THE ORIGIN OF CELESTITE (STRONTIUM SULFATE) ORES IN THE SOUTHWESTERN UNITED STATES AND NORTHERN MEXICO

by

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ABSTRACT

Present and former ore deposits of celestite in Durango, Chihuahua, Coahuila, Mexico and Arizona and California, United States were studied in order to derive a guide for the exploration for additional strontium ore deposits.

The Mexican deposits are localized along the lower Cretaceous Coahuila Peninsula, in what was a shallow water, near shore carbonate environment; the United States deposits are in Tertiary, evaporative lake bed deposits. Fluid inclusions suggest that the former crystallized at or less than 25°C from a water with a low m_{Na^+}/m_{K^+} ratio which is lower than most ground waters and sea water. Petrographic and field evidence indicates that celestite has replaced carbonate material in both the Mexican and American deposits. The American celestite deposits give petrographic evidence of having formed at near chemical equilibrium conditions. Geologic data and geochemical considerations indicate that the celestite ores probably formed by the following diagenetic process: Aragonite containing approximately 9800 ppm strontium in solid solution was deposited from sea water. When fresh, continental waters having a low m_{Na^+}/m_{K^+} ratio contacted the aragonite the orthorhombic $CaCO_3$ converted to calcite, liberating the Sr^{++} to the ground water. In the case of the Mexican deposits the strontium rich ground water then mixed with sea water, in the case of the U.S. deposits the ground water mixed with saline waters from the evaporative lake. As both the sea water and the saline waters were sulfate rich, celestite was deposited. Concurrently, calcite dissolved with mixing of the ground water and saline water because of the rapid depression of the activity coefficient of calcium at relatively constant concentrations of calcium and carbonate ions.

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I. INTRODUCTION

The earliest significant work on the mode of origin of celestite was done by Moore (1935), who studied deposits in Arizona and California. He concluded that the celestite was syngenetic in origin, formed by precipitation from lake waters. Essentially the same deposits were studied by Durrell (1953) who proposed that the ores in southern California were restricted to evaporative lake beds and were definitely epigenetic, probably forming prior to lithification. Durrell did not indicate either a specific process for mineralization, or sources for the strontium and the sulfate. In England, long a major supplier of celestite, the genesis of the ores has never been studied in detail. Thomas (1973) recently postulated a syngenetic origin for such deposits in lagoonal and/or sabkha type facies. $SrSO_4$ occurrences in Canada have been studied by Johnson (1954), Crowell (1971) and Choo (1972). Johnson concluded, based on field work, that the celestite deposits of Port au Port Peninsula, Newfoundland, were epigenetic, formed by waters of meteoric origin. Crowell, who investigated a deposit at Enon Lake, Nova Scotia, reached no conclusions about the genesis of the ore, only mentioning that hydrothermal, syngenetic and diagenetic/epigenetic mechanisms could be proposed to explain the origin of the ore. Choo, who studied this same occurrence, examined thin sections and ore distribution, and, after a very cursory review of pertinent chemical data (albeit the first by a geologist), decided that the Enon Lake deposit was surely syngenetic in origin, with minor remobilization and redeposition of the celestite to explain certain observed phenomena.

The hypotheses proposed for the origin of celestite by these authors and others who worked on non-economic deposits (cf., Krieger, 1933; Morrison, 1935; Kesler, 1944; Muller and Puchelt, 1961; Fishburn and Davis, 1962; Roedder, 1969) may be grouped into four classes.

1. Deposition by hydrothermal solutions, regardless of the solution's source.
2. Deposition in consolidated sediments by either brines or meteorically derived waters.
3. Syngenetic deposition of the ore and the country rock.
4. Diagenetic deposition in a sabkha evaporite facies.

The conclusions put forth by previous workers concerning the genesis of celestite occurrences have been based on field observations, petrographic studies and a cursory review of available chemical evidence.

In this thesis an attempt is made to establish a mode of origin for selected celestite deposits in the southwestern United States of America and northern Mexico, with the hope that such knowledge might be used in guiding the further search for additional deposits. In developing and evaluating hypotheses of origin of celestite, information was obtained from the literature, field observations, petrographic studies, review of published data on the behavior of Sr^{++} in the pertinent environments, fluid inclusion studies and thermodynamic considerations.

Descriptions of the principal characteristics of selected celestite deposits in the United States, Mexico, Canada and England are presented. Based on these characteristics the host rocks of the celestite bodies appear to represent two depositional environments, the near shore, shallow water carbonate facies and the sabkha facies. The behavior of strontium in such environments is then considered within the boundary conditions suggested by the fluid inclusion studies. Finally, mineral stability relationships among the minerals celestite, strontianite, aragonite, calcite, gypsum and anhydrite are considered. Using criteria developed in the preceding sections, various hypotheses for the origin of the ores are analysed. Concluding that no previously proposed mechanism adequately explains the deposits of celestite, a model is proposed that satisfies the known occurrences for the mineral celestite. Finally, using the model developed from this study several ore guides are suggested and potential ore bearing areas are noted.

II. DESCRIPTION OF CELESTITE DEPOSITS AND GENESIS OF THE MINERALIZED COUNTRY ROCKS

Several celestite deposits in the southwestern U.S. and northern Mexico that either were producing or had been productive were visited in order to obtain data for this study. At each deposit the lithologies associated with the celestite, the relationship of the mineralization to structural elements and the distribution and physical nature of the celestite were examined. Hand-samples of celestite and all contiguous lithologies were collected for further studies. It was hoped that such data would provide information useful in evaluating hypotheses concerning the genesis of the mineral celestite. Two other celestite deposits are sufficiently described in the literature to provide some guides concerning their genesis; these deposits are at Enon Lake, Nova Scotia (Crowell, 1971; Choo, 1972) and the English deposits near Bristol (Thomas, 1973). Descriptions of other celestite occurrences may be found in Jayaraman (1940), Hardin and Thurston (1945), Dennis, et al. (1947), Caldwell and Waterman (1950), Fishburn and Davis (1962), Green (1971), and Forghami (1973).

Southwestern United States

Celestite deposits in the Fish Creek Mountains, Avawatz Mountains and at Ludlow, California, and near Gila Bend, Arizona, were visited during July, 1974 (Figure 1). A striking feature of these deposits is the consistent association of the celestite with sedimentary rocks. In all of these localities the celestite is associated with gypsum, usually in separate contiguous beds, although in the Fish Creek

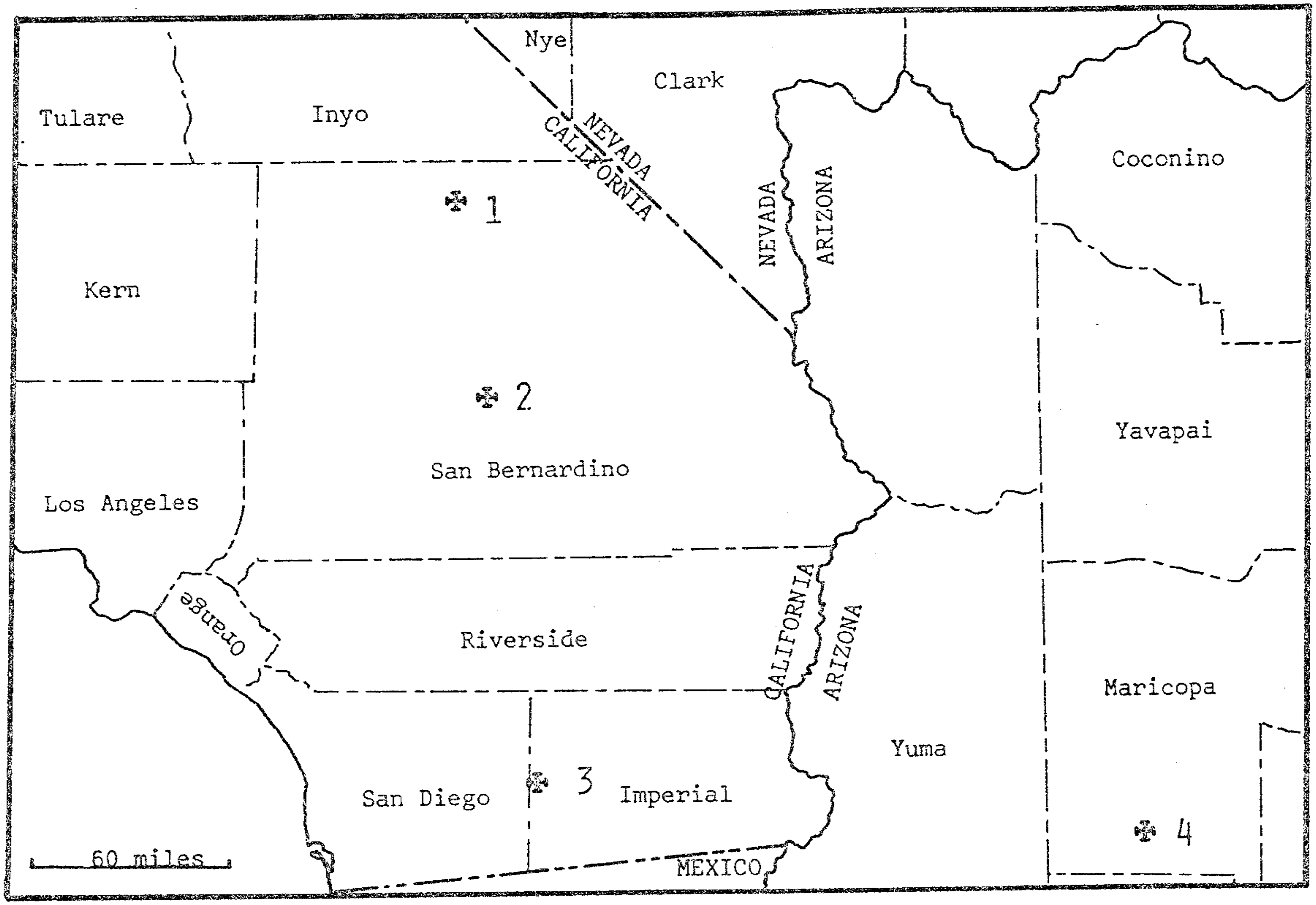

Figure 1. Index map to S.W. U.S. celestite deposits. 1. Avawatz Mtns.; 2. Ludlow; 3. Fish Creek Mtns.; 4. Gils Bend Redrawn from Moore, 1935

Mountains the celestite occurs in massive gypsum. In all but the Fish Creek occurrence the ore is also spatially related to various clastic rocks, typically shales and lithic arenites.

The mode of occurrence of the celestite is also uniform in the deposits. In each deposit the ore forms distinct lenses, beds or layers which are conformable to bedding of adjacent sedimentary units; in no case is it disconformable with the country rock. The nature of the celestite units is also fairly uniform among these deposits. The ore occurs in three basic shapes; lenses, nodules and beds. The latter appear grossly to be composed of and grade laterally into the lenses, which in turn seem to grade into the smaller nodules. This gradation in shape is best shown by the Fish Creek Mountain deposit (Figure 2).

The shape of nodules is best characterized by noting their marked resemblance to potatoes, ranging in size from less than a centimeter to approximately 20 cm. along the major axis. The lenses range in length from 60 cm. to over 2 meters. Typically they display a length to thickness ratio of 4:1, the ratio being slightly greater in the larger lenses. Because the long axes of the lenses are linear (a characteristic also exhibited by the larger nodules) it is not surprising that as the lenses become larger and more abundant, they interlayer and form a single continuous bed. This state of development may be seen best at Ludlow, where a single bed of celestite is as much as 1.3 meters thick. Figures 3, 4 and 5 are photographs of the three shapes: nodules, lenses and beds, respectively. The celestite mineralization has no distinct boundaries, as the richest areas grade slowly outward into lower and lower celestite contents.

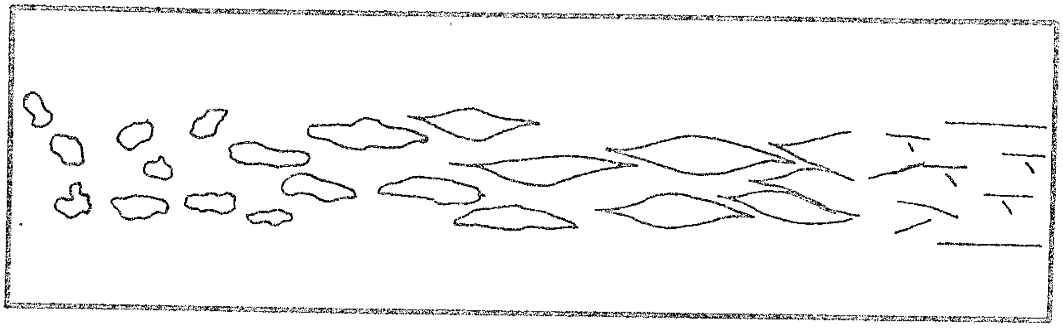

Figure 2a. Schematic view of the development of a celestite bed (on extreme right) from lenses of celestite (center). The lenses in turn are developed from nodular $SrSO_4$ (extreme left).

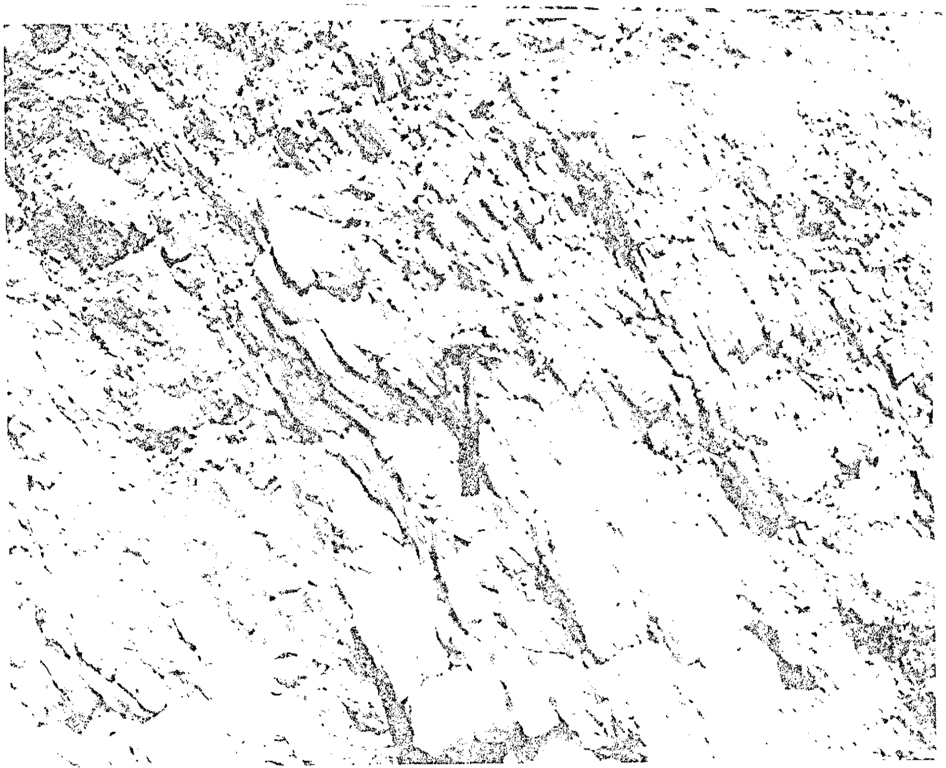

Figure 2b. Lenses of celestite grading into a bed. Two lenses are enclosed by dashed lines, the developing bed by another dashed line. Ludlow, California

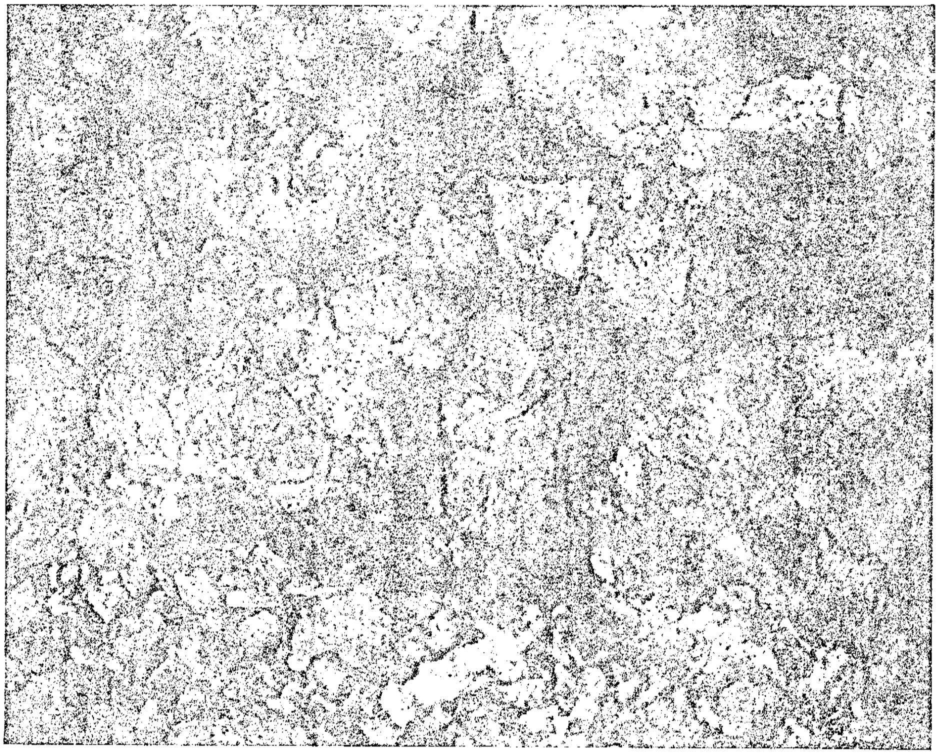

Figure 3. Nodules of celestite in massive gypsum, point of hammer immediately below a nodule. Fish Creek Mtns., California

Figure 4. Lenses of celestite, dashed line encloses a lens. Gila Bend, Arizona.

Figure 5. Beds of celestite, woman standing on bed of celestite and in front of another bed of celestite. Ludlow, California.

Figure 6. Laminated sparite; x-nicols; 15.625 x; Ludlow, California.

In hand sample the celestite from California and Arizona is remarkably uniform in appearance. The rock is fine grained, gray or green in color and, except for the specific gravity, the material could easily be mistaken for limestone.

Field relations and petrographic studies support the conclusion that the sediments in which the celestite occurs are evaporative lake deposits (in one case, Fish Creek Mountains, possibly a marine lagoon) as suggested by Ver Planck (1952, 1954).

Typical sediments include laminated sparites (Figure 6), gypsum, halite, shaly micrite, and feldspathic litharenites (Figure 7). Gradations between these extremes are common. Bedding is uniformly thin, in most cases on the order of a few centimeters; cross-bedding was not observed. The feldspathic litharenite is composed of poorly sorted, subangular to subrounded, elongate to equant grains. The lithic fragments are mostly basalts and ash flow tuffs with rare metamorphic (?) rock fragments. Grains range from clay size to ~ 2 mm. in diameter. Feldspars are mostly oligoclase and labradorite (determined by the Michel-Lévy method) with minor quantities of microcline. Several nearly euhedral feldspar crystals occur in thin section. Also present are zoned augite crystals. Alteration of most of the particles is very slight.

Based on the above evidence the clastics were probably derived from a subaerial volcanic source, transported a relatively short distance, with final deposition in or along the margins of a quiescent lake which, depending on the water balance, precipitated calcium carbonate, gypsum or halite.

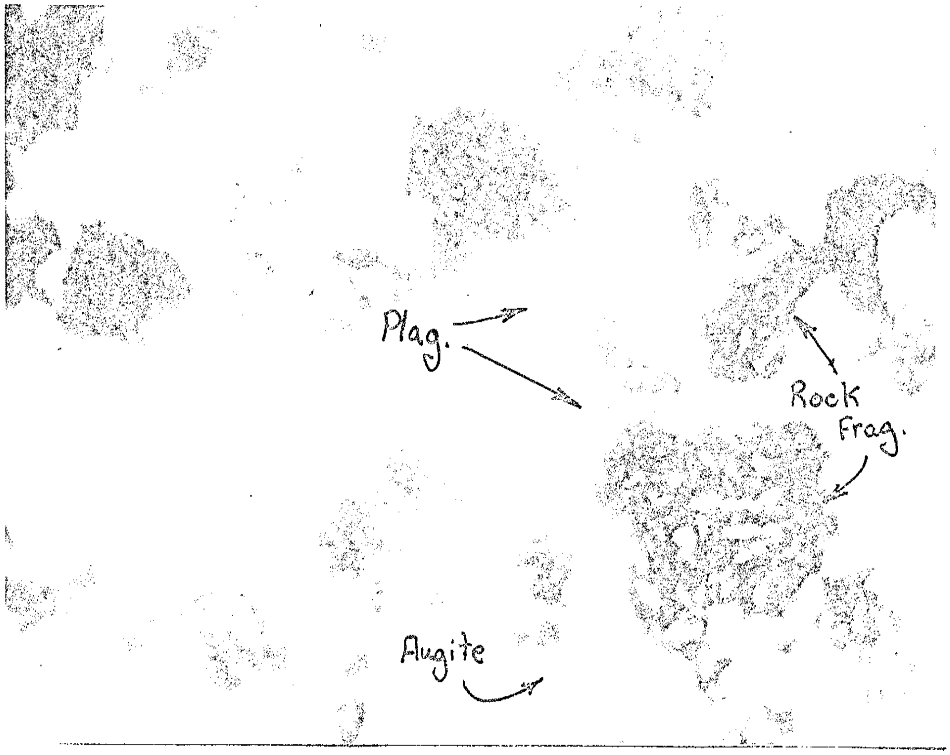

Figure 7. Feldspathic litharenite; crossed nicols; 62.5 x magnification; Ludlow, California.

Figure 8. "Bowtie" structure; crossed nicols; 15.625 x magnification; Fish Creek Mtns., California.

Petrographically there are two important characteristics which suggest that the celestite post dates calcium carbonate deposition: (1) the celestite has pseudomorphously replaced micrite, even in the Fish Creek Mountains, where no megascopic carbonate is evident, and (2) the celestite shows a texture which will be referred to henceforth as "bowtie" structure (Figure 8). Evidences for the celestite replacement of micrite are the euhedral nature of the celestite crystals in a matrix of micrite and isolated carbonate fragments in the celestite. The importance of the replacement phenomenon is that it argues against the possibility of syngenetic precipitation of $SrSO_4$ and country rock as a method of genesis for these deposits. The bowtie structure is significant because it has been reported as a crystal habit for the diagenetic celestite from the sabkhas of the Persian Gulf (Evans and Shearman, 1964). If the associated sediments are evaporative lake deposits and the mineralization postdates the deposition of the carbonate host, but predates the consolidation of the sediments (the problems involved in post-consolidation emplacement of the celestite are discussed in Chapter VI*), a sabkha environment may have existed at the time of ore deposition.

In thin sections the celestite frequently exhibits preferred orientation of elongate crystals. Also, the $SrSO_4$ appears to replace preferentially the calcium carbonate in certain layers of the host rock. The growth of the celestite was not continuous or irreversible, because thin sections display ghost textures suggestive of periods

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of celestite deposition, dissolution and renewed deposition. Evidence for this is the development of one crystal habit of celestite in casts after a different habit of celestite (Figures 9, 10) and the presence of corroded crystals overgrown by fresh celestite. These features suggest a system at or near chemical equilibrium.

Mexico

Papers on the geology of the area in which the major Mexican celestite deposits occur are Kellum (1936) and Kelly (1936) who defined a northward trending peninsula of Lower Cretaceous age around which carbonate sedimentation had occurred. Figure 11 shows the spatial relation of the Mexican deposits described in this study relative to that peninsula. The correlation between the peninsula's shore line and the distribution of the celestite deposits is readily apparent.

The deposits all occur in dark grey, massive, fine-grained limestone containing only a trace of fossil material. Identifiable fossils found include brachiopoda or pelecypoda (only poorly preserved, broken shell fragments were obtained), foraminifera and algal structures. This assemblage of fossils indicates that the carbonates are probably of marine origin though there are nonmarine forms of each type. Thin sections show that the limestone is a fine-grained sparite, usually with a few percent of the total material consisting of clasts or pellets. The material of the clasts is nearly identical with the matrix material. This evidence is suggestive of a high energy environment of deposition, such as a shallow water or near shore environment (Folk, 1974). Supporting this conclusion are the algal

Figure 9. Plain light view of high grade celestite ore, light areas exhibit the morphology of celestite crystals; 25 x magnification; Gila Bend, Arizona.

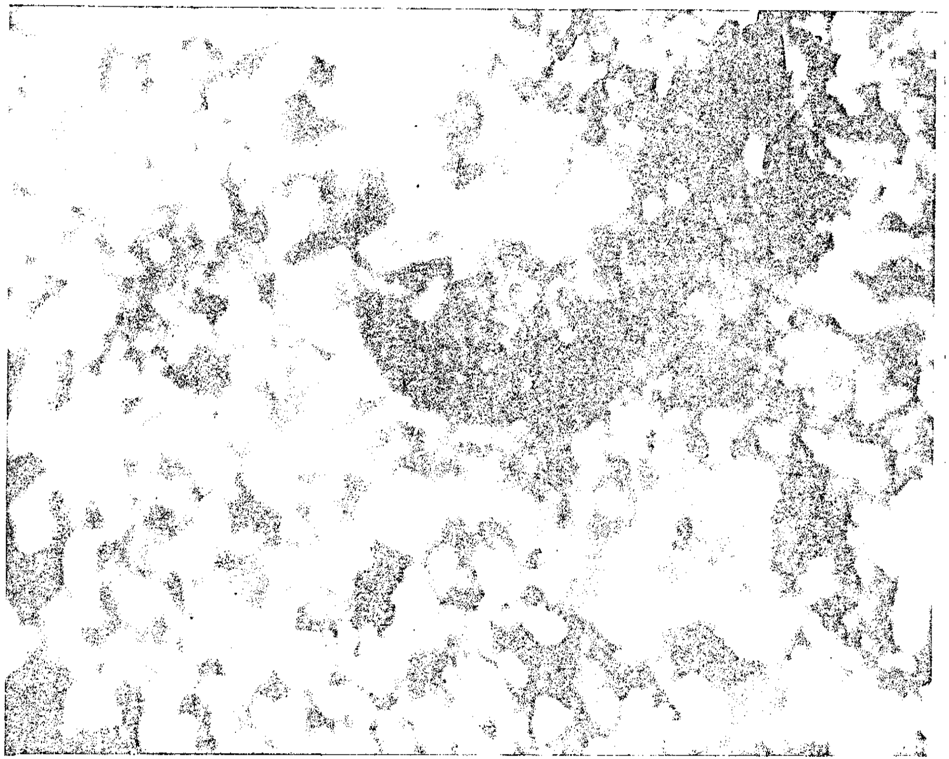


Figure 10. Same view as Figure 9; crossed nicols; large "crystals" of Figure 9 are ghosts, now composed of fine grained celestite; 25 x magnification; Gila Bend, Arizona.

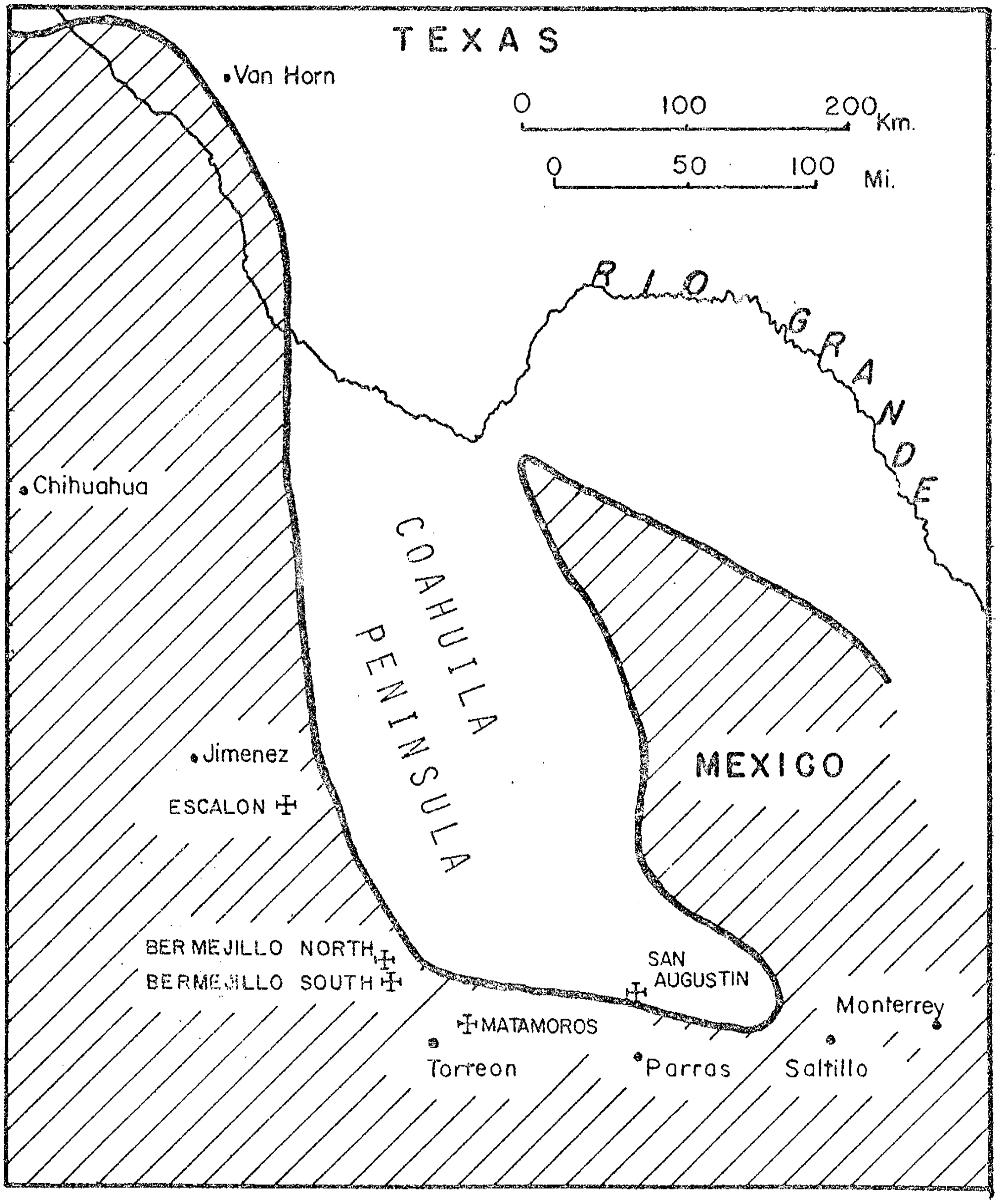


Figure 11. Index map to Mexican celestite deposits and shore line map for the lower Cretaceous, ruled area represents areas of marine deposition, redrawn from Kellum, 1936.

structures from Bermejillo South and San Augustin which, according to Kendall and Skipworth (1968), are typical of tidal flat environments in many parts of the world such as the Bahamas, the south coast of Texas, the Great Salt Lake and the Persian Gulf.

Figure 12 illustrates a type of stromatolite found at the Mexican deposits. The specimen from Bermejillo South is composed of laminated stromatolites which were repeatedly formed, torn loose, deposited, eroded and overlain by new algal mats. This requires a very high energy environment at intermittent intervals with quiescence between the high energy periods. An intertidal flat is just such an environment, where storms may cause sufficient turbulence to disrupt the shallow sediments.

The stromatolites from San Augustin are of the SH-C type described by Logan, et al. (1964). In this paper the authors presented evidence that this morphology is developed in exposed intertidal mud flats.

The ore at San Augustin and Bermejillo North and South is essentially monomineralic, consisting of pure celestite, at Matamoros and Escalon, the celestite is associated with primary calcite, which in both cases is pre-celestite in age. The celestite grows from the terminated faces of calcite scalenohedrons which in turn grow from nucleation centers (Figure 13).

All gypsum in the Mexican celestite deposits appears to be secondary cavity filling material. Typically the gypsum occurs in large masses disconformable to the celestite bearing strata and crystallizes in large, transparent, intergrown crystals. In all cases where macroscopic, euhedral crystals of celestite were observed the gypsum-celestite contact indicated that the celestite had preceded the gypsum.

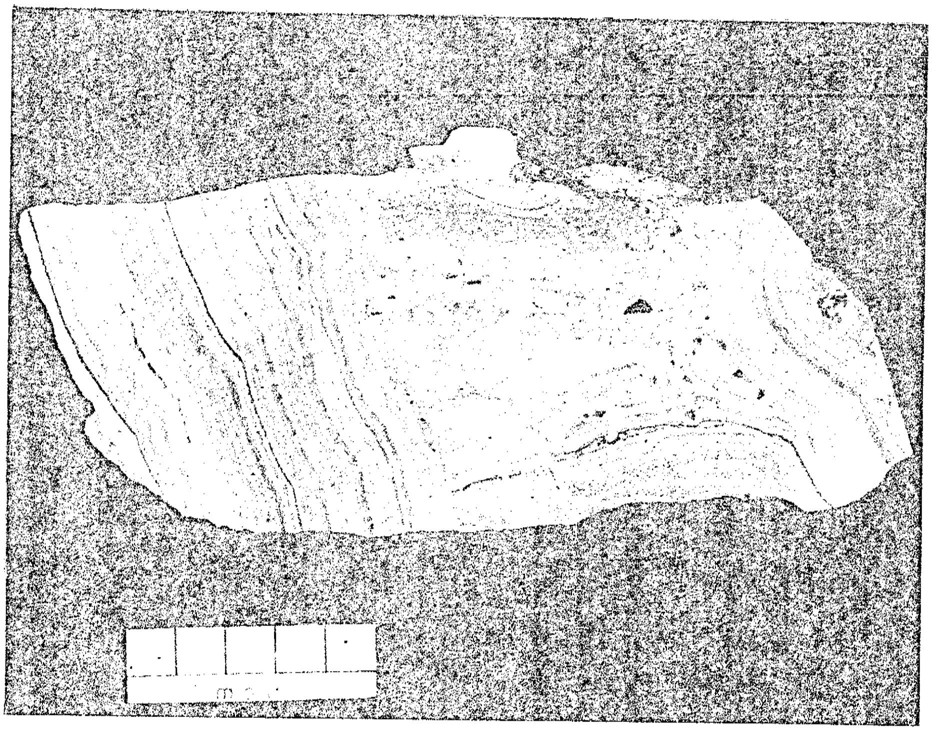


Figure 12. Laminated stromatolite; Bermejillo South, Durango, Mexico. Bar is 5 cm. long.

Figure 13. Celestite growing radially about calcite coating a limestone block; Escalon, Chihuahua, Mexico.

There are two main crystallographic forms of celestite present in the ore; anhedral, equant crystals up to 2 cm. long, and elongate, intergrown blades which are very similar to reported hydrothermal barite (Williams, et al., 1964). The bladed crystals are found only at Bermejillo North and Escalon, where they are the only form of celestite observed and may be up to 7 cm. in length. No preferred orientation of crystals was observed in any deposit except for local uniformly radial crystallization around growth centers (Figure 13). Thin sections of the ore from San Augustin and Bermejillo South exhibit randomly oriented grains of anhedral, equant celestite with a mixture of grain sizes, ranging from a few microns to 5 centimeters.

The ore bodies are typically conformable to the local strata but in a few places cut across bedding planes on a scale of up to a meter in length. Compared to the scale of the deposit this is insignificant. The deposits are from 30 meters to approximately a kilometer in length, and from 1 to 4 meters thick.

A significant problem which any model of genesis of the celestite must explain, are ubiquitous angular blocks of limestone engulfed in the celestite, which are observed in all of the Mexican deposits; these blocks may range in size from 1 cm. to over a meter in diameter. In the Escalon and Matamoros deposits these blocks are rimmed by radially oriented calcite crystals, separating the limestone and the celestite (Figures 13, 14). At San Augustin the limestone shows a thin rim a few millimeters in thickness where the rock has recrystallized, grading from calcite grains 1-2 mm. thick at the rim to grains less than a millimeter in size in the original rock. A thin section across

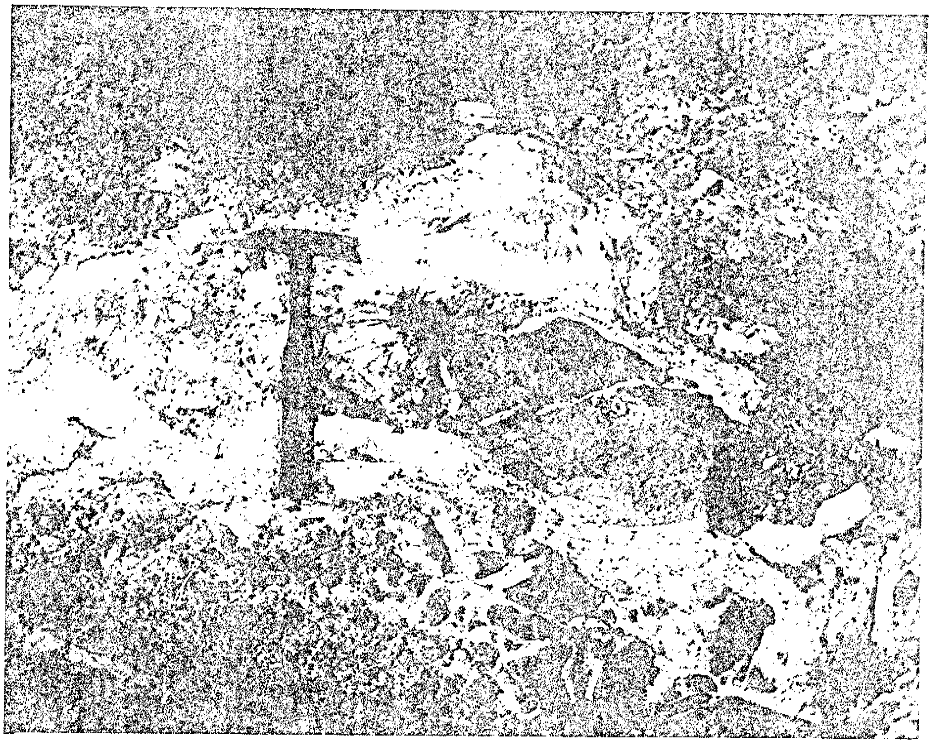


Figure 14. Celestite, white, in a limestone, gray, breccia; Escalon, Chihuahua, Mexico.

a limestone block-celestite contact from Bermejillo South shows that at the contact fine grained celestite replaces limestone followed by recrystallization of celestite into larger crystals, ranging up to one millimeter in length.

The limestone fragments are probably not fault breccia; because they are too randomly distributed in the ore and have no preferred size or shape. The fragments have not been altered except for minor recrystallization, as noted above. In one case in the Bermejillo North deposit the original orientation and position of the limestone blocks is maintained with respect to their orientation and position prior to celestite deposition, a characteristic not typical of a fault generated breccia (Park and MacDiarmid, 1964).

At Matamoros the ore frequently occurs in pre-existing cavities, some quite large. Euhedral celestite crystals grow from the walls of the cavity toward the center but where the cavities were approximately a meter or more in diameter the celestite did not fill the space. Post-ore gypsum often fills the remaining void. In smaller cavities the celestite fills the space completely.

There does not appear to be any structural control of the ore distribution; all faults observed at the deposits are post ore. At Matamoros the ore essentially follows the axial plane of an overturned anticline, but the celestite had to be at least in part pre-folding in age because the celestite is crushed along zones of slippage.

Finally, unlike the United States celestite deposits studied for this thesis, the Mexican deposits have distinct ore-waste boundaries.

Other Localities

The Enon Lake deposit, according to Choo (1972), is localized in a near shore, marine depositional terrain along the flanks of paleo-highs and is almost always associated with limestones of Mississippian age. Crowell (1971) asserts that the celestite grades into, and interfingers with, gypsum. Choo indicates that lithofacies change radically throughout the district, varying from arkose to limestone to gypsum. Choo also observes that some of the celestite had penetrated the weathered basement rocks and locally replaces fossils. He also concludes that the long axis of the ore zones is oriented parallel to either the strike or the dip of the host rocks.

The English deposits in the vicinity of Bristol are described by Thomas (1973). The important features which he discusses are the similarity of the celestite formations to the sabkhas of the Persian Gulf, with respect to the lithologies and the textures of the rocks. The richest celestite ore is associated with basement highs, similar to the relationship between ore and paleo-highs in the Enon Lake deposit.

Comparison of Deposits

It is suggested from the above discussion that there are two fundamentally different types of deposits of celestite which commonly occur and were observed in this study. The deposits of California and Arizona occur in the sediments of evaporative lakes, associated with gypsum and calcite. Such celestite is fine grained and forms nodules, lenses and beds with a gradational ore-gangue contact. In contrast, the ores in Mexico have formed in near shore marine carbonates. The only associated primary mineral is calcite, both as massive country rock and open-space filling crystals. The ore is coarse grained, and has replaced the country rock, at least locally, exhibiting sharp, well defined boundaries to mineralization.

From the brief descriptions available it is probable that the English celestite deposits are more nearly like the southwestern U.S. deposits than those of northern Mexico, but are probably of marine origin. This conclusion is based essentially on the association of both the United States deposits and the English ores with saline type sediments. The Enon Lake material exhibits characteristics of both the United States deposits and the Mexican deposits. The association with gypsum is typical of the former; the purity and mono-mineralic character of the Canadian ore is typical of the Mexican celestite. Possibly all of the deposits studied for this thesis could be viewed as parts of a continuous spectrum of genetic types or a single mechanism responsible for celestite deposition under varying geologic conditions. All the deposits of celestite for which useful data is available are spatially associated with carbonates, usually limestone. In the U.S. and Mexican deposits the celestite definitely replaces limestone, and as nearly as can be established, all of the deposits occur in rocks of shallow water origin.

III. DISCUSSION OF ENVIRONMENTS

Any model for the deposition of celestite must be compatible with the known behavior of strontium in the geologic environments in which the celestite formed.

Nearshore Marine Environment

Calcite and aragonite are the two carbonate phases commonly precipitated from seawater. Lisitzin (1972) indicates that most carbonate deposition occurs in the temperate and tropic zones. If the host rock for the celestite ores formed in shallow waters, it seems probable that the waters in which the carbonate formed were relatively warm. If so, then Winland (1969) indicates that aragonite will be the stable carbonate phase, relative to calcite, which is in agreement with the observed distribution of aragonite and calcite reported by Wagner and Van der Togt (1973) and Rodgers (1957). Thus aragonite is the probable original carbonate phase considering the environments of deposition of country rocks containing celestite ores.

The conversion of aragonite to calcite occurs during diagenesis. This process may take place when the original carbonate material comes into contact with fluids of a composition different than the solution from which they originated (Friedman, 1964; Berner, 1966). The new solution may be either more or less saline than the original solution; thus, diagenesis can occur when marine carbonates are exposed to continental waters or the brines of a sabkha.

In aragonites formed from seawater, strontium levels of 7,500 to 10,000 p.p.m. are typically found (Kinsman, 1969a); calcite under the same conditions will have ≃ 1,200 p.p.m. Sr^{++} (Kinsman, 1969a). Analyses of limestones (Kulp, et al., 1952; Graf, 1960; Blatt, et al., 1972 and Veizer and Demovic, 1974) suggest an average value of about 500 p.p.m. Sr^{++} may be found in such rocks. Obviously the calcitic limestones are depleted in strontium compared to the values in the original carbonate material, particularly if the original carbonate phase was aragonite.

The ratio of concentrations of two elements in a mineral may be greater, equal or less than the ratio of concentration in the solution from which the mineral precipitated. This partitioning may be numerically expressed by the partitioning coefficient, $\overset{\circ}{K}$, defined by the equation:

$$\overset{\circ}{K}{}^{m}_{e1} = \frac{m^{m}_{e1}/m^{m}_{e2}}{m^{sol}_{e1}/m^{sol}_{e2}}$$

where m stands for the mineral of interest and, m^{m}_{e1}, m^{m}_{e2}, m^{sol}_{e1}, and m^{sol}_{e2} are respectively the molality of elements one and two in the mineral, and of elements one and two in the solution. For aragonite (ar), equating e1 to Sr^{++} and e2 to Ca^{++}, Kinsman and Holland (1969) give a value for $\overset{\circ}{K}{}^{ar}_{Sr^{++}}$ of 1.12±0.04 at 25°C for seawater and less saline aqueous solutions. Butler (1974) gives a value of 1.0 for the highly saline brines in sabkhas. For calcite from seawater and dilute aqueous solutions Kinsman (1969a) gives $\overset{\circ}{K}{}^{cal}_{Sr^{++}}$ equal to ≃ 0.14 at 25°C.

The preceding numbers indicate that the Sr^{++}/Ca^{++} ratio in a solution precipitating aragonite will remain constant or decrease slightly. However, if calcite is the generated phase, then the

Sr^{++}/Ca^{++} ratio in the solution precipitating the calcite will increase until, if the system is closed, the Sr^{++}/Ca^{++} ratio in the solution is approximately seven times the starting concentration in the calcite. Further, a conversion of aragonite to calcite will liberate Sr^{++}, owing to the low $\overset{\circ}{K}_{Sr^{++}}$ of the calcite.

The difference between the strontium content of limestones and the strontium content of carbonates precipitated from seawater provides a potential source for the strontium concentrated in the celestite deposits. A partial mechanism for releasing the strontium from the carbonate sediments is apparent from the preceding discussion, i.e. the recrystallization of aragonite to calcite, which owing to the latter's low $\overset{\circ}{K}_{Sr^{++}}$ value, is incapable of retaining as much strontium as the aragonite from which the calcite forms.

Sabkha Environment

Briefly stated, a sabkha occurs where the ground surface is within a few meters of an evaporating water table; for a general discussion of the sabkha environment, see Kinsman (1969b). It should be noted that a sabkha may be formed under continental or coastal marine conditions, and that this environment can produce a suite of minerals ranging from calcite-aragonite through the highly soluble salts of potassium and magnesium (Shearman, 1966).

Either of two fundamental mechanisms of groundwater flow may be associated with a sabkha, capillary action or a gravity flushing mechanism. In the former case waters are drawn up into the vadose zone of the overlying sediments by capillary action to replace interstitial water that has evaporated. The new brine is in turn evaporated, raising dissolved ion concentration which can cause the deposition of the dissolved materials. In the latter mechanism a small pond or brine flat is filled with tidal or storm waters and evaporation produces a dense saline brine which will tend to settle to the bottom of the pool and flow through the underlying sediments. Precipitation of the evaporite minerals gypsum, anhydrite and halite can occur on the bottom of the evaporating pool and in the underlying sediments. As a result of these groundwater flow mechanisms, a common feature of continental or coastal marine sabkhas is the mixing of relatively fresh groundwaters and more saline waters.

The California and Arizona celestite deposits studied, suggest that the sabkha phases pertinent to this study are celestite, calcite, aragonite, gypsum and anhydrite. These are the minerals presently observed or which could have been available at some time in the past to interact to a significant extent with the aqueous solutions present.

Butler (1974) discusses the behavior of strontium in the highly saline sabkha environment, and the following is a summary of his description of some of the processes involving Sr^{++} in a sabkha. The original materials present in a sabkha include terrigenous particles, aragonite and calcite and in the special case of the evaporative lakes, possibly gypsum. As evaporation concentrates the interstitial waters, aragonite will be precipitated until the water is saturated with respect to gypsum or anhydrite, which will then begin forming. As salinity increases, dolomitization will begin, releasing Ca^{++} from calcite and aragonite according to the reaction

$2CaCO_3 + Mg^{++} \rightarrow CaMg(CO_3)_2 + Ca^{++}$, causing gypsum to precipitate. For each of these phases with the exception of aragonite, Butler indicates that $\overset{\circ}{K}_{Sr^{++}}$ will be less than unity; therefore, strontium will be excluded from the mineral phase relative to the solution from which the mineral precipitates. As gypsum and anhydrite form, calcium will be consumed and strontium will concentrate in the remaining aqueous solution. Eventually, at some point the strontium dissolved in the water reaches a sufficiently high concentration and celestite precipitates. This model is certainly partially valid as celestite is a common accessory mineral in the sabkhas of the Persian Gulf (Kinsman, 1969b).

Summary of Discussion of Environments

The behavior of strontium in the shallow water carbonate and the sabkha environments is controlled by the $\overset{\circ}{K}_{Sr^{++}}$ of the minerals forming in the environment, and the minerals which later form during the diagenesis of the sediments deposited. Aragonite, which probably constitutes the major original phase in the former facies, has a $\overset{\circ}{K}_{Sr^{++}}$ close to unity. For the other phases discussed above (calcite, gypsum, anhydrite, and dolomite), $\overset{\circ}{K}_{Sr^{++}}$ is significantly less than unity. Therefore, if aragonite forms from a solution it will have nearly the same Sr^{++}/Ca^{++} ratio as the solution from which the aragonite precipitated; and, the solution's Sr^{++}/Ca^{++} ratio will remain unchanged. If the alternate phases form, Sr^{++} will be concentrated into the aqueous solution from which the new mineral forms.

IV. FLUID INCLUSION DATA

Fluid inclusion analyses were carried out on samples from the Mexican celestite deposits in an effort to ascertain the temperature of formation and the composition of the fluid from which celestite ores are formed. Unfortunately, samples of celestite from the deposits in the U.S. contained too much included material, and the celestite grains were too small to be amenable to the techniques used. Results of the fluid inclusion analyses for this study are presented in Table I. For a discussion of the theory and validity of such analysis and a comparison with other inclusion analyses, see Roedder (1967, 1972).

Homogenization Studies

Thermal measurements for this study were obtained from both an electrical resistance heating stage, and glycerine immersion and acetone immersion freezing stages, all using a type K DS-520 Doric thermocouple, accurate to ± 0.2°C.

It should be noted that temperatures given for the Mexican celestites in Table I are not minimum temperatures of formation as are most fluid inclusion homogenization temperatures. The inclusions exhibited the unusual condition of no gas phase being present at room temperatures, ≈ 25°C. Such results could indicate that the inclusions formed at a higher temperature, but that owing to metastability, the gas phase has not appeared. This possibility is eliminated by results from the freezing stage work. It was noted during attempts to freeze the Mexican material, that a gas phase would appear, and upon warming disappear. This behavior sets a lower limit on the temperature of formation, and allowing for the possibility of minor metastability, 25°C is a reasonable estimation of the temperature of formation of the celestite, if not a maximum value.

In using fluid inclusion homogenization data a correction factor, allowing for hydrostatic pressure at the site of mineralization during the period the fluid inclusion developed, must be applied to obtain the temperature of formation (Roedder, 1967). This correction to the homogenization temperature increases with increasing pressure of formation. It is unnecessary, however, to apply any significant pressure correction to the celestite homogenization data, because of the absence of a gas phase in the celestites studied. If the material had formed in a zone of significantly high pressure, when that pressure was removed, a gas phase would tend to exsolve if the fluid was saturated or nearly saturated with gas. Further evidence of the lack of a high pressure environment for the celestite deposition involves the formation temperature deduced. In an area with an average thermal gradient, a temperature of 25°C is measured within a few thousand feet of the Earth's surface (Howell, 1959). If the celestite had formed at a greater depth under normal geothermal conditions, the fluid inclusions would either exhibit a temperature of formation higher than 25°C.

Fluid Composition

Sodium and potassium analyses were determined on a Perkin-Elmer Model 403 atomic absorption unit with carbon furnace. Samples were hand picked to eliminate macroscopic impurities in the celestite, crushed to fine sand size, leached in hot concentrated $HCl-HNO_3$ to remove any soluble contaminating material, then powdered in HCl solution. The HCl solution was then analysed for sodium and potassium.

The analyses, reported in parts per million, do not represent the actual Na^+ and K^+ concentrations in the fluid inclusions because the percentage of the final analysed solution actually contributed by crushing the fluid inclusions is unknown. However, it must be assumed all of the sodium and potassium in the HCl solution is derived from the opened fluid inclusions. The significance of the sodium and potassium values is in their ratio. As noted in Table I, the molal ratios of Na^+ to K^+ in the celestites analysed is approximately 10. In comparison, the value of this ratio for seawater is ≈ 70 (Park, 1972) and for "connate" ground waters and oil field brines it is 500+ (White, 1965). Indeed, the only class of ground water which exhibits a Na^+/K^+ ratio as low as the celestite fluid inclusion samples is that of shallow groundwaters which have not had sufficient time to chemically equilibrate with their country rocks (Collins and Howard, 1927; Brown, et al., 1962; Skougstad and Horr, 1963; Leve, 1968).

Fluorite Analysis

The San Augustin mine occurs in an area of intense fluorite mineralization. Field evidence is ambiguous as to the genetic relationship between the fluorite and the celestite; the fluid inclusion data, however, serve to clarify the nature of this relationship. Fluid inclusions from fluorite indicate a minimum temperature of formation of 117-144°C, whereas the celestite formed at less than 25°C. Celestite adjacent to the fluorite shows no impression of the much higher temperature of formation of the latter. Thus it can be concluded that the celestite and the fluorite have no direct, obvious genetic relationship, and that their spatial correlation is only coincidental.

In summary, the fluid inclusion analyses for this study indicate that the celestite in the Mexican deposits formed at a low temperature, probably 25°C or less. The fluids from which the celestites crystallized had a low sodium to potassium ratio, ≈ 10. The fluorite ores in the vicinity of the San Augustin mine appear to have no genetic relationship to the celestite ore.

TABLE I

FLUID INCLUSION DATA

Deposit	Mineral	Homogenization Temperature in degrees C	Freezing Temperature in degrees C	p.p.m. Na^+	p.p.m. K^+	m_{Na^+}/m_{K^+}
San Augustin	celestite	25	-	4.25	0.74	9.8
mine immediately above the San Augustin	fluorite	117-144	-24 to -20.5	-	-	-
Bermejillo N.	celestite	25	-	4.1	0.58	12.0
Bermejillo S.	celestite	25	-	-	-	-
Matamoros	celestite	25	-	-	-	-
Matamoros	calcite	25	-	-	-	-
Escalon	celestite	25	-	-	-	-
Escalon	calcite	≈33	-	-	-	-

V. MINERAL STABILITY RELATIONSHIPS

From the previous discussion it is apparent that five phases may be used to define or limit certain chemical parameters occurring during celestite mineralization: i.e. celestite, gypsum, anhydrite, aragonite and calcite. Add to this strontianite, $SrCO_3$, and the list includes all the common Sr^{++}-Ca^{++}-$CO_3^=$-$SO_4^=$ phases.

The chemical stability relationships among these phases are illustrated in Figure 15, using principles discussed by Garrels and Christ (1965). For a given phase plotted on the figure, the relationship between the values of $a_{CO_3^=}$ to $a_{SO_4^=}$ and $a_{Sr^{++}}$ to $a_{Ca^{++}}$ necessary for the phase to be stable with respect to the aqueous solution are illustrated. The validity of the diagram is restricted to the parameters specified to construct the diagram: temperature = 25°C, one atm. of pressure and $a_{H_2O} = 1$ (ubiquitous). The calculations used in constructing Figures 15 and 16 are presented in Appendix B.

The composition of seawater is plotted on the diagram at "A". The point is based on a value of 7.5 p.p.m. total dissolved strontium in seawater (Angino, et al., 1966), which corresponds to a molality of 8.56×10^{-5}.

The molality of an ion is related to the activity of the ion by the equation:

$$a_i = \overset{\circ}{\gamma}_i m_i \tag{1}$$

where a_i is the activity, $\overset{\circ}{\gamma}_i$ is the stoichiometric individual ion activity coefficient, and m_i is the molality of the appropriate ion in the solution. The value of $\overset{\circ}{\gamma}_i$ may be calculated from the formula (Helgeson, 1969):

FIGURE 15

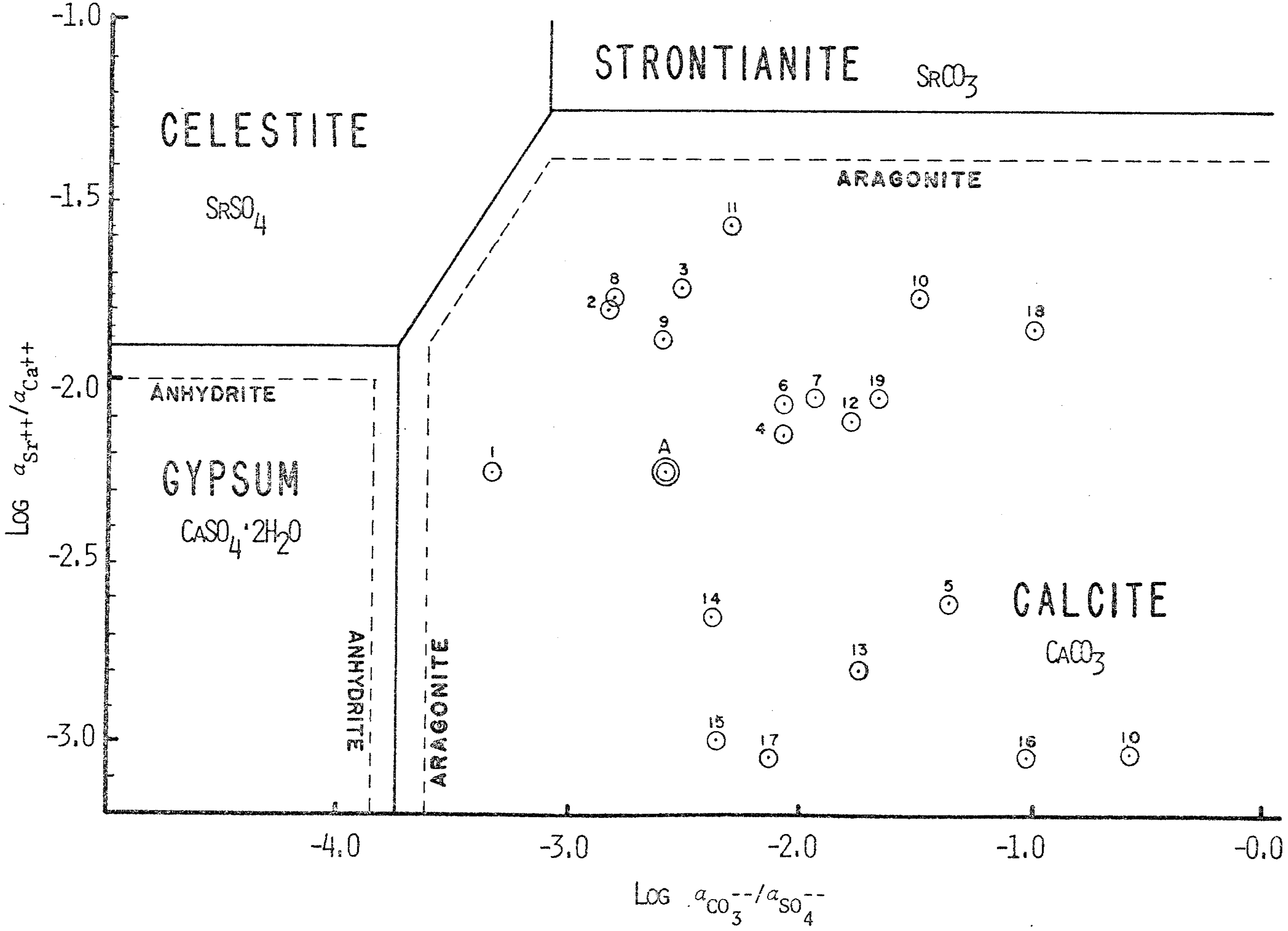
Plot of stability fields of celestite, strontianite, gypsum, anhydrite, calcite and aragonite with selected groundwaters as a function log $a_{Sr^{++}}/a_{Ca^{++}}$ vs. log $a_{CO_3^=}/a_{SO_4^=}$ at 25°C, 1 atm. and $a_{H_2O} = 1$. Anhydrite and aragonite are unstable with respect to gypsum and calcite under the conditions assumed in constructing the diagram; the metastable mineral's boundary lines are shown by dashed lines on the diagram. Points 1-12 are from Skougstad and Horr (1963), 13-19 are from Summers, et al. (1972). For the derivation of A, see text.

Identification of Analyses

A. Seawater

1. Cedar Valley Ls., Adair Cnty., Iowa
2. Galena Dol., Platteville Fm., St. Peter Ss., Louisa Cnty., Iowa
3. Galena Dol., Platteville Fm., St. Peter Ss., Warren Cnty., Iowa
4. Roubidoux Dol., Cherokee Cnty., Kansas
5. Roubidoux Dol., Cherokee Cnty., Kansas
6. Cotter Dol., Crawford Cnty., Kansas
7. Roubidoux Dol., Crawford Cnty., Kansas
8. Long Creek Member of Foraker Ls., Wabaunsee Cnty., Kansas
9. Prairie du Chein Grp., Jordan Ss., St. Lawrence Fm., Marshall Cnty., Iowa
10. Prairie du Chein Grp., Jordan Ss., St. Lawrence Fm., Clinton Cnty., Iowa
11. Ls. and Dol. of Silurian and Devonian age, Blackhawk Cnty., Iowa
12. Cotter Dol., Crawford Cnty., Kansas

13.-19. respectively are Analysis 2, 3, 5, 7, 16, 19, and 29 of Summers, et al.



STRONTIANITE
$SrCO_3$
CELESTITE
$SrSO_4$
ARAGONITE
ANHYDRITE
GYPSUM
$CaSO_4 \cdot 2H_2O$
ANHYDRITE
ARAGONITE
CALCITE
$CaCO_3$
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
10
A
-1.0
-1.5
-2.0
-2.5
-3.0
$\text{LOG } a_{Sr^{++}}/a_{Ca^{++}}$
-4.0
-3.0
-2.0
-1.0
-0.0
$\text{LOG } a_{CO_3^{--}}/a_{SO_4^{--}}$

$$\overset{\circ}{\gamma}_{\varepsilon} = \frac{1}{\dfrac{1}{\overset{*}{\gamma}_{\varepsilon}} + \sum \dfrac{a_{L}^{y}}{\beta_y \overset{*}{\gamma}_y}} \tag{2}$$

where $\overset{*}{\gamma}_{\varepsilon}$ is the individual ion activity coefficient of the central ion ε, a_L^y is the activity of ligand L raised to the stoichiometric coefficient (y) of the ligand in the complex εL_y, β_y is the overall dissociation constant for the aqueous complex εL_y, and $\overset{*}{\gamma}_y$ is the activity coefficient for the species εL_y. Equation (2) takes into account the long range of electrostatic forces which ions exert upon each other, ion-solvent interactions and ion-ion chemical interaction, and, association of the cation under consideration with various ligands.

For Sr^{++} in seawater equation (2) becomes:

$$\overset{\circ}{\gamma}_{Sr^{++}} = \frac{1}{\dfrac{1}{\overset{*}{\gamma}_{Sr^{++}}} + \dfrac{a_{HCO_3^-}}{K_{SrHCO_3^+}\overset{*}{\gamma}_{SrHCO_3^+}} + \dfrac{a_{SO_4^=}}{K_{SrSO_4^o}\overset{*}{\gamma}_{SrSO_4^o}} + \dfrac{a_{CO_3^=}}{K_{SrCO_3^o}\gamma_{SrCO_3^o}}} \tag{3}$$

Values of $a_{HCO_3^-}$, $a_{SO_4^=}$ and $a_{CO_3^=}$ are from Garrels and Thompson (1962), $K_{SrHCO_3^+}$ and $K_{SrCO_3^o}$ from Sonderegger (1974), and $K_{SrSO_4^o}$ is from Garrels and Christ (1965). $\overset{*}{\gamma}_{Sr^{++}}$ and $\overset{*}{\gamma}_{SrHCO_3^+}$ are calculated according to the extended Debye-Hückel equation:

$$-\log \overset{*}{\gamma}_i = \frac{A\, Z_i^2 \sqrt{I}}{1 + \overset{\circ}{a}_i B \sqrt{I}} + B^o I \tag{4}$$

where at 25°C, $A = 0.5085$, $B = 0.3281 \times 10^{-8}$; $B^o = 0.041$; I is the ionic strength of the solution, Z_i is the absolute charge of the ion "i"; and, $\overset{\circ}{a}_i$ is the "effective diameter" of the ion "i" in solution. For Sr^{++}, $\overset{\circ}{a} = 5.0 \times 10^8$ (Garrels and Christ, 1965), for $SrHCO_3^+$, $\overset{\circ}{a} = 5.0 \times 10^8$ was used (Beane, pers. comm.). For the neutral species γ_y^* is assumed to equal the γ^* of CO_2 (Helgeson, 1969). The ionic strength of seawater was taken to be 0.71 after Garrels and Thompson (1962).

The resulting stoichiometric activity coefficient of Sr^{++} in seawater is:

$$\overset{\circ}{\gamma}_{Sr^{++}} = \frac{1}{\frac{1}{.19} + \frac{10^{-2.95}}{10^{-1.2}(.66)} + \frac{10^{-2.74}}{10^{-2.3}(1.2)} + \frac{10^{-5.32}}{10^{-3.1}(1.2)}}$$

$$= 0.179$$

Thus, according to equation (1), using a molality of strontium equal to 8.56×10^{-5} the activity of Sr^{++} in seawater is 1.532×10^{-5}.

Using the values of $a_{Ca^{++}}$, $a_{CO_3^=}$ and $a_{SO_4^=}$ in seawater from Garrels and Thompson (1962), one may calculate log $a_{Sr^{++}}/a_{Ca^{++}}$ and log $a_{CO_3^=}/a_{SO_4^=}$ for normal seawater, yielding values of -2.24 and -2.58 respectively. According to Odum (1951) it is probable that the position of seawater with respect to the vertical axis of Figure 15 has not changed significantly since the end of the Precambrian; if the carbonate/sulfate ratio also has not changed (Krauskopf, 1967), the plot of seawater on the diagram would be same since the beginning of the Cambrian.

Also plotted on Figure 15 are the positions of various low salinity groundwaters using data from Skougstad and Horr (1963) and

Summers, et al. (1972). The analyses of the former are from carbonate sections in Iowa and Kansas, and the latter are from a mountain recharge zone in New Mexico with volcanic and metasedimentary country rocks. The first group of waters have generally reached saturation with respect to calcite, whereas many of the latter have not.

Not shown on the diagram are the compositions of waters from the sabkha environment. This is because of a lack of information on exact water compositions, the complexity of the solutions involved and the wide range in values possible. It is best to simply state that most sabkha and evaporative waters will be in the gypsum field after initial concentration removes the solution from the calcite-aragonite stability field.

VI. THEORIES OF GENESIS AND PROBLEMS

Various hypotheses for the generation of celestite ores in the southwestern U.S.A. and northern Mexico can be evaluated in the light of the evidence presented here.

Hydrothermal Celestite

Deposition from hydrothermal solutions is excluded for numerous reasons: the low temperature of formation indicated by the fluid inclusions; the lack of associated minerals one would normally expect such as fluorite, galena, sphalerite, pyrite, etc. (Park and MacDiarmid, 1965); the solubility of celestite which decreases with increasing temperature (Holland, 1967; Blount and Dickson, 1968), thus making transportation of the $SrSO_4$ difficult at elevated temperatures; and finally, the lack of noticeable alteration zones such as marbleization or sericitization.

Deposition in Consolidated Rock from Ground Waters

The deposition of celestite in a section of consolidated carbonates such as observed at the Mexican and United States deposits involves problems of source and mechanism. A source would need to provide large quantities of $SO_4^=$ and possibly Sr^{++}; both of these components are present in groundwater but below concentrations sufficient to precipitate celestite. Simple concentration, maintaining the relative ratios of all the groundwater components but increasing the absolute concentration, would remain in the calcite field of Figure 15. Therefore, local addition of strontium or sulfate to the groundwater is necessary to create sufficiently high concentrations of the two ions to cause celestite deposition and shift composition out of the calcite field. Either strontium or sulfate added to the groundwater must be derived ultimately from a solid mineral phase; the common sedimentary minerals containing either Sr^{++} or $SO_4^=$ are celestite ($SrSO_4$), and gypsum ($CaSO_4 \cdot 2H_2O$).

Figure 16 is the plot of an hypothetical, average groundwater on the diagram from Figure 15. If an initial groundwater composition, represented by "B" on Figure 16 is assumed, addition to the groundwater of a solution in equilibrium with celestite will tend to cause the groundwater composition B to shift toward the celestite field; as increasing amounts of this Sr^{++} and $SO_4^=$ fluid are introduced the compositional shift will follow a path* as shown by arrow 1 on the diagram. Ultimately the mixed groundwater will reach the celestite - calcite boundary and celestite becomes stable. As more of the celestite stable solution is added to the groundwater, calcite dissolution will occur accompanied by celestite precipitation. This process would yield the paragenesis observed in the celestite occurrences described above calcite → celestite with calcite dissolution. However, the process assumes groundwater mixing with a solution in equilibrium with pure celestite which requires a source containing celestite. All known celestite deposits are mixed with major quantities of calcite or gypsum. If one assumes a mixed celestite - calcite source for the solution added to the groundwater, the final composition of the combined waters would plot at the celestite-calcite boundary on Figure 16 and calcite dissolution would never occur. Changing the assumed composition of the

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*arrows not necessarily linear because axes are logarithmic.

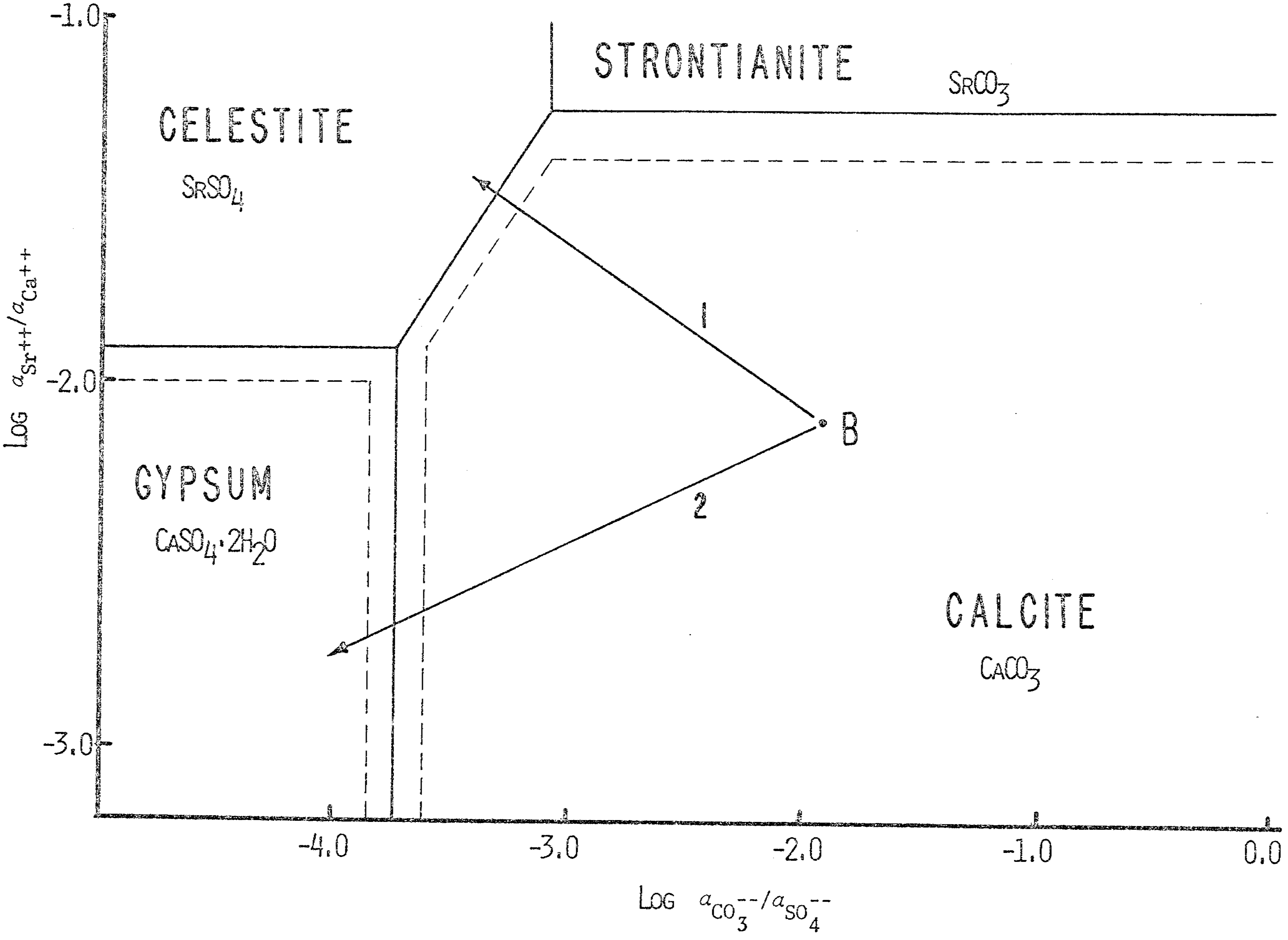
FIGURE 16

Schematic water composition paths as a celestite or gypsum stable solution is added to an assumed groundwater.

B - assumed groundwater composition.

1 → - trend of the plot of groundwater B as a celestite stable solution is added.

2 → - trend of the plot of groundwater B as a gypsum stable solution is added.



STRONTIANITE
$SrCO_3$
CELESTITE
$SrSO_4$
GYPSUM
$CaSO_4 \cdot 2H_2O$
CALCITE
$CaCO_3$
B
1
2
-1.0
-2.0
-3.0
-4.0
-3.0
-2.0
-1.0
0.0
Log $a_{Sr^{++}}/a_{Ca^{++}}$
Log $a_{CO_3^{--}}/a_{SO_4^{--}}$

initial groundwater B does not solve the problem. Increasing the strontium to calcium ratio or the carbonate to sulfate ratio of the groundwater will tend to cause the formation of strontianite as an intermediate product, as celestite solution is added to the groundwater but this phase is not observed in the celestite deposits except as a rare secondary mineral. Lowering the initial strontium to calcium ratio or the carbonate to sulfate ratio of the groundwater would tend to cause gypsum to appear as an intermediate product, but this mineral is not observed to be abundant in the celestite deposits of Mexico.

If a solution in equilibrium with gypsum (or anhydrite) is added to groundwater B, the final solution composition will plot to the lower left side of point B. A continued addition of gypsum stable solution will shift the groundwater composition in the direction indicated by arrow 2 on Figure 16. Eventually the groundwater will reach the gypsum - calcite boundary and if more gypsum stable water is added to the solution, calcite will dissolve; as the process continues, gypsum will eventually replace calcite. At no time will celestite saturate, and no reasonable initial groundwater composition plot in the calcite field will result in celestite becoming stable simply by addition of gypsum stable water.

Theoretically strontium could be added to the groundwater by a solution in equilibrium with strontianite, $SrCO_3$. However, such a solution necessitates having a strontianite source, which is unlikely considering the fact that strontianite is rare and almost always reported as being secondarily derived from weathering of celestite.

Simultaneous Deposition of Celestite and Country Rock

Syngenetic origin of celestite with the host rock is superficially an attractive hypothesis, and is favored by Choo (1972) to explain the ore occurrence at Enon Lake, Nova Scotia. With detailed examination, however, a syngenetic model for the genesis of celestite fails.

The major problem in the case of the Mexican deposits is the presence of the limestone clasts in the ore. It is very difficult to explain these angular blocks by any syngenetic hypothesis because a syngenetic mechanism would generate limestone blocks with rounded edges. Further, any celestite deposit formed in marine rocks is probably not syngenetic, based on experimental and field evidence. In experimental evaporations of seawater, celestite is not mentioned as a product phase (Blatt, et al., 1972; Shearman, 1966; Schmalz, 1969; Stewart, 1963), though it may be too minor a phase to be observed readily. Müller and Puchelt (1961) attempted to precipitate celestite from seawater; they concluded that such precipitation would occur after about two thirds of the water had evaporated, which is about the point gypsum begins appearing (Blatt, et al., 1972), which would lower $a_{SO_4^=}$ significantly . Müller and Puchelt (1961) did not state that they had actually precipitated celestite.

In the deposits of celestite in the United States a syngenetic origin is ruled out because of the petrographic evidence (residual carbonate in celestite crystals, celestite replacing micrite molds of celestite) which indicates that the celestite has replaced prior carbonate sediment. While the data do not eliminate precipitation of celestite from saline lake waters as a possible mechanism, it is apparently uncommon or unlikely as evidenced by the lack of reported modern occurrences of celestite.

Diagenetic Deposition in a Sabkha Environment From Brines

A diagenetic mechanism for the genesis of celestite may explain the United States deposits but not the Mexican deposits studied. That some process or processes produce celestite in the sabkha environment is certain; celestite, as mentioned above, is a common accessory mineral in the sabkha sediments.

Diagenetic formation of gypsum or anhydrite can concentrate Sr^{++} in the brines relative to Ca^{++} since the $\overset{\circ}{K}_{Sr^{++}}$ for both minerals is less than unity; the conversion of aragonite to calcite by brines releases additional Sr^{++} into the water which combines with the readily available $SO_4^=$ in solution to precipitate celestite. Such an hypothesis is tempting, particularly since celestite formation from simple concentration is unlikely in view of considerations discussed previously. Such a mechanism may work on a small scale. There are certain features though, which make it difficult to explain large concentrations of celestite according to the model. For example, as salinities increase, dolomitization of aragonite and calcite begins, liberating Ca^{++} to the solution according to the reaction:

$$2CaCO_3 + Mg^{++} \rightarrow CaMg(CO_3)_2 + Ca^{++} \quad .$$

In a region containing considerable aragonite or calcite, the quantity of Ca^{++} available could be very large relative to the quantity of strontium present in solution. This will tend to prevent the solution from precipitating celestite by maintaining the solution in the gypsum stability field of Figure 15 and suppressing $SO_4^=$.

A second problem is generated by the very process necessary to cause the high salinities in the sabkha waters, which Butler (1973) indicates are necessary for celestite generation. As the brine is concentrated by evaporation its specific gravity will increase, yielding an unstable situation in which dense brine will overlie a brine of lesser density (De Groot, 1973). At some point fluid flow will begin, driven by density differences, thereby providing an upper limit to salinity. Unless the brine can be prevented from sinking away from the evaporating surface, the proper concentrations of strontium in the brine may never be reached.

Recrystallization of Anhydrite - Gypsum

One final mechanism must be mentioned with regard to celestite formation in saline sediments. As previously indicated, anhydrite and gypsum both have $\overset{\circ}{K}_{Sr^{++}}$ less than unity. Therefore, if either mineral should recrystallize in the presence of an aqueous solution strontium would be liberated to the aqueous solution. If the strontium level could build up high enough in the fluid, celestite could precipitate. This is probably the mechanism involved in the trace occurrences of celestite in numerous evaporative sequences (Stewart, 1963).

The mechanism, however, is restricted in applicability to explaining concentrations of celestite by several factors. It is limited by the low strontium content of the gypsum and anhydrite. In the case of the Mexican deposits there is neither gypsum nor anhydrite present and no evidence for their former presence was observed. The deposits of the southwestern U.S. are probably not formed this way because any Sr^{++} released by the recrystallization of gypsum or anhydrite would probably be redeposited quickly in the surrounding sulfate rich zone and would not penetrate and replace the carbonate zones, as was observed in these occurrences.

VII. MODEL FOR GENESIS

A model for celestite deposition must include several observed features:

1) Celestite in both American and Mexican deposits occurs in carbonate sediments.
2) Celestite apparently replaces preexisting carbonate as observed in thin sections of the celestite-carbonate contact.
3) There is no observed evidence of celestite replacing gypsum in the United States deposits.
4) Mexican ore contains clasts of limestone.
5) Fluid inclusions from two of the deposits have a low Na/K ratio relative to most ground-waters and much less than for seawater.
6) Celestite ores have a very simple mineralogy.
7) World-wide, celestite ores are generally associated with carbonates of shallow saline-water origin.

The mechanism proposed to account for the celestite deposits of both Mexico and the United States is the release of strontium through diagenetic conversion of aragonite to calcite by fresh waters which then mix with a minor amount of $SO_4^=$ - rich water, either sea water or water from a saline lake. The suggested process requires fresh, i.e. continental, water and the sabkha environment is a suitable region for such mixing. Celestite deposition is probably restricted to warm shallow marine water or saline lake where aragonite is the original carbonate thus allowing high initial strontium content in the carbonate sediment. Understanding the genetic mechanism is enhanced when the Mexican celestite deposits are fitted to the proposed mechanism.

In Aptian-Albian times aragonite muds were being deposited in shallow marine seas along the Coahuila Peninsula (Figure 11). Prior to celestite deposition, at what was to be the Matamoros and Escalon deposits, cavernous dissolution of the marine carbonate sediment occurred, followed by, or in conjunction with, radial crystallization of calcite.

The water from which the celestite formed was probably continental. The Na^+/K^+ ratio in the fluid inclusions is similar to ratios in groundwaters where insufficient time has passed in order for the solution to totally equilibrate with the country rock. This condition is well typified in the United States by shallow waters in Florida which typically have ionic strengths on the order of 0.001 to 0.005 (cf; Leve, 1968; Collins and Howard, 1927; Brown, et al., 1962; Skougstad and Horr, 1963).

As the fresh water came in contact with the aragonite, recrystallization occurred, yielding calcite and Sr^{++} - rich water. In a closed system, aragonite with an original strontium content of 9800 p.p.m. would recrystallize to calcite, generating a solution with a log $(a_{Sr^{++}}/a_{Ca^{++}})$ value of -1.09 (Kinsman, 1969a). At low ionic strengths the γ^*, individual ion activity coefficient, of Ca^{++} and Sr^{++} are nearly identical owing to the same charge and $\overset{\circ}{a}$; thus this ratio would plot in either the celestite or strontianite fields on Figure 15.

Generally, natural carbonate sediments are not closed systems, particularly because fresh water is favored for the aragonite - calcite transformation (Friedman, 1964). If, however, the fresh water is introduced relatively slowly, the high strontium to calcium ratio described above may be maintained. Kinsman (1969a) indicates that the conversion of only 75 millimoles of aragonite to calcite will produce the above indicated Sr^{++}/Ca^{++} ratio in a liter of water. Thus a system should continue to provide high Sr^{++}/Ca^{++} ratios to a considerable volume of circulating water (Kinsman, 1969a).

Most analyses of low Na^{+}/K^{+} waters from Florida plot to the right of the celestite - strontianite line on Figure 15. Therefore, in order to precipitate celestite the $CO_3^{=}/SO_4^{=}$ ratio of the ground-water which will eventually precipitate celestite must be decreased. The most likely source for sulfate is the immediately adjacent seawater.

Consider, for example, a solution composed of a low salinity groundwater with a low sodium to potassium ratio, having a pH $\approx$ 7.4, a normal pH for such water (Skougstad and Horr, 1963). At this pH HCO_3^{-} will be the dominant carbonate phase, $\approx$ 800 times as prevalent as $CO_3^{=}$. The dominant sulfate species will be $SO_4^{=}$, being greater than HSO_4^{-} by $\approx 10^{5.5}$. If a small quantity of seawater is added to this water of pH $\approx$ 7.4, considerable additional sulfate will be available compared to the added quantity of free $CO_3^{=}$. The chemical consequences of mixing various ratios of groundwater and seawater are developed in Table II.

Table II illustrates the chemical nature of final solutions composed of varying ratios of groundwater and seawater. The groundwater has a composition corresponding to a low ionic strength, low Na^{++}/K^{++}, moderate $SO_4^{=}$ content, pH = 7.4 and low HCO_3^{-} concentration typical of shallow Florida groundwaters. Diagenesis by such a solution of a pure

TABLE II

COMPOSITION OF GROUNDWATER, SEAWATER AND VARIOUS RATIOS OF THE TWO

Data for seawater is from Garrels and Thompson (1962), Krauskopf (1967), the strontium value for seawater is from Angino, et al. (1966), the activity coefficient of strontium in seawater calculated as described in text. Note that the individual ion activity coefficients of Ca^{++} and $SO_4^{=}$ are nearly identical with that of strontium over the range of ionic strengths considered in the groundwater-seawater mixes. For assumptions used in arriving at ion concentrations in the groundwater see text.

TABLE II

	Ground Water	Sea Water	1 99% Ground Water 1% Seawater	2 98% Ground Water 2% Seawater	3 90% Ground Water 10% Seawater	4 88% Ground Water 12% Seawater
Ionic Strength	0.02	0.71	0.0269	0.0338	0.0890	0.1028
$\gamma^*_{Sr^{++}}$	0.58	0.19	0.55	0.52	0.39	0.37
$\gamma^*_{Ca^{++}}$	0.60	0.24	0.56	0.53	0.42	0.40
$\gamma^*_{SO_4^=}$	0.57	0.16	0.53	0.50	0.37	0.35
$\gamma^*_{HCO_3^-}$	0.87	0.68	0.85	0.84	0.78	0.78
pH	7.4	8.1	7.4	7.4	7.5	7.5
HCO_3^- (p.p.m.)	50	145	51	52	60	61
Ca^{++} (p.p.m.)	300	400	301	302	310	312
Sr^{++} (p.p.m.)	53.1	7.5	52.6	52.2	48.5	47.6
$SO_4^=$ (p.p.m.)	50	2726	77	104	318	371
Na^+/K^+ (p.p.m.)	4	27.6	4.2	4.5	6.4	6.8
m_{Na^+}/m_{K^+}	6.8	46.99	7.2	7.6	10.8	11.6
$m_{Sr^{++}}/m_{Ca^{++}}$	0.081	0.008	0.079	0.079	0.072	0.070
$a_{Sr^{++}}/a_{Ca^{++}}$	0.081	0.008	0.079	0.079	0.072	0.070

TABLE II - (continued)

	Ground Water	Sea Water	1 99% Ground Water 1% Seawater	2 98% Ground Water 2% Seawater	3 90% Ground Water 10% Seawater	4 88% Ground Water 12% Seawater
$a_{CO_3^=}/a_{SO_4^=}$	2.97	2.68×10^{-3}	2.03×10^{-3}	1.60×10^{-3}	9.14×10^{-4}	8.65×10^{-4}

aragonite mud derived from normal seawater, will generate the high Ca^{++} and Sr^{++} contents shown in column one.

Table II reveals two significant features. For most of the ions in the table the addition of small amounts of seawater to the postulated groundwater will have little effect upon the concentration of those elements in the groundwater - seawater mixture compared to the pure groundwater; an exception is the content of $SO_4^=$ in the mixture which increases radically compared to the groundwater. Also, the ionic strength of the mixture solution is higher than that for groundwater, thus the activity coefficients of species are somewhat lower.

The major limiting factors on whether or not the solution will deposit celestite are the molalities of Sr^{++} and $SO_4^=$, and the ionic strength of the solution which, according to the extended Debye-Huckel equation (equation 4 page 36), controls the $\gamma^*_{Sr^{++}}$ and $\gamma^*_{SO_4^=}$, which in turn limits $a_{Sr^{++}}$ and $a_{SO_4^=}$ according to equation 1. The ionic strength and the molality of sulfate depend, essentially on the percentage of seawater in the mixture. The strontium concentration is limited by the molality of Ca^{++} because of the low value of partitioning coefficient $\overset{\circ}{K}{}^{cal}_{Sr^{++}}$ (= 0.14), the strontium content of the original aragonite and the rate of fresh water flow relative to the rate of aragonite - calcite inversion. The calcium concentration in turn depends on the pH and the quantity of HCO_3^- present. Therefore the limiting conditions for celestite deposition are an interrelated group of variables. From examination of Table II it appears that the prime characteristics needed for celestite deposition are a groundwater with a low HCO_3^- content (which allows a high Ca^{++} content at a given pH), a low Na^+/K^+ ratio, an aragonite mud of moderately high Sr^{++} content and sufficient time to maintain introduced groundwater solution at maximum Sr^{++} content. Calculations show that mixture of Table II having groundwater: seawater = 7.33 is just saturated with respect to celestite.

Finally, the crystal habit of the celestite may be determined by the amount of over-saturation with respect to celestite achieved in the system, bladed celestite occurring in the richer solutions (Baskakov, et al., 1969).

It is necessary to explain the simultaneous dissolution of calcite with the deposition of celestite evidenced by thin sections of the celestite - calcite contact. One possibility is that the solution is under-saturated with respect to aragonite or calcite. This intuitively may seem unlikely as the seawater is saturated with respect to calcite and so will be the groundwater, or nearly so. However, at the point where seawater and groundwater mix, the ionic strength rises rapidly, causing a relatively rapid drop in the stoichiometric activity coefficients of Ca^{++} and $CO_3^{=}$ to such a point that the solution becomes under-saturated with respect to calcite (this paper). Calculations show this to be the case with the postulated water composition of mixture 4. Thus carbonate dissolution will occur upon mixing at the interface.

If the carbonate mud in which the celestite formed was not of uniform susceptibility to the process of dissolution, isolated fragments of what would become limestone would be left in the celestite zone. Also, if the sediments were crossbedded and individual laminae were differentially soluble, cross-bedding might be preserved as observed at San Augustin (Figure 17).

The preceding process for deposition of celestite depends essentially on three things: the inflow of a low salinity, low HCO_3^- content water; the presence of a strontium-rich aragonite; and an interstitial sulfate-rich saline water. These environmental criteria apply to both the Mexican and the United States celestite deposits.

The only difference between the two varieties of deposits is that in the American deposits celestite probably formed by two mechanisms: the bulk of the ore by the process outlined above, and the "bowties" plus a few percent of the total celestite by the process mentioned under the discussion of the sabkha environment. By this method, the celestite could be formed by the sabkha process, generating "bowties" which could be followed or preceded by the main period of celestite mineralization. At any time, the solutions present could become undersaturated with respect to celestite causing deposition to cease and resolution of the celestite to occur.

Figure 17. Cross-bedding in a mine pillar assaying ~ 95% celestite, San Augustin mine, Coahuila, Mexico.

VIII. GUIDES FOR EXPLORATION

The proposed model suggests several criteria to apply to the search for celestite deposits. The need for aragonite as an original carbonate phase is the first. Likely marine environments are nearshore, shallow waters, shallow carbonate platforms such as the Bahamas, and possibly atolls. Tropical to temperate climates seem to favor the development of the necessary aragonite (Winland, 1969). In the marine environment Kinsman (1969a) indicates that the highest strontium values occur in aragonites, in oolitic aragonites and in lagoonal aragonitic muds. Therefore, such sediment types should be dominant in an exploration target for celestite ores. The most desirable continental environment is a saline lake deposit with considerable aragonite as the original carbonate phase.

To provide or enhance celestite deposition, the sediments must be exposed to fresh waters; therefore, they should be close to a shoreline, bordered by a carbonate provenance with little clastic material, and a low groundwater discharge rate.

In the United States, several post Precambrian areas are potential exploration targets. It should be noted, though, that the requirement of a nearshore environment restricts the possible localities considerably. Potential exploration areas may involve the interpretation that a carbonate bank may become emergent for a short period, subject the sediments to fresh water and resubmerge, all without creating a significant unconformity.

Potentially interesting formations are the Geneva and upper Grand Tower Fms. of Devonian age in Illinois and Indiana (Collinson, 1967); the Amsden Fm., Pennsylvanian age, in the Powder River Basin, Wyoming

(Wilson, 1962); and the Pennsylvanian Round Valley Ls. in southwestern Wyoming and northeastern Utah. Also in the Pennsylvanian, the limestone members of Virgilian age near paleo-highs in the central and northern Rocky Mountains are worthy of investigation (Williams, 1962). The Cambrian of the United States presents several possibilities, having extensive carbonate algal shoals and intertidal rock units (Lochman-Balk, 1971).

If in exploration for celestite, geochemistry is used to delineate terrains of high strontium content, it is important to determine if the strontium is in celestite, which would be favorable, or in the calcite, which would indicate that the strontium never had an opportunity to form celestite.

IX. SUGGESTIONS FOR FURTHER WORK

Three subjects have suggested themselves during the course of research for this thesis as deserving further work.

It has been observed during the course of this study that the celestite ores are frequently reported as being localized around paleo-highs and trend parallel to strike or dip, but not between the two extremes. This suggests that a hydrologic control because of structure localizing water flow, may have acted at the time of ore deposition. A study of this matter might add to further knowledge of celestite ore controls.

The second subject is the association of several deposits with saline materials, which may be a consequence of the need for a high strontium content in the original aragonite according to the model proposed above. If the Sr^{++} levels in the primary carbonate could be raised above the values Kinsman reports as typical, the likelihood of an ore deposit forming from the carbonate would be correspondingly raised. One situation under which this higher initial strontium content might occur is in a slightly restricted zone, such as a bay or lagoon, an assumption based entirely on the association of celestite deposits with moderately saline deposits. The validity of this hypothesis deserves testing.

An investigation into the sulfur isotope ratios present in the celestite ores might be useful. Such a study could substantiate the deposition model proposed in this study by indicating if the sulfur ratios present can be derived from seawater, in the case of the Mexican deposits, or saline lake waters, in the case of the American deposits.

Appendix A

Locations of Celestite Deposits Visited for This Thesis

1. Avawatz Mtns., California	approx. NW¼,Sec.5,T17N,R5E, San Bernadino Cnty., California
2. Gila Bend, Arizona	NW¼,Sec.9,T8S,R5W Maricopa Cnty., Arizona
3. Ludlow, California	S½,S½,Sec.19,T8N,R7E, approx. 6 miles west of Ludlow, California
4. Fish Creek Mtns., California	SW¼,NW¼,Sec.18,T13S,R9E, Imperial Cnty., Ludlow
5. San Augustin mine	approx. 30 miles north of Estation Marté, which is midway between Torreon, Coahuila and Saltillo, Coahuila, Mexico
6. Matamoros	approx. 10 miles NW of Matamoros, Coahuila, also approx. 10 miles from San Pedro, Coahuila, Mexico
7. Bermejillo South	approx. 5 miles WNW of Bermejillo, Durango, Mexico
8. Bermejillo North	approx. 13 miles NW of Bermejillo, Durango, Mexico

9. Escalon	approx. 7 miles NE of Escalon, Chihuahua, Mexico, in the Cerro De Los Remedios

Appendix B

Geochemical Data

all data for 25°C, 1 atm., $a_{H_2O}=1$

	reference
Miscellaneous Data	
$\overset{\circ}{K}{}^{\text{aragonite}}_{\text{Sr}^{++}} = 1.14$	1
$\overset{\circ}{K}{}^{\text{calcite}}_{\text{Sr}^{++}} = 0.14$	2
$\overset{\circ}{K}{}^{\text{gypsum}}_{\text{Sr}^{++}} = 0.18$	3
$\overset{\circ}{K}{}^{\text{anhydrite}}_{\text{Sr}^{++}} = 0.37$	3
Data for Seawater	
$a_{\text{Sr}^{++}} = 1.532 \times 10^{-6}$	4
$a_{\text{Ca}^{++}} = 2.548 \times 10^{-3}$	5
$a_{\text{CO}_3^{=}} = 4.860 \times 10^{-6}$	5
$a_{\text{SO}_4^{=}} = 1.814 \times 10^{-3}$	5
Data for calculation of $\overset{\circ}{\gamma}_{\text{Sr}^{++}}$	
$\overset{\circ}{a}_{\text{Sr}^{++}} = 5.0 \times 10^{8}$	6
$\overset{\circ}{a}_{\text{SrHCO}_3^{+}} = 5.0 \times 10^{8}$	7
$\overset{*}{\gamma}_{\text{SrSO}_4^{0}} = 1.2$	6
$\overset{*}{\gamma}_{\text{SrCO}_3^{0}} = 1.2$	6

Data for extended Debye-Hückel equation

$A = 0.5085$, $B = 0.3281 \times 10^{-8}$ (6), $B^{o} = 0.041$ (8)

Dissociation Constants

	log K	reference
$SrHCO_3^+$	- 1.2	9
$SrSO_4^0$	- 2.3	6
$SrCO_3^0$	- 3.1	9
Aragonite, $CaCO_3$	- 8.22	10
Calcite, $CaCO_3$	- 8.35	10
Strontianite, $SrSO_4$	- 9.6	10
Gypsum, $CaSO_4 \cdot 2H_2O$	- 4.6	10
Anhydrite, $CaSO_4$	- 4.5	10
Celestite, $SrSO_4$	- 6.5	10

The following reactions are used to construct Figures 12 and 13 as described in (6).

	log K for the reaction
1. $SrCO_3 + Ca^{++} \rightarrow CaCO_{3(ar.)} + Sr^{++}$	- 1.38
2. $SrCO_3 + Ca^{++} \rightarrow CaCO_{3(cal.)} + Sr^{++}$	- 1.25
3. $SrCO_3 + SO_4^{=} \rightarrow SrSO_4 + CO_3^{=}$	- 3.1
4. $CaCO_{3(ar.)} + SO_4^{=} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_3^{=}$	- 3.62
5. $CaCO_{3(ar.)} + SO_4^{=} \rightarrow CaSO_4 + CO_3^{=}$	- 3.72
6. $CaCO_{3(ar.)} + Sr^{++} + SO_4^{=} \rightarrow SrSO_4 + Ca^{++} + CO_3^{=}$	- 1.72
7. $CaCO_{3(cal.)} + SO_4^{=} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_3^{=}$	- 3.75
8. $CaCO_{3(ar.)} + SO_4^{=} \rightarrow CaSO_4 + CO_3^{=}$	- 3.85
9. $CaCO_{3(cal.)} + Sr^{++} + SO_4^{=} \rightarrow SrSO_4 + Ca^{++} + CO_3^{=}$	- 1.85

10.	$SrSO_4 + Ca^{++} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Sr^{++}$	- 1.9
11.	$SrSO_4 + Ca^{++} \rightarrow CaSO_4 + Sr^{++}$	- 2.0
12.	$CaCO_{3(ar.)} \rightarrow CaCO_{3(cal.)}$	0.13
13.	$CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$	0.1

1) Kinsman and Holland, 1969
2) Kinsman, 1969a
3) Butler, 1973
4) This paper
5) Garrels and Thompson, 1962
6) Garrels and Christ, 1965
7) Beane, pers. comm.
8) Helgeson, 1969
9) Sonderegger, 1974
10) Krauskopf, 1967

APPENDIX C. ADDITIONAL REFERENCES

Bray, Arthur; 1960; Mining Celestite; Canadian Mining Jour., Vol. 81, p. 68-69.

Brower, H. Elise; 1971; The Barite-Celestite Solid Solution: Measurement of Thermodynamic Properties and Discussion of Their Geochemical Implications; Ph.D. Dissertation, New Mexico Inst. of Mining and Tech., 78 p.

Butler, John C. and Sorrell, Charles A.; 1971; Thermal Expansion and the Orthorhombic-Cubic Transformation of $BaSO_4$ and $SrSO_4$; High Temperature Science, Vol. 3, p. 389-400.

Davis, James W. and Collins, A. Gene; 1971; Solubility of Barium and Strontium in Strong Electrolyte Solutions; Environmental Science and Technology, Vol. 5, No. 10, p. 1039-1043.

Grigor'ev, D. P.; 1961; Ontogeny of Minerals; translated from Russian by the Israel Program for Scientific Translations, Daniel Davey and Co., Inc.

Hamilton, Howard J.; 1950; Notes on the Occurrence of Celestite in Pennsylvania; Rocks and Minerals, Vol. 25, No. 7-8, p. 348-350.

Hanor, Jeffrey S.; 1968; Frequency Distribution of Compositions in the Barite-Celestite Series; Am. Mineral., Vol. 53, p. 1215-1222.

Harness, C. L.; 1949; Strontium Minerals; in Industrial Minerals and Rocks, ed. by S. Dolbear, A.I.M.E., 955 p.

Helz, G. R. and Holland, H. D.; 1965; The Solubility and Geologic Occurrence of Strontianite; Geoch. et Cosmoch. Acta, Vol. 29, p. 1303-1315.

Holland, H. D. et al.; 1963; The Co-precipitation of Sr^{++} with Aragonite and Ca^{++} With Strontianite between 70° and 100°C; Geoch. et Cosmoch. Acta, Vol. 27, p. 957-977.

Holland, H. D. et al.; 1964; The Co-precipitation of Cations with $CaCO_3$ - II: The Co-precipitation of Sr^{++} with Calcite Between 90° and 100°C; Geoch. et Cosmoch. Acta, Vol. 28, p. 1287-1301.

Horr, C. Albert; 1959; A Survey of Analytical Methods for the Determination of Strontium in Natural Water; U.S.G.S. Water-Supply Paper 1496-A, 18 p.

Isetti, Giovanni; 1970; Studio Sulla Colorazione della Celestina; Doriana (Supplemento agli Annali del Museo Civico di Sotria Naturale "G. Doria."); Genoa, Italy, Vol. 4, No. 194, 7 p.

Knopf, A.; 1918; Strontianite Deposits Near Barstow, California; U.S.G.S., Bull. 660, part I, 14 p.

Kraus , E. H.; 1905; The Occurrence and Distribution of Celestite-Bearing Rocks; Am. Jour. Sc., Vol. 19, p. 286-293.

Kraus , E. H. and Hunt, W. F.; 1906; The Occurrence of Sulfur and Celestite at Maybee, Michigan; Am. Jour. Sc., Vol. 21, p. 237-238.

Landes, Kenneth K.; 1929; The Strontium Occurrence Near La Conner, Washington; Am. Mineral., Vol. 14, p. 408-413.

Larsen, E. S. and Pardee, J. T.; 1929; The Stock of Alkaline Rocks Near Libby, Montana; Jour. of Geol., Vol. 37, p. 97-112.

Livingstone, Daniel A.; 1963; Data of Geochemistry, 6th ed., Chapter G: Chemical Composition of Rivers and Lakes; U.S.G.S., Prof. Paper 440-G, 64 p.

Lucchesi, P. J. and Whitney, E. D.; 1962; Solubility of Strontium Sulphate in Water and Aqueous Solutions of Hydrogen Chloride, Sodium Chloride, Sulphuric Acid and Sodium Sulphate by the Radiotracer Method; Jour. of Appl. Chem., Vol. 12, p. 277-279.

May, Irving et al.; 1961; Interaction of Anhydrite with Solutions of Strontium and Cesium; U.S.G.S., Prof. Paper 424-D, p. 336-338.

Maclean, Dermid; 1971; A New Source of Celestite; Rocks and Minerals, Vol. 46, No. 7-8, p. 435-438.

Mitchell, Richard S. and Pharr, Richard F.; 1961; Celestite and Calciostrontianite from Wise County, Virginia; Am. Mineral., Vol. 46, p. 189-195.

North, Neil; 1974; Pressure Dependence of $SrSO_4$ Solubility; Geoch. et Cosmoch. Acta, Vol. 38, p. 1075-1081.

Palache, C., Berman, H. and Frondel, C.; 1951; Dana's System of Minerology, Vol. II Seventh edition; John Wiley and Sons, Inc., p. 415-420.

Phalen, W. C.; 1914; Celestite Deposits in California and Arizona; U.S.G.S., Bull. 540, p. 521-533.

Schreck, Albert E. and Arundale, Joseph C.; 1959; Strontium: A Materials Survey; U.S. Bur. of Mines, Info. Circ. 7933, 45 p.

Sillen, L. G.; 1964; Stability Constants of Meta-Ion Complexes. Section I Inorganic Ligands; Chem. Soc. of London, Spec. Pub. 17, 754 p.

Townley, R. W. et al.; 1937; The Solubilities of Barium and Strontium Carbonates in Aqueous Solutions of Some Alkali Chlorides; Jour. of Am. Chem. Soc., Vol. 59, p. 631-632.

West, I. M.; 1964; Evaporite Diagenesis in the Lower Purbeck Beds of Dorset; Proc. Yorkshire Geol. Soc., Vol. 34, p. 315-326, 330.

unknown; 1943; Strontium in Michigan; Engineering and Mining Jour., Vol. 144, No. 6, p. 69.

REFERENCES CITED

Angino, Ernest E., et al.; 1966; Observed Variations in the Strontium Concentration of Sea Water; Chemical Geology, Vol. 1, p. 145-153.

Baskakov, M. P., et al.; 1969; Effect of Initial Concentration of Solution Components on the Form of Celestite Crystals; abstract from Chem. Abs., Vol. 72, reference number 104737y; from Uzbekskey Geologicheskiy Zhurnel, Vol. 13, No. 3, p. 52-55; 1969.

Berner, R. A.; 1966; Chemical Diagenesis of Some Modern Carbonate Sediments; Am. Jour. Sc., Vol. 264, p. 1-36.

Blatt, Harvey, Middleton, G. and Murray, R.; 1972; Origin of Sedimentary Rock; Prentice-Hall, 634 p.

Blount, Charles W. and Dickson, F. W.; 1968; Solubility of Celestite ($SrSO_4$) in H_2O from 50° to 250°C and 100 to 1500 Bars; abstract in Geol. Soc. of Am., Spec. Paper 101, p. 19-20.

Brown, D. W. et al.; 1962; Water-Resource Records of Brevard County, Florida; Florida Geol. Survey, Info. Circ. 32, 180 p.

Butler, Godfrey P.; 1973; Strontium Geochemistry of Modern and Ancient Calcium Sulphate Minerals; in The Persian Gulf, ed. by Bruce H. Purser, Springer-Verlag, 471 p.

Caldwell, W. E. and Waterman, G. H.; 1950; A Northwest Strontium Mineral Deposit; Science Monthly, Vol. 70, No. 4, p. 267-270.

Choo, Kangsoo; 1972; Celestite Mineralization at Enon Lake, Cape Breton County, Nova Scotia; Masters Thesis, Dalhousie University.

Collins, W. D. and Howard, C. S.; 1927; Chemical Character of Waters of Florida; U.S.G.S. Water-Supply Paper 596, p. 177-234.

Collinson, Charles, et al.; 1967; Devonian of the North-Central Region, United States; in International Symposium on the Devonian System, Calgary, 1967, Vol. 1; Alberta Society of Petroleum Geologists, Calgary, Alberta, Canada.

Crowell, G. D.; 1971; The Kaiser Celestite Operation at Loch Lomond; Canadian Mining and Metallurgical Bulletin, Vol. 64, No. 714, p. 48-52.

De Groot, K.; 1973; Geochemistry of Tidal Flat Brines at Umm Said, SE Qatar, Persian Gulf; in The Persian Gulf, ed. by Bruce H. Purser, Springer-Verlag, 471 p.

Dennis, W. E., Fine, M. M. and O'Meara, R. G.; 1947; Celestite Deposits, Brown, Nolan, Fisher and Coke Counties, Texas; U.S. Bur. Mines, Report of Invest. 4018, 16 p.

Durrell, Cordell; 1953; Geological Investigations of Strontium Deposits in Southern California; California Div. of Mines, Spec. Report 32, 48 p.

Evans, G. and Shearman, D. J.; 1964; Recent Celestine from the Sediments of the Trucial Coast of the Persian Gulf; Nature, Vol. 202, p. 385-386.

Fishburn, Maurice D. and Davis, John C.; 1962; Geology of the Celestite Deposits of Brown County, Kansas; Trans. of the Kansas Academy of Science, Vol. 65, No. 1, p. 47-60.

Folk, Robert L.; 1974; Petrology of Sedimentary Rocks; Hemphill Publishing Company, Austin, Texas, 182 p.

Forghami, Abdol-Hossein, et al.; 1973; The Celestine of Molkabade Mine, Dashte, Kavir. (Central Iran); Rocks and Minerals, Vol. 48, No. 2, p. 82-84.

Friedman, Gerald M.; 1964; Early Diagenesis and Lithification in Carbonate Sediments; Jour. of Sed. Pet., Vol. 34, No. 4, p. 777-813.

Garrels, R. M. and Thompson, M. E.; 1962; A Chemical Model for Sea Water at 25°C and One Atmosphere Total Pressure; Am. Jour. Sc., Vol. 260, p. 57-66.

Garrels, R. M. and Christ, C. L.; 1965; Solutions, Minerals and Equilibria; Harper and Row, 450 p.

Ginsburg, R. N. et al.; 1963; Shallow-water Carbonate Sediments; in The Sea, Vol. 3, ed. by M. N. Hill, Interscience Publishers, p. 554-582.

Graf, Donald L.; 1960; Geochemistry of Carbonate Sediments and Sedimentary Rocks; Ill. State Geol. Survey, Circ. 301, 71 p.

Green, Richard; 1971; Ohio Lime, Woodville; Rocks and Minerals, Vol. 46, No. 4, p. 280-281.

Hardin, G. C. and Thurston, W. R.; 1945; Celestite from Livingston County, Kentucky; Am. Mineral., Vol. 30, p. 639-640.

Helgeson, Harold C.; 1969; Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures; Am. Jour. Sc., Vol. 267, p. 729-801.

Holland, H. D.; 1967; Gangue Minerals in Hydrothermal Deposits; in Geochemistry of Hydrothermal Ore Deposits, ed. by Hubert L. Barnes, Holt, Rinehart and Winston, 670 p.

Howell, Benjamin; 1959; Introduction to Geophysics; McGraw-Hill Book Co., 399 p.

Jayaraman, N.; 1940; Origin of Celestite in the Cretaceous Beds of Trichy; Quart. Jour. Indian Inst. of Sci., Vol. 3, p. 22-27.

Johnson, Helgi; 1954; The Strontium Deposits of Port au Port Peninsula, Newfoundland; Canadian Geol. Survey Bull. 27, 19 p.

Kellum, L. B., et al.; 1936; Evolution of the Coahuila Peninsula, Mexico. Part I; G.S.A. Bull., Vol. 47, p. 969-1008.

Kelly, W. A.; 1936; Evolution of the Coahuila Peninsula, Mexico. Part II; G.S.A. Bull., Vol. 47, p. 1009-1038.

Kendall, Christopher and Skipworth, Patrick; 1968; Recent Algal Mats of a Persian Gulf Lagoon; Journal of Sedimentary Petrology, Vol. 30, p. 1040-1058.

Kesler, Thomas L.; 1944; Celestite in Buffalo Cove, Fentress County, Tennessee; Econ. Geol., Vol. 39, p. 287-309.

King, Robert E., et al.; 1944; Geology and Paleontology of the Permian Area Northwest of Las Delicias, Southwestern Coahuila, Mexico; G.S.A. Spec. Paper 52, p. 1-172.

Kinsman, David; 1969a; Interpretation of Sr^{++} concentrations in Carbonate Minerals and Rocks; Jour. of Sed. Pet., Vol. 39, No. 2, p. 486-508.

Kinsman, David; 1969b; Modes of Formation, Sedimentary Associations, and Diagnostic Features of Shallow-Water and Supratidal Evaporites; A.A.P.G. Bull., Vol. 53, No. 4, p. 830-840.

Kinsman, David and Holland, H. D.; 1969; The Co-precipitation of Cations with $CaCO_3$ - IV: The Co-precipitation of Sr^{++} with Aragonite Between 16° and 96°C; Geoch. et Cosmoch. Acta, Vol. 33, p. 1-17.

Krauskopf, Konrad; 1967; Introduction to Geochemistry; McGraw-Hill, 721 p.

Krieger, Philip; 1933; The Occurrence of Strontianite at Sierra Mojada, Mexico; Am. Mineral., Vol. 18, p. 345-350.

Kulp, Laurence, et al.; 1952; Strontianite Content of Limestones and Fossils; G.S.A. Bull., Vol. 63, p. 701-716.

Leve, Gilbert W.; 1968; Reconnaissance of the Ground-Water Resources of Baker County, Florida; Florida Geol. Survey, Report of Invest. 52, 24 p.

Lisitzin, Alexander P.; 1972; Sedimentation in the World Ocean; Soc. of Econ. Paleont. and Mineral., Spec. Paper 17, 218 p.

Lochman-Balk, Christina; 1971; The Cambrian of the Craton of the United States; in Cambrian of the New World, ed. by C. H. Holland; Wiley-Interscience, 456 p.

Logan, B. W., Rezak, R. and Ginsburg, R. N.; 1964; Classification and Environmental Significance of Algal Stromatolites; Jour. of Geol., Vol. 72, p. 68-83.

Moore, B. N.; 1935; Some Strontium Deposits of California and Arizona; A.I.M.E. Trans., Vol. 115, p. 356-377.

Morrison, Roger B., 1935; The Occurrence and Origin of Celestite and Fluorite at Clay Center, Ohio; Am. Mineral., Vol. 20, p. 780-790.

Müller, G. and Puchelt, H.; 1961; Die Bildung von Coelestin aus Meerwasser; Naturwissenschaften, Vol. 48, p. 301-302.

Odum, Howard; 1951; The Stability of the World Strontium Cycle; Science, Vol. 114, p. 407-411.

Park, Charles F. and MacDiarmid, Roy A.; 1964; Ore Deposits; W. H. Freeman and Company, 522 p.

Park, P. Kilho; 1972; Seawater; in Water and Aqueous Solutions: Structure, Thermodynamics, and Transport Processes, ed. by R. A. Horne, Wiley-Interscience, 837 p.

Rodgers, John; 1957; The Distribution of Marine Carbonate Sediments: A Review; in Regional Aspects of Carbonate Deposition; Soc. of Econ. Paleont. and Mineral., Spec. Pub. No. 5, 178 p.

Roedder, Edwin; 1962; Studies of Fluid Inclusions 1: Low Temperature Application of a Dual-Purpose Freezing and Heating Stage; Econ. Geol., Vol. 57, p. 1045-1061.

______________; 1967; Fluid Inclusions as Samples of Ore Fluids; in Geochemistry of Hydrothermal Ore Deposits, ed. by H. L. Barnes, Holt, Rinehart and Winston, Inc., 670 p.

______________; 1969; Varvelike Banding of Possible Annual Origin in Celestite Crystals from Clay Center, Ohio, and in Other Minerals; Am. Mineral., Vol. 54, p. 796-810.

Schmalz, Robert F.; 1969; Deep-Water Evaporite Deposition: A Genetic Model; A.A.P.G. Bull., Vol. 53, No. 4, p. 798-823.

Shearman, D. J.; 1966; Origin of Marine Evaporites by Diagenesis; Inst. of Mining and Met. Trans., Vol. 75, p. 208-215.

Skougstad, Marvin W. and Horr, C. Albert; 1963; Occurrence and Distribution of Strontium in Natural Water; U.S.G.S. Water-Supply Paper 1496-D, p. 55-97.

Sonderegger, John L.; 1974; A Preliminary Investigation of the Dissolution Kinetics of Strontianite and Witherite; Ph.D. Dissertation, New Mexico Inst. of Mining and Tech. 100 p.

Stewart, Fredrick H.; 1963; Data of Geochemistry, 6th ed., Chapter Y: Marine Evaporites; U.S.G.S. Prof. Paper 440-Y, 53 p.

Summers, W. K., Schwab, G. E. and Brandvold, L. A.; 1972; Ground-Water Characteristics in a Recharge Area, Magdalena Mountains, Socorro County, New Mexico; New Mexico Bur. of Mines and Mineral Resources, Circ. 124, 18 p.

Thomas, I. A.; 1973; Celestite: Including References to Strontianite; Mineral Dossier No. 6, Mineral Resources Consultative Committee, 9 p.

Turekian, Karl K. and Kulp, J. Laurence; 1956; The Geochemistry of Strontium; Geoch. et Cosmoch. Acta, Vol. 10, p. 245-296.

Veizer, Jan and Domovic, Rudolf; 1974; Strontium as a Tool In Facies Analysis; Jour. of Sed. Pet., Vol. 44, No. 1, p. 93-115.

Ver Planck, W. E.; 1952; Gypsum in California; California Div. of Mines, Bull. 163, 151 p.

________________; 1954; Geology of Southern California, Chapter 8; California Division of Mines, Bull. 170, Vol. 1, 74 p.

Wagner, C. W. and Van der Togt, C.; 1973; Holocene Sediment Types and Their Distribution in the Southern Persian Gulf; in The Persian Gulf, ed. by Bruce H. Purser, Springer-Verlag, 471 p.

White, D. E.; 1965; Saline Waters of Sedimentary Rocks; A.A.P.G., Mem. 4, p. 342-366.

Williams, Frank E., Fillo, P. V. and Bloom, P. A.; 1964; Barite Deposits of New Mexico; New Mexico Bur. of Mines and Mineral Resources, 46 p.

Williams, J. Stewart; 1962; Pennsylvanian in Central and Northern Rocky Mountains; in Pennsylvanian System in the United States, ed. by Carl C. Branson, A.A.P.G., 505 p.

Wilson, Philo C.; 1962; Pennsylvanian Stratigraphy of Powder River Basin and Adjoining Areas; in Pennsylvanian System in the United States, ed. by Carl C. Branson, A.A.P.G., 505 p.

Winland, H. Dale; 1969; Stability of Calcium Carbonate Polymorphs in Warm, Shallow Seawater; Jour. of Sed. Pet., Vol. 39, No. 4, p. 1579-1587.

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