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SELECTED DOLOMITES IN THE CAMBRO-ORDOVICIAN CARBONATES OF SOUTHWESTERN OKLAHOMA

By

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SELECTED DOLOMITES IN THE CAMBRO-ORDOVICIAN CARBONATES OF SOUTHWESTERN OKLAHOMA

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TABLE OF CONTENTS

LIST OF TABLES

Table Page

CHAPTER I

INTRODUCTION

Purpose

The purpose of this thesis is to evaluate the petro graphy, sedimentology, trace element content and isotope geochemistry of selected Cambro-Ordovician dolomites that are exposed in the Slick Hills of southwestern Oklahoma, and to relate this data to recently proposed models of dolomitization. The Cambro-Ordovician carbonate sequence is exposed in two areas of southern Oklahoma: the Arbuckle Mountains of south-central Oklahoma and the Slick Hills (to the north of the Wichita Mountain igneous complex) in southwestern Oklahoma. The stratigraphy, paleontology, and sedimentology of these rocks are currently under revision and information on the geochemistry of these rocks is sparse, the only detailed work having been done in the Arbuckle Mountains area by Sargent,(1969; 1974).

Intervals Studied

Intervals from both the Timbered Hills Group and the Arbuckle Group were examined in this study (Figure 1). The lowest interval examined is near the base of the

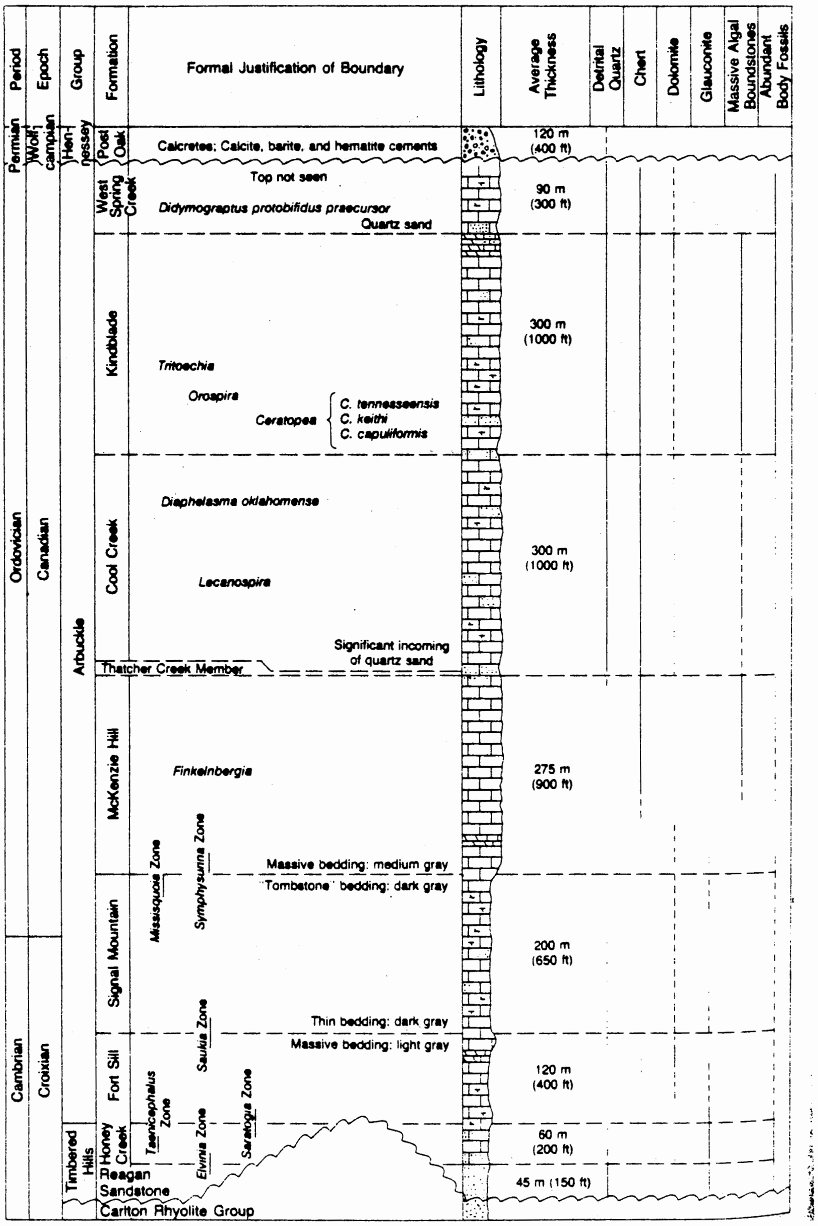


Figure 1. Generalized stratigraphic log for the Slick Hills of southwestern Oklahoma (after Donovan, 1984).

Cambrian Honey Creek Formation, the uppermost formation of the Timbered Hills Group. The three other horizons investigated lie within the Arbuckle Group. From bottom to top these are: 1) the Royer Dolomite of the Fort Sill Formation; 2) part of the Signal Mountain Formation; and 3) a supratidal sequence within the Cool Creek Formation.

Location and Geologic Setting

Although a number of areas in the Slick Hills were visited in this study, the major area of investigation was on Bally Mountain, T.6N., R.14W., Kiowa County, Oklahoma (Figure 2).

The Cambrian and Ordovician rocks of the Slick Hills area have undergone a considerable amount of tectonic deformation in the form of both faulting and folding. As a result dips range from nearly horizontal to vertical and slightly overturned. The area where the majority of the field work for this study was done is essentially homoclinal and gently dipping.

It is interesting to note that although minor amounts of dolomite are present throughout the limestones of the Slick Hills, it is only the northwestern outcrops of the area that contain a significant amount of well developed dolostones.

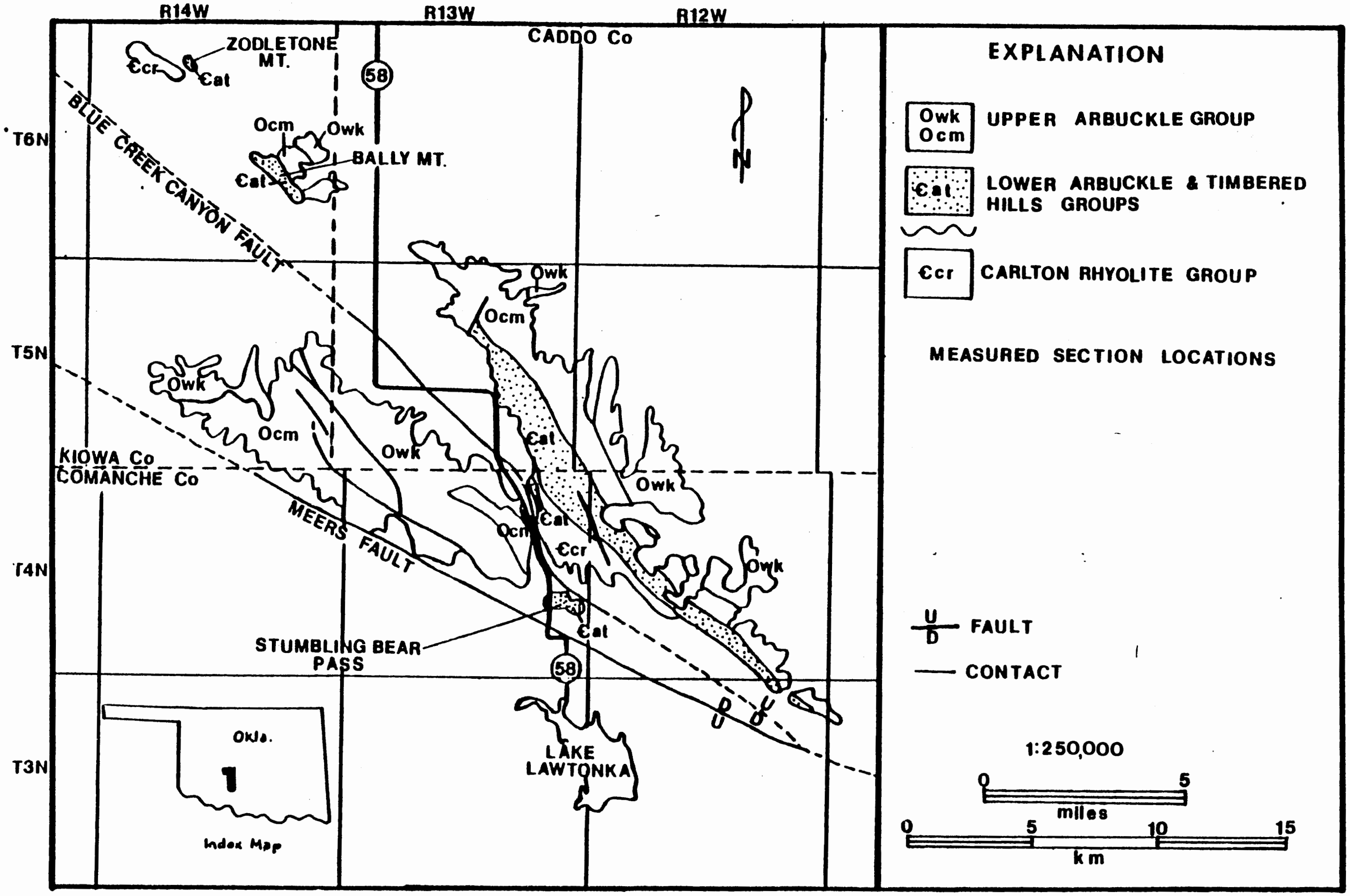


Figure 2. Geologic map of the Slick Hills (after Rafalowski, 1984).

Methods of Study

One detailed section was measured on Bally Mountain within the Cool Creek Formation, and samples were taken at distinct lithologic changes. Sampling intervals varied from less than one foot to as much as ten feet. A short section was also measured and collected near the base of the Honey Creek Formation and samples were taken of the lithologies of interest.

Dolostones in the Fort Sill and Signal Mountain formations do not lend themselves well to section measuring. The Royer Dolomite of the Fort Sill Formation on Bally Mountain is a 220 feet thick, nearly featureless dolostone. Therefore no section was measured, but samples were taken at a number of places both vertically and horizontally along the extent of the Dolomite's exposure. Since the dolomites of the Signal Mountain Formation are thin and texturally heterogeneous, a sampling technique similar to the one used for the Royer was employed. Thin-sections were made and chemical analyses were performed on all samples taken. The thin-sections were stained with alizarin red S and potassium ferrocyanide to permit differentiation of ferroan and non-ferroan varieties of calcite and dolomite (Carver, 1971). The thin-sections were then studied using a petrographic microscope. Samples were prepared and elemental analyses were done using atomic absorption spectrophotometry for the elements iron, manganese, sodium, and strontium. Stable carbon and oxygen isotope analyses, as well as strontium isotope analyses, were done by Lois Jones of Conoco Laboratories in Ponca City, Oklahoma. Cathodoluminescence petrography was done to determine to what extent the dolomites were zoned.

CHAPTER II

PREVIOUS WORKS

Early Works

The earliest work done in the Wichita-Slick Hills area of southwestern Oklahoma was that done by reconnaissance expeditions that travelled through the region. The first such expedition was led by Captain R.B. Marcey. Geologic observations from this expedition were made by George Shumard (1852) who noted the igneous terrane of the Wichita uplands and the sedimentary rocks of the lowlands. In a later survey of the area, Comstock and Cummins (1889) suggested that the geology of the Wichitas is related to that of the Llano area of central Texas. The first petrographic study of these rocks was done by Vaughn (1899). Bain (1900) was the first to recognize and describe the field relationships of the igneous and sedimentary rocks of the region.

Taff and others (1901) completed a general report on the Wichita Mountains. This report included thickness measurements, distributions and stratigraphic relationships of the lower Paleozoic sediments. In 1902 Taff recognized the Arbuckle Limestone as a formal stratigraphic unit with its type locality in the Arbuckle Mountains. In a later report, Taff (1904) subdivided the Arbuckle and described its various members. In a later report, Taff (1904) subdivided the Arbuckle Group to include, from oldest to youngest, the Fort Sill Limestone, Royer Marble, Signal Mountain Limestone, Chapman Ranch Dolomite, McKenzie Hill Limestone and the Wolf Creek Dolomite.

Howell (1922) distinguished the Lower Paleozoic formations of the Wichita Mountains based on textures that he noted in well cuttings. He noted that much of the limestone contained appreciable amounts of magnesium (2-10%), in the form of dolomite. Howell also estimated a total thickness of 6000 feet for the Arbuckle Group.

Gould and Decker (1925) described the Arbuckle Group and correlated it with the terrigenous clastics of southeastern Oklahoma.

Using faunal comparisons, Ulrich (1927) suggested that the lower Paleozoic section of southern Oklahoma represents a transgression from the Pacific side of the continent. In a later report, Ulrich (1932) noted that in the Wichita Mountains the Fort Sill is directly overlain by the Signal Mountain Formation, whereas the two formations are separated by the Royer Marble in the Arbuckles.

Decker and Merritt (1928) described various chemical and physical properties of the Arbuckle Group. They measured a section along highway 77 in the Arbuckles and did thin-section petrography and chemical analyses. Additionally they recognized that dolomite is present throughout the Arbuckle Group and is more abundant in some zones than in others.

Decker (1933) designated type sections for the formations of the Arbuckle Group and described them at these localities, in both the Arbuckle and Wichita Mountains. In a later work Decker (1939) separated the lowest part of the Cambrian section of southern Oklahoma from the Arbuckle Group and called it the Timbered Hills Group. The Timbered Hills Group was subdivided into the Reagan Sandstone and Honey Creek Limestone.

Farmillo (1943) correlated the Royer Dolomite with the Fort Sill Formation based on sponges found in both.

In 1947, Ham and Frederickson correlated the Royer at the Kinblade Ranch in the Wichitas with the Royer of the Arbuckles. This interpretation is based, in part, on the Royer's absence in the Blue Creek Canyon area (Figure 2).

Frederickson (1949) correlated the Honey Creek Formation with the Cap Mountain Sandstone of Texas based on fossil evidence.

Chase and others (1956) gave detailed descriptions and thicknesses of the lower Paleozoic Formation in the Wichita Mountains. Nelms (1958) informally divided the

Fort Sill Formation into three lithologic units. He included the Royer Dolomite in the Upper Fort Sill unit. Fox (1958) discussed the relationship between detrital quartz sand and carbonate components of the Honey Creek Formation. Harlton (1964) subdivided the upper part of the Arbuckle Group based on the type and amount of insoluble residues that he observed.

Later Works

Stitt (1971) described and classified trilobites of the Timbered Hills and lower Arbuckle Groups in the western Arbuckle Mountains. He did a similar study (Stitt, 1977) some years later in the Wichitas. Based on faunal occurrences relative to lithofacies, he suggested that the Franconian transgression progressed from east to west. In his most recent work, Stitt (1978) discussed the biostratigraphy and depositional history of the Timbered Hills and Lower Arbuckle Group in south-central Oklahoma.

Sargent (1974) did a detailed geochemical study of dolomites in the Arbuckle Mountains. In this study he recognized two distinct dolomite types: 1) fine grained "stratigraphic" dolomite; 2) coarse grained "tectonic" dolomite.

St. John and Eby (1978) recognized a number of features (evaporite pseudomorphs, solution collapse breccias, etc.) in the Cool Creek Formation that suggest it was deposited in very shallow water under arid conditions. Ragland (1983) completed a comprehensive facies analysis of the Cool Creek Formation in the Slick Hills-Wichita Mountain area. This study included much detailed work on the stromatolites and other sedimentary features of the Cool Creek Formation. Rafalowski (1984) completed a similar study on the facies relationships of the Honey Creek and Fort Sill formations.

Donovan (1982,1984) described and interpreted many of the sedimentary and structural relationships of the Slick Hills, north of the Wichita Mountains.

CHAPTER III

TRACE ELEMENT GEOCHEMISTRY IN CARBONATES

Theory

Carbonate rocks are made up of a number of minerals. In recent carbonates these minerals include high magnesium calcite, aragonite, low magnesium calcite and dolomite. Ancient carbonates, however, are made up primarily of either low magnesium calcite or dolomite, due to the fact that high magnesium calcite and aragonite are unstable in most post-depositional settings. In addition to calcium, magnesium, and carbonate, the rock forming carbonate minerals contain a number of trace elements. These include strontium, sodium, barium, potassium, iron, manganese and copper.

Trace elements are incorporated into carbonate minerals in the following ways (McIntire, 1963; Zemann, 1969; Veizer, 1983). They may: 1) substitute for calcium or magnesium in the crystal lattice; 2) be present interstitially between lattice planes; 3) occupy lattices which are free due to defects in crystal structure; 4) be adsorbed due to remnant ionic charges; 5) be present in non-carbonate inclusions, such as silicate impurities, fluid or solid inclusions, etc. The only one of these factors that can be quantified with any degree of confidence is lattice substitution. The concentration of a given trace element in the lattice of a carbonate mineral is a function of: 1) the ratio of the trace element to major elements in the solution from which the mineral precipitated; 2) the distribution coefficient of the mineral for that element (Veizer, 1983).

In simple terms, the distribution coefficient is a reflection of the degree to which the mineral discriminates against the incorporation of a trace element into its lattice. It is important to realize that an element whose distribution coefficient exceeds one will have a higher concentration in the precipitate than the water from which it was precipitated, relative to the concentration of the element with which it is substituting. The inverse is true for elements with distributions that are less than one (Veizer, 1983). Although little information is available on factors that control distribution coefficients, they must in part reflect the similarity or difference in valence state and ionic radii between the trace element involved in substitution and the element being replaced in the carbonate lattice.

Since carbonate diagenesis and stabilization takes place through a series of dissolution and re-precipitation events, involving trace elements as well as major carbonate components, a large potential exists for the alteration of the trace element content of these rocks (Bathurst, 1975). This is true even if there is no mineralogical change. The composition of pore water in which these changes take place to a large degree controls the final trace element composition of carbonate minerals involved. Most of this solution re-precipitation takes place below the permanent water table, within the meteoric or mixed meteoric-marine phreatic zones (Land, 1970; Veizer, 1983).

The trace element composition of sea water is well known (Table 1), whereas the chemistry of various meteoric waters is not well known, and in all probability, is highly variable (Table 2). Generally, average surface water, in contrast to sea water, is very dilute (120 ppm vs. 35000 ppm; Veizer, 1983) and the majority of meteoric waters are nearer in composition to surface water than to sea water. It is necessary to realize that it is the trace element to major element ratio that is important, rather than the actual concentration of either. Thus, on the average, the Sr/Ca, Mg/Ca, and Na/Ca ratios are lower and Ba/Ca, Mn/Ca, Zn/Ca, Co/Ca, Cu/Ca and Fe/Ca ratios are higher in meteoric waters than in sea water.

Regardless of the waters composition, if it remains

TABLE I

COMPOSITION OF SEA WATER

Major solutes and nutrients (mg/kg) (ppm)			
Chloride	19,350	Strontium	8
Sodium	10,760	Boron	4.5
Sulfate	2,710	Fluoride	1.3
Magnesium	1,290	Silica	0.5-10
Calcium	411	O_2	0.1-6
Potassium	399	NO_3	0.005-2
Bicarbonate	142	PO_4	0.001-0.05
Bromide	67	Dissolved organic carbon	0.3-2 (as C)
Minor solutes (µg/kg) (ppb)			
Lithium	180	Zirconium	0.03
Beryllium	6×10^{-4}	Niobium	0.01
Aluminum	2	Molybdenum	10
Scandium	6×10^{-4}	Silver	0.04
Titanium	1	Cadmium	0.05
Vanadium	2	Tin	0.01
Chromium	0.3	Antimony	0.2
Manganese	0.2	Iodine	60
Iron	2	Cesium	0.4
Cobalt	0.05	Barium	2
Nickel	0.5	Rare earths	10^{-3} to 10^{-5}
Copper	0.5	Tungsten	0.1
Zinc	2	Gold	4×10^{-3}
Gallium	0.03	Mercury	0.03
Germanium	0.05	Thallium	0.01
Arsenic	4	Lead	0.03
Selenium	0.2	Bismuth	0.02
Rubidium	120	Radium	1×10^{-7}
Yttrium	1×10^{-3}	Uranium	3.3

(after Veizer, 1983)

TABLE II

AVERAGE COMPOSITION OF RIVER WATER

Ca	14.6 ppm
Mg	3.8
Na	5.1

Li	10 ppb	Se	0.2 ppb
B	20	Br	20
F	100	Rb	1
Al	50	Sr	60
Sc	0.004	Y	0.007
Ti	10	Mo	0.5
V	1	Ag	0.3
Cr	1	Sb	1
Mn	8	I	7
Fe	40	Cs	0.03
Co	0.2	Ba	50
Ni	2	REE	0.001-0.1
Cu	7	W	0.03
Zn	30	Au	0.002
Ga	0.1	Mg	0.07
As	2	Pb	1
		Th	0.1
		U	0.1

(after Veizer, 1983)

in contact with the rock long enough an equilibrium situation will develop with respect to the trace elements, in which the solid phase has a composition somewhere between its original composition and the composition of the water. If, however, large volumes of water pass through the rock without ever coming to equilibrium, a drastic change in trace element composition of the rocks could take place providing that the water is of significantly different trace element composition than the rock.

With these principles in mind it is possible to use the concentrations of certain trace elements in carbonate rocks as a clue to their depositional and diagenetic histories.

Use of Certain Trace Elements in Dolomite Geochemistry

Most sedimentary dolomite is thought to form in one of two ways; either through the synsedimentary diagenesis of hypersaline deposits (Friedman and Sanders, 1967; Friedman, 1980) or by postburial diagenesis of normal marine limestones (Hanshaw et al., 1971; Badiozamani, 1973; Folk and Land, 1975). Chemical differences between these two types of dolomite may be determined if considerable recrystallization has not occurred.

Strontium

Since strontium substitutes primarily for calcium in the dolomite lattice, the concentration of strontium in dolomite should be about 1/2 that of calcite formed under similar geochemical conditions. Among ancient dolomites, the early diagenetic (fine grained, layered, of hypersaline origin) type usually contains elevated strontium concentrations compared to its late diagenetic (coarse grained, massive, limpid) counterpart. Strontium concentrations in the early type usually range from 100-1000 ppm, whereas in the later type, they are 30-100 ppm (Veizer and Demovie, 1974; Veizer, 1983). Ancient dolomites with strontium concentrations in excess of 600 ppm must have been precipitated from hypersaline solutions, because in order to precipitate dolomite with such a high strontium concentration it is necessary to raise the strontium to calcium ratio. This may be done by the precipitation of gypsum. The concentration of strontium in dolomite at equilibrium with sea water ranges from 470-550 ppm (Table 3) (Veizer, 1983). The concentrations of strontium in dolomites that formed in mixed marine-meteoric zones, are lower by varying amounts depending on the amount of meteoric water involved (Veizer, 1983).

It must be realized that the concentration of strontium or any other trace element, in ancient

TABLE III

TRACE ELEMENT CONCENTRATIONS IN CARBONATES AT EQUILIBRIUM WITH SEA WATER

Trace Element	Calcite ppm	Aragonite ppm	Dolomite ppm
Sr	1000	7000-9400	470-550
Na	200-300	1500	≤110-160
Mg	16300-75400	750-6300	130400
Fe	2-39	-	3-50
Mn	1	0.1-0.6	1
Zn	10-39	10	24-93
Co	0.1-0.2	-	0.5-1
Cd	0.4-1.5	0.1-0.3	0.3-1
Cu	7-19	0.5-5	110-300
Ba	0.2-0.8	2-4	0.1-0.5
UO_2	<0.1	1-4	-

(after Veizer, 1983)

carbonates, is not only a function of depositional fluids, but is also a function of the composition of diagenetic fluids that have passed through the rock.

Sodium

Sodium, the most abundant cation in sea water, should be a good indicator of the salinity of depositional and diagenetic fluids. The sodium in dolomites can come from three sources: 1) from saline waters, in the form of sodium chloride inclusions; 2) from saline waters in the form of exchanged ions and incorporation into lattice sites; 3) from contamination by non-dolomitic minerals (clays). If the latter is the case, there should be a correlation between insoluable residues and sodium content. Although inner-crystalline inclusions are somewhat unpredictable, they still give some indication of the salinity of the pore fluids at the time of their formation. The most predictable of these factors is the cation exchange within the lattice. This again is directly related to salinity (Fritz and Katz, 1972).

It is unclear if the sodium content in ancient carbonates is a reflection of salinity at the time of deposition, the salinity of diagenetic solutions, or a combination of the two. Since the concentration of sodium in dolomites at equilibrium with sea water is 160 ppm or less (Veizer, 1983) (Table 3), it is clear that dolomites that contain more sodium than this were at some time in their histories in contact with hypersaline solutions. The low sodium content of many ancient dolomites suggests that they are either primary products of solutions containing little sodium, or that they have re-equilibrated with a solution that contained little sodium.

Manganese and Iron

The concentrations of manganese and iron in sedimentary carbonates show considerable similarities. This is probably due to the similar manner in which these elements behave. They are both mobile to significant degrees only in reducing solutions. The concentrations of iron and manganese for dolomite at equilibrium with sea water are 1 ppm, and 3-50 ppm respectively. Meteoric waters contain considerably more manganese and iron than does sea water (Tables 1 and 2).

Ancient carbonates contain higher manganese and iron concentrations than do modern carbonates. There are two possible explanations for this fact: 1) ancient carbonates have undergone considerable recrystallizations in the presence of meteoric waters or subsurface brines; 2) the waters of ancient seas were more reducing than those of modern seas (Fairchild, 1980). Because many dolomites contain three times the iron and manganese that their limestone counterparts contain, the former is more significant (Rao and Naqri, 1977).

Trace Elements in the Arbuckle and Timbered Hills Groups

Sodium

The Cool Creek Formation. The sodium content of the Cool Creek limestones ranges from 160-250 ppm, with the average being 204 (table 4). That of the dolomites ranges from 180-540 ppm, with the average being 290 ppm. The sodium concentration values for calcite and dolomite, at equilibrium with sea water, are 200-300 ppm and 110-160 ppm respectively (Viezer, 1983). The sodium concentrations for modern (hypersaline) dolomites is well in excess of 1000 ppm (Land and Hoops, 1973). These figures indicate that the Cool Creek dolomites and most ancient dolomites were either not formed from hypersaline brines or were recrystallized in the presence of less saline pore waters at some time after deposition.

With one possible exception, it is unlikely that much, if any, sodium was leached from the insoluble portion of these samples. The exception is sample CCB 1, which has the anomalously high sodium concentration of 538 ppm. This sample also yielded 59.7% insoluble residues, which consist primarily of chert. One possible explanation for the unusually high concentrations of sodium and other trace elements is the presence of

TABLE IV

TRACE ELEMENT CONCENTRATIONS OF SAMPLES FROM THE ARBUCKLE GROUP IN PPM

Sample Number	% Insoluble Residue	Strontium	Sodium	Manganese	Iron
CCB 1	59.7	-	538	233	3672
CCB 2	6.3	213	161	99	85
CCB 4	.4	112	206	102	960
CCB 5	14.0	102	244	-	461
CCB 6	7.1	15	240	179	1700
CCB 8	14.4	7	178	110	2662
CCB 10	18.8	-	257	116	643
CCB 13	3.0	107	213	-	519
CCB 14L	.9	6	257	90	666
CCB 14D	3.0	22	293	80	546
CCB 15	4.8	-	408	93	1551
CCB 17	2.0	149	250	96	351
CCB 19	6.9	-	295	102	562
CCB 21	4.0	20	201	21	1040
CCB 23	7.9	108	185	102	541
CCB 25	2.6	73	169	20	216
CCB 26	8.9	16	201	105	588
CCB 27	9.9	-	262	22	519
CCB 28	3.7	-	327	21	1034
CCB 29	.6	-	282	94	177
CCB 32	2.5	-	354	95	803
CCB 34	15.6	27	183	113	2006
CCB 38	40.9	34	197	-	1172
CCB 39	1.5	-	288	-	372
CCB 40	8.8	-	347	21	1098
CCBAR	12.2	27	303	108	93
BDP 1	2.5	-	351	313	1442
BDP 2	.6	60	113	150	240
ROY 1	.2	55	122	164	239
ROY 2	5.1	-	454	323	3380
ROY 3	2.4	-	287	166	2521
ROY 4	.7	-	233	313	1453
ROY 5	4.1	-	367	415	1975
ROY 6	3.1	-	341	321	2287
ROY 7	3.4	-	357	257	2600
ROY 8	.5	-	272	378	2367
SMTL	6.4	179	210	492	4347
SMTD	9.3	86	200	1096	10134

inclusions in the chert. With the exception of this sample, there is no apparent correlation between the sodium concentration and the amount of insoluble components present, which implies that the sodium observed is indeed from the carbonate portion of these rocks.

The Royer and its Associated Pipe Dolomites. The sodium concentration in the limestone samples that are equivalent to the uppermost Royer member ranges from 110-120 ppm, with an average of 115 ppm, whereas the sodium concentrations in the Royer dolomites range from 233-454 ppm, with an average of 329 ppm. These values, like those of the Cool Creek dolomites, are higher than dolomites at equilibrium with seawater but are lower than modern supratidal dolomites. The average value is also higher than that of the Cool Creek dolomites, and is much higher than that of equivalent limestones. There are a number of possible explanations for these facts: 1) the Royer was deposited as a dolomite under more saline conditions than the Cool Creek; 2) the Royer was deposited under similar conditions as the Cool Creek but was not exposed to as much meteoric influence; 3) the Royer was deposited as limestone and was dolomitized by saline fluids; 4) the Royer was deposited as limestone and was dolomitized by mixed meteoric-marine waters and was then recrystallized in the presence of saline pore waters. It is unlikely that the Royer was deposited under similar or more saline conditions than the Cool Creek, since there is evidence for the former presence of evaporites in the Cool Creek but there is no such evidence in the Royer.

The evidence that the Royer was deposited as a limestone is reasonably strong. The Royer truncates the upper Fort Sill Formation. It also contains small amounts of glauconite which has never been reported from sabkha sequences. The coarsely crystalline nature of the Royer also suggests that the Royer, at least in the Slick Hills, is a diagenetic feature. The relatively high concentrations of iron and manganese in the Royer indicate that at some time it was in contact with solutions of nonmarine origin (Veizer, 1983).

It seems most likely from this evidence that the Royer was dolomitized by the mixing of marine and meteoric waters. The relatively high sodium contents might therefore be explained by the more porous (relative to the adjacent limestones) dolomites being infiltrated by saline subsurface waters. Recrystallization in the presence of these waters could be responsible for the sodium concentrations observed.

The Signal Mountain Formation. The limestones in the Signal Mountain Formation have a sodium concentration ranging from 200-220 ppm with an average of 210 ppm. The dolomites range from 200-230 ppm with an average being 213 ppm. Since the dolomite is clearly post-depositional (burrow filling etc.), and yet the limestone and dolomite have such similar sodium concentrations it is likely that this is more a reflection of the chemistry of post-depositional pore waters than of depositional salinity.

Strontium

The Cool Creek Formation. The strontium content of the Cool Creek limestones ranges from 73-213 ppm with an average of 123 ppm. By contrast, the strontium concentration in the Cool Creek dolomites ranges from below the detecable limit (1 ppm) to 34 ppm with an average of 9 ppm. These values are all well below the limit of 100 ppm for ancient hypersaline dolomites as recognised by Veizer (1983). This value of 100 ppm does not take into account the possibility that a supratidal dolomite might have been subjected to meteoric influences or post-depositional recrystallization. These effects could,in the case of the Cool Creek, have significantly lowered the strontium concentrations.

The Royer Member. The strontium content of the limestone equivalents to the uppermost Royer ranges from 50-60 ppm with an average of 56 ppm. All the Royer dolomites have strontium values below the detectable limit. These low values are consistent with a dolomite that formed from warm subsurface waters. Conversely, the strontium may be depleted from the Royer by subsequent recrystallization.

The Signal Mountain Formation. The Signal Mountain limestones analyzed, have a strontium concentration of 150-190 ppm, with an average of 175 ppm. The dolomites have a strontium content of 80-90 ppm, with an average of 86 ppm. These values, though higher than those of either the Cool Creek or the Royer, are still within the range of late dolomite (Veizer, 1983).

Manganese and Iron

The Cool Creek Formation. The iron and manganese concentrations are lower in the Cool Creek than those of any other formation tested (Table 4). The iron concentrations in the limestones are 100-540 ppm, with an average of 360 ppm. The iron concentrations of the dolomites are 177-3671 ppm, with an average of 1180 ppm. The wide range of values might be due to several periods of dolomitization or recrystallization.

Manganese shows a very similar distribution to that of iron in the Cool Creek Formation as well as in the other formations studied. The concentrations of manganese in the Cool Creek are 1-100 ppm for limestone, with the average being 60 ppm. The manganese concentrations in the dolomites are 0-233 ppm, with an average of 83 ppm. These values, although low compared to the other formations studied, are high compared to modern carbonates. Since ground waters of meteoric origin contain more iron and manganese than does seawater (Table 2), it might be concluded that the manganese and iron present in these rocks is due to meteoric influence (Veizer, 1983). There is a general tendency for ancient carbonates to contain higher concentrations of iron and manganese. It has been suggested that this trend might indicate that the ancient atmosphere contained less oxygen, thereby allowing more iron and manganese to be dissolved as Fe++ and Mn++ in the ancient seas (Fairchild, 1980). In addition it is evident that, since the dolomites have higher concentrations than the limestones, the dolomitizing fluids contained more manganese and iron than the original marine pore fluids. This also implies that these later fluids were probably more reducing, since Mn++ and Fe++ are much more mobile than more oxidized ions.

The Royer Member.The Royer dolomites are considerably richer in iron and manganese than those of the Cool Creek. The iron concentrations in the Royer limestone equivalents are 220-240 ppm, with the average being 230 ppm (Table 4). The Royer dolomites contain much more iron than do the limestones, with concentrations of 1400-3380 ppm and an average of 2200 ppm. The manganese concentrations are 0-

170 ppm, with an average of 85 ppm for the limestone, and 166-415 ppm with an average of 315 ppm for dolomites. High concentrations of both iron and manganese indicate that the pore waters were reducing and contained fairly high concentrations of iron and manganese. The source of the iron might in part be the glauconite that is present in minor amounts in the formation. It is difficult to tell when the iron and manganese were introduced into the dolomite lattice. If dolomitization is relatively late, as textural evidence suggests, then it is highly likely that the iron and manganese were introduced by dolomitizing subsurface waters.

The Signal Mountain. Limestones of the Signal Mountain Formation have iron concentrations of 3710-4800 ppm, with an average of 4250 ppm. Dolomites analyzed have iron concentrations of 9500-10100 ppm, with an average of 9900 ppm. The manganese concentrations for limestones were 370-530 ppm, with an average of 450 ppm. The manganese values for the dolomites ranges from 890-1200 ppm, with an average of 1100 ppm. It is necessary to point out that the Signal Mountain samples must have some cross contamination between the limestones and the dolomites, since it was impossible to completely separate the two components. The relatively high manganese and iron concentrations indicate that the pore waters in the Signal Mountain were reducing enough to allow iron and manganese ions to become mobile.

The Honey Creek. The ankerite of the Honey Creek Formation has iron concentrations of 45000-47200 ppm, with an average of 46100 ppm, whereas the calcite has iron concentrations of 5000-7200 ppm, with an average of 6100 ppm. These extremely high iron contents are a reflection of both the calcite and the ankerite having formed in reducing pore waters at the expense of glauconite that is present.

CHAPTER IV

CARBON AND OXYGEN ISOTOPES

Introduction

Isotopes are atoms whose nuclei contain the same number of protons but a different number of neutrons. The isotopes of an element behave almost identically, since chemical behavior is controlled by the structure of the atom's electrons. Although this is true for most experimental systems in the laboratory, it does not apply to many physical, chemical and biological processes in nature. The differences in isotopic mass lead to slight but significant differences in the behavior of the isotopes of an element during natural processes (Anderson and Arthur, 1983).

Since the magnitude of "isotope effects" is proportional to the relative mass difference between isotopes, significant isotopic variations in nature are limited to light elements. Additionally, the elements carbon, hydrogen, nitrogen, oxygen and sulfur occur in relatively high abundance, participate in most important geochemical reactions, and are the most important elements in biological systems, (Anderson and Arthur, 1983).

Isotopic Fractionation

The term "isotopic fractionation" refers to the partial separation of isotopes which can occur during physical and chemical processes. This separation is caused by small differences in the physical and chemical properties of isotopically substituted molecules or crystals. These differences are called isotope effects. Kinetic isotope effects occur when physical processes and chemical reactions of different isotopic species take place at slightly different rates. Equilibrium isotopic fractionation occurs because the thermodynamic properties of isotopically substituted species also differ from one another. In general, light isotopic species will react slightly more readily during a chemical reaction than heavy isotopic species.

The energy of a molecule can be described in terms of: 1) its electronic energy (energy of electrons in relation to one another and to the nucleus); 2) translational energy (that due to linear motion); 3) rotational energy; and 4) vibrational energy (Brownlow, 1979). Isotopic fractionation in chemical and physical processes is due largely to the different frequencies of vibration of heavy and light atoms in a molecule or crystal structure. Atoms of a light isotope vibrate with higher frequencies, therefore they are less strongly bonded to other atoms than atoms of heavy isotopes. The differences in bond strength are appreciable only for isotopes whose atoms have a large relative difference in mass (the elements with relatively low atomic mass). Differences in vibrational frequencies of particles of different masses become smaller at higher temperatures, and the segregation of isotopes is correspondingly less pronounced (Krauskopf,1979).

Oxygen Isotopes

The isotopic composition of oxygen in carbonates precipitated from natural waters is dependant upon the composition of the aqueous phase and temperature. The behaviour of oxygen isotopes in natural waters depends in large part on the fact that $H_2{}^{16}O$ has a slightly greater vapor pressure than the heavier $H_2{}^{18}O$ for a given temperature. For this reason, the processes of evaporation and precipitation are very important controls on the isotopic composition of natural waters, and therefore carbonates. Seawater today has a rather narrow range of isotopic composition, but when extrapolating this composition back in time to non-glacial epochs, a small correction must be made to acount for the volume of isotopically light water released from the melting of glacial ice. Rainwater derived by the evaporation of seawater is depleted with respect to ^{18}O. This effect is more pronounced at high latitudes and altitudes. The light isotopic composition of surface and ground waters is very similar to the composition of the rainwaters from which these waters were derived. This statement may not hold true in areas with arid climates due to the concentration of ^{18}O rich water through evaporation. Brines that are formed from the evaporation of seawater are enriched in ^{18}O and therefore show positive $\delta^{18}O$ values. Deep subsurface waters have undergone the most complex changes since their entrapment as seawater within deposited sediments and may show quite variable isotopic composition.

Carbonates concentrate ^{18}O relative to the water from which they precipitate. This process is inversely proportional to temperature. This provides a paleotemperature scale for marine carbonates and also means that temperature increase caused by burial tends to decrease the $\delta^{18}O$ of late-diagenetic carbonates (Leeder, 1982).

Carbon Isotopes

The two major reservoirs of carbon are those of organic carbonate carbon. Their masses and mean carbon isotopic composition are listed in Table 5. Photosynthetic fixation of carbon from atmospheric CO_2 in organic matter involves a large fractionation of carbon isotopes. In this fractionation ^{12}C is preferentially incorporated into plant tissue. Atmospheric CO_2 has a

TABLE V

ESTIMATED MASS OF CARBON IN VARIOUS RESERVOIRS AND THEIR ISOTOPIC COMPOSITION

	Reservoir	Mass	$\delta^{13}C$‰
1)	Atmosphere (pre-1850 CO_2)	610	-6.0 - -7.0
	(∿290 ppm)	(range: 560-692	
2)	Oceans - TDC	35,000	0
	DOC	1,000	-20
	POC	3	-22
3)	Land Biota (biomass)	(range: 592-976)	-25
		(∿10% may be C_4? plants)	-12
4)	Soil Humus	(range: 1050-3000)	-25
5)	Sediments (Total)[1]	(range: 500,000-10,000,000)	—
	inorganic C	423, 670	+ 1
	organic C	86, 833	-23
6)	Fossil Fuels	>5000	-23

	Fluxes	Rates of Mass Transfer	$\delta^{13}C$‰
1)	Atmosphere/Ocean CO_2 exchange	100	—
2)	Atmosphere/Land Biota - photosynthesis	(range: 53 - 78; avg. 63)	—
	[Estuaries-marshes] ...	(∿1.4)	—
3)	Ocean Photosynthesis	(range: 15 - 126; avg. 45)	—
4)	Land to Ocean	(range: 0.38 - 0.44)	—
	TDC	0.4	-6.0 - -9.0
	DOC	0.1 (0.215)[2]	-25
	POC	0.06 (0.180)[2]	-26
5)	Ocean Deposition	(range: 1 - 10)	—
	inorganic C	(range: 0.5 - 5; probable 1-2)	+ 1.0
	organic C	0.095 (probably too low)	-20
6)	Fossil Fuel Combustion	5	-23
7)	Volcanic CO_2	0.08 (mantle)[3]	- 7
8)	Organic C leaving Photic Zone	4.1 - 10.0	-20

(after Veizer, 1983)

^{13}C of -7 on the PDB scale whereas the $^{13}C:^{12}C$ ratio in plant materials is 2% lower than in the atmosphere due to the fact that more frequent collisions occur between the more energetic $^{12}CO_2$ molecules and in the photosynthesising systems than compared with $^{13}CO_2$. Therefore carbon from organic sources is isotopically light, averaging about $\delta^{13}C$= -24 PDB for land plants (Leeder, 1982).

Extremely light carbon (down to $\delta^{13}C$= -80) is produced in methane derived by anaerobic bacterial degradation of organic materials. Oxidation of this methane forms very light CO_2 that may be taken up into the lattice of carbonate minerals. By contrast, the heavy bicarbonate residue produced by this type of anaerobic degradation can also be involved in carbonate precipitation (Leeder, 1982).

The inorganic precipitation of carbon in the various carbonate minerals involves little fractionation regardless of temperature. Consequently the isotopic composition of the carbon in carbonates is very close to that of the total dissolved carbon in the solution from which it precipitated (Anderson and Arthur, 1983).

Unlike those of oxygen, carbon isotopic ratios usually change very little during diagenesis. This is due to the small amount of carbon that may be dissolved as CO_2 in diagenetic solutions, when compared to the vast amount of carbon tied up in carbonate minerals. The large amount of oxygen in the water molecules of diagenetic solutions is responsible for the relative ease with which oxygen isotopic composition may be changed. By contrast, it is the insolubility of CO_2 that is responsible for the relative difficulty with which carbon isotopic composition of carbonates may be changed during diagenesis.

Expression of Isotopic Data

In geology neither the actual abundance of an isotope nor the exact ratio of one isotope to another is normally sought. Instead the magnitude of the isotopic ratios of a sample is compared to the ratios of some standard. This comparison is calculated in terms of delta (δ), e.g. for stable carbon isotopes,

$$\delta\, {}^{13}C\ 0/00 = \frac{{}^{13}C/{}^{12}C(\text{sample}) - {}^{13}C/{}^{12}C\ (\text{standard})}{{}^{13}C/{}^{12}C(\text{standard})} \quad x1000 \tag{1}$$

and similarly for oxygen, with ${}^{18}O$ and ${}^{13}C$ being substi tuted for ${}^{16}O$ and ${}^{12}C$ respectively. A positive delta value indicates enrichment in the heavy isotope, while a negative delta value indicates a depletion in the heavy isotope. A 1% enrichment of the heavy isotope is equivalent to a delta value of +10 0/00. For carbonates, the PDB standard is commonly used for both carbon and oxygen isotopes. This standard was prepared from

Belemnitella americana, a belemnite from the Cretaceous Peedee Formation of South Carolina. Another standard often used for oxygen isotope determinations is SMOW, or Standard Mean Ocean Water. SMOW values may be converted to PDB values or vice versa using the following equation:

$$\delta^{18}OSMOW = 1.031\,\delta^{18}OPDB + 30.8 \quad \text{(Brownlow, 1979).} \qquad (2)$$

Carbon Oxygen Isotopes of the Cool Creek and Royer Dolomites

The Cool Creek Formation

The Cool Creek carbonates (both limestones and dolomites) exhibit carbon isotopic ratios that are within the range of those marine carbonates (Figure 3). The ^{13}C values for the limestones analyzed are slightly heavier than those for the dolomites (-1.6 to -1.9 vs. -2.1 to 2.8 ^{13}C PDB [0/00]). The slight lightening effect in the dolomites might be the result of meteoric influence or the result of oxidation of hydrocarbons. In either case, the lightening of the carbon isotopes has been very slight due to carbon's strong resistance to isotopic change in carbonates.

Unlike carbon, the oxygen isotopic composition of the Cool Creek carbonates deviates considerably from the values of modern marine carbonates, with $\delta^{18}O$ PDB (0/00) values from -6.4 to -10.1. These unusually negative

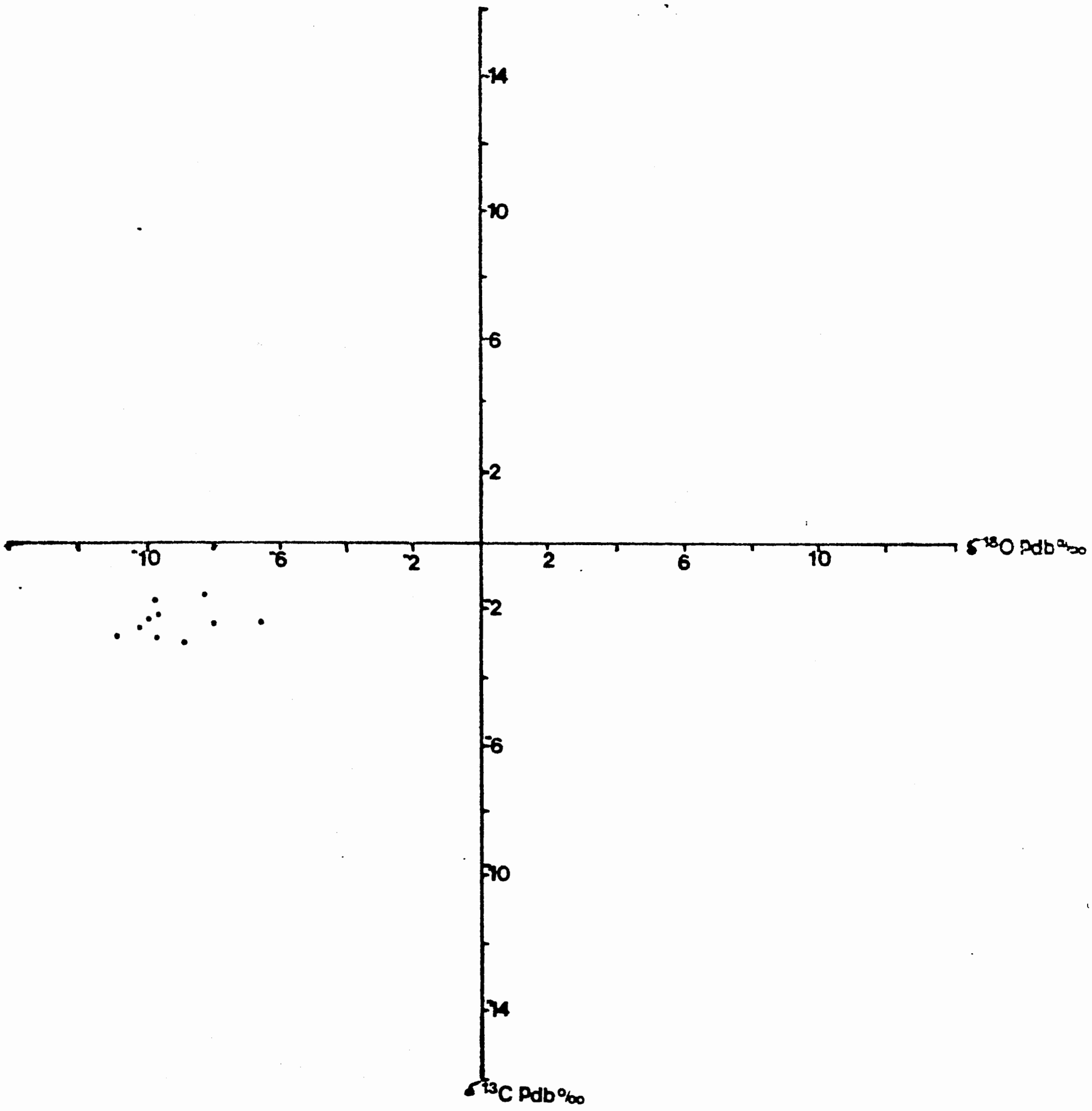


Figure 3. Carbon and oxygen isotopic distribution in Cool Creek Dolomites.

values may be due to a combination of meteoric effects and recrystallization at elevated temperatures after burial.

The Royer Dolomite

The isotopic composition of carbon in the Royer carbonates is slightly heavier than that of the Cool Creek (+.9 to +1.4 δ^{13}C PDB (0/00))(Figure 4). By contrast the oxygen isotopic composition of the Royer is somewhat lighter (-10.4 to -12.1) than that of the Cool Creek. A possible explanation of these variations is that, since the carbon is lighter and the oxygen is heavier in the Cool Creek than in the Royer, the carbon depletion is due to hydrocarbon effects. If this depletion were due to meteoric effects the oxygen depletion should be greater in the Cool Creek due to the fact that carbon isotopic composition is so resistant to change. It is possible that the lighter oxygen isotope values observed in the Royer are due to recrystallization at a higher temperature than in the Cool Creek carbonates, since the Royer was buried deeper than was the Cool Creek.

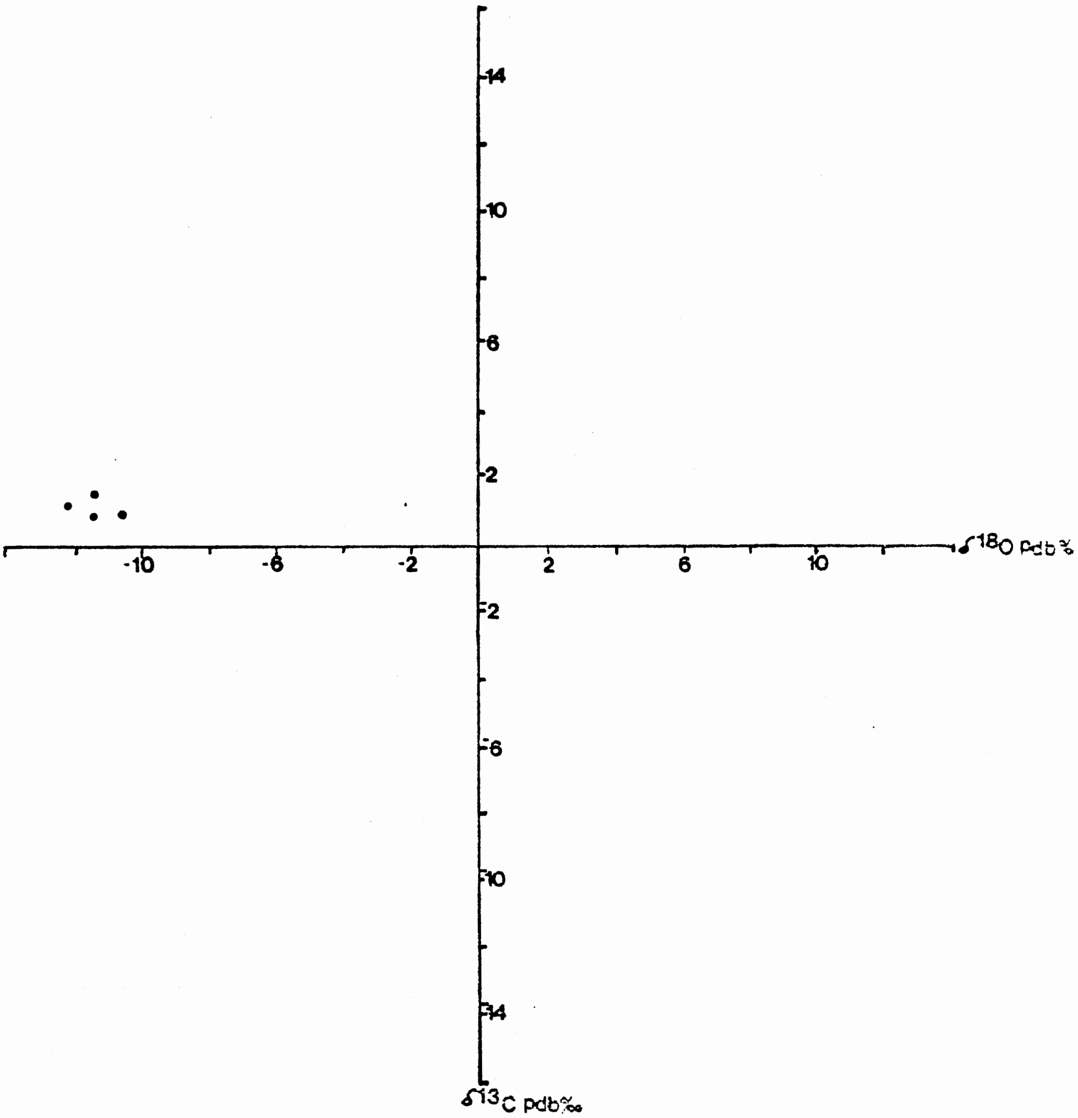


Figure 4. Carbon and oxygen isotopic distribution in the Royer Dolomites.

CHAPTER V

STRONTIUM ISOTOPES

Introduction

In contrast to carbon and oxygen, strontium incorporated into the lattice of carbonate minerals inherits its isotopic composition from the solution of precipitation (Veizer, 1983) The isotopic composition of strontium in seawater is a reflection of four factors: 1) continental river discharge (high $^{87}Sr/Sr^{86}$ compared to seawater; 2) interaction between seawater and oceanic basalts (low $^{87}Sr/Sr^{86}$ compared to seawater; 3) interaction between seawater and carbonate sediments (similar Sr^{87}/Sr^{86} to seawater); 4) subduction of sediments and trapped water in subduction zone (unknown composition) (Veizer, 1983). Through geologic time relative variation of these factors has caused fluctuations in strontium isotopic composition of seawater.

The $^{87}Sr/^{86}Sr$ ratio of seawater today is .709. During the geologic past, it was either similar or less radiogenic (strontium forms as the result of atomic decay of rubidium 87) (Veizer, 1983). By contrast, continental waters are usually more radiogenic. In theory, therefore, strontium isotopes should be a good indicator of the degree of involvement of meteoric water in the diagenesis of carbonates. Unfortunately this is usually not true, because as carbonate sediments stabilize after deposition they lose strontium to pore waters. The pore water system is overwhelmed by this strontium with marine affinities to such a degree that the $Sr^{87}/86$ values will be that of seawater regardless of the actual origin of the diagenetic waters. The meteoric signature may assert itself at a later stage after the original strontium has been lost from the system (Veizer, 1983).

Strontium Isotopes in the Royer Dolomite and Cool Creek Formation

The Cool Creek Formation

Strontium isotope ratio values in the limestones and dolomites of the Cool Creek range from .70868 to .70909 (Table 6), with an average of .70893. There is no apparent difference between dolomites and limestones. Burke (1982) plot the $^{87}Sr/Sr^{86}$ composition of seawater for the early Ordovician seas at .7089. This similarity of values between the Cool Creek and Ordovician seawater suggests that diagenesis took place in pore waters that contained strontium which was similar isotopically to that of seawater.

TABLE VI

ISOTOPIC DATA

SAMPLE NUMBER	^{13}C 0/00 PDB	^{18}O 0/00 PDB	Sr 87/86
CCB 1	-2.4	-6.4	.70897
CCB 2	-1.6	-8.1	.70898
CCB 4	-2.7	-9.2	.70898
CCB 10			.70909
CCB 17	-1.9	-9.8	.70898
CCB 21	-2.6	-10.8	.70868
CCB 26	-2.6	-9.8	.70869
CCB 34	-2.8	-9.4	.70901
CCB 37	+1.4	-11.4	.70875
CCB 40			.70874
CCBAR	-2.8	-8.7	.70900
BDP 1	+1.0	-12.1	.70940
BDP 2	+0.9	10.4	.70910
ROY 1			.70937

The Royer Dolomite

The $^{87}Sr/^{86}Sr$ value of limestone equivalents of the Royer is 0.70918 to .70920 (Table 6), whereas that of the dolomites is 0.70937 to 0.70940. The value that Burke and others (1982) show for late Cambrian seas is 0.7090. The fact the dolomites have more radiogenic values than does the limestone suggests the dolomitization of the Royer most likely involved meteoric waters and took place after much of the strontium from seawater was lost.

CHAPTER VI

FIELD RELATIONSHIPS

The Ankerite Zone

The ankerite zone of the Honey Creek Formation is distinctive in its appearance in the field and marks the transition between the lower portion of the Honey Creek Limestone and the upper portion of the Reagan Sandstone. This transition records a change from siliciclastic to carbonate sedimentation.

The upper Reagan Formation is a peloidal, glauconitic, fine to coarse grained, quartzitic sandstone with abundant phosphatic shell fragments (Lingula sp.) and rhyolite clasts. By contrast, the Honey Creek Formation is a bioclastic limestone consisting largely of pelmatozoan, trilobite, and brachiopod fragments with lesser amounts of peloidal glauconite, rhyolite clasts, phosphatic brachiopods and detrital quartz (Figures 5 and 6). The ankerite zone lies between these lithologies and records the first incoming of carbonate.

The ankerite zone is easily recognized by its characteristic orange color. This characteristic color is due to the oxidation of iron present in the ankerite,

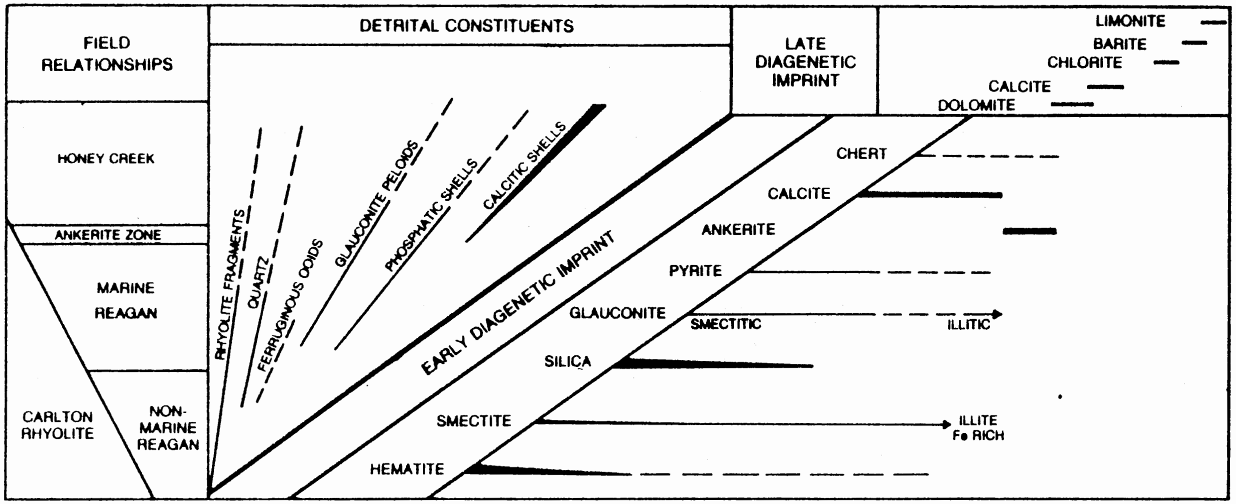


Figure 5. Relative timing of formation of various detrital components and diagenetic phases in the Timbered Hills Group.

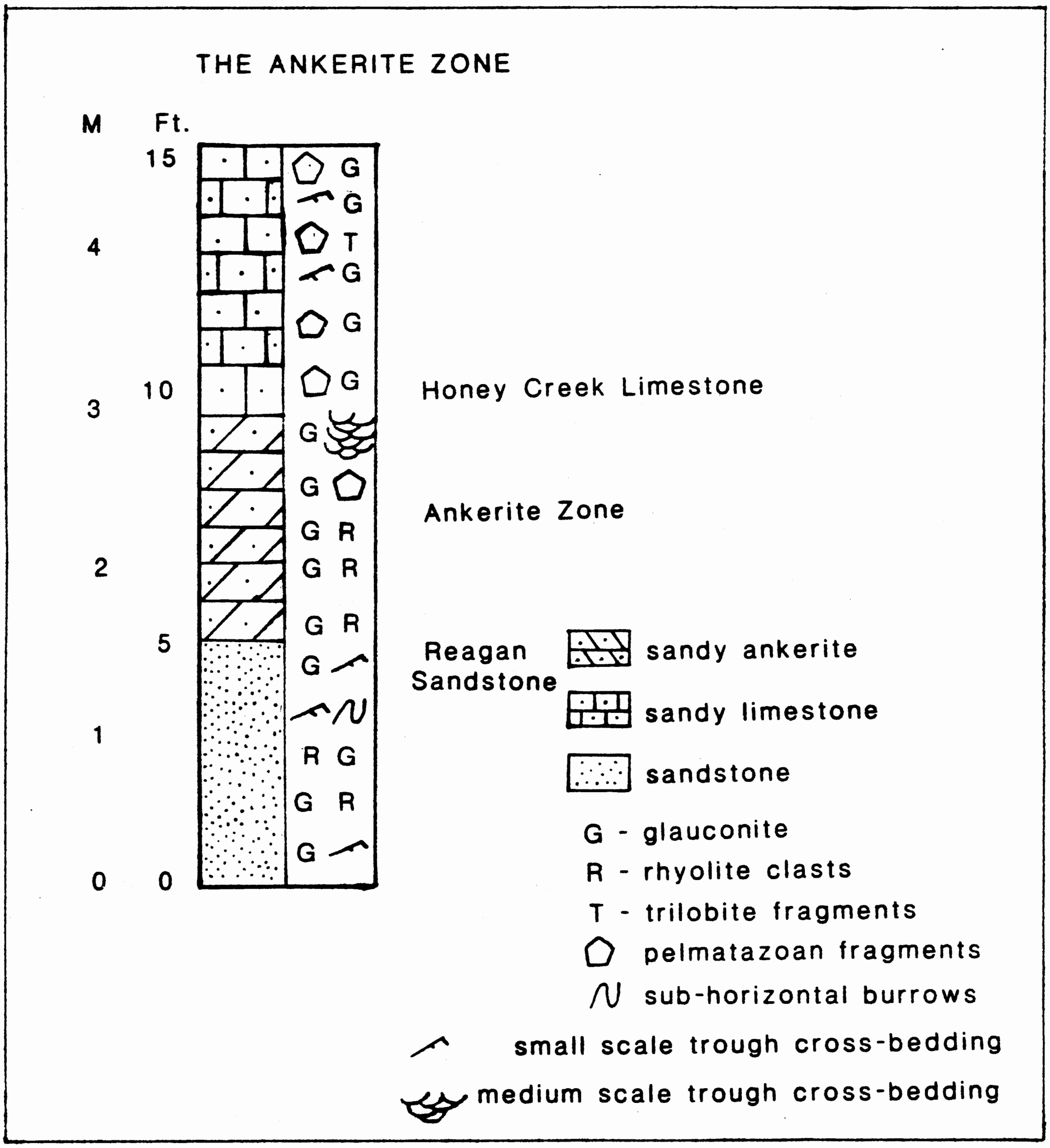


Figure 6. Statigraphic log of the ankerite zone and associated facies on Bally Mountain.

during surficial weathering. This zone is 3 to 5 feet thick and is laterally persistant throughout the Slick Hills area (10's of miles). The contacts between the ankerite zone with overlying and underlying units are sharp but do not always coincide directly with bedding. The slightly discordant nature of the zone as well as its variation in thickness is probably due to permeability differences that existed when diagenetic fluid passed through this unit, forming the ankerite.

Though considerable recrystallization accompanied the formation of ankerite in the Honey Creek, primary sedimentary structures are still present. Medium scale trough cross-stratification is the dominant sedimentary feature present with small scale trough cross-stratification also being present. Cross-sets are accentuated by bands of glauconitic peloids.

The Royer Dolomite

The Royer member of the Signal Mountain Formation, where present, is a 200 foot thick massive, nearly featureless unit made up of buff to brown medium to coarsely crystalline dolomite. Both the upper and lower boundaries are sharp and parallel to subparallel to bedding. Associated with the upper boundary are a number of pipe-like dolostone bodies that are a few 10's of feet wide and extend approximately 100 feet into the overlying rocks.

The dolomite that makes up these pipes is slightly more coarsely crystalline and lighter in color than the dolomite of the Royer itself. The boundaries of the pipes with the adjacent limestones are sharp, however the limestones contain vugs up to 1/2 inch across that are filled with dolomite that is identical to that present in the pipes. In the Royer and its associated pipe dolostones, nearly all primary features have been obliterated. The only vestige of primary textures in the Royer is the rare occurrence of silicified pelmatozoan fragments, glauconite peloids and relict stromatolitic layering.

The Signal Mountain Formation

The dolomite of the Signal Mountain Formation does not form distinct beds, but instead is present as burrow fillings and irregular patches that coalesce to form "pseudolayers". The burrow fillings are 1/4 to 1/2 inch in diameter and 1 to 3 inches in length while the patches and pseudolayers are up to 1.5 inches in thickness and extend laterally for up to 30 feet. These dolomitic areas weather a distinctive orange color that contrasts sharply with the adjacent gray limestones.

The Cool Creek Formation

Dolomite of the upper Cool Creek Formation on Bally Mountain is in a sequence that is made up of 1-6 m thick shallowing upward cycles (Figure 7).

Cycles contain an oōlitic or intraclastic grainstone at their base that is overlain by a stromatolitic or thrombolitic unit (Figure 8). This unit is overlain by massive mudstones grading upward into laminated (mm-cm scale laminations) mudstones. These mudstones typically display fenestral fabrics and are mud cracked in the upper-most portions. Mud cracked laminites are generally overlain by massive or laminated dolomitic mudstones that contain colloform chert nodules that are interperted as having replaced anhydrite. This anhydrite formed by displacive growth within the sediment, prior to compaction, since laminations are compacted around the nodules.

The fine grained dolomite is generally present as either massive mudstones or finely laminated mudstones. Rarely, fine grained dolomite is seen making up dolomitic, intraclastic grainstones or packstones. Fine grained dolomite has also been observed in the form of cement between grains in calcitic grainstones.

Coarse grained dolomites of the Cool Creek include those that are clearly associted with fractures and those that are not. Those that are associated with fractures

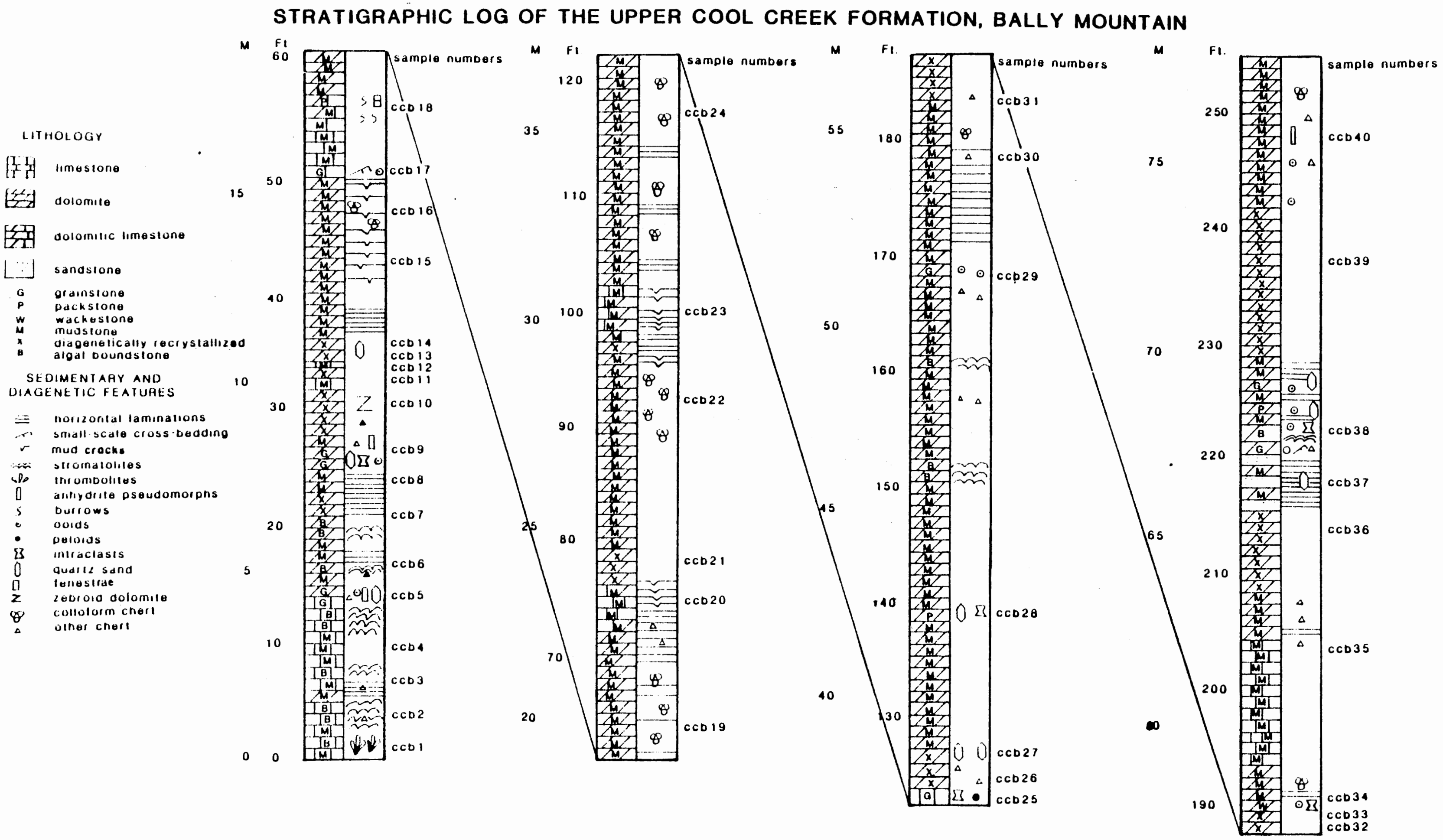


Figure 7. Stratigraphic log of the Upper Cool Creek Formation, Bally Mountain.

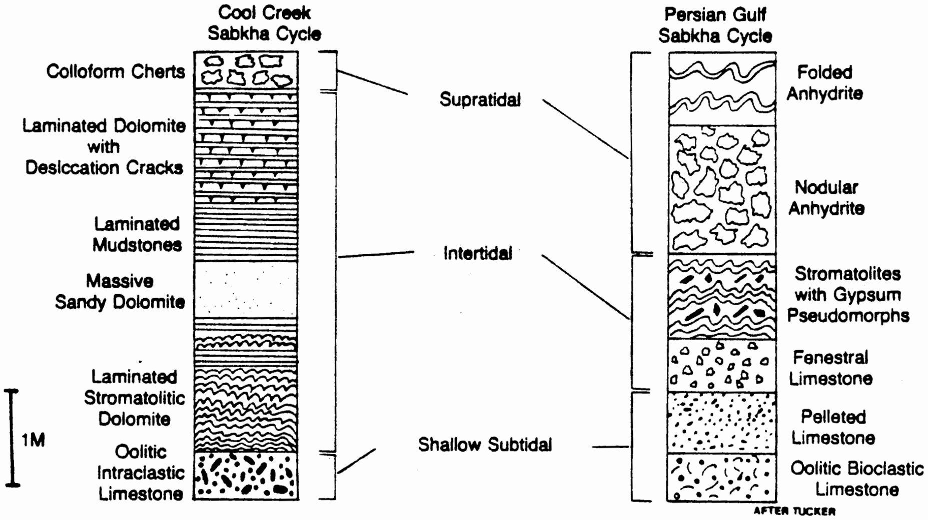


Figure 8. Comparison of a Cool Creek cycle with a Persian Gulf sabkha cycle.

may occur either as passive fracture fills or they may replace either fine grained dolomite or limestone adjacent to the fracture (Figure 9).

Irregularly shaped masses of coarse grained dolomite are common in the Cool Creek of Bally Mountain. These masses cut across bedding and replace both limestone and syndepostional fine grained dolomite (Figure 9). Commonly these irregular masses have no apparent relationship to fractures. This does not necessarily preclude the possibility that these coarse grained masses may have formed through the movement of late diagenetic fluids along fractures. These fractures, if they were present, may have been obliterated along with the sedimentary structures.

Coarse grained dolomite cements, in chert nodules and between grains, clearly are not directly related to fluid migration along fractures.

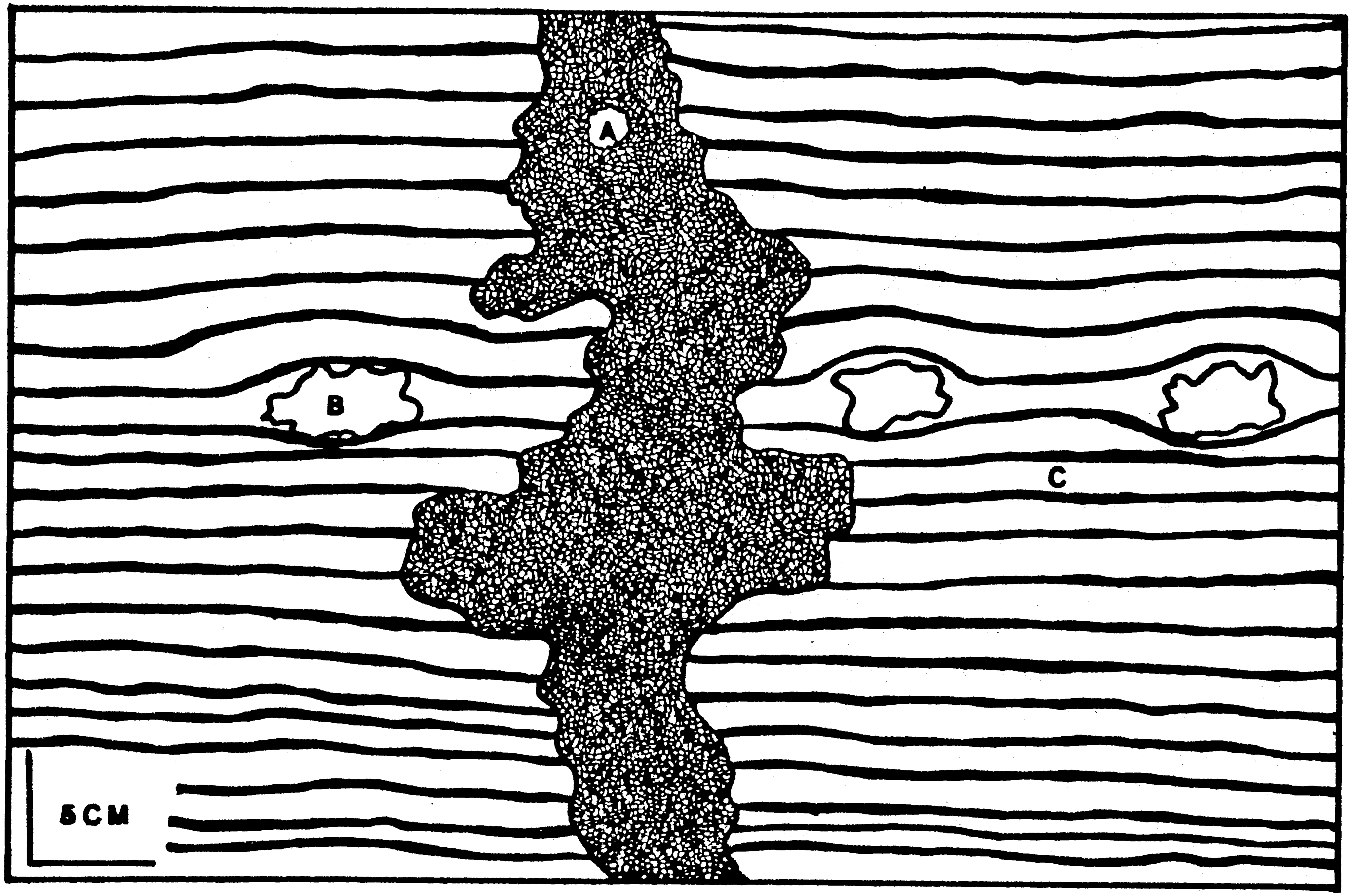


Figure 9. Field relationships of the Cool Creek Dolomites: coarse grained irregular masses that cut bedding (A); chert nodules lined with baroque dolomite (B); and laminated dolomitic mudstone (C).

CHAPTER VII

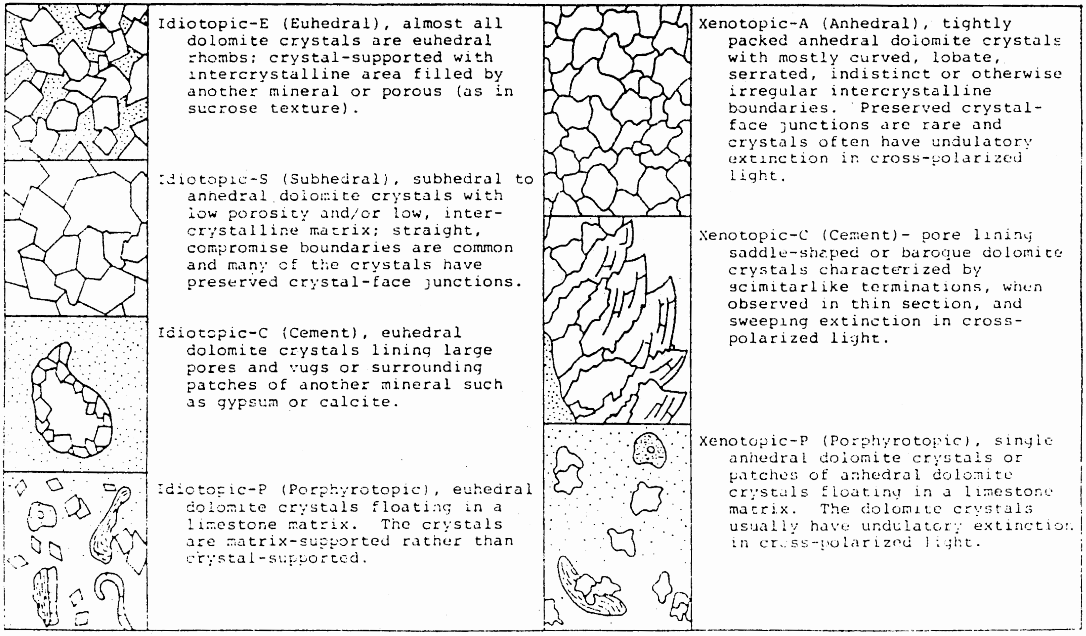
PETROGRAPHY

Introduction

This system subdivides dolomites based on their crystal mor-phology (Figure 10). The two largest divisions in this classification scheme are Idiotopic and Xenotopic. These major divisions are subdivided further based on fine scale crystal morphologies and the interactions between dolomite crystals and/or interactions of dolomite crystals with primary carbonate components.

Xenotopic dolomites are those made up of mosaics of anhedral crystals with irregular or curved intercrystalline boundaries, while idiotopic dolomites are those made up of euhedral to subhedral crystals with straight intercrystalline boundaries (Gregg and Sibley, 1984). Xenotopic dolomites are commonly more inclusion rich than idiotopic dolomites. Refer to Figure 10 for further explanation of Gregg and Sibley's (1984) terminology.

Gregg and Sibley argue that xenotopic dolomites form at higher temperatures (> 50°C), either through the replacement of limestones or by recrystallization of pre-



Idiotopic Dolomite- Rhombic shaped euhedral to subhedral crystals.

Idiotopic-E (Euhedral), almost all dolomite crystals are euhedral rhombs: crystal-supported with intercrystalline area filled by another mineral or porous (as in sucrose texture).

Idiotopic-S (Subhedral), subhedral to anhedral dolomite crystals with low porosity and/or low, intercrystalline matrix; straight, compromise boundaries are common and many of the crystals have preserved crystal-face junctions.

Idiotopic-C (Cement), euhedral dolomite crystals lining large pores and vugs or surrounding patches of another mineral such as gypsum or calcite.

Idiotopic-P (Porphyrotopic), euhedral dolomite crystals floating in a limestone matrix. The crystals are matrix-supported rather than crystal-supported.

Xenotopic Dolomite- Nonrhombic, usually anhedral crystals.

Xenotopic-A (Anhedral), tightly packed anhedral dolomite crystals with mostly curved, lobate, serrated, indistinct or otherwise irregular intercrystalline boundaries. Preserved crystal-face junctions are rare and crystals often have undulatory extinction in cross-polarized light.

Xenotopic-C (Cement)- pore lining saddle-shaped or baroque dolomite crystals characterized by scimitarlike terminations, when observed in thin section, and sweeping extinction in cross-polarized light.

Xenotopic-P (Porphyrotopic), single anhedral dolomite crystals or patches of anhedral dolomite crystals floating in a limestone matrix. The dolomite crystals usually have undulatory extinction in cross-polarized light.

Figure 10. Classification scheme for dolomites (from Gregg and Sibley, 1984).

existing idiotopic dolomite. Idiotopic dolomites are thought to form at lower temperatures.

The Ankerite Zone

Both primary and diagenetic components of the Timbered Hills Group vary systematically through the section (Figure 5). Within the Timbered Hills Group the ankerite zone marks the first incoming of carbonate on the siliciclastic shelf of southern Oklahoma.

Ankerite of the lowermost Honey Creek Formation exhibits idiotopic-e and s (euhedral and subhedral) as well as xenotopic-c (cement) textures. The idiotopic ankerite is made up of large euhedral to subhedral rhombs up to 2 mm across. These rhombs have plane compromise boundaries and exhibit apparent pleochroism in plane polarized light. Xenotopic-c ankerite is made up of large (up to 3 mm in length) scimitar shaped crystals that are characterized by strongly undulose extinction in cross polarized light (Figure 11) and apparent pleochroism in plane polarized light. Both xenotopic and idiotopic ankerite can be seen replacing primary components (primarily skeletal carbonate and glauconitic pellets). The most impor-tant of these processes is the replacement of glauconite, since this is most likely the source of iron for the formation of ankerite.

X-ray diffraction data indicate (Figure 12) that a

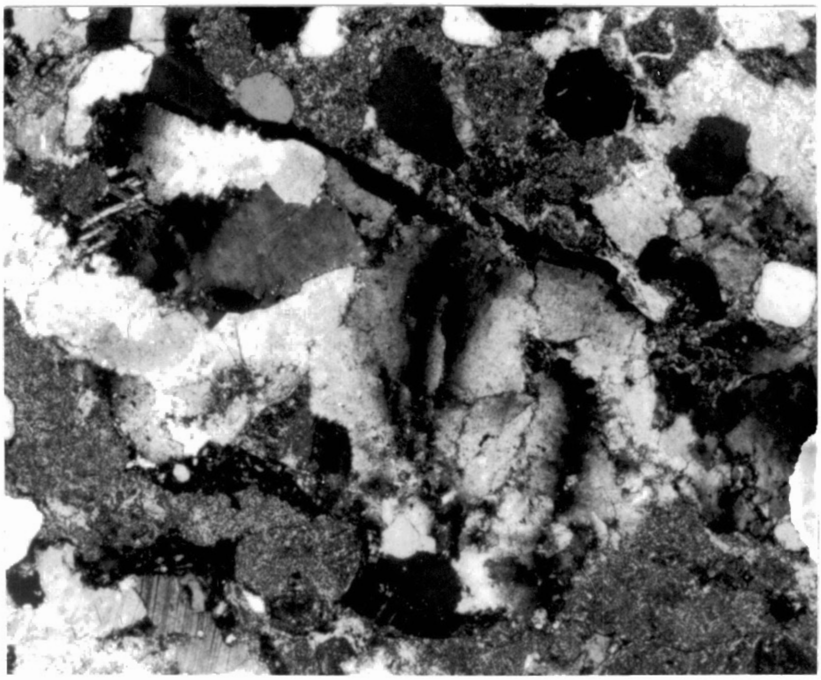


Figure 11. "Baroque" ankerite from the ankerite zone (100 x).

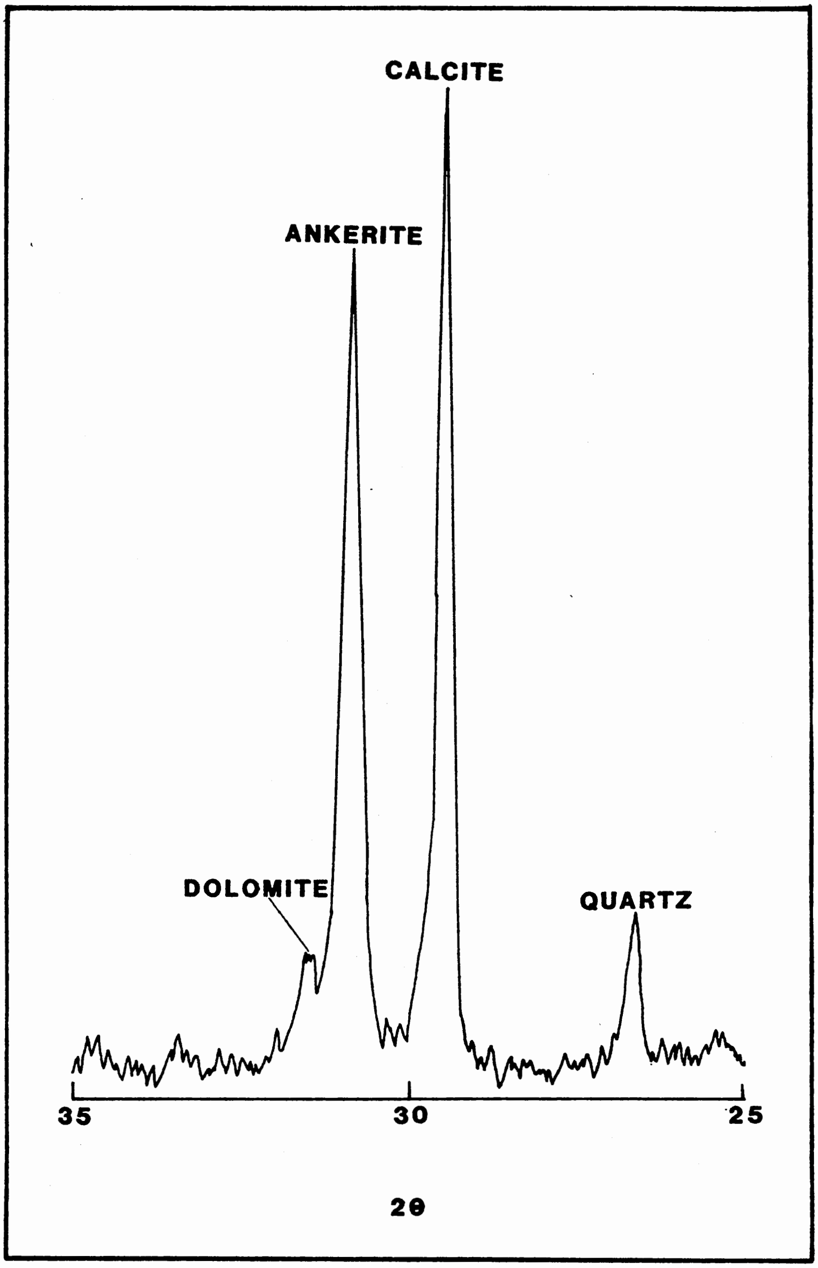


Figure 12. Partial x-ray diffraction pattern for the ankerite zone.

non-ferroan dolomite phase is present in the ankerite zone. In thin-section this is present as minor pore filling cement with xenotopic-c textures. This late pore filling dolomite is volumetrically insignificant (<1%).

The Royer and Its Associated Pipe Dolomites

The Royer is made up of two distinctive dolomite types: 1)xenotopic-c and 2) xenotopic-a. The majority (about 95-98%) of the Royer is made up of xenotopic-a dolomite. Xenotopic-a dolomite of the Royer is typified by anhedral crystals with irregularly sutured crystal boundaries. These crystals range in size from .25mm-1.25mm and contain large amounts of inclusions, giving them a very dull, cloudy appearance (Figure 13). In plane-polarized light these crystals exhibit apparent pleochroism while in cross-polarized light they exhibit slightly undulose extinction.

Dolomite exhibiting xenotopic-c textures comprises the remaining 2-5% of the Royer. Xenotopic-c or "baroque" dolomite of the Royer fills very large pores (up to .75cm across) and consists of scimitar shaped crystals that are up to 3.5mm across (Figure 14). Crystals seem to be slightly pleochroic in plane-polarized light and have very strongly undulose extinction in cross-polarized light. Inclusions are far less common in these pore filling

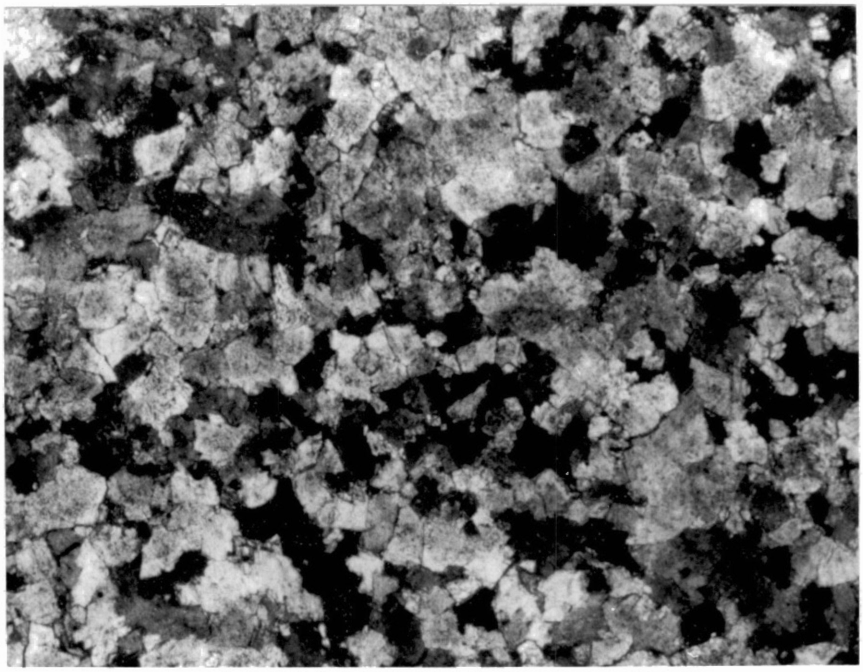


Figure 13. Anhedral xenotopic dolomite of the Royer (100 x).

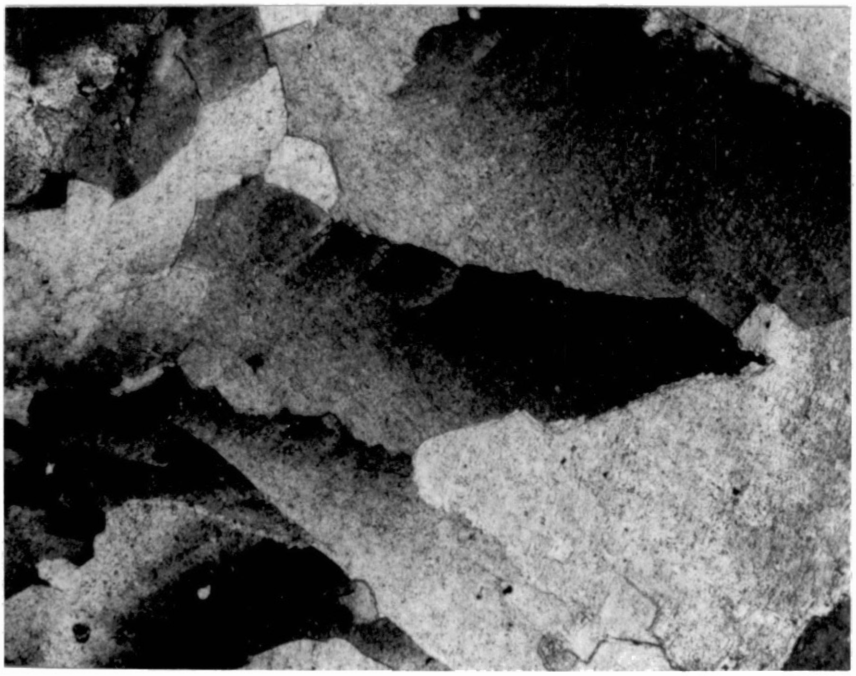


Figure 14. Xenotopic dolomite cement of the Royer (100 x).

cements than in the xenotopic-a dolomites of the Royer, therefore they are much less cloudy. Calcite replacement (dedolomitization) of some of these pore filling dolomite cements has been observed. This calcite preferentially replaces certain growth bands within the dolomite crystals (Figure 15).

The pipe dolomites associated with the upper boundary of the Royer are made up of coarse crystals (up to 2mm across) and exhibit idiotopic-s grading into xenotopic-c textures. These crystals appear slightly pleocroic in plane-polarized light and exhibit extinction that is moderately undulose in cross-polarized light. Crystals contain relatively few inclusions and are therefore fairly clear.

Compromise boundaries are slightly curved and commonly form junctions that approximate 120 angles. Intercrystal areas contain small amounts of illite, fine grained quartz silt, late calcite cement in the form of large equant spar and up to 10% porosity.

The Signal Mountain Formation

The burrow fillings and nodular layers of dolomite in the Signal Mountain Formation are made up of small (30-50 microns) euhedral idiotopic dolomite (Figure 16). Since this dolomite is slightly iron rich it weathers to an

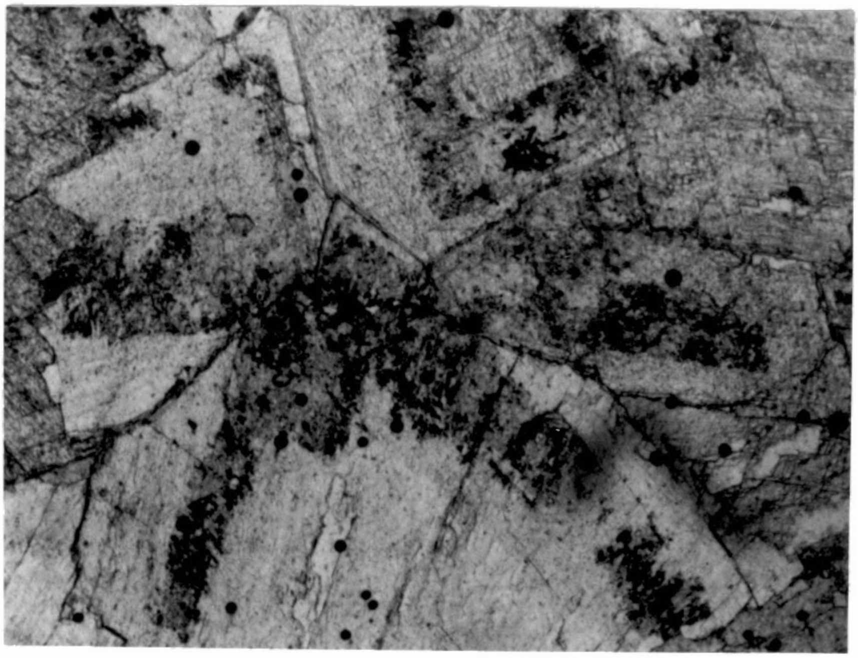


Figure 15. Calcite replacing zones within dolomite crystals (100 x).

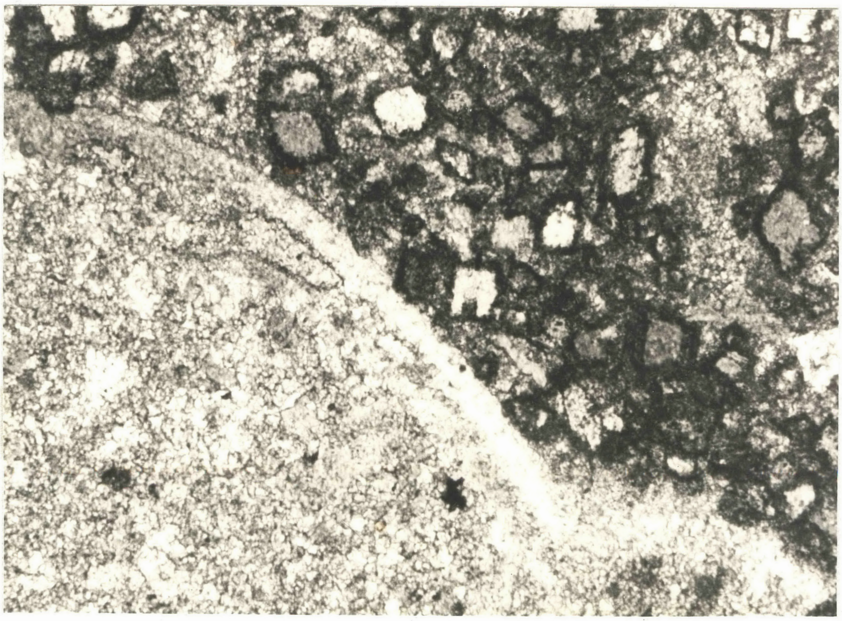


Figure 16. Burrow filling dolomite of the Signal Mountain Formation. Note oxidized rims (200 x).

orange brown color. In thin-section this weathering manifests itself as limonitic rims around individual dolomite crystals (Figure 16).

Though rare, ferroan xenotopic-c dolomite fills voids in the Signal Mountain Formation.

The Cool Creek Formation

Dolomites of the Cool Creek Formation can be divided into two types: 1) fine grained idiotopic dolomites and 2) coarse grained xenotopic dolomites (Gregg and Sibley, 1984). Common textures observed in the fine grained dolomite include idiotopic-c and e. Dolomite exhibiting idiotopic-c textures occur with a variety of relationships. The most common occurrence of idiotopic dolomite cements in the Cool Creek is in the form of equant void fillings in oolitic and intraclastic packstones. These void fillings consist of euhedral to subhedral rhombs .25-.5 mm across. Idiotopic dolomite cements also fill fenestrae in mudstones.

Idiotopic-e (euhedral) dolomite makes up considerable amounts of the upper Cool Creek Formation on Bally Mountain. These generally occur as laminae several mm to 1 cm thick made up of small euhedral rhombs (30-60 microns across) (Figure 17). These layers may make up entire beds several 10's of cm thick or they may alternate with

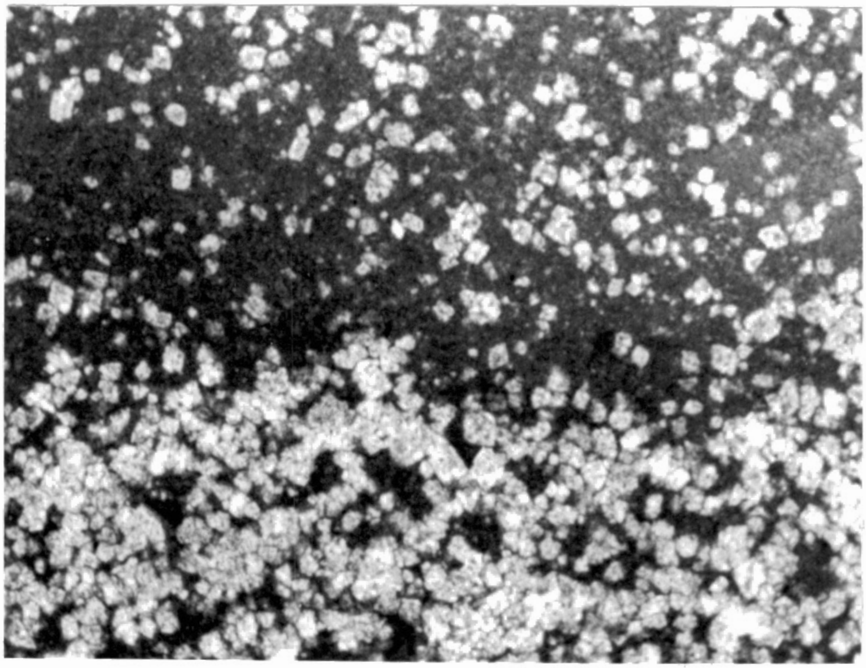


Figure 17. Idiotopic dolomite in a calcite mudstone from the Cool Creek Formation (200 x).

calcitic mudstones.

Colloform chert nodules are intimately associated with the fine grained dolomites of the Cool Creek. Within these nodules a characteristic stratigraphy exists (Figure 18). The outermost layer consists of randomly oriented euhedral rhombs of idiotopic dolomite followed by a layer of chalcedony. The next layer inward is made up of baroque (xenotopic-c) dolomite. The innermost component is either a coarse blocky mosaic of equant calcite or porosity. In some samples the boundary between chalcedony and baroque dolomite contains lath-shaped pseudomorphs (after anhydrite) (Figure 19). The chert layer contains numerous small lath-shaped anhydrite inclusions (Figure 20).

Commonly associated with zones containing chert nodules are small amounts of calcitized rhombs of dolomite (dedolomite). Generally these rhombs have their outer rims replaced by fine grained calcite mosaics while their cores are irregularly shaped single crystals of dolomite (Figure 21).

In addition to its occurrence within chert nodules, coarse grained xenotopic dolomite forms fracture fillings, irregular masses and rarely fills voids in grainstones. Fracture and void fillings are made up of crystals exhibiting typical xenotopic-c (baroque) textures. The crystals are up to 3 mm in length and have characteristic

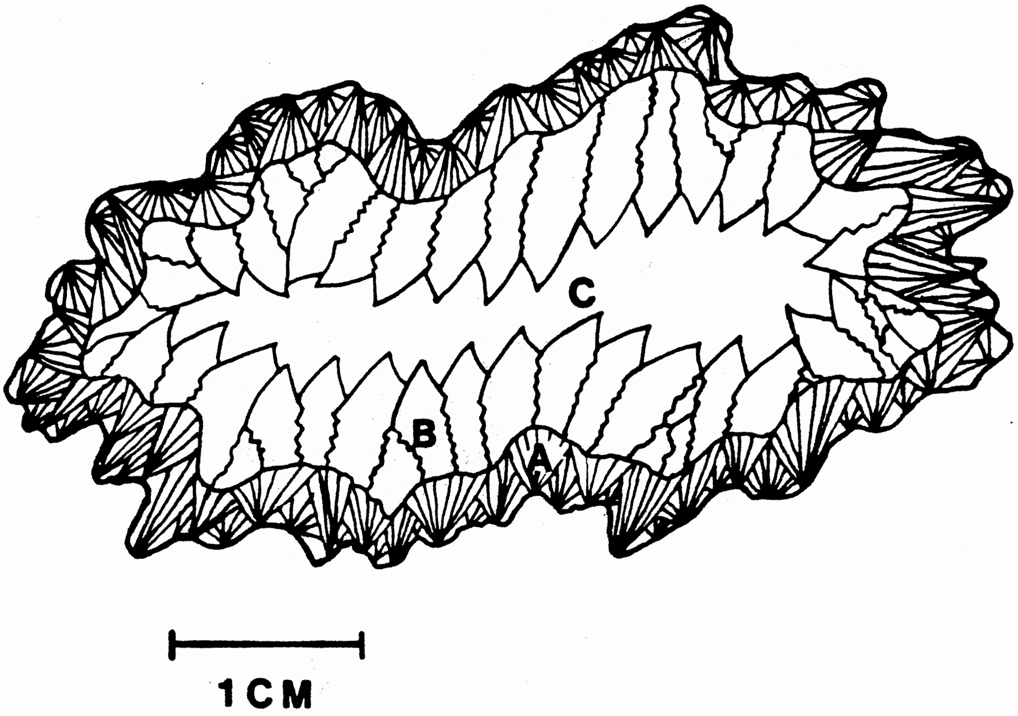


Figure 18. Schematic cross-section through a colloform chert nodule: chalcedony (A); baroque dolomite (B); porosity or calcite spar (C).

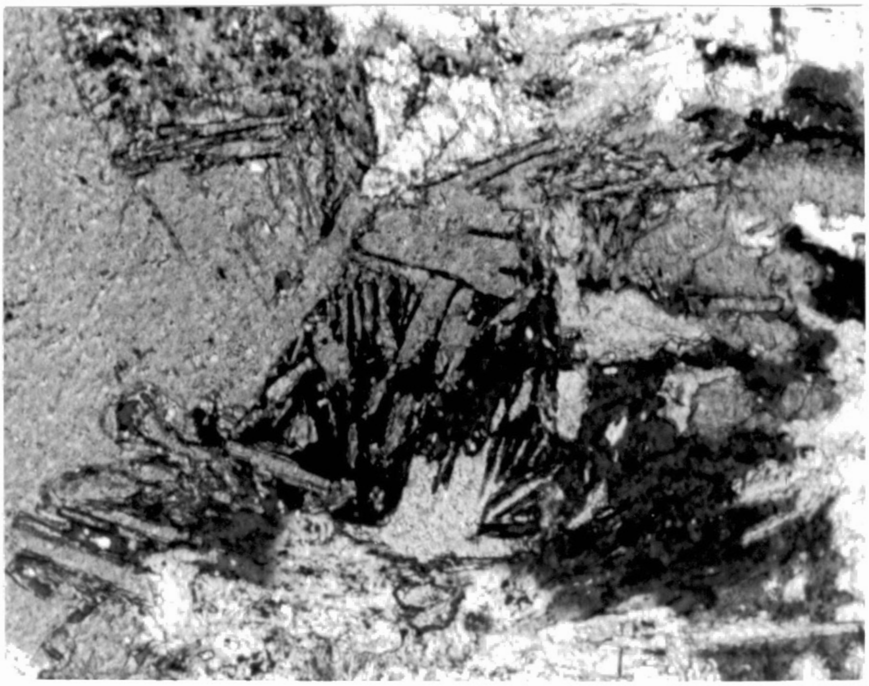


Figure 19. Chert and dolomite pseudomorphing anhydrite (80 x).

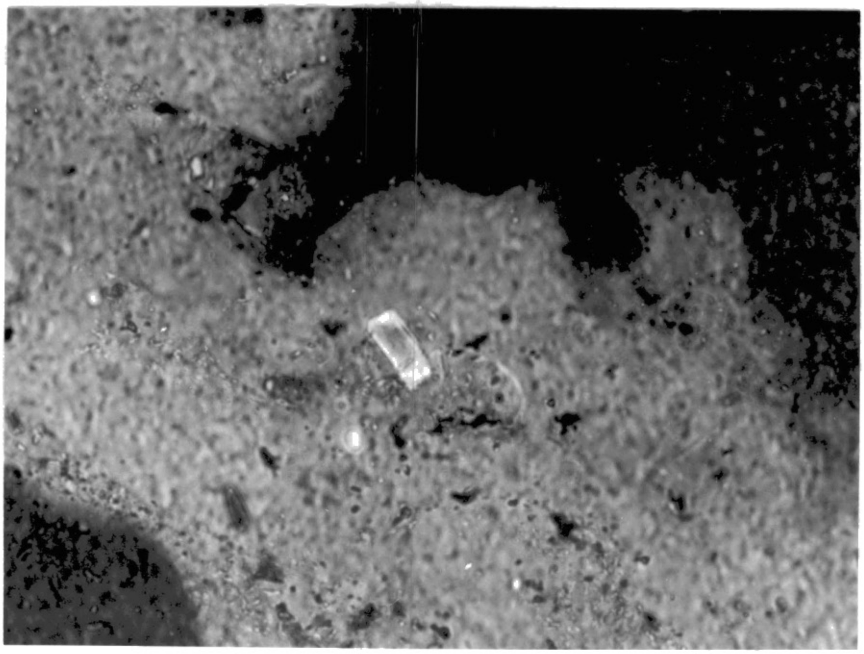


Figure 20. Anhydrite inclusion in chert (400 x).

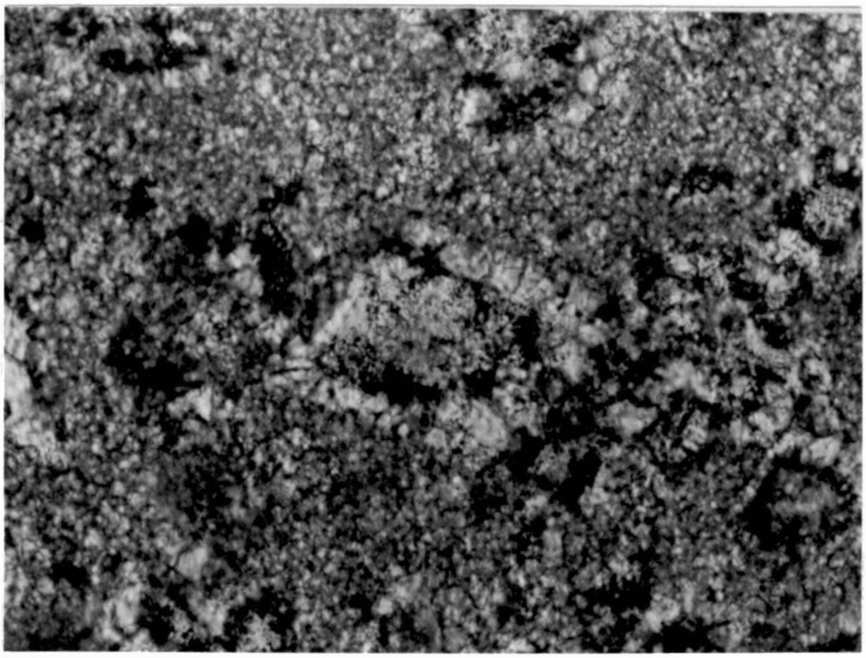


Figure 21. Calcite replacing outer rim of dolomite rhomb (100 x).

scimitar shapes. Undulose extinction in cross-polarized light is typical. Coarse grained dolomites making up irregular masses within the Cool Creek have slightly different textures. A complete range of textures exists from xenotopic-c to idiotopic-s. These crystals have slightly to strongly undulose extinction and slightly curved crystal boundaries. Generally, large crystals are zoned, suggesting pore water chemistry changed through time. Compositional zones are apparent when viewed under cathodoluminescence (Figure 22). "Zebroid" textured dolomites are common in the Cool Creek Formation. This texture is made up of alternating bands of dark fine grained idiotopic dolomite and light coarse grained xenotopic dolomite. These bands are often, but not necessarily, subparallel to bedding. "Zebroid" dolomite has been interpreted as having formed through the growth of dolomite cement (light bands) after an earlier mineral has been dissolved away (Zenger, 1980). Zenger, (1980) suggests that the light bands may represent gypsum that formed through displacive growth. "Zebroid" dolomite has been reported from a number of Mississippi Valley ore deposits (Zenger, 1980).

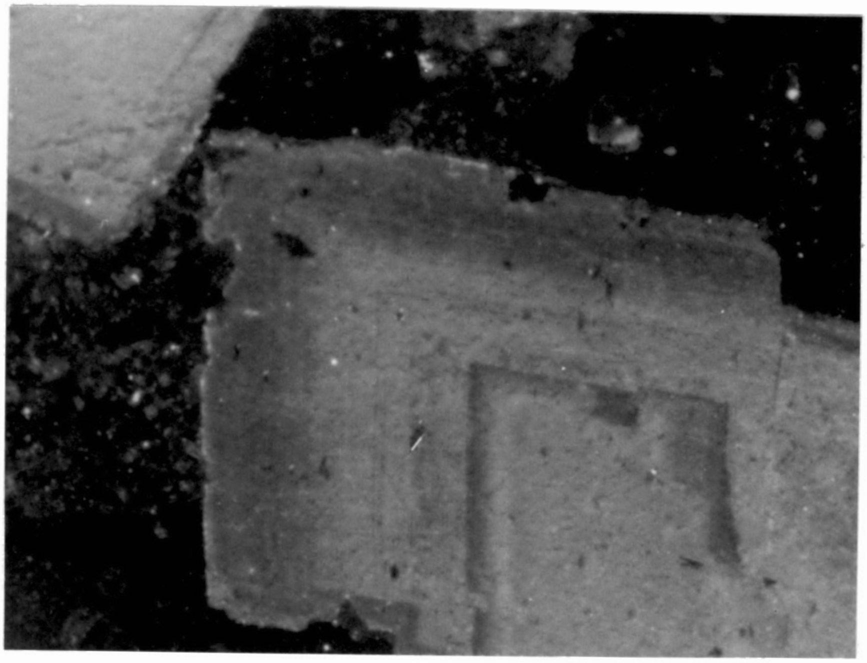


Figure 22. Cathodoluminescence photomicrograph showing zoning in a dolomite crystal (200 x).

CHAPTER VIII

MODELS OF DOLOMITIZATION

Introduction

Dolomite has been reported to have formed in a variety of environments, from relatively fresh ground water zones (Land, 1970) to hypersaline sabkha areas (McKenzie, 1981). In addition to synsedimentary dolomite, dolomite clearly forms under a variety of diagenetic circumstances (Nichols and Silberling, 1980; Mattes and Mountjoy, 1980). Numerous models have been proposed to explain the occurrence of dolomite in both Holocene sediments and in ancient rocks. Several of these models can be used to explain the dolomite and ankerite observed in the Arbuckle and Timbered Hills Groups of southwestern Oklahoma.

The Sabkha Model

Evaporation and therefore climate is the major factor controlling the formation of dolomite in the sabkha model as proposed by Hsu and Siegenthaler (1969). In this model evaporative concentration of seawater that periodically floods the sabkha (marginal marine salt pan) results in the precipitation of aragonite and gypsum (later converting to anhydrite). The gypsum and anhydrite typically form through displacive growth within the sediment resulting in nodules and "chicken wire" textures (Kinsman, 1969). The formation of these minerals removes substantial amounts of calcium from solution thus increasing the magnesium to calcium ratio (to >7) (McKenzie, et al, 1981) of the solution. The brines resulting from this process are then available to dolomitize the existing carbonate sediments (largely aragonite needle mud). This model has been postulated for the modern dolomites of the Persian Gulf region (Hsu and Siegenthaler, 1969) as well as for a number of ancient rock units (Friedman, 1980; Mathis and Radke, 1980).

A number of observed characteristics suggest that the fine grained dolomites of the upper Cool Creek Formation formed along an arid shoreline similar to the sabkhas found along the margin of the modern Persian Gulf. The strongest piece of evidence to support this interpretation is the close association of these fine grained dolomites with colloform chert nodules that mimic chicken wire anhydrite and contain both anhydrite pseudomorphs and small relict anhydrite inclusions (Figures 19 and 20). These nodules also contain length slow chalcedony, a commonly reported replacement of sulfate minerals (Folk and Pittman, 1971; Siedlecka, 1972).

The overall characteristics of the shallowing upward cycles of the Cool Creek Formation are strikingly similar to those observed in the Persian Gulf (Figure 8). Both cycles begin at the base with calcarenites containing ooids and eventually pass upward into stromatolitic layers. The Persian Gulf sequence is capped with "chicken wire" and folded anhydrite, while the Cool Creek sequences are commonly capped by colloform cherts. Both sequences commonly contain fenestral features.

The nearly complete lack of fossils in this section of the Cool Creek is also supportive of a sabkha interpretation as is the presence of algal stromatolites.

The Deep Burial Model

The deep burial model of dolomitization as proposed by Mattes and Mountjoy (1980) calls on a combination of three basic processes for the dolomitizition of basin margin car-bonate sequences: 1) migration of brines from adjacent basin muds undergoing compaction; 2) pressure solution; 3) mixing of near surface waters with deep basinal brines along fracture controlled conduits (Mattes and Mountjoy, 1980).

In this model, temperature increase is the dominant factor allowing for the formation of dolomite through burial diagenesis. This increase in temperature increases reaction rate, thus overcoming the kinetic problems of near surface dolomitization. Mixing of deep subsurface brines with artesian waters and the gradual alteration of brine composition through clay diagenesis and hydrocarbon generation may also be controlling factors. The migration of warm fluids along fracture systems, proposed in this model, make it valuable even in areas where the dolomitized rocks were never buried very deeply but were adjacent to basinal areas where considerable compactional dewatering was taking place.

The Royer Dolomite and its associated pipe dolomites as well as the coarse grained dolomites of the upper Cool Creek Formation and the ankerite of the Timbered Hills Group can easily be explained by this model.

The ankerite of the Timbered Hills Group occurs at a transition from siliciclastic to carbonate sedimentation. This zone must have acted as a permeable conduit through which basinal fluids migrated. The fact that glauconite in these rocks is commonly replaced by ankerite indicates that iron was mobile, therefore the solutions in which these reactions took place were reducing. The coarse crystal size and the baroque morphology of much of the ankerite suggests that these diagenetic solutions were relatively hot (> 50°C) (Mathis and Radke, 1980; Gregg and Sibley, 1984).

Iron has played an important role in the deposition and diagenesis of the ankerite zone. The source of this iron was the pre-Franconian land surface. Locally this surface was made up largely of weathered Carlton Rhyolite. As the Franconian seas transgressed, the residual weathering products were contributed to the marine system. In this system, significant amounts of iron were deposited in the form of hematite and glauconite (Figure 23). Calcite precipitating organisms contributed carbonate to the system. As diagenesis proceeded, these components interacted to form ankerite and small amounts of other minerals.

The dolomite pipes associated with the Royer Dolomite have similar orientations as the fractures of the area (Donovan pers. comm., 1985), suggesting that the Royer and its pipes formed through the circulation of dolomitizing fluids along fracture controlled conduits. The fact that both the Royer and its associated pipe dolomites are coarsely crystalline and exhibit xenotopic textures suggests that the fluids involved in their formation were relatively hot (> 50°C) (Mathis and Radke, 1980; Gregg and Sibley, 1984). This interpretation is supported by the light oxygen isotope values.

Crystal size and morphology along with their association with fractures suggests that the coarse grained dolomites of the Cool Creek Formation formed through the migration of hot (> 50°C) (Mathis and Radke, 1980; Gregg and Sibley, 1984) dolomitizing fluids along

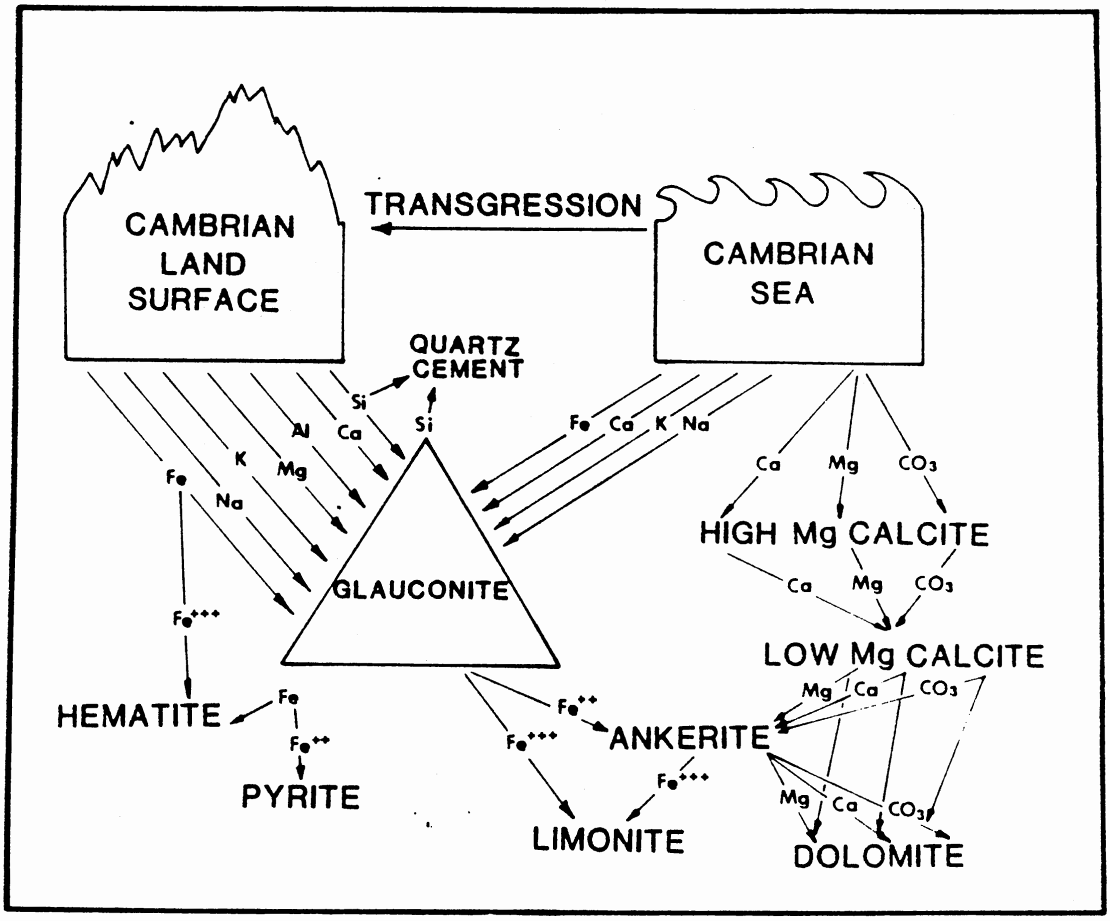


Figure 23. Possible ion pathways in the ankerite zone.

fracture systems. Light oxygen isotope values support the petrographic evidence these fluids were hot (Figure 3). These fluids probably originated as pore water expelled through compaction in the Anadarko Basin.

The Ground Water Mixing Model

The ground water mixing model of dolomitization as proposed by Henshaw and others (1971) calls on the mixing of potable ground water with either seawater or subsurface brines from a brackish zone in which dolomite forms. In this model, both waters being mixed are undersaturated with respect to dolomite while the water that results from their mixing is saturated to supersaturated with respect to dolomite. Folk and Land (1975) suggest that, in such a circumstance, it is the lowering of salinity while maintaining a relatively high magnesium to calcium ratio that allows for the formation of dolomite (Figure 24).

A number of pieces of evidence suggest that dolomite of the Signal Mountain Formation formed through ground water mixing. The dominance of euhedral idiotopic textures in these dolomites suggests that they formed under low temperature, near surface conditions. The lack of any evaporative or desiccation features makes it seem unlikely that the Signal Mountain dolomites formed in a sabkha setting. The relatively high iron concentrations in these dolomites suggests that they formed in a reducing

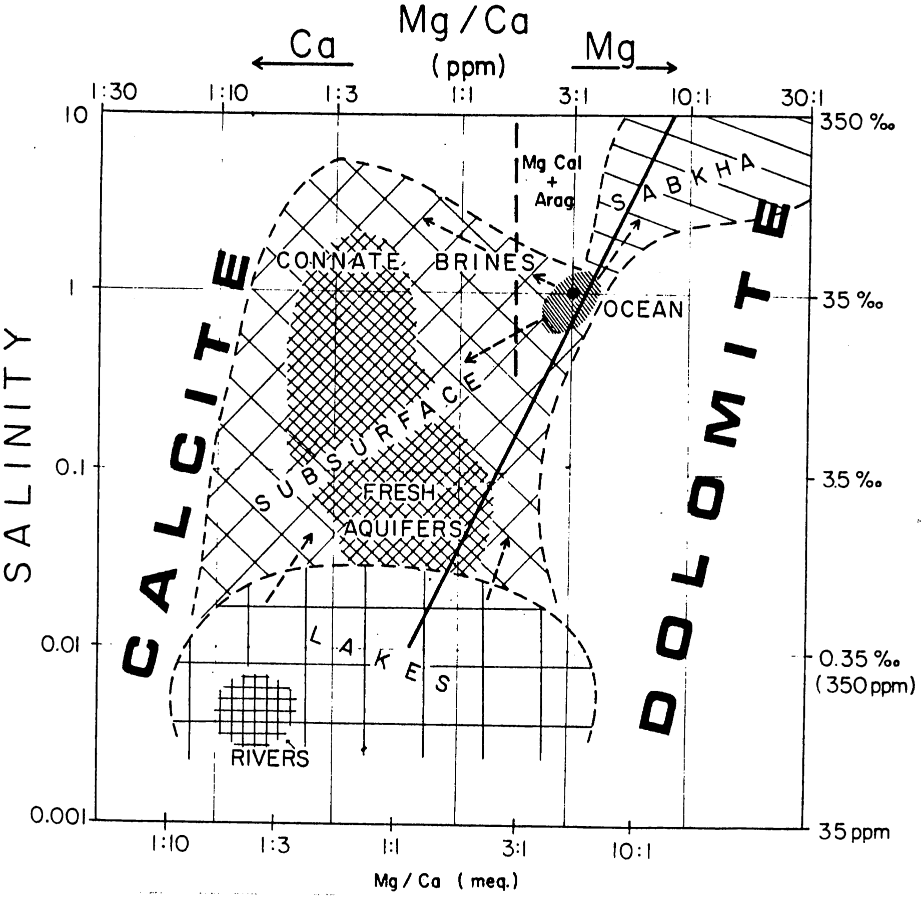


Figure 24. Mg/Ca ratios and salinities of natural waters at equilibrium with calcite and dolomite.

environment. One environment where near surface temperatures and reducing conditions might be maintained is a shallow subsurface aquifer.

CHAPTER IX

SUMMARY AND CONCLUSIONS

The Ankerite Zone

The ankerite zone represents a transition from a siliciclastic dominated to a carbonate dominated shelf setting. This zone records complex interactions between biogenically precipitated carbonate grains and iron silicate mineral grains. The extremely high iron concentrations of the ankerite (as much as 47000 ppm) indicate that it formed in a reducing environment, where iron was mobile in appreciable amounts. Iron present in the ankerite is most likely inherited from the glauconite, which it replaces. The coarse crystal size and xenotopic character of much of the ankerite present indicates that it formed after burial in the presence of hot (> 50°C) fluids (Mathis and Radke, 1980; Gregg and Sibley, 1984; Zenger, 1983). In light of this it seems reasonable to suggest a model similar to that proposed by Mattes and Mountjoy, (1980) for the ankerite zone. The ankerite zone must represent a permeable conduit through which hot basinal fluids migrated. The most likely source for such fluids is the nearby Anadarko Basin. The fact that this zone is restricted to such a narrow stratigraphic interval suggests that the skeletal carbonates overlying this zone were cemented prior to the introduction of basinal fluids while the underlying siliciclastic sediments contained so little carbonate that ankerite could not form.

The Royer and Its Associated Pipe Dolomites

The pipe dolomites associated with the Royer have roughly the same orientation as other lineaments of the area, suggesting a relationship between them. The coarse crystal size and prevalence of xenotopic textures suggests that the fluids from which these dolomites formed were relatively hot (> 50°C) (Zenger, 1983; Gregg and Sibley, 1984). Very light (-10.4 to -10.1 0/00 pdb)$\delta^{18}O$ values also support the interpretation that these dolomites formed at fairly high temperatures, since recrystallization at elevated temperature changes the isotopic composition of the solid phase toward more depleted values (Anderson and Arthur, 1983). Slightly more radiogenic strontium isotope values than either calculated values for Ordovician seawater (.7089) (Burke et al, 1982) or for adjacent limestones may be explained by influences of waters that have been involved with clay diagenesis in the Anadarko Basin. The elevated iron and manganese concentrations of these dolomites (relative to modern carbonates) indicates that they formed in the presence of anoxic subsurface waters. Petrographic as well as geochemical evidence suggests that the Royer formed as the result of hot reducing fluids (> 50°C) migrating along fracture controlled conduits.

The Signal Mountain Formation

Since euhedral idiotopic dolomites are thought to form at low temperatures it seems likely that the burrow filling and nodular layers of dolomite in the Signal Mountain Formation formed near the surface. The lack of evidence of evaporites or exposure makes it unlikely that these dolomites formed along an arid shoreline. Relatively high iron and manganese concentrations indicate that these dolomites formed in the presence of reducing pore fluids. The environment that best satisfies the requirements of both low temperature and low oxygen activity is a shallow subsurface aquifer. The mixing of potable ground waters with either seawater or subsurface brines make this a geochemically feasible environment for the formation of the Signal Mountain dolomites (Henshaw et al, 1971).

The Cool Creek Formation

Dolomites of the upper Cool Creek Formation are of two distinctive types: 1) a fine grained type associated with evaporite related features; 2) a coarse grained type that cuts across bedding and obliterates primary features. The two distinct types owe their characteristics to their vastly different origins.

In thin-section, fine grained dolomites are made up of small euhedral to subhedral rhombs that have straight compromise boundaries. Since dolomites that exhibit idiotopic textures are thought to form at low temperatures it seems likely that the fine grained dolomites of the Cool Creek formed very early in the diagenetic history of the rocks, while they were at or near the surface.

Fine grained dolomites preserve mm-cm scale laminations, extend laterally for long distances and are closely associated with evaporite pseudomorphs, mud-cracked laminites and colloform chert. These dolomites occur in shallowing upward cycles that are strikingly similar to vertical sequences observed in the modern Persian Gulf (Figure 8) (Hsu and Seigenthaler, 1969). It is this similarity along with its close association with evaporite pseudomorphs, mud cracked laminites and colloform chert mimicing chicken wire anhydrite that strongly suggest that the fine grained dolomites of the Cool Creek Formation formed along an arid shoreline similar to the sabkhas of the modern Persian Gulf.

The coarse grained dolomites of the Cool Creek form irregular masses several meters across. These masses are commonly associated with recognizable fractures. The crystals that make up these dolomites are very large (up to 3 mm across) and may be characterized by undulose extinction in cross-polarized light and sutured intercrystalline boundaries. Their xenotopic nature, large crystal size, and association with fractures suggests that these dolomites formed through the movement of hot fluids (> 50°C) through fracture controlled conduits (Mathis and Radke, 1980; Mattes and Mountjoy, 1980; Zenger, 1983; Gregg and Sibley, 1984). Light oxygen isotope values (-6.4 to -10.1 0/00 pdb) support the interpretation that these dolomites formed or were recrystallized at elevated temperatures.

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APPENDIX A

TABLE VII

PETROGRAPHIC DATA

Sample	Rock Type	Dolomite type
CCB 1	Algal Boundstone	I-P
CCB 4	Mudstone	None
CCB 5	Replaced Grainstone	I-S, X-A
CCB 6	Mudstone	I-E
CCB 8	Crystalline Dolomite	I-E
CCB 10	Crystalline Dolomite	I-S, X-C
CCB 12	Crystalline Dolomite	I-S, X-A
CCB 13	Mudstone	None
CCB 14	Crystalline Dolomite	I-S
CCB 15	Crystalline Dolomite	I-S
CCB 16	Crystalline Dolomite	I-E, X-C
CCB 18	Peloidal Packstone	I-C
CCB 19	Crystalline Dolomite	I-S
CCB 20	Mudstone	I-P
CCB 21	Crystalline Dolomite + Chert	I-S, I-E
CCB 25	Peloidal Grainstone	X-C
CCB 27	Crystalline Dolomite	X-A
CCB 28	Intraclastic Wackestone	I-S
CCB 29	Crystalline Dolomite	X-A
CCB 30	Crystalline Dolomite	I-S
CCB 32	Crystalline Dolomite	I-S
CCB 33	Crystalline Dolomite + Chert	X-A, X-C
CCB 37	Crystalline Dolomite	I-S
CCB 38	Crystalline Dolomite	I-S
CCB 40	Silicified Grainstone	X-C
CCBAR	Crystalline dolomite + Chert	X-C
BDP 1	Crystalline Dolomite	I-S, X-C
BDP 2	Crystalline Dolomite	I-S, X-C
BDP 3	Crystalline Dolomite	X-C
BDP 4	Crystalline Dolomite	X-A, X-C
BDP 5	Crystalline Dolomite	X-C
ROY 1	Crystalline Dolomite	X-A
ROY 2	Crystalline Dolomite	X-A
ROY 3	Crystalline Dolomite	X-A
ROY 4	Crystalline Dolomite	I-S, X-A
ROY 5	Crystalline Dolomite	I-S, X-A
ROY 6	Crystalline Dolomite	X-A
ROY 7	Crystalline Dolomite	X-A
ROY 8	Crystalline Dolomite	X-A

APPENDIX B

LAB PROCEDURE FOR TRACE ELEMENT ANALYSIS

All samples were crushed to a fine powder. One gram of powdered sample was digested in 25 ml of 1:1 nitric acid over a hot water bath for about 2 hours in pyrex beakers. The resulting solution was filtered through glass fiber filter paper and the filtrate was brought to 100 ml. Prior to filtering, each sheet of filter paper was labeled, dried and weighed so that after filtration the amount of insoluable residue was determined by drying and weighing. The amount of sample in solution was then determined. Trace element analyses were then done using a Perkin-Elmer model 303 atomic absorption spectrophotometer. Concentrations were calculated for the rock in solution and calculated back to concentrations of trace elements in the rock. These values are reported in parts per million (plus or minus 10%).

VITA 2

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Candidate for the Degree of

Master of Science

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