

GEOCHEMICAL METHOD FOR DETERMINING PALEOSALINITY

by

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ABSTRACT

The boron content of sea water increases linearly with salinity within the range tested. The boron content of the illite minerals in the clay mineral size fraction of many types of sedimentary rocks has been shown to increase with the "geologically known" salinity prevailing during deposition of the rocks. It is believed that boron is abstracted by the illitic clay minerals from sea water in proportion to the salinity of the sea water. This boron content is not substantially changed by other geological processes normally operative in sedimentary rocks. It is concluded that the boron content of illite minerals in sedimentary rocks can be used to evaluate the salinity of the sea prevailing at the time the sediment was deposited.

INTRODUCTION

One of the most important objectives of geochemical work is to provide quantitative methods for evaluating geological processes and specifying geological environments. One of the environmental parameters of biological and geological interest is the salinity of the sea. A method for determining paleosalinities would be not only of great academic interest, because it would provide information of use to the paleontologist, ecologist and paleogeographer, but would also be of considerable practical value in the search for various types of mineral deposits and petroleum. The purpose of this paper is to summarize geochemical work, started in 1956, that was designed to determine paleosalinities quantitatively by making appropriate measurements on sedimentary rocks.

Goldschmidt and Peter (1932) made the first systematic study of boron in sedimentary rocks. They noted a wide variation in the boron content of sediments and observed that a rough relationship existed between the amount of boron and the type of sediment. Later work by Landergren (1945, 1958) showed that much of the boron in sediments existed in the clay-size fraction. In 1877, Dieulfait (see Goldschmidt, 1954, p. 283) made the observation that notable amounts of boron exist in sea water. Goldschmidt and Peters (1932) also made boron determinations from sea water from different places and depths and observed a wide range of values. The observations made by these and other workers suggest that some systematic relationship exists between the boron content of sea water, the sediments formed in this water, and the salinity of the water at the time of deposition.

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PROCEDURE

Relationship Between Boron and Salinity in Sea Water

Bottom-water samples were collected and analyzed to determine the relationship between the salinity of the water and its boron content. The samples were obtained from various shallow-water environments along the Gulf Coast in the vicinity of Port Lavaca and Rockport, Texas. The salinity of the water was measured by determining the density with an immersion hydrometer, correcting for temperature, and referring to curves relating density to salinity (see Harvey, 1955, p. 128). The samples were stored in polyethylene bottles to avoid contamination of the water from boron normally found in glass bottles.

An attempt was made to secure samples from as many environments as possible. Samples were taken from the surf zone, shallow bays, euxinic bayous, rivers and evaporating tidal flats.

The boron content of the samples was determined by emission spectrographic methods. A soluble beryllium salt was used as an internal standard. The samples were analyzed using a high-voltage spark and rotating disk electrodes. Details of the spectrographic technique will be reported elsewhere.

Occurrence of Boron in Sedimentary Rocks

Boron analyses reported here were made using an emission spectrochemical technique adapted from Melvin and O'Connor (1941). The powdered sample was mixed with beryllium and graphite and arced to completion in a high-current D.C. arc. Beryllium was used as the internal standard. The equipment used was the same as that used for the sea water analyses. This technique will be reported also in detail elsewhere.

Illite contents were determined by measuring, with x-ray fluorescence techniques, the potassium content of purified clay. This method was used when x-ray diffraction studies indicated the absence of other potassium minerals in the samples.

The earlier work by Landergren and others indicated that the higher concentrations of boron in sediments occurred in argillaceous sediments. It was suspected, therefore, that the boron was contained in the clay mineral fraction of the sediment. Boron also occurs in tourmaline in sediments. In all the work reported here, however, all the material was carefully sized and it is believed that essentially all tourmaline was removed from the samples. Also, other chemical treatments of the samples indicated the absence of tourmaline in the clay-size fraction.

RESULTS

Boron-Salinity Relationships in Sea Water

The boron content of the water samples is listed in Table 1 and shown in Fig. 1.

TABLE I.—RESULTS OF THE SPECTROCHEMICAL ANALYSES OF BORON IN GULF COAST BOTTOM WATERS

Specimen Number	Total Dissolved Solids (Salinity) in Parts Per Thousand (0/00)	Boron Content in Parts Per Million (ppm)	Environment
1	46.5	6.0	Shallow bay, not over six feet deep, well aerated
2	46.0	6.4	
3	46.0	6.2	
4	46.5	5.8	
5	46.5	6.2	
6	48.0	6.5	
7	6.0	1.0	Bayou, euxinic environment
8	5.0	0.86	
9	8.5	1.3	
10	7.5	1.0	
11	6.5	1.1	
12	38.5	5.0	
13	26.5	3.3	
14	29.0	3.6	
15	27.0	3.3	
16	21.0	3.0	
17	22.5	2.8	
18	50.0	6.5	Shallow bay grading to euxinic bayou
19	51.0	6.6	
20	53.0	6.2	
21	56.0	7.0	
22	55.0	7.8	
23	58.0	7.5	
24	62.0	8.1	
25	63.5	7.8	
26	67.5	8.8	
27	270.0 (saturated)	88.0	Tidal pool: salt bottom
28	2.0	0.20	Colo. River 10 miles from coast
29	22.0	2.9	Euxinic bayou
30	19.5	2.8	
31	18.5	2.7	
32	16.0	2.4	
33	11.5	1.8	
Gulf Water	38.0	5.2	Surf zone of the open Gulf of Mexico

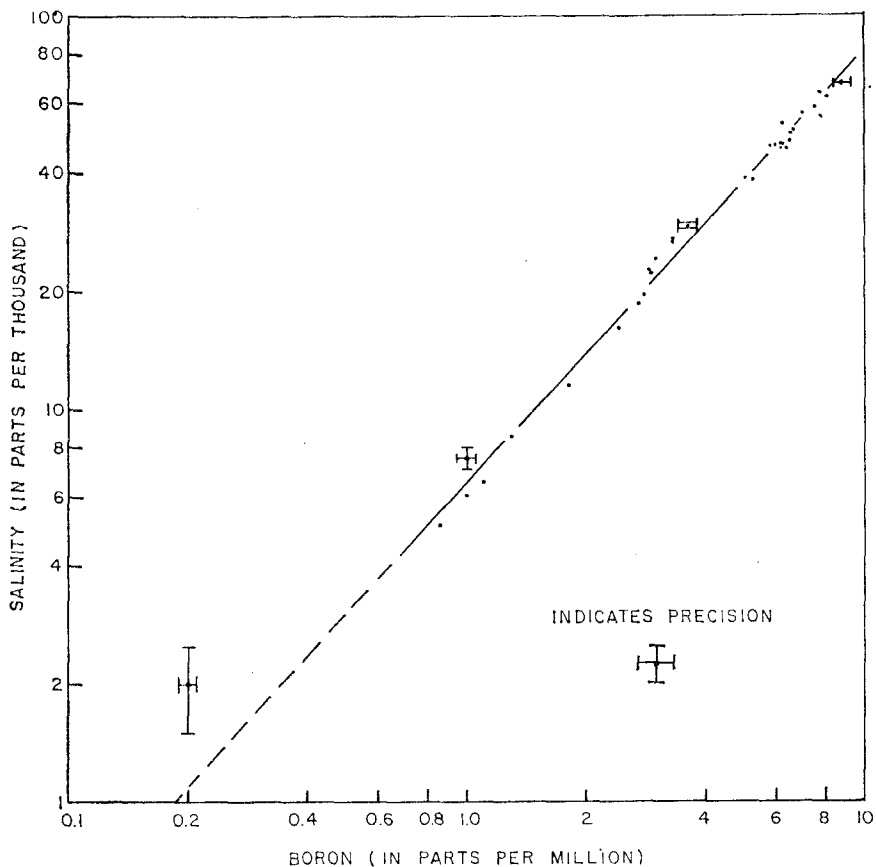


FIGURE 1.—Relationship between boron content and salinity of Gulf of Mexico bottom waters.

Location of Boron in Shale

The amount of boron in some shale samples is plotted against the amounts of kaolinite, illite, and chlorite (Fig. 2). The shale samples were taken from a core of the Cardium formation (Cretaceous) of Alberta. The relative abundances of the clay minerals were estimated by measuring peak areas from x-ray diffractograms prepared from glycol-wet powdered shale that was packed and smoothed into a rectangular sample-holder. Figure 3 shows the

progressive change in diffraction pattern of a Mesaverde shale (Cretaceous, New Mexico) from which clay minerals other than illite were removed by

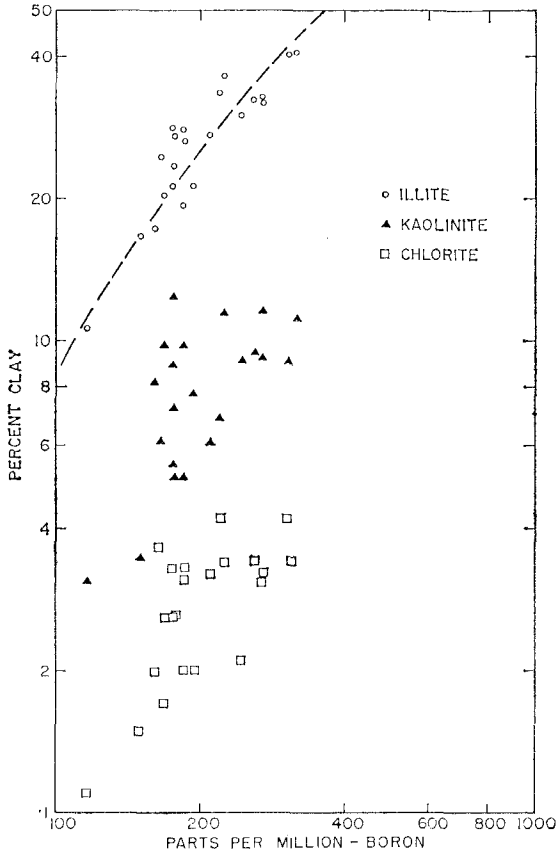


FIGURE 2.—Relationship between clay minerals and boron in Cardium shales.

chemical treatment. The potassium (reported as illite) and boron contents of this sample (Shale 1) before and after treatment are indicated in Table 2 along with potassium and boron data for other shales that were treated in similar fashion.

TABLE 2.—BORON AND ILLITE CONTENT OF SOME SHALES BEFORE AND AFTER CHEMICAL TREATMENT

Sample ¹	Before Treatment		After Treatment	
	Percent Illite	ppm B	Percent Illite	ppm B
Shale 1	50	193	73	217
Shale 2	62	70	81	88
Shale 3	64	160	70	192
Shale 4	64	153	62	154
Shale 5	47	90	53	150

¹ All these samples are Cretaceous shales from New Mexico. The formations represented are the Mesaverde, Greenhorn, Point Lookout, Pictured Cliffs, and Lewis.

Boron Content of Illites from Other Shales

A large number of core and outcrop samples were collected from areas where other geological work has indicated the geological environment to represent fresh water, brackish water, normal marine, or hypersaline conditions. These qualitative environmental evaluations were made by reference to the literature together with noting such details as the texture of the rock, its fossil, coal or organic content, and its general geologic setting. The results of the boron measurement of the illite fraction from these rocks are shown in Fig. 4. Boron concentrations refer to ppm B in pure illite; this "normalized" boron content was calculated according to the following expression: $\text{ppm B} \times 100/\text{percent illite} = \text{ppm B in pure illite}$.

DISCUSSION OF RESULTS

Relationship Between Boron and Salinity in Sea Water

As shown in Fig. 1, a linear relationship exists between boron and salinity in the Gulf of Mexico bottom waters from fresh water to brines containing 70 percent salt. The relationship for more concentrated brines is being determined and no data are yet available. It appears probable that with increases in salinity the boron content of the brine also will increase. The exact relationship can be determined only by experiment.

Extraction of Boron from Sea Water by Clay Minerals

Figure 4 can be interpreted to indicate that illites extract boron from sea water in proportion to the amount present. The exact form of the absorption isotherm or extraction curve is not known at the present time and must be

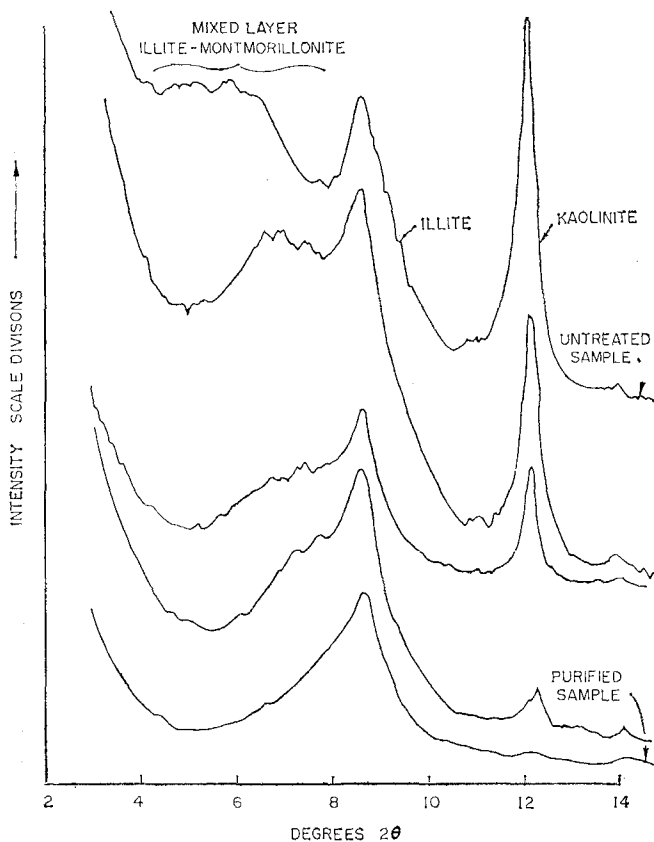


FIGURE 3.—X-Ray patterns showing the progressive removal of clays from illite by appropriate chemical treatment.

determined experimentally. Synthesis experiments to clarify this point are under way and will be reported at a later date. It is also not known whether the boron enters a previously existing clay mineral structure (a "stripped" mica or other detrital mica of some kind) or is incorporated into an illite formed directly from gels and other constituents present on the sea floor and in the sea water. To date, the evidence gives information only on the chemistry of the clay minerals and no direct information on how the clay minerals formed.

Location of Boron in the Cardium Shale

A linear relationship exists between illite, kaolinite and chlorite in the Cardium shales tested (Fig. 2). In these and many other rocks tested, illite

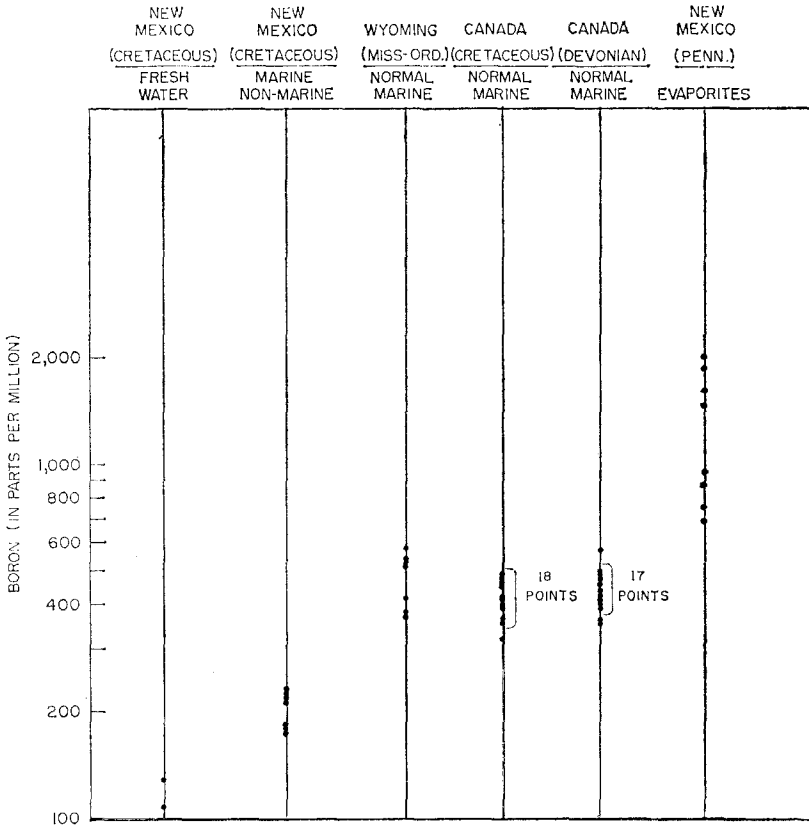


FIGURE 4.—Boron content of purified illites from rocks from "known" geological environments.

and chlorite occur in approximately a fixed ratio, which varies from area to area, irrespective of the total amount of material in the clay mineral fraction of the rocks. The best relationship occurs between illite and boron. These

data have been interpreted as indicating that the boron in the Cardium shales is associated with either mica or illite, both of which are characterized by a 10 \AA diffraction peak. Analyses of micas from other rocks showed boron to be present in very low concentrations. Goldschmidt (1954, p. 282) has found micas to contain less than two ppm B; therefore, there is good evidence that the bulk of the boron in the Cardium shales is associated with the clay mineral illite. To test this hypothesis, the clay-size fractions of several shales were treated chemically in such a way that non-illitic clays were selectively removed. The diffraction patterns of one of these can be seen in Fig. 3 and their boron content noted from Table 2.

For all samples except one, the increased percentage of illite in the clay-mineral fraction resulted in an increase in boron content. The one that remained unchanged (Shale 4) originally contained almost pure illite in the clay fraction. Thus the chemical treatment resulted in essentially no change in illite and hence no change in boron. These experiments indicate that the boron content of the shales tested is contained primarily in the clay mineral illite.

Additional chemical studies have shown that the boron is firmly fixed in the illite structure. One shale sample (Shale 5 of Table 2) was chemically treated so that 85 percent of the sample was decomposed. The residue had the same boron content as the original. Apparently it is not possible to preferentially leach boron from illite by severe chemical treatment. Other chemical attempts to remove boron from shales have failed. Treatment with acid, heating to incandescence, anion and cation exchange experiments and treatment with alkalis have been tried on about 25 shale samples. Significant amounts of boron were not lost from any samples. The conclusion reached is that the boron, once it is fixed into the illite lattice, stays there in substantially the same quantities when the sediment is subjected to other processes normally occurring in sedimentary rocks.

Boron Content in Illites from Other Shales

The boron content of illites separated from shales collected from several "known geological environments" increases with the presumed salinity as shown in Fig. 4.

The scatter in points may actually indicate different salinity conditions. Boron-illite ratios from a series of samples collected from a core (California Standard Fairybank No. 2-8, Canada) plot as a smooth curve (Fig. 5). The curve indicates a gradually increasing salinity from Cooking Lake to Duvernay time. The salinity then gradually decreases until normal sea water ratios are observed. This change in salinity corresponds to the known geological information regarding these rocks. The data in these two figures indicate that a wide range of paleosalinities can be measured by this method and that detailed ratio curves may be of some use to show the salinity behavior in localized areas.

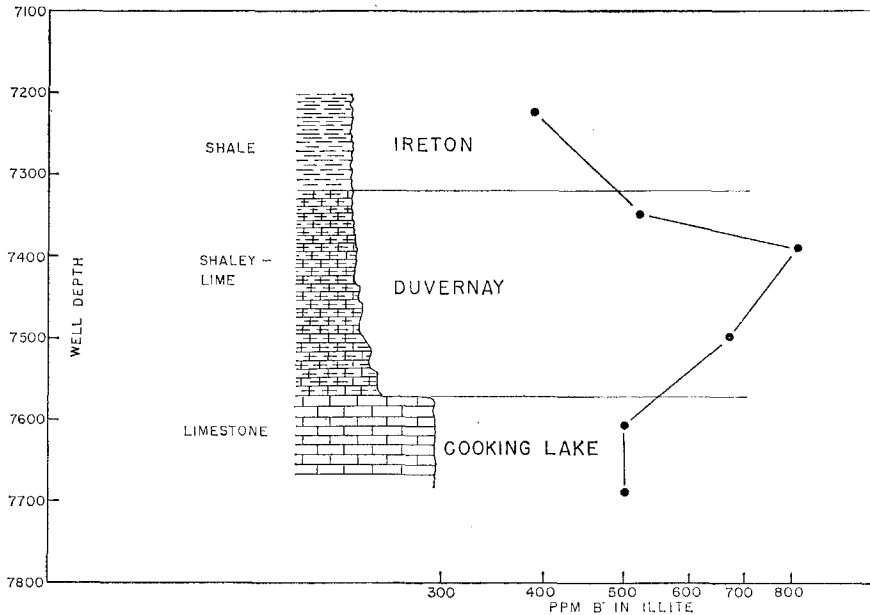


FIGURE 5.—Paleosalinity curve for some Devonian rocks from Canada.

CONCLUSIONS

1. The boron content in brines increases with the salt content (salinity) of the brine over the range studied.
2. Most of the boron in the clay mineral fraction of sedimentary rocks is contained in the clay mineral illite.
3. Boron seems to be extracted from the sea water by illite in proportion to the amount of boron present.
4. The boron is strongly fixed into the illite lattice and the amount of boron is not expected to be substantially changed by the normal geological processes affecting the rocks after their formation.
5. Illites extracted from sedimentary rocks from a wide range of geological environments indicate that their boron content can be used to evaluate the relative salinity of the sea at the time the sediment was formed.

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