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Data of Geochemistry

Sixth Edition

Chapter Y. Marine Evaporites

GEOLOGICAL SURVEY PROFESSIONAL PAPER 440-Y



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Sixth Edition

MICHAEL FLEISCHER, *Technical Editor*

Chapter Y. Marine Evaporites

By FREDERICK H. STEWART

GEOLOGICAL SURVEY PROFESSIONAL PAPER 440-Y



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DATA OF GEOCHEMISTRY, SIXTH EDITION

Michael Fleischer, *Technical Editor*

The first edition of the Data of Geochemistry, by F. W. Clarke, was published in 1908 as U.S. Geological Survey Bulletin 330. Later editions, also by Clarke, were published in 1911, 1916, 1920, and 1924 as Bulletins 491, 616, 695, and 770. This, the sixth edition, has been written by several scientists in the Geological Survey and in other institutions in the United States and abroad, each preparing a chapter on his special field. The current edition is being published in individual chapters, titles of which are listed below. Chapters already published are indicated by boldface.

- CHAPTER A. The chemical elements
- B. Cosmochemistry
- C. Internal structure and composition of the Earth
- D. Composition of the earth's crust
- E. Chemistry of the atmosphere
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- J. Chemistry of rock-forming minerals
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- L. Phase equilibrium relations of the common rock-forming oxides except water
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- N. Chemistry of igneous rocks
- O. Chemistry of rock weathering and soils
- P. Chemistry of bauxites and laterites
- Q. Chemistry of nickel silicate deposits
- R. Chemistry of manganese oxides
- S. **Chemical composition of sandstones—excluding carbonate and volcanic sands**, by F. J. Pettijohn
- T. **Nondetrital siliceous sediments**, by Earle R. Cressman
- U. Chemical composition of shales and related rocks
- V. Chemistry of carbonate rocks
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- X. Chemistry of phosphorites
- Y. **Marine evaporites**, by Frederick H. Stewart
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- AA. Chemistry of coal
- BB. Chemistry of petroleum, natural gas, and miscellaneous carbonaceous substances
- CC. Chemistry of metamorphic rocks
- DD. Abundance and distribution of the chemical elements and their isotopes
- EE. Geochemistry of ore deposits
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DATA OF GEOCHEMISTRY

MARINE EVAPORITES

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ABSTRACT

Marine evaporites are formed initially by the evaporation of sea water in salt pans, marine salinas, lagoons, and relict seas. At various times from the Cambrian onward, thick and extensive evaporites, together with red beds, shales, carbonate rocks, and other sediments, were deposited in basins and shelf areas partly separated from the ocean by clastic, biogenic, or tectonic bars or sills.

More than 80 mineral species (excluding clastic material) have been recorded in marine evaporites, and most of these are chlorides, sulfates, carbonates, and borates; only about 12 rank as major constituents. Many are of secondary origin.

The major elements are those of sea water—sodium, magnesium, calcium, potassium, chlorine, sulfur, carbon, hydrogen, and oxygen. The processes of primary deposition lead to successive layers that are rich in carbonates of calcium and magnesium, sulfates of calcium, sodium chloride, and finally sodium chloride with salts of potassium and magnesium. Primary lateral variation depends on such factors as distance from the shore line, distance from the ocean connection and from rivers, depth of water, configuration of the depositional floor, rates of subsidence, and thermal currents. Vertical repetition of sequence is related to periodic flooding with sea water or fresh water, changes in temperature, and other features.

Among the minor constituents, strontium, barium, and fluorine are concentrated mainly in the earlier products of deposition; bromine and rubidium are concentrated in the later products; and lithium occurs principally in connate waters and in clays. Many of the minor metals are concentrated in the associated clastic material.

Detailed experimental successions at temperatures between 0°C and 110°C are available, and some work has been done on metastable crystallization and on crystallization from solutions with thermal gradients. Although natural successions agree in a broad way with the experimental data, they do not agree in detail. Some of the anomalies can be explained by primary factors such as the contamination of the sea water by addition of terrestrial material during evaporation, but others can only be explained by secondary changes, of which there is abundant petrographic evidence. Penecontemporaneous changes include (1) reaction of minerals with the brines through which they sink; (2) reaction of early-formed minerals with residual liquids; (3) reaction of minerals with early interstitial liquids; (4) changes due to influx of sea water or terrestrial water; and (5) changes due to variations in temperature. Postconsolidation changes include

(6) the effects of burial, involving recrystallization and flow, as well as widespread metasomatism in response to rise of temperature and pressure; (7) the effects of percolating ground water, involving total or selective solution, and metasomatism; (8) thermal metasomatism related to igneous activity; and (9) changes effected by bacteria.

The secondary changes have frequently resulted in large-scale migration of material. Special mention should be made of the removal of the more soluble materials, particularly $MgCl_2$, and to a lesser extent KCl , during leaching by ground water and during the pressing out of brines formed by geothermal metamorphism.

INTRODUCTION AND ACKNOWLEDGMENTS

This paper is concerned with marine evaporites only; continental lacustrine deposits, borate deposits, nitrates, evaporitic carbonates, and the like are discussed in other chapters of this Professional Paper and are therefore not fully discussed here. The original manuscript was completed in 1958, and the work, therefore, contains only a small amount of subsequent data. The stratigraphic nomenclature used is that of the published sources and does not necessarily conform to that of the U.S. Geological Survey.

I am extremely grateful to members of the U.S. Geological Survey and their reviewers for their most valuable help and encouragement in the preparation of this work. Thanks are also due to my colleagues in Durham and Edinburgh for helpful suggestions and discussion. I gratefully acknowledge a grant awarded by the Durham Colleges in the University of Durham to cover costs of translation.

I thank the following for permission to reproduce figures: the American Journal of Science, for figures 1-4; the Staatlichen Geologischen Kommission, Deutschen Demokratischen Republik, for figures 5-9; the Chemical Society (London), for figure 10; the Geological Society of London, for figure 11; the Yorkshire Geological Society, for figure 13; and the New Mexico Geological Society, for plate 1.

DEPOSITIONAL ENVIRONMENT

Although modern evaporite deposits are thin and cover relatively small areas, a glance at the maps of Krumbein (1951), giving the distribution of the older evaporite deposits of the United States, or those of Lotze (1938, p. 155-157), giving the world distribution of evaporites, shows that these rocks are widespread and fairly common types of sediment. Most of the major evaporite bodies are of marine origin, and such bodies occur in all geological systems from Cambrian to Tertiary.

Evaporites form in areas where water lost by evaporation exceeds or equals that supplied by rainfall, rivers, and the open sea. An arid climate is necessary, but the temperature need not be particularly high; drying winds are the most effective agents to ensure rapid evaporation. Many modern evaporites are forming on the leeward sides of mountain chains which cross the path of the prevailing wind and force it to give up its moisture before it reaches the depositional area. In addition to an arid climate, the other essential condition is partial or complete isolation of the evaporating body of water from the open sea, so that free circulation cannot take place.

Deposition sites of modern marine evaporites, which illustrate various ways in which relative isolation is brought about, are placed by Grabau (1920) in the following categories: marginal salt pans, marine salinas, lagoons, and relict seas. Salt bodies of marine type may also form by the concentration of cyclic salts—salts which have been blown inland with spray by the wind and carried into salt lakes by seasonal floods. Such deposits are relatively thin, but the amount of salt may be considerable. For example, analyses of the air show that 13,000 tons of cyclic salts are carried into the Rajputana States annually (Grabau, 1920, p. 156).

"Marginal salt pans" receive sea water during high tides or storms by overwash. The most spectacular example is the Rann of Cutch in northwest India, where an area of about 7,000 square miles is flooded with sea water in the summer. This water evaporates during the winter and leaves a thin crust of salt that reaches a thickness of several feet in some pools. "Marine salinas" receive sea water by percolation through a continuous permeable barrier. The Lake of Larnaca, on Cyprus (Bellamy, 1900), is the type example cited by Grabau. It has an area of 2.1 square miles and is fed by seepage of sea water through permeable layers in a barrier about 1 mile in width that separates the lake from the Mediterranean Sea. Salt is deposited here in the summer. Gypsum and halite are the common minerals of salt pans and salinas; the highly soluble salts of magnesium and potassium are

more rarely found, as, for example, in salt pans in Tunisia.

The deposits of salt pans and salinas cannot reach any great thickness, but those of "relict seas" and "lagoons" may be much larger bodies. Under arid conditions, an arm of the sea that is completely cut off from the ocean by a clastic or orogenic barrier would deposit its salts. If the cut-off area were large and contained a deep depression, the resulting deposit might be very thick over a relatively small area at and near the deepest part. The Salton Sink in California and the Caspian Sea have been cited as modern examples of relict seas, but these have been modified by the addition of terrestrial salts carried by rivers.

The evaporation of a 1,400-foot column of sea water of normal composition would produce a 1-foot bed of anhydrite. To obtain the enormous thicknesses of anhydrite (often many hundreds and sometimes several thousands of feet thick) found over large areas in many parts of the world, the quantity of sea water required would be far greater than that which could be contained in any completely isolated sea of reasonable size. Many of these deposits retain a considerable thickness almost up to the edge of the depositional area, and there is often evidence that they have formed in subsiding regions in relatively shallow water. In order to explain these thick deposits, Ochsenius (1877), developing an earlier idea of Bischof (1864, p. 48), put forward his "bar theory". This theory assumes a lagoonal area cut off from oceanic circulation by a permanent bar, except for one or more narrow and shallow channels through which sea water can enter, offsetting the losses due to evaporation, and through which there is little or no outflow. As more salt is constantly carried into the lagoon, the salinity will increase until salt deposition begins from dense brines that have sunk to the bottom. As long as salt water can enter the basin and the channels remain shallow enough to prevent escape of the dense bottom brines, this process will continue; and eventually the basin will become filled with salts, covered with a sheet of bittern. If uplift or silting up of the channels leads to complete isolation, evaporation can proceed to its limit, with deposition of the highly soluble salts of potassium and magnesium.

As a modern example, Ochsenius cited the Karaboghaz Gulf, which lies on the eastern side of the Caspian Sea and is separated from it by two narrow sand spits, between which passes a shallow channel as much as a few hundred yards in width. Approximately 130×10^6 tons of salt are carried into the gulf each year, and gypsum, halite, and various sulfates of magnesium and sodium are deposited (Urasov and Polyakov, 1956). This is not strictly a marine evapo-

rite deposit, as the Caspian water owes its composition partly to river-carried material. The deposit of the Great Bitter Lake of Suez (Grabau, 1920, p. 139-142) is apparently a recent example of a marine lagoonal deposit. Before being dissolved by the waters of the Suez Canal, the salts had a maximum thickness of 20 m (average 8 m), and covered an area of about 80 sq km. Alternate layers of clay (often fossiliferous), gypsum, and halite were covered with brines rich in potassium and magnesium, and intermittent connection between the Red Sea and the lake presumably existed for a considerable length of time before the lake was completely isolated.

The ideas of Ochsenius were criticized by Walther (1900, 1903; see Ochsenius, 1902, for a reply and Grabau (1913a, 1913b, 1920). Branson (1915) suggested a modification of the bar theory to include a series of water bodies in restricted connection with each other. According to this modified theory, while gypsum was being deposited in one lagoon, the more concentrated brines would pass into a second lagoon and yield halite. In this way, thick unfossiliferous deposits of gypsum without overlying halite, and of halite free from underlying gypsum, could be explained. Such deposits can, however, be formed in a variety of ways. For example, thick beds of gypsum without halite could be formed if the deeper concentrated brines of a barred basin escaped to the ocean through a permeable barrier, or over a barrier whose top was below average wave base but shallow enough to prevent unrestricted circulation, as suggested for the Castile anhydrite of Permian age of Texas and New Mexico (Adams, 1944; King, 1947). The gypsum and halite of mixed deposits can also become separated by contemporaneous or later leaching of the more soluble chlorides and redeposition elsewhere.

Most geologists accept some modification of the bar theory that involves restricted circulation in a subsiding area of deposition in explanation of thick marine evaporite deposits. Some of the thinner deposits, however, may owe their origin to terrestrial concentration of the connate salts enclosed in the pores of marine sediments. The largest deposits occur in intracratonic basins, but extensive evaporites have also been formed in epicontinental-shelf seas (Krumbein, 1951). Restrictions include clastic bars, biogenic reefs, and tectonic sills. American evaporites have been grouped by Sloss (1953) into "intra-basin" and "basin-margin" types, and further classified on the nature of the restriction. Most deposits fall into the "tectonically-silled intra-basin" group. "Reef-enclosed intra-basinal" types include the late Silurian evaporites of the Salina Formation in the Michigan basin. "Back-reef basin-margin" evaporites include some Leonard and Guada-

lupe deposits of the midcontinental and southwestern regions, and some Devonian deposits of Alberta, Montana, and Saskatchewan. "Topographically-silled basin-margin" evaporites are found in the Jurassic of the Wyoming-Montana regions and in the midcontinental and southwestern Permian. Transitions between these and the gypsum-anhydrite "deposits of stable shelf regions" are associated with brackish or non-marine red beds.

Krumbein (1951) considered the succession and types of sediments associated with evaporites; these are commonly red beds with quartzose sandstone or sub-graywacke sandstone, and marine shales and carbonate rocks. The general succession normal marine-evaporites-normal marine occurs typically in intracratonic basins, as, for example, in the Paleozoic evaporites of the Williston and Michigan basins. The successions red beds-evaporites-normal marine and normal marine-evaporites-red beds, are typically on the shelfward margins of intracratonic basins, but some large basinal deposits pass upward from normal marine through evaporites to red beds; for example, the Ochoa of Texas and New Mexico and the Zechstein of central Europe. The succession red beds-evaporites-red beds occurs typically in shelf regions; the deposits are generally relatively thin, but sometimes cover wide areas. Examples are to be found in the Midcontinental Permian of the United States and in the Keuper of Europe. Occasionally black euxinic shales are associated with evaporites, as in the Paradox basin of Colorado and Utah (Wengerd and Strickland, 1954). Black muds are found with some modern evaporites in conditions of chemical reduction (Morris and Dickey, 1957; Moore and Hayes, 1958; Quaide, 1958).

LATERAL VARIATION

Evaporation of a closed body of sea water should give successive layers rich in carbonates of calcium and perhaps magnesium, sulfates of calcium, chloride of sodium, and finally chlorides and sulfates of magnesium and potassium. In natural deposits, the earlier products are common; but in most cases the brines never reached the concentration necessary for deposition of the later potassium and magnesium salts, or else these were removed by later leaching, so that they are relatively rare.

Rapid lateral variation in thickness and type of salts is a common feature of evaporite bodies. In some regions there is a broad lateral zoning from more to less soluble salts as the shoreline is approached. Figure 11 shows a roughly concentric series of such zones in the Zechstein basin, where the chlorides are confined to the inner parts of the basin, but the less soluble sulfates and carbonates occur also in the marginal parts (for more

detailed zoning in various parts of Germany, see Lotze, 1938, p. 400-503). The marginal changes in England are shown by Hollingworth (1942) and Edwards (1951, fig. 38). Within each evaporite bed, the lateral changes include the passage of evaporites into red beds, of chlorides into sulfates, and of sulfates into carbonates in a shoreward direction; the various types show inter-leaving and merging junctions. There are also lateral changes in the nature of minor constituents, magnesite giving place to dolomite, for example, towards the shore (Stewart, 1954). This type of zoning is probably partly a result of progressive desiccation and shrinkage of the area covered by water, so that the sea had almost dried up when the potassium salts were deposited. However, another important factor may have been a density stratification of the brines in the basin. Such a stratification is found in many modern saline lakes (for example, the Dead Sea), where the heavier and more concentrated brines lie in the deeper parts. It is found to a smaller degree even in ocean waters. As a result, the more soluble minerals such as halite may be deposited in the deeper parts of the basin at the same time as the less soluble carbonates and sulfates are accumulating in the shallower marginal parts or over structural highs (Hollingworth, 1942). The depth of water, configuration of the floor, and relative rates of subsidence in different parts of the area of deposition are obviously important factors causing facies variation in evaporites.

A different type of lateral zoning, involving changes from less to more soluble salts from the seaward connections to the inner parts of depositional areas, is well displayed by the Permian of Texas and New Mexico (fig. 12). Adams (1944) gives sections through the Ochoa evaporites of the Delaware basin, which show very clearly a general change from predominantly carbonate facies near the seaward connection at the southern end of the basin, through anhydritic to halitic facies in the interior of the basin (see also the paleogeographic maps in King, 1942). Even more striking, perhaps, are the facies changes of the back-reef Leonard and Guadalupe evaporites (King, 1942, 1948; Adams and Frenzel, 1950; Newell and others, 1953). Here the back-reef limestones pass shoreward into evaporite dolomite rocks, which in turn pass into anhydritic and then halitic evaporites, and finally into near-shore clastics of fine sand and silt. Lang (1937) discussed these changes and pointed out that rapid evaporation would induce a current of water flowing toward the shore. This water would progressively increase in salinity because of evaporation while it flowed, and it would pass successively through a "vitasaline" stage of reef growth, a "penesaline" stage of carbonate and anhydrite deposition, a "saline" stage of anhydrite, halite, and polyhalite deposition, and a "supersaline"

stage, where the bitter salts would be deposited. Red beds would be laid down in a near-shore zone of brackish water formed by the mingling of concentrated brines and terrestrial drainage water. Clifton (1944) applied the term "pseudomarine" to rocks with a normal marine fauna lying between the evaporites and the brackish water sediments. Sloss (1953) gave the following zonary scheme as a modification of Lang's theory:

Normal marine	Reef zone	Penesaline	Saline	Pseudo-marine	Brackish and terrestrial
Fossiliferous limestone and shale.	Dolomitized biostromal limestone.	Dolomite and anhydrite.	Anhydrite and halite.	Limestone, dolomite, shale.	Red beds.

An interesting study of lateral variation of this type in a modern lagoon, the Boccana de Virrila in Peru, has been made by Morris and Dickey (1957). The lagoon is a relict estuary, connected to the Pacific Ocean, with a length of about 27 km and a maximum width of about 2 km. About 20 km from the mouth, a small sill of shallow sand bars and islands separates an outer penesaline environment from an inner saline environment. In 1955 the water was not more than 2 m deep in the penesaline part, and black muds were found near the shore; white marl covered the floor farther from shore. In the saline part, where the water was not more than 1 foot deep, black muds were found just inside the sill; gypsum was being deposited at the margins of islands and near the head of the lagoon; and halite occurred at the extreme inner margins. Drill cores from near the inner end of the lagoon consisted of impure halite above a series of layers with varying proportions of halite, gypsum, and clastic and organic material, indicating past fluctuations in water level and salinity. Table 1 lists chemical analyses of six water samples. Samples A, B, and C are from the saline part, and D and E are from the penesaline part of the lagoon. The approximate distances from the inner end of the lagoon are as follows: location A, 400 m; location B, 1,000 m; location C, 5,000 m; location D, 6,000 m; location E, 13,000 m. The analyses show the initial increase in concentration of ions in lagoon water over the concentration in normal sea water. It also shows the effects of the successive deposition of carbonates, gypsum, and halite that lead ultimately to a sharp rise in concentration of magnesium, potassium, and sulfate ions in the innermost parts of the lagoon.

Facies changes from less to more soluble salts can be related not only to ocean connections, but also to the mouths of terrestrial drainage channels at the margins of basins. Carbonates and sulfates would tend to accumulate in such places, as most terrestrial waters carry these rather than chlorides, and because the

TABLE 1.—*Chemical analyses of Boccana de Virrila water samples*
[From Morris and Dickey (1957, p. 2470)]

Ion	Normal sea water	Location E surface	Location D surface	Location C surface	Location C bottom	Location B surface	Location A surface
Ion concentration expressed as parts per million of water sample							
K ⁺	380	2,314	2,600	1,426	1,912	6,645	9,962
Na ⁺	10,566	26,110	30,150	40,515	58,550	94,176	67,500
Ca ⁺⁺	400	960	1,040	1,000	1,040	300	300
Mg ⁺⁺	1,272	3,446	4,316	5,580	8,340	22,390	39,612
Cl ⁻	18,980	48,990	57,155	74,195	107,920	190,200	190,200
SO ₄ ⁻²	2,649	6,868	7,828	9,567	13,489	31,216	46,417
HCO ₃	140	175	173	171	245	551	948
Total.....	34,387	88,863	103,282	132,454	191,496	345,478	354,939
Ion concentration expressed as percentage of total solids							
K ⁺	1.1	2.6	2.5	1.1	1.0	1.9	2.8
Na ⁺	30.6	29.4	29.2	30.6	30.6	27.2	19.0
Ca ⁺⁺	1.2	1.1	1.01	0.75	0.54	0.1	0.1
Mg ⁺⁺	3.7	3.9	4.17	4.2	4.4	6.5	11.1
Cl ⁻	55.3	55.1	55.3	56.0	56.3	55.1	53.6
SO ₄ ⁻²	7.7	7.7	7.6	7.2	7.0	9.0	13.1
HCO ₃	0.40	0.20	0.17	0.13	0.13	0.16	0.27
Total.....	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Sp gr.....	1.067	1.077	1.094	1.135	1.227	1.243	
pH.....	7.4	7.6	7.8	6.65	7.3	7.1	
Temp.....°C	23	25	25	27	26	27	

relative freshness of the water in such situations would prohibit the precipitation of more soluble salts. Cunningham (1934) showed that polyhalite and anhydrite are concentrated near the margin of the Salado salt basin, where land masses may have been the source of some of the CaSO₄. Following Scruton (1953), Briggs (1958) considered the theoretical distribution of evaporites in a model basin, using Usiglio's chemical data (1849, p. 92, 172), and applied his conclusions to the Upper Silurian Salina Formation in Michigan and neighboring states. This gave convincing evidence as to the position of original marine and river channels.

Other types of lateral variation, including those dependent on thermal currents, later tectonic activity, and secondary reactions, are mentioned below.

VERTICAL REPETITION

Repetitions of sequence are almost universal. Major repetitions, representing major cycles of flooding and desiccation, are common. For example, table 19 lists four such cycles in the Zechstein of Germany, in which thick evaporite beds are separated by carbonate rocks and clays. Three major cycles have been recognized in England.

Within each major cycle there are generally subsidiary cycles of similar type that show repetitions of parts of the salt succession. The lower evaporite bed of the English succession apparently consists of the products of two partial cycles of desiccation, each containing zones of anhydrite followed by anhydrite and halite. The two potash zones of the third evaporite bed of the German succession indicate two

periods of almost complete desiccation. In many districts the Stassfurt potash zone is formed of alternate halite-rich and potassium-rich layers of moderate thickness (not shown in the table). Many such repetitions are found in the Ochoa evaporites of Texas and New Mexico (pl. 1), which include layers of sulfates and chlorides from several feet to more than a hundred feet in thickness (Adams, 1944; Smith, 1933; Cunningham, 1934; Mansfield and Lang, 1935; Kroenlein, 1939). The cycles often commence with thin layers of clay. Repetitions of this kind bear a resemblance to cyclothems and may be due to rhythmic tectonic changes in level of the restricting barrier between the depositional area and the open sea.

The above types of repetition are commonly accompanied by layering on a small scale, in which the thickness of individual beds can be measured in inches or fractions of an inch. This may have been produced in a variety of ways. Minor fluctuations in level of land and sea, or alternate silting-up and breaching of a bar, would lead to periodic influx of normal sea water. This could produce a kind of layering very common in evaporites, consisting of repeated sequences in each of which a thin layer of clastic material is followed by layers of successively more soluble salts. A similar effect would result from flooding with fresh water from the adjacent land mass, and this might be seasonal.

Periodic winds, blowing clastic material into the water, would produce alternate layers rich and poor in clay, silt, or sand, without a repetition of different salts. The Top Anhydrite of the English Zechstein shows a fine banding of red and white anhydrite (about 10 layers to the inch), in which the red type encloses dust particles that may have this origin (Stewart, 1954).

Seasonal changes in temperature may cause small-scale layering of different salts. In the halite-anhydrite rocks of many deposits, halite layers as much as several centimeters in thickness alternate with anhydrite layers which are generally much thinner. In Germany these are particularly well developed in the older halite of the Upper Zechstein, and they have been called Jahresringe. Their origin has been discussed by many workers (for example, van't Hoff, 1912; Zimmermann, 1913; Rozsa, 1917a; Lotze, 1938; Fiege, 1939; D'Ans, 1947b; Kühn, 1953). Some have interpreted them as seasonal effects dependent on the temperature coefficients of the solubilities of the minerals. At some stages of concentration, anhydrite, being more soluble in cold than in hot water, would be deposited in the summer, whereas halite, which is more soluble in hot than in cold water, would be deposited in the winter. However, some workers believe that the "Jahresringe" have a different origin. Recent

work on the bromine content of the layers in the German mines of Salzdettfurth and Wintershall suggests that periodic dilution of the brines by rain water was the significant factor here (Kühn, 1953).

Seasonal variations in temperature above and below the gypsum-anhydrite transition temperature, combined with differences in temperature coefficients of the solubilities of the minerals, have been invoked by the writer (Stewart, 1953) to explain alternations of anhydrite-magnesite, gypsum, and gypsum-halite rocks in the English Zechstein. The effects are complicated by a certain amount of metasomatism (the original gypsum is represented by anhydrite-halite pseudomorphs) and by superimposed layering due to periodic influxes of fresher water.

Yet another way in which seasonal temperature changes can cause layering has been suggested by Dellwig (1955). The evaporites of the Salina Formation of the Michigan basin show thin alternations of layers of cloudy halite with hopper crystals and layers of clear halite. The cloudy halite is believed to have formed by accumulation of surface-formed hopper crystals on the bottom of the basin. Rise in temperature caused partial solution of these crystals, and fall in temperature led to bottom crystallization of clear salt above the cloudy layer. Seasonal changes led to repetition of the two types of salt. Anhydrite-dolomite laminae in the salt are attributed to influxes of normal sea water, and some alternations of anhydrite and dolomite layers are perhaps seasonal effects dependent on the temperature coefficients of the solubilities of these minerals.

One of the most conspicuously layered evaporite deposits in the world is the Castile Formation of Texas and New Mexico, which consists largely of layered anhydrite-calcite rock. Udden (1924, p. 353) found that the anhydrite laminae had a thickness range from 0.2 to 7.0 mm, with an average of 1.63 mm, in Gresham and McAlpine's core test hole Flood No. 1, Culbertson County, Texas. The laminae of bituminous calcite were about half as thick, or less. Udden believed the layers to represent annual cycles of sedimentation and, on this assumption, gave the figure of 360,000 years for the length of Castile time. King (1947) agreed that the layers are of annual type and suggested seasonal variation in temperature as their cause. Adams (1944) considered that each calcite layer was deposited during a summer, but that the anhydrite layers may have taken longer to form. He invoked alternate breaching and sealing of a barrier as the repetitive factor, each new influx of sea water bringing with it a planktonic fauna which would give rise to the bituminous layers. Lang (1950) ascribed the lamination to annual climatic variation and gave

the following types of seasonal rhythms for the Castile and Salado Formations:

1. Castile $\frac{C, Ca}{C, Ca}, \frac{Ca}{C, Ca}, \frac{A}{C, Ca}, \frac{A}{Ca, A}, \frac{A}{A}$ Summer
Winter
2. Salado $\frac{A}{A}, \frac{A}{M}, \frac{A}{M, G}, \frac{H}{M, G}, \frac{H}{H}, \frac{H}{S}$ Summer
Winter

where C=organic material, Ca=calcite, M=magnesite, G=gypsum, A=anhydrite, H=halite, and S=sylvite. He gave the duration of Castile and Salado times as 500,000 years.

It is apparent from the above discussion that many different factors may be responsible for small-scale repetition in evaporites, and that layering of different types may be superposed in the same deposit. It seems probable that all the suggestions mentioned above could possibly apply in certain cases, and each deposit must be considered individually if its history is to be understood. Where several different origins seem possible on ordinary petrographic evidence, further work on minor and trace constituents in layered series may provide more definite results.

MINERALOGY

The minerals of marine evaporites, excluding those of detrital origin, are listed in table 2. Those marked with an asterisk rank as major constituents.

MAJOR ELEMENTS

Ocean water contains about 34.5 parts per thousand of dissolved salts, of which almost 99.7 percent is made up of only seven types of ions. The relative amounts of these major constituents are given in table 3.

As would be expected from these figures, all the major minerals and many of the minor ones in the above list are chlorides, sulfates, or carbonates of sodium, magnesium, calcium, and potassium. Apart from the carbonates, which are considered elsewhere, apthitalite, $(K,Na)_3Na(SO_4)_2$, is the only one of these minerals

TABLE 2.—*Minerals of marine evaporites*
[Those marked with an asterisk rank as major constituents]

<i>Chlorides:</i>	
Halite*	NaCl
Sylvite*	KCl
Bischofite	MgCl ₂ ·6H ₂ O
Koenenite	Mg ₃ Al ₄ Cl ₈ (OH) ₂₂ ·7H ₂ O
Zirklerite	Basic chloride of Al and Fe ⁺² , with minor Ca and Mg.
Chlorocalcite (=hydrophilite).	KCaCl ₃
Carnallite*	KMgCl ₃ ·6H ₂ O
Tachyhydrite	CaMg ₂ Cl ₆ ·12H ₂ O
Douglasite	K ₂ FeCl ₄ ·2H ₂ O?
Erythrosiderite	K ₂ FeCl ₄ ·H ₂ O
Rinneite	NaK ₃ FeCl ₆
<i>Fluorides:</i>	
Fluorite	CaF ₂
Sellaite	MgF ₂

TABLE 2.—Minerals of marine evaporites—Continued
Sulfates:

Aphthitalite (glaserite).....	(K, Na) ₃ Na(SO ₄) ₂
Thenardite.....	Na ₂ SO ₄
Barite.....	BaSO ₄
Celestite.....	SrSO ₄
Anhydrite*.....	CaSO ₄
Vanthoffite.....	Na ₆ Mg(SO ₄) ₄
Glauberite.....	Na ₂ Ca(SO ₄) ₂
Langbeinite*.....	K ₂ Mg ₂ (SO ₄) ₃
Mirabilite.....	Na ₂ SO ₄ ·10H ₂ O
Syngenite.....	K ₂ Ca(SO ₄) ₂ ·H ₂ O
Loewite.....	Na ₄ Mg ₂ (SO ₄) ₄ ·5H ₂ O
Blödite (Astrakanite).....	Na ₂ Mg(SO ₄) ₂ ·4H ₂ O
Leonite.....	K ₂ Mg(SO ₄) ₂ ·4H ₂ O
Pieromerite (Schoenite).....	K ₂ Mg(SO ₄) ₂ ·6H ₂ O
Polyhalite*.....	K ₂ Ca ₂ Mg(SO ₄) ₄ ·2H ₂ O
Görgeyite.....	K ₂ Ca ₃ (SO ₄) ₄ ·H ₂ O
Bassanite.....	2CaSO ₄ ·H ₂ O
Kieserite*.....	MgSO ₄ ·H ₂ O
Sanderite.....	MgSO ₄ ·2H ₂ O
Gypsum*.....	CaSO ₄ ·2H ₂ O
Starkeyite (Leonhardtite).....	MgSO ₄ ·4H ₂ O
Pentahydrate (Allenite).....	MgSO ₄ ·5H ₂ O
Hexahydrate.....	MgSO ₄ ·6H ₂ O
Epsomite (Reichardtite).....	MgSO ₄ ·7H ₂ O
Kainite*.....	KMg(SO ₄)Cl·3H ₂ O
Anhydrokainite.....	KMg(SO ₄)Cl
D'Ansite.....	MgNa ₂₁ (Cl ₃ SO ₄)(SO ₄) ₄

Carbonates:

Calcite*.....	CaCO ₃
Magnesite*.....	MgCO ₃
Siderite.....	FeCO ₃
Aragonite.....	CaCO ₃
Strontianite.....	SrCO ₃
Dolomite*.....	CaMg(CO ₃) ₂
Ankerite.....	Ca(Fe, Mg)(CO ₃) ₂

Borates:

Pinnoite.....	Mg(BO ₂) ₂ ·3H ₂ O
Kurgantaite.....	(Sr, Ca) ₂ B ₄ O ₈ ·H ₂ O
Priceite (Pandermite).....	Ca ₄ B ₁₀ O ₁₉ ·7H ₂ O
Ulexite.....	Na ₂ CaB ₅ O ₉ ·8H ₂ O
p-Veatchite.....	SrB ₅ O ₁₀ ·2H ₂ O
Colemanite.....	Ca ₂ B ₆ O ₁₁ ·5H ₂ O
Hydroboracite.....	CaMgB ₆ O ₁₁ ·6H ₂ O
Inderborite.....	CaMgB ₆ O ₁₁ ·11H ₂ O
Inyoite.....	Ca ₂ B ₆ O ₁₁ ·13H ₂ O
Kurnakovite.....	Mg ₂ B ₆ O ₁₁ ·15H ₂ O
Inderite.....	Mg ₂ B ₆ O ₁₁ ·15H ₂ O
Howlite.....	Ca ₂ SiB ₅ O ₉ (OH) ₅
Paternoite.....	Mg ₂ B ₆ O ₁₃ ·4H ₂ O
Ginorite.....	Ca ₂ B ₁₄ O ₂₃ ·8H ₂ O
(Cryptomorphite).	
Kaliborite.....	KMg ₂ B ₁₁ O ₁₉ ·9H ₂ O
Volkovite.....	Hydrous borate of Sr and K
Ivanovite.....	Hydrous chloroborate of Ca (and K?).

Szaibelyite (Ascharite).....	(Mg)(BO ₂)(OH)
Boracite.....	Mg ₅ B ₇ O ₁₃ Cl
Ericaite.....	(Fe, Mg, Mn) ₃ B ₇ O ₁₃ Cl
Hilgardite.....	Ca ₈ (B ₆ O ₁₁) ₃ Cl ₄ ·4H ₂ O
Parahilgardite.....	Ca ₈ (B ₆ O ₁₁) ₃ Cl ₄ ·4H ₂ O
Strontiohilgardite.....	(Ca, Sr) ₂ [B ₆ O ₈ (OH) ₂ Cl]
Heidornite.....	Na ₂ Ca ₃ Cl(SO ₄) ₂ ·B ₂ O ₃ (OH) ₂
Lueneburgite.....	Mg ₃ B ₂ (OH) ₆ (PO ₄) ₂
Sulphoborite.....	Mg ₆ H ₄ (BO ₃) ₄ (SO ₄) ₂ ·7H ₂ O
Danburite.....	CaSi ₂ B ₂ O ₈

Elements, sulfides, oxides, silicates, phosphates:

Sulfur, pyrite, hauerite, hematite, goethite (limonite), magnetite, quartz, opal, talc, illite, kaolinite, goyazite.	
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TABLE 3.—Major dissolved constituents of sea water as weight percentages of dissolved material

[Based on Sverdrup, Johnson, and Fleming (1942, p. 166)]

Na ⁺	30.61	Cl ⁻	55.04
Mg ²⁺	3.69	SO ₄ ²⁻	7.68
Ca ²⁺	1.16	HCO ₃ ⁻41
K ⁺	1.10		

that shows any considerable variation in chemical composition. This mineral occurs in four different types of environment; marine evaporites, continental evaporites, phosphate deposits, and as an encrustation in volcanic fumaroles. The chemical composition varies with the mode of occurrence. The ammonium ion substitutes for potassium in apthitalite from a phosphate deposit (Fron del, 1950), and small amounts of lead and copper are present in some fumarolic apthitalites (for example, see Zambonini, 1921). In the apthitalites of evaporite deposits, the K₂O:Na₂O ratio is about 4 or 5:1 (Bucking, 1889; Fahey, in Wells, 1937; Foshag, 1920), whereas in those of volcanic origin, it is much more variable and may reach about 1:1. This is in accordance with experimental work in which crystals grown from aqueous solution are limited to between 71 and 75 mol. percent K₂SO₄ at 25°C (Druzhinin, 1938); in the dry system Na₂SO₄-K₂SO₄, a much wider range in composition is possible—between 44 and 75 mol. percent K₂SO₄ below 470°C, and any proportions of the end members above this temperature (Nacken, 1907, 1910; Perrier and Bellanca, 1940; Bellanca, 1942).

A small amount of potassium is sometimes found replacing sodium in blödite, Na₂Mg(SO₄)₂·4H₂O (0.43 percent K₂O in blödite from Kalusz, Galicia, Koechlin, 1902), but the other potassium and sodium minerals of marine evaporites show partially no substitution involving these two elements. This is presumably because the relatively rigid crystal structures at fairly low temperatures of formation prevent replacements that involve such differences in ionic size (Rankama and Sahama, 1950, p. 435).

MINOR ELEMENTS

Of the other 45 or so elements whose concentration in sea water is known, those that form definite compounds in marine evaporites are listed in table 4. Some of the silicon, aluminum, and iron in these minerals certainly has been derived from clay impurities during secondary reactions.

The remaining elements—even including bromine, which is fourth in order of abundance among the anions in sea water (0.19 percent of dissolved constituents)—occur as minor and trace constituents in various salts, except in very special circumstances (such as the formation of galena and sphalerite in evaporites modified by hydrothermal solutions). The distribution of these minor and trace elements in evaporite rocks and minerals is considered later, and only some data that bear on the color of evaporite minerals are given here.

COLOR OF EVAPORITE MINERALS

A remarkable amount of work has been done on the cause of various colors in evaporite minerals, especially

TABLE 4.—Minor elements that form definite compounds in marine evaporites

[Weight percents from Harvey (1955) and Richards (1957)]

Element	Weight percent of dissolved constituents in sea water	Minerals
Sr-----	0.03	Celestite, heidornite, strontianite, p-veatchite, strontiohilgardite, goyazite.
B-----	.01	Many borates.
Si-----	.008	Clay minerals, danburite, howlite, opal, quartz, talc.
F-----	.004	Fluorite, sellaite.
Al-----	.0004	Clay minerals, koeneneite, zirklerite, goyazite.
Ba-----	.0002	Barite.
P-----	.0002	Lueneburgite, goyazite.
Fe-----	.00001	Ankerite, douglasite, ericaite, erythro-siderite, hematite, limonite, magnetite, pyrite, rinneite, siderite, zirklerite.
Mn-----	.000009	Hauerite.

halite, in relation to trace element distribution, and this has been discussed in detailed by Przibram (1953, 1956), one of the chief workers in this field. Many colors can be clearly related to colored inclusions, such as the red and brown hematite inclusions in sylvite and other salts, the gray color imparted by clay inclusions, and the brown and black colors produced by inclusions of carbonaceous material. Some yellow salts, such as tachyhydrite, owe their color to small quantities of FeCl_3 .

Some colors, however, cannot be so readily explained and interest has centered especially on blue and violet halite which occurs fairly commonly in association with sylvite and can often be shown to be of secondary origin. The halite grains are often only partially colored, and the color may occur in zones related to crystallographic planes, or may be patchy and irregular. The associated sylvite is normally red or white. Many suggestions have been made as to the cause of this coloration, and include the presence of traces of gold (Friend and Allchin, 1940), sulfur (Prinz, 1908), and colloidal sodium metal (Siedentopf, 1905). It now seems probable that the blue, violet, and some yellow colorations are due to radiation from occluded radioactive elements, such as K^{40} , U, Th, and Po (Wieninger, 1950; Przibram, 1956; Thomson and Wardle, 1954). In the blue salt there are color centers of colloidal metal.

Determinations of the abundance of radiation sources show that enough energy would have been available in the time since the formation of the salts to produce the effects observed.

There seems to be a definite relation between helium content and color ($\text{He}_{\text{blue}} > \text{He}_{\text{yellow}} > \text{He}_{\text{violet}}$), and Thomson and Wardle (1954) found more helium than can be accounted for by radioactive disintegration of

the uranium and thorium present in the rock. They suggest that some of the helium may be derived from inclusions of brine trapped in the salts during their formation, and that some may have resulted from the inclusion of a lead isotope, radium D (as suggested by Hahn, 1934), during the crystallization of secondary salts from "natural deep" brines rich in radium and radium D (Born, 1934; Hahn and Born, 1935).

To explain why some salt is colored, whereas neighboring salts with just as high a helium content is uncolored, it is necessary to invoke some second factor such as a sensitization of the mineral by some other impurity. Our knowledge of the impurities in halite is not yet sufficient to identify any specific sensitizer,

TABLE 5.—Weight percentages of some trace elements of halite

	Weight percent	Source of data
U-----	1.7×10^{-8}	Thomson and Wardle, 1954
Th-----	$< 2 \times 10^{-7}$	Thomson and Wardle, 1954
U-----	5×10^{-8}	Kemény, 1941
Ra-----	3×10^{-14}	Kemény, 1941
K ¹ -----	0.02–0.5 (avg 0.15)	Aprodiv, 1945; Przibram, 1956; Thomson and Wardle, 1954.

¹ In colored halite.

TABLE 6.—Helium in halite

Color	Number of samples	10 ⁻⁷ cm ³ /g		Source of data
		Range	Average	
White-----	4	0.1–1	0.4	Paneth and Peters (1928).
Blue-----	3	1–7	4	Paneth and Peters (1928).
Violet-----	6	.26–1.0	.67	Thomson and Wardle (1954).
Yellow-----	7	4.0–21.5	8.08	Thomson and Wardle (1954).
Blue-----	3	12.4–15.0	15.9	Thomson and Wardle (1954).
Various-----	8	.55–1.8	1.1	Karlik and Kropf-Duschek (1950).

TABLE 7.—Impurities in halite from Wintershall, Germany (weight percent)

[After Thomson and Wardle, 1954, p. 177]

	Yellow	Violet	Blue
Ag-----	¹ 0.001	¹ 0.0001	-----
Al-----	Trace	Trace	Trace
Ca-----	.001	.001	≈ 1.0
Cu-----	.00005	.02	.0001
Fe-----	.0005	.0002	.002
K-----	.05	.03	≈ .50
Mg-----	.005	.002	> .1
Mn-----	.0002	¹ .0001	-----
Ni-----	¹ .0001	.0001	.0002
Pb-----	¹ .0001	-----	.0001
Rb-----	-----	-----	.0005
Si-----	Trace	-----	.002
Sr-----	-----	-----	.02

¹ Upper limit.

although Thomson and Wardle and others have obtained a certain amount of relevant data in spectrographic analyses (tables 5-7).

It is doubtful whether irradiation colors have been found in natural sylvite. Violet langbeinite may owe its color to inclusions of NaCl. Irradiation may be the cause of the color in lilac kainite, violet anhydrite, and blue celestite (Przibram, 1956).

MODE OF OCCURRENCE OF EVAPORITE MINERALS

CARBONATES

The carbonates are dealt with in Chapter V. However, the list of carbonates of marine evaporites is very small in comparison with that of terrestrial evaporites. Calcite, magnesite, and dolomite are the chief carbonates of marine evaporites. Calcite and dolomite occur in greatest abundance in the lower parts of evaporite successions and in the marginal parts of depositional areas or over structural highs. Magnesite occurs most commonly in regions that contain potassium salts, but it is not restricted to the potassium-rich layers (Schaller and Henderson, 1932; Stewart, 1954). Aragonite, strontianite, ankerite, and siderite are scarce constituents; these occur in the caprock or insoluble residues of some Gulf Coast salt domes and in a few other deposits.

BORATES

These are also discussed in chapter Z. Boracite is the only borate of relatively common occurrence in marine evaporites. Its iron-bearing analog ericaite (with as much as 6.71 percent magnesium and 2.32 percent manganese substituting for iron) has been recorded from the Zechstein deposits of Germany (Heide, 1955; Kühn and Schaacke, 1955). The following also occur in the European Zechstein evaporites: pinnoite, p-veatchite, hydroboracite, kaliborite, szai-belyite, strontiohilgardite, lueneburgite, sulphoborite, danburite, and heidornite. Lueneburgite occurs in the Ochoa evaporites of Texas and New Mexico. These are mainly magnesium borates, and most of them are associated with chlorides. In the bedded gypsum-anhydrite deposits of Nova Scotia and New Brunswick, also presumably of marine origin, the assemblage is quite different and includes several calcium borates more commonly found in terrestrial deposits—ulexite, inyoite, howlite, danburite, and ginorite (How, 1857, 1861, 1877; Hey and Bannister, 1952). The deposits of Inder in Kazakhstan (Boldyreva, 1936; Godlevsky, 1937; Yarzhemskii, 1945, 1952, 1953; Nikolaev, 1946, 1947) in the gypsum caprock of a Lower Permian salt dome and in associated salt beds, include a large assemblage of magnesium and calcium borates—priceite, ulexite, colemanite, hydroboracite,

inderborite, inyoite, kurnakovite, inderite, kaliborite, szai-belyite, ivanovite, kurgantaite, and volkovite.

SULFATES

Gypsum and anhydrite are by far the most abundant and commonly form massive beds overlying the main carbonate zones. The present distribution of these two minerals is largely secondary and bears a close relationship to their depth of burial. Gypsum is predominant in near-surface deposits, and anhydrite is predominant in deeply buried deposits. The primary distribution depends on the temperature and salinity of the brines during deposition; anhydrite is deposited at higher salt concentrations and at higher temperatures than gypsum, assuming conditions of thermodynamic equilibrium. Anhydrite therefore tends to overlie gypsum in a primary sequence. The main calcium sulfates of halite and potassium deposits are normally anhydrite and polyhalite.

Polyhalite is the third most abundant sulfate, and in a primary sequence, assuming equilibrium conditions, it should accompany halite above the halite-anhydrite zone. It is found in notable quantity in such a position in some deposits; for example, below the Stassfurt potassium beds of Germany. Polyhalite of secondary origin has replaced anhydrite in large quantity in the Salado Formation of Texas and New Mexico (Schaller and Henderson, 1932; Cunningham, 1934; Mansfield and Lang, 1935). It also forms exceptionally thick deposits with anhydrite and halite in the Lower Evaporites of the English Zechstein, where much of it is again secondary (Stewart, 1949; Armstrong and others, 1951; Raymond, 1953). It is an important constituent of some Russian salt deposits (Kurnakov, Bokii, and Lepeshkov, 1937; Buyalov and Lepeshkov, 1937; Lepeshkov and Bodaleva, 1940) and occurs as an accessory mineral in many other evaporite bodies.

Langbeinite and kainite occasionally reach the status of major constituents of potassium deposits. Langbeinite is mined in New Mexico, where it occurs with halite and sylvite, and in Germany, where it is associated with carnallite and other minerals. It is at least partly secondary, forming where halite-sylvite rocks have been altered by percolating brines (Borchert, 1940; Borchert and Baier, 1953), but Dunlap (1951) has suggested a primary origin for langbeinite and other potassium salts of New Mexico. Kainite, also mined in Germany, occurs largely as a secondary mineral formed during the leaching of potassium beds by meteoric waters. In New Mexico it is a fairly scarce accessory that partly replaces langbeinite and sylvite (Schaller and Henderson, 1932).

Kieserite is the only magnesium sulfate that occurs in noteworthy quantity in marine evaporites. It is a major constituent of many potassium deposits, where

it is commonly associated with halite and sylvite in the rock called hartsalz. It is also a fairly common accessory mineral in the upper parts of some halite zones below potassium deposits.

The other sulfates are relatively scarce local or minor constituents. Celestite is fairly common as a minor accessory in gypsum and anhydrite deposits, where it may be partly primary. It occurs in greater quantity as secondary masses replacing sulfates. Barite has seldom been found in marine evaporites, but has been recorded from anhydrite deposits (Wetzel, 1938) and salt domes (Hawkins, 1918; Taylor, 1937). Dunham and Purdon (1946; see also Dunham, 1948) suggested that a Middle Devonian barite-pyrite-sphalerite deposit at Meggen, Westphalia, is an evaporite deposit that owes its peculiar composition to the addition, in the basin of deposition, of barium, iron, and zinc from hydrothermal springs. Glauberite is one of the more abundant of the rarer minerals of marine evaporites. It occurs with anhydrite in many deposits, rarely in masses up to several meters in thickness (for example, Hallstadt, Austria), and forms crystals enclosed in halite, often associated with polyhalite, in the upper parts of some halite zones. Glauberite is often of secondary origin, replacing halite, polyhalite, and anhydrite. Görgeyite (Mayrhofer, 1953) is associated with glauberite, halite, polyhalite, and anhydrite in a crush band in salt at Ischl, Austria. It is identical with mikheevite (Nefedov *in* Mokievsky, 1953; Meixner, 1955) recorded from Russian salt deposits. Mirabilite is very scarce in marine evaporites, but occurs in gypsum in Nova Scotia and in Westmorland, England, where it is probably secondary. It also occurs in salt deposits in Austria and Poland and is deposited on rocks along the shore in cold regions such as Antarctica. Thenardite is properly a mineral of continental evaporites and is extremely scarce in those of marine origin. Bassanite ("vibertite") has been recorded by Bundy (1956) as a secondary mineral in gypsum-anhydrite deposits in Indiana, and by Goodman (1957) as replacing anhydrite and gypsum at Nappan, Nova Scotia.

The remaining sulfates occur mainly in or near potash deposits. Vanthoffite and loewite, with langbeinite, occur with halite below the principal potash zones in parts of the German succession. They are associated with blödite (which they partly replace), kainite, and apthitalite (glaserite), in some potash deposits in Germany. Apthitalite is also associated with picromerite, sylvite, and halite in eastern England, with syngenite at Stebnik in Poland, and with halite in New Mexico. It is partly secondary in origin. Blödite (astrakanite) forms secondary(?) coarse crystalline aggregates enclosed in other salts in some halite and

potash deposits. Syngenite is a rare constituent of some Polish evaporites. Leonite is a scarce secondary mineral in potash deposits in Germany and a widespread minor constituent in those of New Mexico. Picromerite (schoenite) forms beds as much as a meter in thickness at Aschersleben in Germany, but is normally a scarce constituent of kainite zones. It occurs in the langbeinite deposits of New Mexico (Cathcart, 1949). Epsomite (reichardtite) occurs as thin layers in carnallite at Stassfurt and elsewhere. Anhydrokainite has been reported from Germany as a metamorphic product of kainite intruded by basalt (Jänecke, 1913; Rozsa, 1916b). Sanderite, starkeyite, pentahydrate, and hexahydrate are not normal minerals of marine evaporites, but occur with epsomite as efflorescences on kieserite and other salts (Leonhardt and Berdesinski, 1951; Berdesinski, 1952a). D'Ansite, found in experimental studies of the system Na-Mg-SO₄-Cl-H₂O, may be the mineral described by Görgey (1909) from Hall, Tyrol, associated with vanthoffite and blödite (Autenrieth and Braune, 1958; Strunz, 1958).

CHLORIDES

Halite forms at least 95 percent of the chloride deposits overlying the gypsum-anhydrite zones of marine evaporites. The other chlorides are largely restricted to the potash zones. They include the most soluble compounds potentially existing in sea water and, with kieserite and kainite, were among the last substances to crystallize. They also include secondary salts formed by reaction of earlier sulfates and chlorides with late percolating brines. Apart from halite, the only chlorides to occur in significant quantity are sylvite and carnallite, which are the major constituents of most potash deposits. Carnallite occurs as a primary constituent, but in part replaces other minerals. Sylvite is probably largely derived from earlier carnallite, but is perhaps in part of primary origin. Sylvite and halite are the major constituents of the rock sylvinite, the principal potassium ore. Bischofite is a rare mineral, at least in part secondary, which replaces carnallite in German deposits (Przibylla, 1904; van't Hoff, 1912). Koenenite occurs in the potash deposits of Germany as an accessory mineral in salt clay, anhydritic hartsalz, and carnallite (Kühn, 1951). Zirklerite (HARBORT, 1928) has been recorded as a secondary mineral in German potash mines, associated with rinneite, halite, anhydrite, quartz, dolomite, and clay. Chlorocalcite (bäumlerite) is intergrown with tachyhydrite in the Desdemona potash mine, Leinetal, Prussia (Renner, 1912). It may be the same as hydrophilite, from Lüneberg, Hannover, originally described as CaCl₂. Tachyhydrite may replace carnallite, and occurs with kainite, sylvite, halite, bischofite, kieserite,

and anhydrite at German localities (Doelter and Leitmeier, 1929, p. 1219; Borchert, 1940; Kling, 1913). Douglasite (Ochsenius, 1878; Boeke, 1909b, c) is recorded with sylvite, carnallite, and halite at Douglas-hall near Stassfurt. Rinneite (Boeke, 1909a, b, c, 1911; Rinne and Kolb, 1911) is a rare mineral of the German Zechstein, but occurs fairly commonly in the English potash field, where it is mainly associated with halite, sylvite, and carnallite, and enters into various replacements (Stewart, 1951a, b, 1956; Armstrong and others, 1951). Erythrosiderite is an alteration product of rinneite.

FLUORIDES

Fluorite occurs very rarely and in small quantity in anhydrite and dolomite deposits. Sellaite (Sahama, 1945; Kühn, 1952b) occurs as a primary mineral with potassium salts at Salzdetfurth in Germany, and with sulfur, fluorite, celestite, and quartz in anhydrite-dolomite rock in a glacial moraine in Savoy, France (Sella, 1887).

OTHER MINERALS

Sulfur is a secondary mineral that occurs fairly commonly in small quantity, and occasionally in bulk, in sulfate and carbonate deposits. There are especially valuable deposits in Sicily (in Miocene limestone and gypsum) and in the caprock of salt domes in Texas and Louisiana, where sulfur is associated with secondary limestone and gypsum. It is partly of bacterial origin and is generally accompanied by bituminous material. Pyrite is a widespread minor accessory of all zones and is sometimes replaced by limonite. Hauerite and marcasite have been found in the water-insoluble residues of salt plugs in Louisiana and Texas. The list of the more common insolubles given by Taylor (1937), in order of abundance, is as follows: Anhydrite (20), dolomite (20), calcite (16), pyrite (13), quartz (19), limonite (11), hauerite (7), sulfur (6), hematite (5), celestite (4), barite (2), marcasite (2), kaolinite (2). The figures refer to the number of plugs, of the twenty studied, in which each mineral occurs.

Hematite is a widespread accessory of marine evaporites, especially in the potash zones. It forms minute plates and rods enclosed in various salts, often in such abundance as to impart a pink or even blood-red color to its host minerals, and a red-brown color to associated clay. Hematite tends to occur in greatest quantity in salts of potassium and magnesium. In the Texas-New Mexico field it is present in much of the polyhalite, carnallite, sylvite, leonite, langbeinite, and glauberite; it is rare in halite and anhydrite (Schaller and Henderson, 1932; Mansfield, 1930). In the evaporites of Yorkshire, England, hematite is

common in sylvite, in some carnallite, and in halite which has replaced these minerals, and occurs rarely in boracite and quartz (Stewart, 1951a, 1956). Schaller and Henderson (1932) suggested that hematite has been deposited from potassium-rich brines by bacterial or algal growth. They found that the greenish clay commonly associated with hematite-rich salts has considerably less total iron than the red-brown clay (table 8), and suggested that ferric iron leached from the red-brown clay was deposited in the salts.

TABLE 8.—Iron content of two clays from the Salado Formation, New Mexico

[E. P. Henderson, analyst]

	Weight percent	
	Fe ₂ O ₃	FeO
Reddish-brown clay-----	5.15	0.96
Greenish-gray clay-----	.44	1.14

Oriented hematite inclusions in carnallite were ascribed by Johnsen (1909) to the oxidation of carnallite that contained some FeCl₂ as an isomorphous replacement of MgCl₂, and it has been suggested (Stewart, 1951a) that some red sylvite may have replaced earlier magnesium-iron carnallite. Marr (1957) also invoked the formation of iron-bearing carnallite to account for a definite association between the content of potassium and Fe₂O₃ in some German mines. Oriented hematite inclusions in sylvite were ascribed by Leonhardt and Tiemeyer (1938) to simultaneous crystallization of the two minerals.

Magnetite is much rarer than hematite in evaporites, but has been recorded as pseudomorphs after hematite (Mügge, 1913) in the German Zechstein, and as minute crystals in anhydrite in the English Zechstein (Stewart, 1949). Quartz, forming well shaped crystals, is a fairly abundant accessory in the English potash field, where it is largely associated with clay and is partly of secondary origin. It has also been recorded in small quantity from many other potash, rock salt, and sulfate deposits. Opal has been found in well cuttings in Texas and New Mexico (Schaller and Henderson, 1932). Talc is a secondary mineral, occurring mainly as plates lying along cleavages of halite and sylvite in New Mexico (Bailey, 1949) and Yorkshire (Stewart, 1949, 1951b). Most evaporites contain patches or layers of clay in which illite, kaolinite, and chlorite have been found mixed with hematite quartz, and carbonates. Goyazite [SrAl₃(PO₄)₂(OH)₅·H₂O] has been reported from the Romny and Issachki salt domes, Ukraine (Pitkovskaya, 1939).

PHYSICAL CHEMISTRY
EXPERIMENTS OF USIGLIO

The first important experiments on the crystallization of sea salts were carried out by Usiglio (1849), who studied the order and quantity of the various salts to separate during the evaporation of water taken, from a depth of 1 meter, several miles from the shore of the Mediterranean near Cette. Analyses of the water itself and of three bitters of different densities, representing different stages of evaporation, are given in table 9, from Clarke (1924).

Clarke pointed out that the figures for bromine are obviously excessive and those for potassium are low, but that otherwise the data agree fairly well with more recent figures. They show the elimination of calcium as carbonate and then as sulfate, the deposition of

sodium chloride, and the accumulation of the more soluble substances in the mother liquor.

Clarke continued (1924, p. 220-221):

In his study of saline deposition Usiglio started with 5 liters of sea water, and determined the character and quantity of the salts laid down at successive stages of concentration. In the following table [table 10] the results of his experiments appear, but are reduced to the initial unit volume of 1 liter. The quantities given are in grams.

Upon further concentration of the mother liquors, Usiglio obtained variable results. Mere cooling from the temperature of day to that of night was sufficient to precipitate additional magnesium sulfate, which redissolved partially the day following. After that more salt was thrown down, then the double sulfate of magnesium and potassium, next the double chloride of the same metals, and finally magnesium chloride crystallized out. In the table of results just given the order of deposition is clearly shown. First, ferric oxide and calcium carbonate; then gypsum; then salt, the latter beginning to appear when the water had been concentrated to about one-tenth of its original volume.

Usiglio established a general order for the deposition of the earlier salts, but the later stages could not be worked out in detail by his methods. Toward the end of the 19th century, van't Hoff and his coworkers started their classic systematic study of the solubility relationships of the principal evaporite minerals, in pure water and in salt solutions at various temperatures. This work was published in 52 papers which were later collected in a separate volume (van't Hoff, 1912; for summary accounts see van't Hoff, 1095, 1909; Jänecke, 1929), and it made a tremendous contribution to our understanding of evaporite deposition and to the economic exploitation of the various salts.

Van't Hoff's solubility studies were carried out mainly at temperatures of 25°C and 83°C, but he also

TABLE 9.—Analyses of Mediterranean water and bitters
[From Clarke, 1924, p. 220. Weight percentages of total solids]

	A	B	C	D
Cl.....	54.39	56.18	49.99	49.13
Br.....	1.15	1.22	2.68	3.03
SO ₄	7.72	5.78	14.64	17.36
CO ₃18			
Na.....	31.08	32.06	20.39	12.89
K.....	.71	.78	2.25	3.31
Ca.....	1.18	.26		
Mg.....	3.59	3.72	10.05	14.28
Total.....	100.00	100.00	100.00	100.00
Salinity, percent....	3.766	27.546	33.712	39.619

A. The water itself, density 1.0258.
B. Bittern of density 1.21.
C. Bittern of density 1.264.
D. Bittern of density 1.32.

TABLE 10.—Salts laid down in concentration of sea water
[Data of Usiglio; quoted from Clarke, 1924, p. 220]

Density ¹	Volume	Fe ₂ O ₃	CaCO ₃	CaSO ₄ ·2H ₂ O	NaCl	MgSO ₄	MgCl ₂	NaBr	KCl
1.0258.....	1.000								
1.0500.....	.533	0.0030	0.0642						
1.0836.....	.316		Trace						
1.1037.....	.245		Trace						
1.1264.....	.190		0.530	0.5600					
1.1604.....	.1445			.5620					
1.1732.....	.131			.1840					
1.2015.....	.112			.1600					
1.2138.....	.095			.0508	3.2614	0.0040	0.0078		
1.2212.....	.064			.1476	9.6500	.0130	.0356		
1.2363.....	.039			.0700	7.8960	.0262	.0434	0.0728	
1.2570.....	.0302			.0144	2.6240	.0174	.0150	.0358	
1.2778.....	.023				2.2720	.0254	.0240	.0518	
1.3069.....	.0162				1.4040	.5382	.0274	.0620	
Total deposit.....		0.0030	0.1172	1.7488	27.1074	0.6242	0.1532	0.2224	
Salts in last bittern.....					2.5885	1.8545	3.1640	.3300	0.5339
Sum.....		0.0030	0.1172	1.7488	29.6959	2.4787	3.3172	0.5524	0.5339

¹ Given by Usiglio in Baumé degrees. Restated here in specific gravities.

determined the transition temperatures of various salts between 10°C and 83°C. Among the considerable number of later workers, D'Ans and his collaborators (1909, 1915, 1933, 1935, 1940, 1944, 1947a, b, 1949, 1950, 1952, 1955) have been especially active, and it is largely because of their work and that of Serowy (1923) and Leimbach (1925) that the main details of stable equilibria in the complex system containing the principal ions of sea water are known at temperatures between 0°C and 110°C. Good summaries of much of this work are given in English by Blasdale (1927) and Phillips (1947), and in more detail in German by Borchert (1940) and Lotze (1957).

The principal ions of sea water are Na^{+1} , Mg^{+2} , Ca^{+2} , K^{+1} , Cl^{-1} , SO_4^{-2} , HCO_3^{-1} , and Br^{-1} . On evaporation, bromine does not form separate compounds, but crystallizes isomorphously with the chlorides. The bulk of the carbonate will normally separate as CaCO_3 before any other salts crystallize. The number of components is therefore reduced to six, together with water. Most of the calcium is precipitated as sulfate (gypsum and anhydrite) before halite starts to separate when the water has reached about 9.5 percent of its original volume. It is therefore convenient to deal first with the experimental data on the early calcium sulfates.

Halite will crystallize throughout the later stages, because sodium and chlorine are so much in excess of the other components, and all salts will form from a solution saturated with sodium chloride. For the main crystallization of the salts of potassium and magnesium, we can therefore consider the part of the quinary system $\text{Mg-Na-K-Cl-SO}_4\text{-H}_2\text{O}$ under conditions of saturation with respect to NaCl . After that we shall discuss briefly the small quantities of calcium salts found at these later stages. Then we shall be in a position to consider theoretical salt successions formed from sea water.

GYP SUM AND ANHYDRITE

In the system $\text{CaSO}_4\text{-H}_2\text{O}$, van't Hoff (1912) and later experimenters have recorded four phases: anhydrite, gypsum, hemihydrate ($2\text{CaSO}_4\cdot\text{H}_2\text{O}$), and "soluble anhydrite" ($\gamma\text{-CaSO}_4$). Two polymorphs each of hemihydrate and soluble CaSO_4 were recorded by Kelley and others (1941), who recognized six solid phases with distinct thermodynamic properties, but there has been some doubt as to the nature of these phases (MacDonald, 1953). Gypsum and anhydrite are the relatively most stable solid phases in the system and the only ones which occur in nature, other than the very rare mineral bassanite ($2\text{CaSO}_4\cdot\text{H}_2\text{O}$).

Posnjak's (1938) diagram of the system $\text{CaSO}_4\text{-H}_2\text{O}$ at atmospheric pressure is given in figure 1. Posnjak found by experimental work that the transition point

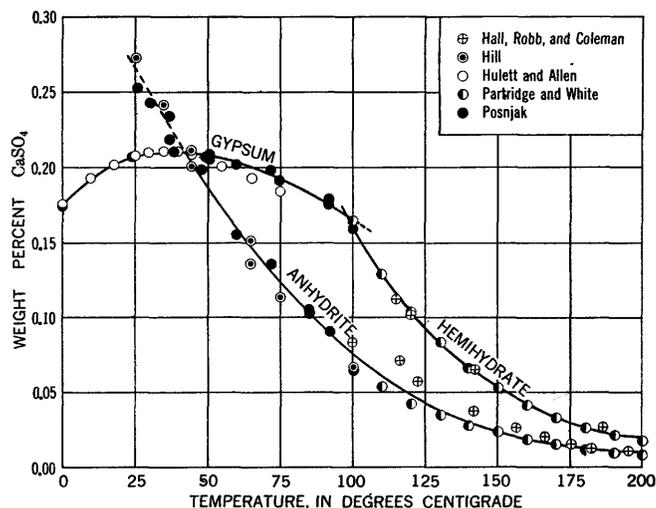


FIGURE 1.—Solubility of gypsum, hemihydrate, and anhydrite in the system $\text{CaSO}_4\text{-H}_2\text{O}$. (Posnjak, 1938, p. 268, fig. 3.)

gypsum-anhydrite at one atmosphere lies at 42°C. Gypsum is truly metastable between this temperature and 97°C, at which it converts to the metastable hemihydrate. Between these temperatures gypsum can change to anhydrite by solution of gypsum and crystallization of anhydrite around preexisting anhydrite nuclei.

Thermodynamic calculations carried out by MacDonald (1953) give the figure of 40°C for the transition point gypsum-anhydrite in the simple system at atmospheric pressure. Increase of total pressure favors the formation of gypsum, the transition temperature being 46°C at 500 bars. MacDonald pointed out that this case would correspond to conditions pertaining during primary deposition of evaporites, but not necessarily to secondary changes due to burial where the water may have free access to the surface. In the latter case, assuming that the rocks under which the evaporites are buried have a mean density of 2.4.

a pressure on the solid phase 2.4 times the pressure on the liquid phase lowers the dehydration temperature of gypsum one degree for 39.45 bars. At a pressure of 500 bars the dehydration temperature is 27°C.

Curves A and B of figure 2 (MacDonald, 1953, p. 888) show the effect of pressure on dehydration of gypsum in this system.

The transition temperature of gypsum-anhydrite is lowered considerably when other salts are present (see for example, Posnjak, 1940; D'Ans, Bredtscheider and others, 1955; Madgin and Swales, 1956a, b). Posnjak (1940) determined the solubility relationships at 30°C in solutions containing NaCl , MgCl_2 , MgSO_4 , and K_2SO_4 in the proportions found in sea water. His results are given in figure 3. In the evaporation of such solutions, gypsum started to crystallize when the salinity had reached 3.35 times the normal salinity of

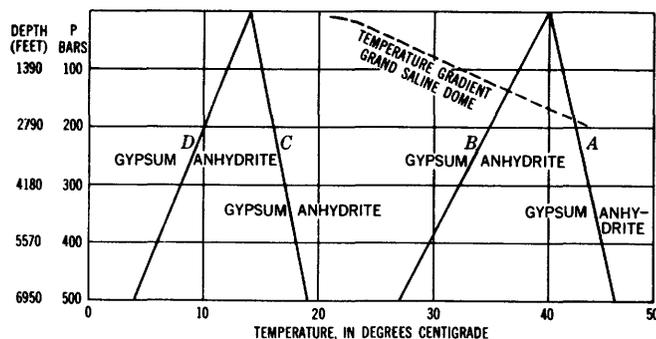


FIGURE 2.—Pressure-temperature relations for the reaction gypsum=anhydrite+water. Curve A, Same pressure acting on all phases, in presence of pure water. Curve B, Rock pressure acting on solid phases, hydrostatic pressure acting on pure water. Curve C, Same pressure acting on all phases in presence of saturated NaCl solution. Curve D, Rock pressure acting on solid phases, hydrostatic pressure acting on saturated NaCl solution. (MacDonald, 1953, p. 888, fig. 2.)

sea water, and anhydrite at 4.8 times the normal salinity.

MacDonald (1953) also considered the effects of dissolved NaCl and of pressure. Using data from the International Critical Tables (1933) and from Adams (1931), he obtained the following results by thermodynamic calculations:

Moles NaCl in solution	Density of solution	Dehydration temperature at one bar	dP/dT in bars per degree for the same pressure acting on all the phases	dP/dT in bars per degree for rock pressure acting on solid phases and hydrostatic pressure on solution
0.90	1.03	37	85.8	-40.6
1.90	1.07	34	86.5	-42.4
3.02	1.11	30	87.7	-44.1
4.28	1.15	25	88.9	-45.9
5.70	1.19	17	90.3	-47.7
6.15 ¹	1.20	14	90.8	-48.3

¹ Saturated.

Figure 4 and curves C and D of figure 2 show graphically the effects of varying NaCl concentration at one bar pressure, and those of varying pressure with saturated NaCl solution.

This work shows clearly that increase in total pressure on all phases favors the stability of gypsum, but increase of NaCl concentration and (or) of differential pressure favors the stability of anhydrite.

THE SYSTEM Mg-Na-K-Cl-SO₄-H₂O, UNDER CONDITIONS OF SATURATION WITH RESPECT TO NaCl

In this system there are 33 invariant points between 0°C and 110°C at which four salts and halite coexist in equilibrium with solution. The position of most of these points have been determined experimentally by van't Hoff, D'Ans, and other workers. The data concerning the points have been tabulated by Borchert (1940) and are reproduced in table 11. Tables 12-15, also based on Borchert (1940), deal with equilibria in the quinary system at 0°C, 25°C, 55°C, and 83°C

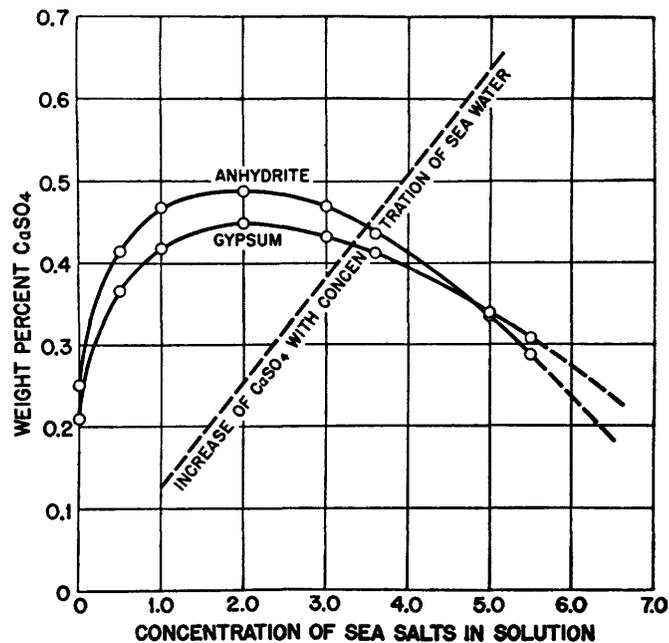


FIGURE 3.—Solubility curves for gypsum and anhydrite in solutions of sea salts. Broken line shows amount of calcium sulfate that is available when ordinary sea water is being evaporated. Concentration is expressed in units of the usual salinity of sea water. (Posnjak, 1940, p. 565, fig. 1.)

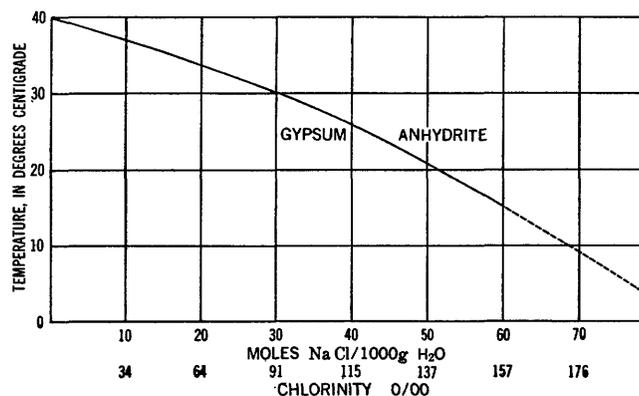


FIGURE 4.—Dependence of the dehydration temperature of gypsum on concentration of NaCl in solution at one bar pressure. (MacDonald, 1953, p. 893, fig. 3.)

(univariant solutions), and the letters in column 2 correspond with those in figures 5-9.

D'Ans' original figures were expressed as the number of moles of Na₂Cl₂, K₂Cl₂, and so forth, in 1,000 moles of water, but all concentrations in tables 11-15 are given in accordance with the units of Jänecke (1923), where K₂+Mg+SO₄=100, and corresponding figures are given for 2Na⁺¹ and H₂O. D'Ans' presentation may be obtained from the Jänecke figures by recalculating on the basis of H₂O=1,000. For example, the first solution in table 12 is in equilibrium with the solid phases of halite, sylvite, mirabilite, and picromerite, and contains 27 moles Na₂Cl₂, 9.7 moles K₂Cl₂, 19.8 moles MgCl₂, and 10.9 moles MgSO₄, in 1,000 moles of water.

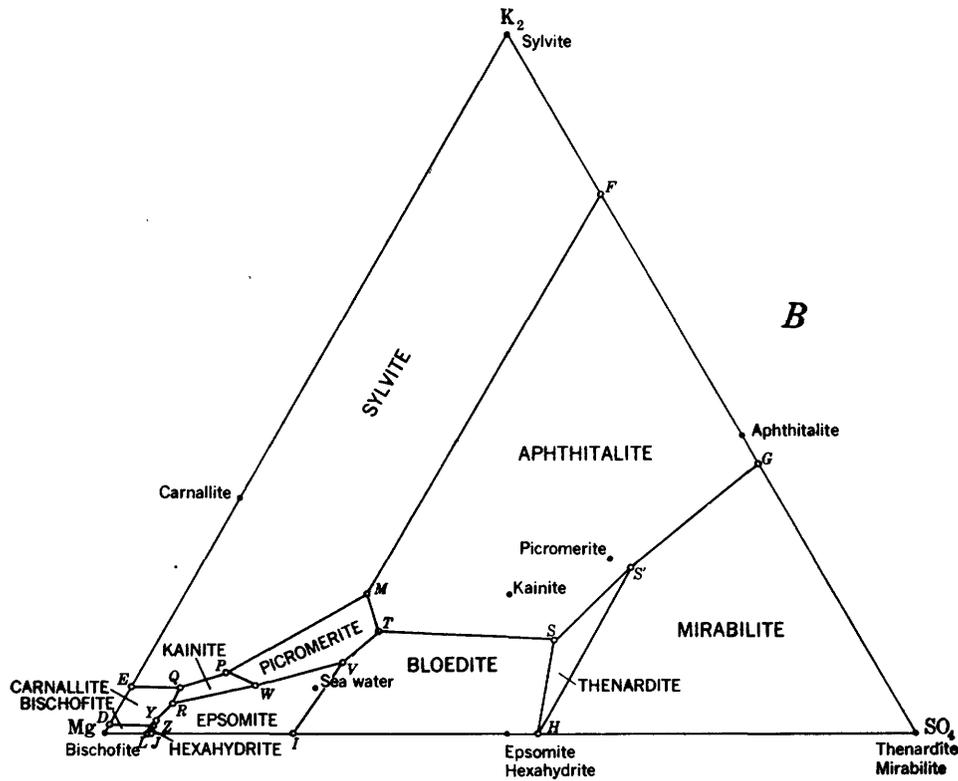
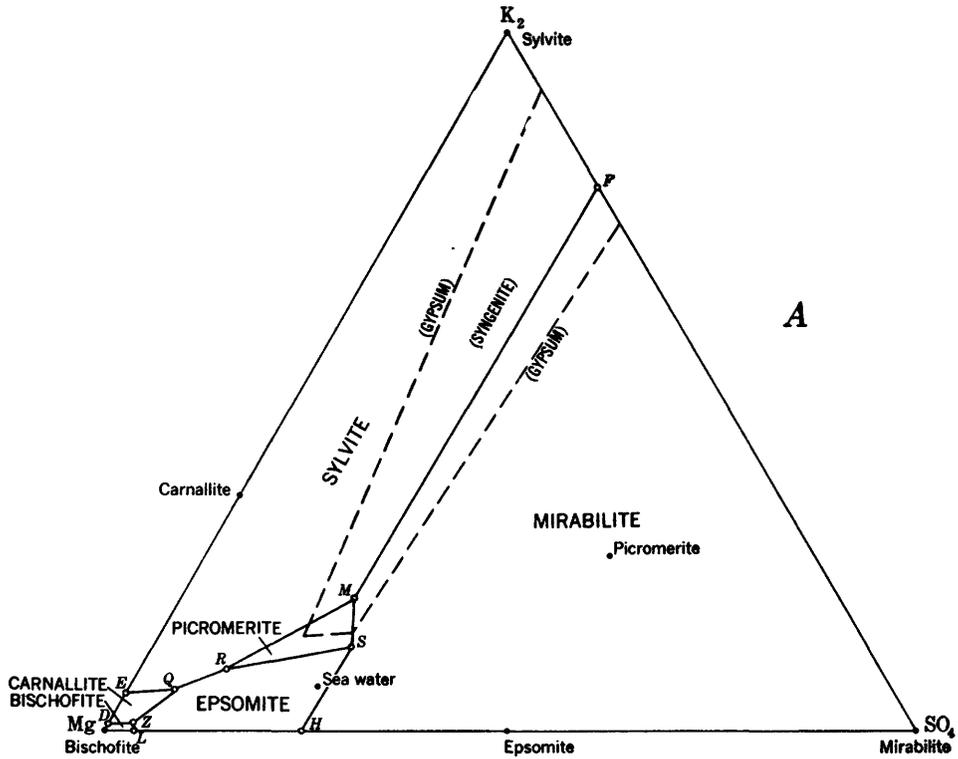


FIGURE 5.—Stability fields of oceanic salts. A, At 0°C, shown on Jänecke-type diagram. The fields for the calcium salts are superposed as dotted lines. B, At 15°C. (Modified after Borchert, 1940.)

TABLE 11.—Transition points in the system Mg-Na-K-Cl-SO₄-H₂O (invariant solutions)[Units of Jänecke (1923), where K₂+Mg+SO₄=100. After Borchert (1940, p. 15-16)]

Transition point	Temp. °C	K ₂	Mg	SO ₄	Na ₂	H ₂ O
Mirabilite+sylvite→aphthitalite+NaCl+(picromerite)-----	2	19.2	59.6	21.2	51	1924
Mirabilite+picromerite→aphthitalite+epsomite+(NaCl)-----	3	12	64	24	35.2	1600
Mirabilite+epsomite→blödite+(NaCl,picromerite)-----	4.5	12.5	65	22.5	36.7	1667
Mirabilite+picromerite→blödite+aphthitalite+(NaCl)-----	6	12.9	62.1	25.0	36.3	1612
Sylvite+epsomite→kainite+4H ₂ O+(NaCl,carnallite)-----	(11)	6.8	87.6	6.8	3.7	1235
Epsomite→hexahydrate+1H ₂ O+(NaCl,carnallite,bischofite)-----	(12.5)					
	(13)	.9	94.5	4.6	4.6	913
Mirabilite→thenardite+10H ₂ O+(NaCl,aphthitalite,blödite)-----	13.5	12.7	38.2	49.1	87.3	1820
Hexahydrate→kieserite+5H ₂ O+(NaCl,carnallite,bischofite)-----	17.5	.9	93.2	4.9	.45	897
Epsomite→hexahydrate+1H ₂ O+(NaCl,kainite,carnallite)-----	18	3	90.5	6.5	2	994
Picromerite→leonite+2H ₂ O+(NaCl,kainite,epsomite)-----	19	8.3	68	23.7	14.2	1182
Picromerite→leonite+2H ₂ O+(NaCl,blödite,epsomite)-----	20	9.6	66.3	24.1	15.7	1204
Picromerite→leonite+2H ₂ O+(NaCl,kainite,sylvite)-----	20	10.2	74.2	15.6	12	1198
Hexahydrate→kieserite+5H ₂ O+(NaCl,kainite,carnallite)-----	23	2.4	90.4	7.2	1.9	966
Picromerite→leonite+2H ₂ O+(NaCl,aphthitalite,sylvite)-----	(25.5)	22.7	55.5	21.8	36	1562
Picromerite→leonite+2H ₂ O+(NaCl,aphthitalite,blödite)-----	26	16.4	54.7	28.9	43.7	1562
Epsomite→hexahydrate+1H ₂ O+(NaCl,leonite,kainite)-----	27	7.5	71.9	20.6	8.6	1082
Epsomite→hexahydrate+1H ₂ O+(NaCl,leonite,blödite)-----	(27.5)	8.3	70.7	21	10	1107
Hexahydrate→kieserite+5H ₂ O+(NaCl,leonite,kainite)-----	(31.5)	6.9	75.6	17.5	6.4	1064
Hexahydrate→kieserite+5H ₂ O+(NaCl,leonite,blödite)-----	(32)	7.6	74.0	18.4	7.6	1082
Leonite+kieserite→langbeinite+5H ₂ O+(NaCl,kainite)-----	37	4.3	81.9	13.8	4.3	1063
Leonite+kieserite→langbeinite+(NaCl,blödite)-----	(37.5)	6.4	79.2	14.4	5.9	1070
Blödite→loeweite+1.5H ₂ O+(NaCl,langbeinite,kieserite)-----	43	8.3	77.5	14.2	5.9	1182
Blödite+2Na ₂ SO ₄ →vanthoffite+4H ₂ O+(NaCl,aphthitalite)-----	46	32.1	25.6	42.3	123	2565
Blödite→loeweite+1.5H ₂ O+(NaCl,langbeinite,leonite)-----	47	12.0	69.4	18.6	14.4	1198
Leonite+kainite→langbeinite+sylvite+(NaCl)-----	55	24.4	56.1	19.5	24.4	1220
Blödite→loeweite+1.5H ₂ O+(NaCl,leonite,aphthitalite)-----	56.5	22.0	47.1	30.9	49.3	1471
Blödite→loeweite+1.5H ₂ O+(NaCl,aphthitalite,vanthoffite)-----	59.5	24.4	41.5	34.1	59.3	1482
Leonite+NaCl→aphthitalite+langbeinite+sylvite-----	60.5	29.9	49.3	20.8	31.8	1300
Leonite+kieserite→langbeinite+aphthitalite+(NaCl)-----	61.5	25.0	46.3	28.7	48.6	1472
Kainite→kieserite+sylvite+2H ₂ O+(NaCl,carnallite)-----	72	10.1	86.9	3.0	3.5	1010
Kainite→kieserite+sylvite+2H ₂ O+(NaCl,langbeinite)-----	83	12.1	84.9	3.0	4.5	1005
Loeweite+aphthitalite→vanthoffite+langbeinite+(NaCl)-----	(98)	39.2	38.5	22.3	40.5	1350
Loeweite→vanthoffite+kieserite+(langbeinite,NaCl)-----	(108)	39.2	39.6	21.2	25	1322

TABLE 12.—Equilibria in the system Mg-Na-K-Cl-SO₄-H₂O at 0°C[Units of Jänecke (1923), where K₂+Mg+SO₄=100. After Borchert, 1940, p. 17]

Saturation with respect to NaCl and	Point	K ₂	Mg	SO ₄	Na ₂	H ₂ O
Sylvite, mirabilite, picromerite-----	M	18.9	59.8	21.3	52	1949
Mirabilite, picromerite, epsomite-----	S	11.9	63.4	24.7	35	1591
Picromerite, epsomite, sylvite-----	R	8.8	80.8	10.4	10.4	1405
	N					
	Q					
Epsomite, sylvite, carnallite-----	T	5.8	88.5	5.7	3.9	1271
	Z	.8	96.2	3.0	.7	955
Epsomite, carnallite, bischofite-----	H		75.6	24.4	51.5	2040
Mirabilite, epsomite-----	L		96.3	3.7	.3	984
Epsomite, bischofite-----	D	.6	99.4		.8	1003
Bischofite, carnallite-----	E	5.2	94.8		5.6	1396
Carnallite, sylvite-----	F	77.9		22.1	302	5900
Sylvite, mirabilite-----	SO ₄			100	2550	45500
Mirabilite-----	Mg		100		.8	1002
Bischofite-----	K ₂	100			395	8060
Sylvite-----						

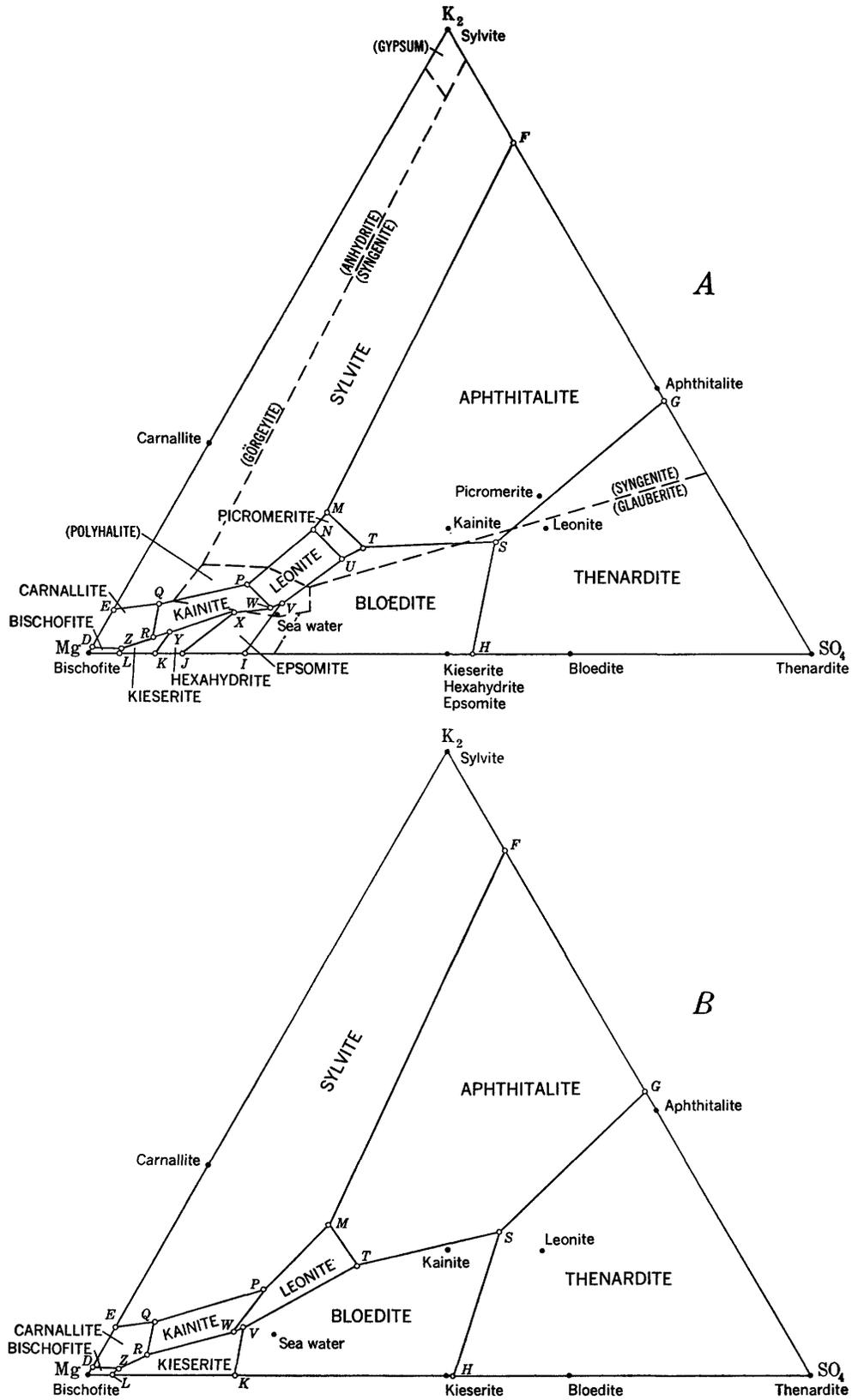


FIGURE 6.—Stability fields of oceanic salts. A, At 25°C. The fields of the calcium salts are superposed as dotted lines. B, At 32.5°C. (Modified after Borchert, 1940.)

TABLE 13.—*Equilibria in the system Mg-Na-K-Cl-SO₄-H₂O at 25°C*[Units of Jänecke (1923), where $K_2+Mg+SO_4=100$. After Borchert, 1940, p. 18-19]

Saturation with respect to NaCl and	Point	K ₂	Mg	SO ₄	Na ₂	H ₂ O	Vapor pressure (mm)
Sylvite, apththitalite, picromerite.....	M	22.3	55.7	22.0	36.1	1571	15.9
Sylvite, picromerite, leonite.....	N	20.2	58.6	21.2	28.3	1461	15.7
Sylvite, leonite, kainite.....	P	10.9	72.2	16.9	11.4	1178	13.4
Sylvite, carnallite, kainite.....	Q	7.5	86.4	6.1	4.0	1178	12.4
Thenardite, apththitalite, blödite.....	S	17.8	34.4	47.8	138.4	2175	16.6
Apththitalite, blödite, picromerite.....	T	17.0	53.2	29.8	44.3	1612	16.1
Blödite, picromerite, leonite.....	U	15.2	56.9	27.9	32.4	1400	15.7
Blödite, leonite, epsomite.....	V	8.4	69.1	22.5	10.8	1100	14.5
Leonite, epsomite, kainite.....	W	7.6	70.8	21.6	9.8	1100	13.4
Epsomite, kainite, hexahydrate.....	X	6.8	76.6	16.6	5.5	1038	12.2
Kainite, hexahydrate, kieserite.....	Y	3.1	87.2	9.7	2.4	974	10.8
Kainite, kieserite, carnallite.....	R	2.4	89.9	7.7	1.6	962	9.5
Kieserite, carnallite, bischofite.....	Z	.8	94.4	4.8	.5	879	7.4
Thenardite, blödite.....	H	-----	46.8	53.2	143.4	2922	17.1
Blödite, epsomite.....	I	-----	78.3	21.7	15.8	1260	17
Epsomite, hexahydrate.....	J	-----	87.0	13.0	4.6	1098	12.2
Hexahydrate, kieserite.....	K	-----	90.9	9.1	1.6	1000	10.8
Kieserite, bischofite.....	L	-----	95.5	4.5	.9	894	7.5
Bischofite, carnallite.....	D	.9	99.1	-----	.5	956	7.5
Carnallite, sylvite.....	E	7.1	92.9	-----	4.8	1297	12.7
Sylvite, apththitalite.....	F	82	-----	18	199	4100	16.84
Apththitalite, thenardite.....	G	40.6	-----	59.4	239.4	4100	17.0
Thenardite.....	SO ₄	-----	100	-----	.6	954	7.63
Sylvite.....	K ₂	100	-----	-----	234	5080	16.84

TABLE 14.—*Equilibria in the system Mg-Na-K-Cl-SO₄-H₂O at 55°C*[Units of Jänecke (1923), where $K_2+Mg+SO_4=100$. After Borchert, 1940, p. 20-21]

Saturation with respect to NaCl and	Point	K ₂	Mg	SO ₄	Na ₂	H ₂ O
Sylvite, apththitalite, leonite.....	M	29.0	50.0	21.0	32.3	1328
Sylvite, leonite, langbeinite, kainite.....	N	24.2	56.2	19.6	24.4	1222
Sylvite, kainite, carnallite.....	Q	9.4	87.1	3.5	3.7	1082
Kainite, carnallite, kieserite.....	R	6.8	89.6	3.6	2.7	1060
Thenardite, vanthoffite, apththitalite.....	S	39.0	22.0	39.0	130	2600
Vanthoffite, apththitalite, blödite.....	T	25.9	38.3	35.8	70.6	1742
Apththitalite, blödite, leonite.....	U	21.5	47.1	31.4	49.1	1462
Blödite, leonite, loeweite.....	V	20.0	51.2	28.8	43.2	1431
Leonite, loeweite, langbeinite.....	W	15.5	59.8	24.7	27.3	1370
Loeweite, kainite, kieserite.....	X	7.0	79.3	13.7	9.4	1068
Kainite, kieserite, langbeinite.....	Y	8.7	80.5	10.8	3.4	1028
Kieserite, carnallite, bischofite.....	Z	1.1	97.1	1.8	.4	857
Thenardite, vanthoffite.....	H	-----	51.8	48.2	156	3085
Vanthoffite, blödite.....	I	-----	60.9	39.1	105	2540
Blödite, loeweite.....	J	-----	74.0	26.0	42.3	1724
Loeweite, kieserite.....	K	-----	85.9	14.1	7.5	1078
Kieserite, bischofite.....	L	-----	96.2	3.8	.6	829
Bischofite, carnallite.....	D	1.1	98.9	-----	.4	874
Carnallite, sylvite.....	E	9.3	90.6	-----	4.1	1164
Sylvite, apththitalite.....	F	88.0	-----	12.0	135.5	3000
Apththitalite, thenardite.....	G	56.0	-----	44.0	213	3760
Thenardite.....	SO ₄	-----	100	-----	677	10760
Bischofite.....	Mg	-----	-----	-----	.45	885
Sylvite.....	K ₂	100	-----	-----	155	3480

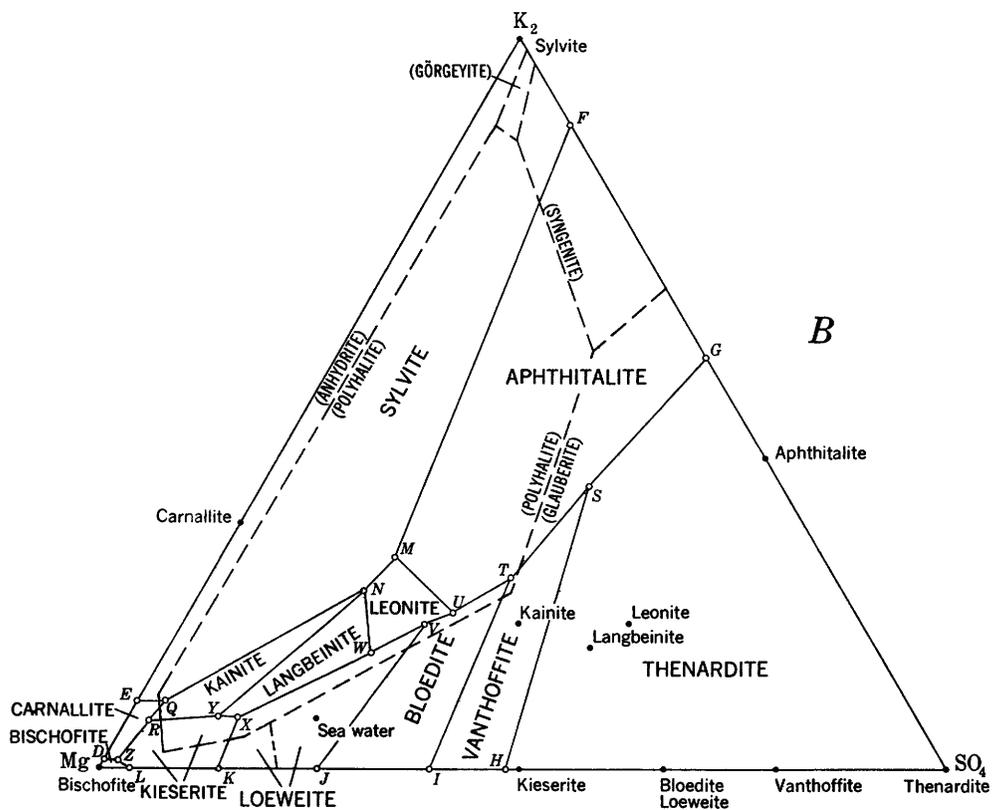
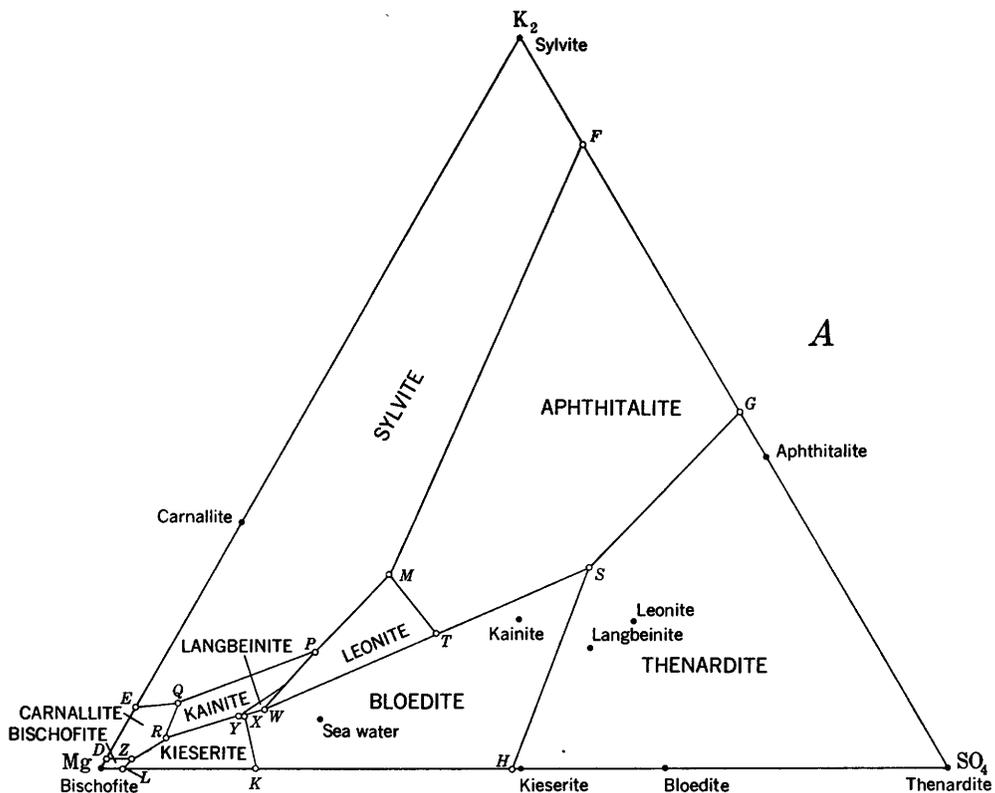


FIGURE 7.—Stability fields of oceanic salts. A, At 40°C. B, At 55°C. The fields of the calcium salts are superposed as dotted lines. (Modified after Borchert, 1940.)

DATA OF GEOCHEMISTRY

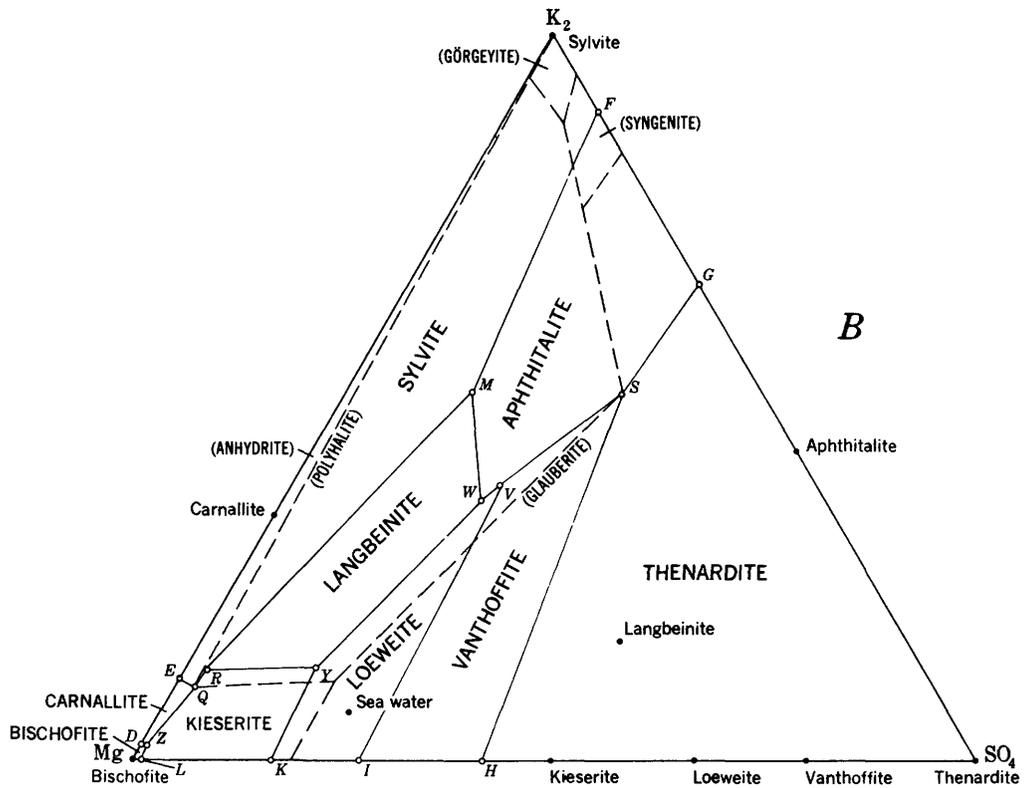
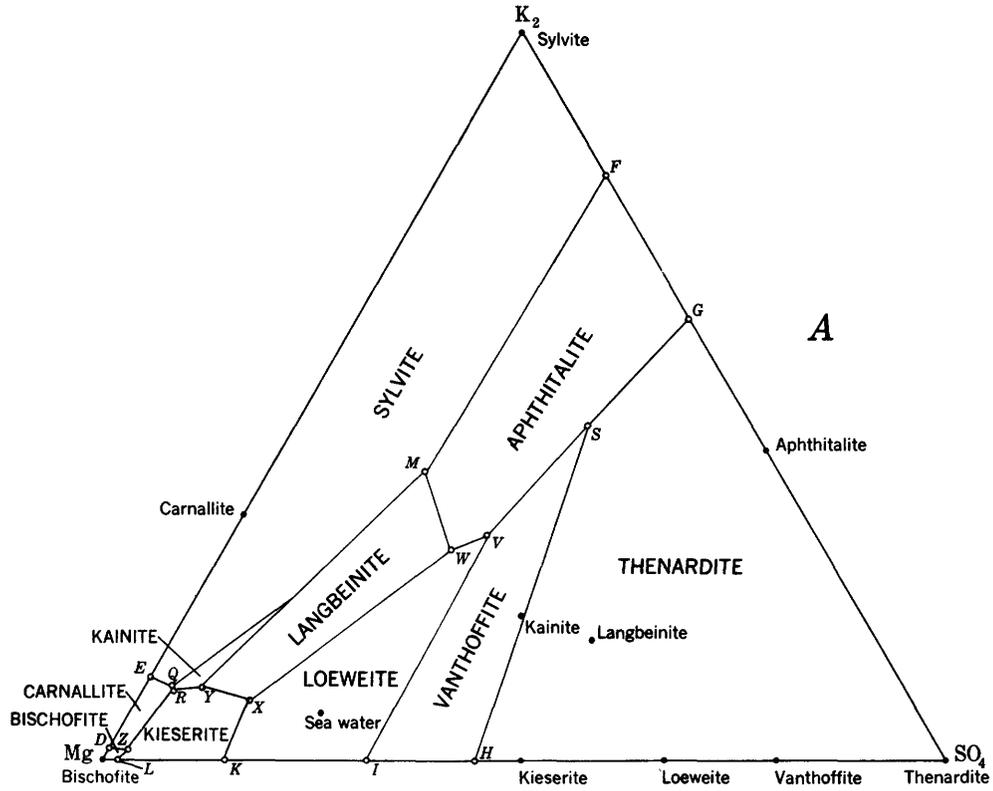


FIGURE 8.—Stability fields of oceanic salts. A, At 70°C. B, At 83°C. The fields of the calcium salts are superposed as dotted lines. (Modified after Borchert, 1940.)

TABLE 15.—Equilibria in the system Mg-Na-K-Cl-SO₄-H₂O at 33°C[Units of Jänecke (1923), where K₂+Mg+SO₄=100. After Borchert, 1940, p. 22]

Saturation with respect to NaCl and	Point	K ₂	Mg	SO ₄	Na ₂	H ₂ O
Sylvite, apththitalite, langbeinite	{M P}	50.6	34.4	15.0	44.7	1509
Apththitalite, thenardite, vanthoffite	S	50.7	16.6	32.7	112.2	2300
Apththitalite, vanthoffite, loeweite	V	37.7	37.4	24.9	49.7	1431
Apththitalite, loeweite, langbeinite	W	35.2	41.2	23.6	43.2	1448
Loeweite, langbeinite, kieserite	Y	12.6	71.8	15.8	24.2	1305
Langbeinite, kainite, kieserite, sylvite	R	11.9	85.0	3.1	4.3	1002
Kieserite, sylvite, carnallite	Q	9.7	87.9	2.4	3.7	976
Kieserite, carnallite, bischofite	Z	1.4	97.8	.8	.5	777
Thenardite, vanthoffite	H		58.8	41.2	203	3970
Vanthoffite, loeweite	I		73.3	26.7	74.6	2120
Loeweite, Kieserite	K		83.6	16.4	26.8	1494
Kieserite, bischofite	L		99.3	.7	.5	789
Bischofite, carnallite	D	1.4	98.6		.55	785
Carnallite, sylvite	E	10.9	89.1		3.9	1128
Sylvite, apththitalite	F	89.7		10.3	104	2355
Apththitalite, thenardite	G	65.2		34.8	169	3080
Thenardite	SO ₄			100	768	12050
Bischofite	Mg		100		.5	796
Sylvite	K ₂	100			114	2680

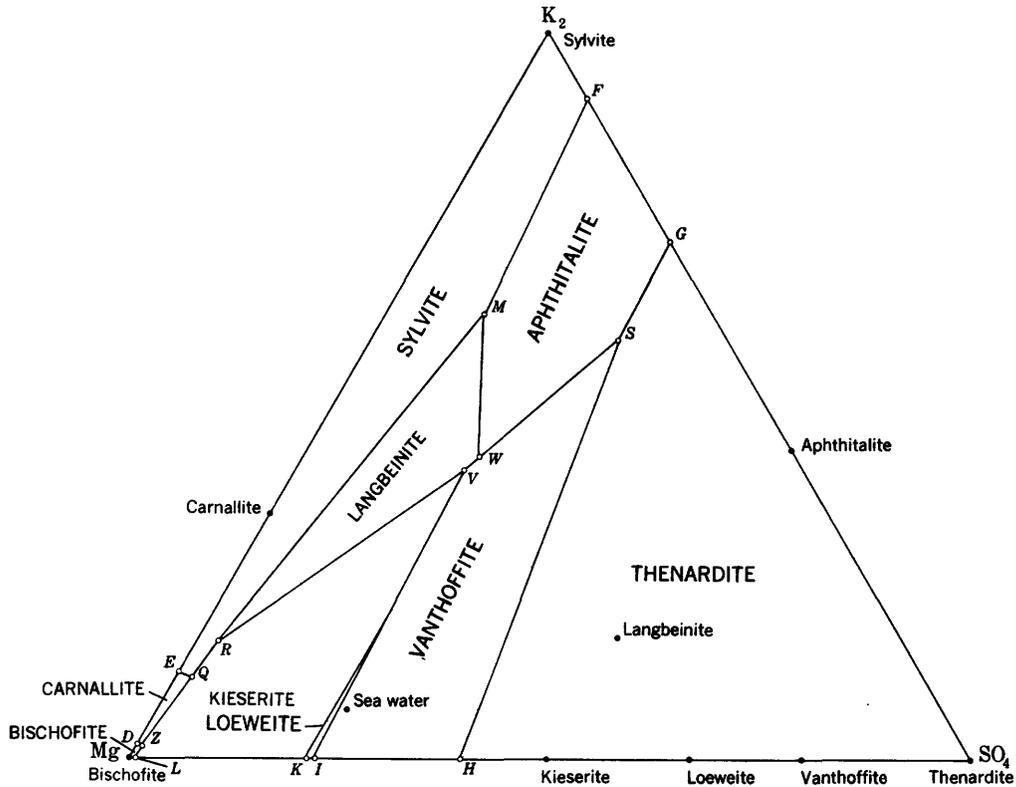


FIGURE 9.—Stability fields of oceanic salts at 110°C. (Modified after Borchert, 1940.)

Various methods have been devised for representing the system graphically, and a convenient one is credited to Jänecke (1923), who expressed the data with a variable water content, the amount needed to produce a saturated solution. Because we are neglecting calcium for the moment and assuming saturation with respect to NaCl, it is possible to construct isothermal triangular diagrams by expressing compositions as mH_2O , xMg , yK_2 , $100-(x+y)SO_4$, zNa_2 . Every composition can then be defined by a point in a triangular diagram with corners K_2 , Mg , and SO_4 , by using the figures for x and y .

In such a diagram the paths of crystallization can be traced as in a simple ternary system, the usual relationships of congruent and incongruent fields still hold, and quantitative information can be derived by application of the center-of-gravity principle. (Phillips, 1947, p. 96).

Isothermal diagrams of this type, for nine different temperatures within the range 0° – $110^\circ C$, are given in figures 5–9 (after Borchert, 1940). In each of these, the point representing sea water (6.7 K_2 , 70.5 Mg , 22.8 SO_4) is given.

These diagrams, of course, give no information about the amount of water or NaCl that could be plotted in a three-dimensional figure. Temperature relations can be shown in a prism constructed by placing the diagrams above one another.

Figure 10 (from Phillips, 1947, p. 98) shows the temperature ranges of formation of the salts in the presence of NaCl.

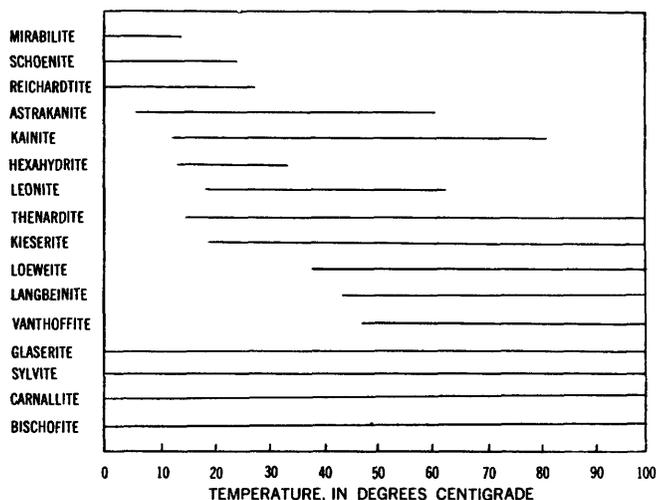


FIGURE 10.—Temperature ranges of formation of oceanic salts between 0° and $100^\circ C$. (From Phillips, 1947, fig. 2, reproduced by permission of the Chemical Society.)

THE LATER CALCIUM SALTS

Before discussing the succession of salts that form when sea water evaporates, a few words should be said about the addition of calcium to the system described above. Most of the calcium in sea water will have been

deposited before the solution is saturated with NaCl and the salts of potassium or magnesium. The small quantity of calcium left will separate as sulfate, and the phases concerned are anhydrite, gypsum, glauberite, syngenite, polyhalite, and görgeyite. The experimental data are not yet adequate to fix the stability fields of these salts accurately, but tentative fields have been superposed by Borchert in four of his triangular diagrams; these are shown here as dotted lines in the diagrams for 0° , 25° , 55° , and $83^\circ C$ (figs. 5A, 6A, 7B, and 8B).

At $0^\circ C$, the fields of stability of the calcium salts are only partly shown. Gypsum and syngenite have large fields; anhydrite has a small field near the Mg corner (not shown); and polyhalite may have a small field in the picromerite-epsomite region. Görgeyite has a small field between those of gypsum and syngenite, as at $25^\circ C$.

At $25^\circ C$, glauberite has become major; the fields of syngenite and anhydrite are larger, and that of gypsum, very much smaller. The sea-water point lies within the polyhalite field, which is fairly small.

At 55° and $83^\circ C$ the fields of syngenite and anhydrite are reduced, and those of polyhalite and glauberite much increased in size.

THEORETICAL SALT SUCCESSIONS FROM SEA WATER

From the data given above, it is possible to work out a series of theoretical salt successions that could be produced by evaporation of sea water at various different temperatures, assuming equilibrium conditions.

The first salts to separate are carbonates. The common carbonates of marine evaporites are calcite and dolomite, but it is probable that much of the dolomite has been formed by secondary replacement of calcite or aragonite. When the water has been evaporated to about 19 percent of its original volume, calcium sulfate starts to separate. Experimental and thermodynamic work indicates that only anhydrite separates from evaporating sea water above about $34^\circ C$; at lower temperatures, gypsum separates first and is followed by anhydrite at a later stage of evaporation.

By the time the solution has been reduced to about 9.5 percent of its original volume, much of the calcium sulfate has been deposited. Halite starts to separate, together with gypsum, at temperatures below about $7^\circ C$, and with anhydrite above that temperature (MacDonald, 1953). When the volume of the solution is less than 5 percent of the original, polyhalite, or at higher temperatures glauberite, takes the place of anhydrite or gypsum. The polyhalite separates together with halite until the solution is saturated with

TABLE 16.—Theoretical successions of precipitation (from bottom to top) up to the stage of saturation with potassium-free magnesium sulfates

0°C	6°C	25°C	35°C
Polyhalite + halite	Polyhalite + halite	Polyhalite + halite	Polyhalite + halite.
Gypsum + halite	Anhydrite + halite	Anhydrite + halite	Anhydrite + halite.
Gypsum	Gypsum + halite	Anhydrite.	
Carbonates of calcium and perhaps of magnesium.	Gypsum	Gypsum	Anhydrite.
	Carbonates of calcium and perhaps of magnesium.	Carbonates of calcium and perhaps of magnesium.	Carbonates of calcium and perhaps of magnesium.

respect to magnesium-bearing sulfates free from calcium and potassium.

Theoretical successions up to the stage of saturation with potassium-free magnesium sulfates, at various temperatures, are given in table 16.

Later stages of deposition can be considered by reference to the triangular diagrams (figs. 5-9). In each of these diagrams the course of crystallization starts at the point representing the composition of sea water and ends at point Z.

If the early salts remain in contact with residual liquids at all stages and react freely with them, the final products of crystallization of the bittern salts are:

0°-13°C	Epsomite + carnallite + bischofite + halite + anhydrite
13°-17.5°C	Hexahydrate + carnallite + bischofite + halite + anhydrite
17.5°-110°C	Kieserite + carnallite + bischofite + halite + anhydrite

If, on the other hand, the earlier salts are prevented from reacting with the residual liquid, either by being crusted over and protected by later salts or by crystal sorting, then the results are much more complex, and the courses of crystallization are as follows:

Figure 5A, 0°C—Across epsomite field to point between R and S (near R), then R, Q, Z.

Figure 5B, 15°C—Across epsomite field to point between V and W, then W, R, Y, Z.

Figure 6A, 25°C—Across blödite and epsomite fields to point between X and W, then X, Y, R, Z.

Figure 6B, 32.5°C—Across blödite field to point practically coincident with V, then W, R, Z.

Figure 7A, 40°C—Across blödite field to point almost coincident with W, then X, Y, R, Z.

Figure 7B, 55°C—Across loeweite field to point between X and W (near X), then across langbeinite field to point almost coincident with Y, then R, Z.

Figure 8A, 70°C—Across loeweite field to point almost coincident with X, then Y, R, Z.

Figure 8B, 83°C—Across loeweite field to point between K and Y, then across kieserite field to point between R and Q, then Q and Z.

Figure 9, 110°C—Across vanthoffite, loeweite, and kieserite fields to point just towards R from Q, then Q, Z.

Table 17 shows the relative volumes of the bittern salts deposited at the nine temperatures, and also the order of deposition. The volumes are expressed as percentages of the salts mentioned, excluding halite and the small amounts of calcium salts which also separate throughout the process. The order of deposition at each temperature is given as 1, 2, 3, and so forth. For example, at 25°C, the first salt to separate is blödite; next is epsomite; then, the pair, epsomite + kainite, and so on.

Table 17 shows clearly that with fractional crystallization a number of successive zones, characterized by the presence of particular minerals, can be predicted. At all the temperatures considered, an early zone containing potassium-free magnesium sulfates, and no potassium-bearing mineral other than polyhalite, is followed by intermediate zones with other potassium minerals. These give place upward to a zone of carnallite with hydrous magnesium sulfates, followed by a thick bischofite zone in which bischofite greatly predominates over carnallite and hydrous magnesium sulfates. Halite, of course, occurs throughout the succession.

In the lowest zone, epsomite, present at low temperatures, gives place at higher temperatures to blödite, and then to loeweite, kieserite, and vanthoffite. In the intermediate zones, picromerite occurs only at relatively low temperatures. Sylvite is present below 11°C and above 72°C, but not at intermediate temperatures. The sylvite-kieserite paragenesis, relatively common in natural potash deposits, is possible in the stable system only above 72°C. Leonite is present in the succession at 32.5°C, and langbeinite, at 40°, 55°, and 70°C. A kainite zone is formed at all temperatures between 11° and 83°C.

It should be pointed out that the successions considered here refer to the evaporation of sea water of normal oceanic composition. It is most unlikely, but possible, that the composition of ocean water has changed sufficiently since the formation of Paleozoic marine evaporites to affect materially the course of crystallization. The water of many areas of evaporite deposition, however, has been modified by river-carried material or by hydrothermal solutions, and this will of

TABLE 17.—Orders of deposition of the bittern salts in the system Mg-Na-K-Cl-SO₄-H₂O with their relative volumes expressed as percentages of total salts, excluding halite and calcium salts

[Figures largely based on Borchert, 1940, p. 43-44. Halite and small quantity of calcium salts crystallize throughout]

	Order of deposition	Bischofite	Blödite	Carnallite	Epsomite	Hexahydrate	Kainite	Kieserite	Langbeinite	Leonite	Loewite	Picromerite	Sylvite	Vant-hoffite	Type of zone
0	5	42.6		0.7	3.0										Bischofite zone. Carnallite zone. Sylvite zone. Picromerite zone. Potassium-free magnesium-sulfate zone.
	4			9.2	3.9										
	3				8.4								2.7		
	2				.05							0.45			
	1				29.0										
Total		42.6		9.9	44.35							0.45	2.7		
15	6	44.9		1.4		6.0									Bischofite zone. Carnallite zone. Kainite zone. Picromerite zone. Potassium-free magnesium-sulfate zone.
	5			1.5		0.5									
	4			3.9	1.3		14.5								
	3				5.8							5.1			
	2				1.0										
Total		44.9		6.8	22.2	6.5	14.5					5.1			
25	7	42.6		0.9				4.9							Bischofite zone. Carnallite zone. Kainite zone. Potassium-free magnesium-sulfate zone.
	6			4.6			2.8	4.8							
	5					1.8	18.6	0.8							
	4				4.2		5.2								
	3				8.4										
Total		42.6	0.4	5.5	12.6	1.8	26.6	10.5							
32.5	5	48.2		1.1				3.8							Bischofite zone. Carnallite zone. Kainite zone. Leonite zone. Potassium-free magnesium-sulfate zone.
	4			4.0			20.5	4.1					3.2		
	3							5.5							
	2							0.1							
	1		9.5												
Total		48.2	9.5	5.1			20.5	13.5		3.2					
40	6	48.3		1.4				2.7							Bischofite zone. Carnallite zone. Kainite zone. Langbeinite zone. Potassium-free magnesium-sulfate zone.
	5			6.2			14.4	3.8							
	4							1.5							
	3							0.8	1.6						
	2		0.1						4.7						
Total		48.3	14.6	7.6			14.4	8.8	6.3						
55	5	44.8		1.7				1.8							Bischofite zone. Carnallite zone. Kainite zone. Langbeinite zone. Potassium-free magnesium-sulfate zone.
	4			11.2				3.1							
	3						6.7	7.3							
	2								7.9				15.5		
	1														
Total		44.8		12.9			6.7	12.2	7.9			15.5			
70	5	43.3		1.7				2.4							Bischofite zone. Carnallite zone. Kainite zone. Langbeinite zone. Potassium-free magnesium-sulfate zone.
	4			18.0				2.4							
	3						4.6	1.2							
	2							13.1	0.1						
	1									0.1			13.2		
Total		43.3		19.7			4.6	19.1	0.1			13.2			
83	5	40.3		1.9				0.6							Bischofite zone. Carnallite zone. Sylvite zone. Potassium-free magnesium-sulfate zone.
	4			15.7				2.7							
	3							0.5					0.9		
	2							24.4							
	1											13.0			
Total		40.3		17.6				28.2				13.0	0.9		
110	6	36.5		1.9				0.4							Bischofite zone. Carnallite zone. Sylvite zone. Potassium-free magnesium-sulfate zone.
	5			16.9				2.45							
	4							0.05					0.3		
	3							39.0							
	2											0.7			
Total		36.5		18.8				41.9				0.7	0.3	1.8	

course alter the resulting salt profiles. For example, the addition of calcium carbonate from rivers may result in the formation of much dolomite at an early stage of deposition, and the resulting removal of magnesium may lead to the later formation of primary sylvite rather than carnallite.

"DYNAMIC-POLYTHEMAL" STUDIES

The experimental work described above is based on experiments carried out at definite temperatures to establish stable equilibria. Since the bulk of the work was completed, two principal lines of research have developed: the "dynamic-polythermal" studies of Borchert and Tollert, and the studies of metastable equilibria by D'Ans and others.

In view of the fact that considerable temperature and concentration gradients, related to climate and topography, exist in large natural bodies of water, Borchert (1933, 1934, 1935, 1940, 1959) carried out a series of experiments in which the temperature varied from one part of the containing vessel to another, and concentration and convection currents were set up. Crystallization in this "dynamic-polythermal" system was rather different from that in the "static" system of van't Hoff, D'Ans, and others. Such work has been continued by Tollert (1950, 1952), who has considered the matter from a thermodynamic point of view.

Under these dynamic conditions a lateral zoning of salts is obtained, and this may be analogous to some types of facies change in natural deposits. Salts with a negative temperature coefficient of solution (called thermophile salts) form in regions of higher temperature. Cryophile salts, with a positive temperature coefficient of solution, form in the regions of lower temperature. The behavior is relative, in that if two cryophile salts are separating, one will behave as thermophile towards the other.

Thermophile salts:	Thenardite, blödite, vanthoffite, loeweite, kainite, langbeinite
Cryophile salts:	Sylvite, picromerite, epsomite, hexahydrate; glauberite is weakly cryophile.

Some salts have a greater range of stability under dynamic than under static conditions. Sylvite, for example, may be deposited from solutions close to the composition of concentrated sea water at moderate temperatures under dynamic conditions. The epsomite-sylvite paragenesis can occur at higher temperatures than 12°C, its limit in the static system. Hexahydrate and the other magnesium sulfates, and picromerite, can exist at much higher temperatures than in the static system. The potassium-magnesium sulfates and kainite have wider ranges of stability, and the fields of the sodium-magnesium sulfates are reduced; a lang-

beinite-carnallite paragenesis is possible with a large temperature gradient. Leonite, kieserite, and polyhalite were not observed within the range 20°-100°C in Borchert's experiments.

Borchert used these results to explain some facies changes in potash mines in Germany—in particular some of the "Vertaubungen" (areas of potassium impoverishment). However, there is still considerable doubt as to how far such conditions can apply to natural deposits of marine evaporites.

METASTABLE PHENOMENA

Recent work on metastable phenomena in oceanic salt systems has shown that some of the salts can form at temperatures considerably above those at which they are stable (Autenrieth, 1953, 1954; D'Ans, 1944, 1947a, 1952; Karsten, 1950; Linstedt, 1955; Tollert, 1956). Picromerite, for example, can form at 55°C—well above its upper limit of stable formation which is 26°C. Kainite can form at 95°C; when in the stable system, it cannot exist above 83°C. In the formation of natural evaporites, if the precipitated salts remain in contact with the residual liquid for a reasonable length of time, the mineralogy should approach that of the stable system. If, however, the precipitates rapidly become solid rock and the residual liquid is removed, then the mineralogy may be different from that of the stable system (Kühn, 1955c). The temperatures of stability of various salts and of characteristic parageneses have been widely used as "geologic thermometers." The recent studies of metastable phenomena throw doubt on their reliability. More work is needed, however, before these problems can be properly evaluated.

SOME MINOR CONSTITUENTS AND FURTHER REFERENCES

Tachyhydrite ($\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$) and chlorocalcite (KCaCl_3) do not appear in the part of the system of sea salts discussed above. D'Ans (1933) gave some data on their conditions of stability, and more recent work on systems containing these minerals includes that of Assarsson, 1950; Assarsson and Balder, 1954, 1955; Igelsrud and Thompson, 1936a, b; Lightfoot and others, 1946, 1949; and Sveshnikova, 1951. These minerals presumably owe their origin to the action of secondary solutions rich in CaCl_2 .

The iron salts of marine evaporites were considered by Boeke (1909b, c, 1911), and D'Ans and Freund (1954) recently studied part of the system $\text{NaCl-KCl-MgCl}_2\text{-FeCl}_2\text{-H}_2\text{O}$, saturated with respect to NaCl , and considered the formation of rinneite ($\text{Na}_2\text{K}_2\text{FeCl}_6$). The lowest concentration of FeCl_2 in equilibrium with rinneite was 21.0 mols FeCl_2 per 1,000 mols H_2O ; the

solution contained 72.5 mols $MgCl_2$, 14.0 mols K_2Cl_2 , and 4.5 mols Na_2Cl_2 , at 83°C. Rinneite has almost certainly formed from secondary solutions, which derived part of their iron content from adjacent nonsaline materials such as the clays associated with the salts.

The literature on the physical chemistry of marine evaporites is very abundant. In addition to those so far mentioned, the following references are included in "Literature Cited": Berdesinski, 1952b; Bodaleva and Lepeshkov, 1956; Bundy and Conley, 1956; Bye and Kiehl, 1948; Campbell, Downes, and Samis, 1934; Conley, Gabriel, and Partridge, 1938; Conley and Partridge, 1944; D'Ans, 1915, 1933, 1935, 1944, 1947a, b, 1949, 1950, 1952; D'Ans, Bredtscheider, Eick, and Freund, 1955; D'Ans, Busse, and Freund, 1955; Faiziev, 1952a, b; Feakes, 1952; Fulda, 1925a, b; Hill, 1937; Hill and Wills, 1938; Ide, 1935; Igelsrud and Thompson, 1936a, b; Ilinskii and Danyushevskaya, 1956a, b; Jänecke, 1913, 1916, 1917, 1923, 1929, 1935, 1950; Kühn, 1952a, b, 1953; Leonhardt, 1951; Leonhardt and Berdesinski, 1949-50, 1951; Lepeshkov and Bodaleva, 1949, 1952; Lightfoot and Prutton, 1946, 1947, 1948; Lightfoot, Prutton, and Meyer, 1949; Lukyanova and others, 1956; Madgin and Swales, 1956a, b; Marsal, 1952; Nikolaev, 1946, 1947; Pelsh, 1953a, b, c; Posnjak, 1938, 1940; Rozsa, 1911, 1914, 1915a, b, 1916a, b, c, d, 1917a, 1919, 1931; Rustamov, 1957a, b; Schaefer, 1920; Serowy, 1922, 1923; Shlezinger and others, 1940; Shternina and Frolova, 1945; Soloveva, 1956; Tanaka and others, 1950; Thompson and Nelson, 1956; Tollert, 1950, 1952, 1956; Tollert and Bruns, 1956; Valyashko, 1951; Valyashko and Nechaeva, 1952; Valyashko and Soloveva, 1949, 1953; Wienert, 1950; Yanateva, 1948, 1949a, b; and Yanateva and Orlova, 1956.

NATURAL DEPOSITS

DISTRIBUTION

Lotze (1938, 1957) gave a detailed account of the world distribution of evaporites, from the Cambrian of Pakistan, Iran, and Siberia to the present day sea-margin deposits of various countries. His work included comprehensive bibliographies. Such an account is beyond the scope of the present work, but it is desirable to give some data showing such general features of evaporite deposits as thickness and frequency of different types, in addition to data on typical natural successions of rock types.

Table 18 is based mainly on the information collected by Krumbein (1951) and shows the distribution in space and time, the thicknesses, and the types of marine evaporites in the conterminous United States. The table shows very clearly the common occurrence of the

less soluble deposits and the rarity of the highly soluble bittern salts. Most natural deposits, in fact, consist of gypsum and (or) anhydrite interbedded with dolomite, limestone, and red beds or other clastic sediments. The bittern salts are found in the conterminous United States in appreciable quantity only in the Prairie Formation (Middle Devonian) of the Williston basin, the Pennsylvanian of the Paradox basin in Utah, and the Permian Salado and Rustler Formations of Texas and New Mexico. Lotze (1957, p. 184-186) listed a total of 42 occurrences of potassium salts in the evaporites of the world, and of these, less than half refer to marine deposits of significant size. The best known are those of the Zechstein of western Europe, the Permian of the Southwestern United States, the Permian of the U.S.S.R. (such as at Solikamsk and Ozinsky), the Oligocene of Spain and Alsace, the Miocene of Poland, and the Devonian of the Williston basin of North Dakota and Saskatchewan.

NATURAL SUCCESSIONS

Many small evaporite bodies show at least the earlier part of the expected succession from carbonate to sulfate, halite, and potash zones, with some repetitions of sequence. In the larger evaporite bodies the sequences are generally complex. The areas of deposition of two of these large bodies—the Zechstein of Europe and the Salado Formation of Texas and New Mexico—are shown in figures 11 and 12. The Zechstein covers an area of about 400,000 square miles, if we accept the submarine extension shown in figure 11. The Salado Formation covers about 50,000 square miles and is underlain in part by an earlier set of carbonate- and sulfate-bearing evaporites (the Castile Formation) which covers about 10,000 square miles. The Salado and Castile have a combined thickness of more than 4,000 feet.

These two great bodies are typical of the more complete evaporite successions. Table 19 shows the general succession of rocks in two regions of the Zechstein basin—the Hanover-Thuringia region and the north of England—with a tentative correlation. The distribution of major and minor mineral constituents in part of the English succession is shown in figure 13. Plate 1 (Jones, 1954) shows the Castile, Salado, and Rustler successions. Much of the complexity is caused by repetitions of the types discussed on pages 5-6, and by the presence of interbedded layers of limestone, dolomite rock, or clastic material. There are gradations between some of the evaporite layers (for example, a halite-anhydrite zone is commonly found between halite and sulfate zones), but, in general, the chemical differentiation between the principal zones has been remarkably effective.

TABLE 18.—*Marine evaporite deposits of the conterminous United States*

(Thicknesses are approximate and include interbedded nonevaporitic sediments. Evaporite types are calcium sulfates, including gypsum and anhydrite, S; halite, H; and bedded bittern salts of potassium and magnesium, B. (After W. C. Krumbein, 1951, with slight modifications.)

Age	Area	Formation or interval	Thickness of evaporite section (ft)	Evaporite type		
Ordovician	Williston basin Illinois basin	Whitewood-Bighorn	25	S		
		Joachim	50	S		
Silurian or Devonian	Williston basin Michigan basin New York West Virginia Iowa-Missouri	Niagaran	25	S		
		Bass Island, Salina	3,000	S, H		
		Camillus, Syracuse	500	S, H		
		Salina	800	S		
		Niagaran-Cayugan?	100	S		
Devonian	Williston basin Iowa Michigan Basin Southwestern Montana	Potlatch, Jefferson	400	S		
		Prairie	600	S, H, B		
		Cedar Valley-Wapsipinicon	50	S		
		Detroit River	1,200	H		
		Three Forks	50	S		
Mississippian	Williston basin Southwestern Montana Iowa Illinois basin Michigan basin Western Virginia	Otter, Charles	1,000	S		
		Kibbey	100	S		
		Keokuk	30	S		
		St. Louis	200	S		
		Michigan	350	H		
		Maccrady	1,000?	S, H		
Pennsylvanian or	Paradox basin, Utah Gypsum basin, Colorado Black Hills region	Paradox	4,000	S, H, B		
		Maroon	500+	S		
		Minnelusa	50	S		
Permian	Michigan basin	Virgilian?	50+	S		
Permian	Black Hills Gypsum basin, Colorado Grand Canyon area Northern New Mexico South central New Mexico Southeastern New Mexico Central Texas Texas Panhandle Oklahoma Panhandle Western Oklahoma West central Kansas Iowa	Minnekahta, Opeche	100	S		
		Maroon	500	S		
		Kaibab, Toroweap	900	S, H		
		San Andres	100	S		
		Yeso, Abo	2,000	S, H		
		Chalk Bluff, Whitehorse	1,000	S, H		
		Rustler, Salado, Castle	4,500	S, H, B		
		San Angelo, Clear Fork, Wichita	1,500	S		
		Pease River, Clear Fork, Wichita	2,000	S		
		Dog Creek, Blaine, Cimarron	1,000	S		
		Blaine, Clear Fork, Wichita	1,500	S, H		
		Harper, Wellington, Marion	800	S, H		
		Leonardian?	50	S		
		or Jurassic	Gulf Coast	Louann, Werner	1,500±	S, H
		Triassic	Wyoming, Nebraska, North and South Dakota.	Chugwater	several hundred	S
		Jurassic	Central Wyoming Central Montana Southeastern Idaho Central Utah South central Utah North central New Mexico East central Colorado Southern Arkansas Northeastern Texas Southwestern Alabama	Gypsum Springs	200	S
Gypsum Springs	100			S		
Preuss	450			S, H		
Arapien	1,000?			H		
Carmel	400			S		
Todilto	100			S		
Summerville equivalent	200			S		
Buckner	350			S		
Buckner	700±			S, H		
Buckner	950			S, H		
Cretaceous	Northwestern Louisiana Southwestern Texas South central Florida Southeastern Florida			Ferry Lake	300±	S
		Fredericksburg	150	S, H		
		Comanchean	6,000	S		
		Comanchean	4,000+	S, H		
Tertiary	Florida	?	several hundred	S		

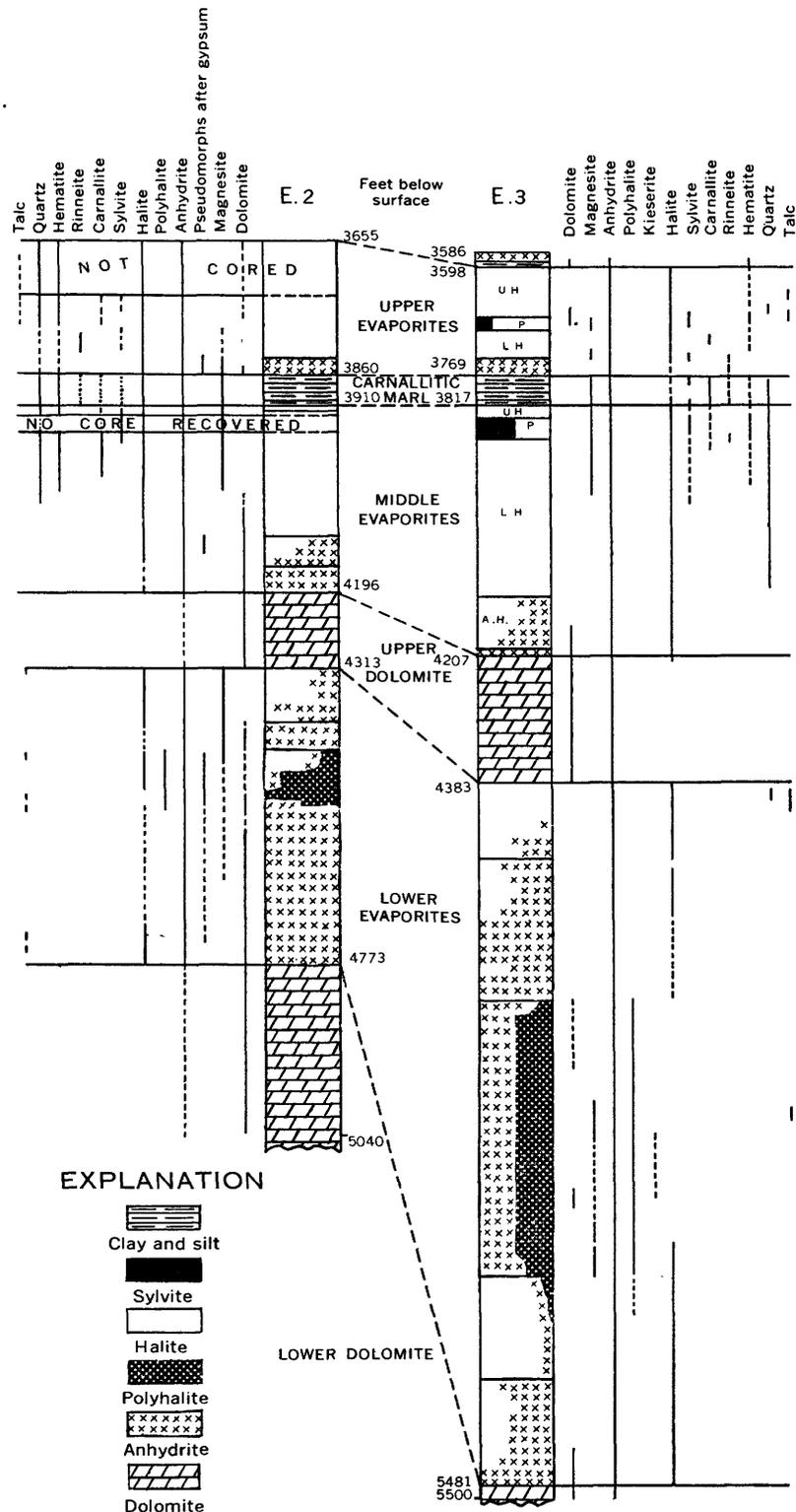


FIGURE 13.—Succession and mineral distribution in the evaporites of two boreholes through the English Zechstein; the E. 2 borehole at Aislaby (based on Stewart, 1949, 1951 a, b) and the E. 3 borehole at Sleights (based on Armstrong and others, 1951), in the Whitby district, Yorkshire. (From Stewart, 1954, fig. 9.)

TABLE 19.—*Evaporite successions in the German and English Zechstein*

[German data based on Hartwig (1941), Lotze (1938), and Fulda (1935). English data from Stewart (1949, 1951a, 1951b, 1954), Armstrong and others (1951), and Raymond (1953). Figures on thicknesses of the English and German successions are approximate, as there is considerable variation from place to place. Correlation based on Lotze (1958), but in absence of reliable paleontological evidence must remain uncertain. Possibly the three principal British cycles correspond generally with the upper three German cycles (Stewart, 1954), but in the present state of knowledge Lotze's correlation is to be preferred]

	Bed	Hanover and Thuringia (normal succession)		Whitby district, England	
			Thickness (ft)		Thickness (ft)
Upper Zechstein		Oberer Zechsteinletten	16	Upper Permian marl	up to 600
	Fourth evaporite	Grenzanhydrit und Tonmischsalz	30	Top anhydrite	2-4
		Jüngstes Steinsalz (with minor potash zone of Ottosshall)	350		
		Pegmatitanhydrit	3-5		
		Jüngerer (Roter) Salzton	50	Salt clay	7-12
	Third evaporite	Tonbrecciensalz	20-50	Upper evaporites	Upper halite 50-90 Potash zone 0-28 Lower halite 41-64 Anhydrite 17-28 Carbonate 2-4
		Oberes Jüngerer Kalilager (Riedel potash zone)	15-30		
		Oberes Jüngerer Steinsalz	230-500		
		Unteres Jüngerer Kalilager (Ronnenberg potash zone)	15-30		
		Unteres Jüngerer Steinsalz Hauptanhydrit	130-165 115		
	Älterer (Grauer) Salzton (dolomite in upper part)	26	Carnallitic marl	31-61	
Second evaporite	Decksteinsalz	3-10	Middle evaporites	Upper halite 0-17 Potash zone 11-13 Lower halite 92-277 Halite-anhydrite } Anhydrite } 50-92	
	Älteres Kalilager (Stassfurt potash zone)	20-65			
	Älteres Steinsalz Basalanhydrit	130-2, 300 6			
	Hauptdolomit und Stinkschiefer, mit Schlamm, Grundkonglomerat	30	Upper Magnesian Limestone (marl in part)	117-183	
Middle Zechstein	First evaporite	Oberer Mittlerer Zechsteinanhydrit	70	Lower evaporites	Upper halite-anhydrite 40-117 Upper anhydrite 40-670 Lower halite-anhydrite } polyhalite in part Lower anhydrite } 46-142 151-309
		Ältestes Steinsalz	20		
		Unterer Mittlerer Zechsteinanhydrit	100		
Lower Zechstein		Zechsteinkalk	13	Lower Magnesian Limestone, with some anhydrite	365±
		Kupferschiefer	1		
		Zechsteinkonglomerat	6		

Table 20 shows estimates of the proportions of the principal rock types in the Salado and Paradox evaporite bodies. The bittern salts are included with halite rock, but from figure 12 and plate 1, and the data given by Smith (1933, 1938), they cannot amount to more than about 0.2 percent of the Salado Formation.

The closest approach, in natural deposits, to the experimental successions of tables 16 and 17 is seen in parts of the Zechstein of Germany and in certain of the Russian deposits. The best known case is the "older" German cycle (cycle 2). There is considerable lateral variation within this cycle, and two of the chief types of succession are given in table 21 (Phillips, 1947).

In the Stassfurt district (Bischof, 1875, Riedel,

TABLE 20.—*Proportion of lithological types in the Salado Formation, New Mexico and Texas, and the Paradox Member of the Hermosa Formation, Colorado and Utah*

[Written communications, 1958, from C. L. Jones (Salado) and E. M. Shoemaker (Paradox) of the U.S. Geol. Survey]

	Salado Formation (percent)	Paradox Member of the Hermosa Formation (percent)
Halide rocks (halite rock, sylvite rock, and others)-----	84	70
Sulfate rocks (anhydrite rock, gypsum rock, and polyhalite rock)-----	12	2
Carbonate rocks (limestone and dolomite rock)-----	0	4
Clastic rocks (sandstone, siltstone, and claystone)-----	4	24

1913; Rozsa, 1914; Lotze, 1938) the following zones or "regions" have been found in the older cycle:

6. Gray salt clay; 5-10 meters thick.
5. Carnallite zone; 15-40 meters thick. Made up of carnallite-halite-kieserite rock, interbedded with halite rock. Average mineral composition (Bischof, 1875; Everding, 1907; Boeke, 1910) is about 55-59 percent carnallite, 22-25 percent halite, 16-17 percent kieserite, 2-4 percent other minerals, including anhydrite, boracite, and clay. In places the carnallite zone is overlain by a cap of secondary kainite formed by leaching of the earlier salts by ground water.
4. Kieserite zone, 20-60 meters thick. Average composition about 65 percent halite, 17 percent kieserite, 13 percent carnallite, 2 percent anhydrite, and 3 percent polyhalite, sylvite, tachyhydrite, bischofite, and others.
3. Polyhalite zone: 40-60 meters thick. Halite with thin layers, patches and disseminated grains of polyhalite. Average composition (Riedel, 1913; Rozsa, 1914) about 93 percent halite, 5 percent polyhalite, 2 percent anhydrite.
2. Anhydrite zone, 300-800 meters thick. Halite with layers of anhydrite which are about 7 mm thick on the average and have been interpreted as annual varves ("Jahresring"). Anhydrite decreases in quantity from about 9 percent near the base to less than 4 percent at the top. Average composition (Riedel, 1913; Rozsa, 1914) is about 96 percent halite, 4 percent anhydrite, with very small amounts of clay and carbonaceous matter, and traces of polyhalite and carnallite.

1. "Older" anhydrite, with some halite and dolomite; as thick as 100 meters.

The kieserite, polyhalite, and anhydrite zones (zones 4, 3, 2) represent the "older rock salt."

These German successions resemble the theoretical successions by having zones that contain anhydrite, polyhalite, and kieserite between the principal potash zone and the calcium sulfate zone. Still, these intermediate zones differ from the theoretical ones in several important respects; for example absence of kainite, blödite, and epsomite. In most natural deposits, however, the intermediate zones are represented by halite rock containing only very small quantities of minerals like polyhalite and carnallite. In the Salado Formation, for example (Adams, 1944; Dunlap, 1951; Kroenlein, 1939; Smith, 1933, 1938), there is a series of many different potassium-rich layers interbedded with halitic and anhydrite-polyhalite layers; but the potassium-rich layers are mainly of one type, sylvite-halite rock (sylvinite). Locally, langbeinite, carnallite, and kieserite are major constituents of the potash zones, but the halite rocks contain only very small quantities of potassium and magnesium-bearing minerals. Polyhalite is mainly secondary, replacing anhydrite.

In many natural potash deposits, potassium and magnesium sulfates are practically absent. In Alsace and Baden (Sturmfels, 1943) and in the Verkhnekama deposits (Preobrazhenskii, 1939), sylvite and carnallite are the only potassium-bearing minerals known to occur in significant quantity. The same is true of the Prairie evaporites of North Dakota and Saskatchewan, and the Paradox evaporites of Utah and Colorado (Dyer, 1945; Hite and Gere, 1958; Tomkins, 1955). In the Upper and Middle Evaporites of the English Zechstein, halite zones with negligible amounts of sulfates are succeeded by halite-sylvite zones, the sylvite of the Middle Evaporites partly replacing earlier carnallite (Stewart, 1956). Even polyhalite is absent.

In summary, it can be said that, neglecting repetitions, most of the more complete natural successions show the upward sequence: carbonate-anhydrite; anhydrite-halite; halite; sylvinite and (or) hartsalz and (or) carnallite-halite rock (\pm kieserite). In some deposits, other minerals, such as langbeinite, are abundant local constituents of potash zones, and polyhalite is a major secondary constituent of sulfate zones. A few deposits (for example, the "Older" cycle of Germany) have a more complete succession, as follows: carbonate; anhydrite; halite-anhydrite; halite-polyhalite; halite-kieserite; halite-kieserite-carnallite and (or) hartsalz. Such salts as langbeinite, loewite, and vanthoffite are local constituents of the inter-

TABLE 21.—Successions in the "older" evaporite cycle of the German Zechstein

[From Phillips, 1947, p. 100]

	Carnallite succession	Hartsalz succession
Older potash beds.	Carnallite with kieserite and halite.	Carnallite with kieserite and halite. Sylvite with kieserite and halite.
Transition beds.	Halite with kieserite and carnallite.	Halite with langbeinite.
	Halite with kieserite and sylvite.	Halite with loewite. Halite with vanthoffite.
	Halite with polyhalite.	
Older rocksalt.	Halite with glauberite. Halite with anhydrite.	

mediate zones, and glauberite is a minor constituent of the lower zones. Kainite may occur in any of the types of deposit, but is of secondary origin. No primary bischofite zone is found.

CHEMICAL COMPOSITION

Chemical analyses of typical evaporite rocks are given in tables 22-26.

In the sulfate zones, most of the calcium, sulfur, and oxygen of evaporites is concentrated, as is much of the hydrogen if the sulfate mineral is gypsum. A good deal of magnesium may be present in dolomite in these zones. The principal rock type is anhydrite rock, and this is often very pure. All stages between anhydrite rock and gypsum rock are found in near-surface deposits. Sometimes a considerable amount of carbonate is present (generally as dolomite, less commonly as calcite or magnesite), and where it is abundant, it is generally (though not always) concentrated in layers, many of which are very thin. Analyses of typical gypsum, gypsum-anhydrite, and anhydrite rocks, with and without carbonate, are given in tables 22 and 23. Secondary polyhalite is sometimes present in the sulfate zones, and all stages between polyhalite rock and anhydrite rock occur. Analyses of typical polyhalite rocks are given in tables 22 and 23. In the Salado Formation (Schaller and Henderson, 1932) and the Lower Evaporites of the English Zechstein (Stewart, 1949), large amounts of potassium and magnesium are fixed in polyhalite.

Most of the sodium and chlorine is concentrated in the halite zones. Some halite rocks are extremely pure (occasionally as much as 99.9 percent NaCl), but most contain a small amount of anhydrite or polyhalite and more or less clastic material. There are all stages between halite rock and salt clay, and between halite rock and anhydrite rock or polyhalite rock, but most of the thick halite zones of the larger deposits are more than 90 percent halite. Analyses of typical halite rocks are given in table 24. Analyses of salt clays and clastic

rocks of evaporite sequences are given in tables 23 and 26.

In the "potash" zones, much of the potassium and magnesium is concentrated, together with chlorine, bromine, sulfur, oxygen, and hydrogen. The rocks are extremely variable in mineral composition; practically all contain halite and many enclose a fair amount of clastic material. The most abundant rock types are halite-sylvite rock (sylvinite), halite-sylvite-kieserite rock (hartsalz), halite-sylvite-anhydrite rock (anhydritic hartsalz), and carnallite-halite-kieserite rock. Less common are halite-sylvite-langbeinite rock (langbeinitic hartsalz), kainite-bearing rocks, and rocks containing the relatively rare salts tachyhydrite, vanthoffite, loeweite, and rinneite. Analyses of the principal rock types are given in table 25, and of average samples of sylvinite zones and of carnallitic clay in table 26.

MINOR AND TRACE ELEMENTS

Our knowledge of the content of minor and trace elements is patchy. The sulfate zones carry barium, fluorine, and strontium. Argon is mainly derived from potassium and is therefore concentrated in potash zones and clays. Bromine and rubidium occur principally in the potash zones, where iron is also locally relatively abundant. Lithium is concentrated in connate inclusions of mother liquor in the potash zones. Many minor elements occur principally in the associated clastic material—for example, chromium, cesium, copper, iron, gallium, manganese, phosphorus, titanium, vanadium, zinc, zirconium, and most of the silicon and aluminum.

Some colorimetric data are given in tables 23 and 24, and spectrographic data in tables 7 and 26. Herrmann (1958) made a detailed spectrographic study of the occurrence of lead, zinc, tin, copper, manganese, silver, aluminum and strontium in halite, sylvite, carnallite, and insoluble residues separated from German Zechstein evaporites. Averages and ranges of composition

TABLE 22.—Chemical analyses of gypsum-, anhydrite-, and polyhalite-bearing rocks of marine evaporites

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
SiO ₂			0.25	0.10		0.51	4.14			Trace					
Al ₂ O ₃	0.10	0.08		.12		.03	.89			Trace	0.03				
Fe ₂ O ₃01		Trace	.09	.10		0.14	Trace					
CaO.....	32.37	32.33	34.20	32.44	32.72	32.49	31.40	35.29	38.46	40.61	42.64	18.71	18.62	18.90	15.33
SrO.....						.10									1.06
MgO.....	Trace	.05	Nil	.33	.41	.92	.99	Trace	.24		.02	6.72	6.47	6.87	8.89
K ₂ O.....									.19			15.64	15.53	15.42	13.31
Na ₂ O.....	.10	.14				Trace			.07			Nil	.01	.02	
H ₂ O.....	20.94	20.96	20.00	20.80	20.20	19.67	18.39	15.88	12.69	1.87		6.08	6.00	5.84	6.25
CO ₂85	1.18	1.54	2.33	.65	7.73		5.15	Trace	Trace	.39	2.66
SO ₂	46.18	46.18	45.50	45.45	45.33	45.07	41.13	48.14	39.53	56.82	51.52	53.04	52.87	52.50	47.36
Cl.....	Trace	.03	Nil						.04			Nil	Nil	Nil	.77
Organic.....						Present		Trace		.46	1.05				
Insoluble.....	.10	.05			.24				.45		1.28	.18	.18	.27	
Total.....	99.79	99.82	99.96	100.09	100.08	100.42	99.37	99.96	99.54	99.76	99.86	100.37	99.68	100.21	95.63

¹ Soluble in chloroform.

² Ignited insoluble in acid.

³ Includes also carbonaceous matter, 0.17.

- A. Gypsum rock. From Hillsboro, New Brunswick, Canada. Analyst: G. Steiger (Clarke, 1915, p. 358).
 B. Gypsum rock. From Alabaster, Mich. Analyst: G. Steiger (Clarke, 1915, p. 358).
 C. Gypsum rock. From Big Horn Basin, Wyo. Analyst: W. C. Wheeler (Wells, 1937, p. 122).
 D. Gypsum rock. From east of Cascade, Black Hills, S. Dak. Analyst: G. Steiger (Clarke, 1915, p. 358).
 E. Gypsum rock. From 60-foot bed near top of Minnelusa sandstone, Sundance Canyon, near Rocky Ford, Wyo. Analyst: J. G. Fairchild (Wells, 1937, p. 122).
 F. Gypsum rock. From Rico-Aspen mine, Rico district, Colorado. Analyst: W. F. Hillebrand (Clarke, 1915, p. 358). Also contains trace of TiO₂.
 G. Gypsum-carbonate rock. From Waterloo Mountain, Montpelier, Idaho. Analyst: W. C. Wheeler (Clarke, 1915, p. 359).
 H. Gypsum-anhydrite rock. From Nephi, Utah. Analyst: E. T. Allen (Adams and others, 1904, p. 106).
 I. Gypsum-anhydrite-calcite rock. From Nephi, Utah. Analyst: E. T. Allen (Adams and others, 1904, p. 106).
 J. Anhydrite rock. From 2½ miles east of Gypsum, Colo. Analyst: J. G. Fairchild (Clarke, 1915, p. 357).
 K. Anhydrite-carbonate rock. Banded material from Caesar Grandi well 1, Eddy County, N. Mex. Analyst: E. T. Erickson (Wells, 1937, p. 120).
 L. Polyhalite rock, formed by secondary replacement of halite rock. From Lower Evaporites (Zechstein), Eskdale No. 2 boring, Aislaby, near Whitby, Yorkshire, England. Analyst: F. H. Stewart (Stewart, 1949, p. 657).
 M. Polyhalite rock, formed by secondary replacement of anhydrite-halite rock. From Lower Evaporites (Zechstein), Eskdale No. 2 boring, Aislaby, near Whitby, Yorkshire, England. Analyst: F. H. Stewart (Stewart, 1949, p. 657).
 N. Polyhalite-dolomite rock, formed by secondary replacement of anhydrite-dolomite rock. From Lower Evaporites (Zechstein), Eskdale No. 2 boring, Aislaby, near Whitby, Yorkshire, England. Analyst: F. H. Stewart (Stewart, 1949, p. 657).
 O. Polyhalite-kieserite rock (partial analysis; material soluble in dilute HCl). From Lower Evaporites (Zechstein), Eskdale No. 3 boring, Sleights, near Whitby, Yorkshire, England. Analyst: W. F. Waters. Spectrographic determinations by J. A. C. McLelland gave: Li, not detected, <0.01; Rb, Cs, not detected, <0.1; Ba, Ti, Pb, not detected; Mn, slight trace; Sr, 0.9; B, approximately 0.02. The analysis has been recast in the form of oxides. (Armstrong and others, 1951, p. 673).

TABLE 23.—Analyses (weight percent) of anhydrite rock, polyhalite rock, and associated sedimentary rocks of the marine evaporite succession of the Paradox basin of Utah, and the Salado Formation of Texas and New Mexico

[From Moore (1960, p. 114-117). Methods development and analyses supervised by F. S. Grimaldi, U.S. Geological Survey]

	A	B	C	D	E	F	G	H	I
Al.....	0.017	0.0042	0.0095	0.0095	1.15	6.12	3.21	1.42	0.95
Ba.....	<.0021	.00062	.0013	.0013	.0071	.0040	.015	.024	.0040
Ba.....	<.0009	.0023	<.0013	.0015	.015	.028	.034	.081	.013
Br.....	<.002	<.002	<.002	<.002	.006	.01	.006	<.002	<.002
(Carbonate.....	1.76	.18	2.82	.041	9.47	2.34	3.38	1.66	.15
(Organic.....	.10	.01	.07	.01	.15	8.23	.01	.04	
(Total.....	1.86	.19	2.89	.052	9.62	10.57	3.39	1.70	.16
Ca.....	27.17	25.44	22.43	11.81	28.32	8.58	3.63	12.60	.19
Cl.....	.15	6.94	2.05	4.71	.47	2.03	2.48	1.69	47.92
Cu.....	.0014	.00046	.00014	.0013	.00013	.0046	.0096	.00056	.0013
F.....	<.001	<.001	.035	.035	.31	.76	.76	.12	.012
Fe.....	1.03	.0020	.0084	.0070	.68	3.18	1.06	.62	.33
H.....	.060	.028	.007	.61	.14	1.06	.38	.66	.16
I.....	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K.....	.17	.025	.075	11.83	.83	3.78	.81	4.08	.78
Mg.....	1.83	.43	5.91	3.90	2.71	2.75	3.00	7.41	1.56
Mn.....	.015	.00014	.00093	.00046	.036	.050	.021	.010	.0039
Mo.....	.00043	<.00003	<.00003	<.00003	.0022	.00050	<.00003	.00010	<.00003
Na.....	.067	4.67	1.31	3.06	.082	.082	.71	.82	30.80
Ni.....	.00012	<.00008	.00008	<.00008	.00079	.0094	.0020	.0012	.00044
O ₁	46.62	41.74	47.13	44.44	47.87	42.40	48.51	48.69	10.69
Pb.....	.00052	.000084	.000074	.000046	<.000009	.00037	.00093	.0011	.00040
S.....	20.04	20.42	17.97	19.48	.87	2.70	.62	13.12	.40
Se.....	<.00005	<.00005	<.00005	<.00005	.00006	<.00005	<.00005	<.00005	<.00005
Si.....	.90	.030	.043	.043	6.54	16.59	24.96	6.98	5.92
Sr.....	.054	.071	.074	.40	.028	.027	.011	.025	.0089
Th.....	<.00002	<.00002	<.00002	<.00002	.00017	.00097	.00045	.00023	.00015
Ti.....	.010	.000078	.0010	.00050	.066	.36	.23	.12	.078
U.....	.000042	.000043	.000025	.000015	.00065	.0025	.00021	.00017	.000048
V.....	.00025	.00003	.00012	<.00003	.00073	.014	.0020	.0012	.00039
Zn.....	.000088	.000034	.00016	.00025	.00021	.0021	.00080	.00028	.00061
Zr.....	.0036	.0013	.0038	.0022	.025	.043	.047	.016	.017

¹ Difference from 100 percent, calculated.

- A. Anhydrite rock. From Paradox Member of the Hermosa Formation of Pennsylvanian age; depth, 3,616 ft; Delhi-Taylor No. 8, sec. 1, T. 25 S., R. 20 E., Grand County, Utah.
 B. Massive anhydrite rock with minor halite inclusions. From Salado Formation of Permian age; depth, 2,452 ft; U.S. Potash Corp. No. 125(S), sec. 25, T. 23 S., R. 34 E., Lea County, N. Mex.
 C. Laminated anhydrite rock (Cowden). From Salado Formation of Permian age; depth, 2,841 ft; U.S. Potash Corp. No. 125(S), sec. 25, T. 23 S., R. 34 E., Lea County, N. Mex.
 D. Polyhalite rock with halite inclusions. From Salado Formation of Permian age; depth, 2,125 ft; U.S. Potash Corp. No. 125(S), sec. 25, T. 23 S., R. 34 E., Lea County, N. Mex.
 E. Limestone. From Paradox Member of the Hermosa Formation of Pennsylvanian age; depth, 3,699 ft; Delhi-Taylor No. 8, sec. 1, T. 25 S., R. 20 E., Grand County, Utah.
 F. Black shale. From Paradox Member of the Hermosa Formation of Pennsylvanian age; depth, 3,788 ft; Delhi-Taylor No. 8, sec. 1, T. 25 S., R. 20 E., Grand County, Utah.
 G. Siltstone. From Paradox Member of the Hermosa Formation of Pennsylvanian age; depth, 3,951 ft; Delhi-Taylor No. 8, sec. 1, T. 25 S., R. 20 E., Grand County, Utah.
 H. Claystone. From Salado Formation of Permian age; depths, 1,860, 1,954, 2,290, 2,333, and 2,361 ft; U.S. Potash Corp. No. 125(S), sec. 25, T. 23 S., R. 34 E., Lea County, N. Mex.
 I. Mixed halite rock, claystone, and siltstone. From Salado Formation of Permian age; depth, 2,142 ft; U.S. Potash Corp. No. 125(S), sec. 25, T. 23 S., R. 34 E., Lea County, N. Mex.

TABLE 24.—Analyses of halite rocks of marine evaporites (weight percent)

[From Moore, (1960, p. 111-113). Methods development and analyses supervised by F. S. Grimaldi, U.S. Geological Survey]

	A	B	C	D	E	F	G
Al.....	0.0023	0.0035	0.0035	0.0011	0.0013	0.0015	0.0011
B.....	.00053	.00016	.00065	.00013	.00011	.00034	.00037
Ba.....	.00027	.00018	.00018	.00009	.00009	.00027	.00027
Br.....	.002	.02	.003	.004	.003	.005	.01
C.....	.006	.01	.006	.01	.006	.006	.006
Ca.....	.47	1.16	.13	1.09	1.54	1.72	.46
Cl.....	59.57	57.94	60.13	58.43	57.71	58.97	59.74
Cu.....	.00065	.00023	.00022	.00055	.00023	.00021	.00010
F.....	.013	.005	<.001	<.001	<.001	<.001	.001
Fe.....	.00077	.0015	.0022	.00091	.00070	.00013	.00063
H.....	.001	.017	.003	.001	.001	.001	.002
I.....	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K.....	.032	.16	.17	.017	.0083	.0027	.0042
Mg.....	.025	.13	.066	.0024	.0097	.010	.011
Mn.....	<.00002	<.00002	<.00002	.00043	.0011	.0020	.00009
Mo.....	<.00003	<.00003	<.00003	<.00003	<.00003	<.00003	<.00003
Na.....	38.61	37.40	38.82	37.92	37.21	37.01	38.64
Ni.....	.00016	.00024	.00020	.00022	.00035	.00023	.00035
O ¹87	2.11	.45	1.63	2.28	2.87	.75
Pb.....	.00012	.00011	.000074	.00054	.00015	.00012	.00066
S.....	.38	1.00	.19	.88	1.22	1.39	.36
Se.....	<.00005	<.00005	<.00005	<.00005	<.00005	<.00005	<.00005
Si.....	.0065	.024	.016	.0022	.0037	.0065	.0032
Sr.....	.0088	.018	.0056	.0062	.0081	.0052	.0048
Th.....	<.00002	<.00002	<.00002	<.00002	<.00002	<.00002	<.00002
Ti.....	.000060	.00016	.00013	.00060	.00096	.00034	.00060
U.....	.0000025	.0000015	.0000015	.0000010	.0000010	.0000010	.0000010
V.....	<.00003	<.00003	<.00003	<.00003	<.00003	<.00003	<.00003
Zn.....	.000056	.000012	.00011	.00012	.00030	.00012	.00008
Zr.....	<.00004	<.00004	<.00004	<.00004	<.00004	<.00004	<.00004

¹ Difference from 100 percent, calculated.

- A. Massive halite rock. From Paradox Member of the Hermosa Formation of Pennsylvanian age; depth 2,394 ft.; Delhi-Taylor No. 8, sec. 1, T. 25 S., R. 20 E., Grand County, Utah.
- B. Thin-bedded halite rock. From Paradox Member of the Hermosa Formation of Pennsylvanian age; depth 2,902 ft.; Delhi-Taylor No. 8, sec. 1, T. 25 S., R. 20 E., Grand County, Utah.
- C. Halite with polyhalite blebs. From Salado Formation of Permian age; depth 1,872 and 1,956 ft.; U.S. Potash Corp. No. 125(S), sec. 25, T. 23 S., R. 34 E., Lea County, N. Mex.
- D. Halite rock. From Orchard salt dome; depth 1,258 to 1,275 ft.; Duval Sulphur and Potash Co., Moore Estate, well no. 554, Fort Bend County, Tex.
- E. Halite rock. From Venice salt dome; depth 2,893 to 2,896 ft.; Tidewater Oil Co., Buras Levee district, no. 5, Plaquemines Parish, La.
- F. Halite rock. From Venice salt dome; depth 3,785 to 3,805 ft.; Tidewater Oil Co., Buras Levee district, no. 5, Plaquemines Parish, La.
- G. Halite rock. From Block 16 salt dome; depth 2,351 to 2,361 ft.; Humble Oil Corp.; lease 800, core test no. 3, Jefferson Parish, La.

TABLE 25.—Analyses of potassium-bearing marine evaporite rocks

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Mg.....	0.02	0.08	0.33	2.48	4.83	0.22	0.34	0.83	0.05	6.58	7.09	6.67	5.40	4.56	8.00
Ca.....	1.09	.15	.18	.50	.59	4.25	4.15	4.33	7.79	.80	.59	.37	.35	-----	.93
Na.....	23.25	35.55	24.39	30.81	17.70	31.49	28.09	20.85	12.66	11.78	6.69	10.74	20.50	22.49	7.45
K.....	15.01	4.58	18.17	2.94	11.71	2.50	6.44	13.50	21.13	8.96	11.40	11.27	8.85	2.78	8.77
SO ₄	2.26	.36	.84	10.28	18.76	11.06	11.16	12.31	18.90	10.96	1.41	26.56	31.06	67.43	9.34
Cl.....	50.23	59.20	54.73	50.53	39.19	50.68	49.11	45.28	38.40	38.70	41.31	27.25	33.07	.73	37.50
H ₂ O.....	.32	.13	1.09	2.59	5.48	.16	.32	2.64	.17	22.03	31.51	14.44	.71	1.80	27.48
SiO ₂	-----	-----	-----	.05	-----	.05	.40	.39	-----	.27	-----	-----	-----	-----	-----
Al ₂ O ₃	-----	-----	-----	.04	-----	.02	.17	.17	-----	.24	-----	-----	-----	-----	-----
Fe ₂ O ₃	-----	-----	-----	.03	-----	.01	.04	.04	-----	.03	-----	-----	-----	-----	-----
Insoluble.....	7.51	.36	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	.30
Clay, waterfree.....	-----	-----	.26	-----	-----	-----	-----	-----	.70	-----	-----	2.71	-----	-----	-----
Total.....	99.69	100.41	99.99	100.25	99.98	100.44	100.22	100.34	99.80	100.25	100.00	100.01	99.94	99.79	99.77

- A. Halite-sylvite rock ("Sylvinit"). From Amelle mine, near Mulhouse, Alsace. Average of two analyses of average samples as mined and shipped. Analyst: E. T. Erickson (Wells, 1937, p. 88).
- B. Halite-sylvite rock, with accessory anhydrite and magnesite. From Malagash, Nova Scotia. (H. C. Rickaby, 1923, p. 46.) Ca and SO₄ given originally as CaO and SO₄.
- C. Halite-sylvite rock ("Sylvinit"). Normal composition, Germany. (Boeke, 1910.) 0.22 Mg is soluble and 0.11 Mg insoluble in alcohol.
- D. Halite-kieserite-sylvite rock ("Kieseritischer Halit"). From Glückauf-Sonderhausen, Germany. (Naumann, 1911, p. 618.) Mineral composition is halite 78.19, sylvite 5.12, kieserite 13.13, anhydrite 1.67, carnallite 1.89.
- E. Halite-sylvite-kieserite rock ("Hartsalz"). Normal composition, Germany. (Boeke, 1910.) In alcohol, 0.44 Mg is soluble and 4.39 Mg insoluble.
- F. Halite-anhydrite-sylvite rock ("Anhydritischer Halit"). From Glückauf-Sonderhausen, Germany. (Naumann, 1911, p. 618.) Mineral composition is halite 79.91, sylvite 4.77, kieserite 1.28, anhydrite 14.41.
- G. Halite-anhydrite-sylvite rock ("Anhydritischer Sylvinit"). From Glückauf-Sonderhausen, Germany. (Naumann, 1911, p. 618.) Mineral composition is halite 71.37, sylvite 12.27, kieserite 1.79, anhydrite 14.08.
- H. Halite-sylvite-anhydrite-carnallite rock ("Anhydritischer Sylvinit"). From Glückauf-Sonderhausen, Germany. (Naumann, 1911, p. 618.) Mineral composition is halite 52.92, sylvite 24.68, kieserite 2.79, anhydrite 14.70, carnallite 3.88.
- I. Sylvite-halite-anhydrite rock ("Anhydritsart"). From Wolframshausen, Germany. (Boeke, 1910.) 0.02 Mg is soluble and 0.03 Mg insoluble in alcohol.
- J. Kieserite-carnallite-halite rock ("Kieseritischer Halitcarnallit"). From Glückauf-Sonderhausen, Germany. (Naumann, 1911, p. 623.)
- K. Carnallite-halite rock ("Halitcarnallit"). Normal composition, Germany. (Boeke, 1910.) 7.09 Mg soluble in alcohol.
- L. Halite-kainite rock ("Halitkainit"). Normal composition, Germany. (Boeke, 1910.) 6.67 Mg insoluble in alcohol.
- M. Langbeinite-halite rock ("Langbeinitthalit"). From Gewerkschaft Friedrich-Franz, Lubtheen, Germany. (Boeke, 1910.) 5.40 Mg insoluble in alcohol.
- N. Vanthoffite rock ("Vanthoffgestein"). From Wilhelmshall, near Anderbeck, Germany. (Boeke, 1910.) In alcohol 4.56 Mg insoluble.
- O. Carnallite-halite-kieserite-tachyhydrite rock. From Mansfelder Mulde, Germany. (Kling, 1915, p. 11.) Calculated mineral composition is carnallite 53.74, halite 18.98, kieserite 13.08, tachyhydrite 10.58, sylvite 2.29, anhydrite 0.37, insoluble 0.30.

TABLE 26.—Analyses of potash zones and salt clays of marine evaporites

[Analyses A, B, and C are from Armstrong and others, 1951, p. 679, 686, 688. Analyst, C. O. Harvey. Semiquantitative spectrographic determinations (marked *) by J. A. C. MacLelland. Water-insoluble material analyzed by semi-micro methods. N.d., not detected. ≈, nearly equal to. Ignition, matter volatile on ignition, other than CO₂ and S (mainly H₂O* [105°C]). The following were looked for, but not found, in the water-soluble parts: I, B*, Ba*, CO₂, Cs*, P₂O₅, Rb*, Tl*. The following were looked for spectrographically, but not found, in the water-insoluble parts of A and B: Be, Bi, Ce, Eu, Ga, Ge, In, La, Mo, Nb, Ni, Sb, Ta, Th, W, Yt, Zr]

	A	B	C	D
CHEMICAL ANALYSES				
Water-soluble matter				
Mg.....	0.09	0.09	0.88	0.19
Ca.....	1.22	.82	1.99	1.23
Na.....	19.47	29.16	6.72	2.07
K.....	21.70	6.73	1.62	2.10
SO ₄	2.74	1.81	2.77	.57
Cl.....	49.83	50.94	15.69	7.37
Br.....	.104	.014	.041	-----
Mn*.....	-----	N.d.	Trace	-----
Sr*.....	Trace	Trace	Trace	-----
Pb*.....	Trace	Trace	Trace	-----
Li*.....	N.d.	N.d.	Trace	-----
Water-insoluble matter				
SiO ₂	2.36	5.91	35.83	25.17
TiO ₂04	.08	.52	-----
Al ₂ O ₃59	1.49	10.47	9.79
B ₂ O ₃ *.....	≈.005	Trace	≈.1	-----
Cr ₂ O ₃	N.d.	N.d.	.01	-----
V ₂ O ₅ *.....	Trace	Trace	-----	-----
Fe ₂ O ₃12	.34	2.28	.82
FeO.....	.09	.19	.74	2.34
MgO.....	.72	.99	6.59	5.81
MnO*.....	-----	Trace	-----	-----
CaO.....	.02	.02	.21	11.63
SrO*.....	Trace	Trace	Trace	-----
BaO*.....	Trace	Trace	.02	-----
Na ₂ O.....	Trace	.02	.17	.07
K ₂ O.....	.04	.60	1.73	4.23
Li ₂ O.....	N.d.	N.d.	.02	-----
P ₂ O ₅	Trace	Trace	.10	-----
CO ₂11	.09	1.42	13.48
SO ₂03	Trace	.14	1.88
Cl.....	Trace	Trace	-----	-----
FeS ₂04	Trace	.04	-----
Ignition.....	.41	.51	3.62	10.10
Total H ₂ O—(105°C).....	.25	.25	5.60	-----
Organic.....	-----	-----	-----	2.01
Total.....	99.98	100.05	99.32	100.36

CALCULATED MINERAL COMPOSITION

	A	B
Halite.....	49.5	74.1
Sylvite.....	40.7	12.5
Carnallite.....	1.0	1.0
Anhydrite.....	4.0	2.6
Magnesite.....	.2	.1
Dolomite.....	-----	-----
Talc.....	2.0	2.9
Ilmenite.....	.08	.1
Hematite.....	.1	.3
Pyrite.....	.04	-----
Silicate minerals.....	1.9	6.8
Total.....	99.5	100.4

¹ Total water.

- A. A average sample of 31-foot bed of halite-sylvite rock; potash zone of Middle Evaporites (Zechstein). From Eskdale No. 3 borehole, Sleights, near Whitby, Yorkshire.
- B. A average sample of 18-foot bed of halite-sylvite rock; potash zone of Upper Evaporites (Zechstein). From Eskdale No. 3 borehole, Sleights, near Whitby, Yorkshire.
- C. A average sample of 40-foot bed of salt clay with about 10 percent carnallite and 17 percent halite; Carnallitic Marl between Upper and Middle Evaporites (Zechstein), from Eskdale No. 4 borehole, Sneaton, near Whitby, Yorkshire.
- D. A average of eight analyses of salt clays (Oligocene) from Wittelsheim, Alsace, selected from the analyses given by Gorgey (1912, p. 443). The content of organic material is exceptionally high.

computed from some of his data are given in tables 31, 32, and 33. Additional data for certain elements are given below.

Alkali metals.—The ionic radius of rubidium (1.49 Å) is not much larger than that of potassium (1.33 Å), which it replaces; natural carnallite contains 0.028–0.035 percent RbCl (Wilke-Dörfurt, 1912; Heyne, 1912). In halite, 0.0005–0.037 percent rubidium has been found (Thomson and Wardle, 1954; Berg, 1929). Cesium (1.65 Å) is very scarce in marine evaporites and is concentrated mainly in the associated clays; 21 ppm Cs₂O have been found in the Younger Salt Clay of the German Zechstein, and 2 ppm CsCl in carnallite (Goldschmidt, 1954; Jander and Busch, 1930). Lithium (0.78 Å) has been detected spectrographically in marine evaporites and is present in the associated clays and clastic material. Connate waters enclosed in the salts are rich in lithium (Fulda, 1939).

Argon.—Minute amounts of atmospheric argon may have been trapped in evaporites during their formation, but the argon present in potash deposits is mainly derived from the K⁴⁰ isotope. It has been used for age determination, and it is interesting that some salts in Permian rocks have given post-Permian ages (for example, Noddack and Zeitler, 1954; Smits and Gentner, 1950; Gentner and others, 1953, 1954). This suggests that such methods may prove useful in dating secondary changes.

Arsenic.—Gautier (1903) found 0.011 ppm arsenic in halite from Stassfurt and 0.03 ppm in salt from the coast of Brittany.

Barium.—Barium replaces calcium in anhydrite and gypsum but is usually much less abundant in halite rock (see tables 23 and 24). In German evaporites, von Engelhardt (1936) found 210 ppm barium in salt clay; 1–3 ppm in anhydrite rock and anhydrite-halite rock; 3–10 ppm in gypsum, polyhalite, some halite, carnallite, and sylvite; and <10 ppm in clear halite.

Boron.—Data on the boron content of minerals and rocks of marine evaporites are summarized in table 27; they were taken from the work of Blitz and Marcus (1911), Harder (1959), Kropachev (1960), and Moore (1960). (See tables 23 and 24.) There is agreement that the salt clays are notably enriched in boron. Harder has shown that this is true of clays in general. The boron contents of the other types of rocks and of the various minerals show very large variations; this might be due in part to irregular disseminations of borate minerals and in part to the presence of clay in the samples. Harder observed a notable enrichment of boron in the Zechstein Basal Anhydrite.

Bromine.—A selection of the numerous data on bromine is given in table 28.

TABLE 27.—Boron in the minerals and rocks of marine evaporites

Material	Number of samples	(ppm) Boron		Source of data
		Range	Average	
Halite rock	6	0-50		Harder, 1959.
Do	2	0-379		
Do	7	0-4		Biltz and Marcus, 1911.
Sylvinite	3	0		
Bischofite	1	3		Moore, 1960.
Sylvite	1	0		
Carnallite	1	0		Biltz and Marcus, 1911.
Carnallite-halite rocks	19	0-625	158	
Halite-kieserite rocks	5	31-152	89	Do.
Halite-polyhalite rock	1	0		
Polyhalite	1	0		Moore, 1960
Do	1	≈800		
Hartsalz	6	0-516	356	Biltz and Marcus 1911.
Do	2	0		
Anhydrite rock	3	6-21	13	Harder, 1959.
Do	62	1-500	68	
Do	22		16	Moore, 1960.
Gypsum rock (epigenetic)	207		17	
Gypsum rock	2	0-14		Do.
Salt clays	8	0-1240	606	

Small amounts of bromine (ionic radius 1.96 Å) replace chlorine (1.81 Å) in all the chlorides. Bischofite, carnallite, some sylvite, and the secondary mineral tachyhydrite contain the element in notable quantity. Practically no bromine separates from the brines during the deposition of the carbonate and sulfate zones of marine evaporites. As soon as deposition of halite begins, bromine is extracted from the liquid, but because of its larger ionic radius, it tends to become concentrated especially in the later products, as the table shows, and the Br:Cl ratio gradually increases in the residual liquid. The bromine content of halite therefore increases steadily toward the top of a primary sequence, whereas in a series of secondary evaporites the bromine content may behave irregularly. Bromine may therefore prove to be a key element in studies of the origin of evaporite rocks, and this has led to much interesting work (D'Ans and Kühn, 1940, 1944; D'Ans, 1947b; Baar, 1954, 1955; Kühn, 1953; 1955a, b, c), which has been recently summarized by Kühn (1955c). The following data (table 29) from the latter publication show how the bromine content of halite increases consistently through the primary sequence at Stassfurt.

Chromium.—Frölich (1960) found 1 ppm chromium in halite rock, sylvite, polyhalite, and gypsum rocks from the Zechstein, but much larger amounts in Zechstein clays.

TABLE 28.—Bromine in the minerals and rocks of marine evaporites

	Bromine Weight percent	Source of data
Bischofite	0.467	Winkler (1917).
Boracite	.005	Kühn (1955a).
Ericaite	.083	Do.
Carnallite	0.07-0.46	Chirkov (1944) Efremov and Veselovski (1928); Kühn (1955a); Lindberg (1946); Winkler (1917).
Halite	0.001-0.069	Chirkov (1944); Kühn (1955a).
Kainite	0.036-0.131	Kühn (1955a).
Koenenite	0.029-0.065	Do.
Langbeinite	.016	Winkler (1917).
Rinneite	0.04-0.065	Boeke (1909b, c); Kühn (1955a).
Sylvite	0.05-0.46	Chirkov (1944); Kühn (1955a); Lindberg (1946); Winkler (1917).
Tachyhydrite	0.18-0.44	Kühn (1955a); Winkler (1917).
Carnallite-bearing rocks	0.01-0.25	Chirkov (1937); Lindberg (1946); Mir (1946).
Halite-sylvite rock	0.014-0.331	Armstrong and others (1951); Chirkov (1944); Lindberg (1946); Mir (1946); Winkler (1917).
Halite-sylvite-kieserite rock	.027	Winkler (1917).
Halite rock	0.002-0.02	Aleksandrov and Levchenko (1953); Moore (1960); Shchepetunin (1937).
Polyhalite rock	<.002	Moore (1960).
Anhydrite rock	<.002	Do.

TABLE 29.—Bromine content of halite of Stassfurt evaporites

Source of halite	Weight percent Br per 100 percent NaCl
Carnallite zone	0.028-0.048
Kieserite zone	.023-.028
Polyhalite zone	.017-.023
Anhydrite zone	.003-.017

Copper.—In the Stassfurt salts, Biltz and Marcus (1909b) found 0.16-0.5 ppm copper in halite rock; 0.6-0.75 ppm in carnallite; 0.75-0.45 ppm in anhydrite rock; and 1.7-6.5 ppm in salt clays. Lietz (1951) found 0.16-0.45 ppm copper in halite rock from the Reitbrook salt dome. Runnels and others (1952) found that copper is concentrated mainly in water-insoluble residues in Kansas salt. In Russian evaporites, Galachowskaya (1953) found 0.019-0.16 (average 0.079) ppm copper in four samples of halite rock, and 0.06-2.76 (average 0.8) ppm in four samples of halite-sylvite rock. Kropachev (1960) reported average contents of 5 ppm copper in 22 anhydrite rocks and 23 ppm copper in 116 epigenetic gypsum rocks (formed by hydration of anhydrite) from the Permian of the fore-Urals. The mechanism of this apparent enrichment in copper (also in manganese and strontium) during the process of hydration is not clear.

Fluorine.—Fluorine occurs principally in sulfate deposits and salt clays, where fluorite and sellaite have been recorded. The following figures for German evaporites are from Koritnig (1951): 0.013–0.087 percent fluorine in gypsum rock; 0.013–0.081 percent in anhydrite rock; 0.089 percent in anhydrite residue from rock salt; 0.0002–0.0057 percent in halite rock; 0.002 percent in polyhalite rock; 0.030 percent in potash zone; and 0.275 percent in gray salt clay. Danilova (1949) reported 0.012 to 0.02 percent fluorine (average 0.0142 percent) in 7 samples of anhydrite, and 0.010–0.015 percent (average 0.0125 percent) in 5 samples of gypsum.

Gallium.—None has been found in the soluble salts, but clay from evaporite deposits contains 5–10 ppm gallium (Goldschmidt, 1954).

Germanium.—Goldschmidt and Peters (1933) recorded 1–5 ppm GeO₂ in German salt clays.

Gold.—Friend and Allchin (1940) reported 23 ppm gold in blue halite, and 4 ppm in blue anhydrite. Gold and silver have been detected in salt dome caprocks (Hanna and Wolf, 1941). (See also Goubeau and Birckenbach, 1938.)

Iodine.—The relatively large ionic radius of iodine impedes its replacement of chlorine and should lead to its concentration in the late liquids. The relatively low I:Cl ratio in marine evaporites relative to that of sea water has been ascribed to loss of iodine to the atmosphere during evaporation (Goldschmidt, 1954). Data on iodine have been collected by the Chilean Iodine Education Bureau (1956). A selection of these data is given in table 30 and is based on the works of Aleksandrov and Levchenko, 1953; Bleyer, 1926; Bohn, 1917; Cavaye and Hoyos, 1953; Eckstein, 1928;

TABLE 30.—Iodine expressed as parts per million, in the minerals and rocks of marine evaporites

	Range	Average	Number of samples
Carnallite.....	0–5. 0	0. 24	57
Kainite.....	0–0. 9	. 23	9
Kieserite.....	0–0. 062	. 020	7
Rinneite.....	0. 026	. 026	1
Sylvite ¹	0–0. 060	. 014	7
Tachyhydrite.....	0–0. 009	. 005	2
Carnallite rock (carnallitite).....	0–0. 09	. 03	6
Halite-sylvite rock (sylvinitite).....	0–0. 133	. 012	43
Halite - sylvite - kieserite rock (hartsalz).....	0–0. 106	. 018	18
Halite-sylvite-langbeinitite rock (langbeinitic hartsalz).....	0–0. 023	. 008	3
Halite rock.....	0–1. 0	. 102	170
Anhydrite rock.....	0.016–0. 3	. 106	7
Gypsum rock.....	0–0. 27	. 065	4

¹ Winkler's values (1916a, b) have been omitted, because they include the extraordinary value of 73.1 ppm.

Efremov and Veselovski, 1928; Fellenberg, 1924; Geilmann and Barttlingck, 1942; Koelichen, 1913; Krafft, 1924; Kraze, 1909; Rădulescu and Georgescu, 1925, 1927; Roeber, 1938 a, b; Rozsa, 1917b, 1924; Scharrer and Schwaibold, 1928; Schreiber, 1926; and Winkler, 1916a, b.

Iron.—Herrmann (1958) detected traces of iron (34.1 ppm average) in 5 out of 21 analyzed samples of halite from the Older Rocksalt of the South Harz in Germany. In three vertical sections through a layered series of halite rocks and hartsalz, he found the following average concentrations: 21 ppm iron in halite from layers of halite rock; 77 ppm in halite from hartsalz layers; and 448 ppm in sylvite from hartsalz layers. In Russian evaporites, Galachowskaya (1953) found 3.7–5.1 (average 4.4) ppm iron in 2 samples of rock salt, and 1.5–7.36 (average 3.3) ppm in 4 samples of halite-sylvite rock.

Lead.—The lead content of German Zechstein evaporites was studied by Born (1934), who found 0.08–0.49 ppm (average 0.17) in 8 samples of halite; 0.01 ppm in 2 samples of blue halite; 3.17 ppm in sylvite associated with blue halite; 0.17–0.27 (average 0.20) ppm in 4 sylvinitite samples; and 0.04 (average) ppm in 4 carnallite samples. Lietz (1951) found 0.76 and 0.17 ppm in halite from the Reitbrook salt dome. In Russian evaporites, Galachowskaya (1953) found 0.0412–0.049 (average 0.045) ppm lead in 2 samples of rock salt, and 0.0076–0.032 (average 0.016) ppm in 4 samples of halite-sylvite rock.

Manganese.—In Russian evaporites, Galachowskaya (1953) found 0.0252–2.38 (average 0.63) ppm in 4 samples of halite rock, and 0.015–0.298 (average 0.17) ppm in 4 samples of halite-sylvite rock. Kropachev (1960) reported averages of 120 ppm manganese in 80 anhydrite rocks, and 370 ppm manganese in 283 epigenetic gypsum rocks from the Permian of the fore-Urals.

Nitrogen.—Biltz and Marcus (1909a) found that NH₃ occurred only in very small quantity in most Stassfurt salts, but that carnallite and sylvite contained up to 77 and 61 ppm NH₃ respectively. They found almost 10 ppm N₂O₅ in salt clay.

Morachevskii and others (1937) recorded the presence of N₂, H₂, and CH₄ in carnallitic rocks that are held at pressures as great as 50 atmospheres in the Verkhnek-amsk district.

Phosphorus.—Phosphorus is concentrated principally in the clays; Koritnig (1951) found 0.092 percent P₂O₅ in gray salt clay and the following percentages in German evaporites: 0–0.006 in gypsum rock; 0–0.005 in anhydrite rock; 0.005 in the anhydrite residue from rock salt; and 0–0.0004 in halite rock.

TABLE 31.—Trace element analyses of halite and water-insoluble material from halite rocks of German Zechstein evaporites (after Herrmann 1958)

[Fe determined colorimetrically; the other elements spectrographically. N.d., not determined; (*), below limit of determination. Averages and ranges of composition computed from Herrmann's tables 14-19, and 22, which give results of individual analyses]

Source and number of samples	A (23)	B (12)	C (7)	D (4)	E (14)	F (4)
In milligrams of elements in 100 g of halite						
Pb.....	0.013 (<0.001-0.060)	0.041 (0.006-0.086)	0.006 (0.003-0.009)	0.002 (0-0.006)	0.026 (0-0.170)	0.003 (0.002-0.005)
Zn.....	.010 (0-0.024)	(*)	.021 (0-0.055)	.001 (0-0.004)	.003 (0-0.010)	.009 (0-0.036)
Sn.....	.0005 (0-0.006)	(*)	(*)	(*)	.0005 (0-0.003)	(*)
Cu.....	.080 (0.009-0.251)	.018 (0.001-0.077)	.056 (0-0.200)	.028 (0.010-0.072)	.040 (0.010-0.090)	.106 (0.014-0.191)
Mn.....	.026 (0-0.135)	.037 (0.005-0.090)	.037 (0.015-0.088)	.007 (0-0.014)	.079 (0.020-0.150)	.075 (0.040-0.116)
Ag.....	.00003 (0-0.0005)	<.002 (0-<0.002)	.0001 (0-0.001)	(*)	.0002 (0-0.0005)	(*)
Al.....	.232 (0-1.125)	.114 (0-0.966)	>.510 (0.053->2.000)	<.020 (0-0.025)	.147 (<0.020-0.743)	.081 (0.033-0.197)
Fe.....	N.d.	N.d.	N.d.	2.36 (1 sample only)	N.d.	N.d.
In parts per million, by weight, of elements in water-insoluble material which includes anhydrite, kieserite, and clay						
Pb.....	<10 (0-10)	<10 (<10-10)	(*)	<10 (<10-10)	<10 (0-10)	<10 (0-<10)
Sn.....	<10 (0-10)	<10 (0-10)	(*)	<10 (0-10)	(*)	(*)
Cu.....	<10 (0-100)	30 (<10-100)	<10 (0-<10)	(0-<1000)	<10 (<10-10)	<10 (<10)
Mn.....	20 (<10-100)	10 (<10-<100)	<10 (0-10)	<10 (<10)	<10 (0-<10)	<10 (<10-10)
Ag.....	(*)	(*)	(*)	(*)	(*)	(*)
Al.....	>500 (10->1000)	(0->1000)	>730 (10->1000)	10-<1000)	(<10-100)	257 (10-1000)
Sr.....	>3000 (<1000->5000)	(4300->5000)	2600 (1200-4000)	(3900->5000)	(1900->5000)	(3700->5000)

A. Older Rocksalt. Kaliwerk "Glückauf" Sondershausen, South Harz region (Herrmann, tables 14, 15, 17).

B. Older Rocksalt. Kaliwerk "Karl Marx", Sollstedt-Craja, South Harz region (Herrmann, 1958, table 16).

C. Younger Rocksalt. Grona 2 and Grona 4 boreholes, Magdeburg-Halberstadt region (Herrmann, 1958, table 17).

D. Halite-rock ("Unstrutbank"). From layers interbedded with halite-carnallite rock in the Older Potash deposits (Stassfurt series): Kaliwerk "Glückauf," Sondershausen

South Harz (Herrmann, 1958, table 18).

E. Halite rock ("Unstrutbank"). From layers interbedded with hartsalz in the Older Potash deposits (Stassfurt series). Kaliwerk "Glückauf," Sondershausen, South Harz

(Herrmann, 1958, table 19).

F. Halite rock. From KCl-poor part of hartsalz bed ("Vertaubung") in the Older Potash deposits (Stassfurt series). Kaliwerk "Glückauf," Sondershausen, South Harz

(Herrmann, 1958, table 22).

TABLE 32.—Trace element analyses of halite, carnallite, and water-insoluble material from carnallite-halite rocks of the German Zechstein evaporites (after Herrmann, 1958)

[Determined spectrographically; (*), below limit of determination. Averages and ranges of composition computed from Herrmann's tables 18, 20, 21, which give the results of individual analyses]

Source of samples	A		B		C	
Mineral and number of samples	Halite (5)	Carnallite (5)	Halite (3)	Carnallite (3)	Halite (3)	Carnallite (3)
In milligrams of elements in 100 g of mineral						
Pb.....	0.006 (0.005-0.008)	(*)	0.010 (0.005-0.019)	0.008 (0.003-0.016)	0.023 (0.012-0.032)	0.003 (0.002-0.004)
Zn.....	(*)	(*)	(*)	.068 (0.022-0.147)	(*)	.028 (0.028-0.029)
Sn.....	(*)	(*)	(*)	(*)	(*)	(*)
Cu.....	.017 (0.007-0.034)	(*)	.061 (0.015-0.091)	.133 (0.064-0.228)	.320 (0.170-0.500)	.276 (0.253-0.312)
Mn.....	.030 (0.017-0.056)	0.0006 (0-0.003)	.044 (one sample)	.011 (0.010-0.013)	.136 (0.072-0.175)	.019 (0.011-0.023)
Ag.....	(*)	(*)	(*)	(*)	<0.002 (0-<0.002)	<0.002 (0-<0.002)
Al.....	<0.020 (0-<0.020)	(*)	.217 (0.070-0.340)	.135 (0.046-0.184)	(0.508->2000)	.519 (0.431-0.626)
In parts per million, by weight, of elements in water-insoluble material, which includes anhydrite, kieserite, and clay						
Pb.....	<10 (0-<10)	(0-100)	(*)	<10 (0-<10)	(*)	(*)
Sn.....	<10 (0-<10)	<10 (0-10)	(*)	(*)	(*)	<10 (0-<10)
Cu.....	55 (10-100)	(0-1000)	(*)	33 (0-100)	<10 (<10-10)	40 (<10-100)
Mn.....	>10 (>10-10)	<10 (<10-10)	(0-100)	<10 (0-<10)	<10 (<10-10)	<10 (0-10)
Ag.....	(*)	<10 (0-<10)	(*)	(*)	(*)	(*)
Al.....	240 (0-1000)	200 (0-1000)	(0->1000)	(0-1000)	(1000->1000)	>1000 (>1000)
Sr.....	(0->5000)	(<1000->5000)	(0-1400)	<1000 (0 <1000)	4500 (4100-5000)	4200 (3900-4900)

A. Carnallite-halite rocks. From layers interbedded with halite rocks (Herrmann, 1958, table 18). Older Potash deposits (Stassfurt series). Kaliwerk "Glückauf," Sondershausen, South Harz.

B. Carnallite-halite rocks. From layer interbedded with hartsalz (Herrmann, 1958, table 20). Same locality.

C. Carnallite-halite breccia ("Trümmercarnallit"). From layers interbedded with hartsalz (Herrmann, 1958, table 21). Same locality.

TABLE 33.—Trace-element analyses of halite, sylvite, and water-insoluble material from hartsalz¹ (halite-sylvite-kieserite-anhydrite rocks) of the German Zechstein evaporites (after Herrmann, 1958)

[Determined spectrographically; (*), below limit of determination. Averages and ranges of composition computed from Herrmann's tables 19, 20, 21, 22, which give the results of individual analyses]

Source of samples— Mineral and num- ber of samples.....	A		B		C		D	
	Halite (18)	Sylvite (15)	Halite (7)	Sylvite (5)	Halite (4)	Sylvite (4)	Halite (3)	Sylvite (3)
In milligrams of element in 100 g of mineral								
Pb.....	0.056 (0.007-0.170)	0.080 (0.004-0.250)	0.011 (0.006-0.35)	0.030 (0.017-0.049)	0.019 (0.015-0.026)	0.094 (0.018-0.181)	0.016 (0.004-0.029)	0.018 (0.009-0.026)
Zn.....	.017 (0-0.115)	.029 (0-0.120)	(*)	(*)	(*)	(*)	.011 (0-0.033)	(*)
Sr.....	.003 (0-0.015)	.007 (0-0.072)	.043 (0.015-0.161)	.054 (0.022-0.111)	.078 (0.033-0.139)	<0.005 (0-0.020)	.059 (0.039-0.077)	.023 (0.007-0.046)
Cu.....	.185 (0.010-755)	.271 (0.032-0.800)	.087 (0.039-0.128)	.041 (0-0.189)	.092 (0.013-0.212)	.064 (0.013-0.091)	.162 (0.156-0.168)	.038 (0.015-0.059)
Mn.....	.265 (0.024-0.980)	.206 (0.037-0.690)	(*)	(*)	(*)	.310 (0.005-0.984)	(*)	(*)
Ag.....	.00005 (0-0.0009)	.0001 (0-0.001)	(*)	(*)	(*)	<0.001 (0-0.002)	(*)	(*)
Al.....	(0.100-2.000)	(0.260-2.000)	.125 (0.026-0.363)	.210 (0.124-0.370)	.158 (0.017-0.328)	.144 (0-0.336)	.271 (0.051-0.578)	.452 (0.170-0.991)
In parts per million, by weight, of elements in water-insoluble material, which includes anhydrite, kieserite, and clay								
Pb.....	<10 (0-0.40)	<10 (0-0.40)	(0-100)	(0-100)	<10 (0-0.10)	(*)	(*)	<10 (0-0.10)
Sr.....	<10 (0-10)	<10 (0-10)	(0-100)	(0-100)	<10 (0-0.10)	<10 (0-10)	<10 (0-10)	(1-100)
Cu.....	<100 (0-100)	420 (0-1000)	(0-100)	(0-100)	<10 (0-10)	<10 (0-10)	40 (10-100)	10 (10)
Mn.....	<10 (0-10)	<10 (0-10)	<10 (0-10)	<10 (0-10)	<10 (0-10)	<10 (0-10)	>1000 (>1000)	>1000 (>1000)
Ag.....	<10 (0-10)	(100-1000)	(1000-1000)	(1000-1000)	>1000 (>1000)	>1000 (>1000)	(100-1000)	(3900-5000)
Al.....	(1600-5000)	(3600-5000)	2600 (<1000-4300)	(2100-5000)	3700 (2700-4600)	(2900-5000)	(3700-5000)	(3900-5000)
St.....								

¹ Older Potash deposits (Stassfurt series): Kallwerk "Glückauf" Sondershausen, South Harz.
 A. Hartsalz. From layers interbedded with halite rocks (Herrmann, 1958, table 19).
 B. Hartsalz. From layers interbedded with halite-carnallite rocks (Herrmann, 1958, table 20).
 C. Hartsalz. From layers interbedded with carnallite-halite breccia (Trümmercarnallit) (Herrmann, 1958, table 21).
 D. Hartsalz. Beside an area in the potash bed which is impoverished in KCl (Herrmann, 1958, table 22).

Selenium.—Less than 0.5 ppm selenium has been reported in anhydrite, polyhalite, kainite, and kieserite (Goldschmidt and Hefter, 1933).

Strontium.—This element occurs in celestite and the very rare heidornite, strontianite, strontiohilgardite, p-veatchite, and goyazite. Most of the strontium of marine evaporites, however, replaces calcium in the sulfates and carbonates. Noll (1934) found 0.17–0.69 percent SrO in anhydrite rock; 0.003–0.13 percent in gypsum rock; 0.12 percent in polyhalite rock; and 0.00002–0.0002 percent in sylvite and carnallite. He found that the gypsum which has replaced earlier anhydrite by hydration at ordinary temperatures cannot always retain all the strontium of the anhydrite, and so celestite is formed. This may provide a clue to the origin of some anhydritic deposits, because primary anhydrite might contain more strontium than anhydrite which has replaced primary gypsum. Kropachev (1960) reported an average of 0.07 percent SrO in 22 anhydrite rocks, and 0.16 percent SrO in 207 epigenetic gypsum rocks from the Permian of the fore-Urals.

Uranium.—Bell (1960) has shown that the average uranium content of evaporitic minerals is less than 0.1 ppm. The uranium of evaporitic rocks is concentrated in clays and organic matter. He found as much as 380 ppm uranium in samples from a clay-rich layer in the Salado potassium-bearing evaporites. The high figures are associated with an exceptionally high phosphate content. Uranium contents of the black shales of the Paradox basin (6–57 ppm) are considerably higher than those of the associated dolomite and anhydrite (1–11 ppm).

Vanadium.—Kropachev (1960) reported no vanadium in 9 anhydrite rocks and an average of 2 ppm vanadium in 17 epigenetic gypsum rocks from the Permian of the fore-Urals.

Zinc.—1.5 and 0.35 ppm zinc were reported in rock salt from the Reitbrook salt dome (Lietz, 1951); 18 and 32 ppm were recorded from German salt clays (Wedepohl, 1953).

Zirconium.—Degenhardt (1957) gives 0.2 and 0.5 ppm zirconium in halite rock, less than 0.1 ppm in sylvite, and 0.1 ppm in sylvinites. All the rocks are from the German Zechstein.

SECONDARY CHANGES

GENERAL

Some of the most noteworthy differences between natural and experimental evaporite successions are as follows:

1. Gypsum is practically absent in nature except in near-surface deposits.
2. Carbonate is more abundant in many sulfate zones than would be expected.

3. Polyhalite is often absent. Where present, it is sometimes associated with anhydrite rather than halite.
4. The potassium-free magnesium sulfate zone is often absent. Where it is present, it does not normally contain salts such as epsomite, blödite, and hexahydrate; their place is taken by kieserite or rarely, langbeinite, loeweite, or vanthoffite.
5. Kainite is generally absent, occurring in significant quantity only in cap zones over potash deposits.
6. Sylvite appears in experimental successions in very small quantity at exceptionally low and high temperatures, but not at all at normal temperatures. Yet sylvite is the most abundant potassium-bearing chloride in natural deposits, and it is frequently associated with kieserite—a paragenesis stable only above 72°C.
7. Other salts not expected on experimental grounds, such as rinneite and tachyhydrite, are present in small quantity in some natural deposits.
8. Bischofite is very rare in natural deposits, although a thick bischofite zone would be expected.
9. Calculations of composition of the more complete natural profiles show large discrepancies between the proportions of some major ions in evaporites and in sea water. Especially obvious is the deficiency of magnesium in most evaporite bodies, brought out very clearly by the ratios given by D'Ans (1915) for the Stassfurt succession:

	<i>Berlepsche, Stassfurt</i>	<i>Sea water</i>
K:Mg	1:4.33	1:10.09
SO ₄ :Mg	1:1.57	1:3

Some of these anomalies can be explained by variations in conditions of deposition, by metastable crystallization or by temperature variations of the type considered by Borchert (see p. 25). The presence of excess carbonate in sulfate zones suggests introduction of terrestrial carbonate into the basin by rivers. This could result in early separation of much calcium and magnesium as carbonate, leading to a deficiency of magnesium in the residual brines, and the separation of sylvite rather than carnallite in the potash zones. The absence of bischofite could be due partly to this; but bischofite is so readily soluble that it would only very rarely be deposited at all, and then would often be redissolved and removed by later surface water. Excess of carbonate could also result from reduction of sulfate by bacteria in the presence of organic matter. The introduction of terrestrial calcium by rivers might lead to early deposition of an abnormal amount of sulfate, resulting in a deficiency of polyhalite, kainite, and other sulfates of magnesium and potassium in the later products. The scarcity of salts like epsomite,

blödite, and hexahydrate may in some cases be due to their reaction with the residual brines, in which the stable magnesium sulfate is kieserite.

Many features remain that cannot easily be explained by depositional factors. The complete absence of gypsum from a primary succession would require a temperature of more than about 34°C, and if the sea water were modified by terrestrial water still higher temperatures would be needed. Such temperatures are too high for this early stage of deposition. It is true that much higher temperatures have been recorded in modern salt lakes (over 70°C in Hungarian salt lakes—Kaleczinsky, 1902), but these high temperatures are found only in exceptional cases, in highly concentrated bitterns where evaporation is very slow and the dense brines absorb the sun's heat. It seems exceedingly unlikely that the temperatures required for the primary formation of such salts as langbeinite, loewite, and vanthoffite, and such parageneses as sylvite–kieserite, would prevail during the relevant stages of evaporation. Nearly all salt geologists accept the fact that secondary changes are responsible for these features.

There is abundant petrographic evidence of secondary changes in the rocks. Recrystallization textures are exceedingly widespread, particularly in the chloride zones, and include platy and linear parallelism of grains, breaking up of relatively brittle sulfate layers and cementing of the broken parts by recrystallized halite, coalescence of small grains to form larger ones which retain the original arrangement of inclusions, and other features. Such evidence is so widespread as to suggest that nearly all the deeper chloride bodies have undergone complete recrystallization, often accompanied by significant flow, since their formation. In a few cases, however, primary structures indicate relatively little disturbance; and, in this connection, the "hopper" structure in the halite of the Salina Formation of Michigan, recorded by Dellwig (1953, 1955), is of considerable interest.

Evidence of replacement is also abundant. It includes pseudomorphs showing the characteristic shape of the original minerals or characteristic structure or arrangement of inclusions, corroded relicts of the replaced minerals, replacement veins with irregular margins, and larger structural features such as the presence of cap salts related to the present land surface, or to unconformities rather than to the bedding of the evaporites. From such evidence it is quite clear that most large evaporite bodies have suffered widespread metasomatic changes since their original formation.

The large-scale changes include dolomitization of limestone at the base of many evaporite sequences, replacement of carbonate rocks by anhydrite (Fowler, 1944; Dunham, 1948; Stewart, 1949, 1951a, b),

replacement of sulfate rocks by halite, and replacement of anhydrite and halite rocks by polyhalite (Schaller and Henderson, 1932; Bessert, 1933; Stewart, 1949). Pseudomorphous structures show that gypsum was once abundant in the sulfate zones of the Salado formation and has been replaced by halite, polyhalite, and other salts (Schaller and Henderson, 1932). Similar pseudomorphs indicate that some of the thick sulfate zones of the English Zechstein originally consisted largely of gypsum but are now entirely replaced, mainly by anhydrite. The replacement sequences gypsum → anhydrite → halite → polyhalite, gypsum → anhydrite → polyhalite, anhydrite → gypsum → anhydrite → polyhalite (Stewart, 1949, 1953), and polyhalite → kieserite (Armstrong and others, 1951) have been recognized here. Pseudomorphs after early gypsum have also been recorded from the German Zechstein (Borchert and Baier, 1953). Gypsum has replaced anhydrite in bulk in many places (for example, Hammerschmidt, 1883; Sherlock and Hollingworth, 1938; Goldman, 1952). Considerable amounts of sulfur have occasionally been formed at the expense of calcium sulfates (for example, see Goldman, 1952).

In the potash zones, a great number of replacements have been recorded. There is convincing evidence of the secondary development in bulk of sylvinite and hartsalz from carnallite–halite rock (Beck, 1912; Naumann, 1913; Repetski, 1926; Bessert, 1933; Baar, 1944; and other authors). Langbeinite has replaced halite and sylvite, and anhydrite and halite have replaced langbeinite (Bessert, 1933; Borchert and Baier, 1953; and other authors). Some of the replacement series are complex; in the Potash zone of the English Middle Evaporites, for example, the replacements involve two generations of carnallite, sylvite, rinneite, and anhydrite, and four generations of halite (Stewart, 1956). In the Carnallitic marl, complex replacements were recorded by Armstrong and others (1951) and involve large amounts of secondary carnallite with sylvite, rinneite, and other minerals.

Many smaller scale replacements have been found in evaporites. In the Salado formation, for example, Schaller and Henderson (1932) have shown that polyhalite has replaced glauberite, kieserite, leonite, and sylvite; anhydrite has replaced halite, leonite, and magnesite; other replacements include glauberite → halite, halite → carnallite, kieserite → leonite, langbeinite → kainite, sylvite → langbeinite. Minor replacements in the English Zechstein include, among others, anhydrite → magnesite, dolomite → halite, anhydrite → sulfur, anhydrite → quartz, halite → quartz, rinneite → halite, rinneite → sylvite, halite → rinneite.

The dating of many of these replacements is extremely difficult, although it has proved possible to place some of them in successive series. It is clear, however, that they have developed in many different ways; the principal possibilities are discussed below.

PENECONTEMPORANEOUS CHANGES

1. *Reaction of minerals with the brines through which they sink*—A mineral may react with the brines through which it sinks. In a density stratified basin, for example, gypsum might form near the surface and be replaced by anhydrite during its downward passage through denser brine.

2. *Reaction of early-formed minerals with residual liquids*—The reaction of early-formed minerals with residual liquids could sometimes result in the conversion of such sulfates as epsomite, hexahydrate, and kainite to kieserite and other salts that are in equilibrium with the latest brines. Widespread metasomatism would result from percolation of supernatant brines through a mesh of early crystals. It is not known how far this would be possible, but at least a certain amount of replacement of gypsum by anhydrite would be expected. It is tempting to regard some dolomitization of limestone as penecontemporaneous reaction with supernatant brines, because this might go a long way toward explaining the deficiency of magnesium in evaporite bodies. Because dolomitization is normally a volume for volume replacement, the introduction of large amounts of magnesium would set free calcium which could result in the precipitation of an abnormally large amount of evaporitic calcium sulfate. This would lead to a deficiency of both sulfate and magnesium in the late salts; to perhaps the virtual absence of kainite, polyhalite, and other sulfates; and to the formation of primary sylvite at a late stage.

3. *Reaction of minerals with early interstitial liquids*—Upward movement of early interstitial liquids into higher strata would result in replacement of more soluble by less soluble minerals. This would probably not become important until postconsolidation squeezing took place, unless compaction were delayed enough to allow the denser brines from above to sink through a permeable crystal mush and displace the lower and less dense brines.

4. *Changes owing to influx of sea water or terrestrial water*—Freshening of the brine by periodic additions of sea water or terrestrial flood water would cause some solution and replacement of more by less soluble salts. Anhydrite, for example, would be replaced by gypsum, which might be converted back to anhydrite after further evaporation. An important change of this type is the formation of sylvite from carnallite,

with the $MgCl_2$ going into solution. This would sometimes result from penecontemporaneous leaching of carnallite by ground water.

5. *Changes due to variations of temperature*—Seasonal, or even diurnal, changes in temperature would be expected to promote some replacements.

POSTCONSOLIDATION CHANGES

6. *Effects of burial*—The effects of burial are exceedingly important. With only a moderate increase in temperature and pressure, which results from burial beneath an appreciable thickness of later rock, evaporites suffer extensive changes.

Familiar pressure effects include the development of structures resembling schistosity and gneissic banding, brecciation of brittle rocks, and flow of chlorides to form salt anticlines, domes, and other structures. These effects will not be discussed here, but it should be noted that selective movement of different salts may result in successions different from the original ones.

Changes that depend to a large extent on rise of temperature have received a great deal of attention, and the literature on geothermal metasomatism is large. Some of the more important work is included in Baar, 1944; Borchert, 1940, 1959; Borchert and Baier, 1953; Geller, 1930; Jänecke, 1916, 1917, 1923, 1929; Lotze, 1957; Rinne, 1914, 1916, 1920; and Rozsa, 1915a, b, 1916a, b, c, 1919, 1931. Experimental work shows that new salts such as langbeinite and vanthofite can be formed by reactions between dry powdered salts at temperatures of about 80°C (Ide, 1935; Leonhardt, 1951; Leonhardt and Berdesinski, 1949–50). Nearly all the natural chlorides contain liquid-filled cavities, however, and most changes are certainly effected by the action of solutions which occur in three different states: (a) Connate brines enclosed in the salts, (b) water of crystallization of the salts, and (c) migrating fluids from the surrounding rocks.

With rising temperatures, many reactions would release a quantity of solution (see, for example, table 12), and the incongruent melting of some salts would give rise to less hydrated salts and solutions. A replacement of gypsum by anhydrite would release about 20 percent water, and this would be expected with burial to a depth of about 2,000 feet (MacDonald, 1953). This change would explain the absence of gypsum in deep-seated deposits. Major changes in the upper zones include the formation of hartsalz at 72°C:

$Carnallite + kainite = kieserite + sylvite + 33.5 \text{ percent solution}$. Bischofite melts at 117°C, corresponding to a depth of about 12,000 feet, and releases $MgCl_2$ solution. Carnallite decomposes above 167.5°C to give sylvite and solution, but the presence of some

apparently primary carnallite in many evaporite deposits indicates that this temperature is very rarely reached.

After consideration of the experimental work, Jänecke gave the following scheme of geothermal metasomatism for the older succession of the German Zechstein (Phillips, 1947):

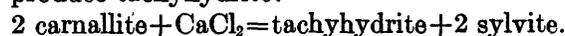
<i>Theoretical profile</i>		<i>Geothermally changed profile</i>
Bischofite zone		Yields $MgCl_2$ solution
Carnallite	→	Carnallite or hartsalz zone
Kainite zone	→	Hartsalz zone
Potassium-free magnesium sulfate zone	→	Loeweite-vanthoffite zone → kieserite zone
Polyhalite zone	→	Polyhalite zone
Anhydrite zone	→	{Glauberite zone Anhydrite zone
Gypsum zone	→	Anhydrite zone

Jänecke considered the initial and final products of metasomatism, and Borchert (1940, 1959) considered in detail the intermediate stages with reference to the experimental work on the quinary system (figs. 5-9). Borchert traced a series of changes of composition of solids and solutions in a "step-metamorphism." In the potassium-free magnesium sulfate zone, for example, the paragenesis thenardite-vanthoffite-halite is an intermediate stage in the transformation of blödite-halite to loeweite-vanthoffite-halite. If the solutions were squeezed out of the rocks during metamorphism, such intermediate stages would be preserved. They are preserved in some cases, but it appears that the solution generally remained long enough for the final stages to be reached. The lack of widespread reversed metamorphism in the German deposits indicates that the solutions were largely pressed out before the removal of much of the overburden by erosion.

Various workers have stressed the importance of the solution set free in the gypsum → anhydrite change. This solution would presumably remain in the sulfate layer until breaks in the impervious salts above were produced by tectonic movements. Then, the large amount of solution often involved would penetrate to and metasomatize the soluble salts above. Some of the barren areas in the German potash mines seem to be related to regions of tectonic weakness where ascending solutions have effected the following changes (Baar, 1944; Borchert and Baier, 1953). Halite-carnallite-kieserite rock → sylvite-rich hartsalz → normal hartsalz → halite-langbeinite-sylvite rock → anhydrite-halite rock. Such changes involve the introduction of considerable amounts of $NaCl$ and $CaSO_4$ and the removal of $MgCl_2$ and KCl in the solution.

By the action of $MgCl_2$ -rich solution on anhydrite, solutions rich in $CaCl_2$ may form and react with carnal-

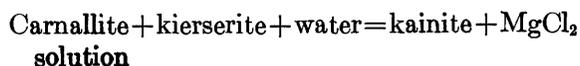
lite to produce tachyhydrite:



Reaction of metamorphic brines with the clastic material enclosed in the salts apparently results in the formation of such minerals as rinneite, hematite, quartz, and talc.

7. *Action of percolating ground water*—Ground water, gaining access to evaporites at any time after their deposition, causes total or selective solution and subsequent reaction between the salts and the solutions. A significant change is the replacement of anhydrite by gypsum. Total or partial hydration of anhydrite takes place in most areas at depths of 1,000 feet or less below the present surface. The depth varies with the composition of the associated solution, the geothermal gradient, and the ratio of hydrostatic to lithostatic pressure (MacDonald, 1953). Some of the depths given for natural deposits are: up to 1,000 feet, Lower Fars evaporites, Iran (Strong, 1937); 1,037 feet, Zechstein evaporites, Cerebos no. 21 boring, northern England (Dunham, 1948); 1,230 feet, Louisiana (Newland, 1921); and rarely below 1,183 feet, gypsum, Sulphur Salt Dome, Louisiana (Goldman, 1952). The exceptional records of gypsum at considerably greater depth (for example, 2,467 feet in Hayton boring, northern England [Dunham, 1948]) may perhaps result from alteration of borehole cores during or after the drilling. It is probable that a great deal of the gypsum now exposed in evaporites has been formed by hydration of earlier anhydrite, and, of course, much of the earlier anhydrite may have replaced primary gypsum during burial.

When ground water enters a zone containing bitter salts, the effects are far-reaching. Bischofite dissolves very readily. Carnallite is changed to sylvite with removal of $MgCl_2$. Kainite is sometimes formed in large quantity at the expense of carnallite, kieserite, and sylvite:



In general, the solutions become enriched in $MgCl_2$ as they percolate downward. Picromerite, apthitalite, blödite, and leonite may form in the upper parts, above secondary kainite, sylvite, and epsomite. The kainite cap zones of the German Zechstein have had considerable economic importance.

Many complex replacements in the cap zones of salt domes have been described (for example, by Goldman, 1952). Especially noteworthy are the removal of chlorides in solution and the accumulation of insoluble residues, especially anhydrite, to form a

cap; the replacement of anhydrite by gypsum; and the replacement of sulfates by carbonates.

8. *Thermal metasomatism related to igneous activity*—Thermal metasomatism related to igneous activity has considerably affected some Zechstein salts in the the Werra and South Harz regions (Dietz, 1928; Bessert, 1933; Storck, 1954; Ahlborn, 1955) and some Tertiary salts of Baden (Hasemann, 1952; Wimmenauer, 1952). Near basalt intrusions, there has been conversion of carnallite-halite rock to sylvite-halite rock (often containing blue halite) and development of kainite at the expense of the sylvite and kieserite of hartsalz. Other reactions include the formation of leonite and apthitalite. In this type of metasomatism, magmatic and connate water and the water of crystallization released from the salts must all play a part.

9. *Changes effected by bacteria*—The agency of bacteria in the formation of some secondary sulfur deposits seems to be well established (Feely and Kulp, 1957; many references to earlier literature are given by them). Experiments indicate that sulfur bodies like those of the Gulf Coast salt domes of Texas and Louisiana could not have been formed by reduction of sulfate by petroleum within the geological time available. However, it would seem that less than a million years would be enough for the formation of these deposits by reduction of sulfate to hydrogen sulfide by bacteria (*Desulfovibrio*), and oxidation of part of the hydrogen sulfide to sulfur by reaction with sulfate ion.

The reality of these processes is supported by evidence from isotopic studies. The experiments show that the S^{32}/S^{34} ratio in the hydrogen sulfide produced by *Desulfovibrio* is increased, with respect to that in the initial sulfate (about 21.85), by at least 2.7 percent with slow bacterial growth. In the water of the caprocks of the Gulf Coast salt domes, the S^{32}/S^{34} ratio of hydrogen sulfide is several percent higher than that of the associated sulfate. The sulfate of the calcite caprock shows a complementary but variable enrichment in sulfur-34 relative to the sulfate of the anhydrite caprock. The C^{13}/C^{12} ratios in calcite and petroleum from the caprocks are similar to one another and as much as 4.3 percent lower than the ratios from sedimentary limestones. This indicates that the calcite caprock resulted from precipitation of carbonate during the oxidation of petroleum by bacteria. The S^{32}/S^{34} ratio of the caprock sulfur is usually a few tenths of a percent lower than that of the hydrogen sulfide of the salt dome and supports the idea of its formation by oxidation of the sulfide by sulfate.

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