

The Sulfate Problem in Marine Evaporites

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ABSTRACT

One of the puzzling characteristics of marine evaporite deposits is sulfate deficiency exclusive of calcium sulfate. Sulfate is the third most abundant ion in seawater, yet less than 40 percent is removed by gypsum/anhydrite precipitation. Therefore, marine evaporites should normally contain an abundance of other sulfate minerals.

An attractive explanation is bacterial reduction of SO_4^{2-} and consequent escape of hydrogen sulfide to the atmosphere, a process observed in modern evaporite environments. Measured rates of reduction in marine systems, however, suggest only a minor effect on brine modification. An additional constraint includes the large volume of organic matter required as an energy source by the bacteria. Furthermore the calcium or magnesium carbonates which are a necessary byproduct of the bacterial process are missing in most deposits. Sulfate depletion can also be brought about by the Haidinger reaction; however, it seems unlikely that sufficient Ca^{2+} would have been available, either from marine influxes or continental runoff, for the reaction to be effective.

It is proposed that the key to sulfate depletion is brine modification through Ca^{2+} enrichment, because the strong at-

traction of Ca^{2+} for SO_4^{2-} can result in all of the sulfate ion being precipitated as gypsum. Several mechanisms can affect Ca^{2+} enrichment, including dolomitization and polyhalitization of previously deposited limestone and gypsum, and substitution of Mg^{2+} , K^+ , and Na^+ for Ca^{2+} in reactions between detrital clay minerals and brine. Geologic evidence in most marine evaporites appears to favor dolomitization. A good example are the middle Pennsylvanian evaporites in the Paradox Basin of southeast Utah, which are notably sulfate deficient. Studies of Paradox evaporite cycles show that the annual supply of CaSO_4 (ASC) in the halite of the oldest cycles was somewhat less than the maximum yield obtainable from evaporation of a seawater brine. It was not until after the deposition of several dolomite units that younger halite beds began to show ASC values in excess of evaporative CaSO_4 . These excess values are believed to represent "reaction" CaSO_4 produced by the reaction of SO_4^{2-} with Ca^{2+} release by dolomitization. Additional evidence for reaction CaSO_4 was obtained from analyses of brine inclusions in halite rock which showed highest Ca^{2+} values in cycles in which the ASC was also high.

STATEMENT OF THE PROBLEM

The seven most abundant ions in seawater include the cations Na^+ , Mg^{2+} , Ca^{2+} , and K^+ and the anions Cl^- , SO_4^{2-} , and HCO_3^- . When seawater is concentrated by evaporation these ions should combine to form a series of minerals which includes a high percentage of magnesium sulfate if evaporation proceeds as far as the potash facies. Most marine evaporite deposits, however, are characterized by a deficiency or sometimes total absence of magnesium sulfate minerals and this constitutes what is generally referred to as the "sulfate problem" in marine evaporites. The magnitude of the problem can be illustrated when the major seawater ions, expressed as milliequivalents per liter, are plotted in histogram fashion. Such a plot (Figure 1) gives a visual accounting of cation-anion balance after precipitation of the early phase evaporite minerals. For example, during evaporation of seawater Ca^{2+} is lost first by precipitation of calcium carbonate, then gypsum. At this

point, the brine is totally depleted in Ca^{2+} but as shown on Figure 1 almost 70 percent of the original SO_4^{2-} still remains in the brine. With further evaporation this SO_4^{2-} will combine with the other cations, principally Mg^{2+} , so that in theory marine evaporite deposits derived from this stage of brine concentration should contain an abundance of magnesium sulfate minerals.

Several theories have been proposed to explain the magnesium sulfate deficiency in marine evaporites. The best known and probably most widely accepted of these is bacterial reduction of sulfate (Borchert, 1940 and 1959). Another intriguing and long standing theory calls for reaction between the sulfate ion in basin evaporite brines and fluvial influxes of calcium bicarbonate (Lorze, 1938; Sturmfels, 1943; D'Ans, 1947; and Valyashko, 1958). Garrett (1970) proposed that deposition of sulfate minerals around the margins of evaporite basins, followed by a later phase of dissolution and basin flushing, could account for the sulfate deficiency. If the composition of an

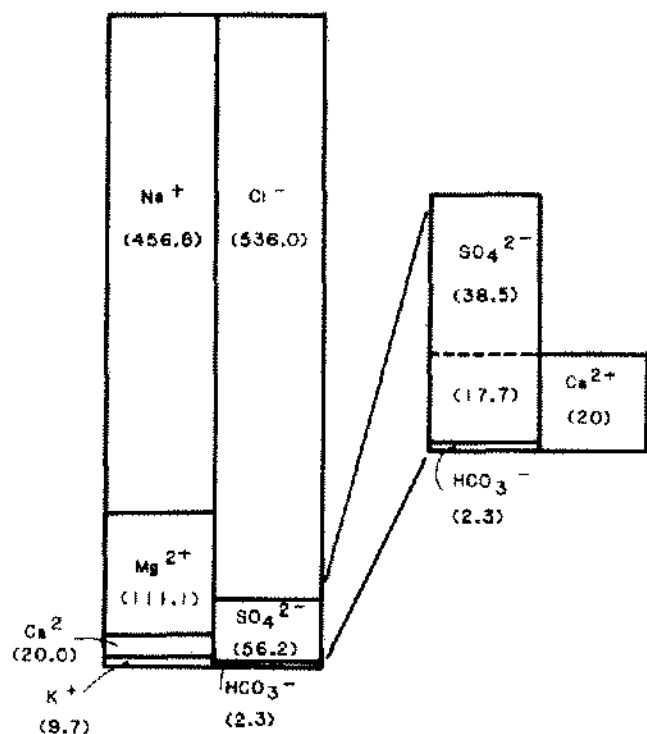


Figure 1. The major ions in seawater. Milligrams per liter converted to milliequivalents per liter.

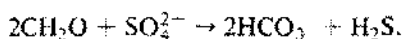
evaporite brine is modified by enrichment in Ca^{2+} from processes such as dolomitization (Braith, 1962) the sulfate can be removed by precipitation as gypsum. This paper will concentrate on explaining the merits of this latter theory and support it with data from several evaporite deposits. In addition, it will be shown why bacterial reduction of sulfate is probably not the answer to the problem.

BACTERIAL REDUCTION OF SULFATE

Although several organisms are capable of sulfate reduction the most important from a geologic standpoint are bacteria belonging to the genus *Desulfovibrio*. These microbes are found in a wide range of anaerobic environments including hypersaline conditions. They derive energy in anaerobic conditions by oxidizing organic compounds with oxygen obtained by reduction of the sulfate ion. Generalized reactions for this process are:



or



Because the H_2S produced by this process could subsequently be lost to the atmosphere, bacterial reduction offers an attractive solution to the sulfate problem. However, evidence from laboratory, natural environments and evaporite deposits suggests that although under some con-

ditions this is an important geologic process, it was not responsible for large-scale removal of sulfate from ancient marine evaporite environments.

RATES OF BACTERIAL REDUCTION OF SULFATE

The amounts of sulfate that must be removed from marine evaporite basins are very large. The effectiveness of bacteria in this removal can be judged only if known modern rates of bacterial reduction of sulfate are considered.

One of the highest known rates of sulfate reduction in a natural environment is in Lake Ain-ez-Zauia, Libya. Butlin and Postgate (1954) reported that in this small lake symbiosis between sulfate reducers and sulfur bacteria produces about 100 tons of elemental sulfur annually. This would require the daily formation of about 55 g/l of H_2S . However, this extremely high rate of production may be misleading because warm springs that feed the lake may supply a significant amount of H_2S (Kuznetsov et al., 1963, p. 108). In certain sulfate lakes in the USSR it was reported that bacterial production of H_2S ranging from 0.0002 to 24.26 mg/l per day (Ivanov, 1961, Table 4). In the Carpathian sulfur deposits, bacteria produce H_2S at the rate of 2 to 3 mg/l per day (Kuznetsov and others, 1963, p. 200).

Under ideal laboratory conditions cultures of sulfate reducing bacteria have produced as much as 3,000 mg/l of H_2S per day (Butlin and Postgate, 1955). Such high rates of sulfate reduction can only be obtained when the cultures are constantly purged of H_2S , otherwise the bacteria would be overcome by the toxicity of their own metabolic wastes. Thus in natural environments, the very nature of the process is self limiting in terms of reduction rates.

After considering the various measured rates of sulfate reduction in natural environments it was concluded that formation of H_2S at the rate of 10 mg/l per day is a relatively high production rate and probably greatly exceeds rates in ancient marine evaporite basins. However, even when this high rate is used, some interesting deductions can be drawn in regard to the effectiveness of microbial sulfate removal from such basins.

In natural subaqueous conditions most bacterial activity is concentrated in the first few centimeters of sediment and the sediment brine interface. A good example is the Dead Sea where Neev and Emery (1967, p. 93) were unable to isolate sulfate reducing bacteria from the water column. They reached the conclusion that organisms capable of producing hydrogen sulfide were present only in the bottom sediments. A similar conclusion was drawn by Nissenbaum (1975). Thus the capacity of an evaporite basin to reduce sulfates is not a function of total volume of brine in the basin, but is probably restricted to no more than a 1 m thick layer of sediment on the basin floor. Keeping this in mind and using the 10 mg/l per day of H_2S production, it is possible to calculate the effectiveness of bacterial reduction in a theoretical marine evaporite basin as follows:

Sulfate Budget for Basin X	
Area of basin = 1 km ²	
Evaporation rate = 2 m/yr (seawater)	
Sulfate reduction rate = 10 mg H ₂ S/l/day (reducing zone of 1 m)	
Sulfate reduction capacity (basin) = 1,063 tons/yr	
Sulfate Balance	(Metric tons/yr)
Influx	5,298
Gypsum precipitation	-1,642
	3,656
Sulfate reduction	-1,063
Surplus	2,693 tons

From these calculations it can be seen that even with a high rate of sulfate reduction a large yearly increment of SO_4^{2-} will accumulate in the evaporite brine.

REQUIRED AMOUNTS OF ORGANIC MATTER

The metabolism of sulfate reducing bacteria is dependent on organic compounds as a source of energy and for carbon for cell growth. Therefore, microbial reduction in an evaporite environment will be limited by the amounts of biomass that are either generated in the basin or are swept in from the sea. Each mole of SO_4^{2-} that is reduced requires oxidation of 2 moles of organic carbon. The actual amount of organic matter is much higher because only part of the organic matter can be utilized by the sulfate-reducing bacteria. The evaporite environment is capable of high organic productivity (Kirkland and Evans, 1981); unfortunately specific rates are generally not well known. Elsewhere the highest known rate of biomass production is 300 g C/m²/yr or more in the areas of oceanic upwelling (Tissot and Welte, 1978, p. 29). Assuming that the productivity of the evaporite environment is not likely to exceed 1,000 g C/m²/yr, this figure can be applied to the previously considered theoretical basin with the following results:

Organic Matter Requirements Basin X	
	Metric tons
Sulfate after gypsum precipitation	3,656
Organic C required for bacterial reduction	$3,656 \times 2 =$
	6,312
Organic C production in basin	-1,000
Deficiency	5,312

Considering the magnitude of organic matter deficiency shown by these calculations it seems unlikely that marine evaporite basins can produce the necessary amounts of organic matter for effective removal of sulfate by bacterial reduction.

THE MISSING EVIDENCE

If bacterial reduction of sulfate was a significant process in the formation of ancient evaporite deposits some geo-

logic evidence of this process should remain in the deposits. For example, as shown in the previously written reaction, bacterial reduction of sulfate results in the formation of the bicarbonate ion. Electrical balance must be maintained in this reaction so the loss of SO_4^{2-} must be replaced by $\text{HS}^- + \text{HCO}_3^-$, or 2HCO_3^- (Braitsch, 1971, p. 246; Berner, 1971; and Carpenter, 1978). In seawater brines, HCO_3^- should combine with Ca^{2+} and Mg^{2+} to form alkaline-earth carbonates (calcite, dolomite, magnesite, etc.). Thus each mole of MgSO_4 missing from an evaporite deposit should be represented by 2 moles of MgCO_3 or CaCO_3 . It is true that carbonate minerals are found in most marine evaporite deposits. Generally, however, these carbonates are not disseminated through the evaporites but occur in discrete layers and more likely represent a depositional response to influxes of bicarbonate-bearing seawater. This interpretation is supported by the fact that the deposition of the carbonate layers was usually preceded and then followed by deposition of calcium sulfate. If the carbonate layers were formed as the result of sulfate reduction and removal then subsequent deposition of calcium sulfate seems unlikely. It is also difficult to accept the explanation that an evaporite-basin periodically undergoes a reducing phase, during which carbonate layers are deposited and the basin brine depleted in sulfate, with the acquired sulfate depletion lasting through a subsequent phase of halite deposition (Borchert and Muir, 1964, p. 120). It is generally accepted that some influx is constant in all marine evaporite basins even during deposition of potash minerals. For that reason, bacterial reduction of sulfate would have to continue at a high rate even during the deposition of the chloride evaporites in order to keep the basin brine depleted in sulfate. Thus, an abundance of carbonate minerals should be disseminated through halite and potash rocks. Most of these rocks, however, contain only trace amounts of carbonates.

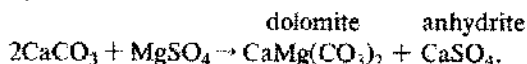
Hydrogen sulfide is very rare as a gas in halite-bearing marine evaporites. When present, it probably represents an introduction of sulfate-reducing bacteria to the deposit by meteoric waters. Because other gases, such as nitrogen, carbon dioxide, methane and hydrogen, which are the by-products of the decay of organic matter, are trapped in these deposits, it seems likely that if sulfate reduction were very active during deposition then some hydrogen sulfide would also be trapped. Hydrogen sulfide released from the floor of an evaporite basin should be oxidized inorganically or by bacteria to elemental sulfur or sulfate when it reaches the oxygenated surface layer. Some of this elemental sulfur should sink back through the brine column and be incorporated in the sediment layer; however, none has been reported in evaporite deposits. In the Dead Sea all of the hydrogen sulfide is probably oxidized to sulfate (Neev and Emery, 1967, p. 94) and is recycled back to the brine. This modern example suggests that even if bacterial reduction of sulfate was taking place at high rates on a basin floor,

significant sulfate removal from the brine might not be possible.

Limited isotopic data from modern marine evaporite environments do not indicate significant bacterial reduction of sulfate. A prime example is the deep brine pools of the Red Sea where Craig (1969, p. 402) observed—"The absence of $\delta^{34}\text{S}$ enrichment in the brine sulfate and the absence also of $\delta^{13}\text{C}$ enrichment in the dissolved carbonate indicate . . . that sulfate was not removed from the original water by reduction processes. . . ." Similar conclusions can be drawn from the isotopic composition of sulfate minerals in ancient marine evaporite deposits. Because all marine evaporite basins were connected to the same surface ocean sulfate system, basins of the same geologic age should show similar $\delta^{34}\text{S}$ values. Only where a particular basin environment was characterized by large-scale bacterial reduction of sulfate would there be sufficient fractionation of the sulfur isotopes to create a notable mismatch with the data from other basins of the same age (Holser, 1979). Extensive sampling of the ancient deposits shows data fitting within a narrow range of values on the $\delta^{34}\text{S}$ isotopic age curve (Claypool and others, 1979). Although the age curve shows wide isotopic variations through geologic time, these variations reflect changes in the total oceanic reservoir (surface) of sulfate rather than change (isotopic fraction by bacterial reduction of sulfate) within individual basins.

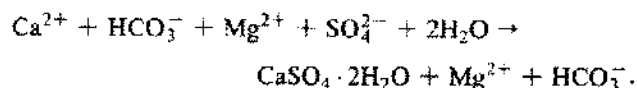
THE HAIDINGER REACTION

The Haidinger reaction, which seems to be better known to carbonate sedimentologists than to evaporite geologists, is also of great importance to evaporite sedimentation. This reaction was named by Krotov (1925) (see Lippman, 1973, p. 150) and was written as:



Although they did not specifically refer to the Haidinger reaction, various authors, notably Lotze (1938), Sturmfels (1943), D'Ans (1947), and Valyashko (1958), have proposed that a similar reaction between influxes of continental calcium bicarbonate waters and basin evaporite brines can deplete brines in sulfate.

Contrary to Borchert and Muir (1964, p. 39) a Haidinger type reaction is a viable mechanism and can be demonstrated in the laboratory. However, experiments by the author showed that calcite or aragonite would not react with a magnesium sulfate brine but that a calcium bicarbonate solution would. In addition, the product of the reaction was gypsum instead of anhydrite, and no carbonate mineral formed. The bicarbonate and magnesium ions stayed in solution for the duration of the experiment. Accordingly then, a modified version of the Haidinger reaction can be written:



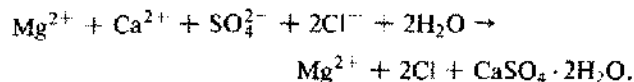
It should also be noted that for the modified Haidinger reaction to take place, an influx of seawater or continental runoff containing Ca^{2+} and HCO_3^- must mix with an evaporite brine that is at the chloride precipitating phase.

Although it can be shown that the modified Haidinger reaction is probably not a significant factor in explaining the magnesium sulfate deficiency in marine evaporites, it nevertheless can bring about some important modifications of brine chemistry involving the bicarbonate ion. Normally, under conditions of static evaporation the early precipitation of calcium carbonate consumes all of the HCO_3^- in seawater (Clarke, 1924, p. 220). Under dynamic conditions, where a halite precipitating brine continues to be replenished by influxes of seawater, the modified Haidinger reaction can actually permit an increase in the amount of HCO_3^- . Thus a seawater brine that originally lost all of its HCO_3^- through precipitation of calcium carbonate can be altered by the modified Haidinger reaction to the extent that the HCO_3^- concentration increases again. This process is well demonstrated by the data of Morris and Dickey (1957) from the Bocana de Virrila of Peru where halite-saturated brine (1.243 sp gr) contained 948 ppm HCO_3^- , or about $6.7 \times$ the bicarbonate content of seawater. It should be noted, however, that the $\text{Cl}^-/\text{HCO}_3^-$ ratio of seawater is 134, compared to about 200 for the Bocana de Virrila brine. Under the dynamic conditions of an evaporite basin, with its nearly constant influx of seawater, the modified Haidinger reaction would produce sediments showing a significant increase in the $\text{CaSO}_4/\text{CaCO}_3$ ratio that is normally obtained from static evaporation of seawater. Furthermore, because the reaction produces brines enriched in Mg^{2+} and HCO_3^- , it seems only logical to assume that it affords a mechanism for the formation of dolomite and magnesite.

Solving the magnesium sulfate problem by the modified Haidinger reaction seems unlikely. The amount of SO_4^{2-} brought into an evaporite basin by influxes of seawater would greatly exceed the amount precipitated by the reaction. Where continental waters are involved, Ca^{2+} is balanced principally by HCO_3^- , and SO_4^{2-} is subordinate (mean composition of river water $\text{HCO}_3^-/\text{SO}_4^{2-} = 5.3$) and the reaction could accomplish the job; however, because of their dilute nature the required volumes of influx would be enormous. The scale of the problem was noted by Garrett (1970), who showed that a flow the size of the Mississippi River would have been needed as a hypothetical Ca^{2+} source for a basin the size of the Devonian Elk Point Basin of Canada. Such a requirement would obviously dilute the basin brine to the extent that deposition of evaporite salts would be prohibited.

BRINE MODIFICATION TO THE CALCIUM CHLORIDE TYPE

Through the years there has been a growing accumulation of data suggesting that enrichment of brine in Ca^{2+} is a common phenomenon in the marine evaporite environment. It is proposed that this form of brine modification is the key to solving the sulfate problem, because when a normal seawater brine ($(\text{Mg}^{2+} + \text{SO}_4^{2-}) \gg \text{Ca}^{2+}$) mixes with a modified evaporite brine ($\text{Ca}^{2+} \gg \text{SO}_4^{2-}$), there is an immediate and dramatic reaction resulting in precipitation of gypsum. This reaction can be written as:



Thus if the brine in an evaporite basin in some manner becomes modified to a calcium chloride type most of the SO_4^{2-} in subsequent seawater influxes will be precipitated as gypsum rather than magnesium sulfate.

Strong evidence for brine modification to the calcium chloride type is provided by the presence of large quantities of tachyhydrite ($\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$) in several marine evaporite deposits. For example, very large deposits of the mineral have been found in the Cretaceous evaporites of the South Atlantic (Wardlaw, 1972; Hite, 1972) as well as in the Cretaceous evaporites of Thailand and Laos (Hite and Japakasetr, 1979). Although tachyhydrite is a major mineral in the aforementioned deposits, it is still somewhat rare in other evaporite deposits. This is not surprising, because extreme desiccation is required for its formation. Most evaporite deposits seldom reached this stage of desiccation, but evidence that the brines from which they formed were enriched in Ca^{2+} is found in chemical analyses of tiny brine inclusions in halite rock (Kramer, 1965; Roedder, 1963, 1979a, and 1979b).

ENRICHMENT MECHANISMS

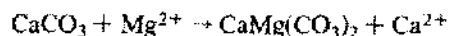
Seawater brines can become enriched in Ca^{2+} several ways. One well-known process is the conversion of gypsum or anhydrite to polyhalite, such as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{K}^+ + \text{Mg}^{2+} \rightarrow \text{Ca}_2\text{K}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O} + 2\text{Ca}^{2+}$, when bittern brines react with these previously deposited sulfates. Polyhalitization could only be a significant factor in enriching evaporite brines in Ca^{2+} where large deposits of the mineral are present. In many evaporite deposits, however, polyhalite is only found as a trace mineral. A notable exception is the Permian Salado Formation of New Mexico which has very large deposits but is characterized by a higher than normal amount of magnesium and potassium sulfates, suggesting that Ca^{2+} enrichment through this process was minimal. Although polyhalitization occurred in some evaporite deposits, it was either on insufficient

scale or was such a late diagenetic event that the host brine layer was relatively unaffected.

The substitution of Na^+ for Ca^{2+} in the exchange sites of continentally derived smectites can also achieve Ca^{2+} enrichment. The evaporite sequences in basins where this process made significant contributions of Ca^{2+} would be characterized by high clay-to-salt ratios. For example, if we assume that the smectites involved have maximum exchange capacity of approximately 150 milliequivalents per 100 g (Grim, 1968, p. 189), then complete SO_4^{2-} removal (5.78 g) from a liter of brine saturated for NaCl would require about 40 g of clay. Expressed in terms of an evaporite sequence, each meter of halite should be balanced by about 0.39 m of claystone. Most evaporite deposits, especially those showing strong evidence of Ca^{2+} enrichment, have much lower clay-to-salt ratios. Although this process probably took place to some extent in all evaporite basins, the required clay:salt ratio, plus the drastic dilution of basin brine by the continental waters necessary to transport the clay, suggest that this process is probably not the major cause of Ca^{2+} enrichment.

The tachyhydrite deposits of the South Atlantic are associated with an iron-rich evaporite sequence. In a paper presented at the 27th Brazilian Geological Congress (Hite, 1975), the author suggested that there might be a direct relationship between the chemistry of iron in the South Atlantic brines and Ca^{2+} enrichment. It was theorized that oxidation of Fe^{2+} in solution in the brine produced the abundant hematite and goethite in the evaporitic sediments and at the same time released H^+ to the brine. The latter then reacted with limestone or dolomite to release Ca^{2+} to the brine. This process can be demonstrated in the laboratory and may have contributed some Ca^{2+} in certain basins, but as pointed out by Peter Szatmari (oral commun., 1978) the amount of iron needed to effect large-scale Ca^{2+} enrichment greatly exceeds the amounts observed in most evaporite deposits, including those of the South Atlantic.

The most common mechanism of Ca^{2+} enrichment, and probably the most logical candidate to bring about large-scale modification of an evaporite brine, is dolomitization. This process, which can be written as:



can only effect Ca^{2+} enrichment when previously deposited limestones, either underlying or adjacent to the brine body, are dolomitized (Braitsch, 1971, p. 248); primary deposition of dolomite will only remove Ca^{2+} from the brine. An examination of many marine evaporite deposits shows that dolomite is present in quantities sufficient to be a major factor in brine modification. A specific example is described in the following section.

PARADOX BASIN EVAPORITES

The Middle Pennsylvanian of the Paradox Basin in south-east Utah and southwest Colorado contains a thick sequence of marine evaporites. This sequence is characterized by a series of potash-bearing evaporite cycles (Hite, 1961), most of which are notably deficient in magnesium sulfate. In addition, carbonate rock, principally dolomite, is an ubiquitous element in each evaporite cycle. Although the brines from which these deposits formed reached very high concentrations, as evidenced by the abundance of potash minerals and by high bromide levels in many halite beds, no tachyhydrite was deposited. However, numerous occurrences of brines with high calcium-to-magnesium ratios have been reported from these deposits (Mayhew and Heylman, 1966). Petrographic relationships, plus numerous plots of the vertical distribution of bromine in the Paradox halite beds (Raup, 1966; Hite, 1983), suggest that this is a primary sequence. Thus, the Paradox Basin evaporites are probably ideally suited to use as a test case for brine modification by dolomitization.

Recently the Department of Energy, as part of a program of evaluation of the suitability of salt deposits in the Paradox Basin for nuclear waste disposal, drilled a deep test hole in the west-central part of the basin on a salt anticline known as Gibson Dome (Figure 2). This hole (GD-1) was cored continuously through the entire evaporite sequence of the Paradox Member of the Hermosa Formation. At the Gibson Dome locality, the Paradox Member includes 19 halite-bearing evaporite cycles (Figure 3). The Paradox Member, as defined in the GD-1 hole, is bounded by the top of Salt 4 and the base of Salt 26 (Hite, 1960). Cumulative lithologies in this interval, as determined by XRD, include: halite (includes some potash), 617 m; anhydrite, 93 m; dolomite and minor limestone, 39 m; and clastics, which consist of about 50 percent clay minerals, 38 m. The entire sequence shows a pronounced deficiency in magnesium sulfate minerals. Kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) was observed only in minor amounts in Salt 6, where it is associated with carnallitic halite.

HALITE-ANHYDRITE COUPLET STUDIES

Similar to many other deposits of marine halite, the halite of the Paradox Member is distinctly banded by anhydrite laminae. The couplets formed by each anhydrite lamina and its adjacent overlying band of halite can be used to calculate the CaSO_4 supply to the evaporite basin, which in turn allows certain conclusions to be drawn regarding modification of the basin brine. Three assumptions are made here about these halite-anhydrite couplets: (1) they are annual, (2) each CaSO_4 lamina represents a new influx of SO_4^{2-} -bearing seawater, and (3) during deposition of these couplets the basin floor was covered by a thick layer of highly concentrated brine. Whether or not these couplets are annual units of sedimentation has never

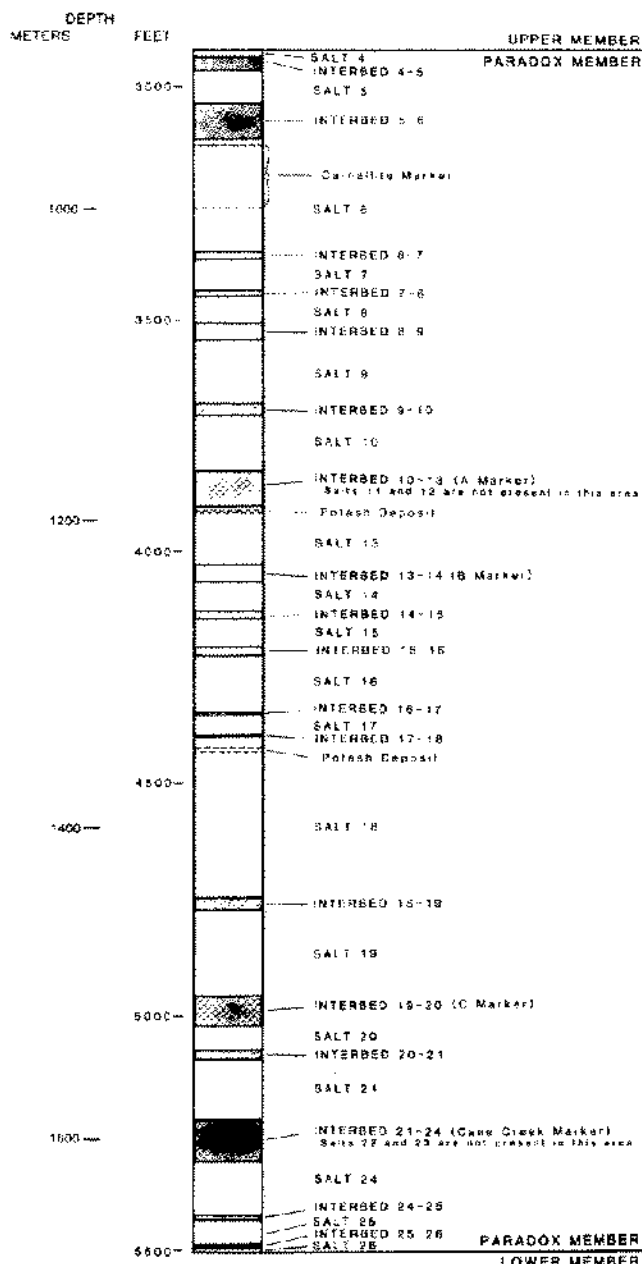


Figure 2. Stratigraphy of the Paradox Member in the GD-1 corehole, Paradox Basin, sec. 21, T. 30 S., R. 21 E., San Juan County, Utah.

been totally resolved (Braitsch, 1971, p. 251, and Shearman, 1970). In the Paradox deposits, however, there is strong evidence for this interpretation. For example, the amount of CaSO_4 present in couplets in the basal halite beds is close to the theoretical amount derived from one year's evaporation of seawater. Many couplets show a regular increase in halite crystal size from base to top, which could only be due to seasonal change in brine temperature or evaporation rates. Furthermore, corrosion surfaces, such as those reported by Wardlaw and Schwerdtner

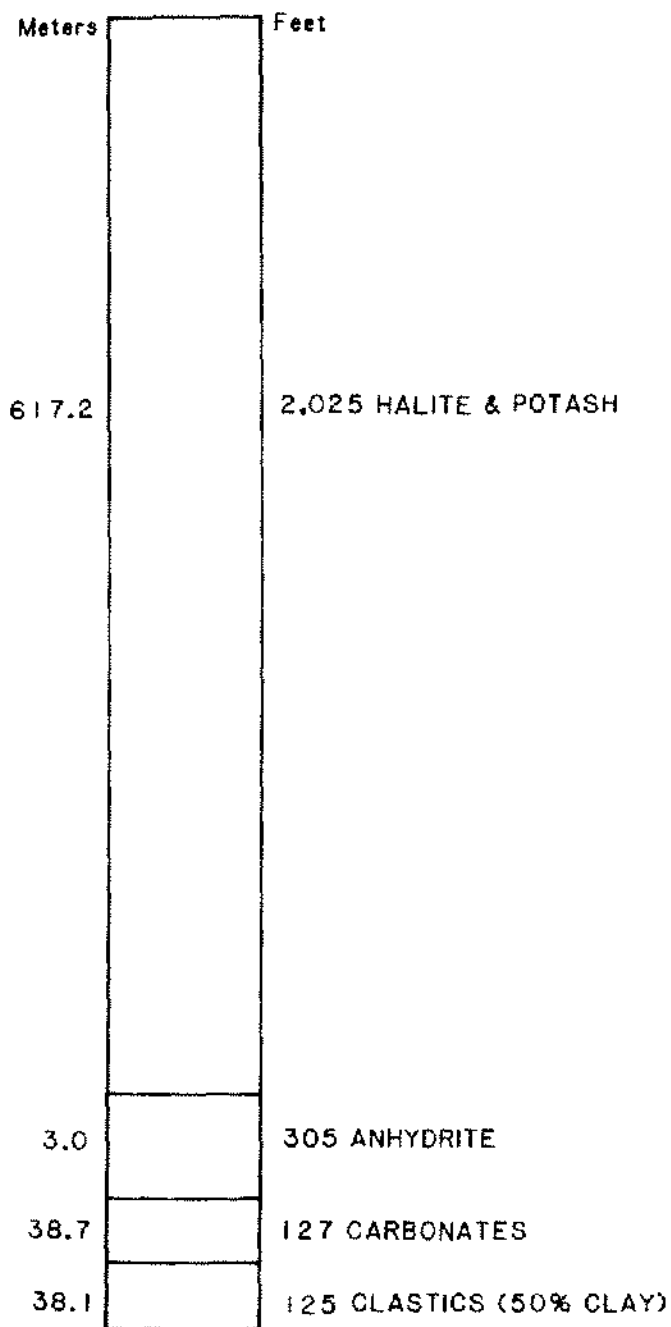


Figure 3. Cumulative lithologies of the Paradox Member in the GD-1 corehole. At this locality the anhydrite to halite and carbonates to halite ratios are 0.152 and 0.063 respectively.

(1966, Figure 4) are very rare in any of the couplet sequences, suggesting that the sedimentational record is essentially complete.

Graphic logs showing the thickness relationships of the halite and anhydrite units of each couplet were prepared for each of the halite beds in the GD-1 core hole. In addition, the water-insoluble content in weight percent was determined for continuous 0.61 m composite samples for

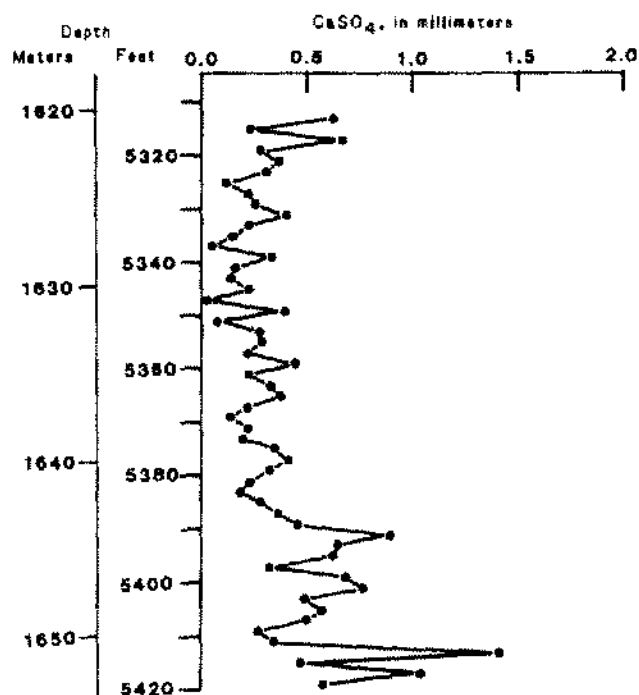


Figure 4. The annual supply of calcium sulfate (ASC) in the halite rock of salt 24 Paradox Member, GD-1 corehole.

all of these beds, and XRD analyses showed that these insoluble residues were generally 95 percent anhydrite. By dividing each weight-percent insoluble value by the number of anhydrite laminae in the same interval, the average annual supply of CaSO_4 (ASC) for each 0.61 m interval was determined for all of the halite beds. When these data were plotted (weight percent was converted to thickness) it became apparent that the CaSO_4 supply changed significantly during the deposition of the Paradox halite beds. In Salt 24, near the base of the sequence (Figure 3), the ASC is rather uniform, and through much of the bed, remains below 0.5 mm (Figure 4). Plots of the ASC for stratigraphically higher halite beds show a much different picture. For example in Salt 19 the ASC starts at about 1.0 mm and shows a gradual upward increase except for the uppermost 10 m where it falls back to a lower range of values (Figure 5). The middle one-third of this bed has many ASC values exceeding 3 mm. Under maximum known rates of evaporation (2.0 m/y), it is possible to obtain an annual precipitate of about 0.715 mm of CaSO_4 from seawater (Braitsch, 1971, p. 254). In the Paradox Basin it is quite likely that pre-concentration of seawater influxes took place on the broad shallow accessways along the southern and southwestern basin margins so that the influx brines were already saturated for CaSO_4 when they reached the Gibson Dome area. In that case, and again at maximum evaporation rates, about 1.6 m of CaSO_4 saturated brine could have evaporated, leaving a 2.0 mm-thick deposit of CaSO_4 . However, under normal conditions the average thickness

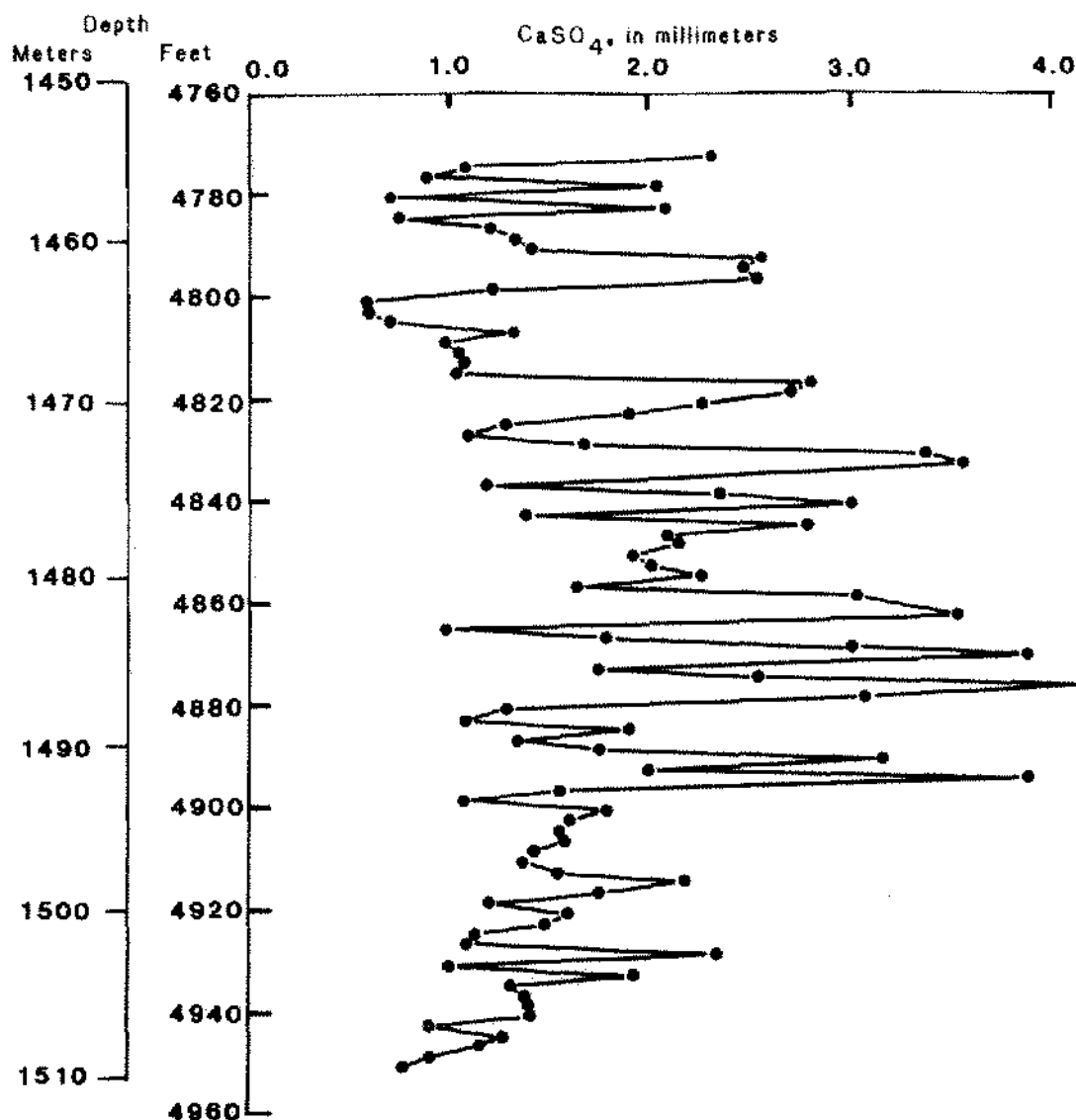


Figure 5. The annual supply of calcium sulfate (ASC) in the halite rock of salt 19, Paradox Member, GD-1 core-hole.

was probably about 1 mm. It becomes apparent then that for halite beds such as Salt 19 there are large yearly surpluses of CaSO_4 . Two explanations for the surplus CaSO_4 seen in the Paradox halite deposits, as well as many other marine halites, can be offered. First, there is the modified Haidinger reaction, which, as previously shown, is likely to have operated to some extent in most marine evaporite basins. This reaction could result in all of the calcium ion in marine influxes being precipitated as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at the expense of CaCO_3 . However, because the ratio of weights of CaCO_3 to CaSO_4 in evaporative seawater is so low (1:12), the modified Haidinger reaction could only account for a small part of the observed excess of CaSO_4 .

The second explanation involves the reaction of influx-
ing SO_4^{2-} with basin brines enriched in Ca^{2+} . Using this

mechanism a logical explanation can be made for the observed ASC relationships in the Paradox deposits. For example, during the deposition of basal halite beds, such as Salt 24, the basin brine was probably not yet enriched in Ca^{2+} and only CaSO_4 produced by surface evaporation was deposited. Later, during the deposition of Salt 19, brine enrichment had taken place so that the CaSO_4 associated with the halite was the product of both evaporation and chemical reaction. Studies of individual halite-anhydrite couplets in Paradox halite rock show that as much CaSO_4 is disseminated through the halite portion of the couplet as is in the anhydrite laminae (Figure 6).

The anhydrite laminae of the couplets probably represent evaporitic CaSO_4 , whereas the anhydrite crystals disseminated through the halite portion of the couplets may

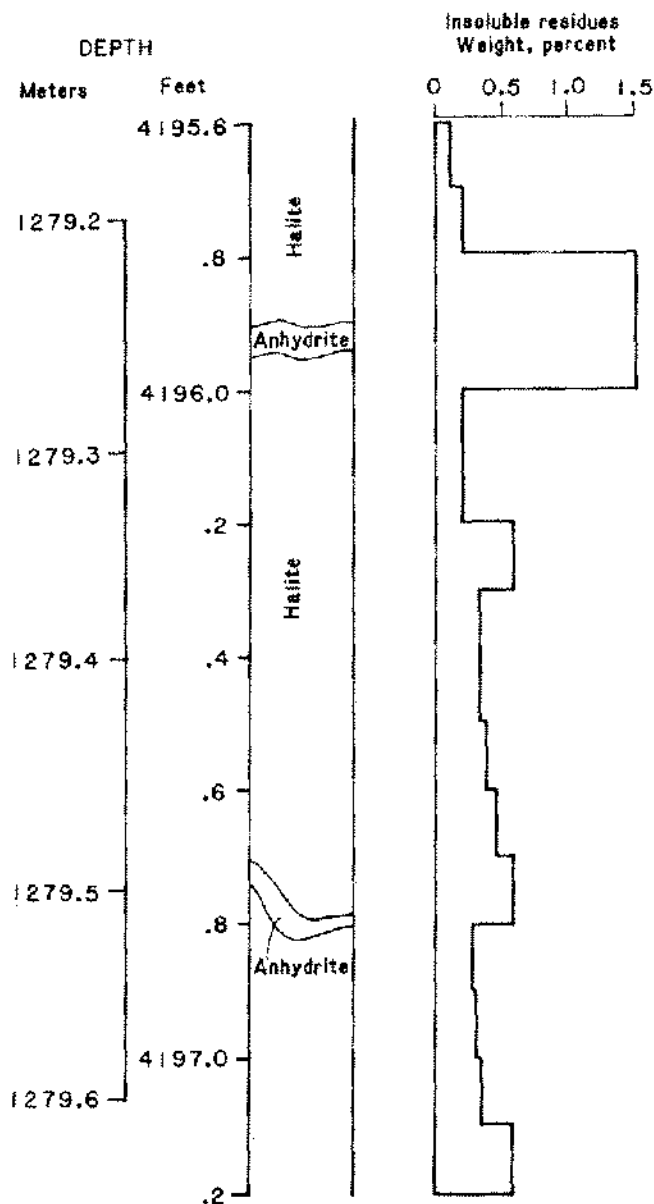


Figure 6. Typical distribution of CaSO_4 in a halite-anhydrite couplet in the Paradox Member, GD-1 corehole.

be mostly "reaction" CaSO_4 . In phase A of this process (Figure 7), a seasonal influx overrides the deeper and more concentrated brine layers in the basin. This thin influx layer loses all of its calcium as CaSO_4 due to surface evaporation. The surface precipitate settles through the brine to the floor of the basin where it forms a thin and essentially monomineralic layer of evaporitic CaSO_4 . With further evaporation the surface brine layer, which would still contain nearly 70 percent of the original influx SO_4^{2-} , becomes heavy and sinks through the chemocline where the SO_4^{2-} reacts with the Ca^{2+} -enriched bottom brines and deposits additional CaSO_4 to the sediment layer. Thus the bottom sediment derived by this model has different spa-

tial as well as temporal origins. Petrographic studies of Paradox Basin halite-anhydrite couplets show that most of the halite in the couplets is the result of basin bottom crystallization. The tops of these bottom-growth halite crystals are frequently sharply outlined, and the microtopography created by their upward projection filled in, by the overlying anhydrite lamina. This suggests that the anhydrite laminae represent rapid surface sedimentation of CaSO_4 , as in phase A of the model (Figure 7). On the other hand, the sedimentation rate of reaction CaSO_4 is controlled largely by slow rates of mixing between the upper sulfate-rich layer and the bottom calcium-rich layer. This slow and rather continuous sedimentation of CaSO_4 , which would be contemporaneous with more rapid halite crystallization on the bottom, would result in the CaSO_4 being widely dispersed through the halite as has been observed in the halite portion of the Paradox couplets (Figure 6).

Considering that the evaporites of the Paradox Member show ample evidence of brine modification by Ca^{2+} enrichment, it remains to examine these deposits in terms of a suitable brine-modification mechanism.

BRINE MODIFICATION BY DOLOMITIZATION IN THE PARADOX BASIN

Because dolomite is a major component of the evaporative sequence of the Paradox Member, the sequence was examined for geochemical and mineralogical characteristics which would test the applicability of the dolomitization mechanism to brine modification in the Paradox Sea.

At least two models of dolomitization may apply to evaporite sequences such as the Paradox Member. One model assumes that dolomite formed during a high sea-level stage when basin influx and reflux were maximal (Figure 8A). Such conditions are strongly indicated by previous studies of lithofacies relationships in the Paradox evaporite cycles (Hite, 1970). Circulation in the basin at this time is anti-estuarine with refluxing light-weight brine sliding back to the sea across a heavy brine trapped behind the basin sill. The model involves dolomitization of slowly settling calcium carbonate particles which are precipitated as the result of evaporative concentration of the surface influx layer. As the particles fall through the chemocline they are dolomitized by the magnesium-rich brine trapped behind the basin sill. This results in the release of calcium ions back to the deep brine body. As long as sea level remains at a relatively high stage, so that reflux is uninhibited, the deep brine body will continue to be enriched in Ca^{2+} . One important aspect of this model is that all of the calcium ion carried in by the influx current can be utilized in brine enrichment while the accompanying sulfate ion would be refluxed. The modified Haidinger reaction would not be a factor because the influx Ca^{2+} would combine with HCO_3^- before there was an opportunity for reaction with deeper brines with high SO_4^{2-} concentra-

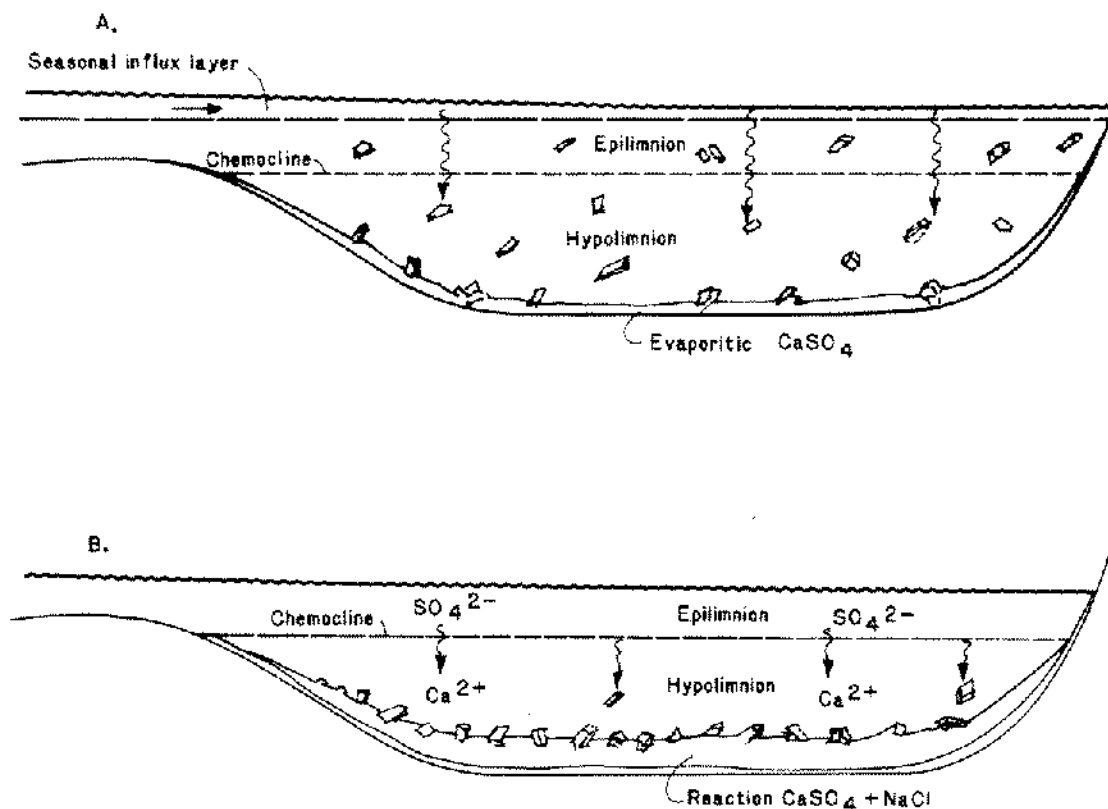


Figure 7. Theoretical models depicting the manner of anhydrite-halite couplet formation in the Paradox Basin. (A) Represents a time of seasonal influx of seawater bringing calcium plus sulfate ions into the evaporite basin. Evaporation of the thin influx layer causes formation of evaporitic CaSO₄. (B) Represents conditions after evaporation of the thin influx layer when further concentration of the epilimnion causes some of the sulfate-bearing brine to sink through the chemocline and react with calcium ions in the dense bottom brine. This forms reaction CaSO₄ which is sedimented contemporaneously with halite crystallizing on the basin floor.

tions. The dolomites of the Paradox Member exhibit petrographic relationships that support this model. These rocks are very fine grained, with high percentages of detrital quartz grains and also dolomite crystals that appear to be detrital. They contain abundant palynomorphs which are preserved with exquisite detail (B. F. Rueger, personal commun., 1983). Normally palynomorphs are poorly preserved in dolomite because of intensive recrystallization. Thus the excellent preservation of the Paradox palynomorphs would be compatible with contemporaneous accumulation with a slowly settling dolomitie sediment such as called for by the model.

It is also possible that dolomitization of previously deposited limestones may have brought about Ca²⁺ enrichment (Figure 8B). In the Paradox Member, however, evidence of a limestone precursor has not been found.

The biggest problem with both models is that dolomitization, at least in the beginning, must start in a high sulfate environment. This would seem incompatible with the findings of Baker and Kastner (1981), who showed that the sulfate ion inhibits dolomite formation. Despite the question of just how dolomitization would begin, once it

began, the consequential depletion of the sulfate ion would probably intensify the process. However the process occurs, it should be remembered that it must take place below or in the deep brine body if the calcium ion is to play a role in sulfate removal.

To appraise the potential of dolomitization as a brine modification mechanism, the evaporite sequence of the Paradox Member was evaluated in terms of volume of dolomite present and the amount of CaSO₄ that could be produced by release of Ca²⁺ back to the brine by the dolomitization process. Figure 9 shows the thickness of CaSO₄ that theoretically could be produced from the underlying dolomite of each Paradox evaporite cycle. The numbers to the right of the curve are the range of calcium values (ppm) that were obtained from the analysis of brine inclusions from halite rock from several cycles. From this figure it is apparent that Ca²⁺ in the brine inclusions increases drastically above cycle 21. Because these inclusions probably represent connate brine trapped during the deposition of the halite, the calcium values probably reflect the potentially large amounts of calcium released back to the brine by dolomitization during cycle 21. Using the potential

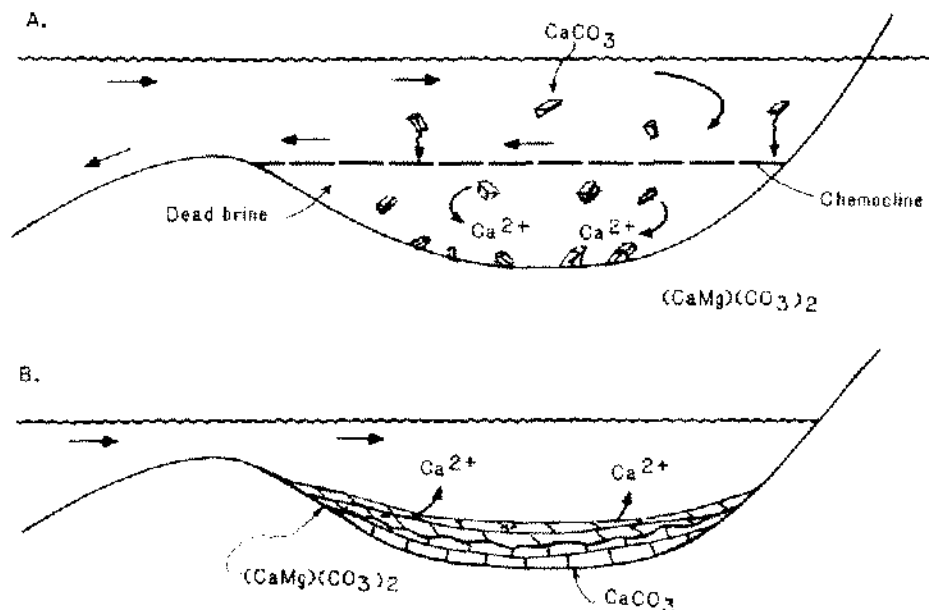


Figure 8. Theoretical model of dolomitization in the Paradox Basin. (A) Represents high sea level stage where calcium carbonate, precipitated as the result of surface evaporation, is dolomitized as it falls through the magnesium-rich chemocline causing enrichment of the brine in the calcium ion. (B) Represents another possible process where a precursor layer of limestone is dolomitized releasing calcium ions back to the brine.

amount of reaction CaSO_4 formed by this process, plus the total amount of CaSO_4 derived from water-insoluble analyses, a CaSO_4 budget for each evaporite cycle in the GD-1 corehole was prepared (Figure 10).

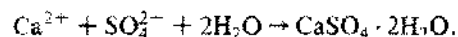
The amount of evaporative CaSO_4 for each cycle was based on the assumption of a yearly precipitate of 1 mm times the number of anhydrite laminae in the halite bed. This value was then subtracted from the total CaSO_4 in the water insoluble residues of the halite rock to give the amount of reaction CaSO_4 for each cycle. The resulting CaSO_4 budget for the Paradox sequence suggests that reaction CaSO_4 did not form in the early cycles because sufficient cumulative enrichment of Ca^{2+} , as the result of dolomitization, had not yet taken effect. Furthermore, the evaporite sequence contains more than enough dolomite to account for all of the reaction CaSO_4 .

Additional evidence that dolomitization was probably the chief means of brine modification in the Paradox Sea are the Mg:Br ratios of several connate brine samples associated with the Paradox Member evaporites. These brines have an average ratio of about 13.0. According to Collins (1975, p. 235) the Mg:Br ratio for seawater brine in which dolomitization has completely removed SO_4^{2-} by reaction with released Ca^{2+} should be about 13.6. If bacterial reduction of SO_4^{2-} is responsible for removal then the ratio should be 20.0.

CONCLUSIONS

Bacterial reduction of sulfate in modern evaporite environments is a well-known process and its existence in the ancient environments is not denied. However, because of questionable adequacies of reduction rates and supply of organic matter, it is unlikely that this process effectively depleted evaporite brines in the sulfate ion. If bacterial reduction of sulfate was quantitatively an important process it should have left behind certain mineralogical or geochemical evidence. This evidence has not been observed in marine evaporite deposits.

The composition of fluid inclusions, associated connate brines, and the mineralogy of many marine evaporite deposits suggest that brines from which these deposits formed were enriched in the calcium ion. Such brines become depleted in the sulfate ion due to the strong reaction



Studies of geochemical and mineralogical relationships in the evaporites of Middle Pennsylvanian age in the Paradox Basin support this mechanism of sulfate depletion and suggest that dolomitization is the principal cause of the Ca^{2+} enrichment. This type of brine modification, rather than bacterial reduction of sulfate, may be largely respon-

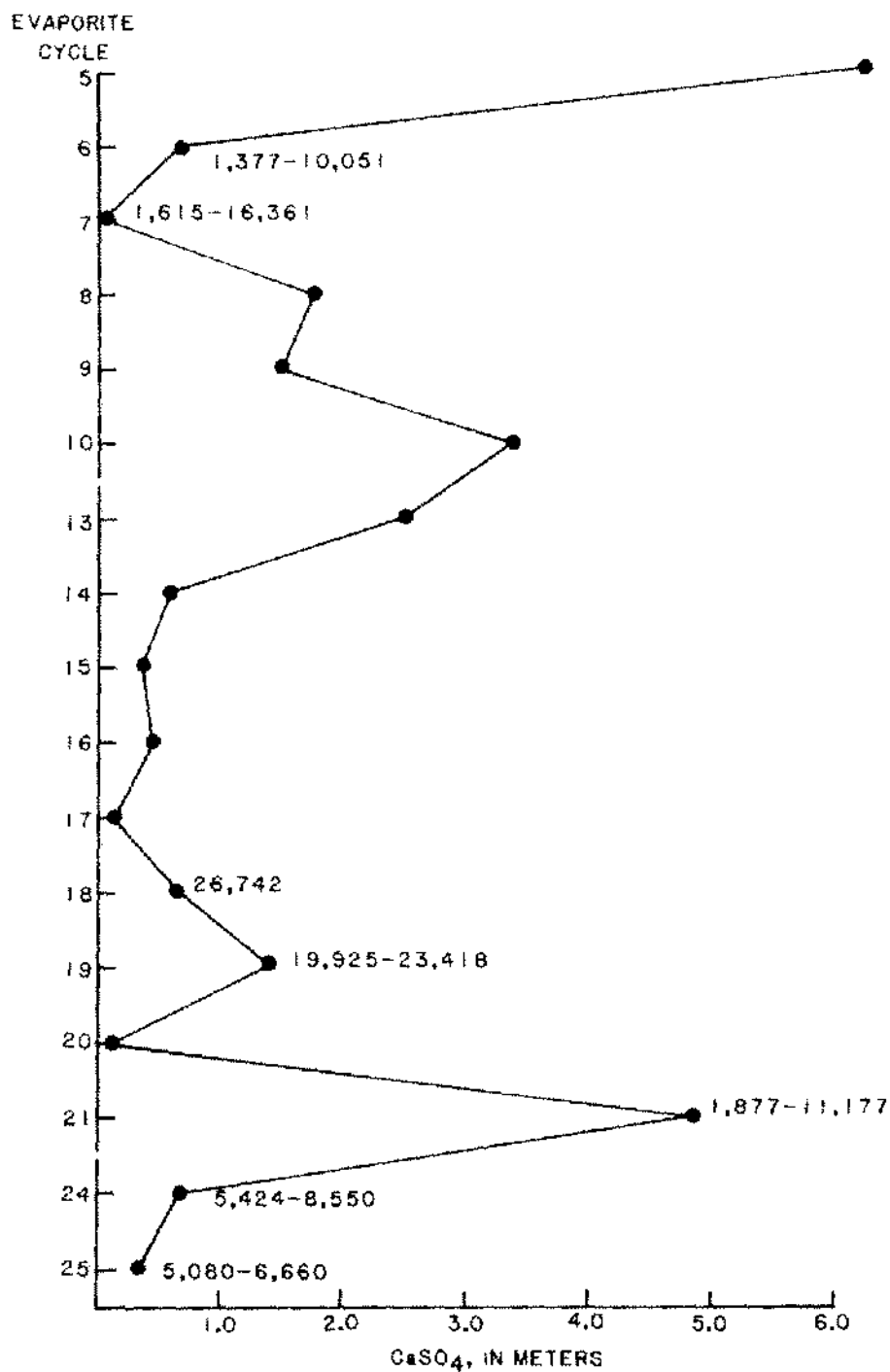


Figure 9. A plot of the potential thickness of CaSO_4 (in meters) that could be produced by Ca^{2+} release from dolomitization of the calcium carbonate in each evaporite cycle of the Paradox Member, GD-1 corehole. Numbers on the right side of the plot are the range of Ca^{2+} values derived from analyses of brine inclusions in the halite rock from that specific cycle.

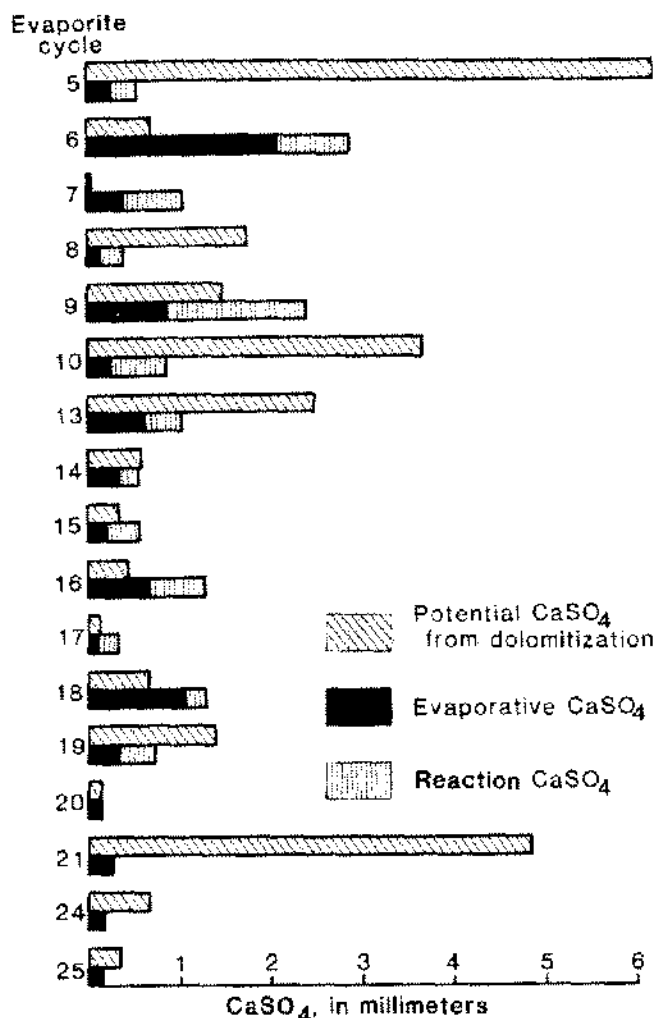


Figure 10. Bar graph showing the theoretical CaSO_4 budget for each evaporite cycle of the Paradox Member in the GD-1 core-hole. All values are given in terms of thickness (millimeters).

sible for the deficiency of magnesium sulfate minerals in marine evaporites.

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