

Lacustrine Deposits of Bromine-Bearing Halite, Green River Formation, Northwestern Colorado¹

John R. Dyni
Robert J. Hite
Omer B. Raup
U.S. Geological Survey
Denver, Colorado

ABSTRACT

Bedded halite and nahcolite (NaHCO_3) form an evaporite facies in the rich oil-shale deposits of the lacustrine Green River Formation of Eocene age in northwestern Colorado. The evaporites consist of thin alternating layers of halite and nahcolite which form couplets that average 5 cm in thickness. These are believed to represent yearly cycles of evaporitive sedimentation and are probably analogous to the varves that characterize the lacustrine marlstones of the formation.

About 170 samples of halite from one core hole drilled near the depocenter of the evaporites in the basin were found to contain bromine in amounts ranging from 15 to 182 ppm. The quantity of bromine in the halite increased progressively from the base to near the top of the halite-bearing section, which in the core hole attains a thickness of about 440 feet. Comparable amounts of bromine ranging from 39 to 157 ppm were found in several core samples of halite from the halite and trona deposits in the Green River Formation, southwestern Wyoming. Contemporaneous volcanic sediments or gaseous emanations and older marine evaporites are suggested sources for the bromine.

Using bromine as a salinity indicator, together with other geologic evidence, the paleosalinities of the ancient lake waters are interpreted to have gradually increased during deposition of the rocks in the lower part of the Parachute Creek Member containing the evaporites. The paleosalinities decreased later in Parachute Creek time during deposition of the rocks of the Mahogany zone which mark a great expansion of the lake.

INTRODUCTION

Rhythmically bedded halite and nahcolite (NaHCO_3) form an evaporite facies in organic-rich marlstones (oil shales) of the lacustrine Green River Formation of Eocene age in northwestern Colorado. Studies of core samples from these evaporites show that the halite contains bromine in amounts ranging from 15 to 182 ppm. Compared with the few published analyses of the bromine content in other halite deposits of continental origin, the amount of bromine in the Green River halite is unusually high.

The stratigraphy and lithology of the Green River evaporite deposits are described and the results of the bromine studies are presented in an attempt to relate the bromine data and other geochemical and mineralogic information to the paleosalinities of ancient Lake Uinta in which the evaporites and associated rocks were deposited.

We thank Mr. Edward Rosar of Wolf Ridge Minerals Corp. and Mr. Joe T. Juhan, Tucson, Ariz., for permission to publish the drill core data on which much of this paper is based. The bromine determinations were made by O.B. Raup, H.L. Groves, Jr., and J.S. Wahlberg of the U.S. Geological Survey. P.L. Hauff, of the U.S. Geological Survey, examined selected samples under the petrographic microscope for mineral contaminants. W.C. Culbertson, of the U.S. Geological Survey, provided core samples of halite from the Wyoming halite-trona deposits.

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

GEOGRAPHIC AND STRUCTURAL SETTING

The Eocene Green River Formation was deposited in several large sedimentary-structural basins in parts of Colorado, Wyoming, and Utah (Fig. 1). The Green River contains extensive

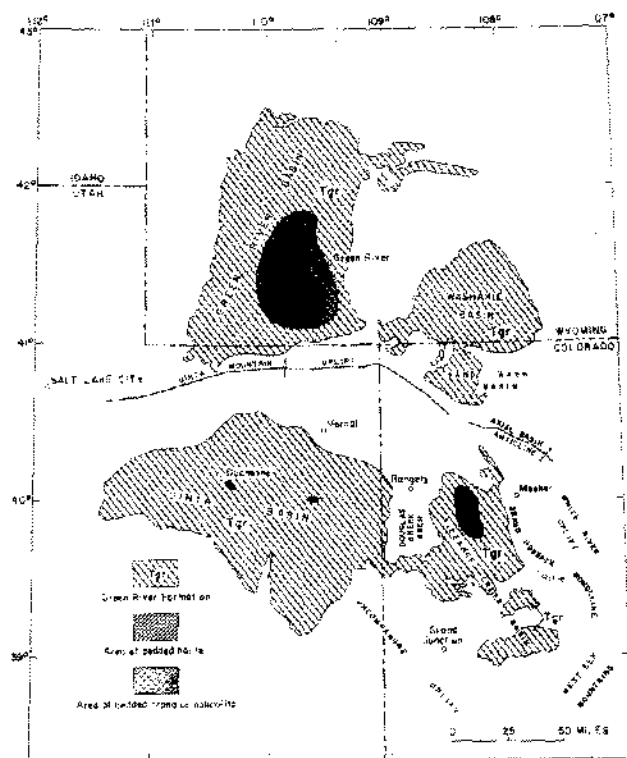


Figure 1. Distribution of bedded salines in the Green River Formation in Colorado, Wyoming, and Utah.

deposits of trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) and halite in southwestern Wyoming (Deardorff, 1963; Culbertson, 1966); nahcolite deposits of unknown areal extent occur at two localities in Utah (Hite, 1964, p. 209, 211). The halite deposits discussed in this paper are in the northern part of the Piceance Creek basin in Rio Blanco County, northwestern Colorado.

The Piceance Creek basin is both a sedimentary and structural basin that attains a maximum width in an east-west direction of about 50 miles and a length in a north-south direction of about 90 miles. Structural features peripheral to the basin include

the Grand Hogback monocline and the White River uplift to the east, the Axial Basin anticline and the Uinta Mountain uplift to the north, and the Douglas Creek arch to the west. The West Elk Mountains, a Tertiary intrusive and volcanic complex, and the Uncompahgre uplift lie to the southeast and southwest, respectively, of the basin.

STRATIGRAPHY

The Green River Formation in the Piceance Creek basin is divided into the following members: the Douglas Creek, Garden Gulch, Parachute Creek, Evacuation Creek, and Anvil Points (Fig. 2). The Anvil Points Member is present along the east side of the basin and is laterally equivalent to parts

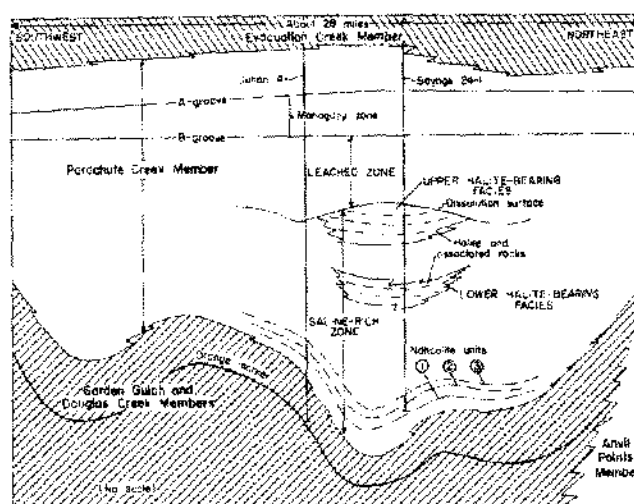


Figure 2. Stratigraphic cross section through the depositional center of the evaporite deposits in the Piceance Creek basin showing the relationship of the halite deposits to the enclosing rocks of the Green River Formation.

of the Douglas Creek, Garden Gulch, and Parachute Creek Members. The orange marker, a distinctive electric log marker in the Garden Gulch Member, is persistent throughout most of the basin and is useful in subsurface correlation.

In the north-central part of the Piceance Creek basin, where the halite deposits are located, the maximum thickness of the Parachute Creek Member is about 2,000 feet. This member contains most of the rich oil shales of the Green River Formation as well as associated deposits of nahcolite, dawsonite [$\text{NaAl}(\text{OH})_2\text{CO}_3$], and halite. The Mahogany zone is a widespread unit, 100 to

200 feet thick, in the upper part of the member and consists of generally rich oil shale. It is bounded at the top and base by units of organic-lean tuffaceous marlstone known as the A-groove and B-groove, respectively.

The Parachute Creek Member below the B-groove can be informally divided into a lower saline-rich zone and an upper leached zone. This informal division is convenient for discussing the sodium-mineral deposits. The saline-rich zone consists of medium- to rich-grade oil shales that contain large amounts of disseminated and bedded nahcolite, disseminated dawsonite, and lesser amounts of bedded halite. Three persistent nahcolite units, numbered 1, 2, and 3, are near the base of the saline-rich zone. Many other nahcolite-bearing units which are present in the saline-rich zone are not shown in the cross section, Figure 2. The base of the saline-rich zone is arbitrarily picked at the base of the continuous rich oil shales which is also the approximate base of the Parachute Creek Member (Fig. 2).

The halite deposits are concentrated in two lenticular sequences in the upper part of the saline-rich zone and are designated herein as the lower and upper halite-bearing facies. The maximum thickness of these deposits is in the vicinity of the John Savage core hole 24-1 in sec. 24, T. 1 S., R. 98 W. This location is the approximate depositional center of the saline deposits in the Piceance Creek basin. In this same well the upper halite-bearing facies is about 200 feet thick and the top occurs about 1,800 to 1,900 feet below the surface. The upper and lower halite-bearing facies are separated by about 150 feet of nahcolitic oil shale which locally contains a thin halite unit. The lower halite-bearing facies is about 100 feet thick. The areal extent of the halite deposits is estimated to be about 50 square miles.

A leached zone of rocks several hundred feet thick consisting of mostly broken and locally brecciated oil shales overlies the saline-rich zone. Open solution cavities in these rocks are common. The base of the leached zone is a dissolution surface which forms a generally sharp contact with the rocks of the underlying unleached saline-rich zone. The dissolution surface is irregular and cuts across rock-stratigraphic units. The upper extent of the leached zone is somewhat indefinite but it probably includes at least the lower part of the Mahogany zone. The leached zone is water bearing,

and removal of water-soluble minerals at the dissolution surface is probably still taking place.

The leached zone probably once contained bedded halite and nahcolite. In the Juhan core hole 4-1, which is located just outside the area of the halite deposits (Fig. 2), unpublished stratigraphic data show that as much as 150 feet of halite and nahcolite was removed by ground-water dissolution. The original thickness and areal extent of the halite and nahcolite deposits prior to leaching are unknown.

Dawsonite, which occurs in oil shales of the saline-rich zone of the Parachute Creek Member (minor amounts are present in younger rocks of the member), is distributed throughout a wide area in the northern part of the Piceance Creek basin (Fig. 3). Maximum concentrations of the mineral are in and adjacent to the area of halite deposition. Although data are incomplete, the distribution of nahcolite is probably similar to that of dawsonite.

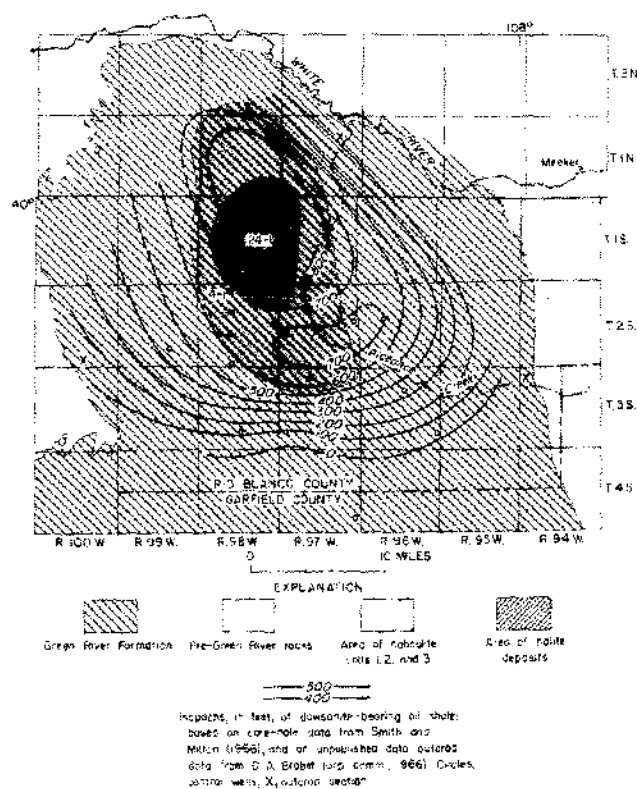


Figure 3. Map of the Green River Formation in the northern part of the Piceance Creek basin showing the distribution of dawsonite, three nahcolite units, and halite.

PETROLOGY

Halite-bearing rocks.

In the Savage core hole 24-1 the upper and lower halite-bearing facies consists of thin-bedded to thinly laminated halite and nahcolite which form units 6 to 70 feet thick that are interstratified with beds of nahcolite-rich oil shale 9 to 24 feet thick. A few fine-grained dense nonlaminated beds tentatively identified as volcanic tuffs, commonly less than 1 inch thick, occur in the rocks between the lower and upper halite-bearing facies. Tuffs become more numerous in the upper part of the Parachute Creek Member above the saline-rich zone.

A typical unit of bedded halite and nahcolite consists of many rhythmically alternating thin beds to thin laminae of halite and nahcolite and some scattered thin beds to laminae of varved oil shale or organic-lean marlstone (Fig. 4). The alternating layers of halite and nahcolite form couplets that range commonly from 2 to 15 cm in thickness, although some are paper thin. Some individual halite and nahcolite beds and laminae show faint to distinct rhythmic stratification caused by small

amounts of brownish organic matter. This is another type of couplet consisting of a slightly organic-enriched layer and an organic-free layer of nahcolite (or halite). Individual layers of halite, in typical halite-nahcolite couplets, commonly range from 2 to 15 cm in thickness; the nahcolite layers are usually thinner and commonly range from about 0.5 to 5 cm in thickness. The thicknesses of 215 couplets were measured in selected parts of the lower halite-bearing facies where the couplets are clearly developed and the following results were obtained:

	Average thickness (cm)
Nahcolite layer	2
Halite layer	3
Halite-nahcolite couplet	5

As determined from these measurements, the ratio of halite to nahcolite in the couplets of the lower halite-bearing facies is 1.5:1. A similar halite-to-nahcolite ratio was obtained in the upper halite-bearing facies.

In a typical couplet the halite is clear to light smoky gray and medium to mostly coarsely crystalline; some halite crystals are as large as 25 mm across. Some halite layers contain brownish cloudy wisps of organic matter. The halite is overlain by a generally thinner layer of dense fine to microcrystalline nahcolite. The nahcolite is commonly colored tan to light brown by small to moderate amounts of disseminated organic matter. The nahcolite is usually gradational with the halite below, but it has a sharp contact with the halite layer in the next couplet above.

Although there are differences in the thickness and mineralogy of the halite-nahcolite couplet and the oil-shale varve, there are some similarities worth noting. According to Bradley (1929, p. 95-96) the varve in Green River oil shale and associated rocks represents a yearly unit of sedimentation which is composed of two thin laminae, one being richer in organic matter. The two laminae are usually sharp and distinct. In some limy lacustrine sandstones the boundary between the two laminae is gradational although the contact between successive varves is sharp. Bradley did not measure the separate thicknesses of the laminae comprising the varves, but he did note that in some limy sandstones the organic-poor layer is two to three times thicker than the organic-rich layer. It seems likely that the halite-nahcolite couplet and the oil-shale varve are analogous units of sedimentation.

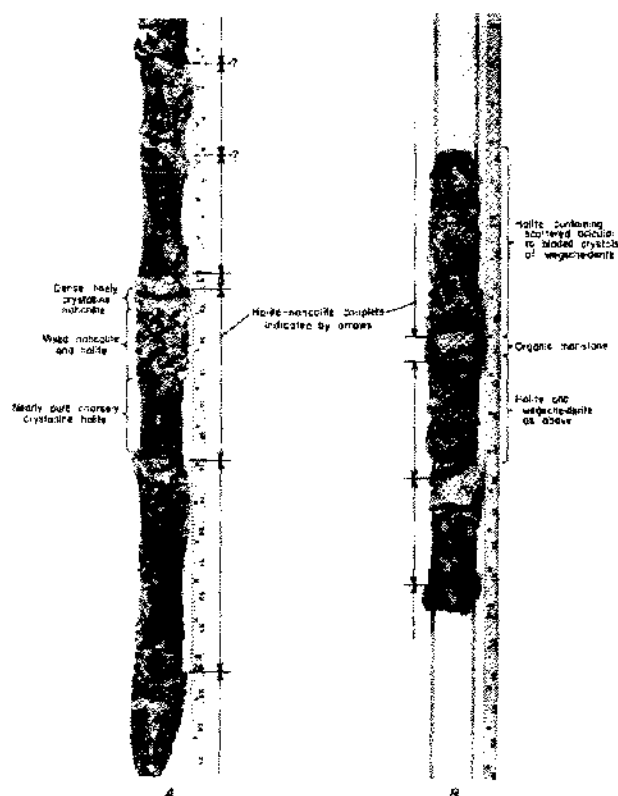


Figure 4. Photographs of core from the Savage core hole 24-1 showing the typical rhythmically bedded character of the halite deposits.

Other workers have demonstrated that individual varves in the Green River oil shales can be traced laterally for many miles (Curry, 1964; Smith, 1969, p. 187). Individual halite-nahcolite couplets also persist laterally and can be correlated in core holes spaced as much as 3 miles apart (Fig. 5).

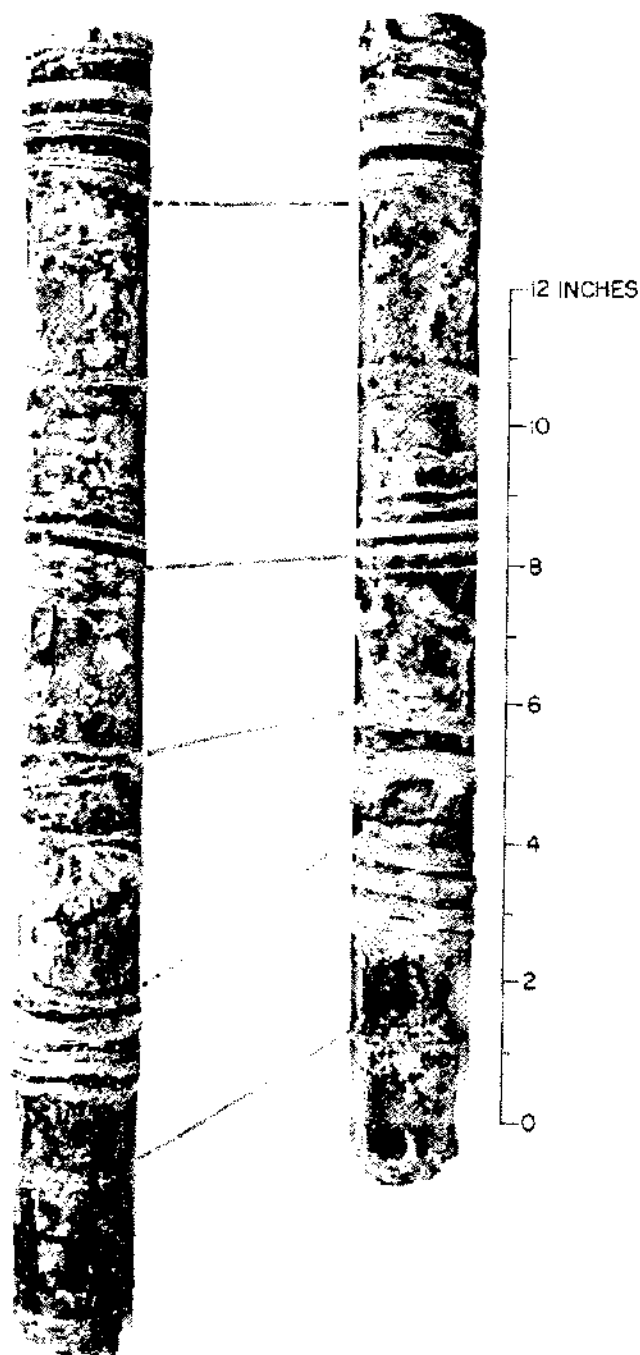


Figure 5. Correlation of halite-nahcolite couplets in cores from two core holes in the Piceance Creek basin spaced about 3 miles apart.

All the evidence indicates that the halite deposits in the Piceance Creek basin are primary evaporites. The rhythmic layering of these deposits as displayed by the halite-nahcolite couplets is believed to represent yearly cycles of evaporative sedimentation which were controlled basically by seasonal variation in temperature and precipitation. Each couplet is probably represented by a varve, or possibly by a diastem, in varved oil shales or organic-lean marlstones laterally adjacent to the halite facies.

Presuming a typical halite-nahcolite couplet grades laterally into an oil-shale varve, a possible microlithofacies relationship between the two units of sedimentation is shown in Figure 6.

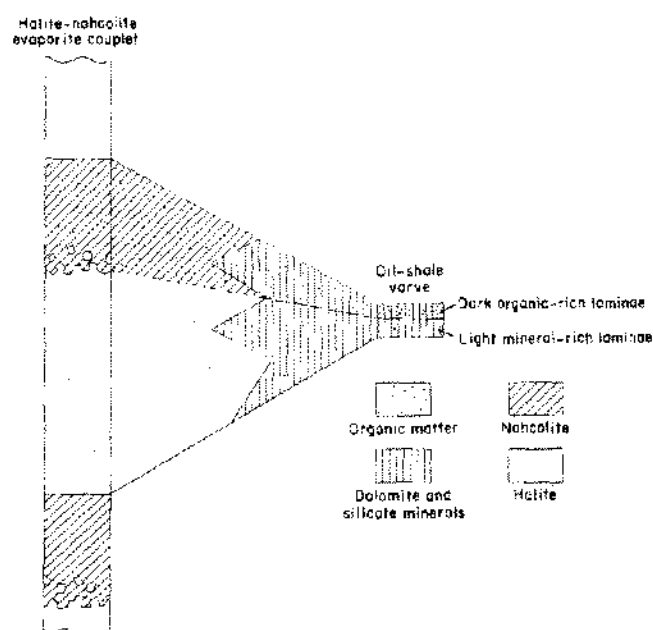


Figure 6. Schematic microlithofacies relationship between a halite-nahcolite couplet and an oil-shale varve.

Rates of sedimentation.

The bedded halite and nahcolite in the basin was deposited at a much faster rate than the laterally equivalent oil shales. This is indicated by isopach data and by comparison of the thicknesses of evaporite couplets and oil-shale varves. Dyni (1969) has shown that the interval of rocks between the B-groove and orange marker, two probable time-stratigraphic markers, thickens in the vicinity of the evaporite deposits. The halite deposits are

within this interval. If the thickness of the bedded halite and nahcolite deposits is subtracted, and making allowances for the irregular thickness of the leached zone, the thickness of the interval of rocks between the B-groove and the orange marker at the basin depocenter for the evaporites would be about the same as that in areas adjacent to the halite deposits.

The average thickness of a halite-nahcolite couplet given previously indicates an average rate of accumulation of 5 cm per year for the bedded halite-nahcolite units. This value is considerably higher than Bradley's estimate of 0.21 cm per year for the rate of accumulation for the bedded trona and halite deposits in the Green River Formation in southwestern Wyoming (Bradley, 1963, p. 632). A reason for the large difference between the two values may be that rhythmic bedding in the Wyoming deposits was not recognized by Bradley. Bradley's value is based on the rate of trona deposition which was calculated by Fahey (1962, p. 44-45) from the percentages of water-insoluble material distributed vertically through the 10-foot-thick trona bed in the Westvaco mine, about 20 miles west of the town of Green River, Wyo. Photographs of the mine face published by Fahey (1962, p. 44-45, Figs. 3, 4), show distinct, possibly annual layers several centimeters thick, which would indicate a more rapid rate of deposition.

At the rate of 5 cm per year, the total time required to deposit only the halite-nahcolite units in the upper and lower halite-bearing facies in the Piceance Creek basin would amount to about 1,200 years. The true value is somewhat greater because no allowance was made for the thin layers of varved oil shale and marlstone which are intercalated with the units of halite and nahcolite.

By comparison, the average thickness of a varve in moderately rich grade Green River oil shale is 0.065 mm (Bradley, 1929, p. 99). At a depositional rate of 0.065 mm per year, the total length of time required for accumulation of the oil-shale units in the lower and upper halite-bearing facies amounts to tens, or hundreds, of thousands of years. However, the rate of accumulation and the time required to deposit these rocks are difficult to estimate because of the presence of beds and non-bedded masses of nahcolite.

Other sodium minerals.

In the Savage core hole 24-1 a number of uncommon sodium minerals are present in small amounts in the upper halite-bearing facies. These include wegscheiderite ($\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$), shortite ($\text{Na}_2\text{CO}_3 \cdot 2\text{CaCO}_3$), northupite ($\text{Na}_2\text{CO}_3 \cdot$

$\text{MgCO}_3 \cdot \text{NaCl}$), and searlesite ($\text{NaBSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) (Hite and Dyni, 1967, p. 31). Wegscheiderite is associated only with halite. Searlesite is present in bedded nahcolite and in oil shale. Most, but not all, of the northupite and shortite is found in oil shale.

Wegscheiderite occurs in halite as acicular to bladed crystalline aggregates and scattered randomly oriented crystals. Some of these crystals are as long as 35 mm, but most are 10 to 15 mm long. Wegscheiderite comprises as much as 25 percent of some halite layers; however, for the entire upper halite-bearing facies, it amounts to probably no more than a few percent. The other three sodium minerals occur only in trace amounts. Searlesite occurs locally as scattered crystals in nahcolite layers and in oil-shale beds. The crystals are colorless, clear, sharply rectangular platelets, some of which measured about 2 mm long, 1 mm wide, and 0.1 mm thick; a few platelets are as long as 15 mm. Shortite forms stubby, colorless to light-brown, wedgelike crystals 2 mm or less in length, which are scattered locally through some of the oil shale. Northupite occurs as well-developed octahedrons about 0.2 to 2 mm across, which are scattered locally through some oil-shale beds. No doubt additional studies of these rocks, especially of the lower halite-bearing facies which has not yet been examined in detail, will reveal the presence of other uncommon minerals that have been reported elsewhere from the Green River Formation.

BROMINE GEOCHEMISTRY

Previous investigations.

Other workers have demonstrated that the distribution of bromine in marine chloride evaporites is useful as a paleosalinity indicator and as a guide in potash exploration. A substantial amount of work has been published on bromine geochemistry of marine evaporites, but there has been little similar work published on continental halite deposits.

Gulyaeva and Parfenskaya (1967, p. 740) reported low bromine values ranging from 0.5 to 7 ppm in Permian halite deposits of possible terrestrial origin from the Chu-Sarysu basin in South Kazakhstan, U.S.S.R. Holser (1969) found bromine in amounts ranging from 6 to 70 ppm in several continental Tertiary to Holocene salt deposits from the Western Interior of the United States. These few published data suggest that continental halite deposits have relatively low bromine values. This is not true, however, for the Green River deposits, which have much higher bromine values.

Methods of sampling and analysis.

About 170 samples of halite from the Savage core were analyzed for bromine by X-ray fluorescence. The core was sampled at approximately 0.5-foot intervals through the upper halite facies, and 1- to 10-foot intervals through the lower halite-bearing facies. Several of the thicker halite layers of individual halite-nahcolite couplets were sampled at 1-inch intervals.

In addition to samples from the Savage core hole, seven samples of halite from the halite-trona deposits in the Green River Formation in southwestern Wyoming were analyzed for bromine. Six of these samples are from the Finley core hole 1 in sec. 8, T. 16 N., R. 110 W., Sweetwater County, Wyo.; the seventh sample is from the Perkins core hole 2 in sec. 32, T. 15 N., R. 109 W., Sweetwater County, Wyo.

Most of the samples were collected by drilling a small hole into the side of the core with an electric hand drill and masonry bit. About 0.5 to 2.5 gm of powder was obtained and saved for analysis. To minimize contamination, the drill bit and core were carefully cleaned prior to drilling each hole. Some of the samples were also collected by chipping off a small piece of core which was ground to a powder before analysis.

The halite samples from the Savage core were examined by petrographic microscope, and, with the exception of 19 samples from the upper halite-bearing facies, were estimated to contain less than 1 to 2 percent contamination by other minerals. The 19 samples contained an estimated 5 to 50 percent carbonate minerals, mainly nahcolite or wegscheiderite. Most of the Wyoming samples contained trona. The trona was removed prior to analysis by treating the samples with room-temperature concentrated hydrochloric acid which was saturated with bromine-free sodium chloride. This reduced the mineral contamination to less than about 5 percent in each sample. Bromine analyses of the Wyoming samples and the 19 samples from the upper halite facies in the Savage core before and after acid treatment showed that small amounts of bromine were removed by the acid. This loss may have been bromine in brine-filled inclusions in the carbonate minerals. The bromine data given in this report are based on untreated samples from the Savage core hole, including the 19 samples mentioned previously, and on acid-treated samples from the Wyoming deposits.

Bromine in the samples from the upper halite-bearing facies in the Savage core hole was determined quantitatively on a Norelco X-ray

fluorescence spectrometer using the method described by Raup (1966, p. 238-239). The samples from the lower halite-bearing facies in the Savage core hole and the Wyoming samples were analyzed on a Picker X-ray fluorescence unit using the method described by Raup, Hite, and Groves (1970), in this symposium.

The precision of the bromine analyses was determined by O.B. Raup to be ± 6 percent for values greater than 80 ppm, and ± 15 percent for values in the range of 30 to 80 ppm. Some bromine determinations used in this report are less than 30 ppm and are subject to greater error. They need checking by more accurate methods.

Bromine analyses.

Figure 7 shows the bromine analyses and their statistically smoothed profiles (5-point moving averages) plotted next to a generalized lithologic section of the halite-bearing rocks in the Savage core hole.

The amount of bromine in the lower halite-bearing facies is relatively low and its distribution is remarkably uniform. The bromine content of 31 samples from these rocks averages 46 ppm. The amount of bromine fluctuates somewhat in the lower one-half of the sequence, but is nearly constant in the upper one-half. In two separate halite layers, each about one-half foot thick, the bromine content varies slightly from the base to the top of the layer, but the maximum variation is relatively low, ranging from somewhat less than 39 to 60 ppm.

Two samples from the 2-foot-thick unit of halite-nahcolite in the middle of the sequence of nahcolitic oil shale separating the lower and upper halite-bearing facies contained 39 and 40 ppm bromine, or about the same as the lower facies.

The distribution of bromine in the upper halite-bearing facies differs significantly from that in the lower halite-bearing facies in several ways: the bromine content has a much broader range, from 15 to 182 ppm; values commonly fluctuate widely from sample to sample; and the amount of bromine gradually increases from the base to near the top of the upper halite-bearing facies. In the lower two halite-nahcolite units of the upper facies, the amount of bromine ranges from 16 to 51 ppm. In the next halite-nahcolite unit above, bromine values vary rather widely between the samples but increase generally upward from 40 to 80 ppm. Bromine values continue to increase upward with many fluctuations through the next higher halite unit, about 70 feet thick, to a maximum of about 150 to 180 ppm about 7 feet

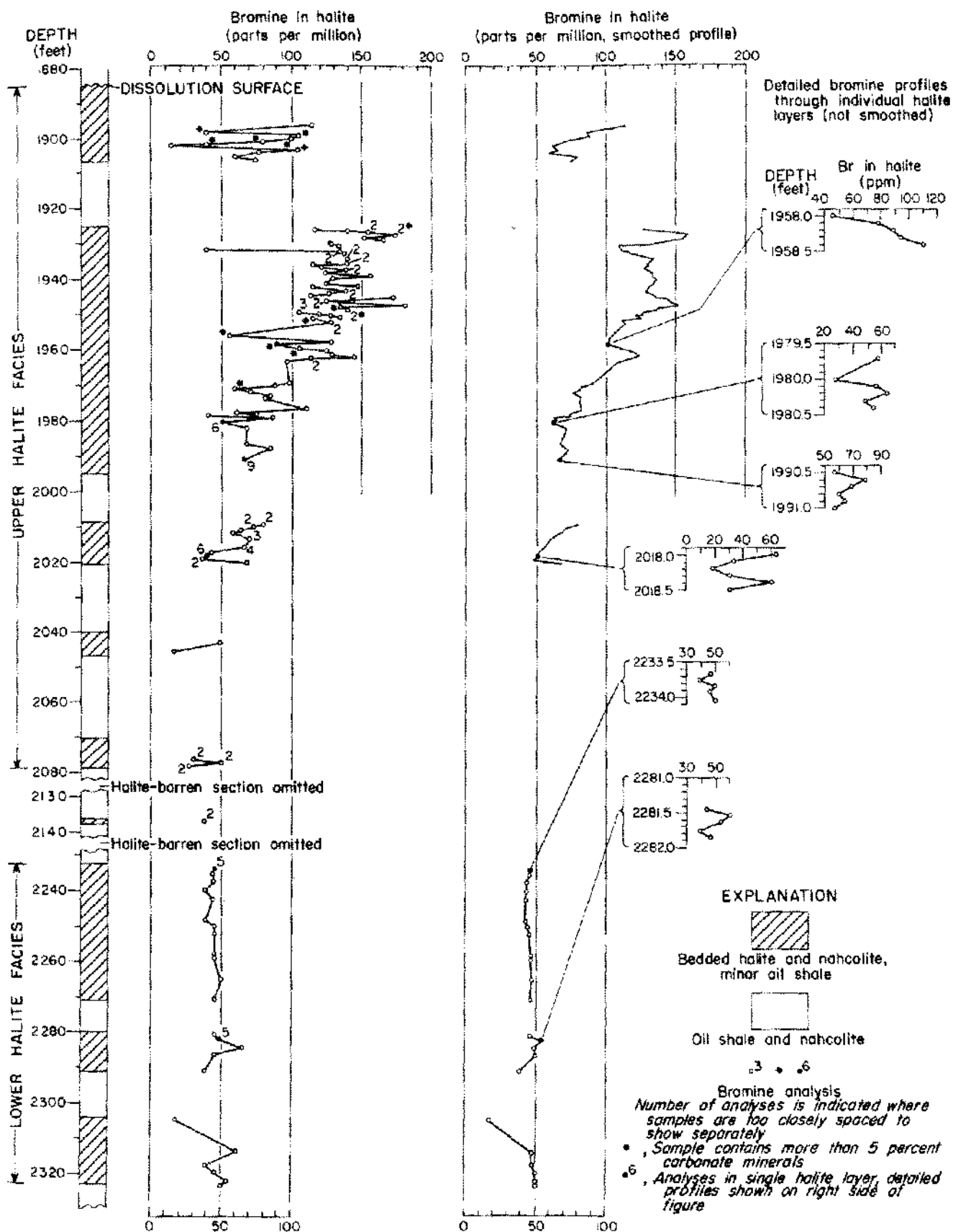


Figure 7. Generalized lithologic section and bromine profiles of halite deposits in the Savage core hole 24-1.

below the top of the unit, then decrease to about 115 ppm in the uppermost few feet of the unit. The maximum concentration of bromine, 182 ppm, was from a sample about 22 feet below the top of the 70-foot-thick halite-nahcolite unit. The amount of bromine decreases markedly by about 40 ppm between the top of the 70-foot-thick unit and the base of the uppermost halite-nahcolite unit in the upper halite-bearing facies. In the highest halite-nahcolite unit at the top of the upper halite-bearing facies the amount of bromine fluctuates widely between samples; values range from 15 to 115 ppm. Although the smoothed bromine profile suggests a general upward increase in bromine, the unit is too thin to confirm this trend. The distribution of bromine in the seasonal halite layers of four separate couplets from the upper halite-bearing facies shows a wider range of values than those in the lower facies. Notably, no two bromine profiles of the individual halite layers in either facies are alike. The bromine profile for the halite layer between the depths of 1,958.0 and 1,958.5 feet is unusual because the amount of bromine decreases upward through the layer and shows a wide range of values.

Analyses of core samples of halite from six selected beds in the halite-trona deposits in the Wilkins Peak Member of the Green River Formation in southwestern Wyoming showed bromine in amounts ranging from 86 to 157 ppm (Fig. 8). A clear layer of halite, a few inches thick, which occurs a few feet above halite-trona bed 18 in the Perkins well 2, contains 39 ppm bromine. It is suspected that this layer is a vein of recrystallized halite because of its purity, veinlike crystal structure (interlocking large crystals elongate perpendicular to bedding), and low bromine content. It was also noted that, when crushed, the other six halite samples emitted a strong hydrogen sulfide odor, whereas the sample from the Perkins well 2 had no detectable odor. The analyses are too few to determine vertical distribution trends for bromine in the Wyoming deposits; however, it is of interest to note that the values are of the same order of magnitude as in the Colorado deposits.

Geochemical cycle of bromine.

Geologic processes which controlled the distribution of bromine in the Green River Formation are uncertain, but most likely they were complex. The original chemical composition of the ancient Green River lake waters, basin configuration and water depths, mixing of waters through interconnection of lake basins, source areas and trace ele-

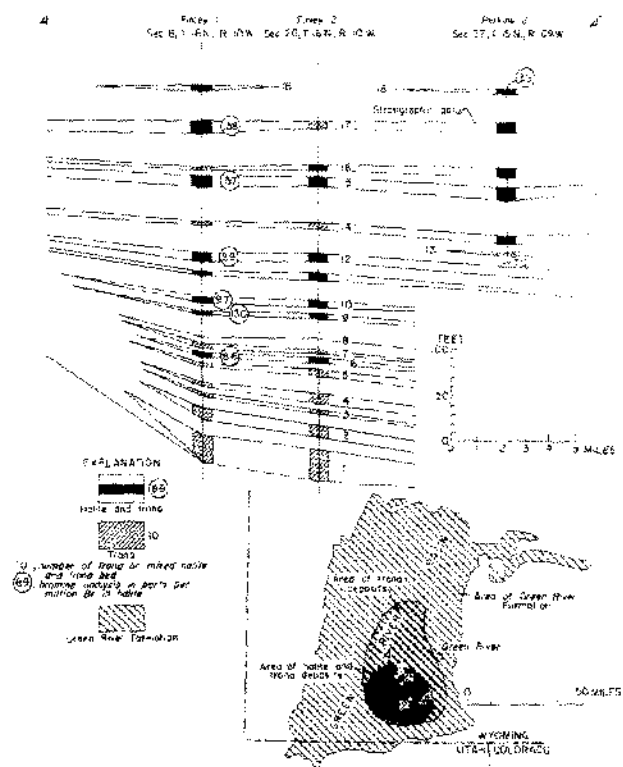


Figure 8. Partial stratigraphic section of the saline facies in the lower part of the Wilkins Peak Member of the Green River Formation southwestern Wyoming, showing bromine analyses of some selected mixed halite and trona beds.

ments including bromine, paleoclimatic conditions and the role of organic matter, especially algae, as a bromine concentrator are largely unknown, but all of these factors may have influenced the geochemical cycle of bromine to some degree.

The possibility that organic matter in the Green River Formation concentrated halogens needs study. Vinogradov (1959, p. 45-51), Gulyaeva and Irkina (1967), and others have shown that organic matter in soils and sedimentary rocks is enriched in bromine and iodine. Of particular interest is the fact that the fresh-water alga, *Cladophora santeri* is a bromine accumulator (Vinogradov, 1959, p. 45). According to Bradley (1931, p. 37-54) mud of the organic matter comprising the Green River oil shales was derived from aquatic microorganisms including algae. It is of interest to note here that 132 ppm bromine was found in an Estonian oil shale (Rankama and Sahama, 1950, p. 767) and 90.6 ppm bromine was reported in a Brazilian oil shale (Behne, 1953, Table 3).

To test the possibility that organic matter in the Green River oil shales concentrated halogens, 11 samples of untreated and water-leached oil shal-

from the Juhan core hole 4-1 were analyzed for chlorine and bromine. The iodine content of six of these samples was also determined. The samples are from the saline-rich zone of oil shale below the halite-bearing facies and from clay-bearing oil shales just below the saline-rich zone. The analyses are given in Table 1.

The concentration of total chlorine in these rocks ranges from 40 to 650 ppm. Total bromine values are uniformly low and range from less than 1 to 10 ppm. The iodine content ranges from 1 to 3 ppm in the six samples analyzed. Much of the chlorine, and probably most of the bromine, is water soluble. These water-soluble halogens may be associated with small amounts of pore water in the oil shale and perhaps with fluid inclusions, especially in nahcolite, which commonly form large crystalline masses and beds in the oil shale.

There is no clear correlation between total chlorine or bromine and the organic content of the oil shale, nor can the abundance of water-insoluble chlorine be directly related to the organic or carbonate mineral content of the oil shale. Although the site of the water-insoluble chlorine is likely the organic matter and possibly the carbonate minerals dawsonite and dolomite, which constitute a large part of the mineral fraction of the rocks, the abundance of chlorine in these rocks seems to be related to other factors.

Figure 9, which is based on the data given in Table 1, shows the vertical distribution of total chlorine in raw samples and chlorine in water-leached samples and their statistically smoothed profiles (five-point moving averages). A bromine

Table 1. Halogen Content of Some Oil-Shale Samples from the Juhan Core Hole 4-1

Sample depth	Untreated samples (ppm)			Water-leached samples ¹ (ppm)		Organic matter (weight percent)
	Cl	Br	I	Cl		
1883-85	650	3		120		12
1907-09	250	10		90		23
2011-13	350	8	1	100		31
2041-43	420	<1		110		45
2075-77	360	<1		70		5
2087-89 ¹	50	<1		30		18
2143-45	290	7	3	100		25
2147-49	540	<1		150		39
2165-67	90	1	1	40		15
2177-79	230	<1		40		13
2231-33 ²	40	<1		60		18
2293-95 ²	230	3		50		21
2313-15	300	5		40		27
2353-55	95	<1	1	40		12
2433-35 ³	100	4	1	30		36
2481-83 ³	240	4	3	110		22

1. All samples contained <2 ppm Br.

2. Sample contains water-soluble nahcolite; remaining samples are essentially nahcolite-free.

3. Sample contains illite; remaining samples contained no X-ray detectable clay minerals.

Notes: Br, Cl, and I were determined by J.S. Wahlberg, U.S. Geological Survey. The method of analysis included concentrating the halogens by fusing 1 or 0.5 gm samples of oil shale with NaOH and precipitating them with AgNO₃. The precipitated halides of silver were then analyzed by X-ray fluorescence. Possibly some of the halogens, especially iodine, were volatilized and lost upon fusion. The estimated instrumental range of accuracy is: Cl, ± 10 ppm; Br and I, ± 1 ppm.

The amount of organic matter was calculated by multiplying the Fischer assay value (gallons of oil per ton) by 0.58, an empirical conversion factor determined by Smith (1966). Although this factor applies more strictly to oil shale from the Mahogany zone, it is approximately correct for deeper oil shales in the basin. The oil yields used to compute the amount of organic matter were determined by the U.S. Bureau of Mines, Laramie, Wyo.

profile was not plotted because many values are near or below detection limits. Although the chlorine values fluctuate considerably, they seemingly increase upward through the section. The stratigraphically lowest sample (2481-83 feet) has a relatively high water-insoluble chlorine content as compared to the next several overlying samples. Perhaps the chlorine in this sample is associated with the abundant illite in the sample. The next higher sample (2433-35 feet) contains only small amounts of chlorine and illite. The highest sample (1883-85 feet) contains the most total chlorine (650 ppm) of the samples tested. Its stratigraphic position is, significantly, only 40 feet below the base of the lower halite-bearing facies, which is leached in the Juhan core hole.

The vertical distribution of total and water-soluble chlorine (and possibly bromine) might be related to the paleosalinities of the ancient Green River lake. The oil shales of the saline-rich zone are essentially impermeable and contain only small or trace amounts of pore water. It is also likely that since lithification there has been little or no movement of pore water in these rocks other than in a few thin leached beds as noted below. If the porosity and pore-water content of these rocks are

relatively uniform, it may be possible to use the chlorine content alone as a paleosalinity indicator. Locally, the oil shales in the saline-rich zone may have anomalous chlorine contents because of leaching. For example, the sample between the depths of 2,087 and 2,089 feet (Table 1) is from a thin brecciated bed of oil shale which has probably been flushed of its original pore water.

Studies by Boeke (1908) indicated that the amount of bromine in halite that is precipitated from a brine increases in successively younger halite layers at a rate which is proportional to the volume of the parent brine. Thus, the amount of bromine accumulating in halite would increase at a slower rate for a large volume of brine and conversely at a faster rate for a small volume of brine.

Brine volume can also be expressed in terms of brine depth. Kühn (1955, p. 658) noted that it may be possible to calculate this depth from the rate of increase in the amount of bromine per unit thickness of halite precipitated by a brine by the

following formula:
$$T = \frac{b_2 m}{b_2 - b_1} \cdot f$$

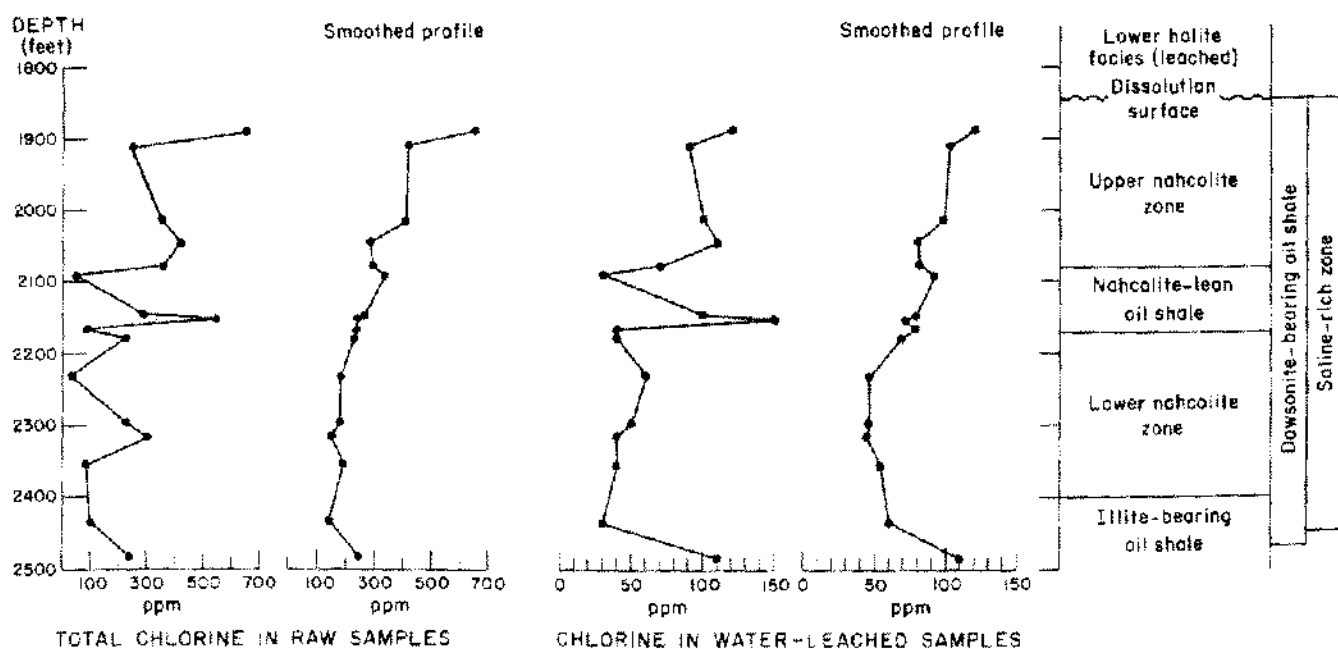


Figure 9. Vertical profiles of total and water-insoluble chlorine in the saline-rich zone, Juhan core hole 4-1.

where

T = thickness of brine layer

b_1 = bromine value of halite sample

b_2 = bromine value of stratigraphically higher halite sample

m = thickness of halite between b_1 and b_2

and

$$f = \frac{d \cdot 100}{s \cdot c}$$

where

d = 2.17, density of halite

s = density of brine

c = weight percent sodium chloride in brine

Kühn's formula was applied to parts of the seasonal halite layers for which detailed bromine profiles were determined (Fig. 7). For the calculations it was assumed that the ancient lake waters during salting stages in the Piceance Creek basin were similar to the theoretical composition of Lake Gosiute, the ancient Green River lake in Wyoming, at trona-halite salting stage as calculated by Bradley and Eugster (1969, Table 18, col. I). Using Bradley and Eugster's data, c was determined to be 21.6 and s was estimated to be 1.2. Applying these values to the Piceance Creek basin halite deposits, the following results were obtained:

The calculated brine depths may be too shallow. Such shallow conditions probably would have lead to complete desiccation of the lake unless a continuous inflow was available. Inflow waters would need to be highly charged with salts; otherwise the brine would never exceed saturation for sodium chloride. Preconcentration of lake waters could have taken place in adjacent lake basins, such as the Uinta basin in Utah.

Although errors in the brine depth determinations may be large, the wide fluctuations in bromine values in the seasonal halite layers of the upper halite facies certainly suggest shallow water, possibly even playalike conditions. The steeper bromine gradients in the seasonal layers of the lower halite facies, as well as the steep bromine gradient for the entire lower halite facies, suggest generally deeper waters, although this is not clearly supported by the water-depth determinations.

Instead of gradual upward increase in bromine values from the base to the top of a seasonal halite layer, as might be expected under conditions of progressive evaporation, most of the detailed bromine profiles show one or more reversals (Fig. 7). Similar reversals in seasonal halite layers in marine evaporites were found by Wardlaw and Schwerdtner (1966) and Kunasz (1970). The reversals in marine halite layers are attributed by these workers to basin influxes of water of varying salinity, variation in rates of evaporation, and partial solution of the halite layer by brines freshened by additions of meteoric waters followed by redeposition of halite. Similar conditions may have obtained in the Piceance Creek basin, except that the sources of influxes of water would be

Thickness of halite (ft)	Range in bromine (ppm)	Calculated depth of brine (ft)	
0.3	27-57	4.8	Upper halite facies
0.2	60-78	7.3	do
0.2	18-63	2.4	do
0.1	30-60	1.7	do
0.01	39-46	5.0	Lower halite facies
0.08	46-50	8.4	do
0.21	39-60	5.0	do

either streams or overflow from other lake basins in the same closed system.

Sources of bromine.

Older marine evaporites and Tertiary volcanic rocks or gaseous emanations are possible sources for the bromine in the Green River halite deposits of the Piceance Creek basin. The marine Eagle Valley Evaporite of Pennsylvanian age crops out on the White River uplift, a Laramide structure, which borders the Piceance Creek basin on the east. In the subsurface this formation contains thick sequences of bedded halite (Bass and Northrop, 1963, p. J4; Mallory, 1966) which is probably bromine-bearing. Whether the timing of uplift and erosion was such that this formation could have contributed sediments to the basin during Parachute Creek time is unknown. However, the proximity of the formation to the basin makes it attractive as a possible source area.

Volcanic tuffs are abundant in the Parachute Creek Member of the Green River Formation. Possibly these tuffs and associated gaseous emanations were sources of halogens, although, judging from the number and distribution of tuffs in the formation, the period of the most intense volcanism postdated deposition of the halitic rocks in the basin.

PALEOSALINITIES

The mineralogy of the saline-rich zone indicates that ancient Lake Uinta in the Piceance Creek basin during Parachute Creek time was essentially an alkaline sodium carbonate-chloride body of water. Figure 10 shows an idealized vertical paleosalinity profile of the lake during part of Green River time as interpreted from lithologic, mineralogical, and geochemical data from the Juhan (Hite and Dyni, 1967) and Savage core holes. The relation of the vertical distribution of some typical minerals (illite, dawsonite, nahcolite, and halite) in the saline-rich zone of the Parachute Creek Member and adjacent rocks to the paleosalinity profile is shown by vertical dashed lines in the figure. Although the genesis of each mineral was different, the distribution of minerals in these rocks probably was controlled primarily by the salinity and pH of the ancient lake waters.

The salinity and pH of Lake Uinta are believed to have generally increased, with many local fluctuations, during the time the rocks in the upper part of the Garden Gulch Member and in the saline-rich zone of the Parachute Creek Member were deposited. The salinity of the lake during the

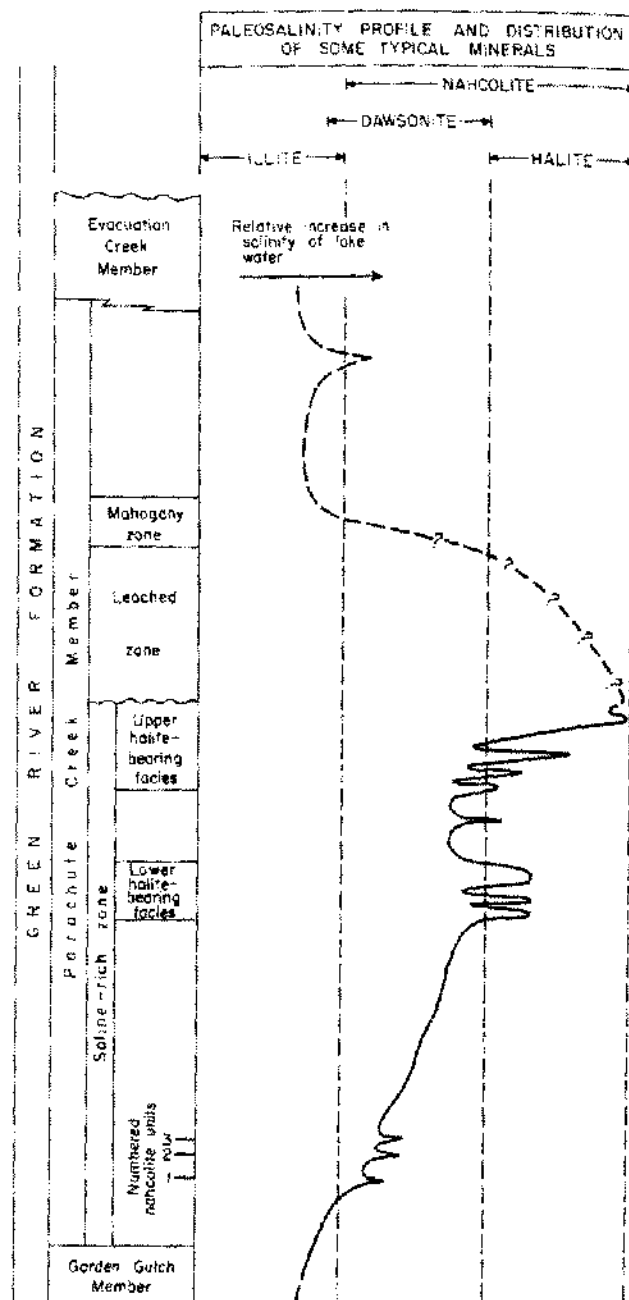


Figure 10. Vertical paleosalinity profile of Lake Uinta during Green River time at the depositional center of the halite deposits in the Piceance Creek basin.

time of deposition of the rocks in the leached zone is conjectural; however, there is ample evidence of the former presence of water-soluble minerals, probably mainly halite and nahcolite, which indicates that salinities were high. Possibly more soluble potassium and magnesium salts may have been precipitated during this time.

The salinity of the lake during the remainder of Parachute Creek time is also largely conjectural, but it probably decreased sharply during early Mahogany zone time because of the reappearance of illite and also because the rocks of the Mahogany zone, which have great areal distribution, mark a period of maximum expansion of the lake. A few crystal cavity zones above the Mahogany zone near the top of the Parachute Creek Member suggest brief periods of high salinity. However, more mineralogical and geochemical data will be needed before a realistic interpretation of paleosalinities during late Parachute Creek time can be made.

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