OCEANIC SALT DEPOSITS

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THE rocks classified by the geologist as sedimentary are formed by the deposition, from transporting agents, of the products of disintegration and chemical decomposition of previously-existing rock masses. Material carried in suspension by rivers is laid down to form clastic sediments—sandstones, clays, etc.—but many of the products of chemical weathering pass into solution and are carried down into lakes or eventually to the sea. Most of these dissolved products are only recovered when laid down as chemical deposits as a consequence of the evaporation of the aqueous solvent. Of such sediments produced by evaporation, the oceanic salt deposits, or *marine evaporites*, are geologically and chemically by far the most important. Though the exact circumstances have been, and to some extent still are, a matter for disputation, it has long been realised by geologists that at several periods during the course of past geological ages large bodies of sea-water have been evaporated sufficiently far to cause at least partial crystallisation of the dissolved salts.

The waters of the present-day oceans, the hydrosphere, in volume about 3×10^8 cubic miles, have been found to display a remarkable degree of constancy in the relative proportions of the more important ions present, though the absolute concentration may vary to some extent. Early analytical work by Forchhammer and others was superseded by the determinations made by W. Dittmar [1] on 77 samples of ocean waters collected during the " Challenger " expedition; it is a tribute to Dittmar's work that later investigations have effected few important modifications of the values which he gave. The complexity of the solution and the difficulty of separation of certain related substances present awkward analytical problems. Even the total salt content cannot be accurately determined by direct evaporation, for it is difficult to drive off all traces of moisture without loss of other constituents. For these reasons, oceanographers use two defined quantities in the discussion of the chemistry of sea-water. The " chlorinity " is determined by precipitation of the halogens with a silver salt, and is essentially the chlorine equivalent, it being assumed that the bromine and iodine have been replaced by chlorine. (For more precise discussion, chlorinity has been redefined [2] in terms of the weight of silver precipitated, and hence is independent of any changes in accepted values of atomic weights.) The " salinity " is also a defined quantity, slightly less than the total weight of dissolved solids, and can be calculated from

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[1] Reports of " Challenger " Expedition, Physics and Chemistry, 1884, **1**, 1—251.

[2] J. Jacobsen and M. Knudsen, *Assoc. d'Oceanog. phys., Union geodes. geophys. intern.*, 1940, Publ. Sci., No. 7.

the chlorinity or determined from a measurement of the density. Both chlorinity and salinity are customarily expressed as g. per kg. of sea-water, using the symbol $^0/_{00}$ (per mille).

A recent tabulation [3] of the proportions of the major constituents of sea-water, for a chlorinity of $19^0/_{00}$, is given below:

Ion.	Cl = $19{\cdot}00^0/_{00}$.	%.	Ion.	Cl = $19{\cdot}00^0/_{00}$.	%.
Na^+	10·556	30·61	Cl^-	18·980	55·04
Mg^{++}	1·272	3·69	$SO_4^=$	2·649	7·68
Ca^{++}	0·400	1·16	HCO_3^-	0·140	0·41
K^+	0·380	1·10	Br^-	0·065	0·19
Sr^{++}	0·013	0·04	F^-	0·001	0·00
H_3BO_3	0·026	0·07	Total	34·482	

The waters of the open oceans thus contain about 34 parts per thousand of dissolved salts, of which about 55% by weight is chlorine and 31% sodium. The salinity varies only slightly except near land masses, where it may be greatly reduced by the influx of river-water. We shall have occasion later to discuss further whether the salinity of sea-water has remained sensibly constant for long geological periods; it is interesting to note here that the contributions received at the present time from river-waters are of quite a different composition from the salt content of the oceans, Ca^{++} constituting about 20% and $CO_3^=$ about 35%, but much of this material is soon abstracted by animals or plants and involved in a biological cycle.

One of the earliest attempts to study the order of separation of salts on the evaporation of sea-water was made by J. Usiglio,[4] who, nearly one hundred years ago, carried out a long series of experiments by evaporating samples of water taken from the Mediterranean. He was able to demonstrate a general succession, calcium carbonate and sulphate being followed by sodium chloride and the sulphates and chlorides of magnesium and potassium. The problem, however, was much too complex for such a direct analytical approach to be successful, and the scientific study of the crystallisation of oceanic salts really began with the classic studies of J. H. van't Hoff and his associates. These studies were directed towards obtaining a closer understanding of the conditions of formation of the salt deposits of the Stassfurt region, at that time the most important potash-producing area in the world. Instead of experimenting, as did Usiglio, with actual sea-water, van't Hoff undertook a systematic study of the solubility relationships of all the salts in question. By working initially under atmospheric pressure and at a single defined temperature (25°), solubilities were determined first in pure water and then in the presence of other salts, full precautions always being taken to maintain saturation by the presence

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[3] H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, "The Oceans," New York, 1942, p. 166.

[4] *Ann. Chim. Phys.*, 1849, **27**, 92—107, 172—191.

of the solids as "Bodensalze," and to ensure the attainment of equilibrium —the slowness of attainment of equilibrium in some instances was one of the reasons why the early experiments of Usiglio could never have been completely successful. A second series of investigations was carried out at a temperature of 83°, and other particular temperatures corresponding to the appearance or disappearance of individual compounds were determined. "It is hard to say how far such researches could have been carried by chemists unacquainted with the phase rule. They would have had no guide to the apparently chaotic results obtained on evaporating mixed salt solutions. The meager results obtained before the problem was taken up by van't Hoff show that little progress could have been made by the older methods of experimentation in which the results and the guiding principles of modern physical chemistry had no place." [4a] A long series of separate contributions were conveniently summarised in extended accounts [5] dealing first with the chlorides and sulphates of sodium, potassium, and magnesium and secondly with the calcium salts and boron compounds. Further work by later investigators, notably J. d'Ans,[6] has established in detail the conditions of equilibrium in the systems involving the chlorides and sulphates of sodium, potassium, magnesium, and calcium over a temperature range of 0—120°. The necessary preliminary work on the simpler systems, whilst having no direct application to the complex problem of the natural deposits, has proved of immense importance in providing the data on which to base the subsequent extraction and refinement of the various salts.

The following table lists the more important salts which may occur in marine evaporites :

Chlorides and sulphates of sodium, potassium, and magnesium

Halite (rock-salt)	$NaCl$
Sylvine	KCl
Bischofite	$MgCl_2,6H_2O$
Carnallite	$KCl,MgCl_2,6H_2O$
Thenardite	Na_2SO_4
Mirabilite (Glaubersalz)	$Na_2SO_4,10H_2O$
Glaserite (aphthitalite)	$(K,Na)_2SO_4$
Kieserite	$MgSO_4,H_2O$
Hexahydrite	$MgSO_4,6H_2O$
Reichardtite (epsomite, Bittersalz)	$MgSO_4,7H_2O$
Vanthoffite	$3Na_2SO_4,MgSO_4$
Astrakanite (bloedite)	$Na_2SO_4,MgSO_4,4H_2O$
Loewite	$2Na_2SO_4,2MgSO_4,5H_2O$
Langbeinite	$K_2SO_4,2MgSO_4$
Leonite	$K_2SO_4,MgSO_4,4H_2O$
Schoenite (picromerite)	$K_2SO_4,MgSO_4,6H_2O$
Kainite	$KCl,MgSO_4,3H_2O$

[4a] W. A. Gale, *Ind. Eng. Chem.*, 1938, **30**, 867.

[5] J. H. van't Hoff, "Die Bildung ozeanischer Salzablagerungen," I and II, Brunswick, 1905, 1909 ; "Untersuchungen über die Bildungsverhältnisse ozeanischer Salzablagerungen," Leipzig, 1912.

[6] "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen," Berlin, 1933.

Calcium salts

Anhydrite	$CaSO_4$
Gypsum	$CaSO_4,2H_2O$
Glauberite	$CaSO_4,Na_2SO_4$
Syngenite	$CaSO_4,K_2SO_4,H_2O$
Polyhalite	$2CaSO_4,MgSO_4,K_2SO_4,2H_2O$
Tachhydrite	$CaCl_2,2MgCl_2,12H_2O$

Boron compounds

Boracite	$5MgO,MgCl_2,7B_2O_3$
Pinnoite	$MgO,B_2O_3,3H_2O$
Ascharite	$2MgO,B_2O_3,H_2O$
Sulphoborite	$2MgSO_4,4HMgBO_3,7H_2O$
Lueneburgite	$3MgO,B_2O_3,P_2O_5,8H_2O$

Iron salts

Rinneite	$NaCl,3KCl,FeCl_2$
Douglasite	$2KCl,FeCl_2,2H_2O$

Certain of these names are applied by systematic mineralogists only to massive material of the kind usually found in marine evaporites, other names (some of which are given above as alternatives) being applied to well-developed crystals, but we shall find it convenient to continue to use those names which are well established in the literature of oceanic salt deposits. It is a fortunate circumstance that, amongst so many possible solid phases, there is only a very limited degree of isomorphous replacement; glaserite shows a limited substitution of potassium by sodium, and very small amounts of sodium may be taken up by leonite and of potassium by astrakanite.

Upon evaporation of sea-water, the first salt to separate is calcium carbonate. The surface layers of ocean waters may, in fact, be considerably supersaturated with calcium carbonate,[7] and in some regions of shallow water, such as the Great Bahama Bank, where the shallowness reduces circulation, precipitation of carbonate is already taking place at the present time. As evaporation proceeds, it is probable that dolomite may be directly precipitated, though it must be admitted that the conditions of formation of dolomite are not yet fully understood and it is often not possible to determine how far a particular dolomite may have been produced by the later alteration of a limestone by saline waters rich in magnesium. The actual quantities involved are small—from a 1000-m. depth of water a limestone only a few cm. thick would be formed, if there were no considerable degree of supersaturation.

As evaporation proceeds, calcium sulphate appears. The conditions determining the separation of gypsum or of anhydrite were studied by van't Hoff, but it has recently been pointed out [8] that his determinations were based on the incorrect assumption that gypsum dissociates directly to form anhydrite. Actually, the hemihydrate $CaSO_4,\frac{1}{2}H_2O$ is always formed first, and gypsum and anhydrite only coexist at a four-phase equilibrium point. In saturated aqueous solutions of gypsum and anhydrite this point lies at

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[7] H. Wattenberg, *Fortschr. Min.*, 1936, **20**, 192.

[8] E. Posnjak, *Amer. J. Sci.*, 1938, **35**, *A*, 247—272.

a temperature of 42°. Investigating the effect on this transition temperature of salt solutions of approximately the composition of sea-water, E. Posnjak [9] showed that at a temperature of 30° gypsum will begin to separate when the salinity has been increased by evaporation to 3·35 times the normal value, and that nearly one-half of the total amount of calcium sulphate present will be deposited as gypsum before the concentration is reached at which anhydrite becomes stable.

As evaporation is continued further, halite eventually separates when the water content has been reduced to less than one-tenth of the original, and anhydrite and halite continue to separate together until the field of stability of polyhalite is reached. The degree of evaporation necessary to precipitate gypsum, or anhydrite, and halite has been attained at various periods in past geological ages, and important deposits of rock-salt are worked in many parts of the world. In this country, the salt industry of Cheshire and Durham is based on occurrences in the Permian and Triassic rocks, and the associated gypsum and anhydrite are also extensively worked, but practically no potassium salts have been found, though polyhalite has recently been recorded.[10]

Only when the evaporating body of sea-water has been reduced to 1·57% of the original volume do the salts of magnesium and potassium begin to appear. Such a high degree of evaporation has only infrequently been reached, and the Permian deposits of Germany still remain the best-known example of natural potash resources. The earliest workings were around Stassfurt, after which the deposits are still popularly known, but subsequent exploration, involving the sinking of over two hundred shafts and some thousands of boreholes, revealed the wide extent of the deposits, both northwards towards Hanover and south of the Harz on both flanks of the Thüringer Wald. The Werra district, between Eisenach and Fulda, has recently become the most important producer. National requirements for potash during two world wars induced extensive exploration in other countries. In the United States of America, isolated records of potassium salts had been known from the Permian Salt Basin of the Texas–New Mexico area since 1912, and after an intensive programme of exploration the first shaft was sunk in 1929 and production begun in 1931.[11] In the U.S.S.R., deposits closely resembling those of Germany were discovered in 1916, in the region around Solikamsk, in the province of Perm, and less important deposits are known also in Alsace, Poland, and Spain.

The detailed study of the further course of crystallisation in the complete system (Na,K,Mg,Ca),(Cl,SO_4) presents considerable practical difficulties, inherent in the diagrammatic representation of a system which, with water, has six independent components. The concentration of calcium at this stage is so low that it may conveniently be left out of account for the present, but we still have to deal with a quinary system. Since further crystallisation occurs always in the presence of excess of sodium chloride, which forms no binary or ternary compounds with any of the other salts, a diagrammatic

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[9] *Ibid.*, 1940, **238**, 559—568.

[10] C. E. Tilley, *Min. Mag.*, 1943, **26**, lvii.

[11] J. W. Turrentine, "Potash in North America," Reinhold, 1943, p. 27.

representation can be effected in terms of $MgCl_2$, Na_2SO_4, and KCl, and van't Hoff constructed various types of isothermal model. He also made extensive use, in his discussions, of plane " paragenetic diagrams " which showed the combinations of salts in equilibrium with halite and saturated solutions at various temperatures, but possessed no quantitative significance. In devising further simplifications, E. Jänecke [12] has been particularly active. Van't Hoff expressed his results in terms of the solubility of the various salts in a constant amount of water, but Jänecke proposed an alternative method with a variable water content, expressing the amount required to produce a saturated solution. The water content is thus treated separately from the composition of the salt mixtures, so that any inaccuracies in determination of the water content are not carried over to statements about the salt contents. The device also leads to a simple graphical procedure. Expressing the composition in the form

$$m\mathrm{H_2O}, x\mathrm{Mg}, y\mathrm{K_2}, (100 - x - y)\mathrm{SO_4}, s\mathrm{Na_2},$$

since only neutral salts are in question, all possible compositions can be plotted on a triangular diagram in terms of K_2, Mg, and SO_4, by using the values of x and y, and an isothermal representation in a plane diagram is thus achieved.

In such a diagram the paths of crystallisation 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 centre-of-gravity principle. For a given temperature, a further quantity such as the water content m or the associated amount of sodium chloride can be plotted as ordinate, whilst if the various isothermal diagrams are set above each other the equilibrium conditions throughout a range of temperatures can be conveniently displayed in a triangular prism. Certain features of the courses of crystallisation can be studied also in projections on a face of the prism. Fig. 1 illustrates such a prism constructed by Jänecke [13] in the form of a wire model.

Within the prism, between 0° and 120°, there are 33 invariant points at which four salts (in addition to halite) co-exist in equilibrium with solution. Amongst these, three important types may be distinguished. At the first, of the type

$$\mathrm{S_1 + S_2 + S_3 \rightleftharpoons S_4 + Solution}$$

a mixture of three salts gives way, on rise of temperature, to the appearance of a new solid phase. As examples may be quoted the reactions

Mirabilite + Reichardtite + Schoenite ⇌ Astrakanite + Solution

marking the appearance of astrakanite at 4·5°, and

Mirabilite + Astrakanite + Glaserite ⇌ Thenardite + Solution

corresponding to the formation of thenardite above 13·5°

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[12] See " Handbuch der Mineralchemie," C. Doelter and H. Leitmeier, 1929, IV, **2**, 86—91, 1253—1258 (a convenient summary of numerous earlier papers).

[13] *Z. Elektrochem.*, 1934, **40**, 741.

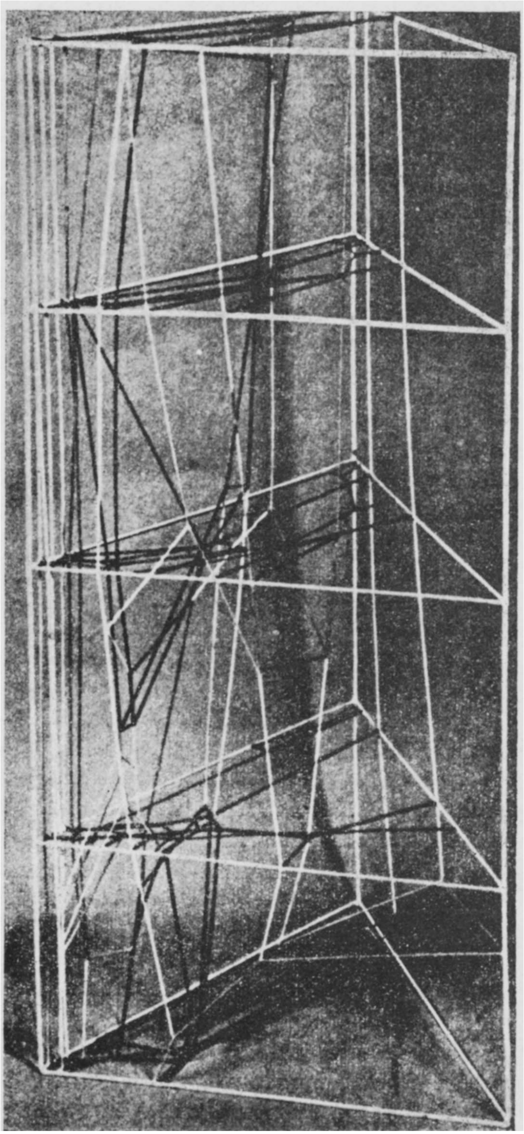

FIG. 1

Solubility of oceanic salts between 0° *and* 120° (*Jänecke*).

Many of the invariant points are of the type

$$S_1 + S_2 \rightleftharpoons S_3 + S_4 + \text{Solution}$$

indicating a change of paragenesis. The important reaction

$$\text{Carnallite} + \text{Kainite} \rightleftharpoons \text{Kieserite} + \text{Sylvine} + \text{Solution}$$

is one example of this kind, taking place at a temperature of 72°.

A third type, $S_1 \rightleftharpoons S_2 + S_3 + S_4 +$ Solution, marks the disappearance of a particular solid phase at higher temperatures, as with schoenite at 26° and kainite at 83°. Fig. 2 shows the temperature ranges of formation, between 0° and 100°, of the various salts in the presence of sodium chloride. It will be seen that, whilst certain salts can crystallise throughout this range, others have a much more limited field, the highly hydrated salts giving place to less hydrated or to anhydrous compounds at higher temperatures. Van't Hoff distinguished three stages; below 37°, schoenite, reichardtite, and hexahydrite disappear, between 37° and 55° loewite, langbeinite, and vanthoffite appear, whilst above 55° astrakanite, leonite, and kainite in succession cease to form. It should perhaps be emphasised that Fig, 2 refers only to temperatures of *formation* of the various salts within the system under consideration; the salts themselves are stable under suitable conditions over much wider ranges, and langbeinite for example will remain unchanged indefinitely in a dry atmosphere at room temperatures.

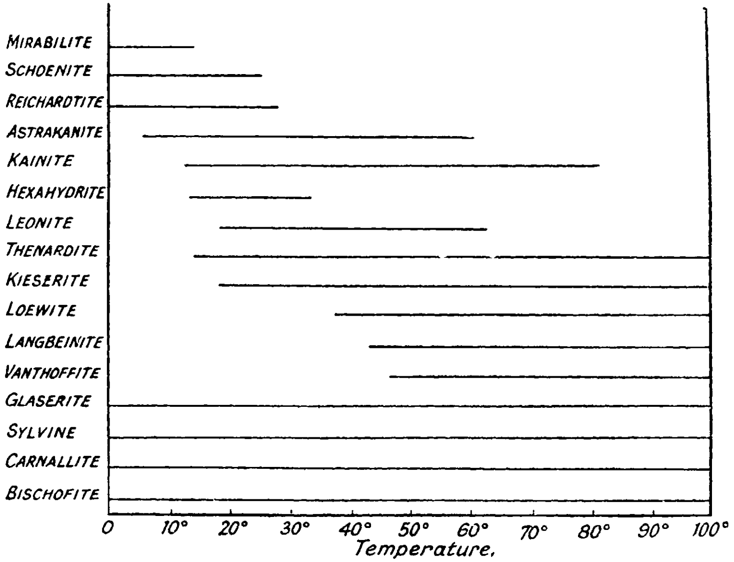

FIG. 2

Temperature ranges of formation of oceanic salts.

If we turn next to the course of crystallisation of a solution of the composition of normal sea-water the possibilities are much restricted. For isothermal evaporation at 25°, the point marking this composition falls just within the field of astrakanite (Fig. 3), which is therefore the first salt to crystallise. The path of crystallisation, following a straight line directly away from the point marking the composition of this salt, soon reaches the boundary of the reichardtite field. Reichardtite begins to separate, and the further course depends upon whether the previously-separated astrakanite remains in contact with the solution. If it does, it will be resorbed as the reichardtite continues to crystallise ; under natural conditions, however, it is likely that the salts already separated will become crusted over and thus be protected from the action of the solution. In either event, the path of crystallisation eventually passes across the field of reichardtite to its boundary with that of kainite. From here, the path lies along the boundary, with the two salts crystallising together. There follow in succession the pairs hexahydrite–kainite, kainite–kieserite, kieserite–carnallite, and finally the three salts kieserite–carnallite–bischofite separating together until the evaporation is complete ; in this mixture of salts the bischofite is, of course, greatly predominant in amount, since the composition is now so close to the Mg vertex.

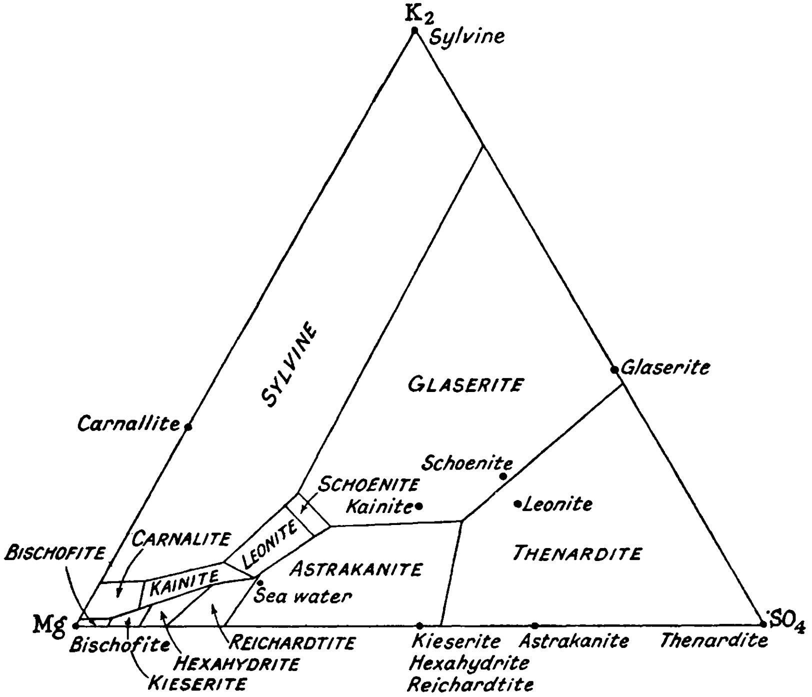

FIG. 3

Stability fields of oceanic salts at 25°.

Throughout this later part of the crystallisation, halite is still separating, together with small further amounts of calcium salts. The fields of stability of these latter can be delineated in a similar Mg, K_2, SO_4 triangle, and in many of the published figures the two isothermal diagrams are superposed (see, for example, Fig. 1). The actual amount of calcium present is so small that its effect on the course of crystallisation is negligible, and the path of crystallisation outlined above can be applied directly to the double scheme.

The polyhalite which is stable when the crystallisation of magnesium salts begins gives way finally to anhydrite during the course of separation of kainite.

We can thus construct a theoretical profile of the salt succession to be expected from this course of crystallisation at 25° :

Kieserite, carnallite, bischofite	Anhydrite	Halite	Bischofite zone
Kieserite, carnallite			Carnallite zone
Kieserite, kainite			Kainite zone
Hexahydrite, kainite			
Reichardtite, kainite			
Reichardtite	Poly-halite		Potash-free magnesium sulphate zone
Astrakanite			
Polyhalite			Polyhalite zone
Anhydrite			Anhydrite zone
Gypsum			Gypsum zone
Carbonates			Basal limestone and dolomite

A comparison of this theoretical profile with the successions in natural deposits reveals in most areas a general correspondence, at least up to a certain stage. Marine limestones or dolomites passing up into anhydrite and halite, with or without polyhalite, are developed, for example, in Germany, in the Texas–New Mexico field, and in this country. The characteristic calcium sulphate of most marine evaporites is anhydrite, however, rather than gypsum. In the succeeding zones, less complete agreement with the theoretical profile is revealed, and in many areas there is profound disagreement. Salts such as astrakanite, reichardtite, kainite, or hexahydrite are rare or absent ; vanthoffite, loewite, langbeinite, and sylvine are found instead. For parts of the German field a succession can be tabulated : [14]

	Carnallite succession.	Hartsalz succession.
Older potash beds	Carnallite with kieserite and halite	Carnallite with kieserite and halite Sylvine with kieserite and halite
Transition beds	Halite with kieserite and carnallite Halite with kieserite and sylvine	Halite with langbeinite Halite with loewite Halite with vanthoffite
	Halite with polyhalite	
Older rock-salt	Halite with glauberite Halite with anhydrite	

Sylvine, which does not appear in the theoretical profile at 25° (in which kainite is the chief carrier of potassium), is a constituent of two of the

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[14] E. Fulda, " Zechstein," Berlin, 1935, 47, 139.

most important ores in most areas—the " Hartsalz " of the German miners, a mixture of sylvine with kieserite and halite, and the rich " Sylvinite," a mixture of sylvine with halite. The latter is of chief economic importance in the Texas–New Mexico district,[15] in the upper parts of the German succession, and in the Solikamsk region. Whether a primary bischofite layer was ever developed is a question which will be referred to later; certainly nothing resembling the thick bischofite zone of the theoretical profile has ever been encountered, but its absence can be readily accounted for on the supposition that in most natural occurrences the evaporation of the mother liquor did not proceed to completion.

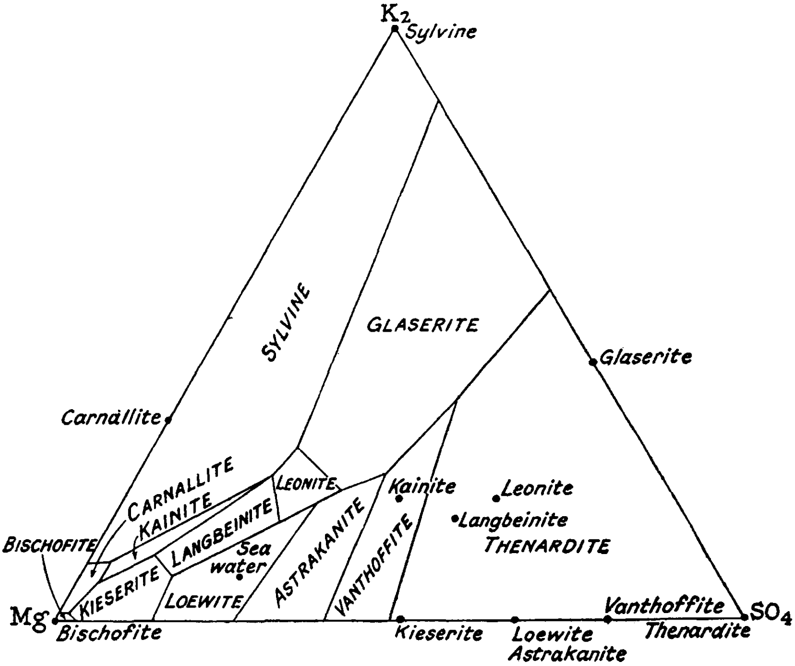

FIG. 4

Stability fields of oceanic salts at 55°.

The first suggestion to arise in an attempt to explain these discrepancies may be that the evaporation took place at higher temperatures, and it was to pursue this suggestion that van't Hoff carried out a second series of experiments at 83°, at which the field of kainite disappears. In Fig. 4 is reproduced the isothermal diagram for a temperature of 55°; loewite is the first salt to separate from normal sea-water at this temperature, and langbeinite also is found in the succession. Sylvine associated with kieserite would need still higher temperatures, since below 72° the field of kainite intervenes. Such high original temperatures appear most unlikely to most

[15] J. W. Turrentine, " Potash in North America," Reinhold, 1943, p. 24.

present-day students of the marine evaporites. Many lines of evidence, such as the characteristic association with "red beds," indicate that most oceanic salt deposits of past ages were laid down in an evaporating basin under an arid continental climate, but E. Fulda [16] is almost alone amongst recent authorities in believing that, as the rapidity of evaporation decreased with increasing concentration, the temperature may have risen sufficiently high to allow the direct crystallisation of these higher-temperature associations. Much of his evidence in support of the contention that the present-day profiles are essentially primary is of a geological character, but reference may be made here to experiments by S. Löwengart [17] on the evaporation of water from the Dead Sea. When the solution had reached a density of 1·35, evaporation came almost to a standstill whilst irradiation served merely to effect a rise of temperature.

Some modifications of the normal profile might be expected if other conditions during the evaporation, apart from the temperature, were different from those which we have assumed. It is possible that extensive resorption of earlier-formed salts may have occurred at a later stage of crystallisation, if they remained as a porous mass permeable by the solution. During the final stages, only kieserite, carnallite, bischofite, halite, and anhydrite are in equilibrium together, and any earlier products now brought into contact with the magnesium-rich liquor will be resorbed and pseudomorphed. It is also possible that a layering of solutions of different concentration may have arisen in the containing basin, and the crystalline products separating from the more concentrated but hotter surface layer may have been resorbed on settling through the underlying layers of differing concentration. A further effect of the setting up of currents of solutions of different concentrations has been specially stressed by H. Borchert.[18] In the course of an investigation of the reasons for the impoverishment of salt-deposits by lateral passage into less rich ores, he has developed a "dynamic-polythermal" study in contrast with the purely static considerations of van't Hoff and d'Ans. Such features as the configuration of the floor of the basin and different rates of evaporation in different areas may set up temperature gradients and circulating currents of solutions of different concentrations. Those compounds which tend to separate in the regions of higher temperature in such a circulatory system are termed *thermophile*, whilst the *cryophile* salts will be precipitated in the colder regions. The fields of formation of some salts under these conditions are considerably modified in comparison with the static system. Sylvine and langbeinite, for example, show much wider possibilities of formation; at high temperatures the langbeinite area is considerably extended towards the Mg apex, and a langbeinite–carnallite paragenesis may then be possible.

It has so far been assumed that the deposition of marine evaporites of past geological periods must be explained in terms of the evaporation of

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[16] *Z. deut. geol. Ges.*, 1924, **76**; Monatsber., 7—30.

[17] *Z. pr. Geol.*, 1928, **36**, 86—89.

[18] *Kali*, 1933, **27**, 97—100, 105—111, 124—127, 139—141, 148—150; 1934, **28**, 290—296, 301—305; 1935, **29**, 1—5; *Arch. Lagerstforsch.*, 1940, No. 67.

a solution similar in composition to present-day sea-water. It is, of course, possible that the composition may have been very different, and the question of the origin of the salt content of the sea is an interesting geochemical problem. On the assumption that the sea was originally fresh, and has gradually acquired its present content of salts from the contributions brought down to it by rivers, geologists have in the past even attempted to derive an estimate of geological time. The salt content of rivers, however, must have been derived from the chemical weathering of previously-existing rocks, and it is particularly difficult to accept that the high chlorine content of the sea can have been produced in this way. V. M. Goldschmidt [19] has examined the availability of a large number of elements in the earth's crust. It would appear that the concentrations of sulphur, chlorine, bromine, and boron in sea-water are such that these elements must already have been present in the primeval ocean.[20] E. J. Conway [21] has recently discussed the probable course of the chemical evolution of the ocean, both on the hypothesis that the halogen content was derived from the original atmosphere and also on the alternative assumption that all the halogen has come from volcanic sources. The probable differences of salt content between the Permian oceans and those of the present day thus revealed are quite insufficient to effect any radical change in the course of crystallisation which we have traced.

Some salt deposits are believed to have been laid down from solutions which derived their salt content, not directly from the ocean but by re-solution of previously-existing marine evaporites. The conditions of deposition then approach those of non-marine evaporites, the formation of which can be studied at the present day in natural salt lakes. In contrast with the uniform composition of oceanic waters, the waters of such lakes show a wide variety of chemical characteristics. In particular, it may be suspected that beds of rock-salt without an associated layer of gypsum or anhydrite below them are of secondary origin.

The discrepancies between the theoretical profile and the natural successions are not merely of a qualitative kind. A difficult quantitative problem is encountered in the vast thicknesses of gypsum, anhydrite or halite often recorded. A bed of halite 100 m. thick would correspond to the evaporation of a column of water some thousands of metres in depth, whilst thicknesses of anhydrite have been recorded which would involve the evaporation of an appreciable fraction of the whole present hydrosphere. Even if these large original volumes in the evaporating basin could be accepted, there should be evidence of marked shrinkage of the ocean as evaporation proceeded ; in actual fact, the beds of anhydrite and halite maintain their thickness close to the margins of the area of deposition. These difficulties find at least a partial explanation in the accepted picture of the conditions under which evaporation in the basin took place. Most geologists adopt, in a more or

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[19] *J.*, 1937, 667.

[20] H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, *op. cit.*, p. 221 ; C. H. White, *Amer. J. Sci.*, 1942, **240**, 714—724.

[21] *Proc. Roy. Irish Acad.*, 1943, **48**, *B* 9, 161—212.

less modified form, the " bar " theory put forward by Bischof and developed by C. Ochsenius [22] in the middle of the last century. Salt deposition is pictured as taking place from the waters of an enclosed lagoon, behind a permanent bar. So long as a constant or intermittent connection with the waters of the open ocean was maintained, an inflowing current of water of normal salinity across the bar would augment the supply of salts to the evaporating waters of the lagoon. In this manner, thick beds of salt could be formed, but the high degree of concentration necessary to precipitate the more soluble salts must eventually have allowed the concentrated mother-liquor to collect in the more depressed parts of the basin. Even at this stage there may have been an occasional influx of new solutions, either from the sea itself, from one basin to another, or as a result of rainfall which dissolved and washed down the salts which had separated earlier on the marginal portions of the area and had been left exposed by the retreat of the water.

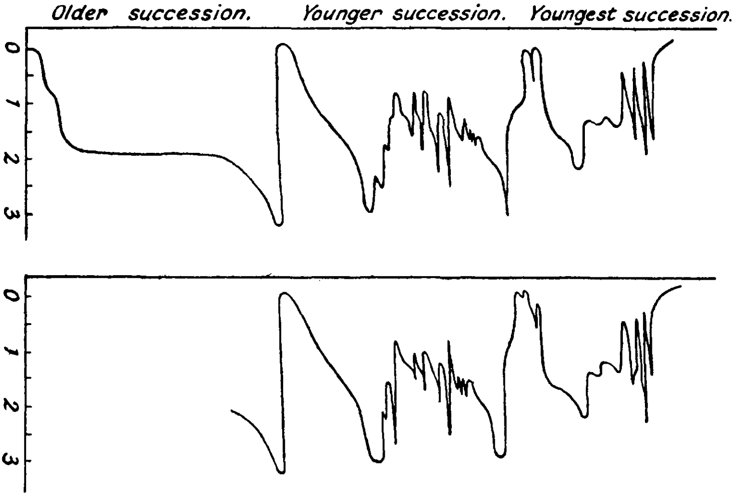

FIG. 5

Depositional rhythms in two salt profiles (Lotze) : 0, *Deposition of non-saline sediments.* 1, *Formation of anhydrite.* 2, *Formation of halite.* 3, *Formation of potassium salts.*

Indisputable evidence of such periodic additions, on both a major and a minor scale, can be found in the deposits themselves. In many parts of the German field a succession, beginning with anhydrite and passing upwards through the deposition of halite to the stage of formation of potash salts, is overlaid by clastic sediments (often a red saline clay) above which follows a more or less complete further cycle. A diagrammatic section by F. Lotze [23] reveals three such cycles (Fig. 5) in one area. In this country, two partial cycles from limestone through anhydrite to salt, followed by a third reaching

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[22] " Die Bildung der Steinsalzlager . . .," Halle, 1877.

[23] " Steinsalz und Kalisalze," Berlin, 1938, p. 151.

the stage of deposition of anhydrite, have been distinguished.[24] Periodicity on a minor scale is seen in the so-called annual rings (" Jahresringe "), a series of thin layers or streaks of anhydrite or of polyhalite in halite. Their name is derived from the belief, still accepted by some geologists, that they represent changes in solubility of calcium sulphate consequent upon annual fluctuations of temperature, but they may equally have arisen from periodic influx of further supplies of sea-water which reduced the concentration below the point of saturation for halite. A similar fine banding by layers of clay particles is sometimes observed, and seems to speak conclusively in favour of the influx of muddy water, possibly consequent upon increased rainfall due to climatic oscillation.

The considerations which we have so far advanced may help to explain in part the features presented by the natural profiles, but it is generally accepted that they provide only a partial clarification, and that an important branch of the study of marine evaporites involves the examination of changes effected subsequently to their deposition by the heat and pressure to which they have been subjected and by reaction with circulating solutions. The salts of the theoretical profile, many of them highly hydrated, will be specially susceptible to rise of temperature consequent upon burial under later overlying sediments—salt deposits have been described as " the liveliest and most temperamental of rocks "—and the importance of subsequent thermal metamorphism was stressed especially by F. Rinne [25] and Jänecke.[26] That many of the present mineral components of the salt deposits are the products of secondary changes seems to be abundantly clear. Lateral changes, such as carnallite passing into Hartsalz, have been frequently demonstrated, and it has been found possible in some areas to trace a number of successive guide-horizons of beds of almost pure halite of great lateral extent which pass unchanged between different zones of potash salts.[27] Examination of the detailed studies by K. Weber [28] of the Stassfurt region, or by W. T. Schaller and E. P. Henderson [29] of the successive replacements in the Texas–New Mexico deposits, will convince most readers that, whatever may have been the original succession, the salts now found are the products of profound alteration.

A purely thermal metamorphism, consequent upon burial, would bring about the successive " melting " of various salts, with the generation of solutions of various compositions. Under a depth of burial of about 3000 m. the change from gypsum to anhydrite would release almost pure water. If a primary bischofite layer were present, this would melt at a depth of about 4200 m. to an almost pure magnesium chloride solution. Jänecke has traced these changes in detail, and put forward the following scheme :

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[24] S. E. Hollingworth, *Proc. Geol. Assoc.*, 1942, **53**, 145.

[25] *Fortschr. Min.*, 1920, **6**, 101—136.

[26] See summary account in " Handbuch der Mineralchemie," C. Doelter and H. Leitmeier, 1929, IV, **2**, 1283—1290.

[27] A. Tinnes, *Arch. Lagerstforsch.*, 1928, No. 38.

[28] *Kali*, 1931, **25**, 17—23, 33—38, 49—55, 65—71, 82—88, 97—104, 122—123.

[29] Geol. Surv. United States, 1932, Bull. No. 833.

Theoretical profile.		Geothermally changed profile.
Bischofite zone	⟶	Yields $MgCl_2$ solution
Carnallite zone	⟶	Carnallite or Hartsalz zone
Kainite zone	⟶	Hartsalz zone
Potash-free magnesium sulphate zone	⟶	Loewite–Vanthoffite zone ⟶ Kieserite zone
Polyhalite zone	⟶	Polyhalite zone
Anhydrite zone	⟶	Glauberite zone Anhydrite zone
Gypsum zone		Anhydrite zone

A specially important change is that by which Hartsalz would be derived at 72°, *viz.*,

$$\text{Kainite} + \text{Carnallite} \rightleftharpoons \text{Kieserite} + \text{Sylvine} + \text{Solution}$$

but much of the Hartsalz shows an apparently primary lamination and would thus appear to be an original formation rather than the product of thermal metamorphism of previously-existing salts.

If the solutions generated during these reactions remained in contact with the salts, they would be available for a reversal of the reaction on declining temperature. Usually, however, they will have been pressed away to other regions, changing their composition by further reactions such as the abstraction of $MgCl_2$ from carnallite and effecting further modifications in the composition of the various zones. The proponents of extensive metamorphism of this kind believe that such residual solutions (" Restlaugen ") have exercised a profound influence on the generation of the present-day profiles of marine evaporites. To those such as Fulda, however, who reject completely the theory of a thermal metamorphism, the only solutions which have been active are the connate solutions (" Urlaugen "), which represent portions of the mother-liquor enclosed with the deposits at the time of their formation, and percolating ground water the action of which will be considered shortly. The details of Jänecke's presentation have been criticised by H. Borchert,[30] who points out that the compositions of residual solutions postulated will in fact be reached only by stages, and it is probably true to say that decreasing reliance is placed on a pure thermal metamorphism at the present time to explain the features of the actual profiles of marine evaporites. Consideration of the changes effected during deformation and earth movement, and of the significance of the plasticity of salt deposits, would lead into a purely geological field, but we may note here that earth movements have probably been responsible for producing the " Haselgebirge," an intimate mixture of salt, gypsum, and clay which is the common salt-producing rock of the Alps.

By reason of their ready solubility, the salt deposits are likely also to suffer further changes in the upper parts of the succession under the action of circulating ground water, unless effectively sealed off by overlying clays. Here belong a number of reactions classified by German geologists as " Hutsalzbildung "—the formation of an altered " cap " analogous with the secondary changes often found close to the surface in other types of ore

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[30] *Kali,* 1938, **32**, 132—135, 143—146, 169—172.

deposits. A re-formation of kainite is especially characteristic of these later changes :

$$KCl,MgCl_2,6H_2O + MgSO_4,H_2O + xH_2O = KCl,MgSO_4,3H_2O + (MgCl_2 + yH_2O)$$

Carnallite + Kieserite + Water = Kainite + Solution

The sylvine and kieserite of Hartsalz may combine to yield kainite :

$$KCl + MgSO_4,H_2O + 2H_2O = KCl,MgSO_4,3H_2O$$

Sylvine + Kieserite + Water = Kainite

Carnallite not accompanied by kieserite may yield sylvine (which, with the associated halite is the sylvinite ore), its $MgCl_2$ content passing into solution. Posthumous kainite and sylvinite thus formed are usually massive and unlaminated. Kainite itself may suffer a further extraction of its chlorine, yielding schoenite :

$$2(KCl,MgSO_4,3H_2O) + xH_2O = K_2SO_4,MgSO_4,6H_2O + (MgCl_2,yH_2O)$$

Kainite + Water = Schoenite + Solution

In the earlier days of the mining industry in Germany, large quantities of these rich kainite rocks from the shallower zones were worked, and sold for use as an artificial fertiliser ; the name has tended to linger on in application to a product which is now often a mixture of salts deriving its potassium content mainly from sylvine and kieserite.

Anhydrite brought within the influence of circulating ground water will be converted into gypsum, and the resultant increase of volume is usually accepted as the cause of the folded and contorted appearance (" enterolithic structure ") of many gypsum beds intercalated in salt deposits. This structure is occasionally found in beds which are now composed of anhydrite, but it is clear that, in the course of the complex history of some of these deposits, an anhydrite rock converted into gypsum at one stage may have been again dehydrated later in its history.

In their studies of metamorphic changes in rocks, geologists have for long been staunch supporters of the axiom " *Corpora non agunt nisi fluida,*" looking always for the presence of a solvent to act as a medium for recrystallisation. During the last two decades, however, more attention has been paid to the possibility of reaction by diffusion in the solid state, and this aspect of the study of oceanic salt deposits has been explored particularly by Leonhardt and his associates.[31] Experiments on mixtures of powdered salts which were compressed and subsequently heated showed that, even in the absence of solutions, compounds such as langbeinite and vanthoffite may begin to form at a temperature of 80°, and this type of reaction may well be important during metamorphism related to earth movements.

Thus far we have considered only those elements present in normal sea-water in relatively high concentrations. Amongst those of medium concentration, considerable interest has centred on boron. Reckoned as H_3BO_3 it ranks fifth amongst the anions with a concentration of 27 mg./kg., and, as we have noted, it must apparently be accepted as an original constituent of the primeval ocean, possibly derived from the presence of BCl_3 in the

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[31] J. Leonhardt, *Fortschr. Min.*, 1935, 19, 37—39 ; H. Ide, *Kali*, 1935, **29**, 83—86, 93—96, 103—105.

original atmosphere.[32] The work of W. Biltz and E. Marcus [33] showed that the boron content of the commoner minerals of the German deposits varies widely. Sporadically, however, a concentration is reached sufficient to allow the formation of boron minerals, of which the most important is boracite. When found as well-developed crystals, boracite has every appearance of being a primary product (though this conclusion has been questioned),[34] but it presents an interesting genetic problem. The external habit of the crystals is in agreement with cubic symmetry, but in section the crystals are seen to be composed of doubly-refracting lamellæ with the symmetry of an orthorhombic structure. When heated in the laboratory, the crystals become truly cubic only at 265° ; it seems unlikely that such a temperature could ever have been reached during burial and metamorphism of the salt deposits, and the explanation must be accepted at present that the crystals are pseudo-cubic polysynthetic twins. Boracite is found also in a massive form, originally named " stassfurtite," either interbedded with carnallite or as concretionary nodules, and most of this material is clearly secondary. Although stassfurtite is readily changed further by the action of circulating ground water, giving rise to other boron minerals such as ascharite, kaliborite, and pinnoite which are found in the Hutsalz, magnesium chloride being carried away in solution, yet the well-crystallised boracite seems to be much more resistant to such changes. Lueneburgite, another rare mineral in the German deposits, has been recorded also from the Texas–New Mexico district.[35]

Of other rare minerals occasionally found in marine evaporites, it will suffice to mention two examples. Tachhydrite may arise from carnallite as a secondary product under the action of solutions containing calcium chloride :

$$\underset{\text{Carnallite}}{2(KCl,MgCl_2,6H_2O)} + CaCl_2 = \underset{\text{Tachhydrite}}{CaCl_2,2MgCl_2,12H_2O} + \underset{\text{Sylvine}}{2KCl}$$

in agreement with the observed paragenesis tachhydrite–sylvine–carnallite–halite. The calcium chloride solution may arise from the action of magnesium chloride solutions on anhydrite :

$$MgCl_2 + CaSO_4 \rightleftharpoons CaCl_2 + MgSO_4$$

and tachhydrite has been recorded in association with kieserite. Rinneite, $NaCl,3KCl,FeCl_2$, is likely to form only where there is a high local concentration of iron. The small amount of iron present in sea-water is commonly represented in the marine evaporites by the particles of hematite which impart to most of the carnallite and many of the other salts a characteristic red colour (good colour photographs illustrating this feature are given by G. R. Mansfield).[36] A regular zonal arrangement of these particles of iron

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[32] H. Wattenberg, *Z. anorg. Chem.*, 1938, **236**, 355.

[33] *Ibid.*, 1911, **72**, 302—312.

[34] H. Werner, *Kali*, 1930, **24**, 129—132.

[35] W. T. Schaller and E. P. Henderson, Geol. Surv. United States, 1932, Bull. No. 833, pp. 47—48.

[36] *J. Chem. Educ.*, 1930, **7**, 737—761.

oxide within the host crystal [37] suggests that they have developed after crystallisation, the iron having originally been present as an isomorphous replacement of some part of the magnesium. In the American potash field, hematite as a red pigment is most abundant in the potash minerals. The insoluble residue left on dissolving away the salt has a stringy structure, and it has been suggested that the hematite is here the result of bacteriologic action.[38] More rarely, carnallite and tachhydrite are coloured yellow by ferric chloride, or the iron may be present as FeS_2 (pyrite) or as Fe_3O_4 (magnetite), colouring carnallite black. During the secondary reactions which have given rise to the cap salts, the iron content of the primary salts seems to pass into solution, and there is often a sharp dividing line between the brightly-coloured primary salts and the colourless overlying secondary products. For the direct formation of a compound such as rinneite it is possible that the presence of organic compounds retarded oxidation.

In all, 44 elements, excluding dissolved gases, have been demonstrated to be present in the water of the oceans, though for some the demonstration is indirect, by way of the examination of the ash of marine organisms. In the marine evaporites, these rarer elements are seldom or never represented by individual compounds, but occur as isomorphous mixtures or as trace elements in the commoner salts. Our present knowledge of their distribution is still very uneven, a systematic investigation of all the minor and trace elements by modern methods having yet to be undertaken. The following table [39] gives the concentration in ocean water of a few of these minor elements to which we may direct attention here :

Element.	Mg./kg.(Cl = 19·00°/₀₀).	Element.	Mg./kg.(Cl = 19·00°/₀₀).
Bromine . . .	65	Iodine . . .	0·05
Strontium . . .	13	Cæsium . . .	(0·002)
Fluorine . . .	1·4	Silver . . .	0·0003
Rubidium . . .	0·2	Gold	0·000006
Lithium . . .	0·1		

Bromine, in spite of its relatively high concentration, does not give rise to distinct bromine compounds, but is found isomorphously replacing chlorine in salts such as carnallite, sylvine, and kainite (ionic radii, Br^- 1·95 A., Cl^- 1·81 A.). Bischofite and tachhydrite may also contain appreciable amounts, but much less replacement is found in halite. Previously to the development of methods for the extraction of bromine from sea-water, Germany possessed an almost complete monopoly based on her Permian salt deposits, using carnallite and sylvine with a bromine content up to 0·4%. An early investigation by H. E. Boeke [40] showed clearly that at Stassfurt the bromine content of a given profile varied regularly with the content of carnallite, and a similar relationship has been demonstrated in the Russian

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[37] A. Johnsen, *Zentr. Min.*, 1909, 168—173.

[38] W. T. Schaller and E. P. Henderson, *loc. cit.*, pp. 11, 38.

[39] H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, *op. cit.*, pp. 176—177.

[40] *Z. Krist.*, 1908, **45**, 346—391.

deposits near Solikamsk, where J. Moratchevsky and A. Fedorova [41] found the bromine content to be independent of the depth but directly related to the carnallite content of the rock. Iodine, with its still larger ionic radius (2·16 A.), does not readily replace chlorine in these salts, and is found only in very small amounts in salt deposits. A detailed study of the iodine content of the German deposits has been made by J. Roeber.[42]

Rubidium and cæsium have also been extracted from carnallite, in which they replace the potassium (ionic radii : K^+ 1·33 A., Rb^+ 1·48 A., Cs^+ 1·69 A.). Rubidium has been found in the waters of the present-day oceans, but the cæsium content of 0·002 mg./kg. quoted in the table above is calculated on the basis of the ratio Cs : Rb in carnallite.[43] G. Heyne [44] found rubidium also in sylvine and langbeinite, but none in the kainite and polyhalite which he examined.

The presence of lithium has been demonstrated spectroscopically, and its occurrence has a practical application. Although the majority of salt mines are quite dry, solutions occasionally break into the workings. If these are connate waters (" Urlaugen ") enclosed with the salts at the time of deposition they will be limited in volume and will eventually drain away harmlessly. If, however, surface water breaks into a salt mine through fissures, the consequences are likely to be disastrous, and may entail the abandonment of the mine. The observation that the harmless Urlaugen are usually notably rich in lithium may hence be put to practical use.[45] The very different proportions of the alkali metals in sea-water and in the marine evaporites, when compared with their concentrations in igneous and sedimentary rocks, are to be referred to the readiness with which they are adsorbed in fine-grained sediments.[46]

Strontium, with a concentration of 13 mg./kg. in sea-water, is the fifth most abundant kation, and in agreement with this relatively high concentration the sulphate, celestine, has been occasionally recorded from salt deposits both in Europe and in America. More usually, strontium is found replacing calcium (ionic radii : Ca^{++} 0·99 A., Sr^{++} 1·13 A.) either in the carbonates, especially aragonite, or in the sulphates. The fact that a higher percentage seems to enter the anhydrite structure, compared with the small amounts usually found in primary gypsum,[47] may be used to study the vexed question of the original form in which the calcium sulphate of oceanic salt deposits was laid down. Anhydrite which has resulted from the dehydration of primary gypsum may be expected to show a low strontium content in comparison with primary anhydrite which separated directly from solution. Some occurrences of gypsum and anhydrite in the Permian deposits of Russia have been investigated from this point of view.[48]

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[41] Abstract in *Neues Jahrb. Min.*, Ref. II, 1929, 686.

[42] *Jahrb. Hallesch. Verb. Erf. mitteldtsch. Bodensch.*, 1938, **16**, 129—196.

[43] H. Wattenberg, *Z. anorg. Chem.*, 1938, **236**, 346.

[44] Abstract in *Neues Jahrb. Min.*, 1913, I, 365.

[45] E. Fulda, *Z. pr. Geol.*, 1939, **47**, 11—14.

[46] W. Noll, *Chem. Erde*, 1931, **6**, 573.

[47] *Idem, ibid.*, 1934, **8**, 559.

[48] L. M. Miropolsky and S. A. Borovick, *Compt. rend. (Doklady) Acad. Sci. U.R.S.S.*, 1943, **38**, 33—36 ; **41**, 382—383.

The high figures sometimes quoted for the supposed gold content of sea-water would suggest that this element also might become strongly concentrated in the residual liquor and thus enriched during the deposition of the oceanic salts. It would appear, however, that these high figures are partly due to faulty analytical methods, and also that much of the gold actually present is not in solution as ions but exists as discrete particles or in organic matter.[49] Such gold would be adsorbed on the finer clastic sediments rather than concentrated in the salts. J. Goubeau and L. Birckenbach [50] found the highest content of precious metals, amongst the salt minerals, in those which were notably coloured by inclusions of fine clay particles, and showed also that the average content of the associated clays was higher than that of the salt minerals themselves.

An attempt has been made in this review to trace the development of the study of marine evaporites, and to outline some of the geochemical problems involved. For recent more extended accounts, written from various points of view, reference may be made to the works of Lotze (1938) and Borchert (1940) cited above, or to two further works by Fulda.[51]

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[49] H. Wattenberg, *Z. anorg. Chem.*, 1938, **236,** 352.

[50] *Ibid.*, pp. 37—44.

[51] " Steinsalz und Kalisalze," Stuttgart, 1938 ; " Die Salzlagerstätten Deutschlands," Berlin, 1940.