

# Trace and Minor Element Variations in the Permian Castile Formation, Delaware Basin, Texas and New Mexico, Revealed by Varve Calibration

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## ABSTRACT

*Calcite-anhydrite varve couplets of the Castile Formation provide a means of calibrating chemical changes which occurred within the Delaware Basin over a period of at least 260,000 years. In addition, individual varve laminae can be correlated for at least 113 km providing close stratigraphic control for observing lateral changes over a wide area.*

*Varve calibration and correlation show that changes in water chemistry, as recorded in short- and long-term variations in major components and trace and minor elements, often occurred rapidly and were synchronous over large areas of the basin. For example, change from predominantly sulfate deposition to predominantly carbonate deposition occurred within a few tens of years as the result of a marked decrease in the rate of sulfate precipitation, and not an increase in the rate of carbonate precipitation. As the rate of sulfate precipitation decreased, the amount of a particular trace or minor element co-precipitated with a unit volume of anhydrite increased by as much as several orders of magnitude, but the actual amount of that element removed from the water per unit time actually decreased. This suggests that trace element incorporation in evaporite minerals may be more closely controlled by precipitation kinetics than by concentration of the element in the aqueous phase.*

## INTRODUCTION

Anderson, et al. (1972) established a detailed varve calibration for the entire Castile Formation (Upper Permian) in the Delaware Basin of Texas and New Mexico. This calibration is based on the assumption that each remarkably distinct couplet of interlaminated calcite-anhydrite or anhydrite-halite represents an annual increment of sedimentation. Anderson and Kirkland (1966), Kirkland and Anderson (1970), and Anderson, et al.

(1972) further demonstrated that individual varve laminae are stratigraphically correlative in cores separated by distances of as much as 113 km, and are probably correlative over most of the basin. The lamination process begins in the pre-evaporite formations underlying the Castile, continues throughout the Castile and into the overlying evaporites of the Salado Formation. In the eastern portion of the basin, the Castile can be subdivided into three halite members and four anhydrite members. In the western portion of the basin, halite units have been dissolved leaving beds of solution breccia (Figure 2). Based on varve calibration, approximately 154,200 years during Castile time were involved in predominantly  $\text{CaSO}_4$  deposition, and approximately 20,700 years involved in predominantly  $\text{NaCl}$  deposition. Within a particular anhydrite member, there are usually a number of salinity cycles represented mainly by variations in relative proportions of calcite and anhydrite. A complete salinity cycle begins with interlamination of organically stained calcite laminae and very thin anhydrite laminae with calcite more abundant than anhydrite. With increasing salinity, more anhydrite is added, and anhydrite becomes the dominant component in the typical calcite-banded anhydrite of the Castile. Further along the salinity cycle, the anhydrite becomes nodular, and, in a complete salinity cycle, the nodular anhydrite is overlain by halite with interlaminae of anhydrite. Correlation of individual laminae has shown that the onset, progression and termination of these salinity cycles occur at approximately the same time in all cores examined for distances up to 113 km.

The purpose of this paper is to examine in detail a part of one of these salinity cycles to determine what effect increasing and decreasing rates of carbonate and sulfate deposition has on the incorporation of trace and minor elements in these two phases. By studying details of the same cycle in three different cores separated by up to 30

km, it was possible to observe regional variations in composition, and in the rate and timing of calcium carbonate and calcium sulfate deposition. Stratigraphic variations in certain trace element concentrations throughout the entire Castile-lower Salado evaporite sequence were also examined. Locations of the cores used for this study are shown in Figure 1.

### METHODS

Prior to analyses, all cores were slabbed, polished, and photographed. Thicknesses of individual calcite-anhydrite varve couplets were measured on enlarged photographs of the cores. Figure 2 shows the thicknesses of varve couplets for the entire 260,000 year time series involving the upper part of the Bell Canyon Formation, all of the Castile Formation, and the lower part of the Salado Formation.

Samples for analyses were cut from the cores at 50-couplet intervals. Detailed short-term analyses were made using this 50-couplet interval. For analyses of long-term variations, a 400-couplet sample interval was obtained by

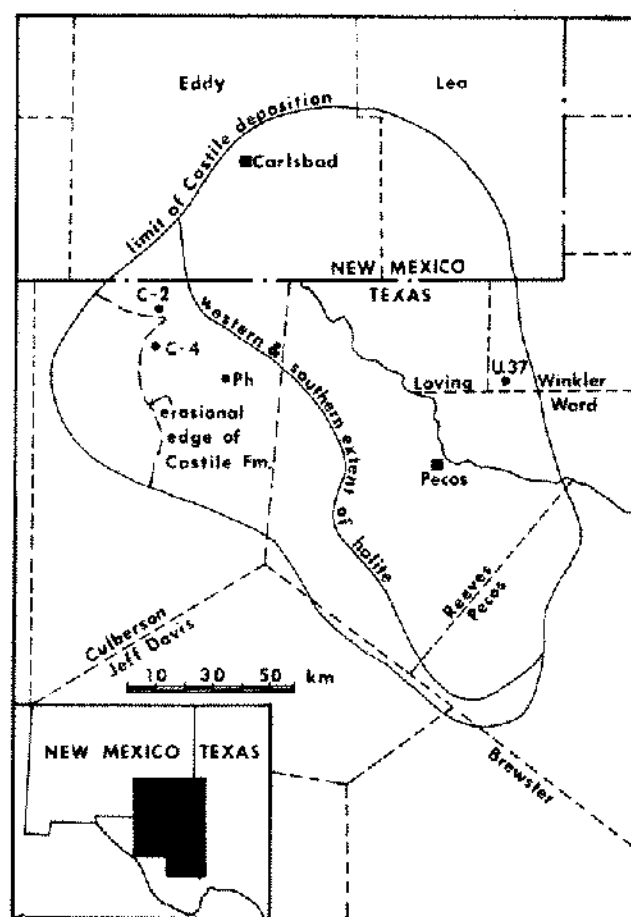


Figure 1. Index map showing the locations of cores used in this investigation. C-2: Cowden no. 2 well; C-4: Cowden no. 4 well; Ph: Phillips no. 1 well; U-37: Union-University "37" no. 4 well. (For more detailed information on core locations, see Anderson, et al., 1972).

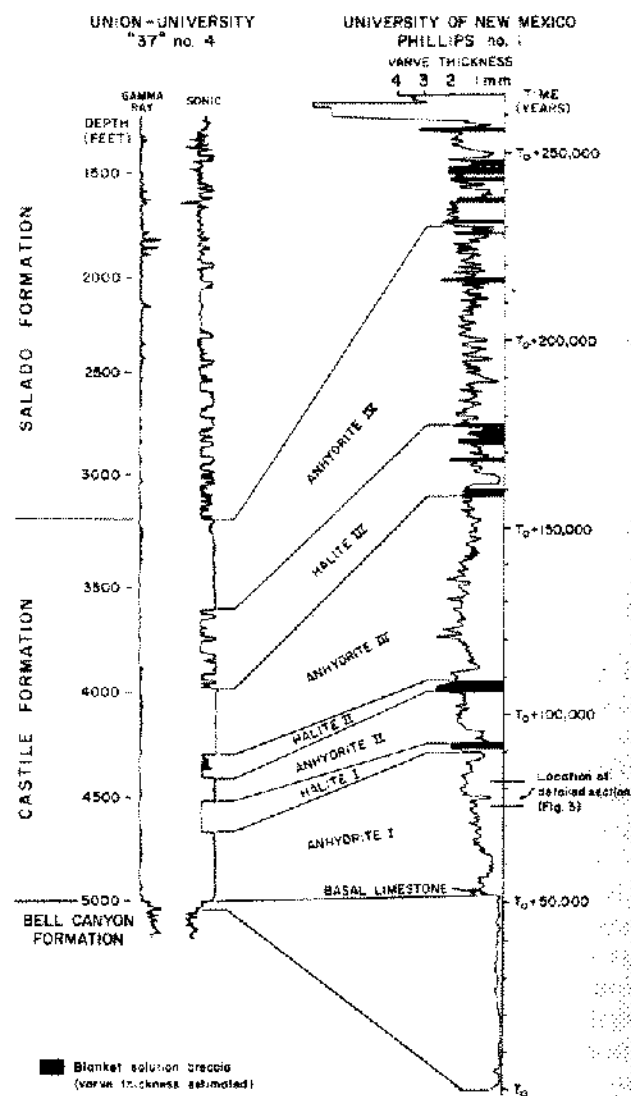


Figure 2. Correlation between gamma ray and sonic logs of the Union-University well and smoothed calcite-anhydrite couplet thickness in the Phillips no. 1 core. Couplet thicknesses are estimated for halite units. (after Anderson, et al., 1972).

homogenizing 8, 50-couplet samples. Preliminary results demonstrated that for resolving long-term variations, very little detail was gained by using a sampling interval shorter than 400 couplets.

All samples are referenced to the master sequence shown in Figure 2. For example, a designation  $T_0 + 25,370 - 25,419$ , Anhydrite I refers to a 50-couplet sample beginning 25,370 couplets above the base of the Anhydrite I Member of the Castile Formation (Fig. 2).

The relative amounts (percent) of organic matter and carbonate in each sample were determined by controlled weight loss on ignition at  $550^\circ\text{C}$  and  $1000^\circ$  respectively. Percent anhydrite was taken as the difference between 100 percent and the sum of organic matter and carbonate percentages (Dean, 1974).

Concentrations of Sr, Mg, Na, and K were determined with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. Whole-rock samples were prepared by dissolving the untreated carbonate-sulfate sample in hot HCl. Anhydrite samples were obtained by dissolving the carbonate fraction in dilute acetic acid. After washing and drying, the anhydrite residue was then dissolved in hot HCl for analysis.

Most chemical and mineralogic analyses are presented as a percent of a certain volume or weight of material. However, the main advantage of a varve sequence is that samples can be collected at equal time intervals even though the amount of material deposited per unit time varies considerably. It is possible, therefore, to convert relative values (percent or ppm), obtained from chemical analyses, into absolute values such as mm  $\text{CaSO}_4$  deposited in 50 years, or mg Sr co-precipitated with  $\text{CaSO}_4$  per  $\text{cm}^2$  per 50 years.

## RESULTS

### Short-term variations

Plots of smoothed couplet thickness for the Anhydrite I,  $T_0 + 24,788 - 26,638$  zone in the Cowden no. 2, Cowden no. 4, and Phillips no. 1 cores of the Castile Formation are shown in Figure 3 (see Figure 2 for location of this zone

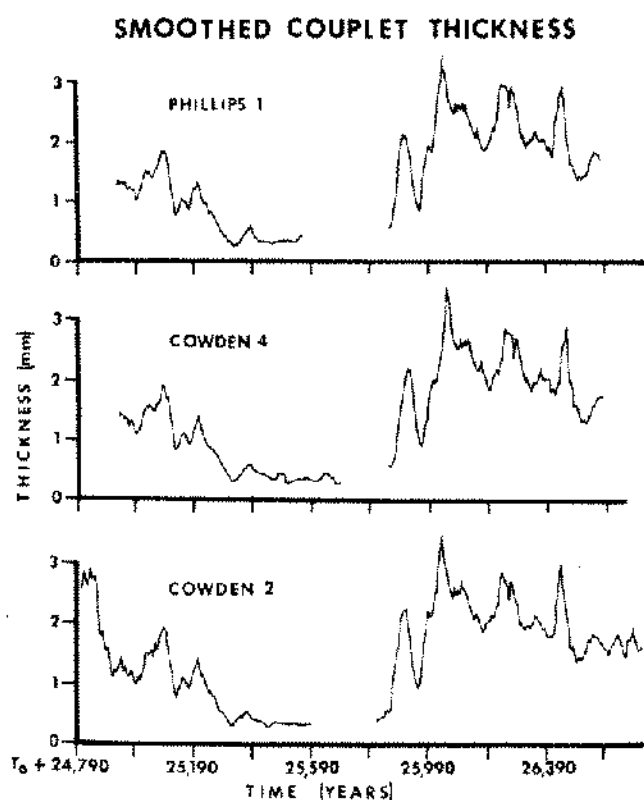


Figure 3. Plots of smoothed carbonate-sulfate couplet thickness for the  $T_0 + 24,788 - 26,638$  zone of Anhydrite I, Cowden no. 2, Cowden no. 4, and Phillips no. 1 cores of the Castile Formation (see Fig. 2 for location in the master time series).

in the master time series). This zone was chosen for detailed analyses because it contains rapid lithologic changes. Within a period of about 100 couplets, the petrology changes from a sequence of typical Castile calcite-banded anhydrite to a laminated limestone. The laminated limestone then grades into an overlying thin nonlaminated limestone which changes back to typical calcite-banded anhydrite within a few tens of couplets. As shown in Figure 3, these changes are essentially synchronous in all three cores. Figure 4 shows that as the couplets become thinner,  $\text{CaCO}_3$  increases from less than 20 percent to more than 80 percent. However, the absolute curves (Fig. 4) show that the change to limestone does not represent an increase in the rate of  $\text{CaCO}_3$  precipitation (expressed as mm  $\text{CaCO}_3$  per 50 years), but rather a rapid decline in the rate of  $\text{CaSO}_4$  precipitation. In fact, the absolute amount of  $\text{CaCO}_3$  actually decreases in the laminated limestone.

The sudden change from predominantly sulfate deposition to predominantly carbonate deposition is interpreted as a decrease in salinity within the basin due to influx of more normal marine water resulting in a decrease in rates of precipitation of both calcite and anhydrite. This conclusion is supported by isotopic data which show that  $\delta\text{O}^{18}$

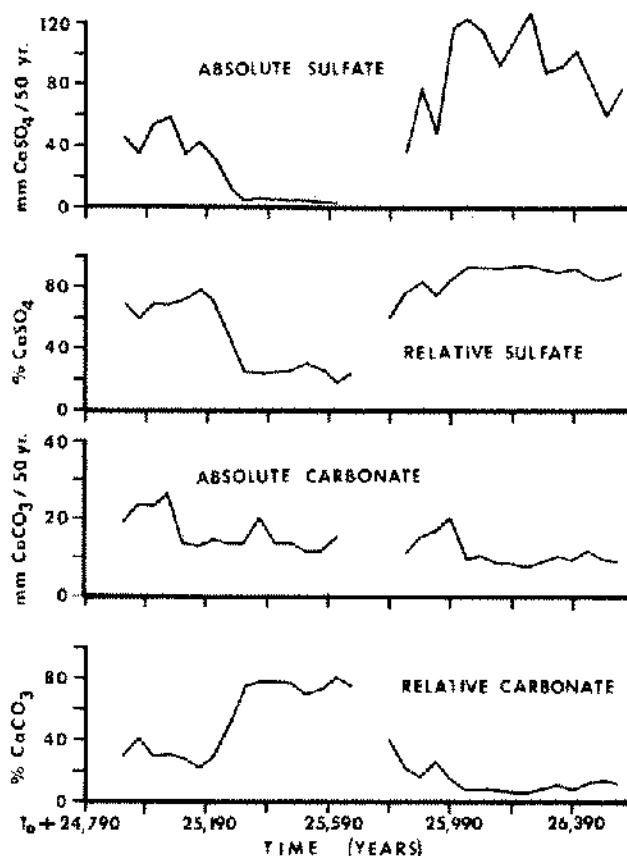


Figure 4. Plots of relative and absolute  $\text{CaCO}_3$  and  $\text{CaSO}_4$  for the  $T_0 + 24,788 - 26,638$  zone of Anhydrite I, Cowden 4 core of the Castile Formation.

decreases by approximately  $1.5^{\circ}/\infty$  (i.e. becomes lighter) in the laminated limestone, and then increases as sulfate deposition once again predominates. A marked decrease in salinity should be accompanied by a decrease in concentrations of Mg, Sr, and K in the water, and result in a decrease in the concentrations of these elements in mineral phases precipitating from the water. However, Figures 5-7 show that the concentrations of these elements in anhydrite and whole-rock samples actually *increase* during low sulfate deposition. Conversely, with increased rate of  $\text{CaSO}_4$  precipitation, the concentrations of Mg, Sr, and K in mineral phases decreased although the amount of a particular element removed per unit time (absolute value) increased. These results are also shown by the strong negative correlation coefficients between percent sulfate and concentrations of Mg, Sr, and K in both anhydrite and whole rock samples (Table I).

A comparison of correlation coefficients (Table II) computed from analyses of carbonate, organic matter, sulfate, Sr, Mg, and K in correlative samples from three cores from the Castile Formation shows remarkable lateral continuity of chemical changes. Of the major components, the organic content is the most variable between cores. Mg is the most variable of the minor elements. Stratigraphic variations in Mg concentration may range over three orders of magnitude whereas concentrations of the other elements are much more constant. Between cores, Mg

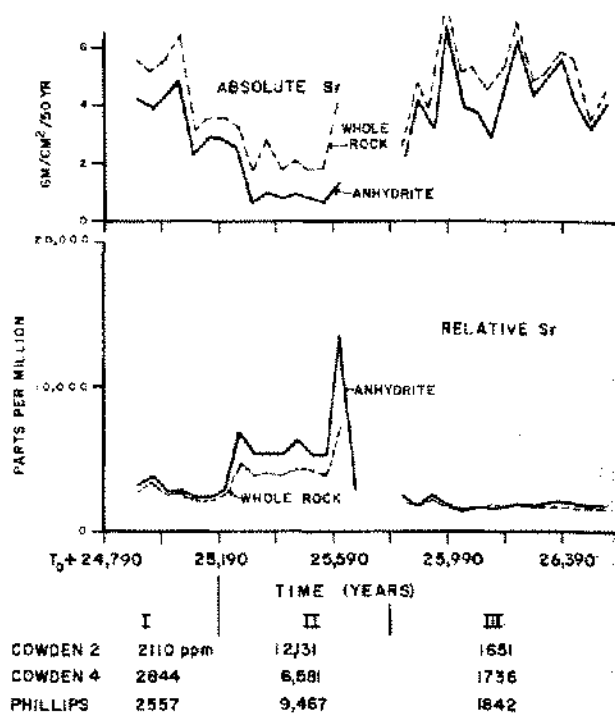


Figure 5. Plots of relative and absolute Sr in anhydrite and whole-rock samples for the  $T_0 + 24,788$ –26,638 zone of Anhydrite I, Cowden no. 4 core of the Castile Formation. Mean values for three parts of this sequence in three different cores are given below the curve for relative Sr.

TABLE I

Correlation coefficients for 50-couplet samples from Anhydrite I,  $T_0 + 24,788$ –26,638, Cowden no. 4 core of the Castile Formation.

Variables:												
1	2	3	4	5	6	7	8	9	10	11	12	13
1 =	2 =	3 =	4 =	5 =	6 =	7 =	8 =	9 =	10 =	11 =	12 =	13 =
couplet thickness	relative (percent) carbonate	relative (percent) organic	relative (percent) sulfate	absolute (mm/50 yr) carbonate	absolute (mm/50 yr) organic	absolute (mm/50 yr) sulfate	ppm Sr (anhydrite)	ppm Mg (anhydrite)	ppm K (anhydrite)	ppm Sr (whole rock)	ppm Mg (whole rock)	ppm K (whole rock)
2	-0.87											
3	0.24	-0.01										
4	0.87	-1.00	0.07									
5	-0.24	0.35	-0.42	-0.35								
6	0.77	-0.63	0.77	0.63	-0.42							
7	0.99	-0.89	0.28	0.88	-0.36	0.79						
8	-0.82	0.94	-0.04	-0.94	0.30	-0.57	-0.83					
9	-0.77	0.93	0.06	-0.93	0.30	-0.50	-0.78	0.86				
10	-0.77	0.93	-0.01	-0.93	0.10	-0.53	-0.75	0.90	0.86			
11	-0.84	0.94	-0.06	-0.94	0.38	-0.58	-0.86	0.99	0.86	0.86		
12	-0.62	0.67	0.16	-0.67	0.31	-0.34	-0.64	0.67	0.84	0.53	0.70	
13	-0.75	0.91	0.05	-0.91	0.26	-0.53	-0.75	0.83	0.83	0.88	0.82	0.55

N = 28; 99% confidence limits =  $\pm 0.50$ ; values which are significant at the 99% level are underlined. Thickness values are summations of 10 individual laminae; carbonate, organic matter, and sulfate were determined by loss on ignition; trace elements were determined by atomic absorption.

TABLE II

Correlation coefficients for 50-couplet samples from Anhydrite I,  $T_0 + 24,788$ –26,638, Cowden no. 2, Cowden no. 4, and Phillips no. 1 cores of the Castile Formation.

Variable	Cowden 2 vs. Cowden 4	Cowden 2 vs. Phillips	Cowden 4 vs. Phillips
Couplet thickness	0.99	0.99	0.99
Percent $\text{CaCO}_3$	0.99	0.99	0.99
Percent Organic	-0.01	0.81	-0.09
Percent $\text{CaSO}_4$	0.99	0.99	0.99
Absolute $\text{CaCO}_3$	0.93	0.94	0.95
Absolute Organic	0.54	0.86	0.55
Absolute $\text{CaSO}_4$	0.99	0.99	0.99
ppm Sr	0.74	0.69	0.77
ppm Mg	0.46	0.29	0.91
ppm K	0.89	0.75	0.85

N = 28; 99% confidence limits =  $\pm 0.50$

Values which are significant at the 99% level are underlined. Thickness values are summations of 50 individual couplets; percent carbonate, organic, and sulfate were determined by loss on ignition; absolute carbonate, organic, and sulfate were calculated by multiplying the percent value by couplet thickness; ppm Sr, Mg, and K were determined by atomic absorption.

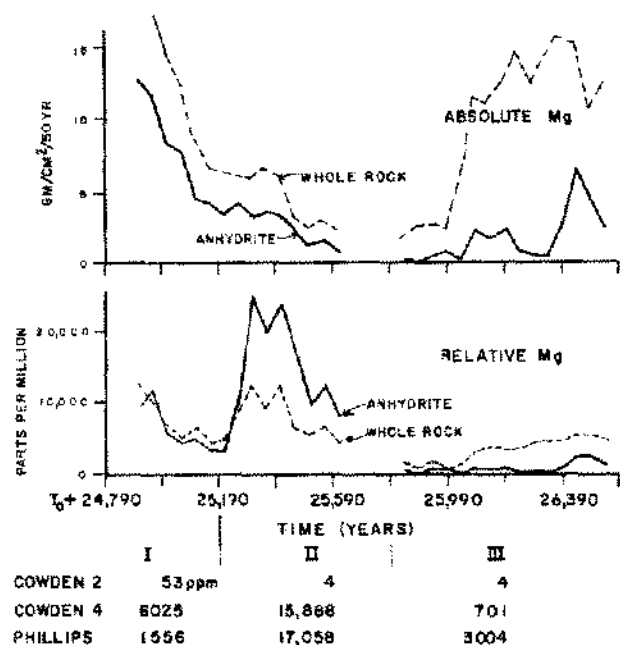


Figure 6. Plots of relative and absolute Mg in anhydrite and whole-rock samples for the  $T_0 + 24,788$ –26,638 zone of Anhydrite I, Cowden no. 4 core of the Castile Formation. Mean values for three parts of the sequence in three different cores are given below the curve for relative Mg.

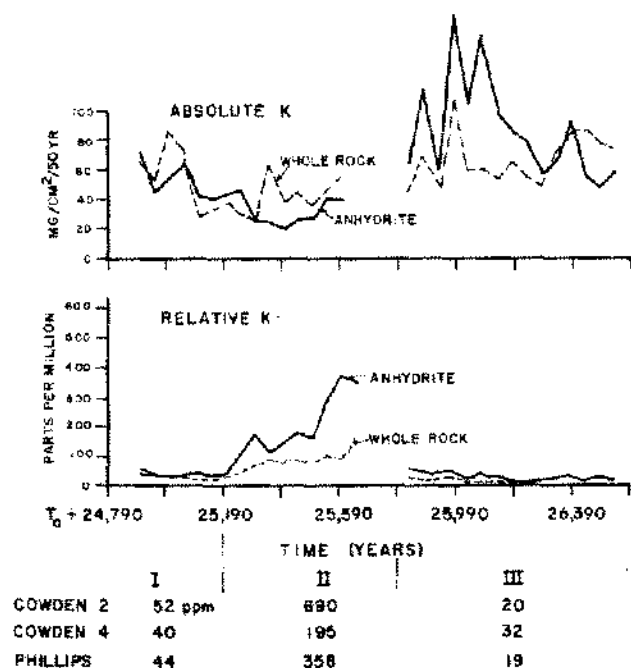


Figure 7. Plots of relative and absolute K in anhydrite and whole-rock samples for the  $T_0 + 24,788$ –26,638 zone of Anhydrite I, Cowden 4 core of the Castile Formation. Mean values for three parts of the sequence in three different cores are given below the curve for relative K.

concentrations may also vary several orders of magnitude even within correlative 50-couplet groups. For example, the lack of correlation (Table II) between Mg concentrations in the Cowden no. 2 core and either the Cowden no. 4 or Phillips no. 1 core is due to the fact that the Mg concentration in the Cowden no. 2 core is consistently several orders of magnitude lower than in either of the other two cores (Fig. 6). Some of the variability in Mg concentration is due to actual differences in Mg concentrations in the anhydrite, but some of the variability is also due to the presence of minor amounts of dolomite. Although most of the carbonate in the Castile is calcite, and no dolomite has been identified by X-ray diffraction, occasional small dolomite crystals have been observed within anhydrite using an electron probe (Fig. 8). Note also (Fig. 8) that the Sr concentration is evenly distributed among the three phases (calcite, dolomite, and anhydrite) whereas the Mg concentration is clearly different. In general, the Mg concentration is greater in calcite than in anhydrite as evidenced by the distribution of Mg (Fig. 8), and by the fact that whole-rock Mg concentrations are generally greater than anhydrite Mg concentrations.

The results plotted in Figures 3–7 show that most chemical changes occurred at approximately the same time and to the same extent in all three cores. Although analyses have not yet been made on correlative samples from the Union-University core, the remarkable similarity in thickness variations between the Union-University core in the eastern portion of the Delaware Basin and cores

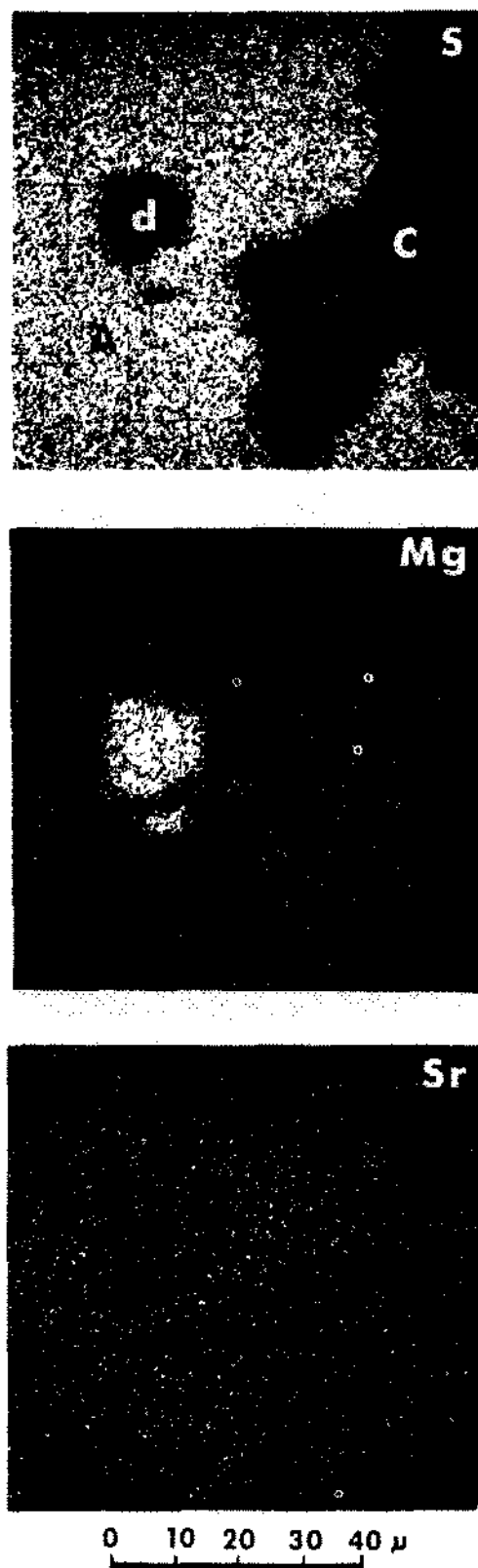


Figure 8. Electron probe X-ray images for S, Mg, and Sr in caliche (C) and anhydrite (A) laminae from the Castile Formation. A rare dolomite crystal (d) is indicated by the high Mg, low S phase.

from the western portion of the basin over 100 km away (Anderson, et al., 1972) suggests that chemical changes within the basin occurred rapidly, and affected the entire basin at approximately the same time. For example, the onset of deposition of the Halite I Member of the Castile began only 15 years earlier in the eastern portion of the basin than in the western portion (Anderson, et al., 1972). This synchronicity of chemical change demonstrates that the classical model of laterally zoned evaporite facies described by Scruton (1953), Briggs (1957), Stewart (1963), Schmalz (1969), and others may not be entirely valid, at least for the Delaware Basin. According to this model, precipitation of halite in the more distal portions of the basin is contemporaneous with sulfate deposition near the center of the basin, and with carbonate deposition closer to the marine inlet. With time and increasing salinity, the depocenters of these facies shift toward the inlet so that a halite bed would be time transgressive and become progressively older toward the distal portions of the basin. Although there is some lateral time zonation within the Castile, for the most part the onset and termination of anhydrite and halite deposition occurred in response to chemical changes which affected most of the basin at essentially the same time.

#### Long-term variations

Analyses of short-term (1000–3000 years) variations revealed an inverse relationship between salinity (as indicated by rate of sulfate precipitation) and trace and minor element concentrations in precipitated mineral phases. To determine if this relationship holds over the entire evaporite sequence, the results of 510, 400-couplet whole-rock samples covering all of the Castile Formation and the basal portion of the Salado Formation, a total of 204,000 years, can be considered.

There is a qualitative difference in the magnitude of salinity oscillations in the first and second halves of the Castile-lower Salado sequence (compare Anhydrites I, II, and III with Anhydrite IV and lower Salado in Fig. 2). Consequently, the correlation coefficients given in Table III were computed on separate halves of the sequence. Coefficients for the lower half of the sequence are the upper set of numbers in each row; the lower set of numbers in each row are correlation coefficients for the upper half of the sequence. Means and standard deviations for concentrations of  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ , Sr, Na, K and Mg in 255 whole rock samples from each half of the sequence are given in Table IV.

The weakest correlations in Table III are for Mg. This undoubtedly is due to the fact that Mg is much more variable than any of the other elements on both a short-term and long-term basis (Fig. 6). Relative concentrations of all four elements tend to be positively correlated with each other, with Na showing the strongest correlations. In

TABLE III

Correlation coefficients for 400-couplet samples from the lower and upper halves of the Castile-lower Salado varved evaporite sequence. Upper set of numbers in each row is for the first half of the sequence; lower set is for the second half. Only coefficients significant at the 95% confidence level ( $\pm 0.125$ ,  $N = 255$ ) are included.

		CaCO <sub>3</sub>	CaSO <sub>4</sub>	Sr	Na	K
ABSOLUTE (mm per year)	CaSO <sub>4</sub>	-----	-----	-----	-----	-----
		-----	-.46	-----	-----	-----
	Sr	+0.19	+0.62	-----	-----	-----
		+0.15	+0.33	-----	-----	-----
	Na	-----	-.61	+0.38	-----	-----
		-----	-.51	+0.49	-----	-----
RELATIVE (percent)	K	-----	-.57	+0.30	+0.35	-----
		-----	-.55	+0.19	+0.24	-----
	Mg	-----	-.28	-.26	+0.66	-----
		-----	-.26	-----	+0.47	+0.15
	CaSO <sub>4</sub>	-----	-----	-----	-----	-----
		-----	-.99	-----	-----	-----
RELATIVE (percent)	Sr	+0.67	-.67	-----	-----	-----
		+0.87	-.88	-----	-----	-----
	Na	-----	-----	-----	-----	-----
		-----	-.71	+0.68	-----	-----
	K	+0.13	-.13	+0.18	-----	-----
		+0.53	-.53	+0.52	+0.33	-----
RELATIVE (percent)	Mg	-----	-----	-----	-.64	-.25
		-----	-----	-----	-.28	+0.16

general, the correlations are best developed in the upper half of the sequence. Also in the upper half, Sr, Na, and K all have strong positive correlations with percent CaCO<sub>3</sub>; Sr is the only element which shows a strong positive correlation with CaCO<sub>3</sub> in the lower half of the sequence. Because we are dealing with essentially a two component system (CaCO<sub>3</sub> and CaSO<sub>4</sub> with minor organic matter), a strong positive correlation of an element with one component results in a strong negative correlation with the other component, in this case CaSO<sub>4</sub>.

Variations in the degree of association between CaSO<sub>4</sub> and a particular trace element over the entire 204,000-year time period can be observed using moving correlation coefficients (Figs. 9-10). For this computation, a time interval of 8,800 years was chosen (i.e. 22 samples of 400 years each). A correlation coefficient is calculated for a pair of variables (e.g. percent CaSO<sub>4</sub> vs. ppm Sr) in samples 1-22, then in samples 3-24, 5-26, and so on. The results can then be plotted to show changes in association between the two variables with time. The plot of relative CaSO<sub>4</sub> vs. relative Sr (Fig. 9A) shows that for the lower half of the sequence the two variables are usually negatively correlated, although there are long periods of time

TABLE IV

Means and standard deviations for % CaCO<sub>3</sub>, % CaSO<sub>4</sub>, ppm Sr, ppm Mg, ppm Na, and ppm K in 510, 400 couplet samples from the Castile-lower Salado varved evaporite sequence.

	CaCO <sub>3</sub> (%)	CaSO <sub>4</sub> (%)	Sr (ppm)	Mg (ppm)	Na (ppm)	K (ppm)
First Half: (N = 255)						
mean	15.6	84.3	1010	4788	307	17
$\sigma$	$\pm 12.2$	$\pm 12.2$	$\pm 456$	$\pm 3054$	$\pm 121$	$\pm 20$
Second Half: (N = 255)						
mean	14.7	85.1	1196	2637	254	13
$\sigma$	$\pm 14.3$	$\pm 14.4$	$\pm 893$	$\pm 2304$	$\pm 105$	$\pm 13$
Total: (N = 510)						
mean	15.1	84.7	1103	3713	280	15
$\sigma$	$\pm 13.3$	$\pm 13.3$	$\pm 675$	$\pm 2679$	$\pm 113$	$\pm 17$

when there is a weak positive association. However, in the upper half, relative sulfate and relative Sr are almost always negatively correlated, and usually strongly so. These variations result in a total correlation coefficient of -0.67 for the lower half and -0.88 for the upper half (Table III). The difference between the lower and upper halves of the sequence are even greater in the correlation plot of relative sulfate vs. relative Na (Fig. 10A). In the lower half, there are periods of strong negative correlation and periods of strong positive correlation, but the overall result is no significant correlation. However, in the upper half of the sequence, correlations are always negative, with an overall correlation coefficient of -0.71. On an absolute basis, sulfate is almost always positively associated with both Na and Sr (Figs. 9B and 10B although there is considerable variation in the degree of association).

The above long-term correlations demonstrate that the same relationship observed for short-term variations holds for the entire sequence, namely that the relative amount (mg/kg or ppm) of a particular trace element co-precipitated with sulfate has a negative association with rate of sulfate deposition. However, on an *absolute* basis, the amount of a particular element co-precipitated per unit time is positively correlated with the rate of sulfate deposition (note positive correlation coefficients in Table III for absolute CaSO<sub>4</sub> vs. absolute Sr, Na, K, and Mg). This means, then, that with an increase in the rate of sulfate precipitation, the amount of a trace element in each gram of CaSO<sub>4</sub> precipitated decreased, but the total amount of the element removed within a given time period increased, simply because more CaSO<sub>4</sub> was precipitated during that time.

## DISCUSSION

The above results have demonstrated that trace element incorporation becomes less during periods of in-

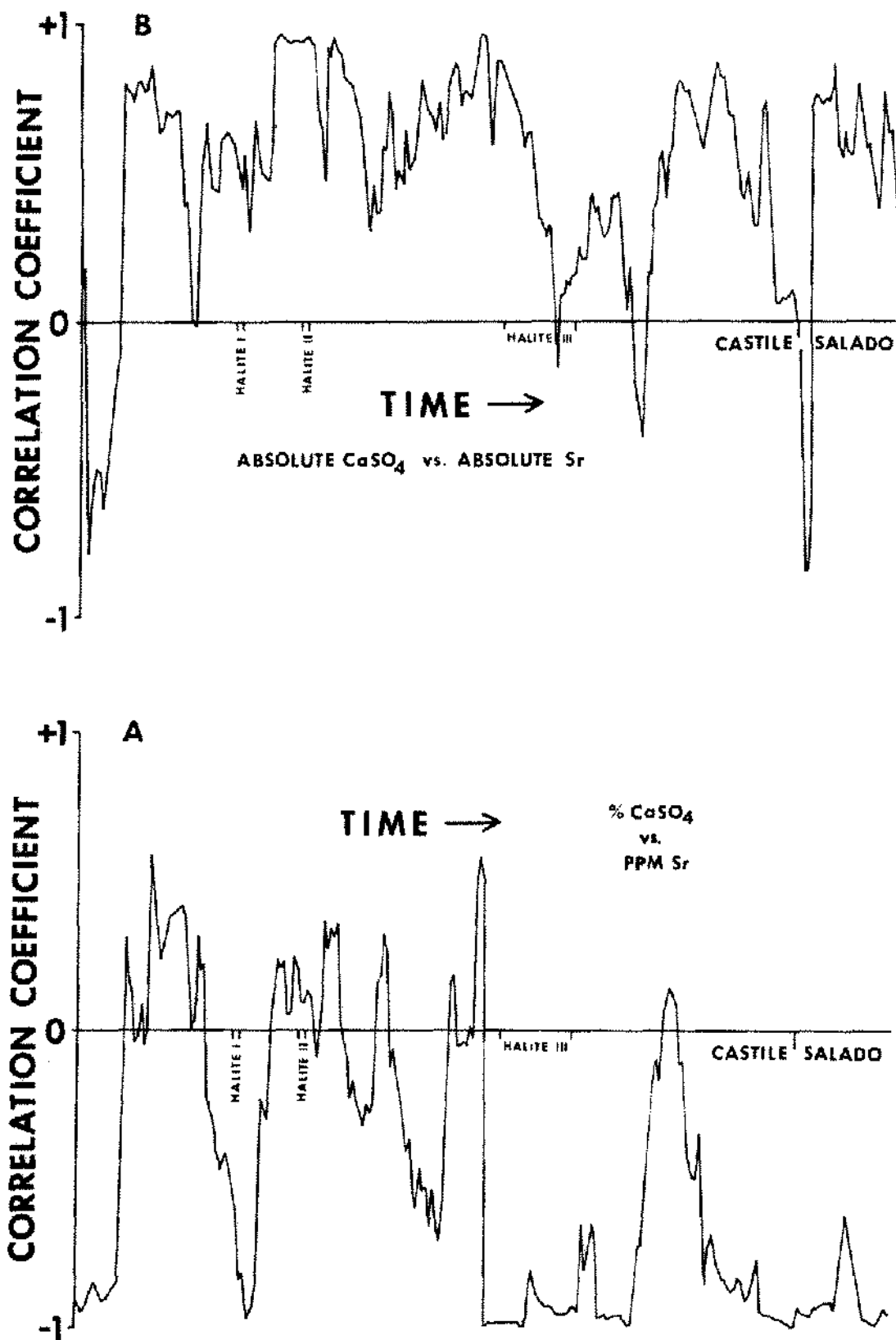


Figure 9. Moving correlation coefficients for relative  $\text{CaSO}_4$  vs. relative Sr (A), and absolute  $\text{CaSO}_4$  vs. absolute Sr (B) for the Castile-Lower Salado varved evaporite sequence in the Phillips no. 1 core, N = 22 (9800 years); see Figure 2 for position within master time series.



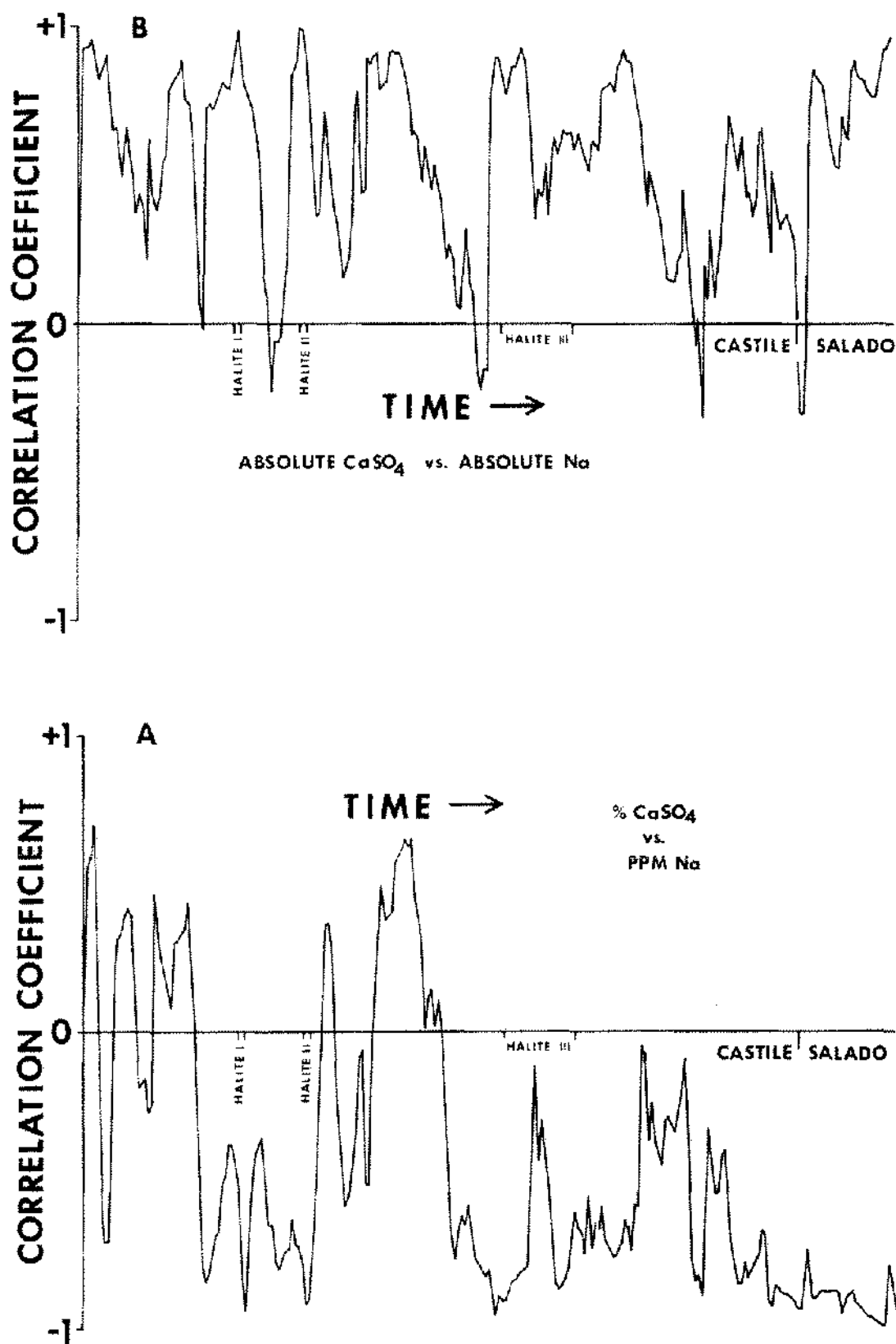


Figure 10. Moving correlation coefficients for relative  $\text{CaSO}_4$  vs. relative Na (A), and absolute  $\text{CaSO}_4$  vs. absolute Na (B) for the Castile-Lower Salado varved evaporite sequence in the Phillips no. 1 core, N = 22 (8800 years); see Figure 2 for position within master time series.

creased sulfate precipitation, and greater (by as much as several orders of magnitude) during decreased sulfate precipitation. One possible explanation for this relationship is that the concentration of a particular element in the water may be less during periods of increased sulfate precipitation, so that the concentration of that element incorporated into calcium sulfate precipitating in equilibrium with the water would also be less. However, of the four minor elements (Sr, Mg, Na, and K) measured in anhydrite and whole-rock samples, three (Mg, Na, and K) occur as major ions in sea water. In addition, none of these three is removed from solution as a major component in a mineral phase until the precipitation of halite. Assuming that increased sulfate precipitation reflects increased salinity in the water, one would expect the concentrations Mg, Na, and K to be actually *higher* in the water during increased sulfate precipitation, not lower. Unlike the other three elements, Sr is a minor element in both sea water and in all precipitating mineral phases. It is possible, therefore, that co-precipitation of Sr with Ca in calcium carbonate and then in calcium sulfate might deplete the water in Sr so that higher salinity waters would be depleted in Sr relative to lower salinity waters. However, Purkayastha and Chatterjee (1966a and 1966b) found that the distribution coefficients for Sr in both gypsum and anhydrite are less than 1.0 (0.44 for gypsum; 0.51 for anhydrite) so that Sr would be enriched in the residual solution, not depleted. For example, Kinsman (1969) reports that with increasing salinity, the molar Sr/Ca ratio increases from about  $8.6 \times 10^{-3}$  for normal sea water to about  $12 \times 10^{-3}$  in 9 times concentrated sea water. Kinsman also gives a range of  $8 \times 10^{-3}$  to  $22 \times 10^{-3}$  for the Sr/Ca ratio in an evaporite area in Baja California and solar salt works in California. Butler (1970) found that waters precipitating calcium sulfate in the sabkha and lagoons of Abu Dhabi had Sr/Ca ratios ranging mostly between  $8 \times 10^{-3}$  to  $13 \times 10^{-3}$ . Therefore, Sr, like Mg, Na, and K would be expected to increase in the water during periods of high sulfate deposition.

Another possibility is that temperature effects are operating on trace element incorporation. Assuming that the  $\text{CaSO}_4 - \text{XSO}_4$  system behaves like most other binary solid solution systems, we would expect to find less trace element (X) substituting in  $\text{CaSO}_4$  at higher temperatures. If increased sulfate precipitation is related to salinity, then it is possible that the increased salinity is due to increased evaporation which might be related to increased temperature. This would provide a change in trace element incorporation in the right direction to explain the observed concentrations. However, it is very unlikely that temperature differences were great enough to explain trace element concentration differences as large as those observed. Similarly, temperature effects on distribution coefficients would also be minimal. For example, Oxburgh, et al.

(1959) found the distribution coefficient for Sr in calcite decreased from 0.11 at 30° C to 0.07 at 95° C. Kinsman and Holland (1969) reported that the distribution coefficient for Sr in aragonite decreases linearly with increasing temperature at a rate of about 0.045 per 10° C. Therefore, an increase in temperature within the range expected for evaporite deposits would have a small effect on distribution coefficients.

A third possibility is that trace element incorporation is most closely related to precipitation kinetics. The observed facts are that when more calcium sulfate is precipitated over a given period of time, trace element concentrations are lower; when calcium sulfate precipitation is slower, trace element concentrations are higher. In the following discussion we will use Sr as an example. Castile anhydrite contains an average Sr concentration of 1100 ppm (Table IV) which corresponds to a Sr/Ca ratio in anhydrite of  $3.7 \times 10^{-3}$ . Assuming a range of  $8 \times 10^{-3}$  to  $22 \times 10^{-3}$  for the Sr/Ca ratio in evaporite-associated brines (Kinsman, 1969; Butler, 1970), and a distribution coefficient for Sr in anhydrite ( $k_{\text{Sr}}^{\text{An}}$ ) of 0.51 (Purkayastha and Chatterjee, 1966), then the predicted range of Sr/Ca ratios in anhydrite (assuming linear equilibrium partitioning) is  $4 \times 10^{-3}$  to  $11 \times 10^{-3}$ , which corresponds to a range of 1180 to 3240 ppm Sr. Butler (1970) found a range of  $1.55 \times 10^{-3}$  to  $12.2 \times 10^{-3}$  for Sr/Ca ratios in recent gypsum from Abu Dhabi, corresponding to Sr concentrations of 360 to 2820 ppm. He found that most recent anhydrite samples from Abu Dhabi had Sr/Ca ratios between  $3.5 \times 10^{-3}$  and  $8.85 \times 10^{-3}$  (1270 to 2600 ppm Sr).

In general, Sr concentrations in Castile anhydrite are lower than theoretically predicted. It is possible that Sr concentrations were higher and have been reduced during open system diagenesis as suggested for carbonates by Kinsman (1969) and for gypsum by Butler (1970). However, the fact that increased Sr concentration in Castile anhydrite correlates closely with reduced rate of sulfate deposition, suggests that variations in Sr measured in Castile anhydrite are a record of variations in rate of Sr incorporation corresponding to variations in the rate of sulfate precipitation.

A recent example of the effect of crystal growth kinetics on trace element incorporation may be represented in Butler's (1970) data on Sr concentration vs. crystal size for Recent gypsum from Abu Dhabi. He found that the Sr/Ca ratio in gypsum dropped off rapidly with increasing size from  $>10 \times 10^{-3}$  for small ( $<0.5$  mm) crystals to  $<5 \times 10^{-3}$  for larger crystals. The Sr/Ca ratios in small crystals are close to those predicted whereas the ratios in large crystals are less than predicted. Butler concluded that the difference was diagenetic. However, another possibility is that growth of the larger crystals was more rapid than for the smaller crystals so that equilibrium was not attained.

Another example of the effect of kinetics on trace element incorporation is provided by Kinsman and Holland (1969). They found that the distribution coefficient for Sr in aragonite is a function of kinetics of crystal growth, and that this kinetic dependence is most critical when the rate of crystallization is greater than the rate of diffusion within the crystal.

In all probability, temperature, salinity, diagenesis, and other factors have all had some effect on the final concentration of Sr measured in Castile anhydrite. However, we have concluded that precipitation kinetics has had the greatest influence on concentrations of Sr, and that the same is true for the other elements we have described as trace and minor elements. During periods of increased sulfate precipitation, there was not enough time for growing crystals to equilibrate with the water, and trace element concentrations are low. During periods of slower sulfate precipitation, equilibrium was more nearly attained, and trace element concentrations are higher, even though the concentrations of the elements in the brine may have been lower.

## CONCLUSIONS

Chemical changes within the Delaware Basin during deposition of the Castile Formation occurred rapidly and affected most of the basin at essentially the same time and to the same extent. Both short- and long-term variations show that co-precipitation of Mg, Sr, Na, and K with a unit volume of anhydrite was greatest during periods of slow sulfate deposition, and lowest during periods of rapid sulfate deposition. However, the *absolute* amount of a given element co-precipitated during a unit time period is directly related to the rate of sulfate precipitation. These associations suggest that trace element incorporation is more closely related to the rate of calcium sulfate precipitation than to the concentration of ions in the brine. This inverse relationship between trace element concentration and rate of sulfate precipitation is best developed during the second half of the varved evaporite sequence (i.e. Upper Castile and Lower Salado) when salinity fluctuations were more rapid and more extreme.

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