

Gypsum and Anhydrite of Recent Age, Trucial Coast, Persian Gulf

David J. J. Kinsman
Department of Geology
Princeton University
Princeton, New Jersey

ABSTRACT

The infilling of lagoons along the Trucial Coast, by Recent carbonate sediments, has produced a supratidal coastal plain, which extends along 150 miles of coastline, is more than 10 miles wide in some places, and covers an area in excess of 1000 square miles. High temperatures and low rainfall give rise to high net evaporation, which results in the formation of concentrated, sea water derived, interstitial brines. Interstitial precipitation of new minerals takes place and reactions occur between brines and initial aragonitic sediments. Widespread dolomitisation occurs and magnesite is locally developed. Gypsum is widely precipitated, mainly in the upper intertidal zone and seaward parts of the coastal plain. Abundant anhydrite is precipitated interstitially in mid and inner parts of the coastal plain, mainly above the water table. The anhydrite is characteristically nodular in form. Other associated diagenetic minerals are celestite, halite, and huntite.

The course of the diagenetic reactions can be closely followed by changes in brine composition, for example, Mg^{++} loss parallels dolomitisation and SO_4 loss parallels sulphate mineral development. Ultimate brines have $^{m}Mg^{++}/^{m}Ca^{++}$ ratios of less than two and SO_4 is present in only trace amounts.

This first widespread development of Recent, natural anhydrite has enabled the stability relationships of gypsum and anhydrite to be defined. It is considered that the relatively high temperatures and high rates of evaporation account for the precipitation of anhydrite.

The supratidal coastal flat environment of the Trucial Coast is compared with similar areas in other parts of the world. In addition, the supratidal flat developments to be expected in carbonate sediment sequences are compared and contrasted with those in noncarbonate sequences. The Trucial Coast developments are proceeding at a rapid rate, and are developed on a geologically significant scale. It is suggested that similar environments in the past can account for the development of penecontemporaneous dolomites, and thin evaporite sequences, particularly of the nodular anhydrite type.

INTRODUCTION

Calcium sulphate minerals are of widespread occurrence throughout much of the geological record. Modern, natural occurrences of these minerals are in general rather restricted and direct comparison with many of the ancient evaporite sequences has not proved possible. The purpose of this paper is to describe an area where the calcium sulphate minerals, gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) have been extensively developed during the past few thousand years. In addition, other Recent occurrences of these minerals will be reviewed. The gypsum-anhydrite equilibrium, about which so much controversy has centered, will be considered in the light of recent laboratory data and the field data from the Trucial Coast. The new data and observations enable at least some of the previous uncertainties, relating to the origin of anhydrite, to be resolved.

A more detailed description and analysis of the sedimentary and diagenetic processes at work along the Trucial Coast of the Persian Gulf is in preparation (Kinsman, 1965a). Only those parts of the study which bear on the development of gypsum and anhydrite are included in this paper, apart from a general introduction to the environment as a whole.

TRUCIAL COAST ENVIRONMENT

General description

The Persian Gulf is a shallow sea, being nowhere deeper than 300 feet. The deep water axis lies relatively close to the northeastern or Iranian shore, whereas water depths off the Arabian shore are generally less than 100 feet. The Trucial Coast Embayment is a broad shelf lying off the Trucial Coast, marine waters shoal gradually shorewards in all directions and along the southern margin the coastline comprises a complex of islands, peninsulas, and lagoons (Fig. 1).

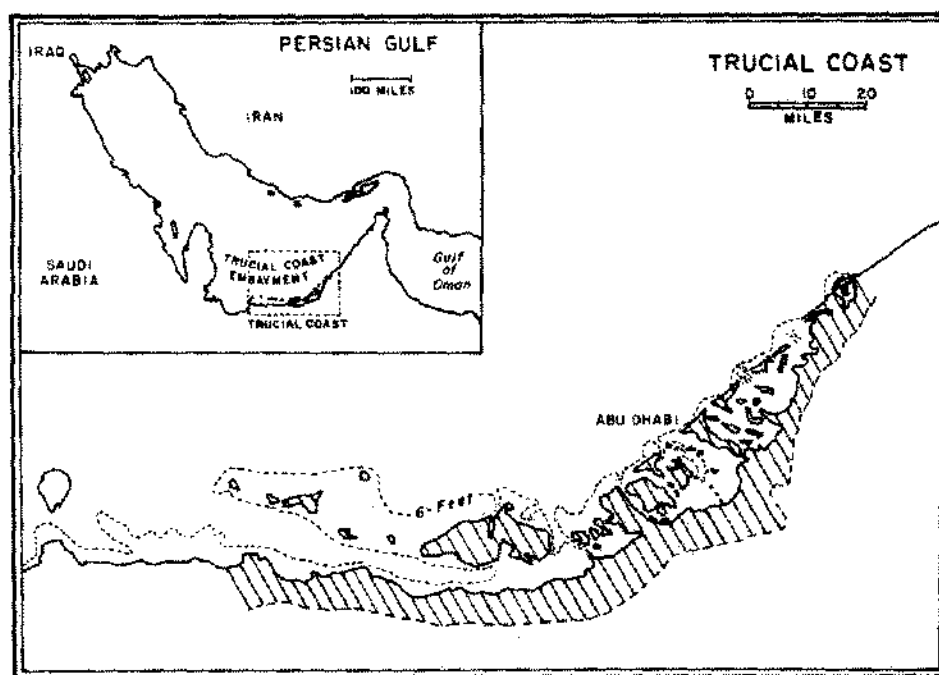


Figure 1. Location map of Persian Gulf and Trucial Coast. Area of supratidal Recent carbonate sediments approximately indicated by diagonal ornament.

The prevailing wind is northwesterly and thus onshore. Annual precipitation averages less than 1.5 inches. Coupled with high rates of evaporation a regime of net evaporation results. Sea water salinities are consequently increased, values ranging from 37-38‰ in the outer shelf areas, to 42-43‰ in the inner shelf areas, to over 60‰ in very restricted lagoons.

Along the Arabian shore the near-shore zone is the site of Recent carbonate sedimentation. Acolian additions are important in some places. Over the Trucial Coast Embayment the bottom sediments are essentially a skeletal facies of coarse sands and even gravels on local sea-floor elevations, and finer sands and carbonate muds in local depressions. The lagoon barrier along the inner shelf is a high energy environment of highly variable sedimentary facies. The barrier islands typically have frontal faces of dune sands of oolite facies. Tidal channels, lined with coarse skeletal lag deposits, cut between the islands and connect the lagoons with the open shelf. Tidal deltas are typically associated with these channels and are sites of oolite formation. Coral reefs are developed in front of most islands and in places behind the tidal deltas, in the outer lagoon areas. The lagoon barrier is thus seen to have a complex geometry and the sedimentary

facies developed vary greatly both across the barrier trend and along its length. The mid-lagoon sediments are essentially a pellet sand facies in very shoal areas or an aragonite mud facies in deeper subtidal areas. In the sheltered inner lagoon, aragonite muds, loosely aggregated and pelleted, are the major sediment type. Algal mats are abundant in intertidal areas of the innermost lagoons and typically form the final lagoon infilling facies.

The lagoons are being actively infilled, although the pattern of infilling is complex. The mainland shore is rapidly building out seawards towards the barrier but active sedimentation is also occurring around almost all the island coasts, particularly those of sheltered aspect. In general, the more sheltered a coastline, the finer-grained are the sediments laid down. Thus along the eastern half of the Trucial Coast the infilling of the sheltered lagoons is essentially achieved by carbonate muds, whereas to the west, the inner coast is less sheltered, as the barrier lies farther offshore, and in this area the sediments are largely skeletal sands and gravels.

Marine sedimentation of this type can obviously only occur up to high water mark, although storm waves will occasionally pile sediment slightly above this level. The result of such sedimentation is the development of a supratidal sediment surface which is only flooded by marine lagoon waters during periods of exceptional storm activity. Along the Trucial Coast the supratidal coastal plain of the mainland is in some places more than 10 miles in width and covers an area in excess of 1000 square miles. Similar areas are present on many of the offshore islands, although they are not as extensively developed. These low-lying areas are normally salt-encrusted and are known locally as "sabkhas" (an Arabic word denoting salt-flat).

Along the present lagoon shores the algal facies closely delimits the mid and upper intertidal zone. This facies has been found in many pits dug in the sabkha, some as far as 7-8 miles back from the present lagoon shores. It can be concluded, therefore, that the sedimentation has been essentially of a similar nature for a considerable period of time. Radiocarbon dates (kindly provided by Dr. M. Rubin of the U.S. Geological Survey) show the sabkha sediments to all be younger than 3-4000 years. A levelled profile across the mainland sabkha near Abu Dhabi showed the intertidal facies to lie at a constant level, near to and above present mean sea level. Several lines of evidence thus indicate the wide supratidal surfaces or sabkhas to be composed of Recent sediments of lagoonal type, developed in response to a constant sea level. The gypsum, anhydrite, and other diagenetic minerals occur within these sediments and are also, therefore, of Recent age. The marine carbonate sedimentation is obviously highly diachronous, and in the later discussion it will be seen that the diagenetic processes are also diachronous.

Sabkha description

The sabkha areas in general have a surface relief of less than two feet, and lie at about 3-5 feet above mean sea level. Factors affecting the absolute height of the upper surface are; the initial height to which normal marine and storm sedimentation proceeded; subsequent sediment compaction; wind erosion of the upper sediments; and the effect of precipitation and the development of new minerals in interstitial positions. There is evidence of a 1-3 feet vertical growth of the surface, resulting largely from the interstitial precipitation of new minerals.

The upper levels of the sabkha comprise an unstable, aeolian facies consisting of marine derived carbonate grains which are being gradually blown across the sabkha surface, commonly to accumulate in downwind areas. On the mainland sabkha the windblown sand layer is only an inch or two thick in the seaward areas but across the greater part of the coastal plain the thickness averages 1-2 feet. This sand ultimately accumulates at the inner margin of the sabkha, against the Tertiary rocks which constituted the old Pleistocene shore line.

Levelled profiles show the ground-water table to lie at depths of 1-4 feet below the surface and to coincide fairly closely with mean sea level. The ground-water table is essentially horizontal and parallels the surface across the outer two-thirds of the mainland sabkha. Where the sabkha surface rises as a result of aeolian accumulations in the innermost areas, the ground-water table is also found to rise. Above the ground-water table is a continuous capillary zone where all interstitial pore spaces are filled with water. Higher again is a discontinuous capillary zone where only thin films of water cover the sediment particles and in the highest levels the sediments are often completely dry.

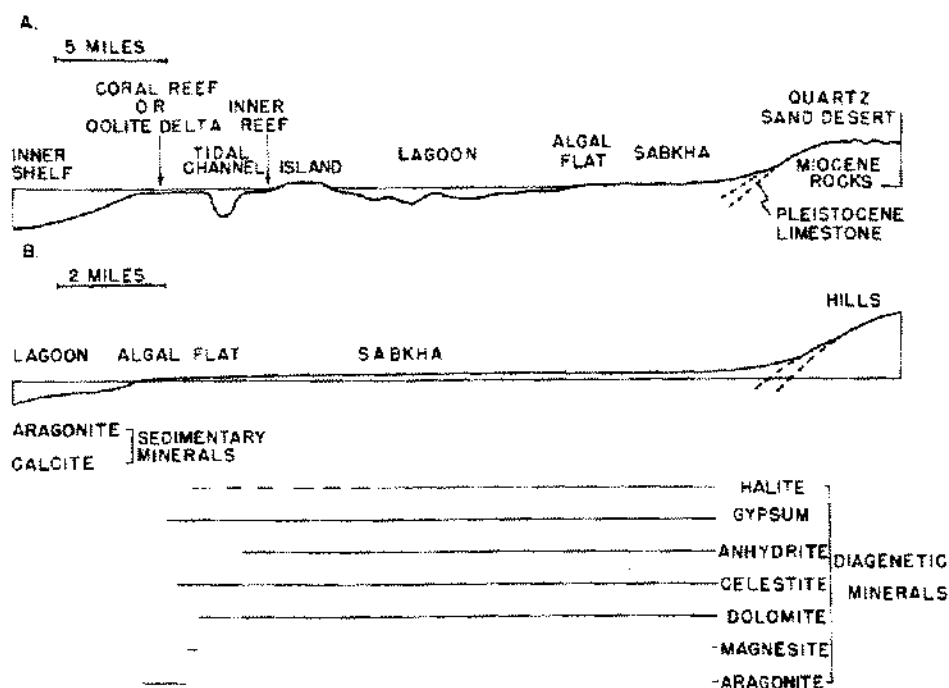


Figure 2. (a) Diagrammatic profile across inner shelf, lagoon barrier, lagoon, and supratidal sediment surface (sabkha).
 (b) Sabkha profile indicating approximate relative positions at which the early diagenetic minerals are developed.

The surface layers of the sabkha are generally loosely cemented together with halite. This halite crust is destroyed when the sabkha is flooded during extreme storm conditions. After flooding, much of the flood water drains back into the lagoons, some percolates into the sediments and some is lost by evaporation. In areas of carbonate muds, there is evidence that surface flooding causes no dilution of the ground water; ground-water concentrations may well be decreased in areas of sandy sediments where the permeability is much greater.

Temperatures of this area are high when compared with most earth surface sedimentary or early diagenetic environments. The intertidal algal mats are dark olive green or brown in color and the sabkha surface is medium to dark brown -- both surfaces will tend to absorb solar radiation. Seasonal air temperatures range 5-47°C, averaging 28°C; it is possible that these dark surfaces reach 60°C (or up to 80°C) during the summer months. The sediments and ground water at 2-4 feet depth range seasonally 26-39°C, averaging 34°C, about 5°C higher than the average temperature of the marine waters of the lagoons.

Evaporation losses from the sabkha surface cause marine lagoon waters to move into the sediments. Within the island sabkhas and across almost the entire width of the mainland sabkha, the ground waters have a marine origin. In the innermost parts of the mainland sabkha the marine derived ground waters mix with ground waters from the Tertiary rocks of the hinterland. The marine derived ground-water brines are found to increase in concentration away from the lagoon shore line, and in any one position an increase in concentration normally occurs from the ground-water table up through the capillary zone. This inward and upward concentration of waters reflects the normal cycle of pore water movement within the sabkha sediments.

As previously discussed, the sediments of the sabkha are entirely marine in aspect, and are almost wholly aragonitic. The evaporitic minerals are all diagenetic, interstitial developments, with the primary marine sediment serving as host site. The diagenetic minerals result from direct precipitation from the concentrated sea water derived brines, and also from brine/sediment reactions. Lithification or the development of surface crusts -- apart from ephemeral halite

crusts -- is not found, except very locally in some algal flat areas; all the diagenetic changes described take place in soft, plastic sediments.

An interesting and informative approach can be made in these studies in the direction of achieving a chemical balance at various stages of the diagenetic reactions. Studies of the marine sediments have enabled their mineralogy and chemistry to be defined. The lagoon waters have been analysed, and so the precursor of the interstitial pore fluids has also been defined. In addition there is almost no evidence of bacterial reduction of SO_4^{2-} within the sabkha environment. Thus although the system is a dynamic one and is open, it can be defined entirely except for those chemical species which exchange with the atmospheric reservoir (H_2O , CO_2 , O_2 , etc.).

Diagenetic minerals

The diagenetic minerals are all developed in interstitial positions within the marine sediments. The diagenetic mineral suite comprises aragonite, dolomite, magnesite, huntite, halite, celestite, gypsum, and anhydrite.

Aragonite

Aragonite is present in the algal flat and sabkha areas mainly as a primary sedimentary mineral. Diagenetic aragonite is precipitated interstitially in some algal flat areas, sometimes resulting in the cementation of the uppermost half inch or so of the sediments. Aragonite is progressively replaced by dolomite during later diagenesis.

Dolomite

Dolomite is not precipitated in the marine environments and first appears in the upper capillary zone at the algal flat-sabkha junction. With increasing distance inland the amount of dolomite at any one horizon increases, and it extends in depth until 7 miles or more from the sea the upper 2-3 feet of sediment are almost entirely dolomitised, and even at 4 feet the initial carbonate sediments are about 50% dolomitised. The dolomite is fine grained ($2-3\mu$), is calcium-rich and has a slightly disordered lattice. In these characteristics it is closely similar to Recent dolomites described from other areas. The dolomite is a replacement product of the original carbonate sediments. In areas where the original carbonate sediments were medium- and coarse-grained sands dolomite is scarce. The fine-grained ($<1-2\mu$) aragonite muds are relatively rapidly dolomitised.

Magnesite and Huntite

These two magnesium carbonate minerals have been described in more detail elsewhere (Kinsman, 1965b). They are very fine-grained ($<2\mu$), are volumetrically unimportant members of the diagenetic mineral suite and are only included here for completeness.

Halite

Halite is an ephemeral, near surface mineral, loosely cementing together the upper aeolian layer. Rarely, small cubic crystals occur in the sediments of the upper capillary zone.

Celestite

Celestite occurs dispersed throughout the sabkha sediments, normally with an abundance of less than 1%. It first occurs in the uppermost algal flats, associated with gypsum. The crystals occur singly and as sheath-like aggregates, with good crystal faces, and elongated parallel to the 'b' axis. Where the carbonate sediments are dolomitised it is abundant, being a by-product of the replacement of high strontium-bearing initial aragonite (up to 7000 ppm Sr) by relatively low strontium-bearing dolomite (<1000 ppm Sr).

Gypsum

Gypsum occurs as a diagenetic mineral in the upper parts of most algal flats or other high intertidal areas, and is present throughout the sabkhas of the islands and mainland. It is always developed in interstitial positions, never as a precipitate upon the upper sediment surface. In some places the gypsum forms more than 50% of the upper 3-4 feet of the sediment. Gypsum is

associated with both sandy and muddy marine sabkha-sediments, and also with the overlying aeolian sand layer. Several distinct stages of gypsum formation may be distinguished, and the associations and habits of the different types are fairly distinct.

The earliest gypsum occurs in the upper algal flats close to mean high water mark. The crystals first appear immediately beneath the uppermost algal mat, but with increasing distance from mean high water mark the gypsum is found to occur at increasingly greater depths below the surface. The gypsum crystals range up to 0.5 inches in diameter and are commonly clear and free from inclusions. Many, however, bear included carbonate particles, often arranged in zonal patterns which possibly represent earlier crystal face positions. The crystals are discoidal in shape, flattened normal or nearly normal to the 'c' axis, and are similar to those from the Laguna Madre described by Masson (1955). In fact, nearly all Recent gypsum occurrences comprise crystals of this habit. Some of the gypsum crystals are deeply corroded by subsequent partial solution. Cores in the uppermost parts of the algal flat environment commonly show successive algal mats underlain by clear discoidal gypsum crystals, associated with greater or lesser amounts of carbonate sediments. Some algal flat areas have gypsum crystal 'mushes' extending 2-3 feet below the surface. Similar crystal mushes occur throughout the width of the sabkha, commonly associated with algal banded sediments. The crystals of the mushes may be variously intermixed with sediment or they may occur almost pure. Sometimes, almost pure gypsum layers are found to alternate with gypsum free or gypsum poor layers, at least to depths of 4 feet.

A later form of discoidal gypsum crystal is represented by the large gypsum sand crystals which occur within the upper sabkha sediments or litter the surface as deflation lag deposits in some places. These crystals have only been found in areas of sandy sediments. The gypsum sand crystals grow within the sediments in all orientations and reach 10 inches in diameter. Included within them are a great diversity of carbonate and noncarbonate grains -- whole gastropods commonly occur. Traces of the original sedimentary stratification can often be seen running through the sand crystals. The sand crystals are of a similar habit to those of the algal flats, being discoidal and flattened normal or near normal to the 'c' axis.

A third type of gypsum comprises extremely flattened, sometimes bladed crystals, up to 4 inches in length, found so far only growing in muddy sabkha sediments of intertidal and lagoon facies, at depths of 1-4 feet. This type may be only a very flattened discoidal crystal with a complex surface pattern of growth lines. The crystals are rarely free from fine-grained included carbonate, commonly arranged in a zonal manner. The crystals grow in all orientations within the sediment and often bear traces of algal laminae (Fig. 3a). Associated with these gypsum crystals are uncommon rosettes, up to 2 inches in diameter, which are intergrowth forms of the basic discoidal crystals, together with single discoidal crystals up to 2 inches in diameter. Discoidal crystals greater than 0.5 inches in diameter are always a later development than the early phase of discoidal crystal formation, found in the algal flat and seaward sabkha areas.

A fourth type of gypsum comprises euhedral crystals, flattened in the 010 plane and similar to the classically described prismatic 'selenite' crystals. This crystal habit has only been found as a development after anhydrite and the crystals are normally crowded with anhydrite inclusions. Such crystals have been found up to 2.5 inches in length, and occur widely at the inner edge of the mainland sabkha where earlier anhydrite is being rehydrated, following contact with dilute ground water from the inland areas.

The earliest gypsum crystals are thus the small discoidal forms of the mid and upper intertidal zone. These small discoidal crystals do not extend in depth down into the older subtidal lagoon sediments. But similar, small discoidal crystals also form throughout the diagenetic sequence in the uppermost levels of the sabkha, in the aeolian sands. The aeolian sand layer is absent in the intertidal zone and thickens inland across the sabkha. Commonly developed within it are abundant small discoidal gypsum crystals, indistinguishable from those which are formed interstitially within the intertidal zone sediments. An example of an extremely late development is illustrated in Fig. 3b which shows discoidal gypsum crystals from the aeolian sand layer near the inner margin of the mainland sabkha, with cores formed by small anhydrite nodules.

The size of individual discoidal crystals within the old intertidal zone sediments does not increase with distance inland away from the shore line. This indicates either that the gypsum



Figure 3. (a) Gypsum crystal of extremely flattened, bladed, or discoidal habit from old intertidal sediments. Upper and lower edges are cleavages; crystal 3 inches in length. Organic algal layers included within crystal.

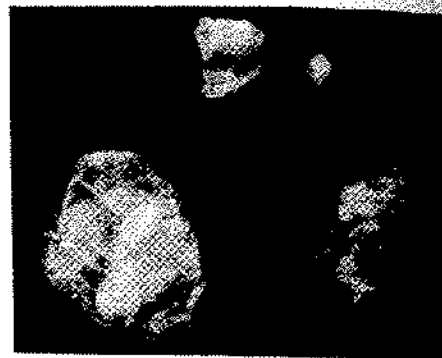


Figure 3. (b) Small discoidal gypsum crystals of late-stage development, partially corroded by solution; opaque white areas are small anhydrite nodules, serving as cores (largest crystal 0.5 inches in length).

precipitation is limited largely to the intertidal zone, or that further precipitation takes place around new nuclei, either at the same levels or at different levels such as in the overlying aeolian sands or in the underlying old lagoon sediments. Brine analyses, in fact, show gypsum precipitation not to be limited to the intertidal zone.

The large gypsum sand crystals and flattened bladed crystals are developed within both intertidal and lagoon facies sediments. Within the modern intertidal zone sediments they are absent and thus they postdate the earliest phase of small discoidal crystal development of the intertidal areas. These larger crystals generally occur singly within the enclosing sediments and do not form dense crystal mushes. The two varieties are roughly coeval and the differences between them may well be a reflection of the type of sediment in which they grew. In muddy sediments, the extremely flattened variety is found, and often included within the crystals, when they are developed in old intertidal sediments, are evidences of primary sediment layering such as algal laminations (Fig. 3a). Within the aragonite muds the only trace of original sedimentary layering is provided by the organic algal laminae; layering within the carbonate sediments is entirely destroyed in shallow lagoon and intertidal facies by organic burrowing activities, particularly by crabs. Sandy sabkha sediments often bear traces of sediment layering additional to that of the algal laminae (Fig. 5: left core). Gypsum sand crystals growing within such sediments are found with the original sedimentary layering preserved within them.

The later discoidal crystals grow to largest size (up to 10 inches in diameter) within sandy sediments. There is evidence of partial shouldering aside of the original sediment grains, but in general the original grains are incorporated within the crystals. The gypsum is in large part an inter-grain void precipitate although each discrete gypsum area has lattice continuity and is a separate crystal. The partial moving aside of some grains indicates also that the crystal in part grows by displacement. In muddy sediments the late, large-sized crystals include within them original organic algal layers but little carbonate mud. In this instance it is not possible to decide from the textural relationships, whether the inter-algal layer gypsum has physically displaced the original aragonite mud, or whether the original carbonate has been replaced by gypsum, by a solution/reprecipitation process.

Concentrations of gypsum crystals are common on the sabkha surface. Wind deflation removes the finer sediment particles, the coarser gypsum crystals becoming concentrated as a surface lag deposit. On the offshore islands, dune sands, downwind of sabkha areas, are commonly found to be rich in wind abraded gypsum crystals. In fact, some dune sands comprise more than 70% gypsum crystals.

anhydrite

The occurrence of anhydrite as a diagenetic mineral within the sabkha environment is of particular interest as this was the first recorded natural occurrence of Recent anhydrite. The mineral was first found in a sabkha core collected by the author in January, 1962. Subsequent field studies have shown it to be of widespread occurrence and to be developed on a geologically significant scale. Recent anhydrite has since been reported from the Sarykamysk Lakes, USSR by Rubanov et al. (1964), and from Nevada by Moiola and Glover (1965), but neither of these occurrences would seem to be as geologically interesting or significant as that of the Trucial Coast.

Anhydrite has so far been found to occur only in the sediments of the mainland sabkha. The fairly extensive sabkhas of some of the offshore islands have so far failed to reveal its presence. As with the gypsum, the initial occurrence is within the uppermost inch or so of the sediment. The anhydrite has been found to always have gypsum lying between it and the intertidal zone. The distance inland from the intertidal zone, to where anhydrite is first encountered, cannot be defined in absolute units as this distance may vary from 2-300 yards to more than a mile.

The earliest anhydrite, in the uppermost few inches of the sabkha sediments has been found as small nodules 0.05 inches in diameter, sometimes associated with a gypsum crystal mush. The nodules comprise a felted mass of small anhydrite laths. Thin sections of core samples have revealed single crystals and multiple aggregates of anhydrite laths to be developing within the sediments. Figure 6d shows the early development of an anhydrite nodule, the aggregate being only 100 μ across.

Further anhydrite development takes a variety of forms, and the mineral has been found to extend to depths exceeding 4 feet in mid and inner parts of the mainland sabkha. In general, the anhydrite occurs within the aeolian sands and old intertidal sediments above the permanent water table, but a few occurrences have been found extending below. In places the upper 3-4 feet of the sabkha is at least 50% anhydrite, but local variation is great, and the detailed sequence in one pit is often not paralleled in a closely situated pit.

Some of the major forms taken by anhydrite are illustrated in Figs. 4 and 5. The nodule is the characteristic form although occasional thin beds do occur. The beds may be up to 6 inches or so thick, but generally are less than 1-2 inches. They may have simple or complex marginal relationships with the sediments in which they occur, and may be horizontal or variously cross-cutting. Within a bed the texture is usually massive (Fig. 4, upper). None of the beds are in any way laminated or banded. The majority of beds are free from foreign grains and appear brilliantly white; on occasions, carbonate and other grains occur mixed with the anhydrite and the bed is then brownish and may have quite diffuse boundaries with the adjacent sediments.

Nodules vary greatly in development. They may range from less than 0.05 inches to more than 6 inches in diameter; shape ranges from spherical to strongly flattened, and they may occur as individuals or as complex, intergrown masses of hundreds of nodules. The latter development commonly gives rise to 'beds' of anhydrite nodules; an example is shown in Fig. 4, middle. Beds of flattened, plate-like nodules are fairly common, but this is a growth form; individual nodules within beds sometimes show a slight tendency towards flattening but this is uncommon -- this flattening may well be mechanically induced. Nodules may be packed tightly together with little or no interstitial material (Fig. 4, lower), or they may be separated by greater or lesser amounts of foreign material (Fig. 4, middle). The former occurrence is common in many ancient evaporites associated with back reef and lagoonal deposits, being termed net or chicken-mesh structure; a Mesozoic example from the Persian Gulf is shown in Fig. 6a.

Nodules are usually free from foreign grains, but on occasions examples are found with included carbonate and noncarbonate sabkha sediment grains (Fig. 5, left). During growth the nodules are evidently able to shoulder the enclosing sediments aside.

Optical and X-ray examination has shown the anhydrite to be normal and to compare closely with published data for ancient anhydrites. The crystals are lath-like, although most fragments are broken along cleavages; on rare occasions when crystal terminations can be seen the crystals are found to be distally spear-shaped. The crystals are colourless, transparent, free from inclusions and are elongated normally parallel to the 'c' axis. Refractive indices are normal. The laths may be extremely thin (<2-3 μ) and show a good pseudo-cubic cleavage (Fig. 6b). Crystal

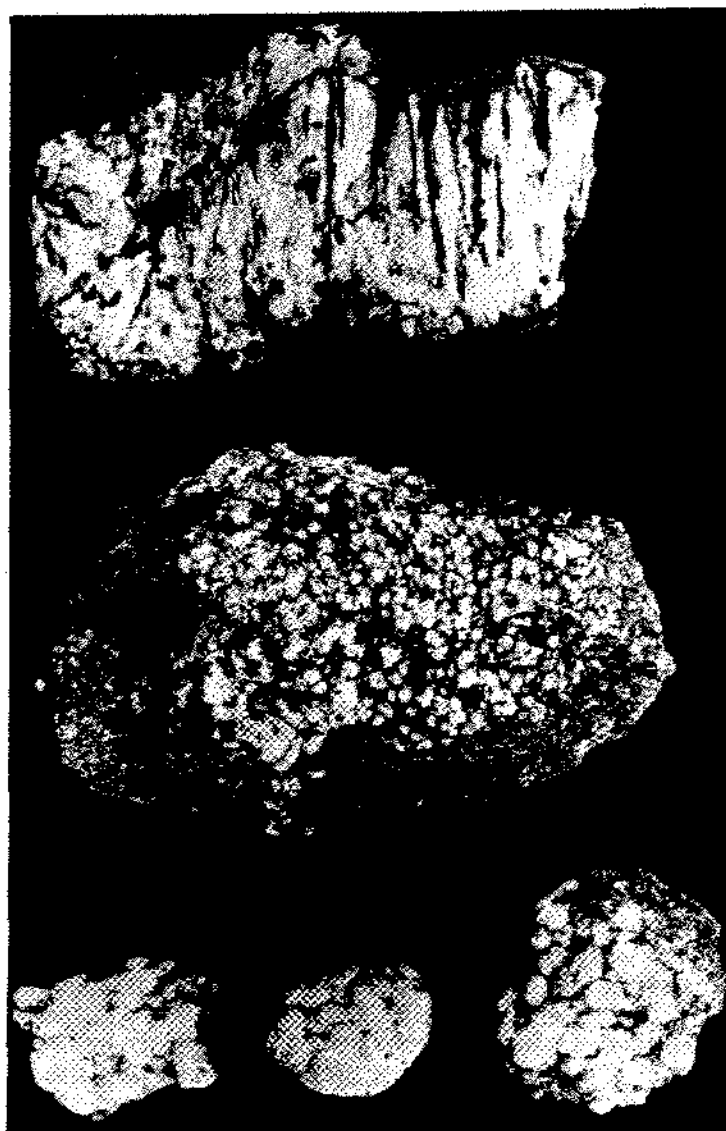


Figure 4. Forms taken by anhydrite (natural size).

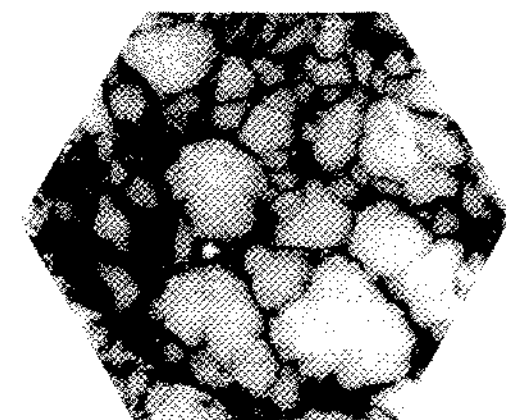
- (a) upper -- a thin bed of anhydrite with no traces of nodular structure.
- (b) middle -- part of a discontinuous layer or 'bed' of anhydrite nodules: such a concentration of relatively small nodules (less than 0.1 inches) is uncommon; individual nodules are free from included foreign grains, internodular material consists of aeolian sand grains, mainly carbonate of marine origin.
- (c) lower -- complex nodules comprising intergrowth of several smaller nodules, internodular material sparse; left-hand specimen planed off to show classical chicken-mesh structure.



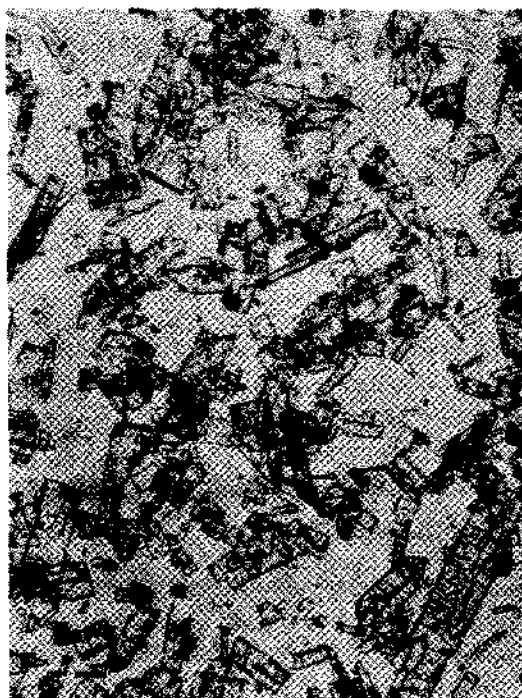
Figure 5. Cores from sabkha area of carbonate sands; note traces of lamination in left core; algal lamination absent from both cores; left core shows transgressive layer of anhydrite nodules, individual nodules with some included carbonate grains; large nodule in right core is completely free from foreign materials. Upper part of right core is a mass of complexly intergrown, very soft anhydrite nodules.

edges are usually straight but on occasions ragged edges are found, the crystals having undergone some secondary solution. Single laths range from less than $2-3\mu$ in length up to a maximum of 0.15 inches. Normal length to width ratios vary from about 5:1 to 10:1. Thickness is dependent on crystal size, but even the largest crystal laths do not exceed $50-60\mu$ in thickness.

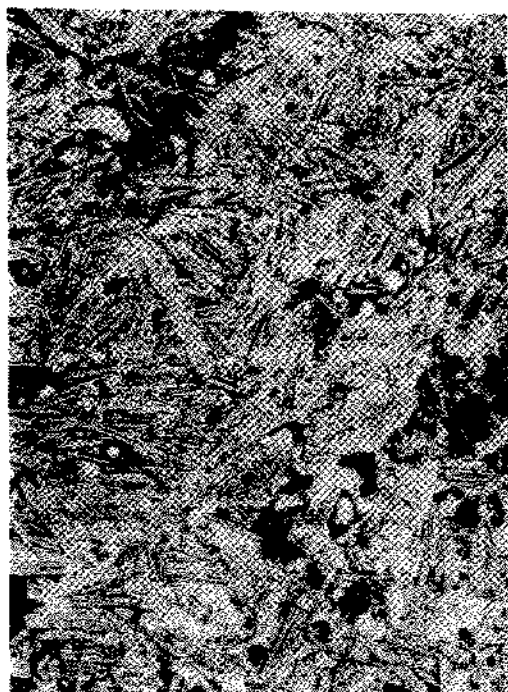
Orientated thin sections of nodules and core samples have shown crystal laths in most instances to be randomly disposed and textures to be identical with those found in ancient nodular anhydrites. An example of an exceptionally coarse-grained anhydrite nodule is shown in Fig. 6c where the large laths have a random orientation. Some anhydrite nodules and beds show arcuate,



(a)



(b)



(c)



(d)

Figure 6. (a) Mesozoic nodular anhydrite showing chicken-mesh structure (compare with Figure 4, lower left). (b) Water mount of anhydrite laths showing pseudo-cubic cleavage (largest lath $200\ \mu$). (c) Thin section of exceptionally coarse-grained anhydrite nodule, showing felted, random texture (largest laths $800\ \mu$ in length). (d) Thin section of very early nodule ($100\ \mu$ in total length), showing sheath-like development of laths: this stage is preceded by single laths and simple sheath developments. Growing in dolomitised intertidal carbonate muds.

sinuous patches of laths with subparallel orientation. Near foreign included grains laths may either show a 'wrap-around' relationship or show no disturbance at all.

Sampling over a wide area of the mainland sabkha has shown that there is little over-all sequence in the arrangement of anhydrite beds, beds of nodules and individual nodules, one form predominating in one area, yet being absent in the next. Similarly, detailed microscopic study has revealed no constant relationship between the crystal form and size and the major field structures. The smallest crystals have been found forming almost pure beds of anhydrite, and the coarsest crystals have been found in anhydrite nodules, but the wide range of intermediate sizes occurs indiscriminately in both beds and nodules.

An unusual occurrence of anhydrite is illustrated in Fig. 3b which shows early anhydrite nodules forming cores to small, discoidal gypsum crystals. The gypsum obviously postdates the anhydrite.

Wind deflation and erosion of the sabkha surface during flooding expose anhydrite at the surface. The nodules are fairly resistant and commonly litter some surfaces of erosion. However, large quantities of anhydrite crystal laths are distributed across the sabkha surface, particularly by the wind, and are a component of the near-surface detrital and aeolian layers.

There is no evidence of the anhydrite being an *in situ* dehydration product of earlier gypsum. If the anhydrite origin were to be explained in this way, it would be reasonable to expect to find gypsum crystals which had not been fully replaced by anhydrite. Such an occurrence is not found, and, therefore, if it were insisted that this was the origin of the anhydrite, it would have to be concluded that once the process started it went to completion very rapidly, so that the chances of ever catching a gypsum crystal 'on-the-hop' would be slim. Such an explanation is most unlikely.

In addition, if early formed gypsum crystals became later replaced *in situ* by anhydrite, then pseudomorphing of the gypsum crystal shape would be expected. No anhydrite nodules have been found with such a shape. The gypsum crystals, if replaced by anhydrite would each be expected to give rise to one anhydrite nodule. The large gypsum crystals are found in all orientations within the sediments, some having their greatest diameter vertical, yet when anhydrite nodules are found which are appreciably flattened, they nearly always have their greatest dimension horizontal. Within the old intertidal sediments and the overlying aeolian sands, most of the gypsum exists as small discoidal crystals, less than 0.5 inches in diameter. If such gypsum were to be replaced by anhydrite then most of the anhydrite should occur as small nodules such as are shown in Fig. 4, centre. In fact, this occurrence of anhydrite is unusual. The anhydrite nodules in general have an individual mean volume at least twice and perhaps as high as 3-4 times that of the gypsum crystals.

The volume change involved when gypsum is replaced by anhydrite is almost 40%. But the initial gypsum crystal is a solid body with zero porosity. The anhydrite nodules are multicrystalline aggregates with a high porosity, at least 40%, maybe as high as 80%. Thus if a gypsum crystal were replaced there would be no over-all reduction in volume. Following from this it is reasonable to expect that if a gypsum was replaced, it would be almost perfectly pseudomorphed. Modification of the anhydrite nodule by compaction would still not mask the shape of the original gypsum crystal, particularly any which had initially been horizontally disposed within the sediments. Such gypsum crystals would be expected to give rise to very thin, flattened anhydrite nodules. Such forms do not occur. If subsequent anhydrite nodules had internal porosities greater than 40%, an increase in volume would occur following replacement of gypsum, but this increase would be insufficient to account for the observed volume differences between individual anhydrite nodules and gypsum crystals.

Many gypsum crystals have included carbonate sediment or aeolian grains within them. If these gypsum crystals were replaced by anhydrite nodules then the resulting nodules would be expected to also have the foreign material included within them. Yet the great bulk of the nodules are entirely free from such included material, indicating that if gypsum crystals had indeed been replaced then the nodules somehow excluded these foreign grains during the replacement process.

In oriented thin sections from cores, single laths and very small rosettes of anhydrite laths ($<50\mu$) can be found within old intertidal sediments and aeolian sands, presumably representing early stages of nodule development. Within the uppermost aeolian layers there are anhydrite

laths which have a detrital origin, having been derived from earlier nodules and reworked by the wind or by the occasional flood waters which inundate and scour the sabkha surface during exceptional storms. But such laths have a near parallel orientation with the surface, as would be expected of detrital particles with a strong shape factor. The single laths which are considered to represent early nodule development, occur in all orientations, some of them even vertical. This arrangement is most unlikely for detrital anhydrite grains. The laths and small rosettes often occur in old intertidal sediments with the nearest gypsum crystal some inches or feet away. The evidence thus suggests primary nucleation and growth of anhydrite to be occurring interstitially within the sediments.

The process of nodule growth would seem to involve further precipitation of anhydrite immediately adjacent to an initially formed crystal. Later lath development must also take place within the complex of earlier laths. In this manner, the grains of the surrounding sediments can be excluded. If addition of new laths took place peripherally then the nodules would probably contain much more foreign material than they do. Even though many of the nodules are soft, some even plastic, when removed from the sediments, they are obviously capable of displacing the surrounding sediments.

It could be argued that the anhydrite represents a replacement of earlier carbonate sediment. Within the aeolian sands, where much of the anhydrite is found, quartz and other noncarbonate grains may amount to 10-20%. If space for the anhydrite were derived by replacement of carbonate grains then the nodules should either be rimmed with a quartz-rich sand layer or actually include within them the noncarbonate grains. Neither situation is found. In fact, those nodules which do contain foreign grains have carbonate and noncarbonate grains in the same proportion as exists in the surrounding sediments. In old intertidal sediments, noncarbonate grains are rare, and so this approach cannot be used. However, by the time the anhydrite first appears within these sediments, they have often been appreciably dolomitised. Under the solution conditions prevailing, dolomite is apparently the stable carbonate mineral, and it would be most unlikely that the dolomite would be replaced. If any remaining aragonite were replaced by anhydrite in the process of anhydrite nodule development then the nodules would be expected to be replete with dolomite. Traces of small ($<2-3\mu$) dolomite grains are sometimes found within the anhydrite nodules but this is uncommon.

In summary, it can be seen that several lines of positive evidence and many lines of negative evidence indicate that the anhydrite nodules represent a primary, early diagenetic, calcium sulphate mineral development. The anhydrite bodies do not have a gypsum precursor.

Interstitial Brine Analyses

Diagenetic changes involving precipitation from the concentrated brines or reaction between brines and original carbonate sediments should be reflected in the brine chemistry. Thus at the inner edge of the algal flats, where gypsum is usually present in fair quantity, the interstitial brines should show a relative loss of Ca^{++} and $\text{SO}_4^{=}$. In areas where dolomitisation is taking place, brines should show relative loss of Mg^{++} . However, all the diagenetic developments first take place in the upper levels of the sediments, above the ground-water table. Thus to follow their course in detail, samples of pore fluids from the capillary zone are required. Even so, ground-water samples should indicate the general picture, in a 'broad-brush' manner, and in this reconnaissance survey only ground-water analyses have been made.

As the ground waters are derived from the marine waters of the lagoons, the latter were analysed. Although concentrated up to salinities of 60‰ these waters showed a simple concentration effect for all major ions except Ca^{++} , which showed a 4% loss. This loss can be correlated with formation of CaCO_3 in the marine environments.

Interstitial ground-water samples were taken from algal flat and sabkha areas and their positions are indicated schematically in Fig. 7a. Methods of analysis and detailed discussion of the analyses will not be given here but are included in a separate publication (Kinsman, 1965a).

The analytical results are given in summary form in Table 1. The innermost pair of samples are slightly contaminated with mainland ground waters, but otherwise the samples are sea water derived brines. Brine concentrations increase away from the shore line, at first rapidly,

Table 1

Analyses of interstitial ground waters from intertidal
algal flat (3) and sabkha environments (5)

Sample type	ALGAL FLAT			SABKHA				
	7	6	12	18	32	30	30	24
Water table depth (inches)	7	6	12	18	32	30	30	24
Field temp. °C	26.7	-	27.5	-	28.4	31.4	30.5	31.2
Field pH	-	7.45	7.10	7.55	6.20	6.10	-	-
Density at 22°C (gms/cc)	1.085	1.087	1.125	1.128	1.183	1.192	1.203	1.211
Cl ⁻ (gms/kgm)	63.8	63.9	90.9	96.3	134.5	151.6	159.1	165.9
SO ₄ ⁼ "	7.66	8.53	11.68	8.57	2.51	1.98	0.44	0.39
Ca ⁺⁺ "	0.92	1.12	0.93	1.22	2.48	2.56	9.00	10.43
Mg ⁺⁺ "	4.07	4.34	6.49	6.00	5.53	6.81	9.51	15.53
Sr ⁺⁺ "	0.02	0.02	0.02	0.03	0.05	0.06	0.21	0.24
K ⁺ "	1.24	1.18	1.64	1.80	2.74	3.84	3.13	4.15
Na ⁺ "	35.9	35.5	50.3	53.3	75.1	81.4	75.1	65.1

then rather more slowly. At the innermost edge of the mainland sabkha plain concentrations fall as the addition of dilute mainland derived ground waters becomes appreciable.

Lagoon waters showed pH values of about 8.3; interstitial algal flat waters have values of about 7.5, and in mid and inner sabkha positions the pH falls to 6.0-6.4.

The ratio mNa^+/mCl^- is constant in all samples except the slightly contaminated innermost pair, and even here it does not depart widely from the sea water value of 0.86.

There is a relative loss of 5-10% of the potassium, associated with organic, algal removal (there are no potassium minerals developed). Analyses for Mg⁺⁺ show a loss to occur almost exactly where the first dolomite is found. The loss continues across the sabkha (Fig. 7b) and amounts to over 40%. Loss of SO₄⁼ from the brines is paralleled by precipitation of gypsum, celestite and anhydrite. (There is apparently little or no bacterial reduction of SO₄⁼.) Ultimate brines have only traces of SO₄⁼.

Analyses for Ca⁺⁺ and Sr⁺⁺ show an initial loss of 4% in marine environments and a further 5-10% in intertidal areas as diagenetic aragonite. Further loss, after brines exceed chlorinities of about 65%, is almost entirely as gypsum and celestite (or anhydrite, after chlorinities exceed about 120-130%). In mid and inner parts of the sabkha there is a relative increase in Ca⁺⁺ and Sr⁺⁺ which can be correlated with the process of dolomitisation. Concentrations of these two ions may increase to fairly high levels as SO₄⁼ is present in only trace amounts and other possible salts of these ions are all very soluble.

The relationships between interstitial solutions and associated minerals enable the diagenetic processes to be closely delimited both as to type and degree. For example, the curve of SO₄⁼ loss can be equated with sulphate mineral precipitation. As the loss continues across the sabkha, with increasing brine concentration, it can be concluded that sulphate minerals are precipitated across almost the entire width of the area. Gypsum is the dominant sulphate mineral in the seaward parts of the sabkha and 80% of the SO₄⁼ loss is associated with gypsum precipitation (minor amounts with celestite). Anhydrite first occurs where chlorinities are about 130%, and where

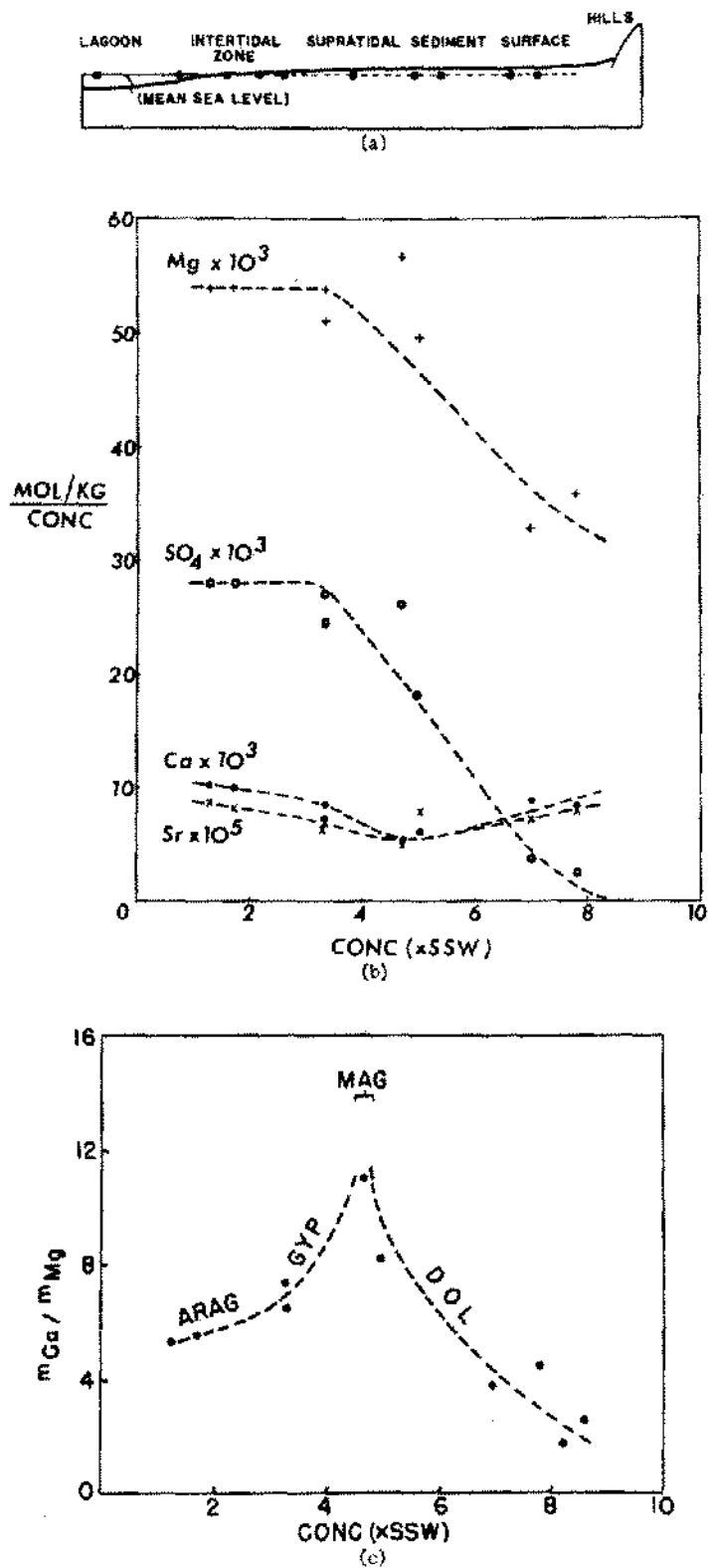


Figure 7

- (a) Diagrammatic representation of water sample positions.
 (b) Analyses of lagoon and interstitial ground waters showing relative loss or gain of various ions.
 (c) mMg^{++}/mCa^{++} ratios in analysed waters. The dominant controls on the ratio are indicated at various stages in brine evolution; ARAG -- aragonite; GYP -- gypsum; DOL -- dolomitisation. (Precipitation of magnesite (MAG) is not a dominant control but occurs at peak mMg^{++}/mCa^{++} ratios.)

$\text{SO}_4^{=}$ concentrations have fallen to 20%. Yet in mid and inner sabkha areas, gypsum is the subordinate mineral, anhydrite being quantitatively much more abundant. The ultimate brines are almost free from $\text{SO}_4^{=}$ and thus the remaining 20% of the available $\text{SO}_4^{=}$ is apparently precipitated largely as anhydrite. Yet, this is an insufficient source for the amounts of anhydrite developed. Thus from a chemical balance standpoint it must be concluded that at high brine concentrations (anhydrite being presumably the stable phase) much of the early formed gypsum is dissolved and the Ca^{++} and $\text{SO}_4^{=}$ reprecipitated as anhydrite. The lack of pseudomorphing of gypsum indicates that the remobilized ions migrate to new sites before anhydrite precipitates.

The ratio ${}^m\text{Mg}^{++}/{}^m\text{Ca}^{++}$ is shown in Fig. 7c to vary greatly during the course of the diagenesis. In the lagoons, the ratio rises from the normal sea water value of 5.3 to 5.5, owing to aragonite precipitation. Further precipitation of aragonite raises the value slightly higher in algal flat ground waters. Precipitation of gypsum at chlorinities above 65% causes the ratio to rise to at least 11 and it is under these conditions of high ${}^m\text{Mg}^{++}/{}^m\text{Ca}^{++}$ ratios that magnesite is formed and dolomitisation begins. The ratio thereafter falls, even though Ca^{++} is precipitated all the while as gypsum or anhydrite. For the ratio ${}^m\text{Mg}^{++}/{}^m\text{Ca}^{++}$ to remain constant whilst dolomitisation and calcium sulphate mineral precipitation are underway, the moles of Ca^{++} lost from solution must equal twice the moles of Mg^{++} lost. (This is because the dolomitisation process is one of replacement of CaCO_3 and for every mole of Mg^{++} lost, a mole of Ca^{++} is added to the solution.)

THE GYPSUM-ANHYDRITE EQUILIBRIUM

The gypsum-anhydrite equilibrium ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4 + 2\text{H}_2\text{O}$ liquid) has been the subject of much research and much controversy for a considerable number of years. One major problem has been the difficulty with which anhydrite may be synthesized at reasonable temperatures (less than 60-70°C) in the laboratory. Another difficulty has been that no Recent occurrence of anhydrite has been available for detailed study, so that apparent equilibria, determined in the laboratory, could be neither confirmed nor refuted. These two problems have, in fact, led several investigators to suggest that anhydrite is never the primary calcium sulphate mineral and that all anhydrite is developed by dehydration of a gypsum precursor. The Trucial Coast anhydrite shows this hypothesis to be incorrect. The occurrence of Recent gypsum and anhydrite along the Trucial Coast has enabled the equilibrium to be fairly closely defined, in terms of temperature and brine concentration.

Solubility Measurements

One approach to defining the gypsum-anhydrite equilibrium has been to determine the solubilities of the two mineral phases at various temperatures and brine concentrations. When the solubilities of the two minerals are equal, the two solids and associated solution and vapour phases are all in equilibrium.

The numerous solubility studies which have been carried out on gypsum and anhydrite have been nearly all from the direction of undersaturation. Gypsum readily nucleates and precipitates when its solubility product is exceeded and thus it is feasible to approach the gypsum solubility from both directions. However, anhydrite has proved almost impossible to precipitate from solution below 80-100°C and this is difficult to explain. Certainly there is great difficulty in initial nucleation but even when anhydrite nuclei are added to a solution which is saturated or supersaturated with respect to anhydrite, gypsum is the usual precipitate. Kinetic factors would seem to be playing a dominant role here. Under natural conditions, a solution continues to evaporate, even though apparently supersaturated with respect to anhydrite, until the gypsum solubility product is exceeded, when gypsum is then precipitated.

This peculiar behaviour puts certain restrictions on what can be achieved with solubility measurements and also affects the type of data and its interpretation. To discuss this, the solubilities of the two minerals in pure water will be considered, although the points raised can be applied to solubilities in any solution. Figure 8 shows the familiar "solubility curves" of gypsum and anhydrite and their intersection at about 42°C. The data of several investigators bracket the gypsum curve quite well, even though they all represent minimum solubility measurements. Zen (1965) has recently redetermined the solubility of gypsum, approaching equilibrium from both

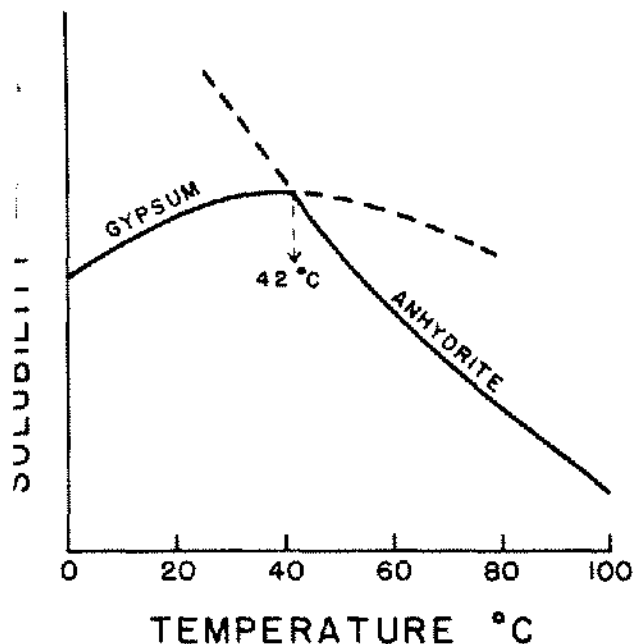


Figure 8. Solubility curves for gypsum and anhydrite in pure water (from Posnjak, 1938 and other published sources). Solid curves -- solubilities of presumed stable minerals. Dashed curves -- solubilities of presumed unstable or metastable minerals. Note solubility curves intersect at 42° C.

solubility, yet this fact seems to have been tacitly ignored by most investigators. Under such conditions, anhydrite initially is dissolved; before equilibrium anhydrite solubility is anywhere near attained, the solubility product of gypsum is exceeded; gypsum can then be expected to precipitate.

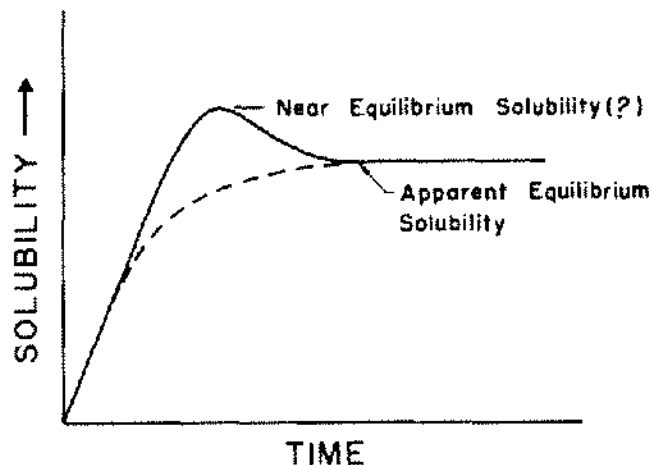


Figure 9. Schematic representation of measured anhydrite solubility. Value regarded as "normal" is probably kinetically controlled by rate of anhydrite dissolution and rate of gypsum precipitation. So-called "abnormal" solubilities may well represent near-equilibrium anhydrite solubility. It is possible that many investigators have not sampled near the peak solubility value and presume a solubility/time relationship indicated by dashed line.

undersaturation and supersaturation, and finds solubilities about 5% higher than most of those previously reported. (The gypsum solubility curve of Fig. 8 is based on the earlier data.) Zen's data are probably nearer to the true equilibrium gypsum solubility; this would shift the intersection with the anhydrite solubility curve to 38°C.

Equilibrium gypsum solubility can only, in fact, be determined when gypsum is the stable mineral (the least soluble mineral -- marked in Fig. 8 by a solid curve). Yet, because of the inability of anhydrite to nucleate and precipitate when it is apparently the least soluble and stable phase, the gypsum solubility measurements can be extended into the anhydrite stability field, although the gypsum is truly metastable under such conditions (indicated by a broken curve in Fig. 8).

Similarly, the anhydrite equilibrium solubilities can only be determined under conditions when anhydrite is the stable mineral phase (solid curve in Fig. 8). Because the anhydrite solubility can only be approached from undersaturation, the determined values will be minimum values. Under conditions when gypsum is the stable mineral it is not possible to determine anhydrite solubility.

This situation is indicated schematically in Fig. 9. The apparent equilibrium solubility value will not be the true equilibrium anhydrite solubility and will be controlled by several factors:

1. rate of anhydrite dissolution,
2. rate of gypsum nucleation and precipitation,
3. initially by supersaturation at which gypsum first nucleates; later by gypsum solubility value.

Some investigators (for example, Hara et al, 1934) have reported anhydrite solubilities 30% higher than "normal values" (apparent equilibrium solubility) and have considered this to be caused entirely by the higher solubility of very fine-grained starting materials. It is well known that fine-grained materials have higher solubilities than coarse-grained materials but this excess of solubility is generally limited to 5-10%. Anhydrite would seem to be unusual in showing such a marked effect. Following the earlier

discussion another possibility becomes evident. The apparently high solubilities may well represent near equilibrium anhydrite solubilities and the subsequent decrease could be caused mainly by gypsum precipitation and the maintenance of some kinetically controlled intermediate solubility lying between the solubilities of both mineral phases.

In most solubility experiments moderately large amounts of starting materials have been used and runs have commonly not been of great duration. In addition, the solubility of gypsum and anhydrite is relatively low. In time, if the above suggestion is correct, the initial anhydrite starting material should become depleted, the solid phase will be entirely gypsum and the ultimate solubility will be that of gypsum. In solubility investigations, the starting material seems rarely to have been minutely examined after the experimental work. If the runs were of short duration and particularly if large quantities of anhydrite were used as starting material, any gypsum produced might well be overlooked. It would seem likely that no runs have been allowed to go to completion as the ultimate solubility value would have probably been recognized as that of gypsum.

Some recent laboratory data (Hardie, 1964) indicate that, in fact, the gypsum-anhydrite equilibrium temperature in pure water is close to 57°C (not 38-42°C). In a subsequent discussion it will be shown that this is a much more probable temperature. Figure 10 shows the gypsum and anhydrite solubility curves from Fig. 8 (light dashed curves); in addition, the new gypsum solubility data of Zen (1965) are shown and are accepted as being more probably correct than the earlier data (even if the old data prove correct the gypsum-anhydrite equilibrium temperature is only shifted about 2-4°C). If the equilibrium temperature is 57°C then we know one point on the anhydrite solubility curve. Three other points at 72°C and 85°C are included; these are the results of runs of one to two years duration and so are probably near equilibrium solubilities (data from Posnjak, 1938). If the gypsum-anhydrite equilibrium lies at 57°C, then anhydrite solubility runs below that temperature will not give equilibrium solubility values.

As the result of a review of the solubility data, W. T. Holser constructed an equilibrium diagram for the calcium sulphate mineral-sea water system, a modified form of which comprises Fig. 11. In pure water the gypsum-anhydrite equilibrium is indicated to lie at about 42°C; when

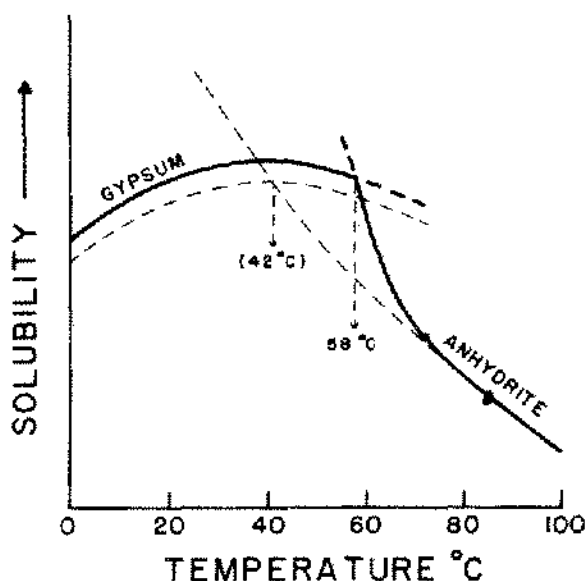


Figure 10. Solubility curves for gypsum and anhydrite in pure water; curves from Figure 8 as light dashes. New data of Zen (1965) plotted for gypsum solubility. Solid curves and heavy dashed curves as for Figure 8. Anhydrite solubility curve derived from three runs of Posnjak (1938) and gypsum-anhydrite equilibrium data of Hardie (1964). Note new intersection of solubility curves at 57°C.

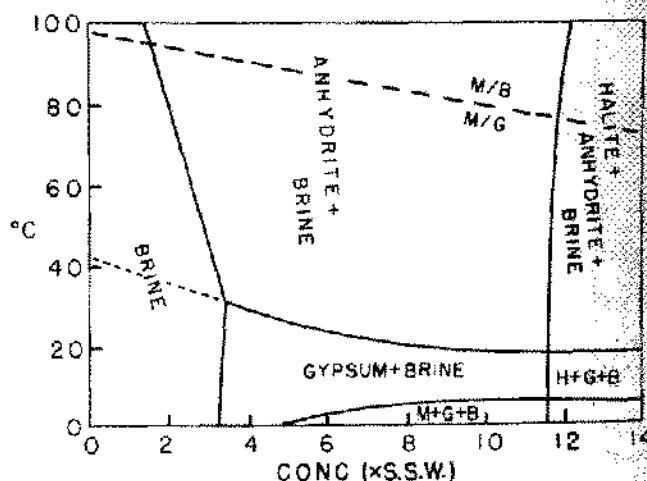


Figure 11. Equilibrium diagram for calcium sulphate minerals constructed from solubility data for pure water and sea water solutions (modified, after W. T. Holser: unpublished report). Note gypsum-anhydrite equilibrium in pure water lies at 42°C; gypsum is metastable throughout the lower part of the anhydrite stability field (M/G) and then dehydrates to metastable bassanite (M/B). At low temperatures mirabilite becomes a component (X).

gypsum first starts to precipitate the equilibrium lies at about 31°C and in halite saturated brine the equilibrium lies apparently at about 18°C.

If the gypsum-anhydrite equilibrium were positioned as indicated by the solubility studies, then we should perhaps expect to find anhydrite as a common sulphate mineral in Recent near surface evaporite deposits. The occurrence of anhydrite along the Trucial Coast, and the studies of Hardie (1964), indicate that the equilibrium indicated by the solubility studies is incorrect and that lack of attainment of equilibrium solubilities is probably the reason.

Thermodynamic Calculations

The thermodynamic properties of gypsum and anhydrite were examined in some detail by Kelley et al (1941). The anhydrite solubility data used in this compilation are almost certainly incorrect, as discussed above. Macdonald (1953), using this data, calculated the temperature of the gypsum-anhydrite equilibrium in pure water to be 40°C.

More recently Zen (1965) has re-examined the data and found it to be internally inconsistent. Using only internally consistent data he has calculated the equilibrium temperature in pure water to be 46±25°C. [Hardie and Eugster (1965), find 46±21°C.]

Re-examination of the Gypsum-Anhydrite Equilibrium

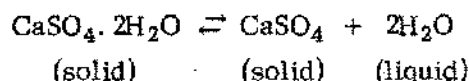
For application to the natural sea water system, the equilibrium needs to be defined in terms of temperature and brine concentration. The equilibrium may be considered from the standpoint of solubilities. For example, the solubility product of gypsum,

$$K_{\text{Gypsum}} = a_{\text{Ca}^{++}} \cdot a_{\text{SO}_4} = \cdot a^2_{\text{H}_2\text{O}}$$

and the solubility product of anhydrite,

$$K_{\text{Anhydrite}} = a_{\text{Ca}^{++}} \cdot a_{\text{SO}_4} =$$

Thus for the reaction:



the equilibrium constant, $K_{(T,P)} = a^2_{\text{H}_2\text{O}}$

As long as no intermediate compounds of different composition are formed, the equilibrium is a function only of the activity of H_2O ($a^2_{\text{H}_2\text{O}}$) and is independent of the other ions in solution, except insofar as they affect $a_{\text{H}_2\text{O}}$.

Conley and Bundy (1958) have suggested that the formation of double salts is involved in the gypsum-anhydrite transition. The compositions of the solutions from which they precipitated the double salts, syngenite, $\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$ and labile salt, $2\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were rather different from those of natural solutions. No double salts were found associated with any of the evaporite minerals of the Trucial Coast. Conley and Bundy also suggested that in dilute solutions, transient surface complexes were involved in the gypsum-anhydrite transition. It seems unnecessary to postulate the presence of such complexes, particularly now that the field occurrence can be reasonably explained in terms of the simple equilibrium relationships.

The value of $a_{\text{H}_2\text{O}}$ of any solution is defined as the ratio,

$$\frac{P_{\text{H}_2\text{O}} (\text{Solution})}{P_{\text{H}_2\text{O}} (\text{Pure water})}$$

For pure water, $a_{\text{H}_2\text{O}} = 1.00$ and with increasing ionic concentration this value decreases. The solutions of greatest importance are brines derived from the evaporation of sea water.

Published data are available for the vapour pressure of concentrated sea water brines (Arons and Kientzler, 1954) in the range of temperatures 10-60°C, the range of particular interest in this study. In addition, standard data are available for the vapour pressure of pure water over a similar range of temperatures (Hodgman, 1962). The sea water brine data are for a sea water which was progressively concentrated, the ionic ratios changing as particular minerals, such as gypsum, were precipitated. The Trucial Coast brines do not have such a simple history. They are indeed sea water derived brines but because of sediment/brine reactions such as dolomitisation, their composition is not exactly what would be predicted if they had merely undergone simple concentration. This difference in composition is unlikely to affect the values of a_{H_2O} by more than their probable error of 2% (Arons and Kientzler, 1954).

Figure 12 shows the vapour pressure curve for pure water between 10-60°C ($a_{H_2O} = 1.00$). Also shown is the vapour pressure curve for a concentrated sea water brine of chlorinity 150‰. Over this range of temperature, the relative lowering of the vapour pressure of this solution is 23% ($a_{H_2O} = 0.77$). Sea water (19‰ chlorinity) and intermediate brines have values of a_{H_2O} between 0.77-1.00.

Values of a_{H_2O} for brines of chlorinity 0-150‰ are shown in Fig. 13. The relationship of a_{H_2O} to brine concentration indicates that the gypsum-anhydrite equilibrium boundary must have a negative slope and curvature. Similarly, the metastable gypsum-metastable bassanite boundary is a function of a_{H_2O} and this boundary should also show a negative slope and curvature.

Hardie (1964) has presented data on the gypsum-anhydrite equilibrium, which he has defined in terms of a_{H_2O} and temperature. The equilibrium was approached from both directions and runs were sometimes as long as one year. Anhydrite was actually produced during the runs. The data on the following page show the three temperatures at which the equilibrium was determined and also the extrapolated points for pure water and halite saturated brine. The sea water brine concentrations have been calculated using the vapour pressure data of Arons and Kientzler (1954). [Hardie and Eugster in a later abstract (1965) have slightly modified the equilibrium temperatures to the following: 53.5, now 55.0°C; 38.5, now 39.0°C; 24.0, now 23.0°C; 19.0, now 18.0°C.]

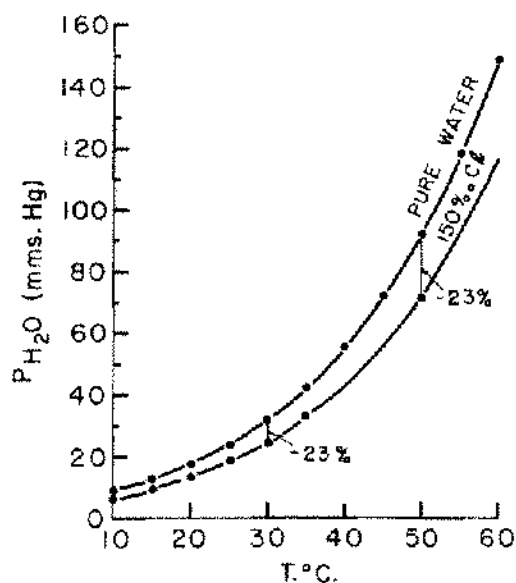


Figure 12. Vapour pressure curves for pure water and a concentrated sea water brine of 150‰. The latter shows a 23% lowering in vapour pressure (i.e., $a_{H_2O} = 0.77$).

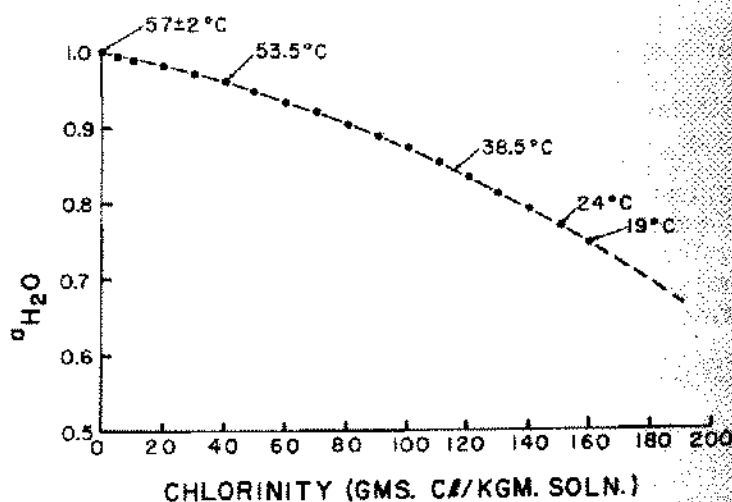


Figure 13. Showing relationship of a_{H_2O} to sea water brine concentration (calculated from vapour pressure data of Arons and Kientzler, 1954). The five temperatures indicated, together with the associated values of a_{H_2O} and brine concentration, define the gypsum-anhydrite equilibrium (initial data from Hardie, 1964).

a_{H_2O}	1.00	0.960	0.845	0.770	0.750
T. °C.	57±2	53.5	38.5	24.0	19.0
% Lowering of a_{H_2O}	0	4.0	15.5	23.0	25.0
Chlorinity %	0	41	115	151	161

By extrapolation

The temperature and a_{H_2O} data determined by Hardie (1964) are included in Fig. 13. Figure 14 shows the gypsum-anhydrite equilibrium boundary superimposed on the stability relationships determined from the solubility measurements. The new position for the equilibrium boundary differs greatly from that indicated by the solubility studies but is within the range of temperatures predicted from the thermodynamic calculations ($46 \pm 25^\circ\text{C}$).

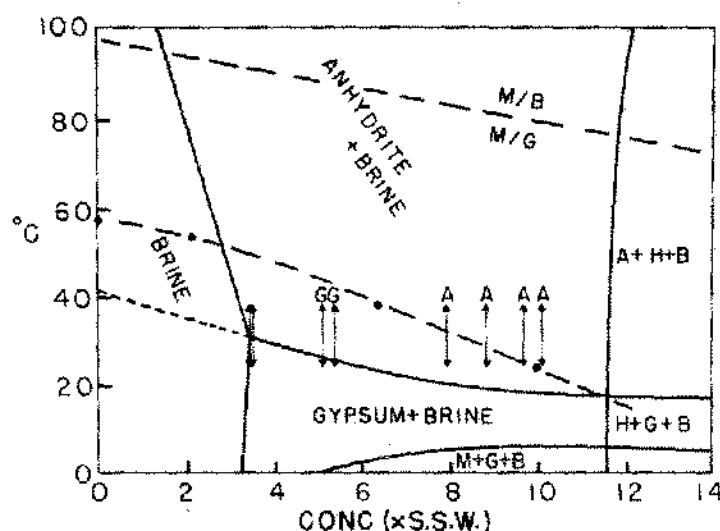


Figure 14. Gypsum-anhydrite equilibrium relationships, showing solubility measurement data (same as Figure 11) and new data of Hardie, 1964 (heavy dashed line). Vertical lines (8) represent Trucial Coast brines associated with either gypsum (G) or anhydrite (A), and annual brine temperature range. Agreement with Hardie's data is excellent.

Also plotted in Fig. 14 is the temperature range and concentration of interstitial ground water brines from the Trucial Coast. The two samples marked "G" are associated with gypsum and the four samples marked "A" are associated with anhydrite. The two samples with gypsum have gypsum above the ground water table level, associated with the slightly more concentrated capillary waters, but also have gypsum below the ground water table indicating probable equilibrium conditions, between gypsum and ground water brine. The two most concentrated brines have anhydrite both above and below the ground water table. The anhydrite below the ground water table level shows no sign of solution (laths with ragged edges, etc.) and can be considered as being in equilibrium with the brines. The other two brines have anhydrite in the capillary zone; thus the concentration of the pore fluids in equilibrium with the anhydrite in these two samples will be slightly greater than the concentration of the ground water brines. In other words from a brine/anhydrite equilibrium standpoint these two samples should be shifted slightly to the right, to higher concentrations. It can be seen that the equilibrium relationships which can be derived from the

Trucial Coast data tie in very closely with the work of Hardie. In fact, even if Hardie's data were not available, the inferred position of the equilibrium boundary would have been in almost exactly the same place.

GENERAL DISCUSSION

Recent Gypsum

Gypsum has been widely reported from Recent sediments of a variety of types. The mineral has been reported from continental areas where it is found in salt lake and playa sediments (for example, Great Salt Lake, Eardley and Stringham, 1952) and as a near-surface caliche-type deposit in many arid regions. In low latitudes, many tidal flats and semi-isolated marine pools and lagoons have gypsum associated with them (Laguna Madre, Masson, 1955; Bonaire Island, Deffeyes et al, 1964; Qatar, Persian Gulf, Wells, 1962; etc.).

In most tidal flats and areas peripheral to surface bodies of concentrated waters, the gypsum is a subsurface, interstitial development and is of displacement rather than replacement origin. Even below some surface bodies of saline water, gypsum crystals develop within the sediments rather than at the sediment/water interface. On the island of Bonaire (Deffeyes et al, 1964), gypsum precipitates both within tidal flat sediments and apparently on the sediment/water interface in surface pools of concentrated sea water brine. In the Bocana de Virrila, Peru (Morris and Dickey, 1957) gypsum precipitates on the bottom from the concentrated brines.

Most of the studies mentioned above have not related the gypsum to a parent brine. On the Trucial Coast this can be achieved and gypsum can be shown to precipitate when its solubility is just exceeded (65% chlorinity). A survey of the other Recent gypsum occurrences, together with the Trucial Coast data and the new gypsum-anhydrite equilibrium data, indicate that gypsum will probably always be the first calcium sulphate mineral to precipitate from a natural solution under earth surface climatic conditions. The equilibrium data indicate that a sea water derived brine would have to exceed 50°C for anhydrite to precipitate and not be preceded by gypsum (Fig. 14). However, because of the difficulty with which anhydrite nucleates, gypsum will be precipitated metastably even above 50°C, certainly from surface bodies of brine. Such water bodies will probably undergo relatively rapid increases in brine concentration, anhydrite solubility will be rapidly exceeded, gypsum solubility attained and gypsum precipitated. Given long enough, anhydrite can obviously nucleate and precipitate and it is possible that such conditions are only attained in interstitial brines where rates of concentration may be slower.

Gypsum is sometimes, therefore, a sedimentary mineral, resulting from precipitation from concentrated surface bodies of brine. In most instances these will be sea water derived brines but occasionally they may be of continental origin, such as playa lake waters. Associated sediments will be evaporitic in nature. Within intertidal and supratidal flat sediments and within sediments below and peripheral to surface bodies of brine, gypsum may develop interstitially as an early diagenetic mineral. Depending on the situation, the associated sediments may obviously range from normal marine, with perhaps abundant faunal remains, to almost azoic saline lake sediments.

Recent Anhydrite and Bassanite

Anhydrite from the Sarykamysh salt lakes (Rubanov et al, 1964) occurs dispersed within the silty residue of halite layers and in the underlying clays, as near cubic crystals 20-40 μ in size. It forms a fraction of a percent of the sediments and the conditions controlling its precipitation are largely unknown.

Recent anhydrite has also been reported from Clayton Playa, Nevada (Moiola and Glover, 1965). Early gypsum crystals have been successively dehydrated to bassanite and anhydrite. In situ dehydration of this kind would ultimately result in pseudomorphing of the original gypsum by anhydrite.

There are several reported occurrences of bassanite in the literature, although some of them may well be the result of sample preparation. However, in the sun, temperatures of at least 80°C can be reached and under such conditions gypsum may be expected to dehydrate. Gypsum

apparently never dehydrates directly to anhydrite. Kelley, et al (1941), experimentally determined the dissociation vapour pressure of the reaction:



It can be calculated from their data that at 80°C, at relative humidities of less than 80%, gypsum should dehydrate. However, the dehydration reactions, gypsum \rightarrow bassanite and bassanite \rightarrow anhydrite are nonequilibrium, kinetically controlled reactions and detailed analysis of controlling factors is probably not very useful or enlightening, at the moment.

On the Trucial Coast, bassanite has not yet been found, although it is possible that gypsum crystals exposed on the surface may at times become partially dehydrated. However, at night, high humidity and falling temperature result in all exposed surfaces being covered with dew and any bassanite formed during the day would probably be rehydrated. No bassanite is found associated with the anhydrite.

The extremely high surface temperatures recorded along the southwestern shore of the Persian Gulf (Bergstrom and Aten, 1964, have recorded 80°C in Kuwait) will extend only a very small depth below the surface, probably less than one inch. Anhydrite laths and very early nodules have been found growing at depths of 15-18 inches, where recorded seasonal temperatures range from 0° to 40°C. Thus, exceptionally high surface temperatures cannot be called upon to explain the development of the Trucial Coast anhydrite. Several lines of evidence thus disprove the suggestions of Ostroff (1964), that the mechanism of anhydrite formation is the successive dehydration of gypsum to bassanite and then to anhydrite, and that in aqueous salt solutions the dehydration occurs at temperatures above 90°C or above 97°C in pure calcium sulphate solutions.

The anhydrite from the Trucial Coast is an early diagenetic mineral, developed in supratidal areas of marine lagoonal carbonate sediments, by displacement. This is obviously one environment in which nodular anhydrite can develop. But it is quite conceivable that nodular anhydrite could develop within the sediments underlying a surface body of brine, particularly if appreciable reflux of concentrated brines through the sediments was taking place. The nodular habit of anhydrite would seem definitely to be a displacement, early diagenetic development within lithified sediments.

Murray (1964) has considered the development of gypsum crystals in exposed supratidal flat environments and considers all nodular anhydrite to represent dehydration of such early formed gypsum crystals. The Trucial Coast nodular anhydrite conclusively disproves the metagypsum origin of all nodular anhydrites. In fact, by applying what can be learned from the Trucial Coast area to ancient occurrences, it becomes likely that the majority of nodular anhydrites were never initially gypsum. Kerr and Thompson (1963) have also argued strongly for a metagypsum origin of most or all nodular anhydrite occurrences. Certainly there are, in the subsurface, evidences of such pseudomorphing of early gypsum by later anhydrite but this is a late diagenetic dehydration associated with burial; the pseudomorphs, although somewhat similar to anhydrite nodules, are rarely able to conceal their original gypsum shapes.

Gypsum and Anhydrite in the Subsurface

In general, gypsum is the common near surface calcium sulphate mineral and anhydrite the mineral of the deeper subsurface. In cores, anhydrite can often be seen to be gradually replaced by gypsum as the surface is approached. The depth of the hydration is generally less than 1,000 feet but there are records of it being deeper (Murray, 1964). Conversely, there is also abundant evidence of early gypsum being replaced by anhydrite after burial.

The preservation of the initial sedimentary or very early diagenetic gypsum or anhydrite will depend on temperature, pressure and pore fluid composition. Because of geothermal heat loss, the temperature gradient increases with depth from the initial mean surface temperature. Thus on the Trucial Coast the geothermal gradient will increase from a mean temperature of 33-35°C (initial temperature will be lower in most other areas). If we consider only the temperature and brine concentration ($a_{\text{H}_2\text{O}}$) variables, and consider a situation of constant $a_{\text{H}_2\text{O}}$, then increase in temperature with burial will favour the replacement of early gypsum by anhydrite, and will also favour the preservation of anhydrite formed in near surface positions.

Changes in the interstitial pore fluids could have a drastic effect on the mineralogy, particularly at shallow depths, before temperatures exceed about 50°C. For example, if flushing of the original pore fluids by dilute water should occur, then early anhydrite might well be replaced by gypsum, but only if temperatures were below about 55° (the more dilute the pore solution, the higher can be the temperature: see equilibrium curve of Fig. 14). If for some reason interstitial brine concentrations increased (a_{H_2O} decreased) then initial anhydrite preservation would be assured, or early formed gypsum would be replaced by anhydrite. Thus various possibilities arise which would either tend to maintain the initial mineralogy or promote one or other replacement. In general, however, during early burial the odds are stacked against prolonged gypsum preservation and surface formed anhydrite is likely to be preserved.

The effect of hydrostatic pressure has been stated to favour the preservation of gypsum (Douglas and Goodman, 1957) as the dehydration of one mole of gypsum to form one mole of anhydrite and two moles of water involves a volume increase of 9%. This would be so only if subsurface systems were closed, but many lines of evidence indicate that most subsurface systems are in fact open and thus the water produced during gypsum dehydration can escape. It is possible that anomalously deep gypsum could be explained in this way, the local system having been essentially closed so that the dehydration reaction could not take place.

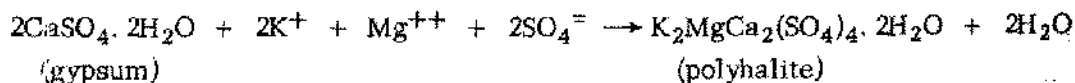
Models for Supratidal Diagenesis

During the past ten years many investigations of intertidal and shallow water sediments have been carried out and analogues have come to be abundantly recognized in ancient rocks. Diagenetic studies in Recent sediments have only just got underway, but it is obvious that on occasions, as in the Trucial Coast area, very early diagenesis is an important geological phenomenon.

The Trucial Coast study has indicated some of the diagenetic developments to be expected in a pure carbonate sequence under climatic conditions of high temperature and net evaporation (probably applicable particularly, for example, to Permian marginal carbonates and evaporites). The carbonate mud area showed rapid dolomitisation to occur, and massive calcium sulphate mineral development; ultimate brines were almost $SO_4^{=}$ free, low in Mg^{++} and rich in Ca^{++} .

Although data are far from sufficient, it might be of interest to point out some of the differences to be expected if we vary the model of supratidal diagenesis in various ways.

The obvious extreme, to contrast with the Trucial Coast would be a climatically similar area but with noncarbonate sediments. Laguna Ojo de Liebre, Baja California, would roughly serve (Phleger and Ewing, 1962). In such an area, supratidal diagenesis will not involve dolomitisation, although gypsum will be widely precipitated. However, if there is no source of additional Ca^{++} , then the maximum amount of $SO_4^{=}$ loss from interstitial brines is 35% as the brine then becomes depleted in Ca^{++} . Ultimate brines in such a diagenetic sequence are Mg^{++} rich, have 60-70% of their original $SO_4^{=}$ and are Ca^{++} free. W. T. Holser (1965) has found Recent polyhalite in this area, replacing early gypsum. From consideration of the interstitial brine composition this is an entirely reasonable development to find:



From the composition of the Trucial Coast brines ($SO_4^{=}$ free, low Mg^{++}) polyhalite would not be expected in such an environment.

In addition, if we compare these two extreme models, the amount of calcium sulphate mineral precipitation is seen to differ by a factor of almost 3. The total calcium sulphate mineral development is a function of Ca^{++} availability and in the one extreme all the Ca^{++} is derived from sea water, in the other, there is an excess supply as a by-product of dolomitisation.

The carbonate model can be subdivided, depending on initial sediment characters, into carbonate muds and carbonate sands. Along the western parts of the Trucial Coast, carbonate sands predominate; dolomitisation is here much retarded, and from reconnaissance field studies the volume of calcium sulphate minerals is less than one half that developed in the east where initially fine-grained carbonate muds have been rapidly dolomitised. Thus the relative rates at which

carbonate sediments are dolomitised, controls the amounts of calcium sulphate minerals developed. It is possible that replacements such as polyhalite replacing early gypsum might be found in areas of slow dolomitisation such as coarse carbonate sands.

Many other variables could be fitted into our models but will only be briefly mentioned. An important one concerns bacterial reduction of $\text{SO}_4^{=}$, which could reduce $\text{SO}_4^{=}$ drastically and thereby affect the volume of sulphate mineral development. If appreciable Ca^{++} is precipitated in marine or interstitial positions as CaCO_3 , before calcium sulphates are precipitated, then this could reduce the volume of calcium sulphate minerals. Climatic factors, permeability and porosity of sediments (particularly with regard to reflux or ion diffusion) and also hinterland relief and water table effects can all be variously juggled. The possible variations in the model are immense and could well account for many or most of the things we see in ancient, marginal, sedimentary sequences, with associated evaporites. The rates at which sedimentation and diagenesis of this type can occur are particularly noteworthy. For example, along the Trucial Coast, the great areas of supratidal carbonate sediments, together with the diagenetic dolomite and evaporitic minerals, have all been developed within the past 3,000-4,000 years, a fleeting moment of time when viewed geologically.

ACKNOWLEDGMENTS

Much of the work reported here was carried out at Imperial College, London. Financial assistance came from NATO and the late Department of Scientific and Industrial Research. Many people have discussed or exchanged ideas and made my views less parochial. Of particular help have been H.D. Holland, W.T. Holser, R.C. Murray, and D.J. Shearman.

REFERENCES

- Arons, A.B., and Kientzler, C.F., 1954, Vapour pressure of sea-salt solutions. *Trans. Amer. Geophys. Union*, vol. 35, pp. 722-728.
- Bergstrom, R.E., and Aten, R.E., 1964, Natural recharge and localization of fresh ground water in Kuwait. *J. Hydro*, vol. 2, pp. 213-231.
- Conley, R.F., and Bundy, W.M., 1958, Mechanism of gypsification. *Geochim. et Cosmochim. Acta*, vol. 15, pp. 57-72.
- Deffeyes, K.S., Lucia, F.J., and Weyl, P.K., 1964, Dolomitisation; observations on the island of Bonaire, Netherlands Antilles. *Science*, vol. 143, no. 3607, pp. 678-679.
- Douglas, G.V., and Goodman, N.R., 1957, The deposition of gypsum and anhydrite. *Econ. Geol.*, vol. 52, pp. 831-837.
- Eardley, A.J., and Stringham, B., 1952, Selenite crystals in the clays of Great Salt Lake. *J. Sed. Pet.*, vol. 22, pp. 234-238.
- Hara, R., Tanaka, Y., and Nakamura, K., 1934, On the calcium sulphate in sea water; I-Solubilities of dihydrate and anhydrite in sea waters of various concentrations at 0-200°C. Sendai Japan, Tech. Reps., Tohoku Uni., vol. 11, pp. 199-221.
- Hardie, L.A., 1964, Gypsum-anhydrite equilibrium at 1 atmosphere pressure. Abstract, GSA Meeting, Miami.
- _____, and Eugster, H.P., 1965, The gypsum-anhydrite equilibrium at 1 atmosphere pressure. *Proc. Second Salt Symposium* (this volume).
- Hodgman, C.D., (Ed.), 1962, Handbook of chemistry and physics. Chemical Rubber Pub. Co., Cleveland.
- Holser, W.T., 1961, Unpublished report, California Research Corporation.
- _____, 1965, Diagenetic polyhalite in Recent salt from Baja California (in press).
- Kelley, K.K., Southard, J.C., and Anderson, C.T., 1941, Thermodynamic properties of gypsum and its dehydration products. U.S. Bur. Mines Tech. paper, 625, 73 pp.

- Kerr, S.D., and Thompson, A., 1963, Origin of nodular and bedded anhydrite in Permian shelf sediments Texas and New Mexico. *Bull. Am. Ass. Pet. Geol.*, vol. 47, pp. 1726-1732.
- Kinsman, D.J.J., 1965a, Recent carbonate sedimentation and diagenesis, Trucial Coast, Persian Gulf, (in press).
- _____, 1965b, Huntite, $Mg_3Ca(CO_3)_4$ and magnesite associated with Recent carbonate and evaporite sediments, Trucial Coast, Persian Gulf (in press).
- Macdonald, G.J.F., 1953, Anhydrite-gypsum equilibrium relations, *Amer. J. Sci.*, vol. 251, pp. 884-898.
- Masson, P.H., 1955, An occurrence of gypsum in southwest Texas. *J. Sed. Pet.*, vol. 25, pp. 72-79.
- Moiola, R.J., and Glover, E.D., 1965, Recent anhydrite from Clayton Playa, Nevada (in press).
- Morris, R.C., and Dickey, P.A., 1957, Modern evaporite deposition in Peru. *Bull. Amer. Assn. Pet. Geol.*, vol. 41, pp. 2467-2474.
- Murray, R.C., 1964, Origin and diagenesis of gypsum and anhydrite. *J. Sed. Pet.*, vol. 34, pp. 512-523.
- Ostroff, A.G., 1964, Conversion of gypsum to anhydrite in aqueous salt solutions. *Geochim. et Cosmochim. Acta*, vol. 28, pp. 1363-1372.
- Phleger, F.B., and Ewing, G.C., 1962, Sedimentology and oceanography of coastal lagoons in Baja California. *Geol. Soc. Amer. Bull.*, vol. 73, pp. 145-182.
- Posnjak, E., 1938, The system, $CaSO_4-H_2O$, *Amer. J. Sci.*, vol. 235-A, pp. 247-272.
- Rubanov, I.V., Mirakhmedov, M., and Sharipova, A., 1964, Anhydrite in the Recent salt deposits of the Sarykamysh Lakes. *Doklady Acad. Nauk, SSSR*, vol. 158, pp. 622-624.
- Wells, A., 1962, Recent dolomite in the Persian Gulf. *Nature*, vol. 194, pp. 274.
- Zen, E-an. 1965, Solubility measurements in the system $CaSO_4-NaCl-H_2O$ at 35°, 50°, and 70°C and one atmosphere pressure. *J. Petrology*, vol. 6, pp. 124-164.