BULLETIN 93

Bromine in the Salado Formation, Carlsbad Potash District, New Mexico

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Abstract

The bromine content of halite and sylvite in the Salado Formation was investigated in drill cores and underground workings of the International Minerals and Chemical Corporation mine in the Carlsbad potash district, southeast New Mexico. The bromine content of halite ranges from 25 to 105 parts per million (0.0025 to 0.0105 weight per cent). This low concentration, in the presence of sylvite, suggests that much of the Salado Formation is second cycle. Changes in the bromine content of halite across stratigraphic boundaries correlate with changes in mineralogy and lithology. This is interpreted as evidence that these features formed during deposition and the bromine content of the halite has not changed substantially since deposition.

The bromine contents of halite and sylvite in the first ore zone, the principal potash bed in the district, suggest that the initial precipitation of a halite-sylvite assemblage was succeeded by the precipitation of halite-carnallite. Carnallite replaced some of the sylvite but was subsequently converted to sylvite during early diagenesis.

The bromine content of halite aids in identifying salt horses in drill cores. Bromine distributions are also of value in regional exploration. Most geochemical processes indicated on the basis of bromine concentrations in halite and sylvite are supported by independent mineralogic, stratigraphic, and textural criteria.

Introduction

The Permian sedimentary basin of the southwestern United States underlies parts of Texas, New Mexico, Oklahoma, Kansas, and Colorado. It has an area of about 155,000 square miles. The Carlsbad potash district may be considered as belonging to the west Texas—southeastern New Mexico part of the basin (fig. l), which covers about 50,000 square miles. Within the more limited area of the Carlsbad potash district (about 1200 square miles), seven companies presently mine potassium salts. This report is based on studies made of the drill cores and underground workings of the International Minerals and Chemical Corporation mine.

Geological investigations of the Permian basin of west Texas and southeastern New Mexico were stimulated first by the discovery of oil and salt and later by the delineation of economic potash deposits. Descriptions of the Permian evaporites have been presented by Lang (1937), Adams et al. (1939), Kroenlein (1939), Hill (1942), King (1942), Lang (1942), Adams (1944), and King (1947). These reports established the general characteristics and distribution of the basin sediments. Other papers dealt more specifically with the nature and distribution of anhydrite, notably Udden (1924), Adams (1944), Kerr and Thomson (1963), and Snider (1966). Less consideration has been given to the extensive beds of halite and associated salts, especially within the Carlsbad district. The most complete petrologic description of these beds was compiled by Schaller and Henderson (1932) from investigations of drill core samples. Madsen (1962) described the petrography of a core recovered from a hole drilled by the Atomic Energy Commission in connection with the Project Gnome underground nuclear explosion. Jones (1954, 1959a,b) gave a brief description of the occurrences and distribution of potassium minerals in the Salado Formation. Ageton (1936), Dunlap (1951), and Linn and Adams (1966) published the results of detailed underground mapping. Brief papers of mineralogic interest have dealt with the occurrence of talc (Bailey, 1949), clay (Grim, Droste, and Bradley, 1961; Fournier, 1961), fractures in langbeinite (Cathcart, 1949), and cryptomelane (Sun, 1961) within the potash ore zones.

In the present study, the bromine content of halite (NaCl) and sylvite (KCl) from the Salado Formation was investigated. It was hoped that such a study would contribute to understanding of the following problems:

(1) The origin and composition of the solutions that deposited the Salado Formation;

(2) the factors that controlled the characteristics of certain mineral assemblages and changes in assemblages both vertically and laterally within the Salado Formation;

(3) the evaluation of the grade and continuity of potash mineralization known only from development drilling; and

(4) the location of potash deposits within unexplored sequences of salt beds.

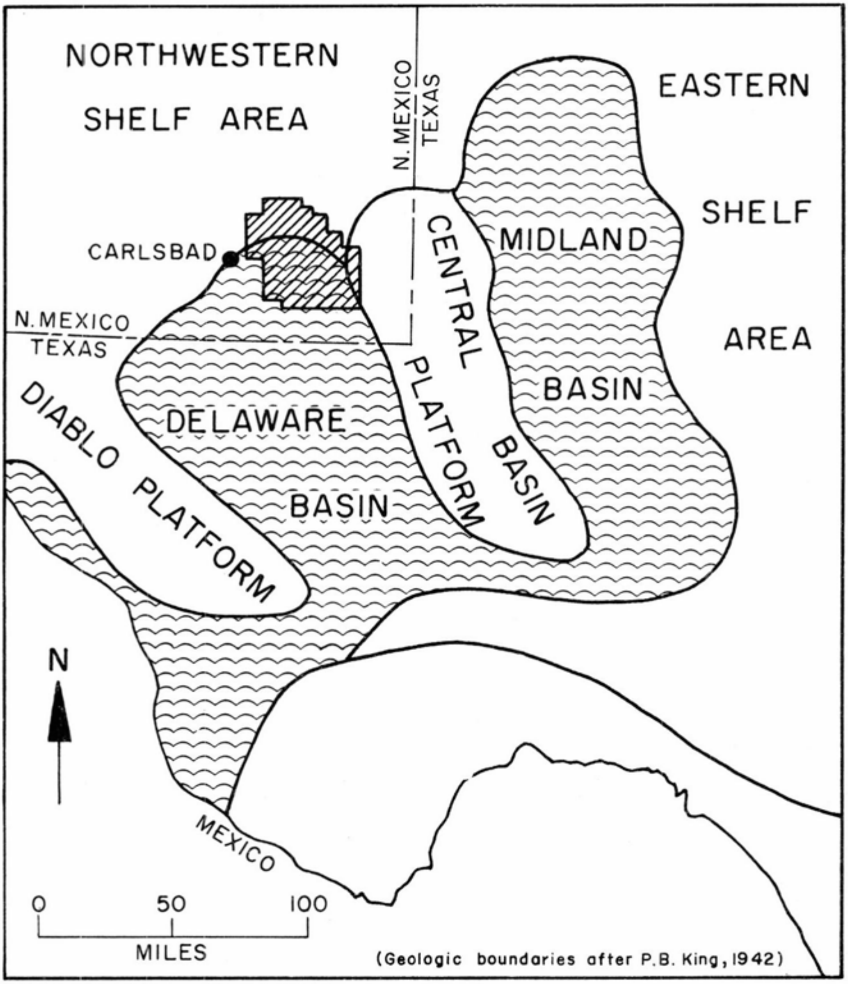


Figure 1

LOCATION MAP OF SEDIMENTARY PROVINCES OF THE PERMIAN BASIN OF SOUTHEAST NEW MEXICO, WEST TEXAS, AND THE CARLSBAD POTASH DISTRICT

(modified after Linn and Adams, 1966)

ACKNOWLEDGMENTS

The writer gratefully acknowledges the support of the International Minerals and Chemical Corporation (IMC). Dr. F. C. Kruger, past vice-president for mining and exploration, and Dr. D. L. Everhart, chief geologist, initially approved and encouraged these geochemical investigations. The Carlsbad Operation of IMC made available the mine workings and drill cores for study and sampling. Many of the bromine analyses and all other analyses were made in the mine laboratory at Carlsbad under the supervision of Mssrs. R. 0. Johnson, R. F. Roe, and M. C. Dodson.

Special thanks go to Dr. K. 0. Linn for profitable discussions of Carlsbad evaporite geology and assistance in collecting samples. The late Dr. 0. Braitsch and Prof. U. Petersen contributed to the writer's understanding of salt systems and Prof. Petersen critically reviewed the manuscript. This text, in essentially this form, was submitted to Harvard University as a Ph.D. thesis.

BRIEF HISTORY OF THE CARLSBAD POTASH DISTRICT

In the early nineteenth century, the manufacture and export of potassium carbonate derived from wood ashes constituted America's most important chemical industry. This industry dwindled rapidly, however, with the discovery of potassium deposits in Germany in 1843. As summarized by Smith (1938, p. 856):

> The search for potash in the Permian Salt Basin was the result of a demand for potash for plant food. Germans discovered in 1840 that potash was essential to plant growth. Potash itself was discovered in Germany in 1843 in the brine of a salt well. In 1857, it was found as a mineral in the course of sinking a shaft for salt. In 1858, potash in soluble mineral form was found to be a satisfactory source of potash for plant growth, and experimental work soon followed for the separation of the potash from the salt. The potash salts obtained incident to shaft sinking were used in this work. The initial production from the mine amounted to 2,293 tons in 1861. Mineral potash was introduced to American agriculture in 1872.

The term *potash* originally denoted potassium carbonate derived from the leaching of wood ashes. It is now used as a general term for potassium-bearing compounds and is expressed in K_2 0 equivalents.

Until 1910, the United States imported potash as potassium chloride from Germany. In that year, the German government cancelled our contracts and our dependence on a foreign source of potash became painfully apparent. In 1911, Congress passed an act providing for "researches with a view to determining conditions favorable to the presence of deposits of potash salts" (Smith, 1933). The execution of this program was initially the responsibility of the U.S. Geological Survey and the Bureau of Soils. All known potential sources of potash were investigated. The U.S. Geological Survey has continued its studies of potash occurrences to the present. The exploration efforts of government agencies and private interests yielded their first significant reward with the discovery of the potash deposits of the Carlsbad district in 1925. Prior to 1911, there had been little exploration for either oil or gas in the Permian basin, though Hill (1878) had called attention to the extensive deposits of salt and gypsum 33 years earlier. The first direct evidence of potash in the Texas Permian evaporites was reported by Udden in December 1912. He obtained a brine sample from a depth of 2220 feet in an oil well drilled by Swenson and Sons near Spur, Dickens County, Texas. The brine contained 5.4 per cent potassium. Subsequently, additional analyses were made of brines from this and other wells, some of which showed the presence of potassium (Udden, 1914, 1915, and 1921; Hoots, 1925; Mansfield and Lang, 1929).

Thick salt in the vicinity of Carlsbad was first discovered in an oil well drilled in 1913. In 1914, the Boden well was completed 23 miles northwest of Amarillo. Samples of salmon-red salt from this well contained 9.2 per cent potash and represent the first discovery of a soluble potassium mineral in the Permian basin. Similar salt was recovered from the Miller well, 18 miles southwest of Amarillo. On the basis of these two holes, the U.S. Geological Survey started a churn drill hole 8 miles northwest of Amarillo in 1915. For lack of funds, the hole was abandoned in 1916 without discovering potash.

Polyhalite ($\mathrm{2CaSO4MgSO4K2S042H2O}$) was the first potassium-bearing mineral to be identified in the Permian evaporites. On February 17, 1921, R. K. Bailey recognized this mineral in cuttings from the Bryant well in Midland County, Texas. Udden had previously suspected the presence of polyhalite, and it was soon discovered in numerous wells in west Texas and southeastern New Mexico. The discovery of oil in 1923 in Regan County, Texas, was in part responsible for the notable increase in exploration drilling that subsequently led to the discovery of the Carlsbad district.

In 1925, the Snowden and McSweeney Company drilled an oil well 20 miles northeast of Carlsbad. In November of that year, R. K. Bailey of the U.S. Geological Survey made the first identification of sylvite (KCl) from the Permian basin in the cuttings from this hole. On August 6, V. H. McNutt, who is generally credited with discovering the district, filed a potash prospecting permit application covering the federal land on which the well was drilled. In 1926, the Snowden and McSweeney Company drilled a core hole 525 feet from the discovery well. In this core, a significant bed of sylvinite (mixture of KCl and NaCl) and the minerals kainite ($\mathrm{KCl{\bullet}MgSO4\ 2.75H_2O}$) and langbeinite ($\mathrm{K_2S0_42MgSO_4}$) were discovered for the first time in the Permian basin (McNutt, 1927). In 1926, the American Potash Company was organized from the Snowden .and McSweeney interests to explore for potash in the vicinity of the McNutt well. By 1929, the new company had completed 12 core tests. Also in 1929, the Gypsy Oil Company began the first of its series of four core tests.

In 1926, Congress appropriated $500,000 for a potash drilling program in the Permian basin to be conducted by the U.S. Geological Survey and U.S. Bureau of Mines. This program was concluded in 1931 after the completion of 13 core tests in New Mexico, 10 in Texas, and 1 in Salt Valley, Utah. Polyhalite was identified in all the core tests in the Permian basin. Twelve of the tests also contained carnallite, sylvite, or langbeinite. The first of these core tests drilled in New Mexico was completed in 1927. The first identification of carnallite in the basin was made in the core from this hole.

Refined potash from the Carlsbad deposits was first produced in 1931 by the United States Potash Company (now the United States Borax and

Chemical Corporation). The Potash Company of America became the second producer in the district in 1934. In 1940, International Minerals and Chemical Corporation produced its first product. In subsequent years, the Duval Corporation (1951), Southwest Potash Corporation (1952), National Potash Corporation (1957), and Kermac (1965), joined the earlier producers to complete the list of presently producing companies. The growth of the district has been remarkable, as indicated by the production data in Figure 2. In 1961, the Carlsbad district achieved the rare distinction of becoming a billion-dollar mining district.

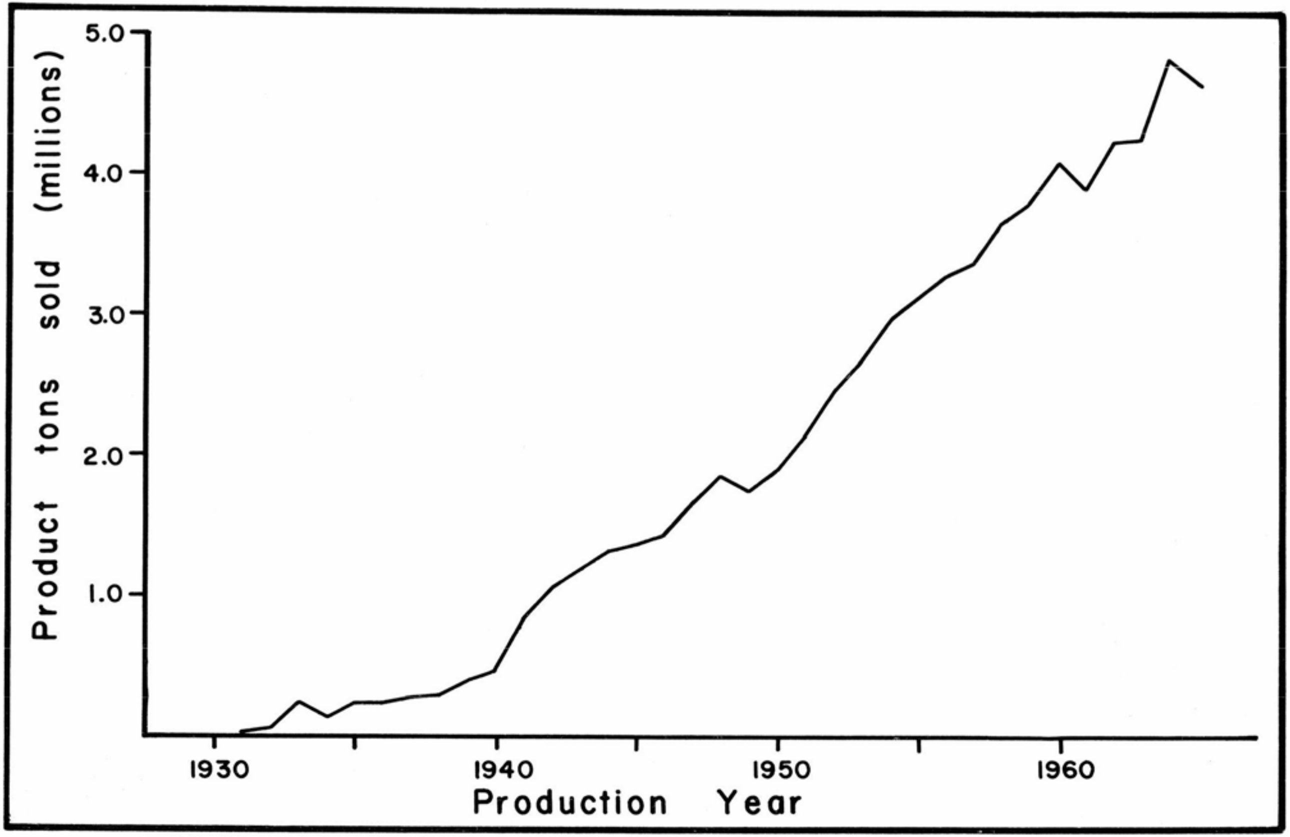


Figure 2
POTASH PRODUCT TONS SOLD FROM THE CARLSBAD DISTRICT

Permian Stratigraphy

EVOLUTION OF PERMIAN SEDIMENTARY PROVINCES

The sediments of the Permian basin of southeastern New Mexico and adjacent west Texas comprise a complex assemblage of chemical and detrital rocks whose distributions were controlled by changing climatic, hydrologic, and tectonic conditions. Numerous publications have considered both the regional and detailed features of the basin; they provide a regional setting in which the geology of the Carlsbad district may be considered in greater detail.

During the Permian, the dominant sedimentary provinces were (fig. l) the Delaware and Midland basins, the Diablo and Central Basin platforms, and the shelf areas to the north and east. Stratigraphic units are thicker and lower in elevation in the basins than equivalent units on the platforms and shelf areas. The platforms were higher than the shelf areas, which sloped gently up onto the craton. These provinces were not static during the Permian. In particular, the basins were continually subsiding relative to the platform and shelf areas.

Within the structural provinces smaller structural features influenced sedimentation for only part of the Permian. During the Guadalupe Epoch, for example, the Delaware basin was rimmed on the north, east, and west by a fringing reef. While the reef was actively growing, it inhibited the transport of sediments into the basin and thereby contributed to the development of sedimentary provinces corresponding to the basin and shelf structural provinces.

Structures during the deposition of the Ochoa Series were generally gentle features resulting from differential subsidence. Areas of more rapid subsidence can be detected on structure contour maps and isopach maps. When the thicknesses of successive intervals are compared, it is apparent that small, local basins were continually being succeeded and offset by younger basins. An exception to this pattern is the Ochoa trough (Snider) on the eastern edge of the Delaware basin. Throughout the Ochoa Epoch, this linear feature subsided continuously and received a thick sequence of evaporites. The position of the trough is indicated in Figure 3.

PRE—OCHOA STRATIGRAPHY

Deposition of the anhydrite and halite of the Castile and Salado Formations was preceded by the deposition of related sediments in other parts of the southwestern United States. Figure 4 shows the distribution of evaporite beds in these sediments and will be of particular interest in later discussions.

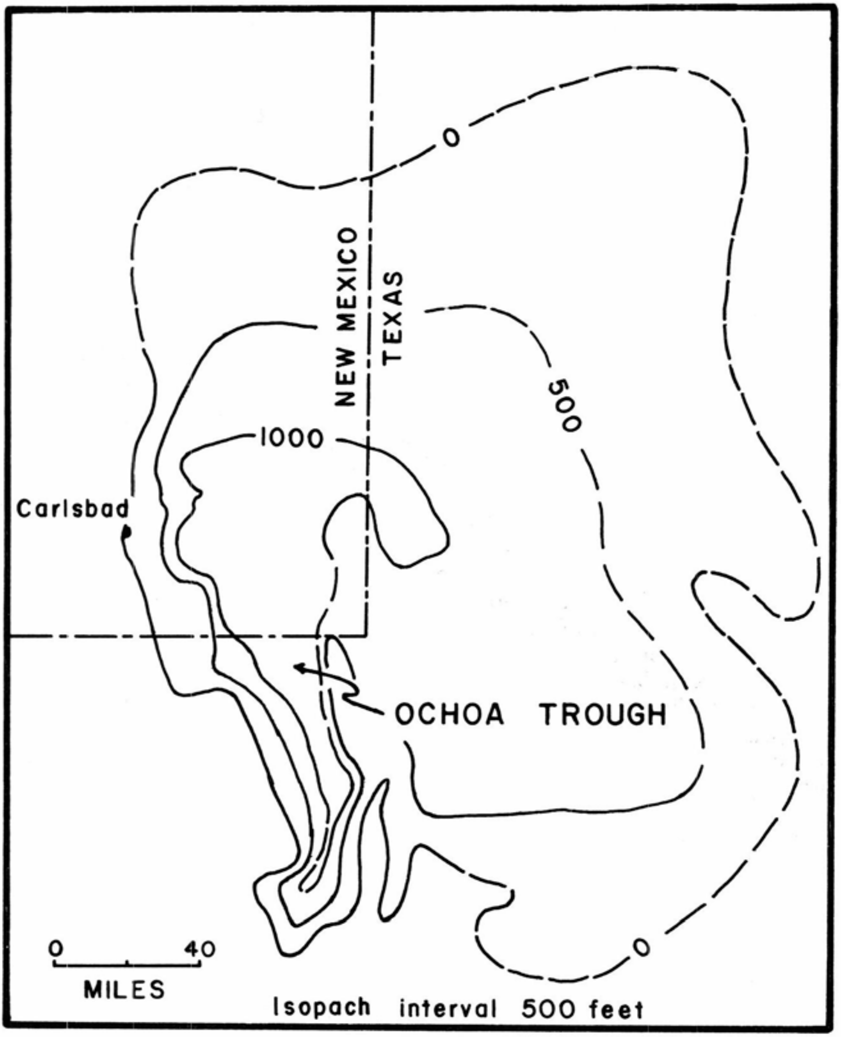
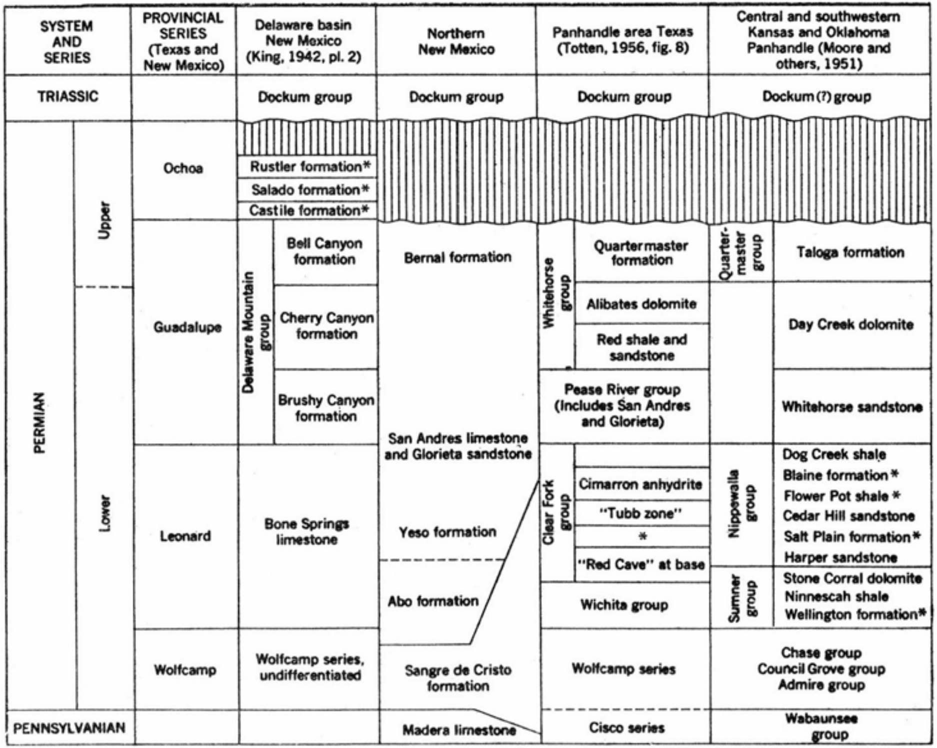


Figure 3

THICKNESS OF THE SALADO FORMATION IN SOUTHEAST NEW MEXICO AND WEST TEXAS

(modified after Pierce and Rich, 1962)



SYSTEM AND SERIES		PROVINCIAL SERIES (Texas and New Mexico)	Delaware basin New Mexico (King, 1942, pl. 2)		Northern New Mexico	Panhandle area Texas (Totten, 1956, fig. 8)		Central and southwestern Kansas and Oklahoma Panhandle (Moore and others, 1951)	
TRIASSIC			Dockum group		Dockum group	Dockum group		Dockum (?) group	
PERMIAN	Upper	Ochoa		Rustler formation*					
				Salado formation*					
				Castile formation*					
		Guadalupe	Delaware Mountain group	Bell Canyon formation	Bernal formation	Whitehorse group	Quartermaster formation	Quarter-master group	Taloga formation
	Lower			Cherry Canyon formation			Alibates dolomite		Day Creek dolomite
							Red shale and sandstone		
				Brushy Canyon formation	San Andres limestone and Glorieta sandstone	Pease River group (Includes San Andres and Glorieta)			Whitehorse sandstone
		Leonard	Bone Springs limestone		Yeso formation	Clear Fork group		Nippewalla group	Dog Creek shale
							Cimarron anhydrite		Blaine formation*
							"Tubb zone"		Flower Pot shale*
							*		Cedar Hill sandstone Salt Plain formation*
							"Red Cave" at base		Harper sandstone
					Abo formation	Wichita group		Sumner group	Stone Corral dolomite Ninnescah shale Wellington formation*
		Wolfcamp	Wolfcamp series, undifferentiated		Sangre de Cristo formation	Wolfcamp series		Chase group Council Grove group Admire group	
PENNSYLVANIAN					Madera limestone	Cisco series		Wabaunsee group	

Figure 4

GENERALIZED STRATIGAPHIC CHART FOR PARTS OF THE PERMIAN BASIN

Asterisk indicates salt-bearing formations (after Pierce and Rich, 1962, p. 29)

TEXAS PANHANDLE, OKLAHOMA, AND KANSAS

During the Wolfcampian, Leonardian, and Guadalupian epochs, shales, sandstones, and limestones were the dominant sediments deposited in the Permian basin of southeast New Mexico and west Texas. At the same time, the northern part of the basin was intermittently receiving evaporite sediments. In Oklahoma and Kansas, the Hutchinson Salt Member of the Wellington Formation (Pierce and Rich, 1962) forms the most widespread zone of salt. This member has an aggregate salt thickness of up to 400 feet. A second salt deposit 200 feet thick occurs about 1000 feet above the Hutchinson Salt Member in Kansas and may belong to the Salt Plain Formation.

In the Texas Panhandle, salt in the Clear Fork Group of the Leonard Series attains a cumulative thickness of more than 650 feet (Pierce and Rich). This salt is interbedded with red shale, anhydrite, and some dolomite and is considered younger than the salt of the Wellington Formation (Sellards, Adkins, and Plummer, 1932).

Considerable Lower Permian salt is also present in the Holbrook basin of northeast Arizona. These evaporites belong to the Supai Formation (Winters, 1963), which is equivalent to the Wolfcampian and Leonardian sediments in New Mexico and Texas.

SOUTHEAST NEW MEXICO AND WEST TEXAS

The Lower Permian Wolfcampian sediments strongly reflect the structural provinces in which they were deposited. The majority of the area received calcareous sediments of some variety. Farther north, these sediments give way to red beds; against the Marathon Fold belt to shale, sandstone, and conglomerate. On the shelves and platforms, limestones were deposited without any apparent development of reefs. The deposits of the Midland and Delaware basins were principally black shales with some interbedded shaley limestone and sandstone. The sediments were deposited in quiet, stagnant, and perhaps relatively deep water.

The sediments deposited during Early Leonardian time were much the same as in the preceding epoch, with the exception that minor amounts of anhydrite, gypsum, and salt were precipitated on the northern shelf. In the Upper Leonardian, the character of the sediments changes greatly. Sandstones were deposited over the northwestern and eastern shelf areas, fading out toward the Midland basin and becoming coarse toward the south The shelf areas then received blanket limestones that interfinger with evaporites and red beds to the north and black limestone and shale toward the basins.

The Guadalupian Epoch was characterized by a restricted marine environment. Sands were deposited in the Delaware basin during Early Guadalupian time. The contact with underlying noncalcareous black shales and limestone is sharp and apparently conformable. During the deposition of sand in the basin, the shelf and platform areas were probably emergent. In Middle Guadalupian time, as the seas readvanced over the shelves, limestone reefs began to develop around the margin of the Delaware basin. The reef continued to develop into Late Gudalupian time, probably in response to continued subsidence of the Delaware basin. In the Late Guadalupian, the shelf waters ceased supporting abundant marine life. The brines became more saline and evaporite deposition began on the northwest shelf, the Central Basin platform, and in the Midland basin. These evaporites, composed of gypsum with minor salt, give way to red beds to the north (Page and Adams, 1940) and are the first significant evaporites in the Permian of west Texas and southeast New Mexico. They signaled the retreat of marine conditions from the area and the advance of the saline environment from the north.

OCHOAN STRATIGRAPHY

The Ochoan Series is composed of, in decreasing order by age, the Castile, Salado, Rustler, and Dewey Lake Formations (fig. 4), composed dominantly of evaporites and representing the final stages of the Permian sea. The Castile Formation is composed mostly of anhydrite; the Salado mostly of salt. The basal clastic beds of the Rustler Formation give way to anhydrite, dolomite, and gypsum in the upper part of this formation. The Dewey Lake Formation is composed of red beds.

All Ochoan formations except the Castile, which is limited to the Delaware basin, are present in the Midland basin and on the Northwest shelf and Central Basin platform. The Ochoan Series crops out in southern Eddy County, New Mexico, with a stratigraphic thickness of about 2000 feet. In the subsurface to the east, where the salt of the formations has not been dissolved, the total thickness is greater than 4500 feet.

The correlation of the Lower Ochoan sediments of the Delaware basin with reef zone and shelf sediments is difficult and several explanations have been offered. Moore (1960) believed that gypsum rock of the Castile Formation may be correlative with the upper part of the Capitan Limestone at the margin of the basin. Snider stated that tracing of marker beds in well logs from Reeves County, Texas, within the Delaware basin to Pecos County, Texas, in the Central Basin platform area led him to a tentative correlation of the Castile with the Seven Rivers (El Capitan) and Lower Yates Formations. He adds that the Salado of the Delaware basin may be correlative with the Upper Yates, Tansill, and Salado of the Midland basin.

CASTILE FORMATION

The Castile Formation was named by Richardson (1904, p. 43) for Castile Spring in east-central Block 61, Township 2, Culberson County, Texas. It is restricted to the Delaware basin, where it attains a maximum thickness of about 2000 feet, and is composed of massive anhydrite, calcite-banded anhydrite, and halite beds. The lower contact is easily recognized against the underlying Delaware sand. The contact with the overlying Salado Formation has been defined as the horizon above which salt is more abundant than anhydrite. This horizon is also generally chosen so that the Castile Formation is limited to the Delaware basin. The application of these definitions is difficult, because near the edges of the basin, halite and anhydrite beds adjacent to the contact thin, coalesce, and pinch out so rapidly that any specific horizon is difficult to follow. As summarized by Hayes (1964, p.

15-16), "until either a transitional or disconformable contact at the base of the Salado Formation in the shelf area can be verified or until the contact of the Castile Formation with the Capitan Limestone can be seen. . .lateral relations of the Castile must be conjectured."

The Castile Formation covers an area of about 10,000 square miles at a thickness between 1300 and 2000 feet (Snider). Along the north and east edges of the basin, it thins abruptly against the Capitan reef. "In the southern and western parts of the Delaware basin, the Castile grades into alternating anhydrite and dolomite, and in the Glass Mountains the Tessey reef dolomite overlying the back-reef Guadalupian dolomite and sandstone is probably in part equivalent to the Castile" (King et al., 1942, p. 554).

Aspects of the lithology, distribution, and origin of the Castile Formation have been discussed by Hill (1942), King (1942), King et al., King (1947), Lang (1935, 1937), Udden (1924), Adams (1944), and Snider. King (1947) estimated that the ratio of anhydrite to halite in the Castile Formation is 5:1. Snider (p. 54) arrived at a ratio of 5.4:1.

SALADO FORMATION

The Salado Formation, named by Lang (1935, 1939) from a subsurface section in the Pinal Dome oil well (Means Well No. 1), Loving County, Texas, is composed of halite and agrillaceous halite with less anhydrite and polyhalite. The contact with the underlying Castile Formation in the Delaware basin has been discussed. The contact with the overlying Rustler Formation is taken as the top of massive salt.

Unlike the Castile, the Salado Formation extends beyond the Delaware basin to within the Midland basin and on the Central Basin platform and the Northwest shelf. Figure 3 shows its thickness and limits. The present western limit is an erosional boundary due principally to the removal by solution of salt in the subsurface; the original western limit of salt is not known. The eastern and northern limits are characterized by facies relations between salt and other sediments, in particular red shales (King et al.). To the south, dolomite becomes interbedded with salt, and the Salado Formation is probably equivalent to the Tessey limestone of the Glass Mountains (King, 1942, p. 666; Adams, 1944, p. 1609).

The Salado Formation is composed almost entirely of evaporite sediments. Halite, the most important mineral, occurs as essentially pure beds and as beds containing several per cent of other minerals, particularly argillaceous and sulfate minerals. The argillaceous material is composed of "clay and silt-sized particles of quartz and silicate minerals" (Jones, 1954, p. 109). The amount of argillaceous material in the impure halite beds ranges from less than 1 to greater than 90 per cent, with an average probably between 1 and 3 per cent.

Sulfate minerals are ubiquitous in halite beds. This writer does not know of any monomineralic halite beds in the Salado Formation. The common sulfate minerals, in order of abundance, are anhydrite and polyhalite. Anhydrite is dominant in the southern Delaware basin and in the bottom third of the section in the Carlsbad district. In the upper two thirds of the section, both minerals are present in 1- to 20-foot massive beds remarkable for their continuity over areas in excess of 12,000 square miles.

The Salado Formation is composed of alternating beds of halite, argillaceous halite, anhydrite, polyhalite, argillaceous material, and soluble potassium minerals. In general, this alternation is not cyclic, although certain lithologic sequences and associations are common. The characteristics of the three most abundant rock types, the chloride, sulfate, and clastic beds, are of prime interest.

Halite is the only regionally important chloride mineral. It occurs in well-defined beds identified by abrupt changes in the crystal size of the halite and the amounts of accessory minerals. The grain size of the halite ranges from less than 5 to greater than 25 mm and may remain constant or change gradually within a bed. Gradual and abrupt changes in the grain size of halite are commonly accompanied by changes in the amounts of polyhalite or anhydrite and argillaceous material.

The distribution of polyhalite and anhydrite in individual halite beds may be erratic, may be evenly disseminated throughout the bed, or may change uniformly from the top to the bottom of the bed. These minerals are commonly so finely disseminated that individual grains are not megascopically visible. In other beds, the sulfate minerals are present as 10- to 20-mm blebs.

The argillaceous minerals are consistently fine-grained (2 mm or less). They are present in the argillaceous halite beds as

(1) a fine dust in the halite grains;

(2) numerous discontinuous thin bands parallel to the bedding;

(3) clots within halite grains; and

(4) thin films and clots between halite grains.

Colors of the argillaceous material include gray, gray-green, and brownish red. Persistent clay seams are commonly present at the top and bottom and sometimes within argillaceous halite beds.

Anhydrite and polyhalite beds are commonly referred to as marker beds or markers because of their wide distribution in units as thin as 4 inches. The contacts between chloride and sulfate beds are sharp. Higher concentrations of disseminated polyhalite or anhydrite are common in the halite beds immediately above sulfate beds. Gray magnesitic clay is concentrated at the base of many sulfate beds in thicknesses proportional to the thickness of the marker.

Polyhalite and anhydrite beds are massive and laminated. The laminations are characteristic of the thicker sulfate beds in which anhydrite alternates with carbonate-rich layers. Halite is generally present in the sulfate beds as scattered crystals and bands parallel to the bedding. Argillaceous material is notably absent from sulfate beds.

Clastic beds constitute a small part of the Salado Formation. Adams (1944, p. 1609-1610) summarized the distribution of clastic beds as follows:

> Salado salts in the south-central part of the Delaware basin are much cleaner than those in the areas near the north rim. . . .
>
> Sands and silts are encountered in many parts of the Salado section. The sands are coarser than most of the Permian sands but they are not characterized by the

> frosted quartz grains so common in the Yates and Dewey Lake Formations. Both red and gray sands are present. A tongue of bedded sandstones extends south from the vicinity of Carlsbad almost to the Pecos County line. The source of supply seems to have been at the north and west. The sands are most extensive near the top of the Salado formation.. . .
>
> Silts and shales are less conspicuous but more generally distributed than sands in the Salado section. Colors include brown, green, blue, gray, red, pink, violet, and black. These finer clastics are commonly lost in cuttings from oil wells but are very conspicuous in the potash core tests. One prominent member near the base of the Salado is named La Huerta silt. Numerous other unnamed members, of equally wide distribution, can be recognized in the upper part of the section.

The relative abundance of the principal rock types in the Salado Formation within the Carlsbad district has been estimated by Jones (1959a, p. 13) as follows:

ROCK TYPE	PER CENT
Halite	38.6
Argillaceous halite	45.0
Sulfate	12.5
Clastic	3.9

RUSTLER FORMATION

Near the Carlsbad potash district, the Rustler Formation ranges in thickness from 100 to 360 feet (Jones, 1959a, p. 10) and conformably overlies the Salado Formation. The accumulation of clastic debris at the contact between the two formations suggests that the boundary may represent considerable pre- and post-Rustler dissolution of argillaceous halite at the top of the Salado Formation.

Jones (1959a, p. 11) recognized five lithologic units from the top of the formation: (1) upper gypsum member (0 to 25 meters); (2) Magenta Dolomite Member of Adams (1944), (0 to 10 meters); (3) middle gypsum member (0 to 30 meters); (4) Culebra Dolomite Member (5 to 10 meters); and (5) lower sandstone member (30 to 60 meters). Each of these members contains some clastic material as clay, silt, and sand. The gypsum members contain significant amounts of salt in the Delaware basin.

Along the western eroded edge of the Salado Formation, the lower part of the Rustler Formation is reduced to collapse breccia. Information on these structures suggests that some dissolution of Salado salt occurred after the deposition of the Rustler Formation. This, in turn, is evidence that the Salado salt originally extended farther west than its present boundary.

DEWEY LAKE FORMATION

Overlying much of the Rustler Formation are the Dewey Lake red beds. According to Jones (1954, p. 107), this formation is composed entirely of red sandstone, siltstone, and minor amounts of shale. These beds probably served as a protective cap over the evaporites of the Rustler and Salado Formations during the period of erosion between the deposition of the Dewey Lake Formation and the overlying Upper Triassic Dockum Group.

Geochemistry of Marine Evaporites

Marine evaporites owe their origin to the evaporation of sea water in restricted environments such as certain epicontinental seas, grabens, salt pans, and lagoons. For salts to accumulate in such environments, the influx of unsaturated solutions (stream runoff, rainfall, ground-water seepage, and sea water influx) must be less than the rate of evaporation and the concentrated brines must be prevented from escaping to the sea. Many salt deposits have been considerably altered by postdepositional metamorphism and metasomatism, whereas others have been derived from the dissolution, transport in solution, and reprecipitation of older marine evaporites. The composition of these secondary or altered evaporites is similar enough to primary marine evaporites to consider them as a single group. Not included with the marine evaporites are deposits of nitrates, borates, sodium carbonates, and other continental evaporites.

Conditions favorable to the deposition of marine evaporites frequently existed for numerous salt deposits, and beds representing the Paleozoic, Mesozoic, and Cenozoic Eras are found in the United States (Stewart, 1963, p. Y27). Investigators have attempted to explain the chemical, stratigraphic, and mineralogic features of ancient evaporites through studies of (1) modern marine evaporites, (2) the present and past compositions of sea water, and (3) experimental investigations of the stable and metastable mineral assemblages formed from the evaporation of sea water at various temperatures. These studies have met with considerable success but have also delineated some substantial differences between natural and theoretical evaporite deposits. Some features of the Ochoan evaporites of southeast New Mexico and west Texas, which depart from theoretical salt sequences, will be considered in later sections. For these discussions, consideration of the following generalizations regarding the origin of evaporite deposits will prove useful.

COMPOSITION OF SEA WATER

Investigations of the chemistry and origin of ancient marine evaporites begin with an assumption about the composition of ancient sea water. In the absence of concrete evidence to the contrary, this has generally stated that the composition of Paleozoic oceans did not differ significantly from present sea water (table 1) and is supported by some aspects of marine evaporites, challenged by others.

Frederickson and Reynolds (1960) used the boron content of illite to investigate the salinity of ancient sediments. To the extent that boron varies with, but is not independent of, the total salinity, this is a good method for determining paleosalinity. From investigations of Precambrian illites, Reynolds (1965, p. 12) concluded that "the boron content of sea water has not varied significantly for the last 2 to 3 billion years." According to Rubey (1951, p. 1111), "lines of evidence now available suggest that the composition of both sea water and atmosphere may have varied somewhat during the past; but the geologic record indicates that these variations have probably been within relatively narrow limits."

TABLE 1. MAJOR CONSTITUTENTS OF SEA WATER
(after Rankama and Sahama, 1950, p. 287)

ION	WEIGHT (%)
Cl^-	1.89799
SO_4^{-2}	0.26486
HCO_3^-	0.01397
Br^-	0.00646
F^-	0.00013
H_3BO_3	0.00260
Na^+	1.05561
Mg^{+2}	0.12720
Ca^{+2}	0.04001
K^+	0.03800
Sr^{+2}	0.00133

Kramer (1965) recently developed constant temperature-pressure models for sea water based on equilibrium with clay minerals, calcite, hydrozylapatite, carbonate-fluor-apatite, phillipsite, gypsum, strontianite, celestite, and aragonite with and without chloride. These models were compared with fluid inclusions from salt and chert from the Silurian Salina and Niagaran Groups of Michigan, Ontario, Ohio, and Wisconsin. Kramer concluded (p. 941) that "the compositions of the liquid inclusions and models do not vary much from the composition of modern sea water, suggesting little change in the composition of sea water in the past."

On the basis of these investigations, the composition of sea water does not appear to have changed significantly since the beginning of the Paleozoic Era. This conclusion is accepted in the ensuing general discussion on marine evaporites and subsequent discussions of the geochemistry of the Permian evaporites of the southwestern United States.

THEORETICAL SALT SEQUENCES

The sequences of salt that may result from the evaporation of sea water are numerous and have been considered by Braitsch (1962), Borchert (1940), and others. Some of the general physical and chemical features in marine evaporite deposits result from the following factors that are important in the development of evaporite deposits:

(1) the regime of the evaporite basin, including such factors as the basin shape and depth and the rate, frequency, and source of influx of solutions;

(2) the temperature of deposition;

(3) the stable and metastable evaporite minerals and mineral assemblages that form with the evaporation of sea water; and

(4) the postdepositional alterations of evaporite deposits.

Table 2 gives the compositions of the marine evaporite minerals referred to.

TABLE 2. SALT MINERALS OF MARINE EVAPORITE DEPOSITS

MINERAL	FORMULA
Anhydrite	$CaSO_4$
Bischofite	$MgCl_2 \cdot 6H_2O$
Blödite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$
Carnallite	$KMgCl_3 \cdot 6H_2O$
D'Ansite	$Na_{21}MgCl_3(SO_4)_{10}$
Epsomite	$MgSO_4 \cdot 7H_2O$
Gypsum	$CaSO_4 \cdot 2H_2O$
Glaserite	$K_3Na(SO_4)_2$
Glauberite	$Na_2Ca(SO_4)_2$
Gorgeyite	$K_2Ca_5(SO_4)_6 \cdot H_2O$
Halite	$NaCl$
Hexahydrite	$MgSO_4 \cdot 6H_2O$
Kainite	$4(KMgClSO_4) \cdot 11H_2O$
Kieserite	$MgSO_4 \cdot H_2O$
Langbeinite	$K_2Mg_2(SO_4)_3$
Leonhardtite	$MgSO_4 \cdot 4H_2O$
Leonite	$K_2Mg(SO_4)_2 \cdot 4H_2O$
Löweite	$6Na_2SO_4 \cdot 7MgSO_4 \cdot 15H_2O$
Mirabilite	$Na_2SO_4 \cdot 10H_2O$
Pentahydrite	$MgSO_4 \cdot 5H_2O$
Polyhalite	$Ca_2K_2Mg(SO_4)_4 \cdot 2H_2O$
Schoenite	$K_2Mg(SO_4)_2 \cdot 6H_2O$
Sylvite	KCl
Syngenite	$K_2Ca(SO_4)_2 \cdot H_2O$
Tachhydrite	$CaMg_2Cl_6 \cdot 12H_2O$
Thenardite	Na_2SO_4
Vanthoffite	$Na_2Mg(SO_4)_4$

The regime of the evaporite basin determines the lithology, thickness, and stratigraphy of the deposit. The regime may be one in which all the incoming sea water evaporates, producing an evaporite deposit in which the salts are in the same ratio as in sea water. The distribution of the salts within this evaporite sequence will depend, among other things, on the number of sea water influxes the basin received, as each influx may produce a separate lithologic cycle.

At the other extreme, the regime of deposition may be telescoped in a series of open systems. As the sea water enters the basin, it begins to precipitate carbonates. The brine continues to move into the basin at the surface, buoyed up by denser subsurface brine, depositing gypsum, anhydrite, and eventually halite as it becomes more concentrated. If such a regime persists, thick deposits of nearly monomineralic evaporites will accumulate. The residual, concentrated brines may deposit magnesium and potassium salts at the far end of the basin, accumulate and eventually precipitate on the basin floor, or reflux to the ocean if the inlet is not obstructed by an impervious barrier. This latter event seems to have occurred frequently in the past, for many deposits of gypsum and anhydrite have no associated halite, and many halite deposits have no associated potassium and magnesium salts. Between these two regimes, many permutations occur; it is not surprising that the bulk composition of most evaporite sequences bears little resemblance to what "should" result from the evaporation of sea water.

The temperature of evaporite deposition, assuming ancient climates were similar to those of today, probably ranged from a low of 10°C to a maximum of 70°C (Borchert and Muir, 1964, p. 15-17), with most precipitation occurring between 25° and 55°C.

van't Hoff (1912) and D'Ans (1933), among others, have investigated the phase equilibria of salt systems important to the study of marine evaporites, including the seven-component system representing sea water (Na, K, Mg, Ca, CI, SO_4, and **$H_2 0$).** Information on the stable and metastable phases in equilibrium with a wide range of solution compositions over the temperature range of interest is of considerable importance when investigating the development of evaporite beds in general and potash beds in particular.

After deposition, evaporite beds undergo slight to intense alteration, depending on their mineralogy and the characteristics of the total evaporite section. Postdepositional changes are most intense in late-stage evaporite assemblages, such as potassium and magnesium chlorides and sulfates.

Considering the many factors that determine the physical and chemical characteristics of an evaporite deposit, it is impossible to compile a definitive list of deposits that might result from the evaporation of sea water. Limiting consideration to the salts that precipitate after the beginning of halite precipitation allows some useful generalizations. These salts are the principal concern when discussing the potash horizons of the Salado Formation.

Table 3 lists some theoretical stable and metastable sequences of mineral assemblages resulting from the evaporation of sea water (Braitsch, 1962, p. 68). The thicknesses for each bed are based on a thickness of 325 feet for the halite interval (A) that would underlie each sequence of assemblages. The interval (B) deposited above the halite bed (A) for both stable and metastable equilibria contains the assemblages halite-blodlite, halite-epsomite, or halite-blodite followed by halite-epsomite. The next interval (C) contains from 1 to 3 assemblages with some combination of halite and kainite, epsomite, sylvite,

TABLE 3. THEORETICAL STABLE AND METASTABLE SEQUENCES OF MINERAL ASSEMBLAGES FORMED FROM THE STATIC EVAPORATION OF SEA WATER

(Bed thicknesses correspond to 325 feet of halite; after Braitsch, 1962, p. 68)

	STABLE EQUILIBRIUM									METASTABLE EQUILIBRIUM					
BED	15° C			25° C			35° C			15° C			25° C		
B$_1$	20 m	33	n	6.3 m	72	n	8.7 m	74	n	20 m	33	n	6.3 m	72	n
		67	e		28	bl		26	bl		67	e		28	bl
B$_2$				4.5 m	20	n							5.8 m	24	n
					80	e								76	e
C$_1$	3.4 m	32	n	6.3 m	29	n	8.5 m	11	n	8.2 m	30	n	4.5 m	33	n
		52	e		30	e		89	k		53	e		47	e
		16	sy		41	k					17	sy		20	le
C$_2$	5 m	33	n	5.7 m	21	n	3.2 m	14	n				3.0 m	22	n
		67	k		3	hx		1	k					58	e
					76	k		85	ks					20	sy
C$_3$				1.7 m	11	n									
					4	ks									
					85	k									
D$_1$	2.9 m	21	n	3.6 m	12	n	4.5 m	12	n	10.3 m	17	n	0.65 m	7	n
		79	c		40	ks		29	ks		23	e		38	e
					48	c		59	c		60	c		55	c
D$_2$	3.3 m	10	n							0.5 m	18	n	14.5 m	7	n
		29	e								39	hx		35	hx
		61	c								43	c		58	c
D$_3$	3.1 m	18	n							0.8 m	17	n	1.95 m	9	n
		30	ks								37	5H		53	5H
		52	c								46	c		38	c
D$_4$										0.4 m	24	n	1.3 m	9	n
											32	lh		62	lh
											44	c		29	c
E	33.5 m	0.5	n	38 m	0.5	n	39 m	0.5	n	34.2 m	0.5	n	34 m	0.5	n
		1.	ks		1.	ks		0.25	ks		4.5	lb		5.	lb
		2.5	c		0.5	c		0.25	c		3.	c		0.5	c
		96.	bi		98	bi		99.	bi		92.	bi		94.	bi

Abbrevitations: bi-bischofite; bl, blödite; c, carnallite; e, epsomite; hx, hexahydrite; k, kainite ks, kieserite; 5H, pentahydrite; le, leonite; lh, leonhardtite; n, halite; sy, sylvite kieserite, and hexahydrite for stable equilibrium or halite and leonite, epsomite and sylvite for metastable equilibrium. In the next interval (D), halite combines with some combination of carnallite, kierserite, and epsomite in stable equilibrium or carnallite, epsomite, hexahydrite, pentahydrite, and leonhardtite in metastable equilibrium. In the fmal interval (E), halite is combined with kieserite, carnallite, and bischofite in stable equilibrium or leonhardtite, carnallite, and bischofite in metastable equilibrium.

These assemblages and sequences of assemblages are derived from calculations based on experimental phase equilibria studies. Such calculations are useful as a basis for the investigation of salt deposits but commonly do not resemble natural evaporite deposits. The assumptions, inherent in all the calculations, that evaporation is isothermal, that reactions do not occur at transition points, and that the basin does not receive intermittent influxes of sea water are probably rarely realized in nature. Rather than try to list all varieties of assemblages and sequences of assemblages that might arise in natural environments, it is more reasonable to interpret the characteristics of each evaporite sequence in terms of the basin regime, temperature, phase equilibrium data, and postdepositional changes.

NATURAL SALT SEQUENCES

The numerous factors involved in the formation of evaporite rocks have produced a wide variety of salt deposits in the geologic column. Many are composed of gypsum, anhydrite, or halite, whereas only a few contain potassium and magnesium salts. The compilation of information on the world evaporite occurrences by Lotze (1938, 1957) and discoveries and reports of the past ten years provide a basis for some generalisation.

Some extensive evaporite deposits, such as the Salina Formation of the Michigan basin and the Wellington Formation of Kansas, contain no bedded potassium and magnesium salts in spite of the large volume of halite. One must assume that the residual potassium- and magnesium-rich brines escaped to the ocean or deposited salts that subsequently dissolved. Other major evaporite deposits contain substantial beds of potassium salts but not at all like those one would expect from preceding discussions. The Paradox Formation of southeast Utah, the Prairie evaporites of North Dakota and Saskatchewan, Alberta, and Manitoba, Canada, and the Salado Formation of Texas and New Mexico are examples of a common type of evaporite deposit in which potassium is present dominantly as sylvite in beds of sylvinite (mixture of halite and sylvite). Absent from these deposits are the magnesium sulfate-bearing mineral assemblages that should underlie the sylvite beds. Furthermore, the majority of the potassium occurs as sylvite rather than the anticipated kainite and carnallite. Herein lies the greatest difference between the theoretical and natural salt sequences; namely, the latter are depleted in phases containing sulfate, especially, magnesium sulfate. This problem has received considerable attention in the literature (Braitsch, 1962; Garrett, 1966) and is discussed again in this study.

Bromine in Marine Evaporites

EXPERIMENTAL INVESTIGATIONS

The first studies of the substitution of bromine for chlorine in potassium, sodium, and magnesium chloride minerals were carried out by Boeke (1908). His results were subsequently modified, extended, and applied to the study of European salt deposits by D'Ans and Kuhn (1940), D'Ans and Hofer (1934), Valyashko (1956), Kuhn (1953), and others. In the past ten years, the bromine contents of North American deposits have been reported in the literature (Holser, 1963, 1966; Raup, 1966; Wardlaw and Watson, 1966). The bromine distributions between crystallizing chloride minerals and brines have also been investigated by Braitsch and Herrmann (1963).

Sea water contains an average of 0.0065 weight per cent (65 ppm) bromine. With an average chloride content of 1.8980 weight per cent, the Cl$^-$/Br$^-$ ratio for the oceans is 304:1. When sea water is evaporated, the chloride ions are incorporated in halite, sylvite, and carnallite. The bromide ions do not form descrete bromide minerals but become concentrated in the residual brine and, to a much lesser extent, substitute for chloride ions in chloride minerals. The increases in the bromine and chlorine concentrations in sea water with artificial evaporation are shown in Figure 5 for a coastal Russian lake fed by sea water (Valyashko). The bromine content of a brine increases most rapidly with static evaporation, at a slower rate (or not at all) with brine reflux and intermittent solution influx. At temperatures important in evaporite deposition, KC1 and KBr form a continuous solid solution series; NaCl and NaBr do not. In natural and artificial chlorides, therefore, bromine substitutes more extensively in potassium than in sodium phases for the same bromine concentration in the solution. Table 4 lists ionic radii for the ions of the common chloride evaporite minerals.

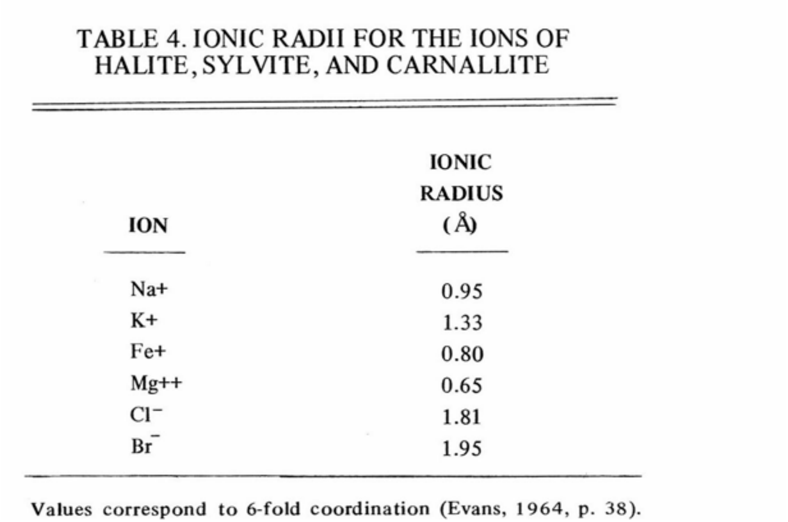


TABLE 4. IONIC RADII FOR THE IONS OF HALITE, SYLVITE, AND CARNALLITE

ION	IONIC RADIUS (Å)
Na+	0.95
K+	1.33
Fe+	0.80
Mg++	0.65
Cl$^-$	1.81
Br$^-$	1.95

Values correspond to 6-fold coordination (Evans, 1964, p. 38).

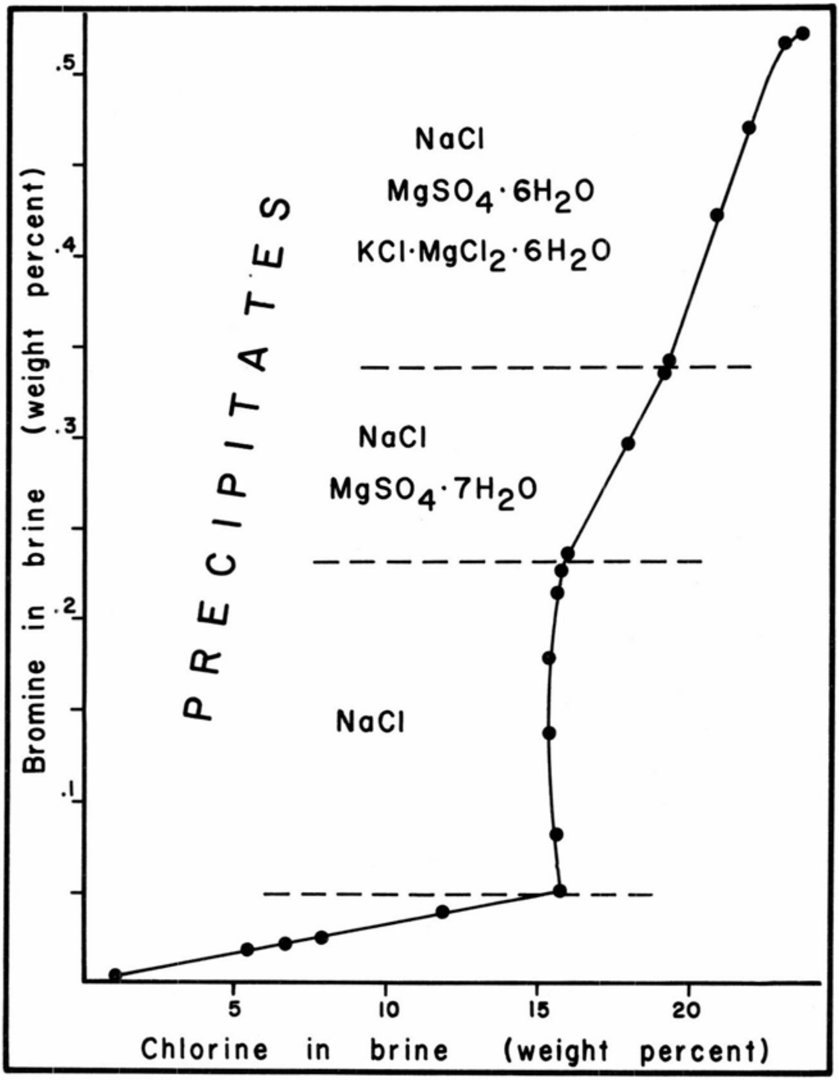


Figure 5

INCREASE IN BROMINE AND CHLORINE WITH EVAPORATION OF SEA WATER FROM A RUSSIAN LAKE

(data from Valyashko, 1956, p. 572)

For each chloride mineral, a bromine distribution coefficient *b* determines the distribution of bromine between a brine and the mineral and is defined as

$$b = \frac{\text{wt \% Br crystal}}{\text{wt \% Br solution}}$$

The magnitudes of the distribution coefficients depend on the composition of the solution and on temperature but are independent of the bromine content of the brine if it is below one per cent. The bromine contents of natural brines are less than one per cent.

Braitsch and Herrmann (1963) determined the bromine distribution coefficients for halite, sylvite, and carnallite under a wide range of temperatures and solution compositions. Under all conditions, the coefficients for these three minerals are less than one. As bromine substitutes for chlorine in one or more precipitating minerals, therefore, its concentration in the brine continues to increase. With this continued increase, so also does the bromine content of the precipitates increase. The distribution coefficients are independent of the bromine content of the brine throughout the concentration range found in natural brines. Figure 6 shows the *b* values for halite, sylvite, and carnallite for a range of bromine concentrations and a variety of solution compositions. The distribution coefficients are also relatively insensitive to changes in temperature. Braitsch and Herrmann (1963) found that over the temperature range 20° to 80°C, the coefficient for halite, carnallite, and sylvite increased 8.2, 15.7, and 11.0 per cent, respectively (fig. 7).

The bromine distribution coefficients are noticeably affected by changes in the $MgC1_2$ content of the brine. Notice in Figure 6, for example, that as the $MgC1_2$ content of the solution increased from zero to saturation with respect to carnallite, the *b* value for halite decreased from approximately 0.16 to 0.073. The coefficient for sylvite shows a similar decrease. The dependence of *b* values on solution composition requires that consideration be given the $MgC1_2$ content of the brine if *b* values are to be selected and used with confidence.

The bromine content of chloride minerals in marine evaporites should provide information on the history of the salt beds when considered in the context of the relations just discussed. With regard to the bromine content of halite,

(1) the stage of brine evaporation should be indicated, assuming the bromine content of the sea water was the same as at present;

(2) in the absence of potassium minerals, their stratigraphic proximity should be indicated by the level of concentration of Br in halite;

(3) vertical and horizontal changes in the Br content should provide information on variations in the brine composition with time and position in the basin;

(4) secondary halite can be identified from primary halite by its lower bromine content; and

KEY TO FIGURE 6

Curve 1	Distribution coefficients for halite in the system Na–Cl–Br–H_2O
Curve 2	Distribution coefficients for halite in the system Na–Mg–Cl–Br–H_2O; $MgCl_2$ concentration corresponds to the beginning of halite precipitation with the evaporation of sea water
Curve 3	Distribution coefficients for halite in the system Na–Mg–Cl–Br–H_2O; $MgCl_2$ concentration at about 11 weight per cent
Curve 4	Distribution coefficients for halite in the system Na–Mg–Cl–Br–H_2O; $MgCl_2$ concentration close to $MgCl_2 \cdot 6H_2O$ saturation
Curve 5	Distribution coefficients for sylvite in the system K–Cl–Br-H_2O
Curve 6	Distribution coefficients for sylvite in the system K–Mg–Cl–Br–H_2O; solution close to carnallite saturation
Curve 7	Distribution coefficients for carnallite in the system K–Mg–Cl–Br–H_2O

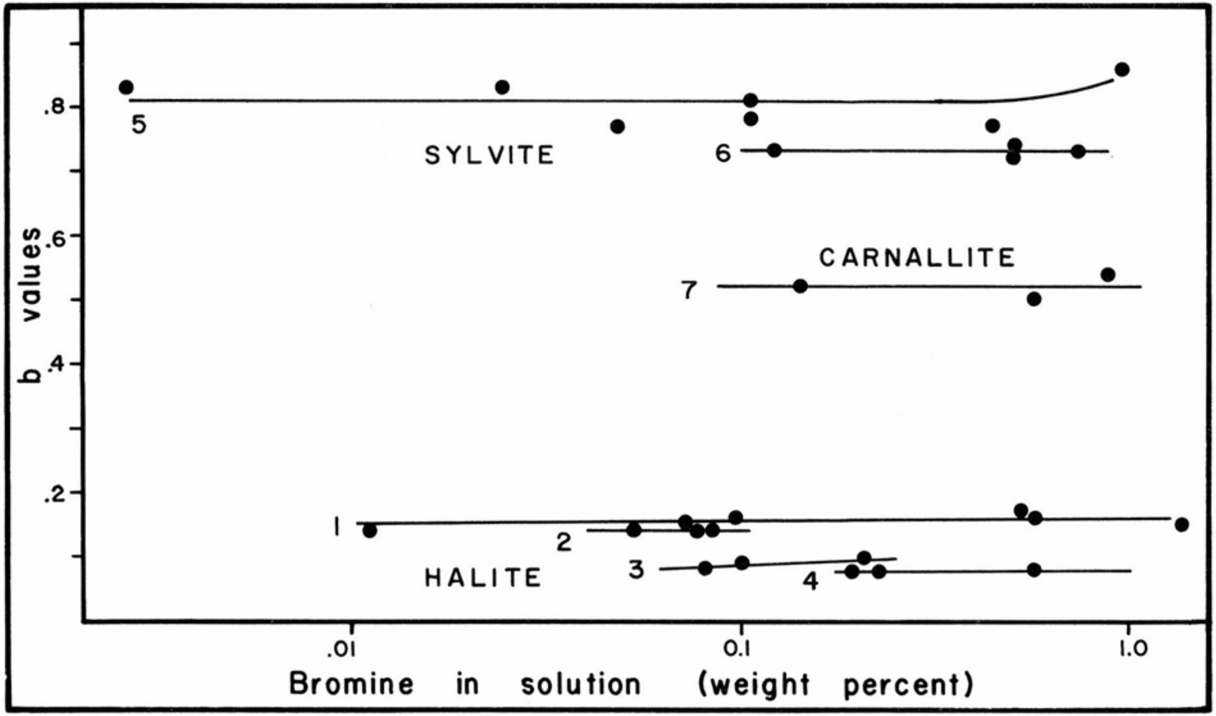


Figure 6

BROMINE DISTRIBUTION COEFFICIENTS (b)

For halite, sylvite, and carnallite with different solution compositions and bromine concentrations at 25°C (modified after Braitsch and Herrmann, 1963).

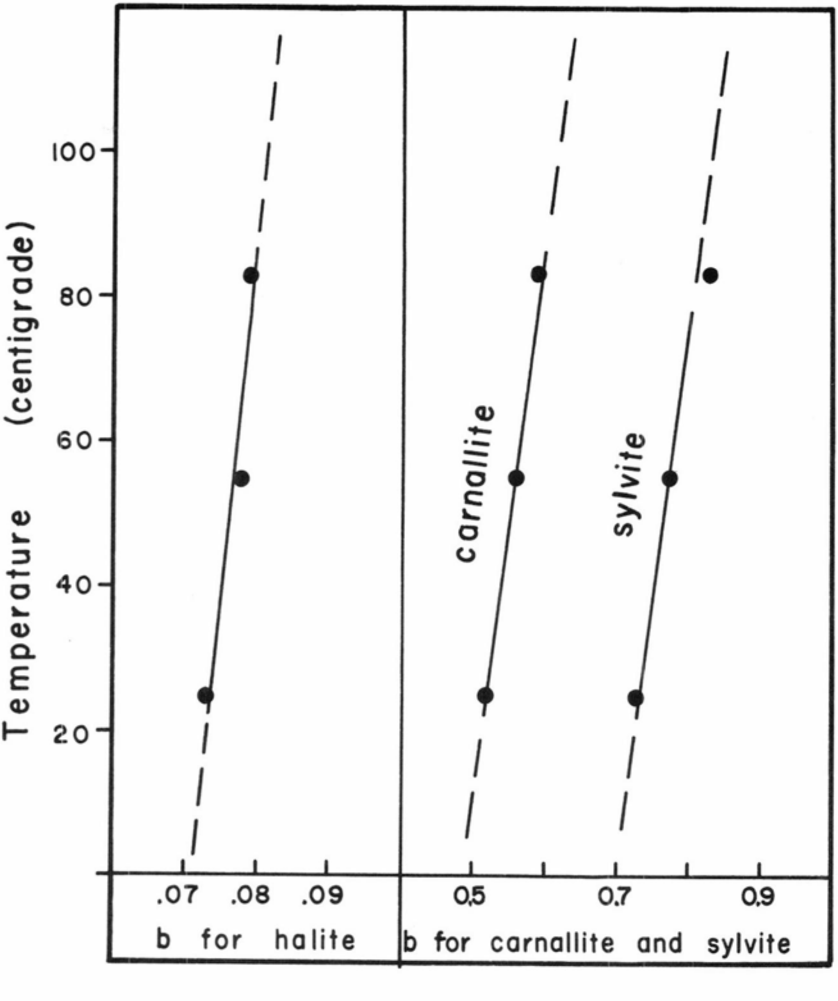


Figure 7

BROMINE DISTRIBUTION COEFFICIENTS (b)

For halite, sylvite, and carnallite as a function of temperature; $MgCl_2$ content of solution for halite and sylvite close to carnallite saturation (after Braitsch and Herrmann, 1963, p. 372)

(5) bromine profiles for an evaporite should supplement lithology as a means of lateral correlation.

The bromine content of coexisting halite and sylvite or halite and carnallite may be used to identify secondary assemblages in which recrystallization or replacement has occurred. Bromine analyses commonly corroborate and augment previously identified lithologic and mineralogic complexities or create confusion where none existed before. When applied as a complement to stratigraphic and mineralogic studies, however, bromine investigations can contribute substantially to the understanding of evaporite deposits.

BROMINE IN NATURAL EVAPORITE DEPOSITS

The bromine contents of natural chloride minerals from many salt deposits have been studied. Baar (1954, 1963) and Schulze (1958) investigated the use of bromine in halite for stratigraphic correlation. Baar (1952, 1954), Kuhn (1955), Kokorsch (1960), and Storck (1954) have applied bromine to the identification and study of postdepositional alteration in the potash beds. Braitsch (1964) studied the temperature of formation of some mineral assemblages.

Bromine profiles have been published for several of the world evaporite deposits. Figure 8 shows generalized bromine profiles (Baar, 1963) for the Werra rock salt (Zechstein 1) of the Werra Basin and the rock salt of the Upper Rhine Oligocene. Notice that the bromine increases from a low of about 70 ppm in both deposits to highs of about 260 ppm and 330 ppm before decreasing again to about 70 ppm. Figure 9 shows a bromine profile of similar shape for rock salt of the Angara—Lena basin of Russia (Ogienko, 1959).

Evaporites of the Mississippian Windsor Formation of Nova Scotia were studied by Baar (1966). Figure 10 presents one bromine profile through the salt section. Van der Plank (1962) analyzed the bromine content of halite from several incomplete potash cores of the Devonian Prairie Evaporite Formation of Saskatchewan, Alberta, and Manitoba, Canada. Schwerdtner and Wardlaw (1963) and Wardlaw (1964) presented bromine profiles for parts of the Prairie evaporites (fig. 11). Special consideration is given to the bromide content of different kinds of halite, including chevron, clear, and brown varieties, by Wardlaw and Watson and Wardlaw and Schwerdtner (1966).

From the major evaporite basins of the United States, the bromine content of the Paradox Member of the Hermosa Formation has been studied by Raup (fig. 12), and Holser (1966) has presented a bromine profile for the Wellington Formation of Kansas (fig. 13).

The first report of bromine in the chlorides of the Salado Formation was made by Schaller and Henderson (p. 23). They stated that bromine was detected only in carnallite-bearing samples and that the concentration was less than 0.1 per cent. Lindberg (1946) analyzed samples containing carnallite, sylvite, and halite and found that the weight per cent increased as the weight per cent carnallite and sylvite increased. Holser (1966) prepared bromine in halite profiles for parts of the Salado and Castile Formations (fig. 14). In the present study, three bromine profiles have been prepared for the Salado Formation, as well as numerous profiles for one potash ore zone.

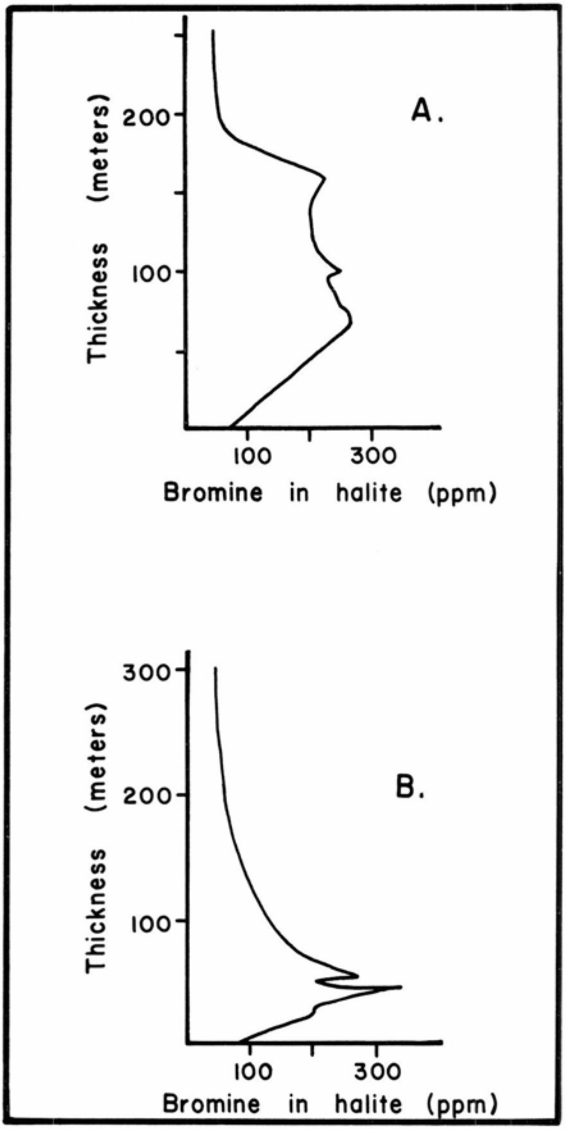


Figure 8

BROMINE PROFILES

A. For the Werra rock salt (Zechstein 1) compiled by Baar (1963) from data of D'Ans and Kühn (1940) and Dittrich (1962).

B. Bromine profile for the Upper Rhine rock salt compiled by Baar (1963) from data of Baar and Kühn (1962) and Manger (1961).

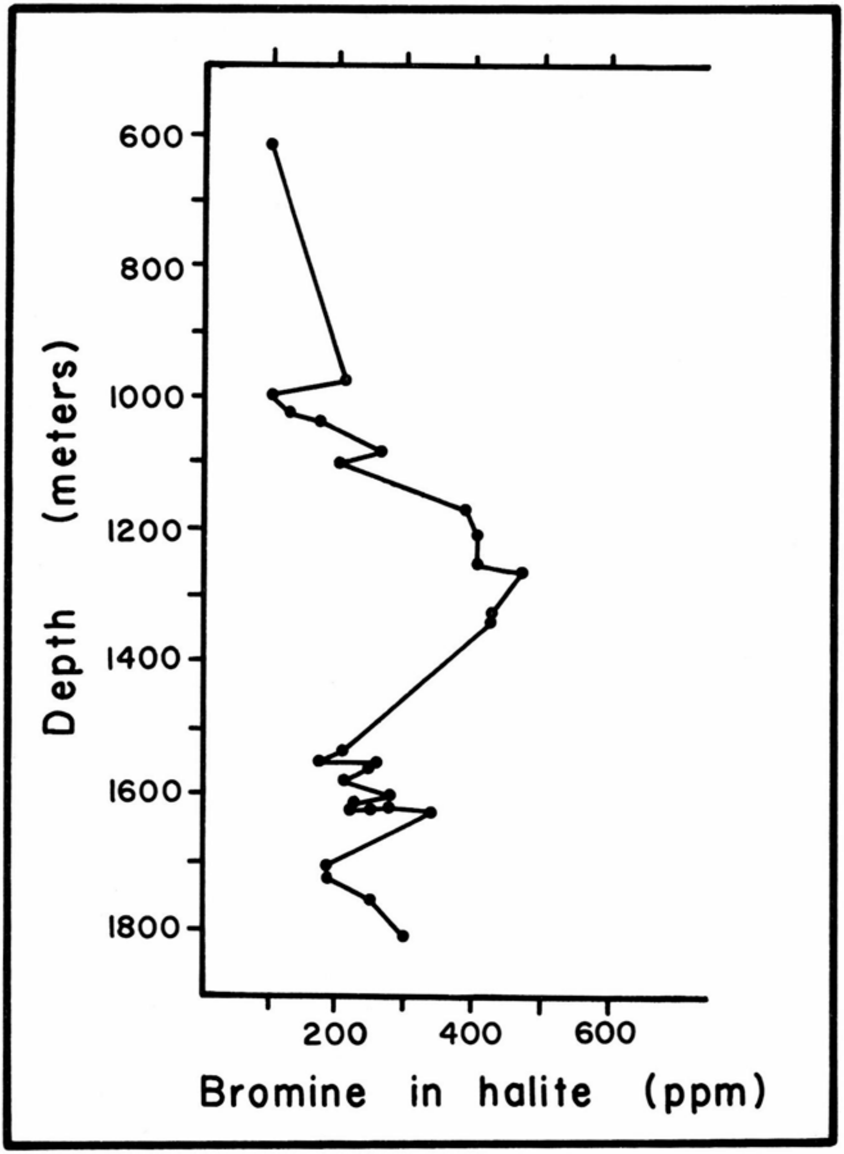


Figure 9
Bromine profile for rock salt of the Angara–Lena Basin, Russia
(modified after Ogienko, 1959)

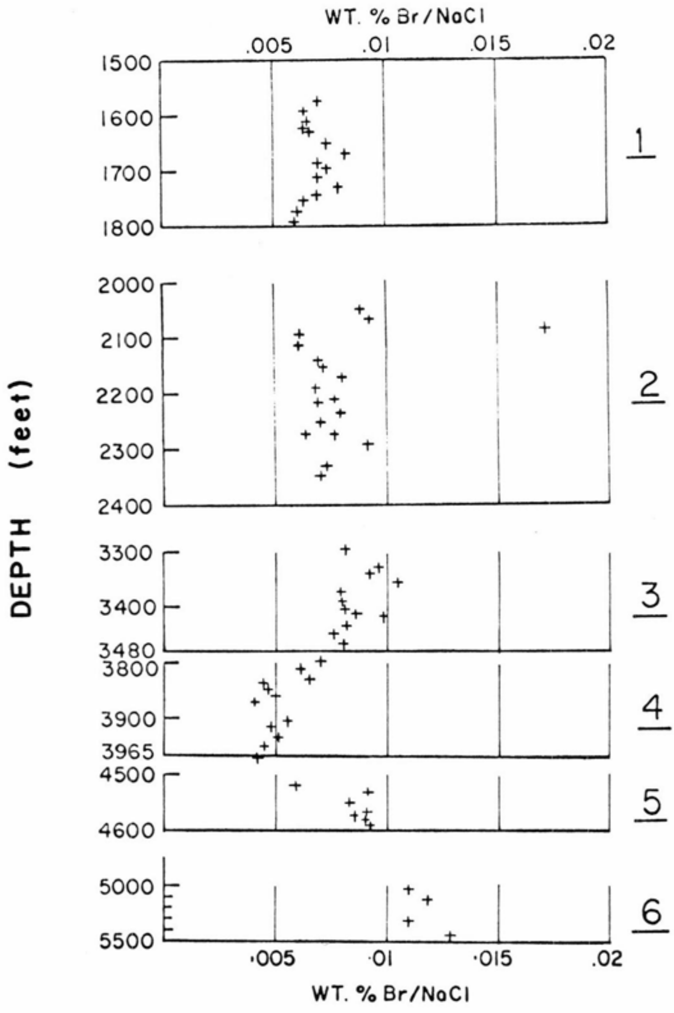


Figure 10

Bromine profile for Halite cuttings from the Windsor evaporites, Sunoco No. 1A, Nappan, Nova Scotia
(after Baar, 1966, p. 289)

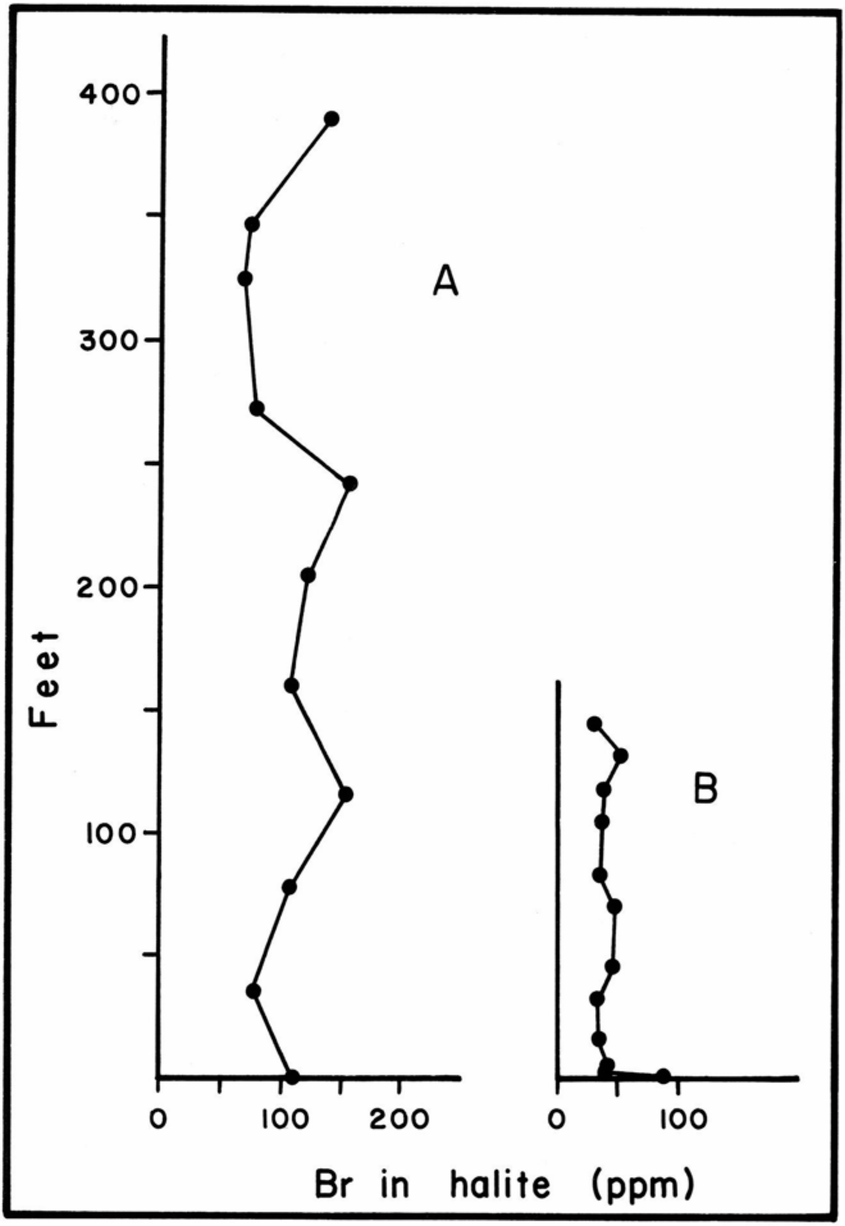


Figure 11

Bromine profiles for the Prairie Evaporite Formation

(A) Winsal Osler and
(B) Tidewater Bryce Lake cores
(after Schwerdtner and Wardlaw, 1963)

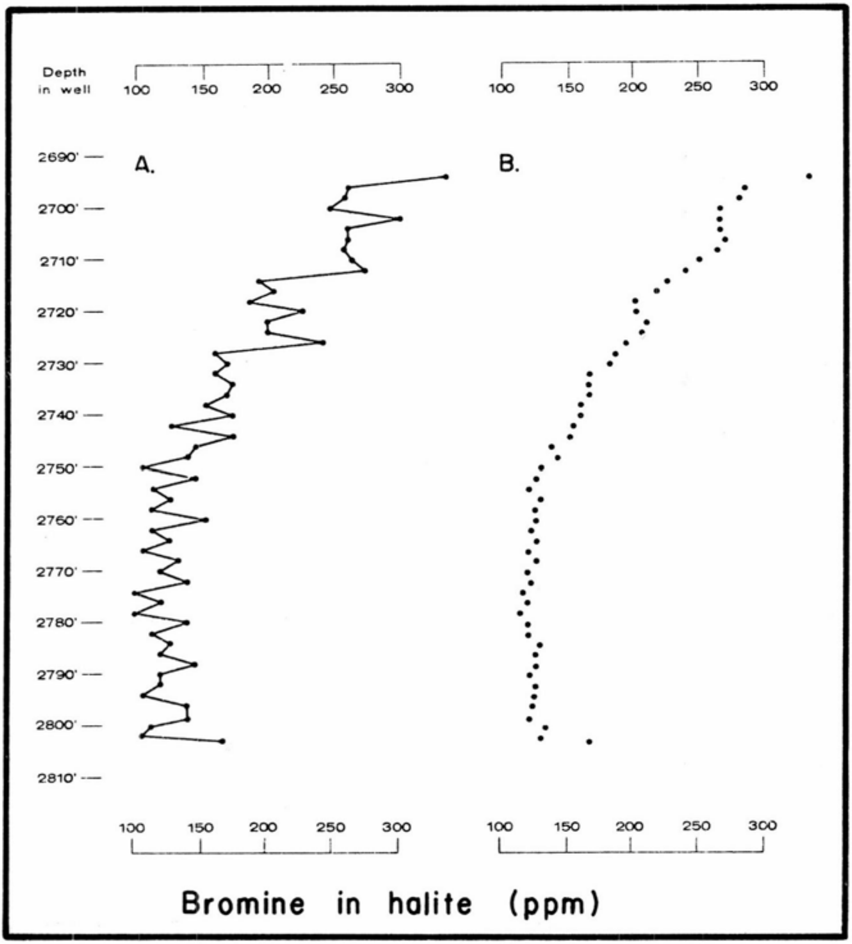


Figure 12

NORMAL (A) AND SMOOTHED (B) BROMINE PROFILE

For salt bed 5, Paradox Member, Hermosa Formation, Utah
(after Raup, 1966)

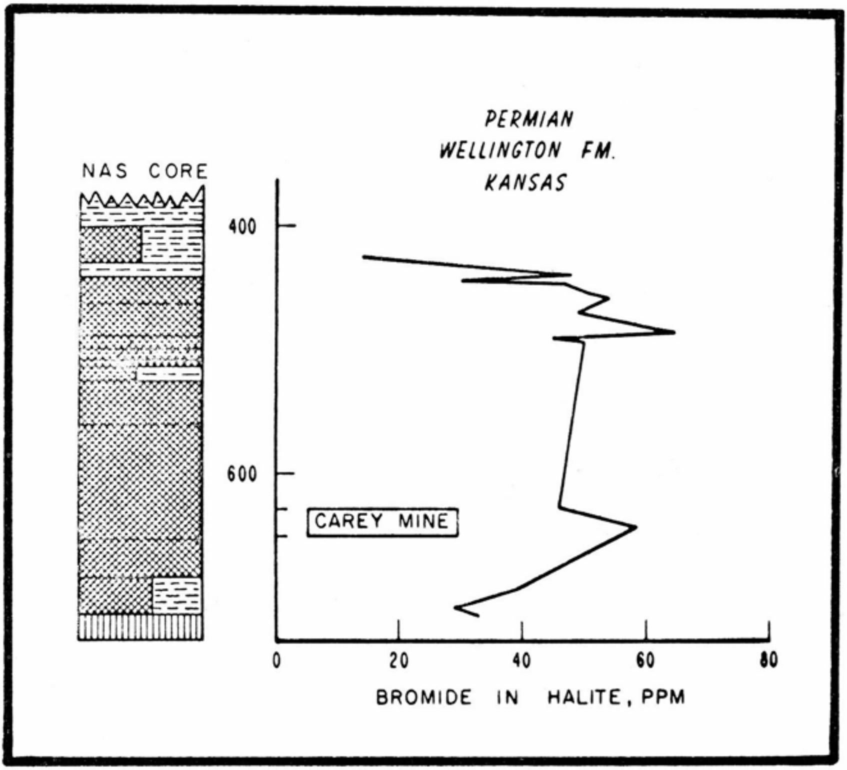


Figure 13
BROMINE PROFILE FOR THE HUTCHINSON SALT MEMBER
Wellington Formation, Kansas
(after Holser, 1966, p. 257)

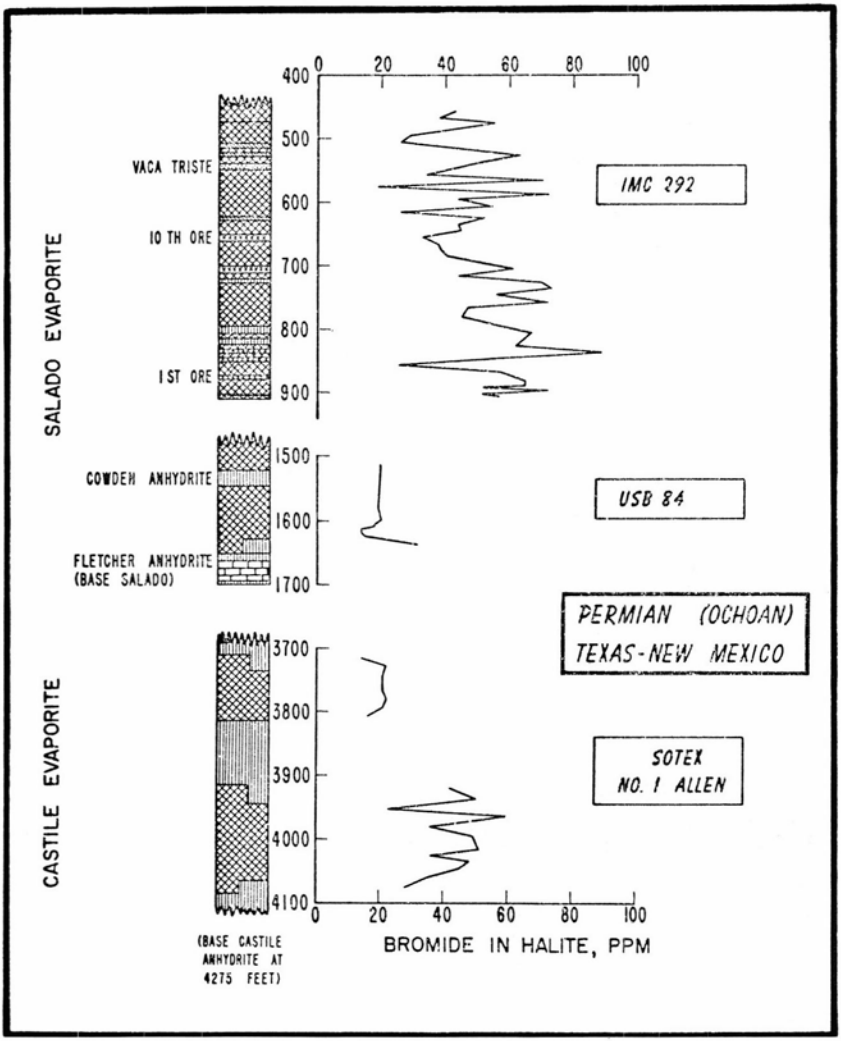


Figure 14

Bromine profiles for parts of the Salado and Castille Formations, Delaware Basin

(after Holser, 1966, p. 263)

Sample Preparation and Analysis

Pure samples of halite and sylvite for bromine analysis were hand-picked from coarsely crushed core and underground samples. Pure mineral samples could be prepared by this method because halite and sylvite differ significantly in color, hardness, crystal habit, and luster. A ten-gram sample of pure mineral was separated, ground to a fine powder in a porcelain mortar, and bottled for analyses.

All bromine analyses were performed according to the method of Willard and Arno (1943). Two hundred analyses were made by the writer in Cambridge, Massachusetts. The remainder of the analyses were by M. C. Dodson and others at the Carlsbad mine site, under the direction of Roy 0. Johnson. By Willard and Arno's analytical method, the sample is weighed and dissolved in water. The bromine is then oxidized to bromate with hypochlorite at a pH between 5.5 and 7.0. After excess hypochlorite has been removed with sodium formate, potassium iodide is added. The iodide is oxidized to iodine by the bromate and titrated with a standard sodium thiosulfate solution.

Analyses performed by this method were repeatedly checked against standard potassium bromide solutions. Recent analyses of standard solutions, typical of the accuracy of the method, were as follows:

Br in Standard Solution (per cent)	Br by Analysis (per cent)
0.0200	0.0201
0.0300	0.0295
0.0500	0.0499

The range of analytical results obtained in this study also checks well with those of other investigators.

The reproducibility of the analytical method was determined by performing several analyses of the same sample. Two groups of analyses of two different samples are tabulated in Table 5. From these data, it seems safe to expect that the analytical error due to inaccuracy and reproducibility will not exceed plus or minus 5 parts per million (0.0005 weight per cent).

Undoubtedly many (in fact, most) samples contained small amounts of contaminants. The most common were clay and polyhalite. Clay is to be avoided because it contains bromine-rich brine; polyhalite acts solely as a dilutent. Fortunately, both of these contaminants are easily recognized and were kept below 5 per cent in the prepared samples.

Sylvite is the most undesirable contaminant in halite because it contains approximately ten times as much bromine and, therefore, contributes disproportionately to the analytical error. Sylvite is easy to recognize in halite if it is red but is more dfifficult to detect when it is milky in color. The preparation of halite concentrates from sylvite-bearing samples required considerable care. Halite samples analyzed for potassium contained less than 0.5 per cent potassium that could not be attributed to polyhalite on the basis of the calcium analysis. This could contribute less than 5 ppm error to the halite analysis, which lies within the range of analytical error.

TABLE 5. MULTIPLE ANALYSES OF TWO HALITE SAMPLES FOR DETERMINATION OF REPRODUCIBILITY OF ANALYTICAL METHOD

Sample 1		Sample 2	
No.	% Br	No.	% Br
SH-1	90	T-1	99
SH-2A	90	T-2	99
SH-2B	90	T-3	103
SH-3	94	T-4	82
SH-4A	94	T-5	100
SH-4B	94		
SH-5	94		
Average	92.3	Average	96.6

Distribution of Bromine in the Salado Formation

BROMINE CONTENT OF SINGLE SAMPLE

Interpretation of the bromine distribution in the Salado Formation depends on how well a bromine analysis represents the bromine content of the sample or bed. To investigate local variations in the bromine content of halite, 26 samples from different locations were collected, and two or more preparations and analyses made. The analyses listed in Table 6 show that the average deviation exceeded that of the analytical method (±5 ppm) for only 5 samples. The deviations exceed the analytical error by more than 2 parts per million for only 2 of these 5 samples. If these figures are representative, 80 per cent of all analyses presented reflect the bromine content of the sample and the local bromine content of the bed within the analytical error.

Where two or more distinct types of halite are present in a bed or sample, it may be necessary to consider their bromine contents separately. The presence of more than one type of halite in a sample may be indicated by color, grain size, or inclusions. A common association in the Salado Formation is coarse-grained halite (15 to 25 mm) with finer-grained halite (5 to 10 mm). The coarser halite is generally clear, whereas the fine-grained halite is commonly buff or orange because of inclusions of polyhalite. Concentrates of both types of halite were prepared from many samples and the analyses are presented in Tables 7 and 8.

The 20 coarse- and fine-grained samples of Table 7 came from a variety of places in the Salado Formation. The fine-grained portion of the samples (average 67 ppm) generally contained slightly more bromine than the coarse-grained fraction (average 62 ppm). The difference between the two exceeded 10 ppm, however, for only 6 samples. Coarse halite in 5 of the 20 samples contains more bromine than the fine halite. The large crystals and generally lower bromine content of coarse-grained halite probably resulted from recrystallization.

The samples in Table 8 came from bed F of the first ore zone (see fig. 20) in ore and waste at underground location 6 (see fig. 25a). The coarse halite of the samples generally contains slightly more bromine than the fine halite in both ore and waste. This is exactly opposite the relation of the samples in Table 7. Recrystallization of halite in the ore zone, particularly in association with salt horses, increases the bromine concentration, whereas outside the ore zone the reverse is true. Recrystallization around and within salt horses also produces erratic bromine variations.

TABLE 6. MULTIPLE SAMPLE PREPARATIONS AND ANALYSES OF HALITE FROM THE SALADO FORMATION

Sample number	Bromine in Halite (ppm) Analyses	Average	Average deviation
9-6	53,88,87	76	15
1A-1	85,88	86	2
52-779.2	64,61	62	2
115-819.3	60,47	53	6
115-419.9	45,58	51	6
115-439.9	64,64	64	0
115-497.0	43,51,42,42	42	1
115-562.7	37,43	40	3
115-598.6	55,55	55	0
115-739.9	38,45	41	3
115-745.0	41,42,42	42	1
115-799.8	72,78	75	3
115-807.2	104,101	102	2
115-809.2	64,65	64	1
6-2-2	59,45	52	7
6-5-6	85,105	95	10
7-1-4	57,51	54	3
7-5-7	70,66	68	2
7-6-9	71,79	75	4
7-8-4	57,59	58	1
8-1-3	61,62	61	1
6-0+65	72,79	75	4
145	63,64	63	1
22	66,69	67	2
218-742.0	69,72	70	3
331-829.8	52,52	52	0

TABLE 7. BROMINE CONTENT OF COARSE (MORE THAN 10 MM) AND FINE (LESS THAN 10 MM) HALITE IN THE SAME SAMPLE FROM THE SALADO FORMATION

Sample number	Bromine Content of Halite (ppm) Fine (HF)	Coarse (HC)	HF–HC
1-1-6	64	66	–2
1-2-2	60	58	2
5-6	72	72	0
6-3-4	54	50	4
6-5-3	91	71	20
7-1-5	66	65	1
7-1-9	59	72	–13
7-1-6	91	66	25
7-3-9	85	84	1
7-4-5	69	60	9
7-4-8	79	66	13
8-1-6	66	66	0
8-2-9	78	72	6
331-529.8	52	52	0
331-839.8	26	32	–6
115-807.2	102	73	29
115-820.9	61	48	13
115-862.5	66	75	–9
331-640.0	32	32	0
331-789.8	65	71	–6
Average	67	62	

TABLE 8. BROMINE CONTENT OF COARSE AND FINE HALITE IN ORE AND WASTE, LOCATION 6, BED F, FIRST ORE ZONE

	Bromine Content of Halite (ppm)		
Sample number	Fine (HF)	Coarse (HC)	HF–HC
	ORE		
6-2	–	59	–
6-3	52	72	–20
6-0+20	–	72	–
6-0+40	–	72	–
6-0+65	72	79	–5
6-0+70	53	–	–
6-0+85	66	66	0
6-1+05	66	–	–
Average	62	70	
	WASTE		
6-1-25	86	86	0
6-5	–	95	–
6-1+45	92	79	+13
6-1+65	80	99	–19
6-1+85	–	99	–
6-6	79	91	–12
6-2+05	79	86	–7
6-2+25	94	72	+22
Average	85	88	

VERTICAL DISTRIBUTION OF BROMINE IN THE SALADO FORMATION

The bromine content of halite in the Salado Formation was investigated over a stratigraphic interval of 460 feet between the 113 and 126 polyhalite beds. Analyses were made of samples collected at 10-foot intervals from the drill cores of IMC core tests 115 and 331.

The bromine contents of samples from IMC 115 are plotted in Figure 15 with the ore zones, polyhalite and anhydrite beds, and clay concentrations. Clay beds are indicated by solid horizontal lines, argillaceous halite intervals by broken lines and blocks.

The bromine content of halite alternately increases and decreases vertically in the Salado Formation. These changes are abrupt for some intervals, gradual for others. It is probable that had samples been taken at sufficiently small intervals, the curve in Figure 15 would be smoother but would contain more inflections. The bromine curve in Figure 16 was constructed with analyses of samples collected at 0.5-foot centers from a part of the interval in Figure 15. This profile demonstrates that gradual bromine variation can be identified With closely spaced analyses. In the discussion that follows, it should be kept in mind that Figure 15 is a generalized bromine profile for the Salado Formation.

The core from the stratigraphic interval represented in Figure 16 was analyzed for K, Mg, Ca, Cl, SO_4, water-insoluble material and combined water in addition to bromine. Table 9 gives the analyses. The mineralogy of the samples (table 10) was calculated from the analyses using the following assumptions:

All calcium in the analysis is from polyhalite (the calcium is then used to calculate the amount of polyhalite in the sample);

All sodium is present as sodium chloride (sodium is calculated as an ion balance, not determined analytically);

The water of crystallization in polyhalite was not obtained in the combined water analysis; the analytical totals, therefore, must be increased by the amount of H2 0 in polyhalite.

The striking aspects of the bromide profile of the Salado Formation include its

irregularity;

the correlation between the bromine content of halite and the mineralogy and changes in mineralogy of the associated rocks; and

the narrow range of the bromine content of halite.

These features may be conveniently discussed by considering the distribution of bromine as a function of lithology.

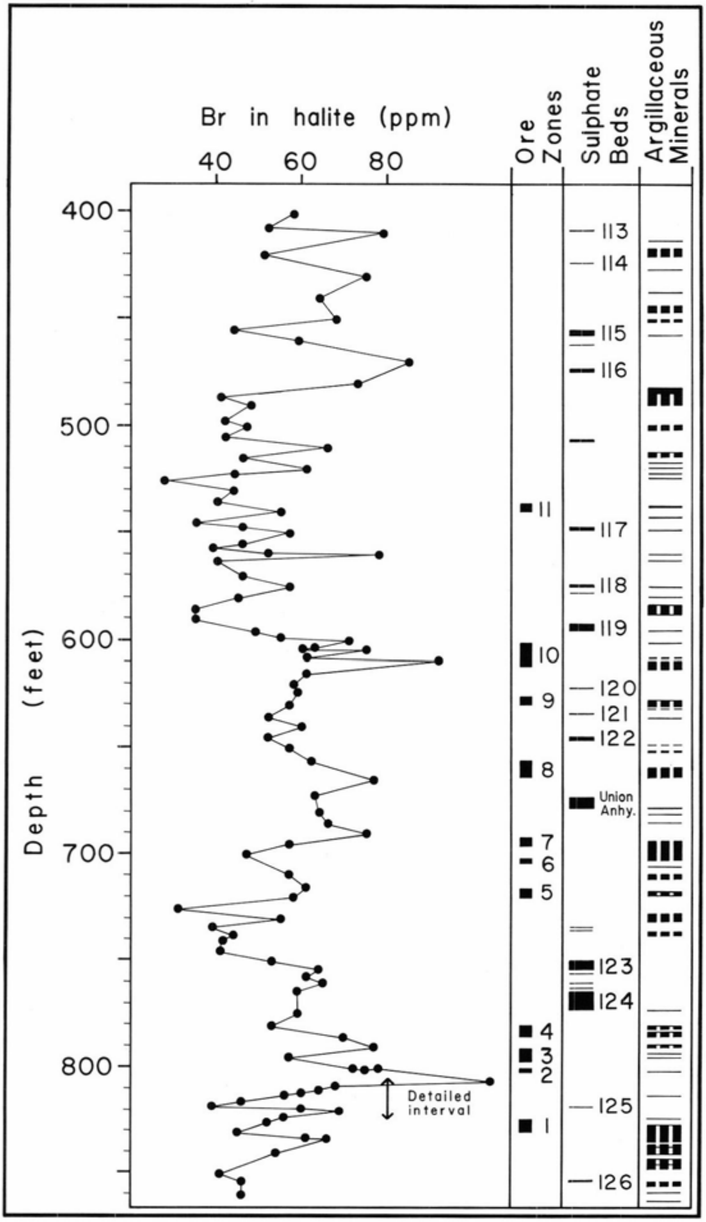


Figure 15

Bromine profile for Halite in the Salado Formation

(Core test IMC 115)

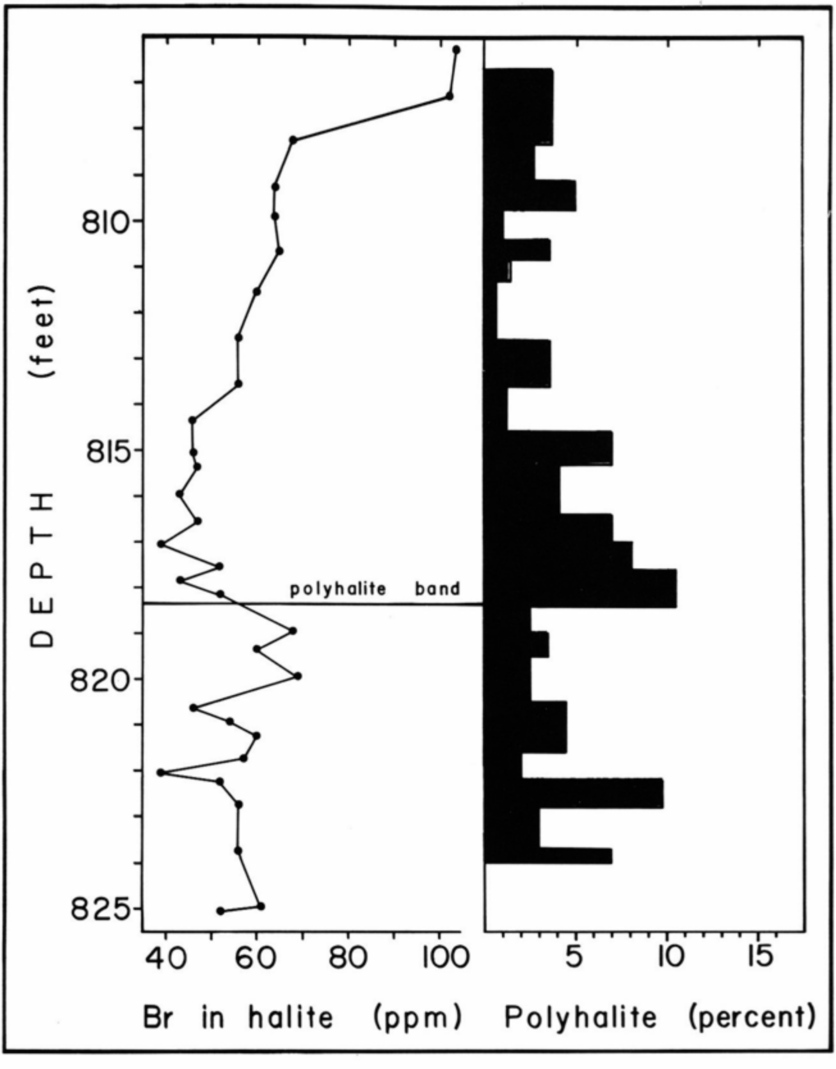


Figure 16

Detailed Bromine profile for part of the Salado Formation

(Core test IMC 115; see fig. 15)

TABLE 9. ANALYSES OF CORE SAMPLES BETWEEN 806.7 AND 824.0 IN CORE TEST IMC 115

	FOOTAGE			WEIGHT PER CENT								
NO.	FROM	TO	INT.	K	Mg	Na	Ca	Cl	SO_4	INSOL.	H_2O	TOTAL
1	806.7	808.3	1.6	0.56	.20	37.53	0.50	58.00	2.50	0.03	.32	99.64
2	808.3	809.1	0.8	.35	.14	38.21	.38	59.00	1.78	.02	.22	100.10
3	809.1	809.7	0.6	.78	.26	36.78	.73	56.80	3.60	.03	.40	99.38
4	809.7	810.4	0.7	.13	.07	38.44	.13	59.40	0.57	.12	.12	98.98
5	810.4	810.8	0.4	.58	.19	37.29	.51	57.60	2.55	.30	.38	99.41
6	810.8	811.3	0.5	.24	.12	38.48	.21	59.50	1.05	.08	.18	99.86
7	811.3	812.6	1.3	.19	.08	37.68	.08	58.30	0.46	1.95	.32	99.06
8	812.6	813.6	1.0	.67	.39	32.94	.51	51.50	2.61	7.40	.78	96.80
9	813.6	814.6	1.0	.10	.08	38.67	.16	59.80	0.70	.22	.16	99.98
10	814.6	815.3	0.7	1.07	.40	35.27	.99	54.60	4.96	1.22	.70	99.21
11	815.3	816.4	1.1	0.70	.20	37.30	.58	57.70	2.78	.08	.36	99.70
12	816.4	817.0	0.6	1.02	.30	36.03	.94	55.70	4.49	.11	.50	99.09
13	187.0	817.6	0.6	1.07	.35	35.48	1.07	54.80	5.14	.27	.56	98.74
14	817.6	818.4	0.8	1.37	.45	34.82	1.42	53.80	6.71	.19	.74	99.50
15	818.4	819.0	0.6	.35	.11	37.68	.33	58.10	1.65	.11	.24	98.57
16	819.0	819.5	0.5	.46	.17	37.63	.46	58.10	2.22	.13	.30	99.47
17	819.5	820.5	1.0	.35	.12	38.05	.33	58.70	1.65	.14	.22	99.56
18	820.5	821.6	1.1	.62	.20	36.97	.61	57.10	2.88	.37	.38	99.13
19	821.6	822.2	0.6	.27	.09	38.23	.26	59.00	1.23	.10	.18	99.36
20	822.2	822.8	0.6	1.37	.43	34.80	1.29	53.90	6.13	.59	.68	99.19
21	822.8	823.7	0.9	.43	.13	37.68	.38	58.20	1.81	.09	.24	98.96
22	823.7	824.0	0.3	.99	.30	36.10	.97	55.80	4.53	.12	.20	99.01

TABLE 10. CALCULATED MINERALOGY FOR ANALYSES IN TABLE 9
(representing samples between 806.7 and 824.0 in core test IMC 115)

	WEIGHT PER CENT MINERAL					
NO.	HALITE	POLY-HALITE	INSOL.	TOTAL (Tm)	ANAL. TOT. (TA) + H_2O POLY.	TOTAL (TA–Tm)
1	95.33	3.76	0.03	99.12	99.86	0.74
2	97.05	2.86	.02	99.93	100.27	0.34
3	93.42	5.49	.03	98.94	99.71	0.77
4	97.64	0.98	.12	98.74	99.04	0.30
5	94.71	3.84	.30	98.85	99.64	0.79
6	97.74	1.58	.08	99.40	99.95	0.55
7	95.71	0.60	1.95	98.26	99.10	0.84
8	83.67	3.84	7.40	94.91	97.03	2.12
9	98.22	1.20	.22	99.64	100.05	0.41
10	89.59	7.45	1.22	98.26	99.65	1.39
11	94.74	4.36	.08	99.18	99.96	0.78
12	91.52	7.07	.11	98.70	99.51	0.81
13	90.12	8.05	.27	98.44	99.22	0.78
14	88.44	10.68	.19	99.31	100.14	0.83
15	95.71	2.48	.11	98.30	98.72	0.38
16	95.58	3.46	.13	99.17	99.68	0.51
17	96.65	2.48	.14	99.27	99.71	0.44
18	93.90	4.59	.37	98.86	99.40	0.54
19	97.10	1.96	.10	99.16	99.48	0.32
20	88.39	9.70	.59	98.68	99.77	1.09
21	95.71	2.86	.09	98.66	99.13	0.47
22	91.69	7.30	.12	99.11	99.45	0.34

BROMINE IN HALITE BEDS

In halite beds free of argillaceous material, the bromine content of halite generally increases from the bottom to the top of the bed. This increase may be uniform or it may be interrupted by short intervals in which the bromine in halite remains constant or decreases. This pattern is readily apparent in Figure 16 and the equivalent interval in Figure 15. The pattern is not apparent throughout most of the curve in Figure 15 because adjacent samples are not from the same clean halite bed but, in most instances, come from adjacent argillaceous halite beds or are separated from each other by sulfate, argillaceous halite, or clay beds. It is probable that the bromine content of halite will change gradually when the samples are collected from the same halite bed. Across bed boundaries, however, the bromine content of halite may be expected to change abruptly and unpredictably.

The gradual increase in the bromine content of halite toward the top of a halite interval is inferred at depths of 420, 520, 560, 670, and 810 feet in Figure 15. Closer spaced analyses for these intervals would probably yield bromine curves much like that in Figure 16.

BROMINE IN ARGILLACEOUS HALITE BEDS

The distribution of bromine is more difficult to study in argillaceous halite than in halite beds because individual argillaceous halite beds are generally thin and the clay must be removed from the sample prior to the bromine analysis. Argillaceous halite intervals are commonly composed of a series of units separated by discontinuous or pronounced clay bands and containing different concentrations of argillaceous material. The distribution of the bromine content of halite in argillaceous halite intervals appears to be erratic (fig. 15). It is probable that this irregularity reflects the composite nature of the argillaceous halite beds and that close-spaced analyses of each unit would produce gradual bromine variations.

Frequency distribution curves for 58 bromine analyses of halite and 37 analyses of argillaceous halite from IMC 115 are plotted in Figure 17. There appears to be no significant difference between the bromine content of halite (average 55 ppm) and argillaceous halite (average 56 ppm).

BROMINE IN POTASSIUM-BEARING BEDS

The distribution of bromine within potassium-bearing beds or ore zones has been investigated in detail only for the first ore zone. Details for this ore zone will be discussed later.

The bromine content of the halite generally increases irregularly up through the halite and argillaceous halite intervals immediately below ore zones. This is true, in Figure 15, for ore zones 1, 2, 5, 7, 8, and 10. Within the ore zones, if data for the first ore zone are representative, the range of the bromine content of halite is as great as it is for the entire Salado Formation. The bromine content of halite decreases abruptly across the upper contact of the ore zones, reflecting the transition from the argillaceous halite and sylvinite of the ore zone to the overlying halite.

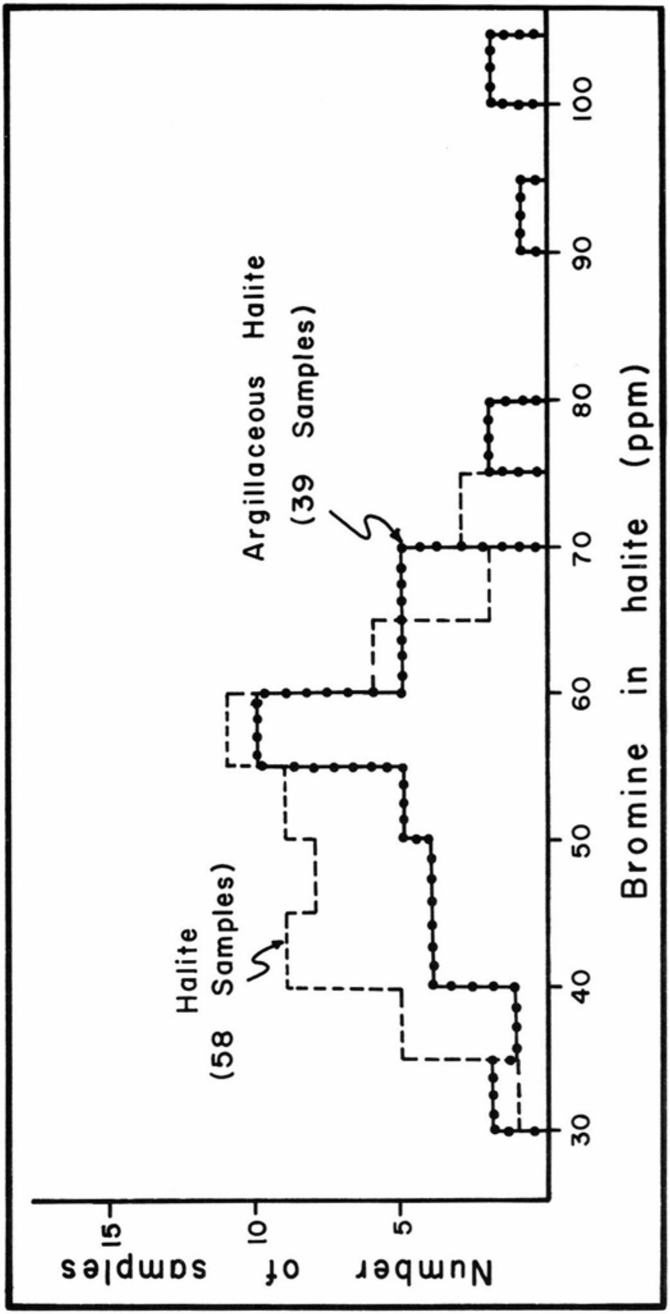


Figure 17

Frequency distribution curves for Halite and Argillaceous Halite

(Core test IMC 115)

BROMINE ADJACENT TO SULFATE AND CLAY BEDS

Sulfate beds rarely contain appreciable halite, so no effort was made to study the distribution of bromine within these beds. It has been noted, however, that significant changes in the bromine content of halite commonly occur in the vicinity of such beds. In exploring this relation, one should recognize two type of sulfate beds: First, those beds that range from discontinuous seams up to 4 inches in thickness and are immediately overlain and underlain by halite. Second, those beds with a thickness range from 4 inches to 10 feet underlain by gray magnesitic clay. The halite rock below this clay may be argillaceous; that above the sulfate bed is free of argillaceous material.

The bromine content of halite beneath thin sulfate beds begins to decrease less than 3 feet below the sulfate-halite contact. The decrease may continue into the halite above the sulfate bed for a few feet before it again increases. This relation is apparent in Figure 16 with respect to the polyhalite bed at 818.3 feet in the section. Notice also the thin polyhalite beds in Figure 15 at footages 462 and 506. The bromine content of halite below thick sulfate beds increases up to the base of the clay bed. The bromine content of halite immediately above these sulfate beds begins lower than at the base and increases up through the overlying halite. This pattern is present across sulfate marker beds 115, 117, 118, and 126.

The antipathy between sulfate minerals and high bromine concentrations in halite may be extended to include disseminated polyhalite present as microscopic grains or 1- to 10-mm blebs in many halite beds. In the interval of stratigraphy shown in Figure 16, the bromine content of halite fluctuates and decreases as the weight per cent polyhalite fluctuates and increases, particularly in the interval between 821 and 823 feet. The following summarizes the relationships between the bromine content of halite and the distribution of sulfate minerals:

> The bromine content of halite generally decreases toward sulfate beds, both from above and from below.
>
> An increase in the disseminated polyhalite content of halite rock generally is attended by a decrease in the bromine content of halite.
>
> Bromine profiles across thin sulfate beds are different from those across thick beds with underclays. The origins of these two types of profiles will be considered in a subsequent section.

Clay beds also produce inflections in the bromine profile of the Salado Formation. The bromine content of halite decreases above the clay beds at the tops of the ore zones. For many of the clay beds shown in Figure 15, however, the bromine concentration appears to remain constant or to increase from halite below to halite above the clay beds. The relationships between the bromine content of halite and clay beds has not been well documented in this study.

RANGE AND RATE OF CHANGE OF BROMINE IN HALITE

All bromine analyses of halite from the Salado Formation fall between 25 and 105 parts per million. The large majority of samples, however, contains between 35 and 70 ppm bromine. This is a remarkably narrow range for 460 feet of salt stratigraphy when halite from other evaporites contains as much as 400 and as little as 25 parts per million bromine. It is also remarkable that the bromine is rather uniformly distributed; that is, there is no gradual increase or decrease in the bromine content of halite toward the top of the Salado Formation. At best, one might say there is a slightly higher average bromine concentration between 400 and 500 feet and between 600 and 700 feet in the core of IMC 115.

The rate of change of bromine in the numerous bromine cycles in Figure 15 is difficult to determine without more detailed sampling. It is estimated that the average rate of change of bromine in halite is approximately 10 to 15 parts per million per 3 feet. The cycles cover the concentration range of 25 to 30 ppm and an interval from 5.9 to 9.8 feet. More accurate figures can be obtained from Figure 16. Over the intervals 821.0 to 819.4, 815.3 to 809.3, and 809.3 to 806.3, the bromine content of halite increases at the rate of 25, 11, and 40 ppm per 3 feet of stratigraphic rise. Over the interval 819.4 to 817.6, the bromine content of halite decreases at the rate of 37 ppm per 3 feet. The rate of change of bromine in halite obviously is not constant. It is probable that the higher rates of change were associated with more concentrated brines; for example, just before or during the deposition of potassium minerals. More thorough sampling could be expected to substantially improve the definition of these relations.

HORIZONTAL DISTRIBUTION OF BROMINE IN THE SALADO FORMATION

The horizontal distribution of bromine may first be investigated by comparing the bromine profiles for two core tests. The profile for IMC 115 (fig. 15) was discussed in the preceding section. The profile for IMC 331, about 7 miles south of IMC 115, is given in Figure 18. Although the sampling for IMC 331 is less complete, it is apparent that the bromine concentrations in halite from equivalent stratigraphic units in the two core tests are similar. It would have been desirable to study the horizontal distribution of bromine with closely spaced samples, but no such samples were available except in the mine workings of the ore zones. The ore zones seemed unacceptable because of postdepositional changes that might have altered the primary bromine distribution. Postdepositional changes in the bromine content of halite in the ore zone probably attended the alteration of the potassium and magnesium chloride minerals. A horizon was selected, therefore, immediately above bed A of the first ore zone, and samples were collected from several core tests. The boundary between bed A and the overlying salt is an erosion surface on which the clay of bed A collected as a residuum, making it a sharp and easily recognized boundary. The halite samples analyzed for bromine represent the first halite deposited after the reattainment of saturation with respect to sodium chloride.

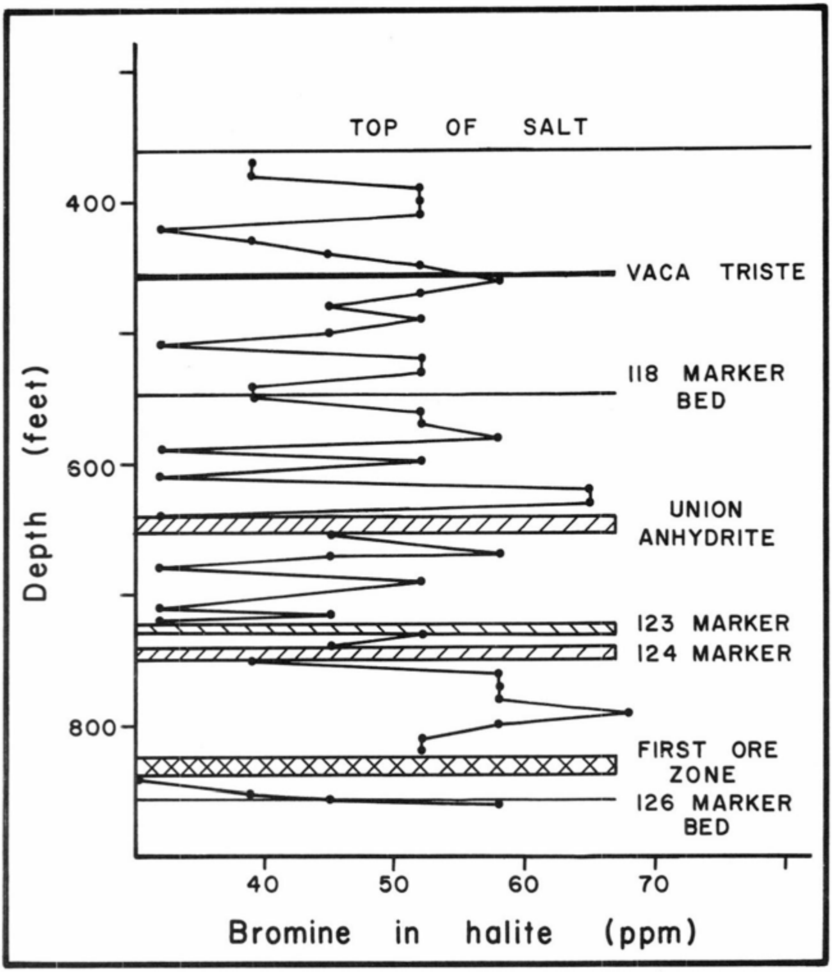


Figure 18
BROMINE PROFILE FOR HALITE IN THE SALADO FORMATION
(Core test IMC 331)

The horizontal distribution of bromine resulting from these analyses is shown in Figure 19. At this horizon, there is a considerable range in the bromine content of halite and the distribution of these values is not random. Near the center of the map, an area of high bromine concentrations in halite (70 to 83 ppm) is entirely surrounded by lower bromine values. The significance of this distribution will not be realized until the area of sampling is enlarged. The data may then provide information on variations in the composition of the brine and the geometry of the basin of deposition.

DISTRIBUTION OF BROMINE IN THE FIRST ORE ZONE

DESCRIPTION OF ROCK TYPES

The first ore zone contains eleven beds within the area of this study. Within some of these beds, one or more lithologic units are generally present. In Figure 20, the beds and common subunits of the ore zone are identified by lithology and letter. The beds may be divided into halite, sylvinite, halite marker, and clay on the basis of their bulk lithology. The contacts between beds and units within them are generally sharp and easy to recognize in the mine.

The lithology for about 10 feet above the ore zone is halite with 0.5 to 11 per cent polyhalite. This interval, shown in Figure 16, was described in an earlier section. Below the first ore zone are about 10 feet of interbedded halite and argillaceous halite containing up to 30 per cent brown clay. Underlying this interval are 5 feet of halite and the 126-polyhalite marker bed.

Clay Beds

Clay in the first ore zone is represented by beds A and D. Because of their dominant brown to reddish-brown color, these two beds have been referred to in the district as the first (or top) and second brown clays. Both beds are composed of 50 to 70 per cent argillaceous material, the balance being halite with traces of polyhalite and other minerals. The argillaceous material is generally brown, but it becomes gray in the extreme southern part of the study area.

The mineralogy of the argillaceous material is assumed to reflect the composition of similar material from other sections of the ore zone and other ore zones, namely, a variety of clay minerals, quartz, and talc.

In both clay beds, the ratio of clay to halite decreases irregularly from the top to the bottom of the bed. The upper few centimeters of the beds contain at least 90 per cent argillaceous material. The percentage decreases to about 10 in the bottom few centimeters. This distribution of argillaceous material is not duplicated in any other bed in the first ore zone but is repeated at the tops of other ore zones. Halite in these clay beds is finer grained (5 mm) than in halite and sylvinite beds. Where the rock is dominantly clay, individual halite grains are scattered through the argillaceous groundmass. As halite becomes more abundant, the clay forms clots between clusters of clay-bearing halite grains and within coarser halite grains.

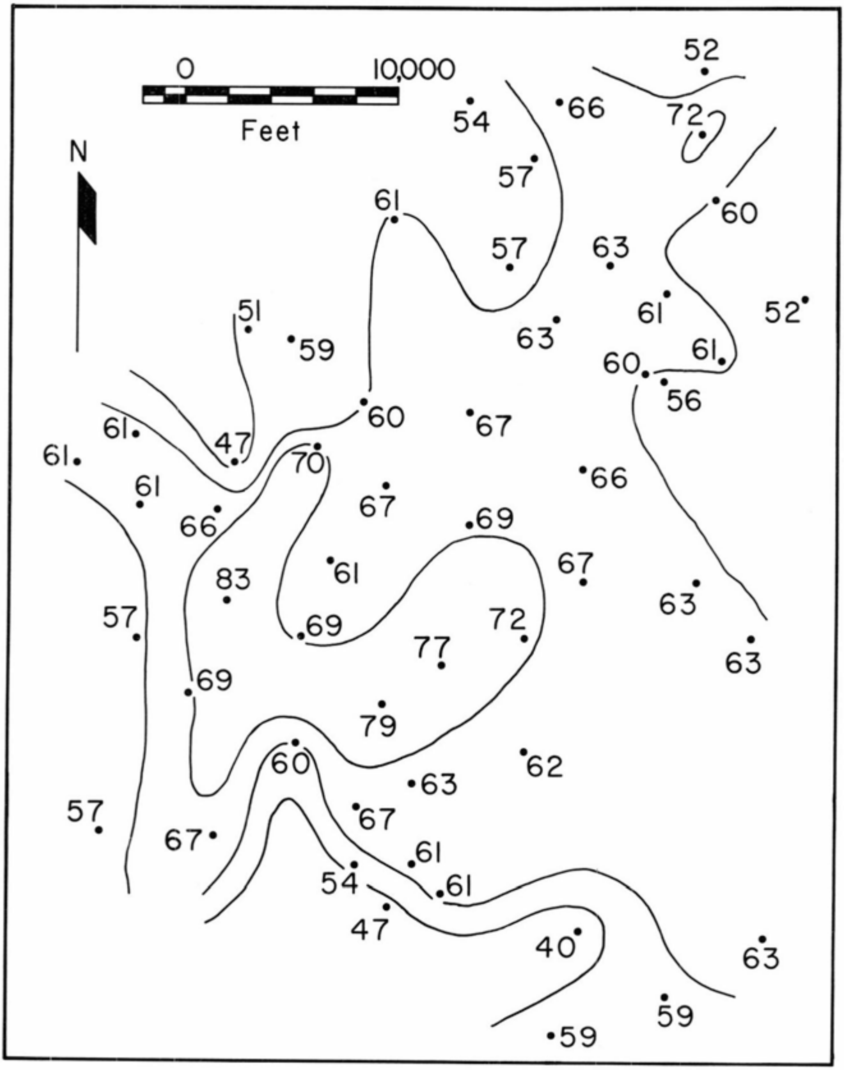


Figure 19

HORIZONTAL DISTRIBUTION OF BROMINE (PPM) IN HALITE

From halite interval immediately above bed A of the first ore zone

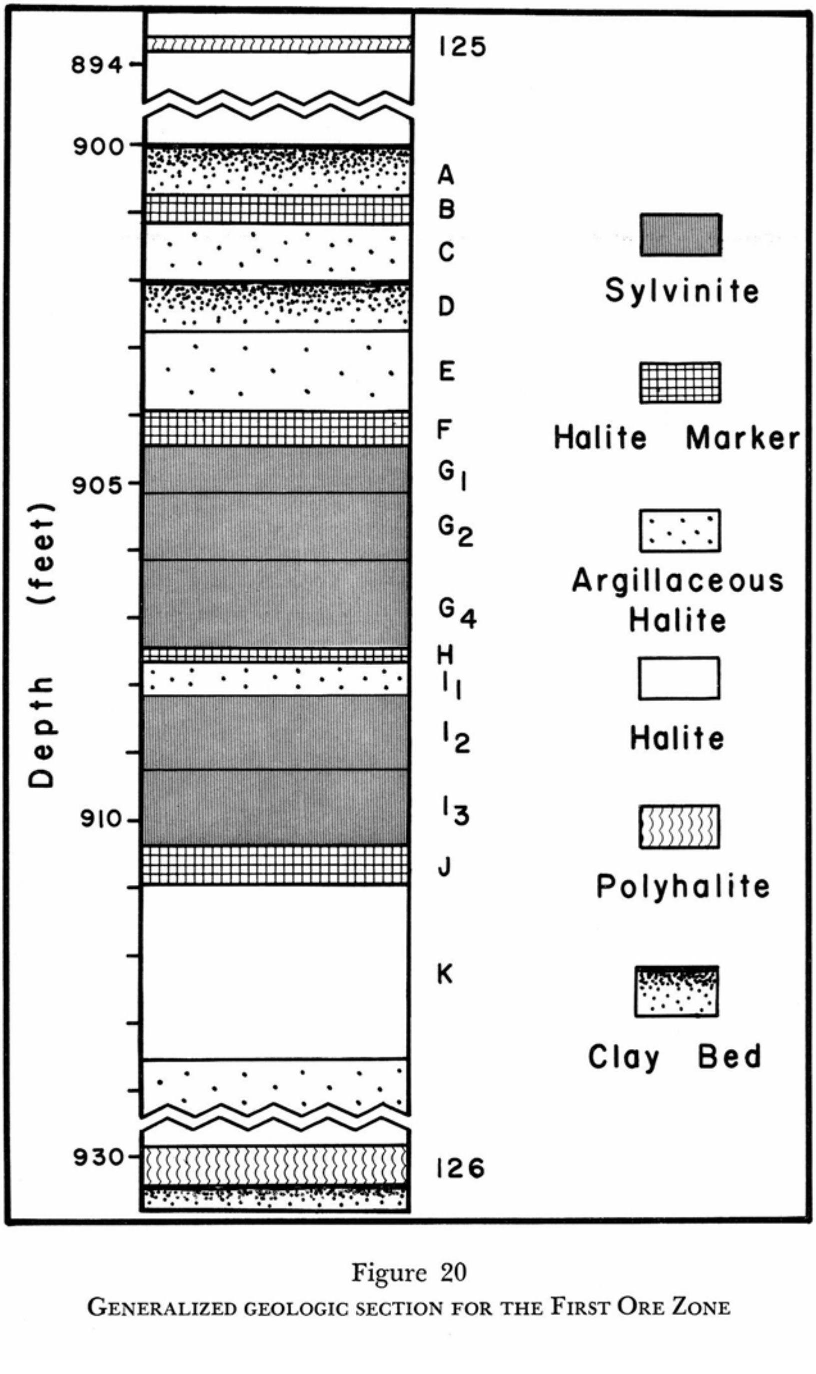


Figure 20
GENERALIZED GEOLOGIC SECTION FOR THE FIRST ORE ZONE

Sylvinite Beds

Sylvinite is a mixture of halite and sylvite, frequently containing small amounts of other minerals. Five beds in the ore zone are included in this category: Beds G, I, and K contain an appreciable amount of sylvite throughout most of the study area. Beds C and E locally contain sylvite; elsewhere, they are best described as argillaceous halite.

The thickness of the sylvinite beds ranges between 28 inches and 40 inches with an average of 34 inches. The principal minerals are halite and sylvite. Sylvite ranges up to about 50 weight per cent but averages about 30 per cent; the remaining 70 per cent is dominantly halite. Argillaceous material amounts to between 0.5 and 4 per cent. Polyhalite is always present in traces, but rarely exceeds 5 weight per cent. Other minerals present in small amounts include leonite, kainite, kierserite, and langbeinite. The majority of these minerals, as will be discussed later, does not represent primary concentrations of sulfate in the ore zone.

The minerals of the sylvinite beds are intergrown in an intimate network. Halite is present in 10- to 20-mm clear, cubic crystals. Sylvite rarely forms cubic crystals but occurs as formless masses between and cementing the halite grains. The other minerals occur either along grain boundaries or disseminated in the halite and sylvite. Halite grains are clear but may contain fluid inclusions and clay disseminated as a fine dust or in clots. Sylvite is either red or milky, never clear. The color of the red sylvite is due to the presence of minute plates of hematite. Red sylvite occurs either as fine-grained crystals (3 to 5 mm) or as rims around coarser grains (10 to 20 mm), the centers of which are milky. Milky sylvite, on the other hand, occurs in large, local, recrystallized masses or as the grain centers just mentioned.

Clay in sylvinite beds is always gray when sylvite is present. If sylvite is absent, the clay is generally brown. Those parts of the beds that lack sylvite are usually thinner than the equivalent stratigraphic interval in ore.

Halite Marker Beds

These beds are remarkable for the uniformity of their dominant features. They are composed almost exclusively of halite and polyhalite. Polyhalite amounts to between 3 and 15 per cent of the bed. Clay is not found in halite marker beds. When sylvite and other sulfate minerals are present, they are secondary in origin and erratic in distribution.

Halite marker beds range from orange to buff in color because of the finely disseminated polyhalite within the halite grains. The halite grains are small (5 mm) and equigranular. The texture frequently approaches that of a sugary sandstone. Where recrystallization has occurred, the halite is coarser (10 to 15 mm) and the polyhalite is present along halite grain boundaries as films and 5- to 10-mm blebs.

STRATIGRAPHY OF THE ORE ZONE

For a discussion of the bromine distribution in the first ore zone, more specific data on the characteristics of beds F through K, sampled for bromine analyses, are given.

Bed F: halite marker bed composed of 5- to 10-mm, buff to orange halite; sylvite, when present, is red and red-rimmed, rarely exceeds 5 per cent

Bed G: sylvinite bed containing four units (fig. 20), G1 and G4 being argillaceous sylvite beds (1 to 3 per cent argillaceous material), whereas G2 contains less than 0.5 per cent argillaceous material; argillaceous unit G3 has limited distribution and is characterized by 0 to 10 per cent leonite and kainite

Bed H: thin halite marker bed frequently broken into discontinuous lenses during compaction

Bed I: like bed G, this sylvinite bed contains several subunits; II contains 10- to 15-mm clear halite, 0 to 10 per cent sylvite (5 to 15 mm, red, and red-rimmed), and 1 to 3 per cent argillaceous material; 12 and 13 contain up to 50 per cent sylvite and differ only in that 12 has a slightly higher average argillaceous content (about 2 per cent contrasted to 1 per cent) and a higher proportion of red to milky sylvite

Bed J: orange, halite marker bed; sylvite, generally present in amounts less than 10 per cent, is 5 to 15 mm in grain size and red to red-rimmed in color

Bed K: poorly exposed in mine working so that reliable subunits have not been chosen; at some underground locations, two or three samples have been collected, but their position depends more on the distance from the base of bed J than recognizable stratigraphic units; this sylvinite bed contains 25 to 35 per cent red-rimmed sylvite and less clay (average about 0.75 per cent) than the upper sylvinite beds

Frequency curves for per cent K, SO_4, and water insoluble or argillaceous material in four intervals of the first ore zone are shown in Figures 21, 22, and 23. The analytical data contained in these curves augment the mineralogic information presented thus far. The stratigraphic intervals represented by the analyses are not in every instance those chosen for bromine analyses. The potassium curves for the four intervals (fig. 21) show that the sylvinite beds (G + **H,** I, and K) contain an average of between 12 and 18 per cent potassium. The inclusion of bed **H** in the G interval slightly decreases the average per cent potassium of the latter. Marker bed **J,** in contrast, contains less than 12 per cent potassium. **All** analyses below 5 per cent potassium have been eliminated, because in the sylvinite beds they generally represent the removal of sylvite through postdepositional leaching. In so doing, however, many bona fide primary potassium analyses for bed **J** were eliminated. The higher percentage of SO_4 in bed K (fig. 22) is also the result of postdepositional processes. The insoluble determination (fig. 23) illustrates two important features of the ore zone: First, bed **J** contains less argillaceous material than the sylvinite beds. Marker beds are remarkably **and** consistently free of clay. Second, the clay content of the sylvinite beds increases from the bottom to the top of the ore zone. The argillaceous mineral content of sylvinite bed G is even higher than indicated, since clay-free **H bed** is included in the analyses.

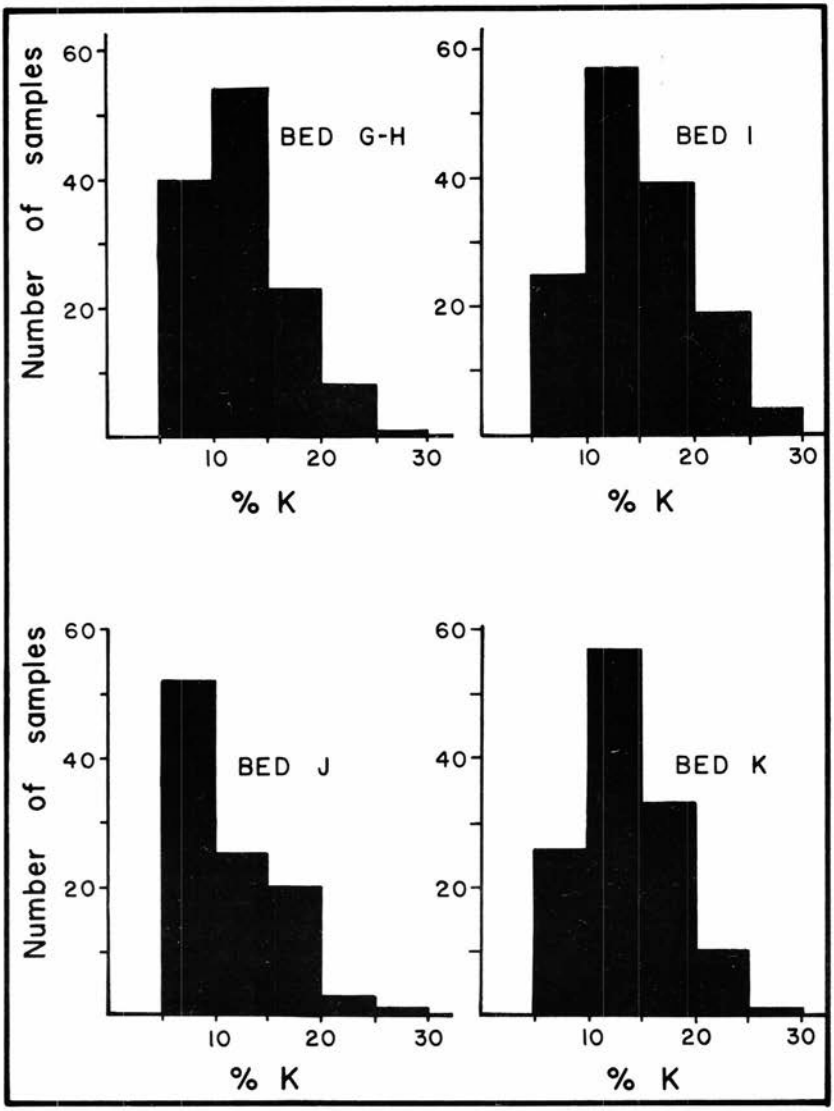


Figure 21

Frequency distribution curves for Potassium analyses

(from four beds of the first ore zone)

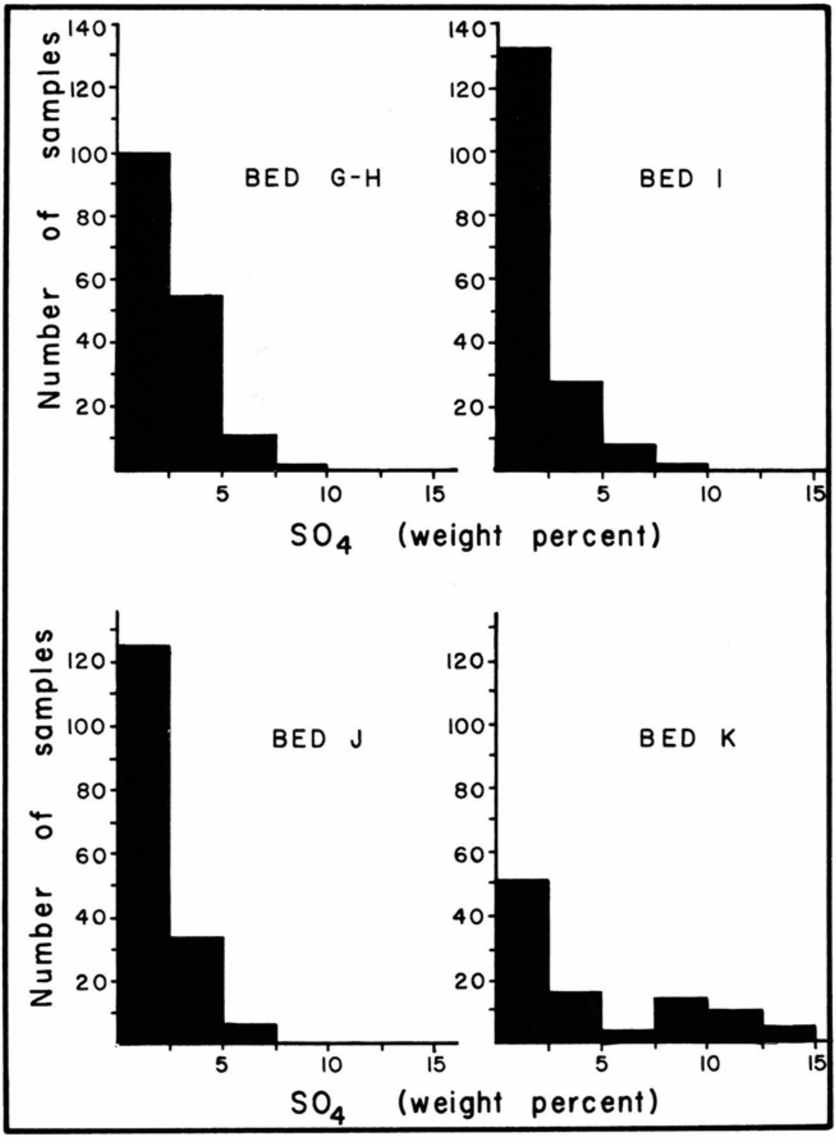


Figure 22

FREQUENCY DISTRIBUTION CURVES FOR SULFATE ANALYSES

(from four beds of the first ore zone)

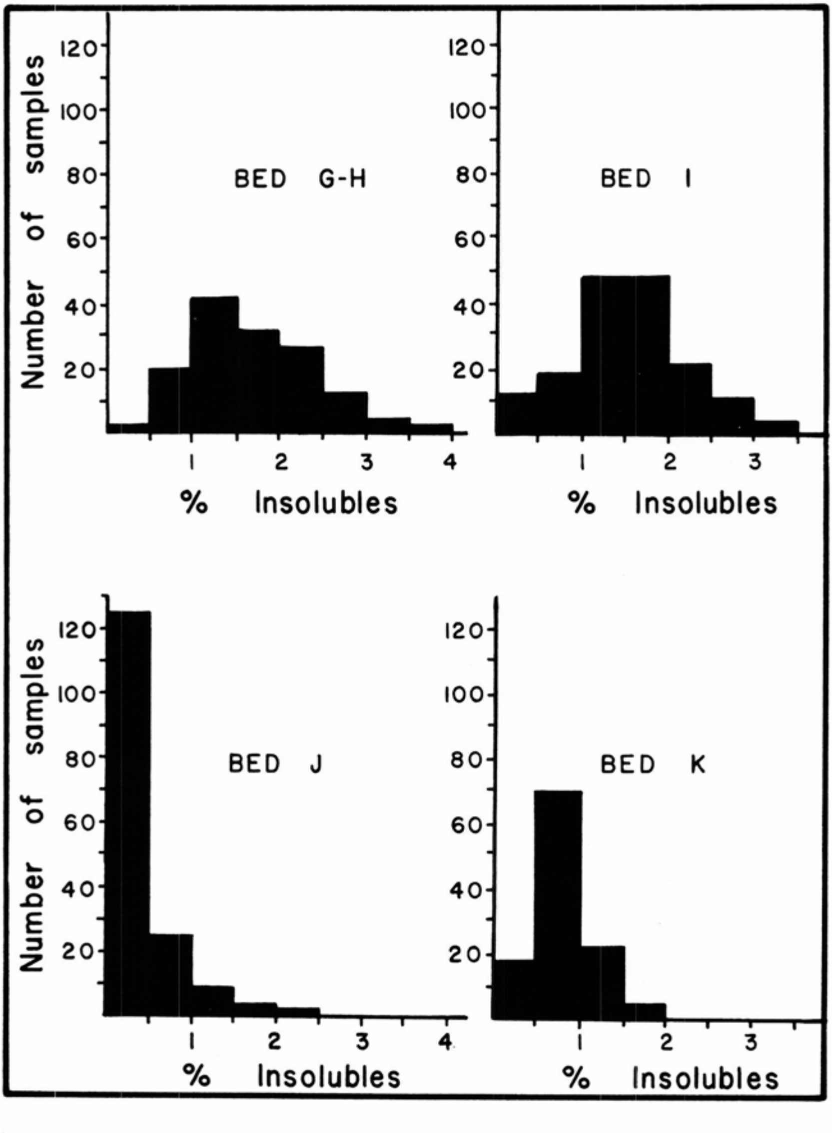


Figure 23
FREQUENCY DISTRIBUTION CURVES FOR WATER—INSOLUBLE DETERMINATIONS
(for four beds of the first ore zone)

HORIZONTAL DISTRIBUTION OF BROMINE IN HALITE

The vertical and horizontal distribution of bromine in the first ore zone was studied by collecting suites of samples at seven underground locations. Underground samples were used because the beds and units could be located with greater certainty than in cores, and unlimited samples were available. Beds F through K were studied because they are persistently mineralized and are exposed in the mine workings. At each underground sample location, halite and sylvite samples were collected from nine to twelve of the stratigraphic units. The bromine contents of the halite samples are tabulated in Table II, together with average values for each stratigrphic unit. The analyses are shown in Fig. 24 as average bromine profiles for each location superimposed on a generalized section of the ore zone. These data indicate that the bromine contents of halite in the units of the ore zone are not constant. The probable bromine ranges within the stratigraphic units reflect one or more of the following conditions:

1. A range in the bromine content of halite over short distances; for example, in a single hand specimen. Such variations were considered in a previous section (table 6), and it was concluded that 80 per cent of all analyses represents the local bromine content of halite in a unit or bed to within 5 ppm. The bromine ranges for nine of the twelve units, however, exceed I0 ppm.

2. Vertical bromine gradients may be present within the units and beds. Samples from different positions within the bed would then contain different bromine concentrations, and the range of values might be expected to increase with the thickness of the bed. Bed H, the thinnest unit sampled, has the smallest bromine range. The correlation between bed thickness and bromine range for the other intervals is poor. Vertical differences in the bromine content of halite contribute to bromine ranges within the beds and units, but probably are not the dominant factor.

3. Horizontal gradients in the bromine content of halite in the beds and units of the ore zone may be present. Horizontal gradients have been identified at the horizon immediately above the first ore zone (fig. I9), and one can test for similar distributions within the ore zone.

At location I *(see* fig. 25), three sample stations were established to test for horizontal bromine variations over relatively short distances. The three stations were about I0 feet apart and samples were collected from 9 litho-logic units at each station. The analyses, compiled in Table 12, illustrate that over short distances, the horizontal bromine gradients in these 9 stratigraphic units are insignificant. The bromine range exceeds the analytical error (plus or minus 5 ppm or a range of 10 ppm) only in beds I_2 and I_3 .

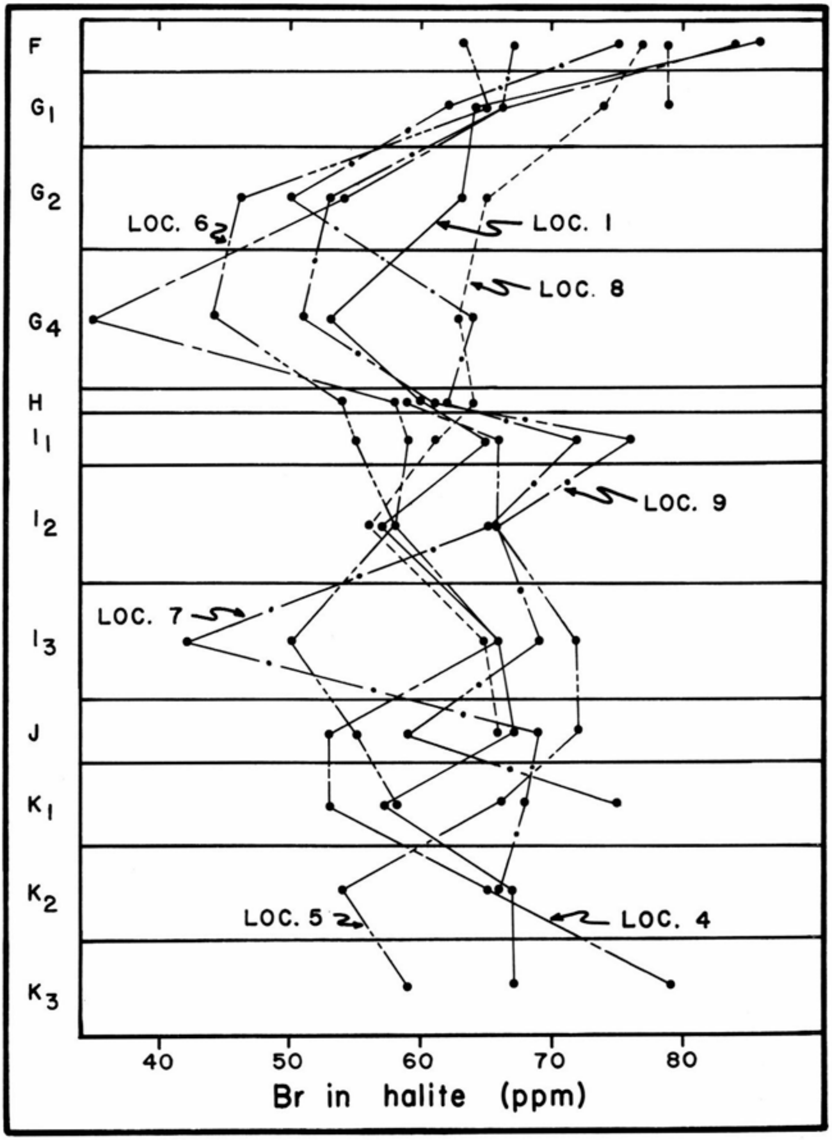


Figure 24
BROMINE PROFILES FOR THE FIRST ORE ZONE AT SEVEN UNDERGROUND LOCATIONS

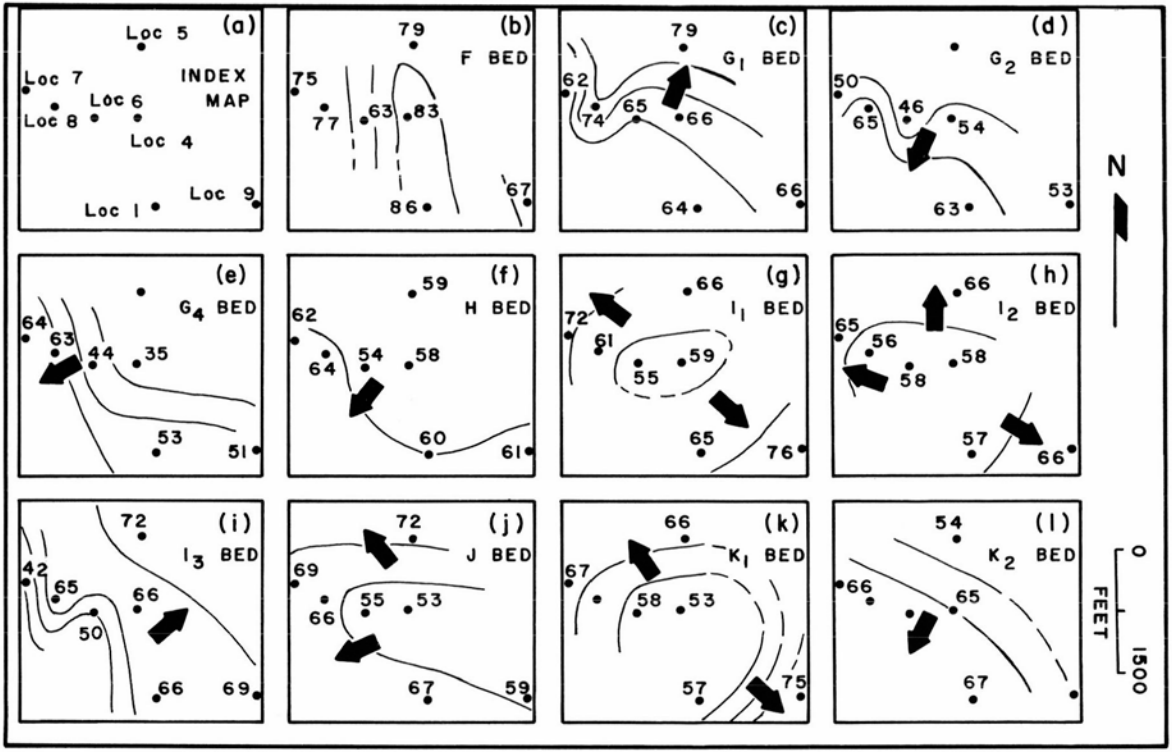


Figure 25

Horizontal distribution of Bromine (ppm) in beds of the First Ore Zone

TABLE 12. BROMINE CONTENT OF HALITE FROM ROWS 1, 2, AND 3, LOCATION 1, FIRST ORE ZONE

	BROMINE IN HALITE (ppm)					
BED	ROW 1	ROW 2	ROW 3	AVG.	AVG. DEV.	RANGE
G_4	56	48	56	53	4	8
H	58	59	64	60	2	6
I_1	70	65	59	65	4	11
I_2	53	54	65	57	5	12
I_3	63	65	69	66	2	6
J	65	65	71	67	3	6
K_1	58	59	54	57	2	5
K_2	67	64	70	67	2	6
K_3	69	65	67	67	1	4

The distribution of bromine in halite over greater distances is reflected in the analytical results from the seven underground sample locations. These results are presented in Figure 25 as twelve maps (an index map and an isobromine map for each stratigraphic interval sampled).

Because of insufficient control points, the reliabilities of the indicated bromide distributions are low, permitting only some general comments:

> Significant horizontal gradients exist in the bromine content of the halite within the stratigraphic units of the ore zone.
>
> The horizontal bromine distribution in the various units appears to change systematically.
>
> The bromine distribution pattern for each unit appears to be related to the patterns for adjacent beds.

The dominant trend of the horizontal bromine gradients is northeast-southwest. In some beds (G_1 and I_3), the bromine content of halite increases toward the northeast; in others (G_2, G_4 H, and K_2), it increases toward the southwest. Between gradients of opposite orientation lie beds in which the bromine distribution is radial, increasing toward the fringes of the map. Between beds K_2 (southwest bromine increase), and I_3 (northeast bromine increase) are the radial distributions of beds J and K_1. Similarly, the radial patterns of beds I_1 and I_2 occur between beds H and I_3. No sample analysis was available for bed G_2 at location 5, which would be necessary to develop a radial pattern between the opposite orientations of beds G_1 and G_4.

Bromine gradients over greater distances may be seen in Figure 26 where the average bromine profile for locations I, 4, 5, 6, 7, 8, and 9 is plotted with the profile for location 86. The locations represented by the average curve lie within 6000 feet of each other, whereas location 86 is about 9000 feet to the southwest. It is apparent that at location 86, the lower part of the ore zone contains less and unit G 4 contains more bromine than the vicinity of the other locations.

VERTICAL DISTRIBUTION OF BROMINE IN HALITE

Figure 24 presents seven vertical bromine profiles for the first ore zone. Figure 26 gives the average for these curves and an additional profile. An examination of these profiles permits the following observations:

> The bromine content of halite in the ore zone covers almost as broad a range as in the entire Salado Formation.
>
> In the lower part of the ore zone (beds H through K), the bromine content of halite is between 50 and 70 ppm, with the average curve (fig. 26) varying from 60 to 68 ppm. Above bed H, the bromine content increases from 45 to 55 ppm (beds G_2 and G_4) to 60 to 85 ppm in beds G_1 and F.
>
> The concentration of bromine in halite does not correlate with the lithology of the beds. Halite marker beds do not contain consistently higher or lower bromine concentrations in halite than the sylvinite beds.
>
> Beds immediately above halite marker beds (G_4 and I_3) show the greatest range (30 ppm) of bromine values for the seven locations. These beds also show a decrease in the bromine content of halite similar to the relation associated with the I25 marker and other thin polyhalite beds.

BROMINE DISTRIBUTION IN THE ASSEMBLAGE HALITE—SYLVITE

BROMINE CONTENT OF SYLVITE

Milky sylvite contains approximately twice as much bromine as red sylvite. Unfortunately, most sylvite in the ore zone is red-rimmed and not amenable to the easy preparation of pure red and pure milky separates. A few pure separates were prepared, but the majority of the sylvite analyses represents samples containing both red and milky sylvite. In discussing the analyses, four sample types are recognized:

(I) Red sylvite: Samples composed of fine-grained red sylvite and/or the red rims from medium to coarse red-rimmed sylvite

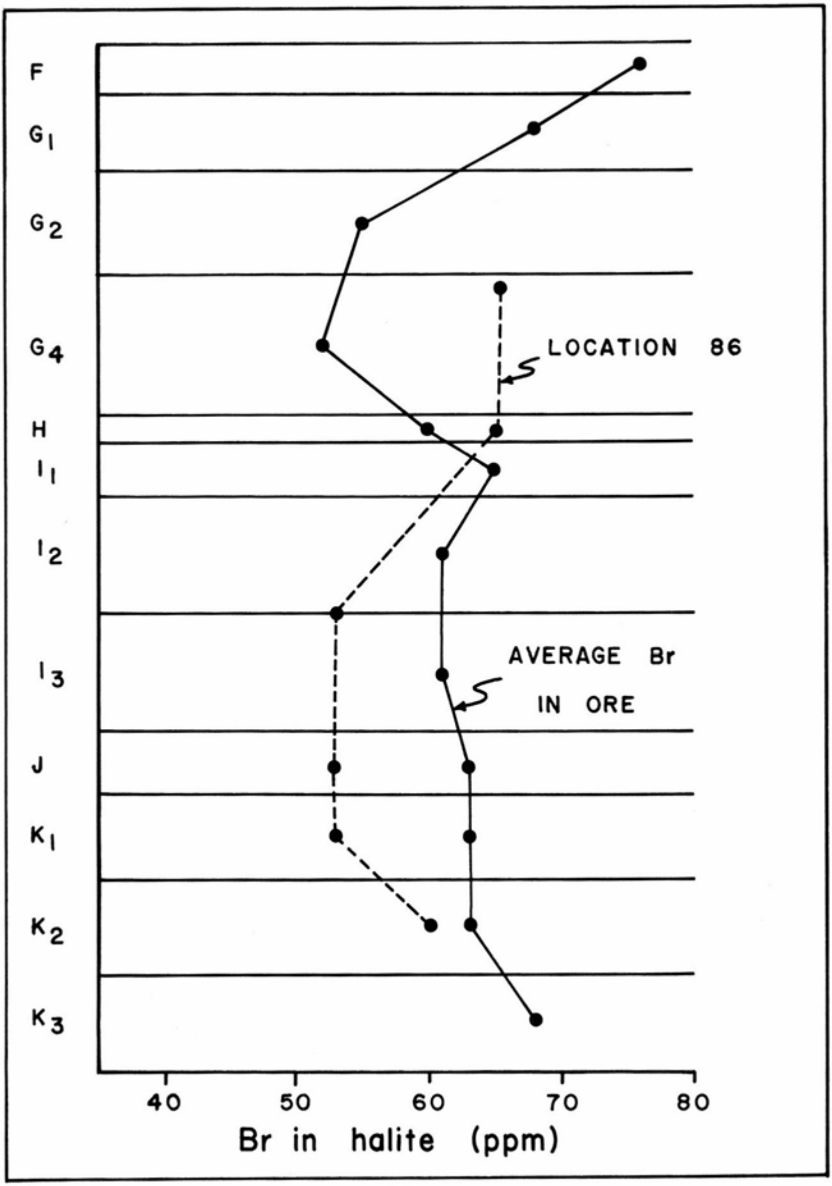


Figure 26
Bromine profiles for Location 86 and average profile for Locations 1 through 9

(2) Red-rimmed sylvite: Samples composed of sylvite containing from 10 to 90 per cent red rims

(3) Slightly red-rimmed sylvite: Samples containing less than I0 per cent red sylvite as rims

(4) Milky sylvite: Samples composed entirely of coarse milky sylvite and/or the milky centers of red-rimmed sylvite

The bromine content of sylvite in the first ore zone correlates more with its color than any other factor, including its stratigraphic position within the ore zone. Frequency curves for analyses of the four sylvite varieties (fig. 27) illustrate this fact. These curves were constructed with I40 analyses distributed as follows: I7 red, 47 red-rimmed, 20 slightly red-rimmed, and 56 milky sylvite samples. The average bromine content of sylvite concentrates (633 ppm) produced by the mine is close to the average of the analyses in Figure 27. It is apparent that red sylvite, with a range of 250 to 550 ppm and an average of 390 ppm, contains consistently less bromine than milky sylvite (range 550 to 950 ppm, average 780 ppm). As would be expected, the bromine content of red-rimmed sylvite (average 500 ppm) is between that of the pure separates. The positive skewness of the curve reflects the fact that toward the higher concentrations, pure milky sylvite samples were prepared in preference to red-rimmed samples and that in other instances, the proportion of red rims was low enough to place the sample in the slightly red-rimmed category.

BROMINE CONTENT OF COEXISTING HALITE AND SYLVITE

Halite and sylvite separates, prepared for I40 samples, were made from I00- to I500-gram samples, taking advantage of the most readily available halite and sylvite. There is no assurance that the mineral concentrates were in physical contact with each other. *Coexisting*, as used subsequently, means that the halite and sylvite separates were prepared from the same hand specimen and were separated by no more than 4 inches.

The bromine contents of coexisting halite and sylvite from the beds of the first ore zone are of interest because they may provide information on the origin of the sylvinite assemblages. For this discussion, the ratio of the bromine content of sylvite to that of halite will be of principal interest rather than the absolute bromine concentrations in the minerals.

Frequency curves for the ratio Br (sylvite)/Br (halite) have been plotted in Figure 28 for each color variety of sylvite. The ratios for red sylvite-halite pairs range from 4 to 9, with an average of 6.3. Milky sylvite-halite pairs have a greater range (8 to 17) and a higher average (I3.2). Red-rimmed sylvitehalite pairs have an intermediate range (4 to 14), similar to the bromine content of red-rimmed sylvite, and an average ratio of 8. The ratios for slightly red-rimmed samples are distributed between 7 and I6, with an average of I2. The bromine ratios for the red sylvite-halite and milky sylvite-halite pairs are as distinctly different as were the bromine contents of these two varieties of sylvite. The average ratios for halite, red sylvite, and milky sylvite are, therefore, I:6.3:I3.2.

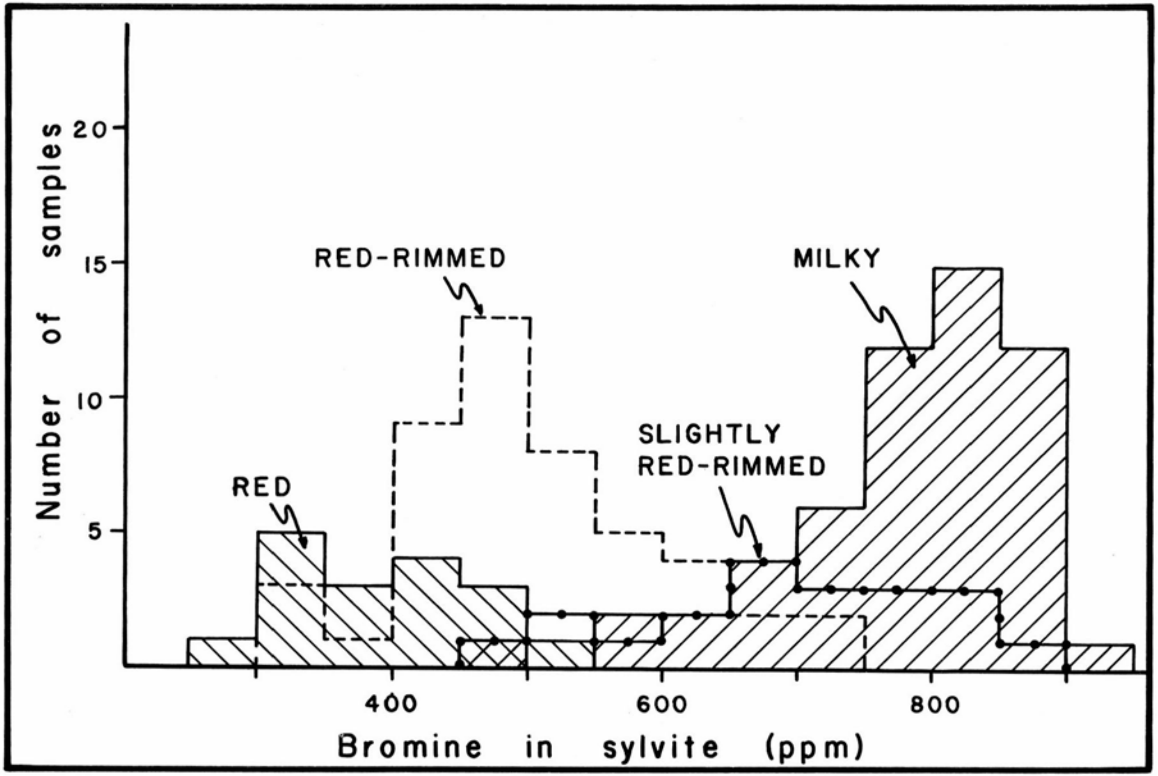


Figure 27
FREQUENCY DISTRIBUTION CURVES FOR THE BROMINE CONTENT OF RED, RED—RIMMED, SLIGHTLY RED—RIMMED, AND MILKY SYLVITE, FIRST ORE ZONE

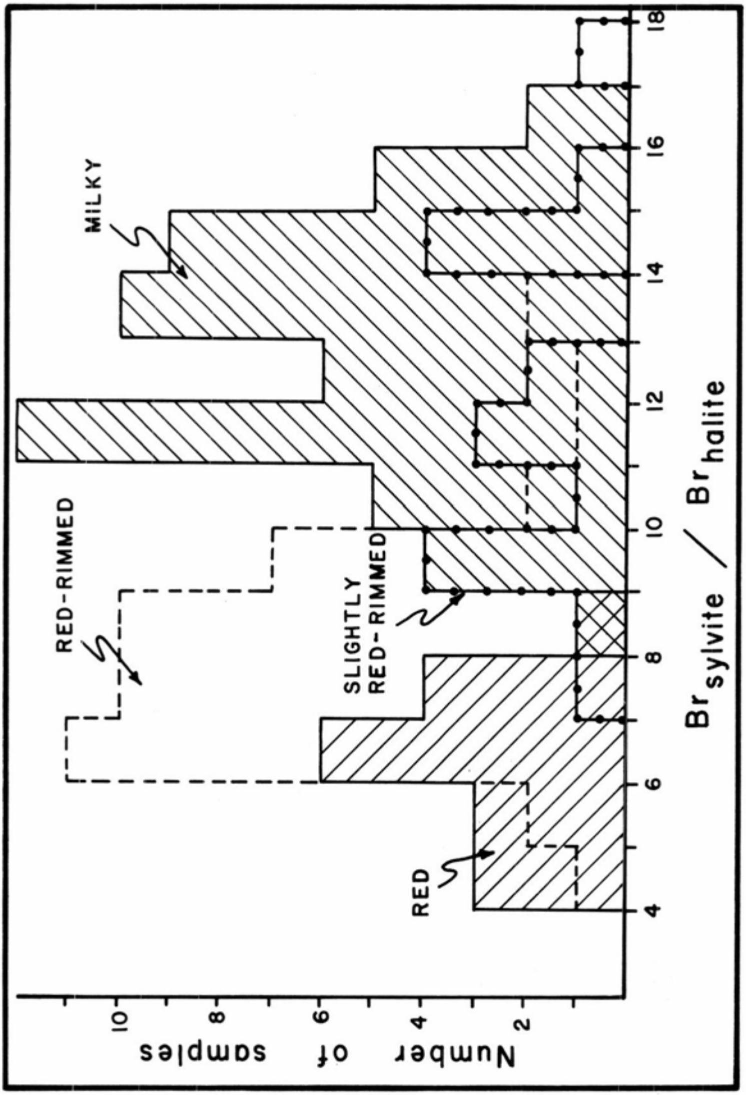


Figure 28

Frequency distribution curves for ratios of the Bromine contents of Red, Red—Rimmed, Slightly Red—Rimmed, or Milky Sylvite

(to that of coexisting halite)

Included in Figure 28 are analyses of nine samples from each of which halite, red sylvite, and milky sylvite separates were prepared. These nine sets of analyses are tabulated in Table I3 with their respective bromine ratios. The average ratio among halite, red sylvite, and milky sylvite is I:6.8:13.I. This ratio is essentially identical to that calculated from the total sample population and given above.

INFLUENCE OF STRATIGRAPHIC POSITION

The bromine and bromine ratio profiles for halite and sylvite from the seven underground sample locations are plotted in Figures 29 through 35. The sylvite analyses are identified as representing milky, slightly red-rimmed, red-rimmed, and red sylvite samples *(see* key in fig. 29). When two sylvite analyses are presented for the same bed (locations I, 4, 6, 7, and 8), notice that the bromine content, with two exceptions, decreases in the order the varieties are listed above. This strong correlation with color may mask correlations between stratigraphy and the bromine content of sylvite. This possibility was explored by constructing average bromine profiles for red and milky sylvite in Figure 36. The number of analyses for each variety of sylvite is also plotted in this figure. These curves indicate that

(1) the bromine content of milky sylvite increases gradually from bed K3 to K1, then decreases in halite marker bed J. A slight increase in beds I_3 and I2 is followed by a decrease in bed I_I below halite marker bed H. A similar decrease occurs from the bottom to the top of bed G;

(2) changes in the bromine content of red sylvite parallel those in milky sylvite where the two curves overlap; and

(3) the number of analyses of each variety of sylvite is only an approximate indication of the ratio of red to milky sylvite in the beds. The preponderance of milky and slightly red-rimmed samples in beds K3 through I_3 indicates, nonetheless, that milky sylvite is more abundant than red sylvite. In beds I_2 , I_I, and H red sylvite exceeds milky sylvite. In bed G, red sylvite is more abundant than milky sylvite except in unit G2.

BROMINE DISTRIBUTION WITHIN AND ADJACENT TO SALT HORSES

Sylvite is locally absent from the beds of the first ore zone. The distribution of these barren areas was studied by Linn and Adams, who mapped ore-waste contacts in detail. They concluded that most of these features, commonly referred to as salt horses, formed by the dissolution of sylvite

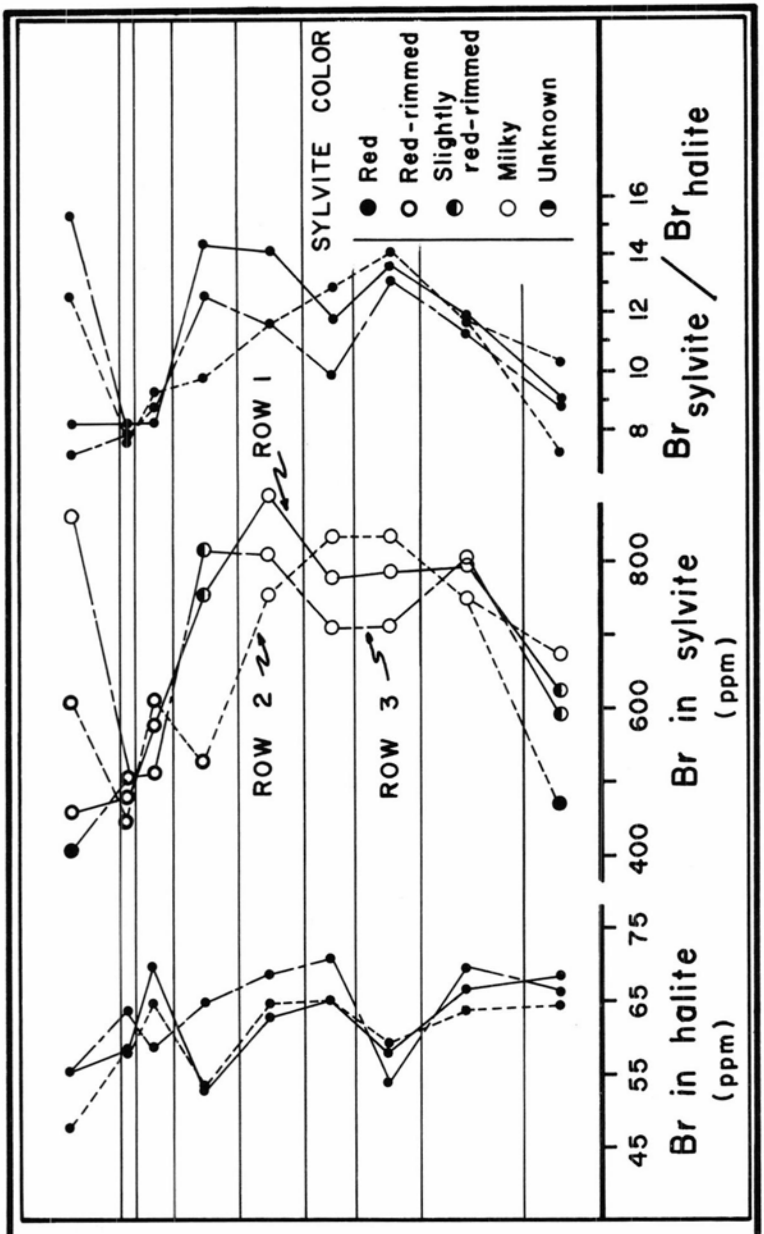


Figure 29
Bromine and Bromine ratio profiles for Halite and Sylvite, Location 1, First Ore Zone

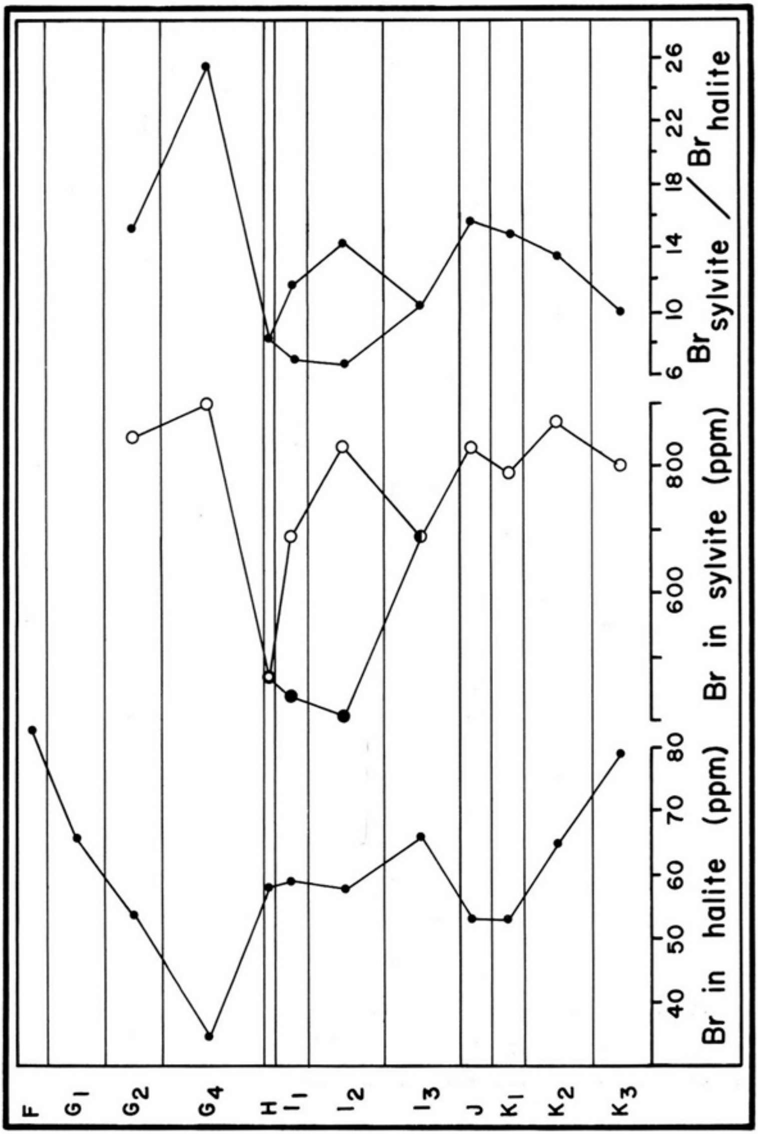


Figure 30

BROMINE AND BROMINE RATIO PROFILES FOR HALITE AND SYLVITE, LOCATION 4, FIRST ORE ZONE

(*See* fig. 29 for sylvite color designations)

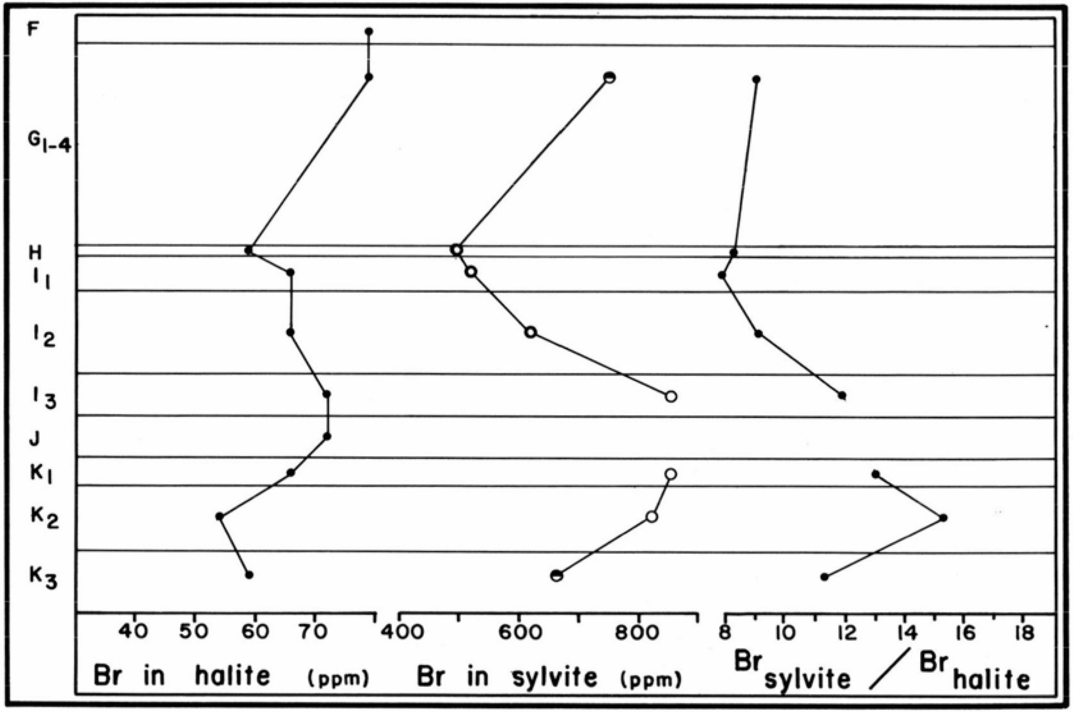


Figure 31

BROMINE AND BROMINE RATIO PROFILES FOR HALITE AND SYLVITE, LOCATION 5, FIRST ORE ZONE

(*See* fig. 29 for sylvite color designations)

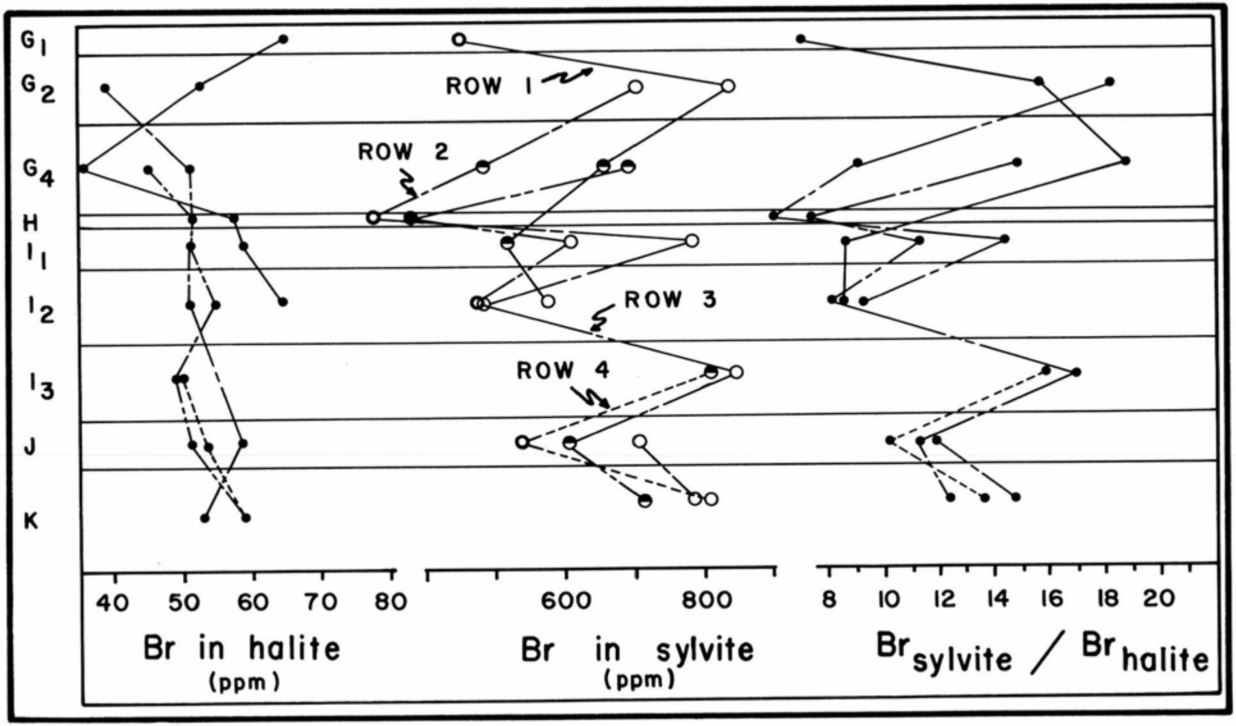


Figure 32

Bromine and Bromine ratio profiles for Halite and Sylvite, Location 6, First Ore Zone

(*See* fig. 29 for sylvite color designations)

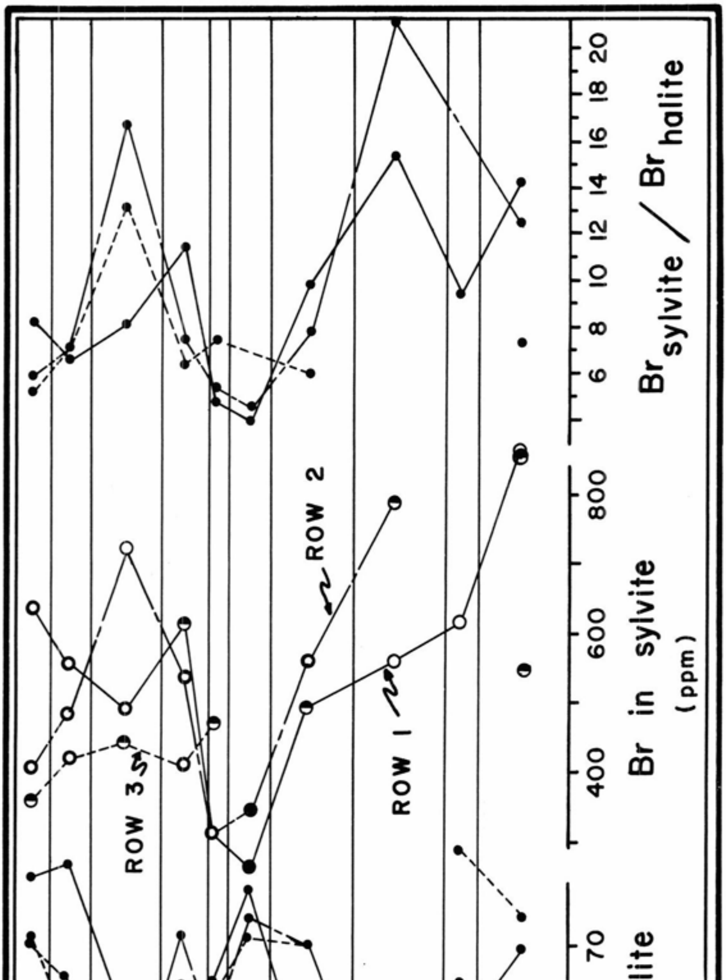


Figure 33

Bromine and Bromine ratio profiles for Halite and Sylvite, Location 7, First Ore Zone

(See fig. 29 for sylvite color designations)

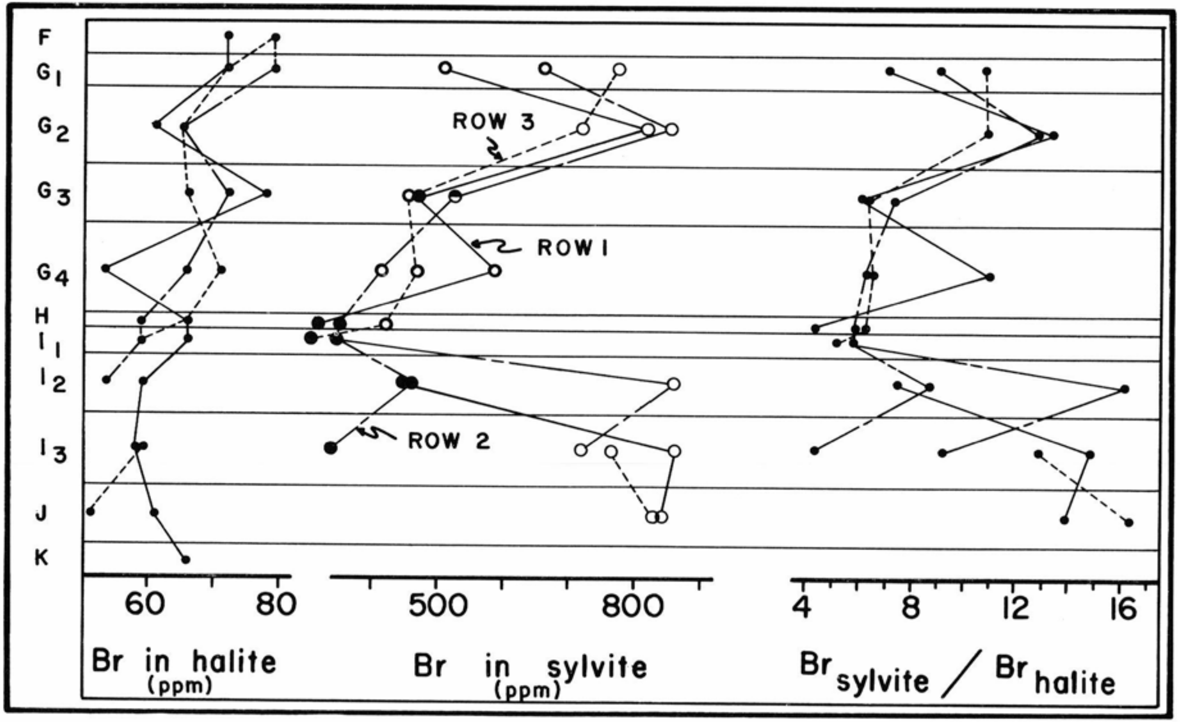


Figure 34

Bromine and Bromine ratio profiles for Halite and Sylvite, Location 8, First Ore Zone

(*See* fig. 29 for sylvite color designations)

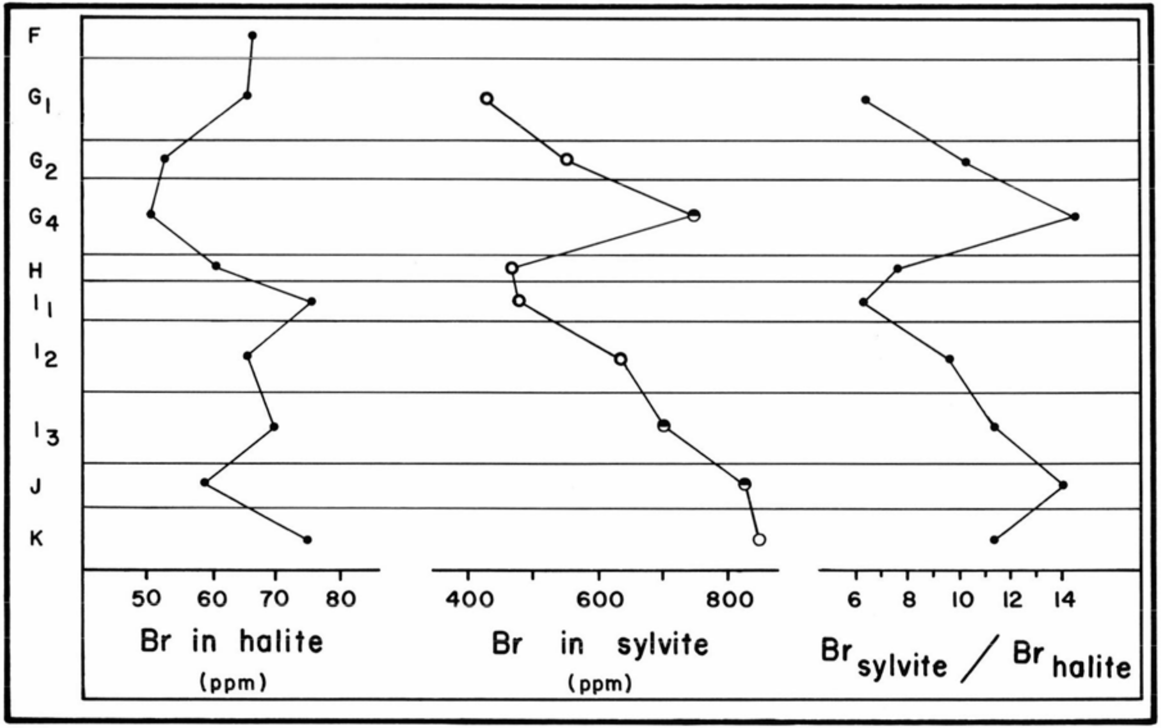


Figure 35

Bromine and Bromine ratio profiles for Halite and Sylvite, Location 9, First Ore Zone

(*See* fig. 29 for sylvite color designations)

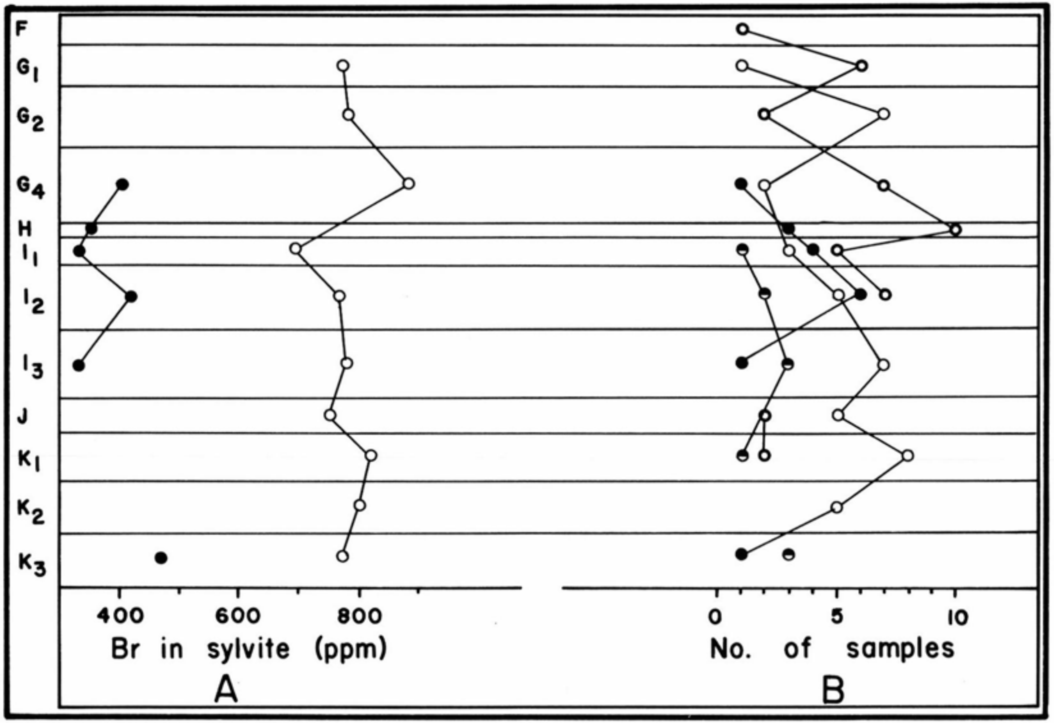


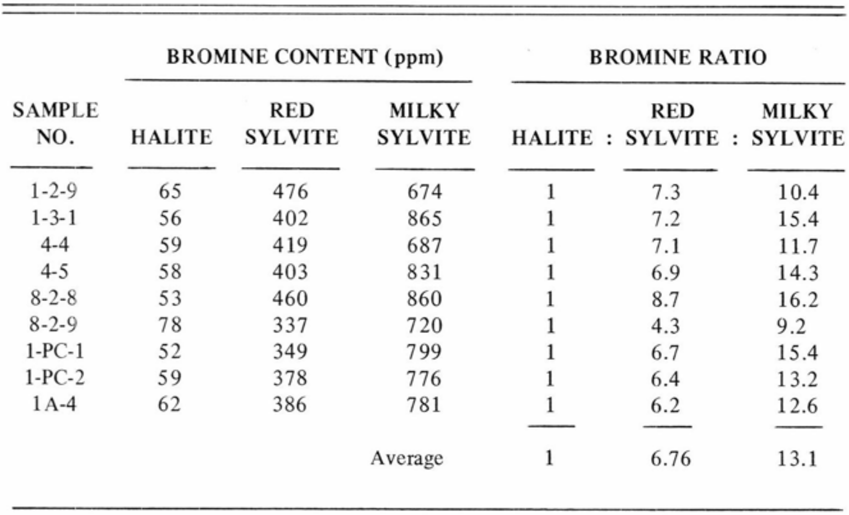
Figure 36

Average Bromine profiles for Red and Milky Sylvite

Curves show the number of analyses of each Sylvite color variety

(*See* fig. 29 for sylvite color designations)

TABLE 13. BROMINE CONTENTS AND RATIOS FOR NINE SAMPLES OF COEXISTING HALITE, RED SYLVITE, AND MILKY SYLVITE



	BROMINE CONTENT (ppm)			BROMINE RATIO		
SAMPLE NO.	HALITE	RED SYLVITE	MILKY SYLVITE	HALITE :	RED SYLVITE :	MILKY SYLVITE
1-2-9	65	476	674	1	7.3	10.4
1-3-1	56	402	865	1	7.2	15.4
4-4	59	419	687	1	7.1	11.7
4-5	58	403	831	1	6.9	14.3
8-2-8	53	460	860	1	8.7	16.2
8-2-9	78	337	720	1	4.3	9.2
1-PC-1	52	349	799	1	6.7	15.4
1-PC-2	59	378	776	1	6.4	13.2
1A-4	62	386	781	1	6.2	12.6
			Average	1	6.76	13.1

from the ore zone by unsaturated solutions rising up through the beds. Evidence supporting this interpretation has been discussed in their paper. It is worthwhile to determine if and in what manner the process of salt-horse formation has been recorded in the distribution of bromine within and around such horses as this may permit the recognition of local salt horses in core tests in contrast to larger areas of sylvite nondeposition.

BROMINE DISTRIBUTION ADJACENT TO SALT HORSES

The distribution of bromine in halite and sylvite of the ore zone was studied within and adjacent to three salt horses. The first (location 6) is about 2000 feet wide. This salt horse is referred to as a "back horse," since the solutions that removed the sylvite apparently entered the ore zone from above. In such a horse, the ore-waste contact generally slopes toward waste (fig. 37). Six sample rows were established across the ore-waste contact. Halite and sylvite (if present) samples were collected from each bed and their bromine contents were determined.

The bromine contents of halite and sylvite from rows 1 through 4 are plotted in Figure 32, together with the bromine ratios for coexisting halite and sylvite. There is no evidence in these profiles that the salt horse had any influence on the bromine content of halite and sylvite in adjacent ore. This conclusion is supported by a study of the ore-waste contact, which is abrupt, with little or no alteration of adjacent ore.

The second salt horse is of the more common "floor horse" variety. It is about 250 feet long and 200 feet wide. A structure cross section through this

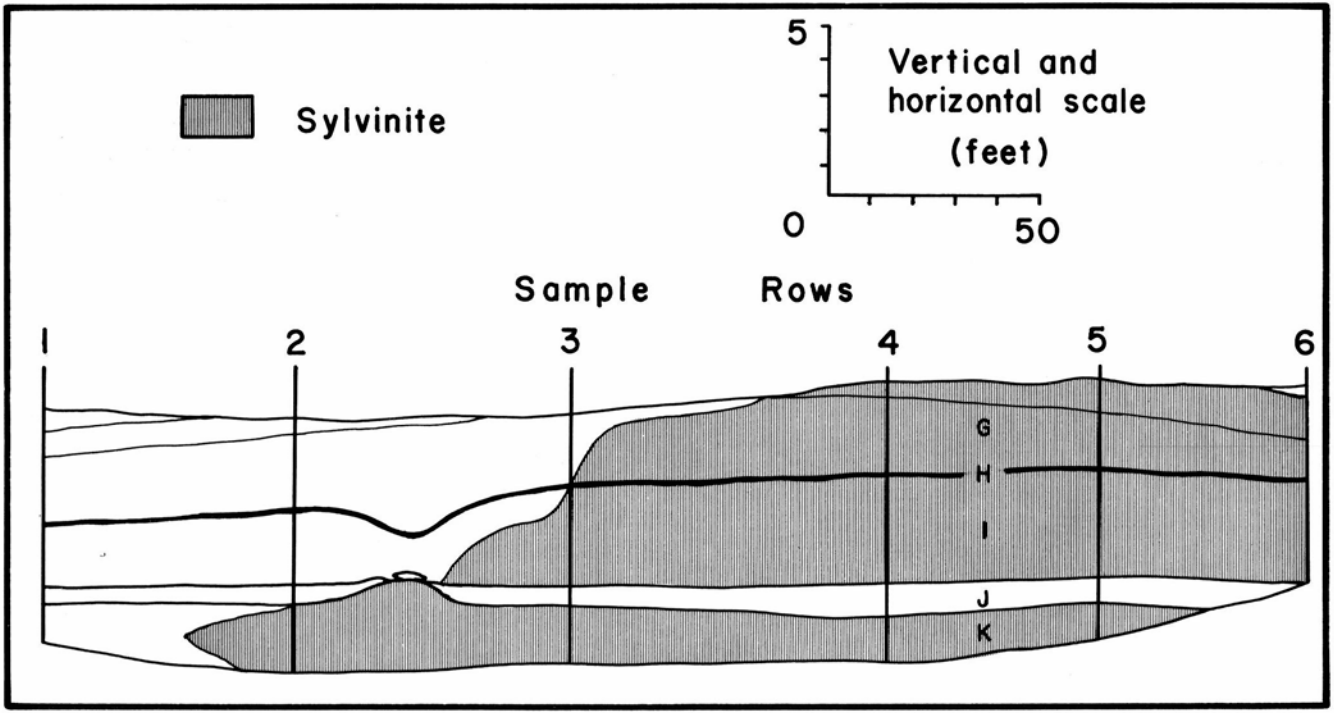


Figure 37
GEOLOGIC SECTION ACROSS ORE—WASTE CONTACT OF "BACK" SALT HORSE AT LOCATION 6, FIRST ORE ZONE

salt horse was presented by Linn and Adams (their figure 14). Samples of halite and sylvite were collected from each bed of the ore zone at eight sample locations. The parts of rows 1, 2, and 3 (fig. 38) in ore are useful for discussing the bromine distribution adjacent to salt horses. The bromine profiles for halite and sylvite from these rows were presented in Figure 33, together with the bromine ratio profiles. It appears that the bromine content of halite decreases toward the salt horse in beds F, G_1 , and G_2. This is compatible with the observation that the ore-waste contact for these beds is more diffuse than normal. Halite in the lower part of the ore zone and sylvite throughout the ore zone show no such trend.

Sylvite was dissolved only from the lower part of the ore zone in the third salt horse studied (location 8). A geologic section across this salt horse and the location of three sample rows are shown in Figure 39. The bromine and bromine ratio profiles for halite and sylvite from the three sample rows are shown in Figure 34. The bromine content of halite and sylvite in ore adjacent to and above the salt horse was apparently unaffected by the process of salt-horse formation. The generally abrupt contacts between ore and waste around these three salt horses must represent equally abrupt chemical boundaries during salt-horse formation.

BROMINE DISTRIBUTION WITHIN SALT HORSES

Data collected from the salt horses at locations 6 and 7 illustrate the distribution of bromine in halite within salt horses. Bromine profiles for the sample rows in waste at these two locations are plotted in Figure 40. There are no apparent regular vertical or horizontal variations in the bromine content of halite within these salt horses. There are two interesting trends:

(1) The bromine content of halite at location 6 (back horse) increases toward the bottom of the bed. At location 7 (floor horse), there is a slight increase toward the top of the bed.

(2) The bromine content of halite increases down and away from the ore-waste contact at location 7 (see rows 4, 5, and 8, fig. 38).

Excepting these trends, the bromine content of halite in salt horses is as uniform between beds of the ore zone as it is within them.

REDISTRIBUTION OF BROMINE DURING SALT-HORSE DEVELOPMENT

The average bromine profiles for ore and waste at locations 6 and 7 (fig. 41) illustrate that halite in salt horses contains more bromine than stratigraphically equivalent halite in adjacent ore and that the increased bromine content of salt-horse halite is not constant. Salt-horse halite is characterized by 20- to 25-mm crystals, compared with 5- to 20-mm crystals for halite in ore. It seems possible that the higher bromine content might be due to a greater abundance of fluid inclusions in the coarser halite. A single large sample of halite was collected from bed 1_3 in the salt horse at location 6. The sample

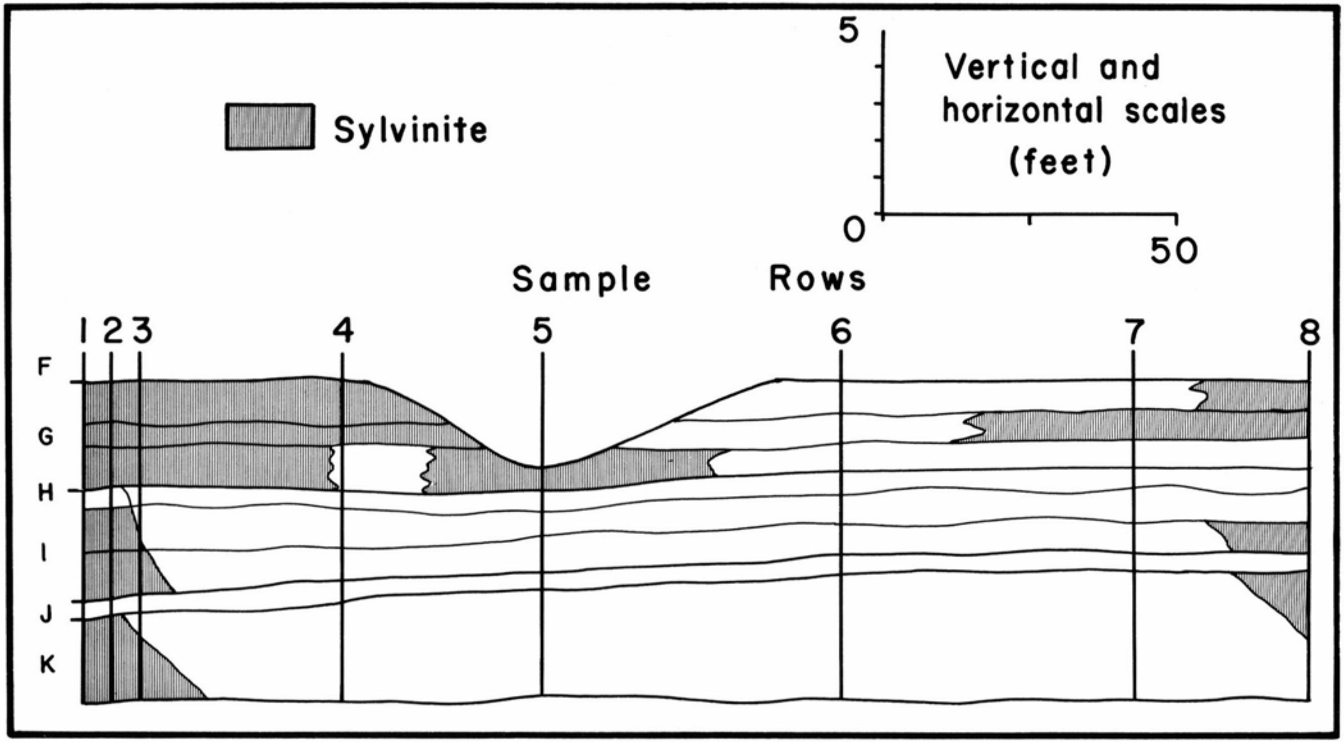


Figure 38

Geologic section across Ore—waste contacts of "floor" Salt Horse at Location 7, First Ore Zone

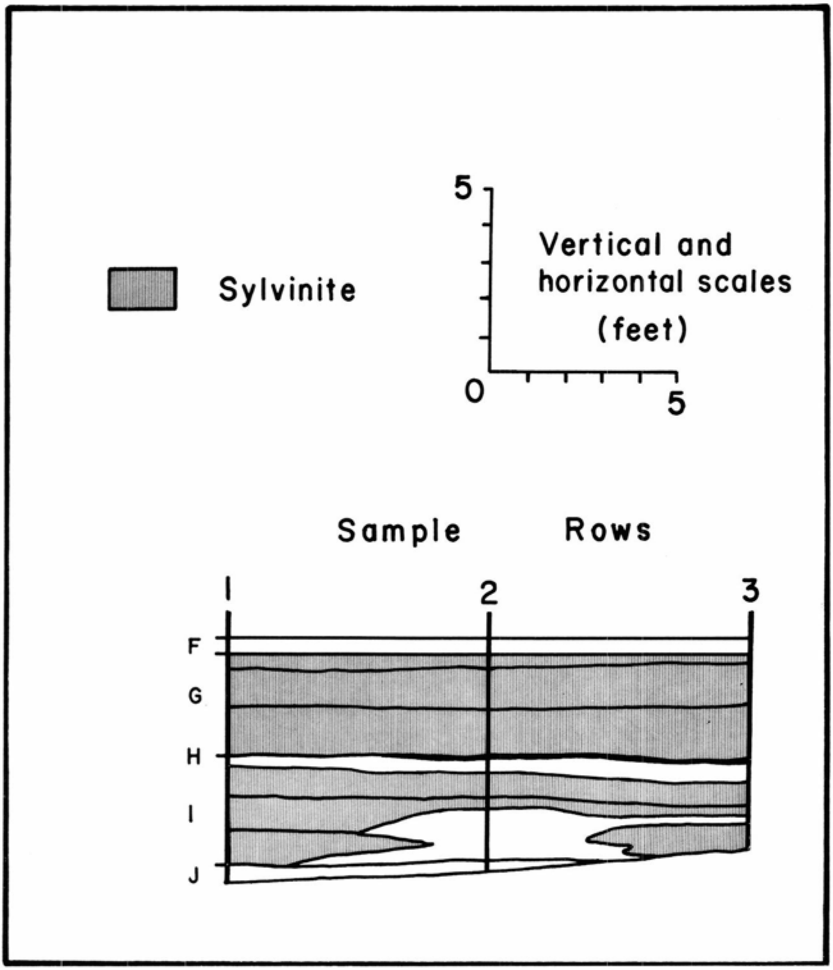


Figure 39
GEOLOGIC SECTION ACROSS ORE—WASTE CONTACTS OF "FLOOR" SALT HORSE AT LOCATION 8, FIRST ORE ZONE

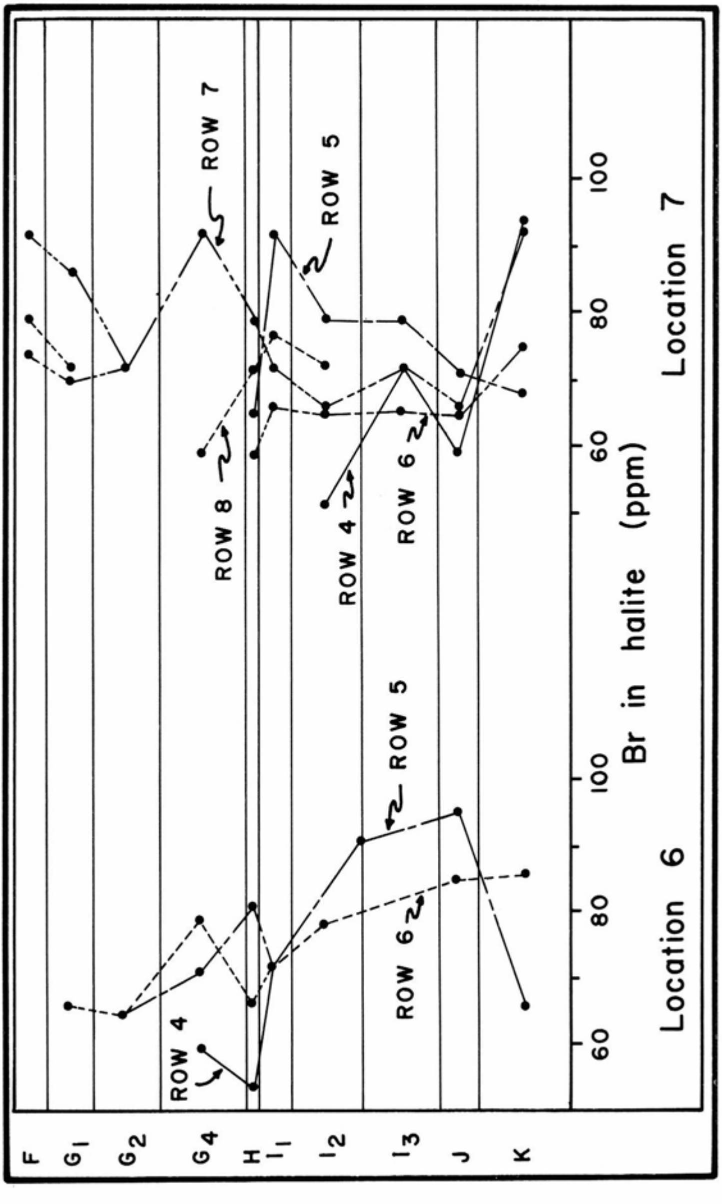


Figure 40

Bromine profiles for Halite in Salt Horses, Locations 6 and 7, First Ore Zone

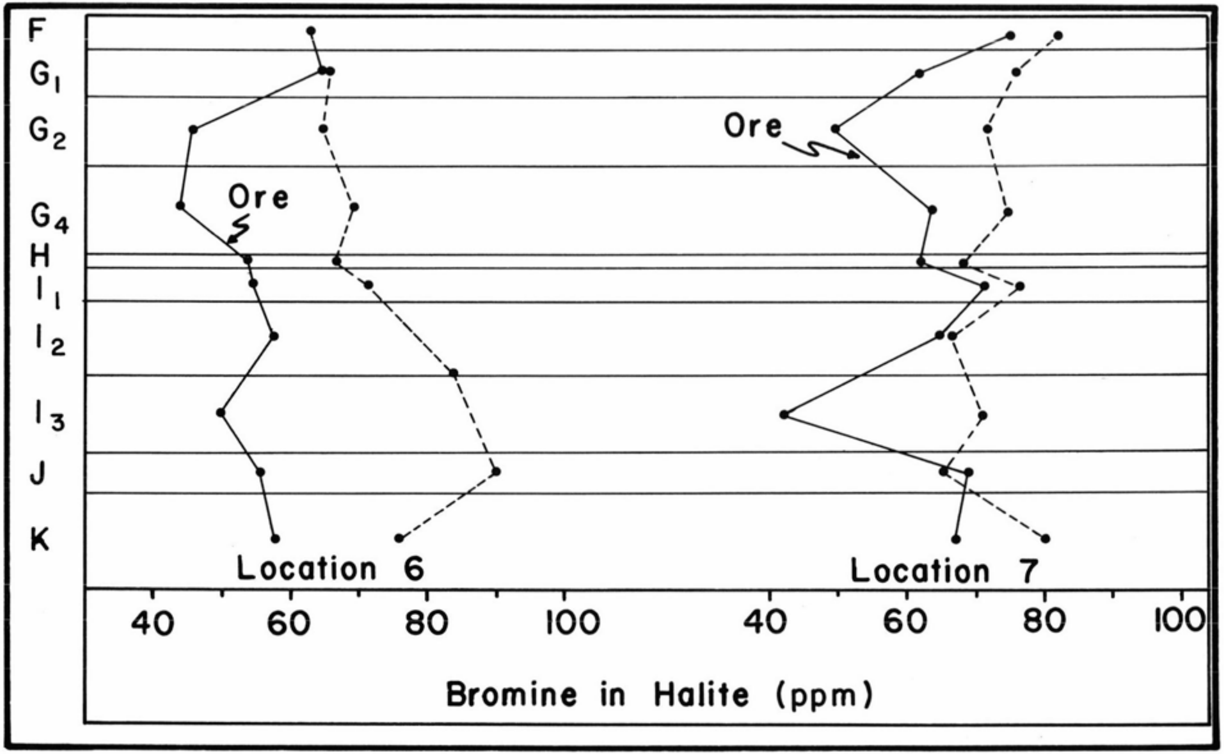


Figure 41
AVERAGE BROMINE PROFILES FOR HALITE IN ORE AND WASTE, LOCATIONS 6 AND 7, FIRST ORE ZONE

was coarsely ground to 1- to 5-centimeter chunks and split into two samples. These two splits were prepared for analysis in the following manner:

Split 1. This sample was finely ground and split into two identical parts (SH-6 and SH-7). The percentage of moisture released at 100°C and 300°C was determined for each sample, as well as the bromide contents of the dried and undried samples and the K, Mg, Ca, Cl, SO_4, and water-soluble material.

Split 2. This sample was finely ground and immediately washed with acetone for three minutes. The remaining acetone was permitted to evaporate and the sample was split into two identical parts (SH-8 and SH-9). Each split was analyzed for K, Mg, Ca, Cl, SO_4, $H_2$0 at 100°C and 300°C, and Br in the dried and undried samples.

The analytical results for these four samples are given in Table 14. The calcium, potassium, magnesium, and sulfate are probably present as polyhalite and in the brine of the inclusions. The acetone wash successfully reduced the bromine content of samples SH-8 and SH-9. It did not, however, remove all the brine and, therefore, all the bromine present other than in substitution for Cl. Assuming equilibrium distribution of bromine between the fluid inclusions and the host crystals, it is possible to determine the magnitude of error resulting from the bromine in the brine by choosing an appropriate distribution coefficient. From Figure 6, a distribution coefficient between 0.075 and 0.14 seems reasonable. At an average bromine content of 87 ppm for the total sample, the lowest bromine content that can be calculated for the crystal strucuture with the preceding assumptions is 83.5 ppm. This concentration is still well above the bromine content of halite from this bed in ore (49 and 50 ppm). For location 7, the calculated decrease (4 to 5 ppm) eliminates the bromine increase in salt-horse halite for four of the nine beds. Much of the halite in salt horses, nonetheless, appears to contain more bromine in lattice substitution than stratigraphically equivalent halite in ore. A similar increase in secondary or recrystallized halite was reported by Holser (1966, p. 268) for pairs of analyses from five separate evaporite formations.

Some possible explanations for the higher bromine content of salt-horse halite may be developed by considering briefly the way in which salt horses are believed to form.

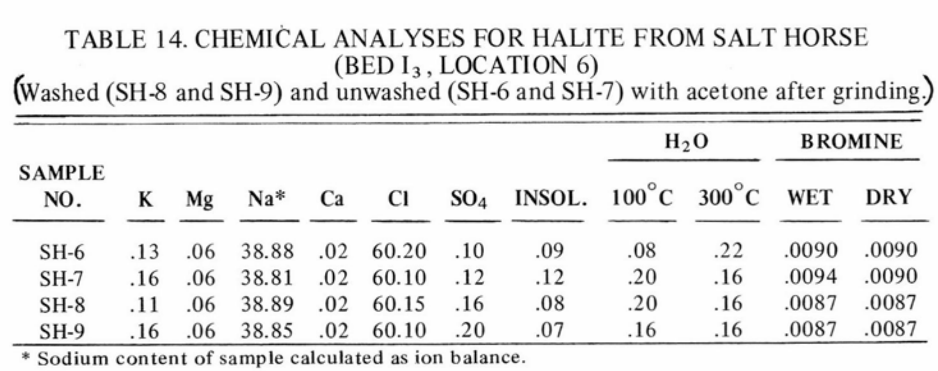


TABLE 14. CHEMICAL ANALYSES FOR HALITE FROM SALT HORSE (BED I_3, LOCATION 6)

(Washed (SH-8 and SH-9) and unwashed (SH-6 and SH-7) with acetone after grinding.)

SAMPLE NO.	K	Mg	Na*	Ca	Cl	SO_4	INSOL.	H_2O 100°C	H_2O 300°C	BROMINE WET	BROMINE DRY
SH-6	.13	.06	38.88	.02	60.20	.10	.09	.08	.22	.0090	.0090
SH-7	.16	.06	38.81	.02	60.10	.12	.12	.20	.16	.0094	.0090
SH-8	.11	.06	38.89	.02	60.15	.16	.08	.20	.16	.0087	.0087
SH-9	.16	.06	38.85	.02	60.10	.20	.07	.16	.16	.0087	.0087

* Sodium content of sample calculated as ion balance.

According to Linn and Adams, "floor" salt horses formed by solutions entering the ore zone from below and dissolving sylvite (with respect to the redistribution of bromine, there should be little difference between "floor" and "back" horses). The most apparent features of salt horses, which form the basis for the hypothesis, include the following:

> The ore-waste contacts are abrupt and crosscut the sylvinite beds. The dissolution of sylvite has been thorough so that residual pods and lenses in the salt horses are rare.
>
> Lenses and pods of leonite, kainite, and langbeinite are commonly present on the flanks of floor horses at the base of the ore zone. These lenses and pods are generally in juxtaposition with sylvite at the ore-waste contact and are zoned with a langbeinite core and an outer mixed zone of leonite and kainite.
>
> The absence of sylvite in the ore zone is attended by a thinning of the sylvinite beds.

The lenses and pods of sulfate minerals on the flanks of "floor" horses suggest that the brines which migrated into the ore zone contained Mg ++ and SO4. As the brine dissolved sylvite, it became saturated with magnesium and sulfate ions, resulting in the precipitation of one or more potassium magnesium sulfate minerals. Assuming that the original sulfate assemblage included leonite, kainite, and langbeinite, limits on the temperature of salt-horse formation and on the composition of the final brine are suggested by the solution equilibria data of D'Ans. Langbeinite is unstable in the presence of a brine below about 37°C. The three sulfate phases must, therefore, have formed above 37°C. As noted above, the sulfate minerals are generally zoned with leonite and kainite separating langbeinite and sylvite. This indicates that either the assemblage formed between 37° and 55°C or a sylvite langbeinite assemblage, formed above 55°C, developed an intermediate leonite-kainite zone upon cooling. The compositions of the solutions in equilibrium with leonite, kainite, sylvite, and halite at 37°C and with leonite, langbeinite, sylvite, and halite at 55°C are given in Table 15. The solution resulting from the formation of the salt horses had a composition similar to these brines.

The composition of the original solution is difficult to estimate. The only two evaporite minerals occurring in abundance below the first ore zone, with respect to which the brine must have been saturated, are halite and poly-halite. Little more can be said than that the potassium was lower and the sodium higher than in the final brine.

The redistribution of bromine during salt-horse formation should be considered in terms of brines similar to those in Table 15. This is impractical because the composition of the original brine and the bromine distribution coefficients applicable to it are only approximately known. Therefore, salt-horse formation will be briefly considered in the simpler $NaCl-KC1-H_2O$ system. This system is appropriate because the principal changes involved in salt-horse formation are the dissolution of sylvite and the precipitation of halite.

TABLE 15. COMPOSITION OF SOLUTIONS IN EQUILIBRIUM
Leonite, kainite, langbeinite, sylvite, and halite
at 55°C and leonite, kainite, sylvite, and halite
at 37°C (data from D'Ans, 1933, graph 21).

	37°C		55°C	
MINERAL	MOLES	WT (%)	MOLES	WT (%)
K	26	3.76	19.5	5.40
Mg	55	4.96	46.0	4.00
Na	24	2.04	19.5	3.20
Cl	130	17.10	69.0	17.50
SO_4	15	5.34	16.0	5.50
H_2O	1000	66.80	1000.0	64.40

The bromine content of the original salt-horse brine can be estimated if one assumes that it was in equilibrium with the bromine content of halite below the ore zone. In this study, halite from 25 feet below the ore zone to the 126-polyhalite bed contained between 30 and 60 ppm Br. Holser (1966) obtained values for the same interval in the range between 50 and 70 ppm. For a much lower stratigraphic interval, between the Cowden and Fletcher anhydrite beds, he presented bromine analyses between 10 and 30 ppm *(see* fig. 14). No bromine determinations are available for the approximately 650 feet of Salado salt between this interval and the 126-polyhalite marker. The average bromine content of halite below the first ore zone is probably between 30 and 80 ppm Br. The distribution of bromine between this halite and an interstitial brine would have been determined by the distribution coefficient *b* as influenced by the $MgC1_2$ content of the brine and the temperature. For the brines in Table 15, between 37° and 55°C, a distribution coefficient between 0.08 and 0.12 would seem appropriate *(see* fig. 6). The bromine content of the brine, in equilibrium with crystals containing 30 to 80 ppm Br, would then fall between 0.02 and 0.12 weight per cent. For convenience, the midpoint of this range will be used as the bromine content of the brine.

The redistribution of bromine during salt-horse formation depended on the KC1 content of the original brine (initial saturation with respect to NaCl assumed), the bromine content of the original brine, the amount of sylvite dissolved, the bromine content of the sylvite dissolved, the amount of halite precipitated, the bromine distribution coefficient for the precipitated halite, and the temperature.

Table 16 tabulates estimated ranges for five of these variables.

TABLE 16. ESTIMATED RANGES OF VARIABLES CONTROLLING BROMINE DISTRIBUTION

During the formation of salt horses in the system $NaCl–KCl–H_2O$

	WEIGHT PER CENT
Bromine content of original brine	0.02 – 0.12
KCl content of original brine	0.00 – 6.00
Bromine content of sylvite in ore zone	0.063
Temperature	37°C – 55°C
Halite bromine distribution coefficient	0.08 – 0.12

The amounts of halite precipitated and sylvite dissolved are functions of temperature and the initial NaCl and KCl concentrations in the brine. When the temperature and initial KCl content of the brine are fixed (at NaCl saturation), the amount of salts dissolved and deposited can be determined from the data of D'Ans (his graph 2, fig. 2).

Calculations based on the data in Table 16 indicate that halite deposited during salt-horse formation could contain between 0.0048 and 0.0075 weight per cent bromine. This range assumes equilibrium throughout the entire volume of altering brine. These calculated values are less than those found in salt-horse halite (fig. 41). If one assumes that primary halite in the ore zone retained its original bromine content, the secondary halite would have to contain between 80 and 100 ppm bromine to yield the present average concentration. The low calculated values may indicate that one or more of the estimates in Table 16 are in error. It is also possible that the halite precipitated during salt-horse formation assumed more than an equilibrium amount of bromine from the sylvite it replaced.

VOLUME CHANGES DURING SALT-HORSE FORMATION

The thickness of sylvinite beds in the first ore zone decreases in salt horses. Such volume changes depend on the percentage of sylvite in the ore zone and, to a lesser extent, on the composition of the initial solution and temperature. The thinning of the beds involves, principally, halite and sylvite and will be considered in the system $NaCl—KCl—H_2O$, using the data of D'Ans (his graph 2, fig. 2).

Halite precipitates from solutions saturated with respect to NaCl when sylvite dissolves. The volume of halite deposited, however, is less than the volume of sylvite dissolved. Over the temperature range 25° to 55°C, the volume per cent of sylvite *not* replaced by halite increases from 65.5 to 66.5. If, for example, a bed containing 30.5 per cent sylvite is attacked by a sufficient volume of sodium-chloride-saturated solution, the resulting decrease in bed volume will be 20 per cent. If this loss of volume occurs as bed thinning, the decrease in thickness of a 6-foot bed will be 14 inches.

The sylvite content and thinning of beds G + H and I associated with the salt horses at locations 6 and 7 were investigated. The percentage decreases in the thickness of bed I at these two locations are respectively 35.6 and 36.7. These values are almost twice the calculated values. The decreases in thickness of beds G + H at locations 6 and 7 are 7.9 and 26 per cent. The thinning of this interval at location 7 is also more than would have been expected. The excess thinning of these beds probably indicates that at the time of salt-horse formation, the ore zone was composed not of a halite-sylvite assemblage but rather a halite-carnallite-sylvite assemblage. This possibility will be discussed later.

To calculate the volume of brine necessary to remove sylvite from the ore zone, from a column of ore 6 feet thick and 1 foot square, the parameters are as follows:

(1) Temperature, 25° to 55°C

(2) KC1 per cent in original brine, 29.95 to 5.87

(3) Original brine at NaCI saturation

(4) Minimum density of original brine, 1.20 to 1.25

(5) KC1 per cent in bed, 30

Under these conditions, between 433 and 1434 liters of brine would be required to leach 0.17 cubic meter of ore. This is equivalent to 117 to 379 gallons of original brine leaching 6 cubic feet of ore. As the temperature of the brine increases and the initial KC1 content decreases, the required volume of brine decreases. The calculated volume range is a maximum, because a minimum brine density range was used.

IDENTIFICATION OF SALT HORSES

A current problem in potash exploration is the difficulty of differentiating in drill cores between a barren hole due to a salt horse and a barren hole due to the nondeposition of potash. The higher bromine content of halite in salt horses and the characteristic bromine profiles that develop in floor and back horses may provide a means of distinguishing between the two types of barren holes. Three bromine profiles are plotted in Figure 42. The average profile was constructed using analyses from the underground sample locations (table 11). Core test IMC 123 is a barren hole about 4 miles northeast of the underground locations. Core test IMC 112, another barren hole, is 4 miles to the southeast. The bromine profile for IMC 112 looks much like a salt horse of the "back" variety (fig. 41). The profile for IMC 123, on the other hand, is uniformly low in bromine and may represent an area of nondeposition of potassium minerals rather than a salt horse.

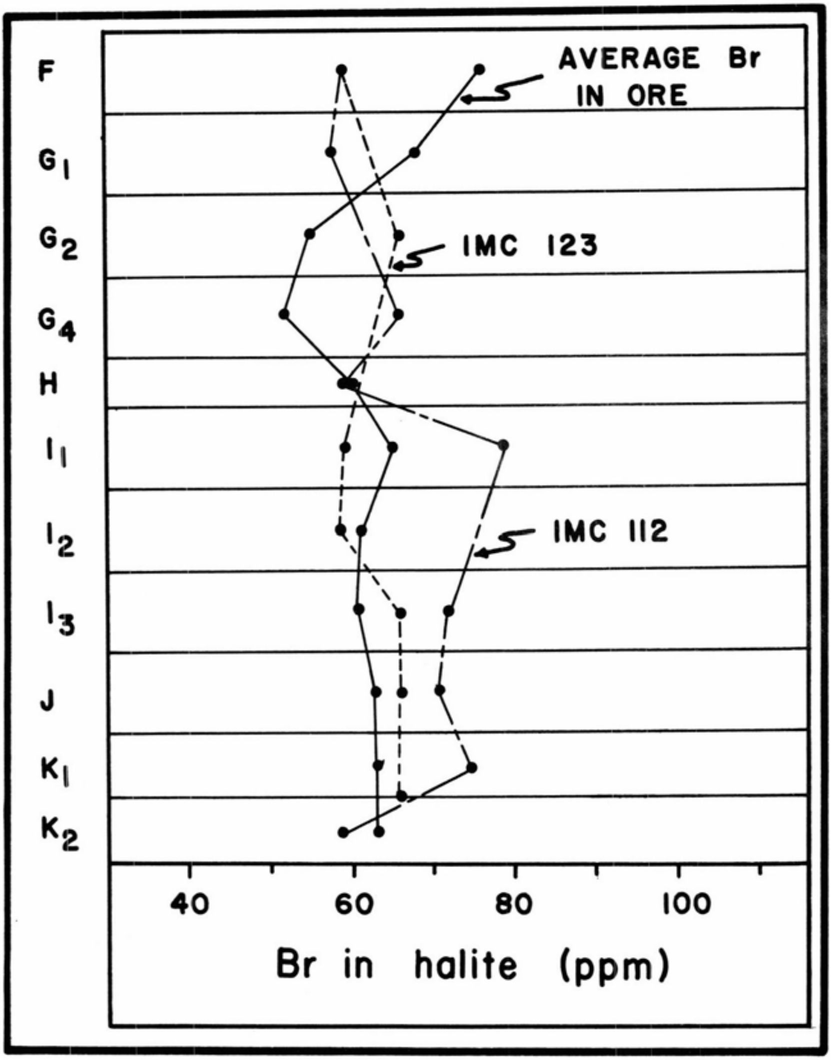


Figure 42
Bromine profiles for the First Ore Zone in core testes IMC 112 and 123 and the average profile for Locations 1 through 9

Origin of the Salado Formation: Lithologic Considerations

Aspects of the stratigraphy and mineralogy of the Salado Formation provide information on the conditions and mechanism of its deposition. The grain size, textures, mineral assemblages, and sequences of rock types are all, to some extent, primary depositional features. Only the gross features of the Salado will be considered.

HALITE BEDS

The grain size of halite is coarser and more uniform in halite than in argillaceous halite beds. The average grain size ranges from 10 to 20 mm, but 1- to 5-centimeter bands of 5- to 10-mm crystals are common. Individual grains are subhedral and clear in color but may contain milky zones because of the presence of minute fluid inclusions.

Halite rock is more closely monomineralic than any other evaporite bed in the Salado Formation. It is not monomineralic, however, as traces of some calcium sulfate mineral are always present. Of twenty-two analyses of the halite interval above the first ore zone, thirteen indicated between 1 and 5 per cent polyhalite (table 10). Anhydrite is the common sulfate mineral in the bottom 410 feet of the formation, whereas polyhalite dominates in the interval containing the ore zones.

Halite rock was deposited during periods when the basin area was greatest and rates of precipitation were high. Both of these factors decreased the rate of accumulation of argillaceous material by displacing its source and decreasing the relative rate of nonchemical sedimentation. Halite grains nucleated on the brine surface, grew into hopper crystals, and coalesced to form plates. As the size of grains and grain aggregates increased, surface tension could no longer hold the particles to the surface, and they settled to the floor of the basin. Crystallization continued on the basin floor both by overgrowth and recrystallization. This process has been observed by the writer in a salt lake near Carlsbad, New Mexico, and was described by Dellwig (1955).

The changes in grain size of halite in halite beds probably resulted from the more rapid accumulation of fine-grained intervals. The absence of hopper crystals and chevron structures (Wardlaw and Schwerdtner), generally considered diagnostic of primary halite, and the generally coarse grain size of halite may indicate that widespread diagenetic or postdepositional recrystallization has occurred.

ARGILLACEOUS HALITE AND CLAY BEDS

COMPOSITION AND MINERALOGY OF ARGILLACEOUS MATERIAL

The argillaceous minerals of the Salado Formation, as determined with the petrographic microscope and X-ray diffraction, are clays and lesser amounts of quartz, talc, magnesite, hematite, and dolomite and perhaps other minerals quartz and hpmatite are aPnPrallv nrecent in arnunintc nn to ahnnt S ner cent. Talc may be present in clean and argillaceous halite beds but is almost exclusively limited to those beds that contain or contained potassium and magnesium chloride minerals. Talc also occurs in some clay beds, notably those at the top of ore zones. The distribution of magnesite and dolomite is not well known. Magnesite is present in clay beds at the base of certain sulfate beds and in at least two of the ore zones.

Clay minerals constitute more than 90 per cent of the argillaceous material of argillaceous halite and clay beds. The mineralogy of these clays has received little attention and the distribution of the various clay minerals is unknown. Two studies have identified specific clay minerals and determined their relative abundances. Grim, Droste, and Bradley concluded that the dominant clay mineral in argillaceous material of the first and seventh ore zones in the United States Borax mine is an interlayered chlorite-vermiculite or chlorite-montmorillonite. Fournier studied the clays of core test AEC No. 1 and found mixed-layer chlorite-vermiculite the most abundant clay. He also identified illite, chlorite, random mixed-layer chlorite-vermiculite, and muscovite-vermiculite or muscovite-montmorillonite. A more thorough investigation is needed, but it is probable that the dominant clay minerals in the Salado Formation are of the mixed-layer type. Studies of other deposits corroborate the conclusion that the common argillaceous minerals of halite rocks are mixed-layer clays, illite, and chlorite (Droste, 1963; Braitsch, 1960; Fuchtbauer and Goldschmidt, 1959; Lounsburg, 1963; Nelson, 1960). The significance of this clay assemblage can be better understood by briefly considering the behavior of clays in the marine environment.

BEHAVIOR OF CLAYS IN THE MARINE ENVIRONMENT

The effect of sea water on clay minerals has been investigated by noting the changes in the clay mineralogy of bottom sediments near the mouths of rivers and by experimentally placing different clays in natural and artificial sea water. Powers (1957) studied clays in Chesapeake Bay and the rivers emptying into the Bay. In the river waters, he found well-formed to weathered illite, minor amounts of kaolinite, and a trace of weathered chlorite. Within the Bay, he found (p. 361) that "a chlorite-like clay is forming from weathered illite through a mixed-layer illite-vermiculite-chlorite stage, and some illite is apparently regenerated to a better illite." Furthermore, he noticed an increase in chloritelike and vermiculite clays toward the mouth of the estuary. Investigations near the Mississippi delta showed montmorillonite and less kaolinite and illite in the fresh water of the river channel. The clays in water with a salinity of 1 to 10 parts per thousand are mixed-layer aggregates of diagenetic chlorite, principally vermiculite. With increased salinity, the thermal stability of the chlorite increases. Powers believed the distribution of clays in these two areas is explained by the diagenetic formation of mixed-layer clays and chlorite through the preferential absorption of Mg^{+2} by montmorillonite and weathered illite. Some illite is also formed by the absorption of $K+$ by weathered illite.

Carroll and Starkey (1960) immersed various clays in samples of sea water for from 10 to 150 days. They found that all clays yielded appreciable amounts of SiO_2, $A1_20_3$, and Fe_20_3 to the sea water. The quantities produced decreased in the order montmorillonite, mixed-layer mineral, illite, kaolinite, and halloysite. They also determined that the order of replacement of the Ir ions in the H-form of the clay minerals was Ca^{+2} >Mg^{+2}>Na^{+}> K^{+}. In sea water, Mg^{+2} occupies most of the sites, however, since the Ca:Mg ratio in sea water is 1:3.

Whitehouse and McCarter (1958) immersed kaolinite, illite, and montmorillonite in artificial sea water for from 6 months to 5 years. Their data support the contention that illite and chlorite clay types can form from montmorillonite in marine environments. They did not note any transformation of illite or kaolinite to other clay types. The initial diagenetic modification of montmorillonite occurred during flocculation and settling in sea water. The extent of modification, they found, depended more upon the magnesium-potassium ratio than upon the total concentration level. The ideal magnesium-potassium ratio was of the order of 9:4, provided the sea water chlorinity was in the range of 7.2 to 19.4 grams per kilogram and the potassium was not less than 0.005 molar.

It is apparent that mixed-layer and chloritelike clays form in marine saline waters from montmorillonite and weathered chlorite by the absorption or exchange of Mg^{+2} in the brine. Kaolinite and crystalline illite may persist in the same environment; the latter may even form from weathered illite. In brines such as those that deposited the ore zones of the Salado Formation, this process would have been accelerated because of the high Mg^{+2} and K^{+} concentrations. The original mineral assemblage of the first ore zone requires a Mg:K ratio in the brine of about 6:1, slightly higher than the ratio of 5:1 in sea water. The clay minerals of the ore zones, therefore, should be chlorite, possibly illite, and some mixed layer; these are in fact the minerals reported (Grim, Droste, and Bradley; Droste).

The diagenesis of clays in a brine produces changes in the chemistry of the brine other than the removal of Mg^{+2} ; Si02 is lost to the brine, especially from montmorillonite (Carroll and Starkey). Whitehouse and McCarter noted that in the alteration of montmorillonite to chlorite, $Si0_2$ platelets similar to those precipitated from sodium silicate solutions formed. Recently, Mackenzie and Garrels (1965) and Mackenzie et al. (1967) demonstrated the rapid reactions between various silicates and sea water.

The fate of iron in the diagenesis of iron-bearing montmorillonites in brine is also of interest. Powers pointed out that all the diagenetic chlorite he produced resulted from the action of sea water on iron-bearing montmorillonite. He also immersed an iron-free montmorillonite in sea water for one year without the formation of any chlorite. No analyses of the initial and final brines or clay were made for iron, so it is not known whether the iron was replaced by Mg^{+2} or whether it merely acted as a catalyst to alteration.

ORIGIN OF CLAY MINERALS IN THE SALADO FORMATION

The identity of clay and other argillaceous minerals in the Salado Formation has been discussed in the preceding paragraphs, together with the behavior of clays in brines. From these discussions, one can summarize the most probable origin for clays in argillaceous assemblages.

Silicate minerals were introduced into an evaporite basin during the precipitation of evaporite minerals. Montmorillonite was probably a major component of these allogenic silicates. The close association between potassium and clay minerals precludes the argillaceous material having been carried by terrestrial streams draining adjacent landmasses. Such solutions would be of low salinity and could not produce the coincidence of argillaceous material and potash mineralization. The silicates in argillaceous sylvinite were probably introduced mostly as airborne dust.

As the silicate minerals entered the basin brine, they began to alter to the argillaceous mineral suite now characteristic of the Salado Formation. The principal alteration products were mixed-layer clay minerals, quartz, and probably iron now present in sylvite as hematite. An authigenic origin for the quartz crystals is supported by their euhedral habit, the absence of pitting and rounding, and their ubiquitous occurrence in argillaceous halite rock. The quartz crystals are also coarser than the clays, which would have led to sorting had the assemblage been washed into the basin.

DISTRIBUTION OF ARGILLACEOUS MATERIAL IN THE SALADO FORMATION

Argillaceous material in the Salado Formation is present as thin bands and is disseminated in halite rock, in potassium-bearing beds, and at the base of sulfate beds. The characteristics of the occurrences in halite and sylvinite beds are summarized below.

Beds within the Salado Formation are recognized by changes in color, grain size, amounts, and distribution of the minerals. The color and distribution of argillaceous material in a bed may be uniform or may increase in amount from the bottom to the top of the bed. Figure 43 shows the possible sequences for these two distributions, together with an argillaceous-free halite bed, and sequences including a sulfate bed as well. The "common" sequences account for the majority of sulfate beds and all sulfate beds more than about 6 inches thick. The less common sequence is typical of sulfate beds less than 6 inches thick. Argillaceous halite immediately above a sulfate bed is uncommon.

The argillaceous material of an argillaceous halite bed may be present in one or more of the following ways:

Disseminated within halite grains
Clots within halite grains
Thin films along halite grain boundaries
Clots between halite grains
Discontinuous 2- to 3-mm-thick bands parallel to the bedding

As the amount of argillaceous material increases, the importance of these modes of occurrence increases approximately in the order listed. The order also corresponds to the progressive recrystallization of an argillaceous halite bed.

The contacts between halite beds are sharp or vague, depending on which beds are juxtaposed. The contact between halite and overlying argillaceous halite may be difficult to determine exactly. On the other hand, the contact between clean halite and underlying argillaceous halite is usually sharp and

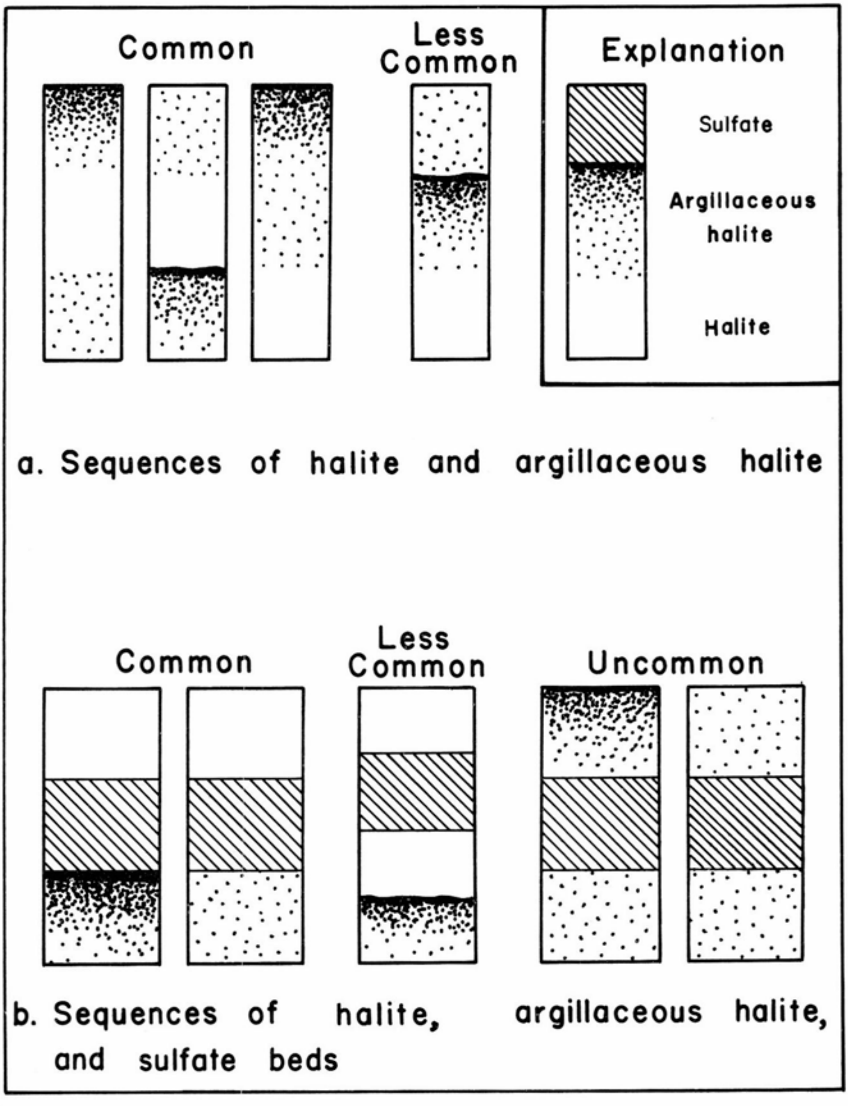


Figure 43
POSSIBLE SEQUENCES OF HALITE, ARGILLACEOUS HALITE, AND SULFATE BEDS IN THE SALADO FORMATION

frequently is occupied by a thin clay seam. Contacts between the two types of argillaceous halite are commonly difficult to locate within a few centimeters.

Potash ore zones are characteristically high in argillaceous material whether or not potassium minerals are present. The average insoluble content of the ore zones ranges from 2 to 5 per cent. The amount of argillaceous material increases from the sulfate-rich ores to those originally deposited as halite-carnallite assemblages.

FORMATION OF ARGILLACEOUS HALITE ROCK

The deposition of argillaceous halite rock, in contrast to halite rock, probably reflects the following conditions at the time of deposition:

> Prolonged evaporation, limited influx, and perhaps reflux reduced the size of the basin. That part in and around the potash district would then have been closer to a source of wind- and stream-transported clastic material.
>
> The rate of chemical sedimentation (halite precipitation) was reduced, whereas the rate of clastic sedimentation was unchanged or accelerated.

The association of argillaceous material and potash beds is not consistent with a stream transport origin for the clastic material. It is more likely that the majority of argillaceous material in the ore zones was carried into the basin by winds. This is supported by the general observation that as individual halite beds become thinner, the bulk clastic material remains about the same while the weight per cent increases. Probably, argillaceous chloride rocks accumulate under conditions of decreased chemical sedimentation rather than increased clastic sedimentation. A decrease in the rate of chemical sedimentation reflects either a higher rate of solution influx into the basin or a decrease in the rate of evaporation. If the decrease in chloride precipitation is due to increased solution influx, a sulfate bed will generally result. This will be considered in a subsequent section. Argillaceous halite intervals not overlain by a sulfate bed probably were deposited under a reduced rate of evaporation.

The rate of evaporation of a brine depends on atmospheric conditions (temperature, per cent humidity, and wind velocity) and the composition of the brine. Evaporation rates are highest when warm, dry air is continually moving across a body of solution. It is likely that these parameters varied many times during deposition of the Salado Formation and that many changes in lithology were the direct result of such variations. It seems unlikely that changes in these parameters fortuitously coincided with potash deposition to produce the argillaceous sylvinite of the ore zones. Rather, argillaceous sylvinite probably reflects slower evaporation rates due to the composition of the brine.

As the concentration of a brine increases, the water vapor pressure in equilibrium with the brine decreases. Brine concentration may be expressed in terms of ionic strength, moles of solute per 1000 moles of water, or other appropriate units. A decrease in vapor pressure means that, for the same atmospheric conditions, the brine will attain equilibrium with the air through the loss of less water than at a higher vapor pressure. Vapor-pressure curves for three saturated brines and water are plotted in Figure 44 as a function of temperature. At a specified temperature, the vapor pressure in equilibrium with these solutions decreases in the order H_20, KCI, NaCl, and $MgC1_2 \cdot 6H_2 0$. If air in equilibrium with pure water were to blow over the three brines, it would successively lose water to the solutions as each attained its equilibrium vapor pressure. If, on the other hand, air in equilibrium with a saturated $MgC1_2$ '6H2O brine passed over the other solutions, it would successively pick up water. For a given set of atmospheric conditions, therefore, the rate of evaporation decreases as the concentration of the brine increases.

The approximate path of sea water evaporation is presented in Figure 45 in terms of the dissolved solids in the brine and its vapor pressure at 25°C. From the beginning of precipitation of magnesium- and potassium-bearing minerals to saturation with respect to carnallite, the vapor pressure decreases from 14.5 to 7.4 mm. A similar decrease must have occurred between the precipitation of clean halite beds and the ore zones in the Salado Formation. This decreased vapor pressure was attended by a decrease in the brine evaporation and sedimentation rates, permitting the relative rate of windblown elastic accumulation to increase.

CALCIUM SULFATE BEDS

The abundant calcium sulfate-bearing minerals in the Salado Formation are anhydrite ($CaSO_4$) and polyhalite (2CaSO4*MgS04 ·K2SO4 2H2O). They are present as disseminated grains in halite and argillaceous halite rock and as numerous, massive, sulfate beds. Most sulfate beds are composed of polyhalite. The few anhydrite beds in the section of the Salado Formation shown in Figure 15 are bounded on their tops and bottoms by polyhalite. Other calcium sulfate minerals, present in small amounts, include glauberite ($CaSO_4$ $2Na_2$ SO_4) and syngenite ($Ca.SO_4.K_2S04$ H_2 0).

SOURCE OF CALCIUM SULFATE SOLUTIONS

A solution precipitating halite cannot proceed to the precipitation of massive polyhalite or anhydrite without the influx of new solutions. Prior to the deposition of each sulfate bed, therefore, a new influx of unsaturated brine entered the basin. The new solutions contained appreciable amounts of calcium and possibly sulfate and became saturated with respect to a calcium sulfate mineral because of evaporation and mixing with the NaCl-saturated basin brine. The exact composition and origin of the influxes cannot be deduced from the rocks, but some limiting observations can be presented:

> Sulfate beds thicker than 2 feet contain appreciable amounts of anhydrite, indicating that with prolonged influx, the solutions did not contain sufficient potassium and magnesium to maintain saturation with respect to polyhalite. This, in turn,

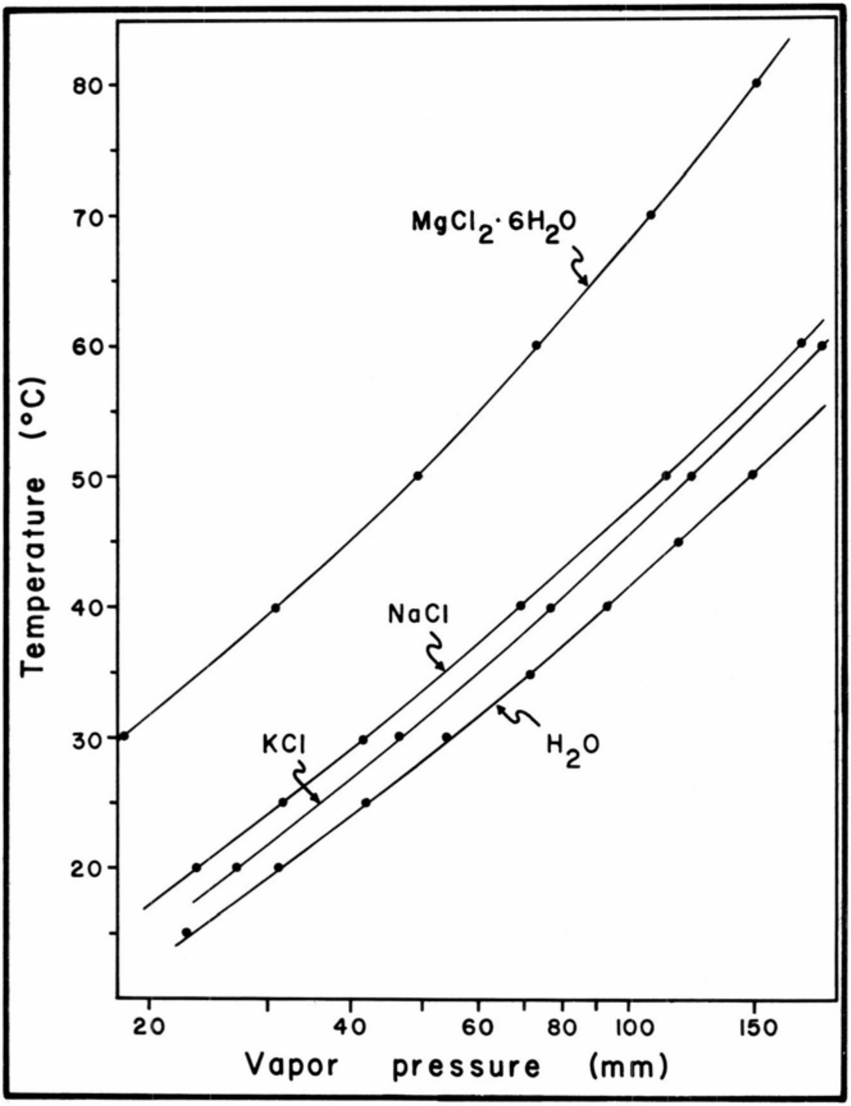


Figure 44

VAPOR PRESSURE OF WATER AND SELECTED SATURATED SALT SOLUTIONS
(Data from International Critical Tables 1926-1933; Olynyk and Gordon, 1943)

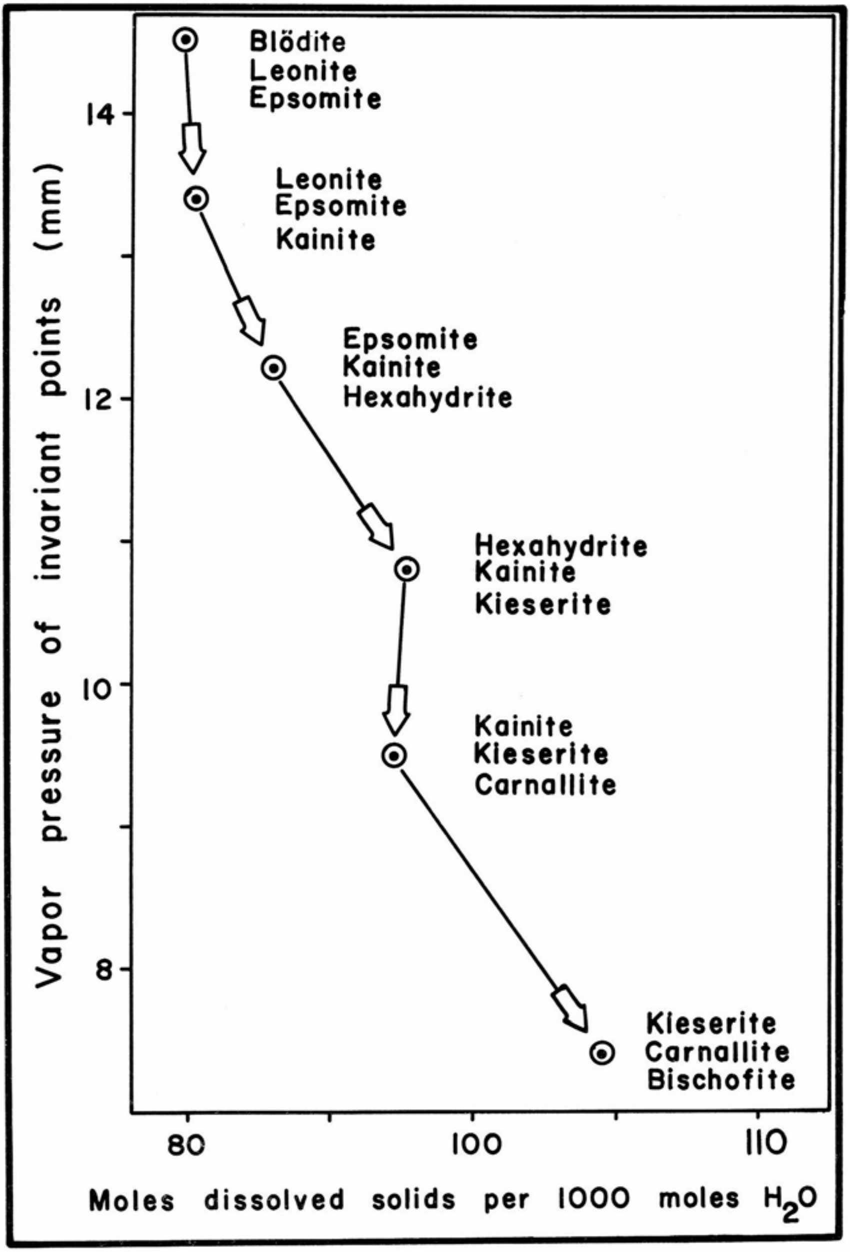


Figure 45

APPROXIMATE EVAPORATION PATH OF SEA WATER

Reflected by invariant points in the system Mg—Na—K—Cl—SO_4H_2O at 25°C

(Data from D'Ans, 1933; Borchert, 1940)

suggests that the potassium and magnesium in the polyhalite was derived from the basin brine.

Sulfate beds thicker than 4 inches generally have underclays containing magnesite. This requires that the influx solutions contained $CO3^{-2}$.

Some of the clay underlying sulfate beds is a residuum from the dissolution of halite by unsaturated influx solutions. This is supported by discontinuous bromine profiles (to be discussed next). The influx solutions, therefore, must not have been saturated with respect to NaCl. Furthermore, had they been saturated with NaCI, they could not have carried the calcium (and sulfate) present in the anhydrite and polyhalite beds. On the other hand, most sulfate beds are overlain by an interval of halite, suggesting that the associated influxes contained some NaCl. This addition of a sodium-calcium-sulfate-carbonate solution reduced the relative concentrations of $MgC1_2$ and KC1 and the total salinity, permitting a higher evaporation rate and the deposition of the clean halite rock. Continental stream waters are typically calcium carbonate solutions and meet all the foregoing requirements except that of NaCl. Sea water and streams exposed to beds of salt meet all the requirements.

RATE OF SOLUTION INFLUX

The rate at which solutions entered the basin was not constant. It is possible that solutions continually entered the basin, but only intermittently at rates sufficient to undersaturate the brine with respect to halite and permit the precipitation of sulfate beds. Intervals of halite rock show evidence, in fact, of influx and dissolution without associated sulfate beds. The balance between influx and evaporation was not the same for all sulfate beds and even changed during the deposition of a single bed. These fluctuations led to the development of the following features:

Thin sulfate beds (0.5 to 10 cm) are not immediately underlain by clay seams, whereas thicker sulfate beds have underclays proportional in thickness to the thickness of the sulfate bed. For thin sulfate beds, the rate of influx was probably slow and prolonged and the volume small. The basin brine was not entirely diluted, averting the dissolution of halite and the accumulation of a clay residuum. The slow influx also permitted mixing and evaporation to precipitate the carbonates closer to the point of entry into the basin. Deposition of thicker sulfate beds was preceded by a large solution influx, dilution of the basin brine, dissolution of halite, and the accumulation of a clay residuum. Some clay may also have been carried in with the solutions. As influx decreased, evaporation and mixing with the original basin brine led to the precipitation of a carbonate mineral and eventually the sulfate bed.

In thick (3- to 10-foot) sulfate beds, in which the sulfate mineral is dominantly anhydrite, numerous 1- to 3-mm magnesite-rich bands are interlayered with 5- to 50-mm bands of anhydrite. Extending up from these magnesite bands in radiating groups are 2- to 50-mm twinned gypsum crystals that have been replaced by halite. These crystals grew on the basin floor during times when the brine was unsaturated with respect to $NaC1$, and the surface nucleation and precipitation of a calcium sulfate mineral was slow.

The halite intervals above many sulfate beds contain more polyhalite or anhydrite than can be explained by coprecipitation of these minerals with halite through evaporation. This suggests that the influx of Ca- or SO_4-bearing solutions had reached such a delicate balance that excess polyhalite or anhydrite was deposited with only intermittent interruption of halite precipitation.

PARAGENESIS OF SULFATE MINERALS

Sulfate minerals commonly form and persist in brines as metastable phases. Interpretations of present sulfate distributions must recognize that, for example, polyhalite that appears to be secondary may have replaced either stable or metastable gypsum or anhydrite. This problem has received little consideration in this study, and the following observations deserve more widespread documentation and investigation.

When a sulfate bed contains both anhydrite and polyhalite, the latter occurs as bands or rims on the top and bottom of the bed. The anhydrite in the center of the bed may be either banded with magnesite or (and) massive anhydrite. It is not known whether these minerals are as they were deposited or whether they owe their relative positions to postdepositional replacements. The influx and evaporation of unsaturated solutions should have led first to the nucleation of calcium sulfate minerals at the brine-air interface. From what we can deduce about the composition of the influx solution, gypsum or anhydrite should have been the first calcium sulfate-bearing mineral to nucleate. As the grains settled through the underlying brine, they should have been converted from gypsum to anhydrite and finally to polyhalite. If the volume of influx solution were large, the deeper brine would have become progressively unsaturated with respect to halite and polyhalite through mixing. Polyhalite would then have ceased to be the stable calcium sulfate mineral on the basin floor, and the central anhydrite part of the bed began to accumulate. As evaporation continued, the salinity of the brine again increased and the top band of polyhalite was deposited, followed by the resumption of halite deposition.

It is also possible that the entire bed accumulated initially as a gypsum or anhydrite interval. The tops and bottom of the bed subsequently altered to polyhalite through exposure to the interstitial potassium-and magnesium-bearing brines of the adjacent halite intervals. The origin of disseminated polyhalite in the halite beds raises the same questions that will be answered only after more work on the stable and metastable ranges of sulfate minerals in brines, the kinetics of sulfate reactions, and the petrography of sulfate rocks.

Origin of the Salado Formation: Geochemical Considerations

SOURCE OF BASIN SOLUTIONS

Evaporation of sea water is the only known geochemical process capable of producing the concentrations of halite, anhydrite, and potassium salts present in the Salado Formation. Two aspects of the chemical composition of the formation, however, are at variance with what would be expected from the evaporation of sea water:

1. The bromine content of halite in the 460 feet of the formation studied does not exceed 105 ppm, even in potassium-bearing mineral assemblages.

2. The magnesium sulfate and potassium magnesium sulfate minerals, which should underlie or occur at the expense of the sylvinite beds, are absent.

If the Salado Formation had been precipitated directly from sea water, the bromine profile in Figure 15 would have more closely approximated those for the Werra (fig. 8a), Upper Rhine (fig. 8b), and Angara—Lena (fig. 9) salt sections. The average bromine content of halite would have been between 100 and 200 ppm, with minimum concentrations of 200 to 250 ppm in potassium- and magnesium-bearing mineral assemblages. The potassium-bearing mineral assemblages would have resembled those in Table 3 and the older cycle of the German Zechstein (Phillips, 1947), the natural evaporite most closely approximating a theoretical succession of mineral assemblages. The low bromine content, high potassium-to-bromine ratio, and the dominance of sylvite as the potassium-bearing phase strongly suggest that a large part of the Salado Formation was derived from the dissolution, transport, and redeposition of an older evaporite deposit.

The dissolution of a primary evaporite deposit, with an average bromine content of 200 ppm, would yield a saturated sodium chloride brine, at 30°C, containing approximately 0.00526 weight per cent bromine. The first salt deposited from this brine, for a distribution coefficient of $b = 0.14$, would contain 7 ppm bromine; depending on the regime of the basin, this concentration would increase slowly or rapidly with further evaporation. The absence thus far of bromine concentrations in this range suggests that the brines derived from the dissolution of previously deposited evaporites were augmented by brine from another source with a slightly higher bromine-to-chlorine ratio, probably sea water.

A likely source for much of the salt in the Salado Formation would have been the older Permian and Pennsylvanian evaporite deposits of Arizona, Utah, Kansas, Oklahoma, Colorado, northern New Mexico, and the Texas Panhandle. The regional tectonic events that gradually uplifted, drained, and exposed these deposits to erosion by continental streams also provided a new and final Permian evaporite basin in the west Texas—New Mexico area in which the secondary brines accumulated. Throughout deposition, the basin received intermittent influxes of secondary brine, sea water, and probably water from calcium carbonate-bearing continental streams, leading to the repetitive halite-sulfate bedding characteristics of the formation.

REGIME OF THE EVAPORITE BASIN

The regime of the Salado evaporite basin was particularly complex because of the plurality of brine sources and influxes. Ideally, one should be able to prepare a material balance for an evaporite basin based on the addition of brines of various compositions and the removal of water through evaporation, salts through precipitation, and brine through reflux. When more detailed data are available on the composition and distribution of rock types, such a material balance may be within reach. The data collected in this study permit only general remarks about some parameters of the basin regime.

RATE AND FREQUENCY OF INFLUX

Sea water and other solutions entering an evaporite basin have a tendency to form a sheet of unsaturated solution over the saturated basin brine. This is because of the greater density of the basin brine and the slow rate of mixing of the two solutions. Evaporation then occurs in the new surface layer, leading to the deposition of sulfate or carbonate minerals on the previously accumulated halite. Continued evaporation and mixing at the solution interface eventually eliminates the NaCl-unsaturated surface layer, and halite precipitation resumes.

The rates of many solution influxes were too slow to replace halite with monomineralic calcium sulfate precipitation throughout the entire basin. Changes in the rate of influx produced facies boundaries between halite and sulfate beds that migrated in response to changes in the balance of influx and evaporation. The use of sulfate beds to identify influxes and realtive changes in the rates of influx and evaporation was discussed earlier. The bromine profile is an even more sensitive recording of these same changes, and each inflection in the profile (fig. 15) corresponds to a change in the rate of influx or evaporation. It is not possible to determine which process fluctuated, for the results are the same for both.

The bromine profile for the upper part of the Salado Formation is extremely irregular by comparison, for example, with the very detailed and regular profile of salt bed 5 in the Paradox Formation (fig. 12). Both profiles, nonetheless, reflect their respective environments of deposition. Evidence that the profile for the Salado Formation is a depositional feature comes principally from correlation of the bromine content of halite and changes in lithology. These correlations reflect the fact that the concentration of bromine in halite and the lithology of the bed both reflect the same conditions of deposition. The source and intermittent influxes and refluxes of solutions prohibit the use of the absolute bromine content of halite as a measure of salinity. The following features of the bromine profile are noteworthy:

The bromine content of halite generally increases toward the top of halite beds. This is consistent with the normal pattern of static or uninterrupted evaporation of a brine.

The bromine content of halite increases irregularly up through halite and argillaceous halite beds to the base of most potash ore zones, indicating that the deposition of argillaceous sylvinite beds occurred during periods of higher salinity.

Throughout the Salado Formation, there is a pronounced antipathy between bromine and calcium sulfate minerals. In the vicinity of all polyhalite and anhydrite beds, the bromine content of halite decreases. This decrease reflects, as do the calcium sulfate minerals, a decrease in the concentration of the basin brine through refreshening. If the rate of influx was slow, the bromine content of halite begins to decrease some centimeters below the base of the sulfate bed and continues to decrease up into the overlying halite for a short distance before increasing again. These sulfate beds are generally composed of polyhalite, are less than 4 inches thick, and have no concentrations of argillaceous material at their bases. If the influx of new solutions was more rapid, the halite on the basin floor dissolved with the accumulation of a residual clay augmented perhaps by clays carried in with the solution. This clay zone, on which the sulfate bed then precipitated, also contains magnesite reflecting the high carbonate content of the influx solution. These sulfate beds are 4 to 16 inches thick, and the associated bromine profile generally increases up to the clay zone, reflecting the truncated nature of the contact. Above the sulfate bed, the profile resumes its increase but at a lower concentration. The extreme irregularity of the bromine profile for the upper part of the Salado Formation reflects the complex depositional history of these evaporite rocks. Correlations between changes in the bromine content of halite and changes in lithology reflect frequent changes in the composition of the basin brine because of repeated influxes of solutions.

DEPTH OF BRINE

Indirect evidence suggests that the basin brine was not deep, ranging perhaps from 0 to 165 feet. The bromine profile is not directly useful in this context because of the numerous influxes of solution. The steeper profiles in Figure 15 argue for a small brine volume. The rate of increase of bromine in halite can be held constant or decreased through dilution and reflux. A high rate of bromine increase, on the other hand, indicates static evaporation and probably a limited brine volume.

Many of the clay seams appear to have formed as residual accumulations from the dissolution of halite. For this to happen, the entire volume of basin brine had to be diluted below saturation with respect to NaCl. It is extremely doubtful that this could have occurred with a brine depth in excess of 165 feet because of the tendency of influx solutions to sheet over the basin rather than to mix with and dilute the basin brine. It is more likely that the brine depth was closer to 15 to 30 feet.

Evidence of erosion of salt is best developed at the top of ore zones where residual clay accumulations are common. In the first ore zone, the tops of beds A and D (fig. 20) are both erosion surfaces. Within these clay concentrations, talc plates show the casts of halite crystals they abutted in sylvinite rock that has eroded. It is not surprising that erosion followed potash deposition because these were the times of greatest basin restriction and, presumably, shallowest brine depth.

The brine depth during evaporite deposition has generally been considered greater than the above observations suggest. Depths of several hundred meters (600 feet) are not considered excessive by Borchert and Muir for most evaporites. They based this principally on the assumption that salts commonly precipitated more rapidly than the basin subsided; hence, thick evaporites must have been deposited in deep basins. The same conclusion has been reached where evaporite rocks overlie euxinic sediments.

The Permian basin of New Mexico and west Texas was probably 500 to 600 feet deep during the Early and Middle Permian. The Castile may even have been deposited in deep water. The Salado Formation, however, was probably deposited from comparatively shallow brine.

TOPOGRAPHY OF BASIN FLOOR

Studies of the horizontal distribution of bromine in halite at specific stratigraphic horizons, within and outside the first ore zone, indicate that the chemical conditions of sedimentation varied horizontally within the basin. Most important, the composition of the brine and perhaps the depth of the basin were not constant. The origin of the composition or concentration gradients is not known, but they may have resulted from currents in the basin that changed with changes in the basin regime. Important factors controlling currents in a shallow, continually subsiding basin include the source, volume, and frequency of influx solutions and the topography of the basin floor. Horizontal variations in the bromine content of halite should provide additional information on the basin regime as more representative samples become available.

Other important aspects of the basin regime include the brine temperature, air temperature, velocity, relative humidity, length and characteristics of seasons, and rates of precipitation and evaporation. The best working hypothesis seems to be that conditions during the Permian were much as they are today in equatorial regions.

FIRST ORE ZONE

STRATIGRAPHY

The first ore zone may be considered as representing a period of potassium and sodium chloride deposition interrupted by solution influxes and deposition of the halite marker beds. The influx solutions contained Na, Cl, Ca, and possibly SO_4. In other ore zones, the abundance of magnesite suggests the intermittent influx of carbonate-rich solutions. It appears that with each major solution influx, sylvinite precipitation ceased while the potassium- and magnesium-poor surface brine coprecipitated halite and polyhalite (anhydrite?) to form the halite marker beds (beds J, H, and F). As soon as the surface brine had dissipated through evaporation and mixing, sylvinite precipitation resumed. The contacts between the two rock types are abrupt, indicating that the solutions either were saturated with sylvite and precipitated it in eutectic proportions with halite (sylvinite beds) or were unsaturated and no sylvite precipitated (halite marker beds).

The bromine profiles for the first ore zone are remarkably uniform from top to bottom, indicating that the regime of the basin was open, thus preventing a steady buildup of bromine. The lowest and most erratic bromine concentrations in halite occur in the units immediately above the halite marker beds. This probably reflects the development of variations in basin composition that attended the solution influxes indicated by the markers.

The distribution of argillaceous material in the ore zone and its association with sylvinite rather than with the halite marker beds should be noted. In that the latter represent pronounced solution influx, the clay would be associated with them were it introduced into the basin primarily in suspension rather than as a windblown dust.

SYLVINITE ASSEMBLAGES

The general features of the three sylvinite beds of the first ore zone have been described. Two characteristics of these beds are not easily explained by the simple evaporation of a brine; namely, (1) the dark red rims around most sylvite grains and (2) the lower bromine content of the red sylvite rims (average 389 ppm Br) compared with the milky centers (average 780 ppm Br).

Schaller and Henderson, in their microscopic investigation of the potash deposits, concluded that two generations of sylvite exist: an older, colorless variety and a later red variety. They believed that the red sylvite developed through a process of coloration by the introduction of hematite into the colorless sylvite. Of importance is the observation that the colorless sylvite appears to have been replaced or encroached upon by the red sylvite rim or, to use their terminology, the hematite. I believe, however, that the apparent replacement was not simply an addition of hematite. The interpretation that red sylvite developed, in part, at the expense of milky sylvite is supported by the distribution of bromine in the two varieties of sylvite and their associated halite.

Sylvite and carnallite commonly contain iron as oriented or deranged plates of hematite. Schaller and Henderson (p. 37-38) noted that the hematite plates in sylvite are hexagonal in outline, with an average size of 0.005 mm. Hematite is also present in rods 0.02 mm long. These observations may be extended to other evaporites (Stewart, 1951), the hematite rods probably representing replaced goethite. The origin of hematite in carnallit! and sylvite has received much speculation but little experimental invest gation. The reasonable hypotheses follow:

$FeC1_2$ was incorporated into the crystal structures during growth, subsequently oxidized to Fe_2O_3, and exsolved along preferred crystal planes.

Hematite plates nucleated on the growing crystal faces of sylvite and carnallite in an epitatic relation.

$FeC1_2$ can readily substitute for $MgC1_2$ in the carnallite lattice (D'Ans and Freund, 1954). This is possible because of the similarity of the ionic radii of Fe ++ and Mg^{++}, as shown in Table 4. $FeC1_2$ cannot be expected to substitute for KC1 in sylvite or carnallite because of the considerable difference in ionic radii and the difference in charge.

Leonhardt and Tiemeyer (1938) reported that hematite in sylvite from Wathlinger, Hanover, is oriented with the (0001) plane parallel to the (100), (111), and (110) planes of the sylvite. They interpreted this to indicate that the hematite plates crystallized on the growing faces of sylvite. Most other investigators reported the orientation of hematite to be deranged or random (Stewart, 1951). Experimental and field data are lacking to support the contention that hematite in sylvite can be explained by epitaxy. It has been demonstrated (D'Ans and Freund) that Fe' will enter the carnallite lattice in substitution for Mg^{++} and that sylvite can replace carnallite. The writer accepts this as the mechanism of incorporation of iron, as hematite, in sylvite.

The oxidization of Fe ++ to the Fe' found in sylvite is poorly understood. Since many carnallite crystals contain hematite, the oxidization may occur before the conversion of carnallite to sylvite. Borshchevskii (1964) contended that the oxidization is associated with the natural radioactive decay of $K^{4\circ}$ with intermediate steps such as $A^{4\circ}$ and $C1_2$.

Braitsch (1962, p. 171-174) summarized data pertaining to the occurrence of iron in brines. He stated that evaporation of sea water would increase the concentration of iron from an initial value of 0.002 ppm to 0.017 ppm at the beginning of halite deposition and 0.17 ppm at the beginning of carnallite deposition. Sea water itself, therefore, provided a negligible source of iron. The solubility of iron in sea water and its evaporation products is much greater than the figures given above, particularly if the environment is sufficiently reducing to maintain iron in the Fe + form. Whitman, Russel, and Davis (1925) determined that the solubility of Fe ++ is further increased in $MgC1_2$ solutions. D'Ans and Freund demonstrated that $Fe(OH)_3$ can be reduced in concentrated $MgC1_2$ solutions in the presence of reducing substances. It appears, therefore, that in reducing saline environments, particularly those rich in $MgC1_2$, abundant iron can be retained in solution. It is also apparent that the iron would have to come from a source other than sea water.

Two samples of red sylvite from the first ore zone contained 0.18 and 0.13 weight per cent iron. If we assume that this iron was precipitated in carnallite, we can determine the approximate iron content of the brine from the date of D'Ans and Freund. They determined that iron substitutes for magnesium in carnallite in amounts up to 25 weight per cent of the iron in solution. If the alteration of carnallite to sylvite involved only the loss of one mole of $MgC1_2$-$6H_20$ for each mole of carnallite, the iron content of the original brine was between 0.139 and 0.193 weight per cent. This is about ten thousand times the iron concentration that results from the evaporation of sea water to carnallite saturation.

The close association of sylvite, particularly red sylvite, and argillaceous material has been noted. Certain other ore zones contain two lo three times as much clay as the first ore zone and red sylvite almost to ill; exclusion of milky sylvite. Within the first ore zone, the average insoluble content increases from about 0.8 per cent in bed K at the base of the ore zone to 1.5 (bed **I)** and 2.0 (beds G + **H)** per cent in the upper sylvinite beds. The proportion of red to milky sylvite increases in the same 5 quence. The deposition of carnallite and argillaceous material is apparently favored by the same environment. Furthermore, the original clays of the argillaceous material probably provided the iron now present in sylvite. 'This iron was released to the basin brine *in situ* by the alteration of an iron-bearing clay to a variety of mixed-layer clays and chlorite.

Oxidization-reduction reactions in saline environments have also received little study. Most of the evaporite minerals are insensitive to the oxidization potential of the brine as long as the sulfate ion is stable. For this reason, there is a paucity of mineral relations that reflect the Eh of deposition. It appears that iron must have been present as Fe^{++} during the formation of the ore zones. Other evidence suggesting a reducing environment includes the presence of **H2** S and minute quantities of pyrite in the ore ::one. **The H_2S** appears to be more abundant in colorless sylvite centers than in the red rims. The importance of bacteria (Flint and Gale, 1958) and algae (Morris and Dickey, 1957) in the evolution of salt beds has been suggested; ancient salt deposits contain numerous varieties of bacteria (Dombrowski, 1966). It seems probable that the ore zones were deposited from brines with a sufficiently low oxidization potential to retain considerable iron in solutior as Fe^{++}. The study of this environment may be materially assisted by the presence of manganese in some sylvite in the form of cryptomelane (Sun).

The interpretation that the red sylvite in the first ore zone was once carnallite finds support in the phase diagrams for the system VIgC1$_2$—KC1—NaCl—H$_2$0. **A** ternary diagram for this system, drawn for 65°C and saturation with respect to NaC1, is presented in Figure 46. Water saturated with NaCl is at point *a*. Moving away from point a into the field of a-e-d-c-b, the solution contains increased amounts of MgC1$_2$ and KCl while maintaining saturation with respect to NaCl. When the solution composition reaches one of the arcuate curves of the line e-d-c-b, it has attained saturation with respect to sylvite, carnallite, or bischofite. Between points *d* and *e,* the solution will be saturated with sylvite and halite; between *c* and *d,* with ^{c}arnallite and halite; and between *b* and *c,* with bischofite and halite. These three parts of the line are called the saturation surfaces of the respective minerals.

A mineral is only stable in contact with a solution when the solution composition falls on the saturation surface of the mineral. Point *d* is common to the sylvite and carnallite saturation surfaces and is called a peritectic point. With a brine composition at this point, further evaporation will move the brine composition onto the carnallite saturation surface, rendering sylvite in contact with the solution no longer stable. Sylvite will then be destroyed or "replaced" by carnallite. Point *c* is a eutectic point. Once the trine composition reaches this point, bischofite and carnallite will precipitate simultaneously (together with NaC1) in such a ratio that the brine composition

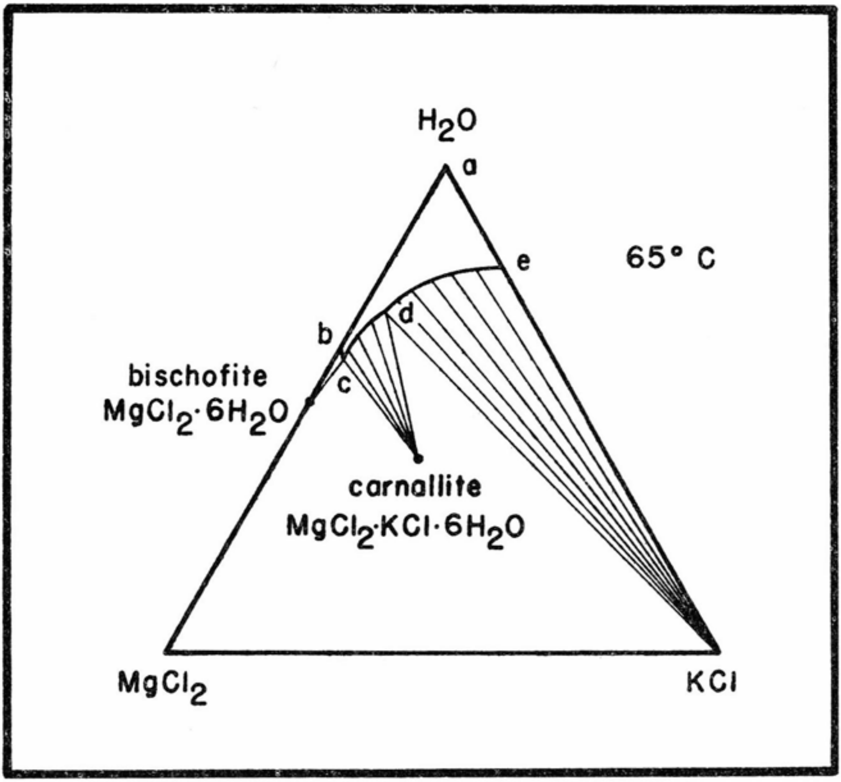


Figure 46

TERNARY DIAGRAM FOR THE SYSTEM Mg—Na—K—Cl—H_2O AT 65°C AND NaCl SATURATION

(Prepared by Adams, 1966, from data of D'Ans, 1933) undergoes no further change until dryness. It should also be noted that the saturation surface of sylvite lies between the composition of carnallite and H_20. If carnallite is placed in pure water or a NaCl-saturated brine, sylvite will be the first potassium phase to precipitate, not carnallite. These relations, although shown for 65°C, are not materially different for the temperature range 25° to 70°C. The significance of these relations is most obvious when one traces the evaporation of a brine such as that which c eposited the sylvinite bed of the first ore zone.

The evaporation of most natural sodium chloride-saturated br ines will first reach the saturation surface of sylvite (d-e), according to this diagram. Halite and sylvite coprecipitate with further evaporation, and the brine composition moves toward point *d*, where carnallite and sylvite are in equilibrium ium with the brine. If evaporation continues, however, the brine composition moves onto the carnallite saturation surface (c-d), and carnallite replaces sylvite as the stable phase. Sylvite exposed to the brine is altered to ca carnallite. This alteration may produce a carnallite rim on the sylvite or sc lid carnallite grains, depending on the sylvite grain size and the time of exposu re. When the sylvite has been completely altered to carnallite or effectively removed from the solution by carnallite rims, further evaporation precipitates primary carnallite. Evaporation may eventually reach the eutectic point *c*, but bischofite-carnallite assemblages are not present in the Salado Formation and are rarely preserved in salt deposits.

Each sylvinite bed in the ore zone contains red-rimmed sylvite, indicating that the bed was deposited initially as a halite-sylvite assemblage. When saturation with respect to carnallite was finally attained, the overlying brine seeped into the halite-sylvite crystal mush, altering the sylvite rims to carnallite and precipitating fine-grained carnallite in the interstices. F ad carnallite saturation been attained during the deposition of the sylvinite beds, the upper part of the beds would contain only red sylvite, which is not true.

During the alteration of sylvite to carnallite, abundant iron must have been available in the brine. This iron was provided by the associated clays that, since deposition, were being altered through the addition of Mg^{++} and the release of Fe^{++} and SiO_2. The concentrations of iron and silica in the interstitial brine may have become substantial, as is known to occur below the brine sediment interface in some saline lakes.

During the period of halite and sylvite deposition, bromine substituted for chlorine in both minerals. The distribution coefficients were close to the minimum values determined by Braitsch because of the high $MgC1_2$ content of the brine. As carnallite replaced sylvite, the bromine was red stributed to approach equilibrium, as determined by the carnallite-brine distribution coefficient. It has not been discovered, on the basis of microscor is studies or bromine determinations, exactly how much carnallite replaced sylvite. The red sylvite present in halite marker beds F, H, and J was probably deposited as carnallite at the same time carnallite was forming in the adjacent sylvinite beds.

Prior to the formation of residual bed A, all carnallite in the ore zone was converted to sylvite. This conversion was probably caused by basin brine, unsaturated with respect to carnallite but saturated with respect to sylvite, seeping into the ore zone. It appears to have been essentially complete because no primary carnallite has yet been reported in the district from the first ore zone. Possibly the carnallite was destroyed by brims rising up through the bed, but there is no apparent relation between this process and salt-horse formation, as one might then expect. The conversion of carnallite to sylvite is remarkable for its completeness.

Another feature of the ore zone, which probably developed during the destruction of carnallite, is the presence of plates and films of talc around the red-rimmed sylvite grains. This talc formed as $MgC1_2$ and H_20, was released by the alteration of carnallite, and encountered the high $Si0_2$ content of the interstitial brine. Such a reaction seems likely because in sylvinite rock the talc is almost exclusively limited to the surfaces of red-rimmed sylvite grains. Talc casts in the insoluble residuum at the top of bed A must have formed prior to the development of this residuum.

SALT HORSES

The characteristics and origin of salt horses were considered in some detail. Most chemical and physical aspects of the salt horses seemed satisfactorily explained by assuming that the ore zone was composed of halite and sylvite at the time of salt-horse formation. One important exception, however, was the excessive shrinkage of bed I at locations 6 and 7 and bed G + **H** at location 7. On the basis of the preceding discussion, it seems possible that some salt-horse development preceded the alteration of carnallite to sylvite and, therefore, could have involved different volume changes.

No volume measurements have been made of the milky and red sylvites in the first ore zone. It is known that the average bromine content of milky sylvite is 780 ppm and that of red sylvite 389 ppm. For the past several years, sylvite concentrates (a mechanical concentrate of all sylvite) in the mill feed have averaged about 633 ppm bromine. It may be estimated that such an average would be derived from 62 per cent milky sylvite and 38 per cent red sylvite. These figures are compatible with visual observations and will be accepted as representative of the ore zone. If the red sylvite (as carnallite) and milky sylvite were dissolved by sodium chloride-saturated solutions to the point of saturation with respect to carnallite, the decrease in bed volume would be 31 per cent for an average ore zone grade of 11 per cent potassium. This is more compatible with the bed thinning in the salt horses at locations 6 and 7 (35.6 and 36.7 per cent) and suggests that salt-horse formation probably occurred before the complete alteration of carnallite to sylvite.

Potash Deposits: Exploration and Evaluation

The bromine content of halite in an evaporite deposit may be an aid in exploration for potash deposits. The bromine concentration in halite formed through the evaporation of sea water should indicate the degree of brine concentration and, therefore, the stratigraphic proximity of potash beds. The bromine profile for a salt section should identify, by higher bromine concentrations, those horizons at which potash might occur in nearby areas. Two or more core tests might establish a horizontal gradient at a favorable horizon, indicating the best direction for further exploration drilling.

These general tests are less applicable to the Salado Formation than to some other salt deposits. The bromine content of halite in the Salado Formation, even in the presence of potash minerals, is uniformly low because the salts are second cycle. Furthermore, the bromine concentration in halite increases only 20 to 30 ppm over short stratigraphic intervals in passing from unmineralized to mineralized halite rock. In the absence of carnallite, langbeinite, and sylvite, the Salado Formation would appear to be a poor unit to explore for potash because the bromine content of the halite is low and the bromine profile lacks peaks 100 to 150 ppm above the background concentration. Clearly, the general bromine tests must be augmented by other data to correctly appraise second-cycle evaporite deposits. The widespread occurrence of polyhalite in the Salado Formation would be sufficient, together with the bromine profile, to recognize the complex origin of this evaporite sequence and its potential for economic potash deposits. In some beds economic concentrations of potash are present with low bromine concentrations in halite and without associated polyhalite. For the appraisal of such deposits, other guides must be developed.

The association of mixed-layer clays with salt deposits and potash beds in particular has been noted. It is possible that the mineralogy and composition of the clay minerals could serve as indicators of the brine composition at the time of deposition. Studies of clay seams and disseminated clay in argillaceous halite could then be used to determine the original brine composition and the proximity to potash deposition. The silicate minerals might be particularly suited to such studies, as they should be less responsive to postdepositional changes than the salt minerals.

Some of the potash deposits in the Carlsbad district contain numerous salt horses. It has not been possible in exploration drilling to determine whether a barren hole intersected a small salt horse in otherwise good ore or an area of potash nondeposition. It is also difficult in the mine workings to predict the proximity, shape, and size of a salt horse. Bromine studies were made to determine whether salt horses could be identified in cores and their limits predicted in the underground workings.

Figure 41 shows bromine profiles through two types of salt horses. It is apparent that halite in both salt horses contains more bromine than the adjacent ore does. The amount of bromine increase is greater at the top of the ore zone for "floor" horses (location 7) and the bottom of the ore zone for "back" horses (location 6). It should be possible, therefore, to differentiate between these two types of salt horses in cores. This is important because floor horses are more numerous but smaller in size than back horses. It is not certain that a bromine profile for the ore zone in an area of potash nondeposition was obtained in this study. The profile for core test IMC 123 in Figure

42 may be such a profile because it does not resemble a salt-horse profile. It seems likely that, given a bromine profile for an ore zone in potash, "floor" and "back" salt horses can be identified in cores.

The distribution of bromine within and adjacent to salt horses was studied to determine whether the proximity of ore-waste contacts could be anticipated. It was concluded that the bromine content of halite and sylvite in ore adjacent to salt horses is not sufficiently altered to predict a salt horse in the mine workings. In a similar way, the horizontal distribution of bromine in halite within salt horses gives no indication of proximity to the edge of the salt horse, except possibly within a few feet of the ore-waste contact.

Summary and Conclusions

Interpretation of the distribution of bromine in the Salado Formation in drill cores and underground workings of the International Minerals and Chemical Corporation mine, Carlsbad potash district, New Mexico, has led to the following conclusions:

1. The uniformly low bromine content of halite in the Salado Formation reflects the second-cycle origin of most of the salt. The close correlation between changes in the bromine content of halite and changes in lithology suggests that the bromine distribution is a sedimentary feature that has been only locally altered by postdepositional processes.

2. The repetitive sequence of halite, argillaceous halite, sylvinite, and sulfate beds indicates that the basin of deposition received many influxes of solution. These influxes are also recorded in the bromine profile as decreases in the b bromine content of halite.

3. Several potash ore zones were deposited during prolonged periods of evaporation and low solution influx. In the first ore zone, sylvite was the first potassium mineral to precipitate. It was followed and in part replaced by carnallite. During early diagenesis, all carnallite was converted to sylvite.

4. Postdepositional changes in the first ore zone locally resulted in the removal of sylvite and carnallite from the ore zone by solutions derived from the overlying and underlying rocks. The barren areas that resulted are referred to as salt horses.

5. The distribution of argillaceous material was controlled more by changes in the rate of chemical sedimentation than by changes in the rate of clastic sedimentation. The argillaceous minerals, principally mixed-layer clays, chlorite, talc, and quartz, resulted from the alteration and reconstitution of the original clastic minerals.

6. Geochemical programs can be of assistance in prospecting for and evaluating potash beds in evaporite sequences. The programs, however, must be designed for the specific deposits and carried out in the context of general geological studies, particularly investigations of evaporite stratigraphy and mineralogy.

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