Bromine Distribution and Paleosalinities from Well Cuttings, Paradox Basin, Utah and Colorado*

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ABSTRACT

Stratigraphic profiles constructed from bromine analyses of cuttings from two wells in the Paradox basin show basin-wide salinity cycles. Periods of influx with reflux, as well as periods of influx with little or no reflux, are demonstrated. The well located closer to the basin center has a higher average bromine content than the well located closer to the shelf, and thus indicates a salinity gradient within the halite facies.

Bromine content was determined for 657 samples of halite from 26 of the 29 depositional cycles of the Paradox Member, Hermosa Formation of Pennsylvanian age. Bromine was determined by X-ray fluorescence in samples collected from 10-foot (3.1-meter) intervals, and the values obtained range from 30 to 316 parts per million. Profiles from well cuttings closely resemble those obtained from cores. The average bromine content was calculated for stratigraphically correlated intervals for each salt bed and used as an index for comparing relative salinities between salt beds.

In most basins core material is either not available or available only to a limited extent. Because bromine profiles from cuttings compare favorably with those from core samples the use of cuttings will allow much broader regional studies of paleosalinities than are possible from just core samples. Good correlation between salt beds with high average bromine content and those known to contain potash salts indicates the potential of bromine distribution studies in the search for potash.

INTRODUCTION

Distribution of bromine in marine evaporite chloride minerals and in solutions from which they crystallized was determined many years ago b H.E. Boeke (1908). He discovered that bromid minerals do not form during the crystallization o salts from sea water. The bromine occurs only i solid solution as a substitute for chlorine in chlc ride minerals. The amount of bromine in the soli phase chlorides depends on the concentration c bromine in the parent solution. Recrystallizatio of salt will affect the bromine content only if th salt is recrystallized in the presence of brines whic contain different bromine contents from that c the original. The Paradox salt beds, in the area c the two wells sampled for this study, lack evidenc of major deformation, recrystallization, or reorga ization of their constituents and one may assum on the basis of present knowledge that their br mine content has remained unchanged.

Theoretical aspects regarding the geochemistı of bromine in the marine evaporite environme have been published in a number of papers (D'A and Höfer, 1934; D'Ans and Kühn, 1940; Küh 1953, 1955, 1968; Baar, 1954; Valyashko, 195 Braitsch, 1962; Braitsch and Herrmann, 196 1963, 1964; and Holser, 1966). These studies ha provided the basis for using bromine distribution marine evaporites as a useful tool in the study stratigraphic problems, paragenesis, depositior environment, salinity gradients, and as an aid prospecting for potash and oil (Baar, 1954, 195

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Valyashko, 1956; Schulze, 1958, 1960; Ogienko, 1959; Holser, 1963; Schwerdtner and Wardlaw, 1963; Braitsch, 1966; Raup, 1966; Wardlaw, 1966, 1968; Adams, 1967; and Hite, this publication).

Most studies of bromine distribution in marine evaporites are based on analyses of core samples or of samples from potash and salt mines. The present study has shown that reliable data on bromine distribution can be derived from well cuttings as well as core samples. Using well cuttings, bromine content was determined for 657 samples of halite from 26 of the 29 depositional cycles of the Paradox Member, Hermosa Formation of Pennsylvanian age in two wells in the Paradox basin. Stratigraphic profiles were constructed from these analyses.

ACKNOWLEDGMENTS

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GEOLOGIC SETTING

Samples for this study are from two wells drilled along the axis of the Paradox basin. The salt basin consists of a deep, elongate trough that trends northwest along the southwest flank of the Uncompahgre uplift and a shallower shelf area to the west, southwest and south (Fig. 1). This trough is characterized by a thick accumulation of evaporite beds and by a series of northwest-trending salt anticlines. The basin covers an area of 11,000 square miles in southeastern Utah and southwestern Colorado. The boundaries of the basin are defined by the limit of the salt deposits in the Paradox Member of the Hermosa Formation of Pennsylvanian age. The original thickness of the Paradox Member ranged from 0 at the basin margins to about 7,000 feet in the deepest part of the basin. Individual salt beds now range in thickness from 20 to 800 feet at the basin center. The salt section has been locally thickened to as much as 14,000 feet in diapiric anticlines (Hite, 1968, p. 321). The saline rocks of the Paradox Member consist of 29 known evaporite cycles. The rock types in these cycles include limestone, silty dolomite, anhydrite, calcareous black and gray shale, and halite with or without potash salts. Hite (1960) has numbered the salt beds of the saline section from 1 through 29 from top to bottom. A diagrammatic stratigraphic section of these rocks is shown in Figure 2.

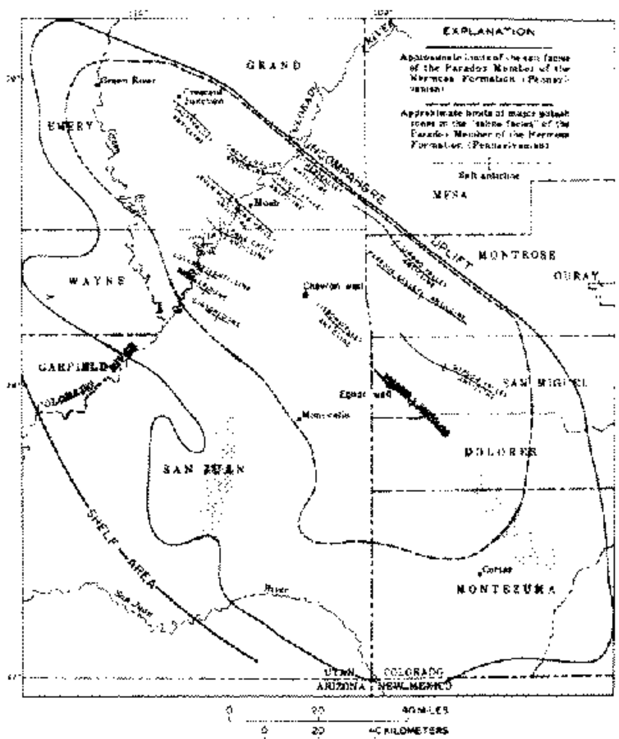

Figure 1. Index map and well locations. Limits of salt and potash from Hite (1961). Arrows show directions of increasing salinity.

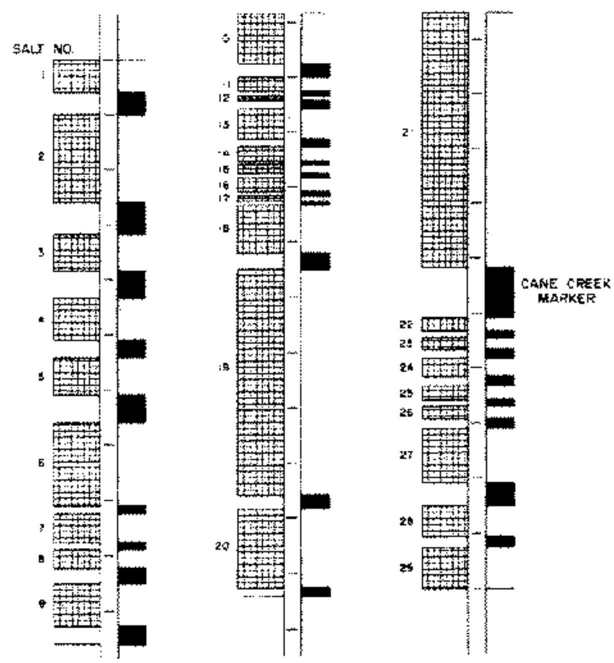

Figure 2. Diagrammatic stratigraphic section of the Paradox Member of the Hermosa Formation, after Hite (1960). Boxes on left side of column represent salt beds. Boxes on the right represent penesaline and clastic intervals between salt beds. Tick-marks in center column are at 200-foot intervals.

The floor of the deep trough of the Paradox basin was very irregular during the deposition of the lower 14 salt beds. This relief was caused by large fault blocks which were pushed upward in the areas that now contain the salt anticlines. Movement of these blocks occurred during the deposition of salt beds 29 through 16 (Hite, unpublished data). The effects of these structural features on the salinity gradient are discussed later.

STRATIGRAPHY

Reynolds Mining Corp., Egnar No. 1 well. This well will be referred to hereafter as the Egnar well. The Egnar well is located in sec. 14, T. 43 N., R. 19 W., San Miguel County, Colorado, near the crest of the Dolores anticline. The Paradox Member occurs between the depths of 5,443 and 9,579 feet, a total thickness of 4,136 feet, and salt beds 4 through 29 were penetrated. At this locality salt beds 1, 2, and 3 are represented by a carbonate facies. Of the 26 salt beds penetrated by this well, 9 contain potash (mostly sylvinite). They are salt beds 5, 6, 7, 9, 14, 16, 19, 21, and 27. Of these, salt beds 7 and 16 contain only a trace of potash.

There is no clear evidence that the beds penetrated by this well are folded or faulted. Salt beds 18 and 27, however, are unusually thick compared to nearby wells, which may be due to steep dips.

Gulf Oil Corp., Chevron Federal No. 1 well. This well will be referred to hereafter as the Chevron well. The Chevron well is located in sec. 24, T. 29 S., R. 23 E., San Juan County, Utah, on the extreme northwest flank of the Lisbon Valley anticline. The Chevron well is 29 miles northwest of the Egnar well. The Paradox Member occurs between the depths of 5,221 and 9,042 feet, a total thickness of 3,821 feet, and salt beds 4 through 28 were penetrated. At this locality salt beds 1, 2, and 3 are represented by a carbonate facies. Of the 25 salt beds penetrated by this well, 9 contain beds of potash (mostly sylvinite). They are salt beds 6, 7, 9, 13, 16, 19, 20, 21, and 24. Of these, salt beds 6, 7, 13, 16, 20, and 21 contain only a trace of potash.

Examination of the gamma ray-neutron logs of this well shows that some strata have been folded and/or faulted. From 6,910 to 7,030 feet an anomalous thickness of anhydrite is the result of recumbent folding near the bottom of salt bed 13. This same folding has thickened the pensaline and clastic interval below salt bed 13. The remainder of the section penetrated by the well seems to be undeformed. Between salt bed 18 and the base of salt bed 29, most of the salt beds and the intervenin penesaline and clastic rocks are thinner than nor mal. Isopach maps (Hite, unpublished data) show that this well is probably located on an old positiv structure. The influence of this structure is no evident in the strata above salt bed 18.

METHODS OF ANALYSIS

Samples from the Egnar well were hand picke under a binocular microscope for bromine analysi: About 6 grams of clean halite was picked from th original sample of 15 to 20 grams. Care was take to select the cleanest halite which was free of ir cluded anhydrite.

Samples from the Chevron well were purified fc X-ray analysis by recrystallization rather than b hand picking. This was done to speed the proce: of sample preparation. Approximately 7 to 8 gram of sample were placed in 100 ml. of distilled wate and stirred to quickly dissolve the halite. A sma amount of anhydrite went into solution; howeve because less than 0.5 percent of the recrystallize salt was calcium sulfate, the contamination is insi nificant for our purpose. The salt solution was fi tered and placed in an evaporating dish lined with commercially available plastic film. The plast keeps the recrystallizing salt from creeping up th sides of the dish and aids in removing salt after th liquid has evaporated. The recrystallized salt scraped and brushed from the plastic film, tho oughly ground and mixed, dried for about 10 mi utes under a heat lamp, and then thorough ground and mixed again. Great care is taken t prevent loss of any recrystallized salt. Because the bromine distribution coefficient between liqu and solid phases, loss of even a small amount late crystallizing salt would adversely affect th bromine content of the sample. The salt was dri again for a few minutes and pelletized at a pressu of 22,000 pounds per square inch (15,5(kg/cm^2). The pellets are stored in a desiccator un they are X-rayed.

Twenty samples from the Egnar well, which ha been prepared for analysis by hand picking, we recrystallized and analyzed again. No significa differences were noted in the bromine content b tween the two methods of sample preparation.

The analyses for bromine were by X-ray flu rescence spectrometer; equipment used was Picker X-ray spectrodiffractometer; analyses we made in air; radiation was from a tungsten tul operated at 50 KV-37.5 Ma; the analyzer cryst was lithium fluoride; the detector was a scintill tion type; a pulse height analyzer circuit was used with window voltages selected to maximize sensitivity for the 11.91 Kev $K\alpha$ energy of bromine; a spinner in the spectrograph rotated the sample during analysis to insure uniform exposure to the X-rays.

Each sample was scanned from 28 to 32 degrees 2θ, at the rate of 1 degree per minute. The bromine peak scanned was $K\alpha_1$, 1st order at 29.96 degrees 2θ. The peak was scanned rather than determined by the fixed count method because there is a shift of the $K\alpha_1$, 1st order peak position, at low concentrations of bromine. The limit of sensitivity for bromine in a matrix of sodium chloride using this equipment and technique is approximately 30 ppm. X-ray traces of the halite samples were compared to traces of artificially prepared standards of known bromine content. The average precision in the range of 30 to 80 ppm bromine is plus or minus 15 percent and in the range of 80 to 310 ppm is plus or minus 6 percent.

BROMINE PROFILES FROM WELL CUTTINGS

Bromine analyses of halite samples from the Egnar and Chevron wells are plotted stratigraphically in Figure 3. The resulting profiles were smoothed by a moving average of five points. The profiles of these analyses are of two major types: (1) those in which the bromine contents show a regular, steady increase or decrease; and (2) those in which the bromine contents of the samples differ greatly so as to produce very irregular profiles.

The analyses that plot into regular profiles are those in which the bromine contents of adjacent samples differ less than 50 ppm; irregular profiles show a greater variation. All salt beds in the Egnar well except 28, and salt beds 4, 6, 8, 10, 14, 15, 16, 18, 23, 25, 26, 27, and 28 in the Chevron well are examples of regular profiles. Gamma ray-neutron logs show that the irregular profiles are due to disruption of normal stratigraphic sequence by either folding or faulting within a salt bed.

There is a wide range of regularity in these profiles. Some profiles have a high degree of regularity, some are regular but a few samples indicate local disruption, and some are irregular throughout the whole salt bed. The fact that most of the profiles have a fairly high degree of regularity, similar to those from core samples (Raup, 1966, p. 236), indicates that cuttings can be used successfully for bromine distribution studies.

Correlations between profiles of the same salt bed in the two wells were made so that the

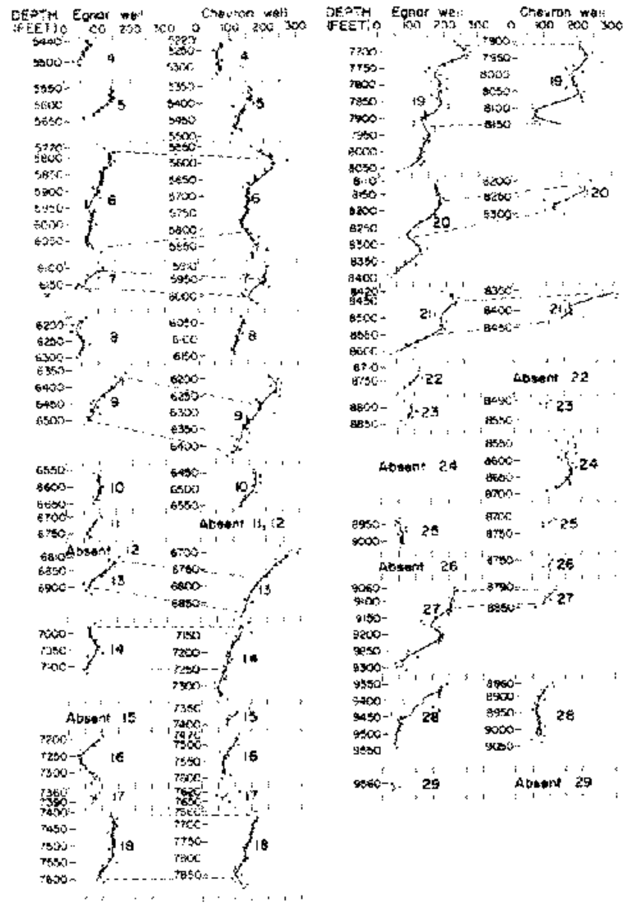

Figure 3. Bromine profiles from cuttings from the Egnar and Chevron wells. Dots indicate X-ray fluorescence analyses for bromine; lines show the smoothed profiles. Dashed lines suggest correlations on the basis of the best reasonable fit. Bromine is in parts per million. Numbers indicate salt beds.

analyses used in calculating the average bromine content would represent the same stratigraphic intervals. These correlations are indicated by dashed lines on Figure 3.

PROFILES OF AVERAGE BROMINE CONTENT

The *average* bromine content for an individual salt bed is a useful salinity index for comparing salt beds between wells. Figure 4 shows stratigraphic plots of the average bromine content of the correlated intervals for each salt bed in the Egnar and Chevron wells.

The average bromine profiles (Fig. 4) show 2 major stratigraphic intervals of high bromine content in both wells. One is the interval between salt beds 5 and 13 and the other between salt beds 18

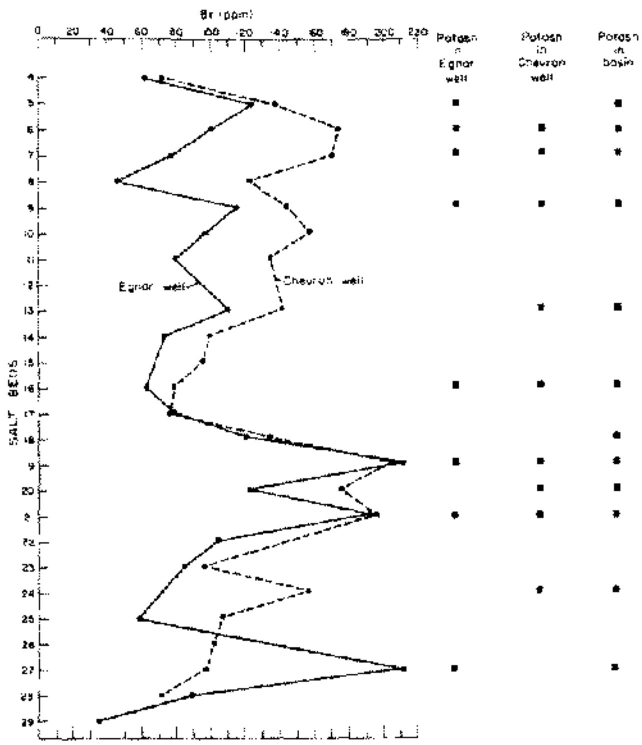

Figure 4. Profiles of average bromine contents from correlated intervals in the Egnar and Chevron wells. Black squares indicate salt beds that contain potash deposits.

and 21. Bed 24 is high in bromine in the Chevron well and bed 27 is high in the Egnar well. Minor cycles are characterized by the shape of the profiles. There is reasonably good correlation between these two profiles. In all but 4 salt beds the average bromine content is higher in the Chevron well than in the Egnar well. These exceptions are salt beds 17, 19, 27 and 28. The significance of the higher bromine content in the Chevron well is discussed in the next section.

The salt beds which contain potash in the Egnar and Chevron wells and elsewhere in the basin are shown to the right of the profiles. There is good correlation between those salt beds that contain potash salts and those salt beds that have a high average bromine content. The one obvious exception is salt bed 16. This salt bed contains potash but the average bromine content is in the range of 62 to 78 ppm. Our data at the present time offer no explanation for this anomaly.

INTERPRETATIONS OF PALEOSALINITIES

The bromine content of halite is indicative of the salinity of the brines from which it crystallized. As the dissolved constituents of sea water becom concentrated through evaporation, bromine in creases from 65 ppm in normal sea water to abou 500 ppm at the beginning of halite precipitation During the stage when only halite is precipitating prior to the appearance of the first potash min erals, bromine in the brine increases from abou 500 ppm to about 2,300 ppm (Valyashko, 1956, p 574) while the bromine content of the halite bein precipitated during this stage increases from abou 65 ppm to 270 ppm (Valyashko, 1956, p. 578 Five of the average bromine contents in salt beds i the Egnar well are below the theoretical minimur of 65 ppm. These are salt beds 4, 8, 16, 25 and 2 Three of these are very close to the theoretic minimum—salt beds 4, 16 and 25 with bromin contents of 61, 62 and 58 respectively. These a close enough to the theoretical minimum so as t be accounted for by analytical error. Salt beds and 29, with bromine averages of 45 and 33 respe tively, are too low to be considered errors. At t present time we cannot suggest a reason for t low bromine contents in these salt beds.

As the average bromine profiles indicate (Fig. 4 the salinity of the brines in the Paradox basin w initially low. This would be expected during t deposition of the first salt in the evaporite s quence. During the deposition of succeeding sa beds the salinity in the basin increased and d creased through two major cycles. The maxima the major cycles comprise salt beds 5 through 1 and 18 through 21. The minor cycles are evide from the profiles for each well.

The salinity of the brine in the basin during t deposition of any given salt bed is the result of t balance between influx of sea water into the bas and reflux of dense, very high salinity brines out the basin (Fig. 5). The balance between influx a reflux was determined by two major factors—s level and sedimentation in the shelf area. Duri periods of high sea level the depth of water in t basin and over the shelf area was at a maximu There was little if any restriction to water flowi into the basin and because of the maximum dep of water over the shelf there was sufficient "spac for dense, high salinity brine to flow out of t basin as an undercurrent. As sea level lowered, t water became shallower over the shelf and it b came increasingly difficult for the refluxing brin to return to the open ocean. As sea level continu to lower, a point was reached where the refluxi brines could not overcome the friction of the fluxing surface currents and reflux stopped. T produced an increase in both salinity and rate evaporite deposition in the basin.

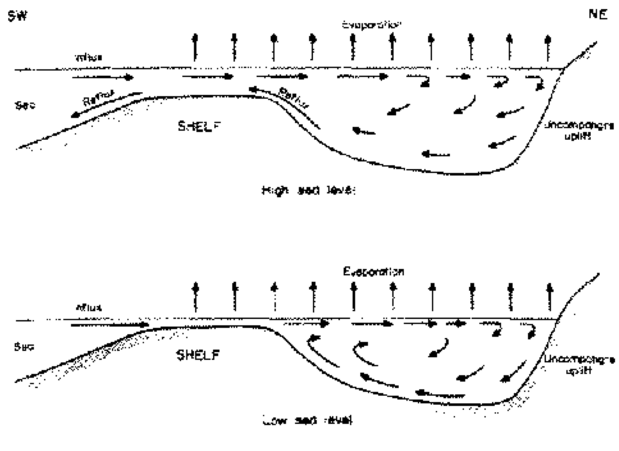

Figure 5. Diagrammatic cross-section of Paradox basin during evaporite deposition showing effects of sea level on influxing and refluxing brines.

Sedimentation on the shelf had the same effect on the influx-reflux balance as lowering sea level. If sea level remained constant and the shelf area was raised by carbonate sedimentation, the water over the shelf became shallower and the "space" necessary for the escape of refluxing brines decreased. This, too, caused an increase of salinity in the basin accompanied by an increase in evaporite deposition. The salinity of the brines in the basin and the conditions of evaporite deposition are controlled by a very delicate balance between changes of sea level and the rates of carbonate sedimentation on the shelf. Conversely, the rate of shelf sedimentation is controlled in part by the refluxing brines that flow out of the basin and back over the shelf. These effects on carbonate sedimentation are discussed in detail by Hite (this publication).

The bromine profiles and the average bromine contents of the salt beds in the basin (Figs. 3, 4) indicate the relative balance between influx and reflux. Where the bromine profile of a salt bed shows no appreciable increase in bromine content during salt deposition, the reflux kept pace with influx so that the salinity of the basin brines remained fairly constant. Profiles which show a rise in bromine content during salt deposition indicate that influx and/or reflux was reduced and the salinity of the basin brine was increasing. This would result during a low sea level stage. Profiles that show a decrease of bromine content indicate that influx and/or reflux increased which lowered the salinity of the brines in the basin. This would result during a high sea level stage. It is assumed in all of these relationships that the rate of evaporation has remained constant. Any changes in the evaporation rate would also affect this balance.

The slope of a bromine profile indicates the *rate of change* in salinity during evaporite deposition, but the average bromine content indicates the *degree* of salinity during any given stratigraphic interval.

A general salinity gradient between the shallower and deeper parts of the basin is indicated by the differences in average bromine content between the Egnar and Chevron profiles. In Figure 4 it is clear that the average bromine content of most of the salt beds in the Chevron well is higher than those in the Egnar well. Figure 6 is a graphic representation of the salinity gradient between the two

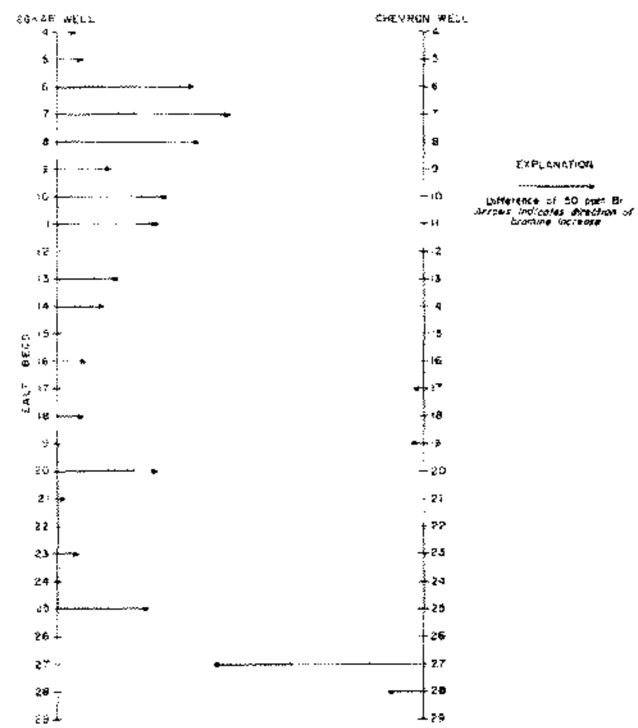

Figure 6. Graphic representation of the salinity gradient between the Egnar and Chevron wells.

wells. The length of each arrow is an index of the difference in salinity and the direction of the arrow indicates the direction of increase in the salinity. Most of the analyses show an increase toward the Chevron well. Two salt beds, however, show a significant gradient in the opposite direction—salt beds 27 and 28. These reversed gradients are the result of *vertical* as well as horizontal variations in salinity within the brines of the basin.

On the basis of facies distribution and geochemical data it appears that the Paradox basin contained fairly deep water during the deposition of the evaporite rocks. The brines were probably strongly stratified which would result in both vertical and horizontal salinity gradients. During deposition of the lower 14 salt beds, the bottom of the basin had considerable relief caused by fault blocks which were pushed upward in the areas that now contain the salt anticlines. Movement of these blocks occurred during the deposition of salt beds 29 through 16. Irregularities in the salinity gradients as represented by average bromine in these salt beds resulted from the irregularities in the basin floor. Although the salinity gradient in the basin as a whole is toward the central deeper part of the basin, local variations in salinity resulted from these structural irregularities. An example of this is shown in salt beds 27 and 28. Even though the general salinity gradient increases from the Egnar well toward the Chevron well the gradients during the deposition of salt beds 27 and 28 were locally reversed. The Chevron well was drilled at the site of one of these large structural blocks. During the deposition of salt beds 27 and 28 the block elevated this part of the basin floor into brines of lower salinity. This resulted in deposition of salt with lower bromine content than the equivalent salt beds in the Egnar well.

ECONOMIC APPLICATIONS

Interpretations of paleosalinities, through bromine distribution studies of the halite rocks of an evaporite basin, yield concepts which are of economic value. In most basins halite samples from core material either is not available or is available only to a limited extent. Because bromine profiles from cuttings compare favorably with those from core samples the use of cuttings will allow much broader regional studies of paleosalinities than are possible from just core samples. The applications of paleosalinity data are useful in two major areas: (1) exploration for potash salts; and (2) exploration for petroleum.

Potash salts are the last products of the evaporation and concentration of sea water in an evaporite basin and are deposited when the salinity of the basin brine is at a maximum. At any given time of salt formation the potash minerals will be deposited in the deepest parts of the basin where the high salinity brines migrate because of their high density. If directions of increasing salinity can be determined for an individual salt bed, then the location of potentially valuable potash salts may be predicted. The salinity gradient observed between the Egnar and Chevron wells confirms this concept. In a basin that is less well known than the Paradox basin, valuable clues to the location of potash might be indicated from the study of cuttings from a few widely spaced drill holes, even though the well samples contain no potash.

R.J. Hite (this publication) shows how paleosalinity data, derived from bromine distribution studies, can be used to reconstruct sedimentation patterns in and around an evaporite basin. This technique could be of great value in the exploration for oil.

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