Bromine Distribution in Some Halite Rocks of the Paradox Member, Hermosa Formation, in Utah[1]

Omer B. Raup
U. S. Geological Survey
Denver, Colorado

ABSTRACT

Bromine content was determined for 301 samples of halite from a well core, Cane Creek anticline, Grand County, Utah. The stratigraphic interval sampled includes the halite units of four depositional cycles of the upper part of the Paradox Member, Hermosa Formation of Pennsylvanian age.

Samples of halite, collected at 2-foot intervals through each salt bed, were analyzed for bromine by X-ray fluorescence; a few samples were rechecked by chemical methods. The bromine values determined range from 80 to 350 parts per million. These values were then plotted with respect to their stratigraphic positions, giving profiles which have been smoothed by a moving average of five points.

The profiles show a systematic increase in bromine from bottom to top of each of the four salt beds. The profiles are grossly similar, but they differ in detail. The general regularity of bromine increase shown by the profiles indicates that each of the four salt beds was deposited during one continuous period, and it can be inferred that there was neither a major change in depositional conditions nor apparent metamorphism of the salt which would tend to upset the steady increase of bromine content from bottom to top of the salt beds.

INTRODUCTION

The evaporites of the Paradox Member of the Hermosa Formation of Pennsylvanian age in southeast Utah and southwest Colorado are direct precipitates from saline water and have been changed only slightly by subsequent events. The content of bromine, which is an indicator of the salinity of the water, is an important clue to understanding the depositional history and the nature of the sedimentary regimen. This paper summarizes preliminary results of a study to determine the bromine distribution in halite rocks represented by 301 halite samples from a well drilled near the crest of the Cane Creek anticline, Grand County, Utah (Fig. 1). The well penetrated the top four salt beds numbered 2, 3, 4, and 5 of the Paradox Member (Fig. 2).

Distribution of bromine in marine evaporite chloride minerals and in the solutions from which they crystallized was determined many years ago by H. E. Boeke (1908). Since then much work has been done in this field by Baar (1954), Block and Schnerb (1953), Braitsch (1962), Braitsch and Herman (1962, 1963, 1964), D'Ans and Höfer (1934), D'Ans and Kühn (1940), Kühn (1953, 1955), and Valyashko (1956). These studies have provided a means for using bromine distribution in marine evaporites as a useful tool in the study of stratigraphic problems and in prospecting for potash deposits (Baar, 1954, 1955; Schulze, 1958, 1960; Ögienko, 1959; and Valyashko, 1956).

[1] Publication authorized by the Director, U. S. Geological Survey.

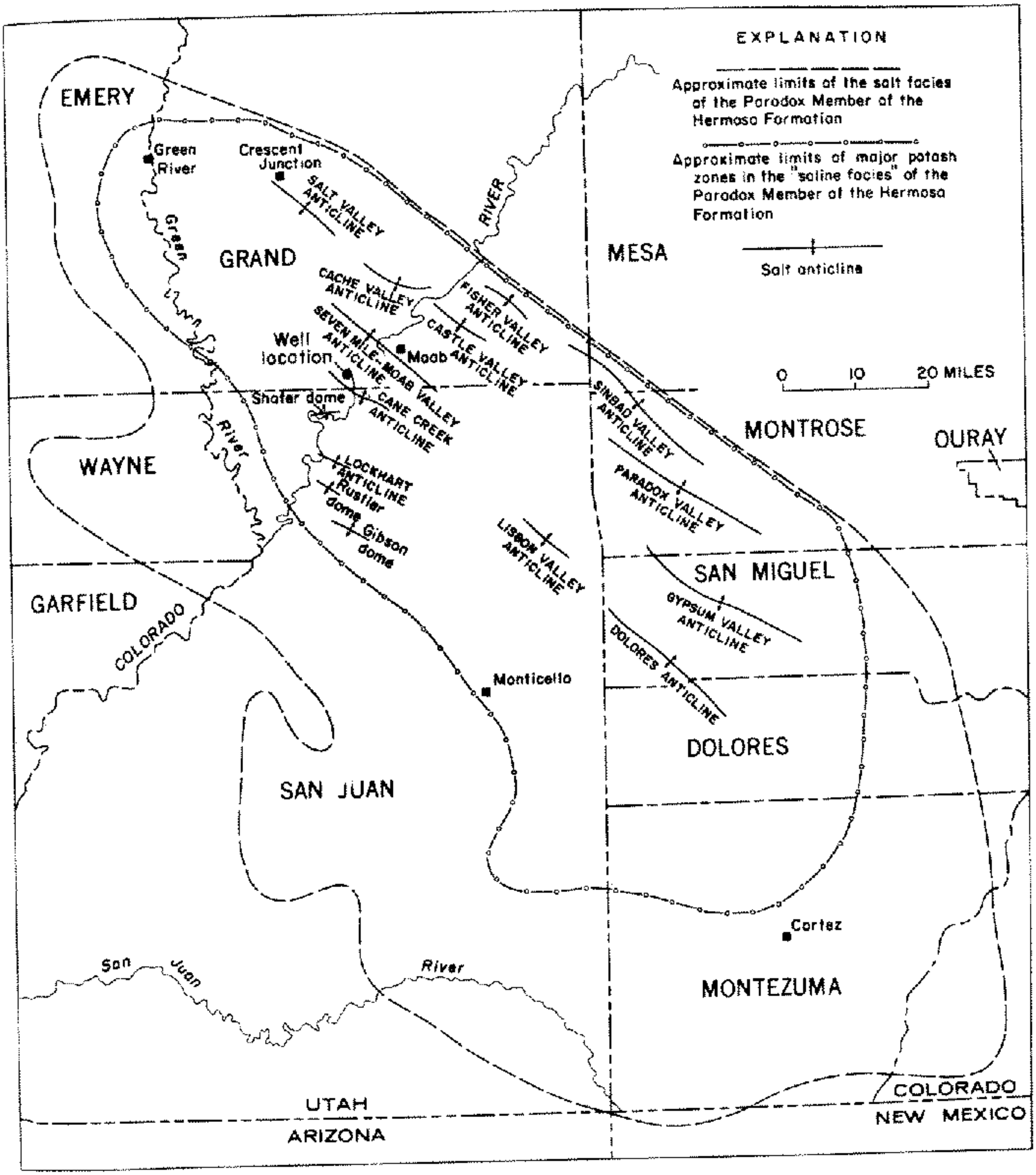

Figure 1. Index map and well location. Limits of salt and potash from Hite, 1961.

ACKNOWLEDGMENTS

I would like to acknowledge the assistance and enthusiastic cooperation of Charles F. Fogarty, Frank E. Tippie, and James H. Ogg of the Texas Gulf Sulphur Company, and Robert R. Norman of the Buttes Gas and Oil Company. Gordon H. Van Sickle of the U.S. Geological Survey made the chemical determinations for bromine.

OCCURRENCE OF BROMINE IN MARINE EVAPORITES

Boeke (1908) discovered that bromide minerals do not form during the crystallization of salts from sea water. The bromine occurs only in solid solution as a replacement of chlorine in chloride minerals. The amount of bromine in the solid phase chlorides depends on the concentration of bromine in the parent solution.

Each of the chloride minerals has its own coefficient of solid solution with regard to bromine. If the amount of bromine that can be taken into solid solution by halite is taken as unity, then the amount taken into solid solution by sylvite (KCl) is 10, carnallite ($KMgCl_3 \cdot 6H_2O$) is 7, and kainite (KCl, $MgSO_4 \cdot 3H_2O$) is 3.5 (Braitsch, 1962, p. 104). When two or more chlorides crystallize simultaneously from a brine, the bromine enters each solid phase according to each mineral's coefficient. Consequently, the abundance of bromine in halite, to which the work described in this paper was limited, is not affected by the presence or absence of other chloride minerals.

As the dissolved constituents of sea water become concentrated through evaporation, bromine increases from 65 parts per million (ppm) in normal sea water to about 500 ppm at the beginning of halite precipitation. During the stage when only halite is precipitating, prior to the appearance of the first potash minerals, bromine in the brine increases from about 500 ppm to about 2300 ppm (Valyashko, p. 574). The bromine content of halite, during the stage when only halite is precipitating, increases from a minimum of 68 ppm to 270 ppm (Valyashko, 1956, p. 578).

Recrystallization or deformation of salt will affect the bromine content only if the salt is recrystallized in the presence of brines which contain different bromine contents from that of the original (Schwertner and Wardlaw, 1963, p. 241). The Paradox salt beds, in the area of the Cane Creek anticline, lack evidence of major deformation or reorganization of their constituents and one may assume on the basis of present knowledge that their bromine content has remained unchanged.

Thus, by using the bromine content of halite to measure the salinity of the brine from which the halite precipitated, one can reconstruct the history of salinity in the basin of deposition. The scope of this paper is limited to the halite stage of precipitation of four salt beds in the upper part of the Paradox Member. Salt beds 2, 3, and 4 are composed only of halite rocks; salt bed 5 contains sylvite in the upper 16 feet.

METHODS OF ANALYSIS

Samples of halite were collected at 2-foot intervals through the total thickness of each salt bed. Approximately 4 grams of material were selected from each sample and crushed to granule size. This material was hand picked to get the purest sample of halite possible from each interval. The selected grains of halite were then ground to a fine powder. Approximately 2 grams of material were used for analysis.

The analyses for bromine were by X-ray fluorescence spectrometer; equipment used was a North American Phillips X-ray fluorescence unit: the spectrograph was a vacuum type (used without vacuum) with inverted optics; radiation was from a tungsten tube operated at 50 KV-40 Ma; the analyzer crystal was lithium fluoride; the detector was a scintillation type; the recorder had an integrating circuit; a spinner in the spectograph rotated the sample during analysis to insure uniform exposure to the X-rays. An aluminum filter was placed over the tungsten tube window. Sample holders were Caplugs covered by Mylar of 0.25 mil thickness.

Each sample was scanned through 4 degrees 2 Θ, from 28 to 32 degrees, at the rate of 4 degrees per minute. The bromine peak scanned was K_{α_1}, 1st order at 29.93 degrees 2 Θ. The limit of sensitivity for bromine in a matrix of sodium chloride is 70 ppm. X-ray traces of the halite samples were compared to traces of artificially prepared standards of known bromine content. The precision of the method is plus or minus 16 per cent.

As a check on the accuracy of the X-ray method, 86 samples were also analyzed chemically using a modification of a method described by Strenger and Kolthoff (1935). The two methods were substantially in agreement, but at the low bromine contents of these samples the X-ray method appears to be less subject to small but noticeable errors than does the chemical method.

DESCRIPTION OF CORE

The halite samples were obtained from the core of a well drilled near the crest of the Cane Creek anticline, Grand County, Utah (Sec. 25, T. 26 S., R. 20 E). Total depth of the well is 2805 feet. The stratigraphic interval discussed in this paper is represented by core between 1800 and 2805 feet (Fig. 2).

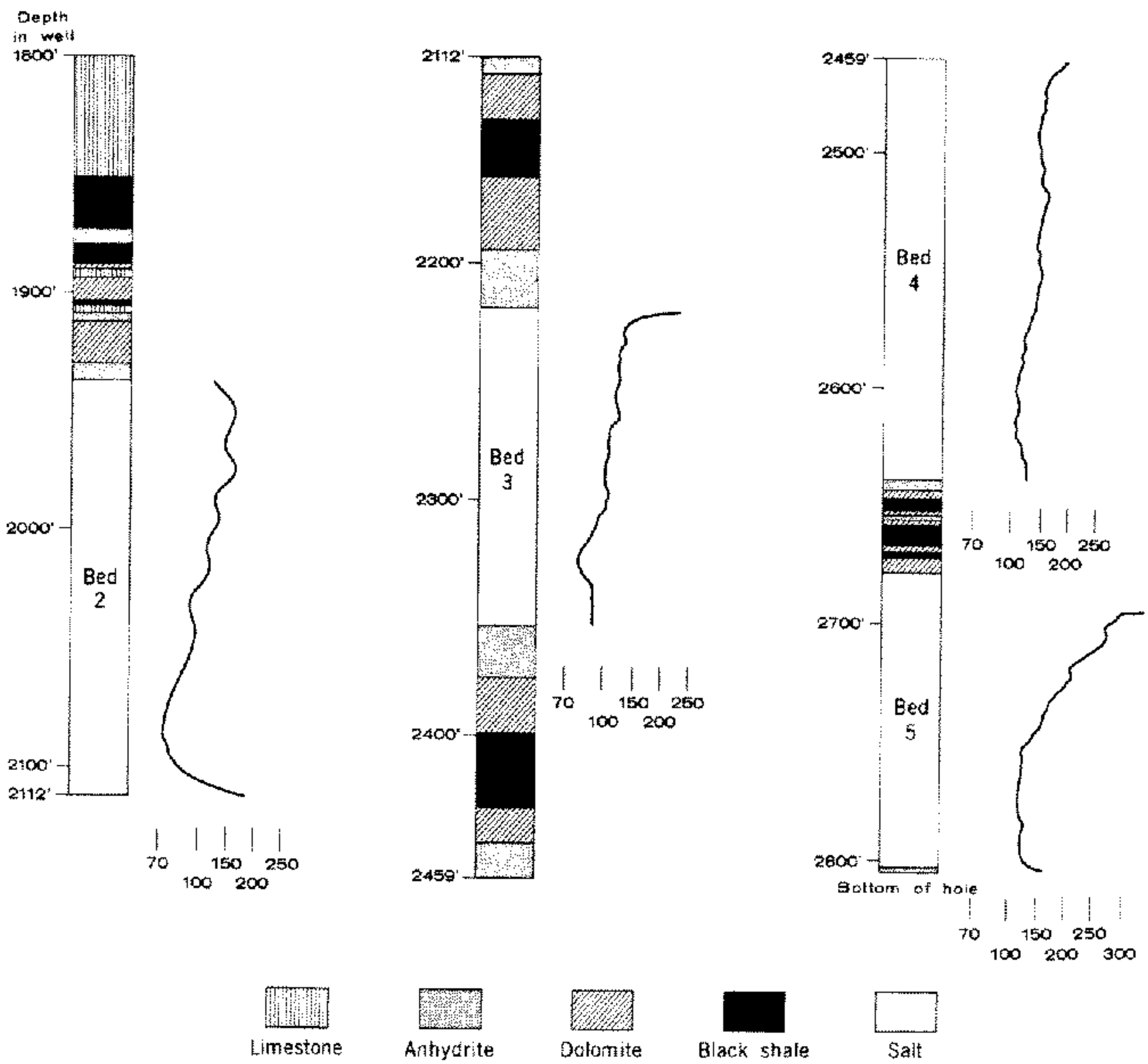

Figure 2. Stratigraphic column represented by well core. Generalized bromine profiles are to the right of each salt bed, bromine content in parts per million.

The section of the Paradox Member penetrated by the well contains four halite beds, each separated from the others by penesaline and clastic beds of anhydrite, silty dolomite, and black shale. The four halite beds are salt beds 2, 3, 4, and 5 in the terminology of Hite (1960). Salt bed 1, the uppermost salt bed in the Paradox Member, is missing in the area of the Cane Creek anticline (Hite, in press). These salt beds are only a few of the many known to exist in the region; a total of 24 are known to be present in the Cane Creek anticline.

The halite in all the salt beds except bed 5 is clear to white, or grayish to white where the rock has disseminated crystals of anhydrite. Salt bed 5 generally is clear to gray or light brown, but has a red tinge near the top of the bed. The upper 16 feet of the bed contains commercial grade sylvite that is being mined by the Texas Gulf Sulphur Company.

The four salt beds have laminae of anhydrite approximately 1/16 of an inch thick. Near the bottom of each bed the laminations are about 1 inch apart; near the top they may be as much as 6 inches apart. The laminations are most widely separated in the potash zone of salt bed 5, where they are as much as 8 inches apart.

The penesaline and clastic intervals between salt beds 2 and 3 and between 3 and 4 have a symmetrical cyclic arrangement (Fig. 2); each has anhydrite on the bottom, overlain successively by silty dolomite, black shale, silty dolomite, and anhydrite. The contact of the lower anhydrite with the underlying halite is abrupt; the upper anhydrite grades into the overlying halite through a thickness of 2 to 3 feet. All contacts within the penesaline and clastic intervals are gradational.

Salt bed 2 is overlain by anhydrite and then dolomite, but above this a cyclic pattern is not evident. Overlying rocks are mostly normal marine fossiliferous limestone. The penesaline and clastic interval between salt beds 4 and 5 is thinner than the other three, and the lithologies are not in a regular cyclic order (Fig. 2).

BROMINE PROFILES

Bromine analyses at 2-foot intervals are plotted in Figs. 3 through 6. The resulting profiles were smoothed by a moving average of five points. The profiles of salt beds 2, 3, and 4 are complete through the entire halite interval. The profile for salt bed 5 lacks data for the upper 16 feet, because this interval is the potash ore zone and core material was unavailable for study.

Salt bed 2 profile. In the profile for salt bed 2 (Fig. 3), the bromine content at the base is 180 ppm and decreases upward to a minimum of 70 ppm at 2088 feet. The bromine content increases from 70 to 160 ppm between 2088 and 1950 feet and again decreases in the upper 14 feet of the salt bed.

These three trends in bromine content -- first a decrease, then an increase, and finally another decrease -- correspond to changes in basin salinity during the deposition of salt bed 2. Initially the salinity was high relative to the total salinity range through which halite precipitates, and, during deposition of the lower 24 feet of halite, the salinity of the parent brine was rapidly decreasing. From 2088 up to 1950 feet the salinity of the brine generally increased, yet from the frequent change in slope of the profile, indicating a rhythmic increase and decrease of bromine in the halite, it is clear that the increase in salinity of the brine was interrupted four times by brine dilution that probably resulted from influx of sea water into the basin. Subsequently, during the deposition of the upper 14 feet of salt bed 2, the salinity of brine decreased rapidly, probably as a result of the return to open sea conditions. Rocks not far above salt bed 2 are dominantly normal marine limestones of the upper member of the Hermosa Formation.

Salt bed 3 profile. The profile of salt bed 3 (Fig. 4) shows a bromine content of 90 ppm in the bottom part of the bed, 2352 to 2336 feet, a decrease to 75 ppm between 2336 and 2325 feet, and an increase for the entire interval from 2325 feet to the top of the bed at 2220 feet. From 2325 to 2230 feet the bromine content increases from 75 to 130 ppm but with enough irregularities to suggest the existence of cycles, similar to those shown more clearly by salt bed 2. The upper 10 feet of this salt bed has a very great increase in bromine content -- so great, in fact, that at the top it falls just short of the salinity necessary for the precipitation of potash minerals.

The 90 ppm bromine content of the halite in the lower 16 feet of salt bed 3 represents a brine salinity that is above the minimum for the deposition of halite, but from 2336 to 2325 feet the

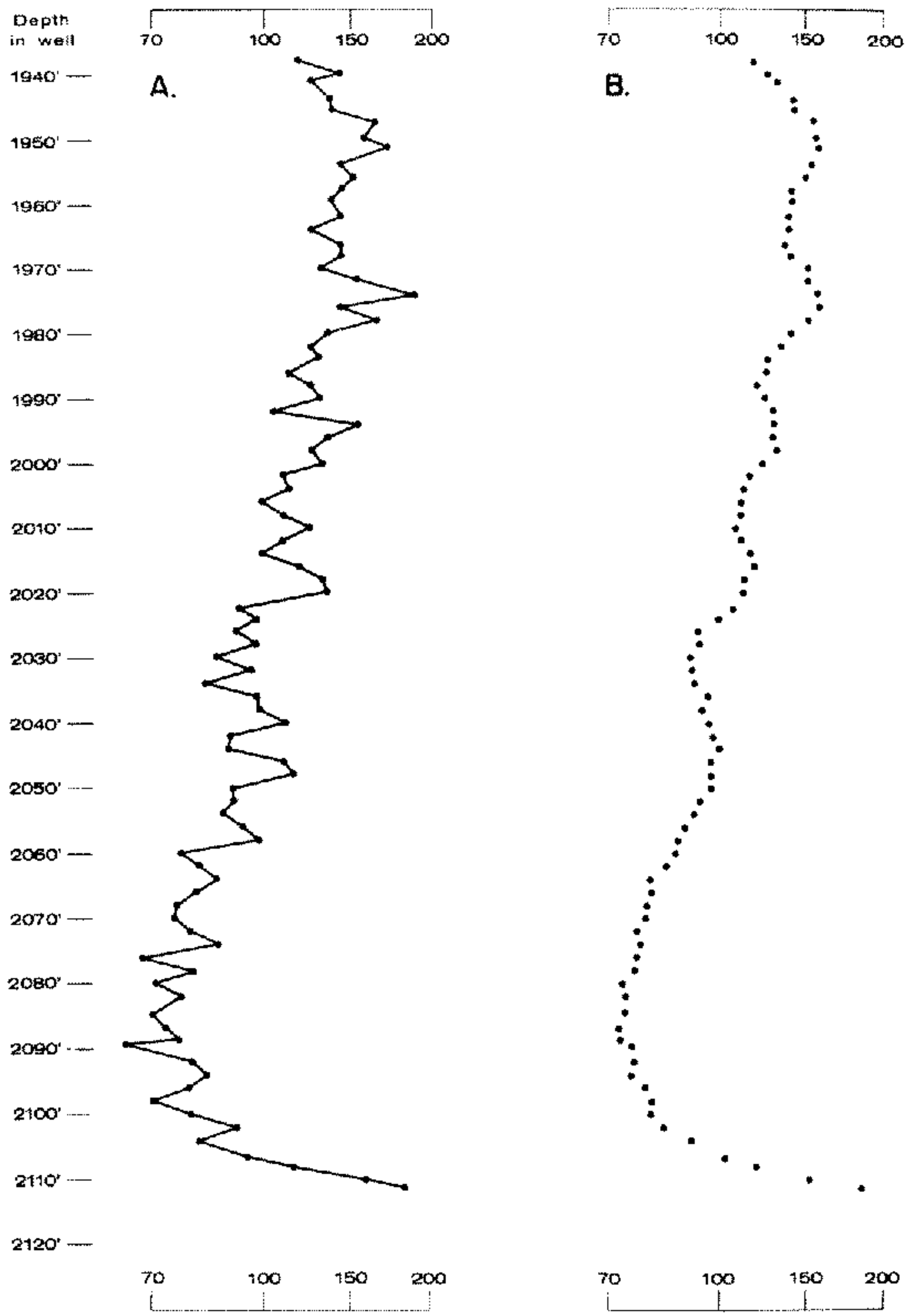

Figure 3. Bromine profile of salt bed 2, content in parts per million.
A. Analysis values ---- B. Smoothed profile.

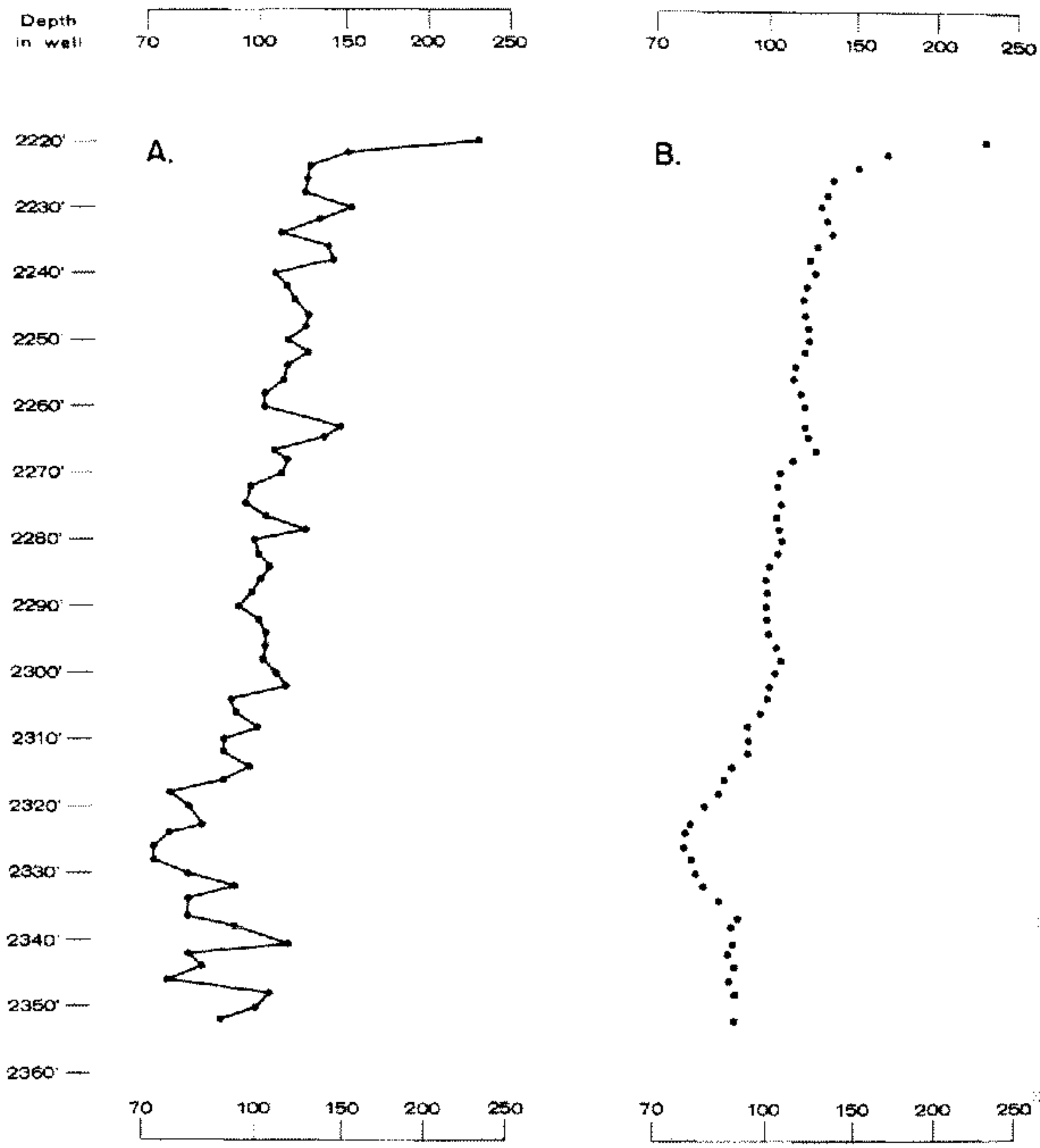

Figure 4. Bromine profile of salt bed 3, content in parts per million.
A. Analysis values ---- B. Smoothed profile.

salinity decreased to a value close to that at which halite would cease to crystallize. From 2325 to 2230 feet the salinity generally increased, but there was occasional influx of fresher brines. The rapid increase in salinity in the upper 10 feet of salt bed 3 is of particular interest. It may mean that the influx of sea water into the basin was entirely cut off or that the movement of water was restricted by more local conditions. Regardless of the cause, this horizon is one worthy of attention in the future exploration for potash.

Salt bed 4 profile. The profile of salt bed 4 (Fig. 5) is similar to that of salt bed 3 and reflects a similar history of salinity. The base of the bed at 2640 feet has only 125 ppm bromine and this decreases to 100 ppm at 2616 feet. From 2616 fo 2520 feet the bromine content gradually increases to 160 ppm, with little evidence of cyclic character. Between 2520 and the top of the bed

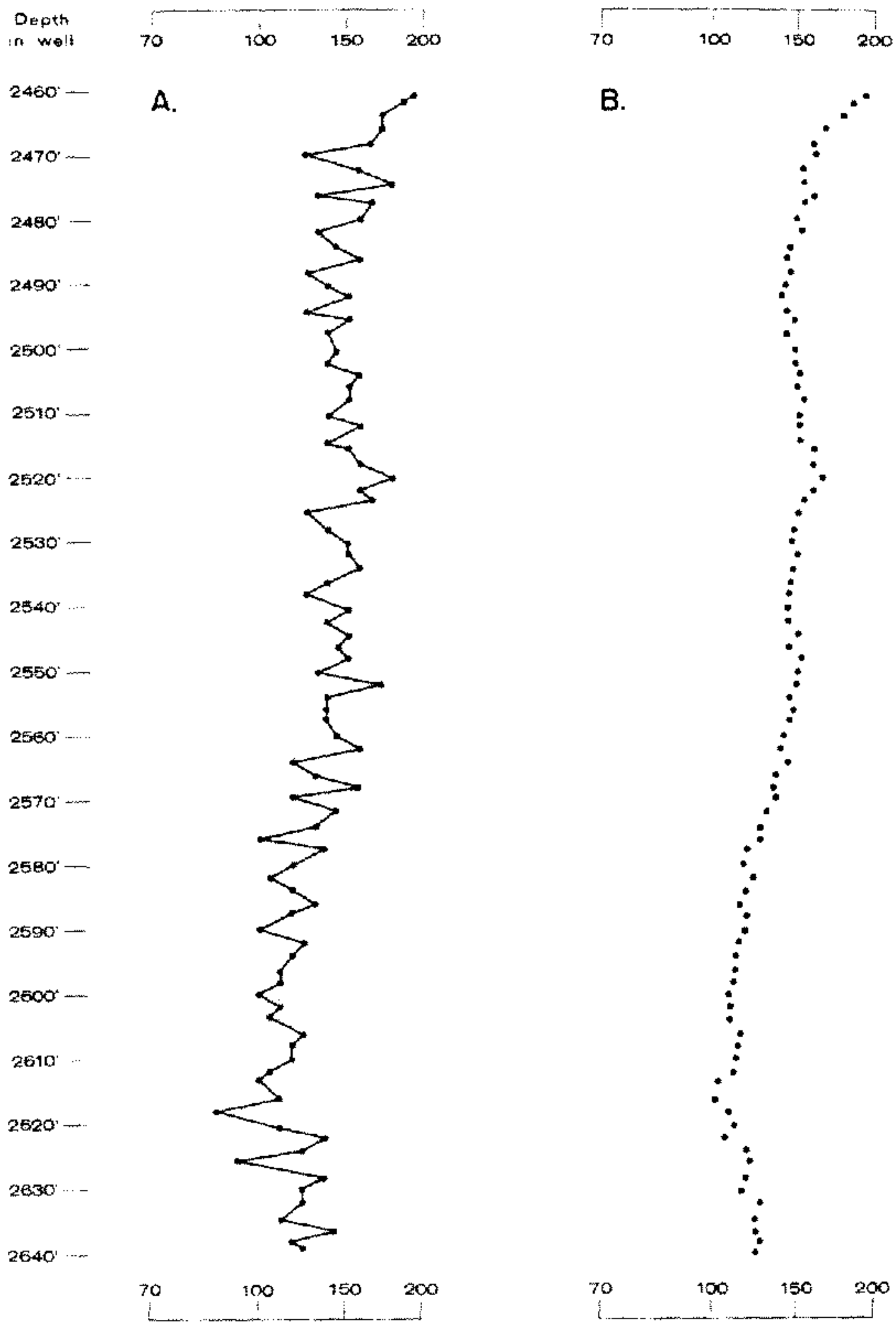

Figure 5. Bromine profile of salt bed 4 content in parts per million.
A. Analysis values ---- B. Smoothed profile.

at 2461 feet the bromine content first decreases slightly to 140 ppm at 2492 feet, then increases to 190 ppm at the upper contact.

The chief difference between this profile and those for salt beds 2 and 3 is that the bromine content of the halite is nearly the same throughout the bed, indicating very little change in salinity of the brine during deposition. Maintaining nearly constant salinity during deposition of 180 feet of halite requires not only flow of sea water into the basin but also reflux of bittern brines out of the basin, for without loss of bittern brines, bromine would have accumulated along with potassium and magnesium and thus increased the total salinity. In short, the nearly vertical bromine profile for salt bed 4 shows that the influx-evaporation-reflux system must have been in very close balance.

Salt bed 5 profile. Salt bed 5 (Fig. 6) has a wider range of bromine values than the other salt beds, yet the shape of the profile and the history of salinity are similar to those of salt bed 3. The bromine content at the base of the bed is 170 ppm but decreases within 5 feet to about 120 ppm

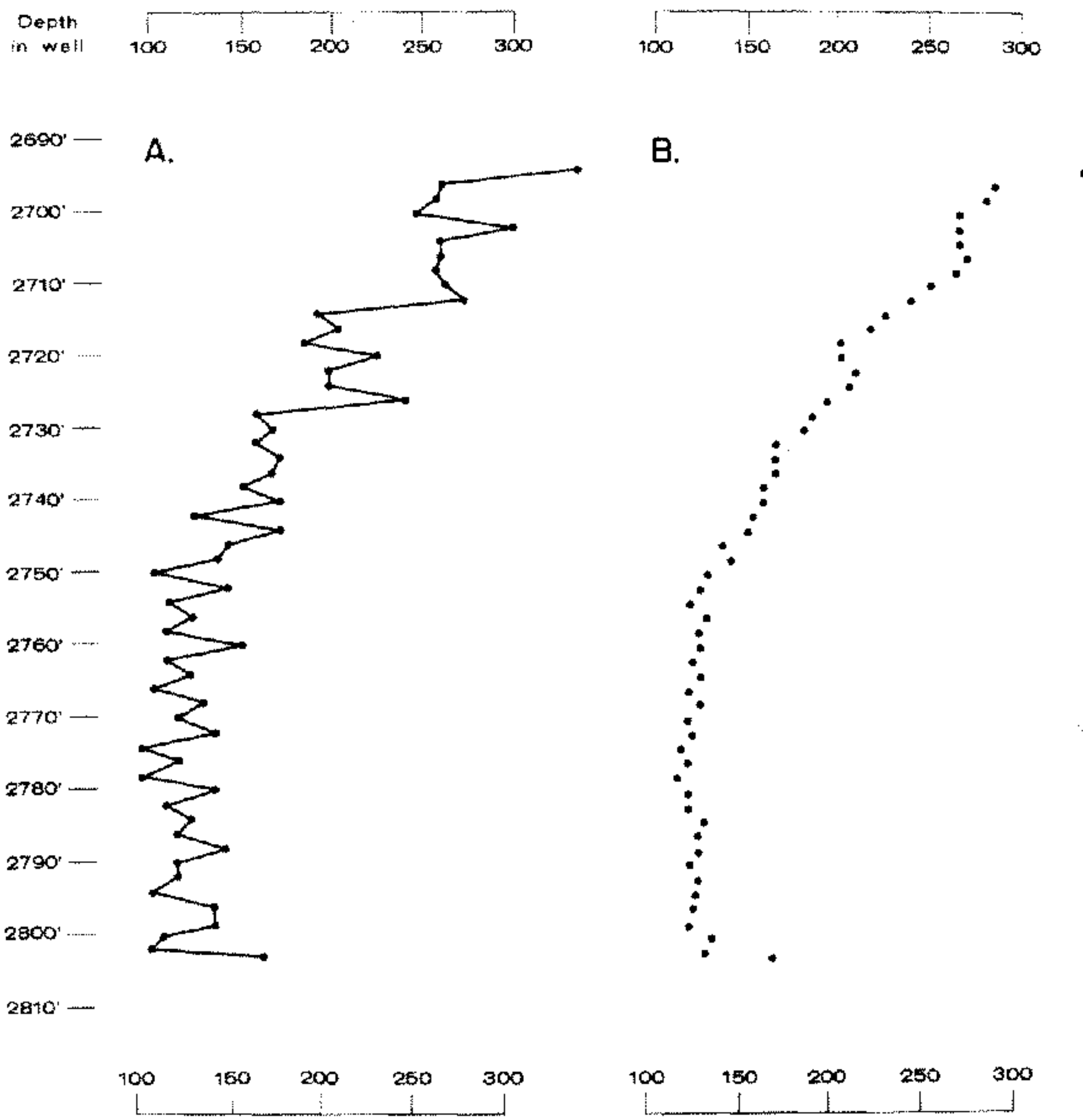

Figure 6. Bromine profile of salt bed 5, content in parts per million.
A. Analysis values ---- B. Smoothed profile.

mains at that level from 2798 to 2754 feet. From 2754 feet to the top of the profile at 2694 e bromine content increases rapidly but with rhythmic increases and decreases like those of ofiles of salt beds 2 and 3. All of these changes in bromine content signify corresponding es in salinity.

A 16-foot sylvite zone lies at above 2694 feet, but core material was unavailable for bro- analysis. Undoubtedly the bromine content of the halite is greater than in the underlying beds ie salinity of the original brine was higher.

The lowest bromine content of this salt bed, 120 ppm, is higher than the minimum values of her three profiles. From this one infers that the salinity of the brine was initially higher the brines from which salt beds 2, 3, and 4 precipitated. In all likelihood, there also was little dilution of brines with normal sea water during the deposition of the penesaline and ic rocks that immediately underlie salt bed 5. During deposition of salt bed 5, a period in h a rapid increase in salinity is indicated by the bromine profile, influx of sea water must been greatly restricted, if not cut off entirely.

Salinity at outset of halite crystallization. The high bromine content at the bottom of each of our salt beds is of particular interest. This feature is especially noticeable in salt bed 2, re the bromine content of the lowest halite is 180 ppm; during the deposition of the lower 24 , the bromine content decreased to 70 ppm. One can infer from this that the salinity of the ie during the initial depositional stages of salt bed 2 was high and that during the deposition of following 24 feet of salt, the brine became diluted nearly to, but not below, the minimum salin- for halite deposition. According to widely accepted general theory, the bromine content at the e of a salt bed should be at the minimum value for the deposition of halite and it should increase ard as the salt is being deposited. Initial high salinity, indicated by high bromine content at base of salt bed 2 requires conditions other than those proposed by the general theory. In ad- on to the aforementioned observation, one must note that the salinity at the top of salt bed 3 s high, indicated by a bromine value of 240 ppm. Considering the conditions of high salinity at end of deposition of salt bed 3 and high salinity at the beginning of salt bed 2, one wonders out the salinity during the deposition of the penesaline and clastic rocks between these salt beds.

In an attempt to solve this problem, samples of the anhydrite, dolomite, and black shale re analyzed for bromine; bromine values for the dolomite and black shale range from 110 to 0 ppm. The manner in which the bromine is held in these rocks is uncertain. Bromine-rich florescences on freshly cut surfaces of the core suggest, however, that the bromine occurs in gh salinity brines, or residues thereof, in the pore spaces in these rocks. The anhydrite con- ins no bromine. Examination of thin sections reveals a lack of porosity in the anhydrite, which obably explains the absence of bromine. High bromine content at the top of salt 3, in the dolo- ite and black shale above salt 3, and in the bottom of salt 2, suggest, therefore, that the salinity f the basin, at least at the solid-liquid interface, remained high throughout deposition of these ocks.

Similar investigations made of the black shale and dolomite between salt beds 3 and 4, and eds 4 and 5 show the same bromine relations; therefore, the history of salinity for these inter- als is the same as that for the interval between salt beds 2 and 3.

CONCLUSIONS

Profiles of the bromine content of the salt beds show a systematic increase from near the bottom of each salt bed to its top. This change reflects increasing salinity of brine during the time the salt was precipitated. The consistency of the results from one salt bed to another indicates that the deposition of each was continuous. Irregularities in the profiles are so small that they can be explained by minor changes in the salinity of the water, rather than by postulating breaks in sedimentation. The bromine values in the upper part of salt bed 5 indicate a great increase in salinity, which ultimately led to the precipitation of sylvite in commercial quantitites. Two other beds show evidence for sharp increases in salinity near their tops but not enough to yield potassium minerals. Still another bed has evidence for decreasing salinity in its upper part. In short, one extreme is represented by salt bed 5, which reflects an environment in which there were severe restrictions on the influx of sea water and the reflux of bittern brines; the other extreme represents the removal of all restrictions and return to salinity conditions normal to the open sea.

The work reported here is no more than a beginning in the use of the bromine distribution technique in interpreting the depositional history of the evaporites in the Hermosa Formation. To do the same work on all 29 salt beds of the basin in many drill holes would be a large undertaking, but results to date suggest that a bromine distribution study would yield an enormous amount of information about lateral as well as vertical changes in the sedimentary regimen. Were this technique to become a routine part of all drilling in the region, it might well point to localities and to horizons worthy of further exploration for potash.

REFERENCES

Baar, A., 1954, Untersuchungen des Bromgehalts im Zechsteinsalz: Bergbautechnik, vol. 4, pp. 284-288.

________, 1955, Zur stratigraphischen Orientierung im Kalibergbau durch den Bromtest: Bergbautechn., vol. 5, pp. 40-47.

Block, M. R., and Schnerb, J., 1953, On the Cl^-/Br^--ratio and the distribution of Br^- ions in liquids and solids during evaporation of bromide-containing chloride solutions: Bull. Research Council Israel, vol. 3, pp. 151-158.

Boeke, H. E., 1908, Über das Kristallisationsschema der Chloride, Bromide, Jodide von Natrium, Kalium und Magnesium, sowie uber das Vorkommen des Broms und das Fehlen von Jod in den Kalisalzlagerstätten: Z. Krsit., vol. 45, pp. 346-391.

Braitsch, O., 1962, Entstehung und Stoffbestand der Salzlagerstätten: Berlin-Gottingen-Heidelberg, Springer Verlag.

__________, and Hermann, A. G., 1962, Zur Bromverteilung in salinaren Salzsystemen bei 25°C: Naturwissenschaften, vol. 49, p. 346.

__________, and Hermann, A. G., 1963, Zur Geochemie des Broms in salinaren Sedimenten, Teil I: Experimentelle Bestimmung der Br-Verteilung in verschiedenen natürlichen Salzsystemen: Geochim. et Cosmochim. Acta, vol. 27, pp. 361-391.

__________, and Hermann, A. G., 1964, Zur Geochemie des Broms in salinaren Sedimenten, Teil II: Die Bildungstemperaturen primärer Sylvin-und Carnallit-Gesteine: Geochim. et Cosmochim. Acta, vol. 28, pp. 1081-1109.

D'Ans, J., and Höfer, P., 1934, Untersuchungen an Brom: Z. f. angew. Chemie, vol. 47, pp. 71-74.

________, and Kühn, R., 1940, Über den Bromgehalt von Salzgesteinen der Kalisalzlagerstätten: Kali, vol. 34, pp. 43-46, 59-64, 77-83.

Hite, R. J., 1960, Stratigraphy of the saline facies of the Paradox Member of the Hermosa Formation of southeastern Utah and southwestern Colorado, in Four Corners Geol. Soc. Guidebook Field Conf. No. 3: Geology of the Paradox basin fold and fault belt, 1960, pp. 86-89.

________, 1961, Potash-bearing evaporite cycles in the salt anticlines of the Paradox basin, Colorado and Utah: Art 337 in U. S. Geol. Survey Prof. Paper 424-D, pp. D135-D138.

________, in press, Salt deposits of the Paradox basin, Southeast Utah and Southwest Colorado, U. S. A.

Kühn, R., 1955a, Über den Bromgehalt von Salzgesteinen, insbesondere die quantitative Ableitung des Bromgehaltes nichtprimärer Harsalze oder Sylvinite aus Carnallit: Kali und Steinsalz, vol. 1, no. 9, pp. 3-16.

________, 1955b, Tiefenberechnung des Zechsteinmeeres nach dem Bromgehalt der Salze: Deutsche geol. Gesell. Zeitschr., vol. 105, pp. 646-663.

Ogienko, V. S., 1959, Distribution of bromine in the rock salt of the Angara-Lena salt basin and the possibility of finding potassium salts: Geochemistry (translated from Russian) no. 8, pp. 893-900.

3., 1958, Beitrag zur Stratigraphie und Genese der Salzserien 1-4 des mitteldeutschen eins, unter besonderer Berücksichtigung der Bromverteilung: Freiberger Forschung- A123.

——, 1960, Stratigraphische und genetische Deutung der Bromverteilung in den mittel- :hen Steinsalzlagern des Zechsteins: Freiberger Forschungshefte, C83, p. 114.

ner, W.M., and Wardlaw, N.C., 1963, Geochemistry of bromine in some salt rocks of :airie Evaporite Formation of Saskatchewan, in Symposium on Salt: Northern Ohio Geol. pp. 240-246.

V.A., and Kolthoff, L.M., 1935, The detection and colorimetric estimation of micro- :ities of bromide: Jour. Am. Chemical Soc., vol. 57, pp. 5, pp. 831-833.

.ko, M.G., 1956, Geochemistry of bromine in the processes of salt deposition and the use e bromine content as a genetic and prospecting criterion: Geochemistry (Geokhimiya) 6, pp. 570-589.