Boron isotope geochemistry as a tracer for the evolution of brines and associated hot springs from the Dead Sea, Israel

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Abstract—A boron isotope study combined with analyses of elemental boron, lithium, and chlorine is 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‰ versus NBS-951) 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.

INTRODUCTION

THE DEAD SEA is a terminal hypersaline lake, located in one of the rhomb-shaped grabens along the Jordan Rift Valley in Israel. The sediments in the lake floor are composed of authigenic aragonite and detrital clay minerals (NISSENBAUM and KAPLAN, 1976). Its brines are characterized by high salinity and are typically Ca-chloridic (STARINSKY, 1974). BENTOR (1961), ZAK (1967), NEEV and EMERY (1967), STARINSKY (1974), and ZAK (1980) suggested that 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 that are recorded in the large salt bodies (mainly halite) of the Mount Sedom Formation (ZAK, 1967). A combination of climatic changes and tectonic movements led to fluctuations in the lake level and eventual isolation from the Mediterranean seawater (ZAK, 1967; NEEV and EMERY, 1967). The Lisan Formation, with an age between 60,000 and 18,000 years B.P. (KAUFMAN, 1971), is the precursor of the modern Dead Sea and reflects deposition during high lake-level conditions. The Lisan sediments are composed of white authigenic varve-like aragonite alternating with detrital laminae (KATZ and KOLODNY, 1989). Using major-element ratios of brines from the Dead Sea, 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 mixtures of freshwaters (e.g., Jordan River) with subsurface hypersaline brines. In contrast, STARINSKY (1974) and ZAK (1980) 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 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 the boron isotopic composition, 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. 1 and Table 1). The chemical characteristics of the waters investigated in this study are summarized in Table 2.

ANALYTICAL PROCEDURES

The determination of boron isotopic compositions was carried out by negative thermal-ionization mass-spectrometry (ZEININGER and HEUMANN, 1983; VENGOSH et al., 1989, and references therein). The high reactivity of boron enables production of BO_2^- ions from untreated solutions which were loaded directly onto filaments in a reverse-polarity mass spectrometer. Isotope ratios are reported as
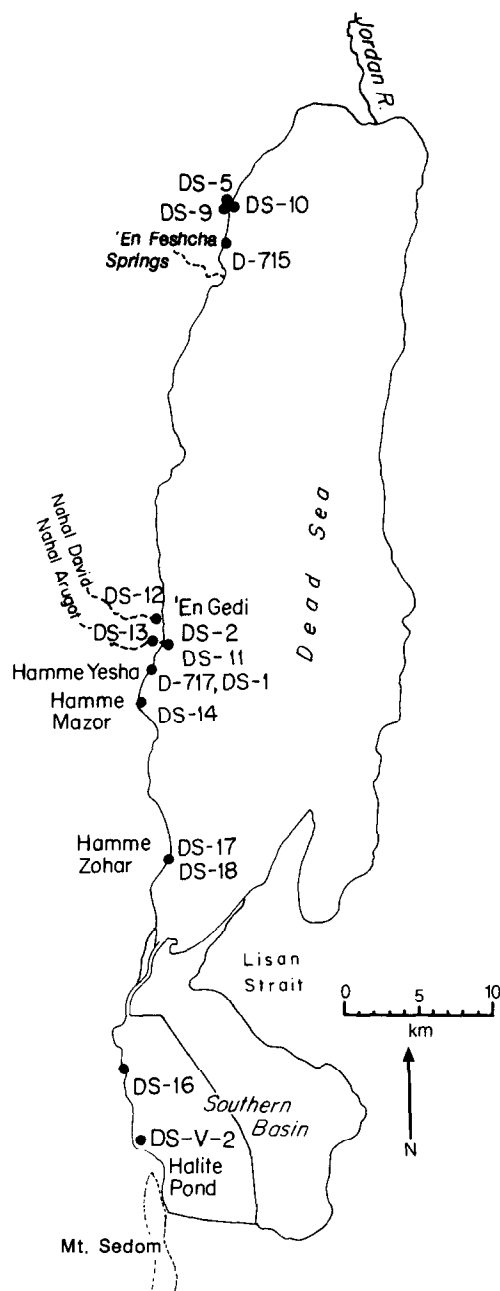
FIG. 1. Location map of the investigated brines and waters. Note that what used to be the southern basin of the Dead Sea is now a large evaporation pond.

permil deviation (δ^{11}B) in the ^{11}B/^{10}B ratios relative to the standard NBS SRM 951:

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

NBS SRM 951 (boric acid power) and seawater samples were repeatedly analysed to determine reproducibility. The 2σ 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). The mean of the absolute ^{11}B/^{10}B ratios of the NBS SRM 951 replicates, detected by the NUCLIDE solid-source mass spectrometer, at the time of this study, is 3.986 ± 0.005. Boron concentrations (Table 3) in brines and waters were determined by isotope-dilution mass spectrometry (VENGOSH et al., 1989), chlorine by Ag-titration, and lithium by ICP.

RESULTS

The isotopic and chemical results are summarized in Table 3. Several groups of waters are recognized:

1) Surface brines from the Dead Sea are characterized by high δ^{11}B values (55.7 to 57.4‰; cf. seawater with δ^{11}B of 39‰), high contents of boron (3.5 to 4.1 mMol/kg-H_2O), lithium (1.8 mMol/kg-H_2O), and chlorine (5000 mMol/ kg-H_2O). The B/Cl ratios are marine but the B/Li ratios (2.3) are lower than that of seawater (15.7). In the southern basin, which presently is an artificial evaporite pond of the Dead Sea Works Ltd, the concentrations of boron (5.2 mMol/kg-H_2O) and chlorine (5571 mMol/kg-H_2O) are higher. The lithium content in the halite pond is also higher than that of the northern basin, in the range of 2.4 to 2.6 mMol/kg-H_2O (GANOR and KATZ, 1989). The δ^{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 δ^{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 δ^{11}B values in the range 51.7 to 54.9‰, B contents of 1.9 to 2.9 mMol/kg-H_2O, Li of 0.8 to 1.1 mMol/kg-H_2O, and Cl of 2791 to 3561 mMol/kg-H_2O. B/Li ratios are in the range of 2.5 to 2.7.

4) The brackish springs from 'En Feshcha have δ^{11}B values of 37.7 and 40.6‰, and B contents of 3.7 × 10^{-2} and 6.5 × 10^{-2} mMol/kg-H_2O, respectively.

5) The δ^{11}B values of meteoric freshwater springs from 'En

TABLE 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 pond
DS-16	Dead Sea surface brine	halite pond, 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

TABLE 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/SO₄
				(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

Dawid and Nahal Arugot are 33.8 and 36.9‰, and their B contents are 9.3 × 10⁻³ and 2.7 × 10⁻² mMol/kg-H₂O, respectively. The B/Cl ratios (9.8 × 10⁻³ and 3.7 × 10⁻³) are higher than that of the Dead Sea and seawater (Table 3).

DISCUSSION

The Origin of Boron in the Dead Sea Brine

The geological and geochemical evidence suggests that brines in the Dead Sea area are a residual product of evaporated seawater that have precipitated halite and interacted with sediments of Mount Sedom Formation and Cenomanian and Turonian limestones (ZAK, 1967; 1980; NEEV and EMERY, 1967; STARINSKY, 1974). In the following section we will show that boron isotopic systematics in the Dead Sea also suggest a marine origin, although the $\delta^{11}B$ value of the Dead Sea brine is higher than that of seawater.

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, is 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 (15.7) and indicate a relative depletion of elemental boron in the Dead Sea by a factor of about 7. This is a minimum estimate, as some Br was coprecipitated in the formation of halite in the Mount Sedom Formation (ZAK, 1967).

The marine B/Cl ratios of the Dead Sea brines and the hot springs (Table 3) do not indicate conservative behaviour of both boron and chlorine in the Dead Sea system. In a plot of Na/Cl vs. B/Cl ratios (Fig. 2), one can see the variations of these parameters during progressive evaporation of seawater: Na/Cl ratios decrease while B/Cl ratios increase (VEN-

GOSH, 1990). 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. 2). Consequently, the "marine" B/Cl ratios indicate a depletion of boron. This is consistent with the low B/Li ratios.

In addition to depletion of elemental boron, the brines from the Dead Sea system are enriched with ^{11}B ($\delta^{11}B$ = 51.7‰ to 57.4‰) relative to seawater ($\delta^{11}B$ = 39‰), indicating that ^{10}B was preferentially removed from the liquid phase. The depletion of elemental boron and ^{10}B in the Dead Sea could be the result of (1) adsorption of boron onto clay minerals (SHERGINA and KAMISKAYA, 1967; 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 (VENGOSH, 1990) it is shown, however, that during evaporation of seawater to its final stages both the $\delta^{11}B$ 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, Lake Lisan (KATZ and KOLODNY, 1989).

The normalization of boron to lithium in the Dead Sea is made because of the conservative behaviour of lithium, as reflected in its isotopic composition. Seawater is enriched with ^7Li relative to submarine hydrothermal solutions, its principal lithium 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 ^6Li from seawater is grossly similar to the processes of depletion of seawater by ^{10}B (SPIVACK and EDMOND, 1987; SPIVACK et al., 1987). The $^6Li/^7Li$ ratios of the Dead Sea

TABLE 3. Boron isotopic and chemical composition of the investigated brines and freshwaters from the Dead Sea region. Boron, lithium and chloride concentrations are in mMol/kg-H₂0, and B/Cl and B/Li ratios are also molality units.

| sample	$\delta^{11}B$ (‰)	B	Li	Cl	B/Li	B/Cl (x10⁻⁴)	density (g/cc)
seawater	39.0	0.4	2.8x10⁻²	530	15.7	8.1	1.023
Dead Sea, northern basin							
DS-11, Dead Sea (north)	57.3±1.0	4.1	1.8	5004	2.3	8.1	1.224
DS-2, Dead Sea (north)	57.2±1.6	3.5	na	na	-	-	-
Dead Sea, southern basin (artificial evaporite pond)							
DS-16, Dead Sea (south)	56.4±1.5	5.2	na	5571	-	9.4	1.243
DS-V-2, Dead Sea (south)	55.7±1.0	na	na	na	-	-	-
Diluted Dead Sea							
DS-10, 'En Feshcha beach	57.4±1.5	1.6	0.8	2028	2.0	7.8	1.083
D-715, saline spring	55.7±1.5	0.8	0.4	1091	2.0	7.3	1.040
Hot Springs							
D-717, Hamme Yesha	52.2±1.5	2.1	na	2820	-	7.3	1.117
DS-1, Hamme Yesha	51.7±1.6	1.9	na	na	-	-	-
DS-14, Hamme Mazor	54.9±1.0	2.0	0.8	2791	2.5	7.1	1.108
DS-17, Hamme Zohar	52.9±1.5	2.1	0.8	1611	2.7	13.1	1.065
DS-18, Hamme Zohar	52.9±1.5	2.9	1.1	3561	2.6	8.2	1.144
'En Feshcha brackish springs							
DS-5, 'En Feshcha	40.6±1.0	4.1x10⁻²	na	33	-	12.3	1.001
DS-9, 'En Feshcha	37.7±1.0	6.5x10⁻²	na	51	-	12.4	1.002
Freshwater springs							
DS-12, 'En Dawid	33.8±1.1	2.8x10⁻²	na	2.4	-	97.5	1.000
DS-13, Nahal Arugot	36.9±1.2	9.3x10⁻²	na	3.3	-	36.8	1.000

na = not analysed
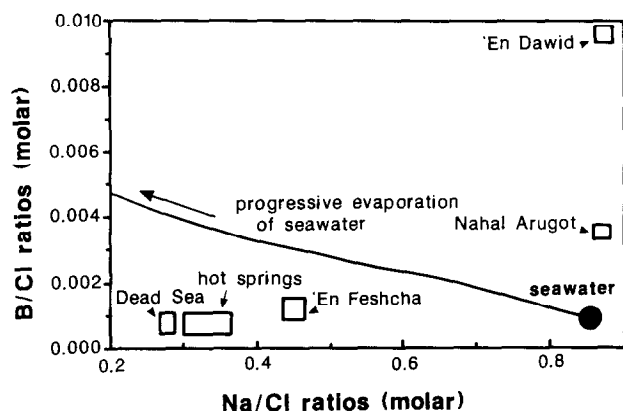
FIG. 2. B/Cl vs. Na/Cl ratios of evaporated seawater, Dead Sea, hot springs, and brackish and freshwater springs at 'En Feshcha, 'En Dawid, and Nahal Arugot. The curve for progressive evaporation of seawater is from VENGOSH (1990). The B/Cl ratios of the Dead Sea and hot springs are typically marine, 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.

brine are similar to that of modern seawater (CHAN and ED-MOND, 1988), indicating that the original marine lithium has accumulated in the brine residues without isotopic exchange. In contrast to lithium, the high $\delta^{11}B$ values of the Dead Sea indicate the non-conservative behaviour of boron.

The interaction of the Dead Sea brine with clay minerals could be completely reversible or it can be assumed that the sediments were isolated from the main brine reservoir due to rapid sedimentation. KATZ and KOLODNY (1989) have shown that the chemical composition of sediment-entrapped brines in the Lisan Formation suggests rapid sedimentation and isolation of the lake deposits from the overlying brine. In the following section we estimate the distribution of boron species in the Dead Sea brine and use the observed boron deficiency and boron isotopic composition to detect the probability of these two scenarios.

The isotopic fractionation during the adsorption of boron onto clay minerals is dependent on the distribution of boron species, temperature, pH, and clay mineralogy (SHERGINA and KAMISKAYA, 1967; SCHWARCZ et al., 1969; KAKIHANA et al., 1977; NOMURA et al., 1982; SPIVACK et al., 1987; PALMER et al., 1987). These workers have shown that during experimental 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. KAKIHANA et al. (1977) and OI et al. (1989) suggested that $B(OH)_3$ species would be always enriched in ^{11}B relative to $B(OH)_4^-$. The estimated fractionation factor (α) for the isotopic exchange of $B(OH)_3$ and $B(OH)_4^-$ species at 25°C is 0.981 according to KAKIHANA et al. (1977), or 0.969, measured by PALMER et al. (1987) in adsorption experiments.

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 (BYRNE and KESTER, 1974; REARDON, 1976; HERSHEY et al., 1986; ROGERS and VAN DEN BERG, 1988). HERSHEY 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 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%).

For the conditions of the Dead Sea of low pH of 6.5 (NEEV and EMERY, 1967; NISSENBAUM, 1969; AMIT and BENTOR, 1971; SASS and BEN-YAAKOV, 1977), ionic strength = 9.5 M, Ca = 0.51 M, Mg = 1.98 M (GAVRIELI et al., 1989), and total B of 0.0049 M, we estimate the distribution of boron species. By using the dissociation constants of boric acid, $CaB(OH)_4^+$ and $MgB(OH)_4^+$, corrected for the high ionic strength and the Na-Ca-Cl matrix of the Dead Sea (HERSHEY et al., 1986), the fractions of boron species in the Dead Sea brines are calculated as $B(OH)_3$ = 0.98, $B(OH)_4^-$ = 1.66 $\times 10^{-3}$, $MgB(OH)_4^+$ = 1.46 $\times 10^{-2}$, $CaB(OH)_4^+$ = 4.92 $\times 10^{-3}$. Consequently, it seems that boric acid is the predominant form of dissolved boron in the Dead Sea.

Considering that dissolved boron in the Dead Sea brine is composed predominantly of boric acid whereas $B(OH)_4^-$ is preferentially adsorbed onto clay minerals, we use the measured B/Li and $\delta^{11}B$ in the modern Dead Sea to estimate the empirical boron-isotope fractionation factor. We assume that (1) the original seawater had B/Li and $\delta^{11}B$ values similar to that of the present ocean; (2) the boron contribution from terrestrial inflows and rocks is negligible; i.e., the Dead Sea brine-sediment is a closed system (KATZ and KOLODNY, 1989); and (3) the effective water/sediment ratio is close to 0. According to the first model, the interaction of the brines with clay minerals is completely reversible and the adsorbed boron is in equilibrium with the dissolved boron. The magnitude of the fractionation factor is thus

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

where $\delta^{11}B_{SW}$ and $\delta^{11}B_{DS}$ represent the boron isotopic composition of seawater and Dead Sea brines, respectively; X is the fraction of boron which remains in the solution, normalized to lithium: $X = (B/Li)_{DS}/(B/Li)_{SW}$ (=0.14 in the Dead Sea); and α is the boron-isotope fractionation factor between dissolved and adsorbed boron (=0.981, using Eqn. 1).

According to the alternative model, adsorbed boron was continuously removed without exchange with the remaining brine. The fractional adsorption scenario can be described by using Rayleigh distillation terminology:

$$(\delta^{11}B_{DS} + 1000) = (\delta^{11}B_{SW} + 1000) X^{\alpha-1}. \quad (2)$$

Using α values of 0.981 (KAKIHANA et al., 1977) and 0.969 (PALMER et al., 1987), and X = 0.14, the calculated $\delta^{11}B$ values of the Dead Sea brine ($\delta^{11}B_{DS}$) are 78.5 and 104.3‰, respectively (Eqn. 2). These values are obviously higher than

the measured $\delta^{11}B$ value in the Dead Sea (57‰) thereby indicating that the fractional adsorption model is not valid for the Dead Sea system. Instead, the magnitude of the empirical boron-isotope fractionation factor, detected by the equilibrium model (0.981) is respectively similar and lower to that suggested by KAKIHANA et al. (1977) and PALMER et al. (1987).

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

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

and

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

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 vs. $\delta^{11}B$ values (Fig. 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. 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. 3). The relatively low $\delta^{11}B$ values of the hot springs, as expected from their B contents, indicate 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 (1970). The deviation of $\delta^{11}B$ values of the hot springs relative to the Dead Sea-freshwater mixing lines is consistent with other chemical tracers.
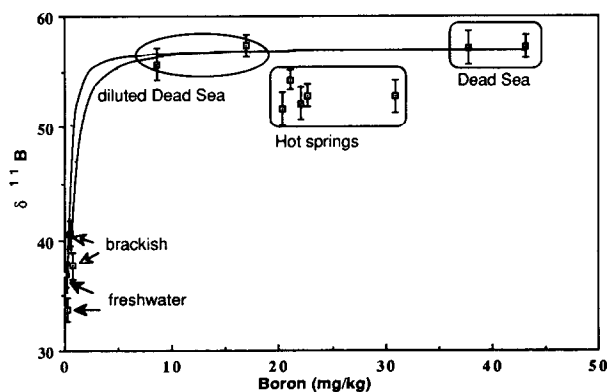

FIG. 3. $\delta^{11}B$ values vs. boron contents of the Dead Sea brines, diluted Dead Sea, hot springs, brackish water ('En Feshcha) and freshwaters in the Dead Sea system. The mixing lines were calculated from mixing equations of the Dead Sea brine with 'En Feshcha springs and with freshwater.

STARINSKY (1974, p. 139) showed mixing curves of Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-, and Br^- that indicate that the hot springs are not mixing product of the Dead Sea and freshwater.

The lower $\delta^{11}B$ values and higher B/Li ratios of the hot springs, relative to those of the Dead Sea (Fig. 4), suggest that the hot springs are the sources of the Dead Sea. The data points in Fig. 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 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. 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. 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 relatively 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 $\delta^{11}B$ 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. In addition, rock leaching would produce a brine with a low $\delta^{11}B$ value and high B/Li or B/Cl ratios. This is reflected in the boron isotopic composition ($\delta^{11}B$ values range from 4 to 12‰; $^{11}B/^{10}B$ ratios are normalized to NBS 951) and high B/Cl ratios (1.8×10^{-2} to 8.5×10^{-2}) of inland hot springs from Japan (KAKIHANA et al., 1987; MUSASHI et al., 1988). As boron is extractable with water that can leach over 50% of total boron in granitic rocks (SAUERER et al., 1990), VENGOSH (1990) has shown that a terrestrial input of boron and lithium would produce a brine with a $\delta^{11}B$ value of ~0‰,
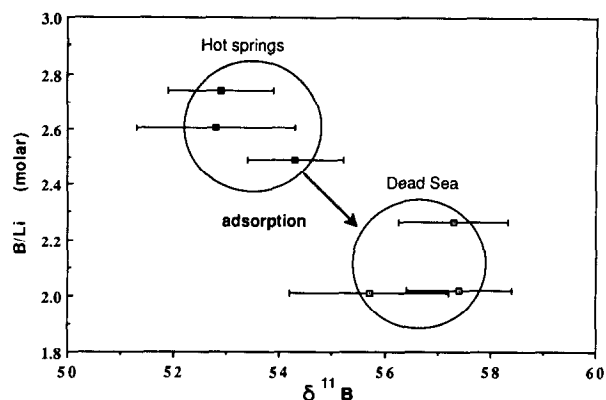
FIG. 4. Boron/lithium ratios vs. $\delta^{11}B$ values of Dead Sea brines (squares) and hot springs (filled squares). The trend of adsorption is suggested by the lower B/Li ratios and higher $\delta^{11}B$ values of the Dead Sea brines relative to those values from the hot springs.

and a high B/Li ratio. The high $\delta^{11}B$ values and the low B/Li ratios, particularly of the subsurface thermal springs, rule out such mechanisms for the origin of salts in the Dead Sea.

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 2) indicate 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 2).

Most of the country rocks in the eastern Judea Desert are composed of Cenomanian and Turonian carbonate rocks. Boron in the freshwater springs in that area could be therefore derived from (1) atmospheric cyclic salts that originated from seawater and have marine $\delta^{11}B$ values. Although SPIVACK (1986) showed that $\delta^{11}B$ values of rainwaters from the Pacific Ocean (4 samples) vary between 1 to 35‰, VENGOSH et al., (1991) suggested that high-$\delta^{11}B$ brines from inland Australian salt lakes are derived from marine cyclic salts; and/or (2) country rocks with low $\delta^{11}B$. VENGOSH (1990) has investigated Cenomanian and Turonian limestone and dolomite rocks from outcrops at the western slopes of the Judea Mountains. The $\delta^{11}B$ values of these rocks ($\delta^{11}B = 1.5$ to 8.4‰) are significantly lower than that of modern carbonate sediments and biogenic calcareous skeletons ($\delta^{11}B = 8.9$ to 31.9‰; VENGOSH, 1990).

The $\delta^{11}B$ values (33.8 to 36.9‰), high B/Cl ratios (higher than that of seawater and the Dead Sea), and the marine Na/Cl ratios of the freshwater (Fig. 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 = 8 × 10⁻⁴, Na/Cl = 0.86), with terrestrial boron, derived from the carbonate rocks. It seems that boron isotopes in the freshwaters are sensitive to rock leaching whereas Na/Cl ratios are not. The terrestrial endmember 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 3; Fig. 2). In addition, their Na/Cl ratios are low (0.38–0.45; Table 2). This could 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. 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.

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 of a brine indicate 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.

4) The $\delta^{11}B$ values of inland brines from the Dead Sea reported in this study and of some salt lakes from Australia (VENGOSH et al., 1991) are higher than that of seawater and are the highest natural ¹¹B-enriched reservoirs known to date.

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