



0016-7037(95)00227-8

## The boron isotope geochemistry of the Kirka borate deposit, western Turkey

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(Received December 1, 1994; accepted in revised form May 19, 1995)

**Abstract**—We have measured the boron isotope composition of seventeen samples of borate minerals (colemanite, ulexite, and borax) and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in thirteen borate samples from the Kirka borate deposit in western Anatolia, Turkey. These Neogene deposits were formed by evaporation of playa lakes fed by geothermal springs. The  $\delta^{11}\text{B}$  values range from  $-14.9\text{‰}$  in colemanite to  $-1.6\text{‰}$  in borax. To a first approximation the relative differences in the  $\delta^{11}\text{B}$  values of the borate minerals are consistent with their basic boron atomic configuration, but the magnitude of the boron isotope fractionation between the three minerals precludes their simultaneous precipitation from a brine with the same boron isotope composition and pH. Rather the data are consistent with precipitation of colemanite from a brine with lower pH than that required for ulexite precipitation, which in turn requires a lower pH than is needed for borax precipitation. The boron isotope data also suggest that the borate minerals did not maintain boron isotopic equilibrium with the brine after they precipitated. Rayleigh fractionation models indicate that during borax precipitation the  $\delta^{11}\text{B}$  value of the brine was slightly heavier than during precipitation of ulexite and colemanite.

### 1. INTRODUCTION

Nonmarine evaporite deposits are of interest for a variety of reasons. Their presence attests to a restricted range of climatic conditions, different types of nonmarine evaporites have origins requiring specific tectonic conditions and the evaporites may contain minerals of economic interest (Smoot and Lowenstein, 1991). Borate deposits are an important category of nonmarine evaporites. The deposits are the largest industrial source of boron in the world today, with the major production coming from the USA and Turkey (Kistler and Helvacı, 1994). Previous studies of boron isotopes in nonmarine evaporites have shown they can reveal information concerning the source of boron and possibly the pH conditions at which the borates were formed (Swihart et al., 1986; Oi et al., 1989). We have carried out a boron isotope study of borates from a Turkish borate deposit at Kirka to constrain the physicochemical conditions during their precipitation.

### 2. GEOLOGICAL SETTING

The Turkish borate deposits occur in western Anatolia in five main districts; Bigadiç, Kestelek, Sultançayırı, Emet, and Kirka (Fig. 1). They formed in a lacustrine environment during periods of calc-alkaline volcanic activity in the Neogene. Although there are differences between the different districts, they are all generally enclosed within limestones and clays and are interbedded with layers of volcanic ash, limestone, marl, and clays. At Kirka this volcanosedimentary sequence lies unconformably on Paleozoic metamorphics, Mesozoic ophiolites, and Eocene limestones. A stratigraphic section of the Kirka deposit is shown in Fig. 2 (Inan et al., 1973; Helvacı, 1977; Sunder, 1980). The main boron mineral is borax with lesser amounts of colemanite and ulexite. A number of other borate minerals have also been found in the deposit, including pandermite, inyoite, meyerhoffertite, tincalconite, kernite, hydroboracite, inderite, inderborite, kurnakovite, and tunnelite (Inan et al., 1973; Helvacı, 1977, 1978, 1983). Broadly speaking, the borax body is surrounded by a thin layer of ulexite, followed by a thin layer of colemanite. The whole borate ore body is enclosed within calcite and limestone. The borate layers contain minor amounts of calcite and dolomite. The clay layers interbedded with the borates consist largely of smectite-group min-

erals with minor illite and chlorite. The clay layers also contain some volcanic tuff (frequently altered to zeolites), quartz, biotite, and feldspar (Helvacı, 1983). The source of the boron is thought to be from geothermal springs associated with the local volcanic activity and the borates were formed when the spring waters underwent evaporation after flowing into shallow playa lakes (Helvacı, 1995).

### 3. EXPERIMENTAL

#### 3.1. Sampling

Samples were collected from seventeen different locations at Kirka and one sample from was collected from Göçenoluk. This is a small deposit to the northwest of Kirka thought to be at the same stratigraphic level as the colemanite layer underlying the borax body at Kirka. In this study we will only consider the principal ore minerals (borax, ulexite, and colemanite). The boron isotope systematics of the minor borates will be considered elsewhere. Several of the samples contain different generations of crystals of the same borate mineral (e.g., as fillings in septarian cracks in nodules). These were separated by handpicking and analysed as different samples. With the exception of the sample from Göçenoluk all the samples were taken from the main pit at Kirka. The borates do not form a continuous body within the Kirka deposit, but are thought to have precipitated in a series of interconnected subbasins (Inan, 1973). The degree of interconnectedness between these subbasins is uncertain, but the gross chemical zoning within the deposit indicates that at any one time the borates within the Kirka deposit were precipitated from a relatively homogeneous brine (Inan et al., 1973). The samples were handpicked under a binocular microscope to ensure the analysed samples were free from adhering clay minerals and were pure mineral separates. A brief description of each sample is given in the Appendix.

#### 3.2. Analytical

The boron was extracted by pyrohydrolysis at  $1400^{\circ}\text{C}$  (Spivack and Edmond, 1986) to ensure all the boron was extracted from the sample. The boron isotope compositions were measured using a modified version (Aggarwal and Palmer, 1995) of the method described by Spivack and Edmond (1986). The data are reported as  $\delta^{11}\text{B}$  values where

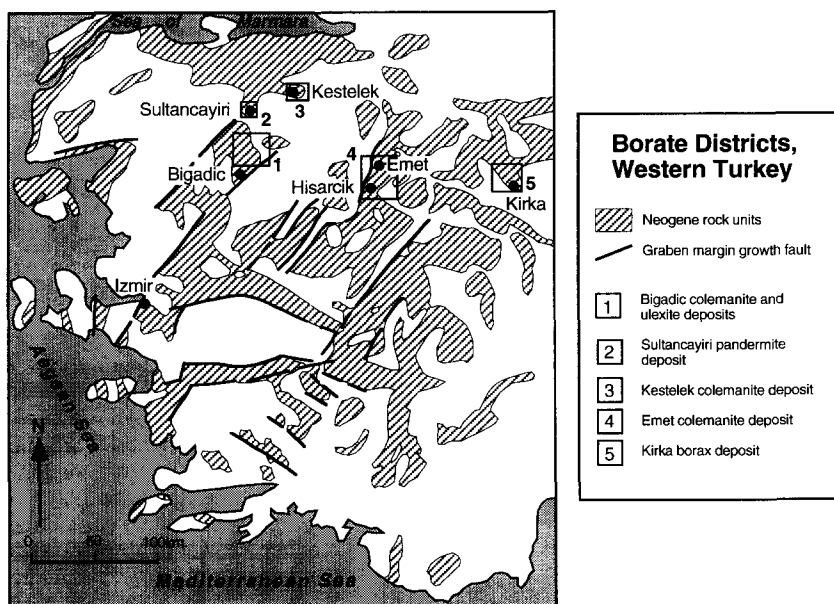


FIG. 1. Location of major borate deposits in western Turkey.

$$\delta^{11}\text{B} = \left[ \left\{ \frac{{}^{11}\text{B}/{}^{10}\text{B}_{\text{sample}}}{{}^{11}\text{B}/{}^{10}\text{B}_{\text{standard}}} \right\} - 1 \right] \times 10^3.$$

The standard is NBS boric acid SRM 951 and as with other isotope standards the measured value varies slightly between laboratories; at our laboratory ~100 analyses of this standard over three years on a VG336 mass spectrometer have yielded an average  ${}^{11}\text{B}/{}^{10}\text{B}$  ratio of  $4.0529 \pm 0.1\%$  ( $2\sigma$ ). The average  $2\sigma$  error of the fifty-four individual measurements is  $\pm 0.32$ . Replicate analyses were made of each sample and the average agreement between these replicates is slightly poorer at  $\pm 0.44$ . This may reflect isotope heterogeneity in some samples together with analytical artefacts. This second value is taken as the true measure of precision.

Strontium isotope ratios were also measured on a selected suite of the samples using the same mass spectrometer. The ratios were normalised to an  ${}^{88}\text{Sr}/{}^{86}\text{Sr}$  ratio of 0.1194 and an  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  value of 0.7080 for the E&A standard. We obtained an average  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  ratio of 0.70795 for ten measurements of this standard.

#### 4. RESULTS

The results are listed in Table 1 and the structural formulae and basic boron atomic structure of the borate minerals considered in this study is given in Table 2. Borax has the heaviest (less negative)  $\delta^{11}\text{B}$  values of the main borate minerals, with ulexite having lighter  $\delta^{11}\text{B}$  values and colemanite having the lightest  $\delta^{11}\text{B}$  values. This is in accord with previous observations and calculations that show that the heavy isotope of boron,  ${}^{11}\text{B}$ , is concentrated in borate minerals with a higher proportion of trigonally coordinated boron (Oi et al., 1989).

#### 5. DISCUSSION

The variation in boron isotope compositions of the borate minerals is a function of several variables. The most important of these are (1) the boron isotope composition of the source of boron to the deposits, (2) the mineralogy of the borate minerals, (3) the temperature of formation of the borates, (4) the pH of the solution during precipitation of the borates, and

(5) the proportion of borates precipitated from the brines (Rayleigh effects).

As noted above, the mineralogy of the borate minerals is important in determining their boron isotope ratios. Boron isotope fractionation arises largely from changes in the symmetry of the boron atom, such that the heavy isotope,  ${}^{11}\text{B}$ , is concentrated in planar  $\text{BO}_3$  and the light isotope,  ${}^{10}\text{B}$ , is concentrated in tetrahedral  $\text{BO}_4$ . As with other stable isotopes the magnitude of the isotope fractionation factor is temperature dependent (e.g., Palmer et al., 1992). There are no experimental data for isotope fractionation factors between different borate minerals, but these can be calculated (Kakihana and Kotaka, 1977; Kakihana et al., 1977) and applied to the boron isotope composition of nonmarine evaporites (e.g., Oi et al., 1989). In addition, the relative proportions of trigonally and tetrahedrally coordinated boron in the dissolved phase are pH dependent (Ingri, 1963; Hershey et al., 1986); hence the extent of boron isotope fractionation between brines and borate minerals will also depend on this variable.

These theoretical calculations show that the extent of isotope fractionation is such that at  $25^\circ\text{C}$  borax should have a  $\delta^{11}\text{B}$  approximately 2‰ higher than that of ulexite, which would in turn be 1.3‰ heavier than colemanite, assuming all three minerals precipitated in equilibrium with one another (Oi et al., 1989). The average  $\delta^{11}\text{B}$  value of borax from Kirka ( $-3.7\%$ ) is 3.6‰ higher than the average  $\delta^{11}\text{B}$  value of ulexite ( $-7.3\%$ ), which is 5.6‰ higher than the average  $\delta^{11}\text{B}$  value of colemanite ( $-12.9\%$ ). The discrepancy between the theoretical isotope fractionation factors between the borate minerals and the differences observed at Kirka could be due to a number of causes. It is possible that the theoretically calculated isotope fractionation factors differ from the empirical fractionation factors. Secondly, if the borates were precipitated at a lower temperature than  $25^\circ\text{C}$  the isotope fractionation factors between the minerals would be greater. Finally, if the borates were not coprecipitated from the same

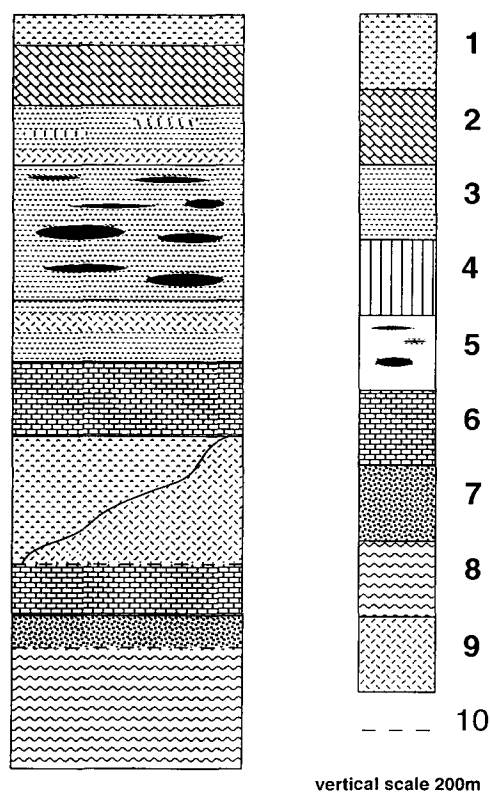


FIG. 2. Schematic stratigraphic section of Kirka borate deposit. 1. volcanic rocks (basalts, andesites and rhyolites) 2. cherty limestone 3. marl and claystone 4. lignite bands 5. borate zone 6. limestone 7. sandstone and conglomerate 8. basement complex: ophiolite, marble, schist 9. tuff 10. unconformity (after Inan, 1973, Helvacı 1977, Sunder 1980).

brine, differences in the chemistry of the brines may also control the  $\delta^{11}\text{B}$  values of the borates.

Empirical studies of boron isotope fractionation between marine carbonates and seawater have shown the theoretical isotope fractionation factors are consistent with the observed data (Hemming and Hanson, 1992). Hence, we do not believe that the greater than predicted isotope fractionation factors at Kirka is due to inaccurate theoretical data. Palmer et al. (1987) obtained higher fractionation factors between the trigonal and tetrahedral dissolved boron phases from experiments of boron adsorbed onto clay minerals. When corrected for the adsorption effect, these data would predict a difference of 2.35‰ between the  $\delta^{11}\text{B}$  values of borax and ulexite and 1.57‰ between ulexite and colemanite. These are still significantly different from the observed data.

To achieve a fractionation factor of 3.6‰ between coexisting borax and ulexite under equilibrium conditions the temperature would have to be less than 0°C (Oi et al., 1989). Evaporites are formed in Antarctica at these temperatures (Burton, 1981), but these conditions clearly did not apply to the Quaternary western Mediterranean.

Hence, we conclude that borax, ulexite, and colemanite were not precipitated from brines with identical chemistry. Differences in brine chemistry may include changes in its bo-

ron isotopic composition, changes in the pH, and/or changes in the major element chemical composition.

As the  $\delta^{11}\text{B}$  values of the borates are sensitive to a number of factors there is no independent monitor of possible changes in the boron isotope composition of the brines during evolution of the deposit. At Kirka the potential source rocks include Paleozoic metamorphics, Mesozoic ophiolites, and Eocene limestones as well as the calc-alkaline volcanics that formed contemporaneously with the borates (Inan et al., 1973; Helvacı, 1977; Sunder, 1980). We do not have geochemical data for these rock types, but among other things they might be expected to have different strontium isotope compositions, and possibly different  $\delta^{11}\text{B}$  values. To determine whether different sources of boron were important in defining the range of  $\delta^{11}\text{B}$  values we measured the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and  $\delta^{11}\text{B}$  values of a suite of samples. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the borates show a narrow range (0.7083–0.7094). There is no obvious correlation between boron and strontium isotope ratios. This is compatible with the hypothesis that there were no major changes in the source of elements to the deposit during precipitation of the borates. It is not possible to dismiss the possibility that there were major changes in the  $\delta^{11}\text{B}$  value of the sources of the brines that are not reflected in the strontium isotopes at this preliminary stage, but there is no evidence to support this hypothesis. There is some evidence for changes in the boron isotope composition of the brines during precipitation (see below), but it is surely beyond coincidence that the relative  $\delta^{11}\text{B}$  values of the borate minerals accord so well with their structural formulae.

Differences in boron isotope composition between minerals precipitated from the same brine can arise if the pH of the fluid changes and/or as a result of more or less complete precipitation of the borate (Rayleigh fractionation).

The nature of changes in the  $\delta^{11}\text{B}$  value of the brines and borates during precipitation depends on whether the borate mineral precipitated from the brine maintains isotopic equilibrium with the brine or whether it is isotopically isolated from the brine following precipitation.

Precipitation of colemanite is favoured by low pH values (Helvacı, 1977) so a brine precipitating colemanite will become progressively enriched in  $^{11}\text{B}$ . If the boron included in colemanite remained isotopically isolated from the brine, later generations of colemanite would have heavier  $\delta^{11}\text{B}$  values than early precipitates. Sample MRP-12 is a colemanite nodule that also contains colemanite in septarian cracks. The colemanite in the cracks clearly formed after the bulk of the nodule, but its fine-grained nature indicates that it is not a secondary recrystallisation product. The bulk of the nodule has a  $\delta^{11}\text{B}$  value of –12.4 to –12.8‰ and the colemanite in the cracks has a  $\delta^{11}\text{B}$  value of –11.3 to –11.4‰. In another case we examined the boron isotope composition of the inner and outer portions of a colemanite nodule (MRP-14). In this case the central portion of the nodule (assumed to have formed first) has a  $\delta^{11}\text{B}$  value of –14.7‰ and the outer portion has a  $\delta^{11}\text{B}$  value of –13.7‰. More evidence is required, but these examples indicate that the earlier precipitated borate remained isotopically isolated from the later brines. In addition, it is difficult to envisage a physical mechanism whereby the centre of a 0.5 m diameter colemanite nodule could remain in isotopic communication with its rim.

Table 1. Boron and strontium isotope compositions of borate minerals from the Kirka deposit, Turkey

Sample	Mineralogy	$\delta^{11}\text{B}$		$^{87}\text{Sr}/^{86}\text{Sr}$
		1st run	2nd run	
CH-8	borax	-1.6 $\pm$ .2	-1.7 $\pm$ .3	0.70891 $\pm$ 30
CH-14	borax	-5.7 $\pm$ .2	-5.0 $\pm$ .2	0.70865 $\pm$ 09
CH-15	borax	-4.9 $\pm$ .2	-5.9 $\pm$ .3	0.70874 $\pm$ 06
CH-18	borax	-5.1 $\pm$ .4	-4.3 $\pm$ .2	0.70943 $\pm$ 07
CH-24	borax	-1.6 $\pm$ .3	-2.4 $\pm$ .3	0.70889 $\pm$ 03
MRP-4	borax	-3.3 $\pm$ .4	-2.6 $\pm$ .2	
MRP-5	borax	-3.3 $\pm$ .2	-4.1 $\pm$ .3	
CH-7	ulexite	-6.2 $\pm$ .2	-6.8 $\pm$ .4	0.70862 $\pm$ 15
CH-10	ulexite	-8.0 $\pm$ .3	-7.5 $\pm$ .4	0.70855 $\pm$ 31
CH-9	ulexite	-10.1 $\pm$ .2	-10.6 $\pm$ .3	0.70890 $\pm$ 09
CH-12	ulexite	-7.8 $\pm$ .3	-7.7 $\pm$ .2	0.70830 $\pm$ 35
CH-17	ulexite	-7.6 $\pm$ .2	-7.5 $\pm$ .2	0.70864 $\pm$ 10
CH-18	ulexite	-7.9 $\pm$ .4	-7.6 $\pm$ .5	0.70941 $\pm$ 06
MRP-11	1° ulexite	-5.7 $\pm$ .4	-6.4 $\pm$ .5	
MRP-11	ulexite in cracks	-5.9 $\pm$ .4	-5.3 $\pm$ .4	
MRP-17	ulexite	-6.7 $\pm$ .3	-6.0 $\pm$ .2	
CH-16	colemanite	-12.9 $\pm$ .3	-13.3 $\pm$ .2	0.70916 $\pm$ 07
CH-17	colemanite	-9.6 $\pm$ .3	-9.9 $\pm$ .4	0.70861 $\pm$ 08
CH-22	colemanite	-13.3 $\pm$ .3	-13.4 $\pm$ .3	
MRP-12	1° colemantite	-12.8 $\pm$ .6	-12.4 $\pm$ .5	
MRP-12	colemantite in cracks	-11.4 $\pm$ .3	-11.3 $\pm$ .4	
MRP-12	2° colemantite	-14.9 $\pm$ .5	-14.7 $\pm$ .3	
MRP-14	central colemantite	-14.7 $\pm$ .4	-14.7 $\pm$ .4	
MRP-14	outer colemantite	-13.7 $\pm$ .2	-13.7 $\pm$ .3	

To what extent can the Kirka dataset be used to constrain the  $\delta^{11}\text{B}$  values of the original brines and the pH of the lakes?

There is minor geothermal activity in the general area of the borate deposits, but there is no certainty that the composition of these fluids are representative of the geothermal activity at the time the borates formed. However, some constraints can be obtained from the borate  $\delta^{11}\text{B}$  values and the boron speciation and isotope fractionation given in Oi et al. (1989). Regardless of the pH, colemantite with a  $\delta^{11}\text{B}$  value of less than -13‰ cannot have precipitated from fluids with  $\delta^{11}\text{B}$  values greater than approximately 0‰. Similarly, borax with a  $\delta^{11}\text{B}$  value of greater than approximately -4‰ could not have precipitated from the fluids with a  $\delta^{11}\text{B}$  value of less than -13‰. This range of 0 to -13‰ includes most of the boron isotope data measured in continental geothermal fluids (e.g., Palmer and Sturchio, 1990) that are the presumed source of boron in the Kirka deposits (Helvacı, 1995).

The effect of pH on the  $\delta^{11}\text{B}$  value of borate minerals precipitated from a brine can be modelled from the theoretical boron isotope fractionation factors and the speciation of borate in solution (Oi et al., 1989). An example is shown in Fig. 3, where it is assumed that the borates are in equilibrium with a brine with a  $\delta^{11}\text{B}$  value of -4‰. There is some overlap, but Fig. 3 indicates that colemantite formed under more acidic conditions (average pH = 8.2) compared to ulexite (8.6) and borax (8.83). This observation is in accord with experimental and theoretical evidence that suggests colemantite precipitated from lower pH solutions than either ulexite or borax (Christ et al., 1967; Helvacı, 1977). (The relative pH order of the

three borate minerals would not be changed if a different brine  $\delta^{11}\text{B}$  value was used in the calculation.)

An additional constraint on fluid compositions is provided by the fact that borax is the dominant borate mineral in the deposit, followed by ulexite and then colemantite (Inan et al., 1973). It is not unreasonable, therefore, to conclude that conditions generally favoured borax precipitation.

The extent of borate precipitation from a parcel of brine can be constrained from the appropriate Rayleigh equation and the assumption that the  $\delta^{11}\text{B}$  values measured in this study are representative of the total range in the deposit. For illustration we consider the model of no boron isotope exchange between precipitated borates and later brines. In this case the appropriate Rayleigh equation is

$$R_m = R_i \alpha f^{\alpha-1},$$

where  $R_m$  is the  $^{11}\text{B}/^{10}\text{B}$  ratio of the borate precipitated at extent  $f$ ,  $R_i$  is the initial  $^{11}\text{B}/^{10}\text{B}$  ratio of the evaporite fluid,  $\alpha$  is the isotope fractionation factor between the fluid and the borate mineral, and  $f$  is the fraction of boron remaining in the brine. The total ranges in  $\delta^{11}\text{B}$  values for each borate mineral are -5.9 to -1.6‰ for borax, -10.6 to -5.3‰ for ulexite, and -14.9 to -9.6‰ for colemantite. The values of  $\alpha$  at pH values of 8.2, 8.6, and 8.83 are taken from Oi et al. (1989). From these data and the Rayleigh equation above it is possible to calculate the fraction of boron removed from solution to yield the observed range in  $\delta^{11}\text{B}$  values at a given pH and starting  $\delta^{11}\text{B}$  value for the brine.

Table 2. Structural formulae and basic boron atomic structure of borate minerals analysed in this study

Boron Mineral	Structural Formula	Basic boron atomic structure
borax	$\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$	$2\text{BO}_3 + 2\text{BO}_4$
ulexite	$\text{NaCaB}_5\text{O}_6(\text{OH})_6 \cdot 5\text{H}_2\text{O}$	$2\text{BO}_3 + 3\text{BO}_4$
colemanite	$\text{Ca}_2[\text{B}_3\text{O}_4(\text{OH})_3]_2 \cdot 2\text{H}_2\text{O}$	$\text{BO}_3 + 2\text{BO}_4$

The results of these calculations are shown in Fig. 4. The calculation indicates that for borax to be the dominant borate mineral requires a high pH and a relatively heavy starting  $\delta^{11}\text{B}$  value for the brine. Colemanite requires the lowest pH in order for it to be the dominant mineral, with ulexite being dominant at intermediate pH. Colemanite and ulexite both require a lighter starting  $\delta^{11}\text{B}$  value than borax for them to be the dominant borate minerals.

It is emphasised that this calculation illustrates general principles rather than providing a unique solution to a multivariant problem. In addition, if more than one borate forms at any one time the boron isotope evolution of the brine will depend on the relative proportions of the precipitating minerals (although individual portions of the deposit are dominated by a single borate mineral, with relatively minor amounts of other borates—Inan et al., 1973; Helvacı, 1977; Sunder, 1980—and none of the paragenetic relationships observed in hand specimen show evidence for *intergrowth* of different borate minerals). In two samples there are coexisting borate minerals. CH-18 is from a point close to the upper borax-ulexite transition zone and consists of a nodular ulexite coating ( $\delta^{11}\text{B}$

value;  $-4.3$  to  $-5.1\text{‰}$ ) on top of a borax layer ( $\delta^{11}\text{B}$  value;  $-7.6$  to  $-7.9\text{‰}$ ). The difference between the isotopic composition of the two minerals is greater than the value ( $\sim 2\text{‰}$ ) for ulexite and borax in equilibrium with one another at  $25^\circ\text{C}$  (Oi et al., 1989), suggesting that they did not form at the same time. CH-17 is from above the main borate body and consists of a large radiating colemanite nodule ( $\delta^{11}\text{B}$ ;  $-9.6$  to  $-9.9\text{‰}$ ) with smaller white nodular ulexite ( $\delta^{11}\text{B}$  value;  $-7.5$  to  $-7.6\text{‰}$ ). Again the difference between the two minerals is greater than the theoretical isotope fractionation factor ( $\sim 1.3\text{‰}$ ) (Oi et al., 1989), suggesting that the ulexite and colemanite did not form at the same time. In addition, theoretical phase relations between the various borate minerals do not favour coprecipitation of different minerals (Christ et al., 1967).

Despite these uncertainties, other example calculations (not shown) indicate that the relative ordering of the pH values remains the same, i.e., borax is precipitated from higher pH brines than is ulexite, with colemanite forming from the lowest pH brines. These calculations also show that either ulexite or colemanite can be the dominant borate min-

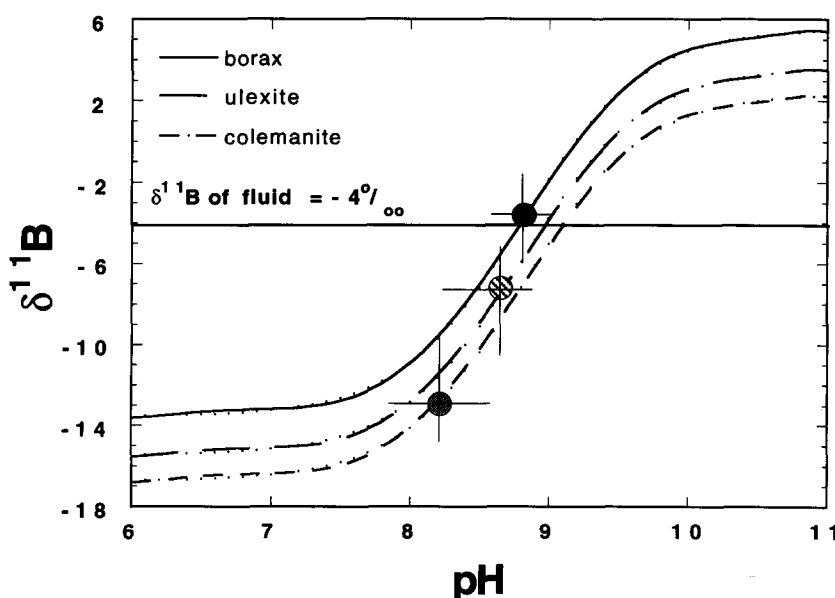


FIG. 3. Variation with pH of boron isotope compositions of borate minerals precipitated from a brine with a  $\delta^{11}\text{B}$  value of  $-4\text{‰}$ . The three curves reflect the different isotope fractionation factors between the solution and the different borate minerals (values from Oi et al., 1989).

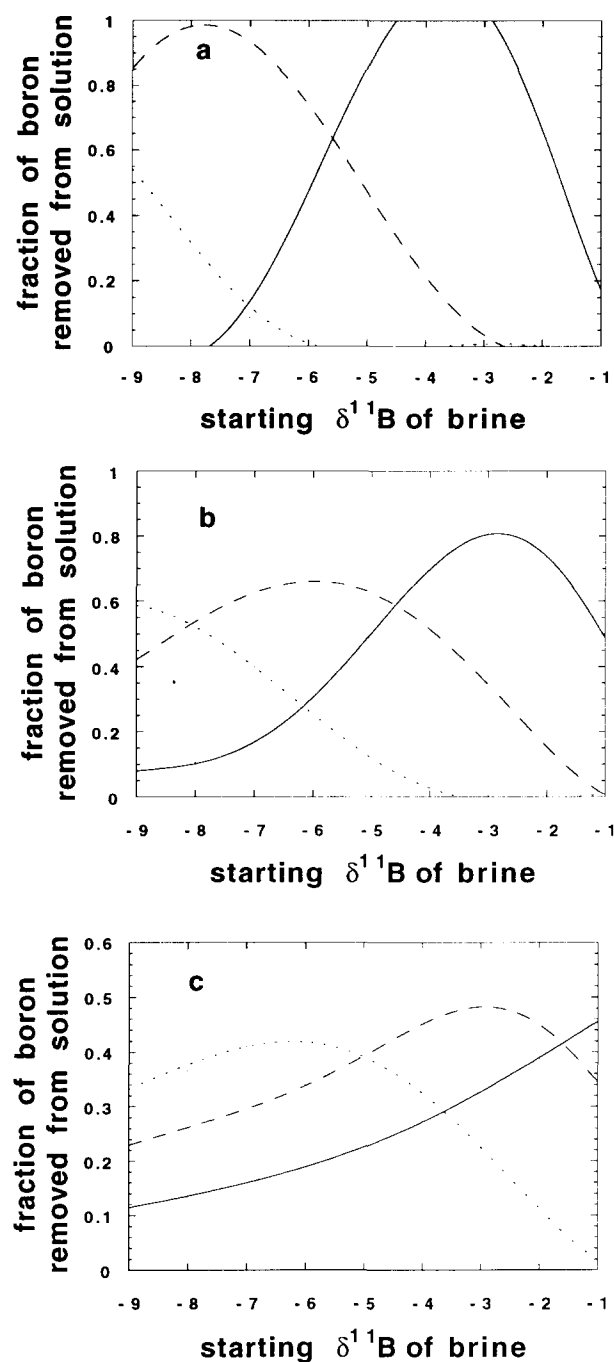


FIG. 4. Fraction of boron removed from solution to yield observed range in  $\delta^{11}\text{B}$  values for given starting  $\delta^{11}\text{B}$  value of brine. Full line is the curve for borax, dashed line is for ulexite and dotted line is for colemanite. (a) pH 8.83, (b) pH 8.6, and (c) pH 8.2 (see text for details).

erals precipitated from a brine with the same starting  $\delta^{11}\text{B}$  value if the pH changes, but for borax to be the dominant borate mineral at Kirka, a heavier  $\delta^{11}\text{B}$  value is required along with a higher pH.

The pH of the brines may have changed as a result of a number of processes, e.g., changes in the pH of geothermal fluids entering the basin, precipitation of carbonates, oxida-

tion of organic matter, etc. It would be of interest to examine pH changes in a modern borate precipitating lake, but we know of no phenomenological study of this type. Oxidation of organic matter would lower the pH without significant change in Na, Ca, and boron concentrations, whereas precipitation of  $\text{CaCO}_3$  would change the pH and lower Ca concentrations.

The pH of the geothermal fluids entering the lake may change as a result of factors, such as, a change in the level of the groundwater table initiating phase separation in the geothermal system. In the Yellowstone geothermal system, high Na/Ca ratios are restricted to high pH fluids (Fournier, 1989) and there is a tendency for the higher pH fluids to have heavier  $\delta^{11}\text{B}$  values (Lewis, 1995) as a result of boron volatilisation during phase separation (Palmer and Sturchio, 1990). These observations are compatible with the boron isotope systematics in the Kirka deposit where borax precipitation is favoured by high pH fluids with relatively heavy  $\delta^{11}\text{B}$  values and high Na/Ca ratios.

## 6. CONCLUSIONS

The  $\delta^{11}\text{B}$  values of colemanite, ulexite, and borax from the Kirka borate deposit in Turkey range from  $-1.6$  to  $-14.9\text{‰}$ . The lack of correlation between boron and strontium isotope ratios for individual minerals suggests that varying sources of boron to the deposits did not play a major role in defining the variations in boron isotope compositions.

The relative differences in the boron isotope compositions of colemanite (average  $\delta^{11}\text{B}$  value;  $-12.9\text{‰}$ ), ulexite (average  $\delta^{11}\text{B}$  value;  $-7.3\text{‰}$ ), and borax (average  $\delta^{11}\text{B}$  value;  $-3.7\text{‰}$ ) are consistent with their boron atomic configurations (Oi et al., 1989). However, the magnitude of the differences in  $\delta^{11}\text{B}$  values between the three minerals is too large for them to have precipitated together from brines with the same boron isotope composition and pH.

The boron isotope data are consistent with colemanite being precipitated from a brine of lower pH than ulexite, with borax being precipitated from a brine of higher pH than ulexite.

Preliminary boron isotope evidence suggests that the borate minerals did not maintain boron isotope equilibrium with the coexisting brine after they precipitated from solution.

Rayleigh fractionation models support the observation that borax was derived from the highest pH fluids and that the  $\delta^{11}\text{B}$  value of the brines that precipitated borax may have been slightly heavier than those that precipitated ulexite and colemanite. These observations are compatible with the boron isotope systematics of modern geothermal systems.

**Acknowledgments**—This work was supported by a NATO grant to MRP and CH and by Royal Society grants to MRP. We are especially grateful to Etibank and the mine manager and geologists for their generosity during fieldwork at the Kirka deposit. Denis Shaw, George Swihart, Marc Chaussidon, and an anonymous reviewer provided constructive reviews of the paper.

**Editorial handling:** D. M. Shaw

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## Appendix

Sample	Mineralogy	Description
CH-7	ulexite	fibrous silky layer of ulexite from below borax zone
CH-8	borax	massive borax from lower part of borax zone
CH-9	ulexite	fibrous layer of primary ulexite from above the borax zone
CH-10	ulexite	powdery ulexite within cavities in upper part of borax zone, possibly secondary after dissolution of borax
CH-12	ulexite	1cm thick layer of ulexite from above the borax zone
CH-14	borax	massive borax from middle of borax zone
CH-15	borax	bedded borax from middle of borax zone
CH-16	colemanite	radiating coemanite nodule 2cm in diameter from top of deposit
CH-17	colemanite	white nodular ulexite growing on radiating crystals of coemanite from just above borax zone
CH-18	ulexite	small (5cm) nodules of ulexite on top of bedded borax
	borax	from top of borax zone
CH-22	colemanite	small (3cm) coemanite nodule from small Göçenoluk deposit northwest of main deposit, thought to correlate with coemanite in main deposit below borax zone
CH24	borax	large (10cm thick) vein of borax cross cutting main borax zone, probably secondary replacement of original borax
MRP-4	borax	bedded borax from main borax zone
MRP-5	borax	thick (15cm) vein of clear borax cross cutting main borax zone, probably formed from recrystallisation of bedded borax
MRP-11	ulexite	small (5cm) discoidal nodule of ulexite with fine grained ulexite infilling septarian cracks, from just above main borax zone
MRP-12	colemanite	large (30cm) nodule of radiating coemanite with cross cutting veins of recrystallised coemanite and fine grain primary coemanite filling septarian cracks, from above main borax zone
MRP-14	colemanite	large (25cm) nodule of radiating coemanite from above main borax zone
MRP-17	ulexite	1cm thick layer of ulexite from above the borax zone