ORIGIN AND DIAGENESIS OF GYPSUM AND ANHYDRITE:

R. C. MURRAY

ABSTRACT

Despite data on the stability of anhydrite at high earth surface temperatures, the observation of Recent gypsum and the evidence for formation and preservation of metastable gypsum suggest that this form may be the common if not universal original calcium sulfate mineral. Gypsum beds can be produced by two mechanisms: (1) Precipitation and sedimentation in a standing body of water subjected to evaporation. Such deposits are original sedimentary facies, contemporaneous with other sedimentary facies. (2) Growth of abundant crystals by displacement of unconsolidated sediment or weathered rocks, which results in beds of gypsum which later is replaced by nodular anhydrite. These nodular anhydrite beds represent a diagenetic facies and postdate the host material. The distinction between sedimented and nodular is important in the interpretation of any given evaporite deposit.

These primary deposits act as a source of calcium sulfate for subsurface growth of replacement and void-filling anhydrite. The latter two secondary types of anhydrite can be distinguished in reflected light, since a dark color is imparted to replacement anhydrite by included material.

From observations in Recent sediments, older outcrops, and the subsurface, there appears to be a characteristic cycle in the diagenesis of gypsum-anhydrite minerals: surface or near-surface gypsum is replaced by anhydrite as a result of burial and is in turn replaced by gypsum if the anhydrite is thereafter brought close to the surface.

ORIGIN OF PRIMARY DEPOSITS

Sedimentary deposits of the calcium sulfate minerals (gypsum and anhydrite) are common throughout much of the geologic record. They are commonly associated with carbonate rocks, especially dolomite and ferruginous clastics. The object of this paper is to examine the evidence regarding which mineralogic form is the primary depositional product and to trace the diagenetic changes that accompany burial and re-exposure of these deposits. This has been the subject of much discussion in the literature with many authors favoring anhydrite as the original form.

Physical Evidence

In general, gypsum is found near the surface and in Recent sediments, whereas anhydrite is the common form of the subsurface. Indeed, it is not uncommon in large gypsum quarries to encounter interbedded anhydrite and gypsum followed by isolated gypsum patches and finally pure anhydrite with depth. Many authors, for example, Sund (1959), argue convincingly for the replacement of anhydrite by gypsum under near-surface conditions. The evidence for this replacement may be observed in all deep quarries and shallow cores where some anhydrite is still preserved. Although the transition commonly takes place within a few hundred feet of the present surface, the replacement of anhydrite by gypsum has been observed as deep as 3500 feet in the Permian San Andres Formation, Dune field, Crane County, Texas (fig. 1).

Bundy (1956) suggested that the gypsum may be the predominant or only form of calcium sulfate precipitated from sea water. Such a generalization is naturally at variance with interpretations of a primary origin of anhydrite. However, studies of Recent evaporite deposits—for example, Fisk (1959), Morris and Dickey (1937), Phleger and Ewing (1952), Mason (1955), Talmage and Wootton (1937), and Wells (1962)—have emphasized the observations that gypsum is the common if not universal form present. It has generally been impossible to determine the specific composition and temperature of the solution at the time the gypsum was precipitated. However, gypsum is forming today in some of the hottest parts of the surface of the earth. Recently, Curtis and others (1963) have reported Recent anhydrite above the free water level in the supratidal flats along the Trucial Coast of the Persian Gulf.

Stewart (1953) observed pseudomorphs of anhydrite after gypsum in the Permian evaporites of northeastern England. These pseudomorphs could only be seen when weathered sur-

1 Manuscript received July 22, 1963.
2 Shell Development Company (A Division of Shell Oil Company), Exploration and Production Research Division, Houston, Texas (Publication No. 354).
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Fig. 1.—Gypsum replacing replacement anhydrite; San Ardores Formation, 3500 feet below the present surface. Gypsum (white) rims and indents a core of subhedral anhydrite. The anhydrite had originally replaced fine sucrose dolomite.

faces of the core were studied. Some of the original crystal outlines were flattened, and in extreme cases the structures were barely detectable. This direct type of observation has seldom been made in massive evaporite beds. The reason must, in part, be ascribed to imperfection of preservation. However, this example is prima facie evidence of the metagypsum origin of these anhydrite beds.

These general observations suggest the generalization that a common diagenetic cycle exists in the calcium sulfate minerals—deposition of gypsum followed, during burial, by replacement of gypsum by anhydrite followed in turn, during uplift and erosion of overlying strata, by replacement of anhydrite by gypsum (fig. 2). Henderson (1954) argued that gypsum in the Stanford Range has never been buried to sufficient depth for replacement of gypsum by anhydrite. If his interpretation based on delicate preservation of textures is correct, these ancient deposits have never passed through the complete cycle.

Chemical Evidence

The physical-chemical environment that favors primary precipitation of gypsum or anhydrite or replacement of one mineral by the other has received much study since the early work of Van't Hoff in the early 1900's. Posnjak (1938) produced data on the stability of gypsum and anhydrite as a function of temperature. These data were obtained only by dissolution. The intersection of the solubility curves for the two minerals defines a temperature above which anhydrite is less soluble than gypsum and thus presumably more stable. The temperature of intersection for distilled water was 42°C; thus, anhydrite should be favored above this temperature. From his earlier work Posnjak recognized that solubility determinations in different concentrations of sea salt solutions could be helpful in interpreting the conditions of deposition of the two minerals from concentrated sea water. He made solubility determinations in solutions of sea salts at 30°C (Posnjak, 1940) and showed that an increase in salt concentration would lower the temperature of equal solubility. He concluded that sedimentary marine deposits of pure anhydrite either must have been partly derived from originally deposited gypsum or must have been formed near or above 42°C. However, from stability considerations some anhydrite could have been formed below 42°C. During his experiments Posnjak observed that
gypsum was very persistent and crystallized easily even in its metastable state. Indeed, evaporation of sea water in the temperature range 60°-80°C produces gypsum rather than anhydrite as a final product. This suggests that factors other than the solubilities of the two minerals may be involved in determining the conditions under which one or the other will be formed.

MacDonald (1953) approached the problem thermodynamically in order to study the effect of concentrated salt solutions and pressure on the gypsum-anhydrite transition temperature. From previously determined thermodynamic properties he calculated a transition temperature of 40°C for the reaction \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{CaSO}_4 + 2\text{H}_2\text{O} \) in pure water. This value corresponds closely with Posnjak's experimental data.

He also demonstrated the effect of pressure on the reaction in pure water. Under hydrostatic conditions the transition curve had a positive slope, indicating that an increase of total pressure would increase the transition temperature and would favor the formation or preservation of gypsum.

From further thermodynamic calculations, MacDonald (1953) produced a graph showing the transition temperature as a function of the concentration of NaCl, which was compared with sea water by corresponding chlorinities. This graph shows the transition temperature decreasing with an increased concentration of salts; thus, theoretically, one could determine the transition temperature of gypsum-anhydrite at any concentration of sea water. With an estimated concentration of 3.35 times that of normal sea water as the saturation point of \( \text{CaSO}_4 \) in the evaporation of sea water, a transition temperature of 34°C was determined. Therefore, if deposition is an equilibrium process, gypsum will be the stable phase and will precipitate out of sea water first at all temperatures less than 34°C, and anhydrite will precipitate out first at all temperatures greater than 34°C.

Henderson (1954) presented additional data on relative solubility of gypsum and anhydrite in salt solutions and concluded that gypsum should be stable to a maximum depth of 2000 feet.

Conley and Bundy (1958) studied the mechanisms involved in converting anhydrite to gypsum. By experimental work they further substantiated Posnjak's observations concerning the persistence and ease of crystallization of gypsum in its metastable state. They also determined
that the reaction of gypsum going to anhydrite plus water is very slow or nonexistent below 42°C. Further, in contrast with Posnjak's and MacDonald's work showing that salt solutions lower the temperature at which anhydrite becomes more stable, they showed that some salts activate rather than inhibit the hydration process in the temperature range studied. In other words, these salts promote the conversion of anhydrite to gypsum, even under conditions theoretically favoring the formation of anhydrite. The best activators were found to be sodium and potassium sulphate.

From their data, Conley and Bundy postulated that it is highly improbable that anhydrite is ever precipitated primarily from sea water because (1) gypsum crystallizes relatively easily in its metastable state, and (2) as soon as crystallites of anhydrite would begin to form in sea water, the activating constituents in the sea water would bring about an almost immediate conversion to gypsum at temperatures below 42°C. They conclude that the thermodynamic applications which predict the formation of anhydrite from gypsum in concentrated salt solutions are incomplete in that they do not incorporate the effect of CaSO₄ activators which influence the reaction kinetics.

Despite the evidence from solubility and thermodynamic calculations that anhydrite is more stable in concentrated salt solutions below 42°C, the observation of common if not universal occurrence of Recent gypsum in brine and the influence of kinetic factors in allowing formation and preservation of metastable gypsum suggest that the primary deposit may almost always be gypsum.

Thus, there is a body of evidence that suggests that under most surface conditions gypsum should be the sedimentary product. Very high temperatures might locally cause formation of some anhydrite at the surface in the presence of gypsum. Indeed, this is happening today on the supratidal flats of the Trucial Coast. However, formation and preservation of gypsum may occur for kinetic reasons when surface temperatures are sufficiently high to make anhydrite the stable phase. With burial, gypsum should be replaced by anhydrite. The minimum depth for the transition should be a temperature of 42°C corrected for the pressure effect at the depth of the transition. Because the rate of the change of gypsum to anhydrite with respect to the rate of subsidence is unknown, this value must remain a minimum depth. Theoretical values for the depth of this transition range around 2000 feet. However, the author is not familiar with any study of gypsum-to-anhydrite transformation in a formation undergoing initial burial. In the deeper subsurface, anhydrite is the almost universal form.

Environments of Formation

Studies of anhydrite in carbonate rocks and in association with carbonate and clastic rocks suggest that a threefold distinction can be made on the basis of the mode of formation. This distinction involves the recognition of (1) bedded anhydrite, (2) pore-filling anhydrite, and (3) replacement anhydrite. The anhydrite beds which represent the sedimentary unit of primary formation and thus generally metagypsum are the obvious source of material for formation of the two secondary types.

From the previous discussion it is apparent that most of the sedimentary units of anhydrite observed in the subsurface are metagypsum. This may be true despite the fact that independent evidence of this replacement in individual examples is relatively rare. The original condition of precipitation involved concentration through evaporation of water, commonly sea water or ground water that has moved through pre-existing evaporite deposits. Such deposits may be of two general types, each with its own significance with respect to paleoenvironment. Although an individual formation may exhibit both types, a distinction between (1) sedimented and (2) nodular fabrics can commonly be recognized.

The sedimented or laminated anhydrite or gypsum beds of which much of the Castile formation (King, 1947) and the Pleistocene Lisan formation of the Dead Sea are composed represents precipitation and sedimentation in a standing body of water. The concentration of the evaporating brine may be maintained within the field of CaSO₄ precipitation by limited flow of new sea water into the body of water and reflux of the heavy brine out through the inlet (King, 1947) or through the underlying sediments and rocks (Adams and Rhodes, 1960; Deffeyes, Lucia, and Weyl, 1964). Such evaporite beds commonly show continuous laminations (fig. 3) and sedimentary structures and should be essentially devoid of uniformly distributed marine fossils. They represent a depositional sedimentary facies, time-contemporaneous with other facies. These other facies may be clastic sediments or even carbonate. The latter is more difficult because extensive carbonate deposition which depends on organic productivity is not possible in concentrated brines.

Nodular anhydrites or gypsum, although they occur in thick units relatively free of carbonate and clastic material, present a different problem.
of genesis. All gradations exist, from isolated nodules in fossiliferous limestone or dolomite to thick beds of clustered nodules with only a thin matrix or sheath of limestone, dolomite, or siliceous clastic material. The crystal fabric of the anhydrite in nodules is similar to that of the sedimented anhydrite. Both exhibit a tightly interlocking fabric of needlelike to tabular crystals commonly preferentially oriented parallel or subparallel to bedding (fig. 4). This preferred fabric may change to an orientation subparallel to the nodule surface near the boundary.

Nodules of anhydrite commonly exist in fossiliferous limestones and fossiliferous limestone replaced by dolomite. However, because of general lack of foreign inclusions or ghosts and the draping of the host rock around the nodule, they do not appear to have formed by replacement of carbonate rock. The similarity of nodule shapes observed in rocks of different age and lithology and the absence of nonfilled vugs of similar shape and size argue against gypsum cementation of large vugs. The thin sheath or matrix of carbonate rock commonly observed between closely spaced nodules excludes the vug origin and suggests a displacement or compactional origin where one nodule has been squeezed against another. These anhydrite nodules appear to exist simply as ovoid masses within carbonate rocks whose origin is inconsistent with an evaporite environment.

Gypsum crystals similar to those found today on the shores of Lake Lucero near White Sands, New Mexico, offer an explanation for the anhydrite nodule origin (fig. 5). These crystals have grown within the Recent alluvial sediments. During growth the crystals physically push aside the silt, sand, and gravel and form clear or nearly clear selenite crystals. When these sediments are buried, the gypsum will be replaced by anhydrite. If compaction of the sediment accompanies this change, draping of sediment both over and under the nodule will result. If the gypsum crystals grew in carbonate sediment, and they do today in most of the arid climate carbonate supratidal flats, the same relations should hold, and the product would be anhydrite nodules within, but not necessarily related by original depositional environment to the carbonate host rocks (figs. 6 and 7). Small gypsum crystals should produce the small pellet-like anhydrite nodules. The larger crystals should produce the larger anhydrite nodules.

The formation of selenite crystals and rosettes by displacement of soft sediments or weathered rocks appears to take place by at least two mechanisms: (1) Evaporation of ground water in the vadose or capillary zone (Talmage and Wootton, 1937). Crystals of this origin are indicative of subaerial exposure of the top of the host rock or sediment. (2) Evaporation of water on a playa or other standing body of water and down-
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Fig. 4.—Small anhydrite nodule; transmitted light. Note the orientation of the individual anhydrite crystals subparallel to the bedding. The host San Andres dolomite is draped around the nodule.

Fig. 5.—Surface of valley fill sediments west of Lake Lucero, New Mexico. The clear gypsum crystals have grown within the sand and silt by displacement. The tops of some crystals have been exposed by erosion.
Fig. 6.—Bed of nodular anhydrite grading into fossiliferous sucrose dolomite; Clear Fork Formation, West Texas.

Fig. 7.—Bed of nodular anhydrite showing thin sheath of original sediment between pure anhydrite nodules; Madison Formation, Montana.
ward movement of the dense hypersaline water into sediment below, with resulting formation of the gypsum crystals. Crystals of this origin are forming in the Laguna Madre tidal flats (Mason, 1955). With either mechanism the presence of the anhydrite nodules is not necessarily indicative of hypersaline water during deposition of the host rock. Thus, the apparent inconsistency of coexisting marine organisms and rocks and hypersaline conditions is satisfied. If the host rock existed at an unconformity that exposed sediments or weathered rocks of different age, the nodular bedded anhydrite would appear to be time-transgressive.

Recently, Kerr and Thomson (1963) have observed pseudomorphs of anhydrite nodules after gypsum crystals, indicating that the gypsum crystal form is not always destroyed in producing anhydrite nodules and presenting prima facie evidence of a metagypsum origin of the anhydrite. Using the Recent analogy of the Laguna Madre gypsum, they point out the association of tidal-flat sediments with nodular anhydrite and suggest that this environment of intermittent inundation with sea water offers an ideal environment for formation of nodular evaporites.

The nodular anhydrite beds thus represent growth of gypsum by displacement of soft sediment after deposition of the host material and must be considered an early diagenetic facies rather than a depositional facies. Many of the examples of Recent evaporites occur on supratidal flats and shallow lakes on supratidal flats rather than in large, deeper-standing bodies of water.

Thus, the conclusion may be drawn that nodular anhydrite is indicative of subaerial exposure of soft sediments with evaporation of CaSO4-bearing water taking place within the sediment. Such conditions commonly exist today on the supratidal flats in arid climates or in desert playas. In the former the source of water is commonly the sea and transport into the supratidal sediments may take place during a large storm or by seepage through the sediments. In the latter the source of the water may be ground water that has passed through older evaporites and
thus represents a reconstructed water. Because nodules may form below standing bodies of water in earlier sediments and because shallow bodies of water may temporarily exist as lakes or sediments, several types of voids can be generated in carbonate or terrigenous clastic sand, intercrystalline space in dolomite, primary cavities in interparticle space occupied by water. These crystals may occur as relatively large clear individuals that fill the pre-existing space or in larger spaces as clusters of clear tabular crystals. However, void-filling anhydrite in carbonate rocks commonly continues to grow by replacement into the rock margin of the pre-existing void (fig. 8).

Replacemnt Anhydrite

Replacement anhydrite crystals grow within the rock and occupy space previously occupied by other minerals and fine pore space. Bioclastic particles appear to be the most commonly replaced material. This process probably takes
place by simultaneous dissolution of the parent rock and precipitation of the anhydrite, as demonstrated by the in-situ distribution of inclusion produced relict patterns. Dissolution is often incomplete, and the anhydrite continues to grow around the more resistant relict calcite, dolomite, and noncarbonate clastic grains, attempting to maintain its rectangular habit, but often the final shape is partially controlled by the shape of the material being replaced. These leftover particles remain within the replacement anhydrite crystal and, if they are large enough, can easily be seen when the anhydrite crystal is turned to extinction. Because of this imperfect replacement, resulting in the inclusion of relict particles within the anhydrite crystal, these crystals are usually cloudy to brown in reflected light. The color, of course, depends on the amount, distribution, and nature of the relict material.

Chemical analyses by emission spectrograph were made of anhydrite samples representing two sets of the three anhydrite types (fig. 9). These samples were prepared by removing all the surrounding carbonate rock with dilute hydrochloric acid. Within the limits of accuracy, the bedded nodular and the pore-filling anhydrites appear quite similar in trace element content. However, the replacement anhydrite from the San Andres dolomite and Charles limestone examples contains excess magnesium, silicon, and aluminum. This undoubtedly represents relicts of nonreplaced dolomite, quartz, and clay minerals within the replacement anhydrite crystals and confirms the nature of the relicts and the cause of the cloudy to brown color. Further confirmation was obtained by X-ray analysis of the three Charles anhydrites. The bedded and pore-filling anhydrite showed only anhydrite, whereas the replacement sample contained between 5 and 10 percent calcite and some quartz.

The three anhydrite types can be distinguished in reflected light because of the textural differences and the presence of inclusions in replacement anhydrite.

Bedded anhydrite is commonly granular to massive and translucent to opaque and may be white or light colored, depending on contained impurities (figs. 10 and 11). Pore- or vug-filling anhydrite commonly occurs as clear single crystals with well-defined cleavage (figs. 10 and 11). Rock-replacement anhydrite, because it often fails to digest completely the rock being replaced, appears as cloudy to brown single crystals (figs. 10-11).
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REFERENCES


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