Boron isotope variations during fractional evaporation of sea water: New constraints on the marine vs. nonmarine debate

Avner Vengosh* Research School of Earth Sciences, Australian National University, G.P.O. Box 4, Canberra, ACT 2601, Australia

Abraham Starinsky Yehoshua Kolodny] Department of Geology, Hebrew University, Jerusalem 91904, Israel

Allan R. Chivas Research School of Earth Sciences, Australian National University, G.P.O. Box 4, Canberra, ACT 2601, Australia

Menahem Raab Geological Survey of Israel, 30 Malkhe Yisrael Street, Jerusalem 95501, Israel

ABSTRACT

Examination of boron isotopes, elemental B, Br, and Li in brines, and coprecipitated salts during fractional evaporation of sea water shows that Br, Li, and B in the evaporated sea water have lower concentrations than expected, as determined from mass-balance calculations. The deficiency is found beyond a degree of evaporation of \sim 30 and is associated with a gradual increase in the δ^{11} B values of the evaporated sea water, from $39^{\circ}_{\circ 00}$ to $54.7^{\circ}_{\circ 00}$ (relative to standard NBS 951). The high δ^{11} B values of the brines and the relatively lower δ^{11} B values of the coexisting precipitates (MgSO₄ and K-MgSO₄ salts; $\delta^{11}B = 11.4^{\circ}/_{\circ 0}$ to 36.0[°]/₀₀) suggest selective uptake of ¹⁰B by the salts. Applying Rayleigh distillation equations, the empirical fractionation factors for the depletion of the salts in ¹¹B are estimated as $30^{\circ}/_{\circ \circ}$ ($\alpha = 0.969$) for the early stages of precipitation (gypsum and halite range) and $20^{\circ}/_{00}$ ($\alpha = 0.981$) for the late stages (K-MgSO₄ minerals). Coprecipitation of $B(OH)_4^-$ species with the salts, and/or precipitation of Mg-borate minerals with a coordination number of 4 are the proposed mechanisms for boron isotope fractionation during fractional evaporation of sea water. The boron isotope composition of sea water ($\delta^{11}B = 39^{0}/_{00}$) is significantly higher than that of continental water $(\delta^{11}B \approx -3^{\circ}/_{00} \pm 5^{\circ}/_{00})$. Our study shows that salt deposits may be depleted in ¹¹B by 20[°]/₀₀ to $30^{\circ}/_{00}$ relative to their parent brines. These variations suggest that boron isotopes can be used to determine the origin (marine vs. nonmarine) of brines and ancient evaporitic environments.

INTRODUCTION

The identification of the origin of evaporites (i.e., marine vs. continental) is important for the interpretation of ancient saline and hypersaline environments. Conventional geochemical methods, such as analysis of bromide content, cannot exclusively distinguish marine from nonmarine sources (Hardie, 1984, 1990; Sonnenfeld, 1985; Holser, 1979; Lowenstein and Spencer, 1990). For example, Hardie (1984, 1990) demonstrated that the compositions of some modern nonmarine saline lakes are similar to that of evaporated sea water. Boron isotope geochemistry can determine the origin of brines and evaporites. Sea water is enriched in ¹¹B relative to both oceanic crust and the continental crust (Spivack and Edmond, 1987; Spivack et al., 1987). The difference is due to isotopic fractionations that occur when boron is removed from sea water onto detrital clays, weathered basalts, and carbonate minerals (Schwarcz et al., 1969; Spivack and Edmond, 1987; Vengosh et al., 1991a). Previous studies showed that ancient marine evaporite borates are enriched in ¹¹B relative to their nonmarine counterparts (Swihart et al., 1986; Oi et al., 1989). Nevertheless, the behavior of boron isotopes during evaporation and crystallization processes has not been studied. The purpose of this study is to examine the variations of boron isotopes, elemental B, Br, and Li in evaporated sea water and coprecipitated salts during artificial evaporation of sea water accompanied by fractional mineral crystallization.

EXPERIMENTAL PROCEDURES

Two sets (Y and R series) of 20 l of Mediterranean sea water were evaporated for 73 days in a clean, air-filtered fume hood. At different stages of evaporation, measured fractions of residual brines and precipitated salts were separated from the main brine reservoir for chemical and isotopic analyses. 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 were reported in Raab and Spiro (1991).

Boron isotope composition was determined by negative thermal-ionization mass spectrometry (Vengosh et al., 1989, and references therein). Brines and H₂O-dissolved salts were deposited directly onto Re filaments and evaporated to dryness before loading into a reverse-polarity, NUCLIDE-type, solid-source mass spectrometer at the Australian National University (Vengosh et al., 1989, 1991a). The ¹¹B/¹⁰B ratios are reported as per mil deviation (δ^{11} B) relative to the standard NBS SRM 951: δ^{11} B = ([¹¹B/¹⁰B_{sample}/¹¹B/¹⁰B_{NBS 951}] - 1) × 1000. The mean of the absolute ¹¹B/¹⁰B ratios of the NBS SRM 951 replicates, analyzed along with the samples, is 3.987 ±0.006. The average δ^{11} B value of 14 sea-water replicates was 37.7%₀₀, with a standard deviation of 1.5%₀₀. Boron concentrations were determined by isotope dilution mass spectrometry (Vengosh et al., 1989), lithium by inductively coupled plasma spectrometry, and bromine by X-ray fluorescence spectroscopy.

RESULTS AND DISCUSSION

The experimental evaporation of Mediterranean sea water yielded progressively concentrated brines and the expected soluble salts for such evaporation, i.e., carbonate, gypsum, halite, MgSO₄, and K-MgSO₄ minerals (Raab and Spiro, 1991). The concentrations of Br, Li, and B, as well as the δ^{11} B values of both the evaporated sea water and salts, increased with evaporation, whereas the salts yielded relatively lower B contents and δ^{11} B values (Table 1). We used the Br, Li, and B contents of the evaporated sea water to detect the degree of evaporation. Assuming that Br, Li, and B accumulate in conservative amounts in the solution, and considering the volume of the brines and the aliquots of the separate fractions that were taken during the experiment for chemical analyses, we calculated the expected concentrations of these elements in each of the evaporation stages. We defined $\epsilon_{(volume)}$, which is the absolute degree of evaporation, as the ratio between the expected concentrations of the conservative elements and their concentrations in ocean water. Although the measured Br, Li, and B contents of the brine increased with evaporation, at late stages of evaporation the measured concentrations were lower than expected. The degree of evaporation calculated for boron (ϵ [B]), lithium (ϵ [Li]), and bromide (ϵ [Br]) were lower than that of the $\epsilon_{(volume)}$ values (Table 1, Fig. 1). Previous investigations, both in artificial and natural conditions, used these elements as indicators for the degree of evaporation of sea water (McCaffrey et al., 1987, and references therein). Our exper-

^{*}Present address: Hydrological Service, Water Commission, Ministry of Agriculture, P.O. Box 6381, Jerusalem 91063, Israel.

iment shows, however, that the three elements are not absolutely conservative—they do not accumulate solely in the liquid phase. In the late stages of evaporation the measured apparent degree of evaporation of lithium was higher than that of boron, which was, in turn, higher than that of bromide (Fig. 1). Thus, considerable amounts of all these elements contribute to the solid phases.

The estimated deficiency of boron in the brines and the gradual increase of B content of the salts suggest removal of boron into the precipitates by two possible mechanisms: (1) incorporation into the mineral lattice and (2) trapping in fluid inclusions. The gradual increase of $\delta^{11}B$ values of the brines from normal sea water from 39^{0}_{00} to 54.7^{0}_{00} and the relatively lower $\delta^{11}B$ values of the coprecipitated salts ($\delta^{11}B =$ 11.4^{0}_{00} to 36.0^{0}_{00} ; Fig. 2) suggest that the boron incorporation into the minerals is associated with isotopic fractionation; therefore, we rule out the second mechanism.

TABLE 1. CONCENTRATIONS OF BORON, LITHIUM, BROMIDE, AND δ^{11} B VALUES IN BRINES AND COPRECIPITATED SALTS DURING FRACTIONAL

| Sample | Brines | | | | | Salts | | | ε (B) | ε (Li) | e (Br) |
|---------------|-------------|--------------|--------------|-------------|------------|-------------|----------|--------|----------|-----------|-----------|
| | B (mg/L) | Li (mg/L) | Br (mg/L) | δ11B (‰) | B (ppm) | δ11B (‰) | ∆ (‰) | (vol.) | | | <u></u> |
| Ocean water | 4.7 | 0.18 | 67 | 39 | - | - | - | | - | - | - |
| Mediterranean | 5.3 | 0.20 | 75 | 37.7 | - | - | - | - | - | - | - |
| sea water | | | | | | | | | | | |
| R-5 (ha) | 53.2 | - | 630 | 41.7 | - | - | - | - | - | - | - |
| Y-11 (ha) | 82.8 | - | 1261 | - | - | - | - | - | - | - | - |
| Y-13 (ha) | 130.9 | - | 1681 | • | - | - | - | 29.3 | 27.9 | • | 25.1 |
| Y-14 (ha) | 158.6 | 7.00 | 1978 | 43.4 | - | 13.2 | 30.2 | 37.3 | 33.3 | 38.8 | 26.4 |
| R-15 (ha) | 152.8 | - | 2169 | 42.9 | | - | - | 39.3 | 32.6 | - | 32.4 |
| R-16 (mg) | 192.3 | 8.29 | 2534 | 46.1 | 2.5 | 14.0 | 32.1 | 48.0 | 41.0 | 46.0 | 37.8 |
| Y-15 (mg) | 222.9 | - | 2766 | | - | - | - | 53.5 | 47.5 | - | 41.3 |
| Y-16 (mg) | 266.4 | 10.63 | 3254 | 44.1 | 8.5 | 11.4 | 32.7 | 62,1 | 56.8 | 59.1 | 48.6 |
| Y-17 (mg) | 369.1 | 14,41 | 4580 | 46.5 | 16.4 | 24.2 | 22.3 | 93.2 | 78.7 | 80.0 | 68.4 |
| R-18 (k, mg) | 603.5 | 23.69 | 7080 | 54.7 | 38.5 | 36.0 | 18.7 | 176.6 | 128.6 | 131.7 | 105.7 |

Note: $\varepsilon(volume)$ is the theoretical ratio between the expected concentrations of a conservative element, as estimated by mass balance, and its concentration in ocean water. $\varepsilon(B)$, $\varepsilon(Li)$ and $\varepsilon(Br)$ are degrees of evaporation calculated for the measured B, Li and Br contents, respectively. The abbreviations for the salts precipitated from each aliquot are: ha = halite; mg = Mg sulfates; k,mg = K and Mg sulfates.

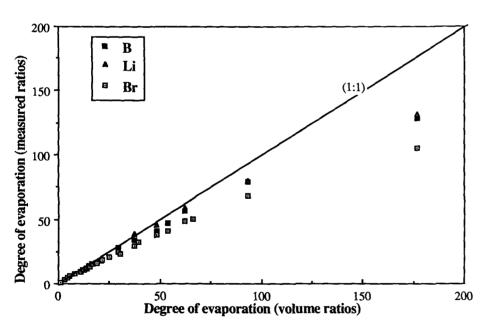


Figure 1. Measured vs. calculated degree of evaporation of B, Br, and Li in evaporated sea water. Theoretical (volume) degree of evaporation was calculated by mass balance, assuming that conservative elements in evaporation experiment do not enter into solid phases. Measured and expected values remain on line with slope of 1 up to degree of evaporation of 30. With further evaporation, degrees of evaporation deviate negatively from that line, indicating depletion of Li, B, and Br relative to expected (absolute) degree of evaporation. Degree of evaporation values were calculated relative to average ocean water (Riley and Chester, 1971; Spivack and Edmond, 1987; Vengosh et al., 1989).

The fractionation of boron isotopes during fractional evaporation of sea water can be described by using the Rayleigh distillation law:

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

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 in the initial sea water, respectively, F is the fraction of boron remaining in the solution, and α is the effective fractionation factor, which is defined as:

$$\alpha = (\delta^{11}\mathbf{B}_s + 1000) / (\delta^{11}\mathbf{B}_b + 1000), \qquad (2)$$

where $\delta^{11}B_s$ is the $\delta^{11}B$ of the precipitating salts. The isotopic fractionation can also be expressed as Δ , which is defined as $\delta^{11}B_{salt} - \delta^{11}B_{brine}$, and is also approximately equal to 1000 ln α . The variations of $\delta^{11}B$ values vs. the fraction of boron remaining in the solution, and the fractionation factors obtained from the brine-salt pairs (equations 1 and 2), are illustrated in Figure 3.

The respective enrichment and depletion of ¹¹B in the brines and precipitates during evaporation and fractional crystallization of sea water (Fig. 2) may be related to the isotopic fractionation between boron species. The B(OH)₃ species tends to be enriched in ¹¹B, whereas the $B(OH)_4^-$ species tends to be enriched in ${}^{10}B$ (Kakihana et al., 1977; Spivack et al., 1987; Palmer et al., 1987; Oi et al., 1989). The distribution of dissolved boron species in a solution is dependent on the pH, ionic strength, and chemical composition of the solution (Byrne and Kester, 19784; Hershey et al., 1986, and references therein). The fraction of boric acid in a solution of high ionic strength and low pH values is relatively high. Therefore, although various boron polymers are formed (Byrne and Kester, 1974), the predominant form (99.9%) of dissolved boron in evaporated sea water is boric acid (Aksenova et al., 1989). Consequently, whereas boron in the solution is mainly composed of boric acid and hence tends to be enriched in ¹¹B, it seems that the borate ion (together with ^{10}B) is preferentially removed from the solution and incorporated into the bulk precipitated salts.

The calculated fractionation factors of the isotopic exchange of B(OH)₃ and B(OH)₄⁻ species at 25 °C has been estimated as 0.981 (Kakihana et al., 1977) or 0.969 (Palmer et al., 1987). The fractionation factors obtained from the brine-salt pairs (Fig. 3) are similar both in sign and magnitude to the predicted ones. At low degrees of evaporation the δ^{11} B values of the evolved brine are closer to the curve defined by $\alpha = 0.969$ (Palmer et al., 1987; $\Delta = -31.7^{\circ}_{/00} \pm 1.3^{\circ}_{/00}$), whereas beyond a degree of evaporation of about 60 (calculated for Br), $\alpha = 0.981$ (Kakihana et al., 1977) models the experimental points ($\Delta = -20.5^{\circ}_{/00} \pm 2.5^{\circ}_{/00}$) better. The observed change in α values may reflect the

GEOLOGY, September 1992

changes in isotopic fractionation with respect to the different minerals precipitated with progressive evaporation. Raab and Spiro (1991) also observed a change in the δ^{34} S values of the evaporated sea water and a reverse fractionation factor of sulfate at the beginning of the Mgsulfate field beyond a degree of evaporation (calculated for Br) of about 60.

Valyashko (1970, and references therein) argued that boron is precipitated mainly in the

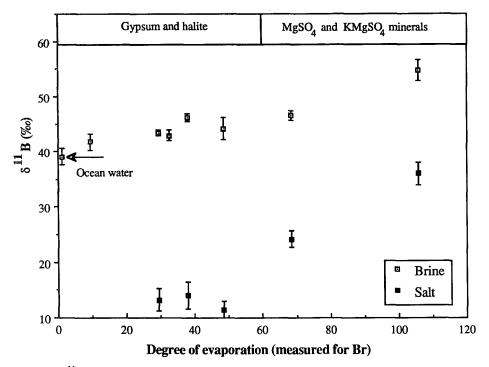


Figure 2. δ^{11} B values of evaporated sea water (open squares with dots) and coexisting precipitated salts (solid squares) vs. degree of evaporation, calculated for bromide concentrations and stability fields of precipitate minerals. Note relative enrichment of ¹¹B in brines relative to salts and difference in magnitude of enrichment during different stages of evaporation and salt precipitation.

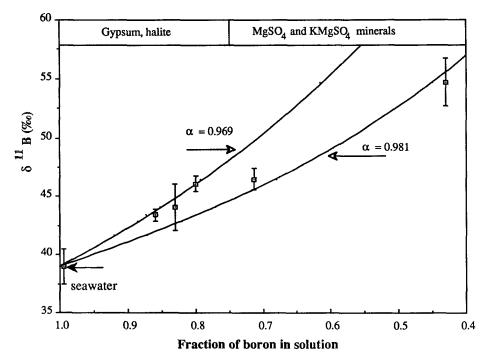


Figure 3. δ^{11} B values of residual evaporated sea water vs. calculated fraction of boron remaining in solution during fractional evaporation of sea water. Two lines were calculated using fractionation factors (α) of 0.981 (Kakihana et al., 1977) and 0.969 (Palmer et al., 1987). Data points were calculated from actual salt-brine pairs.

form of magnesium chloroborate during evaporation of sea water, that in diagenesis is converted to boracite (Mg₃Cl[B₇O₁₃]). In addition, Aksenova et al. (1989) demonstrated that borate minerals can crystallize from evaporated sea water that has not yet reached the eutonic state. Evaporated sea water at the stages where magnesium sulfate and potash salts are deposited is close to saturation with respect to various Mgborate minerals (ascharite, kaliborite, and pinnoite) (Aksenova et al., 1989). The mechanism of boron removal from the highly evaporated sea water may, therefore, be by direct precipitation of Mg-borate minerals and/or formation of a Mg-borate ion pair (MgB[OH]₄⁺) and coprecipitation with the other salts. This is consistent with the coordination number of 4 of boracite (Valyashko, 1970), which allows the preferential removal of ¹⁰B-enriched $B(OH)_{4}$ from the solution. Other borate phases with atomic configurations that include both boron species (Oi et al., 1989) will be less fractionated.

GEOCHEMICAL APPLICATIONS

The observed fractionation of boron isotopes during late stages of evaporation of sea water by $20^{\circ}/_{00}$ to $30^{\circ}/_{00}$ can place additional limitations on the geochemical application of this tracer. The high reactivity of boron and preferential incorporation of ¹⁰B into clay minerals increases the δ^{11} B value of a solution at low water/sediment ratios. In addition, brines with high δ^{11} B values in nonmarine locations can be derived from marine-origin atmospheric salts, as demonstrated for some Australian salt lakes (Vengosh et al., 1991b). Our study indicates that high δ^{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 geologic record. In contrast, in evaporative environments where the brines have evolved only to the stage where halite is precipitated, i.e., up to a degree of evaporation of about 10, the isotopic composition of boron is not controlled by evaporation processes (Vengosh et al., 1991b).

The relation between the "conservative" elements (B, Li, and Br) and $\delta^{11}B$ can be used to infer the origin and history of brines. Brines with high $\delta^{11}B$ values (higher than that of sea water) associated with marine B/Li ratios must have evolved from sea water through evaporation and precipitation of K- and Mg-sulfate salts. In contrast, brines with high $\delta^{11}B$ values associated with low B/Li or B/Cl ratios indicate preferential removal of boron via isotopic fractionation and, hence, interaction with clay minerals (Vengosh et al., 1991b, 1991c).

During fractional evaporation of sea water, salts are depleted in ¹¹B by $20^{\circ}/_{00}$ to $30^{\circ}/_{00}$ relative to the coexisting brines, which is useful in deducing the origin of evaporite deposits. Evap-

oration and salt precipitation of sea water ($\delta^{11}B$ = 39⁰/₀₀) or continental water ($\delta^{11}B = -3^{0}/_{00}$ $\pm 5^{\circ}/_{00}$) in a closed system results in an enrichment of the evaporated brines and depletion of the precipitated salts in ¹¹B, relative to their parent solutions. Using both α values of 0.981 and 0.969 obtained from the evaporation experiment, the marine and nonmarine brines would have $\delta^{11}B$ values in the ranges of $39^{0}/_{00}$ to $70^{\circ}/_{00}$, and $0^{\circ}/_{00}$ to $31^{\circ}/_{00}$, respectively, whereas the coexisting marine and terrestrial precipitates would have δ^{11} B values of 8% to 39% and $-31^{\circ}/_{00}$ to $0^{\circ}/_{00}$, respectively (1000 ln 0.981 = $-19^{\circ}/_{00}$; 1000 ln 0.969 = $-31^{\circ}/_{00}$). The predicted range of δ^{11} B values for the salts overlaps with the measured marine and nonmarine borate minerals, as reported in Swihart et al. (1986) (Fig. 4).

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% BO₄ (boracite), 66% BO₄ (colemanite), 60% BO4 (ulexite), and 50% BO4 (borax) and, hence, are always depleted in ¹¹B relative to their parent brines, which are predominantly composed of boric acid (Aksenova et al., 1989). This is consistent with the low δ^{11} B values (18.2%) and 20.7%) of Permian boracite from Germany, the mostly ¹¹B-depleted marine borate minerals (Swihart et al., 1986). Using the fractionation factors obtained in this study, the conspicuously low $\delta^{11}B$ values of nonmarine borates $(-30^{\circ}/_{00}$ to $8^{\circ}/_{00}$; Swihart et

al., 1986) and of some tourmalines (as low as $-22.8^{0}/_{00}$; Slack et al., 1989; Palmer and Slack, 1989) relative to the δ^{11} B value of the continental crust (δ^{11} B = $-3^{0}/_{00} \pm 5^{0}/_{00}$; Spivack and Edmond, 1987) can be explained if continental water served as the original solution for the evaporation process. Consequently, δ^{11} B variations of borate salts and tourmalines in the geologic record are related both to the boron isotopic composition of their parent brines and to the fractionation of boron isotopes during salt crystallization (Fig. 4).

In conclusion, the agreement between the measured and the predicted δ^{11} B values in borate minerals and common evaporite minerals shows that boron isotopes can distinguish the origin (marine vs. nonmarine) of ancient salt deposits and the nature of their parent brines.

ACKNOWLEDGMENTS

We thank M. Stein, D. M. Fountain, T. E. Cerling, and an anonymous reviewer for critical reading, comments, and suggestions on the manuscript.

REFERENCES CITED

- Aksenova, T.D., Borisenkov, V.I., and Dorofeyeva, V.A., 1989, Stability of natural magnesium borates in marine brines at various stages of halogenesis: Geochemistry International, v. 26, p. 31-39.
- Byrne, R.H., and Kester, D.R., 1974, Inorganic speciation of boron in sea water: Journal of Marine Research, v. 32, p. 119-127.
- Hardie, L.A., 1984, Evaporites: Marine or non-marine?: American Journal of Science, v. 284, p. 193-240.
- Hardie, L.A., 1990, The roles of rifting and hydrothermal CaCl₂ brines in the origin of potash evaporites: An hypothesis: American Journal of Science, v. 290, p. 43-106.
- Hershey, J.P., Fernandez, M., Milne, P.J., and Millero, F.J., 1986. The ionization of boric acid in NaCl, Na-Ca-Cl and Na-Mg-Cl solutions at 25°C: Geochimica et Cosmochimica Acta. v. 50, p. 143-148.

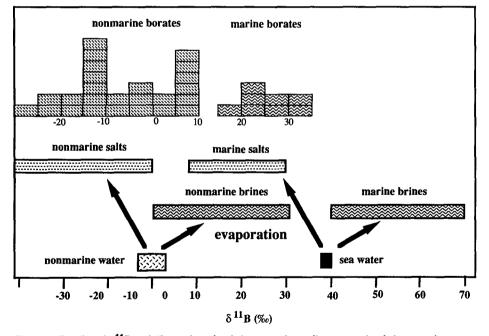


Figure 4. Predicted δ^{11} B variations of marine brines, marine salts, nonmarine brines, and nonmarine salts during evaporation of water from different sources, assuming both fractionation factors (α) of 0.981 and 0.969. Model considers evolution of marine and nonmarine brines in closed systems, in manner similar to sea water-evaporation experiment. Note respective agreement of predicted δ^{11} B values of salts from both environments with those of marine and nonmarine borate minerals, reported by Swihart et al. (1986) and presented in upper histograms.

The interview states and the second states a

- Holser, W.T., 1979, Trace elements and isotopes in evaporites, in Burns, R.G., ed., Marine minerals: Mineral Society of Americs Short Courts Notes v. 6 a 205 246
- ica Short Course Notes, v. 6, p. 295-346. Kakihana, H., Kotaka, M., and Satoh, S., 1977, Fundamental studies on the ion-exchange separation of boron isotopes: Chemical Society of Japan Bulletin, v. 50, p. 158-163.
- Lowenstein, T.K., and Spencer, R.J., 1990, Syndepositional origin of potash evaporites: Petrographic and fluid inclusion evidence: American Journal of Science, v. 290, p. 1–42.
- McCaffrey, M.A., Lazar, B., and Holland, H.D., 1987, The evaporation path of sea water and the coprecipitation of Br- and K+ with halite: Journal of Sedimentary Petrology, v. 57, p. 928-937.
- Oi, T., Nomura, M., Musashi, M., Ossaka, T., Okamoto, M., and Kakihana, H., 1989, Boron isotopic compositions of some boron minerals: Geochimica et Cosmochimica Acta, v. 53, p. 3189-3195.
- Palmer, M.R., and Slack, J.F., 1989, Boron isotopic composition of tourmaline from massive sulfide deposits and tourmalinites: Contributions to Mineralogy and Petrology, v. 103, p. 434-451.
- Palmer, M.R., Spivack, A.J., and Edmond, J.M., 1987, Temperature and pH controls over isotopic fractionation during adsorption of boron on marine clays: Geochimica et Cosmochimica Acta, v. 51, p. 2319–2323.
- Raab, M., and Spiro, B., 1991, Sulfur isotopic variations during sea water evaporation with fractional crystallization: Chemical Geology, Isotope Geoscience Section, v. 86, p. 323-333.
- Riley, J.P., and Chester, R., 1971, Introduction to marine chemistry: New York, Academic Press, 465 p. Schwarcz, H.P., Agyei, E.K., and McMullen, C.C., 1969, Boron
- Schwarcz, H.P., Agyei, E.K., and McMullen, C.C., 1969, Boron isotopic fractionation during adsorption from sea water: Earth and Planetary Science Letters, v. 6, p. 1–5.
- Slack, J.F., Palmer, M.R., and Stevens, B.P.J., 1989, Boron isotope evidence for the involvement of nonmarine evaporites in the origin of the Broken Hill ore deposits: Nature, v. 342, p. 913–916.
- Sonnenfeld, P., 1985, Comment on "Evaporites: Marine or nonmarine?": American Journal of Science, v. 285, p. 661-672.
- Spivack, A.J., and Edmond, J.M., 1987, Boron isotope exchange between sea water and oceanic crust: Geochimica et Cosmochimica Acta, v. 51, p. 1033-1042.
- Spivack, A.J., Palmer, M.R., and Edmond, J.M., 1987, The sedimentary cycle of the boron isotopes: Geochimica et Cosmochimica Acta, v. 51, p. 1939-1950.
- Swihart, G.H., Moore, P.B., and Callis, E.L., 1986, Boron isotopic composition of marine and nonmarine evaporite borates: Geochimica et Cosmochimica Acta, v. 50, p. 1297–1301.
- Valyashko, M.G., 1970, Genesis and exploration of borate deposits related to marine salt origin: International Geological Review, v. 12, p. 711-719.
- Vengosh, A., Chivas, A.R., and McCulloch, M.T., 1989, Direct determination of boron and chlorine isotopes in geological materials by negative thermal-ionization mass spectrometry: Chemical Geology, Isotope Geoscience Section, v. 79, p. 333-343.
- Vengosh, A., Kolodny, Y., Starinsky, A., Chivas, A.R., and McCulloch, M.T., 1991a, Coprecipitation and isotopic fractionation of boron in modern biogenic carbontes: Geochimica et Cosmochimica Acta, v. 55, p. 2901–2910.
- Vengosh, A., Chivas, A.R., McCulloch, M.T., Starinsky, A., and Kolodny, Y., 1991b, Boron isotope geochemistry of Australian salt lakes: Geochimica et Cosmochimica Acta, v. 55, p. 2591-2606.
- Vengosh, A., Starinsky, A., Kolodny, Y., and Chivas, A.R., 1991c, Boron isotope geochemistry as a tracer for the evolution of brines and associated hot springs from the Dead Sea, Israel: Geochimica et Cosmochimica Acta., v. 55, p. 1689–1695.

Manuscript received January 27, 1992 Revised manuscript received May 13, 1992 Manuscript accepted May 21, 1992