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Isotopic compositions of boron in sediments and their implications

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The abundance and isotopic compositions of boron in sediments from the salt lakes of Qaidam Basin, China have been determined by thermal ionization mass spectrometry of cesium borate. The results show large variations in the isotopic compositions of boron. The observed variations of $\delta^{11}\text{B}$, ranging from -25.2% to $+26.08\%$ (relative to NBS SRM 951) indicate both an enrichment and depletion in the lighter isotope (^{10}B) in the lake sediments. The lower $\delta^{11}\text{B}$ values of sediments are mostly closer to the boron isotopic compositions of minerals. Such low $\delta^{11}\text{B}$ values are attributed to the presence of borates, ulexite and other carbonate minerals in sediments of the salt lakes of Qaidam Basin.

BORON is one of the major elements in seawater¹ and is significantly involved in marine biogeochemical cycles^{2,3}. Recent studies have shown that the isotopes of boron act as excellent tracers of geochemical processes⁴⁻⁶. The differences in the behaviour of its two stable isotopes, ^{10}B and ^{11}B , result in the isotopic fractionation of boron during its biogeochemical cycling⁷ and the extent of this fractionation provides insights into the various processes involved.

Although the isotopic studies of boron are being carried out for the past 2–3 decades, the difficulties involved in the accurate measurement of boron isotopic ratios led to a slow progress in this area. However, the recent advancements in the analytical techniques^{8,9} have provided impetus to studies on isotope geochemistry of boron. The isotopic measurements by these techniques have shown wide variations in boron isotopic ratios in nature¹⁰ and indicated distinct differences in the isotopic

compositions of boron between the marine, non-marine and terrestrial samples and between seawater, sediments and the upper oceanic crust^{11,12}.

The hypersaline environments experiencing intense evaporation are excellent sites for isotopic studies of elements as considerable isotopic fractionation occurs during evaporation and precipitation in the brine¹³. The present study is based on the boron isotopic measurements carried out in sediments of the salt lakes of Qaidam Basin, China, from October to December, 1992 to understand their variation and their geochemical implication.

The salt lakes of Qaidam Basin are situated to the north of the Kunlun Tangula mountains in the north-western part of Qinghai Plateau at an altitude of over 2600 m above sea level. This terrestrial basin (Figure 1), evolved during the Jurassic period¹⁴, is typically a continental potassium-bearing basin with an area of $12 \times 10^4 \text{ km}^2$. It is surrounded by the Altun mountains in the northeast and Kunlun mountains in the south. The streams draining from these snow-capped mountains terminate in a series of saline lakes at the margin of the basin.

The basin experiences a typical continental climate with difference in day and night temperatures, reaching as high as 30°C . The climate is arid and cold with an annual precipitation less than 50 mm and annual evaporation far exceeds precipitation. Due to the low air temperatures, high aridity and strong winds, the waters in these lakes have turned into brines.

Sediments were collected from 22 salt lakes in the Qaidam Basin (Figure 1) during 7 July–10 August, 1992. After collection, the brine was drained out and the sediments were oven dried at 60°C . The dried sediments were finely powdered and sieved through a standard 100 mesh. A known quantity of the sieved sample was treated with a minimum quantity of dilute HCl ($< 0.1 \text{ N}$). The acid-washed sediments were filtered and the filtrate was preserved for isotopic measurements. The residue was then washed with distilled water and again filtered. The filtrates were mixed together and made up to 50 ml. Boron contents in the filtrates were determined through mannitol-alkalimetry titration¹⁵. A known quantity of the filtrate was used for the extraction of boron by ion-exchange for isotopic measurements¹⁶.

A mixture of weakly basic anion exchange resin in HCO_3^- form and a strongly acidic cation exchange resin in the H^+ form was poured into a special glass column. The boron-containing solutions were slightly acidified with HCl before passing through the column. After shaking for 7–10 min, boron was eluted with 60 ml high-purity water. The yield of boron recovered from each sample was more than 98%. After elution, the $^{11}\text{B}/^{10}\text{B}$ ratio was measured by a mass spectrometer, model VG 354, based on thermal ionization mass spectrometry of cesium borate using graphite as a substrate

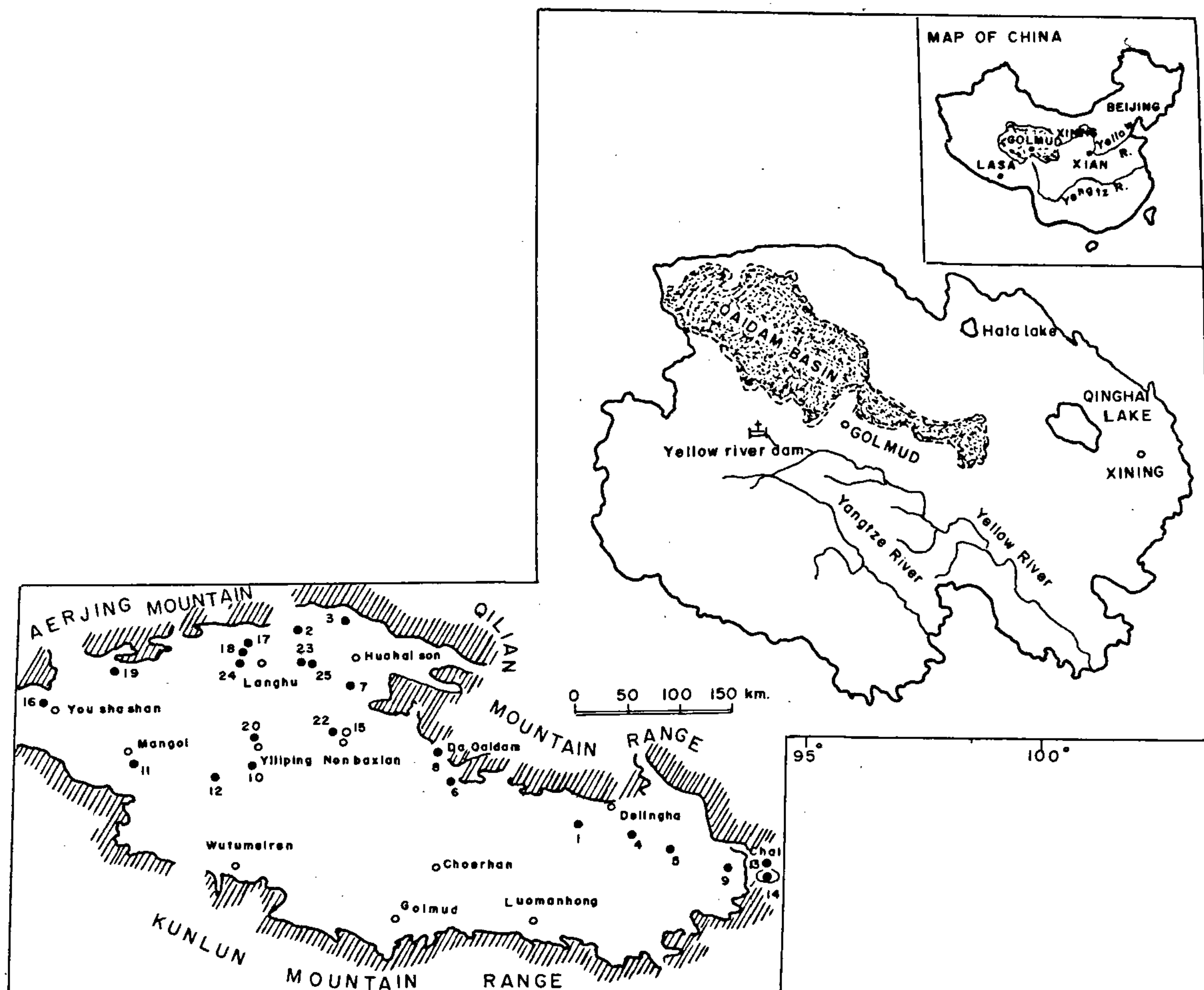


Figure 1. Location of Quidam Basin and the salt lakes in Quidam Basin, China.

for loading⁸. The $^{11}\text{B}/^{10}\text{B}$ ratio of NBS SRM 951 was first obtained and was found to be 4.04362 ± 0.0011 . The isotopic ratios of the samples were then expressed as $\delta^{11}\text{B}$ values (per mil deviation, $\delta^{11}\text{B}$, relative to NBS SRM 951 Boron Standard value of 4.04362), according to the equation

$$\delta^{11}\text{B}(\text{sample}) = \left[\frac{(^{11}\text{B}/^{10}\text{B})_{\text{sam}}}{(^{11}\text{B}/^{10}\text{B})_{\text{std}}} - 1 \right] \times 1000,$$

with a precision of 0.023% (95% confidence limit) for the standard solution while for the samples, the precision was 0.03%.

The $^{11}\text{B}/^{10}\text{B}$ ratios of sediments varied from 3.9416 to 4.1491 with a mean of 4.0431. The $\delta^{11}\text{B}$ values were found to range from -25.21‰ to $+26.08\text{‰}$ (Table 1).

The main components of the salt lake sediments were halite, gypsum and clay minerals. The clay minerals

constituted 5–20% of the sediments; of these, the most abundant were illite (58–78%) and kaolinite (11–42%) (Table 1).

The isotopic compositions of boron showed low (negative) values for most of the sediments from the salt lakes of Qaidam Basin. Even the higher (positive) values of $\delta^{11}\text{B}$ of sediments were much lower than those of the overlying brines, collected simultaneously from the respective salt lakes¹⁷. This reveals the effect of isotopic fractionation of boron wherein the lighter isotope, ^{10}B , is preferentially removed from the overlying brines to sediments. The fractionation of boron has been attributed to its tetrahedral species, $\text{B}(\text{OH})_3$ which is enriched with ^{10}B (ref. 4). Due to the greater affinity of ^{10}B for solids, the borate anion gets preferentially adsorbed onto solid substances when dissolved boron comes in contact with solids¹⁸.

Table 1. Abundance and isotopic compositions of boron and the clay minerals in Salt Lake sediments

Location (lakes)	Boron (mg/kg)	Clay mineral (%)			$^{11}\text{B}/^{10}\text{B}$	$\delta^{11}\text{B}$
		Illite	Kaolinite	Chlorite		
Tuosu	0.18	69	31	–	4.0232	– 5.05
Xiaosugan	0.04	78	22	–	4.0280	– 3.86
Yiligou	0.05	NA	NA	NA	4.0388	– 1.20
Xiao Qaidam	0.78	72	28	–	4.0012	– 10.48
Zhongmahai	0.44	NA	NA	NA	4.0003	– 10.71
Da Qaidam	2.45	74	36	–	4.0549	+ 2.78
Qaikai	0.33	77	23	–	4.0350	– 2.13
Xitaije Ner	1.42	58	42	–	4.0356	– 1.99
Mangai	0.45	NA	NA	–	4.0752	+ 7.80
Tar Din	0.80	NA	NA	NA	3.9416	– 25.21
Keke	0.17	68	32	–	4.0631	+ 4.82
Nanbaxian(I)	0.16	NA	NA	NA	4.0257	– 4.43
Gasikule	0.42	72	28	11	4.0971	+ 13.21
Kunteyie(I)	0.60	NA	NA	NA	4.0246	– 4.71
Potassium(I)	0.62	NA	NA	NA	3.9781	– 16.20
Dalang Tan(I)	1.30	72	11	17	4.1491	+ 26.08
Balunmahai	0.07	70	30	–	4.0329	– 2.65
Nu Lang	0.88	NA	NA	NA	4.1299	+ 21.35
Potassium	0.46	NA	NA	NA	4.1104	+ 16.51
Zhinu	0.83	69	31	–	4.1250	+ 20.12
Jiahu	0.62	68	32	–	3.9781	– 16.20
Dezong	0.47	NA	NA	–	4.0003	– 10.71

I: Interstitial brine.

NA: Not analysed.

Various factors such as pH, temperature, ionic strength, boron concentration of solution and the nature of minerals affect the fractionation of boron^{4,7,12}. The most important factor affecting the speciation of boron is pH as it controls the relative proportion of the two dominant species – $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ (ref. 19). The abundance ratio of $\text{B}(\text{OH})_3$ to $\text{B}(\text{OH})_4^-$ in turn influences the $\delta^{11}\text{B}$ in sediments and minerals. Ingri *et al.*¹⁹ showed that within the pH range of 5–12, the $\text{B}(\text{OH})_3$ to $\text{B}(\text{OH})_4^-$ ratio decreases as the proportion of $\text{B}(\text{OH})_3$ decreases with increasing pH. The pH values of the overlying brines in these lakes¹⁷ were within a comparable range (4.43–8.9). Such a range leads to variable mole fractions of $\text{B}(\text{OH})_3$ in brines and thus to different $^{11}\text{B}/^{10}\text{B}$ ratios and $\delta^{11}\text{B}$ values in sediments.

The $\delta^{11}\text{B}$ values of the salt lake sediments in this study (Table 1) are much lower than those reported for the marine and nonmarine sediments (the nonmarine environment in this case refers to the freshwater environment). However, the salt lakes of Qaidam Basin represent an evaporative environment. In such an environment, boron is not significantly removed by precipitated salts but remains in the brine and gets concentrated in evaporitic clay minerals rich in magnesium, as the tetrahedrally coordinated boron^{20,21}. The studies on the geochemistry of boron³ have shown that the adsorption of boron takes place on sediment particles and the clay minerals are very significant for adsorption. This adsorption leads to isotopic fractionation of boron²².

The clay minerals of the salt lake sediments comprise

58–78% illite, 11–42% kaolinite and 11–17% chlorite (Table 1). The adsorption of boron on these minerals therefore contributes to the lowering of $\delta^{11}\text{B}$ values observed in this study. Apart from this, boron is also taken up by boron minerals and the isotopic composition of borate salts is dependent on their atomic configuration and the proportion of boron species in the mineral²³. The boron (as borate) content of some of its minerals has been given as (100% BO_4) boracite, (66% BO_4) colmanite, (60% BO_4) ulexite and (50% BO_4) borax. These minerals are always depleted in the heavier isotope ^{11}B relative to that in the parent brines²⁴.

Similarly, different minerals are found to have different boron isotopic composition values, e.g. authigenic marine silicates (–38‰); the adsorbed boron onto marine sediments (–25‰) and the modern marine biogenic carbonates (–7 to –25‰). The boron isotopic compositions of some of the boron minerals are: –4‰ (borate); –12.8‰ (ulexite) and from –17.24 to –23.67‰ (pinnoite)^{12,18,24}. As seen from our values in Table 1, the $\delta^{11}\text{B}$ values of the sediments from the Tuosu lake (–5.05‰), Nanbaxian lake (–4.43‰) and the Kunteyi lake (–4.71‰) are closer to those of the borates (–4‰). So also, the $\delta^{11}\text{B}$ values of the sediments from potassium lake (–16.2‰) and the Kunteyi lake (–16.20‰) are closer to that of ulexite (–12.8‰) while the $\delta^{11}\text{B}$ values of many other lake sediments fall in the range for carbonates.

The main boron minerals found in these lake sediments are ulexite, pinnoite, borax and other potash minerals

of chloride and sulphate type. The chloride minerals are carnallite, sylvite, halite and bischofite, whereas the sulphate type are mirabilite, picromerite and polyhalite which are always found in association with epsomite, bloedite, mirabilite or gypsum²⁵⁻²⁷. Oi *et al.*²³ observed that the minerals of marine origin have higher $^{11}\text{B}/^{10}\text{B}$ ratio and higher $\delta^{11}\text{B}$ value than those of the nonmarine origin and the $^{11}\text{B}/^{10}\text{B}$ ratios of minerals from the same geologic origin depends upon the crystal structure. A correlation exists between the crystal structure of the mineral and its $\delta^{11}\text{B}$ values. They attributed it to the reduced partition function ratios (RPFs) of the two species of boron based on the general theory of isotope effects. The RPF of the $\text{B}(\text{OH})_3$ species is larger than that of the $\text{B}(\text{OH})_4^-$ and the mineral having the higher $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$ ratio has larger $^{11}\text{B}/^{10}\text{B}$ ratio and larger $\delta^{11}\text{B}$ value at any temperature. Thus it has been realized that the abundance ratio of $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$ in the solution has a profound effect on the boron isotopic composition of the mineral formed. The varying pH of the overlying brines of these salt lakes (4.43–8.90) may therefore result in differences in the mole fraction of $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ giving rise to different values of $\delta^{11}\text{B}$ for the minerals. So, the slight variation in $\delta^{11}\text{B}$ values observed in our study compared to that of the boron minerals given above, is due to varying pH of the brines of the salt lakes and different origin. These $\delta^{11}\text{B}$ values can therefore be attributed to the presence of borates, ulexite and other carbonate minerals and as such assume greater importance in the exploration of minerals and the characterization of environmental samples.

In conclusion, the boron isotopic compositions of the salt lake sediments indicate the presence of borate, ulexite and other carbonate minerals. During the formation and transformation of minerals in sediments (particularly boron minerals), substantial element exchange takes place. This leads to the isotopic fractionation of boron. So, the boron isotopic study of sediments can give an understanding of sediment diageneses. Measurement of the boron isotopic composition of sediments by mass spectrometry can serve the dual purpose of detecting the minerals and the isotopic composition of the sample.

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