

USING CYCLOTHERMIC BLACK SHALES TO
CREATE A PROXY CALCULATION FOR BOREHOLE
TOC ESTIMATES

By

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Bachelor of Science in Geology

Fort Hays State University

Hays, KS

2006

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
July, 2011

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ACKNOWLEDGMENTS

Thank you to Mr. David Delosier of the Anchor Quarry, Owasso, Oklahoma and Mr. Chad Browne, APAC Quarry, Catoosa, Oklahoma. Thank you to Dr. Jen Latimer and Ms. Windy McBride of Indiana State University for performing the phosphate analysis, on my shale samples. I would also like to thank Jami Tolle, Dr. Hendrata Ali, and Melissa Mikesell for their help as field assistants and sounding boards; who put up with blistering temperatures, hauling heavy equipment, gathering rock samples and generally agreeing to play in the dirt so I could complete my work. The greatest thank you of all goes out to my wonderful husband Matt, who endured field work, countless hours of banter about shales and without whom this work would not have been what it is. Thanks for pushing me to be the best.

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CHAPTER I

INTRODUCTION

In addition to their role as source rocks, black shales have traditionally been regarded by geologists as important marker beds in the petroleum industry. Organic-rich black shales are important for a wide variety of reasons, including but not limited to, their role as hosts for ore deposits and use as subsurface markers (e.g. Murphy et al., 2000; Sageman, 2003; Tourtelot and Meier, 1976; Weller, 1930).

Black shales are often enriched in many trace metals, such as uranium, which can be easily measured in outcrops and in well bores using spectral gamma ray spectrometry (SGR); (Brumsack, 1980; Vine and Tourtelot, 1970). Previous studies have shown that uranium can often be strongly correlated with total organic carbon (TOC) (e.g. Anderson, 1989; Leventhal, 1981; Schmoker, 1981a). The historical Schmoker (1981a) study shows this relationship very well. These observations of the relationship between U and TOC have lead workers to propose a mechanism in which scavenging of U by organic compounds controls its fixation in sediments (Algeo and Maynard, 2004; Anderson, 1982; Elbaz-Poulichet et al., 2005; McManus et al., 2005; Zheng et al., 2002b). However, there are variations in the strength of this correlation, and the correlation does not always exist as shown in Figure 1 (e.g.,Cruse and Lyons, 2004; Elbaz-Poulichet et al., 2005; Leventhal, 1981). One potential cause of such variations in the strength of the

correlation could be the scavenging of U by phosphate, which can also be present in relatively high concentrations in black shales (Doveton and Merriam, 2004).

Understanding the relationships between U, P, and organic carbon serves to strengthen the use of spectral gamma ray results as a proxy for source rock characterization, as well as basin wide correlations of black shales.

Pennsylvanian cyclothemic black shales are often phosphatic and the PO_4 can be a host for U, and can scavenge it on its own, separate from TOC. To test the hypothesis that presence of phosphate can also control uranium concentrations in black shales in different depositional environments, rather than total organic carbon, I have undertaken a geochemical study of the Pennsylvanian (Desmoinesian) Excello Shale. The Excello is a cyclothemic black shale that is well defined both lithologically and stratigraphically, and has a wide geographic distribution, from Indiana in the north to Texas in the south, and Colorado in the west to Indiana in the east (Heckel, 1980). Thus, variations in uranium, total organic carbon and phosphorus concentrations with respect to depositional environments (i.e. distance to shore) can be examined, and used to create a model for uranium fixation in organic-rich shales. Ultimately, such a model can be used to enhance subsurface interpretations and predictions of depositional environment from wireline logs.

The overall objectives of this study are to determine uranium concentrations and their relationship to total organic carbon concentrations and phosphate concentrations and speciation in several outcrops of the Excello Shale. Outcrop stratigraphy and lithology will be used to provide a framework within which to interpret geochemical signals. The study includes outcrop data from south-eastern Kansas and north-eastern Oklahoma that

represent a range of environments from near shore to offshore (Fig. 2). The methods used include determination of total organic carbon concentrations, measurements of phosphorus concentration and speciation, and outcrop spectral gamma ray spectroscopy. The data is used to determine the relationship of uranium with total organic carbon, and phosphate concentrations in the shale, which is interpreted within the context provided by outcrop lithology. A refined conceptual model for uranium fixation in ancient marine sediments is developed that can be used to predict shale behavior in the subsurface using well log data.

CHAPTER II

BACKGROUND

Black Shale Formation

The processes by which organic-rich black shales form have been the subject of a long-standing debate, largely centered around the importance of preservation of organic matter (e.g. Demaison and Moore, 1980) as compared to enhanced water-column productivity (e.g., Pedersen and Calvert, 1990). The preservation model, as presented by Demaison and Moore (1980) and supported by the work of Gelinias (2001), is based on the idea that bottom water anoxia beneath a permanent pycnocline leads to the formation of organic-rich sediments because organic matter (OM) is not decayed. Key to this model is the idea that anaerobic metabolism is slower than aerobic metabolism, and that anaerobic bacteria are not as efficient at OM consumption as compared to aerobes (Volkov, 1984). At the other end of the spectrum, enhanced water-column productivity is thought to be critical to the formation of black shales (Pedersen and Calvert, 1990). In the productivity model, high concentrations of organic matter are produced in surface waters in high concentrations, and subsequently settle below the mixed layer where this organic matter undergoes aerobic degradation. The process of aerobic degradation is catalyzed by oxygen-consuming microbes. If the input of organic matter outpaces the renewal of dissolved oxygen, high concentrations of organic matter can persist in the

underlying sediments. In recent years, many works have shown that these two end-member models cannot fully explain the formation of black shales and that both processes are in some ways intertwined (e.g. Murphy et al., 2000). Additionally, the role of sedimentation rate must also be considered (Sageman, 2003). Variations in sedimentation rate affect the preservation of organic matter in several ways. First, relatively rapid sedimentation rates can help preserve organic matter by burying it below the depth to which oxygen penetrates into sediments. However, very rapid sedimentation rates can also serve to dilute the organic matter delivered to the sediments, thus reducing the concentrations of preserved OM. The presence of anoxia—whether it develops in response to external forcing or in response to an increased sedimentary organic carbon load— also has important implications for the cycling of U and phosphate (Filippelli, 1997; Ruttenger, 2004).

Cyclothems

Cyclothems are cyclic successions of shales and limestones thought to have been formed by repeated transgression and regression of the Pennsylvanian interior sea in response to glacial dynamics (Algeo, 2008; Heckel, 1977; Wenger et al., 1988). This cyclic depositional pattern was first described by Weller (1930), with the term “cyclothem” first used by Wanless and Shepard (1936). Heckel (1977) established the classic model of a “Kansas-type” Cyclothem, which includes two outside shale members, a middle limestone member, a core shale member, and an upper limestone member (Fig. 3). These members are interpreted to represent deposition through a full transgressive and regressive cycle (Heckel, 1977, 1980; 1986). Locally, in areas proximal to ancient

shorelines, variations in this classic model can be observed, due to processes such as the formation of deltas or incised valleys (e.g. Feldman, 2005; Klein and Kupperman, 1992).

The Excello Shale is the core shale member of the Cherokee group cyclothem (James, 1972). The core shale member often consists of a condensed, phosphatic, laminated black shale, described as a thin (0.3 to 2.0 m thick), nearly non sandy, dark marine shale, over- and underlain by a bioturbated gray shale (Heckel, 1977). The core shales range from abundantly to sparsely fossiliferous, and typically contain a black fissile facies that lacks benthic quartz in the lower to middle part (Heckel, 1980). The core shales are considered the most anoxic portion of the cyclothem (Algeo et al., 2004; Cruse and Lyons, 2004; Heckel, 1977). These core shales fit the typical black shale depositional model of very slow sedimentation far from detrital influx and from shore in relatively deep water (Algeo, 2008).

The Excello Shale has a large depositional extent (approximately 264,600 km²) including much of the midcontinent region and the Illinois basin (Fig. 2; Wenger, 1987). The Excello Shale is found as far east as Iowa and Missouri, and as far west as Kansas and Oklahoma. This extent is more than 1.5 times larger than other classic core shales, such as the Hushpuckney or Stark Shales. These core shales are thought to have been deposited by glacially driven transgressive high stands. This high stand was caused by melting of a larger portion of the polar ice caps to produce higher water levels leading to a larger area flooding during Excello Shale deposition (Heckel, 1986). The western extent of the Excello Shale was limited by relatively fast subsidence in the Arkoma Basin and the erosion of the Amarillo uplift to the southwest causing conditions unsuitable for preservation. This was due to mixing of the organic rich sediments with those sediments

being eroded from the uplift, in western parts of Oklahoma and Texas (Algeo, 2008). The southeastern extent is limited by the Ouachitas where elevations were too high for deposition to occur even at high stand (Heckel, 1977).

Modern Geochemical Cycling

Carbon

The carbon on the earth's surface is primarily preserved in sedimentary rocks, with nearly 90% being preserved as kerogen, while only 0.1% cycles in active surface pools (Hedges, 1995). These surface pools include dissolved and particulate organic carbon in seawater, atmospheric CO₂, soil carbonate, land plant biomass, soil humus, dissolved organic matter in seawater, and carbon in surface marine sediments. In these surface pools the carbon exists as a mixture of poorly recognizable biochemical and degraded substances (Hedges, 1995).

Riverine influx provides the major conduit for the preservation of terrigenous organic matter in marine sediments. Broad differences exist between terrestrial and marine organic matter. For example, according to Hedges and Keil (1997, pg. 195)

“Terrestrial organic matter, which is generally derived from higher order vascular plants, contains high concentrations of recalcitrant, nitrogen-free biomacromolecules such as lignin, tannin, suberin, and cutin (de Leeuw and Largeau, 1993). These plants also have distinctive stable carbon isotope compositions (Fry and Sherr, 1984) and produce unique lipids (Peltzer and Gagosian, 1989)”

The nitrogen-free biomacromolecules are absent in the lower order marine plants that source the marine organic matter (Garcette-Lepecq et al., 2000). Less than one third of the organic matter delivered via river discharge is preserved in marine sediments, indicating that this organic matter is rapidly remineralized by growing phytoplankton

(Hedges, 1995). The phytoplankton are subsequently grazed by zooplankton and protozoa. Deltaic deposits account for a large amount of the riverine deposition of carbon overall. Of the organic matter that is transported in by rivers the continental slope and shelf contain two to three times more carbon than deltaic deposits. Less than 10% of the global productivity of the total amount of organic matter reaches the ocean floor, and less than 0.5% is preserved in marine sediments. Overall only 0.1% is preserved under anoxic bottom water conditions, although such deposits appear to be the critical precursors to black shale formation (Hedges et al., 1997). Such anoxic environments also appear to be critical in the cycles of uranium and phosphorus.

Uranium

Uranium is a conservative element in seawater and is present in the +4 valence state under oxic conditions. In modern seawater, U is found as the $\text{UO}_2(\text{CO}_3)$ complex, which is very stable and unreactive, leading to its long residence time of 3 to 6×10^5 years (McManus et al., 2005). In contrast to shales, modern sediments contain only a small fraction of the total sedimentary U is found associated with the organic matter in the marine environments (Anderson, 1982; Zheng et al., 2002a). The primary removal method of aqueous U in seawater is uptake across the sediment water interface (Barnes and Cochran, 1990). Under anoxic conditions (i.e., Eh values associated with iron reductions) U(VI) is reduced to U(IV), which is fixed in sediments (McManus et al., 2005). The exact mechanism by which U is fixed in sediments remains unclear. Processes such as bacterial-catalyzed reduction (Lovley et al., 1991), adsorption to organic matter (Adams and Weaver, 1958), and direct precipitation as uraninite (McManus et al., 2005) have all been proposed as critical mechanisms. Regardless,

empirical observations in modern settings (Anderson, 1989; Zheng et al., 2002b) support a model where high concentrations of U in ancient marine sediments are interpreted as representing more reducing environments (Leventhal, 1981, 1986; Wignall and Maynard, 1993; Zheng et al., 2002a, b).

Uranium is also found associated with phosphates; this uranium phosphate relationship is established by the work of Barnes and Cochran (1990). This documented uranium phosphate relationship shows that in high concentrations phosphate can affect the fixation of uranium in some instances, rather than the organic matter in the sediment during preservation (Pliler and Adams, 1962).

Phosphate

Phosphate in the marine system is derived from two primary sources. These sources include new phosphate which enters the system primarily, but not exclusively, via transport from the terrestrial realm in association with organic matter, or recycled phosphate associated with marine organic matter in the water column. Terrestrial phosphate is ultimately derived from weathering of sediments and transport of detrital material by both wind and rivers (Ruttenberg, 2004). The phosphate is then delivered to the sediment by way of settling through the water column, in the form of both inorganic and organic phosphorous and organic matter (Ruttenberg, 1992). The other source of phosphate is recycled phosphate derived from both aerobic and anaerobic microbial processes which act both at the sediment water interface and throughout the water column. During settling, phosphorus can be regenerated to the water column by decay of organic matter through microbial respiration (Ingall et al., 1993). Such phosphorus can be returned to the photic zone by upwelling. The recycled phosphate is ultimately

expelled from surface waters by the formation of fecal pellets which subsequently settles to the seafloor. Note that atmospheric transport is a very minor portion of the phosphate influx, which deposits particles in the water which subsequently filter down through the water column and are deposited in the sediments (Ruttenberg, 2004).

Phosphorus is also found as a critical component of organic matter. Thus, organic matter that survives transport to the sediment-water interface is also subject to aerobic and anaerobic respiration, which results in the buildup of phosphate concentrations in pore waters (Ruttenberg, 2004). Such concentrations can build to levels high enough to cause diffusion of phosphate from pore waters back to bottom waters. Phosphate that is not regenerated by respiration can also be remobilized by sediment transport, and resuspension of sediments (Ruttenberg, 1990). Because of the strong coupling between organic matter and phosphorus the carbon: phosphate ratio (C: P ratio) can be used to fingerprint organic matter sources. For example the C:P ratio of marine phytoplankton is near 106: 1 (Redfield, 1958). However the C: P ratio for terrestrial organic matter tends toward much higher values i.e. 1:800 to 1:2050 (Ingall and Van Cappellen, 1990).

Sedimentary phosphate is found in a variety of phases, both organic and inorganic. Organic phosphate is most commonly found associated with organic matter (Ingall et al., 1990). Inorganic phosphorus is typically separated into different reservoirs by chemical techniques. The typical fractions are: oxide-associated, authigenic, and detrital (Latimer et al., 2006; Ruttenberg, 2004). The oxide-associated phosphate occurs with authigenic iron oxides. The authigenic phosphate occurs as authigenic carbonic fluorapatite, biogenic apatite (organically derived phosphate), and in association with calcium carbonate. This material forms during diagenesis by

cyanobacterial mat growth (Filippelli and Ruttenger, 1997) or released during organic matter decomposition (Ingall and Jahnke, 1997). The detrital phosphate is derived from the weathering of terrestrial material and delivered to the sediments via aeolian or riverine transport.

Spectral Gamma Ray

Gamma radiation is given off by a wide variety of elements. Those of importance to geology are U, K and Th. Common gamma ray detectors use a scintillation crystal which detects ionizing radiation, that is proportional to the relative abundances of each element (Ellis, 1987). Spectral gamma-ray spectrometry (SGR) has the advantage of being a relatively quick (~1-2 minutes) analytical method, using a handheld SGR unit, that requires no sample preparation, beyond removal of weathered material from the outcrop. One disadvantage is the large volume of rock from which gamma rays are measured (21 to 512 cubic inches, EnviSpec Product website). U and Th concentrations are often reported in ppm units, while K is reported in weight % units. However, such concentration units are converted into API values to allow for the comparison of concentration measurements from different brands of detector. API units are based on an artificially radioactive concrete block at the University of Houston, Texas, USA, that is defined to have a radioactivity of 200 American Petroleum Institute (API) units, which is considered to be equivalent to twice the radioactivity of a typical shale. API values are calculated as:

$$\gamma_{API} = 4*Th + 8*U + 16*K \quad (1)$$

where the thorium (Th) and uranium (U) concentrations are in ppm units, and the potassium (K) concentrations are in wt. %. The API units are derived from the study of

average gamma ray readings for typical shale (Belknap, 1959). The Belknap study quantified and normalized the gamma ray readings based on average spectral readings of gray shales.

SGR data is used in a variety of applications. For example, high API readings (> 150 API) are often associated with organic-rich shale beds that contain high U concentrations are known as “hot shales”. Such signals on well logs can be used to correlate subsurface marker beds over basin-scale regions (Asquith, 1982; Doveton, 2004; Hilchie, 1989). Historically, the Th/U ratio has been used to determine depositional environment, including distance to shore given that thorium is sourced only from the detrital pool (Adams and Weaver, 1958; Cochran et al., 1986). These depositional interpretations are based on fundamental differences in the geochemical cycling of U and Th. As discussed above, U is fixed in sediments under anoxic conditions (Pliler and Adams, 1962). Under anoxic conditions, U is found as a uranyl ion, which is fixed in sediments in association with organic matter and/or phosphate. On the other hand, Th is generally unreactive at the Earth’s surface (Goodell, 1986).

Gamma ray measurements have been used in borehole readings since 1939 by Well Services Inc. (Hilchie, 1979). Improvements in gamma ray detectors over time have given the opportunity to gather spectral gamma ray measurements (separate concentrations of U, K, and Th) (Asquith, 1982). The widespread usage of SGR in borehole logging suites and the demonstrated relationship between the uranium and thorium can be used for distance-to-shore calculations. There is a previous study by Schmoker (1981a) showing the use of SGR readings to calculate total organic carbon of the formation. The Schmoker (1981b) study was conducted on Devonian aged shales

throughout the Appalachian Basin. With these historical studies in mind the model I will develop will ultimately be used to determine organic carbon in the subsurface based on the gamma ray logs, or specifically the uranium portion of the gamma ray logs. It is understood there is variation in the strength of this model and the model may not be applicable in all situations, due to facies variations in the shale. My model is constructed using a range of equations that can be applied to further refine the predicted values down hole, which will serve to make the model more accurate for application in different depositional environments. One average equation, based on my model, could be developed for use in the field, for applications where the data gathered is not detailed enough (i.e. total gamma ray rather than SGR) to allow further refinement for application of the model. The use of one equation would make the application process so there is no need to calibrate for each bore hole, giving the advantage to the evaluator with less investment needed to apply the model.

CHAPTER III

METHODOLOGY

Outcrop Investigations

Three outcrops of the Excello Shale were selected Tulsa, Oklahoma, APAC Quarry, Catoosa, Oklahoma, and Oswego, Kansas (Fig. 2). The outcrops were selected to provide a transect of near-shore to deep-water deposition. Also, a fourth outcrop was selected to serve as a test site, for the accuracy of the model. This test site is an example of the Little Osage Shale, which is stratigraphically younger than the Excello, at the Anchor Quarry near Owasso, Oklahoma (Fig. 2). Prior to SGR analysis and sample collection, the outcrops were dugout to a depth of at least 5 to 15 cm to remove the outer weathered material, or until the oxidized and/or discolored shales were removed. Spectral gamma ray measurements were taken every 10 cm for 1 minute using an Exploranium GR 320 enviSPEC

Sample Collection and Preparation

Samples were collected from the same horizons as SGR data was obtained, and stored in plastic zip-loc bags until processed. Samples were first crushed by hand to 1-2 cm using a ceramic mortar and pestle, and further pulverized using a Spex mill with a stainless steel vial set. The samples were pulverized in five-minute intervals until the entire sample would pass through a 2360 micron sieve.

Powdered samples were stored in glass jars capped with Teflon-lined lids.

Carbon Analysis

Total and inorganic carbon concentrations were determined by coulometric titration using a CM 5014 Coulometer. Total carbon (C_{tot}) was determined by combustion at 950°C for 15 minutes, while inorganic carbon (C_{inorg}) concentrations were determined via acidification with 2 N perchloric acid. Total organic carbon (TOC) concentrations were determined by difference, and analyses of calcite standards were better than 95% accurate.

Phosphate Analysis

Analyses of phosphate concentrations were performed in the laboratory of Dr. Jennifer Latimer at Indiana State University. Phosphorus concentrations in four operationally-defined fractions (oxide-associated, detrital, authigenic, and organic) were determined using a sequential leach technique, modified from Ruttenberg (1992) by Anderson (2000). After isolation, P concentrations were quantified using the molybdate blue technique (Mortlock and Froelich, 1989) on a Shimadzu scanning UV-Visible spectrophotometer. This method gives an accuracy of greater than 94% based on replicate analyses.

CHAPTER IV

RESULTS

All of the results are presented in Tables 1 through 4 located in the Appendix. The results are reported by outcrop and arranged by element. Table 1 contains the results from the Tulsa outcrop. Table 2 contains the Oswego outcrop results. Table 3 contains the results from the APAC Quarry outcrop. Table 4 contains the results from the Anchor Quarry outcrop.

The uranium values used in all the plots are only for the authigenic portion of the uranium, calculated using the Post Archean Average Shale (PAAS) value of 0.31 ppm/wt/% and adjusting the concentrations for the calculated authigenic portion (Taylor and McClennan, 1985). The equation to obtain the U_{auth} values is:

$$U_{\text{auth}} = U_{\text{meas}} - (U_{\text{meas}} * 0.31) \quad (2)$$

The authigenic portions only are used to exclude any detrital uranium that may have been detected by the gamma ray unit.

Tulsa

The Tulsa outcrop is 281 cm thick and contains a lithologic succession of micritic limestone, gray shale, limestone, black shale, gray shale, and a second limestone (Fig. 4). The black shale is 100 cm thick and is fissile. The outcrop contains abundant phosphate nodules, which are predominately more round than oblong and range in size from one to three centimeters in diameter. The weathered face of the outcrop has a red brown oxide

stain, while the non- weathered surface is black and smells of hydrocarbons.

Thorium concentrations range from 3.8 ppm to 11.1 ppm, and U concentrations range from 3.1 ppm to 22.7 ppm. Potassium concentrations range between 0.06 and 2.2 wt. %. Calculated API values range between 83.2 and 717.6., with the highest values located in the black shale (Table 1).

The total extractable phosphorous (P_{tot}) concentrations are generally low and vary with lithology, ranging between 2.61 and 369 $\mu\text{mol/g}$ (Fig. 5). The organic phosphorous (P_{org}) concentrations are generally low, ranging between 0 to 45.72 $\mu\text{mol/g}$. The TOC concentrations range from 0.40 to 17.14 wt. %, with the highest value found at 149 cm height above base (Fig. 5).

Oswego

The Oswego, KS outcrop contains a succession of gray shale, black shale, gray shale which is overlain by limestone. The black shale is marked by iron staining on the face of the outcrop, is fissile, and contains phosphate nodules (Fig. 6). The phosphate nodules are more round than oblong and generally range from one to two and a half centimeters in diameter. The measured thickness of the section totals 205 centimeters, with the black shale occupying 125 centimeters of the total section.

Thorium concentrations range from 9.4 ppm to 16.0 ppm, while the U concentrations range from 6.3 ppm to 54.9 ppm (Table 2). The potassium values range from 2.1 to 3.6 wt. %. The calculated API values range between 149.6 and 512.0, with the highest values found in the black shale (Fig. 6).

The total extractable phosphorous (P_{tot}) concentrations are generally low and vary with lithology, specifically, the higher organic contents correlate with the higher phosphate values (Fig. 7), with values ranging from 1.37 to 672.94 $\mu\text{mol/g}$. The organic phosphorous (P_{org}) values range between 0.20 and 6.29 $\mu\text{mol/g}$. The TOC values range from 0 to 25.26 with the highest values occurring at 70 and 97cm above the base (Fig. 7) in the black shale.

APAC Quarry, Catoosa, OK

The lithology of the APAC outcrop is a micritic limestone overlain by a thin black phosphatic shale, overlain by a second micritic limestone (Fig. 8). The black shale is 65 cm thick and has no discernable weathering on the face, given that it has been exposed for a relatively short period of time from the quarrying activities. The black shale is fissile and contains phosphate nodules throughout; nodules are both round and oblong ranging from one to four centimeters in diameter and up to eight centimeters in length. Both the upper and lower limestones contain shell fragments as well.

Thorium concentrations range from 9.2 ppm to 13.8 ppm, while the U concentrations range from 15.6 ppm to 33.9 ppm (Table 3). The potassium concentrations range from 2.4 to 3.3 wt. %. The Calculated API values were the lowest of all three outcrops, ranging between 209.3 and 230.8, with all of the values recorded in the black shale as shown in Figure 8. No readings were taken in the limestone because the lower limestone was the base of the quarry, and the upper limestone was part of a sheer wall and safety regulations did not allow for access to obtain measurements.

The total extractable phosphorous (P_{tot}) concentrations are generally low, with values ranging between 11.74 and 503.44 $\mu\text{mol/g}$. The organic phosphorous (P_{org}) values range between 1.92 to 3.95 $\mu\text{mol/g}$. The TOC values range from 6.31 to 11.91% with the highest value occurring at 20 cm above the base (Fig. 9) in black shale.

Anchor Quarry, Owasso, Oklahoma

The lithology of the Anchor Quarry outcrop is a micritic limestone overlain by a thin black phosphatic shale, overlain by a second micritic limestone (Fig. 10). The black shale is 70 cm thick and has no discernable weathering on the face given, that it has been exposed a relatively short period of time from the quarrying activities. The black shale is fissile and contains phosphate nodules throughout; nodules are both round and oblong ranging from one to four centimeters in diameter and up to six centimeters in length.

Thorium concentrations range from 6.8 ppm to 14.9 ppm, while the U concentrations range from 9.92 ppm to 18.07 ppm (Table 4). The potassium concentrations range from 1.5 to 3.3 wt. % (Fig. 10). The Calculated API values range between 130.6 and 245.3, with all of the values recorded in the black shale as shown in Table 4.

The total extractable phosphorous (P_{tot}) concentrations are generally low, with values ranging between 9.59 and 116.78 $\mu\text{mol/g}$. The organic phosphorous (P_{org}) values range between 1.75 to 3.35 $\mu\text{mol/g}$. The TOC values range from 5.78 to 12.76% (Fig. 11) with the highest value occurring at 25 cm above the base (Table 4) in the black shale.

CHAPTER V

DISCUSSION

Uranium concentrations are thought to be controlled by organic carbon either directly or indirectly, so that spectral gamma ray data may be a good predictor of organic carbon values in the subsurface (Schmoker, 1981a). Uranium is also found associated with phosphate so establishing the strength of the U-TOC relationship will also improve the strength of the model I developed in the subsurface. This study includes outcrop data from south eastern Kansas, and north eastern Oklahoma that represent a transect from near shore to off shore. For the purposes of this discussion, all of the following plots (Fig. 13-23) show only the black shale data (Fig. 2). The gray shale values were excluded in the analysis because anoxia is required for the uranium to be fixed with the total organic carbon in the rocks (Leventhal, 1981). The ichnofacies observations (e.g., homogeneous bedding) preclude the presence of anoxia during deposition of the gray shales.

Depositional Environment

Lithologic Interpretation

The depositional environment of the Excello shale is considered by most workers to be deep-water anoxic marine. Knight (1985) identified the Excello as a core shale from a "Kansas-type" cyclothem, which is defined as a deep-water marine facies in the

original depositional model (Heckel, 1977). Wenger (1987) and Algeo and Maynard (2004) also support this depositional interpretation. Knight (1985) also points to the thinning of the Excello to the south of the type locality in Oklahoma (specifically in Tulsa County—the location of the Tulsa outcrop in this study), as evidence for a relatively shallower depositional environment. The existence of the Schell City – Rich Hill Anticline in northern Oklahoma at the time of deposition may have caused the thinning beds in the Tulsa area (Knight, 1985). The area around the Kansas-Oklahoma boarder is considered to be a topographic low which accounts for thicker deposition in Kansas (Knight, 1985). In this study, the depositional environment of the Excello, specifically water depth, was interpreted based on lithologic observations at each outcrop, supplemented by inferences from geochemical proxies.

The Tulsa site contains 100 centimeters of fissile black shale. The shale also contains several beds of phosphate nodules no more than 5 cm thick (131 cm, 151 cm, 162 cm, and 184 cm above the base), with a sharp contact between the black shale and underlying Breezy Hill Limestone. In contrast, the upper contact grades to a gray shale which has a gradational contact with the overlying Black Jack Creek Limestone. The overlying Black Jack Creek Limestone is 56 centimeters thick, contains few fossils, and has a somewhat blocky appearance. The underlying Breezy Hill Limestone is 55 centimeters thick and, once again contains few fossils, such as mollusks, fusulinids, and echinoderms, and has a weathered gray appearance. A relatively slower rate of regression as compared to the transgression is inferred from the presence of the gray shale at the top of the black shale. The presence of the gray shale is missing from the lower black shale boundary, showing a more rapid transgression.

The Oswego site is interpreted to have been deposited in the deepest water, and therefore, is assumed to be the furthest from shore. The shale unit is 125 cm thick, is fissile with layers of phosphate nodules no more than 5 cm thick (40 cm, 65 cm, 93 cm, 114 cm and 139 cm above the base), with the shale grading from black to gray in color both at the top and bottom contacts. The lower and upper contacts are with the Black Jack Creek Limestone above and the Breezy Hill Limestone below, though the full thicknesses of the limestones were not exposed. The Black Jack Creek Limestone was mildly fossiliferous and contained *Lophophillidium* horn coral. This specific horn coral is found associated with reef environments, and in this case is predominately replaced with calcite. This depositional environment can be interpreted as a reef environment due to the presence of the horn coral (Knight, 1985). The gray shales over and under-lying the black shale member, are interpreted as strong evidence for deposition further from shore than both the Tulsa and APAC Quarry sites. This relatively deeper depositional environment allowed the more gradual change from black to gray shale, to limestone. The change in water depth is not as dramatic or rapid at this site because the change was not as great compared to the water depth. For example, in 100 m of water, a 1 m decrease in sea-level is 1%, but is a 10% change in a water depth of 10 m.

The APAC site is depositionally the most different of the three sites in this study. The black shale unit is only 65 cm thick, is highly siliceous and contains phosphate nodules throughout, rather than at a few discrete intervals. Also, the overlying and underlying limestones are much thicker than at the Tulsa or Oswego sites. The two limestones are approximately 22 feet thick above the shale, and 35 feet below the shale (Chad Browne, 2009, personal communication). The upper Black Jack Creek Limestone

is micritic and fossiliferous, primarily made up of shell hash, with fractures running throughout the unit. The lower Breezy Hill Limestone is micritic with less fossil material and a blockier appearance. It appears that the APAC site is probably a shoal, given the sharp contacts and fossil material contained in the limestones, and relatively thin shale deposit. Thus it is likely that this site is in the shallowest water and therefore closest to shore compared to the Oswego and Tulsa sites.

Interpretation based on Gamma Ray Data

The gamma ray log is a part of the most common set of downhole logs obtained when drilling wells. Gamma ray logs are measured in API units, which are calculated from the concentrations of uranium, potassium and thorium in the rock. Of the three elements measured, the uranium concentrations have the greatest influence on the calculated API values for the samples in this study (Tables 1, 2, and 3). When the concentrations of uranium, potassium, and thorium are measured and reported separately, the result is a spectral gamma ray log. Several interpretational applications have been developed for data on SGR logs, including distance-to shore-calculations (Cochran et al., 1986). The distance-to-shore calculations can be performed using the uranium/ thorium ratio. Historically Adams and Weaver (1958) were the first to show the validity of the uranium/ thorium ratio as a proxy for distance to shoreline. More recently, the work of Cochran and Carey (1986) have supported the earlier findings by Adams and Weaver (1958). The the U/Th ratio generally increases with increasing distance from shore (Adams and Weaver, 1958; Cochran et al., 1986). The U/Th ratios are plotted in Figure 12, and in relative distance to shore the APAC calculates the closest followed by Tulsa, and then Oswego plots relatively furthest from shore. These relative distances are

consistent with the interpretations based on lithologic observations in this case. Since TOC and uranium are sequestered in sediments under similar conditions, the relationship between TOC and uranium is explored next.

Total organic carbon and gamma ray

The uranium and total organic carbon data can be used as the basis for a subsurface predictive model. The spectral gamma ray data was analyzed to assess the correlation between uranium and total organic carbon concentrations. Additionally total gamma ray values were analyzed to establish correlation with the total organic carbon concentrations. The total gamma ray values are assessed because in historical fields, only total gamma ray logs are available rather than spectral gamma ray logs.

Figure 13 shows the correlations between TOC and U for each site. In these rocks, there is generally a good correlation with the exception of the APAC site ($R^2 = 0.35$), with R^2 values ranging from 0.85 to 0.59. The Tulsa site and the Oswego site give the best examples of a possible model to use in borehole situations; the variation between the correlations of these two sites can be accounted for by the difference in distance to shore. I would probably use the site with the highest correlative value which is the Oswego Site. The APAC site is interpreted as the closest site to shore given the relative abundance of Th in the samples and the lower concentrations of U. There is a question as to the validity of the APAC data to use for modeling, because of the low R^2 value ($R^2 = 0.35$) and low sample density. Compare that value to the Oswego and Tulsa sites which have better R^2 values at 0.85 and 0.59 respectively. The lower correlative value of $R^2 = 0.59$ at the Tulsa site can be accounted for by its deposition relatively closer to shore than the Oswego site.

The previous paragraph shows that there is a relationship between the uranium values and the TOC concentrations. Also the relationships between total gamma ray and TOC are examined, because when assessing older areas/fields there most likely is only a total gamma ray log rather than a spectral log for the wells. This will make the model applicable with a wide variety of historical datasets. When the TOC concentrations and the gamma ray values are plotted, using only the black shale values (Fig. 14), the R^2 values range between 0.84 and 0.28. The low correlation value for the APAC site can be accounted for because of its relatively near shore deposition and low data density, characterized by low U concentrations.

Phosphate-Uranium Relationships

Phosphate is found associated with organic matter before and during deposition (Ingall and Van Cappellen, 1990), therefore one would expect to find a strong correlation between the organic phosphate (P_{org}) and the total organic carbon (TOC) concentrations in the black shales. Uranium has also been known to be associated with P_{org} , so that there may also be a relationship between P_{org} and U. The relationship between the U and the P_{org} could vary with the concentration of the P_{org} in rock.

The organic phosphate values were compared with the organic carbon concentrations, using only the data for the black shales at each site (Fig. 15). There is a poor correlation between P_{org} and TOC for each site, with correlation coefficients ranging between 0.02 and 0.0009. This apparent lack of correlation indicates a disassociation between the organic phosphate and the preserved organic matter in the time since deposition, possibly from diagenetic processes deposition and or burial. This

disassociation makes it apparent the phosphate has no direct correlation to the organic carbon.

There is also no correlation between P_{org} and U concentrations (Fig. 16) in the black shales, with correlation coefficients that range between 0.46 and 0.0003. APAC, which has been interpreted to be deposited in a nearshore environment as compared to Tulsa or Oswego, has the highest correlation coefficient at 0.46. The phosphate in this case for APAC may be more closely associated with the uranium because of the sites relative distance to shore. The lower values of TOC in this depositional area allows the phosphate to fix the U as well.

General subsurface model

With the previous examples of uranium and TOC being geochemically related such as the work by Schmoker (1981a); the relationship established between U and TOC in this study can be used to develop a predictive subsurface model. Also the previous cross plots in Figure 14, show there is a relationship between the TOC and the U in the study area. The distance-to-shore proxy calculations given by the U/Th ratios are used to determine in which rocks the proposed model equation is most applicable.

The values obtained when the known data is modeled provides a simplified calculation for TOC concentrations estimates in the rock from uranium concentrations (Fig. 13). The Tulsa site gives a predictive equation:

$$\text{TOC (wt. \%)} = 0.50 X \quad (3)$$

where X is the concentration of U in ppm. At the APAC site the TOC equation is:

$$\text{TOC (wt. \%)} = 0.62X \quad (4)$$

Finally, the Oswego site gives the following equation:

$$\text{TOC (wt. \%)} = 0.46 X \quad (5)$$

These equations were forced through zero because of the assumption that if there is no TOC present then there will be no U fixed. The changes in slope between the three sites are accounted for by the change in distance to shore. The greater the distance to shore, anoxia increases in the bottom waters which allows for greater preservation of TOC, which leads to more U being fixed. With the data from the three outcrop sites, the model gives a range of calculations to be used along a transect that ranges from more shoreward to more basin-ward. For the predicted concentrations of the assessed data TOC values below 5% would be outside of the range of what should be considered to be applicable for this model, because at 5% the shales could model with negative TOC values.

The Little Osage Shale from the Anchor Quarry site is stratigraphically younger than the Excello. This outcrop is geographically three miles from the APAC site. Given its average Th/U ratio of 1:1.16 (Fig. 18), it is interpreted as having been deposited closest to the APAC site but relatively more shoreward as shown in Figure 2. The TOC values calculated from Equation 4 and measured U concentrations are plotted in Figure 19. The variation ranges from as little as 0.36% to 5.17%. Note that as the TOC concentration increases the correlation between the measured and predicted concentrations improves. Such a level of uncertainty is within the range of analytical uncertainties, and appears to be reasonable for evaluation purposes in the field when analyzing gamma ray log signatures for black shale.

Again, on older logs, the total gamma ray values are often the only data available. So, equations between TOC and total gamma ray were also derived. The equations are shown in Figure 14. The equation for the Tulsa site is:

$$\text{TOC (wt. \%)} = 0.045 X \quad (6)$$

with X being the measured API values. The equation for the APAC Quarry site is:

$$\text{TOC (wt. \%)} = 0.040 X \quad (7)$$

The equation for the Oswego site is:

$$\text{TOC (wt. \%)} = 0.046 X \quad (8)$$

The values for the model use equation 7 from the APAC quarry site (Fig. 14). The overall accuracy of concentrations predicted from API values as compared to those calculated from U concentration are more accurate. For the Anchor site, the calculated values differ from the measured values by 0.81 to 4.18 %, with the largest variation in the predicted values from the API calculations being less than those of the U predictions. A correlation between the TOC concentrations and the thorium concentrations could explain this improved correlation (Fig. 20). In Figure 20, the R^2 values for the three sites range from 0.13 to 0.62, and the R^2 values decrease with distance to shore. The APAC data ($R^2 = 0.62$) shows why the data modeled with the total gamma ray values are more accurate. The equations using the API values gives the user more versatility in the field when using such calculations for TOC estimates, given that older logs/wells generally have only total gamma ray values. On a practical note, this also allows for a less expensive way for one to decide whether or not to spend more money to assess the potential of a particular formation for possible development in the petroleum field.

These equations could be very useful in risk analysis, helping to establish the probability of success when applied to the potential source rock. Variables in the risk equation include probability of a source rock, probability of a seal, and probability of a reservoir (Rose, 2001). If used in risk analysis the calculated values from the model are used in one or two of the variables of the risk equation. Depending upon what shale is considered, whether it is the source rock or both the source and reservoir rock, will change the number of variables in the risk analysis that are accounted for by the data.

In the modeled data from the Excello, the gamma ray values were driven by the U concentrations. A second test data set, the Caney Shale, was chosen because it has thorium-driven API values. The second test data set, was used to determine what sort of error might occur in shale units where API values are not driven by U. The second data set is a test to see if it is necessary to recalibrate the model every time a new area is assessed. This test data is an unpublished data set from the Mississippian Caney Shale (Bryan, 2011; Personal Communication). The Th/U ratio for the data set was plotted (Fig. 21). The average Th/U ratio for the Caney Shale is 1.26, which is most similar to the value for APAC = 1.40, so the equation from the APAC site was used to model the Caney data. The equation used was chosen because it was most similar to the Th/U ratio of the test site. The modeled data from the Caney using uranium concentrations shows a large variation from the measured values of 0.04 to 17.66 % (Fig. 22). The calculated TOC values from the Caney using the total gamma ray values show a large variation from the measured values of 0.08 to 22.43 % (Fig. 23). Thus the equations do not work well with the Caney Shale data, despite the similar Th/ U ratios. The change in the primary driving force behind the API values changed the accuracy of the model. This

change is due to the fact that the Th and U are preserved in different ways and different depositional environments. Thorium is found in a single insoluble +4 valence state; this is sourced from surface weathering of resistate minerals (Doveton, 2004; Jones and Manning, 1994). Thorium is found in the detrital fraction of the rock associated with the heavy minerals or clays (Jones and Manning, 1994). Uranium is found in the +4 valence state as well and is predominately lost during weathering of surface minerals, because it is also found in a highly soluble +2 and +6 valence state (Doveton, 2004; Dypvik and Harris, 2001). Different from Th, U is reduced and precipitated or adsorbed on or with organic matter in a reducing environment (Dypvik and Harris, 2001).

CHAPTER VI

CONCLUSION

The hypothesis of this work is that presence of phosphate can also control uranium concentrations in black shales in different depositional environments, rather than total organic carbon. The data gathered for this study showed that the phosphate has no direct bearing on the relationship between uranium and total organic carbon. The results for the phosphate, uranium, and TOC show the complete lack of relationship between these three elements. The hypothesis was refined to U is associated with TOC in shales regardless of the presence of absence of phosphate. The new hypothesis was then used to generate two general mathematical models (Fig 13 and 14) using both U and total gamma ray values to model TOC values in shales. The borehole TOC calculations appear to work well with shales of similar geologic age, and depositional environment. The modeled data using the U concentrations, had predicted values of TOC that range from 0.36 to 5.2% different from the measured concentrations. The model using the API calculations works with relative accuracy of 0.81 to 4.3 % different from the measured concentrations. The model was also tested using the Caney Shale data that has a gamma ray signature driven by Th. This resulted in larger variations from the measured TOC concentrations of up to 22 %. This makes the model a useful tool for an initial evaluation in the case of new shales in similar depositional environments. TOC estimates generated

from the model could prove to be a useful tool to provide a company with a starting point when evaluating shale plays and source rock characteristics. This leaves the evaluator a considerably more economic and time effective stopping point in the process. If the shale proves to have lower TOC values than considered acceptable after the accuracy of the model is taken into consideration, then the evaluation process can be stopped. This model improves the assessment of whether or not more work needs to be done with a particular shale, or whether that particular shale is not worth the extra expense of further evaluation.

The model quality could be improved further still to more data points with increased depositional range and down hole data. The additional data would serve to improve the accuracy of the model. With this improved accuracy, the model would then be tested extensively to see if there is a variation in the accuracy of the model with regards to age, testing with both geologically older and younger rocks would preformed.

In addition to work with improving the quality of the model, work to understand the relationship between the gamma ray and total organic carbon concentrations should be completed. The relationship between the three elements in the study appears to be more complex than first thought at the outset of this work. A better understanding of this relationship could also improve how the model is constructed and therefore further improve the accuracy for application purposes.

REFERENCES

- Adams, J. A. S., and C. E. Weaver, 1958, Thorium-to-uranium ratios as indicators of sedimentary processes; example of concept of geochemical facies, United States, American Association of Petroleum Geologists : Tulsa, OK, United States, p. 387-430.
- Algeo, T. J., 2008, The Late Pennsylvanian Midcontinent Sea of North America; a review, *in* P. H. Heckel, ed., Palaeogeography, Palaeoclimatology, Palaeoecology, Netherlands, Elsevier : Amsterdam, Netherlands, p. 205-221.
- Algeo, T. J., and J. B. Maynard, 2004, Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems: *Chemical Geology*, v. 206, p. 289-318.
- Algeo, T. J., L. Schwark, and J. C. Hower, 2004, High-resolution geochemistry and sequence stratigraphy of the Hushpuckney Shale (Swope Formation, eastern Kansas): implications for climato-environmental dynamics of the Late Pennsylvanian Midcontinent Seaway: *Chemical Geology*, v. 206, p. 259-288.
- Anderson, L. D., 2000, Sequential extraction and analysis of phosphorus in marine sediments; streamlining of the SEDEX procedure, *in* M. L. Delaney, ed., United States, American Society of Limnology and Oceanography : Ann Arbor, MI, United States, p. 509-515.
- Anderson, R. F., 1982, Concentration and flux of particulate uranium in the ocean, *Eos*, Transactions, American Geophysical Union, United States, American Geophysical Union : Washington, DC, United States, p. 82-82.
- Anderson, R. F., 1989, Concentration, oxidation state, and particulate flux of uranium in the Black Sea, *in* M. Q. Fleisher, and A. P. LeHuray, eds., *Geochimica et Cosmochimica Acta*, International, Pergamon : Oxford, International, p. 2215-2224.
- Asquith, G. B., 1982, Basic well log analysis for geologists *Methods in exploration series*: United States, Am. Assoc. Pet. Geol. : Tulsa, OK, United States.
- Barnes, C. E., and J. K. Cochran, 1990, Uranium removal in oceanic sediments and the oceanic U balance: *Earth and Planetary Science Letters*, v. 97, p. 94-101.
- Belknap, W. B., et al., 1959, API Calibration Facility for Nuclear Logs: *Drilling and Production Practices*, Houston, API.
- Brumsack, H. J., 1980, Geochemistry of Cretaceous black shales from the Atlantic Ocean (DSDP Legs 11, 14, 36 and 41): *Chemical Geology*, v. 31, p. 1-25.
- Cochran, J. K., A. E. Carey, E. R. Sholkovitz, and L. D. Surprenant, 1986, The geochemistry of uranium and thorium in coastal marine sediments and sediment pore waters: *Geochimica et Cosmochimica Acta*, v. 50, p. 663-680.

- Cruse, A. M., and T. W. Lyons, 2004, Trace metal records of regional paleoenvironmental variability in Pennsylvanian (Upper Carboniferous) black shales: *Chemical Geology*, v. 206, p. 319-345.
- Doveton, J. H., 2004, Borehole petrophysical chemostratigraphy of Pennsylvanian black shales in the Kansas subsurface, *in* D. F. Merriam, ed., *Chemical Geology*, Netherlands, Elsevier : Amsterdam, Netherlands, p. 249-258.
- Doveton, J. H., and D. F. Merriam, 2004, Borehole petrophysical chemostratigraphy of Pennsylvanian black shales in the Kansas subsurface: *Chemical Geology*, v. 206, p. 249-258.
- Dypvik, H., and N. B. Harris, 2001, Geochemical facies analysis of fine-grained siliciclastics using Th/U, Zr/Rb and (Zr+Rb)/Sr ratios: *Chemical Geology*, v. 181, p. 131-146.
- Elbaz-Poulichet, F., J. L. Seidel, D. Jézéquel, E. Metzger, F. Prévot, C. Simonucci, G. Sarazin, E. Viollier, H. Etcheber, J.-M. Jouanneau, O. Weber, and O. Radakovitch, 2005, Sedimentary record of redox-sensitive elements (U, Mn, Mo) in a transitory anoxic basin (the Thau lagoon, France): *Marine Chemistry*, v. 95, p. 271-281.
- Ellis, D. V., 1987, *Well logging for earth scientists*: New York, Elsevier, xiv, 532 p. p.
- Feldman, H. R., 2005, Impact of longer-term modest climate shifts on architecture of high-frequency sequences (cyclothems), Pennsylvanian of Midcontinent U.S.A, *in* E. K. Franseen, R. M. Joeckel, and P. H. Heckel, eds., *Journal of Sedimentary Research*, United States, Society of Economic Paleontologists and Mineralogists : Tulsa, OK, United States, p. 350-368.
- Filippelli, G. M., 1997, Controls on phosphorus concentration and accumulation in oceanic sediments, Netherlands, Elsevier : Amsterdam, Netherlands, p. 231-240.
- Filippelli, G. M., and K. C. Ruttenberg, 1997, Phosphorous cycling and sedimentation in marine and freshwater systems: *Marine Geology*, v. 139, p. 1-4.
- Garcette-Lepecq, A., S. Derenne, C. Largeau, I. Bouloubassi, and A. Saliot, 2000, Origin and formation pathways of kerogen-like organic matter in recent sediments off the Danube delta (northwestern Black Sea): *Organic Geochemistry*, v. 31, p. 1663-1683.
- Gelinas, Y., 2001, Organic carbon composition of marine sediments; effect of oxygen exposure on oil generation potential, *in* J. A. Baldock, and J. I. Hedges, eds., *Science*, United States, American Association for the Advancement of Science : Washington, DC, United States, p. 145-148.
- Goodell, P. C., 1986, Differential geochemical mobility of uranium, thorium, and potassium used as geologic environment indicators and explorations tools, *AAPG Bulletin*, United States, American Association of Petroleum Geologists : Tulsa, OK, United States, p. 595-596.
- Heckel, P. H., 1977, Origin of phosphatic black shale facies in Pennsylvanian cyclothems of mid-continent North America, *AAPG Bulletin*, United States, American Association of Petroleum Geologists : Tulsa, OK, United States, p. 1045-1068.
- Heckel, P. H., 1980, Paleogeography of eustatic model for deposition of Mid-Continent Upper Pennsylvanian cyclothems, *AAPG Bulletin*, United States, American Association of Petroleum Geologists : Tulsa, OK, United States, p. 721-721.
- Heckel, P. H., 1986, Sea-level curve for Pennsylvanian eustatic marine transgressive-regressive depositional cycles along Midcontinent outcrop belt, North America, *Geology* [Boulder], United States, Geological Society of America (GSA) : Boulder, CO, United States, p. 330-334.
- Hedges, J. I., 1995, Sedimentary organic matter preservation; an assessment and speculative

- synthesis, *in* R. G. Keil, ed., *Marine Chemistry*, Netherlands, Elsevier : Amsterdam, Netherlands, p. 81-115.
- Hedges, J. I., R. G. Keil, and R. Benner, 1997, What happens to terrestrial organic matter in the ocean?: *Organic Geochemistry*, v. 27, p. 195-212.
- Hilchie, D. W., 1979, *Old electrical log interpretation: United States*, IED Explor. : Tulsa, OK, United States.
- Hilchie, D. W., 1989, *Advanced well log interpretation: United States*, Douglas W. Hilchie : Boulder, CO, United States.
- Ingall, E., and R. Jahnke, 1997, Influence of water-column anoxia on the elemental fractionation of carbon and phosphorus during sediment diagenesis: *Marine Geology*, v. 139, p. 219-229.
- Ingall, E. D., R. M. Bustin, and P. Van Cappellen, 1993, Influence of water column anoxia on the burial and preservation of carbon and phosphorus in marine shales: *Geochimica et Cosmochimica Acta*, v. 57, p. 303-316.
- Ingall, E. D., P. A. Schroeder, and R. A. Berner, 1990, Characterization of organic phosphorus in marine sediments by ³¹P NMR: *Chemical Geology*, v. 84, p. 220-223.
- Ingall, E. D., and P. Van Cappellen, 1990, Relation between sedimentation rate and burial of organic phosphorus and organic carbon in marine sediments: *Geochimica et Cosmochimica Acta*, v. 54, p. 373-386.
- Jones, B., and D. A. C. Manning, 1994, Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones: *Chemical Geology*, v. 111, p. 111-129.
- Klein, G. D., and J. B. Kupperman, 1992, Pennsylvanian cyclothems; methods of distinguishing tectonically induced changes in sea level from climatically induced changes, *Geological Society of America Bulletin*, United States, Geological Society of America (GSA) : Boulder, CO, United States, p. 166-175.
- Knight, K. L., 1985, *Stratigraphy, depositional and diagenetic history of three Middle Pennsylvanian cyclothems (Breezy Hill and Fort Scott limestones)*, Midcontinent North America, United States.
- Latimer, J. C., G. M. Filippelli, I. Hendy, and D. R. Newkirk, 2006, Opal-associated particulate phosphorus: Implications for the marine P cycle: *Geochimica et Cosmochimica Acta*, v. 70, p. 3843-3854.
- Leventhal, J. S., 1981, Pyrolysis gas chromatography-mass spectrometry to characterize organic matter and its relationship to uranium content of Appalachian Devonian black shales: *Geochimica et Cosmochimica Acta*, v. 45, p. 883-889.
- Leventhal, J. S., 1986, Organic geochemical analysis of sedimentary organic matter associated with uranium, *in* T. A. Daws, and J. S. Frye, eds., *Applied Geochemistry*, International, Pergamon : Oxford-New York-Beijing, International, p. 241-247.
- Lovley, D. R., E. J. P. Phillips, Y. A. Gorby, and E. R. Landa, 1991, Microbial reduction of uranium: *Nature*, v. 350, p. 413-416.
- McManus, J., W. M. Berelson, G. P. Klinkhammer, D. E. Hammond, and C. Holm, 2005, Authigenic uranium: Relationship to oxygen penetration depth and organic carbon rain: *Geochimica et Cosmochimica Acta*, v. 69, p. 95-108.
- Mortlock, R. A., and P. N. Froelich, 1989, A simple method for the rapid determination of biogenic opal in pelagic marine sediments: *Deep Sea Research Part A. Oceanographic Research Papers*, v. 36, p. 1415-1426.

- Murphy, A. E., B. B. Sageman, D. J. Hollander, T. W. Lyons, and C. E. Brett, 2000, Black shale deposition and faunal overturn in the Devonian Appalachian Basin; clastic starvation, seasonal water-column mixing, and efficient biolimiting nutrient recycling, *Paleoceanography*, United States, American Geophysical Union : Washington, DC, United States, p. 280-291.
- Pedersen, T. F., and S. E. Calvert, 1990, Anoxia vs productivity; what controls the formation of organic-carbon-rich sediments and sedimentary rocks?, *AAPG Bulletin*, United States, American Association of Petroleum Geologists : Tulsa, OK, United States, p. 454-466.
- Pliler, R., and J. A. S. Adams, 1962, The distribution of thorium and uranium in a Pennsylvanian weathering profile: *Geochimica et Cosmochimica Acta*, v. 26, p. 1137-1146.
- Redfield, A. C., 1958, The biological control of chemical factors in the environment, United States, Sigma Xi, The Scientific Research Society : New Haven, CT, United States, p. 205-221.
- Ruttenberg, K. C., 1990, Diagenesis and burial of phosphorus in marine sediments; implications for the marine phosphorus budget, United States.
- Ruttenberg, K. C., 1992, Development of a sequential extraction method for different forms of phosphorus in marine sediments, *Limnology and Oceanography*, United States, American Society of Limnology and Oceanography : Ann Arbor, MI, United States, p. 1460-1482.
- Ruttenberg, K. C., 2004, The global phosphorus cycle *Treatise on geochemistry*: United Kingdom, Elsevier : Oxford, United Kingdom, 585-643 p.
- Sageman, B. B., 2003, A tale of shales; the relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, Middle-Upper Devonian, Appalachian Basin, *in* A. E. Murphy, J. P. Werne, C. A. Ver Straeten, D. J. Hollander, and T. W. Lyons, eds., *Chemical Geology*, Netherlands, Elsevier : Amsterdam, Netherlands, p. 229-273.
- Schmoker, J. W., 1981a, Determination of organic-matter content of Appalachian Devonian shales from gamma-ray logs, *AAPG Bulletin*, United States, American Association of Petroleum Geologists : Tulsa, OK, United States, p. 1285-1298.
- Schmoker, J. W., 1981b, Determination of organic-matter content of Devonian shale, U. S. Geological Survey Professional Paper, United States, U. S. Geological Survey : Reston, VA, United States, p. 37-37.
- Taylor, S. R., and S. M. McClennan, 1985, The continental crust; its composition and evolution; an examination of the geochemical record preserved in sedimentary rocks *Geoscience texts*: United Kingdom, Blackwell Sci. Publ. : Oxford, United Kingdom.
- Tourtlot, H. A., and A. L. Meier, 1976, Lithium in clayey rocks of Pennsylvanian age, western Pennsylvania, United States, U. S. Geological Survey : Reston, VA, United States, p. 128-137.
- Vine, J. D., and E. B. Tourtelot, 1970, Geochemistry of black shale deposits; a summary report, United States, Economic Geology Publishing Company : Lancaster, PA, United States, p. 253-272.
- Volkov, I. I., 1984, Organic matter consumption during anaerobic diagenesis in world ocean sediments: *Geochemistry International*, v. 21, p. 146-157.
- Wanless, H. R., and F. P. Shepard, 1936, Sea level and climatic changes related to late Paleozoic cycles, *Geological Society of America Bulletin*, United States, Geological Society of America (GSA) : Boulder, CO, United States, p. 1177-1206.
- Weller, J. M., 1930, Cyclical sedimentation of the Pennsylvanian period and its significance,

- Journal of Geology, United States, University of Chicago Press : Chicago, IL, United States, p. 97-135.
- Wenger, L. M., D. R. Baker, H. M. Chung, and T. H. McCulloh, 1988, Environmental control of carbon isotope variations in Pennsylvanian black-shale sequences, Midcontinent, U.S.A, Organic Geochemistry, International, Pergamon : Oxford-New York, International, p. 765-771.
- Wenger, L. M., Jr., 1987, Variations in organic geochemistry of anoxic-oxic black shale-carbonate sequences in the Pennsylvanian of the Midcontinent, U.S.A, United States.
- Wignall, P. B., and J. R. Maynard, 1993, The sequence stratigraphy of transgressive black shales, AAPG Studies in Geology, United States, American Association of Petroleum Geologists : Tulsa, OK, United States, p. 35-47.
- Zheng, Y., R. F. Anderson, A. van Geen, and M. Q. Fleisher, 2002a, Preservation of particulate non-lithogenic uranium in marine sediments: *Geochimica et Cosmochimica Acta*, v. 66, p. 3085-3092.
- Zheng, Y., R. F. Anderson, A. van Geen, and M. Q. Fleisher, 2002b, Remobilization of authigenic uranium in marine sediments by bioturbation: *Geochimica et Cosmochimica Acta*, v. 66, p. 1759-1772.

TABLES

Table 1. Tulsa, OK Outcrop Data

Sample No.	Sample Ht. (cm)	K (wt. %)	Th (ppm)	U AUTH ⁺ (ppm)	Total GR* (API units ¹)	Total P (umol/g)	Organic P (umol/g)	TOC (wt. %)	U/Th Ratio
8060701	45	1.3	4.4	5.7	84.0	16.96	1.35	2.59	1.30
8060702	60	1.6	7.6	4.8	94.4	22.84	6.43	1.36	0.63
8060703	109	0.7	6.0	3.9	66.4	20.67	0.00	0.41	0.65
8060704	123	0.8	6.1	5.8	83.6	44.26	0.00	1.07	0.95
8060705	133	1.1	7.3	8.5	114.8	69.89	15.86	2.01	1.16
8060706	148	2.9	13.3	27.0	315.6	120.91	45.72	15.01	2.03
8060713	167	2.8	13.3	27.0	314.0	7.94	2.88	0.45	2.03
8060712	188	2.9	12.0	30.8	340.8	19.28	10.47	15.81	2.57
8060711	195	2.5	11.4	31.9	340.8	3.83	1.38	15.39	2.80
8060710	211	2.6	12.9	30.7	338.8	3.88	0.71	16.34	2.38
8060709	220	3.0	16.6	23.8	304.8	5.35	0.00	17.14	1.43
8060708	223	2.7	14.0	21.4	270.4	14.37	3.03	15.27	1.53
8060707	235	2.4	11.5	19.0	236.4	59.91	1.82	16.73	1.65

+ Calculated according to equation 2 (see text for discussion)

* GR: gamma Ray

¹ Equation 1 (see text)

Table 2. Oswego, KS Outcrop Data

Sample No.	Sample Ht. (cm)	K (wt.%)	Th (ppm)	U AUTH ⁺ (ppm)	Total GR* (API units ¹)	Total P (umol/g)	Organic P (umol/g)	TOC (wt. %)	U/Th Ratio
8230801	5	2.2	13.6	8.8	159.7	7.15	0.79	0.35	0.64
8230802	20	2.8	15.2	9.0	177.7	5.95	0.84	1.08	0.59
8230803	30	3.0	16.0	14.9	231.5	32.32	2.10	1.25	0.93
8230804	52	2.7	13.1	27.6	316.4	672.94	6.79	14.53	2.11
8230805	62	2.5	12.4	34.3	363.8	193.38	2.74	22.49	2.76
8230806	70	2.2	9.4	54.3	506.8	1.37	0.20	25.26	5.77
8230807	80	2.1	14.1	44.0	442.4	59.34	2.76	15.76	3.12
8230808	90	2.9	12.9	31.8	352.3	57.93	3.54	14.59	2.46
9200802	97	2.7	15.0	35.7	389.1	104.43	2.97	24.03	2.38
9200803	107	3.1	10.5	30.0	331.3	19.52	1.29	17.12	2.85
9200804	118	2.9	9.9	20.1	247.1	5.69	1.53	12.42	2.03
9200805	127	3.1	11.3	8.3	161.3	18.98	1.98	2.81	0.74
9200806	147	3.3	11.2	6.4	148.4	9.57	2.43	0.68	0.57
9200807	157	3.6	10.4	5.3	141.4	24.71	3.27	0.00	0.51

+ Calculated according to equation 2 (see text for discussion)

* GR: gamma Ray

¹ Equation 1 (see text)

Table 3. APAC Quarry, Catoosa, OK data table

Sample No.	Sample Ht. (cm)	K (wt. %)	Th (ppm)	U AUTH ⁺ (ppm)	Total GR* (API units ¹)	Total P (umol/g)	Organic P (umol/g)	TOC (wt. %)	U/Th Ratio
2040901	5	2.4	9.2	16.0	203.1	9.82	1.92	11.905	1.74
2040902	20	3.3	13.8	17.0	244.1	509.32	3.95	10.9881	1.23
2040903	36	2.6	11.7	16.9	223.6	519.76	2.46	6.3062	1.44
2040904	43	2.4	11.3	15.7	208.8	529.90	2.05	11.4275	1.38

+ Calculated according to equation 2 (see text for discussion)

* GR: gamma Ray

¹Equation 1 (see text)

Table 4. Anchor Quarry, Owasso, OK Data Table.

Sample No.	Sample Ht. (cm)	K (wt.%)	Th (ppm)	U AUTH ⁺ (ppm)	Total GR* (API units ¹)	Total P (umol/g)	Organic P (umol/g)	TOC (wt. %)	U/Th Ratio
11210801	5	1.5	6.8	9.92	130.6	10.48	1.87	8.79	1.46
11210802	15	3.3	12.3	10.72	187.8	9.35	2.04	11.43	0.87
11210803	25	2.8	12.2	11.76	187.7	5.62	1.75	12.47	0.96
11210804	37	3	14.9	17.21	245.3	7.46	2.12	10.97	1.15
11210805	47	3	12.1	18.07	241.0	16.35	1.92	12.32	1.49
11210806	55	2.3	12.5	15.36	209.6	113.43	3.35	5.79	1.23

+ Calculated according to equation 2 (see text for discussion)

* GR: gamma Ray

¹ Equation 1 (see text)

FIGURES

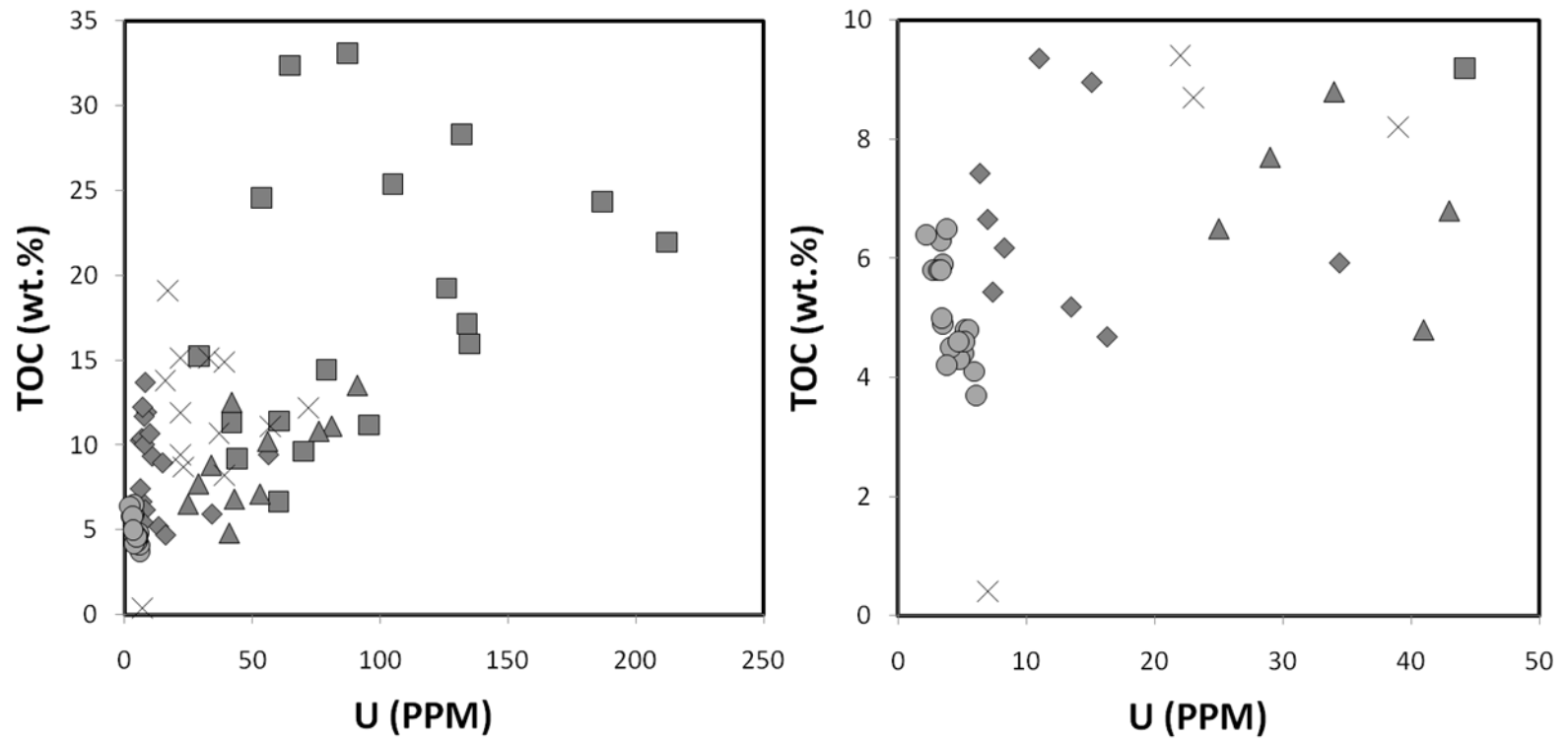


Fig.1. Data from Cruse and Lyons (2004) Pennsylvanian (Squares (Hushpuckney) and Diamonds (Coffeyville Fm.)), Leventhal (1981) Devonian and Mississippian (Triangles (Devonian Shales) and X's (Sunbury and Ohio Shales)), and Elbaz-Poulichet (2005) (Circles (C5 Data set)). A) Shows all data plotted in large scale B) Shows a close up view of the Elbaz-Poulichet data (circles) showing the correlation between the U and TOC.

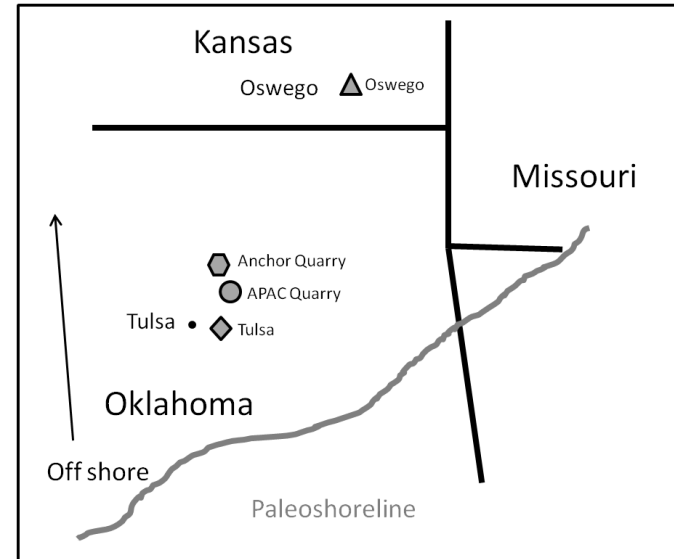


Fig. 2. United States map showing paleoshoreline and depositional extent of the Excello shale modified from (Blakely, 2011). Study area map showing sample sites and the interpreted paleoshoreline.

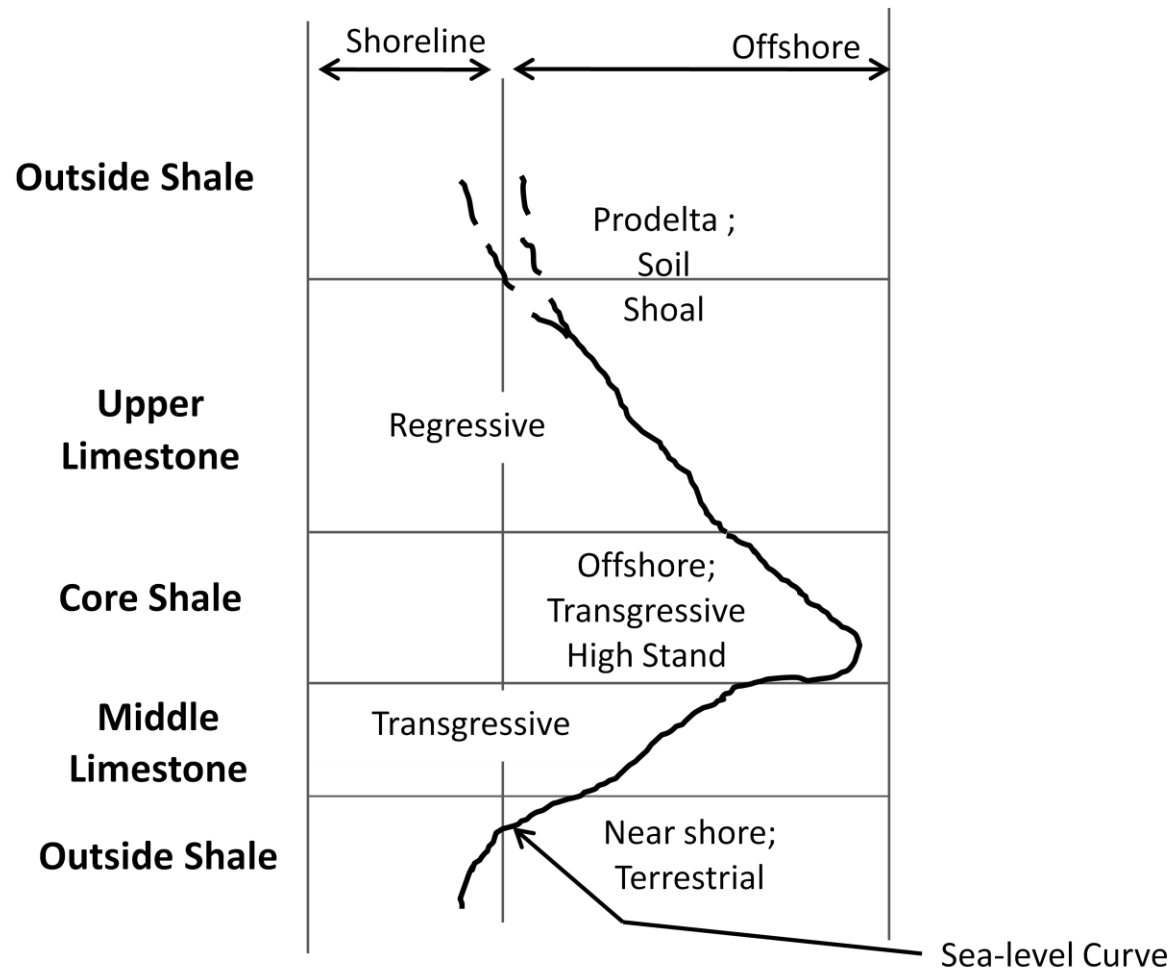


Fig.3. Model of a typical “Kansas-type” cyclothem, showing an interpreted sea-level curve. Modified from Heckel (1977).

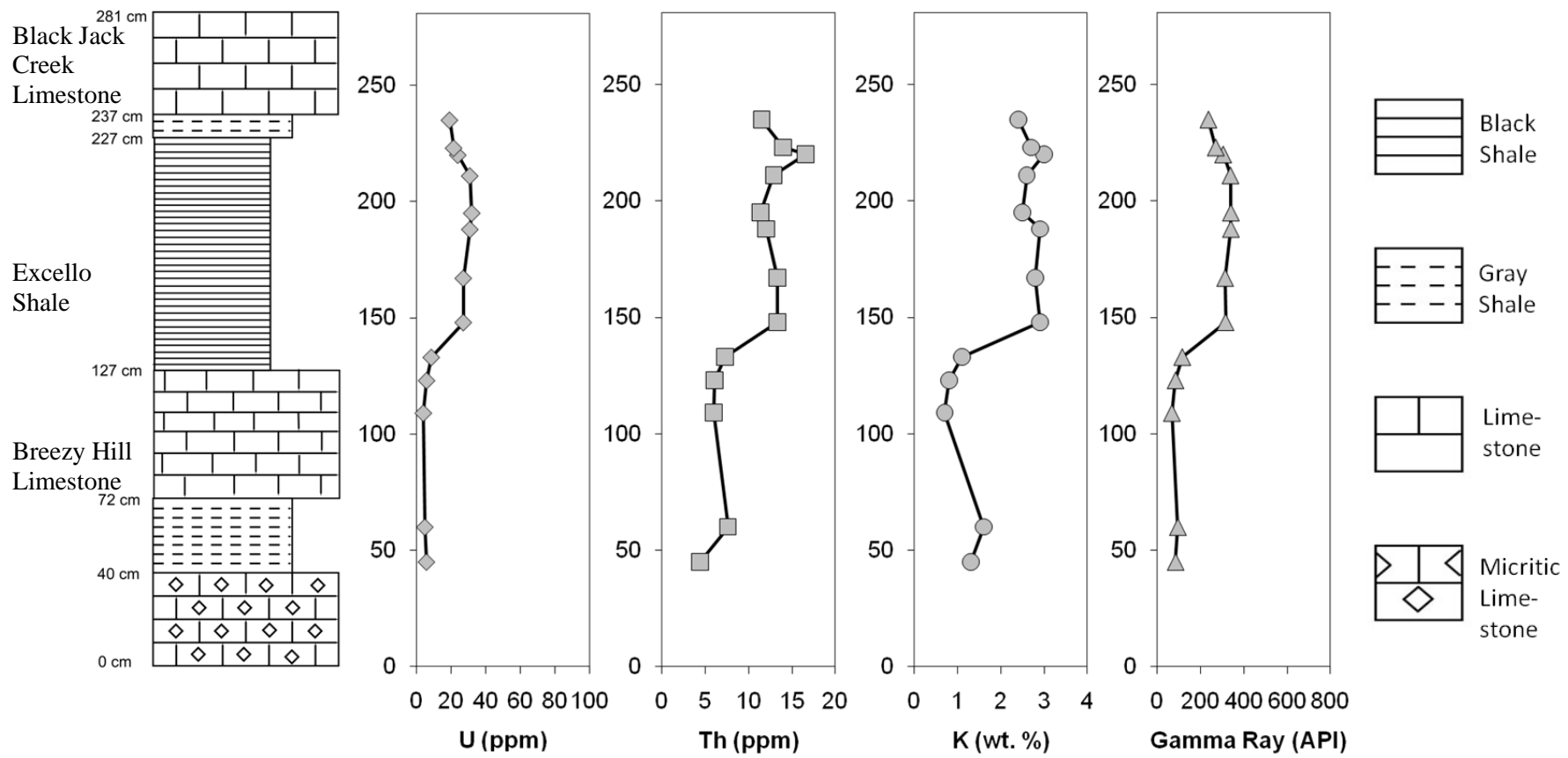


Fig. 4 Plots of the spectral gamma ray data at the Tulsa site in scale with the stratigraphic column.

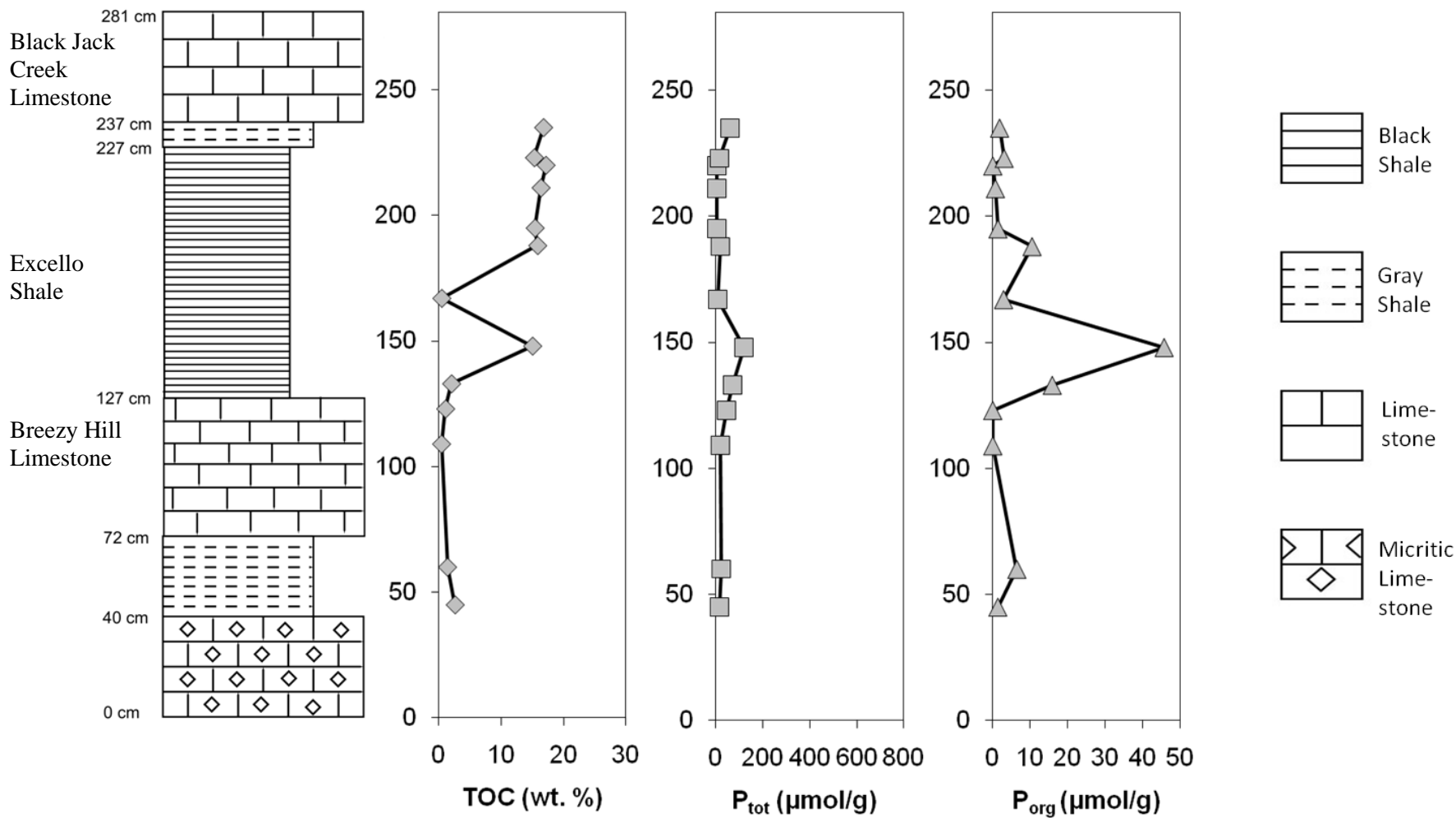


Fig. 5. Plots showing the phosphate and TOC data at the Tulsa site. Note the low data point in the black shale is a gray shale stringer.

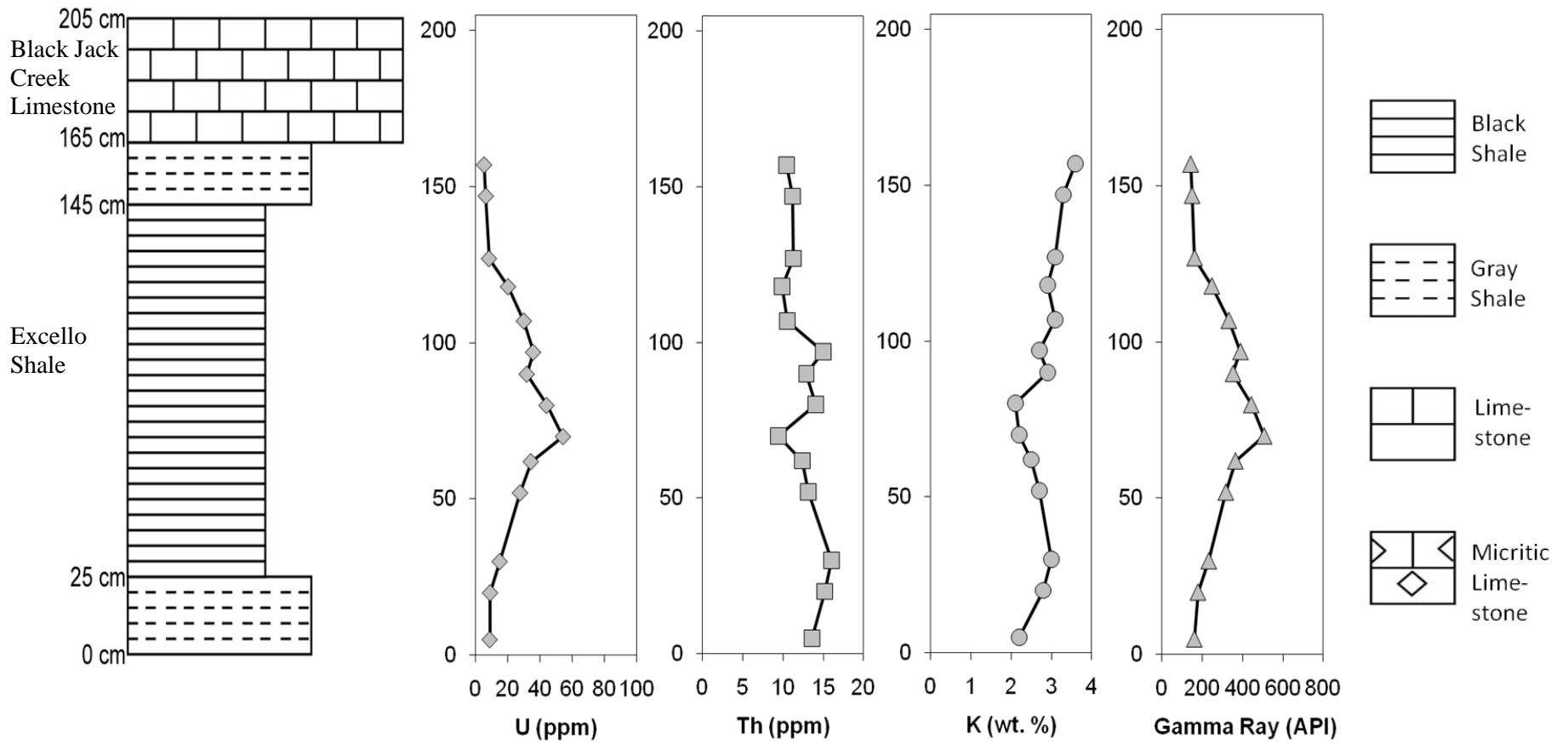


Fig. 6. Plots of the spectral gamma ray data at the Oswego site.

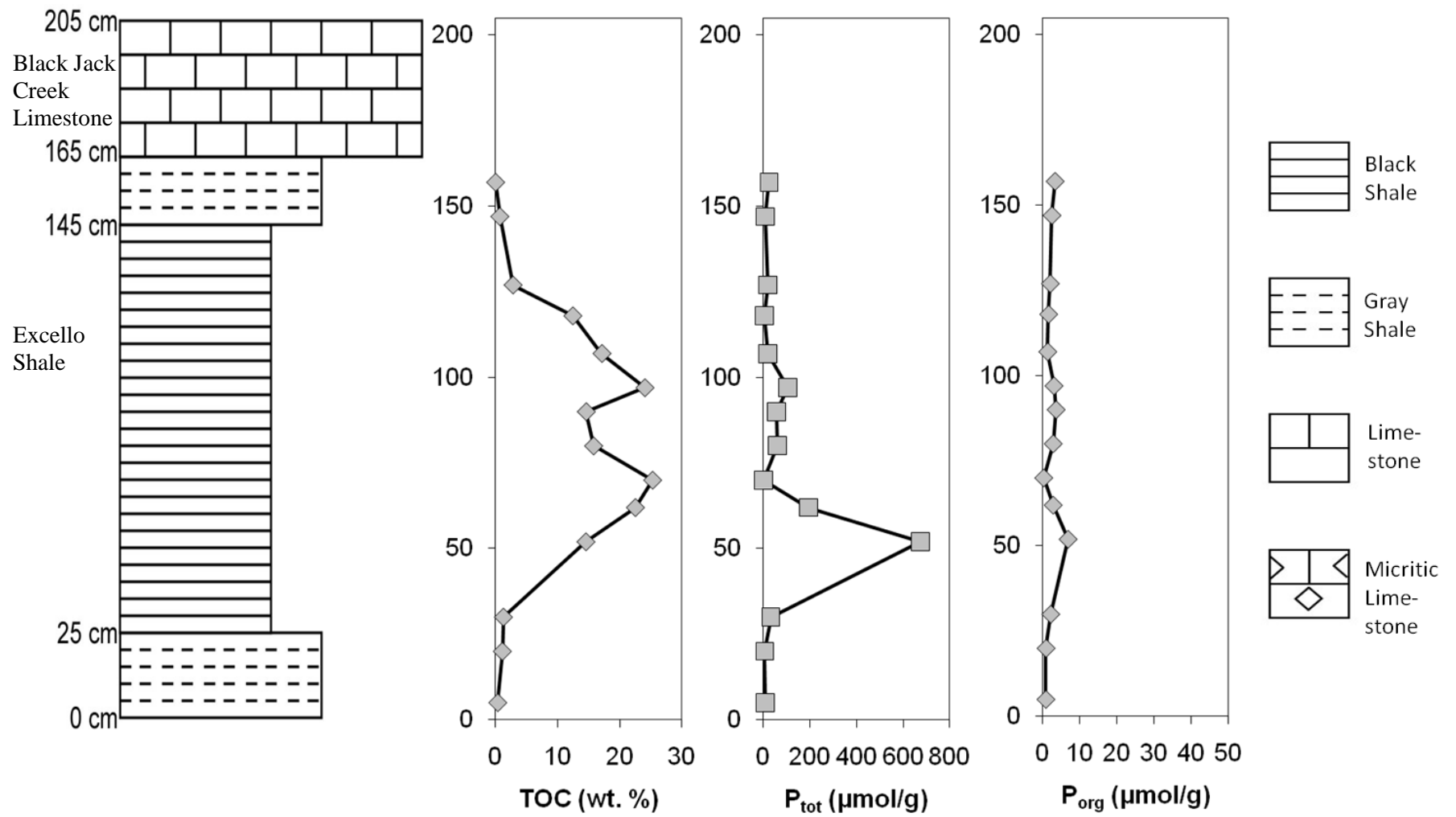


Fig. 7. Plots showing the phosphate and TOC data at the Oswego site.

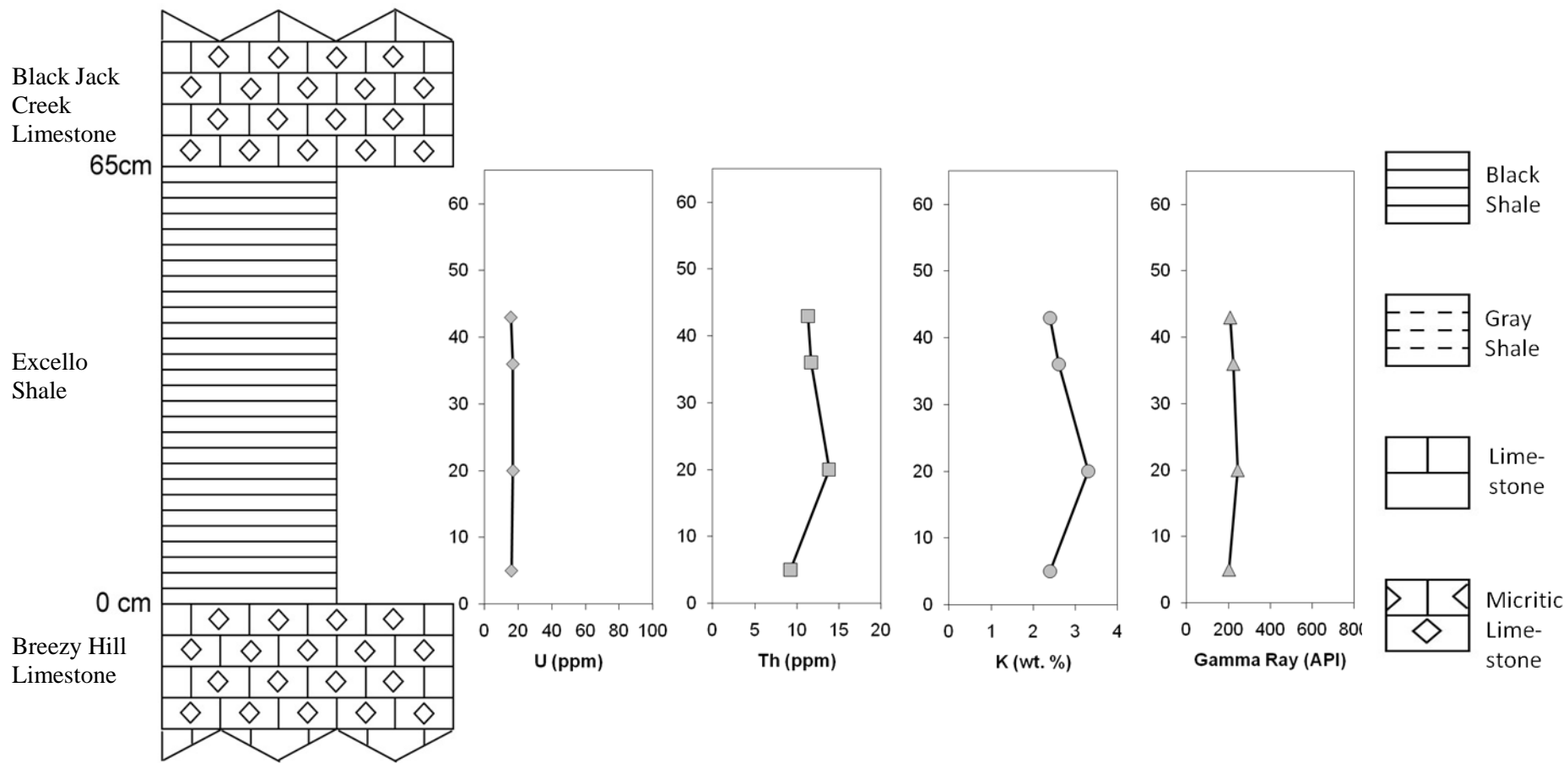


Fig. 8. Plots of the spectral gamma ray data at the APAC Quarry site.

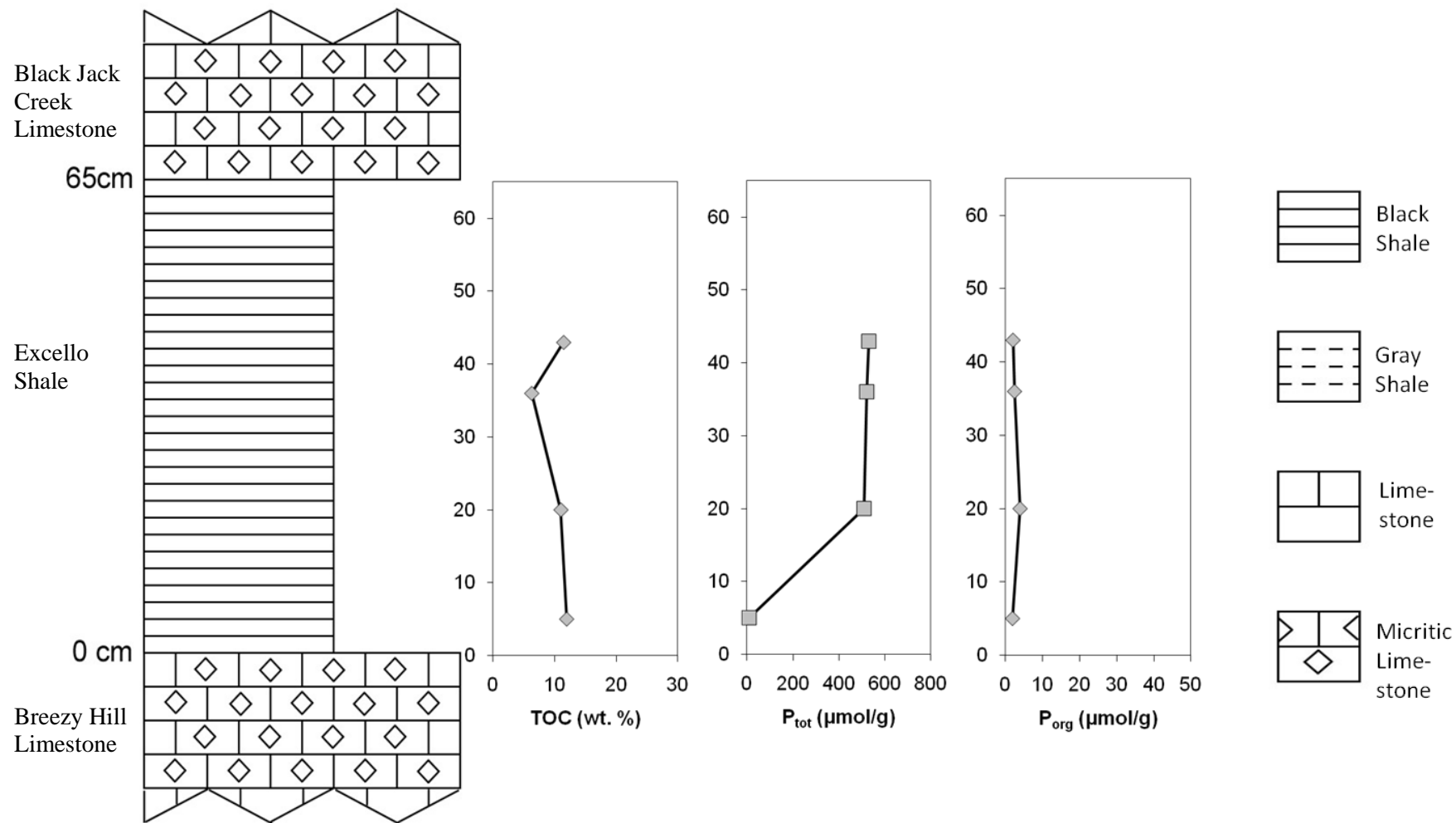


Fig. 9. Plots showing the phosphate and TOC data at the APAC Quarry site in scale.

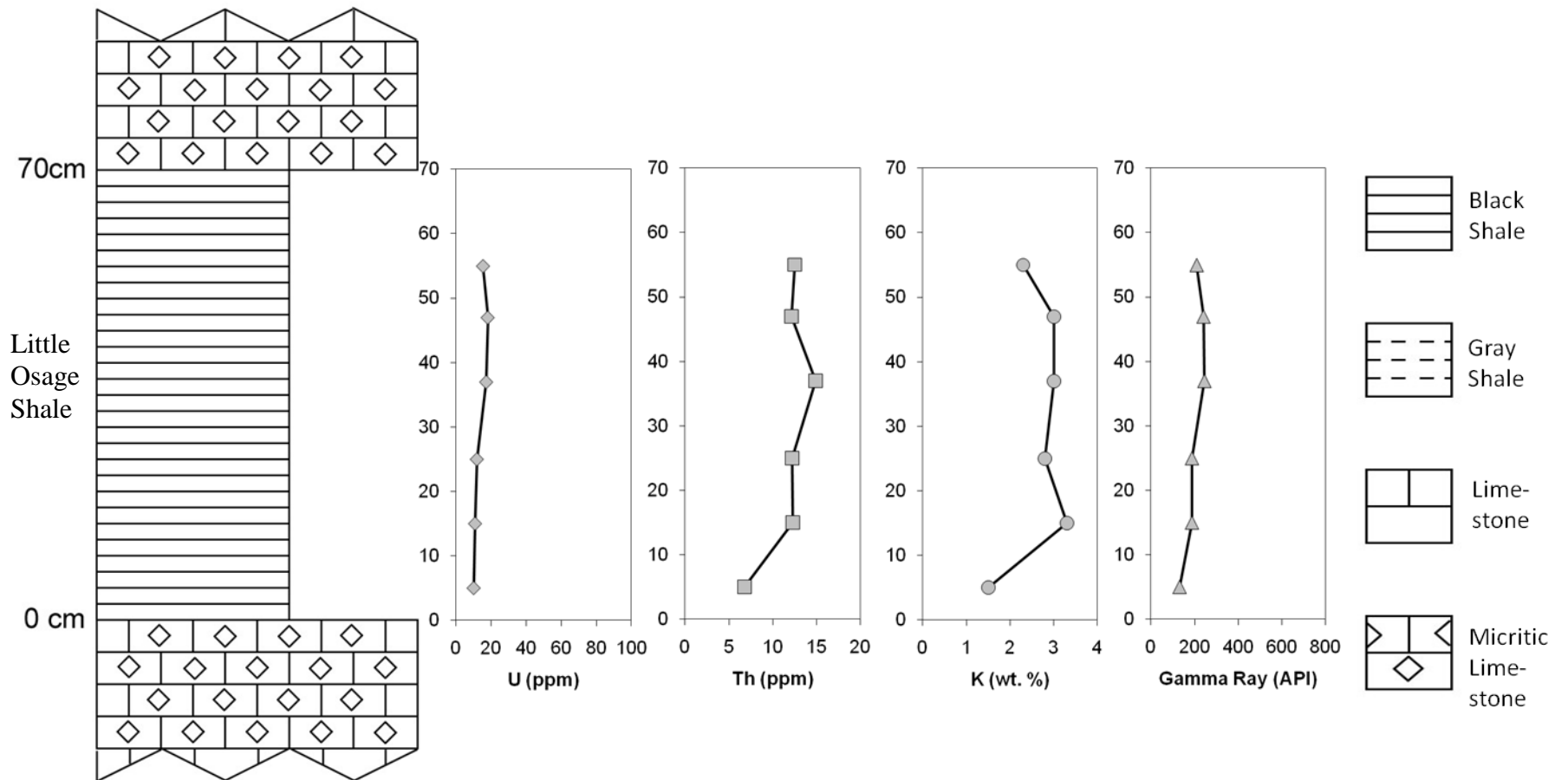


Fig. 10. Plots of the spectral gamma ray data at the Anchor Quarry site.

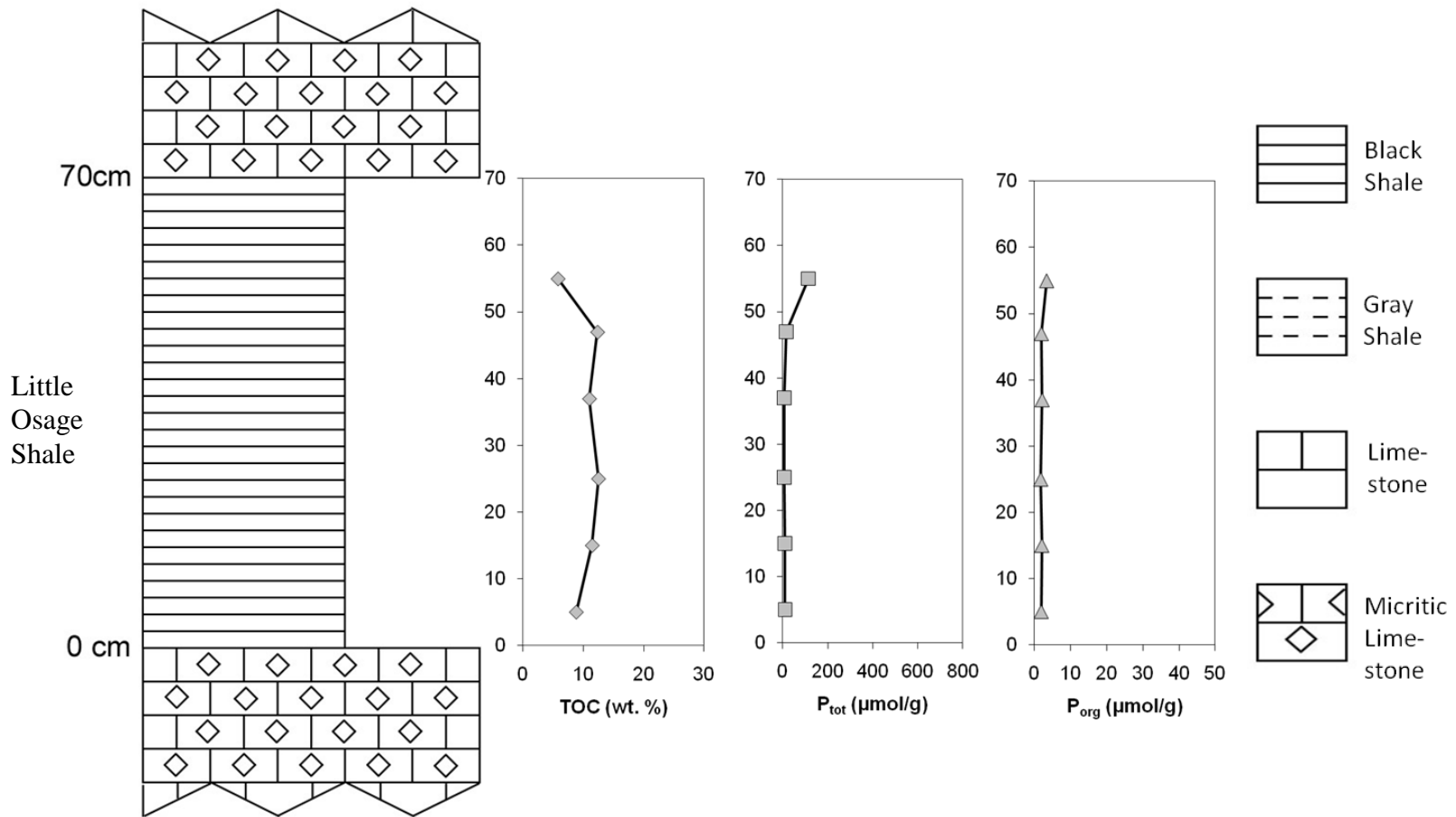


Fig. 11. Plots showing the phosphate and TOC data at the Anchor Quarry site.

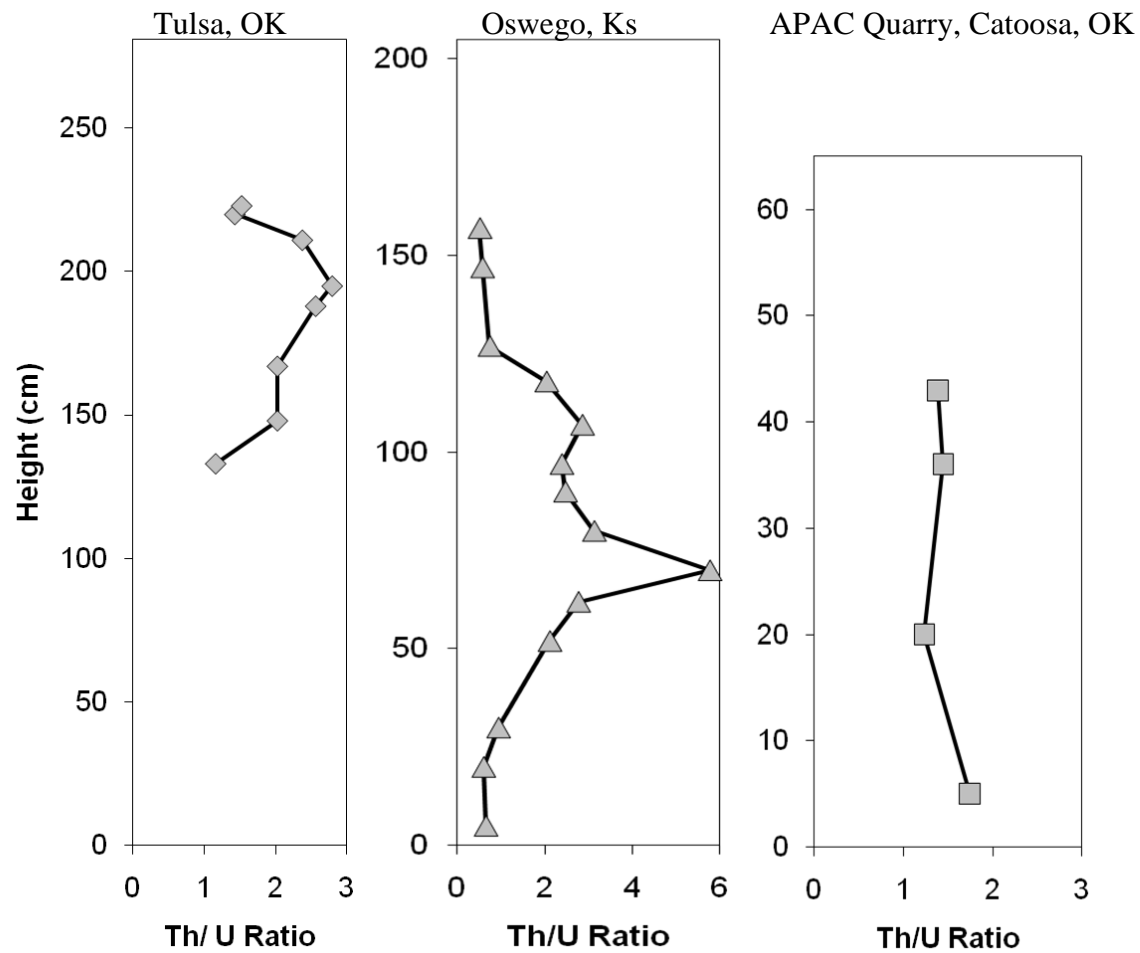


Fig. 12. Plots of Th/U ratios versus height giving proxy distance to shore, A) Tulsa, shown in diamond with an average of 1.99 , B) Oswego shown in Triangles with an average of 1.82, and C) APAC shown in squares with an average of 1.40. Notice that the data are not in scale.

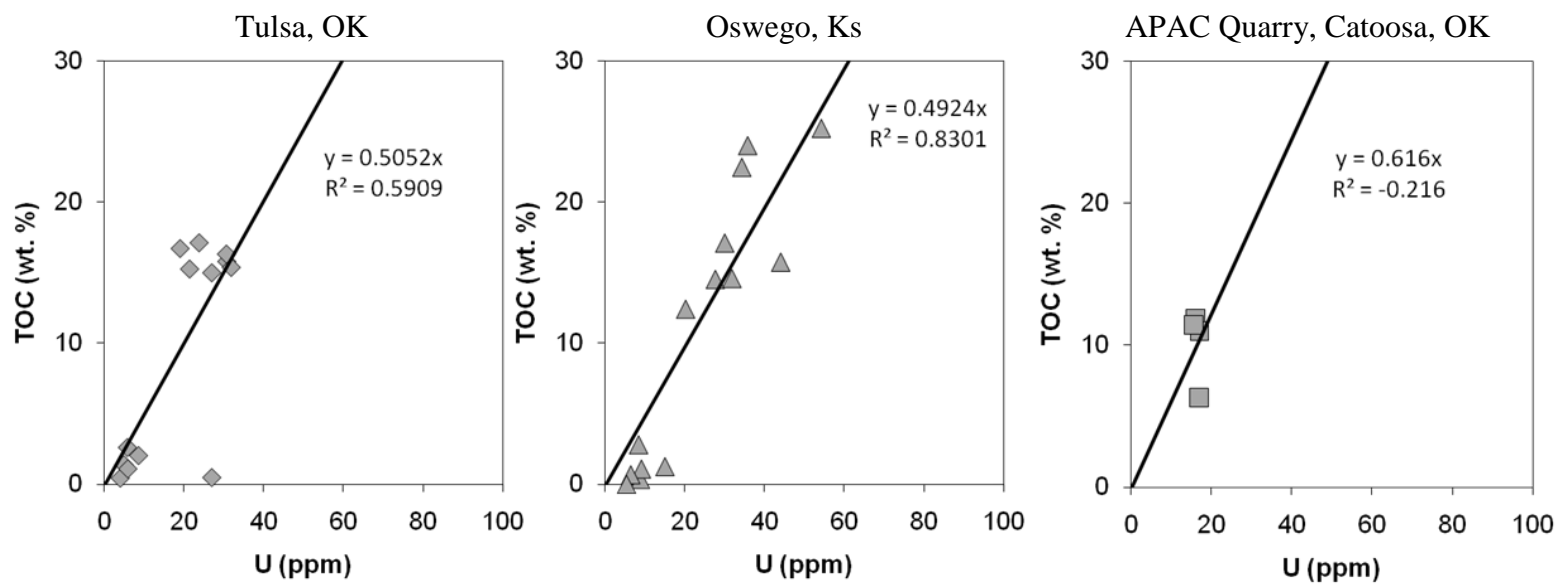


Fig. 13. Cross plots of Uranium versus TOC, A) Tulsa, shown in diamonds, B) Oswego shown in Triangles, and C) APAC shown in squares. Notice the change in slope between the three sites.

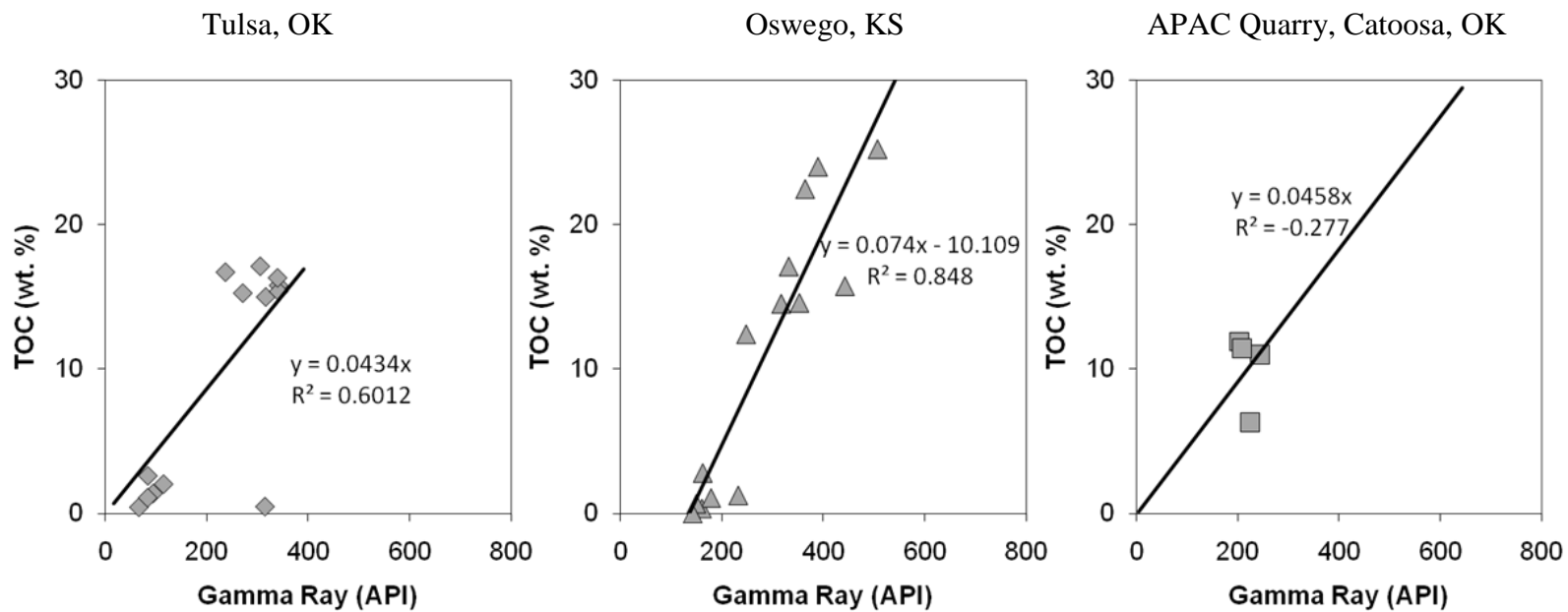


Fig. 14. Cross plots of gamma ray versus TOC, A) Tulsa, shown in diamonds, B) Oswego shown in Triangles, and C) APAC shown in squares.

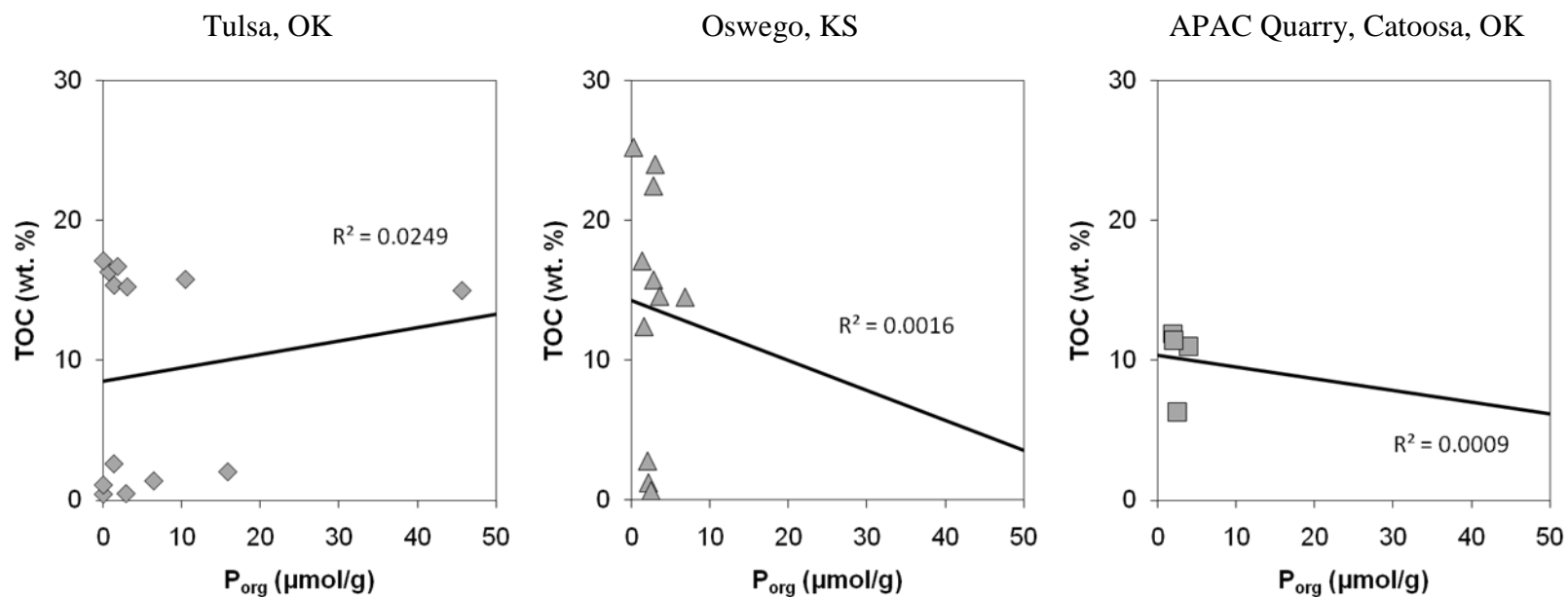


Fig. 15. Cross plots of organic phosphate and TOC, A) Tulsa, shown in diamonds, B) Oswego shown in Triangles, and C) APAC shown in squares. Notice the complete lack of correlation.

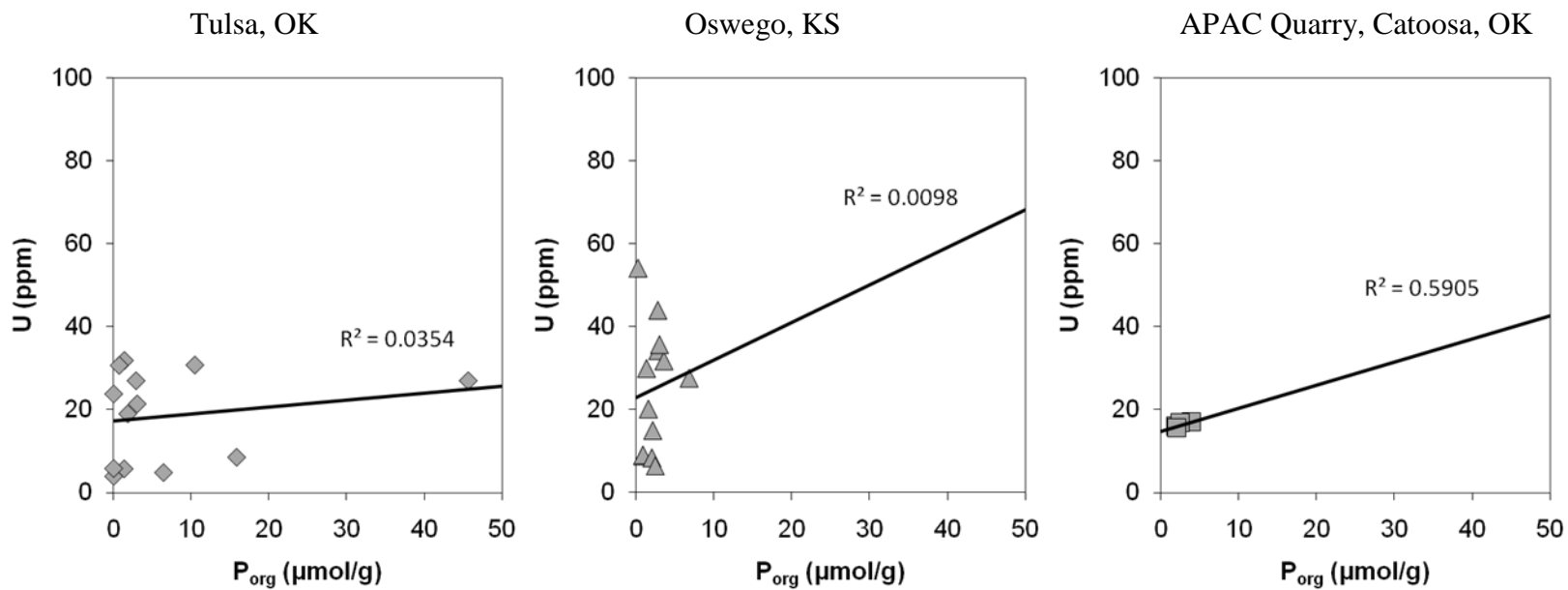


Fig. 16. Cross plots showing Organic Phosphate versus Uranium, A) Tulsa, shown in diamonds, B) Oswego shown in Triangles, and C) APAC shown in squares. Notice the lack of correlation in the Tulsa and Oswego sites.

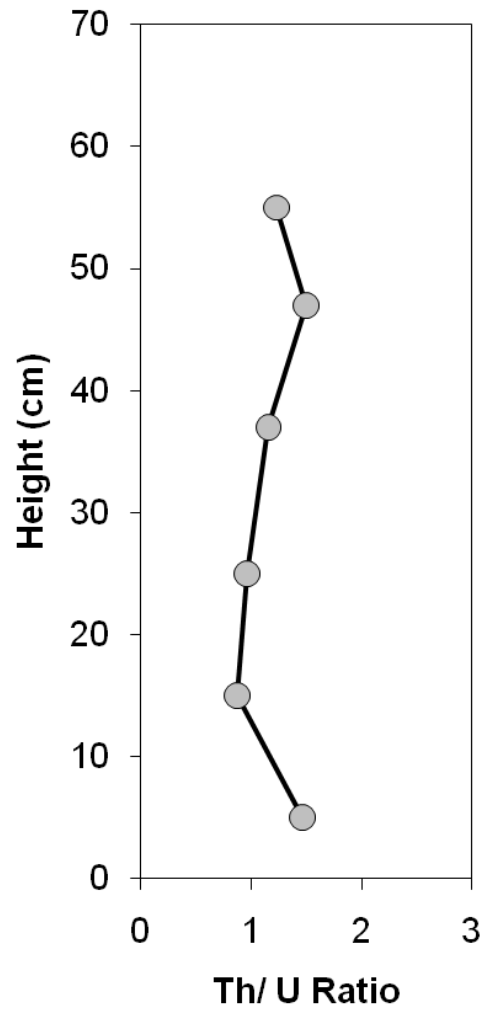


Fig.17. Plot of Th/U ratios versus height for the Anchor Quarry site, average Th/U ratio is 1.16.

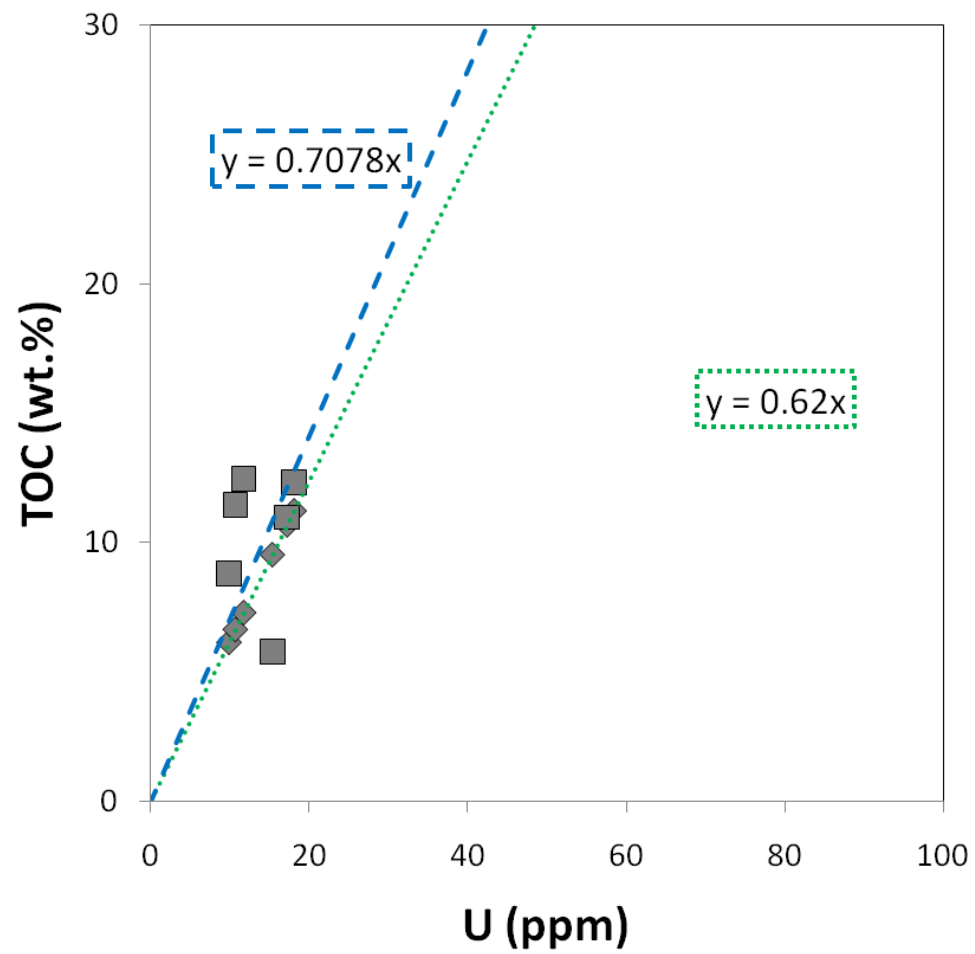


Fig 18. TOC concentrations versus uranium concentrations for Anchor quarry with measured values in squares and calculated values in diamonds. Calculated concentrations are shown by the dotted line, and measured concentrations are shown by the dashed line.

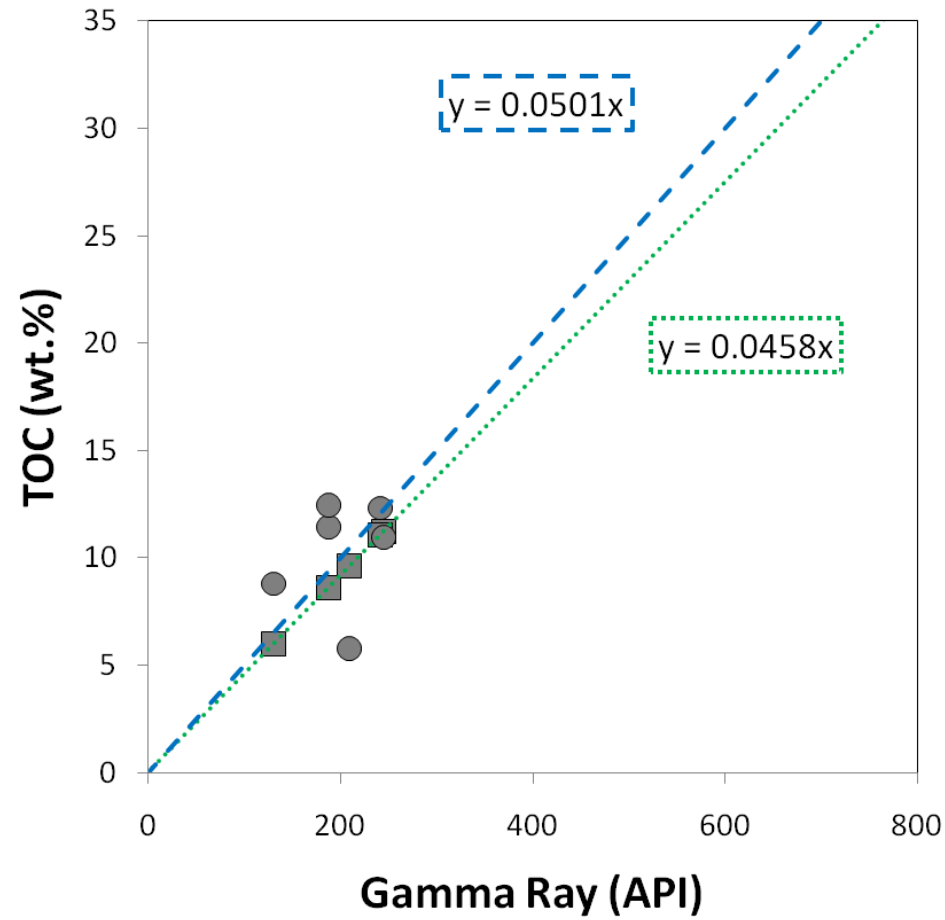


Fig. 19. Gamma Ray concentrations versus TOC concentrations for Anchor Quarry with measured values in square and calculated values in diamonds. Calculated concentrations are shown by the dotted line, and measured concentrations are shown by the dashed line.

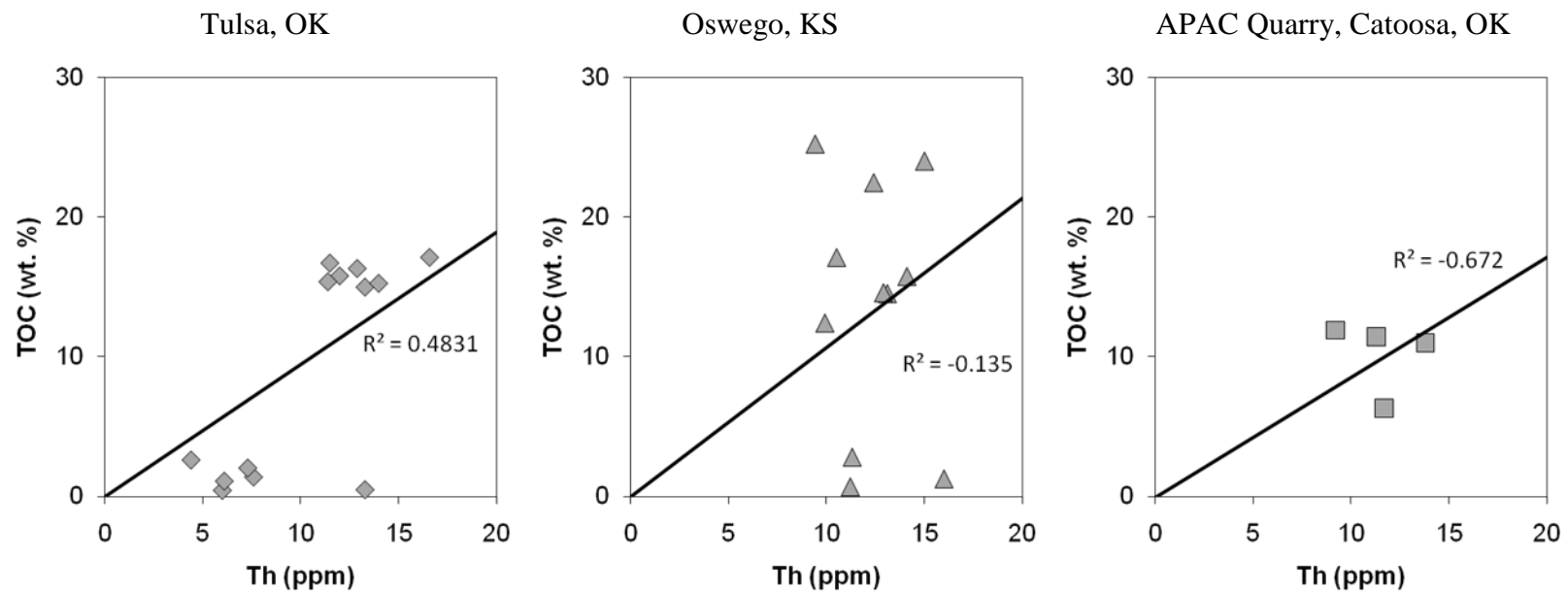


Fig. 20. Cross plots of Th versus TOC showing the relationship between the values. A) Tulsa, OK B) Oswego, KS C) APAC Quarry, Catoosa, OK.

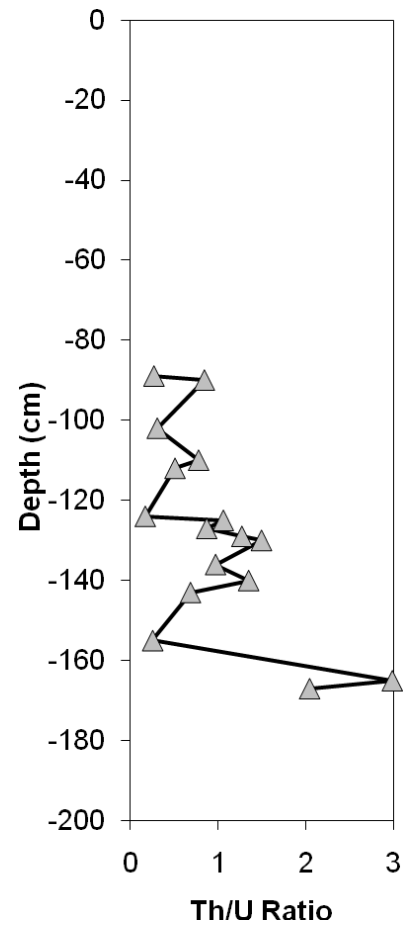


Fig. 21. Plot of Th/U ratios versus depth for the Caney Shale (Bryan, 2011), average Th/U ratio is 1.27.

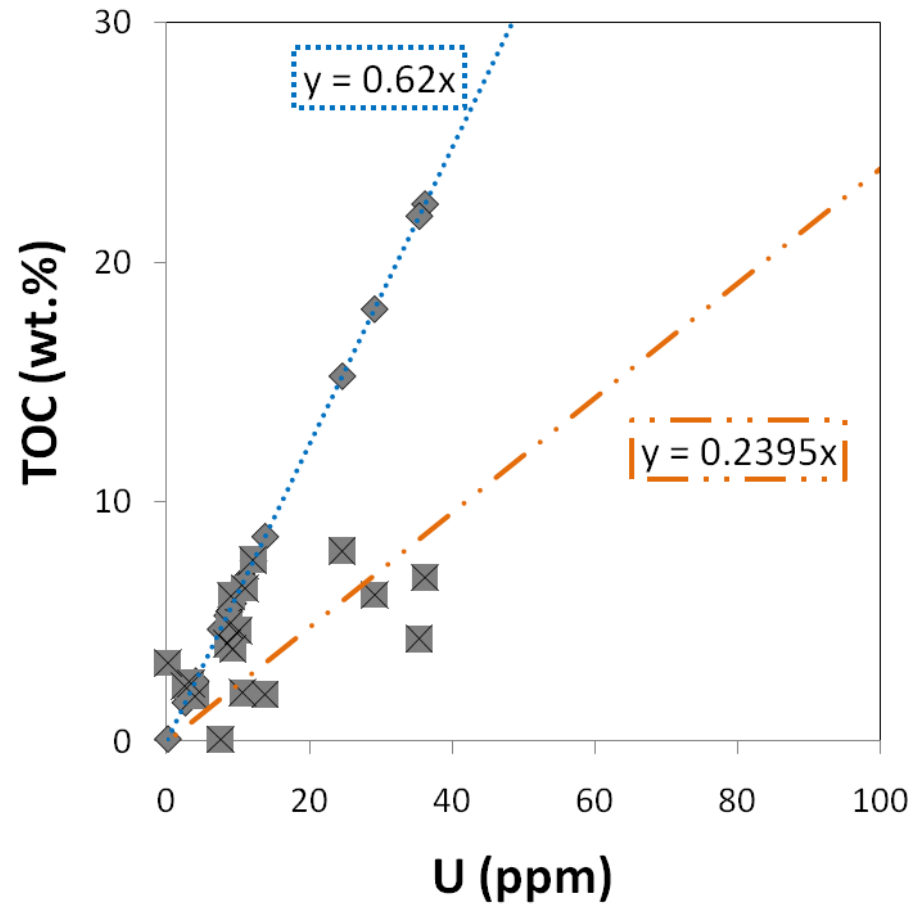


Fig. 22. Uranium concentrations versus TOC concentrations for Caney Shale with measured values in X's and calculated values in diamonds. Calculated concentrations are shown by the dotted line, and measured concentrations are shown by the dotted and dashed line.

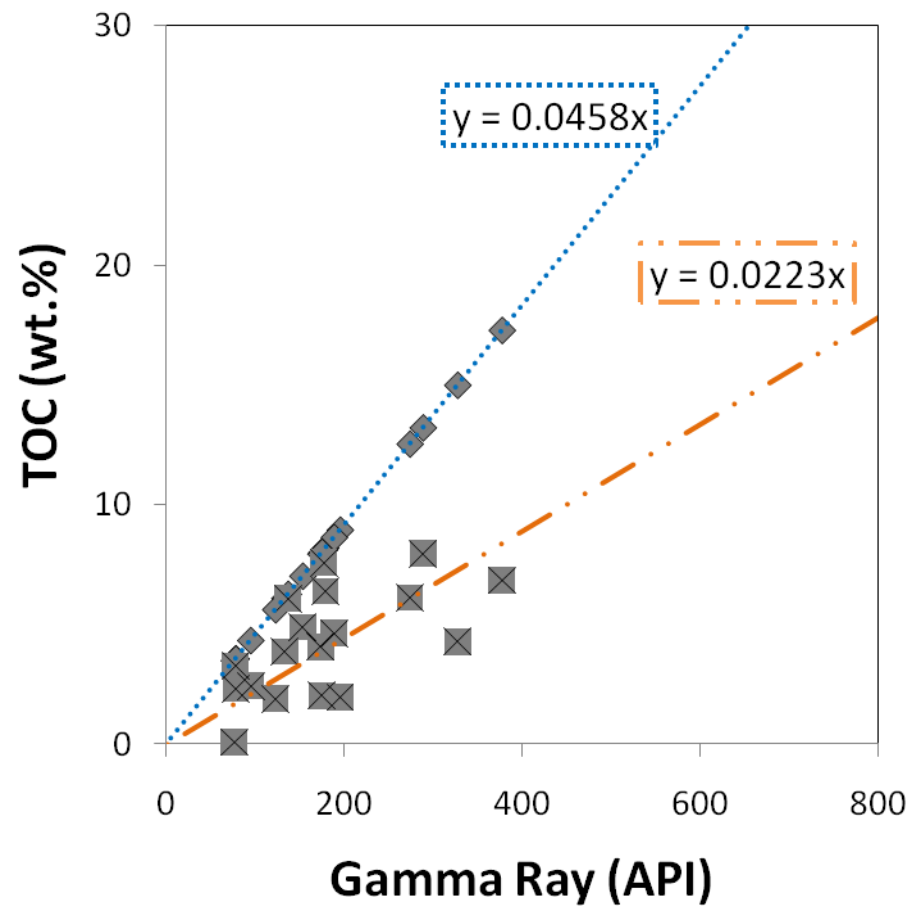


Fig. 23. Gamma ray concentrations versus TOC concentrations for Caney Shale with measured values in X's and calculated values in diamonds. Calculated concentrations are shown by the dotted line, and measured concentrations are shown by the dotted and dashed line.

VITA

Mindi Jo Parsell

Candidate for the Degree of

Master of Science

Thesis: USING CYCLOTHERMIC BLACK SHALES TO CREATE A PROXY
CALCULATION FOR BOREHOLE TOC ESTIMATES

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Date of Degree: July, 2011

Institution: Oklahoma State University

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Title of Study: USING CYCLOTHERMIC BLACK SHALES TO CREATE A PROXY
CALCULATION FOR BOREHOLE TOC ESTIMATES

Pages in Study: 66

Candidate for the Degree of Master of Science

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Black shales are important to the petroleum industry as both source rocks and subsurface marker beds. Black shales are enriched in trace metals, especially uranium (U), which is easily measured in outcrops and wells by spectral gamma-ray spectrometry (SGR). Previous studies have shown that U can be correlated with total organic carbon (TOC), presumably due to scavenging of the U by the organic compounds. Observed variations could be caused by the presence of phosphate, which is often enriched in black shales and strongly scavenges U. The Excello Shale is a Pennsylvanian (Desmoinesian) black shale, found from Iowa to Oklahoma. The Excello is well defined stratigraphically and lithologically, which makes a perfect candidate to test variations in U and TOC with respect to depositional environments. This study tests the hypothesis that that presence of phosphate can also control uranium concentrations in black shales in different depositional environments, rather than total organic carbon.

The objectives of this study are to determine the uranium concentration and its relationship to TOC, and phosphate speciation and concentrations. The study includes outcrop data from southeastern Kansas and northeastern Oklahoma. The methods include phosphorus speciation, SGR and coulometric titration. Data was used to determine the correlation of U, TOC and phosphate concentrations in the shale. Data was used to model a predicted shale behavior in the subsurface using well log data, and depositional changes based on geochemical parameters.

The findings from this study improve well log based basin correlations, and identification of sub surface source rocks. Understanding these variables will help improve SGR proxy calculations for TOC

ADVISER'S APPROVAL: Dr. Anna Cruse
