

# Sedimentology and Bromine Geochemistry of Marine and Continental Evaporites in the Dead Sea Basin

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## ABSTRACT

*A thick mass of evaporites, shale and conglomerate of the Dead Sea Group, of Plio-Pleistocene to Recent age, forms the sedimentary fill, up to 8–10 km thick, of the Dead Sea trough in the Jordan Rift Valley. The history of this evaporite basin, origin of salts, basin morphology, depth of brine and conditions of influx-evaporation-reflux system, is examined, by comparing sedimentological and bromine data and existing data from marine evaporites.*

*Cyclic sedimentation in the Dead Sea Group, of thick rocksalt units alternating with thinner shale units is considered to have been deposited mainly in shallow water with occasional exposure and dessication. In later stages the basin was cut off from the sea with playa, lagoonal, sabkha and fluvial conditions prevailing. Rare occasional influxes of the sea occurred. Seasonal and cyclic sedimentation proceeds through the carbonate and sulfate phases, continuing in the deeper areas to the halite phase and rarely reaching conditions of dessication.*

*The bromine content in the rocksalt, 40–600 ppm, is within the range of salt of marine origin. The general trend of bromine concentration is a progressive increase up the sequence. Bromine profiles are semi-regular with occasional high peaks indicating dessication episodes, verified by characteristic sedimentary structures.*

Bromine ratios ( $\frac{\text{Br} \times 1000}{\text{Cl}}$  weight ratios)

*of connate salts in carbonates and clays range from 4.3 to 19. These and bromine ratios in salt units, are as expected from distribution of bromine between brine of seawater origin and the paragenetic halite respectively. Since these sediments also do not show any diagenesis, it is assumed that the soluble connate salts are from the brines from which the adjacent evaporites have precipitated.*

## INTRODUCTION

The Jordan Rift Valley was formed along a major N-S active sinistral strike slip fault. The Dead Sea deep trough developed in the central part of the rift. The deep part of the rift is thought to continuously shift to NNE due to slight relative rotational movement of the eastern, Arabian block (Freund and Zak, 1973). The present configuration of this trough is that of the Dead Sea Basin (Fig. 1) being bounded by steep sided high escarpments in the west and east. The western escarpment is limited to the border of the Dead Sea, disappearing to the N and S. The basin consists of a deep trough in the northern Dead Sea surrounded by shallow sedimentary, narrow shoulders along the escarpments and broad plains near Jericho and Sedom (Southern Dead Sea).

A thick mass of evaporites, shales and conglomerates of the Dead Sea Group, of Plio-Pleistocene to Recent age forms the sedimentary fill of the trough. These sediments are known from the surface and from wells which penetrated to the depth of 3600 m. The total thickness is thought to be up to 8–10 km, as interpreted from geophysical (gravity and seismic) structural and stratigraphic evidence. Part of the sequence within these sediments, a thickness of about 2500 m (Fig. 2) is exposed at the surface in the salt diapir of Mount Sedom and in the pierced, tilted and uplifted beds surrounding it.

Several problems concerning the development of this thick sequence are dealt with herein using bromine as an indicator in the evolution of evaporites and brines, together with other sedimentological and chemical characteristics. These problems include: (a) marine or continental origin of evaporites; (b) range of salinity; (c) tracing of connate salts of paleo-brines and correlation with the evaporite section; (d) order of succession and bottom and top of rocksalt beds; (e) depths of the paleo-

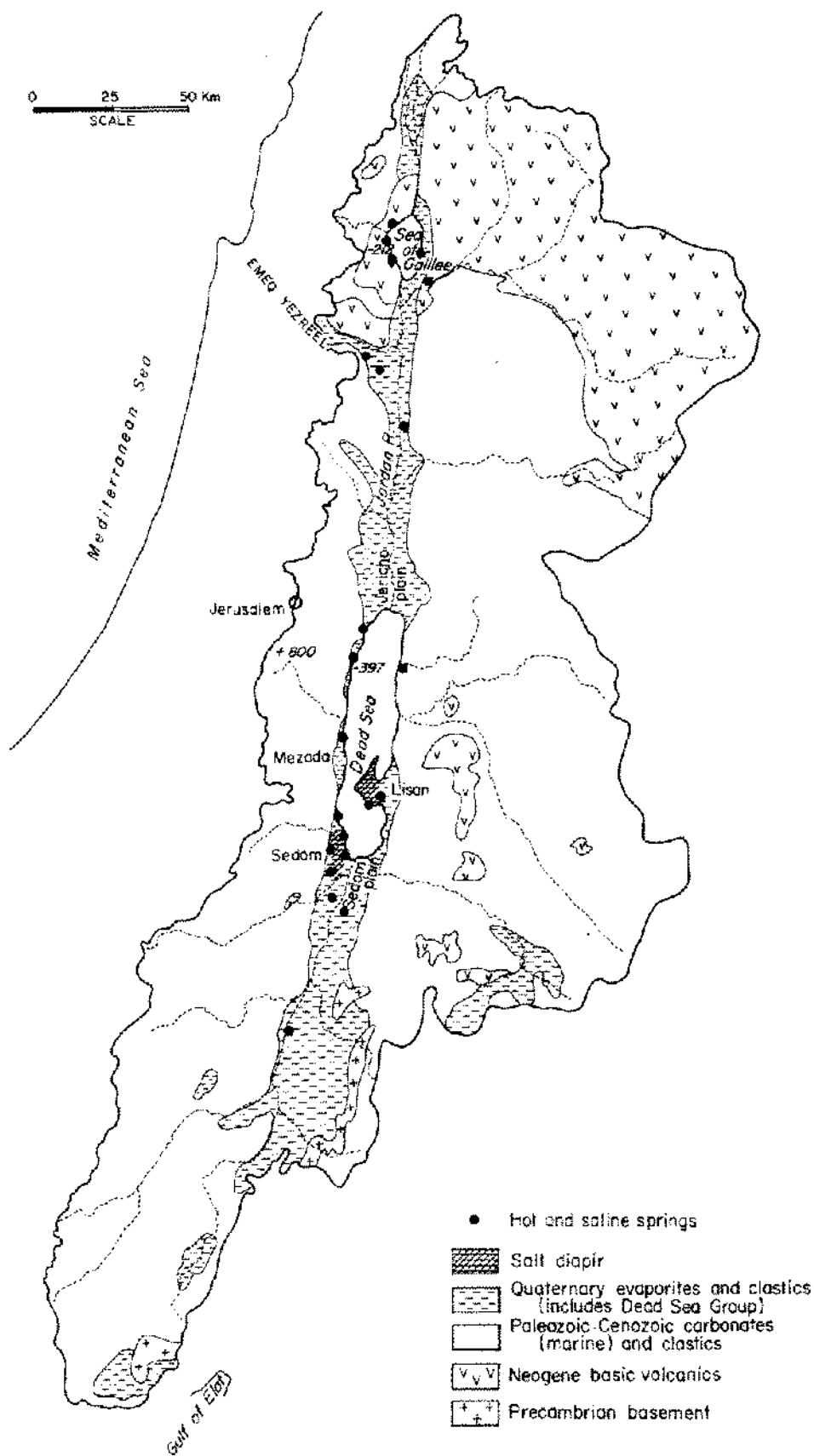


Figure 1. Dead Sea catchment area (after Bentor, 1961).

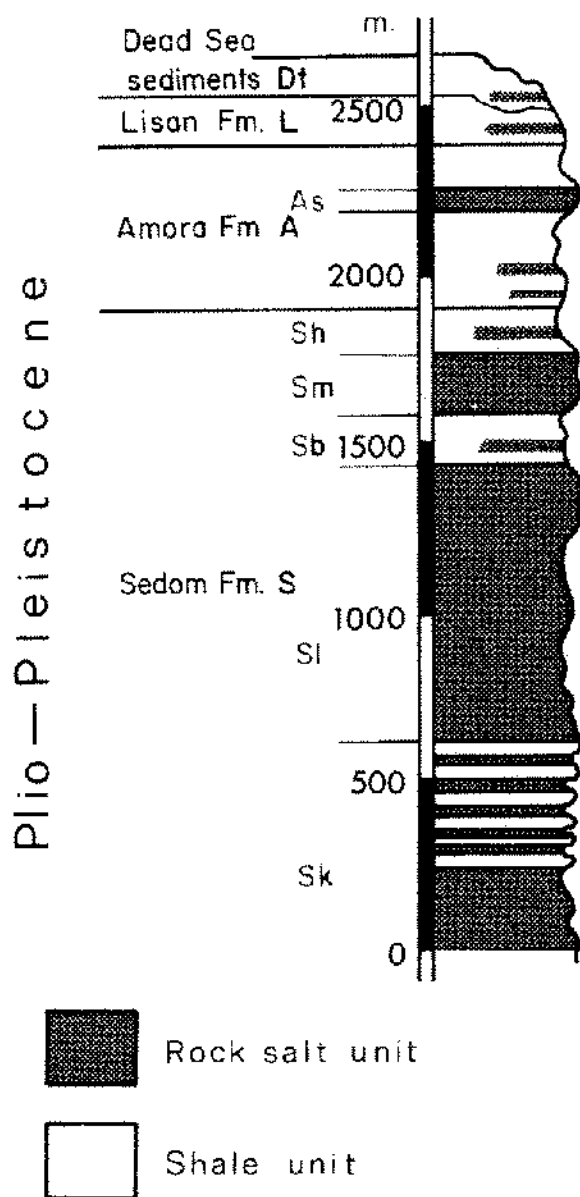


Figure 2. Composite columnar section, Dead Sea Group, Mount Sedom.

water body and configuration of the basin; (f) existence of dessication episodes and potassium salts in the sedimentary fill, and (g) source of salts of the present Dead Sea.

Bromine distribution between chloridic brines and mineral phases has been used in established methods in the study of chloridic evaporite sequences and brines (Boeke, 1908; D'Ans and Kühn, 1940; Bloch and Schnerb, 1953; Baar, 1954; Valyashko, 1956; Braitsch, 1962; Ognieko, 1959; Schwerdtner and Wardlaw, 1963; Wardlaw, 1964; Holser, 1966; Raup, 1966 and others). Bromine ion enters diadochically into solid chlorides. In chlorides crystallizing from sea water or natural brines where the Br/Cl ratio is low, the distribution coefficient of bromine between solid and solution,

$$J = \frac{C_{Br \text{ mineral}}}{C_{Br \text{ solution}}}$$

is constant and  $J < 1$ . In a progressive process of evaporation of natural brine the bromine concentration increases gradually in the residual brine and consequently also in the successively crystallizing chlorides. Therefore, in general, increase and decrease trends of bromine content in rocksalt directly correspond to changes in the mother liquor salinity during deposition of chloride evaporites.

A notable increase of bromine content (in a profile) indicates restriction of inflow of sea water into the basin or even complete isolation. Conversely, decreasing bromine content is suggestive of interruption of progressive salinity in a basin, by brine dilution that probably results from influx of sea water into the basin.

The bromine content as well as Br/Cl ratio in the salt units and shale units of the Dead Sea Group and in natural water sources has been determined and used in clarifying various problems. Results have been compared with primary and secondary sedimentological features.

Analysis of bromine was carried out using the method described by Van der Meulen (1931) and modified by D'Ans and Höfer (1934). The method is based on the oxidation of bromide to bromate by sodium hypochlorite solution. The bromate thus formed is determined iodometrically after the removal of the excess of hypochlorite.

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## DESCRIPTION OF THE DEAD SEA GROUP

The studied section of the Dead Sea Group consists of rocksalt and shale of the Sedom Formation forming the *Sedom salt diapir*, overlain by carbonates, sulfates, shales and some rocksalt of the pierced Amora and the Lisan Formations. Subrecent to Recent carbonates, shales and rocksalt are found in still subsiding areas along the central part of the Dead Sea trough and in peripheral sinks wherefrom salt has been migrating since middle Pleistocene times.

### Sedom formation

This formation consists of alternating salt and shale units reaching an exposed thickness of 1850 m (Table I).

The *salt units*. 20 to 700 m thick each, contain rocksalt beds, 10–60 cm thick, with interlayers of anhydrite, dolomite, clay and silt, 1–10 mm thick. The interlayers occasionally form thicker beds, several meters thick.

TABLE I  
Lithological composition of the Sedom and Amora Formations, Sedom Salt Diapir.

	Sedom Fm %	Amora Fm %
Rock salt	77	8
Carbonates, sulfates	7	59
Clays	9	17
Sands, conglomerates	7	16
	100	100
Total thickness (meters)	1850	410

Composite rocksalt beds are characterized by laminations, mostly 1–5 cm thick (single beds), distinguished by light and dark coloring with parallel variations in dispersed occluded minerals. The beds are occasionally separated by very thin, 0.1–1 mm, anhydrite or clay laminae. Dessication polygons and mudcracks are found in the rocksalt beds and these as well as ripple marks are rarely found in the shaly interlayers. The bedding planes in the rocksalt are mainly tabular, smooth or slightly rumpled.

The salt is a white to gray compact, crystalline aggregate. The halite crystals are mainly anhedral and interlocking, their size usually 1–5 mm. Clear euhedral halite crystals are occasionally found along bedding planes and cubes up to 20 cm and even larger are found along open foliation cracks. These are evidently the result of secondary recrystallization. Impurities are found dispersed within the rocksalt generally forming 1–4% of the total rock mass. These are mainly anhydrite, some dolomite as well as quartz grains, clay, rare flakes of hematite and limonite, apatite and sulfur. Rare zones with traces of dispersed and disseminated sylvite and pockets of carnallite and sylvite are found, usually characterized by pink to reddish colored bands in the rocksalt. Unconformable lenticular pockets of contorted beds of anhydrite and shale, few to tens of meters long, are sometimes found between rocksalt beds close to the occurrence of dispersed sylvite and carnallite.

**The shale units.** These are 10 to 150 m thick each, and contain mudstone, dolomite and clay, silt and sandstone, anhydrite, gypsum and some rocksalt, with rare zones of grit and pebbles of dolomite and chert. Bedding is fine to laminar, 0.1 to 10 mm, and massive, 1–60 cm thick. Mixed or graded bedding is found. Cross bedding, symmetric and asymmetric ripple marks, mudcracks, load and flow structures are found in the mudstone and sandy layers.

Cyclic sedimentary groups are recognized within the shale units being 5–20 m thick and consist of: (a) white and gray sandstone and silt fine to massive bedded, cemented by halite, anhydrite or marl; (b) anhydrite and gypsum, white to gray, fine to massive bedded and silt, clay and dolomite interlayers containing anhydrite and gypsum concretions and veins; (c) red, limonitic sandstone and silt, mostly massive bedded; (d) clayey, dolomitic

mudstone, brown and green, some intergrowth of dolomite with anhydrite, fine to massive bedded; some ripple marks and animal and bird tracks; (e) laminated dolomite and clay containing fish and plant remains, some of freshwater environment, rare birds and insects.

The cycles are quasi-symmetric but mostly incomplete or asymmetric, being better developed in the Sb Shale Member of the Sedom Formation.

The relationship of salt to shale units is also of a cyclic nature, the transition between them being generally gradual with appearance of sulfates, rocksalt and halite cementation, alternating with shales, sandstones and silts.

Sedimentation occurred mainly in an overall hypersaline environment under changing degrees of circulation with the open sea and climatic and seasonal variations, all superimposed on rate of subsidence of the basin. Cycles are thus considered to have been deposited mainly in shallow water with occasional exposure and dessication.

#### Amora formation

The formation consists mainly of marl and chalk, yellow-gray, brown and white, with anhydrite, gypsum, silt, sand, conglomerate and some rocksalt (Table I). The thickness is over 400 m in the exposed uplifted section and much greater (more than two thousand meters?) in wells located in the still subsiding central parts of the Dead Sea basin.

Bedding is mostly laminar but also massive, mainly in the lower and central parts of the section. The laminated sediments consist of aragonite, calcite, dolomite, gypsum, anhydrite, halite, clay, silt, limonite and organic matter, alternating in various bi- or poly-laminated combinations. Sulfur concretions, some having a limonitic-gypseous crust with or without a pyrite core occur in the laminated zones. Small acicular crystals of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  salts are dispersed in the laminated sediments more often in the upper part of the section. The salts also appear in efflorescence on outcrops. Plant remains are rarely found between the laminae. The massive beds (a few cms to several meters thick) are silt, sandstone and conglomerate, often cemented by halite or by gypsum, and anhydrite beds. Occasional massive to thin beds occur, consisting of aggregates of large (up to 10 cm) twinned, clear and smoky white gypsum crystals in part cemented by red-brown limonitic, sandy marl reminiscent of fossil soil.

A rocksalt member (As) up to 10 m thick in outcrop appears in the central part of the section. Salt beds are 0.1 to 0.8 m thick, with interlayers of laminated marl, aragonite, dolomite and anhydrite, a few mm to 10 cm thick. The halite is coarsely crystalline, interlocked, gray to white, with occasional pink bands.

The Amora Formation demonstrates seasonal and cyclic sedimentation in mainly a hypersaline environment. It is partly of a playa type as well as lagoonal, sabkha and

fluvial with occasional influxes of the sea in which case it resembles the environment of the Sedom Formation. Sedimentation is thought to be controlled by climate, seasons and tectonics with short episodes of connection with the sea and development of brines and evaporites of marine origin.

#### Lisan formation

The Lisan Formation consists of chalk, marly chalk, gypsum, rare halite as well as silt, sand and conglomerate closer to the marginal areas of the Dead Sea basin. The thickness is about 40 m in outcrop, outside the active subsiding Dead Sea basin, and thicker in more basinal areas. The section is characterized by alternating white and dark, gray-green laminae, 0.1 to 2 mm thick, occasionally thicker and massively bedded. The white laminae consist mainly of aragonite, and the gray-green laminae contain calcite, aragonite and some clay, quartz and dolomite. Interlayers of laminated and thicker beds of gypsum, calcite, clay and silt as well as halite and dolomite are present. Occasional laminae of organic matter and zones with sulfur concretions are found in the laminated parts. Zones with diatoms are abundant in places (Ehrlich, in: Begin et al., in press) and in others rare fish and plant remains may occur. Tufa and algal calcareous mounds, some having stromatolitic-like structure, a few meters in diameter and height, appear in places, mostly along the marginal areas of the basin. Zones of mudcracks and dessication features are found in places together with laminated and disseminated  $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$  and  $\text{KCl}$  salts, in distinct laminae. Laminated units, 1–200 cm thick, with slump structures are common.

Sediments of the Lisan Formation are found in the Jordan Rift Valley from a height of about -180 m m.s.l., dipping towards the deep trough. The sediments are of an inland hypersaline lake with varying fluvial contributions.

Seasonal and cyclic sedimentation proceeded through the carbonate and sulfate phases continuing in the deeper areas to the halite phase and rarely reaching conditions of dessication. The alternating white and gray-green laminae correspond to dry hot summer and rainy cold winter. The formation is composed of a major by-phase cycle, in which the lower part of the formation contains relatively thicker gray-green laminae while in the upper part the white laminae are thicker. Within this there exists small scale sub-cycles of alternating zones of dominant gray-green and dominant white laminae.

The bi-phase cycle (and to a lesser extent the sub-cycles) is thought to have formed as a result of a major fluvial period, with dilution of the brine in the rising lake, succeeded by a major dry, hot period, with lowering of the water level, and rise in salinity. During the dryer periods playa like conditions were formed with local mar-

ginal areas cut off from the main basin influenced by local fluvial conditions near the mouth of wadis or very dry up to dessication conditions in isolated areas. Along the marginal areas surface and underwater brackish or fresh water springs evolved as a result of the hydrostatic head in the bordering mountains. Tufa and algal calcareous mounds have formed at the outlet of springs (Scholl and Taft, 1964).

#### Subrecent to Recent

At least 70 m of carbonate, clay and sulfate and salt, with bands containing organic matter, some silt, sand and conglomerate accumulated in the still subsiding Dead Sea area. These resemble the Lisan sediments, though are in part unconsolidated (Neev and Emery, 1967). In the southern Dead Sea basin sediments include thick, highly porous beds of halite, consisting of self-supporting cubes, a few mm in size. Halite cubes, up to 10 cm in size, with all six faces having a well developed hopper structure are found scattered in uncompacted highly wet marl. It should be noted that similar but smaller cubes of dolomite pseudomorphs after halite, are found in the lower shale units of Sedom Formation.

### BROMINE PROFILES IN THE DEAD SEA GROUP AND THEIR SEDIMENTOLOGICAL SIGNIFICANCE

#### Bromine in rocksalt

Concentrations of bromine in rocksalt beds of the Dead Sea Group range from 40 to 600 ppm (Table II) and conform to those of marine halite (Valyashko, 1956; Holser, 1966). Ranges and median bromine content in the members and formations are shown in Fig. 3 and Table II, where also general analyses are given. The general trend of bromine concentration is a progressive increase from the base of the Sedom Formation to the Subrecent and Recent sediments. A break in the trend is noted at the top of the Sedom Formation where there is a sudden decrease followed by renewal of the upward trend (Fig. 3). It is of interest to note that apart from geological data the bromine value also indicates that the base of the salt sequence has not been reached. The bromine values throughout are (with only few exceptions) higher than those (30–50 ppm) given by Holser (1966) for the base of a rocksalt sequence of marine origin. The bromine profiles of individual salt units are nearly vertical with irregular variations (Figs. 4, 5). No notable break is seen in profiles in passing from rocksalt of salt units to rocksalt and sand salts of shale units. These profiles are mostly intermediate between regular and irregular types (Holser, 1966). The bromine profile of the Sk Salt Member, of the Sedom Formation (Fig. 4) determined in Sedom 1 well shows bromine values ranging from 80 to 150 ppm, peaks up to 330 ppm (median

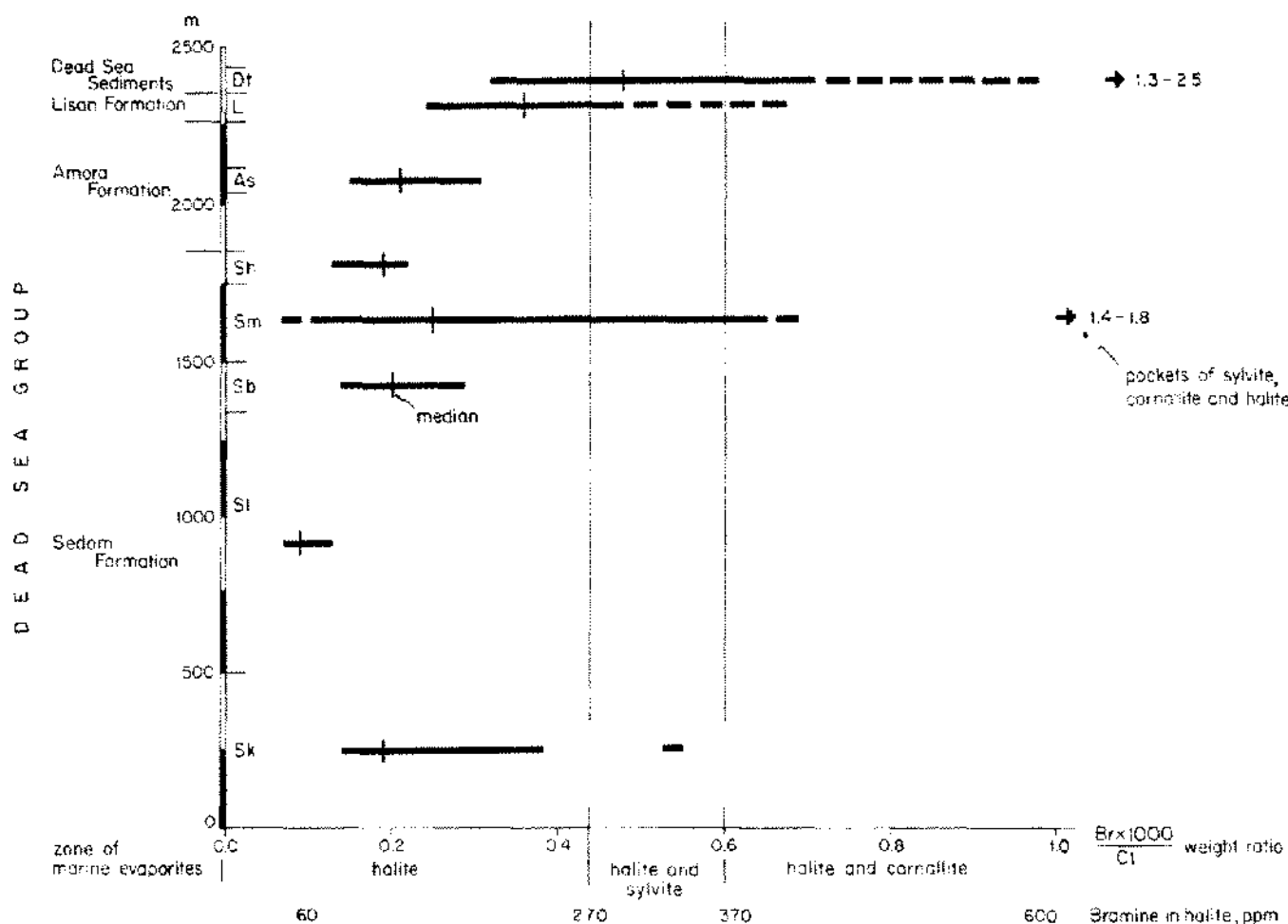


Figure 3. Bromine ratio in rocksalt of the Dead Sea Basin.

content 95 ppm). The bromine values in the Sm Salt Member profile (Fig. 5) are somewhat higher, ranging from 40 to 280 ppm, peaks up to 400 ppm (median content 130 ppm). There is no distinction between bromine values of the sandy salt of the Sb Shale Member and those of the Sm Salt Member (Fig. 5).

Bromine content of sylvite is about 10 times higher than that of paragenetic halite (Braitsch, 1962). Nevertheless, the high bromine values in the rocksalt are not attributed to disseminated sylvite, since the potassium concentration is generally less than 0.5% and rarely exceeds 1-2% (except for pockets of potassium minerals). Furthermore, the higher potassium concentrations are not necessarily correlated with the higher bromine peaks in the profiles. Therefore, bromine contribution by sylvite may be at most up to 10-20% of the bromine present.

The nearly vertical bromine profiles of the salt members indicate a long term relatively fine balance of the system influx-evaporation-reflux (Raup, 1966). Two conspicuous zones of high bromine peaks are suggestive of major approach to dessication.

The first zone in the Sm Salt Member is noted where

peaks in the profile (Fig. 5) probably indicate a rather rapid high increase in salinity as a result of greatly restricted influx of sea water or complete isolation. Returning to a vertical profile in the upper part of the Sedom Formation and in the Amora Formation probably indicates restored influx of sea water into the basin.

The second zone is in the upper part of the Lisan Formation and in Subrecent to Recent sediments (Fig. 3) (see also Neev and Emery, 1967). It probably corresponds to development of arid conditions, and is accentuated in the shallow southern Dead Sea, which is intermittently cut off from the northern, deeper basin.

Bromine content of salt in shale units determined on a halite basis, is in the same range as that in the underlying and overlying salt units (Fig. 5). This indicates that no distinct compositional break occurred in the mother liquor except for dilution.

#### Bromine in diagenesis

Diagenesis in rocksalt involves recrystallization, which in presence of liquid phase brings about redistribution of bromine according to the distribution coefficient, between

TABLE II  
Average chemical composition of salt rocks of the Dead Sea Group (wt %)

Group	Thickness m	Number of Analyses	Water Soluble Salts							Insoluble Residue	Br in Halite, ppm	
			Na	K	Mg	Ca	Cl	Br*	SO <sub>4</sub>		Median	Range
Dead Sea sediments (Dt)	70+	23(19)*	21.6	0.05	0.12	0.53	33.3	0.0160	0.8	—	292	194-594
Lisan Formation (L)	40+	7(4)	12.9	0.13	0.17	0.59	21.8	0.0075	0.7	—	209	146-291
Amora Formation (As)	400+	16(6)	37.7	0.03	0.02	0.18	58.6	0.0113	0.2	2.75	117	92-188
Mezadza SH 1, 2 wells (As?)	300	6	37.1	0.01	0.06	0.37	58.4	0.0159	1.0	1.08	165	139-188
Sh Shale and Salt Member	90	5(2)	37.3	0.02	0.03	0.71	57.8	0.0110	1.7	2.37	115	79-133
Sm Salt Member	250-300	115(105)	36.6	0.57	0.10	0.62	56.6	0.0142	1.4	2.66	152	42-418
Sb Shale Member	150-170	9(3)	36.4	—	—	—	56.1	0.0112	—	3.28	122	85-176
Sl Salt Member	650-1000	19(9)	36.4	0.02	0.02	0.47	56.3	0.0052	1.3	3.46	56	42-79
Lisan 1 well, Sk Member	3500+	2	36.5	0.32	0.11	0.35	59.2	0.0100	0.2	—	103	—
Sedom 1 well, Sk Member	2500+	101(91)	37.6	0.16	0.07	0.52	57.9	0.0098	1.4	1.45	103	85-230

(19)\* Only analyzed for Br, Cl and K or Na. For bromine median content is given.

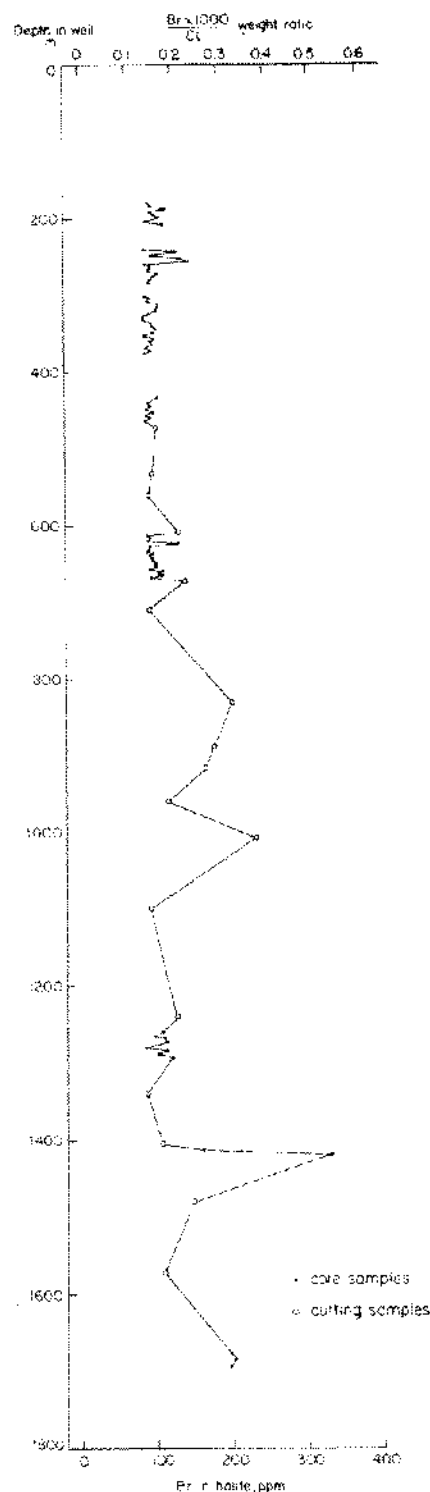


Figure 4. Bromine profile of Sk Salt Member, Sedom Formation, Sedom 1 well.

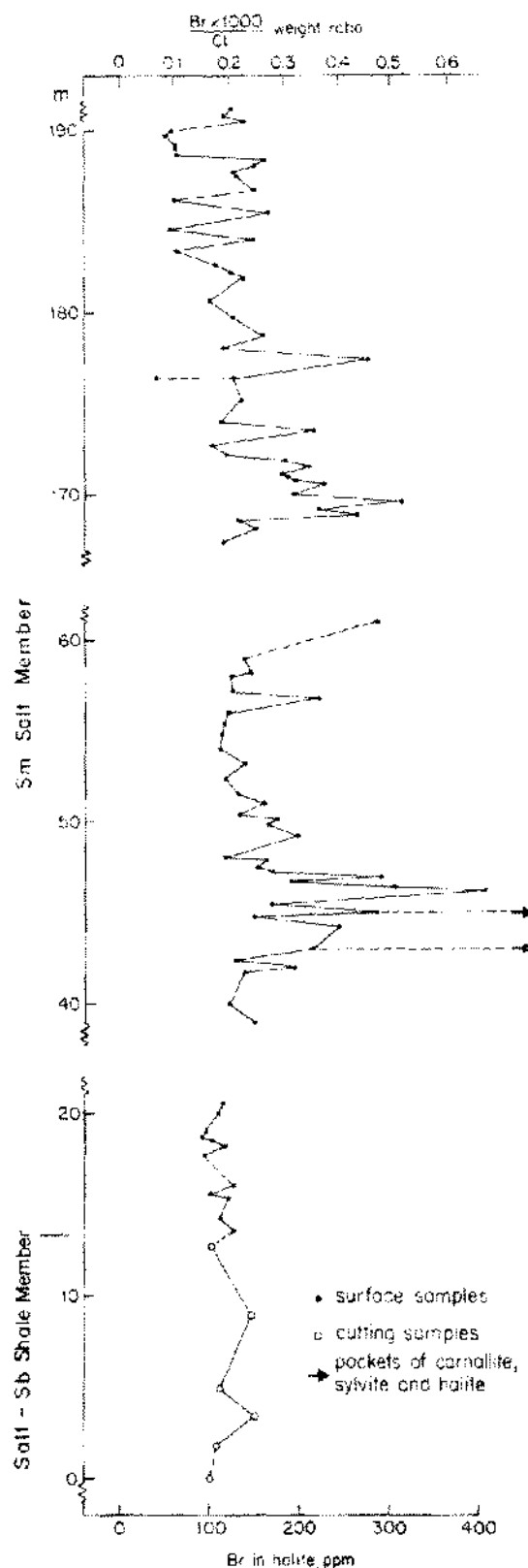


Figure 5. Bromine profile of Sb Shale and Sm Salt Members, Sedom Formation.

halite and solution. Thus, bromine content in recrystallized halite depends on conditions of the system, the relative amounts of solid and liquid phases involved and their bromine pre-concentration. Bromine content in halite will be more affected the more open the system is, for solutions. Whether bromine content in halite will decrease or increase depends on respective bromine content, low or high, in the involved brine.

Deformation and recrystallization is known in rock salt of the Dead Sea Group, but generally bromine content does not seem to have been appreciably affected. It is therefore concluded that recrystallization occurred in a closed system with only a small volume of liquid phase existing (Schwerdtner and Wardlaw, 1963).

Low bromine concentrations indicating diagenesis in an open system, in presence of low bromine solutions, or secondary cycle halite (Holser, 1966) are rare in the Dead Sea Group. However, several phenomena do occur. In some cases bromine values in outcrops are up to 10–30% lower than those in correlatable wells and quarries. This could result from recrystallization at or close to rock surface, with fresh water involved. The lower bromine content in the outcropping Sl Salt Member (Table II and Fig. 3) may be attributed to this fact.

Second cycle halite (Holser, 1966) with low bromine contents, 25–60 ppm, are occasionally found in clear large euhedral halite crystals at the surfaces of open foliation cracks (see Fig. 5, height 176 m). Second cycle halite with a bromine content less than 15 ppm is found in recent stalactites developing in caves and on hanging rock salt walls. On the other hand high bromine contents, 300 ppm and higher, are found in efflorescent salts (see Raup, 1966). Both later phenomena are restricted to karstic features.

#### Bromine in shale

Bromine and chlorine were determined in water soluble salts from carbonates, sulfates and clays of the shale units and interlayers within the salt units. The *bromine ratios*\* are in the range 4.3–19 (Cl/Br 50–230), showing a general trend of rising bromine up the section as is seen with bromine in rock salt. The spread of data within shale is relatively wide and overlap exists between adjacent members and formations (Table III and Fig. 6). The *bromine ratios* are much higher than in adjacent rock salt (0.2–0.6) but comparable to ratios in brines from which these salts should have crystallized. It is therefore assumed that these soluble salts originate from the connate brines from which the adjacent evaporites have precipitated and no important diagenesis or exchange reaction involving the Cl and Br took place at least with regard to laminated carbonate and marly sediments. Further analyses are required to verify this assumption.

\*For the purpose of abbreviation, *bromine ratio* refers to

$$\frac{\text{Br} \times 1000}{\text{Cl}} \text{ weight ratio.}$$



TABLE III

Suggested correlation of  $\frac{\text{Br} \times 1000}{\text{Cl}}$  weight ratios in brines, fresh water and salts.

Evaporation Stage	Dead Sea	Dead Sea and Lisan Sediments	Amora	Sedom	"Normal Marine"
Median for salt units		0.48    0.36	0.24	0.21	
Range for calculated paleo-brines		12-15	6.5- 8.5	5.1-8	
Range for connate salts		8.3-19	5.5-10.5	4.3-8.3	
Springs and other water sources	range 21-27 median 24	9-17 12.5	5.9- 9 7.4	4.1-5.9 5.3	3.3-4.1 3.7

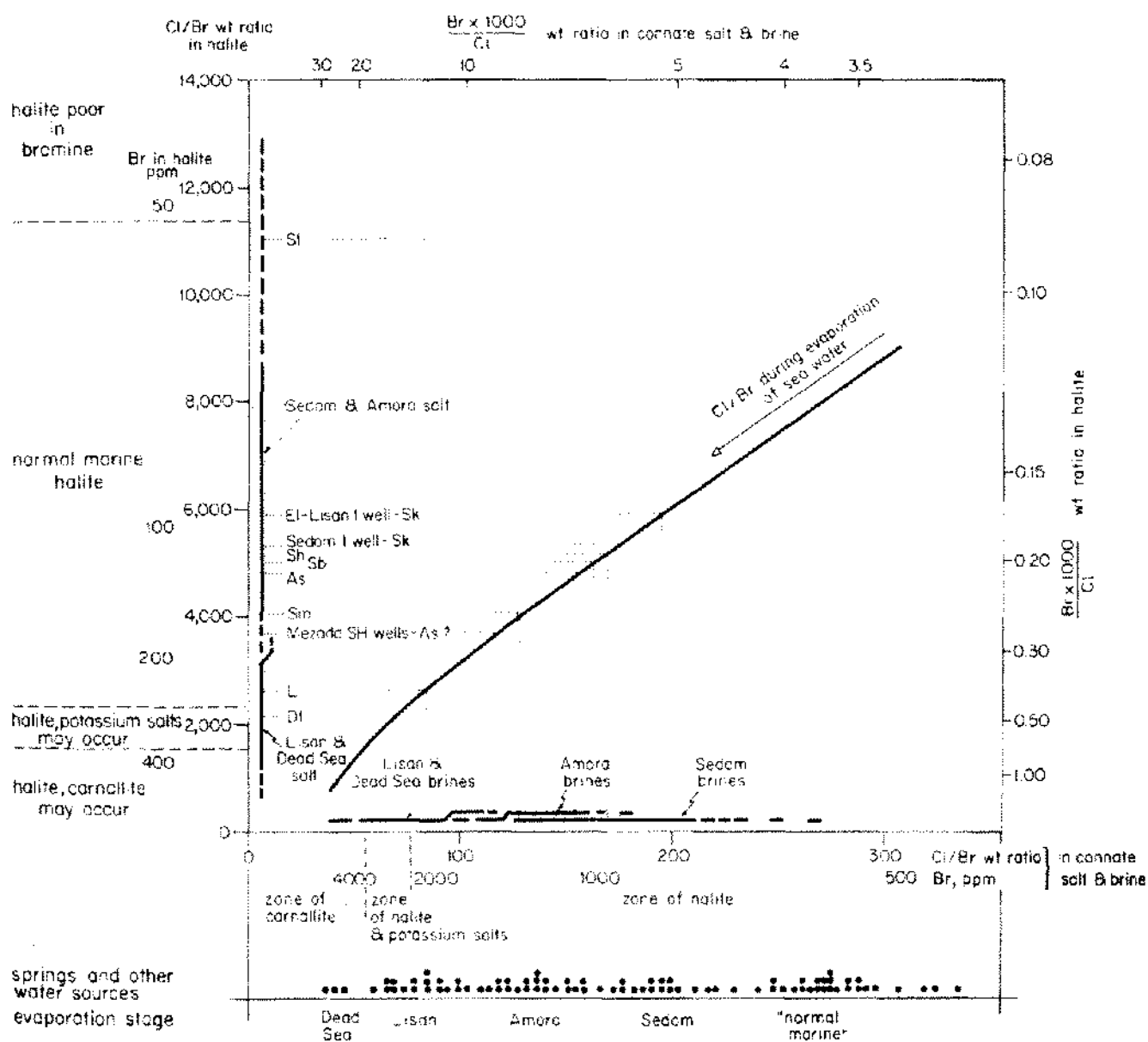


Figure 6. Correlation of bromine weight ratios, in waters and salts of the Dead Sea Basin (diagram modified from Valyashko, 1956).

Fig. 6 shows correlation of bromine content (and *bromine ratio*) in connate salts within shales, with that of rocksalt, as related to the evolutionary path of corresponding brines and related salts of marine origin (Valyashko, 1956).

**Bromine and non-diagenesis.** Diagenesis in the carbonates and shales is generally limited in the Amora and Lisan Formations. This, however, is not the case within the sulfates or shale units in the Sedom Formation, which underwent diagenetic changes to some extent. Non-diagenesis is inferred from the preservation of aragonite laminae alternating with laminae of calcite, some aragonite and clay and of halite, some containing specific concentrations of  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and  $\text{KCl}$  salts. Thus, adjacent laminae occasionally differ considerably in their *bromine ratio*, which in halite is 0.2 - 0.6, in minerals of dessication 1.3 - 2.5, and in connate salts of interstitial mother liquor 4.3 - 19. The conservation of aragonite is considered as indicating that diagenesis has been prevented (Katz et al, in preparation). However, it is not sufficient to show aragonite conservation as indicating non-diagenesis in dealing with an evaporite environment. In such an environment concentration and composition of water soluble salts in the laminae may change, though substitution of aragonite by calcite might be prevented by Mg-rich percolating brines. That this has not taken place is shown by the distinct difference between salt composition of the different laminae.

#### Saline waters

The bromine content was determined in water from springs, wells and brine seepages and the Dead Sea itself (Fig. 1). *Bromine ratios* are in the range 3.3 - 27, grouped around the mode values 3.7, 5.3, 7.4 and 12.5 (Fig. 6). The highest ratios were determined in the density stratified Dead Sea, 21(3380ppm) in the upper mass and up to 27 (4700 ppm) in the lower mass (Bentor, 1961; Neev and Emery, 1967).

In Table III range and median *bromine ratios* for springs and other water sources are given together with ranges for connate salts, and calculated values for paleo-brines (Fig. 6). From this it may be seen that the Br/Cl ratio in springs and other water sources ranges from that of normal sea water, through progressively developing brines from which halite was precipitated, to the Dead Sea brines. No *bromine ratios* indicating halite dissolution are noted in saline waters or connate salts of the Jordan Rift Valley. Thus comparing the *bromine ratios* of saline waters to those of salts (Table III and Fig. 6), a direct correlation is indicated.

### SPECIFIC DEPOSITIONAL PHENOMENA

#### Single and composite rocksalt beds

Bromine content was determined in thin slices (1-2 mm and up to 5 mm thickness) ground parallel to bedding

of rocksalt beds. The rocksalt occurs mainly in *composite beds* and in each *single bed* the bromine content increases upwards (Fig. 7a and b) or remains uniform. No regularity exists in the bromine content of successive *single beds* in the same *composite bed* (Fig. 7c and d).

It is assumed that *single beds* were deposited during a single season, with progressive evaporation and halite crystallization, and consequent increase in bromine content. Each *single bed* corresponds to one influx phase controlled by varying degrees of evaporation. On the other hand, it is assumed that the *composite beds* represent a deposit resulting from several independent influxes of seawater into the basin. This served as a method of determining top and bottom of rocksalt beds in the Sedom salt diapir. The top and bottom relationships were verified by observed indicative sedimentary structures in adjacent shale units (Zak et al, 1968). The increase in bromine content of a *single bed* is only within a narrow range of concentration necessitating repeated, closely spaced, determinations to ascertain the direction of increase.

#### Depth of mother liquor

Kühn (1970, personal communication) analyzed some of the data from *single* and *composite beds* and calculated the depth of mother liquor applying his method. Using an "anhydrite region" factor (Kühn, 1953) shallow depths of the order of few meters were calculated to allow the deposition of salt beds with the aforementioned bromine gradients. This conforms to field evidence which indicates shallow depths with even occasional exposure above water level. Field evidence includes dessication polygons in the salt section and ripple marks, land animal tracks and plant remains in the shales.

Braitsch (1962) proposed particular environmental limitations by which the water depth can be given for stages of bromine concentration. That is only in conditions of purely static evaporation of seawater or the evaporation of fresh or partially concentrated influxes which restore the original sea level without refluxing of concentrated solutions.

Kühn's calculations are confirmed herein by sedimentary structures existing in the Dead Sea Group and since the Dead Sea basin was a long, narrow, shallow gulf, Braitsch's particular environment is also applicable.

#### Potassium salts and dessication phenomena

High bromine peaks in halites of the Dead Sea Group are well within the zone of expected sylvite and also carnallite (Valyashko, 1956; Raup, 1966). Nevertheless only rare occurrences of dispersed sylvite and pockets with sylvite, carnallite and halite were found (Figs. 3 and 5). Bromine content in the pockets (850-1500 ppm) indicates a possible related paragenetic origin for the minerals and the host rocksalt. The accompanying bromine peaks, as expressed in profiles such as Fig. 4 and 5 are narrow and may easily be missed without detailed sampling. However,

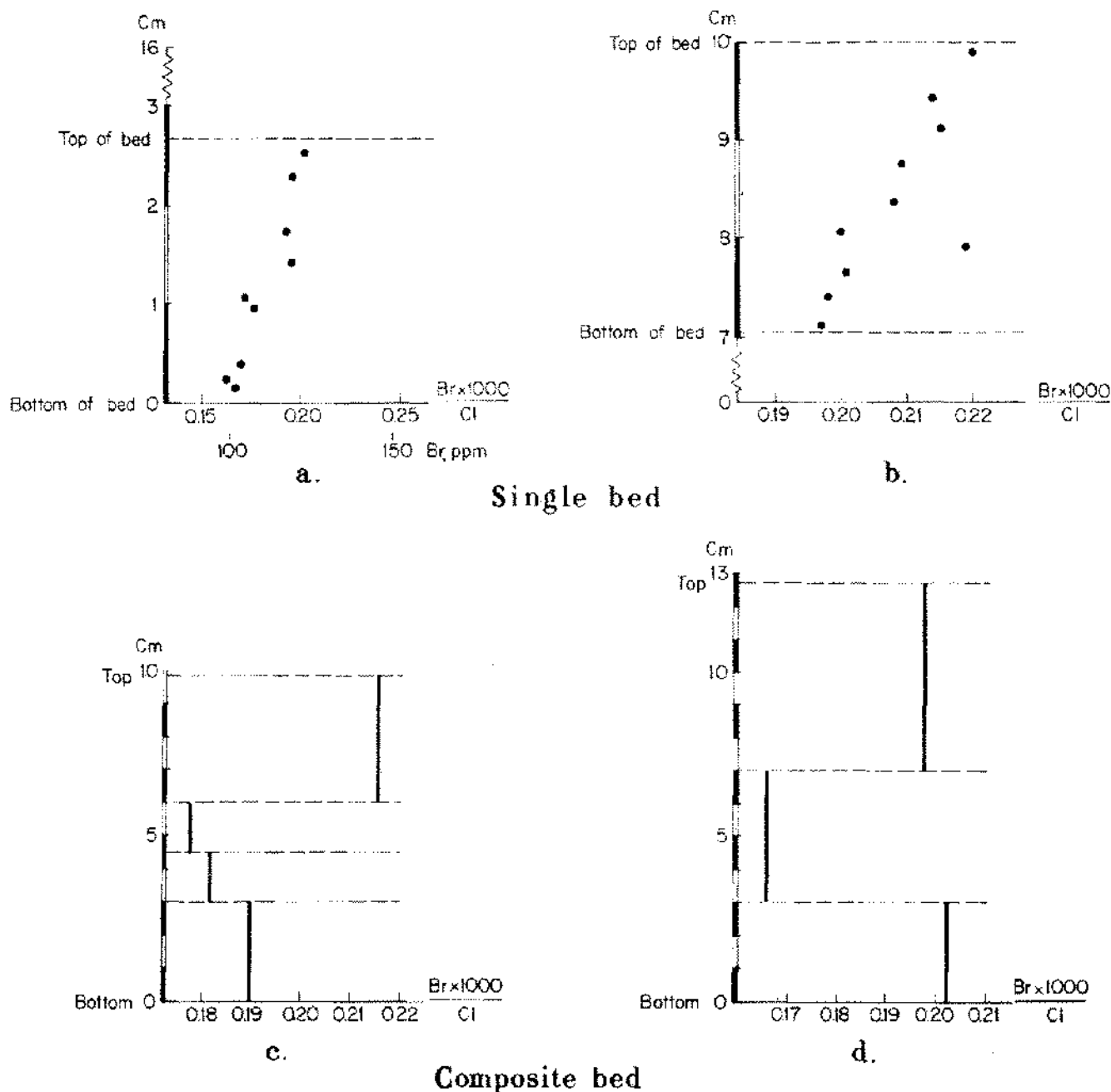


Figure 7. Bromine ratio in composite and single rock salt beds of the Sedom Formation.

several characteristic features mainly related to dessication episodes may be recognized in the halite approaching a high bromine peak and a zone of potassium minerals. These include dessication polygons found in successive beds; residuum such as hematite and limonite flakes and unconformable lenses of contorted beds of anhydrite and clay which are probably residuals of zones which contained highly soluble chloride minerals. Dessication is also probably indicated by the occurrence of  $MgCl_2$ ,  $CaCl_2$ ,  $KCl$  salts, concentrated in distinct laminae.

These dessication features are directly related to the

existence of potassium salts in the Sedom salt diapir. Seepages of brines enriched in K, Mg and Ca chlorides found in the Sedom salt diapir, however, probably indicate solution metamorphism of later salts, including potassium salts, from deep seated zones. It is suspected, therefore, that potassium salts were deposited to a greater extent in the deeper parts of the basin.

### SUMMARY AND CONCLUSIONS

The evaporites in the Sedom Formation and probably in the lower Amora Formation are of marine origin. Later

evaporites were formed in a closed continental basin, with some marine influxes. Much of the thousands of meters of rock salt and shales were deposited in shallow waters and occasionally exposed or underwent progressive dessication. Sedimentation in shallow depth with a high rate of deposition, indicates rapid subsidence.

The bromine content in the rock salt, 40–600 ppm, is within the range of salt of marine origin. Bromine profiles are semi-regular, with occasional high peaks indicating dessication episodes, with a paragenetic association of potassium salts. Bromine profiles of rock salt do not show any distinct break in passing from salt units into shale units. Also bromine in connate salts of supposedly interstitial brines in the shales conforms to that of adjacent rock salt, as expected by its distribution between brine and halite. Rhythmic lamination in the rock salt is considered to be due to seasonal changes in the rate of evaporation of sea water and rate of circulation with the open sea. Slower rate of halite precipitation or increasing rate of shale sedimentation is explained by restriction on influx of sea water into the basin, being balanced, or also induced, by land water, giving rise to cyclic sedimentation.

Bromine content in rock salts indicates marine origin for the chlorides, even in sediments of accepted continental origin. This is explained by the inherited thick sequence of marine chloride sediments with interstitial brines. These, through compaction, diagenesis and metamorphism, serve as the source for an important quantity of recycling chlorides, which contain bromine, of marine like composition. Thus, a more useful way for distinction between marine and closed inland lake would be the mass and ratios of carbonates, sulfates, chlorides and detrital sediments in the basin as compared to provenance lithology in the catchment area on one side and to marine evaporites on the other. Therefore, under conditions such as those of the Dead Sea basin (Fig. 1) a distinction between sediments forming a sea gulf and an inland basin would be mainly by the relative abundance of halite and carbonates respectively. Sulfates though mostly of marine origin nevertheless are in part land derived, from older marine deposits, and therefore are of secondary significance. Shales are of even less significance as they are land derived in both inland lake and sea gulf evaporitic environments.

The occurrence of seasonal laminae enriched in  $\text{CaCl}_2$  salts, which are thought to be products of  $\text{Mg} \rightleftharpoons \text{Ca}$  exchange in calcareous formations (Loewengart, 1962; Loewengart and Zak, in preparation), is considered to be indicative of a closed inland basin environment, entirely cut off from the sea. Similar  $\text{CaCl}_2$  salt occurrences are found in Lower Cretaceous evaporite sequences on both sides of the Atlantic Ocean, in the coastal regions of Sergipe (Brazil) and Congo and Gabon (West Africa) (Wardlaw, 1972).

Potassium salts appear only rarely in the studied sedi-

ments of the Dead Sea Group, though expected on basis of occasional high bromine concentrations. It is suspected that potassium salts were deposited to a greater extent but are restricted to the deeper parts of the basin, as a result of shrinking of the brine level down from the shoulders, during periods of partial dessication. Possible burial of considerable masses of potassium salts in the Dead Sea basin is suspected due to potassium depletion relative to Br and Mg in the Dead Sea mother liquor. This can be explained by solution metamorphism of deep seated carnallite into sylvite. The solutions enriched in  $\text{MgCl}_2$ , KCl and also  $\text{CaCl}_2$  are recycled to the Dead Sea.

## REFERENCES

- Baar, A., 1954. Untersuchungen des Bromgehalts im Zechstein-salz. *Bergbautechnik*, 4:284–288.
- Begin, Z. B., Ehrlich, A. and Nathan, Y., The Lisan Lake, the Pleistocene precursor of the Dead Sea. *Israel Geol. Surv. Bull.* (in press).
- Bentor, Y. K., 1961. Some geochemical aspects of the Dead Sea and the question of its age. *Geochim. Cosmochim. Acta*, 25:239–260.
- Bloch, M. R. and Schnerb, I., 1953. On the  $\text{Cl}^-/\text{Br}^-$  ratio and the distribution of Br-ions in liquids and solids during evaporation of bromide-containing chloride solutions. *Bull. Res. Council Israel*, 3:151–158.
- Boeke, H. E., 1908. Über das Kristallisationsschema der Chloride, Bromide, Iodide von Natrium, Kalium und Magnesium, sowie über das Vorkommen des Broms und das Fehlen von Jod in den Kalisalzlaggestätten. *Z. Krist.*, 45:346–391.
- Braitsch, O., 1962. *Entstehung und Stoffbestand der Salzlagerstätten*. Berlin, Springer-Verlag, 232 pp.
- D'Ans, J. and Höfer, P., 1934. Untersuchungen an Brom. *Z. f. angew. Chemie*, 47:71–74.
- , and Kühn, R., 1940. Über den Bromgehalt von Salzgesteinen der Kalisalzlaggestätten. *Kali*, 34:43–46, 59–64, 77–83.
- Freund, R. and Zak, I., 1973. Migration of folding and faulting along some geological structures in Israel. *Teva Ve'erez* (in Hebrew, in press).
- Holser, W. T., 1966. Bromide geochemistry of salt rocks. *Symp. Salt*, 2nd, Cleveland, Ohio, 1965:248–275.
- Katz, A., Kolodny, Y., Nissenbaum, A. and Zak, I., The geochemistry and stable isotopes of the Lisan Formation, Jordan-Dead Sea Valley (in preparation).
- Kühn, R., 1953. Tiefenberechnung des Zechsteinmeeres nach dem Bromgehalt der Salze. *Z. deut. geol. Ges.*, 105:646–663.
- , 1970. A letter to the author.
- Loewengart, S., 1962. The geochemical evolution of the Dead Sea Basin. *Bull. Res. Council Israel*, 11G:85–96.
- and Zak, I.,  $\text{Ca} \rightleftharpoons \text{Mg}$  exchange between subsurface waters and carbonate sedimentary rocks (in preparation).
- Neev, D., and Emery, K. O., 1967. The Dead Sea: Depositional

- processes and environments of evaporites. *Israel Geol. Surv. Bull.*, 41:147 pp.
- Ogienko, V. S., 1959. Distribution of bromine in the rock salt of the Angara-Lena Salt basin and the possibility of finding potassium salts. *Geochemistry*, 8:893-900.
- Raup, O. B., 1966. Bromine distribution in some halite rocks of the Paradox Member, Hermosa Formation, in Utah. *Symp. Salt*, 2nd, Cleveland, Ohio, 1965:236-247.
- Scholl, D. W. and Taft, W. H., 1964. Algae contributors to the formation of calcareous tufa, Mono Lake, California. *J. Sed. Pet.*, 34:309-319.
- Schwerdtner, W. M. and Wardlaw, N. C., 1963. Geochemistry of bromine in some salt rocks of the Prairie Evaporite Formation of Saskatchewan. *Symp. Salt*, North Ohio Geol. Soc.: 240-246.
- Valyashko, M. G., 1956. Geochemistry of bromine in the processes of salt deposition and the use of the bromine content as a genetic and prospecting criterion. *Geochemistry*, 6:570-589.
- Van der Meulen, J. H., 1931. Bromo-Jodometrische onderzoeken. *Chem. Weekblad*, 28:82-86.
- Wardlaw, N. C., 1964. Bromide in some Middle Devonian salt rocks of Alberta and Saskatchewan. *International Williston Basin Symp.*, 3rd:270-273.
- , 1972. Unusual marine evaporites with salts of calcium and magnesium chloride in Cretaceous basins of Sergipe, Brazil. *Econ. Geol.*, 67:156-168.
- Zak, I., Karcz, I. and Key, C. A., 1968. Significance of some sedimentary structures from Mount Sedom. *Israel J. Earth Sci.*, 17:1-8.