

Bromide Geochemistry of Salt Rocks

William T. Holser
Chevron Research Company
La Habra, California

ABSTRACT

Starting with the experimental distribution coefficient and various geological models, theoretical profiles of bromide content against salt thickness are derived. For a constant regime of inflow, evaporation and reflux all profiles are monotonic logarithmic functions, without extrema or inflections.

A Recent salt pan in Baja California has bromide between the 75 ppm predicted by the distribution coefficient of Braitsch and Herrmann and the 38 ppm in the evaporation experiments of Bloch and Scherb. The value to be expected in basal salt is still indeterminate within this range and may be a function of crystallization conditions. Most basal salts of earlier geological ages fall in this range and show no trend with geological time that would imply a change in the Cl/Br of the oceans.

Published profiles of the Stassfurt salt are regular, with two inflection points interpreted as simple changes of evaporation-inflow regime. Most bromide profiles are much more irregular. The most common type (Wellington, Castile, Salina, Prairie) have irregular profiles with most values in the range 30-80 ppm and occasional spikes up to 150 ppm. In the Salado salt the halite is mostly below 70 ppm even in the potash zone, and sylvite is also low -- almost in paragenetic ratio. Apparently most evaporite basins do not represent a simple inflow-evaporation-reflux cell, but have suffered multiple incursions of sea water with recycling (surface or alteration) of earlier salts and nearly complete loss of bitterns. Meteoric water may also be important in the recycling, as indicated by the extremely low bromide content throughout the Lower Elk Point and at the top of the Wellington.

The theory of profiles permits explicit calculation of brine depth from the basal halite/initial slope ratio, independent of the evaporation-flow regime. To the extent that the lowermost profiles may be primary, this relation suggests initial brine depths in the range 20-200 meters for various evaporite basins, but these depths are somewhat less than the final salt thicknesses.

INTRODUCTION

This paper reviews a several years' reconnaissance, to find out what sort of geological information could be derived from the distribution of a solid-solution element in chemical precipitates. When this work was begun in 1959, there was already available more information about the distribution of bromide in salt rocks than about any other evaporite mineral. Since Boeckle (1908), German geologists had intensively studied the distribution of bromide, both experimentally and in the Zechstein rocks. During the past 20 years, Soviet geologists, particularly M. G. Valiashko (1958), applied bromide geochemistry in their own area, particularly in prospecting for potash. I have tried to develop, from first principles, a general model for the distribution of trace elements in precipitates, and to use this model to interpret analyses of bromide in salt rocks throughout North America. The emphasis in this study has been on the distribution of this single

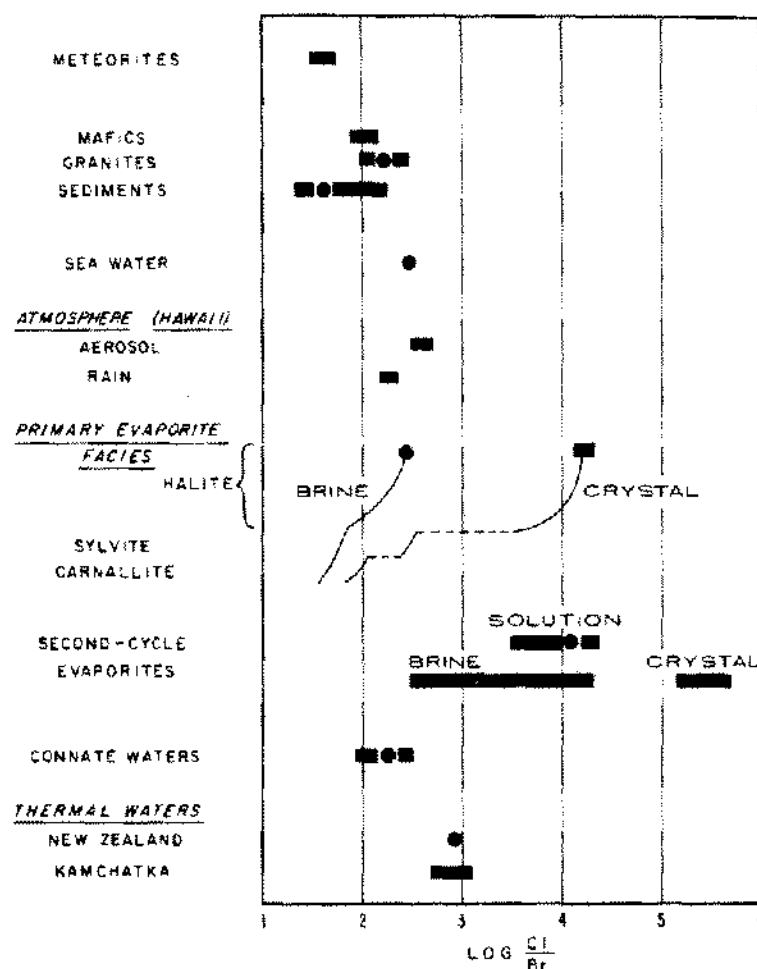


Figure 1. General geochemistry of bromine.

concentrations, as enumerated in Fig. 2. It is well known that in a closed system this relationship leads to a logarithmic decrement or increase of a trace element, depending upon the value of K :

$$\ln \left[\frac{r_c}{r_{co}} \right] = (K - 1) \ln \left[\frac{M_o - M_c}{M_o} \right] \quad (2)$$

where m_o and m_c are the total mass of crystallizing component and the mass crystallized at any given time respectively.

While this equation is perhaps applicable to crystallization in a beaker, or even to some magmatic minerals, a model that will be of general application to evaporite situations must account for the inflow of sea water into a basin, and for the reflux of concentrated brine back to the sea. For this purpose, I assume in Fig. 3 a weighted average of the inflow and reflux, and characterize this as a net flow dW_f , with a concentration of main component A_f and trace element ratio r_f . The relative importance of all factors in the regime, including net flow, dW_f , water evaporation dW_e , and saturation concentration A_1 , is characterized in a way as to best simplify the equations that follow, as the flow-crystallization factor,

$$g = \frac{\text{change of amount of main component A in reservoir}}{\text{change of amount of main component A in crystals}} \\ = \frac{A_1 (dW_e + dW_f)}{A_1 (dW_e + dW_f) - A_f dW_f} \quad (3)$$

element in one mineral -- halite, as a model for application to other mineral-element pairs. This paper reviews the results on mainly marine evaporites; other work on nonmarine evaporites of the Western Interior United States will be published elsewhere.

This study was greatly aided by numerous companies and individuals who furnished samples or provided access to them: J. E. Adams, Standard Oil Co. of Texas, Midland; L. I. Briggs, University of Michigan; L. F. Dellwig, University of Kansas; T. L. Gambill, United States Borax and Chemical Corp., Carlsbad, New Mexico; W. B. Heroy, Geotechnical Corp., Garland, Texas; R. W. Hougland, International Mining and Chemical Co., Carlsbad, New Mexico; S. B. Horrell, Carey Salt Co., Hutchinson, Kansas; A. A. Ivanov, VSEGEI, Leningrad; J. R. Kramer, University of Western Ontario, London, Ont.; F. W. Lines, California Standard Co., Calgary; W. R. Muehlberger, University of Texas; F. L. Parker, Oak Ridge National Laboratory, Oak Ridge, Tenn.; the Alberta Oil and Gas Conservation Board; and Sifto Mines, Goderich, Ontario. I am particularly indebted to various individuals for stimulating discussion of the problems uncovered in these samples: Otto Braitsch, C. L. Jones, Robert Kühn, R. W. Rex, W. F. Schwerdtmer, and N. C. Wardlaw.

I begin with a review of the general geochemistry of bromide, give the results of a general model developed for trace element precipitation, present bromide profiles measured in a wide variety of evaporite basins, and, finally, review some of the general geological and geochemical problems in which bromide geochemistry has been informative. In describing the evaporite profiles, I will make only summary reference to the geological and petrographical relations that have been considered in their evaluation.

BROMIDE GEOCHEMISTRY

Bromide is a unique element because it is not very reactive, and ordinarily follows chloride through the geochemical cycle. Practically the only situation in which there is fractionation of the chloride/bromide ratio is in the crystallization of evaporite minerals, where generally chloride is removed in the solid phase in preference to bromide. Figure 1 is an over-all view of the distribution of bromide in all kinds of rocks. There you see four general groups in terms of the ratio Cl/Br: most igneous rocks, sediments, and meteorites, with a Cl/Br of about 100, brines, atmospheric halides, and connate waters, Cl/Br = 200-400, thermal waters, Cl/Br = about 900, and salt rocks, Cl/Br > 5,000. From this simple diagram, one can draw several interesting conclusions: (1) neither mafic igneous rocks nor meteorites can represent primordial halides in the earth (the meteorite analyses should be re-examined); (2) the intermediate position of thermal waters between the two main reservoirs of halides in the crust, sea water and salt rock, suggest that volcanism represents average halides, either because they represent juvenile halides degassed from the crust, or because they represent an average of halides regenerated from both connate waters and salt rocks during deep crustal metamorphism; (3) if thermal waters are representative of average halide in the crust, then the mass balance requires that there be about twice as much chloride present in salt rocks as there is in the present sea (this is not unreasonable, inasmuch as the volume of evaporites in the Gulf Coast Jurassic alone represents five per cent of the chloride in sea water); (4) second cycle (descendent) waters formed by the solution of salt rock are unique in their very high Cl/Br ration, and second cycle salt rocks deposited from such waters have an even higher ratio; (5) most connate waters are neither second-cycle solution waters nor are they bitterns residual to the crystallization of salt rock.

TRACE ELEMENT PRECIPITATION

Fractionation in simple evaporation. Now let's consider how a trace element will distribute in a series of solid solutions crystallized from a brine. A distribution coefficient

$$K = \frac{r_c}{r_1} = \frac{B_c/A_c}{B_1/A_1} \quad (1)$$

is strictly defined as a thermodynamic constant (at a given temperature) in terms of activities of the components, but for the present we will consider these ratios equivalent to those involved in

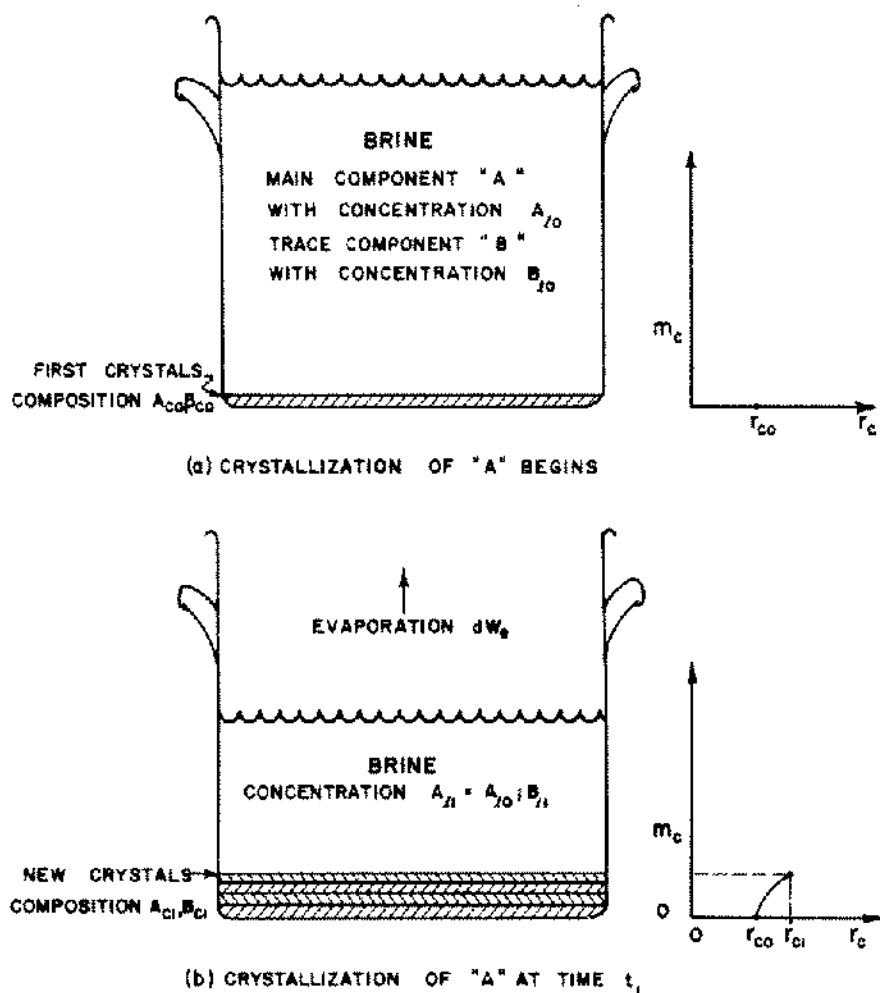


Figure 2. A simple evaporation model for the crystallization of a solid solution of a trace component B in A, showing the development of a trace element profile.

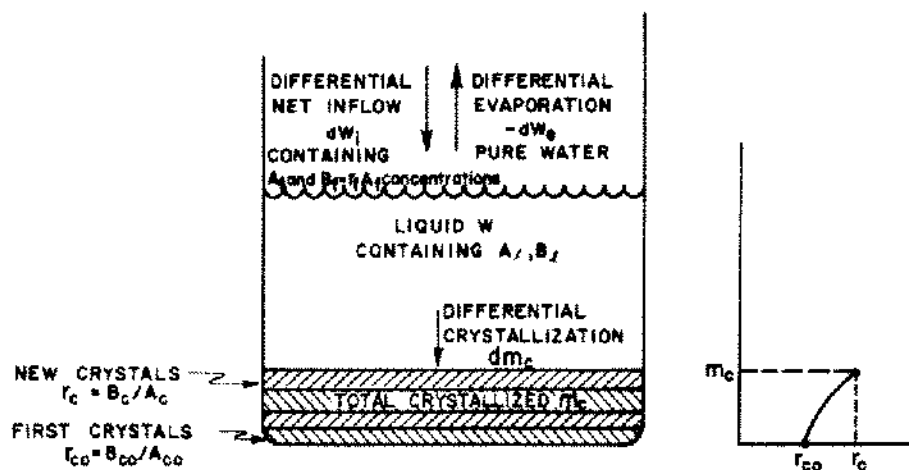


Figure 3. Model for a general open system analogous to Figure 2. Note that signs for flows dW_e and dW_i are both positive for increase in basin volume, that is, dW_e is always negative.

Specifically, $g = 0$ for simple evaporation, $1 > g > 0$ for basins in which evaporation exceeds net inflow, $g = 1$ for the important geological case of constant brine volume in the basin, and $g > 1$ if net inflow exceeds evaporation. The consequent general relation between trace element content and the mass of salt crystallized is

$$\ln \left[\frac{r_c (K - g) + (g - 1) K r_f}{r_{co} (K - g) + (g - 1) K r_f} \right] = \frac{K - g}{g} \ln \left[\frac{m_o - g m_c}{m_o} \right] \quad (4)$$

The full development of this mathematical model will be published elsewhere; I here give only the results. This rather formidable general equation reduces, for the case of straight evaporation ($g = 0$), to equation (2). The constant volume case ($g = 1$) is a singular point at which the particular solution is

$$\ln \frac{r_c - r_f}{r_{co} - r_f} = K \frac{m_c}{m_o} \quad (5)$$

Figure 4 sketches the shapes of trace element profiles for various K 's at a particular g , while Fig. 5 shows curves for various values of g at constant K .

An important generalization can be derived from this general model of trace element precipitation. If the regime (g) of net inflow and evaporation remains constant during the deposition of any particular sequence of rocks, then the trace element profile will be a logarithmic curve with no maxima, no minima, and no inflections, that is, no changes in the signs of slope or

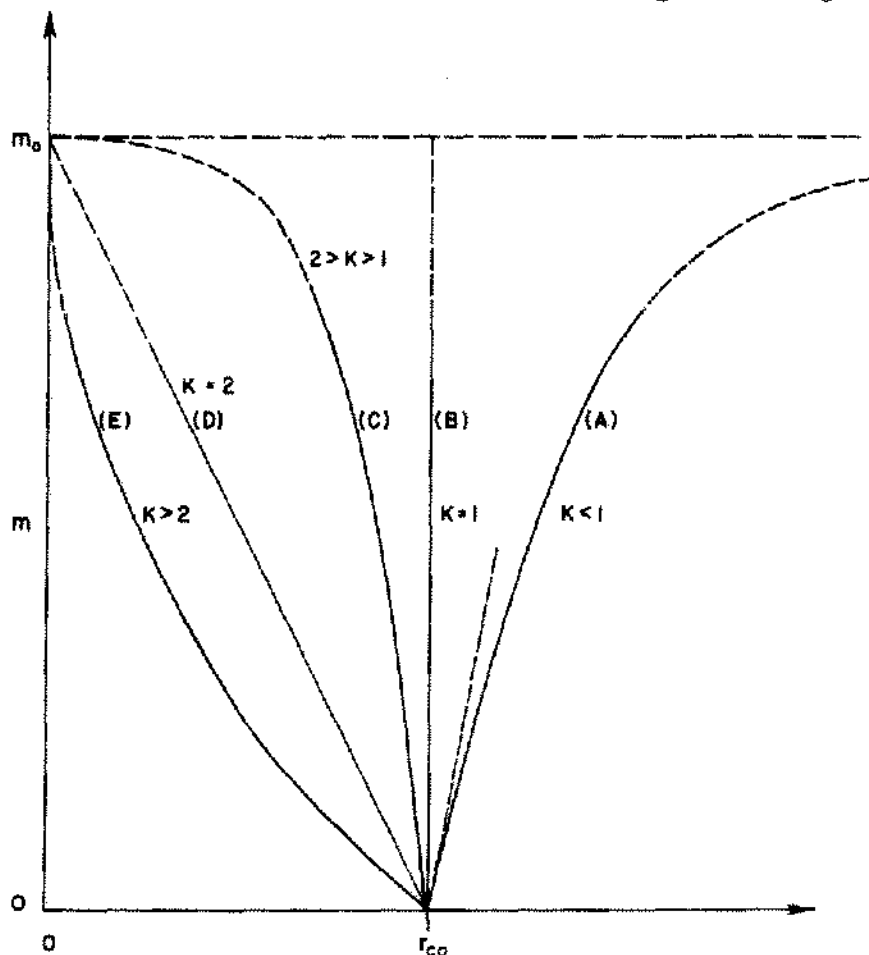


Figure 4. Effect of the distribution coefficient, K , on profiles for simple evaporation (Eq. 2). Dashed upper portions of the curves will generally not be attained due to the intervention of a new facies or change of conditions.

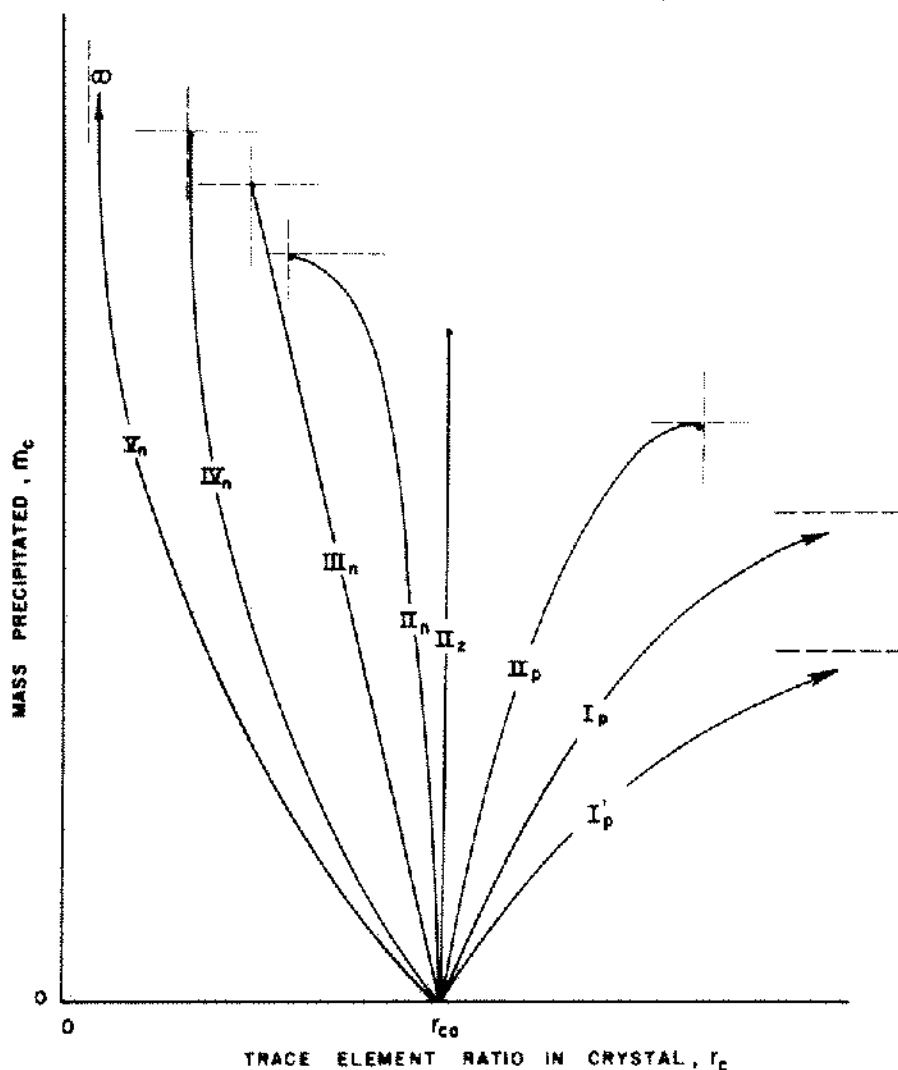


Figure 5. Profiles in an open system with low distribution coefficient, \underline{K} , and low trace element concentration of inflow r_p . The curves illustrate the effect of increasing importance of inflow vs. evaporation (the $\frac{1}{\underline{K}}$ factor) from right to left.

curvature. Conversely, extrema or inflections positively signify a change in the net inflow-evaporation regime of an evaporite basin, regardless of the geological conditions.

Bromide as a trace element. The distribution coefficient \underline{K} for bromide in halite has been extensively studied in various laboratories recently, and definitively by Braitsch and Herrmann (1963). The essential results are shown in Fig. 6, where the distribution coefficient, stated now as \underline{k} in terms of bromide weight concentrations, varies from 0.16 in a pure NaCl solution, decreasing to 0.14 when the magnesium concentration reaches that at the beginning of the halite facies (evaporation of normal sea water), and continuing to decrease to a value of 0.07 by the beginning of the potash-magnesia facies. At that time, other chlorides may begin to precipitate, and the situation gets more complicated.

The general model discussed above did not allow for variations in \underline{k} , but it is still applicable for short ranges of evaporation of sea water. If account is taken of the variation of \underline{k} , theoretical bromide profiles will be like those shown in Fig. 7. The first salt to be expected in an evaporite basin, as found by applying $\underline{k} = 0.14$ to the level of bromide in modern sea water at the beginning of the halite facies, gives 75 ppm Br in the halite.

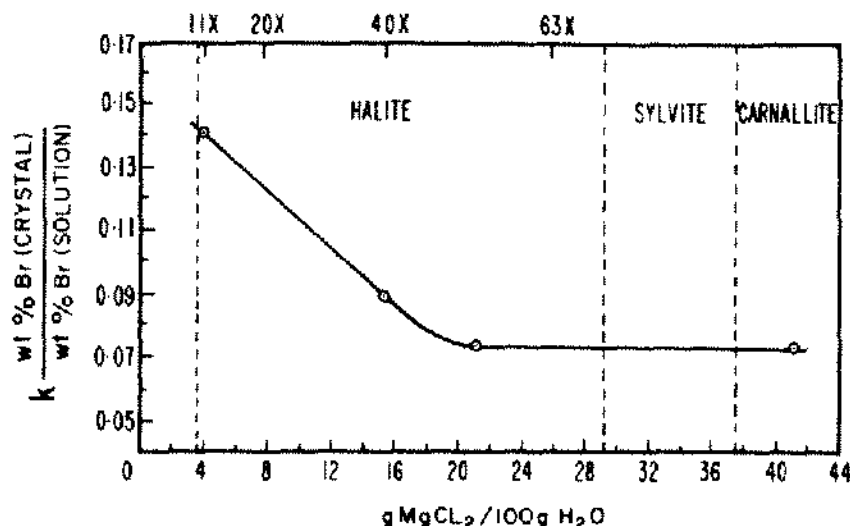


Figure 6. Distribution coefficient k , for bromide in halite, as a function of MgCl_2 concentration (lower scale) (Brairsch and Hermann, 1963, p. 371), or corresponding sea water concentration (upper scale).

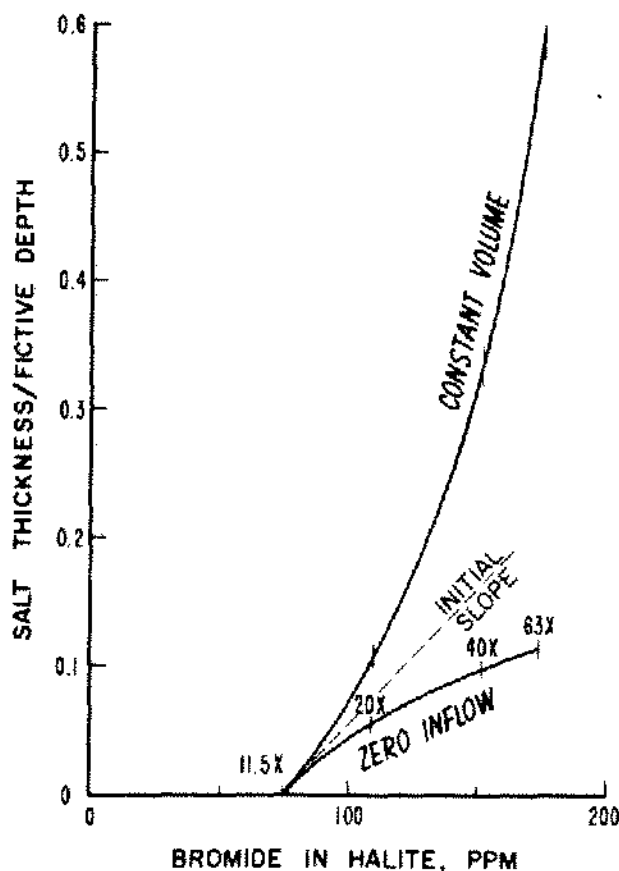


Figure 7. Theoretical bromide profiles in halite, corrected for the variation in distribution coefficient with brine concentration. The ordinate represents the fraction to which an original fictive depth of brine has been filled by solid salt at any point during the sequence of salt crystallization.

It is important to note that the bromide content in halite is constant for any net amount of evaporation accumulated by the brine remaining in the basin, regardless of the inflow-evaporation regime. One hundred and ten ppm bromide means a 20X concentration of sea water [= (total mass of water, present and evaporated)/(Mass of water present)], no matter whether there has been inflow, constant volume, or any other regime. At constant volume, as shown in Fig. 7, the thickness of salt in which this bromide profile is distributed is simply stretched out. The ordinate in Fig. 7 is the ratio of the thickness of salt deposited (at any stage) to the fictive depth of brine, here defined as the depth the brine would have had in the beginning if the basin were cylindrical.

Analysis for bromide. In order to put all analyses on a constant basis of ppm bromide in halite, in the easiest way, samples were redissolved in water, filtered, and recrystallized as NaCl, then carefully remixed before weighing for analysis.

Early in the program we settled on a colorimetric procedure for the determination of bromide that was sufficiently free of interferences and sensitive enough to determine bromide in second-cycle salts and in relatively fresh waters. The method is adapted from that published by Balatre (1936), in which bromide is oxidized with chloramine-T in the presence of phenol-red and a pH 5 buffer. Color

development is carefully timed and the complex measured at 595 nm in a Bausch & Lomb Spectronic colorimeter with a 1-inch test tube.

The analytical method was developed with Mr. Gale Baker of Chevron Research Company, and he made most of the analyses reported here. A standard sample ("analytical reagent" KCl, with a bromide content of 150 ppm) was included in each batch of analyses, and over a 5 year period, including several recalibrations, the standard deviation on this sample was $\pm 4\%$. Replication is a little better, about $\pm 3\%$.

Where contamination by potassium salts was important, two salt samples were picked visually and both analyzed for bromide and for their mineralogy by quantitative X-ray diffraction. Bromide concentrations in halite and, say, sylvite, were then calculated by the method of moments (Kühn, 1962). If contamination by potash salts was merely suspected, perhaps because of a high bromide content, the potassium content of the sample could be quickly checked on a Fisher clinical flame photometer, using the same solution that had been analyzed for bromide. Where contamination by fluid inclusions was suspected, the total water content of the sample was determined in an apparatus designed for other studies of water in salt: melting in a vacuum, freezing in a cold finger, reducing to hydrogen over hot uranium, and measurement in a calibrated-volume manometer. This result, combined with extensive experience in the chemical analysis of brine inclusions (Holser, 1963), served as criteria for confidence in the bromide analysis of halite.

Colored soluble material interferes with the analysis, but it is usually either organic material or iron in solution. Either one is removed by roasting the recrystallized sample at 500°C in air, redissolving, and filtering. Standard addition tests indicate that this treatment does not lose any bromide.

BROMIDE DISTRIBUTION IN SALT ROCKS

Recent salt. Halite and gypsum are now being deposited on extensive tidal flats at the upper end of Laguna Ojo de Liebre, Baja California (Phleger and Ewing, 1962; Holser, 1962). They are underlain by up to 2 meters of porous bedded evaporites, interbedded with sands, and permeated by bitterns whose stage of evaporation increases with distance from the lagoon. Frequent tidal- and wind-driven inflows continually evaporate and begin to crystallize both salt and gypsum about 2 km from the beach, both on the surface of the brine and also on the bottom beneath the few centimeters of brine. Halite from such a locality has about 50 ppm Br. Comparable data from other Recent salt deposits do not seem to be published. This level is considerably below the 75 ppm calculated from a distribution coefficient carefully measured in the laboratory on synthetic solutions, as described above. However, experiments with the direct evaporation of Mediterranean water (with the same Cl/Br as modern ocean water) gave a first halite of only 38 ppm (Bloch and Scherb, 1953, p. 156). Comparable data from other Recent salt deposits do not seem to have been published. Apparently the value for the first halite from modern sea water is still indeterminate by a factor of two, either because some important component has not been included in the laboratory determination of distribution coefficients, or, even more likely, because the value actually varies within the rate or other conditions of crystallization. Hard salt flats 4-15 km from Laguna Ojo de Liebre apparently experience inflows only during occasional storm tides. In that area, one ordinarily finds several centimeters below the surface a brine that is very highly concentrated, in some cases nearly into the potash-magnesia facies (concentration 60X sea water), and gypsum is pseudomorphically replaced by polyhalite. Halite from such localities have the highest bromide in this deposit, but this is still only about 90 ppm, about half the amount expected from equilibrium with such a brine (Fig. 7). Capillary evaporation may have been an important part of the history of this deposit, resulting in a higher stage of evaporation of the brine, with the deposition of only a small quantity of late-stage, high-bromide halite around the pores. Whether or not this is the case, the remarkable thing is that this concentrated brine has not been able to raise the bromide content of the porous salt to its equilibrium level, even after hundreds of years. The possible importance of these processes in ancient evaporites should not be overlooked. Work is continuing on a large collection of samples from surface and cores in this area.

Normally regular profiles. Bromide distribution has been studied intensively in the Permian Zechstein of Germany (Kühn, 1962; Braitsch, 1962, pp. 151-159; geology reviewed by Borchert and Muir, 1964, pp. 44-57; Richter-Bernburg, 1957). This first work on bromide was, in some

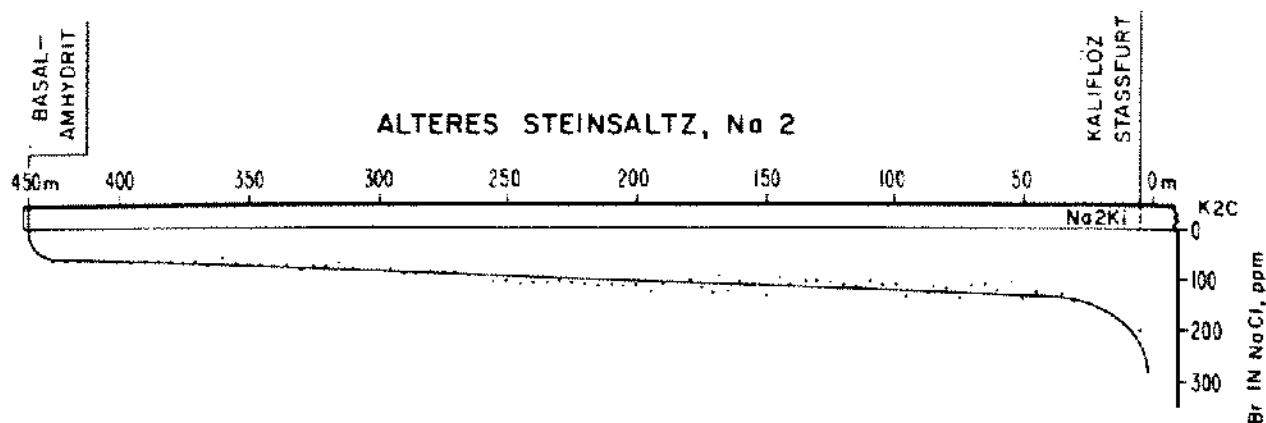


Figure 8. Typical "normally regular" bromide profile from the second salt of the Zechstein series, after Schulze (1960, p. 99). Thirty meters below the top of the profile, the slow, regular climb of bromide content curves sharply to the right, probably because of a change to simple evaporation, finally leading to the Stassfurt potash bed at the top.

respects, a lucky choice, in that at least some of the bromide profiles resemble the ideal profiles of Fig. 7. I choose just one illustration, from a large number published by Schulze (1960, p. 99). Using the principles outlined above, this profile can evidently be divided into three sections, differing from one another in their inflow-evaporation regimes. The short section at the base has the characteristics of a constant volume reservoir of rather small depth (as discussed in a later section). The sharp rightward curvature of the upper section suggests that most or all of the inflow of sea water was cut off while evaporation proceeded rapidly to finally deposit the potash bed near the top of the section. Interpretation of the long steady rise in the main center section is not so clear: possibly it represents a shift to a more efficient reflux of concentrated brine back to the sea, that is, a smaller r_f . If my interpretation of this bromide profile is correct, the implication is that final formation of the potash bed at the top of the sequence was almost an accident that depended upon cutting off access to the sea, after a moderate concentration level had been built up in the brine over hundred of years (see also d'Ans and Kühn, 1960). Indications of the high brine concentrations necessary for potash crystallization are evident only above this final break in the curve; no hint of them is given in the bromide distribution of the main part of the salt section.

Similar curves are found in many localities for this second of the four main evaporite cycles of the Zechstein series. Data, from near and in the potash facies only, in the Paradox Formation of Utah (Lindberg, 1946; Raup, 1965) and the Oligocene of the Upper Rhine valley (Barr and Kühn, 1962, p. 298) suggests that these profiles may also be fairly regular. Some other parts of the Zechstein salts also have a regular development of this sort, but much of the salt rock in the upper two evaporite cycles has very irregular profiles. These are well displayed in the literature, and my results from many basins in the United States and Canada suggest that irregular profiles are actually more usual than the ones found for the Stassfurt series.

A regular and low bromide content also prevails through the small sampling available from the Triassic-Jurassic salt of the Gulf Coast. General geology of this evaporite province has been ably surveyed by Murray (1961), pp. 202-287. The undisturbed Louann salt is seldom seen, in a few wells along the north edge of the basin, and no cores of this were available to me. However, many sections of the salt are well displayed in two extensive belts of salt domes. Kupfer (1963, 1965) and Muehlberger (1959, 1965) have graphically described the intensely folded vertical structures of these piercement domes. In several mines samples were taken using this kind of structural data so that, insofar as possible, they represented a section across the bedding. Although the sequences covered distances of hundreds of feet, it is impossible to guess the original stratigraphic thickness to which they correspond. The sequence at Grand Saline, Texas, is typical: 44, 50, 47, 46 ppm bromide probably on one fold from bottom to top; on other folds: 39, 39, 42, 38, 39 ppm. At Weeks Island, Louisiana, a sequence is 49, 51, 47, 45 ppm; single values from other domes are 34, 49, and 89 ppm bromide. The original Louann salt in this basin apparently

covered 150,000-200,000 square miles, with a thickness up to 5,000 feet (Murray, 1965), so what we have here doesn't represent much of a sample. It is sufficient, however, to suggest a low and regular bromide content for part of this formation.

Commonly irregular profiles. A profile through the Hutchinson salt member of the Wellington Formation, in the Permian of Kansas, illustrates the highly irregular form that is more common than any other in bromide profiles. The distribution of the Hutchinson salt is described by Kulstad (1959), and its textural features are interpreted in terms of environment by Dellwig (1963). The samples analyzed in this study were collected in the Carey Mine, and from a continuous core cut 8 miles south at the Naval Air Station. The petrography of this core has been described in detail recently by Jones (1965), and at the previous Symposium I discussed our chemical analyses of fluid inclusions from this locality (Holser, 1963).

Much of the Hutchinson salt is nicely interbedded with thinner layers of clay, anhydrite, or carbonate, and exposures in the Carey Mine show that many of these are continuous for at least hundreds of feet. Occasional masses of white to clear, very coarsely crystalline salt were probably, to judge by the chemistry of their included brines (Holser, 1963), formed by recrystallization in place (see below). Much of the Hutchinson salt shows the chevron textures indicative (Dellwig, 1955, 1963; Wardlaw, 1964) of primary crystallization. Samples were chosen to represent a variety of these textures and stratigraphic situations in the sequence of salts and interbeds.

The profile, as shown in Fig. 9, starts out in a normal fashion, gradually rising to almost 60 ppm at about the Carey mine level. Small-scale sampling in the mine indicates no substantial variations in a horizontal or vertical direction, within a short sequence of salt layers. Most of the rest of the core has bromide values that are all low, but very irregular in their sequence, until they decrease generally near the top of the section. The last salt at the top of the section has only 10 ppm bromide, indicating that it must have suffered recrystallization and probably redeposition -- a "second cycle" salt.

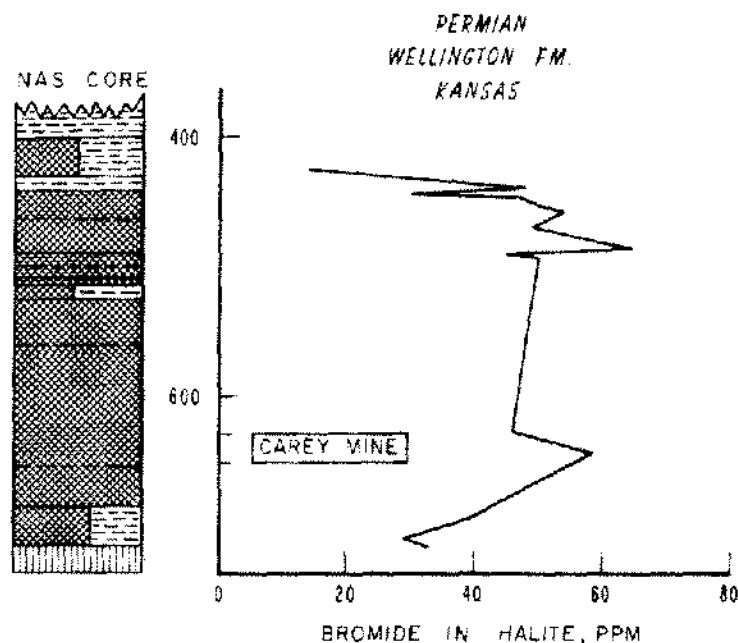


Figure 9. Bromide profile through the Hutchinson salt member of the Wellington Formation, Permian of Kansas. Crosshatching is mainly salt, vertical lines are anhydrite, and dashed lines are shale, all highly generalized. A detailed section has been published by Jones (1965, pp. 55-65).

The Salina Formation of Michigan and Ontario is another example of this sort of profile. The general distribution of salt is shown in Fig. 10, and the stratigraphic sequence of salt beds is

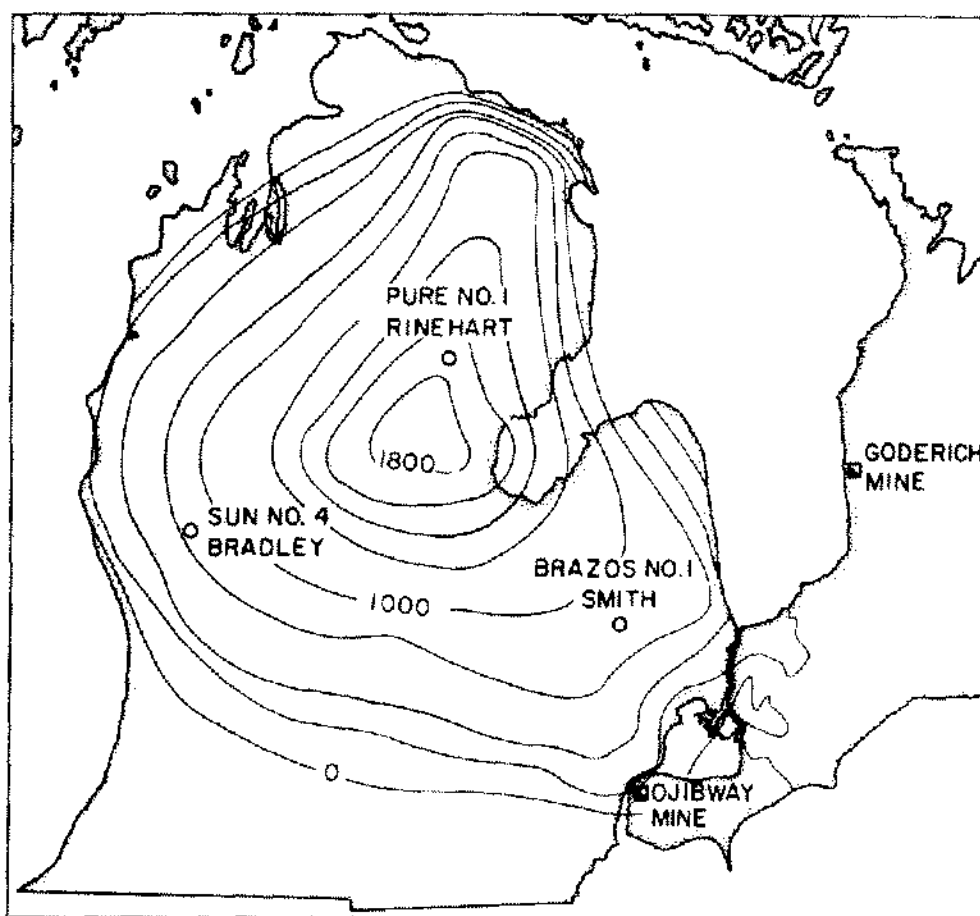
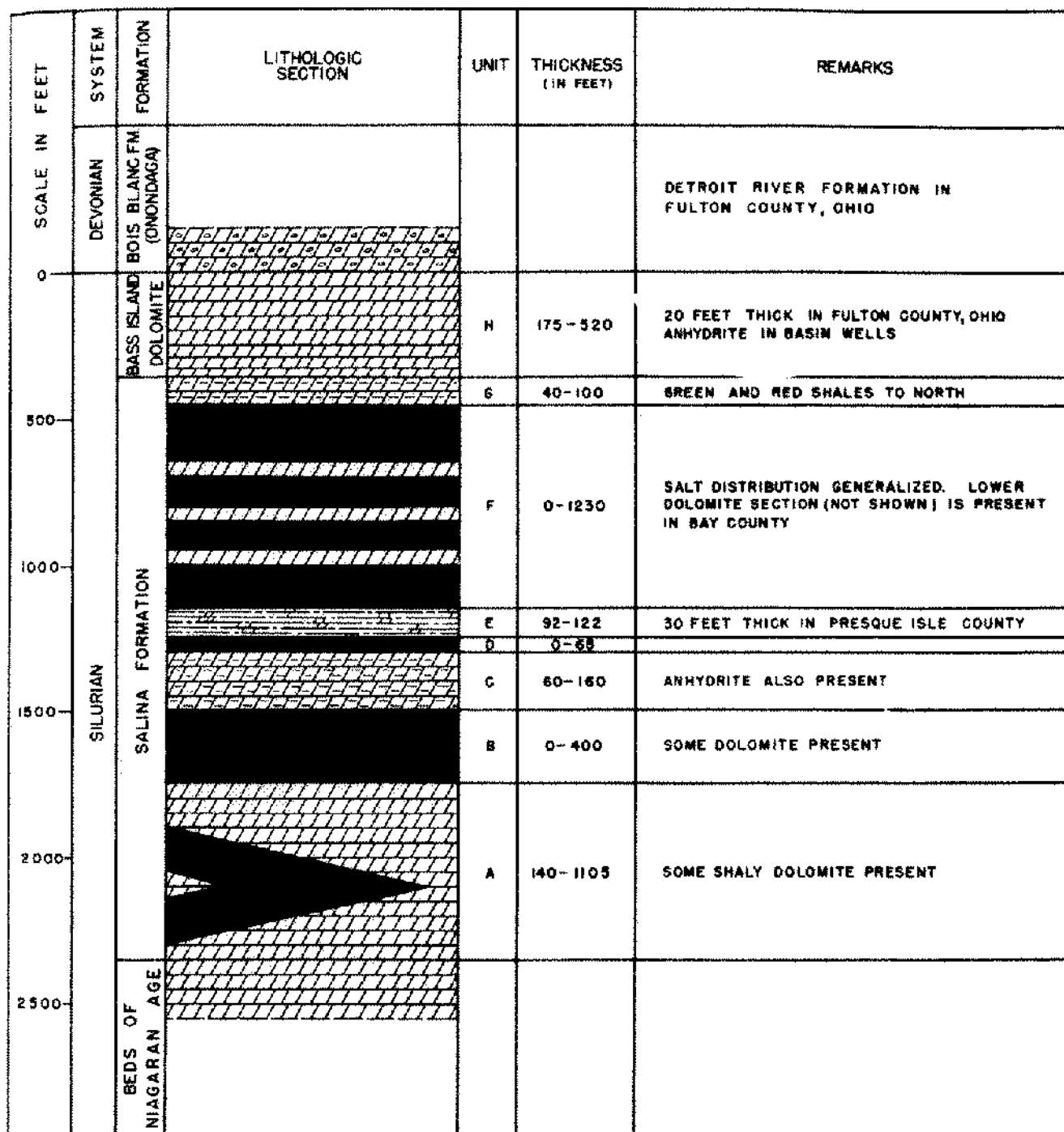


Figure 10. Aggregate thickness of all salt in the Salina Formation of Michigan and Ontario (Landes, 1945). Sample localities are indicated.

indicated in Fig. 11. The paleogeography and general evaporite conditions have been discussed fully by Ailing and Briggs (1961), and Dellwig (1955) gives considerable detailed petrography and interpretation from a core out of the Sun #4 Bradley well in the western part of the basin (Fig. 10). My samples came from two mines very close to the eastern edge of the basin (Hewitt, 1962), and two wells on the slope and in the center of the basin. Where exposed in the mines, salt in both the bottom and top beds shows excellent and continuous bedding, mainly accentuated by anhydrite concentrations. At the basin center the first, or A_1 , salt starts out with the usual 40 ppm bromide, but rises near the top of this bed to values high enough to suggest the presence of potash in this part of the basin. The rest of this profile is irregular, and, like that at Hutchinson, rather low. For the most part, salt toward the edge of the basin is even lower in any given bed. In connection with these profiles, a piece of core from Pure No. 1 Rinehardt in the Devonian Lucas salt (2500 feet above the top of the profile in Fig. 12) analyzed 69 ppm Br. Evidently this salt is marine and cannot have any substantial second cycle contribution by solution of the Salina salt, as hypothesized by Landes (1951, p. 19).

Many large salt sections apparently have a bromide content that lies generally below the minimum value of 75 ppm expected from the crystallization of sea water, and many of these profiles are very irregular in the long run, while being homogeneous on a small scale. This requires



EXPLANATION

- | | |
|---|--|
|  DOLOMITE |  DOLOMITE, CHERTY |
|  DOLOMITE, SHALY |  SHALE, DOLOMITIC |
|  SALT | |

Figure 11. Generalized stratigraphic section of the Salina Formation (Landes, 1945).

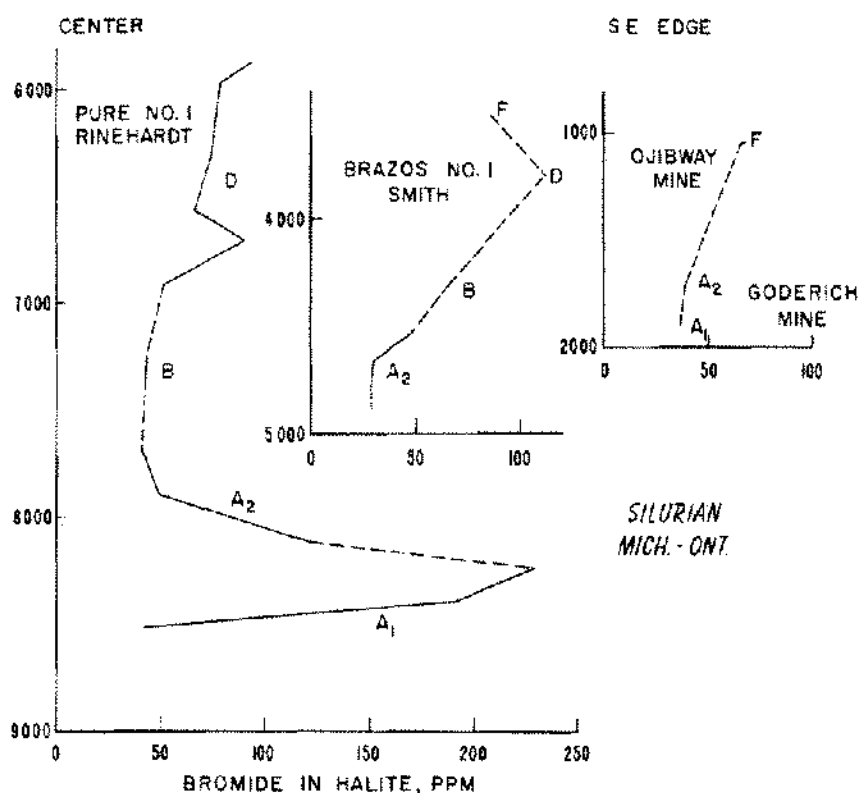


Figure 12. Bromide profiles in the Salina salt in various parts of the Michigan basin.

a modification of the conventional picture of an evaporite basin with uniform inflow and reflux. Perhaps these basins suffered multiple separate incursions of sea water, each one of which may have dissolved and redeposited some of the salt previously deposited, and each of which lost most of its bitterns and consequently its bromide by subsequent outflow or flushing. It is difficult to see how the irregularities observed could be perpetuated in the presence of the flywheel-effect of a body of brine continually overlying the depositing body of salt.

Uncommonly problematical profiles. As irregular as the above profiles may be, they do not present such startling problems as do profiles from the two largest evaporite basins in North America: the Permian Delaware basin in Texas-New Mexico, and the Devonian Alberta basin in Canada.

The geology of the Delaware basin was reviewed by Adams (1963) in the first Salt Symposium and the Carlsbad potash district was described in this symposium by Linn and Adams (also Jones, 1954, 1962). Figs. 13 and 14 show the great horizontal and vertical extent of this series. The Delaware basin itself is a deep basin in front of the high Capitan reef. This pre-existing basin was filled by evaporites of the Castile Formation, including thick sections of primary laminated anhydrite, as well as salt of undetermined texture. The overlying Salado evaporites covered the Castile and extended north and east over the back-reef and shelf areas for considerable distance, beyond the edges of Figs. 13 and 14. Anhydrite here was subordinate to salt, but the anhydrite beds are very persistent throughout the basin. In an area around Carlsbad, New Mexico, both in front of and behind the reef (Figs. 13, 14), potash mineralogy is developed through a considerable part of the Salado evaporite section. Most of the salt in the Salado Formation, both within the potash zone and outside of it, is coarsely crystalline and never shows the chevron textures that would prove primary deposition.

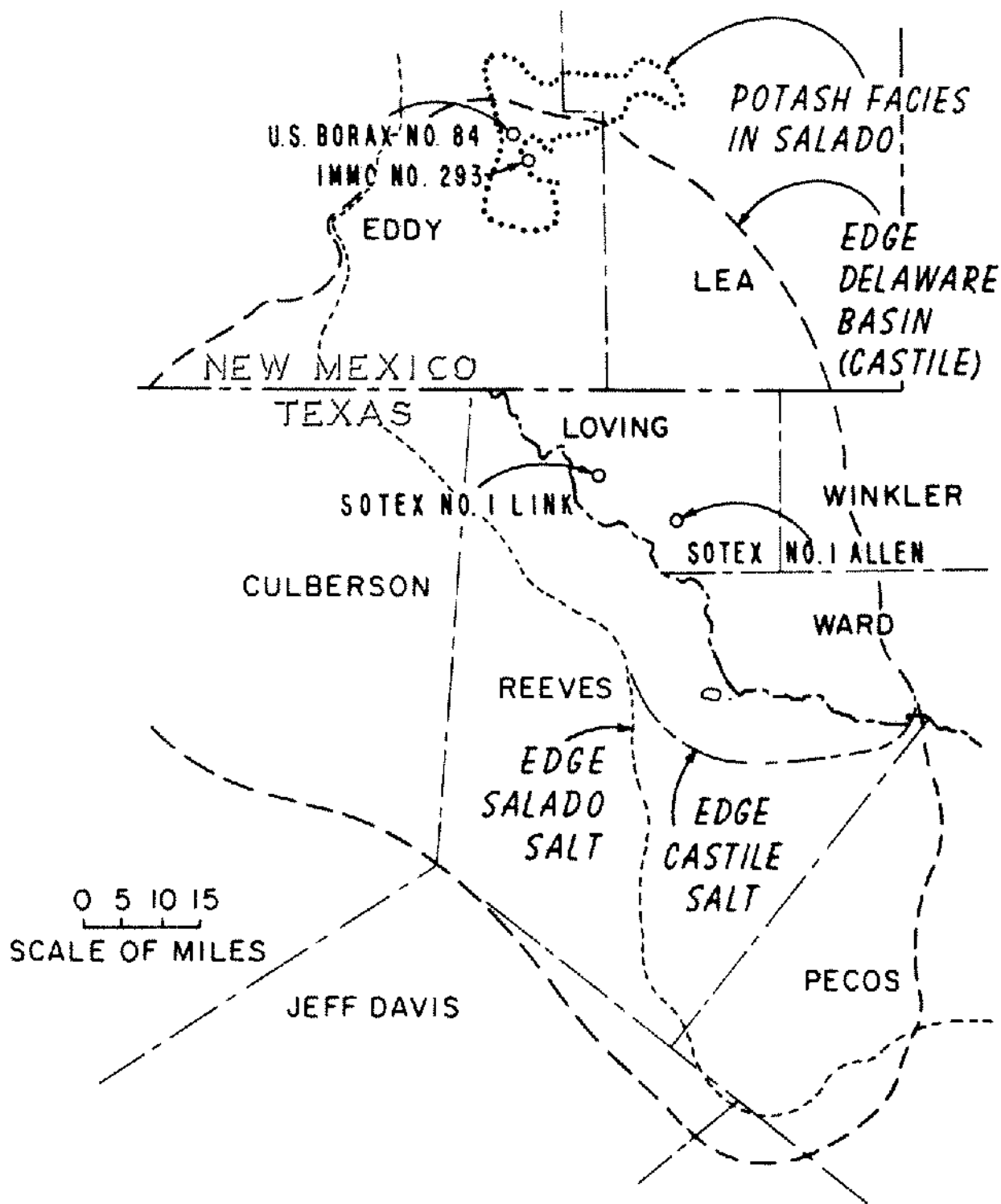


Figure 13. Evaporites of the Ochoa series in the Delaware basin, Texas, and New Mexico, showing sample localities.

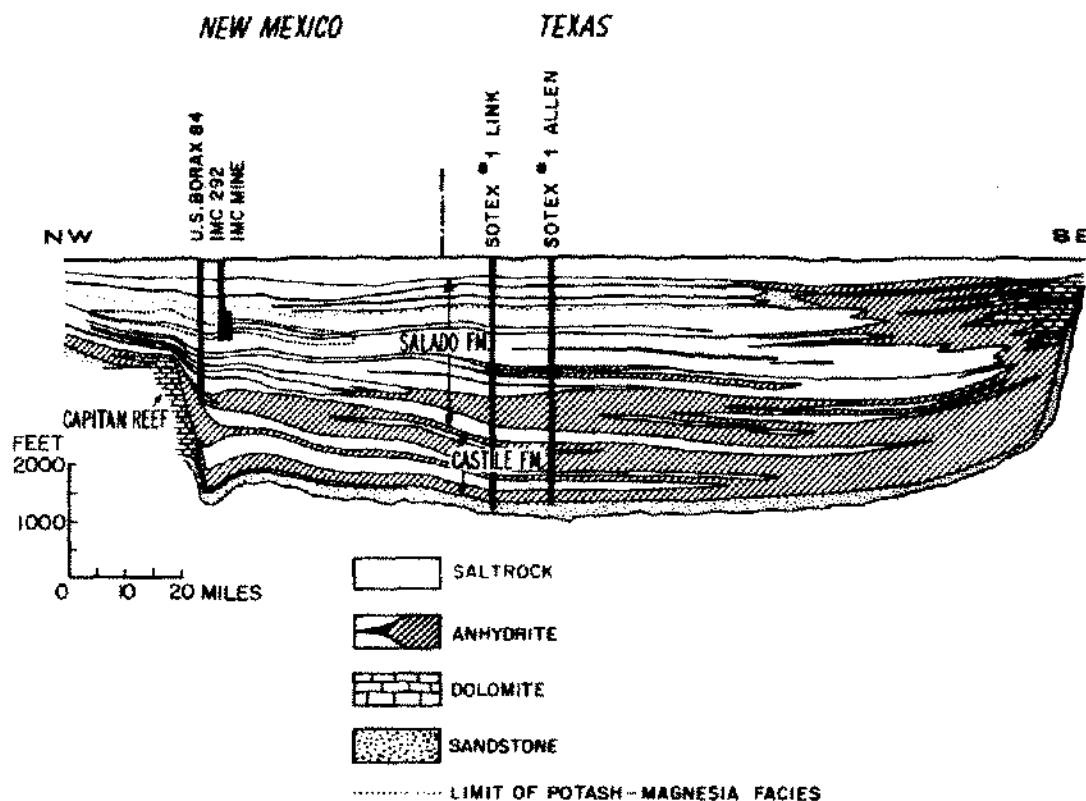


Figure 14. Generalized cross section through the Delaware basin, Texas, and New Mexico.

Some profiles from the Delaware basin are shown in Fig. 15. In the Castile salt no cores were available, so cuttings from two old churn-drill holes were analyzed, at locations indicated on Fig. 13. The lowermost Castile salt might well be classified with the above "commonly irregular profiles," including the characteristics of a normal beginning and a continuing irregular curve in the range 30-50 ppm. A second Castile salt, as well as the base of the Salado Formation (far below the potash zone) is even lower in bromide, in the range of 20 ppm. Although my main interest was in halite, these results posed the interesting question as to just how far up the section one had to go before finding the rise in bromide content expected to accompany potash deposition (Figs. 7, 8). The answer turned out to be, as you see in the upper section of the Salado profile (Fig. 15), that such high values never are attained. Halite continues to show the irregular values of a common profile even through the potash zone, with most values below 70 ppm. This raised the further question as to the bromide content of the potash minerals. Four sylvite/halite pairs were found to have $Br_{syl} = 200, 450, 740, \text{ and } 780 \text{ ppm}$, with ratios Br_{syl}/Br_{hal} of 10, 12, 22, and 30, respectively. The bromide in sylvite is far below the more than 1500 ppm expected by either metastable crystallization from the sea water brines or by thermal decomposition of carnallite (Braitsch, 1962, pp. 105-113; Kühn, 1962), while the ratios approach the theoretical value of 10 ± 1 . Generally low bromide in the salts from carnallite, sylvite, and halite in Carlsbad was already recognized in the earliest analyses (Lindberg, 1946; Lang, 1954). These data suggest a rather closely related origin for the halite and sylvite minerals that we see in Carlsbad today. Fluid inclusions from Carlsbad salts are also very low in bromide, with Cl/Br near that of sea water, but with higher magnesium content (Holser, 1963, pp. 90-91).

These data all indicate that the evaporites in the Carlsbad area were (most recently) crystallized from a second cycle of new water, low in bromide. The bromide content is not so low but that this new cycle of crystallization could have been caused by sea water, but there is no question that it must have been a fresh cycle of sea water, with the earlier concentrations of bromide removed. There is a further question as to whether the second cycle crystallization occurred

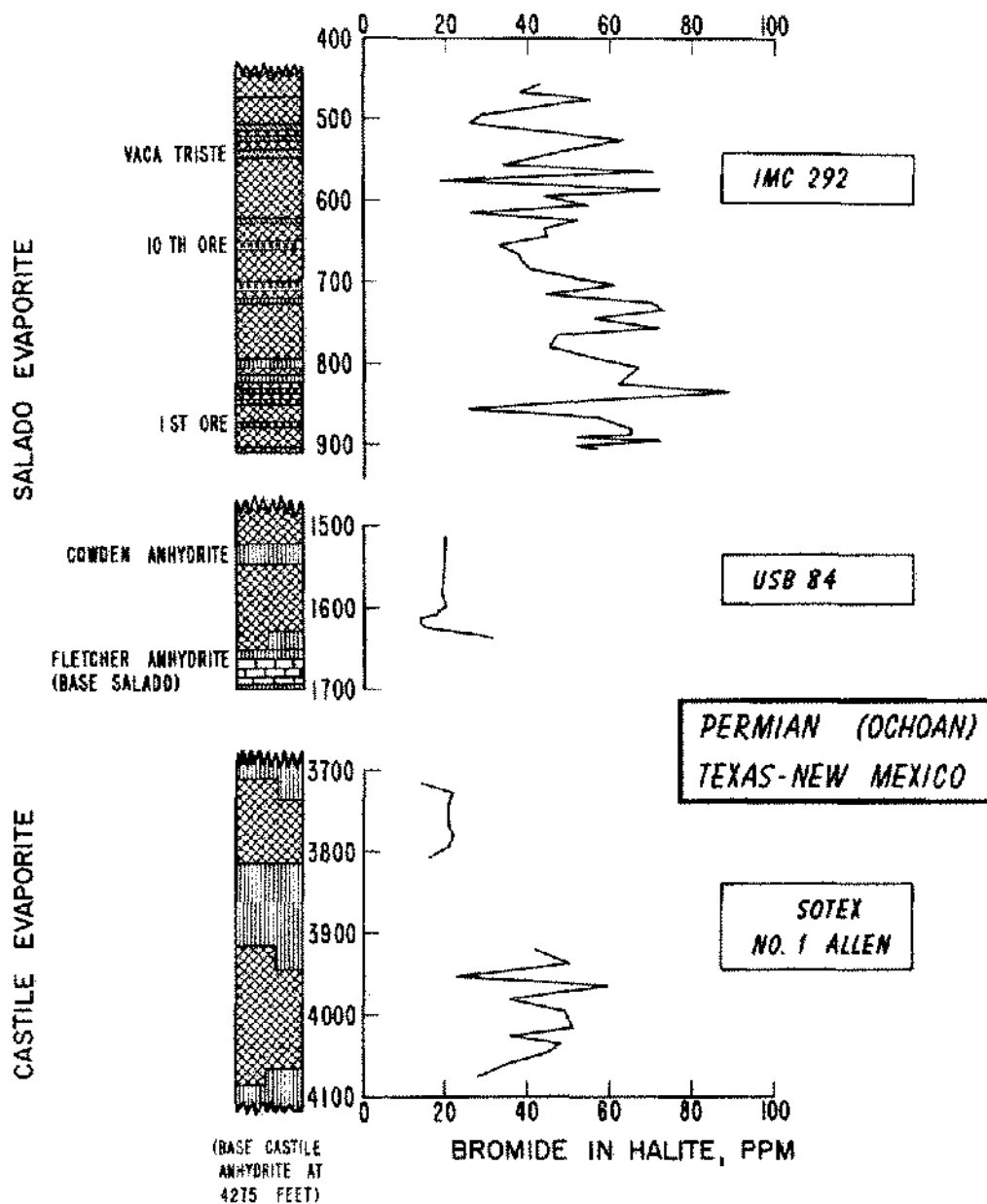


Figure 15. Bromide profiles through the Ochoa series in the Delaware basin, at localities indicated in Figures 13 and 14. Symbols for the generalized cross section are as in Figure 9; crosses indicate the thickest potash ore beds.

in place, or whether the salt was dissolved elsewhere by the water and newly crystallized here. Detailed mapping and petrography (Jones, 1962) seem to support the first idea, although in that case one might have expected a much smoother bromide profile, as well as an even greater incidence of solution-collapse than is found in the area (Maley and Huffington, 1953). Hopefully, the detailed studies still in progress in the area may shed further light on this question, which is a critical one in evaluating the origin and history of these important deposits.¹

¹ Discussion at the Salt Symposium with Mr. S. S. Adams of International Mining and Chemical Company, Carlsbad, who is completing a very detailed study of bromide distribution in their mine, confirms low and irregular nature of the bromide in the potash zone.

The second profile is even more problematical. Evaporites of the Devonian Elk Point group extend across the western interior all the way from North Dakota to the Northwest Territories (Pearson, 1963; Grayston, Sherwin, and Allen, 1964); a part of this section is shown schematically in Fig. 16. The most widespread salt formation is the Prairie evaporite which, in Saskatchewan, also includes very extensive bodies of potash minerals. The bromide profile of Fig. 17 through the Prairie evaporite in Anglo-Canadian No. 1 Elk Point, east-central Alberta, is typical for this formation. A profile through Vermillion Consolidated Oil No. 15, south above the Prairie Plateau, as well as profiles in Saskatchewan published by Schwerdtner and Wardlaw (1963) and Wardlaw (1964) are only qualitatively similar to this one. The profile in the Elk Point well is of

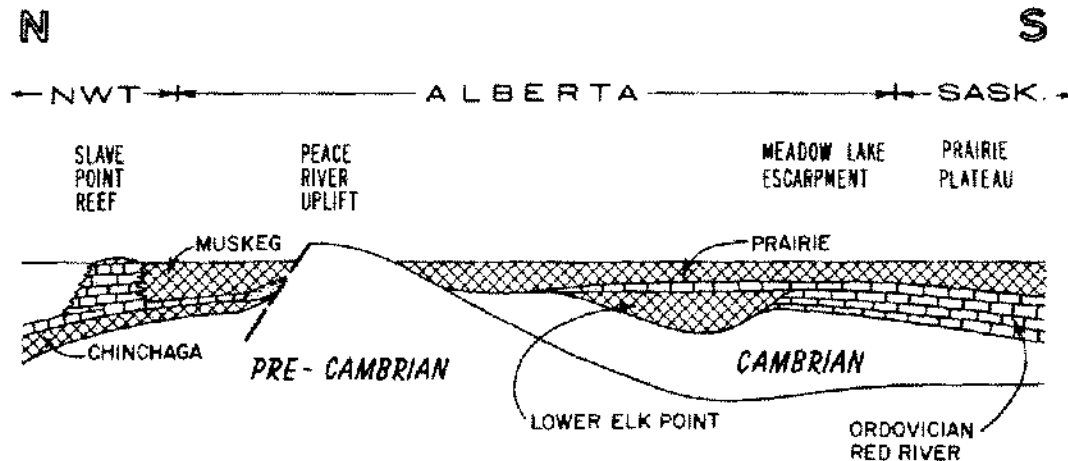


Figure 16. Schematic cross section through the lower Paleozoic of western Canada, referred to the top of the Prairie Formation.

the "commonly irregular" sort, although in the slightly higher range 60-100 ppm, with a number of spikes up to 150 ppm. This is rather reminiscent of the Salado profile, although here in Alberta only traces of potash minerals are present. The large variations are found even in the rather fine sampling shown by the inset on Fig. 17. W.M. Schwerdtner (1964, p. 1114) found low bromide in the Prairie evaporite potash zone in Saskatchewan, although not so low as I found in the Salado.

The startling feature of the Elk Point evaporites, however, is the two earlier salts, which only fill in the Alberta basin (actually two connected basins). These salts have an extraordinarily low bromide content, in the range 2-6 ppm, that is continuous almost without exception through the entire salt section. Again, no regular trends are evident within this low range of values. The purity of this salt can be appreciated when I tell you that a typical analytical-grade sodium chloride has 15 ppm bromide. Two or more cycles of crystallization are certainly necessary for the purification of salt to this low a level. Furthermore, the amount of bromide in sea water prevents reduction below 7 ppm no matter how many cycles of fresh sea water are involved. Consequently, recrystallization by meteoric waters is required for the formation of this salt. Possibly this is some sort of playa-lake deposit deriving its halides from evaporites of the Ordovician Red River Formation on the Prairie plateau to the south. Red bed character of the surrounding and interbedded sediments and nearly complete absence of anhydrite, support this model, but fragmentary marine fossils in the salt argue against it. It is also possible that recrystallization of these salt beds by the action of meteoric water took place in their present position after initial marine deposition. One other profile, in thin salts deposited far to the north in the Mackenzie basin, correlative with the Lower Elk Point, showed a more common irregular profile in the range 40-70 ppm

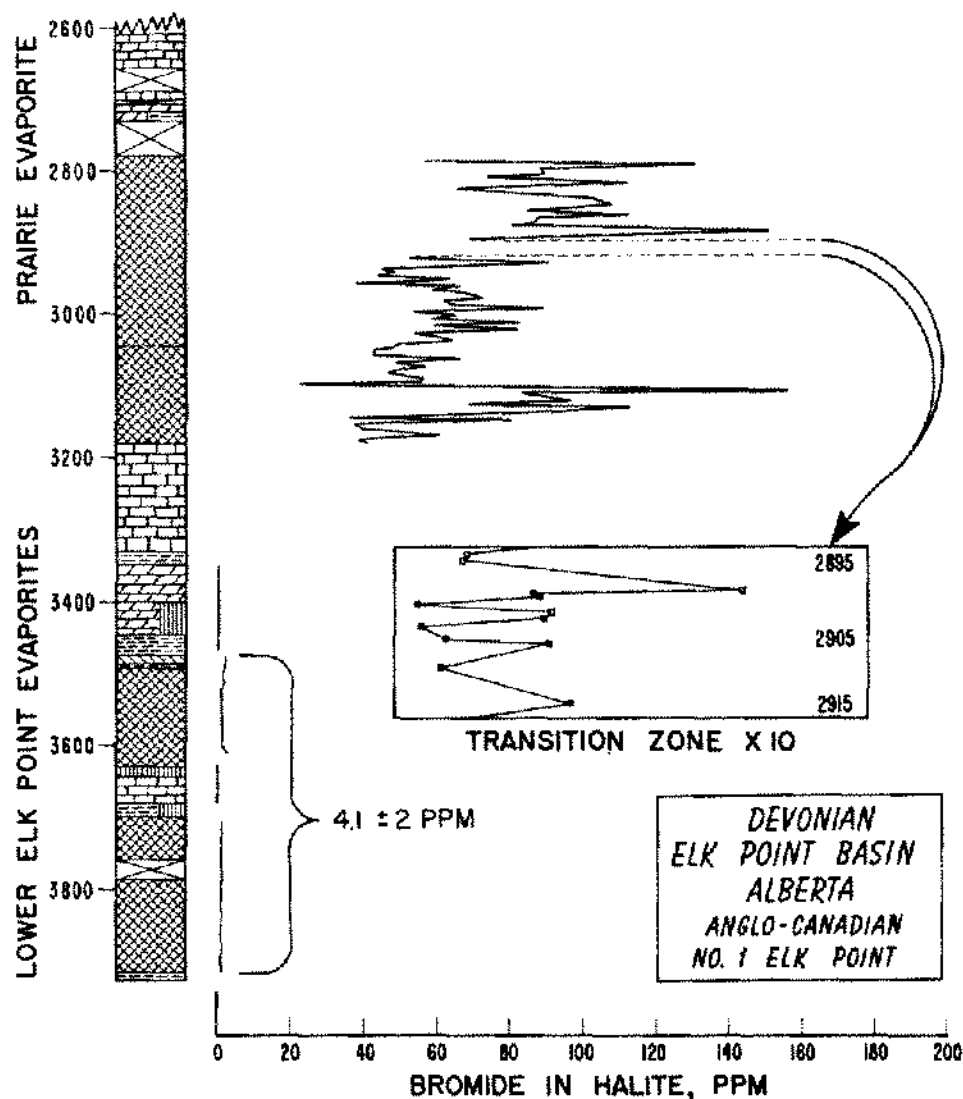


Figure 17. Bromide profile through the Elk Point Group in the Alberta basin, just northwest of the Meadow Lake escarpment (Figure 16). Detailed analysis for one 10 foot zone is shown on an enlarged scale, with dark symbols indicating gray, cloudy, possibly primary salt and open symbols indicating clear, white, possibly recrystallized salt.

bromide. It will be interesting to determine the extent of the extremely low bromide content in the Alberta basin, as more sample material becomes available in the future.²

I might mention in passing a problematical profile at the other end of the scale, from the depths of Siberia. The thick (up to 1000 m) and extensive lower Cambrian evaporites of this area were reviewed by Ivanov and Levitskii (1960, pp. 8-31) and by Yanshin (1962). Bromide profiles published by Ogienko (1959, pp. 895-898) and one which I did on a set of core samples (obtained for another purpose) show 120 to 200 ppm Br at the base, rising irregularly to 300-400 ppm Br at 600 meters above the base in a 700-meter section. Most of the halites have enough bromide to be

² Discussion at the Symposium revealed that D. W. Watson, working with N. C. Wardlaw at the University of Saskatchewan, had sampled the same core in Anglo-Canadian No. 1 Elk Point. They also found an extremely low bromide content, although it was below the sensitivity of their conventional van der Meulen procedure so that an actual profile was not obtained. They got similar results in Anglo-Canadian No. 2 Elk Point, about seven miles to the northwest. We are publishing a joint paper discussing the details of this low-bromide profile and its paleogeographical implications (Holser, Watson, and Wardlaw, in preparation).

in the potash facies, yet no sylvite was evident in the samples, and core analysis showed only traces of potassium. As of 1962 (Yanshin, 1962, pp. 2137-2140) no substantial deposits of potash had been discovered in the basin, although they certainly are expected. It is difficult to visualize a mechanism by which bromide can be so highly concentrated in halite without also depositing potash salts. Possibly the latter were diagenetically leached by solutions that did not stay around long enough to come equilibrate with the remaining halite. Or is it possible that K/Br was actually lower in the Cambrian sea than today in spite of the occurrence of high-K glauconite in Cambrian strata (Yanshin, p. 2138)?

SOME PROBLEMS IN BROMIDE GEOCHEMISTRY

I would like to go back over the details of some particular aspects of bromide geochemistry that could only be touched upon incidentally in the general geological descriptions of bromide profiles.

Origin of common bromide profiles. Most of the common type of bromide profiles in salt rock share some or all of the following characteristics:

1. The profile begins with a basal bromide content in the range 30-50 ppm, comparable with that found on evaporation of modern sea water both in the laboratory and in a Recent salt deposit, but far below the 75 ppm predicted by laboratory experiments on distribution coefficients.
2. The profile rises regularly for a few meters above the base.
3. The profile is very irregular through most of its duration, commonly in the range 30-80 ppm, with occasional spikes up to 150 ppm.
4. These relatively low and irregular bromide levels may continue into the potash zone, if there is one.
5. Limited sampling indicates homogeneity over several feet vertically, and at least that far horizontally.

In some cases the irregularity could be explained as simply due to repeated incursions of new sea water with efficient flushing of the old bromide-rich bitterns. It could also be explained as a result of one or more subsequent cycles of crystallization, which would also serve to explain point (4). Furthermore, such an explanation conforms with the recycling that is certainly required by the extremely low bromide content of the Lower Elk Point subgroup in Alberta (Fig. 17), and of the top of the Hutchinson salt of Kansas (Fig. 9). Although common bromide profiles show effects of multiple cycles of crystallization, the bromide analyses themselves cannot determine whether the new cycle of crystallization occurred by the circulation of new waters (sea water, meteoric waters, or metamorphic water from gypsum dehydration) through solid but porous salt, or whether the salt was actually dissolved in one place and redeposited elsewhere as a "descendent" salt. More needs to be known about the three-dimensional distribution of bromide on a large scale, and its relation to bedding and other structures, before this question can be settled. In the Carlsbad potash zone (and in Zechstein 3 and 4) good horizontal uniformity over short distances and at least rough correlations over hundreds of feet (horizontally) suggest that the salts were sedimented in their present condition on the surface, but in the Prairie evaporite potash zone of Saskatchewan Schwerdner (1964, pp. 1111-1113) finds considerable inhomogeneity of bromide content even on a small scale, as well as petrographic evidence of secondary alteration in place. This question must be considered still open.

Recrystallization of halite. Dellwig (1955), Gottesman (1963), and Wardlaw (1964) have described patterns of fluid inclusions that are indicative of various growth forms in halite crystals, and are consequently firm evidence for primary crystallization of these particular rocks. These patterns of inclusions are in marked contrast to other salts that have apparently undergone some form of recrystallization, where inclusions are segregated to grain boundaries. Some salts that have undergone extensive plastic deformation also show inclusions along (110) or irrational inter-crystalline shear planes. There are a number of other characteristics of certain salt rocks that may be correlative with this distinction between "recrystallized" salt and "probably primary"

salt: clear vs. cloudy color, coarse (2-200 cm) vs. medium- to fine-grained crystallinity, friable vs. compact texture, and crosscutting vs. bedding structure. Even casual observation will soon make it evident that not all of these characteristics go together, yet collectively they represent a suite of attributes that possibly indicate growth of new crystals in halite at some time after original crystallization. The friable salt, for example, I have so far seen only in mines in two Gulf Coast salt domes. This salt has been so well recrystallized that each single crystal is bounded by a set of plane or slightly convex polygons, unrelated to crystal faces, apparently in surface tension equilibrium (Smith, 1951, pp. 1-20). A large chunk of such rock easily disaggregates into the single crystals if you kick it. Crosscutting structures commonly transect the bedding in flat-lying formations of many evaporite basins, as well as occasionally being evident in salt domes. Figure 18 illustrates one of these bodies in the Salina salt of the Michigan basin. It may be useful to point out that in a core such salt would probably be logged as a differently textured salt bed, when actually it is not a bed at all.

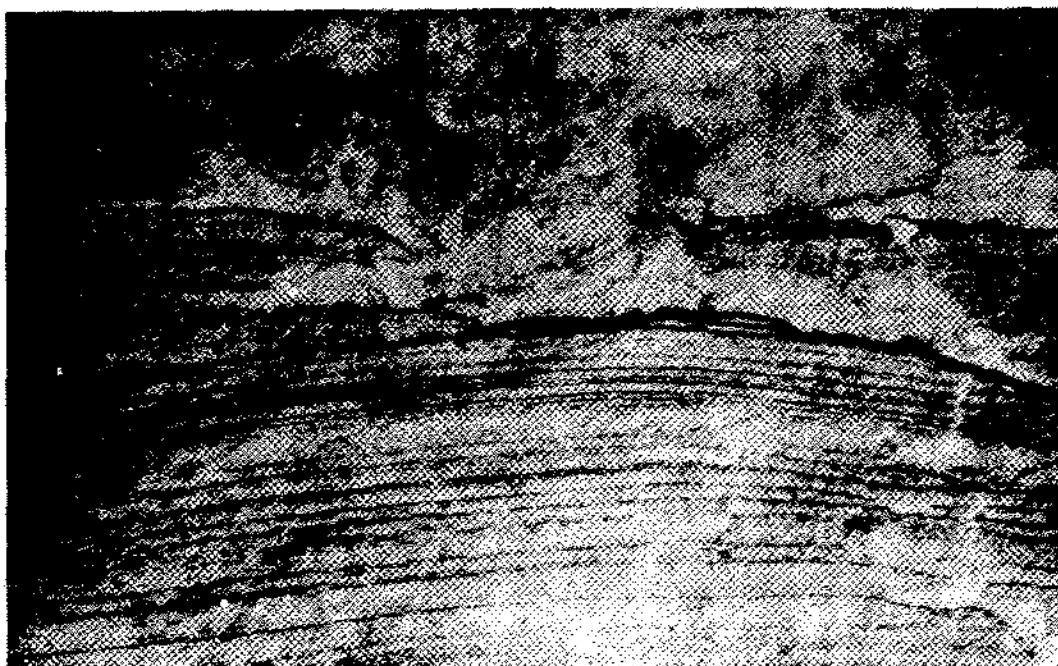


Figure 18. Mass of white, coarsely crystalline, recrystallized salt crosscutting well-defined bedding of Salina unit F in the Ojibway Mine, Ontario. Area is about 8 feet wide.

It was rather interesting to discover that some of these clear-to-white, coarsely crystalline, crosscutting bodies, which seem to have been formed by some kind of recrystallization, actually had a higher rather than a lower bromide content compared with the surrounding bedded salt. In Table 1, I have collected a number of pairs, from a wide variety of occurrences, and find that in nearly all of these bromide increased in the "recrystallized" salt by a factor of up to 3. Figure 19 shows one situation studied in detail. The salt was homogeneous in bromide content throughout both the horizontal cross section of a 3-inch core, and for distances of a foot or more vertically, transecting several varve lamellae. Furthermore, grain size showed good negative correlation with bromide content. Considering the diversity of the pairs in Table 1, and the probability that they do not all represent the same process, their consistency is surprising. I have no explanation to offer for this relationship.³

³ Discussion at the Symposium revealed that similarly high bromide in "recrystallized" halite had been found in the Prairie evaporite of Saskatchewan-Alberta by N. C. Wardlaw and in the Windsor evaporites of the Canadian Maritime provinces by C. A. Barr.

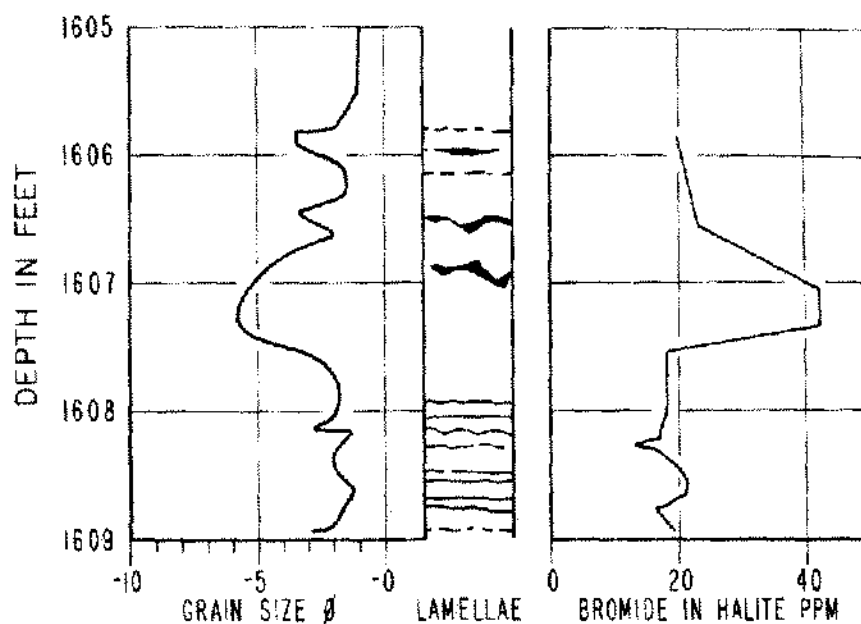
TABLE 1
BROMIDE IN RECRYSTALLIZED HALITE

Formation	Location	Bromide in ppm		Rextall Normal
		"Normal"	"Rextall"	
Salado	Carlsbad, N. Mex.	18	42	2.3
Wellington	Hutchinson, Kans.	30-65	65	1-3
Prairie	Alberta	22-90	70-155	1.0-2.9
Salina	Goderich, Ont.	36-46	88-131	1.9-3.6
Salina	Windsor, Ont.	66-68	85	1.3
Salina	Fairport, Ohio	69	113-121	1.6-1.8
Louann	Grand Saline, Tex.	39-51	39	0.8-1.0

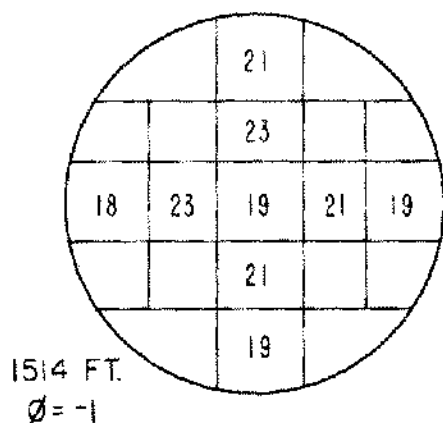
Basal halite. Presumably the first salt to crystallize in an evaporite basin should have a bromide content that was determined only by the bromide/chloride ratio in the water coming into the basin. If the salt had not been recrystallized or otherwise altered, and if the halides were predominately marine, this ratio should now allow us to calculate (equation 1) the bromide/chloride ratio in the ocean of that time. The problem is that we do not yet know the reason why evaporation of modern sea water, both natural and experimental, gives substantially lower bromide than the 75 ppm calculated from measured distribution coefficients. But it is interesting to see whether basal halites even lie within this range between 35 and 75 ppm.

Figure 20 collects data on basal halites, both from my own profiles and a few published ones. Formation names and locations refer to profiles published elsewhere in this paper, except for the following: Cheshire, England (Haslam, Allberry, and Moses, 1950; also letter of November 19, 1959 from J. Haslam); Hall, Austria: Kühn (1955b, p. 65); Germany: Schulze (1960), d'Ans and Kühn (1940), Barr (1954), Kühn (1962); Prairie, Saskatchewan: Schwerdtner and Wardlaw (1963), Wardlaw (1964). The scatter is very wide, even allowing for the fact that most of these "basal" salts, although they are all from the base of the salt section in that profile, are not usually from the deepest known part of the basin. The basal values for the Leine series of the Zechstein were extrapolated (Schulze and Seyfert, 1959; Kühn, 1959; Schulze, 1960, p. 44) through a sharp high at the base inherited from the underlying Stassfurt potash zone. If we eliminate the Lower Elk Point subgroup of Alberta, which must be a second cycle salt involving meteoric water, there does seem to be a general tendency for basal salts to lie in the range 30-50 ppm. I suggest that whatever process made the modern Baja California salts lower than the theoretical 75 ppm, could also have operated, sometimes to a greater extent, to cause the series of values displayed in Fig. 20.

There are two reasons that we might expect some variations in the bromide/chloride ratio of ancient sea waters. Both elements are "excess volatiles" in the sense that the present amounts in the hydrosphere and sediments cannot have been contributed by the weathering of igneous rocks, but must have been a product of volcanic degassing of the crust and mantle throughout their history. Modern vulcanism and hot springs emanate halites with a substantially higher chloride/bromide ratio than modern sea water (Fig. 1), so one might suppose either that a large slug of halite of low Cl/Br ratio was contributed by a primeval ocean (Ellis and Anderson, 1961, p. 427), or that the composition of volcanic emanations had been changing with time. This might be a reason to look for some regular trend in the halite ratios of basal salts through geological time, although the amount of time even back to the Cambrian represents only a rather small fraction of the total



VERTICAL SECTION



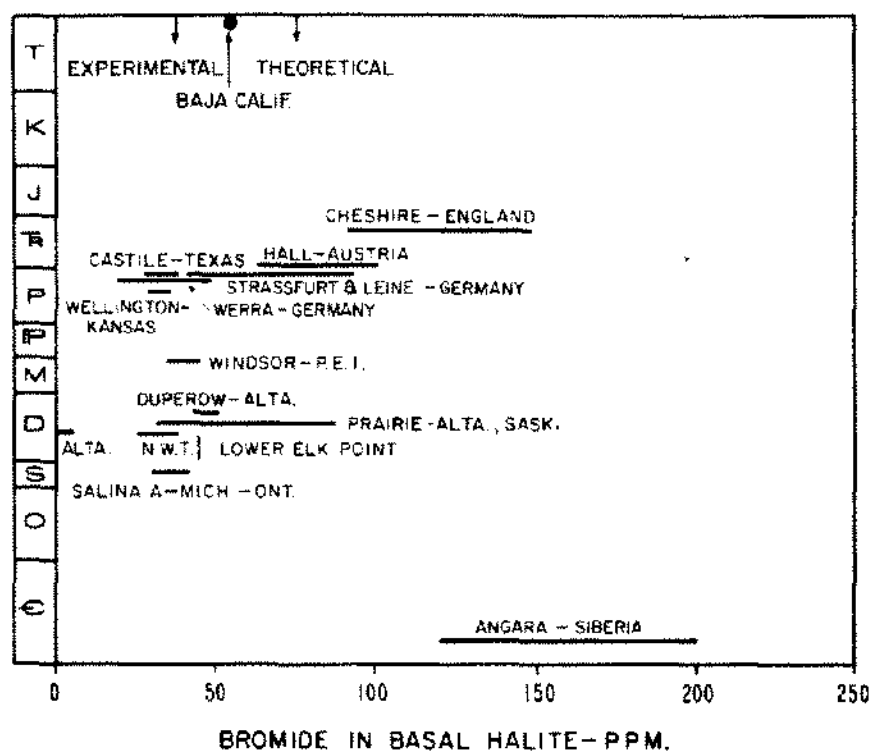
BROMIDE IN PPM
HORIZONTAL SECTION

HOMOGENEITY
TEST
USB-84
SALADO - PERMIAN
NEW MEXICO

Figure 19. Vertical and horizontal homogeneity of bromide concentration, shown by detailed horizontal and vertical sampling of a core in the lower part of the Salado Formation. Note that the bromide content is relatively constant across the interbedded lamellae (mainly carbonate), but increase sharply with increasing grain size (decreasing ϕ). This homogeneity in a short section of core is only an episode in very large variations seen on the smaller scale display of Figure 15, both above and below this level in the evaporite.

time during which volcanic emanations have probably been accumulating. Certainly no regular trend can be demonstrated by the scatter of data presently available, as shown in Fig. 20.

The other viewpoint, adopted earlier in this paper, is that perhaps volcanic halides, whether they are primeval or simply recycled crustal material, may represent some kind of an average for the crust. If so, the volume of chloride stored up in evaporite rocks is at least as great, and probably greater, than the volume presently in the sea. This, then, leads to the interesting conclusion that as the proportion of evaporite and sea water chloride shifted throughout geological



time, through the ever-changing relations of evaporite formation and salt rock erosion, both the chloride content and the chloride/bromide ratio should have been changing in the sea. That is, during periods when more salt rock was being eroded than was being deposited in evaporites, the Cl concentration and the Cl/Br ratio in sea water should have risen, and consequently the bromide content at the base of a salt profile should have begun at a smaller value. Periods of increasing evaporite deposition throughout the world, relative to rock salt erosion, should have increasing values in the basal salt bromide. This situation is strictly analogous to the sulfur isotope ratio in anhydrites, for which an age curve has now been fairly well established (Holser, Kaplan, and Silverman, 1963; Thode and Monster, 1964). The scatter of Fig. 20 gives no evidence that the sea was any richer in bromide at the end of the Permian, certainly a time when a very large amount of evaporites had been accumulated, than it is today. However, this possibility is something to look for in the future as we accumulate more data from profiles in a variety of basins, and with perhaps better petrographic control of the primary nature of the rocks.

Initial slope. Analysis of equations (2) to (5) for the general model of evaporite trace element deposition shows that, other conditions being uniform, the slope should be proportional to the mass of chloride into which the excess bromide is being rejected. In other words, if the fluid reservoir is large, the amount of bromide rejected during the crystallization of one meter of salt will not be of much consequence, and the bromide content of succeeding layers of salt will rise only slowly; whereas if only a thin layer of brine is present, this rejection of bromide will cause the brine composition, and consequently later salt layers, to be richer in bromide at a faster rate.

Using a similar concept, Kühn (1955a, 1962) has calculated depths of the Zechstein sea from bromide profiles. Braitsch (1962, pp. 157-158) has criticized Kühn's approach on the basis that Kühn's model takes no account of the reflux of bromide-rich brines back to the sea, and concludes that the latter effect is so indeterminate that depths cannot be calculated. However, the generation of my equation (4) takes into account any amount and concentration of reflux by weighting it with the inflow to give a net inflow. Now if we differentiate equation (4) at the base, we find for the slope

$$\left[\frac{dr_c}{dm_c} \right]_{m_c = 0} = \frac{(g - K) r_{co} + (1 - g) K r_f}{m_u} \quad (6)$$

In order to apply these equations to calculate a fictive depth from the ratio of basal bromide content to initial slope, we need only assume what I will call concordant inflow: that the regime of evaporation and inflow was constant just before and through the period taken for the initial slope. Under conditions like these, where crystallization is just starting in the basin, the trace element ratio in the inflow, that at the point of crystallization, and that in the outflow are all the same,

$$r_f = r_{co} / K \quad (7)$$

It does not matter what the conditions (g) are, so long as they remain the same just after the beginning of salt crystallization in the basin, as they were before the crystallization started. Later, after the brine builds up an appreciable excess of trace element (assuming $K < 1$), equation (7) may no longer be a good approximation and in fact $r_f < r_{co} / K$. Now substituting (7) in the general equation (6)

$$\left[\frac{dr_c}{dm_c} \right]_{m_c = 0} = \frac{(1 - K) r_{co}}{m_c} \quad (8)$$

Thus this assumption of concordant inflow allows an explicit solution for the fictive depth under any initially constant conditions, by measuring the initial value and initial slope of the trace element, and knowing the distribution coefficient for bromide in halite (including its variation with $MgCl_2$ concentration), and convenient units may be taken into account by determining the initial slope graphically in Fig. 7, whence

$$\text{Fictive depth in meters} = \frac{4.8 \times (\text{Initial value Br/NaCl in ppm})}{(\text{Initial slope Br/NaCl in ppm/meter of NaCl})} \quad (9)$$

Falling back on the sometimes shaky assumption that the salts are primary, fictive depths were calculated from some of the bromide profiles in this and other published papers (Stassfurt: Schulze, 1960, p. 99; Prairie Industrial Minerals #3: Wardlaw, 1964, p. 272), as shown in Table 2. These must be considered doubly tentative in view of the scarcity of data and its wide variation, as a scan of the profiles will demonstrate. The recycling of salts discussed in previous sections would also complicate this model, although if the recycling were a sufficiently uniform process it would still come under equations (7) to (9). Even for the regular profiles of Zechstein 2 Braitsch (1962, p. 152) suggests that Schulze should have looked for petrographic evidence of diagenetic alteration in the lowermost section, because the bromide content was below 75 ppm. The shallow depths of 25-35 meters calculated here are well within the wide range of 2 to 130 meters (mean 20 meters) depth calculated by Kühn (1955a, pp. 659-662) using the bromide oscillations within single yearly varves of the upper part of the Stassfurt salt (various areas), and assuming no reflux. If I assume that the lower segment of the Stassfurt profiles is secondary, and that the very gradual rise of the middle segment can be extrapolated to the base of the section as a concordant flow, the depths calculated by equation (9) are over a thousand meters. If nothing else, this discussion demonstrates the sensitivity of such calculations to purely geological information and assumptions.

TABLE 2
FICTIVE BRINE DEPTHS FROM INITIAL SLOPES

Formation	Location	Basal Halite ppm	Initial Slope ppm/m	Fictive Depth m
Castile	Sotex #1 Allen	27	1.6	80
Stassfurt	Schierstadt 1/55	30	6.7	20
	Schierstadt 2/55	25	5.3	25
	Schierstadt 3/56	60	1.4	210
	Bernberger	35	5.0	35
Wellington	NAS Hutchinson	30	1.3	110
Prairie	I.M. #3 Ft. McMurray	32	0.62	250
	A.C. #1 Elk Point	40	2.	100
Salina	Pure #1 Rinehardt	42	4.	50

It should be further remarked that the fictive depths calculated in Table 2 are less than the thickness of the overlying salt formation (except the Prairie Formation at Ft. McMurray), so that if they bear any relation to reality, subsidence of the basin would seem to be required to keep it from filling up. Richter-Bernburg (1955a, p. 622) has emphasized that the very fast rate of salt deposition, say 0.05 m/yr. would on the other hand require a previously formed basin.

The principle of concordant inflow may be found useful when better data can be assembled.

CONCLUSIONS

If this paper has demonstrated anything, I think it is that bromide geochemistry of salt rocks is a lot more complicated than it may have seemed from the first research work on the Zechstein evaporates. Some very interesting questions have been raised, and only a few tentative answers have come out of this work. But there is no question that bromide has a unique place in geochemistry as an indicator for a history of halides in salt rock, potash, and brines. A great deal more work needs to be done before the full story can be untangled.

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