CHEMOSTRATIGRAPHY AND PALEOENVIRONMENTAL SIGNIFICANCE

OF THE PENNSYLVANIAN SMITHWICK FORMATION,

NORTHEN LLANO UPLIFT REGION,

TEXAS

by

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ABSTRACT

CHEMOSTRATIGRAPHY AND PALEOENVIRONMENTAL IMPLICATIONS
OF THE PENNSYLVANIAN SMITHWICK FORMATION,
NORTHEN LLANO UPLIFT REGION,
TEXAS

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The Early Pennsylvanian (Bashkirian-Moscovian) Smithwick Formation of Central Texas has been previously described as a marine transgressive, fairly homogeneous and fine-grained dark shale sequence with varying local depositional lithofacies. The deposition of the Smithwick shale through the southern margin of the Fort Worth Basin (FWB) has shown large variability in thickness and deposition style. Lithological heterogeneity of the bounding units throughout the basin is inferred to be the result of a combination of depositional, tectonic and eustatic variations. Regional structural instability from Late Mississippian to Early Pennsylvanian is linked to the reactivation of the Ouachita geosyncline and thrust front, causing deformation of foreland structures, a large influx of sediment from the northern and eastern boundaries, and reported syndepositional faulting (Keller and Cebull, 1973; Trice and Grayson, 1985; Grayson *et al.*, 1990; Pollastro *et al.*, 2003).

The current interest in the evaluation and characterization of the Smithwick Formation is based on good core and well-log coverage, revealing its importance as an analogue for studying similar shale sections, and to better understand the structural and depositional constraints of the FWB, and the Pennsylvanian marginal-marine conditions.

The purpose of the present study is to acquire and analyze geochemical data from two drill-cores retrieved from Brown and McCulloch counties, in Central Texas, and to correlate these drill-cores to previously published studies and well data. The multi-proxy approach can lead us toward a better understanding of the local subsurface geology, geochemical patterns, and environmental processes that occurred during the Early Pennsylvanian in Central Texas.

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CHAPTER 1

INTRODUCTION

1.1 Project Outline

Fine-grained rocks, also referred to as "mudrocks", represent a large portion of the sedimentary record and Earth's time. Marine mudrocks tend to preserve organic matter and enrich in metals by a combination of processes that influence the organic productivity near-surface, the clastic sediment supply, and levels of oxidation that influence organic matter destruction at depth. Marine black shales (Tourtelot, 1979; Piper and Calvert, 2009) are mostly attributed to bathymetrically-deeper realms of deposition, where preservation of organic content and metal enrichment are responsible for hydrocarbon and metalliferous deposits.

The research interest in the Smithwick Formation is largely attributed to its time of deposition and the available geochemical proxies for the interpretation of marine conditions and environments (Hughes, 2011; Algeo *et al.*, 2012). These paleoenvironmental reconstructions can be used to interpret geological events at local or global scales, as well as in hydrocarbon systems. Mudrocks have proven versatile as sources, reservoirs, and seal-rocks in hydrocarbon systems, thus the benefit in their better understanding. The study of the Pennsylvanian Smithwick Formation, and the stratigraphic sequences presented in this study, correspond to Mid-Carboniferous strata deposited during a period greatly influenced by changes in global glacio-eustasy and regional tectonic activity (Brown, 1973; Kier, 1980; Boardman and Heckel, 1989; Fielding *et al.*, 2008).

The current research project will initially evaluate two well-cores from Central Texas, the Scoggins A-2-1 from McCulloch County, and the Stevens B-8-1 from Brown County.

The evaluation is intended to compare the subsurface geology on the basis of chemostratigraphic analysis and well-log correlation. The quantitative analysis for major elements is acquired *via* energy-dispersive x-ray fluorescence (ED-XRF) spectrometer. Other sets of available geochemical data (Hughes, 2011), as well as borehole logs, are incorporated into the study to provide a better understanding of the lithological and depositional differences throughout the study area.

1.1.1 Study area

The area of emphasis for the study is located in North-Central Texas, on the northern boundary of the Llano Uplift, and is comprised of the McCulloch, Brown, and San Saba counties (Figure 1.1). Local interaction of geological processes, such as folding and faulting, are documented in the area, and associated with the thickness, as well as depositional differences, in Pennsylvanian rocks (Plummer, 1947; Grayson *et al*., 1990; Erlich and Coleman, 2005).

The exposures of Paleozoic rocks in the study area along faults and the Colorado River Valley make it possible to compare and relate surface to subsurface geology. The exposures along the Colorado River Valley were the focus of the earliest studies on Carboniferous rocks in the region (e.g., Hill, 1889; Cummins, 1890; Paige, 1912; More and Plummer, 1922).

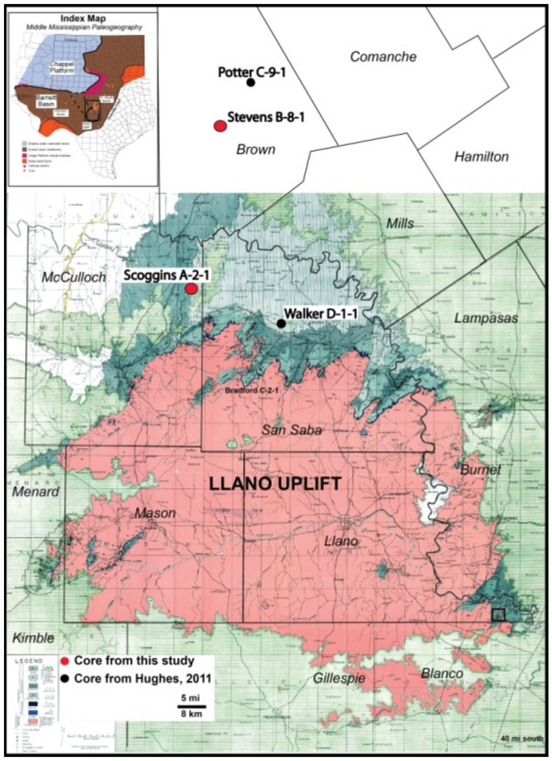


Figure 1.1 Study area and core locations.

1.2 Geological Setting

The study area is located at the intersection of different regional structural features (i.e., Llano Uplift, Bend Arch, Concho Arch). These features caused the Smithwick Formation, as well as other Carboniferous rocks, to be deposited and constrained by the regional geological structures (Figure 1.2), and influenced by eustatic as well as tectonic elements (Crosby and Mapel, 1975; Kier, 1980; Erlich and Coleman, 2005).

The most prominent of the regional structures is the Precambrian Llano Uplift (Figure 1.4). This structure has acted as a mildly positive, stable buttress for the deposition and erosion of a variety of marine environments throughout the Phanerozoic (Grayson, 1990). The cratonic stability of the region infers that changes in global eustasy and pre-existing structural bathymetry played a large role in the deposition of major marine carbonate-shale sequences.

Located northeast of the study area is the FWB (Figure 1.4), which developed as one of the Late Paleozoic foreland basins, forming in conjunction with the reactivation of the Ouachita structural belt. The dynamic conditions of the FWB during the Carboniferous were caused by the tectonic convergence of Laurussia and Gondwana, and the activation of the Ouachita thrust front in the Late-Mississippian to Early Pennsylvanian (Figure 1.2). The main structural elements that actively influenced the geology of Central Texas in the mid-Carboniferous are, from east to west: the Ouachita structural belt, the FWB, and the Concho Platform (Figure 1.4) (Adams, 1962; Grayson *et al*., 1990).

It is the geology of the Bend Arch and Concho Platform, with their local structural elements, that is thought to have affected the timing, as well as the depositional style of the Smithwick, North of the Llano Uplift (Cleaves, 1982; Erlich and Coleman, 2005). The Bend Arch consists of a complex North-plunging structural trend that spans northward from the Llano uplift (Figure 1.4). The Bend Arch acted as the outer shelf-margin that separated the Concho Platform to the West and the FWB to the East. The Bend Arch, also referred as Bend Flexure (Brown, 1973; Crosby and Mapel, 1975; Cleaves, 1982), is interpreted to be the hinge of the downwarp in the outer shelf of the Concho Platform. Interpretation of the depositional thickness of the underlying Mississippian-age Barnett Formation gives evidence of an older, oblique, northeast-trending bathymetric high located North of the Llano uplift in the southeastern half of Brown and South Comanche counties. This structural high is expressed by thinning deposition (<100 feet) of Barnett Formation toward the South. Folding of Ordovician and younger strata at the end of the Atoka (Plummer and Moore, 1921) is thought to have developed the broad north-plunging Bend Arch as a separate structure. The Concho Arch (Kier, 1980; Pollastro *et al*., 2007) describes the older, northwest-trending, positive element that is located northwest of the Llano region. North of the Concho Arch is the Concho Platform, which is identified as the stable structure present through most of the Paleozoic as the Texas Arch, until later affected by subsidence of the FWB, coupled with flexural loading (Cleaves, 1982; Walper, 1982; Erlich and Coleman, 2005).

The northward development of the Bend Arch as a long, flexural hinge occurred likely due to transpressional tectonic stresses that affected the Llano Block in early Pennsylvanian time (Walper 1982; Algeo, 1992; Erlich and Coleman, 2005). Reactivation of the Ouachita foldbelt in Mississippian times caused an initial tectonic uplift of the Llano Block (Algeo, 1992; Erlich and Coleman, 2005) on Early Paleozoic normal faults. The compressional and transtensional tectonic stresses that affected the western part of Llano block during Atokan and early Desmoinesian are thought to have caused a net uplift of <50 meters/Ma in areas of the Llano Block during the Atokan (Kluth, 1986). Uplift of the Llano Block and further uplift of the fold front in the Bend Arch is thought to have restricted most of the Atokan clastic sediment influx from the Ouachita foldbelt to the east of the Bend Arch (Crosby and Mapel, 1975). The formation of a series of N-S to NE-SW oriented horst and grabens, coupled with right-lateral strike-slip motion, influenced deposition, as well as the extensions, of north trending ridges (Caran *et al.*, 1981; Algeo, 1992). These faulted anticlinal ridges or uplifts correspond from west to east to the Cavern, San Saba, and Lampass Ridges, which extend north from the Llano uplift, into Comanche, Hamilton and Coryell Counties (Caran *et al*., 1981; Walper, 1982).

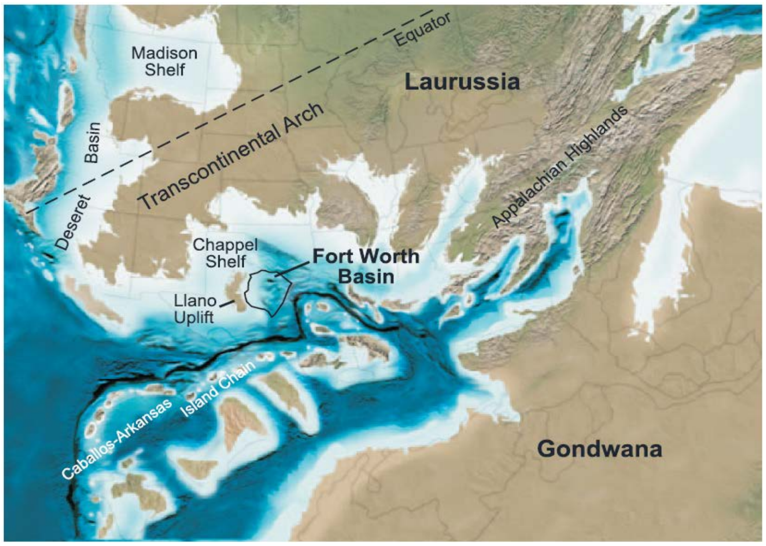


Figure 1.2 Paleogeographic reconstruction of Laurussia and Gondwana during the late Mississippian (325Ma) with approximate location of the Fort Worth Basin (Blakey 2005; Loucks and Ruppel, 2007).

1.2.1 Stratigraphy

The basal rocks of the area correspond to a suite of poly-deformed Precambrian rocks related to the Grenville-aged orogenic event, which is expressed along the southern margin of Laurentia (Roback *et al*., 1999; Mosher, 2008). This group of poly-deformed gneiss, schists, and granites (ca. 1326-1120 Ma) represents a continent-arc-continent convergence, being different in placement, age, and composition to the Granite-Rhyolite Province of the mid-continent (Mosher, 1998; Bartholomew and Hatcher, 2010). Non-comformable deposition of overlying Cambrian and Ordovician strata is variable, representing a long span of erosion and nondeposition on a stable cratonic shelf. Widespread deposition of the epeiric shelf carbonates of the Ordovician Ellenburger Group is common around the Llano region and FWB (Kier, 1980; Pollastro *et al.*, 2003; Erlich and Coleman, 2005). The unconformable contact between Ellenburger carbonates and overlying Carboniferous strata is thought to have been caused by eustatic, as well as topographic changes. A major sea-level drop at the end of the Ordovician brought parts of the Ellenburger carbonate platform to subaereal exposure, developing karst features. Later erosion of any overlying Silurian and Devonian strata is associated with different erosional events. Some of these erosional unconformities have a possible association to periodic upwarping of the Bend flexure or Concho Arch (Herkomer and Denke, 1982; Pollastro *et al.*, 2007). The Mississippian Barnett Formation is deposited over the Ordovician-Mississippian unconformity, representing a major marine transgression around the FWB and Llano region (Figure 1.4). The Barnett Formation consists mostly of organic-rich, black shales with thin shell layers and thin muddy limestone beds at the top of the formation. The deposition of Barnett Shale north of the Llano uplift is thought to have occurred under changing marine conditions, from anoxic/euxinic restricted to open marine (Loucks and Ruppel, 2007; Rowe *et al*., 2008). The end of the Mississippian is usually defined at the top of the Barnett Formation, or if present, the Comyn Formation, which consists of an upper limestone with underlying interbedded dark limestones and gray-black shales, included with the earliest Pennsylvanian Marble Falls (Pollastro *et al.*, 2007).

The basal Pennsylvanian (Morrowan) Marble Falls Formation is widely deposited as a stable open-shelf limestone environment over the Llano Uplift. The Marble Falls Group is generally subdivided into the Upper and Lower Marble Falls, which are usually separated by a middle shale section of variable thickness (Namy, 1982). The Upper Marble Falls becomes progressively younger toward the West, causing the earliest Pennsylvanian limestone in McCulloch County to be mostly or wholly Atoka in age (Crosby and Mapel, 1975; Kier, 1980). The decrease in age of the strata toward the West is inferred to be caused by the time-transgressive deposition of Atokan facies toward the West (Figure 1.3), from their source at the Ouachita structural belt to the East, and the uplifted Muenster arch to the North (Flippin, 1982). The westward shift of depositional environments is influenced by the large sediment influx, a northwestern shift of the basin axis, and reduced subsidence of the FWB. The contact between the underlying Marble Falls and the Smithwick is mostly conformable in the region (Kier, 1980). The progressive westward shift of the lower Pennsylvanian carbonates caused the Upper Marble Falls hinge-line to give way to the Big Saline hinge line further west during Atokan time. This subsequently led to the progradation of the Smithwick and Strawn facies over the Upper Marble Falls (Namy, 1982; Grayson *et al.*, 1990).

The Smithwick Formation around the Llano area consists of a black to gray, slightly calcareous, brittle, fissile clay-shale with subordinate amounts of limestone, sandstone, and siltstone (Plummer and Moore, 1921; Plummer, 1950; McBride and Kimberly, 1963; Kier, 1980). In addition, previous workers (Plummer and Moore, 1922; Cheney 1940; Plummer, 1950) have used the Smithwick nomenclature to include the black shales located above the Marble Falls, and below the sandstones and sandy shales of the Strawn Group. Some of the exposures of Smithwick Formation on the North and northwest sides of the Llano Uplift consist of a lower black shale unit with interbedded thin layers of spiculitic limestone, a middle black shale, as well as an upper silty shale interbedded with thin siltstone and sandstone layers (Turner, 1970; Kier, 1972). Some of the distinguishing features of the Smithwick Formation are: 1) the absence of hard limestone beds, but may contain limestone lentils and siltstones, 2) it may contain rather large, brick-red ferruginous concretions, and it is 3) generally blacker with more organic matter and silica, and less calcite than Upper Atokan and Strawn mudstones (Plummer, 1950).

In the present study, further geochemical characterization of Smithwick Formation defines it as the dark shale section below the detrital brown shale (brown layer) and the lithologically similar Atokan clastics. The time-transgressive deposition of the Atoka/Strawn groups and their relationship to the Smithwick basinal facies is observed across the FWB (Figure 1.3). Westward prograding deltas, as well as the prodelta facies from sediment sources to the North and East (Figure 1.4), were deposited across the slowly subsiding FWB. The delta and prodelta facies then became intertongued with shelf-edge carbonates at the Bend Arch shelf-margin (Brown, 1973; Walper, 1982; Grayson *et al.*, 1990).

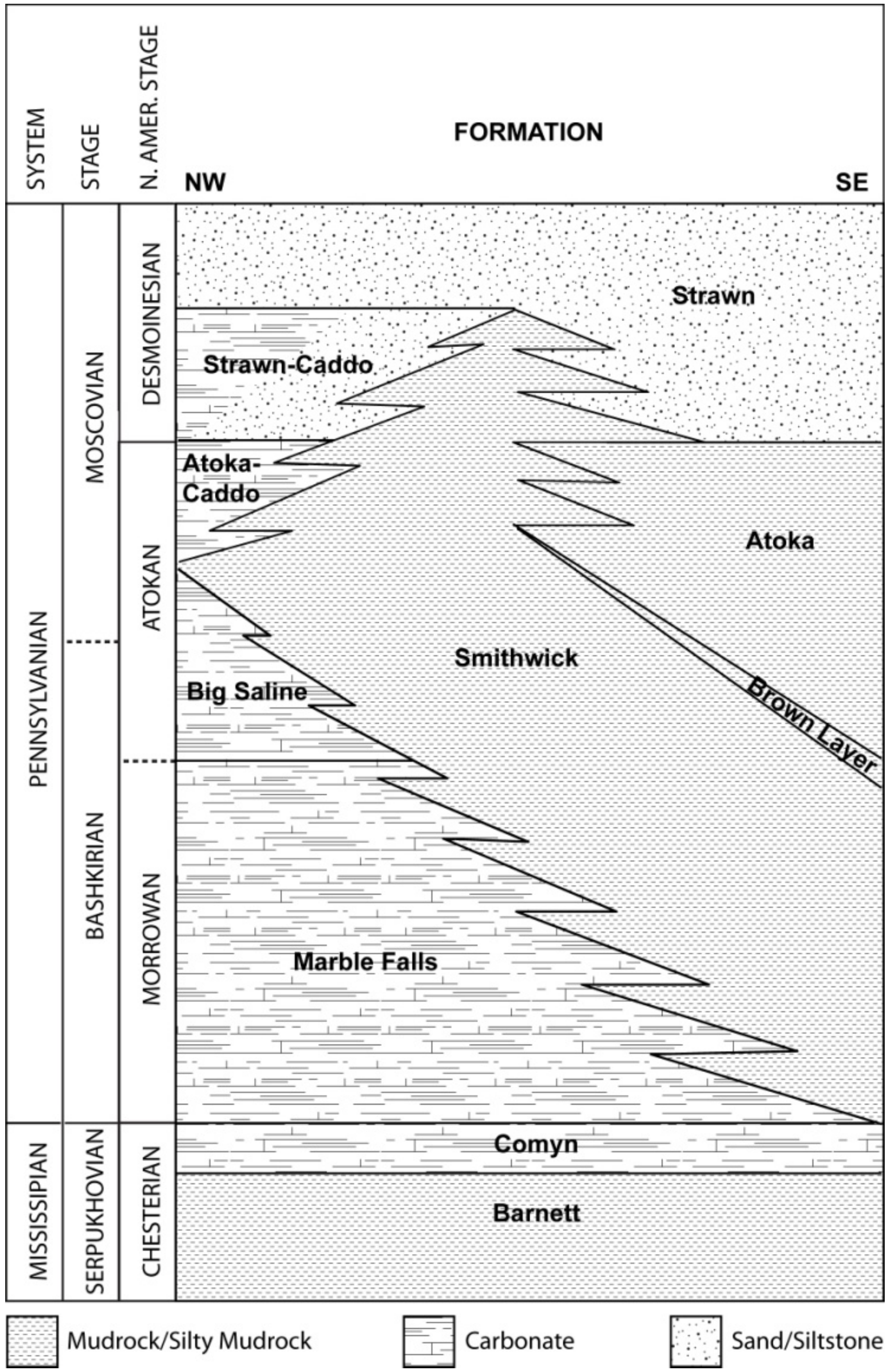


Figure 1.3. Generalized stratigraphy of the Fort Worth Basin along the NW-SE in the western margin of the basin, North of the Llano Uplift (Hughes, 2011; based on descriptions and illustrations from Kier *et al*, 1979; Lovick *et al*, 1982; Walper, 1982; Pollastro *et al*, 2003; Erlich and Coleman, 2005; Jarvie *et al*, 2007).

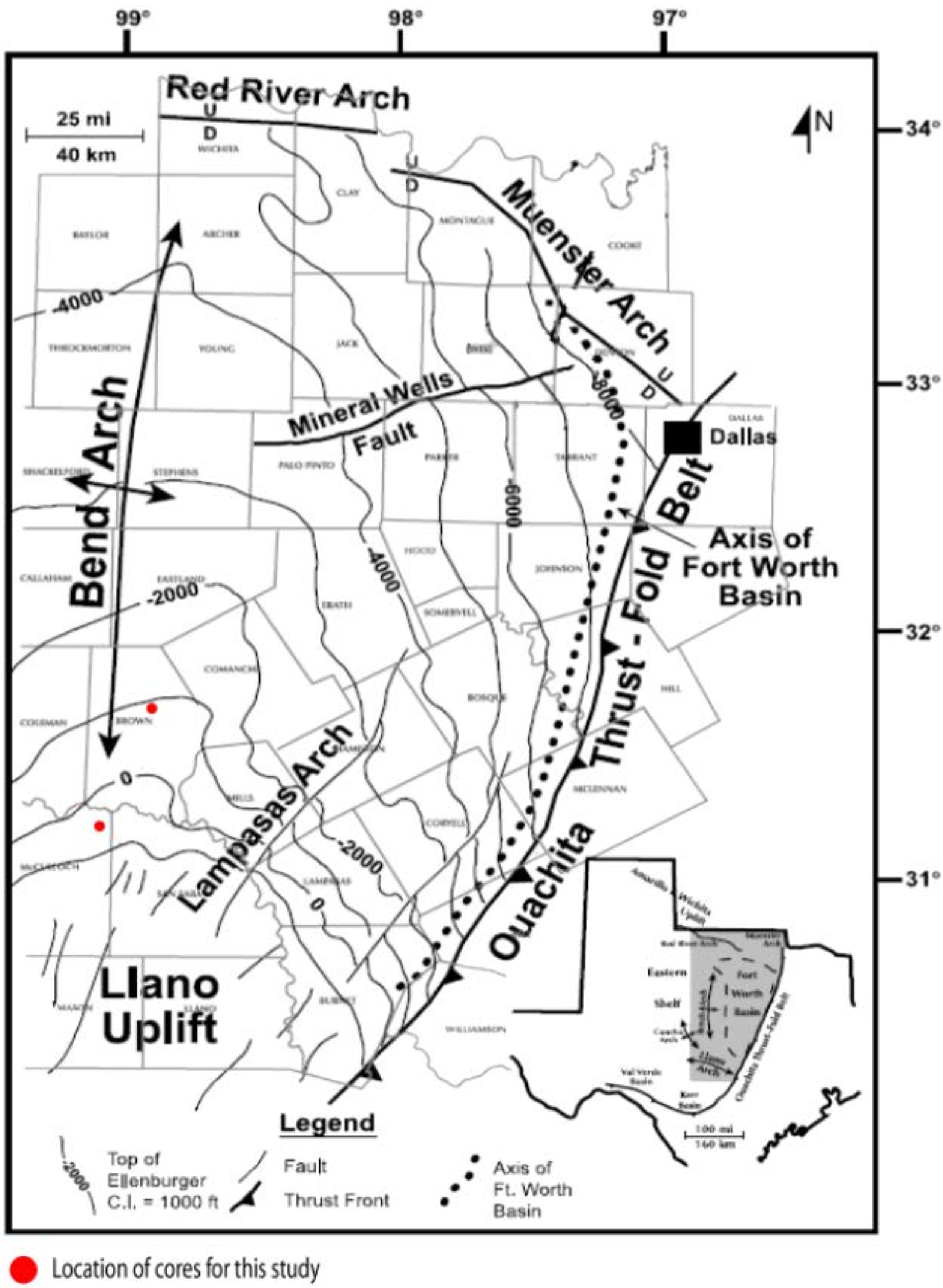


Figure 1.4. Structural features and boundaries of the Fort Worth Basin, Texas (Modified from Montgomery *et al*., 2005; Pollastro *et al.*, 2007).

1.2.2 Glacio-eustasy

Recent work on the Late Paleozoic Ice Age (LPIA), constrained between Visean (Middle Mississippian) and Capitanian/earliest Wuchiapingian ages (Middle-earliest Late Permian), has identified several glacial intervals related to diachronous waxing and waning of ice centers across Gondwana (Bishop 2009; Isbell *et al*., 2012). These glacial-interglacial intervals spanning 1-8 million years (Fielding *et al.*, 2008) represent an alternate view of a single, long-lasting ice sheet with minor changes in ice masses (Cromwell, 1999). The Mississippian-Pennsylvanian boundary is correlated with the beginning of a widespread Gondwanan glaciation period, when glaciers expanded in southern and western South America, and first appeared in eastern Australia (Fielding, 2008; Isbell *et al., 2012)*. Theoretically, some of the glaciation pulses during the Pennsylvanian (Figure 1.4) (Veevers and Powell 1987; Cromwell, 1999; Bishop *et al.*, 2009) could be identified in the sequence stratigraphy of the study area. The Late-Mississippian glacial pulse (ending Earliest Pennsylvanian) is expressed as the Mississippian-Pennsylvanian contact by a marine regression from the Barnett to the Marble Falls facies, identified in European and North American marine records (Davydov *et al.*, 2012; Martin *et al.*, 2012).

The lowest stage of the Pennsylvanian System, Morrowan North American Stage, is linked to a marine low-stand and gradual increase in sea level. This increase in sea level is due to a non-glacial period identified in South America and eastern Australia (Isbell *et al.*, 2012). This diachronous period of marine transgression, occurring during mid-Morrowan time continued well into the mid-Atoka North American Stage, and its observed in the stratigraphic record across North America in the Desert Basin, Nevada (Martin *et al.*, 2012), Permian Basin, and in the Llano area with the deposition of the Smithwick Formation (Figure 1.3). An overall rising sea level, increased tectonic activity and transitional climate are characteristic of the Atoka deposition around the Ouachita structural belt (Coleman Jr., 2000).

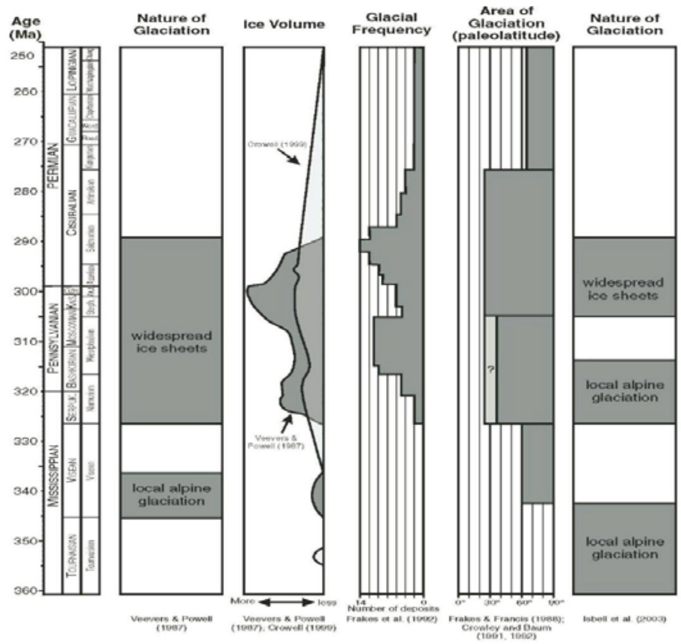


Figure 1.5. Stratigraphic column depicting Late Paleozoic Ice Age (LPIA) glaciations throughout the Carboniferous and Permian system. (Fielding *et al*., 2008)

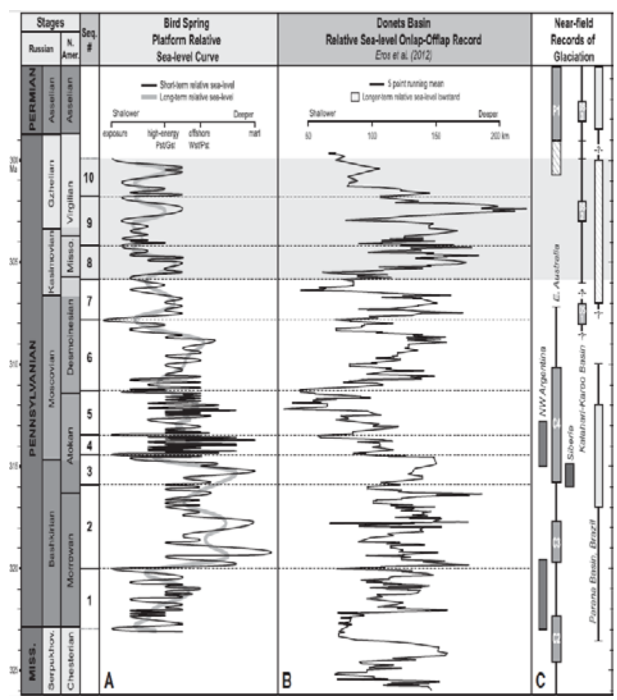


Figure 1.6. Relative Sea-level changes for Pennsylvanian times in (A)Nevada (B)Ukraine, and from (C) records of glaciations in Godwanan basins (from Martin *et al*., 2012)

1.3 Study Objectives

The objective of the present study was to better understand the depositional environments of the Smithwick Formation and its bounding units on the northern margin of the Llano Uplift in Central Texas. The study infers that the lateral variability in the deposition of the Smithwick Formation is based on structural features, which can be characterized by geochemical signatures and depositional patterns. The research project was accomplished by acquiring and examining geochemical data, lithological observations, and linking them to borehole data as well as published studies. The data were subsequently interpreted with an emphasis on marine-depositional processes, sediment influx, as well as temporal and spatial changes in basin evolution, and global glacio-eustasy. Analyses of the rapid changes and trends in rock geochemistry can provide insight on lithological changes and stratigraphic boundaries, whereas trends can constrain depositional patterns.

CHAPTER 2

METHODS

2.1 Well and Core information

Core analysis and borehole logging were used to correlate across the study area. Two well cores, housed in the core repository of the Bureau of Economic Geology (BEG), in Austin, Texas, were prepared for the acquisition of chemical ED-XRF data.

Table 2.1 Detail of cores analyzed (a) in this study, and (b) XRF cores from Hughes (2011).

a)

Core Name	**Scoggins A-2-1**	**Stevens B-8-1**
API	42-307-30447	42-049-31646
Location	McCulloch County, Texas	Brown County, Texas
Depth Interval for XRF	188 meters (30-218 m) 615 feet (100-715 ft)	231 meters (412-643 m) 759 feet (1351-2110 ft)
Smithwick Interval	60 m (198 ft)	65 m (213 ft)
Box Numbers	7-70	29-105
Number of Samples	451	759
Core Conditions	Primarily uncut	Mostly slabbed, also uncut

b)

Core Name	**Walker D-1-1**	**Potter C-9-1**
API	42-411-30100	42-049-31769
Location	San Saba County, Texas	Brown County, Texas
Depth Interval for XRF	271 meters (59-330 m) 888 feet (195-1083 ft)	185 meters (456-641 m) 607 feet (1497-2104 ft)
Smithwick Interval	146 m (481 ft)	41 m (136 ft)
Box Numbers	16-106	15-76
Number of Samples	921	620
Core Conditions	Uncut	Primarily uncut, also slabbed

ED-XRF sampling requires a smooth and clean surface of the rock in order to avoid the puncture of the film that covers the beam area (Figure 2.1D), and minimize the loss of instrument sensitivity. The use of a sample platform on the nose of the instrument (Figure 2.1A) offers stability and a flat surface for timed sampling. Quality-control sampling of a mudrock pellet is performed every 6 hours of sampling, and timed to 180 seconds; whereas regular sampling is done at 60 seconds.

The Scoggins A-2-1 (Scoggins) core from McCulloch County (Table 2.1) was scanned at 1-foot (~0.3m) intervals from the bottom of the core to the top of the Smithwick Fm. A 2-foot (~0.6 meter) sampling interval was used in the clastic strata overlying the Smithwick Fm. The Stevens B-8-1 (Stevens) core from Brown County was scanned at a 2-foot (~0.6m) interval in the lowest 80 feet of the core (~24.5m), into the lower Marble Falls, and at 1-foot (~0.3m) interval to the top of the sampling interval.

Major-element geochemical datasets from two previously studied cores (Hughes, 2011), the Walker D-1-1 (Walker) core from San Saba County and the Potter C-9-1 (Potter) core from Brown County (Figure 1.1), were provided for the present study by Dr. Scott Hamlin of the Bureau of Economic Geology. Correlations between the Walker and Scoggins cores are shown due to their proximity to the Llano Uplift, whereas correlations between the Potter and Stevens cores in Brown County are applied due to their proximity to each other.

2.1.1. Wellbore Logs

Another method to compare our geochemical data is the acquisition of borehole logs of oil-and-gas wells in the vicinity of the examined drill-cores. The correlation of chemical signatures, sedimentary units, and certain log responses are used in the study to identify depositional patterns. The use of gamma-ray (GR) well-logs for subsurface correlation is widely applied in the industry due to the radioactive nature of mudrocks. The lower electrical resistivity (RES) in shales is due to clay-bounded water performing surface conduction (Asquith and Krygowski, 2004). Well-correlation evaluates the log responses and elemental geochemistry as a method of paired subsurface analysis for the identification and differentiation of the Smithwick Formation and other mudrocks present in the area.

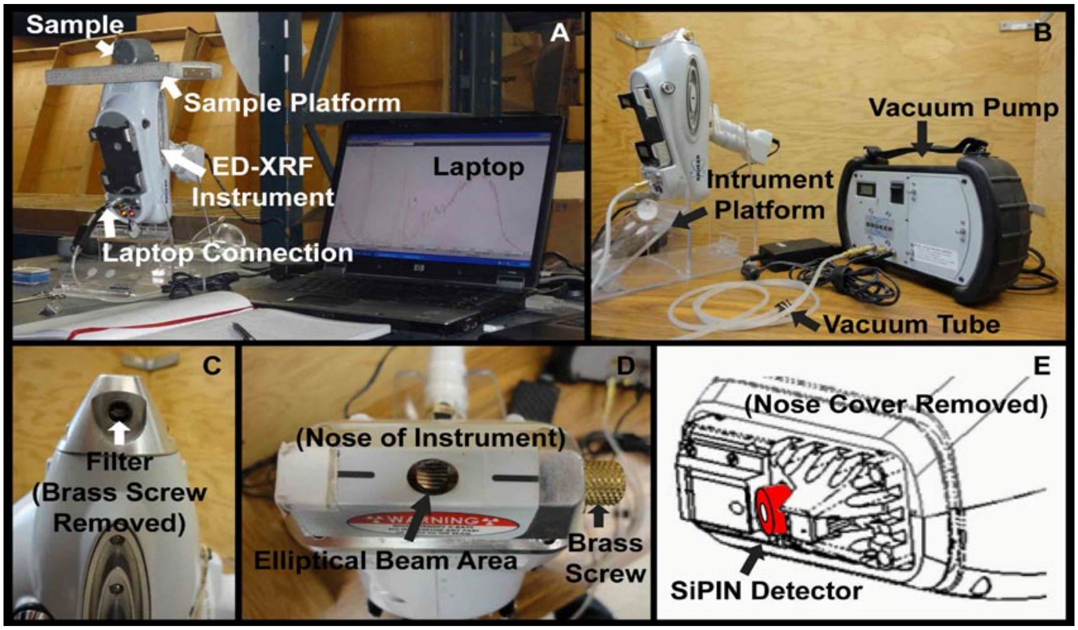


Figure 2.1 Overview of ED-XRF instrumentation and sampling. Illustrating (a) core samples laid directly on nose of instrument with aid of a platform while data are recorded on a laptop, (b) the instrument platform used in (a) to keep the instrument immobile and upright alongside the vacuum pump used in low-energy acquisitions, (c) the filter used in high-energy acquisitions, (d) the nose of the instrument where the beam is emitted, and (e) the SiPIN detector below the beam area (drawn from Brüker manual, Kaiser, 2008)(from Hughes, 2011).

2.2 Energy Dispersive X-Ray Fluorescence (ED-XRF)

There is a variety of analytical techniques used to quantify the chemical composition of rock samples, where hand-held energy dispersive fluorescence (ED-XRF) presents some advantages. Additional benefits are the relatively rapid time of sampling (60-180 seconds), the portability of hand-held ED-XRF, and the non-destructive nature of the sampling. Furthermore, advances in equipment technology, and better calibration standards permit us to quantify chemical concentrations of rock samples through emitted-fluorescence energy, and wavelength spectra (Jan Weltje and Tjallingii, 2008; Rowe *et al*., 2012). The quantifiable analyses of major chemical elements were performed using a Bruker Tracer III-V handheld ED-XRF spectrometer and expressed in weight percentage (wt%) for elements such as magnesium (Mg), aluminum (Al), silicon (Si), phosphorus (P), potassium (K), calcium (Ca), titanium (Ti), manganese (Mn), and iron (Fe); and, where applicable, parts-per-million (ppm) of Vanadium (V), and Chromium

(Cr). The detailed composition of these samples can provide a multi-proxy tool to identify, classify, or characterize lithological units and their origins by chemical composition.

2.2.1 Calibration of ED-XRF

The fairly homogeneous and fine-grained nature of mudrocks presents a high variability in their composition. This variability requires a calibration reference suite that provides an ample range of different chemical compositions (Rowe *et al.*, 2012). The composition of the standard mudrock suite (Table 2.2) used for the calibration of the ED-XRF instrument contains 90 reference samples, including both Barnett and Smithwick shales, which should increase the accuracy of the sampling.

Table 2.2 Tally of minimum and maximum elemental concentrations for the suite of calibration standards and in-house reference materials from Rowe *et al*. (2012).

Standards and reference materials												
	Standards[a]		Woodford Fm.[b]		Ohio Shale[c]		Barnett Fm.[d]		Smithwick Fm.[e]		Eagle Ford Fm.[f]	
n[g]	5		27		7		16		20		15	
Element	Range of values for each formation											
	Min[h]	Max[h]	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Mg (%)	0.93	4.89	0.27	**10.25**	0.66	1.08	0.52	2.64	0.63	1.88	**0.24**	0.66
Al (%)	3.45	9.96	**0.64**	7.62	6.87	10.77	1.20	8.47	1.00	**13.07**	1.07	5.98
Si (%)	13.2	29.3	5.89	**38.2**	26.8	28.8	6.22	32.7	8.79	34.8	**3.75**	22.6
P (%)	0.02	0.14	**0.01**	0.48	0.02	0.17	0.07	**0.98**	0.03	0.12	0.02	0.15
S (%)	0.01	5.35	0.46	5.32	0.72	2.25	0.25	2.24	0.02	2.00	0.33	3.81
K (%)	1.15	3.45	0.17	3.51	2.92	**4.32**	0.27	1.83	0.22	3.12	**0.14**	1.61
Ca (%)	0.43	5.99	**0.07**	18.1	0.19	0.71	2.77	31.2	0.32	27.7	9.36	**34.7**
Ti (%)	0.16	0.43	**0.04**	0.33	0.40	0.53	0.07	0.46	0.05	**0.53**	0.04	0.39
Mn (%)	0.015	0.046	**0.008**	**0.325**	0.008	0.031	0.008	0.031	0.008	0.147	0.008	0.023
Fe (%)	2.12	**6.53**	0.61	4.92	3.09	4.60	0.64	3.54	1.66	6.38	**0.43**	3.57
Ba (ppm)	290	820	842	5750	434.3	562	63.5	625	357	**9050**	**30.3**	295
V (ppm)	87	160	51	**1720**	141	385.5	**22**	165	24	196	41	899
Cr (ppm)	30	123	20	260	62	96	40	**295**	40	120	**10**	100
Ni (ppm)	27	122	17	**302**	33.5	136.8	26	168	22	144	**11**	155
Cu (ppm)	28.7	66	8	**485**	22.3	60.5	12	83.5	8	54	**5**	66
Zn (ppm)	55	103	24	**1220**	77.1	505.3	57	387	45	301	**20**	503
Th (ppm)	4.8	12.8	**1.3**	10.7	9.1	14	2	12.9	2.1	**14.6**	1.6	9.9
Rb (ppm)	59	205	13.9	200	140.8	**224.1**	16.5	121	15.3	167	**6.4**	91.7
U (ppm)	1.5	48.8	3.36	**66**	7.2	37.3	**1.22**	11.4	1.81	6.62	1.67	14
Sr (ppm)	54	420	**36.4**	483	105.3	145	248	**869**	107	518	329	791
Y (ppm)	13	40.6	**5.8**	52.7	26.2	37.2	10.9	**62**	20	35.3	7.6	22.3
Zr (ppm)	53	165	**15.5**	122	133.9	217.7	25	146	17.2	**338**	32.6	215
Nb (ppm)	5.2	14.3	**2**	13	14	16	2	15	2	15	3	**22**
Mo (ppm)	1.4	134	9	**166**	**1.3**	153.7	2	13	2	3	3	95
Total min/max[i]	0	1	10	9	1	2	2	4	0	5	10	2

[a] International standards are SARM-41, SDO-1, Sco-1, SGR-1, and GBW-07107.
[b] Woodford Formation reference materials obtained from Reliance Triple Crown #1 core, Pecos County, TX.
[c] Ohio Shale reference materials obtained from core D4, Powell County, KY.
[d] Barnett Formation reference materials obtained from 1-Blakely core, Wise County, Texas.
[e] Smithwick Formation references obtained from Walker D-1-1 core, San Saba County, Texas.
[f] Eagle Ford Formation reference materials obtained from Leppard core, Bee County, Texas.
[g] "n" is the number of references from each unit.
[h] Minimum and maximum elemental concentrations for the entire suite are designated by bolded and underlined bolded, respectively.
[i] The total number of minimum and maximum elemental concentrations for each group of references is tallied at the bottom of the table.

CHAPTER 3

RESULTS

Geochemical data from the ED-XRF sampling is analyzed to acquire direct and proxy information regarding the lithological as well as depositional variations. Direct lithological observations are associated with the geochemical analysis to better characterize and understand changes. Major element concentrations are quantified in the study by weight percentage (%wt) for Mg, Al, Si, K, Ca, Ti, Mn, and Fe; and where applicable, parts-per-million (ppm) of V and Cr. Subsurface correlations of the cores are presented with nearby wellbore data, and with interpretations of the log responses.

The interpretation of the major lithogenic elements (Al-Si-Ca) is applied to determine basic lithological composition. The limited dissolution of Fe in seawater and its relationship to certain carbonate facies (Ca, Mg, Mn) can represent changes in paleoenvironment or water conditions. Furthermore, detrital influx is evaluated by the main elements of important terrigenous minerals such as quartz (Si), feldspar (K), plagioclase and clay (Al). Geochemical proxies such as Ti/Al, K/Al, Mg/Al, and Si/Al are then used to determine characteristics of the detrital influx and provenance.

3.1 Core Chemostratigraphy

The correlation of geochemical trends and lithological changes is applied to identify and describe some of the differences between the stratigraphic units in both cores of this study. Cores are individually covered and explained to contrast and identify similarities between them.

a) Scoggins core

The Scoggins A-2-1 (Scoggins) core contains a Smithwick Formation section of 60 m (~198 ft) in the depth interval ranging from 132 to 192m (435 to 632 ft). This section of Smithwick is underlain by limestone beds of varying thickness, assigned to the Marble Falls Group. The lower contact of the Smithwick interval with the underlying Marble Falls is interpreted to be gradational. The gradational contact is interpreted due to the progressive upward decrease in %Ca and thickness of limestone beds in the Marble Falls.

The Smithwick Shale preserved in the Scoggins core contains several layers of increased %Ca (5-15%), which are deposited as irregular, thin laminations caused by fracture porosity or associated to ferromanganoan carbonates. The upper contact of the Smithwick Formation in the Scoggins core is marked by the deposition of 2m (~ 6 ft) of a brown silty layer.

The "brown layer" is characterized by an abrupt increase in %Al and %Ti, with a noticeable decrease of %Si (Figure 3.1). The deposition of the clay-rich "brown layer" establishes the boundary between the overlying laminated sandstones with mudstones and the Smithwick dark shale. This "brown layer" is present in all the cores of the study, at different depths and presenting varying thickness as well as composition. The first distinctive unit above the "brown layer" on the Scoggins core corresponds to an interval of thinly bedded mudstones bounded by sandstone beds. This "Unit A" is found at the core depth interval between 120 to 130m (396 to 427ft).The geochemical characteristics of "Unit A" are marked by lower concentrations of %Al, %Fe, %K, and %Ti than its bounding units (Figure 3.1). Above "Unit A", cyclical, light-tan and reddish mudstone laminations are assigned to the Strawn Group of submarine fans and turbidites. The lower section of the Strawn Unit contains highly-oscillating interbedding of thin Si-rich silts and of mudstones containing increased %Al, %K, %Ti, and % Fe concentrations. The upper section of the Strawn Unit contain thicker units (~10ft) of uniform geochemical composition consisting of mudstones with increased %Al, %Ti, %K, and thin sandstones. The presence of a dolomitic (Mg-rich) limestone bed separates the Strawn Unit with overlying Upper Strawn section.

b) Stevens core

In the Stevens core, the Smithwick Formation section measures ~47 m (155 ft), in the depth interval between 500 to 547m (1643-1798 ft). The Smithwick is deposited sharply over thick (~20ft) limestone beds of the Big Saline Formation. The Big Saline is interpreted to be part of the Upper Marble Falls Group (Lovick *et al.*, 1982), and deposited in the northeast-southwest trend of the Bend Arch (Namy, 1982). The upper contact of the Smithwick Shale is acknowledged by the presence of ~9 meters (~29ft) of “brown layer” mudrock at a subsurface depth between 491 and 500m (1613-1642ft). The “brown layer” is expressed in this core as brown shale, differing from the clay layer on the Scoggins. Above the “brown layer”, a section spanning ~8m (25ft) of mudstones lithologically similar to the Smithwick represents the Atokan clastics. The boundary between the Atokan clastic section and overlying fossiliferous Ca-rich mudstones and muddy limestones is defined at the first competent limestone bed at a depth of ~ 485 m (1590 ft). This section of interbedded limestones and mudstones is representative of the Caddo Lime which grades upward into the Si-rich Strawn facies. The Atoka-Caddo facies contain higher Ca and lower Al concentrations than the overlying Strawn-Caddo.

The chemostratigraphic representation of major mineral-forming elements (Si-Ca-Al) for Scoggins and Steven cores are shown in Figure 3.1 and Figure 3.2. Chemostratigraphic interpretation of formations for the Potter (Figure 3.3) and Walker (Figure 3.4) cores as described by Hughes (2011) are also displayed. The Marble Falls-Smithwick contact present in all the cores is expressed by a progressive decrease in %Ca, and steady increase of %Al and %Fe upwards on the Marble Falls Group (Figure 3.1 and Figure 3.3). The Scoggins core presents a markedly reduced thickness of the “brown layer” (~6 feet), and lack of overlying Atokan clastics. The presence of “Unit A” in the Scoggins core is identified as sandstones with interbedded mudstones overlying the “brown layer”, presenting markedly lower %Fe, %K and

%Ti (Figure 3.7). These lower concentrations of %Fe, %K and %Ti above the “brown layer” are also expressed in the Stevens and Potter cores. The Potter core contains an equivalent and similar stratigraphic section to the one present on the Stevens core. The Walker core contains the thickest Smithwick section (~500ft) of all the cores. The Walker core also contains a significant section of Atokan clastics, which is compositionally similar to the Smithwick Fm. but possessing higher %Si.

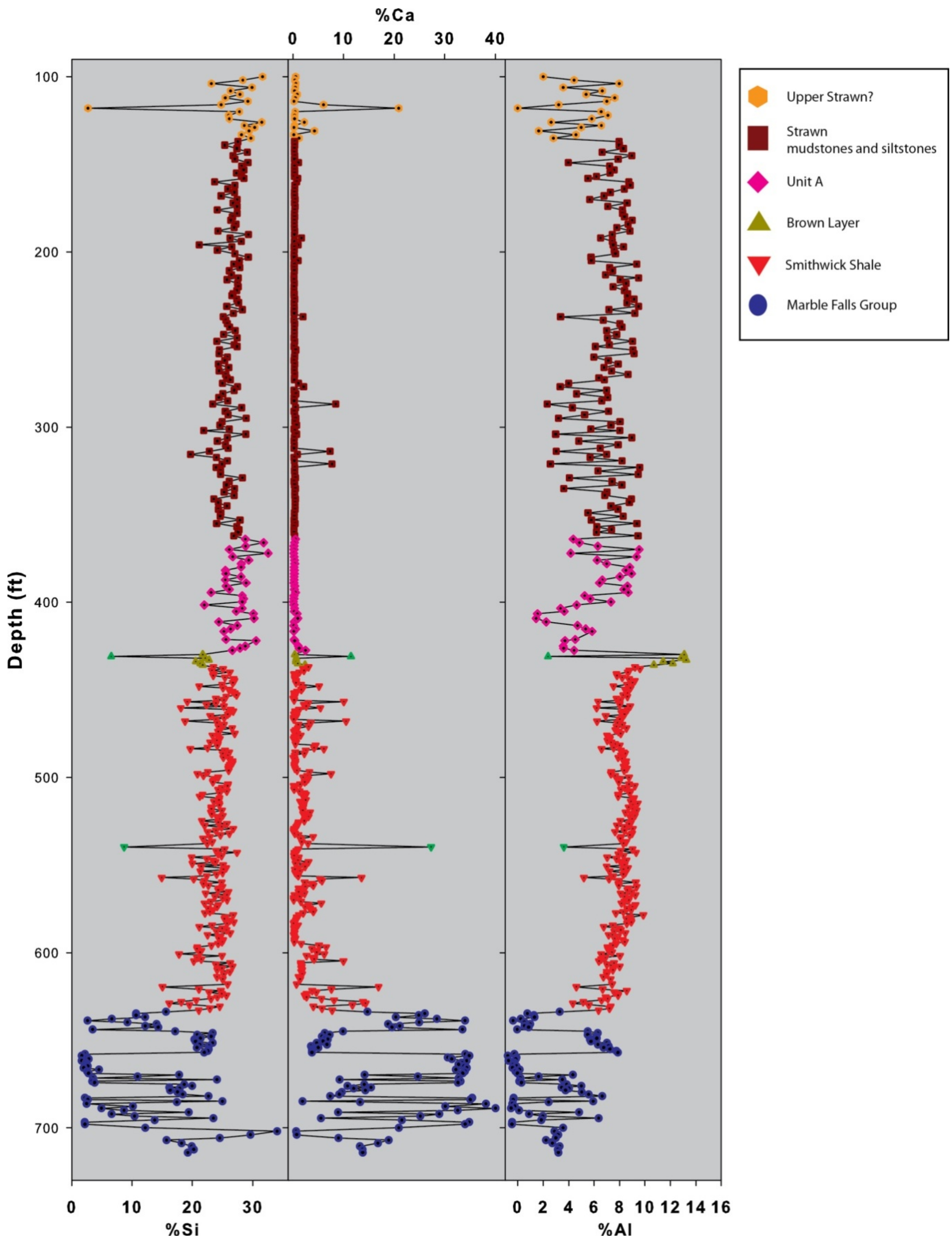


Figure 3.1 Major element (Si, Ca, Al) chemostratigraphic interpretation for the Scoggins core.

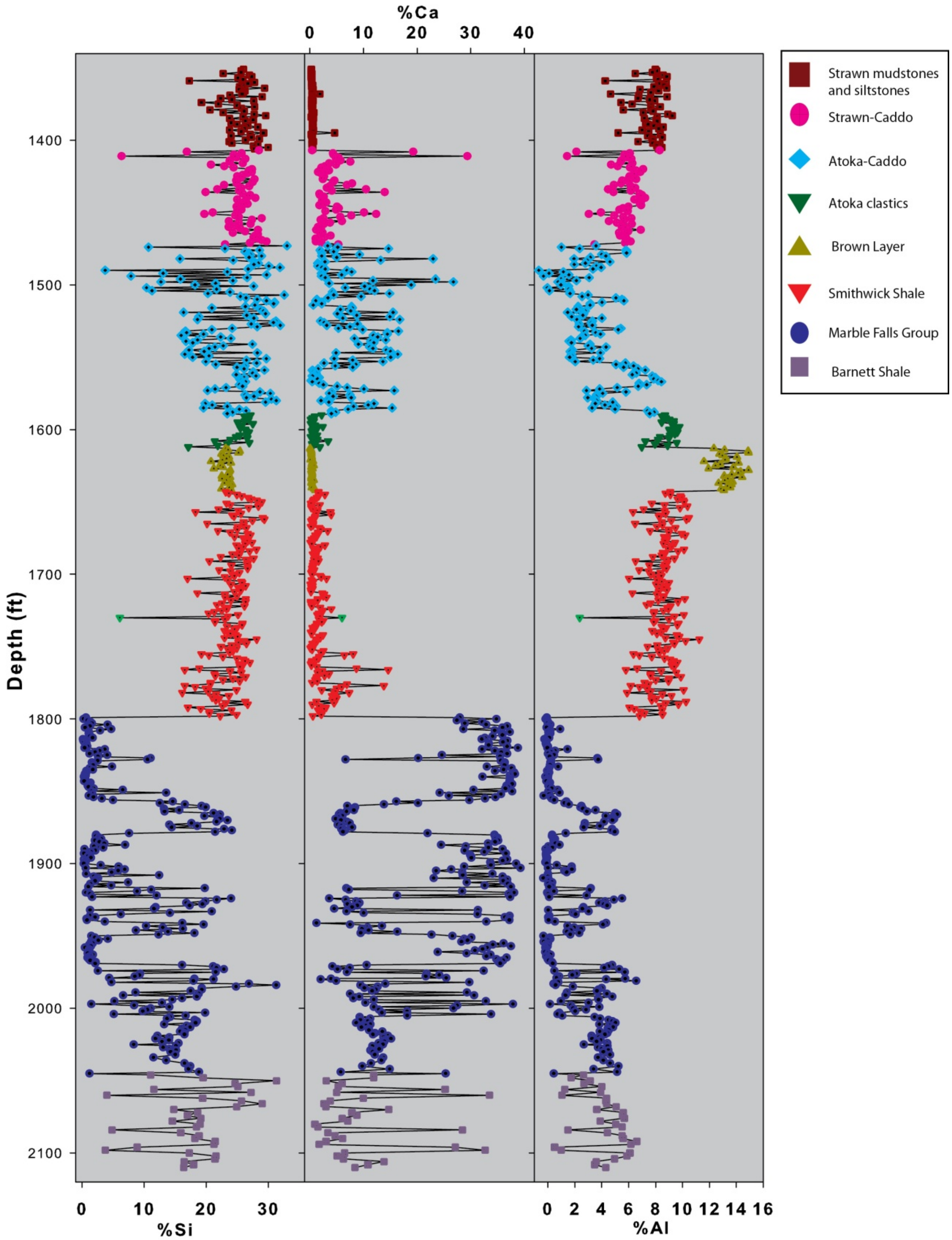


Figure 3.2 Major element (Si, Ca, Al) chemostratigraphic interpretation for the Stevens core.

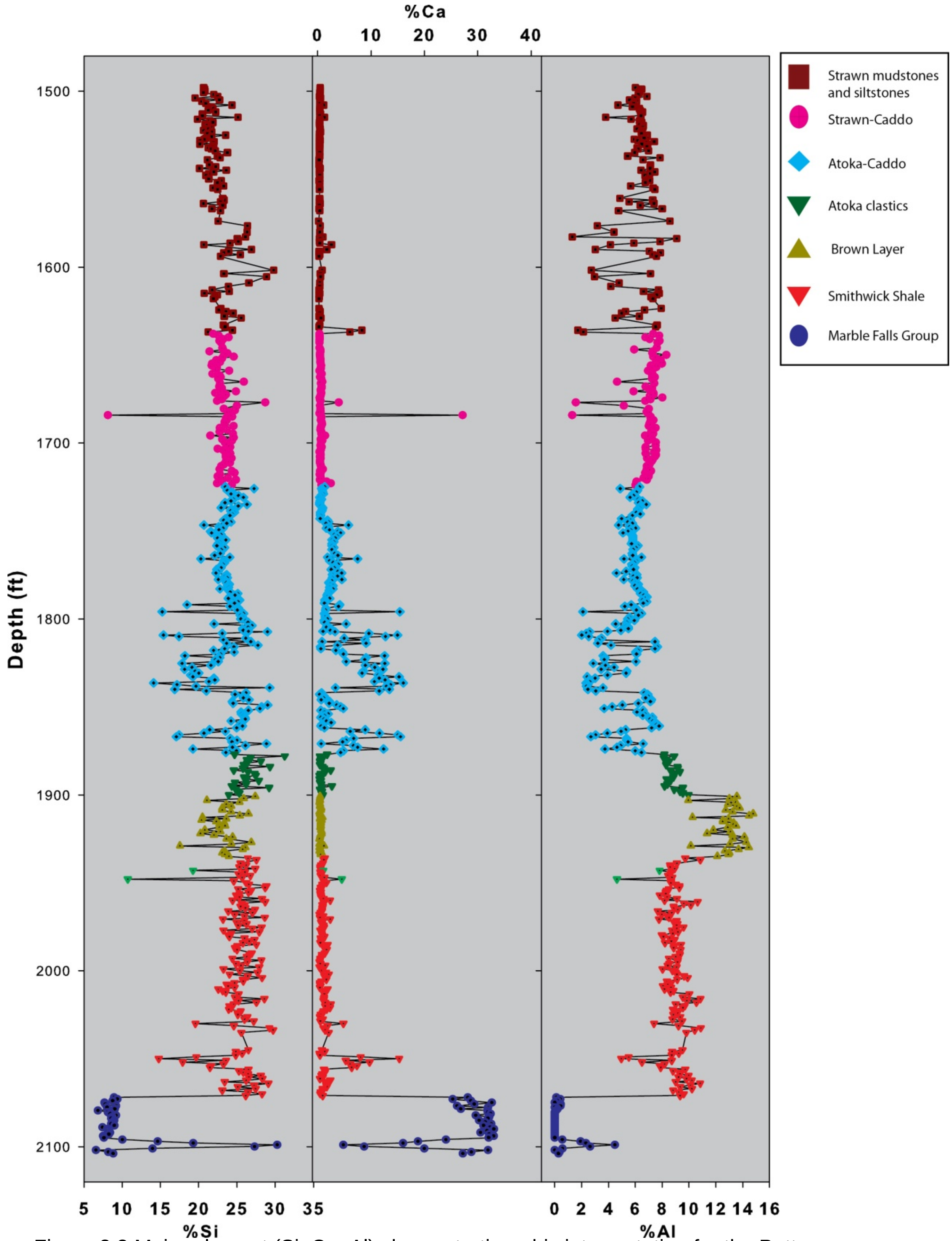


Figure 3.3 Major element (Si, Ca, Al) chemostratigraphic interpretation for the Potter core.

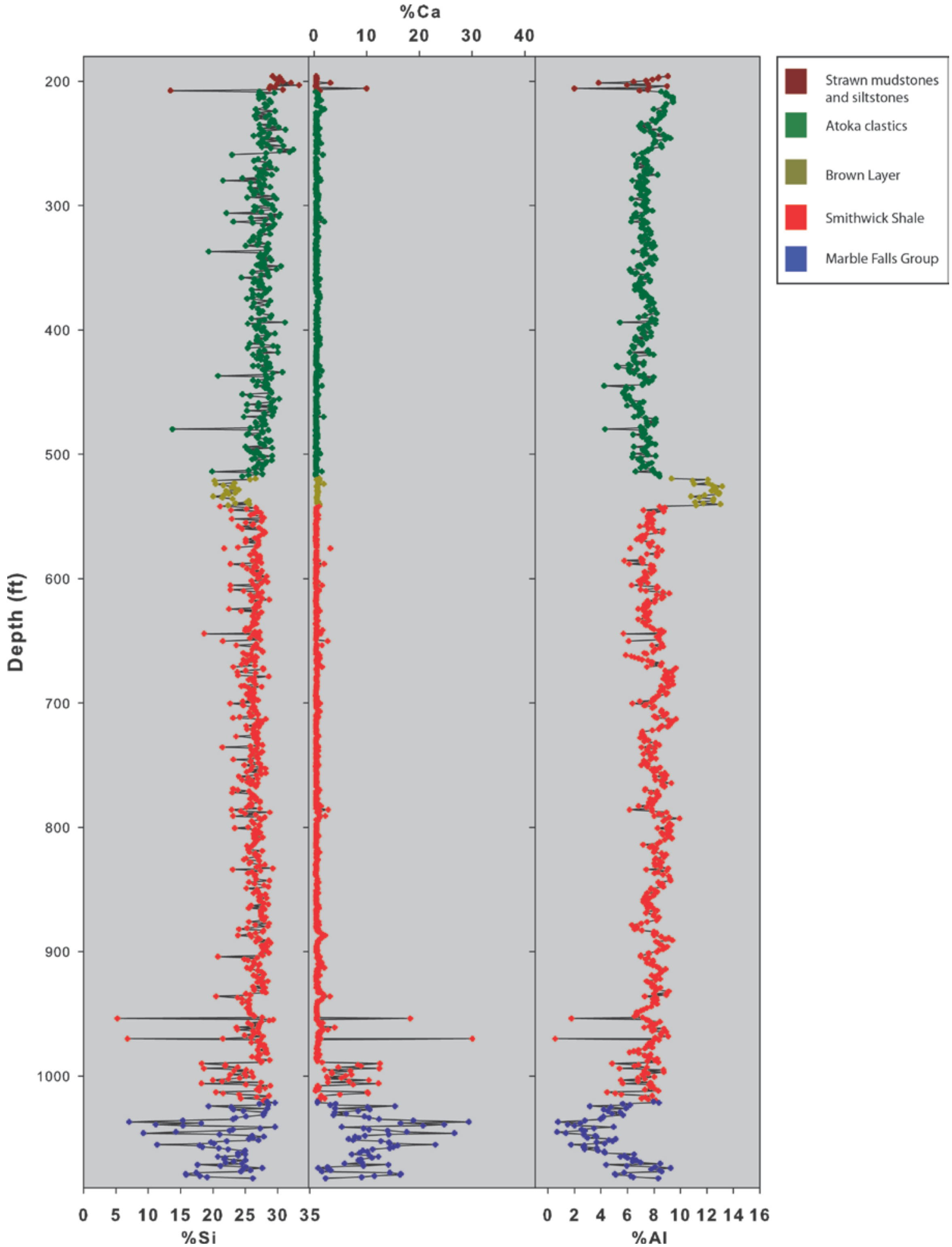


Figure 3.4 Major element (Si, Ca, Al) chemostratigraphic interpretation for the Walker core.

3.1.1 Geochemical Characterization

Chemical element concentrations from the stratigraphic units of interest can be characterized by arithmetic methods. The arithmetic representations of wt% for the Smithwick Fm. and "brown layer" unit from the cores are shown in Table 3.1. These representations are primarily for reference, having into consideration the varying thickness of the units sampling is uniformly performed at one sample (n) per foot.

Table 3.1 XRF-Generated concentrations (%) for major elements (Al, Si, Ca, Mg, Mn, Fe, Ti and K). Siderite-rich samples were separated and not included in formation calculations. Highest concentration values per row in bold.

	Formation	**Smithwick**	**Smithwick**		**Brown Layer**	**Brown Layer**
	Core	SCOGGINS	STEVENS		SCOGGINS	STEVENS
	n=	199	155		5	29
% Al	Mean	8.030	**8.470**		12.556	**13.404**
	Median	8.114	**8.596**		12.844	**13.290**
Range	Max	10.698	**11.251**		13.235	**14.913**
	Min	**4.325**	2.355		11.427	**11.608**
% Si	Mean	23.840	**23.896**		21.689	**23.226**
	Median	24.271	**24.480**		21.704	**23.331**
Range	Max	27.389	**29.344**		22.738	**25.402**
	Min	**14.934**	6.101		20.558	**20.761**
% Ca	Mean	**2.317**	1.839		**0.634**	0.371
	Median	**1.547**	1.267		**0.621**	0.322
Range	Max	**16.930**	14.611		0.958	**0.991**
	Min	0.107	**0.119**		**0.390**	0.004
% Fe	Mean	4.362	**4.482**		**4.674**	4.409
	Median	**4.286**	4.195		**4.758**	4.174
Range	Max	8.189	**17.442**		5.941	**6.686**
	Min	2.554	**2.822**		**3.702**	3.189
% Mg	Mean	**1.172**	0.606		**0.684**	0.426
	Median	**1.156**	0.575		**0.616**	0.432
Range	Max	**3.339**	1.353		**1.068**	0.609
	Min	**0.275**	0.254		**0.305**	0.259
% Mn	Mean	0.033	**0.034**		**0.041**	0.036
	Median	**0.028**	0.026		**0.042**	0.037
Range	Max	**0.282**	0.243		**0.065**	0.060
	Min	**0.014**	0.009		**0.016**	0.015
% Ti	Mean	0.411	**0.430**		0.550	**0.595**
	Median	0.418	**0.441**		0.538	**0.596**
Range	Max	0.486	**0.488**		0.585	**0.671**
	Min	**0.222**	0.201		0.532	**0.537**
% K	Mean	**3.032**	2.692		**2.766**	2.491
	Median	**3.080**	2.778		**2.761**	2.511
Range	Max	**3.569**	3.172		2.931	**2.981**
	Min	**1.713**	0.476		**2.656**	2.088

3.1.2 Detrital fraction

Marine mudrocks are primarily composed of clay minerals, fine-grained quartz and biogenic material (Bohacs, 1998). The terrigenous minerals contribute large amounts of silica and aluminum to the overall mudrock composition, this being represented by their elevated concentrations. The aluminum (Al) content of marine sediments is mainly associated with the detrital fraction, this due to the general immobility of Al and its aluminosilicate affiliation in clays (Tribovillard *et al*, 2006). The presence of titanium (Ti), which occurs at much lower concentrations than aluminum, is a good indicator of detrital input due to lack of participation of Ti in biological cycles, as well as its ultra-low seawater abundance (Li, 1982). The correlation between iron (Fe) concentration and Si/Al ratio is established to determine the provenance of the iron of the detrital fraction. Elements that have a significant participation in detrital material (Fe, Si, K, and Ti) are plotted against %Al to identify their trends and concentrations in the detrital clay fraction. As shown for the Scoggins and Stevens cores in Figure 3.5 and Figure 3.6, the Smithwick Fm. groups on the higher-Al end of the plots (~8%), surpassed only by the "brown layer". A linear and positive relationship between Ti/Al and K/Al is observed in both cores. The %Ti for the Smithwick on both cores averages between 0.4-0.5%. The %K shows a higher end-range and mean value in the Scoggins core. The "brown layer" represents a distinctive lithologic unit marked by a direct correlation between the highest concentrations of %Al, and %Ti in both Scoggins and Stevens cores.

Cross-plot relationships for the Scoggins core (Figure 3.5) show the Smithwick at the intersection of different Si/Al trends. The high-Si/low-Al trend expressed by the "Unit A" and Strawn facies increases in %Al and decreases in %Si toward the Smithwick Fm. Decreasing Si and Al concentrations in the Smithwick follow the dissolution trend into the Marble Falls. Concentrations of Fe in the Smithwick are similar to the values present in the Strawn and the "brown layer", and higher than in the Marble Falls and "Unit A". The "brown layer" contained in the Scoggins core presents lower concentrations of Al and Ti than in the Stevens core.

The cross-plots for the Stevens core (Figure 3.6) show distinctive Si/Al proportions and trends for the different formations. The higher Si/Al ratio is expressed by the Atoka-Caddo Formation, whereas the lower Si/Al corresponds to the “brown layer”. The presence of different stratigraphic units containing interbedded mudstones and limestones, such as the Barnett Shale, Marble Falls and Caddo. These units present similar trends of proportional Ti/Al and K/Al increases. From these units, the Barnett Fm. and Marble Falls Group contain overall lower Ti and Al concentrations. The %Al cross-plots show the Barnett Fm. having lower concentrations of Al, Si, and Ti than the Smithwick Fm. (Figure 3.6). The Atoka-Caddo and Strawn-Caddo follow a similar trend of Ti/Al, where the Strawn-Caddo contains the higher ratio. The Atoka-Caddo shows a lower %Al than the Strawn-Caddo, which correlates with a higher abundance of Ca in this formation.

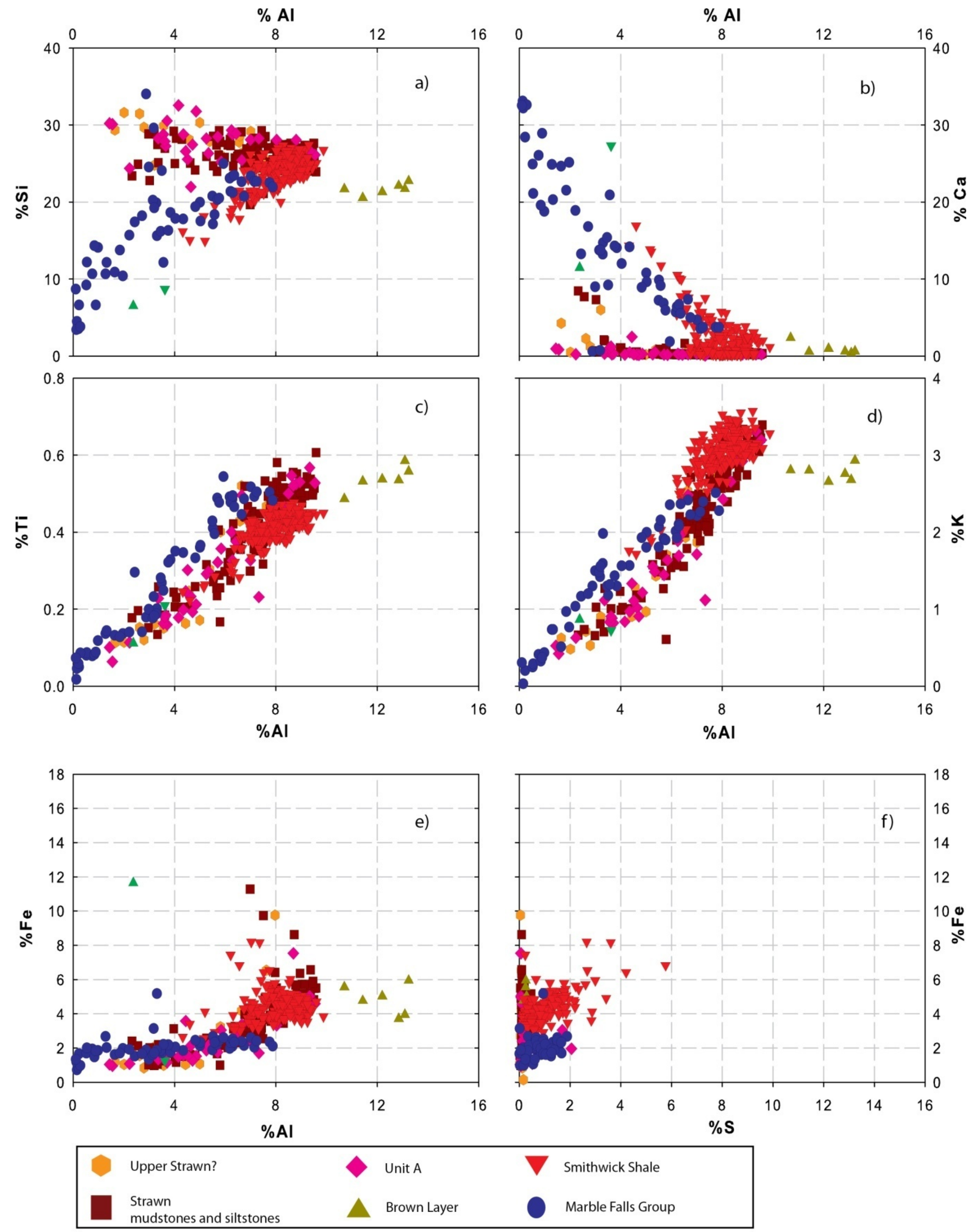


Figure 3.5 Cross-plots of potentially detrital elements (a)Si, (b)Ca, (c)Ti, (d)K, and (e)Fe against %Al, and (f) showing Fe/S. Legend by formation for the Scoggins core.

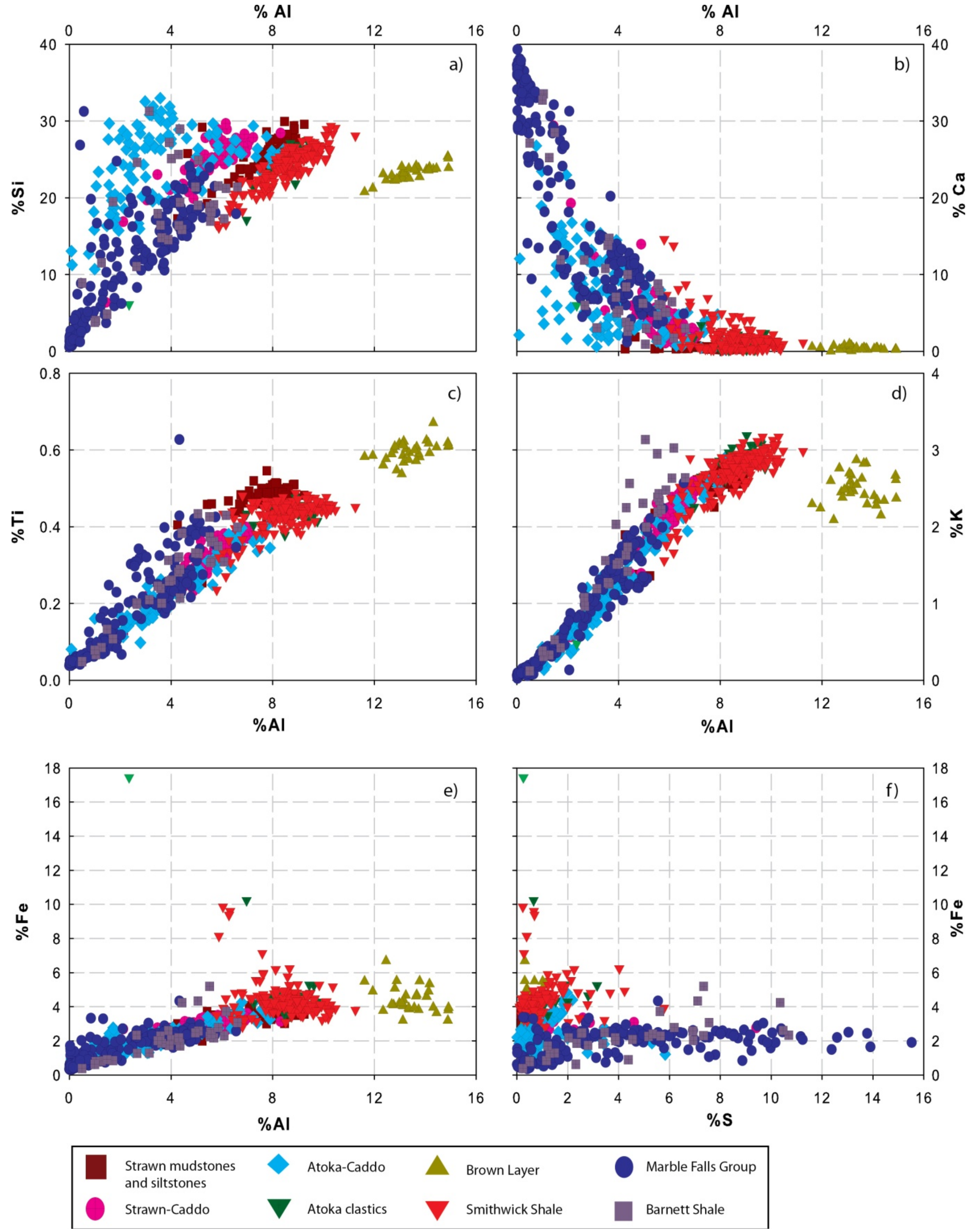


Figure 3.6 Cross-plots of potentially detrital elements (a)Si, (b)Ca, (c)Ti, (d)K, and (e)Fe against %Al, and (f) showing Fe/S. Legend by formation for the Stevens core.

3.1.3 Carbonates and Iron

The carbonate facies are expressed by the affiliation of certain metallic elements (Mg, Mn, Fe) that replace Ca to form carbonate minerals. The carbonate matrix of siderite ($FeCO_3$) is susceptible to the incorporation and substitution of Fe with other elements such as Mn and Mg. The variation in composition of these siderites is closely related to different depositional environments and water chemistry (Mozley, 1989). The %Ca cross-plots show the relationships of the above mentioned elements. Selected carbonate samples with increased %Mn, %Fe, and %Mg are graphed as bright green dots to show variability in concentration.

In the Scoggins core (Figure 3.7), the Marble Falls records a decrease in %Si and %Al, inversely related with an increase in %Ca. The high-Ca samples in the Marble Falls indicate the limestone facies present in the unit, showing a uniform decreasing trend of Ca-dilution towards the dark mudrock facies. The Smithwick Fm. presents a higher mean of %Ca in the Scoggins core (~2.3%) than in the Stevens (~1.8%). The Smithwick Fm. section contained in the Scoggins core presents half the samples of higher Fe (>8%) and Mn(>0.1%) found in the Stevens core. The Ca cross-plots for the Stevens core (Figure 3.8) show the specific compositional characteristics of the formations present. The Marble Falls Group contains the samples with the highest %Ca and lowest %Si on the Stevens core. The Smithwick Fm. contained in the Stevens core shows low geochemical variability. The presence of Smithwick samples showing high %Fe and %Mn, correlates with a moderate presence of Ca (<10%). The higher concentrations of Mg (2-7%) present in the Marble Falls Group contrast with the lower Mg concentrations (<2%) in the Smithwick. The Atoka-Caddo records an overall higher-Si and higher-Ca for the mudstone facies.

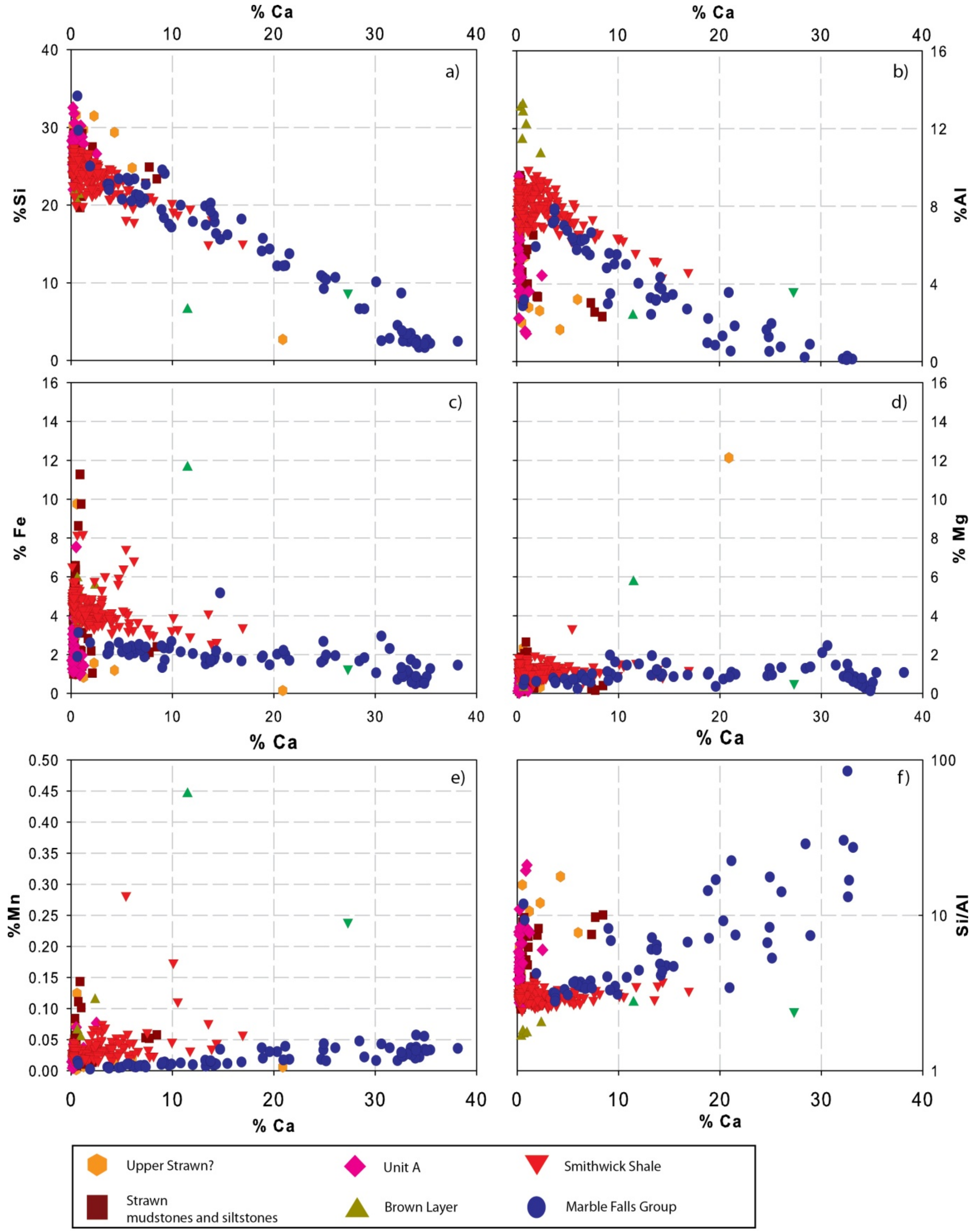


Figure 3.7 Cross-plots of elements with Ca-affinity (a)Si, (b)Al, (c)Fe, (d)Mg, (e)Mn, and (f)Si/Al against %Ca. Legend by formation for the Scoggins core.

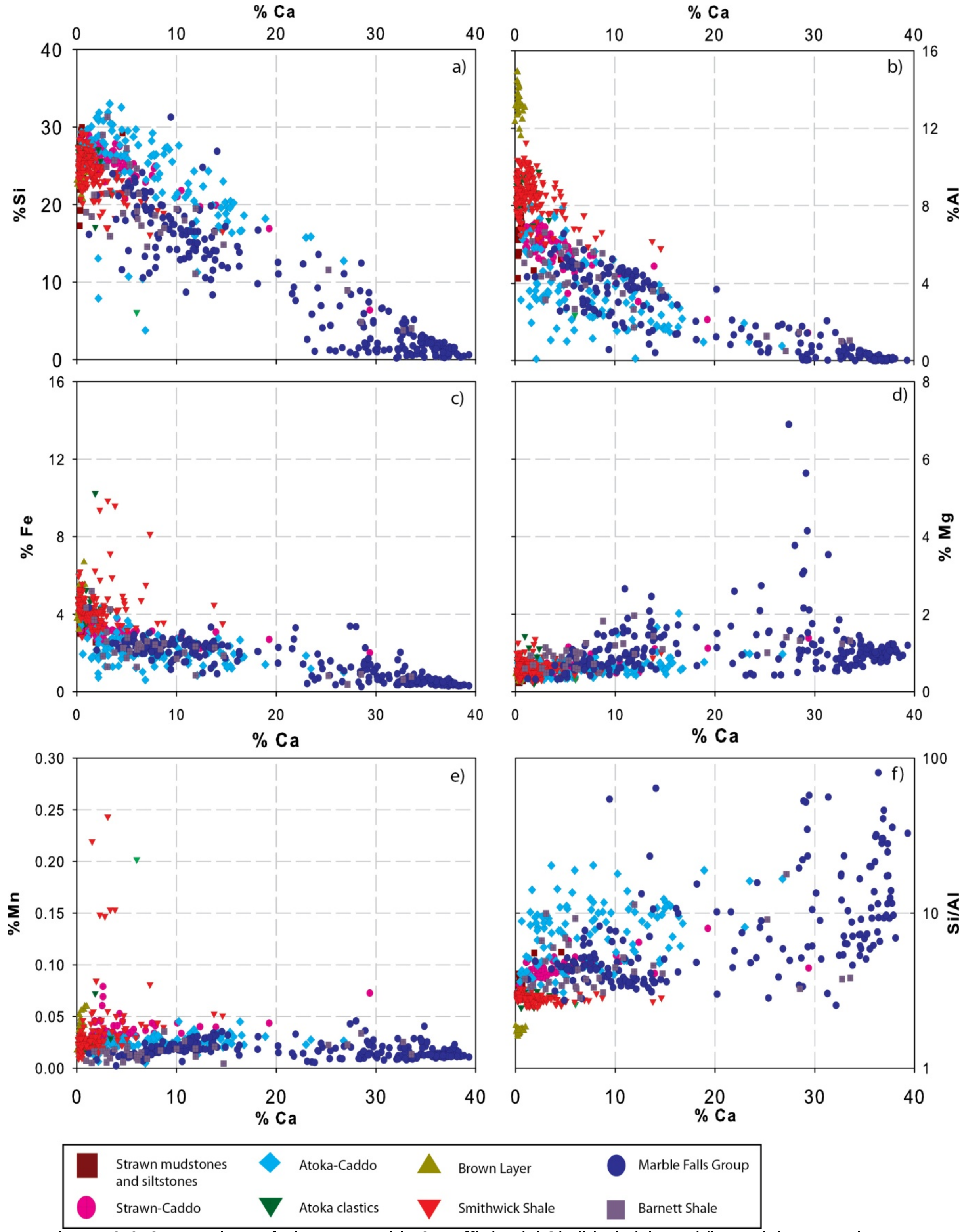


Figure 3.8 Cross-plots of elements with Ca-affinity (a)Si, (b)Al, (c)Fe, (d)Mg, (e)Mn, and (f)Si/Al against %Ca. Legend by formation for the Stevens core.

3.1.4 Inter-core relationships

ED-XRF data acquired for the present study are evaluated in conjunction with a previous local study (Hughes, 2011), providing four cores with geochemical data. All these cores (Scoggins, Stevens, Potter, and Walker) contain significant sections of Smithwick Fm., and their elemental characteristics are compared in cross-plots (Figure 3.9). The elemental concentrations for the Smithwick Fm. correspond to the mean values calculated from the Smithwick sections present in each core. The highest mean of %Si is contained in the Walker core, whereas the lowest mean %Si is expressed in the Scoggins. Mean %Al concentrations in the Smithwick are highest in the Potter core, and lowest in the Walker core. The mean %Ca concentration is highest in the Scoggins, while lowest in the Walker core. Mean %Ti concentrations for the Smithwick are highest in the Walker core, while the lowest mean corresponds to the Scoggins. The highest mean value for %K is present in the Scoggins, while the lowest mean corresponds to the Walker core. Pertaining Mg concentrations, the highest mean is present in the Potter, while the lowest mean for Mg corresponds to the Stevens. The Walker core contains the highest mean of %Mn, while the Scoggins core the lowest. The %Fe data from Walker and Potter cores presents a numerical bias since siderite intervals were removed from the calculations. The Walker core present the highest Si/Al ratio and %Ti between the cores, this is hypothesized to be due to the proximity to sediment sources, and structural constrains that could have also increased the thicknesses of the Smithwick and Atoka clastics in this core.

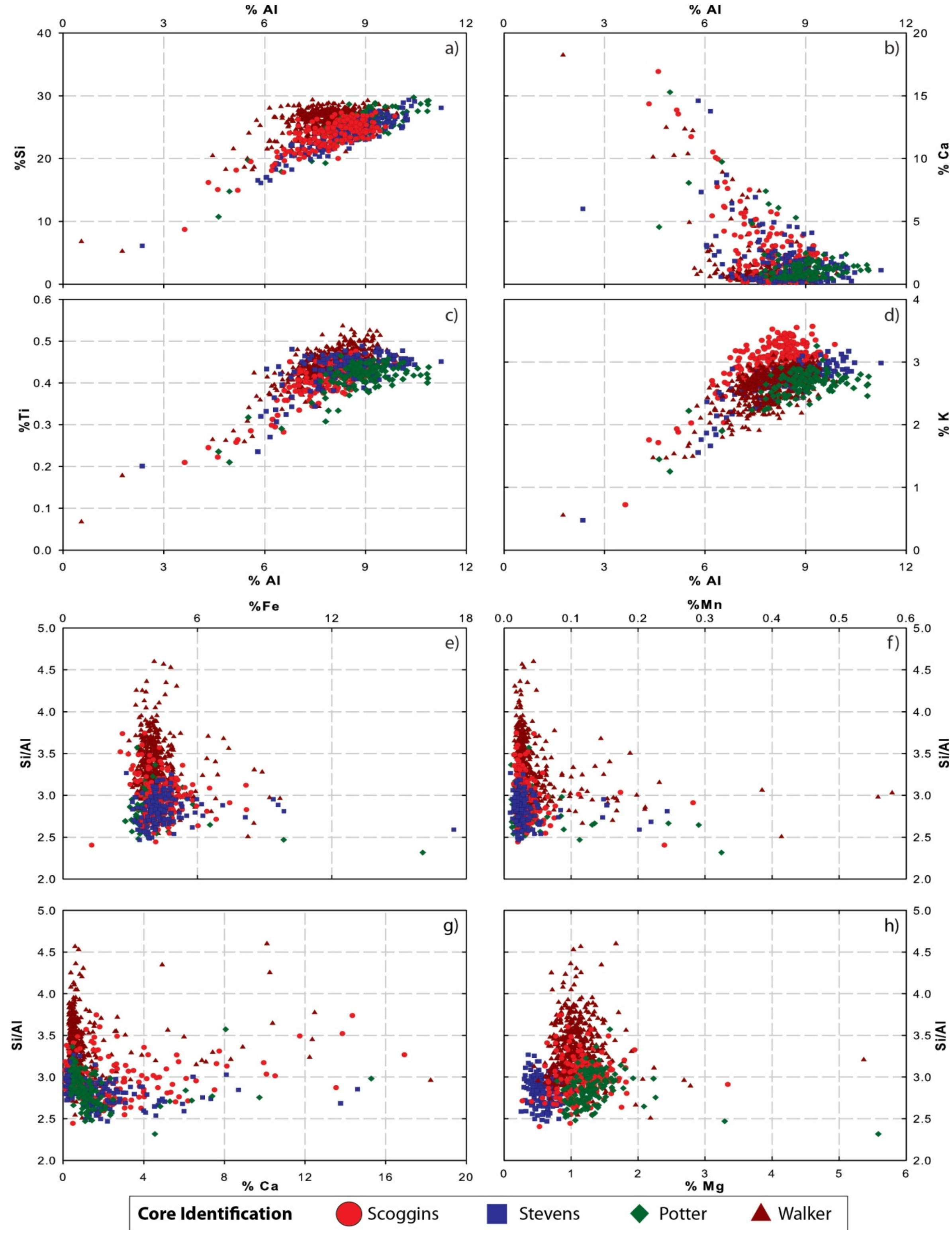


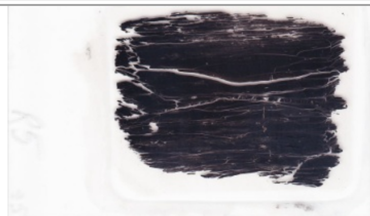
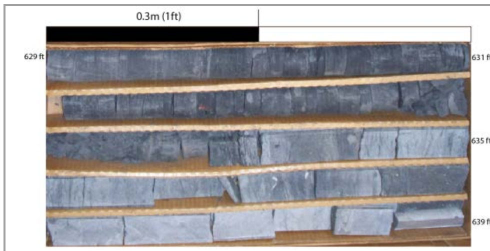
Figure 3.9 Cross-plots of major elemental relationships (a)Si/Al, (b)Ca/Al, (c)Ti/Al. d)K/Al, (e)Si/Al vs. Fe, (f)Si/Al vs. Mn, (g)Si/Al vs. Ca, and (h)Si/Al vs Mg, between all four cores.

3.2 Lithological Observations

Lithological observations from the Scoggins core were performed to better display the variability and degree of change between stratigraphic units.

Table 3.2 Scoggins samples.

Subsurface Depth (ft)	Sample Description	
100		Core segment (~8cm) of fine tan sand and reddish mud laminations. Sand on the uppermost section of the core (~10ft) progressively coarses up.
229		Predominantly brown/red muds and silt laminations. Orange layer in middle shows siderite accretion.
396		Chaotic flow structures on tan silt and darker mud
425-435		Box 41 (425-435ft). Core section showing the changes from “brown layer” mudstone in the lower 6ft, through white sulfate layers, to the overlying sands of “Unit A”. Next to 431ft depth marker, a 10cm siderite layer.

477		Thinly laminated, bluish-black homogeneous clayshale. Slick waxy texture in hand sample.
595		Black fossiliferous mudstone (sponge spicules and radiolarians), presents intervals (<5cm) of sub-horizontal calcite-filled thin (<5mm) fractures.
629-639		Box 62 (629-639ft). Core section showing the upward mud-enrichment of the Marble Falls limestone beds

3.3 Well Log Correlation and Cross Sections

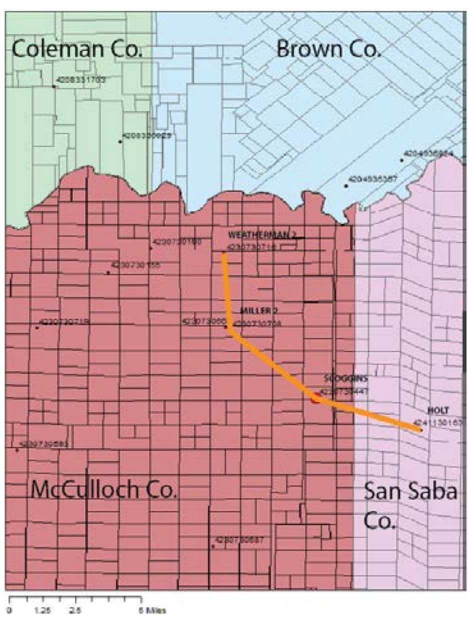
3.3.1 Wellbore Logs

Two areas of interest where studied cores and borehole data are available for correlation are shown in Figure 3.9. Figure 3.9a shows the location of the Scoggins core and the wells used for correlation. Figure 3.9b shows the cross-section located in Brown County and that encompasses both Stevens and Potter cores. The proximity of the wells to the locations of the examined cores, and their setting in local and regional trends are evaluated in structural (Figures 3.10, 3.11) and stratigraphic transects (see apendix). Identification of changes in log responses, thicknesses of units, and vertical displacement between wells are further discussed.

3.3.2 Cross-Sections

Well cross-sections across the area (Figure 3.10) yield evidence of the lithological changes observed in the cores. The Smithwick Fm. is consistently deposited overlying the predominantly carbonate units of the Marble Falls. Below the interbedded carbonate and shales of the Marble Falls Group, the Barnett Fm. is identified. The characteristic high gamma-ray (GR) count of the Barnett contrasts with the underlying low-GR/high-Resistivity (RES) log response of the carbonates in the Ellenburger Group. Changes in chemical composition, depositional trends, and thicknesses are observed in both of the local cross-sections, inferring different structural features. The cross-section containing the Scoggins (Figure 3.10a, Figure 3.11, Appendix C) has a larger spacing between wells (3-4 miles), while the cross-section containing the Stevens and Potter cores (Figure 3.10b, Figure 3.12, Appendix D) have a closer arrangement of wells and cores (0.5-3.5 miles).

a)



b)

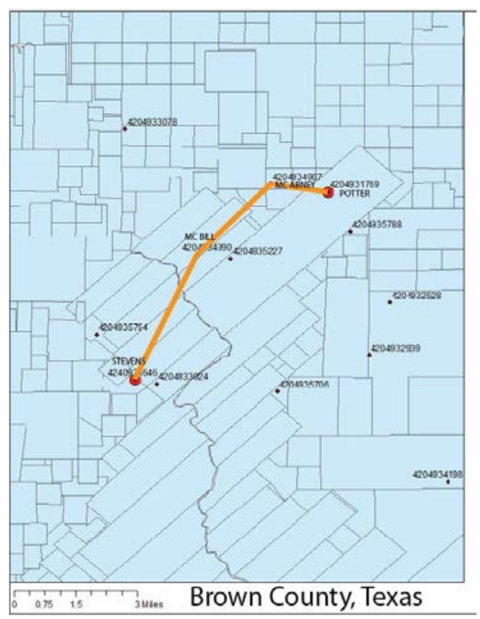


Figure 3.10 Cross-section locations for (a)Scoggins, and (b)Stevens cores.

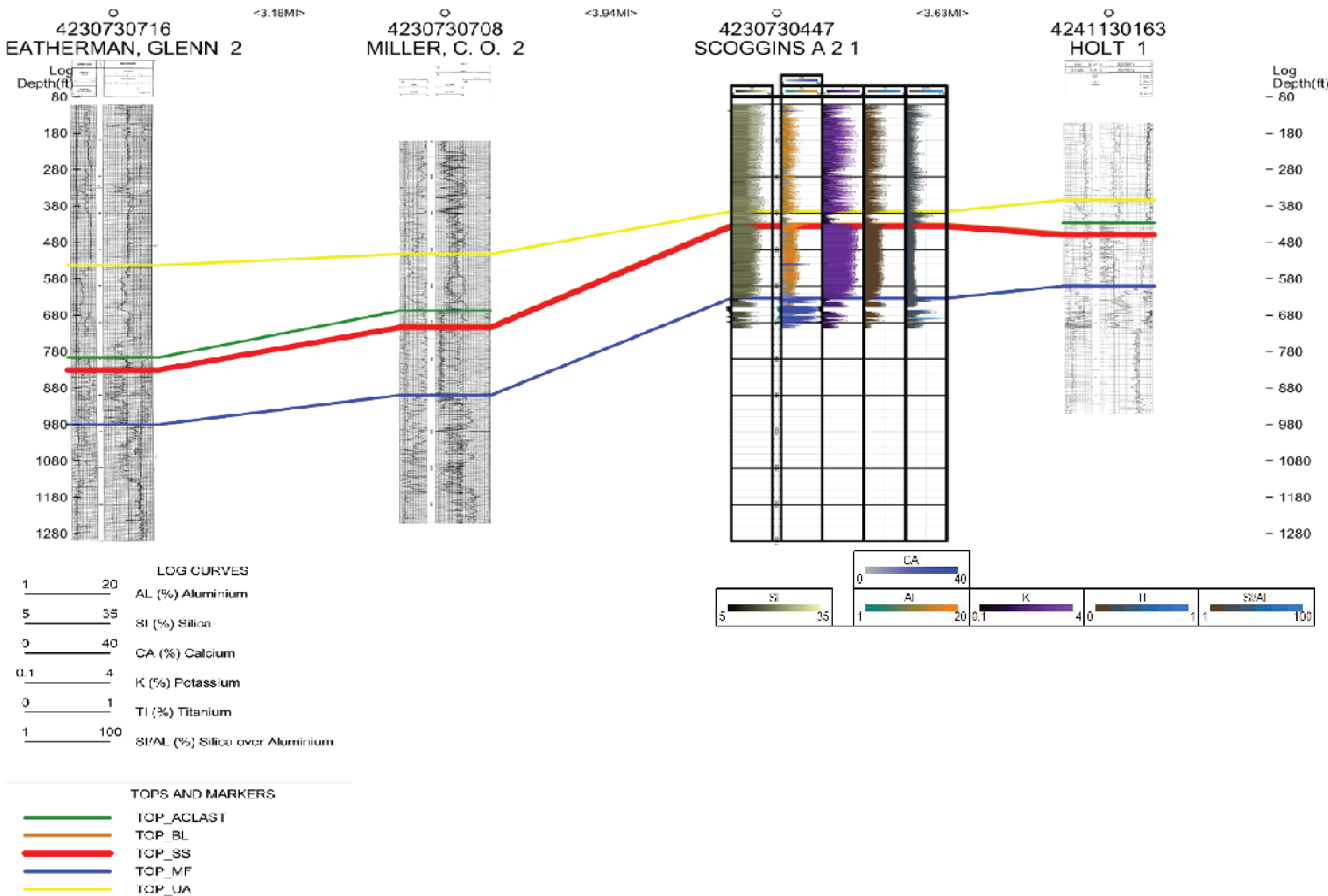


Figure 3.11 NW-SE Structural cross-section in McCulloch and San Saba counties, with Scoggins (Si-Ca-Al) core.

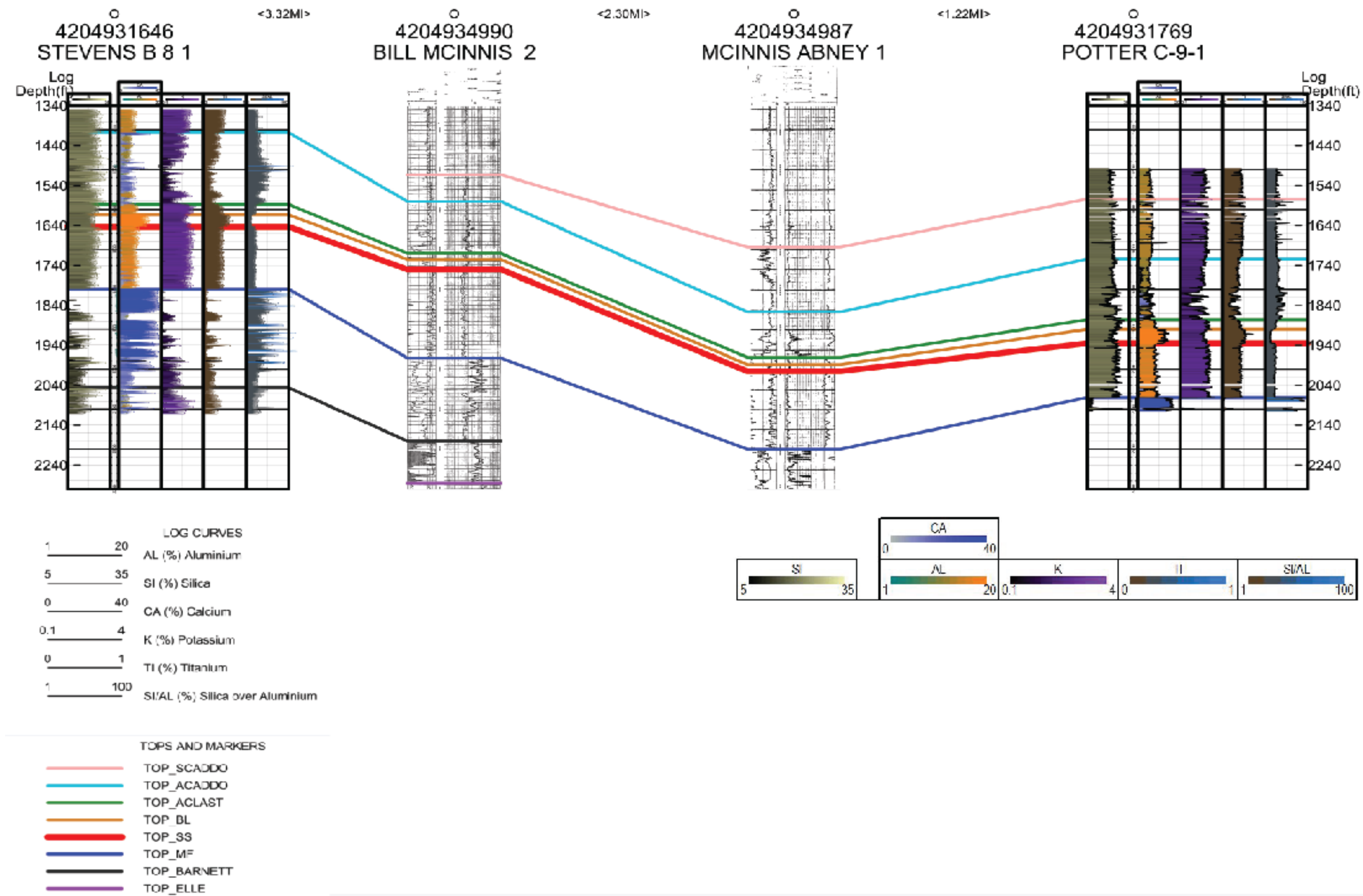


Figure 3.12 SW-NE Structural cross-section in Brown County, between Stevens and Potter (Si-Ca-Al) cores.

CHAPTER 4

DISCUSSION

The discussion will focus on the results for the Smithwick Formation, and the geochemistry of its bounding units. All of the cores presented in the study (Scoggins, Stevens, Walker, and Potter) present Smithwick Fm. sections, expressed at different depths and with subtle changes in lithology.

Changes and co-variance in elemental composition are used as proxy indicators of depositional and lithological changes among the studied cores and formations. Chemostratigraphic interpretation of the formations is based on these geochemical changes, with some of them presenting subtle changes not identifiable in borehole logs. Major lithogenic elements (Si-Ca-Al) are used to characterize the generalized lithology of the formations, whereas secondary elements can provide insight of changes and trends. Cross-plot graphs for Si/Al and Ca/Al show the relationship between these elements and their significance for the characterization of major geological units.

Variations in the rocks contained in both Scoggins and Stevens core, are interpreted to be caused by different depositional environments. Observations from the Scoggins, such as lower overall %K concentrations, the truncating character of the “brown layer”, the presence of authigenic (siderites and ferromanganoan concretions), can provide evidence of a marginal-marine to non-marine environment due to the excess of terrestrial influence and oxygen levels (Bohacs, 1998). The spatial location of the Scoggins core on the proximity of the Llano Uplift could be associated of the low-energy, shallow and restricted-marine deposition in the area.

The Stevens core presents characteristics of a shelfal-marine depositional environment. The presence of Atoka-Caddo carbonates, and the inferred reworking of Atoka-aged sediments (shown as the lower concentrations of Al, Ti, and K present in the Atoka-Caddo unit), is congruent with the abundance of fine-grained pelagic components (biogenic material and marine organic content).

4.1 Elemental Geochemistry

The lithologies and formations of the present study are characterized by the range and average values of elemental concentrations. Variations in elemental percentages do occur in the examined cores, but they are mostly constrained by mineralogy or depositional patterns.

4.1.1 Major Elements

The overall abundance of Si-Ca-Al is used in the generalized interpretation of the lithological character of the units. Some of the units of the study are well constrained by their chemical composition, where specific values are environment-dependant.

In the Scoggins core, the lowest formation corresponds to the Marble Falls Group. This unit presents limestone beds with %Ca concentrations greater than 18%, and mudstones with %Al lower than 8%. The Smithwick Fm. in the Scoggins core contains a moderately uniform concentration of Al, with a median and mean %Al slightly above 8% (see Table 3.1).

The sandstone beds usually consists of %Si greater than 28%, and a Si/Al ratio usually larger than 5:1. Limestone beds present variable concentrations of Ca, but can be characterized by amounts greater than 15%, and a Si/Al ratio of at least 4:1. Generally, the mudstones in the Scoggins core (dark shales and turbidite facies) contain significant amount of %Al (greater than 5%) and %Si less than 29%.

The lowermost unit in the Stevens core corresponds to the Barnett Formation. This formation consists predominately of dark mudstone with sparse microfossils, and it is distinctly capped by 20ft of Si-rich (20-30 %Si) dark mudstone. The lowest part of the Marble Falls consists of dark mudstones similar to the underlying Barnett but with abundant macrofossil fauna (crinoids, foraminifers, and gastropods). Variations of the carbonate facies within the Marble Falls consists of pelmicrites, biomicrites, wackstones, and packstones. An abrupt decrease in fossil fauna within the dark mudstones, and absence of limestone beds mark the upward transition into the Smithwick Formation. The Smithwick Formation contains considerable higher %Al (normally greater than 8%) and %K concentrations (predominantly above 2%), these elemental concentrations being distinctly higher than the mudstones within the Marble Falls or Barnett Formation.

The presence of the “brown layer” in all the studied cores seems to represent a regional change in climatic or tectonic conditions. The increased influx of terrigenous sediment across the area can be attributed to an increase in relief of the source and wetter climate. The observed variation of the dominant clay-mineral in the units of interest, from illite in the Smithwick to kaolinite in the “brown layer”, gives evidence of a change in environmental conditions. The deposition of kaolinite is associated with an increase in chemical weathering, and it is linked to a more humid climate. Inferred higher rainfall and increasing relief of the sediment source could explain the increased detrital character of the “brown layer”. The detrital character of the ‘brown layer” could be explained by paleoenvironmental changes, drastic eustasy variations, increased tectonic activity, or a combination of these factors.

4.1.2 Terrigenous Elements

Changes in the compositional patterns for Al and Ti, both elements directly associated to the terrigenous fraction, can be attributed to factors such as the distance from and the mineralogical characteristic of the sediment source, bottom-energy levels and transport mechanisms. The “Unit A” identified in the Scoggins core was previously defined as sandstones with interbedded mudstones lying directly above the “brown layer”. The “Unit A” presents comparatively lower concentration of K (below 2%), and Ti (below 0.3%) than the bounding mudstones of the Smithwick and Strawn. These sandstone/mudstones beds occur in the interval overlying the ‘brown layer”, and express a less detrital character than the Strawn submarine fans and turbidite facies. An inferred correlation between the “Unit A” from the Scoggins and the Atoka-Caddo in the Stevens is proposed due to the observed lower concentrations of Al, K, and Ti. The mudstone laminations present in the Strawn facies become thicker upward, with increasing concentrations of Al, K, Ti, and Fe. Potassium-enrichment in marine shales is well represented in this study, with the higher average %K corresponding to the Scoggins. The considerable higher %K in the Scoggins could be explained by increased potassium metasomatism (Hutcheon *et al.*, 2000) due to the closer distance to the Llano core.

4.2 Cross-sections

The cross-section containing the Scoggins core (Figure 3.10a, Figure 3.11, Appendix C) shows the correlation of the core with three well in the proximity. The two southernmost wells (Scoggins and Holt #1) are structurally higher, being closer in the cratonic shelf, to the Llano Uplift. Uniform deposition of the Smithwick across the region is evidence of the extensive marine transgression across the region, and possible post-depositional uplift. Thicker sections of the Smithwick in this cross-section (Appendix C) could be related to penecontemporaneous faulting or structural uplift. The increase in thickness of Unit A toward the northeast could represent the marine high-stand at the end of the Atoka and distal sediments reaching from across the FWB to higher paleobathymetrical relief. Si-enrichment in the sandstones of Unit A, coupled with a lower concentration of other detrital elements such as Ti, K, and Fe/S ratio could be accounted by marine high-stand rework of clastic material, with a lower influx of terrigenous sediment. Changes in the Smithwick are also observed in the cross-section containing the Stevens and Potter cores (Figure 3.10b, Figure 3.12, Appendix D). The wells between the two cores show a thicker Smithwick and underlying strata, inferring two structural elements between them.

CHAPTER 5

CONCLUSIONS

5.1 Remarks on the Smithwick Formation

The Smithwick Formation was deposited in the Fort Worth Basin (FWB) and surrounding areas during Early to Early Mid Pennsylvanian (Plummer, 1950; Kier, 1980; Walper, 1982; Grayson *et al.*, 1990; Erlich and Coleman, 2005). The Smithwick Formation consists predominantly of dark to gray mudstone shales, with minor amounts of sandstone and limestone. The continental convergence of Gondwana and Laurussia in mid-Carboniferous caused the FWB to develop in front of the advancing Ouachita thrust-belt, influencing the structural development of the region (Wickham *et al.*, 1976; Algeo, 1992; Erlich and Coleman, 2005). The tectonic reactivation of the area is thought to have caused the further development and subsidence of the FWB, while large amounts of sediments were originated at regions of active uplift around it (Walper, 1982; Grayson *et al.*, 1990). Atokan marine and distal siliciclastic facies progressively covered the FWB, migrating further westward due to basin infilling and decreased basin subsidence. Marine transgression in the region is recorded by the deposition of the Smithwick Fm. and Atoka siliciclastic rocks. The dynamic climate regime and tectonic activity of the region are expressed in the increased sediment supply and changes in lithofacies around the time of deposition of the Smithwick.

The stratigraphic upward decrease in %Si and the rapidly decreased abundance of fossils preserved in the Smithwick is indicative of a marine-transgressive unit, where thickening of the units is associated with increased basin subsidence. The geochemical composition of the mudrock matrix of the Smithwick is largely invariant, supporting a singular sediment source, probably from the Ouachita thrust belt. An important sediment source to the East is also supported by the higher %Ti, and Si/Al ratios between the cores, where the easternmost (Walker) had the higher concentrations.

Structural features and pre-existing bathymetry is likely to have affected the influx of sediments and the local depositional style. Reactivation of tectonic stresses throughout Pennsylvanian times is likely a major component for faulting, and reactivation of older faults, while causing some of the observed thickness differences of the Smithwick. The occurrence of siderite-rich intervals and minor fluctuations in the chemostratigraphy is potentially the result of episodic uplift of the Ouachita thrust belt and other sediment sources, but can also reflect paleoenvironmental changes due to climate processes, or a combination of both.

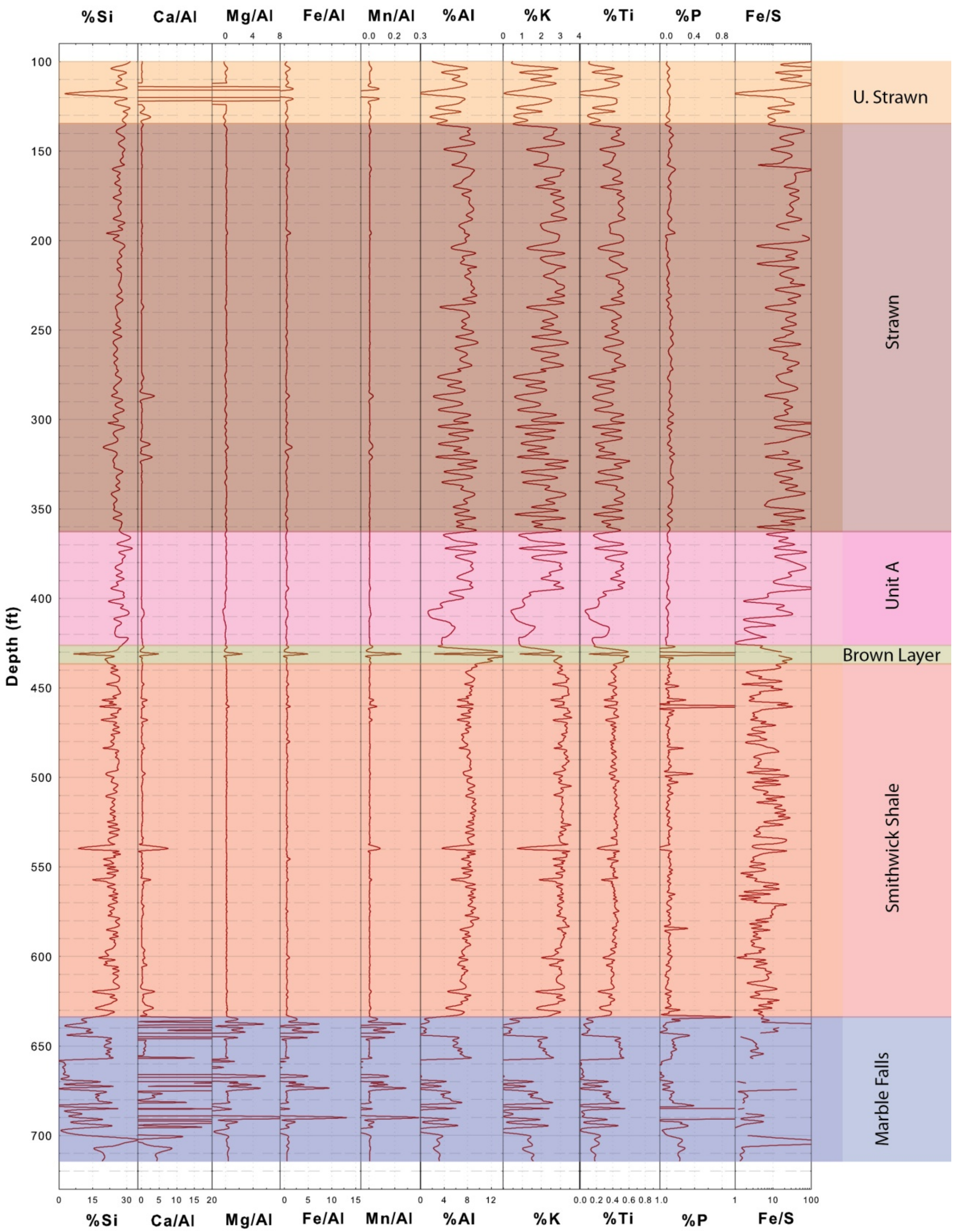
Paleoenvironmental changes for this period are largely associated to fluctuations of the LPIA and the arrangement of continental mass. The large volume of muds and layered clays deposited in the study area from early-to-mid Pennsylvanian are a direct indicator of the predominant wet conditions, which associated with increased terrigenous influx can lead to the deposition of siderites in the Smithwick, and iron-rich, colored clays in the Strawn. The emergence and uplift of the Ouachita Mountains likely acted as an atmospheric barrier for the surrounding warm water to condensate, providing a synergic combination of a large sediment supply, and yield, due to increasing relief and rainfall.

5.2 Future Work

The Smithwick Shale was deposited in a time of dynamic sea-level variations in combination with active local tectonic activity. These synchronous changes in environment provide mixed deposition signals (Erlich and Coleman, 2005), that need to be better understood through subtle changes and patterns in elemental geochemistry. Further development of geochemical proxies can help identify and differentiate the biogenic vs. the terrigenous fractions of the total quantified silica present in the samples. The presence and abundance of certain trace-elements in marine mudrocks has been linked to certain depositional environments with large variations in oxygenation and bacterial activity. Some of the proxies used to identify organic productivity, such as %P, %S, and to a minor extent, Ba, Cr, and U concentrations, need to be more accurately quantified to yield better details of the organic productivity and bottom-water conditions.

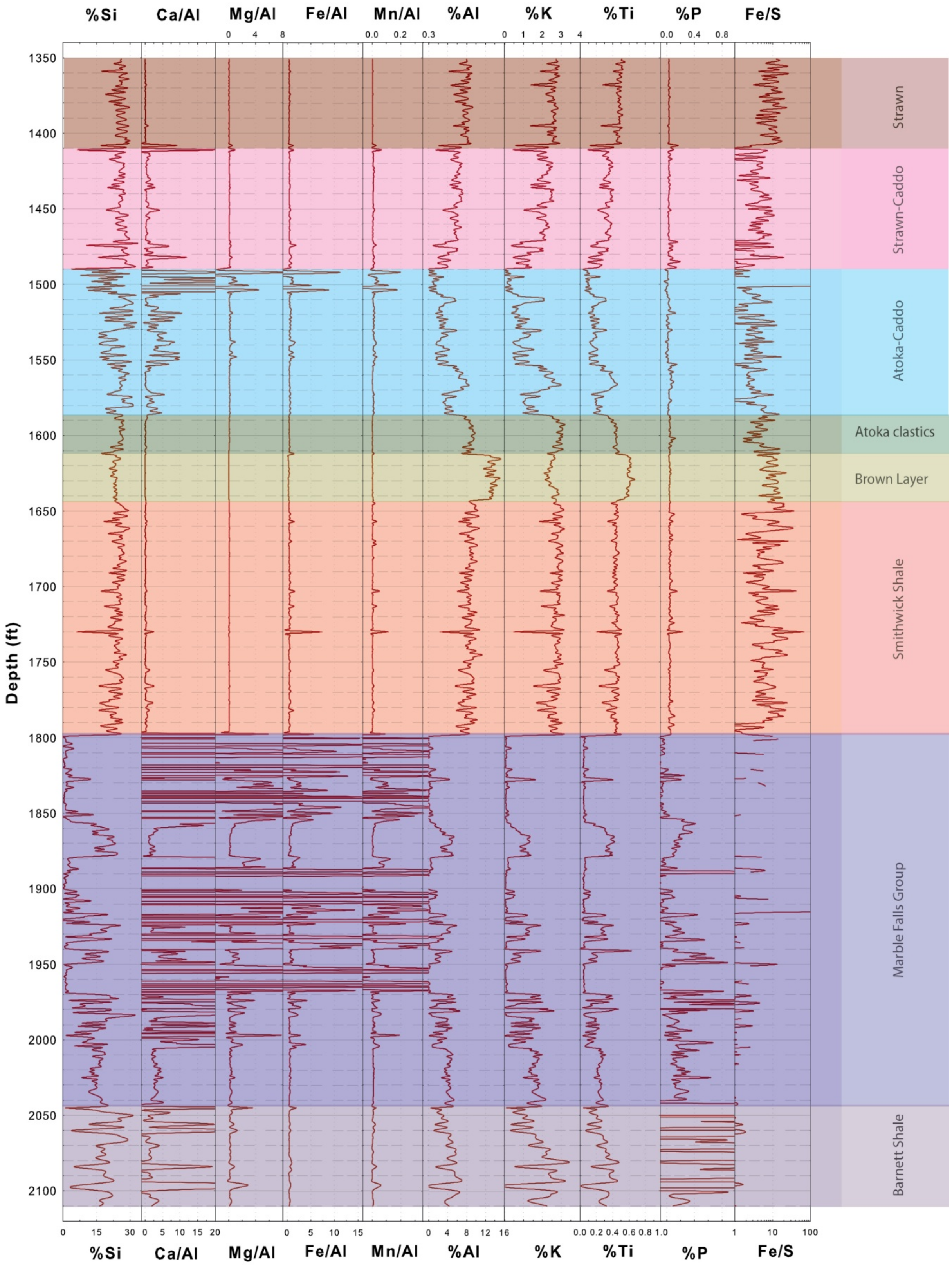
APPENDIX A

GENERAL CHEMOSTRATIGRAPHY OF THE SCOGGINS A-2-1 CORE


%Si
Ca/Al
Mg/Al
Fe/Al
Mn/Al
%Al
%K
%Ti
%P
Fe/S
Depth (ft)
U. Strawn
Strawn
Unit A
Brown Layer
Smithwick Shale
Marble Falls

APPENDIX B

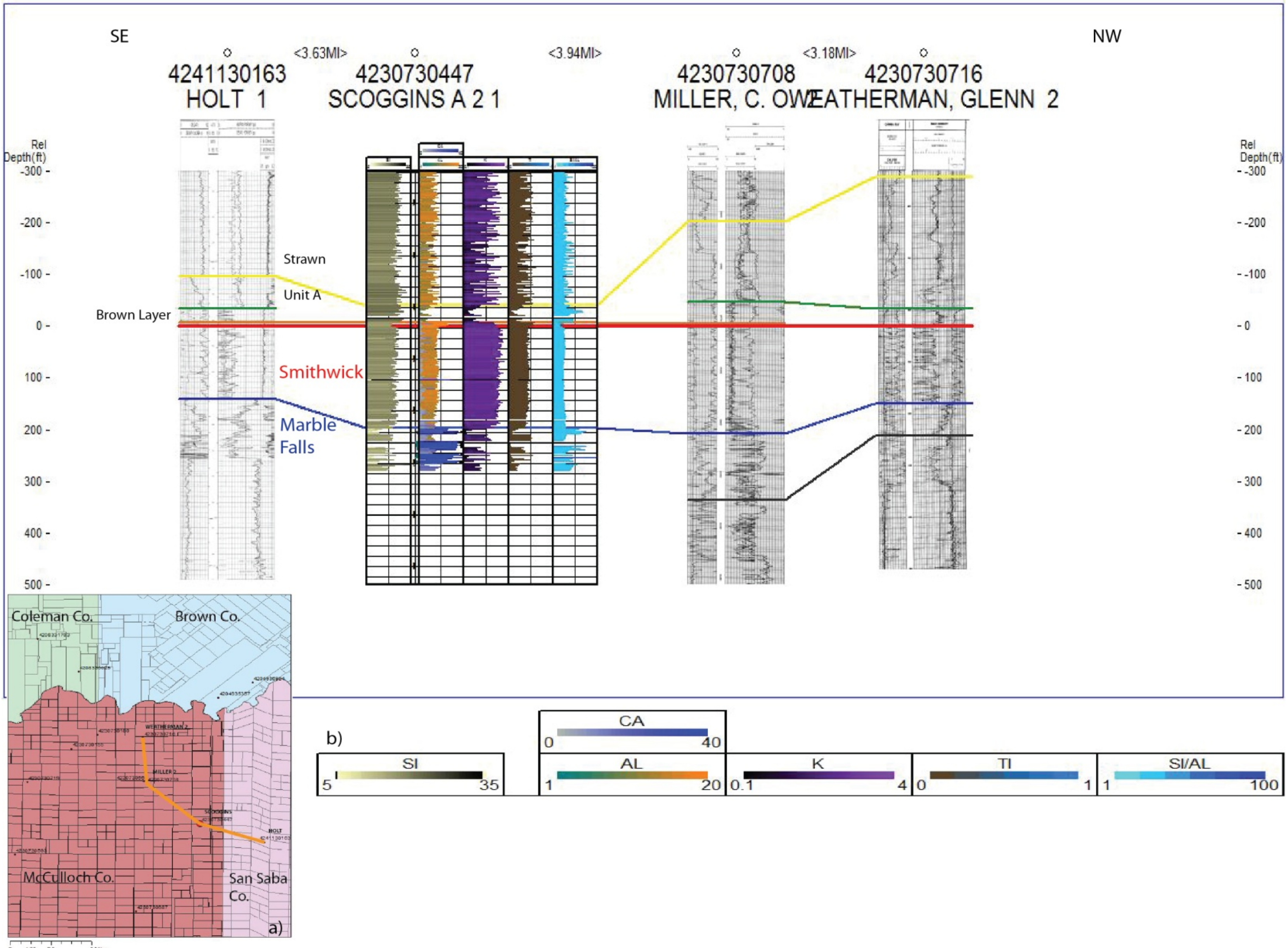
GENERAL CHEMOSTRATIGRAPHY OF THE STEVENS B-8-1 CORE



%Si
Ca/Al
Mg/Al
Fe/Al
Mn/Al
%Al
%K
%Ti
%P
Fe/S
Depth (ft)
Strawn
Strawn-Caddo
Atoka-Caddo
Atoka clastics
Brown Layer
Smithwick Shale
Marble Falls Group
Barnett Shale

APPENDIX C

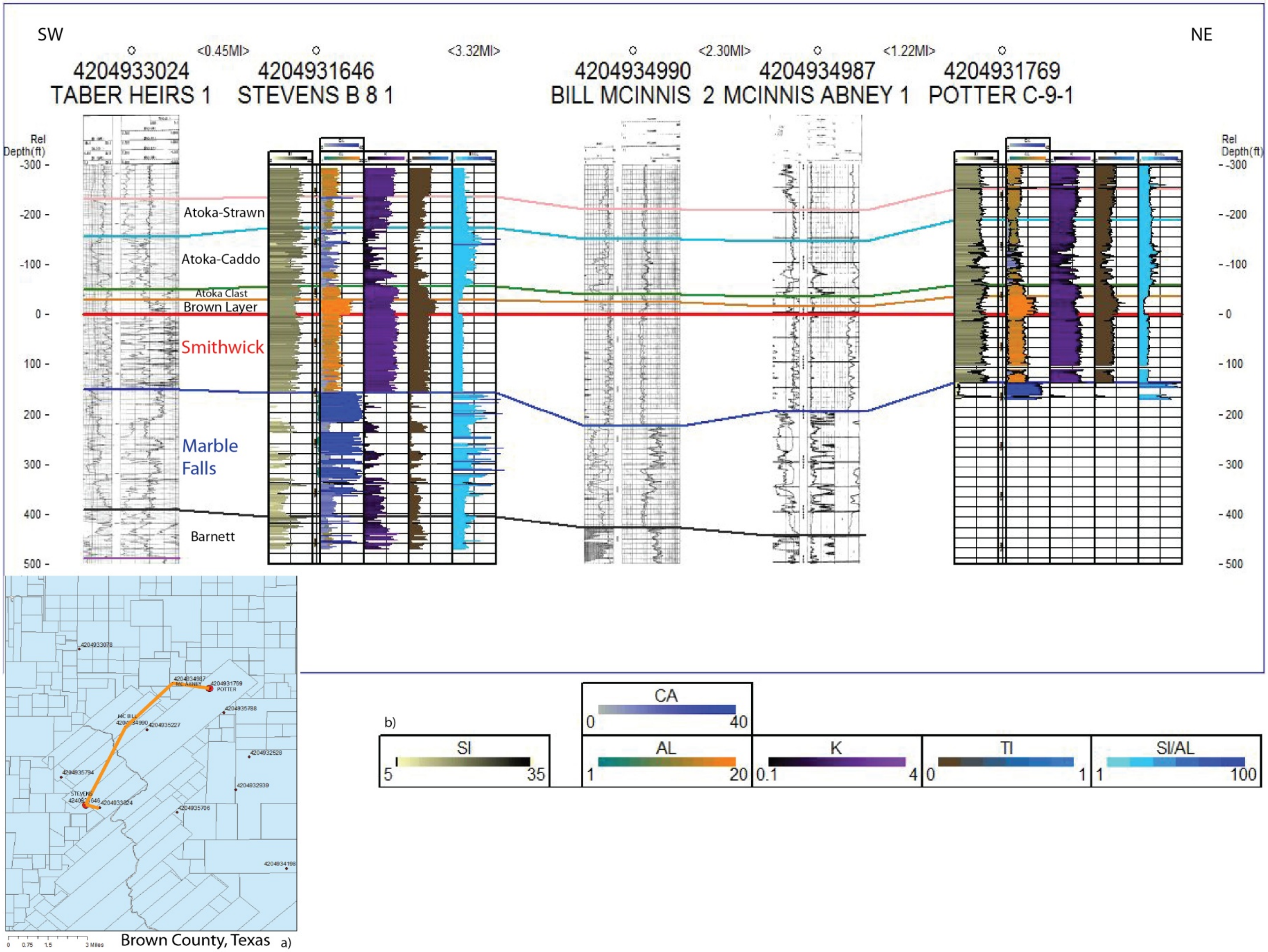
NW-SE STRATIGRAPHIC CROSS-SECTION IN MCCULLOCH AND SAN SABA COUNTIES WITH SCOGGINS CORE, (A)REGIONAL LOCATION, AND (B)GEOCHEMICAL LEGEND



SE
NW
<3.63MI>
<3.94MI>
<3.18MI>
4241130163
HOLT 1
4230730447
SCOGGINS A 2 1
4230730708
MILLER, C. OW2
4230730716
WEATHERMAN, GLENN 2
Rel Depth(ft)
-300
-200
-100
0
100
200
300
400
500
Strawn
Unit A
Brown Layer
Smithwick
Marble Falls
Coleman Co.
Brown Co.
McCulloch Co.
San Saba Co.
a)
b)
CA
0
40
SI
5
35
AL
1
20
K
0.1
4
TI
0
1
SI/AL
1
100

APPENDIX D

SW-NE STRATIGRAPHIC CROSS-SECTION IN BROWN COUNTY WITH STEVENS AND POTTER CORES, (A)REGIONAL LOCATION, AND (B)GEOCHEMICAL LEGEND



SW
NE
<0.45MI>
<3.32MI>
<2.30MI>
<1.22MI>
4204933024
TABER HEIRS 1
4204931646
STEVENS B 8 1
4204934990
BILL MCINNIS 2
4204934987
MCINNIS ABNEY 1
4204931769
POTTER C-9-1
Rel Depth(ft)
-300
-200
-100
0
100
200
300
400
500
Atoka-Strawn
Atoka-Caddo
Atoka Clast
Brown Layer
Smithwick
Marble Falls
Barnett
Brown County, Texas
a)
b)
CA
0
40
SI
5
35
AL
1
20
K
0.1
4
TI
0
1
SI/AL
1
100

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BIOGRAPHICAL INFORMATION

Rene B. Ovalle graduated with a BS in Geology from UT Arlington. A well-balanced curriculum in marine and atmospheric geology, and their application on hydrocarbon exploration fomented a further pursuit in education. Graduate courses in oceanography, carbonate deposition, and environmental geochemistry developed his research interest to better understand fine-grained marine rocks. The application of marine geochemistry in paleoenvironmental reconstructions, and its potential in exploration of hydrocarbon systems, is one of Rene's research interests that he hopes to further develop in his professional career. Other interests are related to unconventional energy resources, and multidisciplinary approaches to diverse challenging projects and objectives.