

# Significance of Laminations in the Upper Silurian Evaporite Deposit of the Michigan Basin

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## ABSTRACT

*Halite exposed in the subsurface workings of the Canadian Rock Salt Co., Windsor, Ontario, and the International Salt Company, Detroit, Michigan, occurs cyclicly interlaminated with dolomite and anhydrite. This association has been attributed to seasonal changes in the basinal environment and to the influx of normal sea water.*

*Bromide data recorded from samples of individual layers indicate:*

*(1) The bromide content of halite overlying the dolomite-anhydrite laminations falls below the theoretical minimum of 75 ppm predicted by the distribution coefficient.*

*(2) The maximum bromide value does not occur at the top of the halite layers as expected under conditions of progressive concentration, but at an intermediate position within each layer. Above this maximum, the bromide diminishes.*

*(3) The bromide values in any given halite layer decrease toward the margins of the basin.*

*The bromide trends suggest two "seasons" of deposition:*

*(1) A dry "season" characterized by high rates of evaporation marked by the deposition of the dolomite-anhydrite lamination and of the lower part of the halite layer in which the bromide trend is positive.*

*(2) A wet "season" which resulted in the deposition of the upper part of the halite in which the bromide trend is negative.*

*The low overall bromide values recorded suggest deposition in a semirestricted basin into which*

*salt-saturated meteoric water was introduced at seasonally varying rates. Solution and redeposition rather than primary precipitation appears to have been the main mechanism of marginal salt accumulation.*

## INTRODUCTION

Studies of bromide geochemistry have contributed much to our understanding of the characteristics of brines from which highly soluble salts are precipitated. Experimental studies have shown that a direct relationship exists between the amount of bromide which can substitute for chloride in the halite structure and the salinity of the solution from which halite is derived.

Recent data on evaporites show bromide distributions which are considerably different from those predicted by the distribution coefficient (Holser, 1966, Wardlaw and Schwerdtner, 1966, Wardlaw and Watson, 1966).

Dellwig (1955) has indicated that, in the Michigan basin, the halite in the deeper portions of the basin differs in appearance from the halite which occurs near the margins. Near shore, clear halite, considered secondary, predominates over hopper halite which forms as pyramidal crystals on the surface of the brine. Fragmented hopper crystals, as well as halite truncated by dolomite-anhydrite laminations, are also found. These observations suggest that solution may have been important in the near shore areas of the basin.

The research project, therefore, was aimed at the following objectives:

(1) To investigate the vertical and lateral chemical variations in individual salt laminations in an

effort to understand the nature of the controlling variations in the parent brines and their evolution through time.

(2) To investigate the importance of solution and reprecipitation.

(3) To quantitatively relate the cyclical occurrence of dolomite and anhydrite to the salinity stages of the brine.

(4) To develop a model of marginal salt accumulation.

### LOCATION OF THE AREA

The area selected for study is located in the southeastern portion of the Michigan basin. Work was conducted in two salt mines (Fig. 1):

(1) International Salt Company, located in Detroit, Michigan.

(2) Canadian Rock Salt Company, Limited, located in Windsor, Ontario, Canada.

Both companies mine the same salt sequence—the Upper Silurian Salina F salt as defined by Landes (1945). Sampling probably was confined to the F<sub>2</sub> subunit.

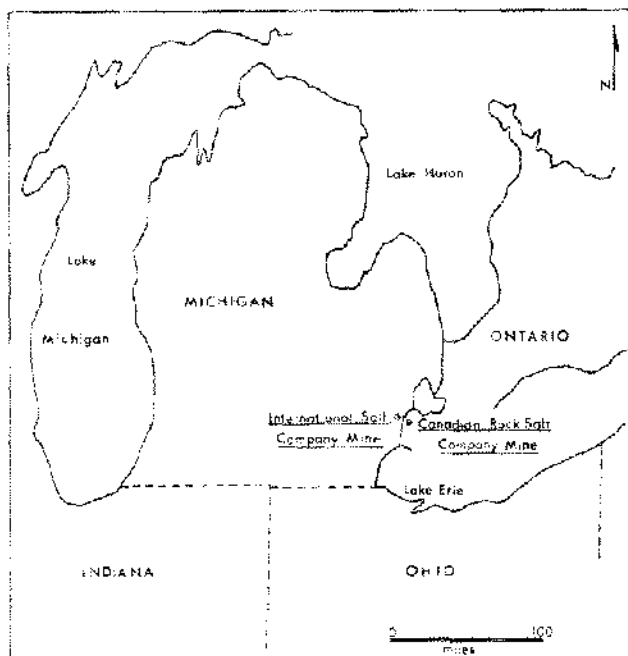


Figure 1. Location map of the two mines investigated.

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### PROCEDURE

#### *Sample collection.*

Two sets of samples were collected from working faces. One set of samples, consisting of a vertical sequence of thirteen stratigraphically equivalent units, was obtained at two localities, one in each mine. Another set of samples of a selected lamination (no. 2 of Fig. 4) was collected from the Canadian Rock Salt mine at intervals of about 1000 feet.

#### *Sample preparation.*

Powdered halite samples used for the determination of bromide concentrations were taken at random vertical intervals by drilling parallel to the bedding using a rotary drill.

Samples for the analysis of insolubles (dolomite and anhydrite) in the dark laminations were collected by drilling through the laminations perpendicular to bedding. Drilling was begun well in the overlying halite layer and ended in the underlying halite layer. Since the boundaries of the dark laminations are indistinct, this procedure ensured the collection of the total insolubles contained in them. As the drilling of each sample was done with the same drill bit, this method provides a basis for comparison of the amount of insolubles among the samples. Variations within the selected laminations may therefore be examined.

#### *Analytical methods.*

The amount of insolubles (dolomite and anhydrite) in dark laminations and the concentration of bromide in halite layers were obtained in duplicate by volumetric analyses. Averages are reported. Averages obtained from two significantly different analytical values are followed by a question mark.

The amount of insolubles in a given sample was determined by weighing the sample, analyzing

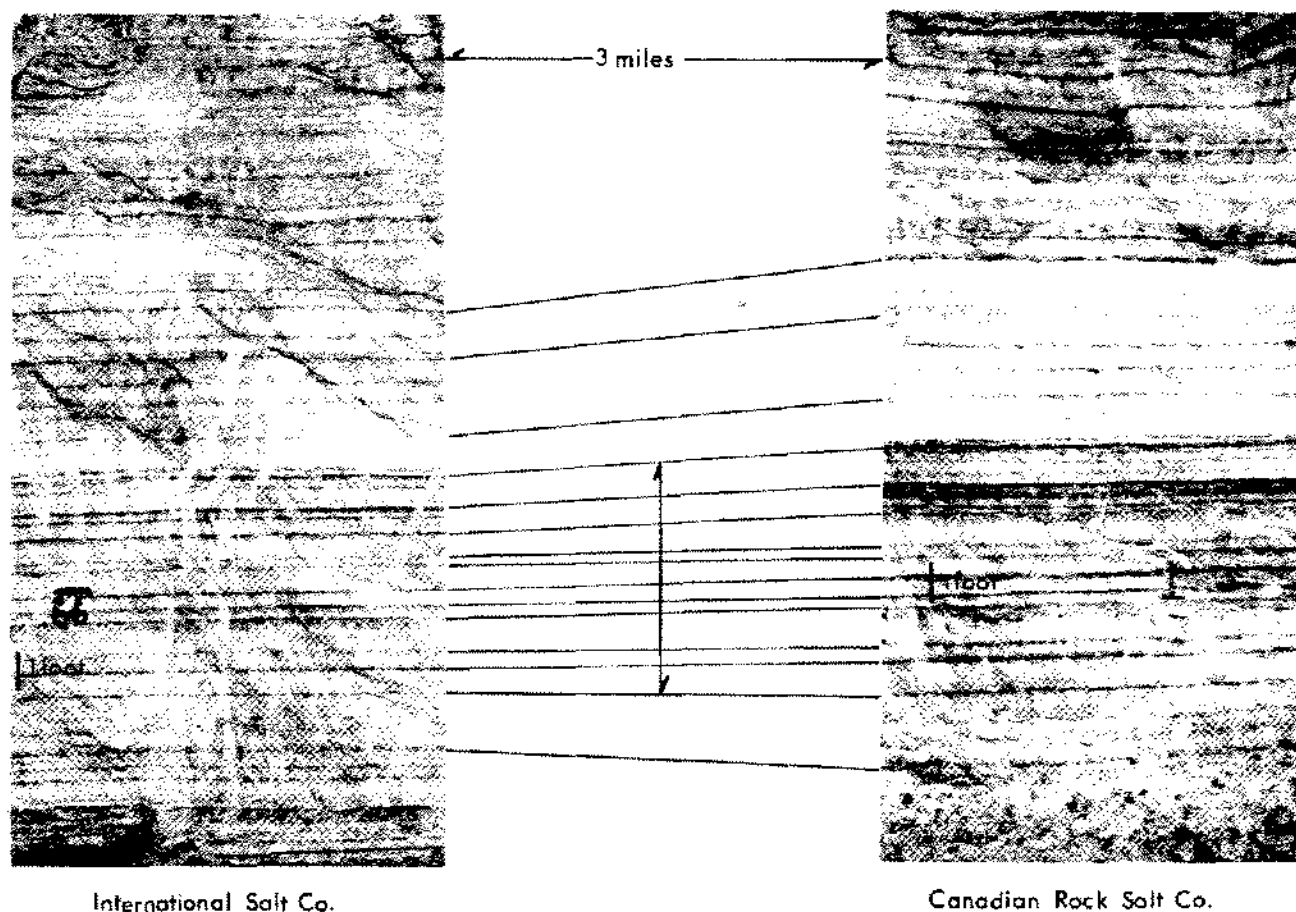


Figure 2. Working faces in investigated salt mines. Correlation lines are drawn between the more obvious laminations. Vertical arrow indicates the sampled interval. Lowermost lamination in interval is lamination no. 1.

sodium chloride content by the standard silver nitrate method, and subtracting the latter from the weight of the sample. The amount of insolubles is reported as milligrams of dolomite and anhydrite per sample.

Bromide was determined indirectly by its quantitative reaction as the bromate with iodide to precipitate iodine which is titrated with sodium thiosulfate. The analytical method has been described by d'Ans and Hofer (1934; English translation by Schwerdtner, 1963) and by Kolthoff and Yutzy (1937). Bromide concentrations are reported as parts per million by weight in halite. Sodium chloride analyses were made on all samples collected directly above or below a dolomite-anhydrite lamination in order to correct for impurities.

## THEORETICAL ASPECTS

The geochemical aspects of bromine have been extensively discussed in the literature (Valyashko, 1956, Braitsch, 1962, Holser, 1966). Therefore, only the general aspects are reviewed in this paper.

Bromine present in sea water in the form of bromide substitutes for chloride in the halite and other halogen structures. The amount of bromine which precipitates in solid solution is directly proportional to the concentration of bromide in the brine, and, therefore, to salinity. The relationship is quantitative and is expressed by a distribution coefficient. The coefficient is constant for a given chloride. It varies from 0.14 at the beginning of halite precipitation to 0.07 during the precipitation of sylvite and carnallite (Braitsch, 1962). The

coefficient predicts that the first halite to precipitate above a dolomite-anhydrite lamination should contain 75 ppm bromide.

The implications of this relationship are significant. Since the coefficient is less than one, the concentration of bromide in the brine increases although some is removed by precipitating halite. Furthermore, since the coefficient is constant, subsequently precipitated halite must be enriched in bromide (Fig. 3).

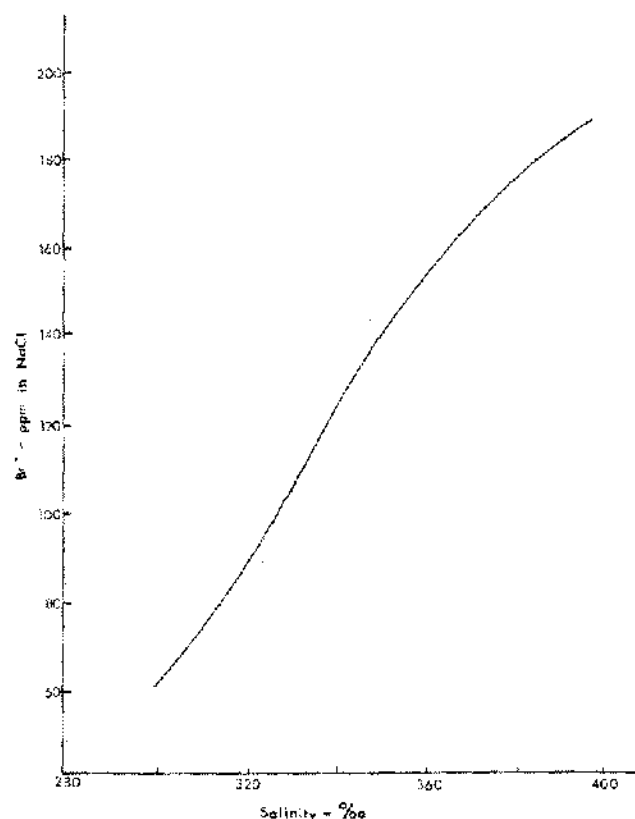


Figure 3. Normal increase of bromide in solid solution in halite as a function of salinity (modified after Holser, 1963).

Holser (1966) points out that a discrepancy exists between the 75 ppm bromide predicted by the distribution coefficient and the 38 ppm bromide recorded in halite precipitated from Mediterranean Sea water by Bloch and Scherb (1953). Similarly low concentrations (50 ppm) have been recorded by Holser in Laguna de Liebre, Baja California, and by Wardlaw and Schwerdtner (1966) in Canada.

Since Mediterranean Sea water has the same bromide to chloride ratio as other modern sea water, the 38 ppm value appears significant. If truly representative, the distribution coefficient should be reevaluated. If, on the other hand, 75 ppm bromide is the correct value, then it is possible that conditions and rates of crystallization affect the amount of bromide which precipitates with halite. Since a critical evaluation is not possible, the discussion of results will be based on the 75 ppm predicted by the distribution coefficient. Whichever value is correct, it does not alter the process of progressive enrichment of bromide in the solid phase.

## ANALYTICAL RESULTS

### *General bromide values.*

Analyses of the collected samples indicates that the bromide concentrations in the first halite above a dolomite-anhydrite lamination are anomalous as they differ from the predicted concentration of 75 ppm bromide by weight (Fig. 4). Samples collected at the International Salt mine and the Canadian Rock Salt mine yielded bromide values ranging from 38 ppm to 59 ppm and 35 ppm to 55 ppm respectively.

### *Bromide profiles.*

Not only does the initial bromide content fall short of 75 ppm, but the bromide trend does not exhibit a progressive increase, as would be expected under conditions of increasing salinities. In both mines, the maximum bromide value occurs well below the top of the each halite layer examined. The general trend is one of bromide concentration above a dolomite-anhydrite lamination increasing toward a maximum at an intermediate position within the salt layer followed by a decrease toward the overlying dolomite-anhydrite lamination (Fig. 4).

The detailed studies of Wardlaw and Schwerdtner (1966) and of Wardlaw and Watson (1966) of the Devonian Prairie Evaporite of Saskatchewan and Alberta also revealed low bromide values and bromide profiles comparable to those of the present investigation.

Two additional observations can be made on the basis of Figure 4:

(1) In the two vertical sections analyzed, the halite shows no evidence of any progressive enrichment or depletion of bromide.

(2) The bromide concentration in stratigraphically equivalent units (Fig. 4: Units 1, 2, 3, 4, 7, )

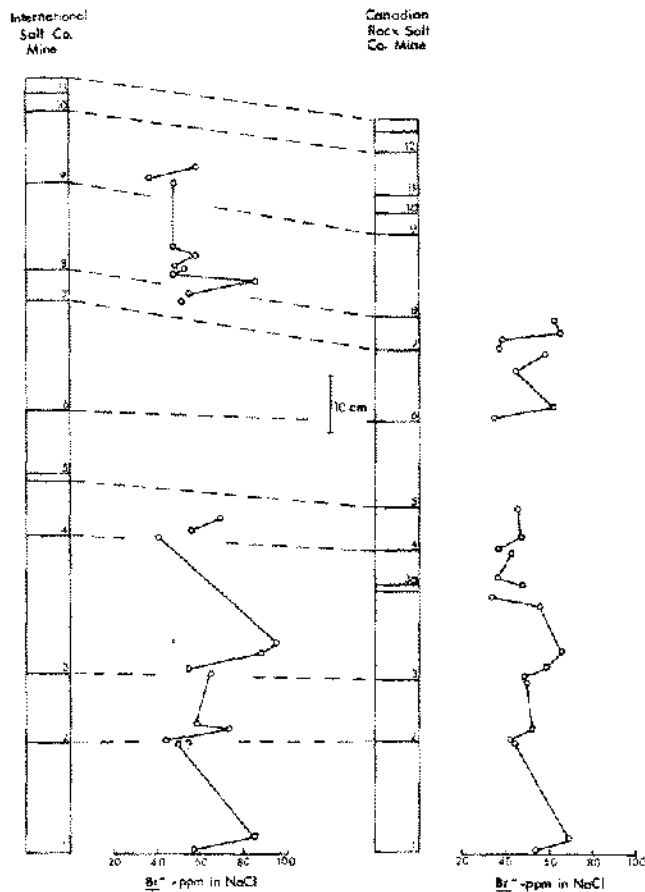


Figure 4. Detailed bromide profiles for halite layers. Horizontal lines represent dolomite-anhydrite laminations. Correlation lines have been drawn between the more obvious laminations.

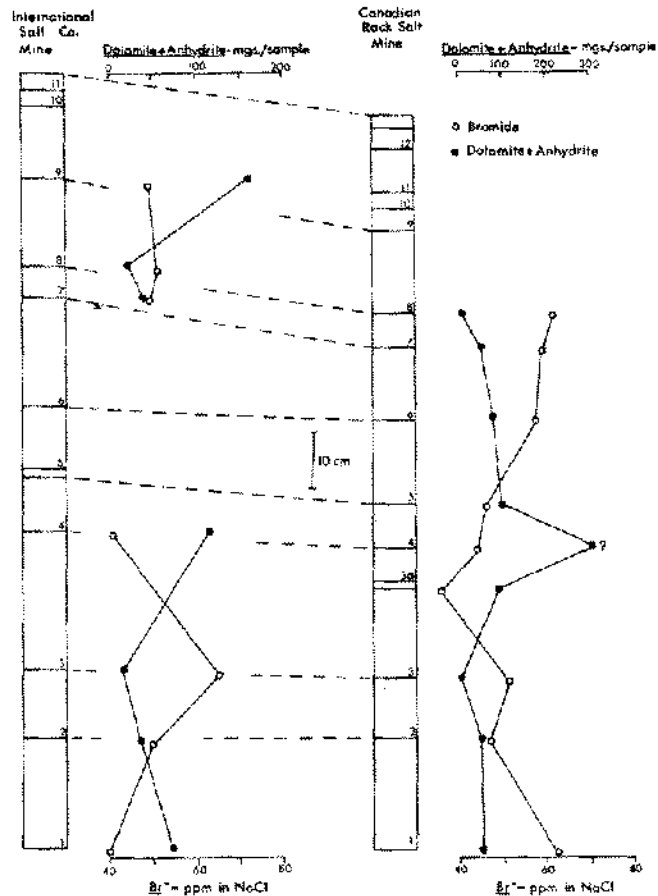


Figure 5. Relationship between the insoluble content of dark laminations and the bromide concentration of the underlying halite layers. Correlation lines have been drawn between the more obvious laminations.

is lower in the Canadian Rock Salt mine than in the International Salt mine. Since the former is closer to the basin margin (Fig. 1), the differences in concentrations agree with Holser's (1966) observation that bromide values in any halite bed decrease toward the edge of the basin.

#### *Insolubles vs. bromide.*

The relationship between the insoluble content (dolomite and anhydrite) of dark laminations and the bromide concentrations of halite directly beneath them was investigated vertically in both mines (Figs. 5, 6) and laterally in the Canadian Rock Salt mine (Fig. 7). The relationship is inverse.

### SIGNIFICANCE OF THE DATA

The low bromide values recorded possibly are attributable to a lower bromide to chloride ratio of the Late Silurian sea water than that of modern sea

water. It is also possible that the coefficient of distribution is incorrect. If, on the other hand, the bromide to chloride ratio has always been essentially the same as that of present day sea water, the existence of a special mechanism responsible for bromide deficiency is implied.

The considerable departure of the recorded bromide values from those predicted by the distribution coefficient certainly appears to support the first possibility. However, since the coefficient is less than one, and constant for halite, the process of bromide enrichment in the solid phase remains unaltered. A lower bromide to chloride ratio in the parent brine would simply shift all the values down. It could not, however, result in an inverse bromide trend.

If the distribution coefficient is, indeed, incorrect, this would either raise or lower the bromide values in halite. Bloch and Scherb's data suggest

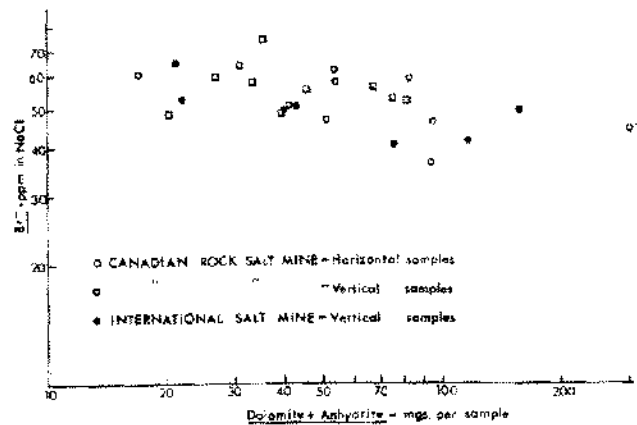


Figure 6. Relationship between the insoluble content of dark laminations and the bromide concentration of the underlying halite layers.

the latter. In this case, the effect would be the same as a lower bromide to chloride ratio in the brine. Although this alternative does account for the low bromide values, it fails to explain the trend reversal.

The inverse bromide trend present in the upper parts of the halite laminations suggests the following possibilities:

- (1) Cyclical changes in the bromide to chloride ratio of the inflowing sea water.
- (2) The existence of a semi-restricted basin into which normal sea water was introduced at seasonally varying rates.
- (3) The existence of a semi-restricted basin into which salt-saturated meteoric water was introduced at seasonally changing rates.

If changes in bromide trends are attributable to the first possibility, the composition of sea water must have fluctuated during the precipitation of each salt layer. Considering the infinite volume of sea water involved and its self-buffering capacity, a change in the bromide to chloride ratio within the time represented by a salt layer seems unlikely. Even more fortuitous would be the repetition of this alternation from layer to layer. A more reasonable postulation in accord with Rubey (1953) is that the composition of sea water has remained constant throughout geologic time.

A model of a semi-restricted basin receiving seasonally variable amounts of normal sea water has been proposed for the Devonian Prairie Evaporite of Canada by Wardlaw and Schwerdtner (1966). The rise in bromide above a dolomite-anhydrite lamination is explained by a period of high evapo-

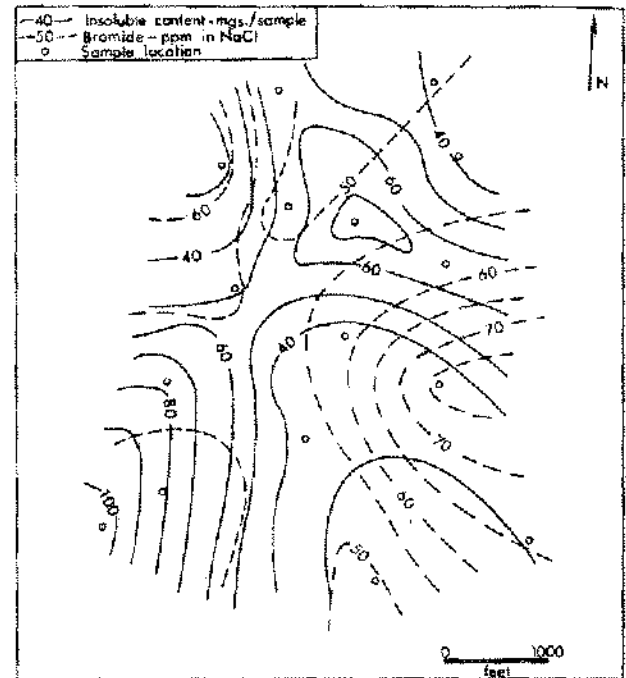


Figure 7. Canadian Rock Salt Company mine—Lateral variation of the insoluble content of dolomite-anhydrite lamination no. 2 (see Fig. 2) and of the bromide concentration of the underlying halite layer.

ration during which normal sea water is preconcentrated in a forebasin before entering the evaporitic basin. The inverse bromide trend is explained by a decrease in the rate of evaporation resulting in a greater inflow of normal sea water. However, in the Michigan basin, the low bromide values, the decrease of bromide concentration and the increase of the amount of insolubles toward the shore of the basin, are difficult to reconcile with such a mechanism.

On the other hand, low bromide concentrations may be obtained if salt-saturated meteoric water is introduced into the basin at seasonally changing rates. This mechanism appears to be the only satisfactory one since it allows for an absence of bromide in the extreme case and at the same time provides an explanation for the inverse bromide trend. It is proposed therefore to examine the last model in greater detail.

## MECHANISM OF HALITE DEPOSITION

### *Dry phase.*

Data obtained from the lower portions of the halite layers are compatible with the established observation that as halite precipitates its bromide

content increases. Therefore, the initial positive bromide trend of each halite lamination may be attributed to a progressive increase in salinity brought about by high rates of evaporation during a period of dryness.

If applied to the Michigan basin, Scruton's model of flow patterns over a sill offers a more adequate explanation for the observed rise in bromide than preconcentration in a forebasin as proposed by Wardlaw and Schwerdtner (1966). A high rate of evaporation over the basin produces higher salinities away from the source of normal sea water. This creates a slope in the surface waters which causes a basinward flow of normal sea water due to hydrostatic pressure. This pressure difference is balanced by a flow of concentrated brine toward the sill. Mixing of outflowing basinal brine and of inflowing sea water over a sill modifies the character of each of these waters and leads to an increase in salinity of the inflowing sea water. The increase in salinity will promote higher rates of halite precipitation and result in a bromide increase more rapid than that derived from normal sea water precipitation. As this mechanism must lead to values higher than 75 ppm, the low bromide concentrations recorded remain to be explained.

Because higher salinities develop earlier at the distal end of the basin than near the inlet region, halite precipitation will begin there. Figure 8 illustrates the behavior of the brine near the margin of the basin during the dry phase. When the brine level decreases to  $T_1$ , an amount of halite  $H_1$  is precipitated. The coefficient of distribution predicts that halite  $H_1$  should contain 75 ppm bromide by weight. As evaporation continues, the brine level drops to  $T_2$  leading to the deposition of halite layer  $H_2$ . Since this halite is precipitated from a more concentrated brine, it follows that its bromide content should be greater than 75 ppm. As the brine level continues to decrease, halite with

a progressively higher bromide content will be deposited. With each lowering of the brine level, halite precipitated during the previous interval of evaporation becomes exposed. The areal extent of halite exposed on the shores is determined by the length of the dry season and by the rates of evaporation.

#### *Wet phase.*

During the wet phase, solution by meteoric water of halite exposed during the previous interval or present in shallow near-shore waters will create a brine markedly deficient in bromide. The bromide to chloride ratio of such a meteoric brine is approximately 1:5000 as compared to 1:280 for normal sea water (Holser, 1966). When washed back into the basin, mixing of the meteoric brine with the basinal brine must result in a net lowering of the overall bromide to chloride ratio. If we assume that meteoric water dissolves halite to the point of saturation, halite precipitation is not interrupted although rates of precipitation due to lower evaporation are likely to be reduced.

The distribution coefficient requires that halite precipitated from such a mixed brine must have a low bromide content. As more halite is dissolved and more meteoric brine is introduced into the basin, subsequent halite precipitation must result in an inverse bromide trend as recorded in the upper part of the salt layers. As the supply of halite is not inexhaustible, this process may eventually lead to undersaturation of the meteoric brine. Halite precipitation may be interrupted and some solution of halite may take place in the basin. When sufficient dilution has occurred, normal sea water containing low solubility carbonate and sulfate salts may be introduced into the area.

The bromide trend recorded in the upper part of halite layers can therefore be attributed to an interaction between the basinal and meteoric brines. A

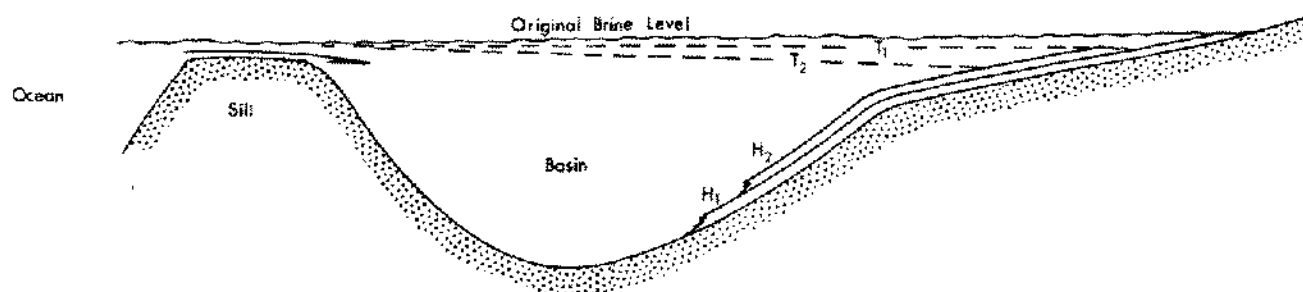


Figure 8. Idealized marginal conditions of deposition associated with the progressive lowering of the brine level during the dry "season."

negative bromide trend reflects a supply of meteoric brine sufficient to create a bromide deficiency. A positive trend (units 3A, 6, 7) represents a very low supply of meteoric brine. An invariable trend (unit 8) suggests a balance between the two brines.

If a brine created by meteoric water mixes with a basinal brine, the degree of dilution and, therefore, the degree of bromide deficiency should be greater in the near-shore halite than in the halite deposited elsewhere in the basin. The bromide data recorded in the two mines investigated indicates such a relationship. Bromide values in stratigraphically equivalent laminations are consistently lower in the Canadian Rock Salt mine than in the International Salt mine (Fig. 4). Paleogeographic studies (Alling and Briggs, 1961) indicate that the Canadian Rock Salt mine is, indeed, the more marginal of the two.

### OCCURRENCE OF DOLOMITE AND ANHYDRITE

If solution was a major mechanism in the formation of the near-shore evaporites of the Michigan basin, it must also permit the formation of the low solubility dolomite and anhydrite salts which are cyclicly interbedded with halite.

As the bromide content of halite directly underlying the dolomite-anhydrite laminations reflects the last stage of salinity of the brine during the wet phase, one would reasonably assume that this value represents a salinity of 353 parts per thousand, the transition salinity from anhydrite to halite. However, since the recorded bromide values depart so much from those predicted by the distribution coefficient, they are inaccurate indicators of salinity. The bromide values, however, may be useful in detecting the relative dilution of the basinal brine. The rate of bromide decrease in the upper part of the halite layers may be used as a qualitative indication of the degree of dilution. Where the bromide value near the top of a halite layer is relatively low, dilution was probably high, suggesting that normal sea water had intermixed with basin brine. This would also explain increased quantities of dolomite and anhydrite in the low bromide halite. Conversely, where the bromide value is high, less dilution is implied, resulting in the precipitation of smaller quantities of dolomite and anhydrite. Such an inverse relationship between the insoluble content (dolomite and anhydrite) of dark laminations and the bromide concentration of the underlying halite is, indeed, present (Figs. 5, 6). Furthermore, data compiled

from a selected dolomite-anhydrite lamination readily identifiable in the Canadian Rock Salt mine and from the halite present directly beneath the lamination indicates a generally inverse correlation (Fig. 7) throughout the area of exposure.

This appears to fit the environmental conditions which may have existed in the basin. It would be unreasonable to expect a uniform density throughout the brine body. Differences in salinity could develop as a result of differential dilution by meteoric water. This would lead to a dynamic differentiation brought about by differences in densities. Therefore, there would be a greater tendency for the more dilute inflowing sea water to move into areas of lower densities resulting in the accumulation of greater quantities of carbonates and sulfates. However, the increase in dolomite and anhydrite towards the margin of the basin (Dellwig, 1955) requires an explanation.

Paleogeographic studies by Briggs (1958) and by Alling and Briggs (1961) suggest that sea water was fed through two major inlets into the Michigan basin: one on the south margin and the other on the northeast margin of the basin.

In such a morphological setting the area investigated is situated at a considerable distance from these inlets. Normal sea water fed through these inlets probably would have lost the carbonate and the sulfate fraction by precipitation before the area under investigation was reached. Although inflowing sea water, being of lower density, could flow over the denser basinal brine, convectional mixing in the basin and over the sill would certainly lead to the precipitation of all the carbonates and most of the sulfates.

An alternate source for the low solubility salts has been recently suggested by Briggs (1967) through a model study of the Michigan basin using computer methods. Results of his research indicate that the two major inlets were supplemented by numerous inlets present in the reef girdle which restricted the basin. Such inlets would certainly be plausible areas for carbonate and sulfate deposition.

The morphological relationship between the basin, reef girdle, and the open sea may well be paralleled in the Great Bahama Bank off the coast of Florida. Ocean water flowing over the Great Bank becomes progressively more saline. In such a morphological setting, evaporation rates over the reef fringe surrounding the Michigan basin may have been high enough to remove the carbonate and sulfate fraction from the sea water. The effectiveness of removal would be determined by the



intensity of evaporation, the depth of water over the reef and the width of the reef complex. Carbonates and sulfates could be introduced into the basin when evaporation rates were lower and sufficient dilution took place.

### DEFINITION OF THE EVAPORITIC CYCLE

The cyclical association of dolomite, anhydrite, and halite in evaporitic sequences has been often interpreted to represent seasonal deposition comparable to varves. Whereas a varve represents a finite time interval (a year), single laminations in evaporite deposits have remained generally unassigned to specific units of time. Richter-Bernburg (1950) has suggested, however, that a sequence composed of dolomite, anhydrite, and halite represents annual deposition and time estimates of evaporitic deposition have been based upon this assumption.

Regardless of the specific amount of time indicated by such a sequence, a dolomite-anhydrite and halite layered-pair is generally believed to indicate a duality of seasons. Since dolomite and anhydrite are low solubility salts, they have been associated with a wet season when sufficient dilution permitted their introduction into the basin. The following dry season led to the deposition of the high solubility salt—halite.

The bromide profiles and petrographic data suggest that the evaporitic cycle should be defined in the following manner (Fig. 9):

(1) Dry season: dolomite-anhydrite lamination and halite unit up to the bromide inflexion point.

(2) Wet season: halite unit from the inflexion point to the overlying dolomite-anhydrite lamination.

At the peak of the wet season, as the supply of exposed halite is exhausted, introduction of

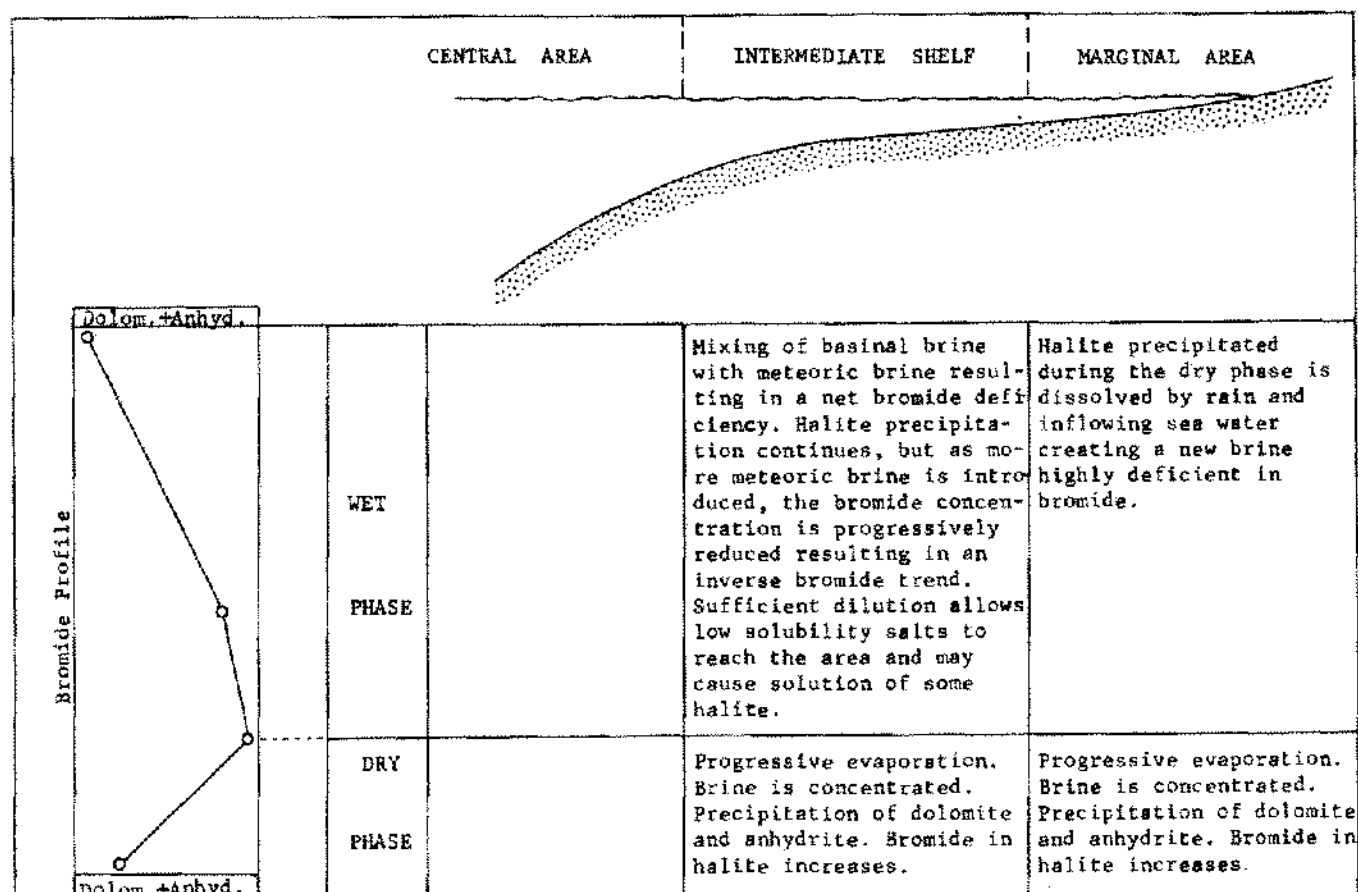


Figure 9. Environments of halite deposition in peripheral areas of the Michigan basin.

meteoric water may have caused sufficient dilution of the basinal brine to redissolve the upper portion of the halite layer. Hopper crystals truncated by dolomite-anhydrite laminae (Dellwig, 1955) and chevron grains truncated by clay layers (Wardlaw and Schwerdtner, 1966) suggest a diastem (?) between some halite layers and the respective overlying dolomite-anhydrite laminations.

The precipitation of the carbonate and sulfate fractions introduced at the end of the wet season, marks the beginning of a dry season. Halite precipitation follows and is characterized by a progressive bromide enrichment.

### SUMMARY AND CONCLUSIONS

Analytical data recorded in portions of the Upper Silurian Salina F salt indicate:

(1) The bromide content of halite overlying the dolomite-anhydrite laminations falls below the 75 ppm bromide predicted by the distribution coefficient.

(2) The maximum bromide value does not occur at the top of the halite layers as expected under conditions of progressive concentration, but at an intermediate position within the layer. Above this maximum the bromide values decrease progressively.

(3) The bromide values nearer to the margins of the basin are lower in any given halite layer.

(4) The dolomite-anhydrite content of dark laminations is inversely proportional to the bromide concentration of the halite underlying them.

The bromide trends suggest that the "seasons" were present during the deposition of the evaporitic cycles. The dry "season" characterized by high rates of evaporation led to the deposition of the dolomite-anhydrite lamination and of the lower portion of the halite layer where the bromide trend is positive. The wet "season" resulted in dilution of the brine and led to the deposition of the upper part of the halite layer. The mechanism causing dilution appears to have been meteoric water which dissolved halite exposed during the dry "season" and recycled it into the basin.

Dolomite and anhydrite and the associated inverse bromide trend suggest the presence, as postulated by Briggs (1967), of additional peripheral inlets through which normal sea water could be introduced in quantities proportional to the stage of dilution of the basinal brine.

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