

# Calcium Sulphate Minerals of Evaporite Deposits: Their Primary Mineralogy

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## ABSTRACT

*Equilibrium relationships between calcium sulphate minerals are briefly reviewed and compared with measured physical and chemical parameters from the sabkha environments of the Persian Gulf and Baja California. The laboratory and field data agree well but emphasize that reaction kinetics play an important role in the widespread occurrence of metastable phases. The data suggest that gypsum will probably always be the phase precipitated from standing bodies of brine but that both primary anhydrite and penecontemporaneous anhydrite after gypsum are very common products of the sabkha environment.*

## INTRODUCTION

The purpose of this paper is to very briefly review the status of our understanding of the natural occurrence of calcium sulphate minerals. The laboratory studies are first summarized and then compared with physical and chemical parameters of the sabkha environments of the Persian Gulf and Baja California, where gypsum, bassanite and anhydrite are all actively forming today.

## LABORATORY STUDIES

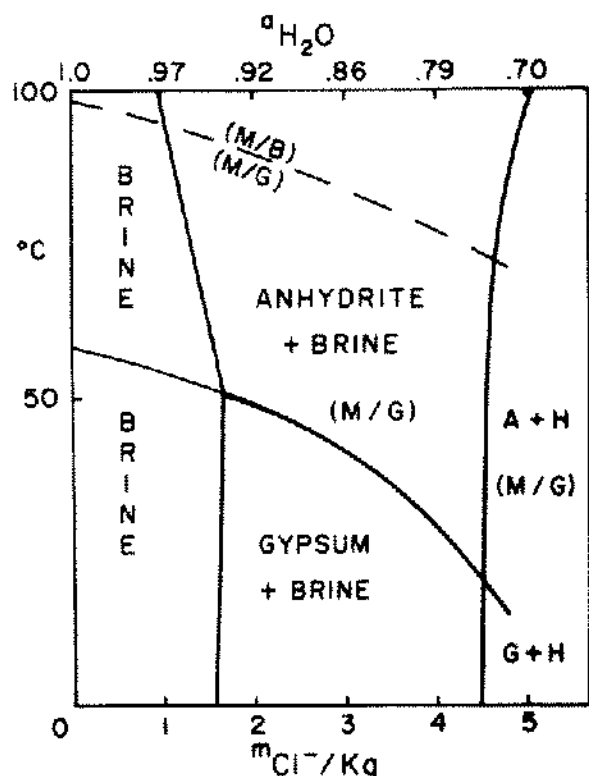
An extensive literature has developed describing laboratory studies of the equilibria between the calcium sulphate minerals and this has been fairly adequately reviewed in several papers, from which the many references to the original studies may be obtained (Gay, 1965; Zen, 1965; Kinsman, 1966, 1967; Hardie, 1967). Gay (1965) recognized four discrete solid phases in the system  $\text{CaSO}_4\text{-H}_2\text{O}$ ; gypsum, bassanite (hemihydrate), insoluble anhydrite and soluble anhydrite. The first three are all naturally occurring minerals but the latter is known only from laboratory studies. The solid phases in certain reac-

tions are a solid state dehydration or rehydration sequence but in other reactions dissolution of one phase is followed by nucleation and crystal growth of the succeeding phase.

As long as no intermediate compounds are formed, such as double salts, then equilibria between the mineral phases are a function only of the activity of water in solution-mineral reactions, or of the relative humidity in vapour-mineral reactions, irrespective of whether the equilibria are stable or metastable. Using stability data largely qualitatively it can be shown that gypsum and anhydrite may be stable minerals within the near-surface earth environment, whereas bassanite will always be metastable.

Most early studies of the gypsum-anhydrite equilibrium were indirect, using solubility data and because of the great difficulty experienced in precipitating anhydrite from supersaturated solutions even in the presence of anhydrite seed nuclei, most of the solubility data represent minimum values because the mineral solubility could only be determined from undersaturation. Even gypsum solubility data are all from undersaturation only, except for the study by Zen (1965). However, Hardie (1964, 1967) succeeded in determining the equilibrium directly, converting one solid phase into the other in solutions of known water activity. I have recalculated his data for application to sea water solutions and the resulting gypsum-anhydrite equilibrium for sea water brines is shown in Figure 1. The equilibria are shown in a similar but slightly different way in Figure 2, where mineral-vapour reactions are considered; this figure is mainly of value for its description of the metastable gypsum—metastable bassanite reaction, which can only take place at earth surface conditions of rather low relative humidity.

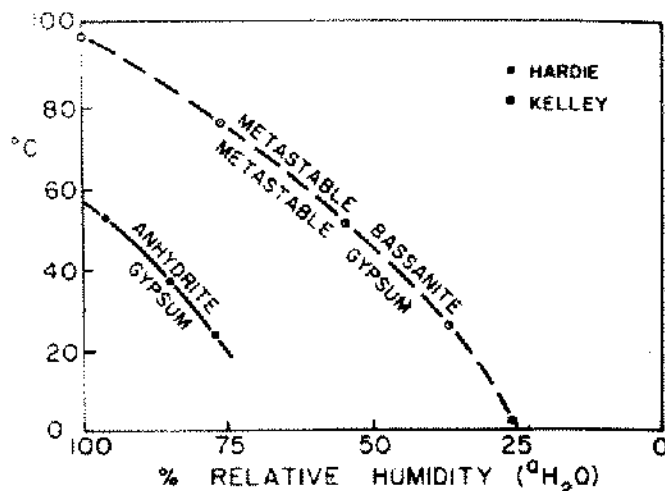
The reaction gypsum  $\rightarrow$  anhydrite in the absence of liquid water requires that bassanite be an intermediate phase. Experimental dehydration of bassanite below tem-



**Figure 1.** Equilibria between the calcium sulphate minerals gypsum (G), anhydrite (A) and bassanite (B) in diluted seawater, seawater and seawater brines. Solution salinities are described as moles of chloride per kilogram of solution and the activity of water in these solutions is shown at the top of the figure. Through much of the lower part of the anhydrite stability field gypsum may be present as a metastable phase (M/G) but at higher temperatures it dehydrates to metastable bassanite (M/B). At chloride concentrations between four and five moles/kg halite (H) is precipitated as an additional solid phase (figure modified from Kinsman, 1966).

peratures of 130°C always yields soluble anhydrite which has not so far been recorded as a natural mineral. Insoluble anhydrite only results after prolonged high temperature (>150°C) dehydration of bassanite. The reaction gypsum → anhydrite in the presence of liquid water and below the metastable gypsum → bassanite reaction temperature results in the formation of insoluble anhydrite by a dissolution-reprecipitation mechanism, although the detailed nature of the anhydrite nucleation is not understood (a fragment of gypsum crystal lattice may serve as nucleus for anhydrite crystal growth).

Of critical significance to the gypsum-anhydrite problem is an understanding of the nucleation of anhydrite. The problem may be one of kinetics of nucleation, or it may be dependent on the differential stability (higher solubility) of nuclei compared with large crystals of the solid phase. The solubility curves of gypsum and anhydrite are fairly similar (Figure 3) and do not diverge rapidly where both phases are nearly in equilibrium with each other.



**Figure 2.** Equilibria between the calcium sulphate minerals expressed in terms of temperature and water vapour pressure. Water vapour pressure may be described as % relative humidity, which is also equivalent to water activity. Equilibria at relative humidities less than 75% (equivalent to water activities less than 0.75) are for water vapour-mineral reactions; data above 75% relative humidity or 0.75 water activity may describe equilibria between saline solutions and solid phases or water vapour and solid phases. The gypsum-anhydrite equilibrium boundary shown is the same boundary which is shown in Figure 1. (Figure from Kinsman, 1967)

Thus when anhydrite is the stable phase (has the lower solubility) an evaporating solution may cross the anhydrite equilibrium solubility curve and shortly thereafter also cross the metastable gypsum solubility curve, if no anhydrite precipitation takes place. If the critical supersaturation for gypsum nucleation is reached before that for anhydrite nucleation, then gypsum will precipitate metastably. This explanation would fit the widespread metastable precipitation of gypsum found in laboratory studies and in natural environments. As the solubilities of the two minerals are rather similar, solutions which continue precipitating metastable gypsum will never become very highly supersaturated with respect to anhydrite. Another significant difficulty in the formation of an anhydrous mineral such as anhydrite probably relates to the desolvation of the aqueous calcium ion.

### CRITICAL ENVIRONMENTAL VARIABLES

The variables to be defined are temperature,  $a_{H_2O}$  and relative humidity. In areas adjacent to the sea, relative humidities rarely fall below 75%; values below 50% occur only in continental deserts and rain shadow areas. These relative humidity values refer to the air mass 1-2 meters above the ground, a typical vertical profile showing higher values over the lower few centimeters. In pore spaces, unless the water table is very deep, pore atmospheres are saturated (but presence of halite means that maximum

$^a\text{H}_2\text{O}$  or relative humidity will be 0.75 or 75%). Values of  $^a\text{H}_2\text{O}$  for marine brines range 0.9-0.75 whilst calcium sulphate minerals are being actively precipitated. Even in fairly late stage brines values only fall to 0.65-0.70. Continental playa waters may have  $^a\text{H}_2\text{O}$  values as low as about 0.6.

Highest mean annual air temperature today is 31°C. In coastal areas air temperatures generally do not exceed 50°C, but values of 60°C may be reached in continental areas. Minimum air temperatures for evaporite forming areas are less well defined but may be 10°C in coastal areas and 5°C or lower in continental areas. Brine body temperatures may exceptionally reach 80°C for short periods but a more common upper limit would be 50-60°C; lower limit is variable, maybe say 10-15°C, dependent on climate and features of the brine body such as size and seasonal mixing. Salt flat surfaces may reach 80°C or more but temperatures above 50°C penetrate only the upper few centimeters. Albedo and thermal diffusivity characteristics generally result in mean ground surface, and ultimately shallow subsurface temperatures, exceeding mean air temperatures in areas of high insolation (by as much as 7°C).

### RECENT OCCURRENCES OF CALCIUM SULPHATE MINERALS

Gypsum is widely precipitated in arid coastal regions of the world and in many continental basins of internal drainage. Gypsum is by far the most abundant calcium sulphate mineral of the earth surface and near-surface environments and forms by direct precipitation from standing bodies of brine and by interstitial precipitation in sabkha environments.

Bassanite has been reported from arid region surface efflorescences; also from Death Valley, California and from Clayton Playa, Nevada. I have recorded bassanite from the Persian Gulf sabkhas, Great Salt Lake, Utah, and two areas in Baja California, Mexico (unpublished). Bassanite is always closely associated with gypsum and seems without doubt a dehydration product of a gypsum precursor. In most arid regions, where gypsum lies exposed to the sun, bassanite will probably be developed, though may be only seasonally.

Anhydrite of Recent age has been reported from several localities (always insoluble anhydrite). At Clayton Playa and Death Valley the anhydrite occurs apparently as a surface dehydration product of a gypsum precursor. The dehydration of gypsum  $\rightarrow$  bassanite  $\rightarrow$  anhydrite, which seems to be indicated, certainly by the Clayton Playa occurrence, does not fit with the experimental data. Either a solution phase was involved or we have more to learn about dehydration processes in the absence of a liquid phase. Several other minor occurrences of anhydrite

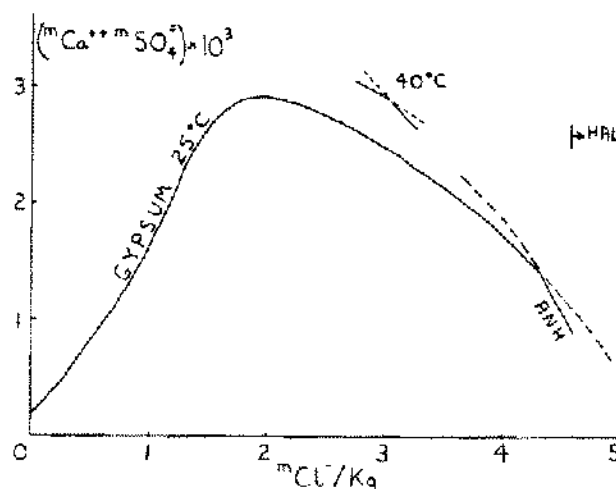


Figure 3. Solubilities of gypsum and anhydrite at 25°C and 40°C in seawater solutions. Solubility of stable phase (least soluble phase) at any temperature is indicated by solid line; metastable phase solubilities shown by dashed line. Intersection of solubility curves marks position of the four-phase equilibrium at any temperature (gypsum-anhydrite-solution-vapour). Note the acute angle of the solubility curves at their intersections indicating that a solution in metastable equilibrium with say gypsum is only slightly supersaturated with respect to the stable phase anhydrite.

Solubilities are expressed in terms of molar product  $m\text{Ca}^{++} \cdot m\text{SO}_4^{--}$  and solution salinities in terms of moles of chloride per kilogram of solution. At salinities somewhat less than five molar, halite (HAL) is precipitated.

have also been reported but generally without sufficient background environmental data to interpret the occurrence very usefully. However, two fairly major occurrences of Recent anhydrite have been reported from Baja California and the Persian Gulf (Kinsman, 1966, 1969). The anhydrite is developed as an early diagenetic mineral in extensive supratidal salt flats or sabkhas. It occurs typically as nodules, layers of nodules or contorted layers which have physically displaced the host sediments (in Baja California the host sediments are terrigenous muds, silts and sands; in the Persian Gulf the host sediments are carbonate muds and sands which are being extensively dolomitised). Near surface bassanite occurs in both areas as a solid state dehydration product of gypsum. Gypsum occurs widely in both areas, also precipitated as an interstitial displacement mineral. In the first studies of the Persian Gulf anhydrite I concluded that there was no evidence of pseudomorphing of earlier gypsum but that much of the early formed gypsum later dissolved, the ions migrating to new sites and there precipitating as anhydrite. In a later study Butler (1969) showed conclusive evidence of pseudomorphing of gypsum by anhydrite in certain areas of the Abu Dhabi sabkhas and from this evidence generalized that all anhydrite of the sabkhas was a diagenetic replacement of earlier gypsum. Later more detailed studies by R. Park, R. Patterson and myself have

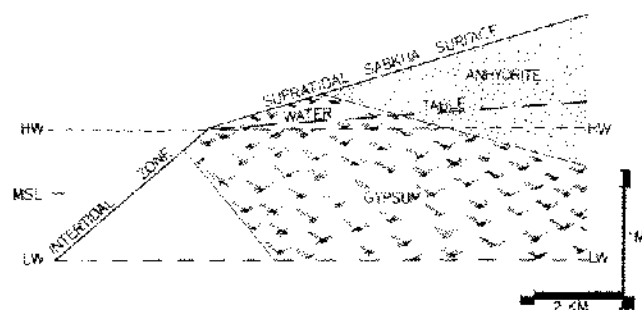
confirmed that the earliest anhydrite of the Persian Gulf sabkha environments forms as a pseudomorphic replacement of gypsum and that a considerable amount of the earlier formed gypsum crystal mushes is later replaced by anhydrite. However, the supratidal unit of non-marine sediments, in which most of the contorted, layered and coarsely nodular anhydrite occurs, never has gypsum developed within it and thus this anhydrite is of primary origin. Figures 4 and 5 summarize the Persian Gulf distribution of gypsum and anhydrite.

Pore fluid studies show that most Persian Gulf sabkha brines are gypsum/anhydrite saturated (Figure 6). Figure 7 shows pore fluid data for fluids squeezed from samples of specific mineralogies; the data of both figures 6 and 7 confirm the laboratory determinations which are summarized in Figure 3.

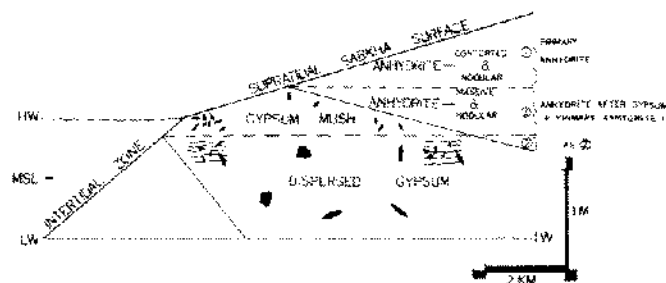
The Persian Gulf field data are summarized in Figure 8 which emphasizes that although the equilibrium data of Hardie (1967) are confirmed, metastable reactions commonly dominate. Reaction kinetics of the replacements are evidently very asymmetric.

### CONCLUSIONS ON THE PRIMARY MINERALOGY OF CALCIUM SULPHATE DEPOSITS

Marine brines of solar salt ponds and natural standing bodies of brine today all precipitate gypsum rather than anhydrite, whatever the brine salinity or temperature. In sabkhas or salt flats both gypsum and anhydrite are formed, together with small amounts of bassanite. These environments provide examples of the primary precipita-



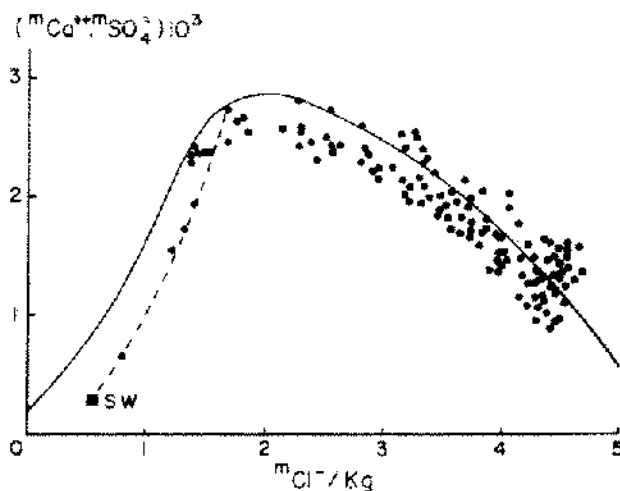
**Figure 4.** Cartoon of gypsum and anhydrite distribution within the sabkha environment of the Trucial Coast, Persian Gulf. All precipitation is from subsurface interstitial brines. Gypsum forms crystal mushes up to 40 cm thick just above water mark (HW) and extending down to mean sea level (MSL). Later interstitial precipitation occurs throughout the intertidal facies carbonate host sediments. Anhydrite first occurs as a near surface pseudomorphic replacement of gypsum and the dissolution-reprecipitation reaction continues with passage of time to greater depths, the entire gypsum mush being replaced by net-textured anhydrite within a 2,000 year period. The bulk of the anhydrite within the slowly accreting supratidal aeolian sediments is primary anhydrite. Note the greatly different horizontal and vertical scales of the figure; the surface slope of the sabkha is close to 1:4000.



**Figure 5.** A more detailed schematic description of the gypsum and anhydrite of the Trucial Coast sabkhas. The gypsum occurs as lenticular or lensoid crystals or as large formless lumps. The gypsum crystal mush is ultimately entirely replaced by anhydrite (zone two) and the replacement even extends down into the stromatolite facies carbonate sediments in which layers of lenticular gypsum crystals occur between the algal mat laminae (zone three). Within zone two, a fairly large amount of primary anhydrite is also thought to be formed (anhydrite without a gypsum precursor). Within zone three only primary anhydrite is formed.

tion of both gypsum and anhydrite, of the solid state dehydration sequence gypsum-bassanite-anhydrite, and of the dissolution-precipitation replacement of gypsum by anhydrite and anhydrite by gypsum.

Temperature and chemistry of associated brines confirm previously published data on the solubility of gypsum and provide new data on the solubility of anhydrite. The solution-mineral data also confirm Hardie's (1967) published equilibrium relationships between gypsum and anhydrite, but give new emphasis to the problems of kinetics as they affect the distribution of gypsum and anhydrite in



**Figure 6.** Persian Gulf brines in presumed equilibrium with gypsum and/or anhydrite. Solid curve from Figure 3. Brine samples were all close to 30°C when collected. Field data fit experimental curve fairly well. Dashed curve is calculated curve for seawater evaporation. Samples lying on this curve are undersaturated with respect to any calcium sulphate mineral. Samples to the left of the dashed line but close to the gypsum saturation curve are continental brines rather than marine brines.

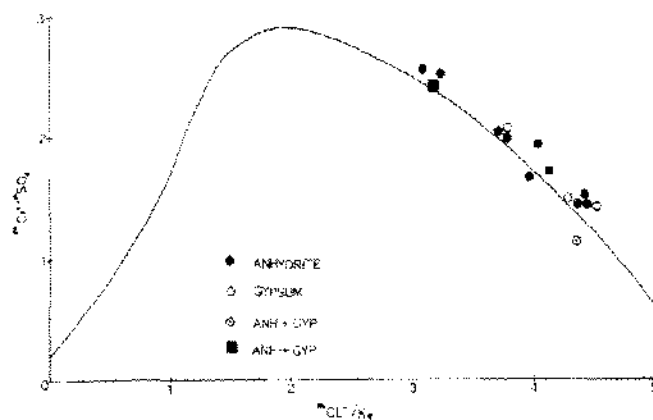


Figure 7. Similar to Figure 4 but solubility data here are for specific solid phases; pore waters were carefully squeezed from gypsum or anhydrite crystal sediments, or from samples where either both phases were present or one phase was being obviously replaced by the other. All data are for approximately 30 °C and show that the solubilities of both gypsum and anhydrite are very similar (analytical errors mask what differences do exist).

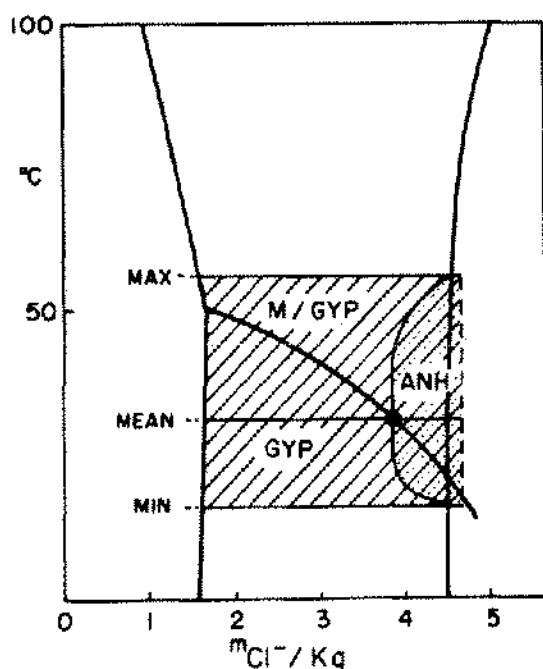


Figure 8. Gypsum-anhydrite equilibria in marine brines, as in Figure 1. The diagonally hatched area is the Persian Gulf sabkha temperature envelope. Gypsum occurs as a stable phase in the lower part of the figure and as a metastable phase above the gypsum-anhydrite equilibrium boundary. The temperature and brine conditions where anhydrite exists are enclosed by the near-vertical curving line inside which a dot and hachure ornament is present. The anhydrite first precipitates in the upper high temperature and high salinity corner of this area but once formed can exist throughout the anhydrite subfield marked by the dotted line. Under mean temperature conditions anhydrite is replaced by gypsum at chloride concentrations less than 3.85 moles per kilogram (marked by large dot). Only very brief exposure of anhydrite in the gypsum stability field suffices for it to be replaced by gypsum.

natural environments. It has become obvious that gypsum can exist metastably within the anhydrite stability field for tens or may be hundreds of years, without being replaced by anhydrite, yet anhydrite is replaced by gypsum within days or weeks should it become the unstable phase.

The precipitation of metastable phases is a commonly observed phenomenon from solutions at earth surface temperatures, especially where relatively high supersaturations are achieved. However, the natural mineral-brine data suggest that high supersaturations are never achieved with respect to gypsum as it nucleates and grows rapidly enough to relieve supersaturation fairly readily. The new mineral-brine data suggest that the solubilities of gypsum and anhydrite at 20-40°C in natural brines of ~4 molal  $\text{Cl}^-$  are sufficiently similar that a solution never becomes excessively supersaturated with respect to anhydrite, before it reaches metastable gypsum saturation. The relatively high temperature (~35°C) and low water activity (~0.77) at which natural anhydrite crystals apparently nucleate and grow suggest that desolvation of aqueous  $\text{Ca}^{++}$  may be the major kinetic barrier to the formation of the anhydrous calcium sulphate phase. The kinetic requirements leading to anhydrite precipitation occur today only in the sabkha environment. However, if isolated standing bodies of marine brine existed well below sea level, as recently suggested for the Mediterranean during the Messinian, then temperatures could be high enough for the precipitation of anhydrite as a primary phase from a standing body of brine.

## ACKNOWLEDGEMENT

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