic composition. Processes that occur within the oceanic environment such as adsorption onto clay minerals can also take place in the terrestrial environment (VENGOSH et al., 1989; Chapter 2) and hence the $\delta^{11}B$ value of the end-products, the rivers, will be consequently enriched in ^{11}B relative to the bulk terrestrial crust.

The observed large oceanic boron sink attributed to $CaCO_3$ may have a significant role in the balance of the boron budget in the oceans through geological time. Throughout the Phanerozoic the boron budget in the oceans could be effected by a combination of: (1) variations in rates of seafloor spreading and hence hydrothermal activity; (2) continent configuration, climate, and hence fluviatile runoff; (3) variations in sea level and formation of shallow epicontinental seas; and (4) deposition of $CaCO_3$ on continental shelves. As the hydrothermal flux of boron to the oceans is not significant (Table 8.4) the boron budget seems to be balanced by the fluviatile input and the boron sinks. During the Cretaceous for example, the combination of high sea-level, intensive $CaCO_3$ deposition, high rate of seafloor spreading and consequently intensive oceanic crust alteration may have effected both the boron content and the $\delta^{11}B$ value of seawater compared to today's values. The low marine $^{87}Sr/^{86}Sr$ ratios through the Cretaceous suggest dominance of mafic sources over continental (higher $^{87}Sr/^{86}Sr$) input (BURKE et al., 1982). Consequently, a constant or even reduced fluviatile boron input relative to more intense removal of boron by altered basalts and calcium carbonate may deplete and enrich seawater in elemental boron content and ^{11}B, respectively.

8.4.3. Possible palaeoenvironmental applications

In order to evaluate the potential of the isotopic composition of boron in calcium carbonate as a palaeoenvironmental tracer, we examined the variations of $\delta^{11}B$ of some biogenic skeletons from the Gulf of Carpentaria, Australia and in limestone and dolomitic rocks from Cretaceous strata in Israel.

The Gulf of Carpentaria, Australia. The Gulf of Carpentaria is a shallow, epicontinental sea separating Australia and New Guinea. During glacial times in the Late Quaternary the Gulf was isolated from the ocean due to lowering sea-level and became a large closed-basin lake (TORGERSEN et al., 1988). The lacustrine environment is reflected in non-marine Mg/Ca and Sr/Ca ratios (DE DECKKER et al., 1988) and high $^{87}Sr/^{86}Sr$ ratios (McCULLOCH et al., 1989) of ostracod shells from piston core sediments.

Modern Ostracoda and benthic Foraminifera from the upper part of core GC-2 from the centre of the Gulf of Carpentaria have $\delta^{11}B$ values of 17.6‰ and 13.3‰, respectively (Table 8.1). The $^{87}Sr/^{86}Sr$ ratios of these shells have modern seawater values (0.70912; McCULLOCH et al., 1989). From a depth of 97.5 cm (~ 18,000 yr BP) in the same core, the $\delta^{11}B$ values of Ostracoda and benthic Foraminifera are 4.0‰ and 4.9‰, respectively (Table 8.1). The lower $\delta^{11}B$ values occur at a time of low sea-level, where the carbonate shells record also high $^{87}Sr/^{86}Sr$ ratios (0.7100 to 0.7103: McCULLOCH et al., 1989), and were formed in a perched lacustrine basin.

The difference in $\delta^{11}B$ values between the modern and ancient shells is 13.6‰ for ostracods and 18.2‰ for foraminifers. We suggest that these shifts reflect variations in the isotopic composition of the waters of the ancient "Lake" Carpentaria. Consequently the $\delta^{11}B$ value of the ancient lacustrine water is estimated at 21‰ to 25‰.

By simple mass-balance, the estimated low $\delta^{11}B$ value of the ancient lacustrine water may indicate a terrestrial boron fraction of 0.4 to 0.6 for fluviatile fluxes with $\delta^{11}B$ values of 0‰ to 15‰, respectively. For comparison, assuming that the rivers from northern Australia and Papua New Guinea had a $^{87}Sr/^{86}Sr$ ratio similar to the average global runoff of 0.7119 (PALMER and EDMOND, 1989), the highest $^{87}Sr/^{86}Sr$ ratio recorded in the ostracod shells (0.71039; McCULLOCH et al., 1989) can be represented as reflecting a terrestrial fraction of 0.4 for strontium.

A decrease in the pH of the ancient lake to a degree where the $B(OH)_3$ species composed the bulk of the dissolved boron would decrease the $\delta^{11}B$ value of the $B(OH)_4^-$ species to 7‰. Hence, the even lower measured $\delta^{11}B$ values of 4.0‰ and 4.9‰ recorded in the glacial-age shells can not be accounted for simply by low pH in the ancient lake.

Cretaceous carbonate rocks. The $\delta^{11}B$ values of Cretaceous limestones and dolomites from the Judea Mountains (Table 8.3; $\delta^{11}B$= 1.5‰ to 8.4‰) are lower than those of modern sediments ($\delta^{11}B$= 8.9‰ to 26.2‰) and modern biogenic calcareous skeletons (Fig. 8.1). Except for one sample, the carbonate rocks also have relatively lower boron concentrations (Table 8.3). The low boron content of these rocks cannot be accounted for by a large fraction of biogenic skeletons that preferentially excluded boron, e.g. Gastropoda (Fig. 8.2), as the $\delta^{11}B$ values of modern gastropod shells are higher (20‰ and 31.5‰). The depletion of elemental B and ^{11}B may be, however, the result of:

(1) recrystallization of the calcite in the presence of groundwater depleted in boron and having a "terrestrial", low-$\delta^{11}B$ signature; (2) water-rock interactions in which a new isotopic equilibrium has been established: ^{10}B would partitioned into the tetrahedral species that incorporates preferentially into the carbonate, while ^{11}B would partitioned into the trigonal species that would remain in the liquid phase in an aquatic environment of pH lower than 7; and (3) secular variations in seawater $\delta^{11}B$ values and

boron contents that are reflected in the shallow-water shelf environment of the Cretaceous of Israel.

8.5. CONCLUSIONS

1) The abundances of boron in several groups of biogenic calcareous skeletons show large variations between 1 ppm (Gastropoda) and 80 ppm (corals). The variations are not related to the mineralogical composition and probably reflect biological ("vital") effects.

2) Variations in the boron isotopic composition of the biogenic carbonates suggest preferential incorporation of boron species, in particular the tetrahedral species.

3) The estimated global boron sink by biogenic calcium carbonate in the ocean is larger than previously estimated, and may have exerted an important control on the oceanic boron budget throughout geological time.

4) The boron isotopic composition of well preserved, ancient biogenic skeletons may provide information on the chemistry of their host waters. In particular, the sensitivity of boron isotopes to terrestrial input may be used to detect isolation of epicontinental basins from the ocean and hence sea-level changes.

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