

ABSTRACT

Abundance and Character of Organic Matter in Cretaceous Rocks of Central Texas.

Stephen M. Clark, M.S.

Committee Chairperson: Steve I. Dworkin, Ph.D.

One of the basic tenants of organic geochemistry states that significant accumulation of organic matter will not occur in well-oxygenated aqueous environments. Changing abundance of sedimentary organic material, therefore, probably reflects changes in marine and terrestrial conditions on Earth. This study will document the abundance and character of sedimentary organic matter in Cretaceous rocks of central Texas with the goal of reconstructing the environmental, chemical, and depositional conditions responsible for organic carbon accumulation.

Organic carbon content in Central Texas ranges from .2 to over 1.5 weight percent. C/N ratios range from 5 to over 25. The C/N ratios are low in the Grayson and Pearsall formations whereas high C/N ratios are characteristic of the Walnut Clay and Lake Waco formations. Carbon isotope ratios of organic matter range from -28.8 to -22.7‰ (VPDB) with lower values occurring in the middle-Cretaceous. Lastly, most $\delta^{15}\text{N}$ values of organic matter hover between 1 to 3‰.

Although these data could suggest a terrestrial source, the influence of Cretaceous oceanic anoxic events could be causing a marine signature to appear terrestrial.

Abundance and Character of Organic Matter in Cretaceous Rocks of Central Texas

by

Stephen Clark, B.S.

A Thesis

Approved by the Department of Geology

Steven D. Driese, Ph.D., Chairperson

Submitted to the Graduate Faculty of
Baylor University in Partial Fulfillment of the
Requirements for the Degree
of
Master of Science

Approved by the Thesis Committee

Stephen I. Dworkin, Ph.D., Chairperson

Steven D. Driese, Ph.D.

Joseph White, Ph.D.

Accepted by the Graduate School
December 2009

J. Larry Lyon, Ph.D., Dean

Copyright © 2009 by Stephen M. Clark

All rights reserved

TABLE OF CONTENTS

	Page
List of Figures	v
List of Tables	viii
Chapter One: Introduction	1
Chapter Two: Regional Geology	4
• Trinity Group	6
• Fredricksburg Group	7
• Washita Group	10
• Pepper Shale	13
• Eagle Ford Group	14
• Austin Chalk	14
• Taylor Group	15
• Navarro Group	17
Chapter Three: Methods	19
Chapter Four: Organic Matter Production, Preservation, and	
Source Identification	21
• Geochemical Proxies in Organic Matter used for source Identification	24
○ Carbon Isotopic Ratios in Organic Matter Identification	24
○ C/N ratios in Organic Matter Source Identification	25
○ Nitrogen Stable Isotope Ratios in Organic Matter Source	27
Identification	

• Oceanic Anoxic Events	28
Chapter Five: Results	30
• Total Organic Carbon, Nitrogen abundance, and C/N ratios	30
• Isotopic Composition of Organic Matter	38
• Correlation between the Trends in $\delta^{13}\text{C}$ (PDB) and $\delta^{15}\text{N}$ (AIR)	42
Chapter Six: Discussion	46
Chapter Seven: Conclusions	53
Appendix A	54
References	59

LIST OF FIGURES

	Page
1. Stratigraphic column for Central Texas Cretaceous rocks (modified from Barnes 1972 and Owens 1979).	5
2. Study Area Map.	19
3. Elemental (atomic C/N ratio) and isotopic identifiers of bulk organic matter. (Meyers 1997).	26
4. TOC measurements by formation.	31
5. TOC formational averages.	32
6. Wt. % nitrogen by formation.	34
7. Nitrogen formational averages.	35
8. C/N formational averages.	35
9. C/N ratios by formation.	36
10. $\delta_{13}\text{C}$ (pdb) values by formation.	40
11. $\delta^{15}\text{N}$ (air) values by formation.	42
12. Formational averages for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$.	43
13. $\delta^{13}\text{C}$ vs. C/N plot. (modified from Meyers 1997)	48
14. Chart of sea level change and stagnation intensity during the Cretaceous (Arthur 1979)	49

TABLES

	Page
1. List of documented Cretaceous anoxic events	29
2. Total organic carbon, total nitrogen, and C/N ratios of sampled formations.	37
3. Averaged carbon, nitrogen, and C/N ratios for each formation with standard deviation.	39
4. Carbon and nitrogen isotopic data for sampled formations.	44
5. Formation isotopic averages with standard deviation.	46

CHAPTER ONE

Introduction

Organic matter typically makes up a very small percentage of a sedimentary rock's total volume. Even in sediments deposited in productive environments, concentrations of organic matter greater than 1 or 2% are generally considered to be high. Despite its relatively low abundance, organic matter in sedimentary rocks is extremely important because it is the source of liquid and gaseous hydrocarbons. This study focuses on the origin and paleoceanographic conditions that resulted in the organic matter found in the Cretaceous rocks of Central Texas.

The abundance and character of organic matter within a marine sedimentary rock lends insight into the environmental conditions that existed at the time of formation. The wide variety of proxies contained within the organic matter of marine sedimentary rocks, sometimes referred to as geochemical fossils, is useful in reconstructing the paleoceanographic and paleoclimatic conditions during the time of deposition (Meyers 1997). Under normal marine conditions, most organic matter is biosynthesized near the ocean's surface (within the photic zone) by marine algae and subsequently sinks to the seafloor. The vast majority of this organic matter is oxidized and destroyed by bacterial decomposition both while sinking to the seafloor and during the time in which the organic sediment sits within the bioturbated benthic layer. Only about six percent of the original volume of produced organic matter makes its way into sedimentary rocks (Meyers 1993, Suess 1980, Wakeham et al. 1980, Knauer and Martin 1981, Easie et al.

1980, Emerson and Hedges 1988). The primary destruction of organic matter involves an efficient aerobic process (mediated by bacteria) that draws oxygen from the surrounding water column. In the absence of oxygen, anaerobic processes involving nitrate, Mn(IV) oxides, Fe(III) oxides, and sulfate continue to aid in the destruction of organic material within the bioturbated benthic layer, although these processes are vastly less efficient (Meyers 1997, Twichell 2002)). Therefore, if a sedimentary rock has a high concentration of organic matter, it implies that either the paleoproductivity rates were high enough to overwhelm the environment's ability to decompose it, or anoxic conditions resulted in a lower degree of oxidative decomposition.

Stable isotope ratios of the carbon and nitrogen in organic matter are another powerful proxy that can provide insight into paleoenvironmental conditions. In the case of carbon, there should be a distinct difference between the carbon isotopic signature of marine algae and land plants. Photosynthetic land plants during the Cretaceous used the C₃ (Calvin) pathway to incorporate carbon from the atmospheric CO₂ ($\delta^{13}\text{C} \approx -7\text{‰}$). The Calvin Pathway biochemically discriminates against C¹³ resulting in a -20‰ shift in $\delta^{13}\text{C}$ from the composition of atmospheric CO₂ (Meyers, 1997). Typical $\delta^{13}\text{C}$ values for terrestrial organic matter in the Cretaceous should, therefore, be about -27‰ . Marine algae, on the other hand, acquires carbon from dissolved bicarbonate ($\delta^{13}\text{C} \approx 0$) and, therefore, generally has a $\delta^{13}\text{C}$ value of $\sim -20\text{‰}$. The 7‰ difference has been used to differentiate the sources of organic matter in near-shore marine sediments (Meyers 1993, Meyers 1997, Hunt 1970, Newman et al. 1973, Gearing et al. 1977, Twichell 2002, Hoef 2004, Lamb 2006). It should be noted, however, that there is often an overlap between the $\delta^{13}\text{C}$ values of marine and terrestrial sediments. Therefore, carbon isotope ratios

should be evaluated in conjunction with C/N ratios in order to accurately determine their source. This is because terrestrial plants have cellulose (absent in algae) as a key structural component. As a result, terrestrial plants' C/N ratio is 20 or greater while algae's C/N ratio ranges between 4 and 10 (Meyers 1993, Meyers 1997, Ertel and Hedges 1985).

Nitrogen isotopes can also be used to elucidate the source and decomposition history of organic matter within sediments. Dissolved nitrogen within seawater has $\delta^{15}\text{N}$ value of about +5‰ while the atmosphere (from which terrestrial plants acquire their nitrogen) has a $\delta^{15}\text{N}$ value of 0‰ (Meyers 2006, Sigman et al. 2000, Altabet and Francois 1994). Despite a number of complications (discussed later), the nitrogen isotope system, especially when used in conjunction with carbon isotopes and C/N ratios, can provide good insight into the source of organic matter and the paleoenvironmental conditions in which it was deposited.

The goal of this study is to use these attributes of organic matter in sedimentary rocks to understand the paleoceanographic conditions that resulted in the abundance and character of organic matter in the Cretaceous rocks of Central Texas. This study provides a unique perspective on this topic because virtually all the rocks within the study areas were deposited in fairly shallow epicontinental seas as opposed to the more commonly studied deep-water sediments.

CHAPTER TWO

Regional Stratigraphy

Marine rocks including limestones, marls, and mudrocks dominate the Cretaceous section in Central Texas. This is thought to be the result of a second order transgression that began in the early Jurassic and reached a maximum at about the Cenomanian/Turonian boundary (~92 Ma) (Skelton et al. 2003). This transgression followed the destruction of the supercontinent Pangaea and was accompanied by variations in the rates of sea-floor spreading creating a massive waterway known as the Western Interior Seaway that cut North America in two and connected what is now the Gulf of Mexico to the Arctic Ocean (Skelton et al. 2003). Though the oceans began to recede toward the end of the Cretaceous, the remaining Central Texas Upper Cretaceous units were deposited in shallow marine environments (Sellards et. al. 1932). Due to the large-scale nature of the transgression, however, the area of the submerged shelf was greatly expanded and sediments deposited in shallow water environments were not necessarily deposited near shore. Clastic sediment supply varied greatly and was very abundant during some time periods (Navarro and Eagle Ford Groups) and was virtually non-existent in others (Edwards Limestone and Austin Chalk).

The stratigraphic nomenclature of the Central Texas formations dates back more than 100 years. Described by R. T. Hill in an 1899 USGS report, the Cretaceous in Central Texas was again extensively described by E.H. Sellards, W.S. Adkins, and F.B. Plummer in a 1932 (re-printed in 1958) University of Texas bulletin entitled *The Geology*

of Texas. Throughout the 1970s, 80s, and 90s, more specific studies examined individual groups and formations leaving us with the nomenclature used today (see the stratigraphic column in fig. 1).

	Stage	Group	Formation
65	Maestrichtian	Navarro	Kemp Clay
			Corsicana
			Neylandville
75	Campanian	Taylor	Marlbrook
			Wolfe City
			Ozan
85	Santonian	Austin	Austin Chalk
	Coniacian		
	Turonian	Eagle Ford	South Bosque
			Lake Waco
			Pepper Shale
95	Cenomanian	Washita	Buda Limestone
			Grayson
			Georgetown
105	Albian	Fredricksburg	Edwards Limestone
			Comanche Peak
			Walnut Clay
			Paluxy Sand
115	Aptian	Trinity	Glen Rose Limestone
			Hensel Sand
			Pearsall
	Barremian		Sligo Limestone
125	Hauterivian		Hosston Sand
	Valanginian		
	Berriasian		
135			

Figure 1. Stratigraphic column for Central Texas Cretaceous rocks (modified from Barnes 1972 and Owens 1979)

Primary groups within the study area (in ascending order) include the Trinity, Fredricksburg, Washita, Eagle Ford, Taylor, and Navarro groups. As a general rule, the lower Cretaceous units in Central Texas tend to be more carbonate-rich while the middle to upper Cretaceous units tend to be dominated by shales and mudstones. Detailed lithologic descriptions of the geologic units sampled in this study are presented below.

Trinity Group

The Trinity Group is geographically extensive in Central and South-central Texas and, along with the Edwards Formation (or Group in South Central Texas), make up an important regional aquifer system. Within the Study area, the Trinity Group includes the Hosston Sand, Sligo Formation, Pearsall Formation, Hensel Sand, and Glen Rose Limestone. The Hosston and Sligo Formations were not sampled in this study due to the very low abundance of organic matter.

The Pearsall Formation is about 140 ft. thick in the subsurface of Waco and thins to the north and west where the Sycamore Conglomerate replaces it (Boone 1968). It is composed of fine sand and silty mud. Sedimentary structures include abundant current ripples and horizontal burrows. The environment of deposition is interpreted to be deltaic (delta plain to delta front). This is consistent with the Pearsall's fluvial conglomerate up-dip equivalent.

The Hensel Sand is thickest (162 ft.) in the subsurface McLennan County and thins to the northwest (Boone 1968). It consists of fine to medium grained sand with some pebble conglomerates scattered throughout (Boone 1968). Small-scale ripple marks can be found as well as with reduction halos and root traces. The Hensel Sand is the result of a fluvial depositional setting and it has little, if any, organic matter. It is for

this reason that the remaining sandstones within the Cretaceous section of the study area were not sampled.

The Glen Rose Limestone is probably the most extensively exposed formation of the Trinity Group and expresses itself in a wide range of lithologies. The Glen Rose is generally divided into an upper and lower member separated by the Corbula Bed, a widespread marker bed recognized by F. L. Whitney (Debout 1977). Depositional environments for both members of the Glen Rose vary greatly, depending on location, but are most often characterized by a shallow to middle shelf marine environment. Sampling in the Glen Rose was biased to the interbedded shales because they had the highest abundance of organic matter. The limestones (mudstones to wackestones) are largely devoid of recognizable sedimentary structures. Burrows are limited to the *Cruziana* ichnofacies. The environment of deposition for the Glen Rose was probably a middle shelf marine environment that had punctuated clastic input. The muddier samples examined for this study probably represent slightly deeper water conditions than the “cleaner” carbonates.

Fredericksburg Group

The Paluxy Sandstone was not sampled for this study because it has little or no organic matter. The Paluxy Formation is a terrigenous sandstone prevalent in the far western section of the study area at the bottom of the Fredricksburg Group in the Lampasas Cut Plain region (Lampasas and Mills County).

The Walnut Clay makes up the base of the Fredricksburg Group in the eastern portion of the study area and is in contact with the underlying Glen Rose Limestone when the Paluxy Sandstone is absent (Moore 1969). The Walnut thins considerably to the

West of I-35 corridor and eventually merges with the Comanche Peak Formation. The Walnut is composed of 4 members (Bull Creek, Bee Cave, Cedar Park, and Keys Valley). The Bull Creek is composed of ooid grainstones and has marine hardgrounds at its top with terrestrial fossils and dinosaur tracks and is interpreted to have been deposited in a very shallow, carbonate marine environment that shallowed upward to an exposure surface containing footprints and mudcracks at its top (Moore 1969, Moore 1996, Talbert 2000). The Bee Cave is composed of fossiliferous marls with a fauna suggestive of a moderately deep and open marine environment dominated by clastics (Moore 1969, Moore 1996). The Cedar Park and Keys Valley Members seem to mimic the Underlying Bull Creek and Bee Cave in that the Cedar Park is composed of shallow marine carbonates (though not quite as shallow) and the Keys Valley contains deeper water marls. The most prominent environmental shift occurs between the Bull Creek and Bee Cave and represents a maximum flooding surface where the underlying transgressive trend ends and the overlying highstand trend begins. The carbonates are obviously from shallow water warm marine environments, however the marls contain fauna like *Texigryphaea* and *Oxytropidoceras* which are characteristic of muddy marine environments (Moore 1969, Moore 1996). Overall, the Walnut Formation seems to have been deposited under normal marine shelf conditions with the occurrence of mudrocks arising from variable terrigenous clastics input enhanced by changes in sea level.

The Comanche Peak Formation sits below the Edwards Limestone and is combined with the Walnut Clay to the west in Comanche and Mills Counties. It is composed of nodular limestones (mudstones and wackestones). Although the faunal content is more or less the same as the Walnut formations, there is a much lower

abundance of skeletal remains (Moore 1969). The Comanche Peak also has a greatly reduced abundance of terrigenous clastics and thus is dominated by carbonates (Moore 1969). Sedimentary structures include massive bedding and burrows of the *Cruziana* ichnofacies. The most likely depositional environment was middle to outer shelf open marine environment with minor inputs of terrigenous clastics (Moore 1969, Corwin 1982).

The Edwards Limestone is very extensive and outcrops over a significant portion of south-central Texas. Toward the southern end of Austin it is redesignated as its own Group and makes up one of the largest aquifers in the state. Within the study area, the Edwards Formation makes up the uppermost formation of the Fredricksburg Group thinning toward the north. In a gross sense, the Edwards within the study area can be subdivided into 3 main groups: a rudist sequence at the base overlain by fine-grained dolomites with miliolid lime grainstones at the top (Moore 1967). Most of the time, the Edwards Formation is composed of grainstones with abundant rudist fossils and *Cruziana* trace fossils. The Edwards is generally thought of as a rudist reef complex within a shallow marine carbonate environment.

Washita Group

The Georgetown Formation is the lowermost formation of the Washita Group and has been extensively studied. The formation is divided into seven members (Kiamichi Clay, Duck Creek Limestone, Fort Worth Limestone, Denton Shale, Weno Member, Pawpaw Shale, and Mainstreet Limestone). The outcrop descriptions made by Brown in 1971 were confirmed at sampled outcrops and are as follows:

- Kiamichi
 - Dominated by gray, calcareous shales, the Kiamichi Formation represents the base of both the Georgetown Formation and the Washita Group. The shales are clay dominated and contain pyrite nodules (Flournoy 1991 as well as Brown 1971). Abundant burrowing and *Gyrphaea* beds can be found along with dark, wavy laminations. The depositional environment was likely shallow marine with heavy brackish influence like a bay or estuary with possible fluvial influence.
- Duck Creek
 - The Duck Creek is about 32 ft. thick at north side of Lake Whitney and thins to the south. It's composed almost entirely of limestone (wackestones to with a few interbedded shales) and is fairly uniform throughout. The limestone beds can be highly thick and resistant, contain few visible structures, and contain *Gryphaea* beds.
- Ft. Worth
 - The Ft. Worth is about 20 ft. thick in Central Texas which tends to hold in the subsurface. While at the surface, however, this member tends to erode faster than other limestone units. Limestones (wackestones) and closely interbedded shales dominate this unit. There are a higher proportion of shales than in the underlying Duck Creek. Fossils include *Gryphaea* beds and the *Cruziana* trace fossil assemblage. Abundant burrowing, appears to have destroyed any structures that might have otherwise been visible.

- Denton Shale
 - The Denton Shale is the thinnest (only about 5 ft. thick thinning to 3 ft. beneath Bell County) member of the Georgetown Formation and always found beneath the overhanging Weno Limestone. It is almost completely laminated shale (silty with some clay) with only a few soft, conchoidal limestones. Fossils are very low in diversity but high in abundance and include *Gryphaea* and *Textularid* forams.
- Weno
 - The thickest and most variable member of the Georgetown Formation, the Weno is 40 ft. thick toward the north. The proportion of interbedded shales decreases to the south effectively decreasing the overall thickness (about 20-25 ft. beneath Bell county) to the south. The Weno consists of limestones (mudstones to wackestones) with a varying proportion of interbedded shales. Dominant fossils include *Gryphaea*, *Lenticulina* and *Globigerina* forams, and the *Cruziana* trace fossil assemblage. Abundant burrowing makes further structures difficult to identify.
- Pawpaw Shale
 - Located between 2 fairly resistant limestones (Weno and Mainstreet), the Pawpaw consists of silty shale and thins to the south of Tarrant County. Although there are a few soft limestones present, the member is about 95% shale. Fossils include ammonites and *Gryphaea* with some burrowing. Laminations are the only structure readily visible.

- Mainstreet Limestone
 - The Mainstreet Limestone is about 45 ft. thick in Hill County thinning southward to about 25 ft. thick beneath Bell County. With very few shales, the member is dominantly limestone (wackestones) with iron stains and weathered pyrite nodules. Dominant fossils include *Gryphaea* and *Globigerina* forams with some burrowing. The member is massively bedded with few other apparent structures.

The Georgetown Formation's depositional environment is interpreted to be warm, low-energy, and open marine settings below fair-weather wavebase. The change between the limestone and clastic members is likely the result of varied terrestrial clastic input.

The Grayson Formation (sometimes called the Del Rio) is about 80-100 ft. thick and conformably overlies the Mainstreet Member of the Georgetown Formation and conformably underlies the Buda Limestone. Where the Buda is eroded, it unconformably underlies the Pepper Shale (Mancini 1974). The Grayson is composed of dark shales with interbedded calcareous claystones and pyrite nodules. Fossils are abundant and include *Texigryphaea*, and a high diversity of foraminiferal fauna (*Textularia rionosis* and *Gaudryinella delrioensis*) characteristic of Cretaceous inner to middle shelf conditions (Mancini 1974, Burnaby 1961, Sliter and Baker 1972). The Grayson is interpreted to have been deposited under normal marine inner to middle neritic conditions with variable terrigenous clastics input (Mancini 1974, Brown 1971).

The Buda Limestone is very sparse and thin throughout McLennan County and thickens rapidly to the southeast reaching a thickness of about 7 ft. in northern Bell County and about 70 ft. in the subsurface of Falls County (Brown 1971). The limestone

is composed of wackestones and packstones with a slightly orange color and dark red spots from weathered hematite. Commonly occurring fossils include *Gryphaea*, *Exogyra* and ammonites. Sedimentary structures are very difficult to identify and were likely destroyed by burrowing. The lack of interbedded shales and abundant fossils indicate a stable, near-shore marine environment far from river mouths. The large size of the oysters suggests an environment varying between normal and brackish waters such as a lagoon lacking significant fluvial input. The Buda, after acid treatment, did not yield enough organic matter to analyze and, as such, is not discussed further.

Pepper Shale

There is some debate as to whether or not the Pepper Shale (also called the Woodbine) should be included in the Eagle Ford Group. It rests directly beneath the Lake Waco Formation and shares many characteristics with its overlying neighbor. It is dominated by laminated black shales and contains the *Chondrites* trace fossil assemblage. It is very organic rich, has few fossils, and is calcite free. Its environment of deposition was likely similar to the deep marine, distal shelf environment of the Lake Waco Formation.

Eagle Ford Group

Near Dallas, the Eagle Ford Group includes three formations (Tarrant, Britton, and Arcadia Park) and is about 145 meters thick. In Austin, it thins to only 15-20 meters thick and has two formations (Lake Waco and South Bosque) (Dawson 1997). The sampled outcrops near Waco included the Lake Waco and South Bosque formations. Both formations were dominantly shales, although the upper Lake Waco also contains

interbedded quartz siltstones and a few bioclastic limestones (Dawson 1997). The *Chondrites* trace fossil assemblage (indicative of a low-oxygen environment) can be found throughout the Lake Waco and underlying Pepper Shale while the South Bosque has *Thallasinoides* burrows and abundant *Inoceramus* fossils (Dawson 1997). The environment of deposition for the Lake Waco Formation seems to be deep-water, distal shelf with reduced oxygen conditions (this formation does fall within Oceanic Anoxic Event-2). The features of the South Bosque indicate that it was deposited in shallower water marine shelf setting like a delta front or lagoon (Silver 1963).

Austin Chalk

The Austin Chalk is a distinct, cliff forming limestone. The erosional contact with both the overlying Taylor and underlying Eagle Ford Groups is non-conformable. Thicknesses in the subsurface of Ellis County reach 500 ft. while the unit thins to the south. The Austin Chalk outcrops in Central Texas from Austin to Dallas. The Austin Chalk is composed of coccolith-rich white chalk beds with interbedded gray marl. Largely homogenous in character, the abundance of marls increases toward the middle of the formation (Reaser 1987). The chalk is massively bedded and filled with *Inoceramus* fossils. This deep-water formation was deposited in an open marine outer-shelf environment (Reaser 1987). The thin walls of the *Inoceramids* suggest low oxygen conditions (Hovorka 1994).

Taylor Group

The Ozan formation is about 500 ft. thick in the subsurface of Ellis County and thins to the west. Its contacts with the overlying Wolfe City and underlying Austin

Chalk are unconformable and gradational respectively (Raney 1987, Jackson 1983). The Ozan consists of well-laminated mudrocks (mixed clay and silt) and is largely homogeneous. There are also some interbedded marls and calcareous mudstones (Raney 1987). The only fossils observed were a few re-worked *Inoceramus* shells toward the bottom of the Ozan. The environment of deposition was an inner to middle shelf marine environment representative of a low energy perideltaic, neritic environment.

The Wolfe City Formation conformably overlies the Ozan Formation and is laterally gradational with the Pecan Gap Formation. It consists of sandy calcareous clay and is interbedded with fine-grained, glauconitic quartz arenite that thins to the east (Raney 1987, Reaser et al. 1983). Hard sandstones can form lenses of varying thickness from .25 in. to 1.5 ft. (Pate 1999). Sedimentary structures within the Wolfe City include hummucky cross-stratification and some trough cross-stratification. *Cruziana* is the dominant trace fossil assemblage, although *Skolithos* and *Zoophycos* can also be found (Pate 1999). The presence and preservation of hummocks means the environment of deposition must have been between fair-weather and storm wavebase. The abundance of quartz sand probably indicates nearby fluvial input and, thus, the paleoshoreline was probably nearby.

The Pecan Gap formation (often referred to as the upper Taylor Marl) conformably underlies the Marlbrook Formation and is laterally gradational with the Wolfe City Formation. It is generally thickest where the Wolfe City is thinnest (Beall 1964). The Pecan Gap consists of chalky marls composed of microcrystalline calcite (along with fossil fragments) with massive bedding as the only apparent structure. The lower Pecan Gap is mostly chalk grading into mostly marl in the upper Pecan Gap. The

majority of the fossils include ostracods such as *Amphicytheruar dubia*. These sediments were likely deposited below storm wavebase in a low-energy, neritic marine environment on the middle shelf.

At the top of the Taylor Group, the Marlbrook Formation (sometimes referred to as the upper Taylor Marl in conjunction with the Pecan Gap Formation) grades conformably into the overlying Neylandville (Beall 1964). As with many of the upper Cretaceous shales, it weathers easily making outcrops difficult to find. It is composed, mostly, of clay and silt as well as some pyrite nodules. Common fossils in the Marlbrook include *Inoceramus* and *Baculites* as well as some vertebrate remains (Beall 1964). Structures were not readily apparent in observed outcrops. The depositional environment was likely low-energy, brackish, and near-shore marine below fair-weather wavebase.

Navarro Group

Despite debate regarding their individual classification, the marls, shales, and sands resting atop the Taylor Group represent the uppermost units of the Cretaceous with the K/T boundary immediately above the Kemp Clay. The three main formations within the Navarro Group are the Neylandville (sometimes called the Bergstrom), the Corsicana (sometimes called the Nacotosh Sand), and the Kemp Clay. Outcrops for all three formations are difficult to find, as the landscape of Central Texas is quite flat and all three formations weather easily. Isolated outcrops in stream are often the only available outcrops.

The Neylandville Formation, sometimes referred to as the Bergstrom, is found at the bottom of the Navarro Group and is composed of gray calcareous (light effervescence in dilute HCl) clay, with small amounts of silt. Isolated fine to very fine sand lenses can

also be found (Chimene 1984). Sedimentary structures are largely absent with only a few, isolated, millimeter laminations to be found. Flora is mostly limited to a late Maastrichtian microfossil assemblages (Keller et al. 2006). The environment of deposition is a low-energy marine environment likely located on the inner to middle shelf.

The Corsicana, otherwise known as the Nacotosh, formation is made up black, argillaceous marl with a glauconitic, sandy bed at the bottom and a greater proportion of very fine to fine sand overall (Chimene 1984). Sedimentary structures included millimeter and centimeter laminations (discontinuous) and hummocks in the sandier areas (Chimene 1984). Fossils here include the same late Maastrichtian microfossil assemblages as well as a few *Inoceramus* shells. The depositional environment was apparently still a marine shelf environment below fair-weather wavebase and above storm wavebase but was likely closer to shore and had more brackish influence.

The Kemp clay is the uppermost formation in both the Navarro Group and the Cretaceous section as a whole in Central Texas. It consists of a gray (weathers to red) clay (little to no silt) and is fairly uniform in composition from base to top. Impact glass can be found toward the top at the famous K/T boundary (Chimene 1984). Sedimentary structures are highly limited and include only a few laminations here and there. Fossils here include late Maastrichtian fossil assemblages and *Lenticulina* in particular (Keller 2006). The Kemp was likely deposited in a low-energy marine shelf environment similar to that of the Neylandville.

CHAPTER THREE

Methods

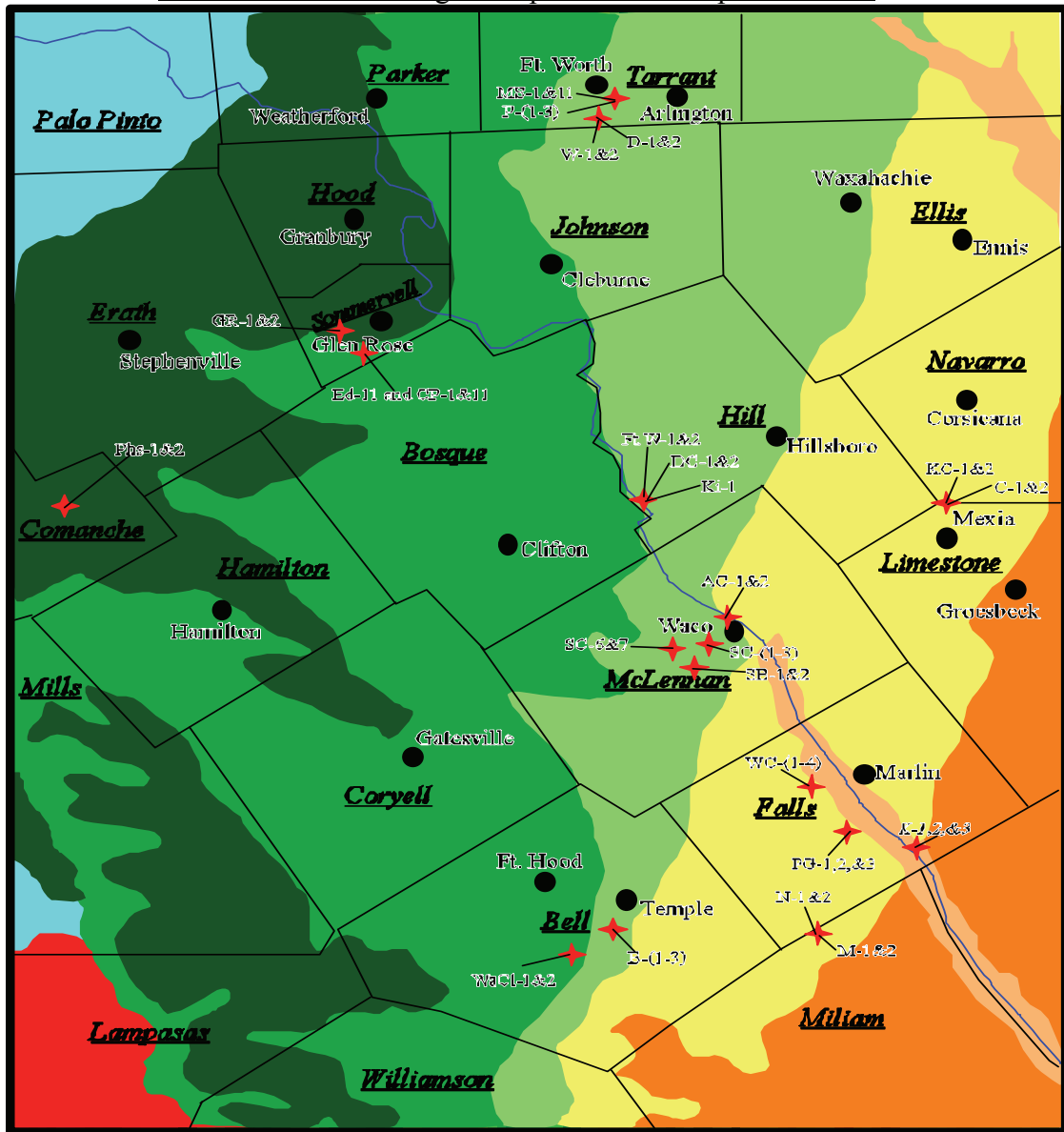
Sampling and Analysis

All samples used in this study were gathered from outcrops in Central Texas (see Figure 2). Great care was taken at each outcrop to insure that the sample being collected was unweathered to avoid weathering effects. In the case of shales exposed in hillsides or streambeds, this meant digging back into the formation several feet in order to obtain a fresh sample. Additionally, samples that appeared to have greater organic content were preferentially sampled over those without much apparent organic content. Therefore, the organic carbon concentrations presented in this study should be considered maximum amounts. Many of the limestones, however, yielded too little organic matter to be useful for this study. A complete list of outcrop localities is presented in Appendix A.

Samples were dried for 24 hours in an oven at 70°C and crushed to a fine powder with a planetary ball mill. Once crushed, a portion of each sample was treated with 10% HCl until all calcite was destroyed leaving behind only organic carbon. After being treated with acid, the samples were rinsed with DI water and re-dried in the oven for 24 hours.

For total organic carbon analysis, both an acid-treated and non acid-treated aliquot of each sample was analyzed on an elemental analyzer (Flash EA). Because the acid-treated sample is devoid of any carbonate carbon constituents, the difference in wt. % between the two values was, after being corrected for the loss of calcite mass during acid

Central Texas Geologic Map with Outcrop Localities



Modified for the Bureau of Economic Geology Geology of Texas state map (1992).

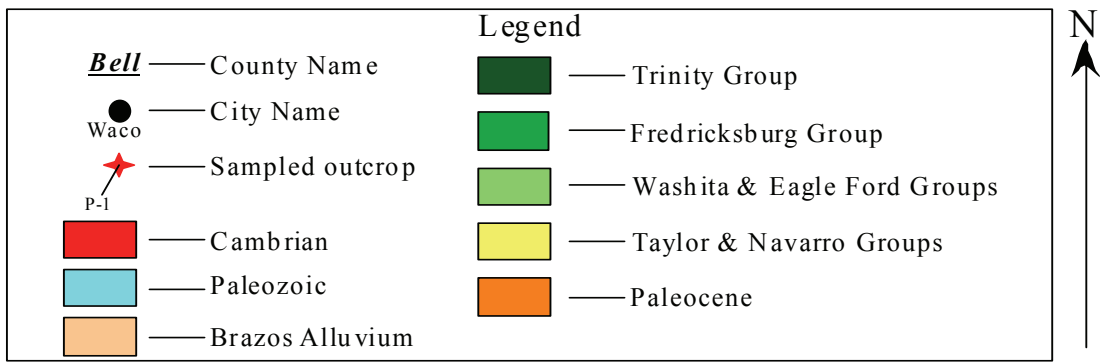


Figure 2. Study area map.

treatment, used to calculate the original total organic carbon (TOC). These calculated values for TOC were then used, in conjunction with the nitrogen measurements (unaffected by acid treatment) generated by the elemental analyzer to calculate C/N values.

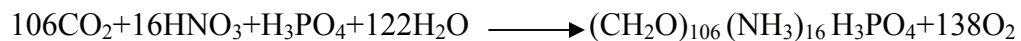
Acid-treated samples were also sent to the Ecosystems Center's Marine Biological Laboratory in Woods Hole, Massachusetts for carbon and nitrogen stable isotope analysis. Dr. Marshall Otter at Woods Hole reports the precision of the analysis to be better than $\pm 0.1\%$.

CHAPTER FOUR

Controls on the Organic Matter Production, Preservation, and Source Identification

Organic Matter Production and Preservation

Living organisms create organic matter. Whether in the marine or the terrestrial realm, organisms ranging from land plants and animals to algae and bacteria live and die and their remains can be preserved within the rock record. In general, the remains of the smaller, more abundant organisms such as algae and bacteria make up the bulk of preserved organic matter in marine sedimentary rocks. Animals rarely contribute a significant amount of organic material to the total world organic reservoir. Within the marine realm, photosynthetic production by algae in surface waters is the dominant source of primary organic matter (Meyers 1993, Meyers 1997, Meyers 2006). Meyers summarized the formation of organic matter as follows (notice that the C/N for the algae is 6.6):



This photosynthetic process requires light in order to proceed. Light, although abundantly available in the terrestrial realm, is only capable of penetrating clear water to a depth of about 100 meters. This depth is often reduced further by turbid conditions to tens of meters. The zone of aquatic light penetration, referred to as the “photic zone”, is where photosynthetic marine organic matter production takes place. Chemosynthesis, a process in which chemical energy is released by oxidation of reduced substrates, can occur in deep water (outside of the photic zone) although this process is not nearly as

efficient making it a minor, and often insignificant, contributor to the total organic matter pool (Meyers 1997, Meyers 2006).

Organic matter from land plants can sometimes contribute significantly to the organic matter preserved in the rock record, even in the marine realm. Areas near river mouths or terrestrial environments that have been recently flooded during transgression often have significant amounts of terrestrial organic matter. These areas often have elevated nutrient levels, which leads to elevated organic productivity.

Nutrient supply is also important to the production of organic matter. The proper proportions of carbon, hydrogen, nitrogen, oxygen, and phosphorous are needed to produce organic matter although nitrogen and phosphorous are often the growth limiting nutrients (Meyers 1997, Meyers 2006). These nutrients exist in variable supply in the world's oceans. Generally, coastal areas, especially those with significant fluvial input, have vastly greater supplies than the open oceans. Vertical mixing of the water column is also an important factor in the efficiency of recycling dissolved nutrients to the photic zone (Meyers 1997, Meyers 2006). As phytoplankton and algae remove nutrients from the water, they die and sink thus depleting the available nutrient pool and further limit organic production. Their decomposition while sinking can also leave the water column oxygen depleted. Density stratification often limits vertical mixing within the water columns of deep-water environments trapping many of these dissolved nutrients on the ocean floor (Meyers 1997, Meyers 2006). In shallower water environments, the shortened water column allows for greater vertical mixing of both oxygen and vital nutrients. Oxygenated surface waters are brought to the bottom while vital nutrients are brought to the photic zone. Carbon and nitrogen are the nutrients of particular interest to

this study because of the way their isotopes are fractionated during the creation and destruction of organic matter.

Carbon, in the marine realm, is generally acquired from dissolved bicarbonate (HCO_3^-) and less commonly from dissolved carbon dioxide (CO_2) whereas land plants obtain their carbon mostly from atmospheric CO_2 . Terrestrial plants acquire their nitrogen almost exclusively from soil microbes that can fix atmospheric N_2 into bioavailable nitrate. In the marine realm, algae usually acquire their nitrogen from dissolved nitrate although cyanobacteria are capable of fixing nitrate directly from atmospheric N_2 .

Because organic matter is composed of a reduced form of carbon at an elevated free energy state, it is intrinsically unstable in oxidizing environments (Meyers 1997, Meyers 2006). As a consequence, only a small amount of the original organic matter survives decomposition in an oxygenated environment. Most of the organic material that does make it to the sea floor is then destroyed by benthic metabolism (it is consumed by creatures living on the ocean bottom) resulting in only small amounts of burial and preservation. Of the organic matter destroyed during its decent through the water column, most of it is lost within the photic zone with oxidative decomposition rates decreasing with increased depth (Meyers 1997, Meyers 2006, Twichell 2002).

Under anoxic conditions, however, organic matter tends to have a much higher rate of preservation both in the water column and in the bioturbated benthic layer. Rapid burial can also improve the rate of organic matter preservation by limiting or even eliminating the time it must spend in the bioturbated benthic layer. Turbidite prone deep-sea basins are an example of an environment where rapid burial preservation could occur.

Ultimately, the ideal marine environment for organic matter preservation would be one with high surface productivity rates, a vertically well-mixed water column, low oxygen levels, and rapid burial rates in the benthic layer.

Geochemical Proxies in Organic Matter used for Source Identification

Two valuable proxies that have been used as indicators of the source of the organic matter within marine sedimentary rocks are stable carbon isotope ratios ($\delta^{13}\text{C}$ (PDB)) and bulk C/N ratios. One significant advantage of these chemical proxies is that they both do not significantly change during diagenesis and generally retain their original source information (Meyers 1993, Meyers 1997, Hunt 1970, Newman et al. 1973, Gearing et al. 1977, Twichell 2002, Hoef 2004, Lamb 2006). These proxies were developed for use on organic matter found in marine or lacustrine environments and are thus appropriate for this study.

Carbon Isotope Ratios in Organic Matter Source Identification

As mentioned earlier, organic matter within marine sediments is either biosynthesized in the photic zone of the water column or transported in from terrestrial settings. In both cases, photosynthesis will preferentially incorporate ^{12}C over ^{13}C resulting in a -20‰ fractionation from the carbon source. The isotopic distinction between terrestrial and marine sources arises from the different carbon source from which land plants and marine plankton and algae acquire their carbon. In the case of C_3 land plants (C_4 land plants had not yet evolved in the Cretaceous), carbon is acquired from atmospheric CO_2 ($\delta^{13}\text{C} = -7\text{‰}$) and incorporated via the Calvin Pathway giving organic matter produced by C_3 land plants an average $\delta^{13}\text{C}$ value of -27‰ . Marine plankton and

algae, however, acquire carbon from dissolved bicarbonate (HCO_3^-) which, when it is in equilibrium with the atmosphere, has a $\delta^{13}\text{C}$ values of about 0‰ giving organic matter produced by marine plankton and algae an average $\delta^{13}\text{C}$ value of -20 ‰. This 7‰ difference has been successfully used to trace the sources of organic matter in ocean sediments (Meyers 1993, Meyers 1997, Twitchell 2002, Lamb 2006, Hoefs 2004). This method can be compromised in polar regions where marine algal $\delta^{13}\text{C}$ values have been measured as low as -28 ‰ (Meyers 1997). This is because colder water can hold substantially more dissolved CO_2 allowing for greater isotopic discrimination by the algae (Meyers 1997). Additionally, a high pCO_2 in the atmosphere will lead to a greater availability of dissolved CO_2 leading again to a greater discrimination in favor of ^{12}C causing the isotope signal of marine organic matter to mimic that of C_3 land plants (Meyers 1997, Meyers 2006, Dean et al. 1986). The impact of polar regions on organic matter source signals should not be an issue with this study area, however, the high atmospheric pCO_2 at the time of deposition may result in reduced $\delta^{13}\text{C}$ values.

C/N Ratios in Organic Matter Source Identification

C/N ratios represent the amount of carbon (organic carbon in this case) versus the amount of nitrogen present in a given sample. Algae typically have a C/N value that ranges from 4 to 10. Land plants, on the other hand, have C/N ratios of >20 . The differences in C/N stoichiometry arise from the fact that land plants have cellulose (absent in algae) as a critical structural component (Prahl et al. 1980, Premuzic et al. 1982, Ishiwatari and Uzaki 1980, Jasper and Gagosian 1982, Prahl et al. 1994, Meyers 1993, Silliman et al. 1996, Twitchell 2002, Meyers 1997). Although diagenesis does have the ability to modify C/N ratios in soils (C/N ratios can decrease with diagenesis), the

original signal does appear to be preserved in sub-aqueous environments (Meyers 1997). However, in anoxic conditions, sub-oxic microbial degradation via denitrification preferentially destroys nitrogen-rich amino acids resulting in C/N ratios that increase over time. The range of elevation depends on the degree of degradation (Twichell 2002).

The combined use of C/N ratios and $\delta^{13}\text{C}$ of organic matter is a powerful tool for identifying the source of organic matter. Philip Meyers, in a 1997 paper published in *Organic Geochemistry*, identified four areas on a $\delta^{13}\text{C}$ vs. C/N plot that correspond to particular sources of organic matter found in marine sediments (figure 3).

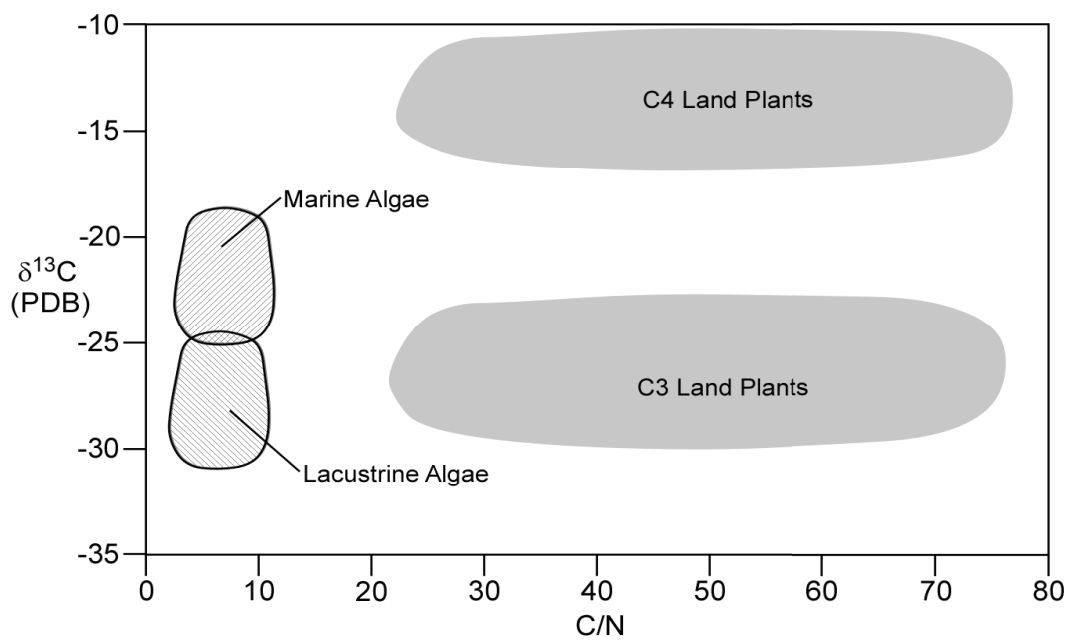


Figure 3. Elemental (atomic C/N ratio) and isotopic identifiers of bulk organic matter. (Meyers 1997)

Nitrogen Isotope Ratios in Organic Matter Source Identification

Despite being more complicated than the carbon system, the nitrogen isotope system can also be used to determine the source of organic matter in marine sediments.

As with carbon, the identification of the isotopic signals of land plants and marine plankton and algae stems from where the different organisms acquire their nitrogen. About 99% of nitrogen on Earth exists in the atmosphere or the ocean as N_2 gas ($\delta^{15}N = \sim 0\text{‰}$) (Hoefs 2004). Nitrogen gas (N_2), however, is inert and bio-unavailable to both plant and animal life. A process called nitrogen fixation takes N_2 and chemically converts it into biologically usable forms of nitrogen such as ammonia (NH_3), which is quickly turned into ammonium (NH_4^+). These products are, in turn, used in a multi-step oxidation process called nitrification that is mediated by a number of autotrophic organisms. The first step involves oxidation by *Nitrosomas* (NH_4^+ to NO_2^-) and the second step involving oxidation by *Nitrobacter* (NO_2^- to NO_3^-). Denitrification, on the other hand, is capable of reducing mineralized nitrogen molecules back to the atmosphere (or oceans) as N_2 . Without denitrification, atmospheric nitrogen would be exhausted within 100 million years (Hoefs 2004, Leng 2006). Marine plankton inherit the nitrogen isotopic signal of dissolved nitrate ($\delta^{15}N = \sim 4.8\text{‰}$) while C3 land plants reflect the atmospheric N_2 $\delta^{15}N$ value of 0 to 1‰ (Meyers 2006, Sigman et al. 2000, Altabet and Francois 1994). A variety of conditions, however, can alter these “normal” isotopic values. Denitrification of organic matter in oxygen-depleted waters can selectively release ^{14}N as N_2 gas leaving the water column enriched in ^{15}N and thus raising the $\delta^{15}N$ of organic matter values to between 7‰ and 10‰. Conversely, the marine $\delta^{15}N$ signal can be depressed to between 1‰ and –4‰ by utilization of dissolved N_2 by nitrogen fixing cyanobacteria. Notable, conditions favoring nitrogen-fixing bacteria include a stratified water column, reduced ocean circulation, and a low availability of nitrate (these conditions can also lead to anoxia). (Meyers 1997, Meyers 2006, Dumitrescu 2006,

Slomp et al. 2002). Diagenesis can also increase $\delta^{15}\text{N}$ values by 1-3‰ through the release of isotopically light NH_4^+ . If this happens on the seafloor, however, the NH_4^+ is often absorbed by the clay minerals leaving the bulk isotopic signal intact (Sigman et al. 1995, Freudenthal et al. 2001, Junium and Arthur 2007).

Oceanic Anoxic Events

The occurrence of at least 8 distinct oceanic anoxic events (OAE) has been identified within the Cretaceous. An OAE is a punctuated period during which the oxygen minimum zone within the water column has been significantly expanded. The oxygen minimum zone describes a section of the water column between 200 meters and 1000 meters which is depleted with respect to oxygen. As organic matter, produced in the photic zone, sinks through this layer of the water column, it is destroyed by bacteria in an aerobic process. The water above the oxygen minimum zone has its oxygen replenished by the atmosphere and deep ocean currents replenish the water below. Anoxic events can be caused by a number of processes. One model suggests that an upwelling of nutrients from the ocean bottom can lead to a boom in organic production at the surface. In this case, the decomposition of the large amount organic matter overwhelms the water column's ability to replenish its supply of oxygen (Twichell 2002). Another model suggests that stratification of the water column as a result of reduced ocean circulation causing anoxia. The loss of ocean circulation can be the result of several conditions including (but not limited to) the position of the continents, the absence of polar ice caps, or changes in global climate. Finally, significant transgressions can also cause an oceanic anoxic event. As sea level rises, coastal terrestrial areas (deltas, tidal flats, coastal plains, ect...) are flooded and large quantities of plant material

are transported out to sea. Transgressions can also increase the production of organic matter in surface waters by providing a vast, shallow shelf area upon which nutrients can be more easily recycled to the surface (Jenkyns 1980). The list of documented Cretaceous Anoxic Events is presented in Table 1.

Table 1. List of documented Oceanic Anoxic Events in the Cretaceous (Jenkyns 1980)

<i>Event</i>	<i>Common Name</i>	<i>Geologic Stage</i>	<i>Duration</i>
OAE 3	none	Coniacian-Santonian	87.3-84.6 Ma
OAE 2	Bonarelli event	Latest Cenomanian	93.8-93.5 Ma
OAE 1d	Breistroffer event	Late Albian	100.6-100.2 Ma
OAE 1c	Tollebuc event	Late Albian	103.7-103.4 Ma
OAE 1b series			
	Urbino event	Early Albian	110.9-110.6 Ma
	Paquier event	Early Albian	112-111.6 Ma
	Jacob event	Late Aptian	113.6-113.2 Ma
OAE 1a	Selli event	Early Aptian	124.2-123.4 Ma

CHAPTER FIVE

Results

Organic Carbon, Nitrogen Abundance, and C/N ratios

Organic carbon concentrations varied from an average value of 1.5% in the Pepper Shale to below the detection limits of the elemental analyzer in the Ft. Worth Member of the Georgetown Formation. Many of the sampled formations (see Table 2) had TOC concentrations between .1% and .6% with the average for the entire analyzed section being 0.38%. Organic carbon contents for multiple samples within the same formation were, generally, similar (see Figure 4). Notable exceptions include the Austin Chalk, Lake Waco Formation, and the Glen Rose Formation (see st. deviation values in Table 3). This is due to very different lithologies being present within the same formation. Additionally, dramatic positive excursions (spikes) in averaged TOC concentrations (Figure 5) occur at about 110 Ma, 93 Ma, and 85 Ma (see Figure 5). The interbedded shales of the Glen Rose Formation are responsible for the 110 Ma spike and have an average TOC of 0.98%. The second spike at 93 Ma is the result of the Pepper Shale at the base of the Eagle Ford Group. With an average TOC value of 1.5%, the Pepper Shale has the highest average TOC wt. % in the dataset. The overlying Lake Waco Formation (also part of the Eagle Ford Group) had some TOC values as high as 0.7%, but most values had considerably less organic matter. One of the Lake Waco samples had only 0.14% TOC decreasing the average TOC for the Formation to 0.42%.

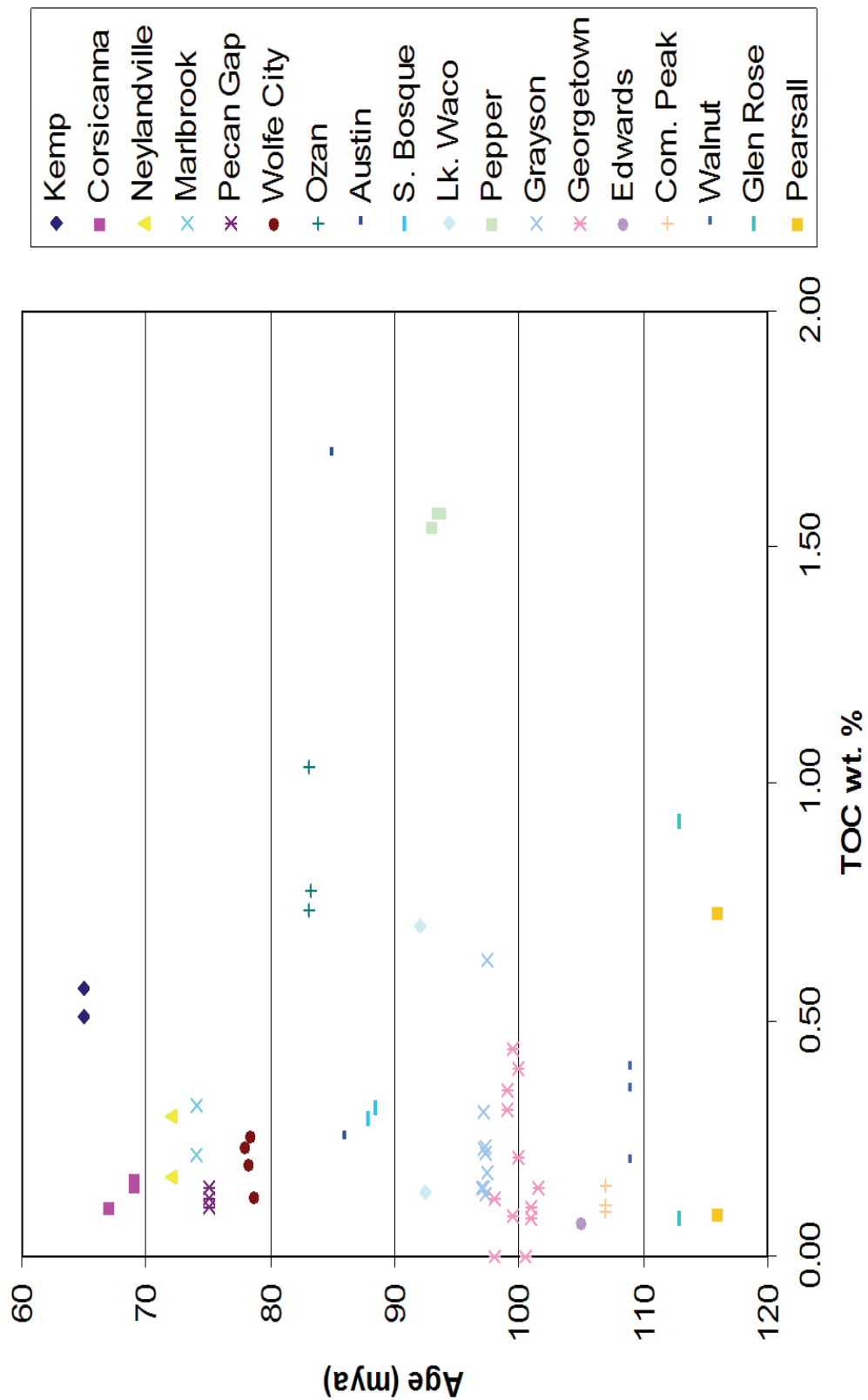


Figure 4: Total organic carbon measurements by formation.

The final spike at 85-84 Ma represents the interbedded marls of the Austin Chalk and the overlying Ozan Formation. Although the marls of the Austin Chalk had the highest overall sample TOC value (1.7%), they weren't consistently that high (the chalk layers were not included as they usually contained too little organic matter to analyze). The average for the formation was 0.98%. The overlying Ozan Formation didn't have some of the high single sample values of the Austin Chalk, but its single sample values were much more consistent (1.03%, 0.73%, and 0.78%). The average TOC value for the Ozan formation was 0.85%. These three spikes seem to correlate with documented (see Table 1) Cretaceous Oceanic Anoxic Events (absolute ages assigned to each formation are tentative). Specifically, the Glen Rose spike probably correlates with the Jacob Event from the OAE 1b series, the Pepper Shale spike probably correlates with the Bonarelli Event of OAE 2, and the Austin/Ozan spike probably represents the less widespread and unnamed OAE 3.

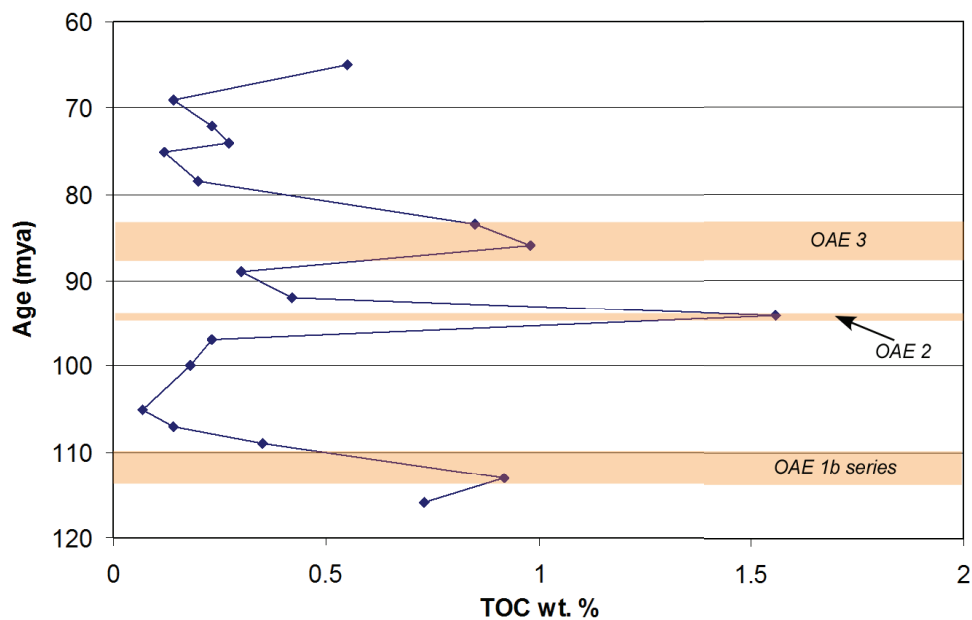


Figure 5: Total organic carbon formational averages (sandstones excluded).

Throughout the Central Texas Cretaceous section, nitrogen concentrations are between 0.025% and 0.05% (see table 2). Notable exceptions include the Pepper Shale and Austin Chalk. It should be noted that the average nitrogen concentration for the Austin Chalk is derived from only two samples. One had a nitrogen concentration of 0.53% (see table 2 as this value is not included on figure 6) while the other had 0.04%. Average nitrogen concentrations by formation are presented in Figure 8.

C/N ratios ranged widely from a maximum average of 36.7 in the Walnut Formation to undeterminable values in the Hensel (nitrogen concentrations were below detection limits). The average C/N ratio for the entire section is 14.7. Most of the lower C/N ratios are found in the upper Cretaceous with the latest Formations (Pecan Gap to the Kemp Clay) ranging between 5 and 15 (see Figure 9). Throughout the middle and lower Cretaceous, the Pearsall, Grayson, and South Bosque also fall within the 5-10 range of C/N ratios. All C/N data is presented in Table 2 and 3.

The spikes in average C/N values also seem to correlate with OAE 1b, OAE 2, and OAE 3 (see Figure 8). In this case, however, the correlation is not quite as close as it was with the TOC data. The spikes for 109 Ma and 92 Ma seem to trail OAE 1b and OAE 2 by 2 to 3 million years rather than directly line up with them. The spike at 86 Ma, on the other hand, falls right in the middle of OAE 3.

The Walnut and Comanche Peak Formations, representing the 109-107 Ma spike, trail the OAE 1b series by about 1 to 3 million years, the Pepper and Lake Waco Formations are probably responsible for the ~92 Ma spike, and the Austin Chalk is probably responsible for the 86 Ma spike.

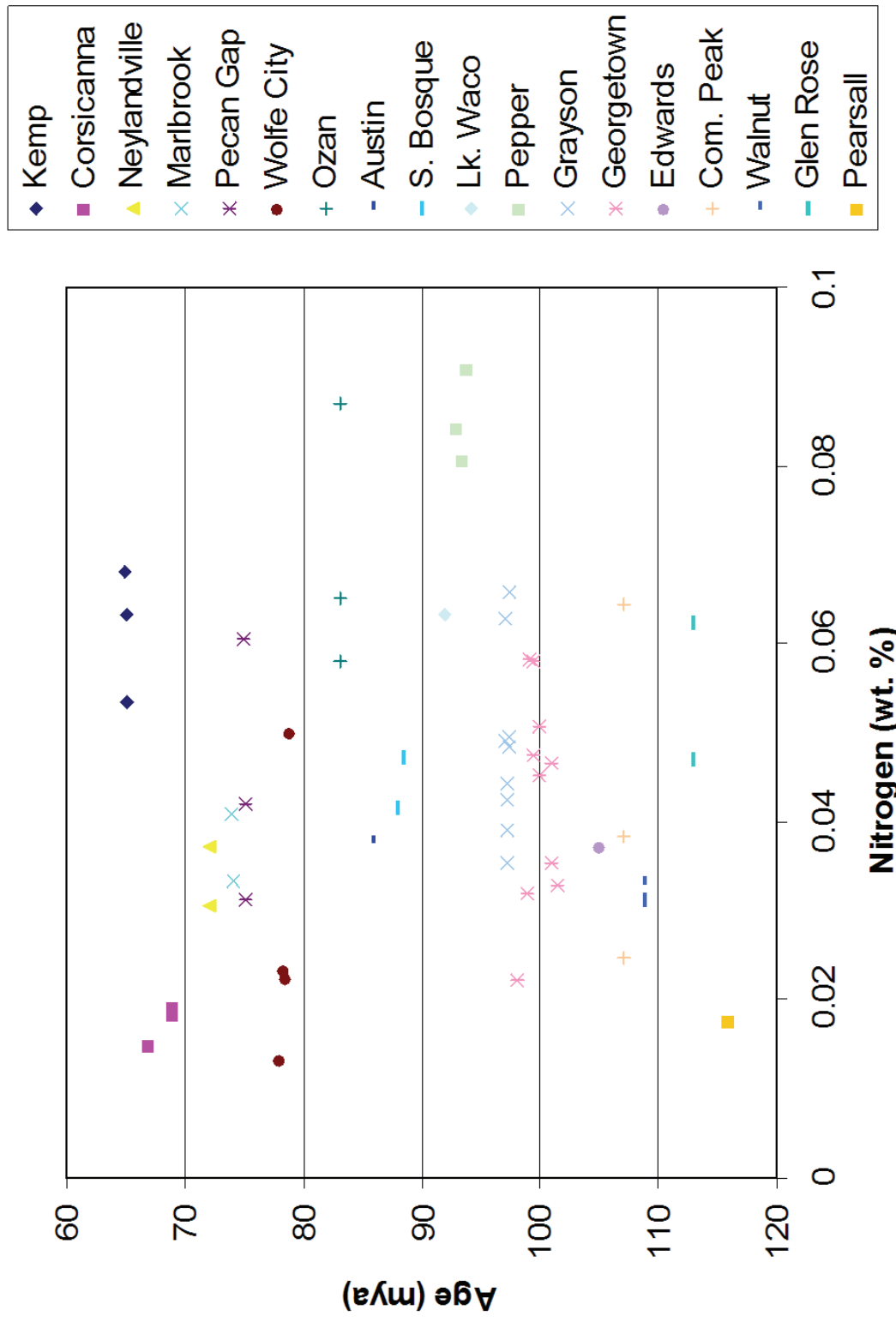


Figure 6: wt.% Nitrogen by formation

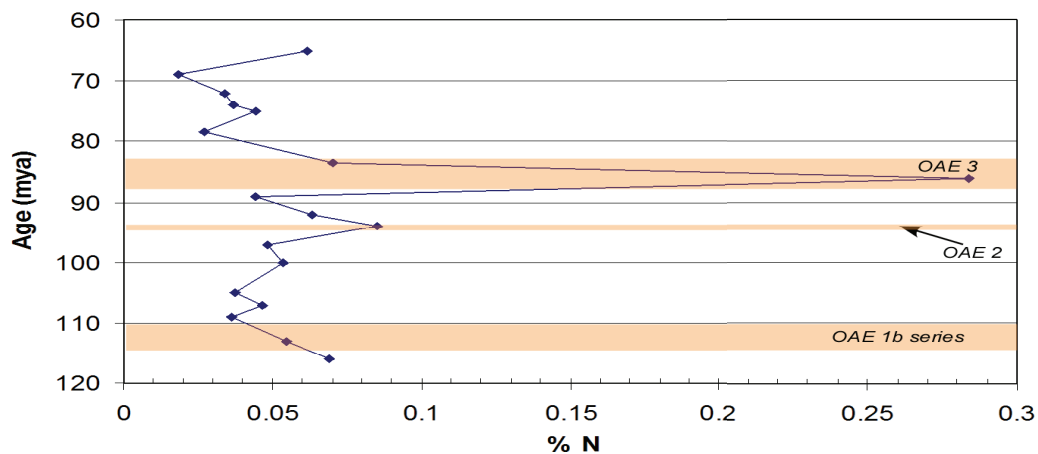


Figure 7: Total nitrogen averaged by formation.

For the most part, the individual samples used to calculate formational C/N average values were consistent. Notable exceptions include the Walnut Formation and Comanche Peak Formations. The Walnut Formation had a low value of 17.4 and a high of 69.7 with an average of 36.7 (the average would be 25.7 excluding the high sample value of 69.7). The Comanche Peak Formation's maximum and minimum values were 49.6 and 25.9 respectively with an average of 33.5.

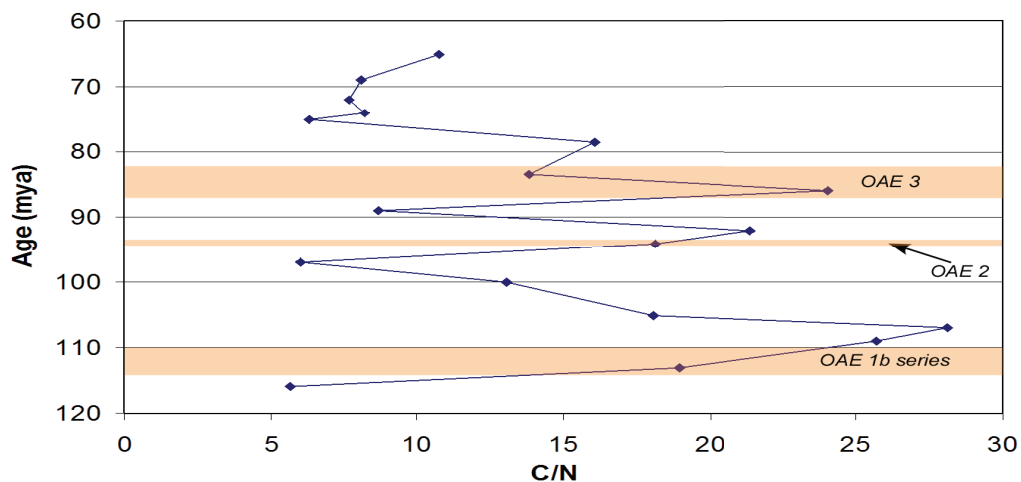


Figure 8: C/N ratios averaged by formation.

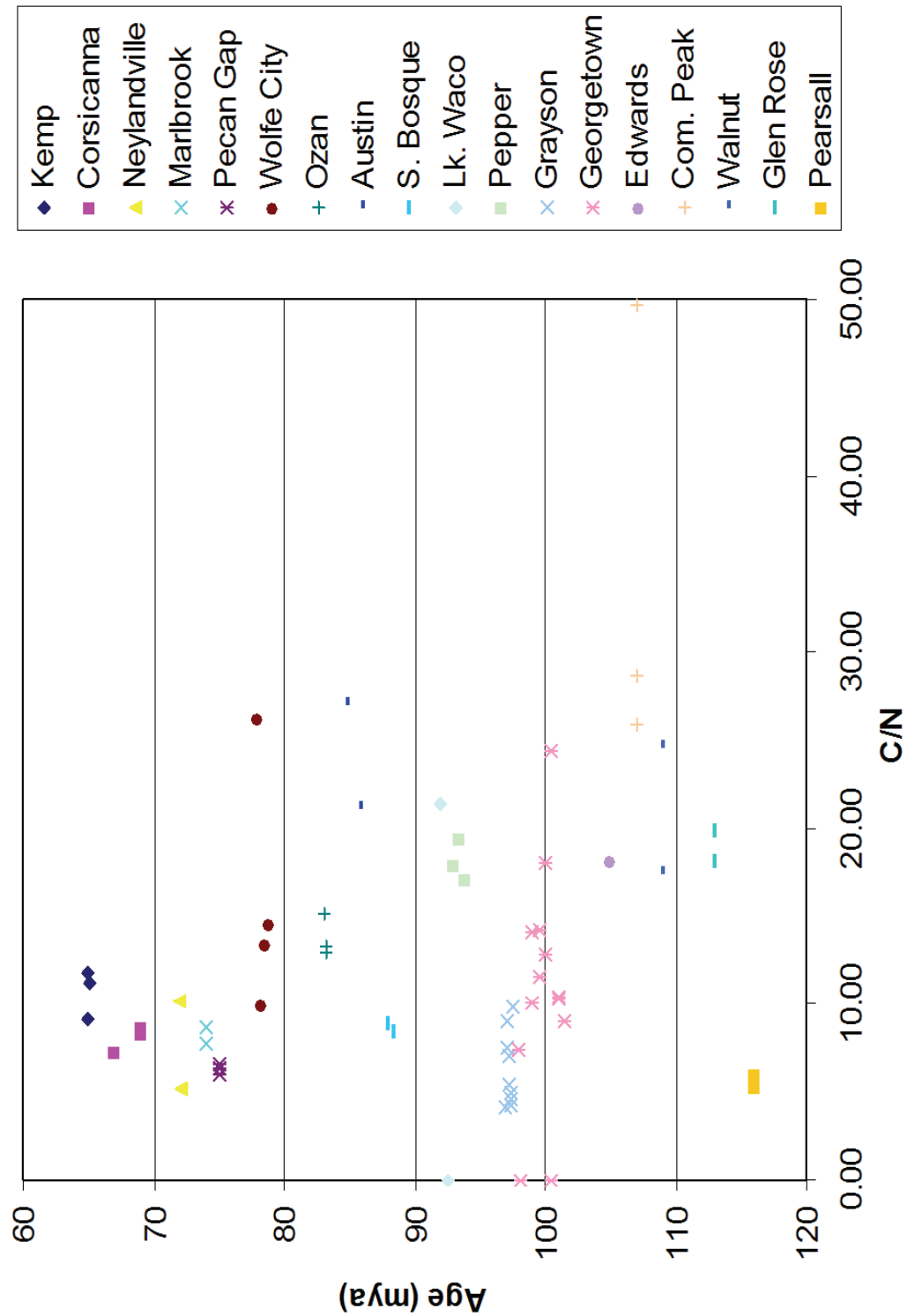


Figure 9: C/N ratios by formation.

Table 2: Total organic carbon, total nitrogen, and C/N ratios of sampled formations

Sample	OC	Wt % N	C/N
	Wt %	treated	
K-1 (Kemp)	0.565492298	0.068058088	9.171655635
K-2	0.506098398	0.053512082	11.81474262
K-3	0.569469874	0.063144118	11.1781684
KC-1 (Corsicana)	0.104593717	0.014751442	7.275486793
C-1	0.165472747	0.019159067	8.620228561
C-2	0.151863102	0.018254807	8.305812729
N-1 (Neylandville)	0.297215311	0.030524764	10.19978755
N-2	0.167999942	0.037214387	5.174693835
M-1 (Marlbrook)	0.318774051	0.040970415	8.708846637
M-2	0.216895344	0.033233464	7.725682208
PG-1 (Pecan Gap)	0.146325438	0.060499966	5.998913279
PG-2	0.103215826	0.031271465	6.586180383
PG-3	0.124650191	0.041954041	6.322049958
WC-1 (Wolfe City)	0.235127412	0.01318	26.25948407
WC-2	0.197999314	0.02323	9.97417133
WC-3	0.257039722	0.022376	13.44297462
WC-4	0.126577712	0.049985	14.51835551
Oz-2 (Ozan)	0.733931124	0.057937	15.16990869
Oz-3	1.032723011	0.0871	12.98920781
Oz-4	0.77511424	0.06508	13.24938537
AC-1 (Austin)	1.699608372	0.52973187	26.98464642
AC-2	0.251457306	0.037578505	21.09274226
SB-1 (S. Bosque)	0.29128901	0.04146	8.860588519
SB-2	0.317519843	0.04715	8.460233298
SC-4 (Lake Waco)	0.698206086	0.06323	21.38383679
SC-5 (Lake Waco)	0.136852025	0	#DIV/0!
SC-1 (Pepper)	1.542781817	0.08431	17.92195469
SC-2 (Pepper)	1.573639225	0.0807	19.41511772
SC-3 (Pepper)	1.575546092	0.09096	17.08443272
SC-7 (Del Rio/Grayson)	0.147420202	0.0489856	4.115903449
SC-6 (Del Rio/Grayson)	0.308689655	0.06283	7.490052523
G-1 (Grayson)	0.228182379	0.0355	9.005352113
G-2	0.145382315	0.039	5.433333333
G-3	0.231866124	0.0443965	7.06136745

Table 2-continued : Total organic carbon, total nitrogen, and C/N ratios of sampled formations.

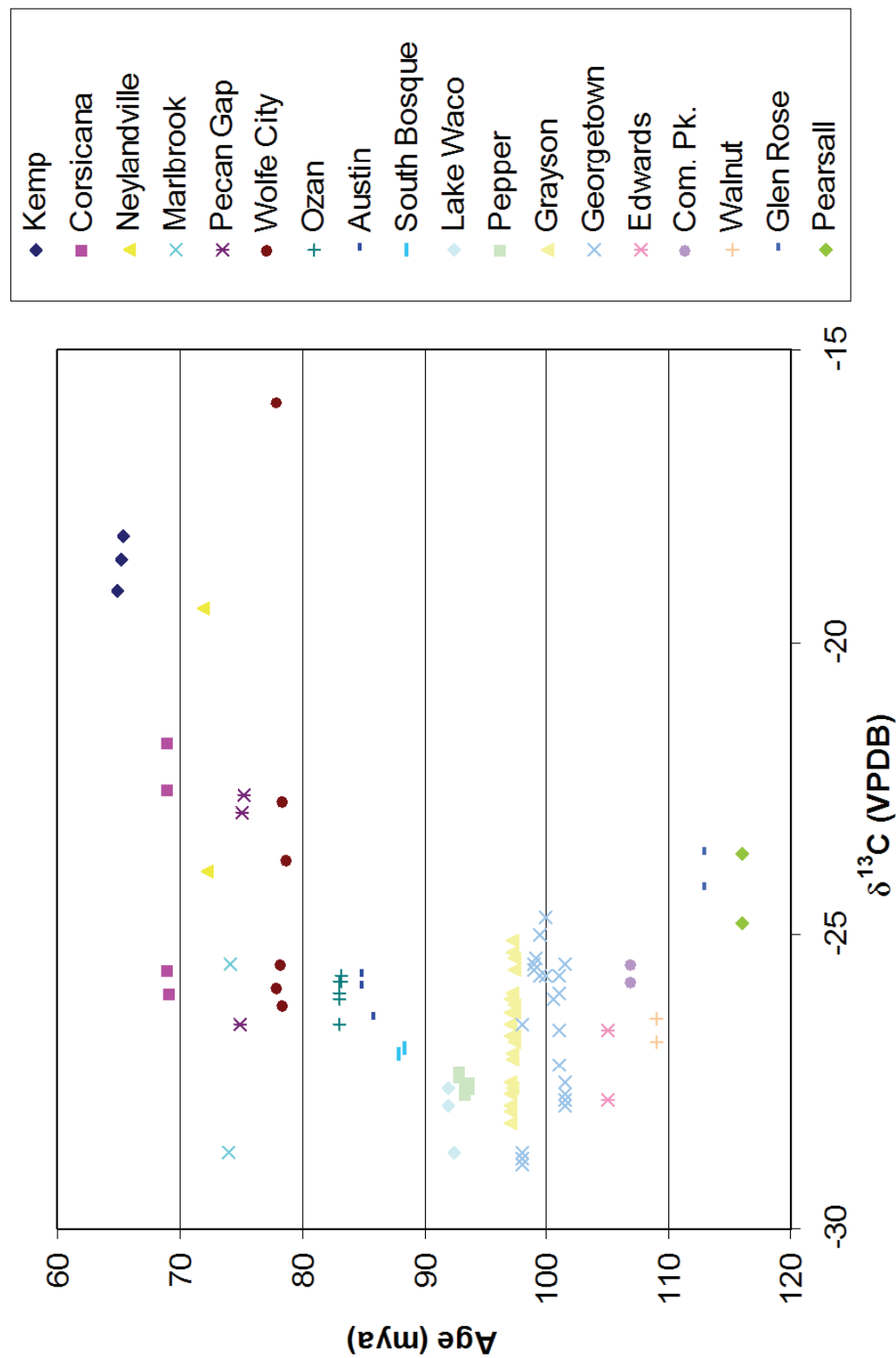
Sample	OC	Wt % N	C/N
	Wt %	treated	
G-4	0.134385127	0.042572	4.268063516
G-5	0.219621499	0.049555	4.652810009
G-6	0.177524673	0.048295	4.954964282
G-7	0.626434598	0.0657682	9.867534766
SC-8 (Mainstreet)	0.123315779	0.02204	7.406079855
MS-11	0		#DIV/0!
P-1 (Pawpaw)	0.311155708	0.03185	14.04081633
P-3	0.35286596	0.05823	9.998282672
W-1 (Weno)	0.088928636	0.058068067	14.20027195
W-2	0.441363739	0.047440548	11.55710545
D-1 (Denton)	0.400095514	0.050739404	12.81374299
D-2	0.210403739	0.045214359	17.9773743
Ft. W-1 (Ft. Worth))	-0.056590892	0.159973502	24.34973897
Ft. W-2	0		#DIV/0!
DC-1 (Duck Creek)	0.083491812	0.035385244	10.2485687
DC-2	0.104374057	0.046601653	10.35159351
SC-9 (Kiamichi)	0.144612145	0.03299	8.969687784
SC-10 (Edwards)	0.071225025	0.037236	18.07444409
Cp-11 (Com. Peak)	0.110676979	0.024676973	49.6075868
Cp-11(2)	0.151178527	0.038431183	25.91684994
Cp-1	0.096386568	0.064296804	28.62476506
Cp-1r	0.204830975	0.059138224	29.85148125
WaCl-1 (Walnut)	0.199238797	0.03131	17.41137017
WaCl-1r	0.35298468	0.033114675	24.63836442
WaCl-2	0.399337266	0.03065	69.7096248
WaCl-2r	0.428853144	0.048532896	35.02171003
GR-1 (Glen Rose)	0.919402262	0.06222	19.82594021
GR-2	0.083531983	0.04703	18.08420157
H-1 (Hensel)	0.044743474	BDL	BDL
H-2	0.056388622	BDL	BDL
H-3	0.034573312	BDL	BDL
H-4	0.057576596	BDL	BDL
Phs-1 (Pearsall)	0.092630922	0.017498	5.286318436
Phs-2	0.725797553	0.120331	6.000947387

Table 3: Averaged carbon, nitrogen, and C/N for each formation with standard deviation

Formation	OC% (average)	C/N (average)	N (average)	St. Deviation OC	St. Deviation C/N	St. Deviation N	Approximate Age
kemp	0.55	10.72	0.06	0.04	1.38	0.01	65
corsicana	0.14	8.07	0.02	0.03	0.70	0.00	69
neylandville	0.23	7.69	0.03	0.09	3.55	0.00	72
marlbroke	0.27	8.22	0.04	0.07	0.70	0.01	74
pecan gap	0.12	6.30	0.04	0.02	0.29	0.02	75
wolfe city	0.20	16.05	0.03	0.06	7.08	0.02	78.5
ozan	0.85	13.80	0.07	0.16	1.19	0.02	83.5
austin	0.98	24.04	0.28	1.02	4.17	0.35	86
south bosque	0.30	8.66	0.04	0.02	0.28	0.00	89
lake waco	0.42	21.38	0.03	0.40		0.04	92
pepper	1.56	18.14	0.09	0.02	1.18	0.01	94
grayson	0.23	6.02	0.05	0.17	2.13	0.01	97
georgetown	0.18	13.05	0.05	0.16		0.04	100
edwards	0.07	18.07	0.04				105
comanche peak	0.14	33.50	0.05	0.05	10.86	0.02	107
walnut	0.35	36.70	0.04	0.10	23.17	0.01	109
glen rose	0.92	18.96	0.05	0.59	1.23	0.01	113
hensel	0.05	BDL	BDL	0.01	BDL	BDL	114
pearsall	0.73	5.64	0.07	0.45	0.51	0.07	116

Isotopic Composition of Organic Matter

The majority of carbon isotopic values of the organic matter in Central Texas Cretaceous rocks fall between -25‰ and -28‰ (see Figure 10). Starting with the Wolfe City Formation (-23.3‰), the formations of the upper Cretaceous show a positive excursion (except for the -27.1‰ Marlbrook Formation) with the Kemp Clay (-18.6‰) being the lightest (complete data set for both carbon and nitrogen isotopic measurements presented in tables 3 and 4). Individual samples making up formation $\delta^{13}\text{C}$ averages (presented alongside the averaged $\delta^{15}\text{N}$ values in Figure 13) were fairly consistent with the Wolfe City Formation's average value having the highest standard deviation (3.8‰). Formations of the lower Cretaceous that have average $\delta^{13}\text{C}$ values outside the -25‰ to -28‰ range include the Pearsall Formation and Glen Rose Formation.



In general, the Cretaceous section starts out with organic matter in the -25‰ range (Pearsall and Glen Rose) which then decreases to ~-27‰ during the middle Cretaceous (109 to 92 Ma). Starting with the South Bosque Formation and Austin Chalk, the upper Cretaceous returns to the heavier -25‰ value and continues with more positive $\delta^{13}\text{C}$ values to the K/T boundary. There does not appear to be any discernable relationship between $\delta^{13}\text{C}$ values and the documented oceanic anoxic events of the Cretaceous.

$\delta^{15}\text{N}$ values range from 6.33‰ in the Kemp Clay to -0.35‰ in the Lake Waco Formation with an average value for the entire section of 2.68‰ (see Figure 11). As with $\delta^{13}\text{C}$ values, values making up $\delta^{15}\text{N}$ formation averages were quite consistent (see tables 3 and 4) with the average value of the Lake Waco Formation having the highest standard deviation (2.19‰). Most of the $\delta^{15}\text{N}$ average values in the lower Cretaceous, from the Grayson to the Pearsall (with the exception of the Hensell), fall between 4‰ and 1.5‰. Above that, there is a sharp drop through the Pepper Shale (.92‰) to the Lake Waco Formation (-.35‰). After a brief jump in the South Bosque Formation (2.5‰), $\delta^{15}\text{N}$ values sharply drop again in the Austin Chalk (.08‰). In the Upper Cretaceous after the Austin Chalk, $\delta^{15}\text{N}$ values begin to rise to ~2‰ in the Ozan (1.94‰) and Wolfe City (2.23‰) followed by another sharp rise in the Pecan Gap (4.23‰). After a brief drop in the Marlbrook (3.6‰), $\delta^{15}\text{N}$ values rise again in the Neylandville (5.4‰). The Corsicana drops $\delta^{15}\text{N}$ values down to 3.525‰ before the Kemp brings them to their highest in the section at 6.33‰. Although there is no discernable correlation with OAE 1b, OAE 2 and OAE 3 are marked by a sharp drop in $\delta^{15}\text{N}$ values to nearly 0‰.

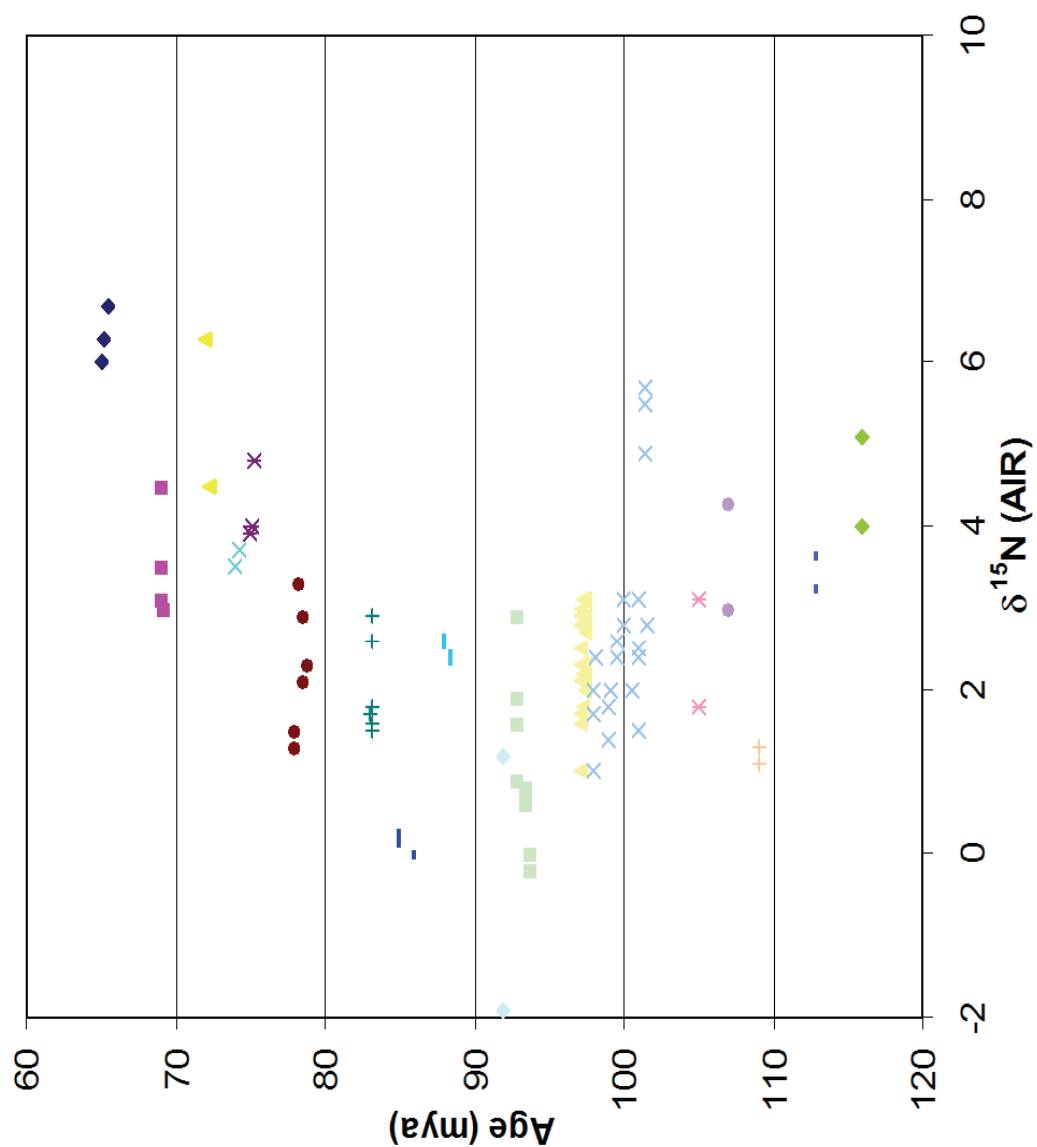


Figure 11: $\delta^{15}\text{N}$ (AIR) by formation.

Correlation Between the Trends in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$.

From the Pearsall Formation (~116 Ma) at the bottom of the section to the South Bosque Formation (~89.5 Ma), the averaged nitrogen and carbon isotopic plots (see figure 12), though offset, mimic each other in terms of relative increase and decrease between formations.

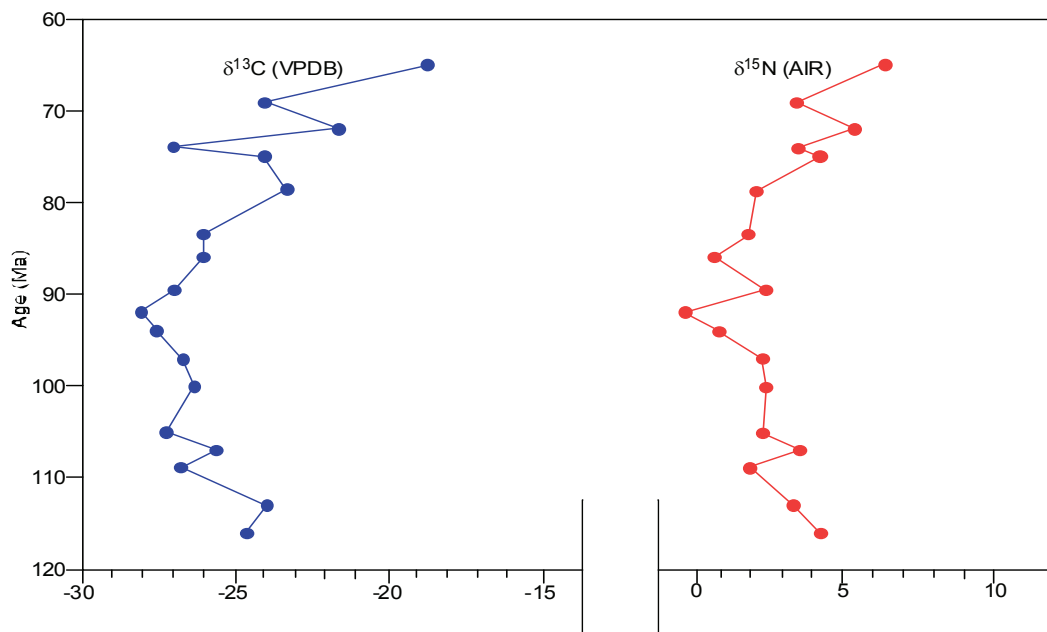


Figure 12: Formational averages for $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$.

This similar trend is also present in the upper Cretaceous from the Pecan Gap (~75 Ma) to the Kemp Clay (~65 Ma) top of the Cretaceous. The only time during which the averaged carbon and nitrogen isotopic trends do not mimic each other is the ~14.5 million year period during which the Austin Chalk, Ozan Formation, and Wolfe City Formations were deposited. This time interval also includes OAE 3 (~87.3-84.6 Ma). In general, the changes in the carbon isotopic compositions were more dramatic than those of the averaged nitrogen isotopic compositions.

Table 4: Carbon and nitrogen isotopic data for sampled formations

Formation	Age (Ma) (approximate)	Sample ID	$\delta^{13}\text{C}$ (vs. PDB)	$\delta^{15}\text{N}$ (vs. air)
Kemp Clay	65	K-1	-19.1	6
		K-2	-18.6	6.3
		K-3	-18.2	6.7
Corsicana	69	KC-1	-21.7	3.5
		KC-1 dup	-22.5	3.1
		C-1	-25.6	4.5
		C-2	-26	3
Neylandville	72	N-1	-19.4	6.3
		N-2	-23.9	4.5
Marlbrook	74	M-1	-28.7	3.5
		M-2	-25.5	3.7
Pecan Gap	75	PG-1	-26.5	3.9
		PG-2	-22.9	4
		PG-3	-22.6	4.8
Wolfe City	78.5	WC-1	-15.9	1.5
		WC-1r	-25.9	1.3
		WC-2	-25.5	3.3
		WC-3	-22.7	2.9
		WC-3r	-26.2	2.1
		WC-4	-23.7	2.3
Ozan	83.5	Oz-1	-26.5	1.7
		Oz-2	-26	1.5
		Oz-2r	-26	2.9
		Oz-3	-26.1	1.6
		Oz-3r	-25.8	2.6
		Oz-4	-25.8	1.8
		Oz-4r	-25.7	1.5
Austin Chalk	86	AC-1	-25.9	0.2
		AC-1 dup	-25.7	0.1
		AC-2	-26.4	-0.06
South Bosque	89.5	SB-1	-27	2.6
		SB-2	-26.9	2.4
Lake Waco Fm.	92	SC-4	-27.9	1.2
		SC-4	-27.6	-1.9
		SC-5	-28.7	
Pepper Shale	94	SC-1	-27.4	1.9
		SC-1	-27.4	0.9
		SC-1	-27.3	2.9
		SC-1	-27.3	1.6
Pepper Shale		SC-2	-27.5	0.6
		SC-2	-27.5	
		SC-2	-27.6	0.8
		SC-2	-27.7	0.7
Pepper Shale		SC-3	-27.6	
		SC-3	-27.6	0
		SC-3	-27.5	0
		SC-3	-27.6	-0.2

Table 4-continued: Carbon and nitrogen isotopic data for sampled formations

Formation	Age (Ma) (approximate)	Sample ID	$\delta^{13}\text{C}$ (vs. PDB)	$\delta^{15}\text{N}$ (vs. air)
Del Rio (Grayson)	97	SC-7	-27.7	2.8
		SC-7	-28	3
		SC-7	-28.2	2.3
		SC-7	-27.7	2.9
Del Rio (Grayson)		SC-6	-26.7	1
		SC-6	-26.7	1.7
		SC-6	-26.5	
		SC-6	-26.3	1.6
Grayson		G-1	-26.1	2.1
		G-1r	-27.5	2.5
		G-1r dup	-27.9	1.6
		G-2	-25.1	3.1
		G-2r	-27.6	1.8
		G-3	-26	2.8
		G-3r	-27.1	2.1
		G-4	-25.3	2.2
		G-4r	-27	2.1
		G-5	-25.4	2.9
		G-5r	-26.8	2
		G-6	-26.7	3.1
		G-6r	-26.2	2.7
		G-7	-25.6	2.1
		G-7r	-26.3	2.3
Mainstreet Lm.	98	SC-8	-28.8	2
		SC-8	-28.7	1.7
		SC-8	-28.8	1
		SC-8	-28.9	1
		MS-11	-26.5	2.4
Pawpaw Shale	99	P-1	-25.5	1.4
		P-1 dup	-25.6	1.8
		P-3	-25.4	2
Weno Lm.	99.5	W-1	-25.7	2.6
		W-2	-25	2.4
Denton Shale	100	D-1	-24.7	2.8
		D-2	-25.7	3.1
Ft. Worth	100.5	Ft. W-1 (bot)		
		Ft. W-2 (top)	-26.1	2
Duck Creek Limestone	101	DC-1	-27.2	1.5
		DC-1r	-26.6	3.1
		DC-2	-26	2.4
		DC-2r	-25.7	2.5
Kiamichi Fm.	101.5	SC-9	-27.8	5.7
		SC-9	-27.9	4.9
		SC-9	-27.7	5.5
		SC-9	-27.5	5.5
		KI-1	-25.5	2.8
Edwards Fm.	105	SC-10	-27.8	1.8
		Ed-11	-26.6	3.1

Table 4-continued: Carbon and nitrogen isotopic data for sampled formations

Formation	Age (Ma) (approximate)	Sample ID	$\delta^{13}\text{C}$ (vs. PDB)	$\delta^{15}\text{N}$ (vs. air)
Comanche Peak	107	Cp-11 (top)	-25.8	4.3
		Cp-11(2)	-25.5	3
		Cp-1 (bot)		
Walnut Clay	109	WaCl-1	-26.8	1.1
		WaCl-1r	-27	3.5
		WaCl-2	-26.4	1.3
Glen Rose	113	GR-1	-24.2	3.2
		GR-2	-23.6	3.6
Hensel	114	H-1	-28.4	0.7
		H-2	-27.2	0.3
		H-3	-27.1	0.9
		H-3 dup	-28.4	0.2
		H-4	-29.2	0.5
Pearsall	116	Phs-1	-24.8	4
		Phs-1 dup	-25.4	3.7
		Phs-2	-23.6	5.1

Table 5: Formational isotopic averages with standard deviation.

Formation	average $\delta^{15}\text{N}$	average $\delta^{13}\text{C}$	age	St. Deviation $\delta^{13}\text{C}$	St. Deviation $\delta^{15}\text{N}$
kemp	6.33	-18.63	65.00	0.45	0.35
corsicana	3.53	-23.95	69.00	2.17	0.68
neylandville	5.40	-21.65	72.00	3.18	1.27
marlbrooke	3.60	-27.10	74.00	2.26	0.14
pecan gap	4.23	-24.00	75.00	2.17	0.49
wolfe city	2.23	-23.32	78.50	3.88	0.78
ozan	1.94	-25.99	83.50	0.27	0.57
austin	0.08	-26.00	86.00	0.36	0.13
south bosque	2.50	-26.95	89.50	0.07	0.14
lake waco	-0.35	-28.07	92.00	0.57	2.19
pepper	0.92	-27.50	94.00	0.13	0.97
grayson	2.30	-26.71	97.00	0.90	0.57
mainstreet	1.62	-28.34	98.00	1.03	0.62
pawpaw	1.73	-25.50	99.00	0.10	0.31
weno	2.50	-25.35	99.50	0.49	0.14
denton	2.95	-25.20	100.00	0.71	0.21
ft. worth	2.00	-26.10	100.50	#DIV/0!	#DIV/0!
duck creek	2.38	-26.38	101.00	0.67	0.66
kiamichi	4.88	-27.28	101.50	1.01	1.20
edwards	2.45	-27.20	105.00	0.85	0.92
comanche peak	3.65	-25.65	107.00	0.21	0.92
walnut	1.97	-26.73	109.00	0.31	1.33
glen rose	3.40	-23.90	113.00	0.42	0.28
hensel	0.52	-28.06	114.00	0.89	0.29
pearsall	4.27	-24.60	116.00	0.92	0.74

CHAPTER SIX

Discussion

For rocks deposited in a marine environment, there is an expected geochemical signal that indicates “normal” paleoceanographic conditions. For organic matter derived from a marine source, C/N ratios should be below 10, $\delta^{13}\text{C}$ values should be $>-25\text{‰}$, and $\delta^{15}\text{N}$ compositions should be about 4.8‰ . Terrestrially derived organic matter, on the other hand, should have C/N ratios >20 , $\delta^{13}\text{C}$ compositions $<-25\text{‰}$, and $\delta^{15}\text{N}$ compositions in equilibrium with atmospheric N_2 (about 0‰). Lastly, oceanic anoxic events have the potential to impart a lighter than normal $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signature (by allowing nitrogen-fixing organisms to flourish) while also imparting a higher than normal C/N ratio. Whether the source is terrestrial or marine, there should not be significant accumulations of organic matter in the presence of a well-oxygenated and vertically well-mixed water column.

Formations from the Central Texas Cretaceous section with organic matter exhibiting the normal marine geochemical signal are the Pearsall Formation, Pecan Gap Formation, Neylandville Formation, and Corsicana formation. Formations that contain organic matter exhibiting a geochemical signature indicative of terrestrial organic input include the Walnut Formation, Comanche Peak Formation, Lake Waco Formation, and Austin Chalk. Of the formations with organic matter seemingly of terrestrial origin, only the Lake Waco Formation does not occur within or closely following an OAE. All other formations not mentioned above fall somewhere between the traditional terrestrial and

marine geochemical signals. In general, the lower and middle Cretaceous tends to exhibit a mixed signal while the upper Cretaceous appears to be distinctly more marine dominated (see figure 13).

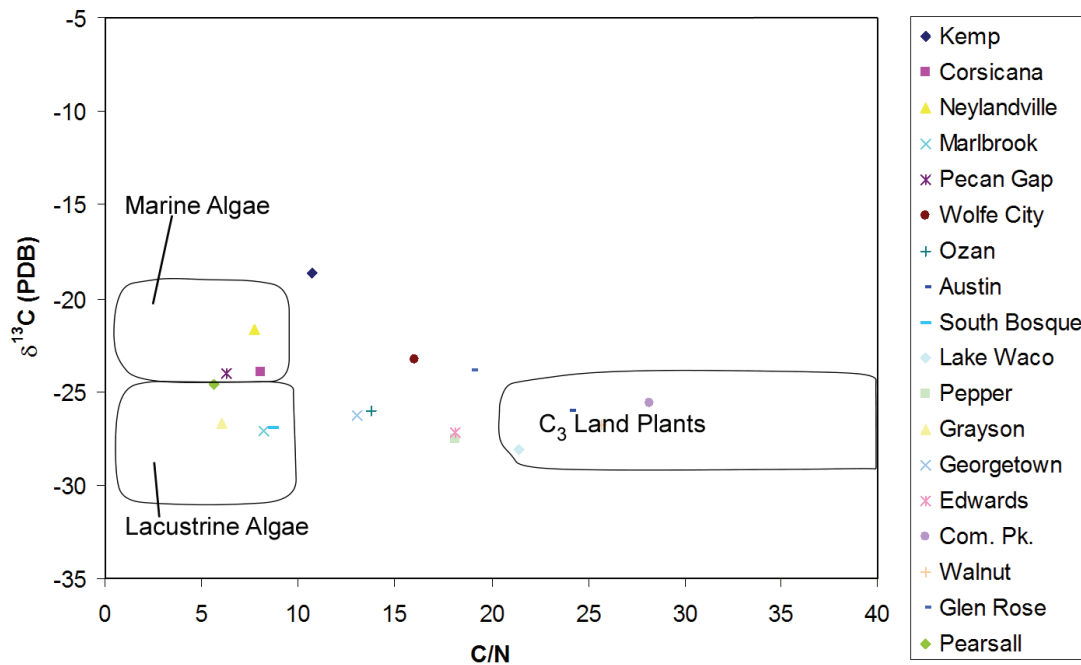


Figure 13: $\delta^{13}\text{C}$ vs. C/N. Modified from Meyers 1997.

As shown in figure 5, the spikes in TOC values for the Central Texas Cretaceous formations seem to correlate OAE 1b, OAE 2, and OAE 3. Two of the primary drivers for oceanic anoxic events are increased production and/or delivery of organic matter and a stratified water column resulting from reduced ocean circulation. The Cretaceous is well known as a time period of greenhouse climate with little to no polar ice accompanied by a period of extensive transgression (Skelton et al. 2003). Figure 14 illustrates both the rise in sea level throughout the early to middle Cretaceous as well as the relative position of OAE 1,2,and 3.

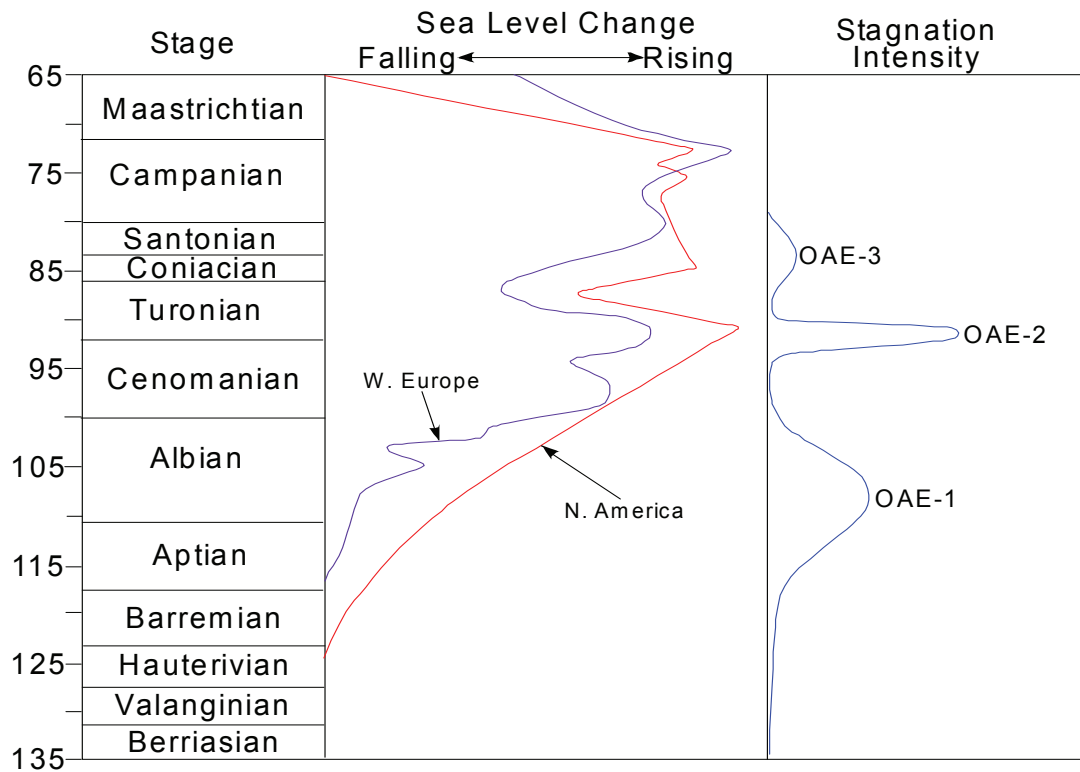


Figure 14. Chart of sea level change and stagnation intensity during the Cretaceous (Arthur 1979)

With no polar ice and the extended shelf area that existed in the Cretaceous in Central

Texas, it's unlikely there were thermal ocean currents comparable to those of today.

However, if ocean stratification as a result of low ocean circulation was the sole cause of increased marine organic matter production, there should be consistently higher TOC

values correlating to a general condition of anoxia throughout the Cretaceous as opposed

to punctuated events correlated to spikes in the TOC plot. The C/N plots (see figure 8)

also seem to correlate with OAE 1b, OAE 2, and OAE 3. The high C/N ratios at 109-107

Ma (Com. Pk. And Walnut Formations) and at 93 Ma (Pepper Shale) seem to closely trail

OAE 1b and OAE 2, respectively, instead of matching up directly with them. The Austin

Chalk positive excursion, on the other hand, does seem to match up directly with OAE 3.

The TOC values and C/N ratios could have been caused by inflated by sub-oxic microbial

degradation of organic matter. This process targets nitrogen-rich amino acids leaving the remains enriched in carbon relative to nitrogen (Twichell 2002, Meyers 1997, Meyers 2006). This would depend on how long anoxic ocean conditions existed at the ocean floor after the OAE itself has subsided. If a stratified water column was to solely blame for the anoxic conditions, the elevated TOC and C/N values should be more consistent. The observed data could be the result both a stratified water column and elevated organic input. The stratified water column could have created a situation where the water column, while not really anoxic, had lower oxygen levels than normal. This way, any period of increased organic matter delivery, whether allogenic or autogenic, would easily overwhelm the already partially depleted and poorly circulated water column and result in a period of anoxia.

Although marine organic matter will be a significant portion of the preserved organic matter in any marine environment, areas with significant fluvial input can also have a substantial input of terrestrially derived organic as well. According to the $\delta^{13}\text{C}$ plot (see figure 10), the entire lower Cretaceous portion of the studied interval (except the Glen Rose), falls within the traditionally defined range of C_3 land plants. This seems to be consistent with studies by Meyers and others with marine sediments exhibiting a terrestrial $\delta^{13}\text{C}$ signature in organic matter. If the organic matter in the study area really was being mostly derived from allogenic C_3 material, the C/N ratios should also reflect this by being consistently greater than 20. When plotted Meyers' C/N vs. $\delta^{13}\text{C}$ plot (figure 13), only a handful of formations fall within the realm of terrestrial plants (Walnut, Comanche Peak, Edwards, Glen Rose, and Pepper) and, of those, only the Edwards Formation is not related to an oceanic anoxic event (during which C/N ratios

can be inflated by sub-oxic microbial degradation). Additionally, greenhouse climates, which are characterized by high pCO₂ (like the one which existed throughout the cretaceous), allow for greater isotopic discrimination in favor of ¹²C thus artificially decreasing $\delta^{13}\text{C}$ values.

The average value for the entire section was 2.7‰ punctuated by drastic negative excursions during OAE 2 and 3. Under normal conditions, the $\delta^{15}\text{N}$ values of marine organic matter and C₃ plants are 4.8‰ and ~0‰ respectively (Meyers 2006, Sigman et al. 2000, Altabet and Francois 1994). Based on the carbon isotopic and C/N data, it's unlikely that the input of C₃ plants caused such light values in the nitrogen isotopic signal. Such a light average value for the section suggests atmospheric nitrogen fixation by cyanobacteria. This makes sense in that the photic zone in a stratified water column would be depleted in dissolved nutrients creating an environment in which nitrogen-fixing organisms like cyanobacteria could thrive. It seems that nitrogen fixation was particularly pronounced during OAE 2 and 3 (see figure 11).

Although the organic matter of the Central Texas Cretaceous formations appears to be mostly marine (especially in the upper Cretaceous), there appears to be a contribution of terrestrial organic matter. The $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ data in figure 12 mimic each other with respect to relative change between formations (not true for the period between 86 and 78.5Ma). An influx of terrestrial organic matter would drive both the $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ signatures to more negative values, which might explain the parallel shifts in both isotope ratios. As stated earlier, the majority of the organic matter within these sediments is likely marine in origin. However, for both the carbon and nitrogen isotopic signals to match up like that for all but 3 formations of the section, there must have been

some organic input from the terrestrial realm. It is also clear that the isotopic signatures of the upper Cretaceous formations return to traditional marine values. It also appears as if nitrogen-fixing organisms remained prevalent at least until the deposition of the Pecan Gap Formation (~75Ma). After the Pecan Gap, sea level began to recede and no longer provided the terrestrial organic matter that the transgression did causing the carbon and nitrogen isotopic signatures to return to traditional marine values.

CHAPTER SEVEN

Conclusions

Significant increases in the preservation of organic matter seem to be directly related to OAE 1b, 2, and 3. This is particularly significant in that OAE influence has generally been thought to be limited to deep ocean basins. The formations studied here were deposited on the Cretaceous continental shelf and clearly have a direct relationship between TOC values and OAE occurrence. The OAE 1b, 2, and 3 also appear to be responsible for the positive excursions in C/N ratios by virtue of sub-oxic microbial decomposition targeting the nitrogen-rich amino acids of organic matter. These oceanic anoxic events appear to be the result of a stratified water column caused by reduced global ocean currents. The global nature of the OAE's makes sudden, massive input of organic matter (either terrestrial or marine) unlikely.

Although there does seem to be a terrestrial contribution to the preserved organic matter, the marine geochemical signature dominates. The high pCO₂ of the time would make the carbon isotopic signal of marine organic matter resemble that of terrestrial organic matter. Additionally, the stratified water column would limit the recycling of nutrients to the photic zone creating an ideal environment for nitrogen-fixing bacteria to flourish. This seems to be why the nitrogen signal is so light in spite of the sub-oxic decomposition of organic matter on the sea floor.

APPENDIX

APPENDIX A

Outcrop Localities

Kemp Clay

Samples K-1, K-2, and K-3 collected in Falls County half a mile upstream of the Brazos River from its intersection with FM 1373.

Corsicana

Samples KC-1 and KC-2 collected in Limestone County in a stream cut of Pin Oak Creek ~4 miles southwest of HW 638. Samples C-1 and C-2 collected in Limestone County in a stream cut of Pin Oak Creek at its intersection with HW 638.

Neylandville and Marlbrook

Samples N-1, N-2, M-1, and M-2 collected in Milam County in a stream cut 100 yards north of the intersection of HW 77 and Little Pond Creek.

Pecan Gap

Samples PG-1, PG-2, and PG-3 collected in Falls County in a stream cut of Poole Creek 2 miles north of Cedar Springs along FM 2028.

Wolfe City

Samples WC-1, WC-2, WC-3, and WC-4 collected in Falls County in a stream cut of Deer Creek 250 yards upstream from HW 320.

Austin Chalk

Samples AC-1 and AC-2 collected in McLennan County at the Lovers Leap cliffs in Cameron Park.

South Bosque

Samples SB-1 and SB-2 collected in McLennan County in a river cut 75 yards upstream from FM 2837 in the South Bosque River just off HW 84.

Pepper Shale

Samples SC-1, SC-2, and SC-3 collected in McLennan County on a slope above the South Bosque River. Take the turnaround under HW 84 just before (as you're going west from Waco) the FM 2837 exit.

Buda Limestone

Samples B-1, B-2, and B-3 collected in Bell County under a freeway bridge spanning Leon Creek under HW 93E in Belton.

Grayson

Samples G-1, G-2, G-3, G-4, G-5, G-6, G-6, and G-7 collected in McLennan County in the US Army Corps of Engineers shale pit near the Waco Regional Airport.

Grayson

Samples SC-6 and SC-7 collected in McLennan County in a river cut of the South Bosque River at its intersection with FM 2416.

Pawpaw Shale and Mainstreet Limestone (Georgetown Formation)

Samples MS-1, MS-11, SC-8, P-1, P-2, and P-3 collected in Tarrant County in a road cut (more a slope) between the Beach and Oakland exits along I-30 east of downtown Ft. Worth.

Denton Shale and Weno Limestone (Georgetown Formation)

Samples D-1, D-2, W-1, and W-2 collected in Tarrant County in a river cut 50 yards north of the intersection of Sycamore Creek and Seminary Dr. This is just to the east of I-35N .

Kiamichi, Duck Creek, Ft. Worth (Georgetown)

Samples Ki-1, DC-1, DC-2, Ft. W-1, and Ft. W-2 collected in Hill County, at the Soldiers Bluff outcrop in Laguna Park at the Lake Whitney Dam.

Kiamichi (Georgetown)

Sample SC-9

McLennan County

Edwards and Comanche Peak

Samples Ed-11, CP-11, and CP-1 collected in Somervall County in a road cut about 12 miles west-southwest of Glen Rose on HW-67.

Glen Rose

Samples GR-1 and GR-2 collected in Somervall County just off FM205 in the Cedar Brake Girls Scout camp entrance west of Glen Rose.

Pearsall

Samples Phs-1 and Phs-2 collected in Comanche County in a stream cut along the Leon River off an un-named county road about 1-2 miles north of HW36.

REFERENCES

- Altabet, M., Francois, R., 1994, Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization: *Global Biogeochemical Cycles*, v. 8, p. 103-116.
- Authur, M., Schlanger, S., 1979, Cretaceous “oceanic anoxic events” as causal factors in development of reef-reservoired giant oil fields: *AAPG bulletin*, v. 63, p. 870-885.
- Barnes, V., 1967, *Geologic atlas of Texas*, scale=1:250,000: University of Texas at Austin, Bureau of Economic Geology.
- Beall, A. jr., 1964, Stratigraphy of the Taylor Formation (upper Cretaceous), East central Texas: *Baylor Geological Studies bulletin*, v. 6, p. 34
- Boone, P., 1968, Stratigraphy of the basal Trinity (lower Cretaceous) sands of Central Texas: *Baylor Geological Studies bulletin*, No. 15.
- Brown, T., 1971, Stratigraphy of the Washita Group in central Texas, *Baylor Geological Studies bulletin*, No. 21.
- Burnaby, T., 1961, The paleoecology of the foraminifera of the chalky marl: *Paleontology*, v.4, p. 599-608.
- Chimene, J., Maddocks, R., 1984, Ostracod biostratigraphy and paleoecology of the upper Taylor Group (Campion, upper Cretaceous) in Central Texas: *Transactions of the Gulf Coast Association of Geological Societies*, v. XXXIV, p. 311-320.
- Corwin, L., 1982, Stratigraphy of the Fredricksburg Group north of the Colorado River, Texas: *Baylor Geological Studies bulletin*, No. 40.
- Dawson, W., 1997, Limestone microfacies and sequence stratigraphy: Eagle Ford Group (Cenomanian/Turonian) North-central Texas outcrops: *Transactions of the Gulf Coast Association of Geological Societies*, v. XLVII, p. 99-106.
- Dean, W., Arthur, M., Claypool, G., 1986, Depletion of ^{13}C in Cretaceous marine organic matter: source, diagenetic, or environmental signal?: *Marine Geology*, v. 70, p. 119-157.
- Dumitrescu, M., Brassel, S., 2006, Compositional and isotopic characteristics of organic matter for the early Aptian Oceanic Event at Shatsky Rise, ODP Leg 198: *Paleogeography, Paleoclimatology, Paleoecology*, v. 235, p. 168-191.

- Eadie, B., Chambers, R., Gardner, W., W.S. and Bell, G., 1984, Sediment trap studies in Lake Michigan: resuspension and chemical fluxes in the southern basin: *J. Great Lakes Res.*, v. 10, p. 307-321.
- Emerson, S., Hedges, J., 1988, Processes controlling the organic carbon content of open ocean sediments: *Paleoceanography*, v. 3, p. 621-634.
- Ertel, J., Hedges, J., 1985, Sources of sedimentary humic substances: vascular plant debris: *Geochim. cosmochim. Acta.*, v. 49, p. 2097-2107.
- Flournoy, G., 1991, Edwards (Cretaceous) shelf margin and platform facies and depositional environments: relationships to petroleum occurrence, south-central and east Texas: unpublished masters thesis, Baylor University, Waco, TX.
- Freudenthall, T., Wagner, T., Wenzhofer, F., Zabel, M., Wefer, G., 2001, Early diagenesis of organic material from sediments of the eastern sub-tropical Atlantic: evidence from stable nitrogen and carbon isotopes: *Geochimica et Acta*, v. 65, p. 1795-1808.
- Gearing, P., Plucker, F., Parker, P., 1977, Organic carbon stable isotope ratios of marine sediments: *Mar. Chem.*, v. 5, p. 251-266.
- Hoefs, J., 2004, Stable isotope geochemistry, 5th revised and updated edition: published by Springer
- Hovorka, S., Nance, H., 1994, Dynamic depositional and early diagenetic processes in a deep-water shelf setting, upper Cretaceous Austin Chalk, North Texas: *Transactions of the Gulf Coast Association of Geological Societies*, v. XLIV, p. 269-276.
- Hunt, J., 1970, The significance of carbon isotope variations in marine sediments. In: G.D. Hobson and G.C. Spears (editors), *Advances in Organic Geochemistry*, 1966. Pergamon, Oxford, p. 27-35.
- Ishiwatari, R., Uzaki, M., 1987, Diagenetic changes of the lignin compounds in a more than 0.6 million-year-old lacustrine sediment (Lake Biwa, Japan): *Geochimica. et Cosmochimica Acta.*, v. 51, p. 321-328.
- Jackson, R., 1983, The stratigraphy of the Gulfian series (upper Cretaceous), East central Texas: unpublished masters thesis, Baylor University, Waco, TX.
- Jasper, J., Gagosian, R., 1990, Alkenone molecular stratigraphy in an oceanic environment affected by glacial freshwater events: *Paleoceanography*, v. 4, p. 603-614.

- Jenkyns, H. C., 1980, Cretaceous anoxic events: from continents to oceans: J. geological society of London, v. 137, p. 171-188.
- Junium, C., Arthur, M., 2007, Nitrogen cycling during the Cretaceous, Cenomanian-Turonian oceanic anoxic event 2: Geochemistry, Geophysics, Geosystems, v. 8, QO3002.
- Keller, G., Adatte, T., Berner, Z., Harting, M., Baum, G., Prasuu, M., Tantawy, A., Stueben, D., 2007, Chicxulub impact predates the K-T boundary: New evidence from Brazos, Texas: Earth and Planetary Letters, v. 255, p. 339-356.
- Knauer, G., Martin, J., 1981, Primary production and carbon/nitrogen fluxes in the upper 1500 m of the northwest Pacific, Limnol: Oceanography, v. 26, p. 181-186.
- Lamb, A., Wilson, G., Leng, M., 2006, A review of paleoclimate and relative sea level reconstructions using $\delta^{13}\text{C}$ and C/N ratio in organic material: Earth Science Reviews, v. 75, p. 29-57.
- Leng, M., 2006, Isotopes in paleoenvironmental research: published by Springer.
- Mancini, E., 1974, Depositional environment of the Grayson Formation (upper Cretaceous) of Texas: Transactions of the Gulf Coast Association of Geological Societies, v. 27, p. 334-351.
- Meyers, P., 1993, Preservation of elemental and isotopic source identification of sedimentary organic matter: Chemical Geology, v. 114, p. 289-302.
- Meyers, P., 1997, Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes: Organic Geochemistry, v. 27, p. 213-250.
- Meyers, P., Bernasconi, S., Yum, J., 2006, 20 My of nitrogen fixation during deposition of mid-Cretaceous black shales on the Demerara Rise, equatorial Atlantic Ocean: Organic Geochemistry, v. 40, p. 1958-1966.
- Moore, C., 1969, Guidebook to the depositional environments and depositional history, lower Cretaceous shallow shelf carbonate sequence, west-central Texas: published by the Dallas Geological Society for the AAPG and Society of Economic Paleontologists and Mineralogists 1969 annual meeting.
- Moore, C., 1996, Anatomy of a sequence boundary – lower Cretaceous Glen Rose/Fredricksburg, Central Texas platform: Transactions of the Gulf Coast Association of Geological Societies, v. XLVI, p. 313-320.
- Newman, J., Parker, P., Behrens, E., 1973, Organic carbon isotope ratios in Quaternary cores from the Gulf of Mexico: Geochim. Cosmochim. Acta., v. 37, p. 225-238.

- Owen, M., 1979, The Paluxy Sand in north-central Texas: Baylor Geological Studies bulletin, No. 36.
- Pate, K., 1999, Trace fossils and their significance in the upper Cretaceous, (Gulfian), Wolfe City Sand, Central Texas: unpublished undergraduate thesis, Baylor University, Waco, TX.
- Prahl, F., Bennet, J., Carpenter, R., 1980, The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay, Washington: *Geochimica. et Cosmochimica. Acta.*, v. 44, p. 1967-1976.
- Prahl, F., Ertel, J., Goni, M., Sparrow, M., Eversmeyer, B., 1994, Terrestrial organic carbon contributions to sediments on the Washington margin: *Geochimica. et Cosmochimica Acta.*, v. 58, p. 3048-3055.
- Premuzic, E., Benkovitz, C., Gaffney, J., Walsh, J., 1982, The nature and distribution of organic matter in the sediments of world oceans and seas: *Organic Geochemistry*, v. 4, p. 63-77.
- Raney, J., Allen, P., Reaser, D., Collins, E., 1987, Geology and Technical considerations for the SSC site in Texas: Geologic Review of proposed Dallas/Ft. Worth area site for the superconducting super collider (SSC): material presented at the meeting of the underground tunneling advisory panel on 4/30/89 at the SSC laboratory Lawrence Berkeley Laboratory.
- Reaser D., 1983, Stratigraphic and structural overview of upper Cretaceous rocks exposed in the Dallas vicinity: SEPM field trip, Dallas Geological Society.
- Sellards, E., Adkins, W., Plummer, F., 1932, The geology of Texas, volume 1 "stratigraphy": University of Texas bulletin, No. 3232, 4th printing, 1958.
- Sigman, D., Altabet, M., Francois, R., 2000, The isotopic composition of diatom-bound nitrogen in southern ocean sediments: *Paleoceanography*, v. 14, p. 118-134.
- Silliman, J., Meyers, P., Bourbonniere, R., 1996, Record of post-glacial organic matter delivery and burial in sediments of Lake Ontario: *Organic Geochemistry*, v. 24, p. 463-472.
- Silver, B., 1963, The Bluebonnet Member, Lake Waco Formation (upper Cretaceous,, central Texas—A lagoonal deposit: Baylor Geological Studies bulletin, No. 4.
- Skelton, P., Spicer, R., Kelley, S., Gilmour, I., 2003, *The Cretaceous World*: published by the press syndicate of the University of Cambridge.
- Sliter, W., Baker, R., 1972, Cretaceous bathymetric distribution of benthonic foraminifers: *Jour. Foram. Res.*, v.2, p. 167-183.

- Slomp, C., Thompson, J., de Lange, G., 2004, Controls on phosphorous regeneration and burial during formation of eastern Mediterranean sapropels: *Marine Geology*, v. 203, p. 141-159.
- Sues, E., 1980, Particulate organic carbon flux in the oceans – surface productivity and oxygen utilization: *Nature (London)*, v. 288, p. 260-263.
- Talbert, S., 2000, Sequence stratigraphy of the Fredricksburg Group, central and north Texas: unpublished masters thesis, Baylor University, Waco, TX.
- Twichell, S., Meyers, P., 2002, Significance of high C/N ratios in organic-carbon-rich Neogene sediments under the Benguele Current upwelling system: *Organic Geochemistry*, v. 33, p. 715-722.
- Wakeham, S., Farrington, J., Gagosian, R., Lee, C., De Barr, H., Nigrelli, G., Tripp, B., Smith, S., Frew, N., 1980, Organic matter fluxes from sediment traps in the equatorial Atlantic Ocean: *Nature (London)*, v. 286, p. 798-200.