DEPOSITION OF CALCIUM SULFATE FROM SEA WATER.

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ABSTRACT. Stability relations of gypsum and anhydrite in solutions of sea salts are of considerable geological interest as many deposits of these minerals are generally considered to be of marine origin. Since it has been shown that the transition point, gypsum—anhydrite, is not governed by a dissociation pressure relationship, but by a four-phase equilibrium, only relative solubilities establish their stability either alone or in presence of other salts. The present determinations in solutions of sea salts were made at 30°. The solubility of gypsum as well as that of anhydrite first increases rapidly in the presence of increasing amounts of sea salts, goes through a maximum at about twice the usual salinity of sea water, and then gradually decreases. However, the decrease is more rapid for anhydrite and an intersection of the two curves takes place at approximately 4.8 times the usual salinity, the point at which anhydrite becomes the stable phase.

Sea water is unsaturated with respect to calcium sulfate, and only after its salt content has increased by evaporation to 3.35 times the usual salinity can deposition take place. Between this concentration and the one required for stable deposition of anhydrite nearly one-half of the total amount of calcium sulfate present in sea water will be deposited at 30° in the form of gypsum. Since at a somewhat lower temperature at which evaporation of a marine basin may be assumed to have taken place the conditions in all probability will not be greatly modified, a large portion of calcium sulfate may always be expected to be deposited as gypsum. Sedimentary marine deposits of pure anhydrite must therefore either be at least partly derived from originally deposited gypsum, or have been formed close to or above 42°—the transition point of the two minerals.

INTRODUCTION.

DEPOSITS of calcium sulfate either in the form of gypsum or of anhydrite are very common in nature. Many of them, by their association with other salt deposits, are recognized to be of marine origin, and therefore the conditions which govern the formation of each of these minerals are of considerable geological significance. The classical investigations of the Stassfurt salt deposits by van't Hoff and his co-workers,[1] in which also the stability relations of the various calcium sulfates were studied, was supposed to have answered the question regarding the conditions under which gypsum and anhydrite were deposited. Later investigators,[2] however,

[1] van't Hoff, J. H., Armstrong, E. F., Hinrichsen, W., Weigert, F., and Just, G.: Z. phys. Chem., 45, 257, 1903; also van't Hoff, J. H.: Bildungsverhältnisse d. ozeanischen Salzablagerungen, Leipzig, 1912.

[2] See citations in ref. 3.

obtained different values for the transition points of the various calcium sulfates, which brought about much doubt of the correctness of van't Hoff's data, and resulted in a continued uncertainty regarding the true relationships in the system calcium sulfate—water. A reinvestigation made recently[3] showed that the incorrectness of the data given by van't Hoff and his associates resulted from their assumption that gypsum dissociates directly to form anhydrite. Hemihydrate, however, though an unstable phase, is always formed first when dissociation of gypsum takes place, and for this reason no three-phase equilibrium curve, gypsum—anhydrite—vapor, can exist under ordinary conditions or intersect the transition point, gypsum—anhydrite.

The coexistence of gypsum and anhydrite takes place only at a four-phase equilibrium point, the two solids—liquid—vapor, and is thus governed solely by the intersection of the solubility curves of the two solids. For the saturated aqueous solutions of gypsum and anhydrite this point lies at 42°, and not at 66° as had been deduced by van't Hoff and his co-workers from vapor pressure measurements of solutions with which, as they thought, gypsum and anhydrite were in equilibrium, and had for this reason assumed that they should have, therefore, a dissociation pressure that is equal to the vapor pressure of the solution. However, in the absence of direct dissociation of gypsum to anhydrite this reasoning is unjustified, and the data for the dissociation pressure curve which they gave are obviously based on purely imaginary equilibria.

To ascertain the effect of some salt solution on the transition temperature of gypsum—anhydrite it is necessary to determine their actual solubility curves in such a solution. The effect of the presence of other solutes on the transition temperature depends in general on the relative change in the solubilities of the two solids in such solutions, and three possibilities are then open. The first is when the solubility of gypsum is increased relatively more than that of anhydrite, and this will result in a lowering of the transition temperature. The second, which represents the reverse of the first in respect to relative solubilities, would result in a raising of the transition temperature. The third possibility appears when the solubilities of both are either increased or decreased in a relatively equal amount, in

[3] Posnjak, E.: This Journal, 35-A, 247, 1938.

which case their transition temperature will of course remain unchanged.

From the above it is obvious that in order to obtain information concerning the form in which calcium sulfate shall be deposited in nature under some assumed conditions, actual determinations of the solubilities of gypsum and of anhydrite under these conditions must be made. Early experiments by Usiglio[4] on the deposition of salts from sea water by evaporation were not carried out under sufficiently controlled conditions to establish exact knowledge. In recent years determinations of the solubility of gypsum and of anhydrite in sea water of various concentrations have been carried out by a number of Japanese investigators.[5] However, they made the solubility determinations for anhydrite only above 40°, and though they found the data for the transition temperatures in the system calcium sulfate—water, given by van't Hoff and his co-workers to be erroneous, their own conclusions regarding the stability relations of gypsum and anhydrite in sea water of various concentrations rest on calculations which are also based on the assumption made previously by van't Hoff, namely, that the dissociation of gypsum to anhydrite takes place directly, and that at the transition point this dissociation pressure is equal to the vapor pressure of the solution. Thus the transition temperatures that they give for the various concentrations of sea water are not determined directly but are derived from calculations which rest on determinations of vapor pressure values obtained by them for these solutions. Since, however, as was pointed out above, no direct dissociation of gypsum to anhydrite does take place, and therefore no dissociation pressure curve intersects the transition point of these two solids, their calculated values are obviously unreliable. Information regarding deposition of gypsum and of anhydrite from solutions of sea salts to be dependable must be based on direct solubility determinations of these substances in such solutions. The intersection of the solubility curves thus determined will

[4] Usiglio, J.: Ann. chim. phys., 27, 172, 1849.

[5] Tanaka, Y., Nakamura, K., and Hara, R.: J. Soc. Chem. Ind. Japan, 34, 284, 1931; Hara, R., Nakamura, K., and Higashi, K.: Tech. Repts. Tohoku Imp. Univ., 10, 433, 1932; Hara, R., Tanaka, Y., and Nakamura, K.: Tech. Repts. Tohoku Imp. Univ., 11, 87, 1934; Toriumi, T., and Hara, R.: Tech. Repts. Tohoku Imp. Univ., 12, 72, 1938.

establish the conditions for their transition. Determinations of the solubilities of gypsum and of anhydrite in solutions of sea salts at 30° are the subject of the present paper, and the results given establish definitely the stable form in which calcium sulfate is deposited under these conditions.

EXPERIMENTAL.

Many analyses of the composition of sea water from various parts of the oceans have been recorded, and the data collected by the *Challenger* expedition are generally accepted as representative. These data show that except in closed or nearly closed basins sea water is of very uniform composition. The salt content is approximately 35 parts per 1,000 parts of solution, and, omitting the very minor salt constituents, consists chiefly of sodium chloride, magnesium chloride, magnesium sulfate, calcium sulfate, potassium sulfate, and small amounts of calcium carbonate and magnesium bromide.

The present experiments were carried out with solutions containing the right proportion of the main salts found in sea water, as natural sea water was not conveniently available. For a solution corresponding to normal sea water the composition given in Table I was used, and fractions or multiples of

TABLE I.

Composition of sea water and solution used in solubility determinations.

	Sea water composition, *Challenger* expedition parts per liter	"Normal" solution used parts per liter
$NaCl$	27.213	27.2
$MgCl_2$	3.807	3.8
$MgSO_4$	1.658	1.7
$CaSO_4$	1.260	...
K_2SO_4	0.863	0.9
$CaCO_3$	0.123	...
$MgBr_2$	0.076	...

these salt contents were used for the various concentrations that may result from the dilution or concentration of sea water. Thus the concentrations of the solutions of sea salts were expressed by designating that corresponding to normal by one, and others by fractions or multiples of this concentration.

As may be noted, the solutions of sea salts that were used

contained no salts of calcium. In natural sea water only about 0.12 parts of calcium carbonate per 1,000 are present. Its omission in the present experiments is insufficient to modify appreciably the behavior of sea water in respect to the two forms of calcium sulfate which were the object of these experiments, and was obviously done to simplify the analytical procedure.

Calcium sulfate is present in sea water to the amount of 1.26 parts per 1,000. This amount is less than its normal solubility in water, and as will be seen below, the solubility of calcium sulfate is greatly increased in sea water of normal salinity. Ordinary sea water is therefore very far from being saturated with respect to calcium sulfate.

For the solubility determinations of gypsum and of anhydrite natural minerals of high purity were used. The gypsum was clear selenite from Wayne County, Utah, and the anhydrite was from Midland, California. Each was finely ground for solubility determinations which were carried out in glass-stoppered Pyrex bottles rotated in a thermostat which was kept constant to better than 0.1°. Experiments showed that two to three weeks' rotation was usually required to attain equilibrium. For gypsum no difficulty presents itself when more time is allowed, as it does not undergo a change even when it becomes the unstable phase. However, anhydrite as an unstable phase readily changes to gypsum, and it is therefore necessary to attain the solubility value in a given solution before the formation of gypsum begins by following the increasing calcium sulfate content of the solution to its maximum value.

Two sources of difficulty must be guarded against in the determination of calcium sulfate in solutions of sea water. One lies in the presence of magnesium especially at the higher concentrations of sea salts, and the other is connected with the general tendency toward too high values for the solubility of gypsum and anhydrite. The reason for this has been attributed to the greater solubility of fine particles which, as Hulett[6] has shown, may result in the case of gypsum in a 20 per cent increase of its solubility. While there is no doubt that fine particles may produce initially supersaturation, it has been pointed out in connection with solubility determinations in the system $CaSO_4-H_2O$,[7] that the high values of many investiga-

[6] Hulett, G. E.: Z. phys. Chem., 37, 385, 1901.
[7] Posnjak, E.: op. cit.

tors resulted not so much from higher solubility—gypsum recrystallizes very readily and it is necessary only to allow sufficient time for the solution to come to equilibrium with the solid—as from imperfect separation of some of the fine suspended solid from the solution. As was shown, solubility determinations on finely ground gypsum were in complete agreement with the results obtained by Hulett, where fine particles were carefully excluded, when the separation of the solution was carried out by means of silica filters of fine porosity. Accordingly the same procedure was used here as before. Samples of the solution were taken at the temperature of the experiment. After allowing a short time for the solid to settle, the stopper of the bottle was replaced quickly by one enclosing the stem of a small immersion filter, which was connected to the stopcock of an evacuated bottle that received the sample of solution. Duplicates taken in this way gave concordant results.

The separation of calcium from magnesium by the oxalate method was found to give satisfactory results provided double, and for the higher concentrations of sea salts triple, precipitation was made. Blanks showed that with high dilution of the solutions, to keep magnesium within the concentration usually recommended for this separation, reliable values could be obtained.

SOLUBILITY DETERMINATIONS.

Results of solubility determinations on gypsum and on anhydrite at 30° are given in Table II and are shown graphically on Fig. 1. It will be noticed that in the presence of sea

TABLE II.

Solubilities of gypsum and of anhydrite in sea salt solutions.

Concentration of sea salt solution	Gypsum	Anhydrite
	grams per 100 grams H_2O	
0.0	0.209	0.250
0.5	0.366	0.414
1.0	0.418	0.468
2.0	0.449	0.488
3.0	0.432	0.470
3.6	0.412	0.436
5.0	0.339	0.336
5.5	0.308	0.288

salts the solubility of gypsum and of anhydrite increases very rapidly up to about the normal salinity of sea water. From then on it increases only slightly, reaching a maximum at

approximately twice the normal salinity, beyond which the solubilities of both begin to decrease. However, the decrease in solubility of anhydrite proceeds more rapidly so that its solubility curve intersects that of gypsum at a concentration of approximately 4.8 times normal salinity. At 30° gypsum is thus the stable phase up to this concentration of sea salts,

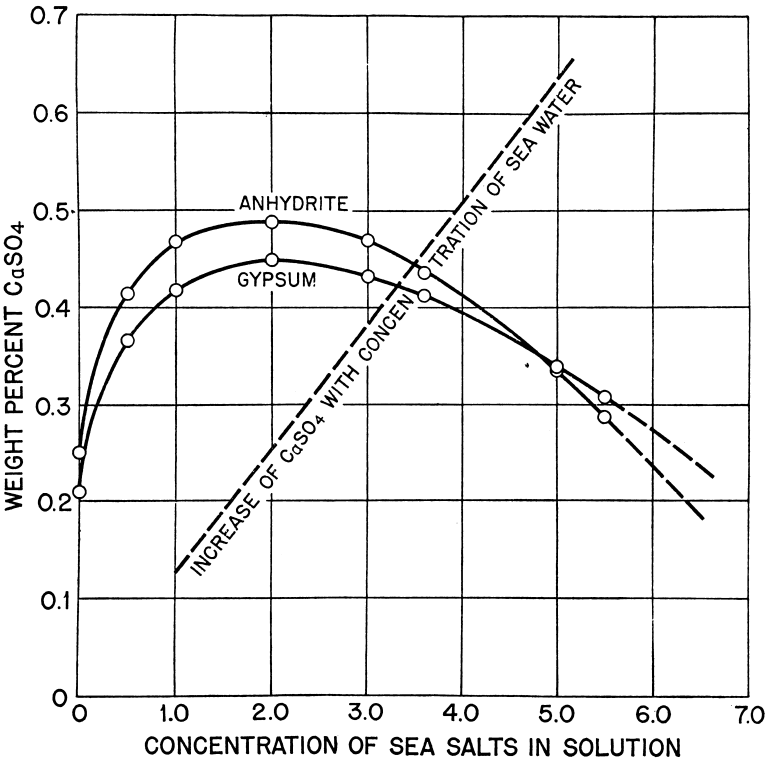

Fig. 1. Solubility curves for gypsum and anhydrite in solutions of sea salts. Broken line shows amount of calcium sulfate that is available when ordinary sea water is being evaporated. Concentration is expressed in units of the usual salinity of sea water.

above which concentration anhydrite becomes the stable phase. While this is a considerable lowering of the transition temperature, the salt concentration is still very far (less than one-half) from saturation with sodium chloride.

As mentioned above, sea water contains only 1.26 parts per thousand of calcium sulfate, and, as may be seen from the diagram Fig. 1, this concentration is very far from the satura-

tion point in such solution. The broken line of this diagram represents the increase of calcium sulfate as evaporation of sea water takes place, and this line, as will be seen, intersects the solubility line of the stable phase—gypsum—at a salinity of 3.35 times the normal concentration of sea water. Therefore when sea water evaporates at 30° gypsum will always be deposited when the brine attains the above salinity, and it will continue to deposit gypsum until the salinity reaches the value of approximately 4.8 times the normal salinity of sea water. Beyond this point the brine will deposit the calcium sulfate in the form of anhydrite.

DISCUSSION.

While evaporation of a marine basin may take place at a temperature that is somewhat lower than 30° C., the solubility data arrived at by the above experiments for this temperature would in all probability not be changed greatly by a decrease of about 10 to 15°. They may therefore be used with reasonable certainty as a basis for discussion of the deposition of calcium sulfate in such basins. It is then evident that when sea water is evaporating somewhat below a temperature of 42° calcium sulfate must always be expected to be deposited at first in the form of gypsum. At 30° somewhat less than one-half of all the calcium sulfate present in the original sea water will be deposited in this form, and only after the volume of sea water has been shrunk by evaporation to nearly one-fifth can direct deposition of anhydrite begin to take place. The often-made assumption that all anhydrite may have been deposited below 42° C. by evaporation of a marine basin and is primary, must then apparently be modified by the additional assumption that the part of calcium sulfate originally deposited in the form of gypsum subsequently was changed to anhydrite.

The problem regarding the conditions of formation of the anhydrite deposits of marine origin remains open. This applies not only to the temperature at which deposition may have taken place, but also to the accumulation of the extraordinarily large deposits of calcium sulfate, the amount of which is out of proportion to the other salts with which they are genetically connected. The bar theory of Ochsenius which is commonly used by geologists to account for the accumulation of calcium sulfate suggests a way for the formation of large deposits

of marine origin but does not give a plausible explanation for its disproportionate amount in such salt deposits. Modification of the bar theory by Branson,[8] postulating separation of salts by a series of connecting lagoons, requires such special conditions that Grabau[9] said that "it might be questioned if such nice balancing of conditions could ever be maintained for any great length of time."

Moreover, the bar theory does not account for deposition of anhydrite as long as it is assumed that its deposition has taken place at a temperature below 42° C., the transition point of gypsum—anhydrite, for any addition of sea water to the solution depositing calcium sulfate would always result in additional deposition of gypsum, until evaporation reached the much more highly concentrated brine required for the formation of anhydrite. The best example illustrating the bar-theory process at present was found by Ochsenius in the salt concentration that is taking place in the Gulf of Karabugas on the eastern side of the Caspian Sea. Here "gypsum forms in considerable quantity along the shallow shores of the Bar in the gulf, as well as everywhere along the shores of the gulf itself at a distance from the mouth of the strait. It forms a white crust of pure gypsum, or binds the sands along the shores into a solid rock mass. When the water level falls in summer, great stretches of flat coast covered by a black sand with numerous gypsum crystals and scattered shells of *Cardium edule* L. are exposed. Gypsum is also found near the margin where the salinity is less (16°-17° Bé.), and farther in, a bed of this salt occurs."[10] Another example is the deposit formed in the Great Bitter lake of Suez which according to Grabau (Op. cit., p. 139) "seems to fill all the requirements of the bar theory and may be used as an illustration of a nearly completed series of this type." Here again gypsum was found, and though it is even interlain with rock salt no mention is made of the presence of any anhydrite.

Only by postulating that deposition of calcium sulfate from sea water has taken place at or above 42° could the formation of beds of anhydrite such as are found, for example, at Stass-

[8] Branson, E. B.: Origin of thick gypsum and salt deposits, Bull. Geol. Soc. Am., Vol. 26, 1915.

[9] Grabau, A. W.: Principles of Salt Deposition, New York, p. 143, 1920.

[10] Grabau, A. W.: op. cit., p. 136.

furt[11] be thought of as being completely primary in their origin. Otherwise, and leaving open the question of the accumulation of the amount of calcium sulfate, it must be assumed that part of it originally deposited as gypsum has later been converted into anhydrite.[12]

[11] It may be pointed out that other salts found there require according to the investigations of van't Hoff and his co-workers even higher temperatures.

[12] In discussing the effects of salt solutions on the transition, gypsum—anhydrite, the present author suggested (Op. cit., p. 270) that a relatively small amount of potassium sulfate may greatly lower this transition. This suggestion was based on a few solubility determinations on gypsum and anhydrite by E. A. Hill (J. Am. Chem. Soc., 59, 2242, 1937) in dilute solutions of potassium sulfate which according to his statement gave for each values lying on straight lines. However, experiments which the author has made since then show that their solubility values were not lying on straight lines, and that the former extrapolation to higher concentrations leads, therefore, to an erroneous result. No intersection of the solubility curves for gypsum and anhydrite even at much higher concentrations of potassium sulfate takes place, anhydrite remaining the unstable phase. At a concentration of approximately three per cent the solubility curve for gypsum terminates with the formation of the double salt syngenite.

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