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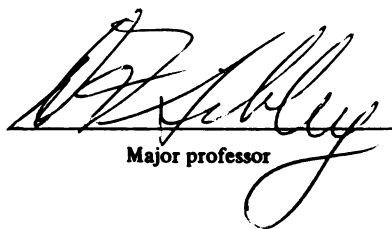
Sulfur in Dolomite

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Keith Charles Hill

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SULFUR IN DOLOMITE

By

Keith Charles Hill

A THESIS

Submitted to
Michigan State University
in partial fulfillment
for the degree of

MASTER OF SCIENCE

1985

ABSTRACT

SULFUR IN DOLOMITE

By

Keith Charles Hill

The purpose of this study is to differentiate dolomites formed in different natural waters by examining their sulfur content. Dolomites and limestones from thirteen formations ranging from Proterozoic to Holocene in age were analyzed for sulfur abundance and oxidation state. These values were compared to the sulfur content predicted by the sulfur chemistry of the various waters in natural environments of dolomitization.

The results of this study are that sulfur is of little or no use as a trace element in differentiating dolomites formed in different environments. The sulfur concentration fields defined by dolomites presumed to be formed by different environments showed no discernable separation. There was also a wide scatter of sulfur concentrations within individual formations. Dolomites and limestones showed no appreciable difference in sulfur values. This evidence contradicts the occult gypsum method used by Beales and Hardy (1980) to assign a hypersaline origin to most dolomites.

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Bob "Jaws" Dedoes, Mike "Reb" Miller, Steve "Mongo" Mattson and Gary "must-have" Lunsky.

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I. INTRODUCTION

The purpose of this study is to differentiate dolomites formed in different natural waters based on their sulfur abundances and oxidation states. The amount and oxidation state of sulfur incorporated into the dolomite crystal will be proportional to the amount and oxidation state of the sulfur in the dolomitizing solution. Because the primary models of dolomitization differ widely in the distribution of sulfur in the dolomitizing fluid, this study proposes to test the hypothesis that this sulfur signature can be used to distinguish between dolomite types.

The structure of this paper will be; 1) to define the models of dolomitization considered and delineate the sulfur chemistry of the pore waters in these environments; 2) to briefly describe the samples analyzed (extensive formations descriptions are included in Appendix A); 3) describe the methods used for sulfur analysis; and 4) to report the results of the analyses and interpret the sulfur distribution.

Models of Dolomitization

Four models of dolomitization are be considered in this study; 1) the hypersaline brine model; 2) the

mixed-water or Dorag model; 3) the organic influence model; and 4) normal seawater dolomitization .

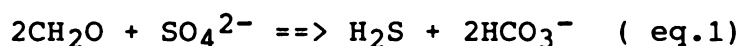
The hypersaline brine model (Adams and Rhodes, 1960) consists of a dolomitizing fluid composed of seawater that has evaporated to the point of gypsum precipitation. The removal of calcium ions due to this precipitation raises the magnesium-calcium ratio in the solution and thus is thermodynamically favored for dolomitization. One strong evidence for the plausibility of this model is that dolomite is forming today in modern sabkhas which is believed to be a result of this model (Illing et. al., 1965; Patterson and Kinsman, 1982; Butler, 1969). The periodic dilution of these brines by seawater and/or freshwater to produce a schizohaline environment may also be important (Folk and Land, 1975).

The mixed-water or Dorag model (Land, 1973a; Badiozamani, 1973; Back and Hanshaw, 1970) involves a dolomitizing fluid that is a mixture of seawater and freshwater. This fluid is supposed to be undersaturated with respect to calcite and supersaturated with respect to dolomite thus favoring replacement. The solution is also dilute which may lessen the negative effect of interfering ions on the replacement reaction (Folk and Land, 1975). Few examples of dolomite forming in modern mixing zone environments have been documented (Land , 1973b; Gebelein et. al., 1980)

The organic influence model consists of two organically

controlled processes which may favor dolomitization. The first of these is sulfate reduction. Sulfate reduction occurs in anoxic waters where bacteria use the oxygen in SO_4^{2-} to convert organic material to CO_2 (Drever, 1982). Baker and Kastner (1981) found that the presence of sulfate ions inhibited dolomitization in hydrothermal bomb experiments. They believe that the large sulfate ions "poison" the lattice sites on the growing dolomite crystal. Therefore, a solution which has the sulfate reduced by bacterial processes would be more favorable for dolomitization.

Another important effect of sulfate reduction is the increase in carbonate alkalinity (Lippman, 1973; Baker and Kastner, 1981). The sulfate reduction reaction can be written as follows (Berner, 1984):



The increase in carbonate alkalinity caused by this reaction favors dolomitization by increasing the activity of the carbonate ion (Lippman, 1973). Figure 1 shows the relationship between SO_4^{2-} decrease and alkalinity increase for certain environments.

The second biologically controlled process which may favor dolomitization is methanogenesis. Methane producing bacteria may not be able to grow in areas where dissolved sulfate is present (Claypool and Kaplan, 1974). This

Figure 1. Changes in carbonate alkalinity and sulfate abundances with depth; a) Abu Dhabi Sabkha (data from Patterson and Kinsman, 1982); b) Bahama mixing zone hammocks, depth of 1 meter estimated (data from Gebelein et. al., 1980); c) Gulf of California (data from Goldhaber and Kaplan, 1980).

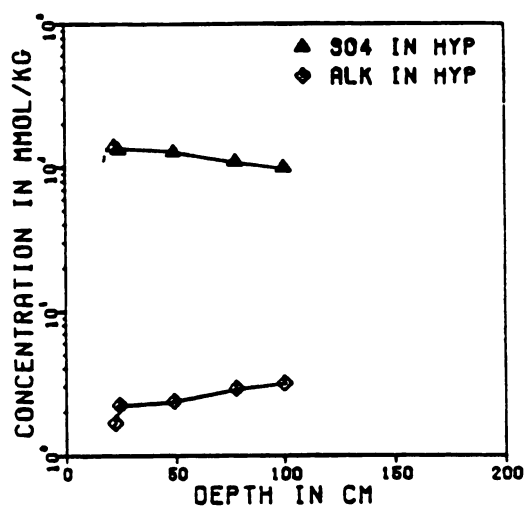


Figure 1a

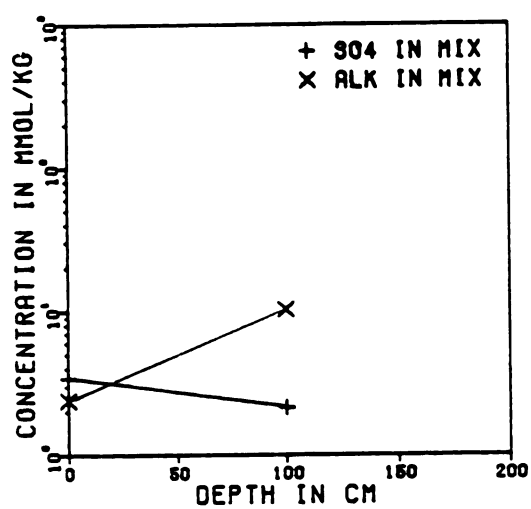


Figure 1b

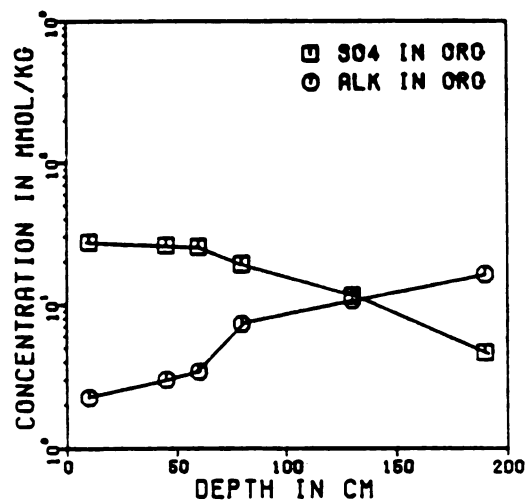


Figure 1c

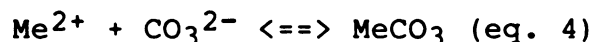
causes a natural segregation of sulfate reduction and methanogenesis environments (Fig. 2). As sediments are buried and pass into the zone of methanogenesis, methane production will proceed according to this equation (Claypool and Kaplan, 1974):



The high HCO_3^- content of the pore fluids due to the overlying sulfate reduction zone (Fig. 3) provides the necessary HCO_3^- . The bacterially controlled, non-equilibrium reaction for methane production (eq. 2), and the resulting increase in OH^- raises the pH of the solution and causes this reaction to occur:



This will favor the precipitation of carbonate minerals:



Me^{2+} can be Ca^{2+} and/or Mg^{2+} so dolomite may be precipitating. These two processes will deplete the HCO_3^- content of the pore fluids (Fig. 3) but other factors such as biogenic decarboxylation may act as a source of carbonate (Irwin, 1980).

The fourth model of dolomitization considered here is

Figure 2. Sedimentary column showing processes and dissolved species in an organic influence environment (from Claypool and Kaplan, 1974).

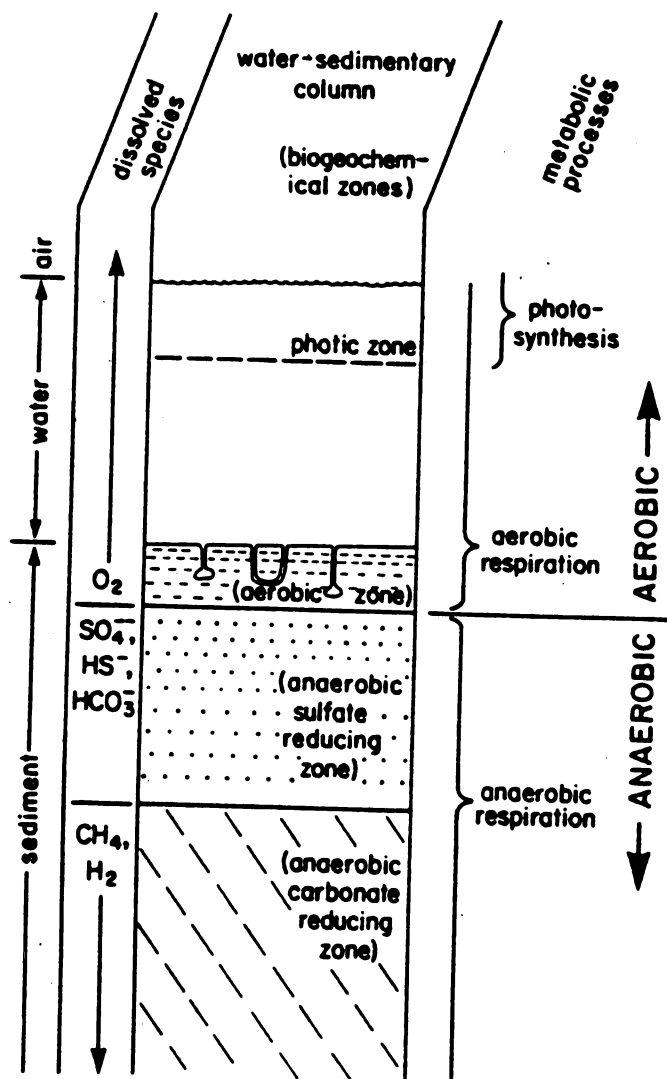


Figure 2

Figure 3. Changes with depth of the concentration of SO_4^{2-} and carbonate alkalinity and carbon isotopes of the dissolved CO_2 in the interstitial water of South Guyamas Basin sediments, Gulf of California (from Claypool and Kaplan, 1974 using data from Goldhaber, 1974). Note the changes in carbon isotopes and titration alkalinity at the depth where SO_4^{2-} is removed and methanogenesis commences.

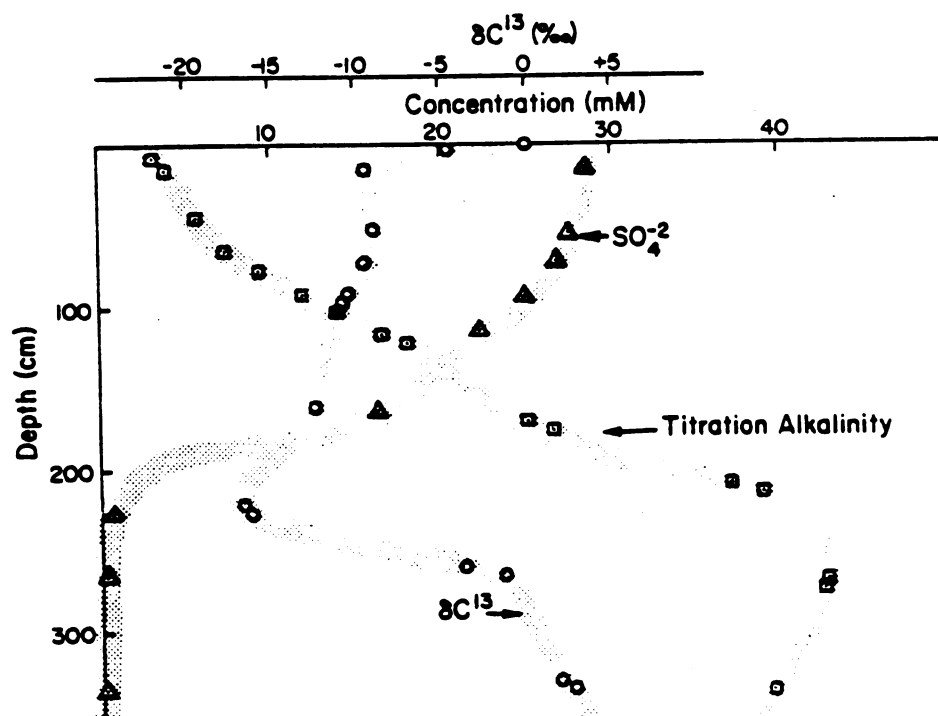


Figure 3

dolomitization by normal seawater. Until recently this model had received little consideration due mainly to the fact that there are a large number of carbonate sediments in contact with seawater which remain undolomitized (Land, 1980 and others). Two recent papers have demonstrated the possibility that relatively unaltered seawater may be responsible for dolomitization.

Saller (1984) studied dolomite found in cores on Enewetak Atoll and concluded that cold normal seawater was the dolomitizing solution. By examining the petrography and strontium isotopes of the dolomite, he showed that the dolomitization occurred no later than middle to late Miocene. This would place the sediments at a depth of more than 900m, far below the expected depth of a mixing zone or hypersaline brine. The temperature profile of the well and the observations of tidal fluctuations within the well suggests it is in communication with the surrounding seawater. The oxygen isotopes of the dolomite are consistent with dolomitization by cold normal seawater. These factors taken together present good evidence for Saller's conclusion.

Carbello and Land (1984) reported dolomite forming crusts in Sugarloaf Key, Florida which they believe to be the result of tidal pumping of normal seawater. The highest concentrations of dolomite were found in the areas of most active tidal pumping. Water analyses showed the surface and subsurface waters were essentially normal

seawater but evidence of sulfate reduction is present.

Water Chemistry

With the exception of normal seawater, pore fluid sulfur in the various dolomitizing environments is difficult to characterize due to the effects of sulfate reduction. Estimates of the sulfur hydrochemistry of the various models are given in Table 1 and shown in Figure 4.

Hypersaline brine waters are enriched in sulfate due to evaporative concentration. Sulfate values in the pore waters of the upper 20cm range from 60 to 140 mmol/kg and are reduced down to 35 to 109 mmol/kg at a depth of 70 cm in areas of dolomite formation (Patterson and Kinsman, 1982; Butler, 1969).

Dissolved sulfide in hypersaline pore waters is much more difficult to characterize. In oxic environments dissolved sulfide is extremely low to non-existent (Berner, 1972; Goldhaber and Kaplan, 1974; Horne, 1969). So essentially all dissolved H_2S is the result of processes occurring in anoxic environments, namely sulfate reduction. As H_2S is produced during sulfate reduction it will immediately react with iron minerals or dissolved iron to form iron sulfides, the most abundant of which is pyrite (Goldhaber and Kaplan, 1974; Drever, 1982). Because seawater is extremely low in dissolved iron (.036 mmol/kg; Drever, 1982) and there are few reports of iron minerals in

Table 1. Estimated dissolved sulfur content in waters
 from the various environments of dolomitization.

TABLE 1

<u>Environment</u>	<u>SO₄²⁻ (mmol/kg)</u>	<u>H₂S (mmol/kg)</u>
Seawater	28 ¹	0
Freshwater	< 1% of SW ¹	variable
Hypersaline Brine		
Surface	60-140 ²	0
Pore Water	35-109 ²	2.5-25 ⁶
Mixing Zone	2.67 ⁴ 1.19-2.15 ⁵	.57-1.27 ⁶
Organic Influence		
Sulfate Reduction	5-25 ⁷	0-.05 ⁷
Methanogenesis	0 ⁷	0 ⁷

¹Berner (1984)

²Patterson and Kinsman (1982); Butler (1969): Persian Gulf sabkha, Kuwait

⁴Back and Hanshaw (1970) Isla Mujeres, Yucatan Peninsula

⁵Gebelein et. al. (1980) North Hawk Creek, Andros Island, Bahamas

⁶Calculated from alkalinity increase and sulfate decrease (see text)

⁷Goldhaber and Kaplan (1980): Gulf of California

*note- the values calculated for H₂S assume no reaction with iron mineral or loss to surface and thus represent a maximum that is probably much too large (see text)

Figure 4. Estimates of sulfur hydrochemistry for the various dolomitizing environments (data from Table 1).

□ SEAWATER
 ○ HYPERSALINE
 ▲ MIXING ZONE
 + SULFATE REDUCTION
 X METHANOGENESIS

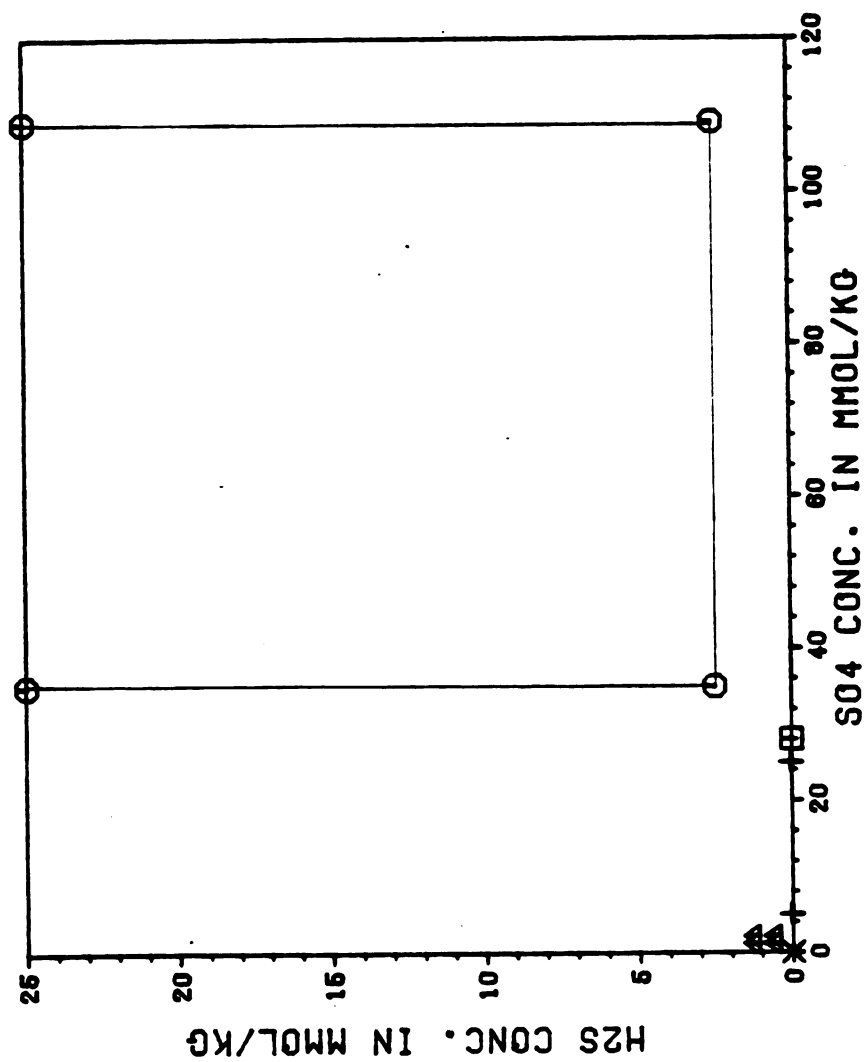


Figure 4

recent sabkha environments, dissolved sulfide cannot be easily removed by precipitation of iron sulfides.

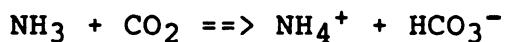
It is possible to make an estimation of the amount of dissolved sulfide in hypersaline pore waters by setting a minimum and maximum value for them. The maximum amount of H_2S produced is the amount of sulfate sulfur lost with depth. This value must be used with caution however, because gypsum precipitation may account for a large part of it (Butler, 1969). Using data from Patterson and Kinsman (1982) the maximum amount of H_2S produced in three sabkha wells would be 25mmols/kg.

In areas containing few iron minerals, the minimum value can be obtained by using the increase in alkalinity and assuming that the alkalinity increase is proportional to the dissolved H_2S at a ratio of 2:1 (fig.5, eq.1) (Goldhaber and Kaplan, 1974). This value may be low due to loss of CO_3^{2-} via the precipitation of carbonate minerals. Again using data from the same wells of Patterson and Kinsman (1982) this yields a value of 2.5 mmols/kg for dissolved H_2S .

The maximum and minimum values obtained here may both be too large due to the fact that H_2S may simply diffuse upward and become oxidized upon contact with seawater (Aharon et. al., 1977; Jorgensen, 1979).

The values obtained here may not be applicable to all hypersaline environments but they at least put a constraint of one order of magnitude on one of the most studied ones.

Figure 5. Changes in carbonate alkalinity with depth (left to right) versus dissolved sulfides. The values must be corrected for NH_4^+ due to the fact that there is some nitrogen in organic materials that will be converted to NH_3 . This will react according to this equation:



which gives anomalously high values (Goldhaber and Kaplan, 1974). The data points are from a carbonate mud in Devil's Hole, Bermuda and the line drawn is the predicted relationship assuming a closed system and eq. 1. (from Goldhaber and Kaplan, 1974 using data from Thorstenson and MacKenzie, 1971).

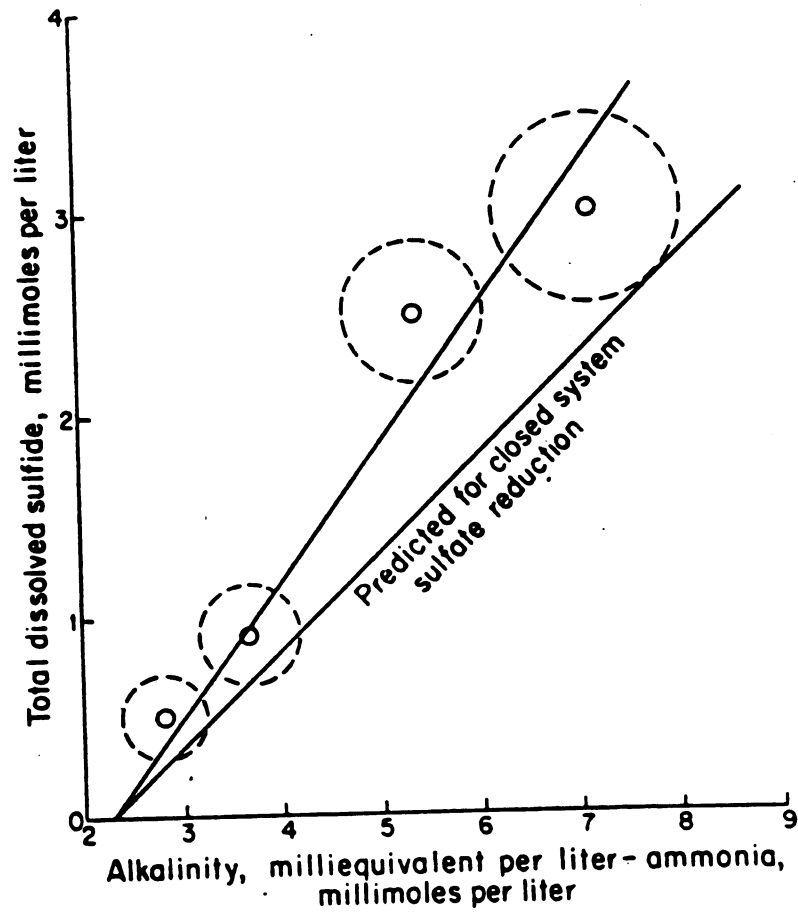


Figure 5

Mixing zone pore fluids have a much lower concentration of sulfate than other models due to the fact that freshwater contains less than 1% the amount of sulfate that seawater contains (Berner, 1984). The dissolved sulfide concentration is also poorly understood but using the amount of sulfate lost reported in Gebelein et. al. (1980) this yields a value of 0.57 to 1.27 mmol/kg mmol/kg for the Bahama mixing zone.

Organic influence waters go through a wide range of dissolved sulfur contents with depth. Examples of sulfur contents with depth are given in Figure 6. In the upper zone, sulfate is gradually depleted with depth from its initial seawater concentration by sulfate reduction. This may or may not be accompanied by an increase in dissolved H_2S depending on the availability of iron minerals for reaction (Berner, 1981; Golhaber and Kaplan, 1974). In some instances there is a buildup of dissolved H_2S where the production by bacterial reduction is greater than the removal rate by reaction with iron minerals (Berner, 1972) (see figure 6) . Below this zone the sulfate is completely removed and there are essentially no dissolved sulfur species in the pore water (Gieskes et. al., 1981). Therefore a dolomite forming in the sulfate reduction zone may have a wide range of sulfur signatures and one forming in the zone of methanogenesis should have essentially no sulfur.

The chemistry of surface seawater is fairly constant

Figure 6. Changes in dissolved sulfur species with depth in three organic-rich, anoxic basins; a) and b) Gulf of California, c) Santa Barbara Basin (from Goldhaber and Kaplan, 1974).

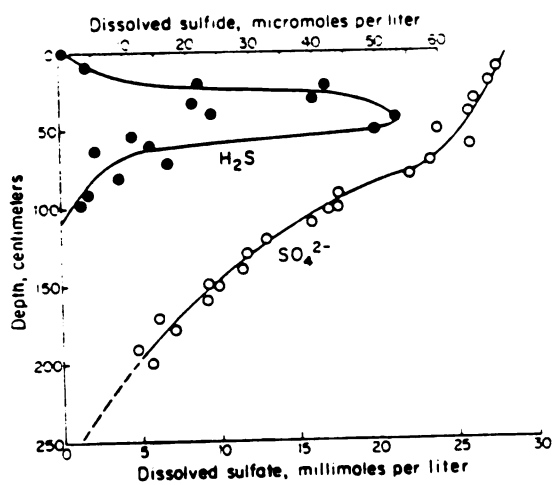


Figure 6a

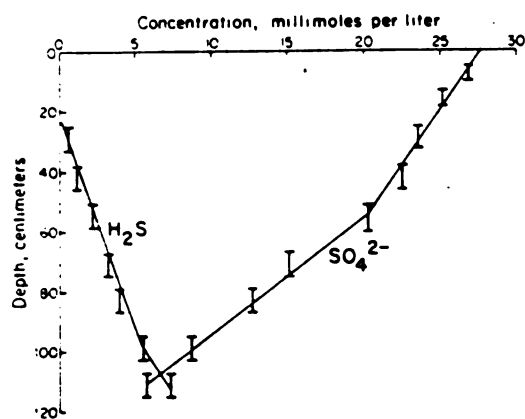


Figure 6b

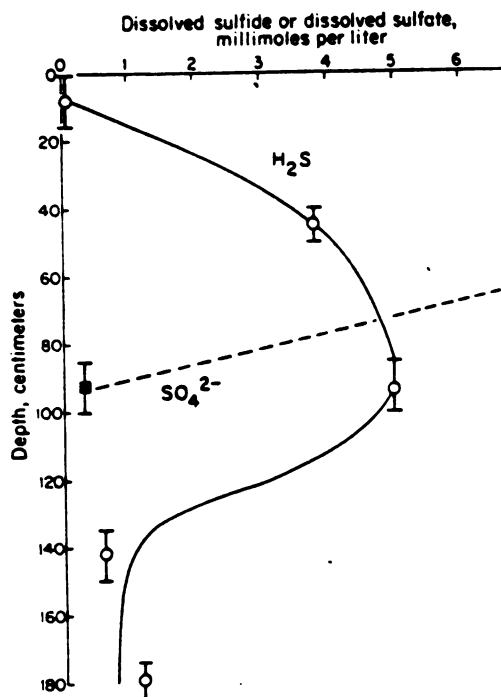


Figure 6c

throughout the world (Holland, 1978). Since it is an oxic environment there is little or no dissolved sulfide.

IV. SAMPLES USED IN THIS STUDY

Sixty-seven samples from 13 formations were analyzed in this study. They are listed by proposed dolomite type in Table 3. Most samples are >90% dolomite although some limestones were analyzed to detect any sulfur content differences. The samples range from Middle Proterozoic to Holocene in age. Formation descriptions of the depositional environment and evidences for the proposed model dolomitization are given in Appendix A.

Table 2. Samples used in this study grouped by proposed model of dolomitization (for evidences see individual formation descriptions in Appendix A).

TABLE 2

<u>Dolomitization</u> <u>Model</u>	<u>Formation</u>	<u>Age</u>	<u>Location</u>	<u>#</u> <u>Dol</u>	<u>#</u> <u>Ls</u>
Hypersaline Brine					
	Yalco	Proterozoic	Australia	4	0
	Muck	Jurassic	Scotland	1	0
	Edwards	Cretaceous	Texas	4	1
	Bahama Crust	Holocene	Bahamas	2	0
	Persian Gulf	Holocene	Abu Dhabi	1	0
Mixing Zone					
	Hope Gate	Pleistocene	Jamaica	6	4
	Seroe Domi	Pliocene	Bonaire	6	4
Organic Influence					
	Monterey	Miocene	California	3	0
	Gulf of Calif.	Quaternary	DSDP #478	2	0
Uncertain					
	Bonneterre	Cambrian	Missouri	3	1
	Galena	Ordovician	Iowa	4	1
	Niagara	Silurian	Mich. Basin	11	3
	Plomo	Miocene	Spain	3	4

V. METHODS

The samples in this study were originally intended to be analyzed using the occult gypsum method (Beales and Hardy, 1977; 1980). When this method proved inadequate, quantitative methods of analyses for sulfur abundance and oxidation state were employed.

Occult Gypsum Method

The first method attempted in this study was the occult gypsum method (Beales and Hardy, 1977; 1980). Occult gypsums are inclusions of gypsum within the dolomite which are too small to be detected by conventional means but which can be "cultivated" to form larger detectable crystals. These inclusions are thought to indicate a hypersaline origin for the dolomite.

The method proposed by Beales and Hardy (1977) was to first dissolve the dolomite in dilute hydrochloric acid. Then the insoluble residue is washed with distilled water to remove the acid and placed in a watchglass filled with distilled water. As the solution evaporates, small gypsum crystallites should form around the edges.

This method was attempted on a number of samples from the Bonneterre, Galena and Seroe Domi formations. Small crystallites which had the form of gypsum were observed in

some samples from all formations. These were difficult to identify because they were so delicate that when extraction on a needle point was attempted for microprobe examination the crystallites shattered on contact. The solution was filtered and the cultured insoluble residue was analyzed by x-ray diffraction but no gypsum peaks were found.

To determine whether or not the the "occult gypsum" crystals observed in the above experiments were actually from the dolomite, a stoichiometric mixture of reagent grade calcium carbonate and magnesium carbonate was run through the procedure as a blank. Small crystallites with the occult gypsum form were observed. This prompted a more detailed look into the mechanism of occult gypsum formation.

There are several problems with the "occult gypsum" method. The main problem concerns the solubility of gypsum in the solution used to dissolve the rock sample. It was found that 250 ml of 5% HCl was needed to completely dissolve 2 grams of dolomite. Solubility calculations (see Appendix B), which were supported by laboratory experiments, show that .718 grams of gypsum can be added to the dissolution solution before it becomes saturated. Therefore, in dolomites containing less than .718 grams (or 35.9 weight percent) of gypsum, the gypsum will all go into solution and will be lost during the washing stage. Dolomites with gypsum concentrations higher than 35.9% would be easily discernable in thin section.

In an attempt to overcome this problem of losing gypsum in solution, experiments were run in which the dissolving solution was retained. This resulted in many crystals having roughly the form of occult gypsums which were shown to be CaCl_2 by microprobe analysis. The large number of these crystals (both large and small) prohibited the identification of gypsum crystallites if present.

Another problem discovered with this method is the reaction of other sulfur bearing minerals to the dissolution process. Some metal sulfides, such as galena and sphalerite, are soluble in HCl and will become oxidized to SO_4^{2-} in the dissolution fluid. Pyrite is exempt from this problem as it is virtually insoluble in HCl. This sulfate from oxidation of sulfide minerals could combine with the abundant Ca^{2+} ions from the dissolved dolomite to form gypsum. Although galena and spalerite are not widespread minerals in carbonates and thus would not be a problem in most dolomite analysis, they are a common component of Mississippi valley-type ore host dolomites which were emphasized in Beales and Hardy (1980).

There also may be contributions to the sulfate content of the solution by other sulfate minerals such as barite or celestite but these are probably not volumetricly important.

The main difficulty with this method is that even if the aforementioned problems are insignificant, it is at best a semi-quantitative method for sulfate analyses.

Therefore, it was concluded that the use of quantitative sulfur analyses would be more useful in this study.

Sulfur Analyses

Carbonate samples were first crushed in a chipmunk jaw crusher and then ground using a rotary disc mill pulverizer. For sulfate analysis, which required finer grain sizes, the samples were powdered using a ball mill.

The samples were originally intended to be leached with EDTA to remove calcite from the dolomite (Videtich, 1981). This process was foregone due to the fact that sulfur inclusions in the limestone, especially pyrite, would be concentrated in the dolomite residual giving anomalous values. It was decided to use pure end members of dolomite and limestone.

Total Sulfur Method

Total sulfur was analyzed using a Leco induction furnace. A weighed quantity of sample is mixed with a conducting flux of pure iron, tin and copper. This mixture is then placed within an induction coil. Oxygen is passed over the mixture and power is applied to the coil. The flux melts under the strong electromagnetic field decomposing the sample. All forms of sulfur are gassed off as sulfur dioxide. This gas is dissolved in a weakly acid

solution and is measured by titration with a standardized solution of potassium iodate in the presence of potassium iodide and starch. The analytical error of this method for replicant samples was .004 weight percent.

Oxidation State

The method used to quantify the oxidation state of the sulfur is to analyze the amount of sulfur in a particular oxidation state (either oxidized or reduced) and subtract this value from the total sulfur value to obtain the amount of sulfur in the other oxidation state (Ricke, 1960).

Methods for obtaining the percentage of sulfur in a particular oxidation state were attempted by myself and two commercial chemical laboratories.

The method I used was that of Murthy et. al. (1956) in which powdered rock sample is decomposed in hydriodic acid in a nitrogen atmosphere. Metal sulfides will react to form H_2S . This gas is then washed through two gas washing bottles filled with cadmium hydroxide. The gas reacts to form cadmium sulfide and water. The amount of sulfide sulfur can then be determined iodimetricly. This process was standardized using analytical reagent grade magnesium carbonate and calcium carbonate and analytical reagent grade zinc sulfide as the spiking agent. The results of these experiments were in agreement with the predicted values with a standard deviation of .002 weight

percent. However, when actual dolomite samples were tested (some with pyrite or sphalerite spikes) or pyrite was used in the reagent matrix, the values were significantly lower than predicted. Insoluble residues from pyrite spiked samples contained pyrite which demonstrates incomplete dissolution even though the recommended mercury catalyst for pyrite decomposition was used (Murthy and Sharada, 1960).

A similar process was attempted by a commercial laboratory using a slightly different acid mixture and more vigorous heating. They too had problems with poor recovery of sulfide standards and were unable to achieve satisfactory results after 2 1/2 months despite numerous adaptations on the method. They noted the appearance of a condensate on the apparatus which they believed was mercuric sulfide. This could explain the poor recovery.

An alternative method was attempted by another laboratory which analyzed for sulfate sulfur by a leaching process with sodium carbonate. A weighed quantity of sample was leached for one hour with a boiling solution of 2% sodium carbonate solution. The filtrate was acidified with HCl and the sulfate separated by precipitation as barium sulfate. This precipitate was filtered off, ignited and weighed to determine sulfate. These results were much more satisfactory with an analytical error of .004 weight percent for replicant samples.

V. EXPERIMENTAL RESULTS

The results of the sulfur analyses are given in Table 3 and shown in figures 7-9. Figure 7 shows all dolomites, Figure 8 shows all limestones analyzed in this study. Figure 9 shows dolomites grouped by proposed dolomite type.

There are a few interesting features to note in the distribution of sulfur contents of the various samples. In Figure 7 it can be seen that there is a wide scatter of sulfur signatures but there is a concentration of dolomites with no appreciable sulfate which plot along the y-axis. This may be due to leaching of evaporitive minerals by groundwater. There are a few dolomites with extremely high contents of both oxidation states (Gulf of California, Persian Gulf, Monterey).

The limestones (Figure 8) show approximately the same distribution but with less points exhibiting extremely high values, especially in sulfate contents. A t-test showed no difference in the dolomite and limestone populations with respect to both forms of sulfur. In fact, the percentage of limestones exhibiting appreciable sulfate is essentially the same as the dolomites (5 of 18 for limestones as opposed to 16 of 42 for dolomites) although not as high.

In Figure 9 it can be seen that there is a wide distribution of sulfur contents not only within dolomites

Table 3. Sulfur analyses for all samples used in this study.

Table 3Dolomites

<u>Formation</u>	<u>Sample #</u>	<u>%Total Sulfur</u>	<u>%Sulfate</u>	<u>%Sulfide</u>
Yalco	1	.007	.003	.004
	2	.006	<.001	.006
	3	.025	<.001	.025
	4	.006	.003	.003
Bonneterre	25	.009	<.001	.009
	26	.002	<.001	.002
	29	.006	<.001	.006
Galena	18	.005	<.001	.005
	66	.005	<.001	.005
	67	.003	<.001	.003
	68	.002	<.001	.002
Niagara	54	.012	.002	.010
	55	.017	.002	.015
	56	.002	<.001	.002
	57	.017	<.001	.063
	61	.063	<.001	.063
Muck	5	.016	<.001	.016
Edwards	45	.067	<.001	.067
	46	.084	.005	.079
	48	.010	<.001	.010
	49	.007	<.001	.007
Plomo	69	.092	.003	.089
	70	.092	.009	.083
	71	.141	.004	.137
Monterey	42	.002	<.001	.002
	43	.047	.044	.003
	44	.169	.031	.138
Seroe Domi	36	.019	<.001	.019
	38	.022	<.001	.022
	39	.017	<.001	.017
	40	.020	<.001	.020
	41	.018	<.001	.018
Hope Gate	11	.006	<.001	.006
	12	.015	<.001	.015
	13	.022	<.001	.022
	14	.017	<.001	.017
	15	.040	.029	.011
	17	.018	.006	.012

Table 3 (cont.)Dolomites (cont.)

<u>Formation</u>	<u>Sample #</u>	<u>%Total Sulfur</u>	<u>%Sulfate</u>	<u>%Sulfide</u>
Gulf of Calif.	50	.152	.026	.074
	51	1.40	.800	.600
Bahama Crust	6	.065	.028	.037
Persian Gulf	72	.460	.322	.138

Limestones

Bonneterre	28	.003	<.001	.003
Galena	23	.051	<.001	.051
Niagara	58	.007	<.001	.007
	59	.001	<.001	.001
	60	.008	<.001	.008
Edwards	47	.006	<.001	.006
Plomo	83	.072	<.001	.072
	84	.046	.011	.035
	85	.020	.003	.017
	86	.032	.003	.029
Seroe Domi	37	.013	<.001	.013
	62	.005	.002	.003
	63	.006	<.001	.006
	64	.022	<.001	.022
Hope Gate	16	.046	.039	.007
	80	.012	<.001	.012
	81	.038	<.001	.038
	82	.012	<.001	.012

Figure 7. Sulfur chemistry of all dolomite samples used in this study.

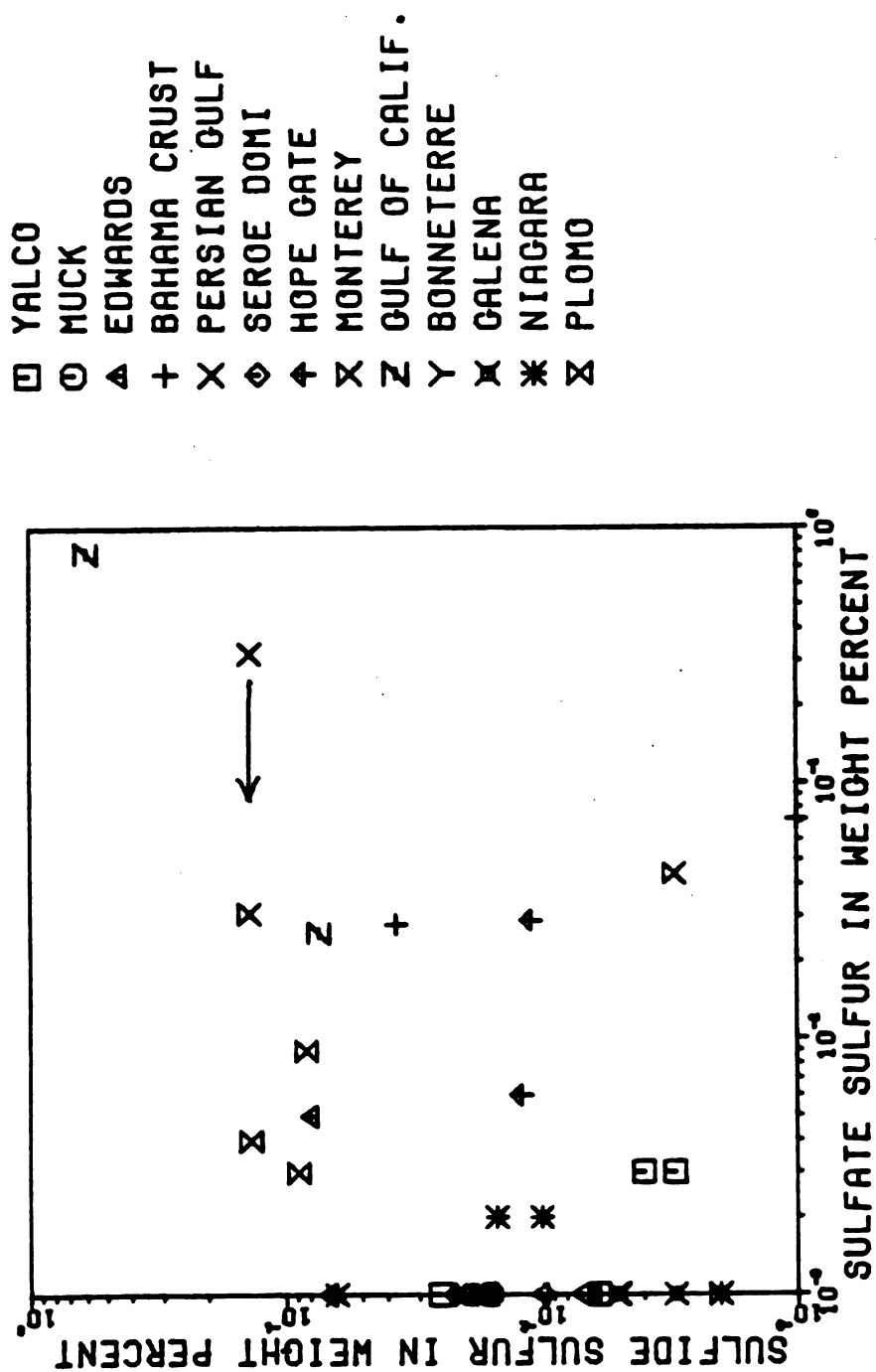


Figure 7

Figure 8. Sulfur chemistry of limestones used in this study.

Y BONNETERRE
 X GALENA
 * NIAGARA
 ▲ EDWARDS
 X PLOMO
 ◆ SEROE DOMI
 † HOPE GATE

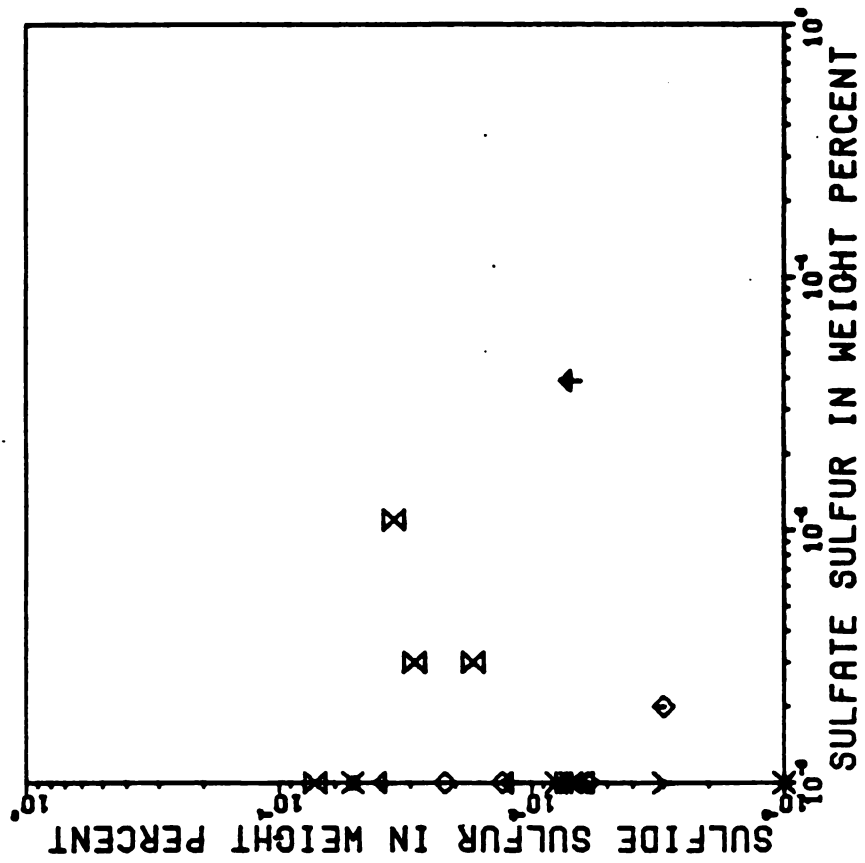


Figure 8

Figure 9. Sulfur chemistry of dolomites grouped by proposed model of dolomitization; a) hypersaline brine; b) mixing zone; and c) organic influence.

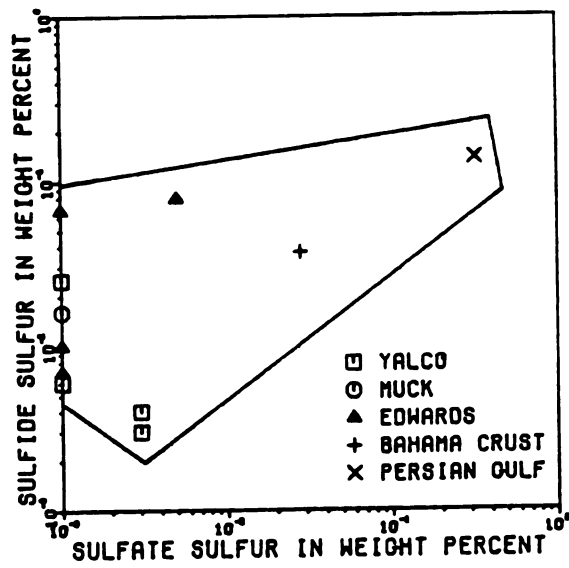


Figure 9a

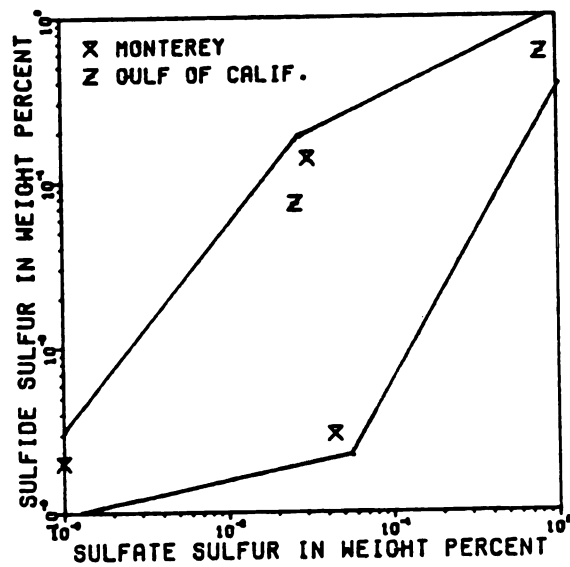


Figure 9c

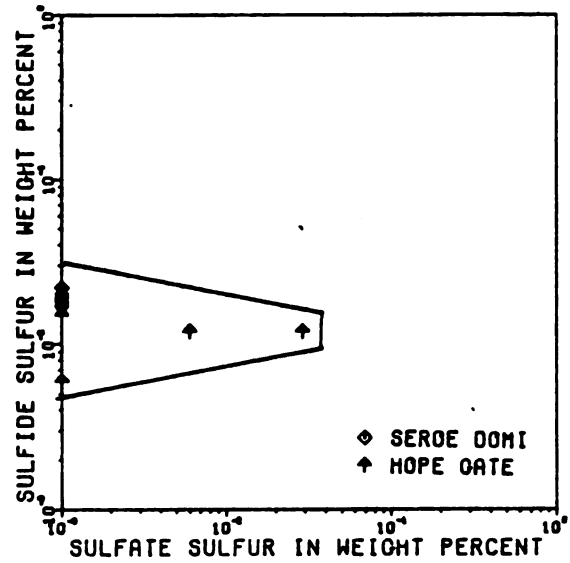


Figure 9b

formed by the same model but also within dolomites from the same formation. The Monterey formation shows probably the largest variation with a point near the origin and a point high in both forms of sulfur. This variation causes the fields delineated by the different models to be large and poorly defined.

The mixing zone dolomites have a fairly tight distribution but there are a few anomalous points. They are dominantly sulfate free as might be expected due to the fresh water influence (freshwater contains less than 1% the amount of dissolved sulfate found in seawater).

The high sulfate content in the organic influence dolomites is rather hard to explain considering the highly reducing conditions that are believed to exist in these environments. There are reports of anhydrite beds in a neighboring drill hole of the Gulf of California dolomites which are believed to be the result of evaporation of seawater during intrusion of dolerite dikes (Shanks and Niemitz, 1981).

VI. DISCUSSION

From a consideration of the sulfur distribution of the various dolomite types as shown in Figure 9, it appears that sulfur is of little use as a trace element in separating dolomites formed by the models considered in this study. There is no separable variation between the fields defined for the dolomites from the three different models (Figure 10).

The reason for the non-conformity of the data to the proposed distribution based on the sulfur hydrochemistry of the pore fluids (Figure 4) is probably due to one or more of the following factors; 1) Inhibition of sulfur incorporation into the dolomite crystal; 2) post-dolomitization leaching or precipitation of sulfur compounds by pore fluids; and 3) recrystallization of the dolomite at depth.

Sulfate ions will not be easily incorporated into the dolomite lattice because they are so much larger than the carbonate ions for which they might substitute. Sulfate will probably be present only as cryptocrystalline or fluid inclusions which may be more susceptible to alteration than a lattice substituting trace element such as strontium. Sulfide ions are small enough to fit in the carbonate sites, but they may be so small that they are not tightly

Figure 10. Fields of sulfur chemistry for dolomites
proposed to be formed by the various models
(based on Figure 9).

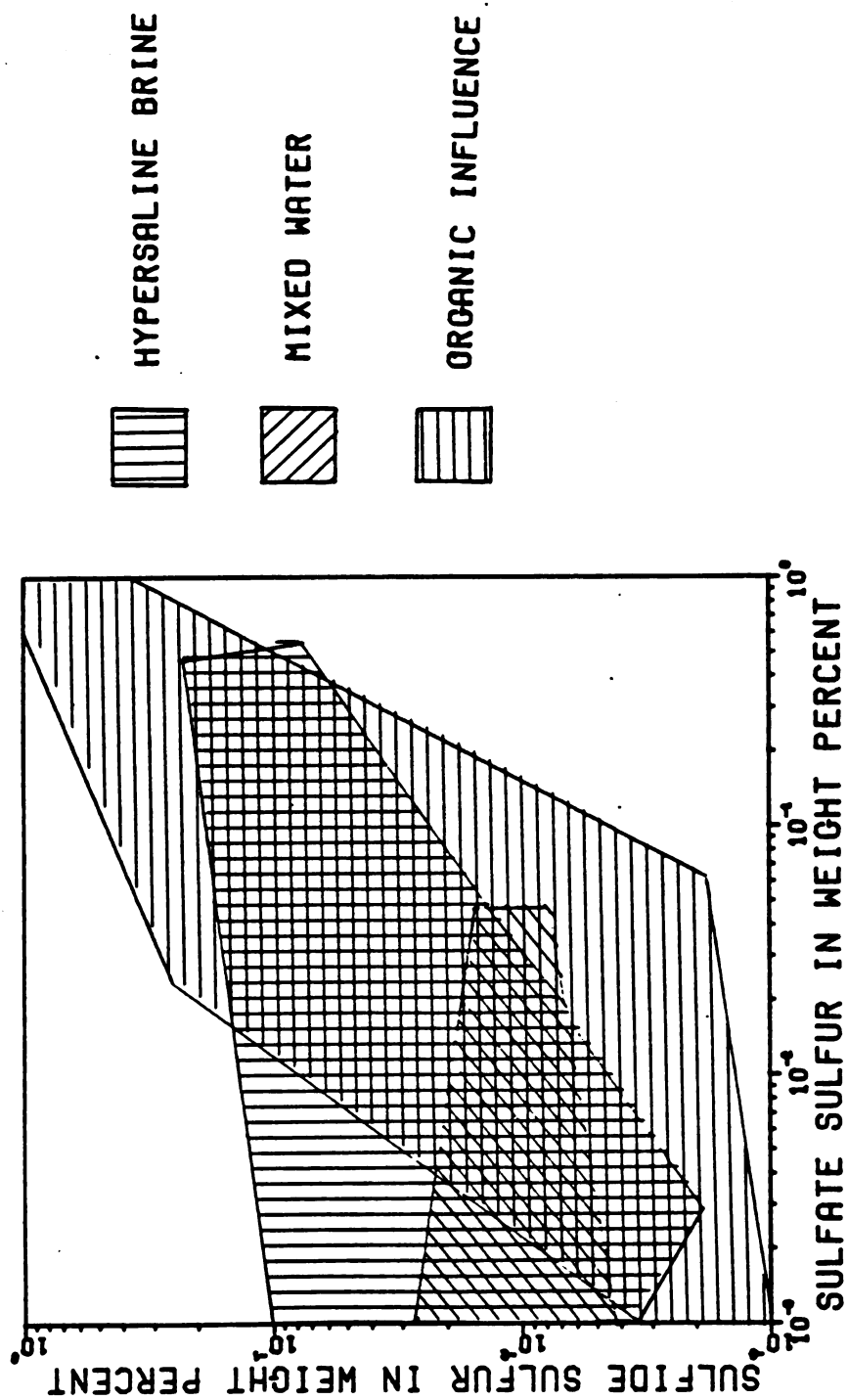


Figure 10

bound.

Sulfate leaching by porewaters is believed to be quite extensive (Beales and Hardy, 1980). This could account for the high amount of samples in Figures 7 & 8 which plot on or near the y-axis. Using a small amount of imagination and Figure 7, it is possible to distinguish a trend in sulfur contents from the different formations. If we consider the Persian Gulf dolomites as a good example of a recent hypersaline brine dolomite we can trace the concentration path during sulfate leaching (arrow on Figure 7). Since sulfide minerals (dominantly pyrite in carbonate rocks) are relatively stable above a pH of 3 (which includes most natural waters), the concentration path will be driven towards the y-axis. There are two hypersaline dolomites that would lie along that pathway, the Plomo Formation and the Edwards Formation. The three dolomites decrease not only in sulfate content but also in age from Recent to Miocene to Cretaceous. This may suggest that there is gradual sulfate depletion through time. Obviously a much larger data set including shorter time intervals than used in this study would be necessary to conclusively prove this hypothesis.

Another interesting feature in Figure 7 is the location of the points for the Bonneterre and Galena formations. They exhibit the lowest average sulfur values of all formations even though the Bonneterre dolomite is suspected of originally being hypersaline in origin. One feature

these two formations have in common (besides old age), is that both are believed to have undergone some growth and/or recrystallization by hydrothermal solutions (see Appendix A). Recrystallization at this elevated temperature could account for this lack of sulfur inclusions.

There may also be post-dolomitization precipitation of sulfur minerals as pore-lining cements. This would mask the original sulfur signature imparted to the rocks during dolomitization. These cements were not observed in thin section for any of the rocks used in this study, but they may have been too small to be distinguishable.

CONCLUSIONS

Based on the distribution of sulfur abundances and oxidation states in the dolomites studied, it appears that sulfur is of little or no use as a dolomitization environment indicator. There was no significant difference between the sulfur concentration fields defined by dolomites that were presumed to be of different origins. Nor is there a significant difference between limestones and dolomites. There was also a large variation of sulfur contents within dolomite fields considered to be of the same origin as well as dolomites from the same formation.

In view of the wide scatter of the sulfur data and the aforementioned problems with the occult gypsum method, the conclusion reached by Beales and Hardy (1980) that dolomite is formed predominantly by hypersaline brines appears to be invalid.

The reason for the non-conformity of the sulfur data to the proposed model based on the sulfur hydrochemistry of the pore waters is believed to be due to; 1) difficulty in sulfur incorporation into the growing dolomite crystal; and/or 2) leaching of evaporite minerals by groundwater; and/or 3) loss during recrystallization at elevated temperatures.

APPENDIX A

Formation Descriptions of Samples Used in this Study

YALCO FORMATION

The Yalco Formation (Middle Proterozoic) is found in Northern Australia. It is overlain by the cross-bedded quartz-rich Stretton sandstone and underlain by the evaporitic and dolomitic Lynott Formation. Muir et. al. (1980) proposed these rocks as an ancient analog to the modern Coorong lagoon. The Coorong Holocene dolomites show tidal flat characteristics alternating with estuarine conditions. There are numerous stromatolites and algal laminations along with dessication features such as polygonal mudcracks (Muir et. al., 1980). The Yalco Formation is remarkably similar to the Coorong dolomite showing all these tidal flat features as well as a lack of evaporites.

The Coorong lagoon is believed to have been dolomitized by a form of the hypersaline brine model in which seawater and freshwater is collected in coastal lakes during the humid summer months and then evaporates during the dry winter months. This forms a concentrated brine believed responsible for the dolomitization (von der Borch, 1976). One effect of the freshwater influence is to add organically derived CO₂ thus raising the bicarbonate content (Botz and von der Borch, 1984). A second effect may be to create a mixing zone environment during the rainy

season. Few if any evaporites are found in the sediment. This could be attributed to dissolution during the wet season or the low concentration of sulfate in the fresh water.

There were four core samples analyzed in this study which came from the Amoco DDH 82-6 well. They consist mainly of dolomitized algal breccia with silica cements of varying amounts as well as a small amount of detrital silica.

BONNETERRE FORMATION

The Bonneterre Formation (Upper Cambrian) contains the Mississippi Valley-type ores in the Viburnum lead-zinc province. There are four main facies in this district which represent a transgressing sea onto the cratonic shelf. The St. Francois mountains which formed a Precambrian high served as a minor shelf area on which the Bonneterre was deposited as an intertidal to supratidal facies. Around this high is a stromatolitic reef with associated oolite facies. The remainder of the Bonneterre is a deep water micrite and shale facies (Larsen, 1977). The facies distribution is given in Figure 1A.

The method of dolomitization is under debate but may be due to hypersaline brines associated with the supratidal facies (Beales and Hardy, 1980). There is a great deal of mineralization which was associated with hydrothermal

Figure 1A. Facies distribution in the Bonnetterre formation
(from Larsen, 1977).

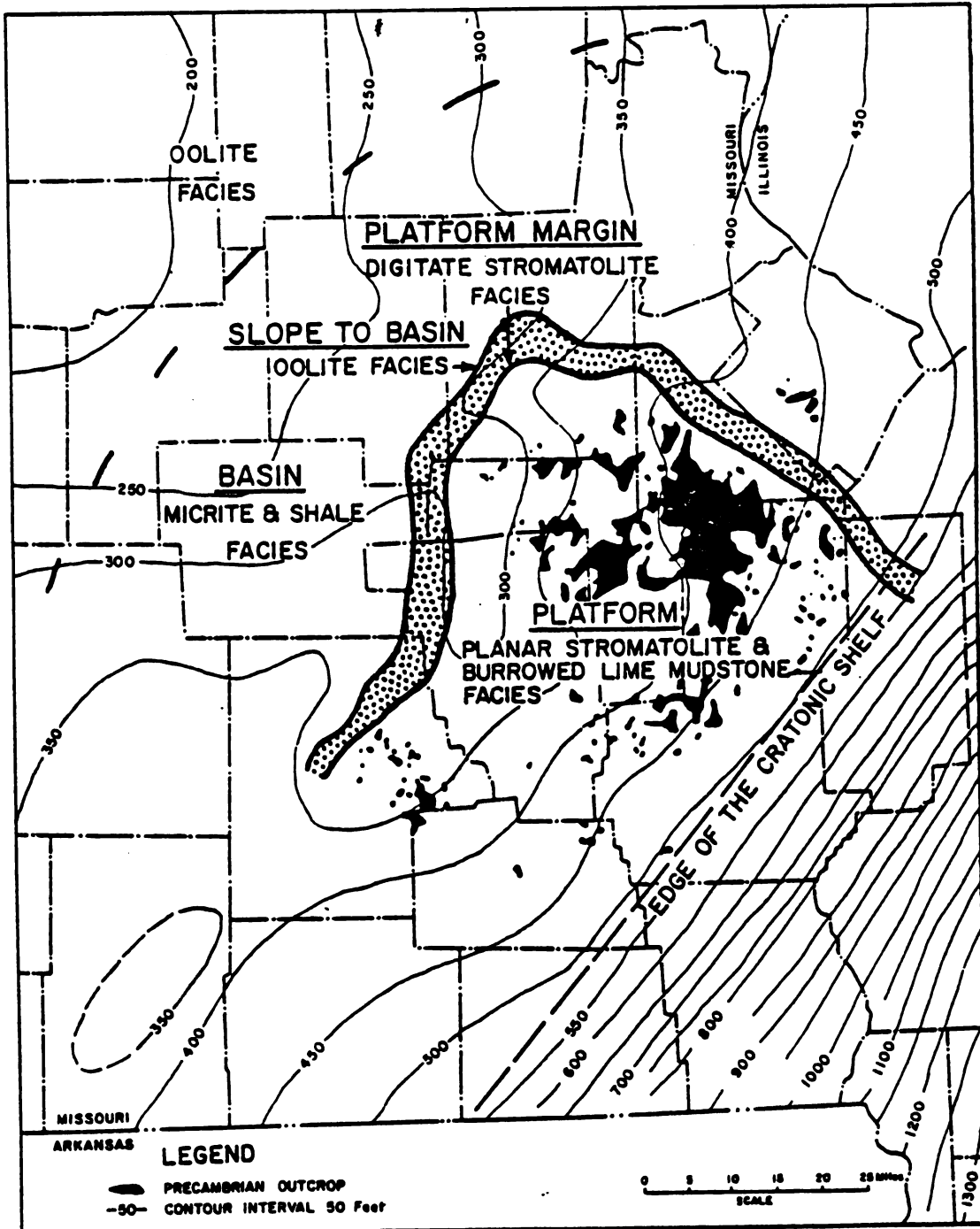


Figure 1A

solutions and it is possible that this solution was responsible for some of the dolomitization. Baroque or saddle dolomite is quite common and may indicate formation at elevated temperatures (Gregg and Sibley, 1984; Radke and Mathis, 1980).

The rocks in this study consist of four samples from the platform or "white rock" facies. There are three dolomites, one of which has baroque dolomite and one peloidal limestone. The dolomites appear to have been dominantly algal material and mud but much of the original texture has been obliterated by dolomitization.

GALENA FORMATION

The Galena Group (Ordovician) is found in the Upper Mississippi Valley. It is a series of limestones and dolomites which represent deposition on a shallow broad shelf area (Delgado, 1983). The rocks are 95% bioturbate mudstones and wackestones or their dolomitized equivalents. The other 5% are grainstones which are thought to be the result of storm deposits. The lack of sedimentary structures such as ripples or rip up clasts combined with the faunal assemblage and lack of exposure features indicates that these deposits formed below wave base (Delgado, 1983).

The mineralogy of the section at Guttenburg Iowa ranges from 100% porous, vuggy dolomite at the top of the section

to mottled partially dolomitized areas in the middle of the section to only slightly dolomitized limestones at the base of the section. There are numerous chert nodules in the middle of the section which are concentrated along bedding planes.

The method of dolomitization was originally believed to be the result of a mixing zone model (Badiozamani, 1973). This was based on the low sodium (190 ppm) and strontium (37 ppm) contents as well as carbon and oxygen isotopes. Recent evidence implies that the dolomite has undergone neomorphism by hot waters associated with lead-zinc mineralization (Gregg and Sibley, 1984). In fact, Figure 2A from Badiozamani (1973) shows that the carbon and oxygen isotopes of the Mifflin member fall in the range of hydrothermally alteration, not in between freshwater and seawater as you would expect from a mixing zone model. This neomorphism and other recrystallizations with depth of the original dolomite could account for the low sodium and strontium values. Therefore, the origin of the original regional dolomitization in the Galena Formation is still uncertain.

There were five samples from the Galena Group analyzed in this study. They consist of four 100% dolomite samples from the upper porous unit and one fossiliferous limestone wackestone from the base of the unit. The dolomite samples consisted entirely of cloudy dolomite rhombs with good porosity and the limestone sample consisted of large

Figure 2A. Isotope data from the Mifflin member in relation to carbonates precipitated from other environments (from Badiozamani, 1973).

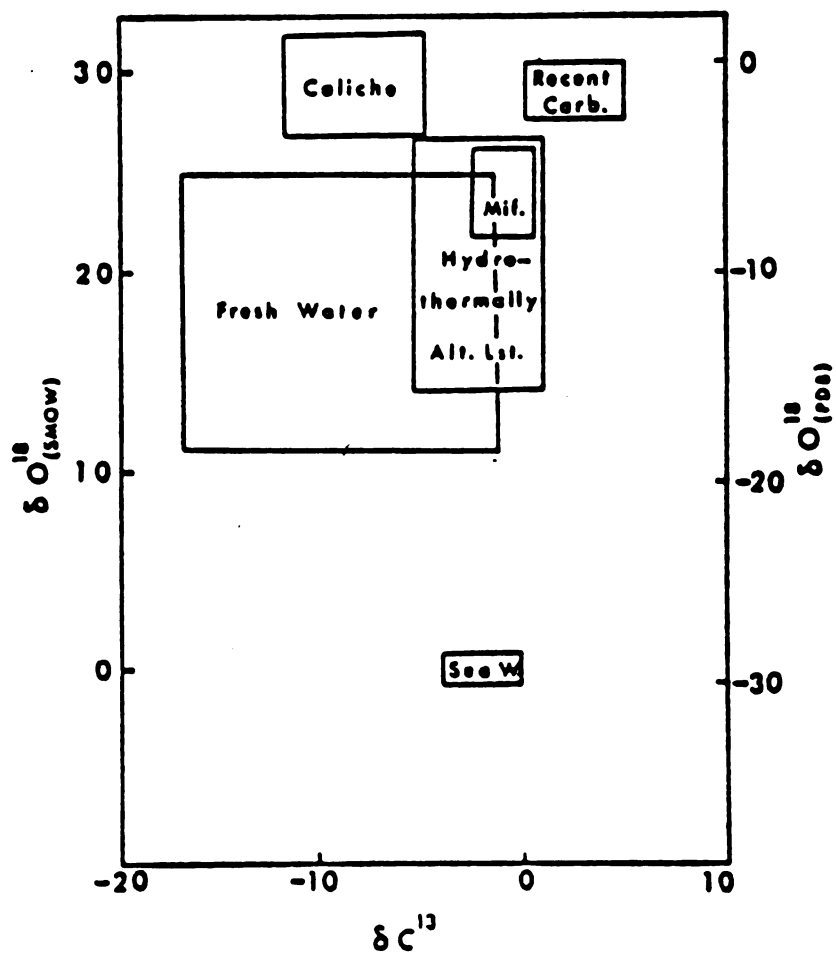


Figure 2A

gastropods, brachiopods and trilobites in a lime mud matrix.

NIAGARAN FORMATION

The Niagara Formation (Middle Silurian) consists of carbonates and evaporites deposited in a epicontinental sea (Sears and Lucia, 1980). There was prolific reef growth associated with the margins and shelf areas of the developing intracratonic basins (Fig. 3A). In the Michigan Basin a number of pinnacle reefs developed basinward of the main reef trend. In Indiana, the reefs were characterized by broad platform reefs and scattered patch reefs (Shaver and Sunderman, 1982). This reef growth was inhibited and eventually stopped by restriction and a sea level drop which resulted in the A-1 and A-2 Evaporite deposition which overlies the reefs (Briggs, 1980). The A-1 Carbonate was deposited in between these two evaporite sequences during a sea-level rise (Sears and Lucia, 1980).

The reefs are composed of stromatoporoid and coral framework infilled with interreef sediments and mud. They are surrounded by a reef flank facies consisting of crinoidal debris in the pinnacle reef zones (Sears and Lucia, 1980) and echinoderm, brachiopod and gastropod debris in the Indiana reefs (Shaver and Sunderman, 1982). There are deeper-water mudstone facies away from the reefs.

The samples from the Niagaran used in this study come

Figure 3A. Niagaran reef growth associated with basin margins and shelf areas during Silurian time; dots are discrete reefs, stipples are carbonate banks or barrier reefs (from Shaver et. al., 1978).

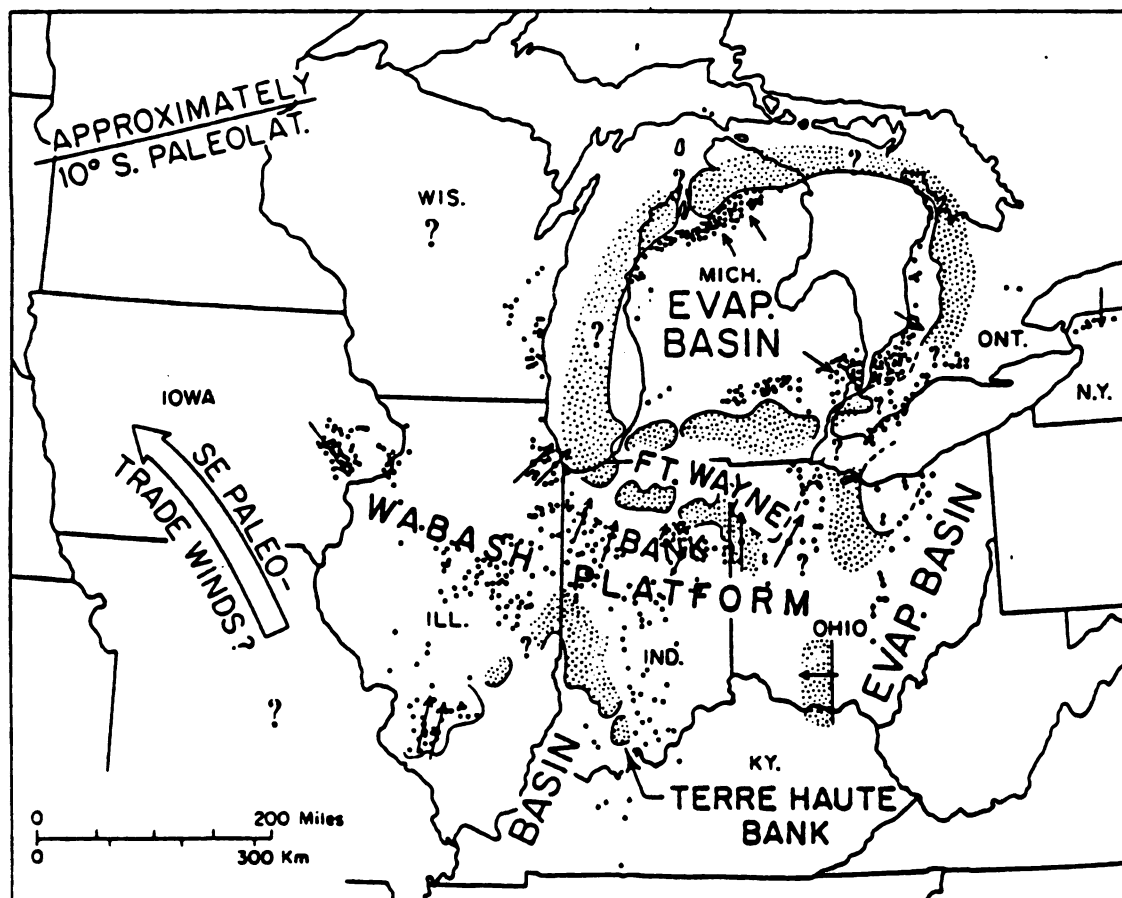


Figure 3A

from a Northern Michigan pinnacle reef and two quarries in North Central Indiana. The pinnacle reef samples are from the Shell State Union 1-8 well in Grand Traverse County, Michigan. This reef is approximately 130 meters thick and is overlain by the A-1 Carbonate (Cercione, 1984). There is an abrupt contact between the top of the reef and the overlying A-1 Carbonate (Cercione, 1984). The A-1 Carbonate is a dark algal mudstone which shows evidence of subaerial exposure (Sears and Lucia, 1980).

There are two petrographically distinct dolomite types found in these pinnacle reefs (Sears and Lucia, 1980). One type consists of clear euhedral rhombs which usually comprise no more than 30% of the whole rock, the remainder being calcite. The other consists of a brownish cloudy anhedral dolomite which usually comprises 90-100% of the rock. The clear dolomite appears to have predated extensive freshwater neomorphism whereas the cloudy dolomite appears to postdate it (Sears and Lucia, 1980).

Sears and Lucia (1980) believe the clear dolomite is of mixed water origin mostly due to the lack of inclusions which Folk and Land (1975) attributed to a dilute solution. They believe the cloudy dolomite is the result of hypersaline brines. Their evidence for this is that there are evaporites overlying the dolomitized A-1 Carbonate which is petrographically similar to the cloudy Niagara dolomite. The dolomitization pattern of the A-1 Carbonate and the Niagaran Formation coincides (see Figure

Figure 4A. Dolomitization patterns from the A-1 Carbonate and the Niagaran Formation in the pinnacle reef trend, Northern Michigan (from Sears and Lucia, 1980).

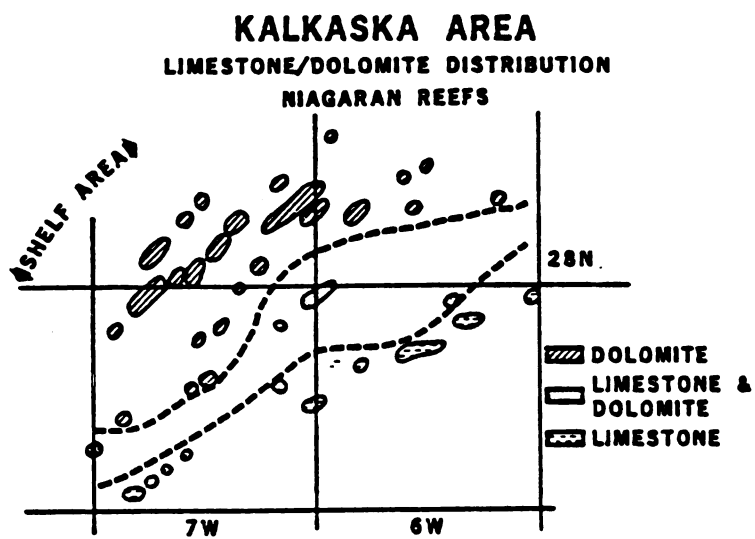
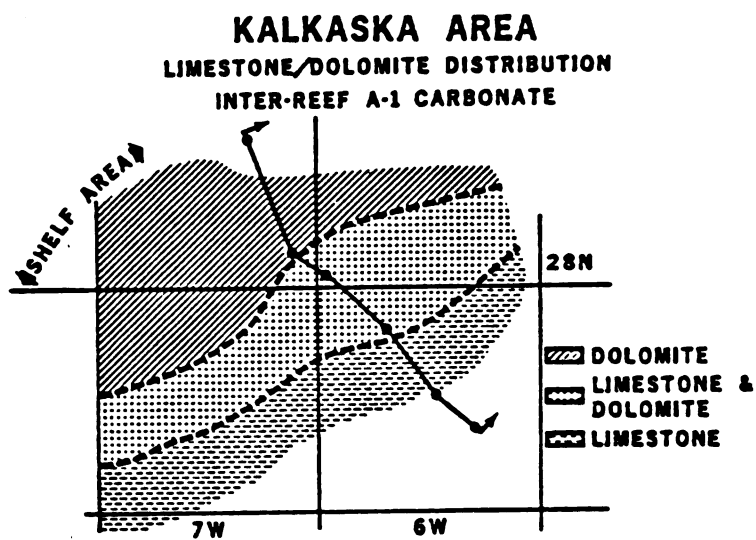


Figure 4A

4A). Carbon isotopes of the cloudy dolomite are slightly heavy (+3.7 PDB) which may suggest a methanogenesis influence (Sears and Lucia, 1980). Strontium concentrations are quite low for a hypersaline dolomite (74 ppm) compared to the predicted value of 600-700 ppm (Behrens and Land, 1973). They believe this is due to recrystallization of the dolomite and/or precursor limestone.

Six samples were analyzed from this core. Three samples (#10, 73, 79) are of the completely dolomitized cloudy type (#10 is A-1 carbonate) and three are of the clear partially dolomitized type (#74, 75, 77). With the exception of #10, all are from the pinnacle reef facies and consist of coral-stromatoporoid wackstones and packstones.

The second suite of samples from the Niagara Formation is from two quarries in Indiana, the Pipe Creek Jr. and Delphi quarries. The two quarries expose two reefs which have had their tops truncated by erosion. They are also coral-stromatoporoid reefs and are flanked by echinoderm, brachiopod and mollusc debris (Shaver and Sunderman, 1982).

An interesting feature about these two localities which are only about 40 miles apart is that the Delphi reef is almost completely dolomitized and the Pipe Creek Jr. reef is almost all limestone (Shaver and Sunderman, 1982). The reason for this difference is believed to be early cementation of the Pipe Creek Jr. reef which decreased permeability and hence inhibited dolomitization (Lehmann,

1978). The method of dolomitization is unclear but evaporites are found directly above the reefs (Shaver and Sunderman, 1982) which may indicate hypersaline brine dolomitization.

MUCK DOLOMITE

The Muck Dolomite (Middle Jurassic) is found in North-West Scotland on the island of Muck. It is a part of the Ostracod Limestone which is a member of the Great Estuarine Series. As the name implies, these deposits were formed in marginal marine to brackish water coastal lagoons (Tan and Hudson, 1974). The water depth was quite shallow and periods of evaporation are marked by mudcracks and brecciation (Tan and Hudson, 1971). The faunal assemblage is non-marine and shows conditions of variable salinity (Tan and Hudson, 1971). The rocks themselves are dominantly mudstones and mostly pure dolomite.

The dolomitization is believed by Tan and Hudson (1971) to have taken place early in diagenesis and to be the result of evaporation and concentration of the lagoon. Their main evidence is the enrichment in isotope values (-0.4 ppm PDB as compared to -2.4 PDB of the limestones and -3.0 ppm PDB of other dolomites in the area) as well as mudcracks and brecciation indicating evaporation. The carbon isotopes in this locality show little organic influence (-2.4 PDB) although other members of the series

have very light carbon isotopes (-14.1 PDB).

There is only one sample of the Muck Dolomite analyzed in this study. It consists of a dolomitized mudstone.

EDWARDS FORMATION

The Edwards Formation (Lower Cretaceous) covers a large part of Central Texas. It was deposited on a large platform in shallow water which periodically experienced conditions of restriction during which time evaporites were deposited (Fisher and Rodda, 1969). Figure 5A shows the distribution of the Edwards facies which were primarily rudist reefs, carbonate grainstone interreef facies and lagoonal deposits on the platform.

Dolomitization is associated with the evaporite lagoons (Fig. 6A). Based on its stratigraphic distribution and the presence of collapse breccias, the dolomite is believed to be a classic example of the hypersaline brine model of dolomitization (Fisher and Rodda, 1969).

There were five samples analyzed from the Edwards Formation. They consist of four dolomites and one limestone. There are evaporites or solution breccias associated with the dolomite samples.

PLOMO FORMATION

The Plomo Formation (Late Miocene) forms a series of

Figure 5A. Distribution of facies in the Edwards Formation
(from Fisher and Rodda, 1969).

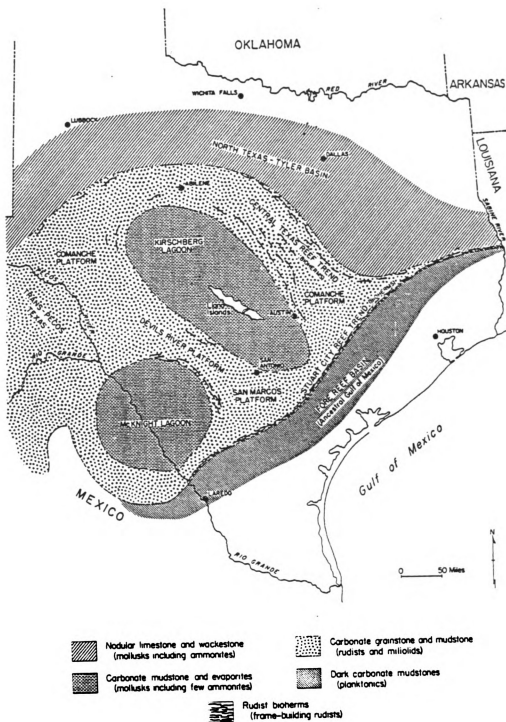


Figure 5A

Figure 6A. Dolomitization of the Edwards Formation with respect to the Kirschberg evaporite lagoon (from Fisher and Rodda, 1969).

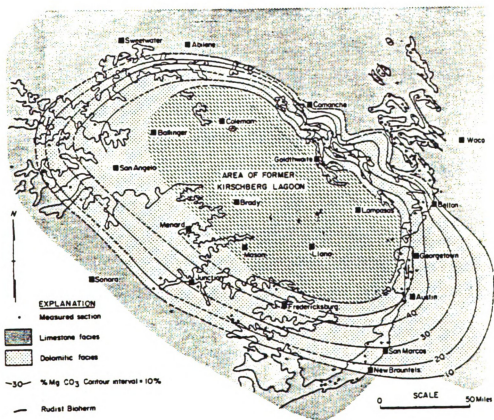


Figure 6A

reefs with interreef facies on the southern coast of Spain. These reefs were deposited in extremely shallow water on the margin of the former straits which connected the Atlantic Ocean and Medditerranean Sea (Addicott et. al., 1978).

The rocks of the Plomo Formation consists of reefs built with predominatly porites framework corals and forereef debris. The porites framework is infilled with halimeda, molluscs, coralline alga and lime mud (Addicott et. al., 1978).

The diagenesis of this unit began with submarine cementation and micritization of fossil fragments. This was followed by extensive dolomitization (Armstrong et. al., 1980). The mechanism of dolomitization is unclear but there is a massive gypsum unit in the overlying beds that represents the Messina salinity crisis (Estaban et. al. 1977). This crisis would have generated a large volume of hypersaline fluid which could be responsible for dolomitization.

There are seven samples from the Plomo Formation analyzed in this study. They consist of three dolomites and four limestones.

MONTEREY FORMATION

The Monterey Formation (Miocene, California) is an organic rich marine shale that was deposited in an

extensive anoxic ocean basin (Friedman and Murata, 1979). Dolomite and limestone occur as beds, lenses and concretions within the shale. The dolomite appears to be concentrated along zones of denser carbonate fossils, but is believed to be primarily a cement (Murata et. al., 1969).

The dolomitization appears to be controlled by organic processes. The carbon isotopes show extreme variability from highly positive (+21 ppt PDB) to highly negative (-30 ppt PDB) (Pisciotta and Mahoney, 1981). The light carbon values are thought to reflect dolomite formed in the sulfate reduction zone (Pisciotta and Mahoney, 1981). The heavy carbon dolomites are probably the result of methanogenesis (Pisciotta and Mahoney, 1981). During methane production the light carbon is preferentially removed leaving heavy carbon a residual (Irwin, 1980).

The samples analyzed in this study consists of three outcrop samples from southern California. All occurred as concretions. They consist of dolomite which appears to be mostly a cement and contained siliceous mud. These rocks did have carbon isotopic analyses which yielded two very positive samples (#42 and 44) and one which was variable from highly positive to negative (#43) (see petrographic reports).

The Seroe Domi Formation (Pliocene to Plietocene) outcrops on the western coast of Bonaire, Netherlands Antilles. The rocks represent carbonates deposited on a Cretaceous volcanic island during a sea level rise (Bandoian and Murray, 1974). The rocks represent a build-up of fore-reef carbonates up to a shallow-water platform at the top (Bandoian and Murray, 1974).

Dolomitization of the platform carbonates is quite extensive and was first thought to be the result of hypersaline brines (Deffeyes et. al., 1965). This hypothesis was developed mainly on the presence of hypersaline lakes on the southern end of the island which contained dolomite in the bottom sediments. Deffeyes et. al. (1965) believed that these lakes were a recent analog to the environment which dolomitized the Seroe Domi. Recent evidence has cast doubt on this model for the Bonaire dolomites. There are few or no evaporites found outside of the hypersaline lakes (Sibley, 1980) and the hydrology of the lakes does not appear consistent with the extensive refluxing conditions necessary for large scale hypersaline dolomitization (Murray, 1969). The sodium content of the dolomite is quite low which suggests fresh water influence and there is freshwater cement included within the dolomite (Sibley, 1980). Oxygen isotopes are high (+2.1 to +4.1 PDB) but could be explained by evaporation of freshwater (Sibley, 1980). These evidences favor a mixed-water model for dolomitization of the Seroe

Domi Formation.

Ten samples from the Seroe Domi Formation were analyzed in this study. They were all collected in the Santa Barbara Hill area. They consist of six dolomites and four limestones.

HOPE GATE FORMATION

The Hope Gate Formation (Middle Pliocene, North Jamaica) consists of a large reef system deposited on Miocene pelagic chalks during a period of high sea level (Land, 1973a). The rocks consist of reef debris such as corals, red algae, foraminifera, molluscs and echinoderms in a micrite supported matrix.

Dolomitization of these rocks is believed to be a result of mixing-zone fluids by Land (1973a). His main evidences are; 1) lack of associated supratidal sediments or evaporites and 2) sodium (400 ppm), strontium (220 ppm) and carbon-oxygen isotopes (+1.2 and +2.2 PDB respectively) which point to a freshwater influence on the dolomitizing fluid. These rocks are similar to the Seroe Domi Formation and Bahaman dolomites both depositionally and diagenetically (Sibley, 1980).

Ten samples were analyzed in this study from the Hope Gate Formation. They were collected on the north coast of Jamaica. They consist of six dolomites and four limestones. All samples contain some sparry calcite cement

(less than 10%) and the limestones appear to have been totally replaced by low magnesian calcite.

GULF OF CALIFORNIA DOLOMITES

Dolomite occurs in Gulf of California sediments which are Quaternary in age and consist of organic-carbon rich, hemipelagic diatomaceous oozes. They were deposited in deep quiet water anoxic basins similar to the Monterrey formation environments (Kelts and McKenzie, 1982).

The dolomite occurs as thin beds within the mud and is believed to form primarily as a cement with some replacement of the small amount of calcium carbonate fossils (Kelts and McKenzie, 1982). Although originally interpreted as a product of sulfate reduction by Baker and Kastner (1981), the dominance of heavy carbon isotopes suggests methanogenesis is important in the dolomite formation (Kelts and McKenzie, 1982).

Two samples consisting of mostly dolomite with some silica were analyzed from the Gulf of California. The samples are from site 478 of Leg 64 of the Deep Sea Drilling Project. The dolomite is fine grained with no discernable fossils or sedimentary structures. Sample #51 contained a small amount of pyrite visible in hand sample.

BAHAMA CRUST DOLOMITES

Holocene dolomite crusts are found on Andros Island in the Bahamas. The crusts are composed mostly of intertidal sediments which are washed up onto the supratidal zone by high tides and storms. The sediments consist of mainly peloidal carbonate mud with algal mats, roots, land snails and a few marine foraminifera and gastropods. Subaerial features such as polygonal desiccation cracks and karst features are widespread (Shinn et. al., 1965).

The mineralogy consists of poorly ordered dolomite with aragonite and calcite cements and grains. The dolomitization is believed to be the result of evaporation concentrated brines which are brought up to the surface by capillary action (Shinn et. al., 1965). Shinn et. al. (1965) found that the magnesium-calcium ratio of this fluid was in excess of 40 to 1 with salinities 5 to 6 times that of seawater thus making it an excellent hypersaline brine for dolomitization.

Two samples of the Bahama crust dolomites were analyzed in this study. They are from Andros Island and contain poorly ordered dolomite and calcite. The textures are poorly preserved but peloids and mollusc fragments are discernable. The calcite is found primarily as a cement but is also found in original grains.

Persian Gulf

Recent dolomite has been reported forming in the

Persian Gulf (Butler, 1969; Patterson and Kinsman, 1982). It is supratidal and is found in sabkhas which is strong evidence for a hypersaline origin.

One sample of this dolomite was analyzed in this study and comes from the Abu Dhabi sabkha.

APPENDIX B

Solubility Calculations in Occult Gypsum Solution

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Solubility Calculations in Occult Gypsum Solution

I. Solubility product of gypsum at 25°C = $10^{-4.61}$
 (Drever, 1982)

II. Activity coefficient calculations

$$\text{Ionic strength (I)} = 1/2 \sum m_i z_i^2$$

If no gypsum were present, the only input of ions would be from the dissolving dolomite and the 5% HCl solution.

$$\begin{aligned} \text{Input from dolomite} &= 2\text{g dol} \times 1 \text{ mol}/184.3\text{g} \\ &= 1.09 \times 10^{-2} \text{ moles} \end{aligned}$$

so, this would contribute 1.09×10^{-2} moles of Ca^{2+} and Mg^{2+} ions and 2.18×10^{-2} moles of CO_3^{2-} (some CO_3^{2-} will be lost due to shifting of the carbonate equilibrium and CO_2 evolution)

$$\begin{aligned} \text{Input from HCl} &= 38\% \text{ HCl} \times 5\% \text{ sol.} \times 1.18\text{g/ml} \times 250\text{ml} \\ &= 5.61\text{g HCl} \times 1 \text{ mol}/36.5\text{g} \\ &= 1.54 \times 10^{-1} \text{ moles} \end{aligned}$$

so this would contribute 1.54×10^{-2} moles of H^+ and Cl^- ions

multiplying the number of moles by 4 (to get molarities for a 250 ml solution) this yields for I:

$$\begin{aligned} I &= 1/2 ([4.36 \times 10^{-2} \times 4] + [4.36 \times 10^{-2} \times 4] + \\ &\quad [8.72 \times 10^{-2} \times 4] + [6.14 \times 10^{-1} \times 1] + \\ &\quad [6.14 \times 10^{-1} \times 1]) \\ &= 9.97 \times 10^{-1} \end{aligned}$$

Using the modified Debye-Huckel equation for activity coefficients ($\log a_{\text{ci}} = -A z_i^2 I / 1 + B a_{\text{ci}}$):

$$\begin{aligned} A &= .5085; B = .3281 \times 10^8 \text{ at } 25^\circ\text{C} \\ a_{\text{O}}(\text{Ca}) &= 6 \times 10^{-8}; a_{\text{O}}(\text{SO}_4) = 4 \times 10^{-8} \\ &(\text{Drever, 1982}) \end{aligned}$$

$$\begin{aligned} \text{this yields: } a_{\text{O}}(\text{SO}_4) &= .134 \\ a_{\text{O}}(\text{Ca}) &= .209 \end{aligned}$$

III. Saturation state calculations

The sulfate in solution is contributed by the acid:

$$\begin{aligned} m_{\text{SO}_4} &= .00002\% \text{ SO}_4 \text{ in acid} \times 5\% \text{ solution} \times \\ &\quad 1.18\text{g/ml} \times 250\text{ml} \times 1 \text{ mol SO}_4/96\text{g} \\ &= 3.07 \times 10^{-8} \text{ moles} \times 4(250\text{ml solution}) \\ &= 1.23 \times 10^{-7} \text{ moles/l} \end{aligned}$$

The IAP for gypsum in this solution is:

$$\begin{aligned} \text{IAP}_{\text{gyp}} &= (4.36 \times 10^{-2}) (.209) (1.23 \times 10^{-7}) (.134) \\ &= 1.47 \times 10^{-10} \end{aligned}$$

to reach equilibrium $\text{IAP} = K_{\text{sp}} = 10^{-4.61}$

so, to reach equilibrium, the amount of gypsum that must be added is:

$$\begin{aligned} (4.36 \times 10^{-2} + m_{\text{Ca}}) (.209) (1.23 \times 10^{-7} + m_{\text{SO}_4}) \\ (.134) &= 2.45 \times 10^{-5} \end{aligned}$$

$$m_{\text{Ca}} = m_{\text{SO}_4} = X$$

multiplying this out yeilds:

$$2.80 \times 10^{-2} x^2 + 1.22 \times 10^{-3} x - 2.45 \times 10^{-5} = 0$$

solving by the quadratic equation yeilds:

$$X = 1.50 \times 10^{-2} \text{ m}_{\text{SO}_4}/\text{l}$$

Converting to grams:

$$\begin{aligned} \text{wt. of gyp} &= (1.50 \times 10^{-2} \text{ m}_{\text{SO}_4}/\text{l}) (.25\text{l}) (172\text{g/mol}) \\ &= 6.43 \times 10^{-1} \text{g CaSO}_4 \cdot 2\text{H}_2\text{O} \end{aligned}$$

this corresponds to 32.1 wt. % in the analyzed sample

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