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THE URANIUM-LEAD GEOCHEMISTRY OF THE MOUNT McRAE SHALE FORMATION,
HAMERSLEY BASIN, WESTERN AUSTRALIA

by

JENNIFER GAIL FISHER

Under the Co-Direction of Dr. W.C. Elliott and Dr. Eirik J. Krogstad

ABSTRACT

The late Archean Mount McRae Shale of the Hamersley Basin in Western Australia may record the presence of oxygen in the atmosphere before the Great Oxidation Event (2.4-2.3 Ga). Several prior studies (Anbar et al., 2007; Blum and Anbar, 2010; Duan et al., 2010; Kakegawa et al., 1998; McManus et al., 2006) have used isotopic systems to analyze the Mount McRae Shale and conclude that there was a presence of oxygen before the Great Oxidation Event. The purpose of this study is to determine if the U-Pb system can be used to see through later events to the initial conditions. The uranium-lead values of the Mt McRae Shale provide evidence of the mobilization of U and Pb gain. The geochemical disturbances have been linked to the tectonic activity (460 Ma) in the neighboring Canning basin, which could have possibly opened the geochemical system. In terms of the depositional environment the U-Pb data gathered here do not point to oxygenation of the atmosphere.

INDEX WORDS: Mount McRae Shale, Hamersley basin, Geochemistry, Uranium-lead system, Paleoclimate proxy

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by

JENNIFER GAIL FISHER

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science

in the College of Arts and Sciences

Georgia State University

2012

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Jennifer Gail Fisher
2012

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DEDICATION

This thesis is dedicated to my friends and family who have always given me their love and support. To my parents, Gail R Fisher and Joe Fisher, who have constantly been there for me with words of encouragement. They have always pushed me to go for my dreams and graduate school was no different. They gave me a place to stay and helped me to find my way. To my friends Sabrina Jarvis, Leighann Dorough, and Justina Pierce who have been there to make sure I don't take life so seriously and stop to have fun. We've grown up together and no matter how far apart we are, they are always there for me. To my friend Kelly Carroll we bonded over our love of geology and found a true friendship. He has been there to listen to me and provide support when I thought that I couldn't do it. To my Cousin, friend and one of the strongest women I know, Sarah Berry. Her strength has always inspired me to find my own. To Baxter who always greets me with a wagging tail, has a constant calming effect and never judges me. To my grandparents (Paul and Doris Russell and Juanita Fisher) I miss you each and every day and I wouldn't be who I am without you. Lastly I would like to thank Jacob Roth. I am more thankful for his support and belief in me than he could ever know. He has a way of brightening my day and making me laugh when I need it the most. Through him I have found a greater capacity to love and internal strength that I didn't know I had. I'm so excited that I get to be part of his family, who has welcomed me with opened arms. I look forward to spending the rest of my life with him.

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LIST OF ABBREVIATIONS

amu: Atomic Mass Unit

GSU: Georgia State University

Ga: gigaannum, unit of time equal to 10^9 years

GOE: Great Oxidation Event

κ_a : Time-integrated Th/U

Mo: Molybdenum

MSWD: Mean Square Weighted Deviation

μ : $^{238}\text{U}/^{204}\text{Pb}$

Pb: Lead

REE: Rare Earth Elements

Ratios with asterisk ($^{207}\text{Pb}^*$ and $^{206}\text{Pb}^*$): asterisk identifies radiogenic isotope

Rh: Rhenium

SRM: Standard Reference Material

S: Sulfur

Th: Thorium

U: Uranium

Wt %: Weight Percent

1 INTRODUCTION

The Mount McRae Shale, whose depositional age is 2.5 Ga, may record evidence of an oxygenated atmosphere before the Great Oxidation Event (GOE), thereby altering our understanding of its timing and possibly nature. The GOE occurred between 2.4 and 2.3 Ga and signaled the rise of oxygen in Earth's atmosphere which caused significant changes in the chemistry of Earth's seawater and atmosphere (Duan et al., 2010; Pufahl and Hiatt, 2012). It also allowed for oxidative chemical weathering and the evolution of multicellular life (Pufahl and Hiatt, 2012). The study of the abundance of redox sensitive elements in formations predating the GOE has become an active area of research (Duan et al., 2010). Previous isotopic data from the Mount McRae Shale have been used as marine paleoclimate proxies (Anbar et al., 2007; Blum and Anbar, 2010; Duan et al., 2010; McManus et al., 2006). The studies by Anbar (2007), Pollack (2008), and Duan et al. (2010) are the most relevant to this study because they both speak of redox sensitive elements in the Mount McRae Shale and potential oxidation of the atmosphere prior to the GOE.

Anbar et al., (2007) used the concentration of molybdenum (Mo), which is sensitive to oxidative weathering to interpret mild oxidation. Molybdenum accumulates in the ocean and is removed from solution by sorption to organic carbon. During weathering in anoxic atmospheric conditions, Mo would be mostly held in sulfide minerals, so sediment deposited under of this type of atmosphere would have little to no enrichment of Mo compared to equivalent deposits after the GOE. Anbar et al. (2007) reported data on sulfur (S), rhenium (Re), and uranium (U). Sulfur because it acts similar to Mo in anoxic environments and the later two, Re and U because their aqueous geochemistry is similar to that of Mo. Due to the coherent behavior of the three elements Anbar et al. planned to use Re/Os geochronometry to verify that the element abundances were unaffected by remobilization. The results of their study supported the hypothesis of mild oxidation (or a "whiff" of oxygen) before the GOE. A study by Duan et al. (2010) also reached this conclusion with the use of Mo isotope evidence in the Mount McRae Shale.

Kauffman et al. (2007) collected S isotopic data as well as mineralogical and elemental data from both the Mount McRae Shale and equivalent strata from South Africa. Kauffman et al. (2007) concluded that there was a change in the redox state of shallow oceans before the GOE.

Some studies claim to have found evidence of oxygen before the GOE while others call these results into question. Pollack (2008) evaluated the geochemistry of the Mount McRae shale as well. The reported data for U-Th-Pb system and rare earth elements (REE) analysis and found that the k_a values are not representative of the sedimentary processes ca. 2.5 Ga (Pollack 2008). The results could indicate the enrichment of U during sedimentation, post-depositional alteration, or multiple detrital sources of U-Th-Pb and REE. The potential for several contradictory interpretations of the data raise the issue of suitability for these and other geochemical systems as paleoredox indicators. The results of Pollack's study do not further constrain the timing of the rise of atmospheric oxygen concentrations, but they do show the effectiveness of using the U-Th-Pb system to determine what stratigraphic units are appropriate for study.

Ultimately, Pollack's study raises questions of how other studies have been in reporting geochemical evidence of oxygen before the GOE, especially in samples of the Mount McRae Shale. The effectiveness of the U-Th-Pb and REE systems is demonstrated on samples from the 2.15 Ga Sengoma Argillite Formation, Botswana (Pollack et al., 2009). These organic-rich shales were formed during the GOE and provide evidence of oxidative continental weathering. This study attempts to determine if the U-Pb system can be used as a paleoredox indicator capable of preserving a signal of paleoclimate conditions despite later geochemical disturbances. U-Pb isotopic data from the 2.5 Ga Mount McRae Shale will be examined to see if it records evidence of a "whiff" of oxygen before the GOE.

1.1 Uranium-Thorium-Lead Systematics

Isotopic compositions of bulk sediment samples can be used to calculate the age of deposition. For the isotopic data to be meaningful the parent and daughter ratios must be part of a closed system. The Pb-Pb System lacks dependence on the present-day closed system of the parent and daughter isotopes and

is therefore preferred to other isotopic systems. Then if the system behaves openly or mobile it is interpreted as representing the presence of oxidative conditions, water temperature and other conditions during source weathering, diagenesis, metamorphism, and metasomatism (where Pb is mobile particularly when in the presence of Cl rich brines) (Krogstad et al., 2004).

Geochemistry of U and Th

Uranium is a redox sensitive element with two common oxidative states, tetravalent (4^+) and hexavalent (6^+), while thorium has one common tetravalent oxidative state. Uranium has a long residence time in present day oceans due to the stability of U^{6+} in oxidizing conditions. However, in early Earth history the lack of oxygen in the atmosphere made U^{4+} the abundant form of U (Krogstad et al., 2004). U^{4+} behaves geochemically like Th^{4+} . This similar geochemical behavior is due to the fact that both U and Th appear in nature in a tetravalent oxidative state, belong to the actinide series, and have similar chemical properties due to their ionic charge, ionic radius, and coordination number (Faure and Mensing, 2005; Krogstad et al., 2004; Pollack, 2008). These similar features allow them to readily substitute for one another. Useful minerals for U-Th-Pb methods include zircon, baddeleyite, monazite, apatite, and sphene. In oxidizing conditions: U has a hexavalent oxidation state, while Th remains tetravalent. Uranium is a mobile element in oxic environments in its hexavalent state while Th^{4+} remains generally insoluble (Faure and Mensing, 2005).

Decay of U and Th to Pb

Uranium has two prominent naturally occurring isotopes (^{238}U and ^{235}U) which are radioactive. Thorium is chiefly found as ^{232}Th , a radioactive nuclide, although there are 5 additional isotopes of Th that occur as short-lived intermediate daughters (Faure and Mensing, 2005). The principle isotopes of U (^{238}U and ^{235}U) and Th (^{232}Th) are each the parent of a chain of radioactive daughters ending with a stable isotope of Pb. Uranium has two decay series: the uranium series resulting from the

decay of ^{238}U (including ^{234}U as an intermediate daughter) to the stable ^{206}Pb and the actinium series resulting from the decay of ^{235}U to stable ^{207}Pb . Th has only one decay series, that of ^{232}Th to the stable ^{208}Pb . Although these three decay series are complex, each parent always leads to the formation of a unique stable Pb daughter isotope. Therefore the isotopic composition of Pb is time-sensitive (Faure and Mensing, 2005). The radioactive decay equations are written in terms of ^{204}Pb because it is the only natural, stable non-radiogenic isotope of Pb. It is typically assumed when using this method that the samples remained closed with respect to U, Th, Pb, and intermediate daughters (Faure and Mensing, 2005). The Pb-Pb isotopic system seems to be the most resistant to complete resetting of all the isotopic systems. The differing behavior of the parent and daughter isotopes will record changes in the chemical or physical environments during deposition and post depositional. The system is also considered able to record the post-depositional geochemical changes

1.2 Purpose of the Study

The purpose of this project is to study the Pb and U isotopic compositions of the Mount McRae Shale in Western Australia. It tests concepts regarding the record of the rise in atmospheric oxygen on Earth during the Precambrian. As well as testing the U-Pb system to determine if the U-(Th)-Pb system can be used to see through later events to the depositional paleoclimate conditions and records any geological disturbances subsequent to deposition.

1.3 Geologic Setting

Western Australia is dominated by early Archean rocks of the Pilbara Craton as well as younger rock deposited in superimposed basins such as the Hamersley Basin (Figure 1). During the later part of the Archean, the Hamersley Basin formed on the Pilbara Craton and contains units of the Mount Bruce Super Group (Anbar et al., 2007). The middle unit of the super group is the Hamersley Group and has been interpreted as a deep marine basin depositional environment that has been subjected to prehnite-pumpellyite facies, and locally greenschist facies metamorphism (Blake and Barley, 1992; Hassler, 1993; Pollack, 2008). The Mount McRae Shale is a 60-meter thick organic-rich shale within the ca. 2.5 Ga

Hamersley Group (underlain by the Mt. Sylvia Formation and overlain by the Dales Gorge Member of the Brockman Iron Formation) of Western Australia (Anbar et al., 2007; Pollack, 2008) (Figure 2). The depositional age of the Mount McRae Shale has been determined by direct radiometric Re-Os dating of whole-rock drill core samples of the Mount McRae Shale (2501 ± 8.2 Ma; (Anbar et al., 2007)) and U-Pb dating of zircon (2504 ± 5 Ma; (Rasmussen et al., 2005)). The Mount McRae Shale is approximately 60 meters thick and is underlain by the Mt. Sylvia Formation and overlain by Dales Gorge Member of the Brockman Iron Formation (Pollack, 2008).

The upper part of the Mount McRae Shale is characterized as a grey/black shale with interbedded carbonates and little pyrite that transitions to a black shale with increasing pyrite content as you more down the formation (Anbar et al., 2007; supporting material). Farther down massive pyrite nodules (1-10 cm radius) occur followed by a thick section of black shale with pyrite laminae and nodules and yet farther down the pyrite content drops as the lithology transitions to a siderite banded iron formation (BIF) (Kakegawa et al., 1998). The formation has a high concentration of organic carbon (2-8 wt %) and the disseminated pyrite constitutes 1-10 wt % S in the bulk rocks.

1.4 Mount McRae Shale Samples

The samples for this study come from two cores (WLT-02 and WLT-10) that were drilled by the Rio Tinto Iron Ore Company from exploration drill holes in the vicinity Perth, Western Australia. The core contains the Dales Gorge Iron Formation and a portion of the Mount McRae Shale. The upper portion of the Mount McRae Shale was weathered and oxidized so the samples selected were below this zone (Pollack, 2008). Samples were assigned sample numbers based on the core and collection depth by the Rio Tinto Ore Company (Table 1).

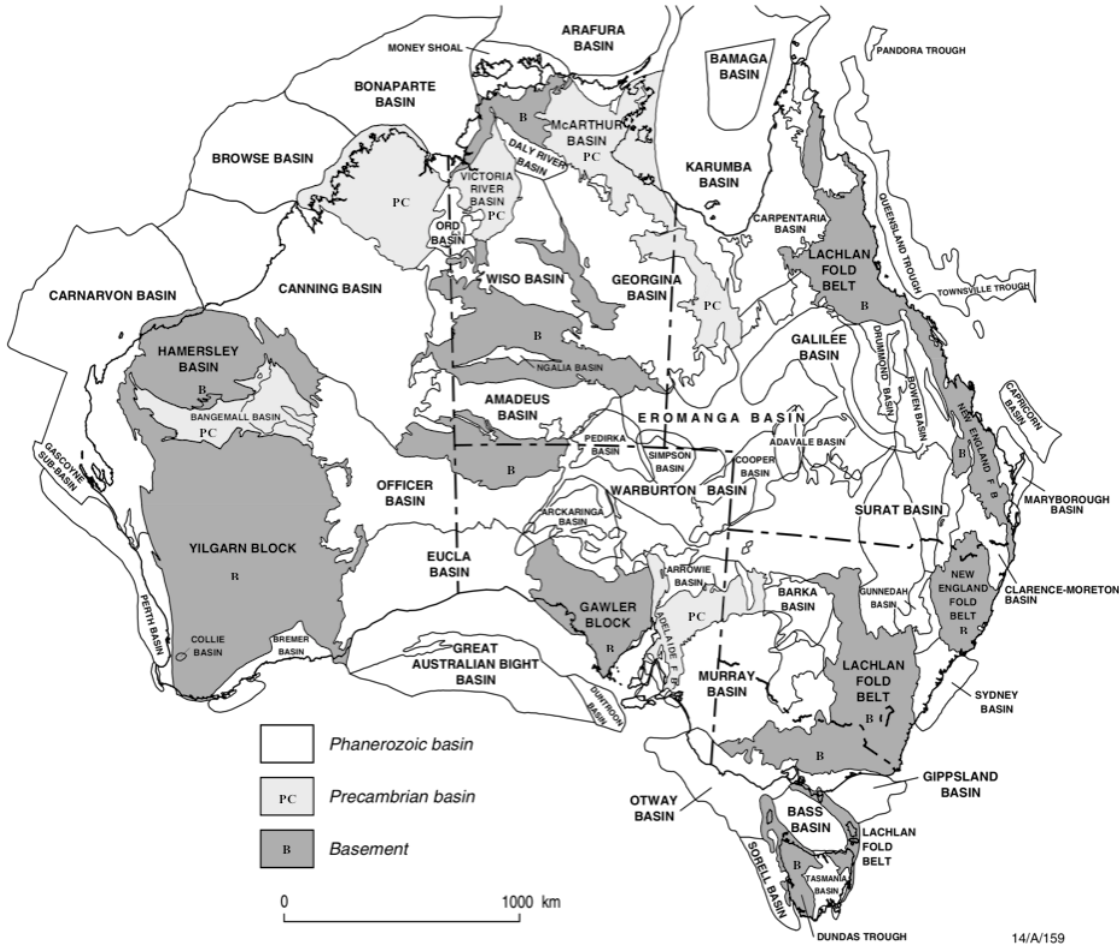


Figure 1: Australia's Sedimentary Basins (adapted from Petrie et al., 2001)
The location of the Hamersley Basin in Western Australia

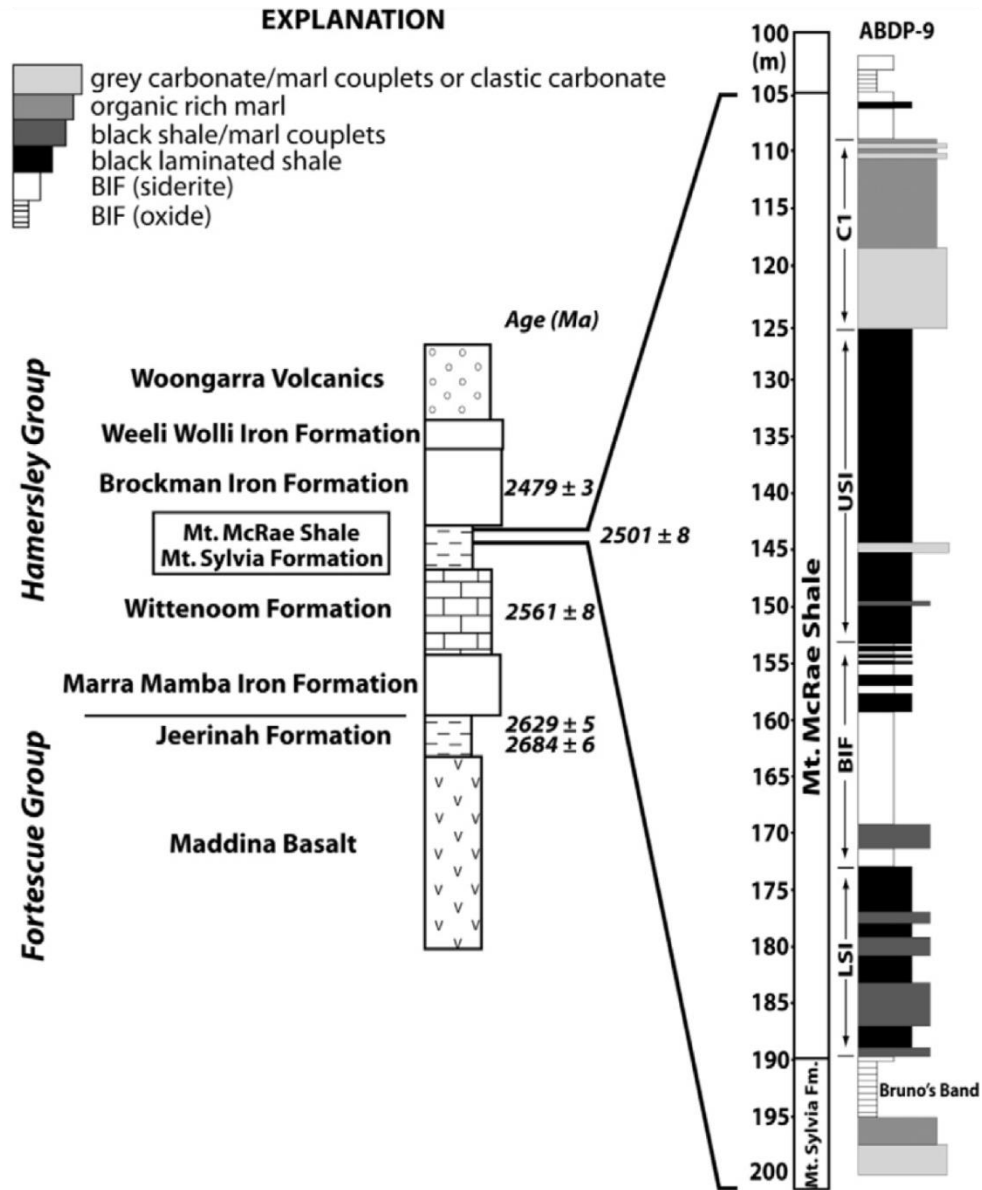


Figure 2: Stratigraphic Column Mount McRae Shale (Raiswell et al., 2011).
The ABDP-9 core of the Mount McRae Shale Formation is represented by this stratigraphic column.

Table 1: Mount McRae Shale Samples

Mount McRae Shale				
Sample Identification*	Sample Name**	Drill Core	Depth (m)	Inspection Notes***
MMS1	WLT-02-142.2	WLT-02	142.2	Small veins on left side of core
MMS2	WLT-02-145.9	WLT-02	145.9	Small hetero in center right of core
MMS3	WLT-02-146.4	WLT-02	146.4	
MMS4	WLT-02-147.3	WLT-02	147.3	
MMS5	WLT-02-147.5	WLT-02	147.5	Two parallel white strata across top
MMS6	WLT-02-148.0	WLT-02	148.0	Three parallel goldish strata about 11mm apart
MMS7	WLT-02-148.1	WLT-02	148.1	Two goldish strata, one with diagonal branch
MMS8	WLT-10-379.9	WLT-10	379.9	Vertical white streak
MMS9	WLT-10-381.0	WLT-10	381.0	One thick and one thin goldish strata
MMS10	WLT-10-383.8	WLT-10	383.8	Thin vertical white fracture, small goldish
MMS11	WLT-10-387.4	WLT-10	387.4	

Notes as provided by Dr. Eirik J. Krogstad

*Georgia State University (GSU) Lab Numbers

**Numbers also used in Pollack, 2008

***Author of log notes unknown

2 METHODS

2.1 Sample Preparation

Samples from both drill cores (WLT-02 and WLT-10) were powdered using a high strength steel stamp mill and shatter box (Pollack, 2008). The upper portion of the Mount McRae Shale was weathered and oxidized, so samples were selected from the unweathered and unoxidized parent below this zone (Pollack, 2008). Samples were assigned GSU lab numbers based on the core and collection depth (Table 1). For this study the powdered samples were worked with as received. The eleven samples were analyzed to determine their Pb isotopic compositions and bulk U, Pb concentrations. The isotope dilution technique was used to determine the concentrations of U and Pb in the samples as well as U and Pb ratios.

The powdered samples were weighed on a Denver Instrument M-220D balance (with tenth milligram accuracy). The rock powders were sampled from several places in the container to obtain a representative sample. The weighed samples were then spiked with 2 to 3 drops (0.0275 g to 0.1592 g) of a mixture composed of ^{205}Pb (0.77%) and ^{235}U (0.98%) and the spiked weight recorded. The sample was then digested in 7 mL Savillex® vials with a mixture of 4:1 reagent Optima® HF (28.9M) and Optima® HNO_3 (15.6M). For digestion, the capped vials were then moved to a hot plate (approximately 95°C and measured with a spring loaded thermometer) and allowed to digest overnight. After digestion, the sample still contained a black residue thought to be graphite or another form of carbon. This residue was allowed to settle out of solution. The clarified solution was then siphoned off by micropipette and placed on anion resin ion exchange columns containing BioRad AG1X8 200/400 mesh resin to separate the Pb and U (see detailed steps in Appendix A). Duplicates for six of the eleven samples were done and their data are presented in Appendix B. Each duplicate was derived by taking a second aliquot of powdered sample and processing it as described above.

2.2 Instrumentation

Concentrations of U and Pb samples were measured on the ThermoFisher Scientific MAT Element 2 High-Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS) in the Isotope

Geochemistry Laboratory at Georgia State University. The HR-ICP-MS is located in 613 Kell Hall and was maintained by Dr. E.J. Krogstad. Mass spectrometry was utilized because the method produces data with high precision and accuracy (Greaves et al., 1989; Pollack, 2008). The precision of this method is demonstrated with the analysis of NIST standards SRM-981 and SRM-982.

2.3 SRM Tabulation

During each run on the HR-ICP-MS reference NIST Pb standards SRM-981 and SRM-982 (Catanzaro, et al.) were analyzed to estimate precision and accuracy. The standard deviation of the results was calculated for both SRM-982 and SRM-981. The standard deviation and error (2σ) of $^{204}\text{Pb}/^{206}\text{Pb}$ was done by first taking the $^{206}\text{Pb}/^{204}\text{Pb}$ data that was reported and taking the inverse of the number so it was in the same format as the standard. The results, standard deviation and 2σ error for $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ for SRM-981 and SRM-982 are shown in Table 2 and Table 3 respectively. The standard deviation for SRM-981 ranges from 2.18×10^{-3} to 9.30×10^{-3} with the 2σ error ranging from 0.48% to 0.90%. The standard deviation for SRM-981 ranges from 7.89×10^{-5} to 3.33×10^{-3} with the 2σ error ranging from 0.33% to 0.67%.

Table 2: SRM-981 Pb Isotope Ratios

File name (Date)	SRM	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{204}\text{Pb}/^{206}\text{Pb}^{\#}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	
EJK 100630 U-Pb (June 30, 2010)	981-1	16.9151	0.0591	0.9134	2.1610	
EJK 100721 U-Pb (July 21, 2010)	981-1	16.7629	0.0597	0.9102	2.1403	
	981-2	16.7550	0.0597	0.9104	2.1404	
	981-3	16.7410	0.0597	0.9106	2.1416	
EJK 100713 U-Pb (July 13, 2010)	981-1	16.6902	0.0599	0.9146	2.1583	
	981-2	16.7830	0.0596	0.9148	2.1487	
EJK 100714 U-Pb (July 14, 2010)**						
EJK 100702 U-Pb (July 02, 2010)**						
FAV20110203 and others (February 03, 2011)**						
FAV 20110210MMS+MQ (February 10, 2011)**						
JF20110216MMSU (February 16, 2011)**						
			0.0596	0.9123	2.1484	Mean
			7.16×10^{-08}	4.73×10^{-06}	8.65×10^{-05}	Variance
			2.68×10^{-04}	2.18×10^{-03}	9.30×10^{-03}	Standard Deviation
			0.90%	0.48%	0.87%	Error (2σ)
			0.059042	0.91464	2.1681	NIST SRM 981 (Accepted)
			0.97%	0.25%	0.91%	Percent Error (from Standard)

$^{\#}$ (calculated from inverse of $^{206}\text{Pb}/^{204}\text{Pb}$)

** No SRM-981 measured

Table 3: SRM-982 Pb Isotope Ratios

File name	SRM	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{204}\text{Pb}/^{206}\text{Pb}^{\#}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	
EJK 100630 U-Pb (June 30, 2010)	982-1	36.6682	0.0273	0.4672	0.9995	
	982-2	36.6638	0.0273	0.4667	0.9983	
EJK 100702 U-Pb (July 02, 2010)	982-1	36.6130	0.0273	0.4660	0.9969	
EJK 100713 U-Pb (July 13, 2010)	982-1	36.5966	0.0273	0.4661	0.9941	
	982-2	36.6338	0.0273	0.4648	0.9887	
	982-2	36.6394	0.0273	0.4663	0.9961	
	982-2-1	36.6704	0.0273	0.4662	0.9958	
EJK 100714 U-Pb (July 14, 2010)	982-1	36.6678	0.0273	0.4666	0.9984	
EJK 100721 U-Pb (July 21, 2010)	982-1	36.3385	0.0275	0.4653	0.9925	
	982-2	36.3854	0.0275	0.4646	0.9895	
	982-3	36.4658	0.0274	0.4648	0.9897	
FAV20110203 and others (February 03, 2011)	982-1	36.4835	0.0274	0.4660	0.9933	
	982-2	36.5148	0.0274	0.4668	0.9971	
FAV 20110210MMS+MQ (February 10, 2011)	982-1	36.4835	0.0274	0.4660	0.9963	
	982-2	36.5666	0.0273	0.4665	0.9968	
JF20110216MMSU (February 16, 2011)	982-1	36.5170	0.0274	0.4658	0.9940	
			Mean	0.0274	0.4660	0.9948
			Variance	2.73×10^{-02}	5.79×10^{-07}	1.11×10^{-05}
			Standard Deviation	7.89×10^{-05}	7.61×10^{-04}	3.33×10^{-03}
			Error (2σ)	0.58%	0.33%	0.67%
			NIST SRM 982 (Accepted)	0.027219	0.46707	1.00016
			Percent Error (from Standard)	0.50%	0.23%	0.53%

[#](calculated from inverse of $^{206}\text{Pb}/^{204}\text{Pb}$)

2.4 Data Refinement

Once the samples were run on the HR-ICP-MS, the data were reported by the Element 3.0 ICP-MS Software, Results Display, Version: 3.0.6. These results were then put into an Excel spreadsheet along with the SRM-981 and SRM-982 measurements conducted periodically during the entire run of sample measurements. The results for SRM-982 were then used to determine the average fractionation per mass unit. This was done by determining the percent difference between the measured and the certified (accepted) amounts of $^{208}\text{Pb}/^{206}\text{Pb}$ in SRM-982, dividing the result by 2 (the difference in atomic mass units (amu) for ^{208}Pb and ^{206}Pb) and averaging all of the SRM-982 measurements. This average fractionation was then used to correct the SRM-981 data when they were available and the sample data. This was done by taking the amu's apart for each Pb ratio and multiplying that by the average fractionation to get the fractionation per amu (for samples that had no SRM-981 data the SRM-982 mass fractionation was used for the final step). Finally the average fractionation per amu was multiplied by the measured ratio and added to the measured ratio to get the mass fractionation correction for the sample.

After correcting the data for mass fractionation it was corrected for the spike. This step mathematically removed the Pb in the spike so that the data show what was originally in the sample. This step was performed using excel. Lastly the data for the samples (Pb and U ratios, sample weight and spike weight) were put in an isotope dilution excel spreadsheet (provided by E.J. Krogstad). The isotope dilution spreadsheet calculated U ppm, Pb ppm, μ , $^{206}\text{Pb}^*/^{238}\text{U}$ ages, $^{207}\text{Pb}^*/^{235}\text{U}$ ages, and $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ (the asterisk identifies the radiogenic isotope).

2.5 κ_a Calculation

The age of the Mount McRae Shale is $2501\text{Ma} \pm 8$ (Anbar et al., 2007) and κ_a values were calculated for all eleven samples for their maximum, average, and minimum ages. The evaluation of Th/U ratios can be difficult because the U-Th-Pb system must remain closed to be accurate. Any post-depositional alteration may affect the data (Pollack, 2008). Uranogenic Pb changes can be seen in the

$^{206}\text{Pb}/^{204}\text{Pb}$ ratio while $^{208}\text{Pb}/^{204}\text{Pb}$ shows changes in thorogenic Pb. These ratios can be used to determine time-integrated U-Th ratios; this is referred to as the average model

Equation 1.

$$\kappa_a = \frac{\lambda_{238}}{\lambda_{232}} \times \frac{\left(\frac{^{208}\text{Pb}}{^{204}\text{Pb}}\right)_m - \left(\frac{^{208}\text{Pb}}{^{204}\text{Pb}}\right)_i}{\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_m - \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_i}$$

where i is the model initial and m is the measured value (Faure and Mensing, 2005; Pollack, 2008).

3 RESULTS

3.1 Pb Isotope Ratios, Concentrations, and κ_a

The Pb isotope data as well as κ_a for the eleven whole rock Mount McRae Samples are presented in Table 4. The κ_a values range from 2.20 to 2.98 and have an average value of 2.71 for the entire set of samples. The κ_a values were calculated using the accepted age of the Mount McRae Shale as well as the minimum and maximum error for the age (± 8 million years) and can be viewed in Appendix B. Differences in the κ_a values between the average, maximum and minimum results varied by no more than one in the one-tenth decimal place. Figure 3 illustrates how κ_a values change in relation to depth.

The Pb isotope ratios for the samples are plotted on a $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ diagram with a two-stage Pb-isotope growth-curve from Stacey and Kramers (1975) values in Figure 4. The best fit slope is 0.140 and corresponds to an age of 2236 ± 920 Ma to present (MSWD = 26). The age represented by the line is not an isochron because it would need to have less scatter resulting in a MSWD less than 1.5 (Pollack, 2008). The age and its error that results from the graph do fall within the previously determined age by Anbar et al (2007). Figure 5 is also a $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ diagram with a single-stage Pb-isotope growth-curve from Stacey and Kramers (1975) values. However in this diagram the outlying points (WLT-02, 145.9m and WLT-10, 379.9) has been removed since they lie past the present on the

graph. This results in a graph whose best fit line has a slope of 0.180 and an age of 2657 ± 230 Ma to present (MSWD = 2.0).

In Figure 6 Pb isotope ratios for all eleven samples are plotted on a $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagram. This resulted in a best fit line whose slope is 1.084 (MSWD = 168). Again the outlying points were removed, this resulted in a slope of 1.033 with a MSWD of 35 (Figure 7).

The concentrations for Pb in ppm are shown in Table 5. The concentrations range from 9.51 ppm to 28.61 ppm with an average of 18.29 ppm. All of the values lie above the Kramers and Tolstikhin (1997) model value for Pb of 8.03 ppm.

3.2 U Isotope Ratios and Concentrations

The $^{235}\text{U}/^{238}\text{U}$ ratios for the Mount McRae Shale (Figure 4) range from 0.0025 to 0.0709 with a difference of 0.0709 and an average of 0.0545. The U concentrations in ppm are shown in Table 5. The concentrations range from 1.18 ppm to 3.64 ppm with an average of 2.46 ppm. Seven of the samples lie above the Kramers and Tolstikhin (1997) model value for U of 2.22 ppm while four lie below. The U and Pb concentrations versus depth are shown in Figure 8.

3.3 μ ($^{238}\text{U}/^{204}\text{Pb}$)

The values of μ for all samples are shown in Table 6. The values range from 4.02 to 19.47 with an average of 9.12. All but one of the values falls below the Kramers and Tolstikhin (1997) model value for μ of 13.70, μ vs. depth are shown in Figure 9.

Table 4: Whole Rock Pb Isotope Ratios and κ_a Results for the Mount McRae Shale

	Depth (m)	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	κ_a^*	$^{235}\text{U}/^{238}\text{U}$
WLT-02	142.2	18.50	15.74	37.67	2.91	0.0559
	145.9	20.52	15.74	38.01	2.20	0.0025
	146.4	18.82	15.77	37.66	2.72	0.0323
	147.3	18.46	15.74	37.10	2.55	0.0479
	147.5	18.66	15.79	37.61	2.78	0.0561
	148.0	18.88	15.88	38.14	2.98	0.0733
	148.1	18.98	15.81	38.18	2.95	0.0733
WLT-10	379.9	20.57	15.79	38.17	2.26	0.0733
	381.0	17.18	15.53	35.79	2.30	0.0616
	383.8	20.35	15.70	40.53	3.45	0.0490
	387.4	15.79	15.26	35.05	2.75	0.0733

* κ_a based on a depositional age of 2501 Ma

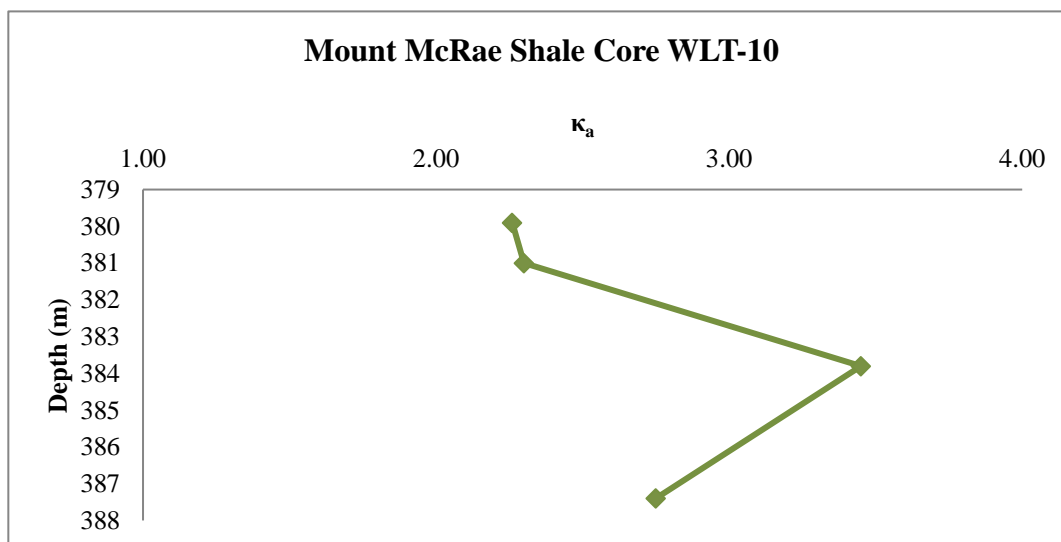
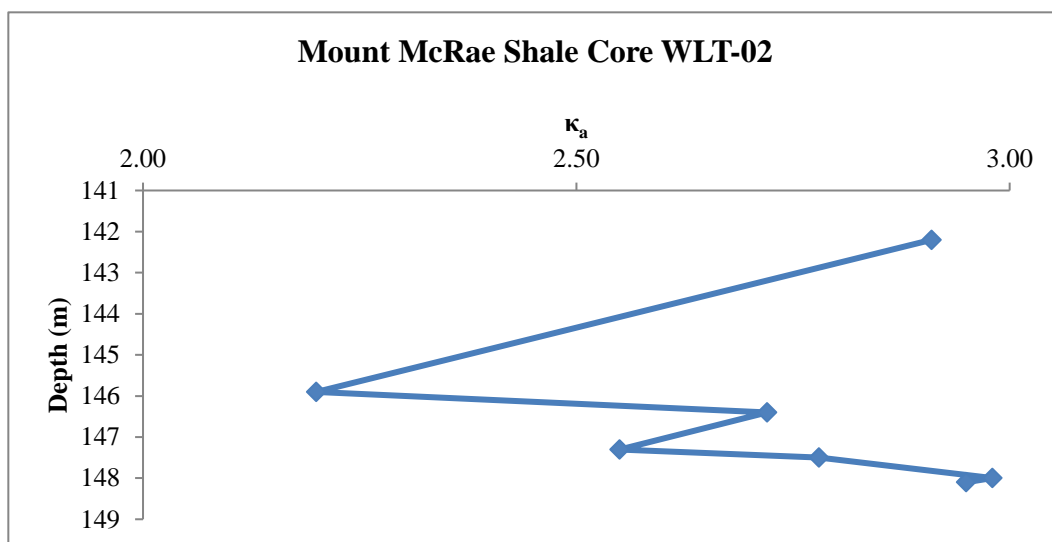


Figure 3: κ_a versus Depth (m) for WLT-02 and WLT-10 cores of the Mount McRae Shale
The κ_a values are based on a depositional age of 2501 Ma

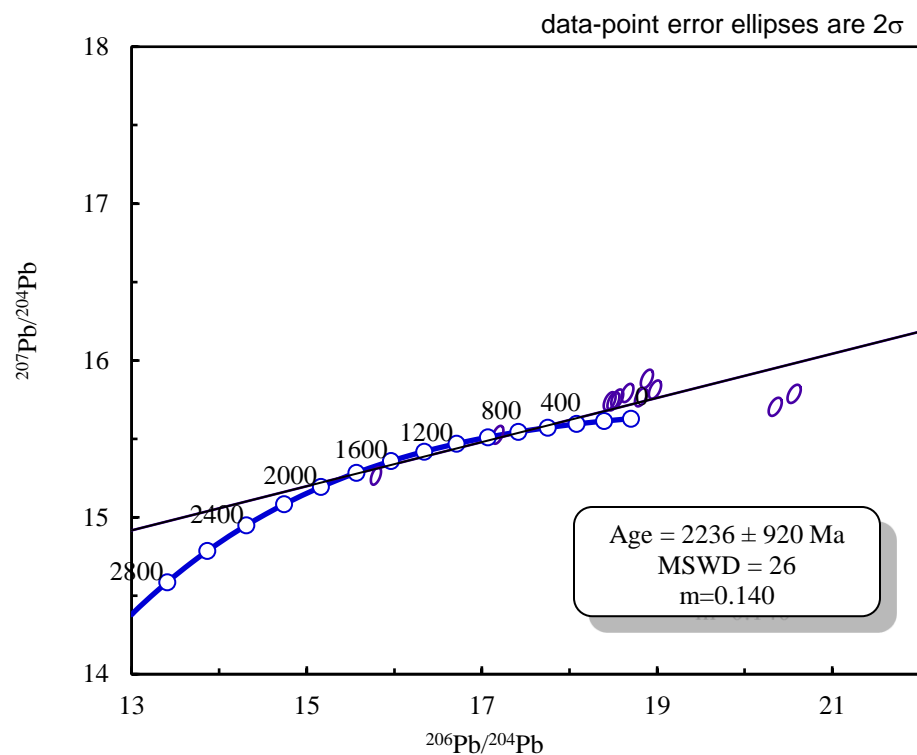


Figure 4: $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{207}\text{Pb}/^{204}\text{Pb}$ plot for the Mount McRae Shale

The $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{207}\text{Pb}/^{204}\text{Pb}$ plot for the whole rock samples of the Mount McRae Shale was made on Isoplot® and the curve represents the Kramers and Tolstikhin (1997) growth model. The slope of the data represents a Pb-Pb age of 2236 ± 920 Ma. This age corresponds to the Anbar et al. (2007) age of 2501 ± 8 Ma Re-Os age. Two points (samples WLT-02, 145.9 m and WLT-10, 379.9 m) do not lie along the general trend of the other points.

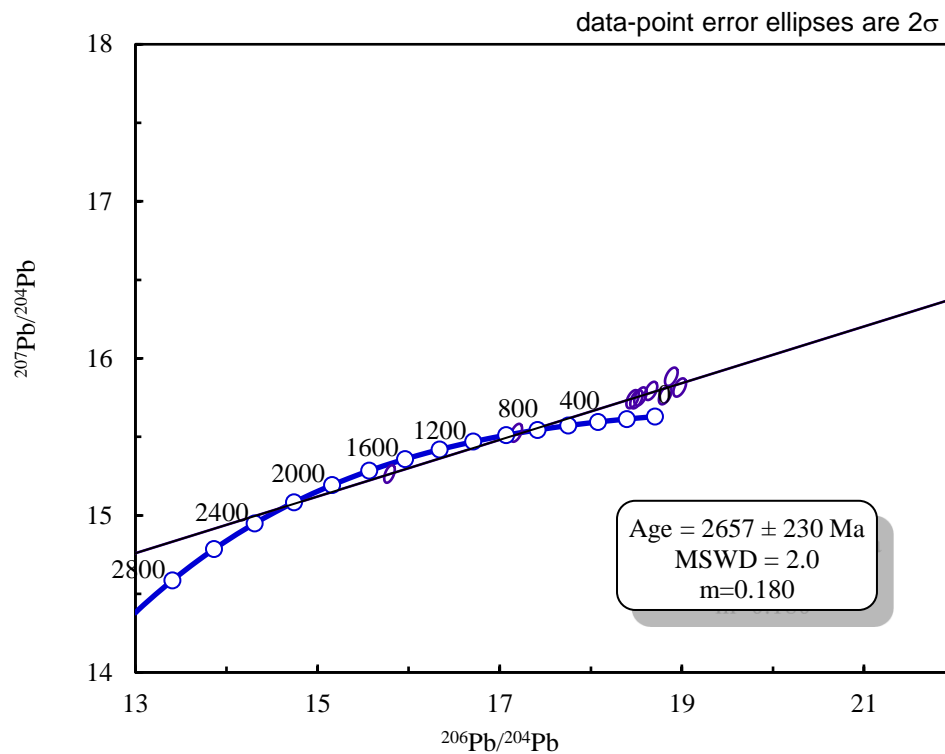


Figure 5: $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{207}\text{Pb}/^{204}\text{Pb}$ plot for the Mount McRae Shale with the two outlying points (WLT-02, 145.9m and WLT-10, 379.9) removed.

The $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{207}\text{Pb}/^{204}\text{Pb}$ plot for the whole rock samples of the Mount McRae Shale was made on Isoplot © and the curve represents the Kramers and Tolstikhin (1997) growth model. The slope of the data represents a Pb-Pb age of 2657 ± 230 Ma. This age also corresponds to the Anbar et al (2007) age of 2501 ± 8 Ma Re-Os age. By removing the two points the data are better constrained.

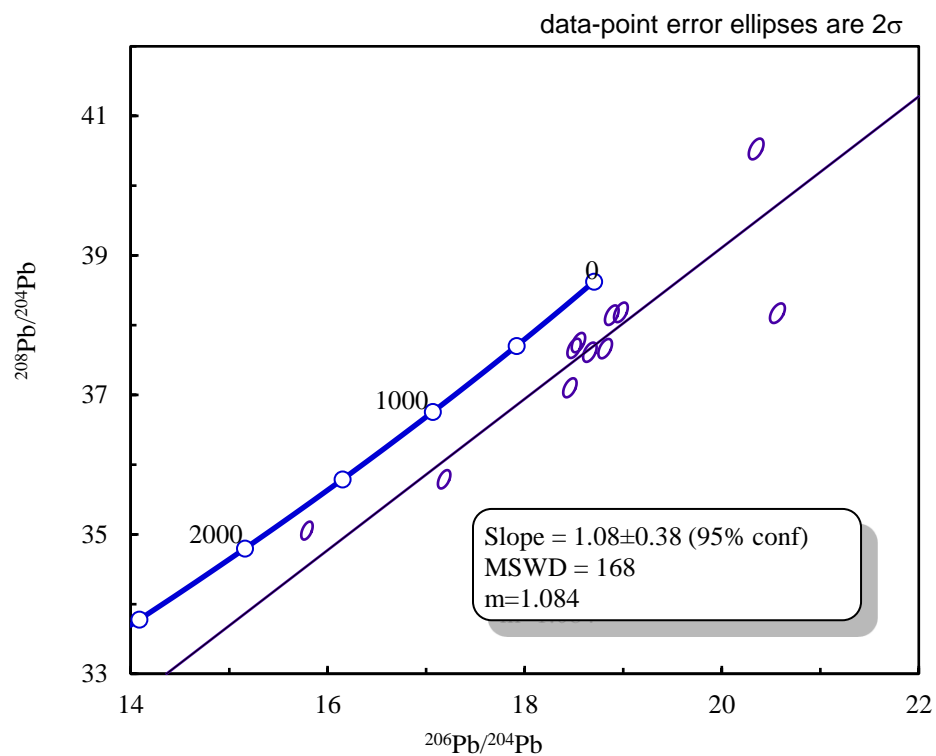


Figure 6: $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{208}\text{Pb}/^{204}\text{Pb}$ plot for the Mount McRae Shale.

The $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{208}\text{Pb}/^{204}\text{Pb}$ plot for the whole rock samples of the Mount McRae Shale was made on Isoplot® and the curve represents the Kramers and Tolstikhin (1997) growth model. The two points that don't follow the trend of the other data are samples WLT-02, 145.9m and WLT-10, 379.9.

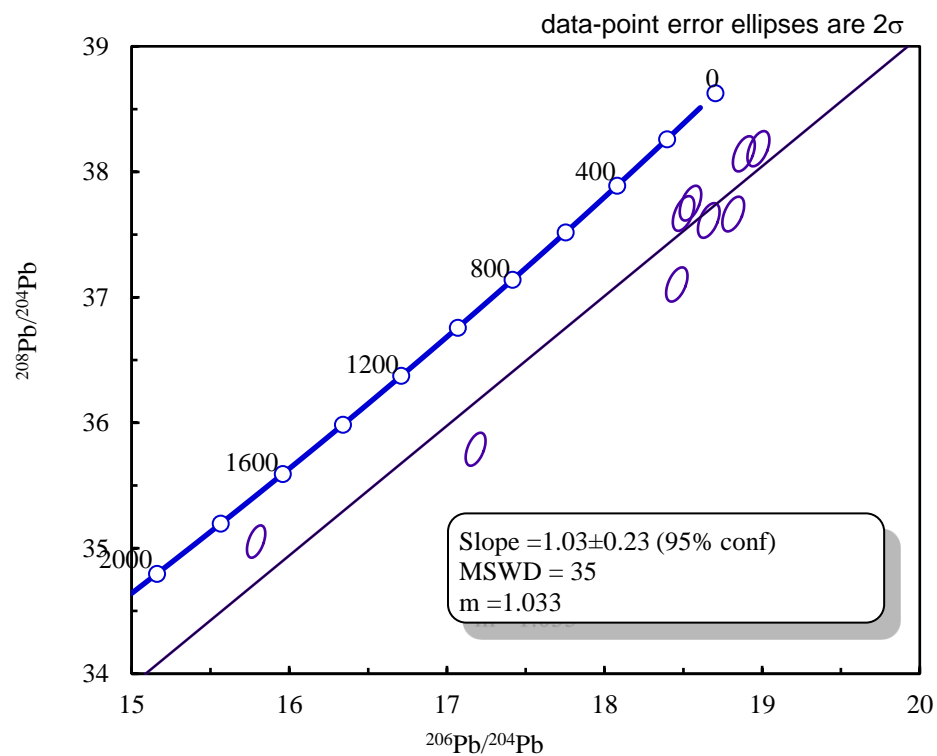


Figure 7: $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{208}\text{Pb}/^{204}\text{Pb}$ plot for the Mount McRae Shale.

The $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{208}\text{Pb}/^{204}\text{Pb}$ plot for the whole rock samples of the Mount McRae Shale.

was made on Isoplot® and the curve represents the Kramers and Tolstikhin (1997) growth model. The two points that don't follow the trend of the other data are samples WLT-02, 145.9m and WLT-10, 379.9 were removed.

Table 5: Concentration of U and Pb for the Mount McRae Shale

	Depth (m)	U (ppm)	Pb (ppm)
WLT-02	142.2	2.87	18.37
	145.9	1.76	27.64
	146.4	3.64	11.84
	147.3	3.30	17.56
	147.5	2.03	12.93
	148.0	1.47	12.70
	148.1	1.63	13.96
	Mean	2.39	16.43
WLT-10	379.9	1.18	9.51
	381.0	2.97	21.75
	383.8	3.13	26.31
	387.4	3.06	28.61
	Mean	2.58	21.54

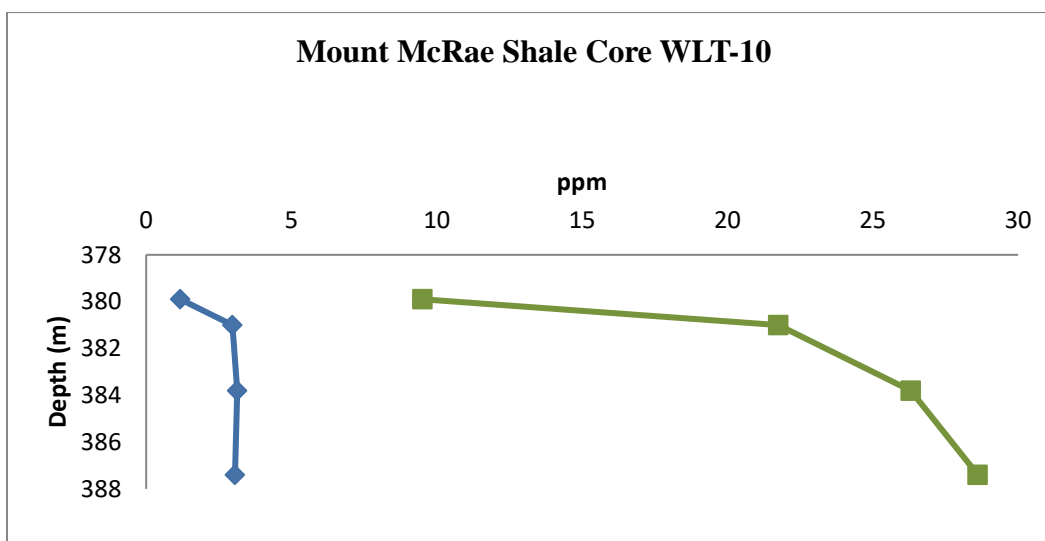
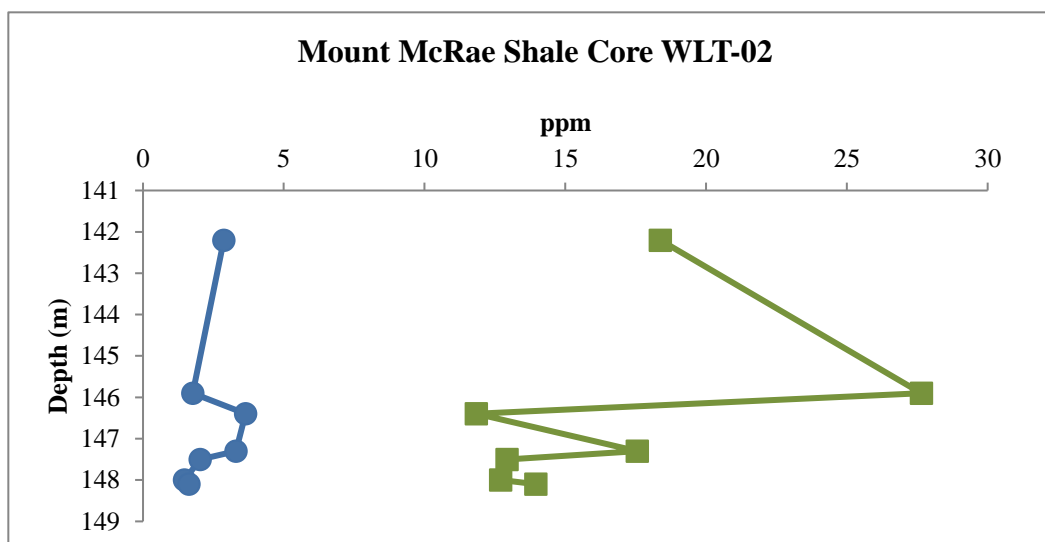


Figure 8: U and Pb Concentrations versus depth for the WLT-02 and WLT-10 Mount McRae Shale Cores

Table 6: μ Values for the Mount McRae Shale

	Depth (m)	μ
WLT-02	142.2	9.85
	145.9	4.02
	146.4	19.47
	147.3	11.75
	147.5	9.89
	148.0	7.41
	148.1	7.45
	Mean	9.98
WLT-10	379.9	8.07
	381.0	8.20
	383.8	7.98
	387.4	6.20
		Mean

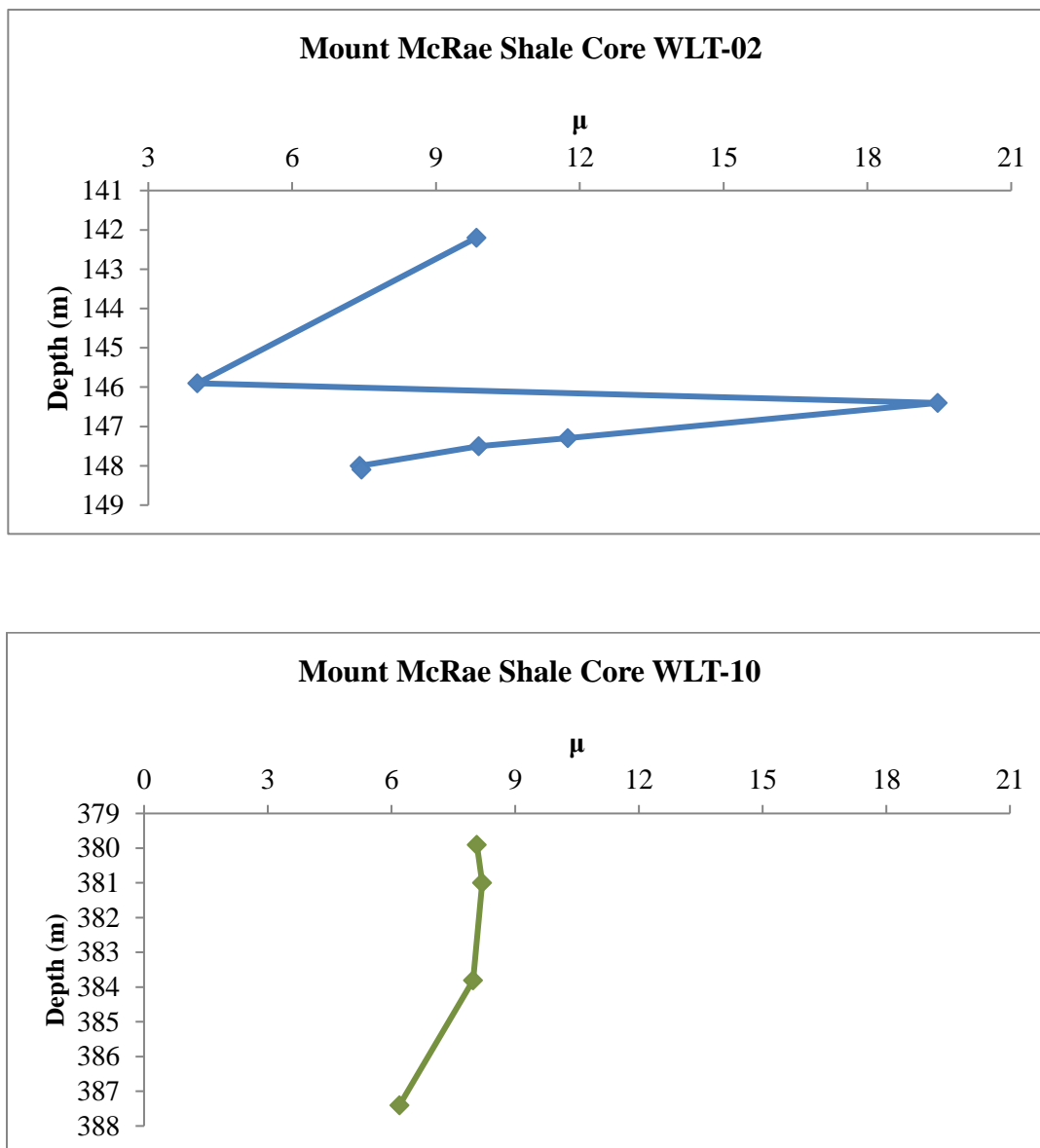


Figure 9: μ values versus depth(m) for the WLT-02 and WLT-10 Mount McRae Shale Cores

4 DISCUSSION

The data for the Mount McRae Shale cores (WLT-02 and WLT-10) cannot be stratigraphically correlated based on their respective depths because it is not known what portions of the formation they contain. Additionally they cannot be stratigraphically correlated to other cores for the same reason. Internal general trends for each of the cores are compared when looking at data by depth.

Figure 4 shows the Mount McRae Shale data plotted on a $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ diagram. The data represents a Pb-Pb slope age of $2236 \pm 920\text{Ma}$. Two of the points (WLT-02, 145.9m and WLT-10, 379.9) lie off the general trend of the curve as well as beyond the present day point on the model Pb growth curve. The Pb isotope values should not have evolved to their measured values considering one has a low μ (WLT-02-145.9m, $\mu = 4.02$) and one has a moderate μ (WLT-10-379.9, $\mu = 8.07$). There are other points that fit with the general trend that lie beyond the present day point on the model Pb growth curve. This data suggests the system started with variable μ values, is the result of source heterogeneity, or experienced post-depositional U mobilization. The hypothesis of variable μ values can be eliminated because the μ values place us into the future. The hypothesis of that the source was heterogeneous can be proven false from the REE data from Pollack (2008). That leaves the hypothesis that the U was mobilized in the Mount McRae Shale. If the two outlying points are removed from the graph as in Figure 5 the resulting age is 2657 ± 230 and the MSWD drops from 26 to 2. Removing the two outlying points from the group is supported by their differing Pb ratios but not their interelement REE ratios. In addition there may be U mobilization which is often not linked with REE mobilization (Pollack, 2008). This age and error is in agreement with the Re-Os age determined by Anbar et al (2007) of $2501 \pm 8\text{Ma}$ which supports the idea that Pb isotope growth was “initiated during sedimentary processes and that κ_a values might represent the time-integrated Th/U ratio associated with sedimentary events” (Pollack, 2008).

κ_a values for this study range from 2.20 to 2.98 with an average of 2.71. These values differ from the values reported by Pollack (2008), who modeled κ_a , with a range of 2.14 to 3.33 with an average value

of 2.80. Both the values reported here and by Pollack (2008) are below the average κ_a (Th/U ratio) of the Taylor and McLennan Model (1985) of 3.8 for Post-Archean shales and the Kramers and Tolstikhin (1997) model result of 3.89 for sedimentary rocks at 2.5 Ga (Pollack, 2008). Since the κ_a values are below the Kramers and Tolstikhin (1997) model values, this suggests the presence of variable redox conditions or multiple sources. The hypothesis of multiple sources can be dismissed because Pollack (2008) used REE values of the Mount McRae Shale to show that there are not different detrital sources of U (Figure 11). Different sources on a REE graph wouldn't appear flattened and congruent. The study did so by determining that at least four different sources were needed to explain the variation observed and that it was more likely that bimodal source mixing resulted in the REE ratios (Pollack 2008). Therefore, the observed variation in κ_a values is most likely related to post-depositional addition of U and/or subtraction of Pb. For the κ_a values to vary there has to be either an addition of U or subtraction of Pb.

The measured U ppm values have an average of 2.71 and 4 samples are below the Kramers and Tolstikhin (1997) model value of 2.22. The concentrations of Pb vary 9.51-28.61 ppm with all values above the Kramers and Tolstikhin (1997) model value of 8.03 ppm. This is interpreted as a gain in U for 7 samples and a gain of Pb for all of the samples.

The gain or loss of either U and Pb on an isochron is impossible to differentiate and result in either a higher or lower μ . High μ values result in higher isotope values so while the slope of the array doesn't change the position of the points does. Samples with a higher μ record U gain or Pb loss while samples with a lower μ record Pb gain or U loss (Lev et al., 2000). All but one of the samples has a μ under the Kramers and Tolstikhin (1997) model value of 13.70 suggesting an overall Pb gain or U loss.

A possible source of U oxidation is the neighboring Canning Basin (Figure 1), which was tectonically active 460 Ma and may have driven hot fluids through the Hamersley Basin. These hot fluids may have carried U and have the potential to mobilize other elements (Oliver, 1986; Pollack, 2008). Pollack (2008) also found a disturbance at 460 Ma recorded by the uranogenic Pb and REE patterns Mount McRae Shale. In addition a study by Webb et al. (2004) found evidence in their study area, also

located in the Hamersley Basin, of carbonate alteration by fluids driving carbonate replacement of silica bearing phases.

The U and Pb concentrations of both cores do not show the same trend in data. However a gain in U is recorded for 7 of the samples and a loss in U for the remaining 4 (compared to the Kramers and Tolstikhin (1997) model value of 2.22 ppm). While the Pb concentrations vary greatly, the average for the WLT-02 core is 16.43 ppm and the WLT-10 core average is 21.54 ppm, the Kramers and Tolstikhin (1997) model value of 8.03 ppm places the entire suite of samples above what is to be expected and records a gain in Pb. The samples that demonstrate unusually high Pb concentration ratios may be caused by the fact that the powdered sample is heterogeneous. However replicates in this study and others (Pollack, 2008) follow the same trend and support adequate homogeneity for this study. The data for the Mount McRae Shale is interpreted as recording a U gain and Pb gain. This implies that the Mount McRae Shale is not an appropriate formation for the study of oxygenation of the atmosphere prior to the GOE.

Future Work

Further study is warranted in the Mount McRae Shale to determine if it is an important paleoclimate indicator. It would be helpful to analyze the minerals in the Mount McRae Shale to know where the U and Pb are being held in the sample. If the U and Pb are being preferentially held in diagenetically formed minerals, such as pyrite or calcite, then this would suggest that the Mount McRae shale experienced post-depositional alteration. In addition the black residue, thought to be graphite, in the samples after digestion could be identified as well. Also working on a larger core of the Mount McRae Shale for study that can be stratigraphically correlated would be more useful in drawing conclusions. Sampling in a smaller and regular interval would help distinguish any trends in data and if the changes in the data are part of an overall trend, an anomaly of sampling, or due to lithology.

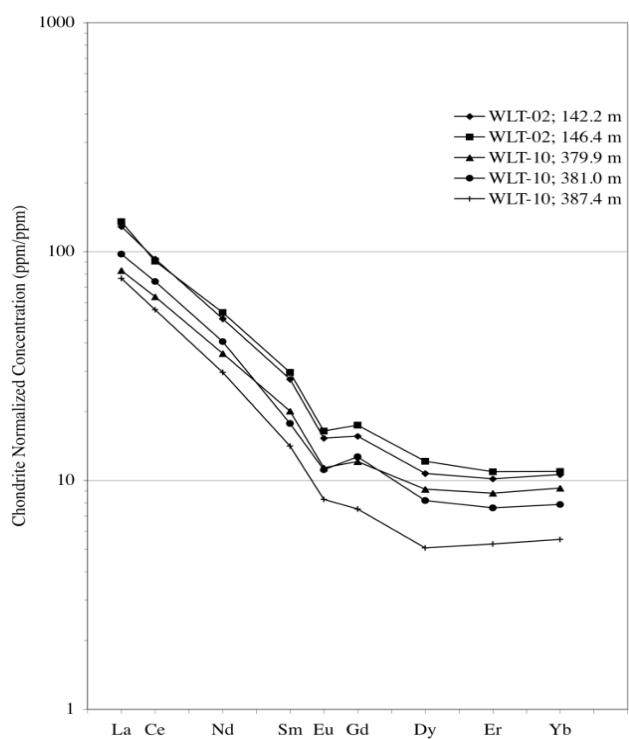


Figure 10: Rare Earth Element Analysis of Selected Mount McRae Shale Samples (Pollack, 2008)

The chondrite-normalized samples were determined by ID-ICP-MS (their errors are smaller than the symbols used), so the errors of the individual points are smaller than the symbols used (Pollack, 2008).

5 CONCLUSIONS

The following conclusions can be derived from this study:

- The data for the Mount McRae Shale suggest three hypotheses for the system:
 1. The system started with variable μ values;
 2. The data reflects source heterogeneity;
 3. The system experienced post-depositional U mobilization.

The data allow for the elimination of the first two hypotheses. The first hypothesis can be eliminated because two of the μ values for the Mount McRae Shale occur in the future which is not possible and the second one because REE data from Pollack (2008) provide evidence for a homogeneous source. Therefore the Mount McRae Shale has experienced U mobilization in its history. The U-Pb data of the Mount McRae Shale provides evidence of U mobilization. If a first approximate of the system presents evidence that it hasn't remained closed then it is unlikely that the Mount McRae Shale can serve as a paleoredox indicator. The age of the disturbance best corresponds with tectonic activity in the Canning Basin which could have added U as part of a roll-front deposit. Therefore it is likely that the recorded "whiff" was caused by post depositional alteration and not early oxidation of the Earth's atmosphere.

- The U ppm concentration records a gain for seven of the eleven total samples. The Pb ppm concentration records a gain of all of the samples.
- The κ_a values are below the model value and are interpreted as representing post depositional variable redox conditions. Since the κ_a values are below the model value they represent a gain in U for the system.
- The μ values for the study represent an overall Pb gain of U loss. This study interprets the former because the concentration of U suggests that there was an addition of U as well.

- The $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ graph has two points that branch off from the others. These points are interpreted as recording the mobilization of U.

If the U-Pb geochemistry of the Mount McRae Shale has been disturbed post-depositionally then studies that use the formation to interpret the climate at the time of deposition must be called in to question. Additional work should be done to resolve what minerals in the formation are holding U and Pb. If these minerals are diagenetically formed then it would provide greater evidence that the U-Pb system cannot be used to say something about the climate during deposition.

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APPENDICES

Appendix A. Analytical Methods

A.1.1 Column Preparation (Krogstad, 2009)

Columns are 1 milliliter pipette tips with quartz wool frit in the tip and approximately 200 microliters of BioRad AGIX8 200/400 mesh resin. The columns reservoir holds approximately 1.5 milliliters.

1. “Float” Columns in Milli-Q Water

Floating the column puts the resin beads into solution by suspending them in water. This is done by “quickly taking up some of the water in a transfer pipette and then squeezing it back into the column.”(Pollack, 2008)

2. Wash columns in 1 reservoir volume of 6.0M Optima® HCl
3. Wash Column in 1 reservoir volume Milli-Q water
4. Equilibrate Column with ½ reservoir volume of 0.5M Optima® HBr

A.1.2 Lead Column Chemistry (to follow Column Cleaning)

1. Place the vial that will collect the U enriched elutant (later referred to as U vial) under the column
2. Load Sample on Column (2 reservoirs volumes)
3. 1 reservoir volume 0.5 Optima® HBr
4. ½ Reservoir Volume 2M Optima® HCl
5. Remove U vial, Place on hot plate to dry

When moving from the hood to the hot plate place the cap on the vial to avoid contamination.

6. Place the vial that will collect the Pb enriched elutant (later referred to as Pb vial) under the column
7. Elute Pb with 1 reservoir volume of 6M Optima® HCl
8. Add 2 drops 14M Optima® HNO₃ to the Pb vial
9. Place Pb Vial on hot plate to dry
10. Place waste containers under columns
11. 1 reservoir volume Milli-Q Water
12. 1 reservoir volume 7M Optima® HNO₃
13. Once u vial is dry add 1mL 7M Optima® HNO₃
 - a. In some cases added 14M Optima® HNO₃ until no fumes were emitted from the vial
14. U vial-everything is now in solution
15. Load sample on column and wash with 1 reservoir volume 7M Optima® HNO₃
16. Add 1mL of 1.96M Optima® HNO₃ (trace metal grade) to empty U vial, Place on hot plate to clean
17. Rinse U vial with Milli-Q Water
18. Place U vial under column
19. Elute U with I reservoir volume Milli-Q Water
20. Put on hot plate to dry (optional)
21. Once Pb vial is dry add 1 drop of 1.96M Optima® HNO₃ and let dry
22. Add 1 drop of 14M Optima® HNO₃ and swirl to dissolve sample
23. Add 1 mL Milli-Q Water (level should be at the vertical sides of the column)
24. Cap and Remove Pb vial from hot plate

Appendix B. Additional Data

Duplicate Data for Whole Sample Mount McRae Shale

	Depth (m)	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{235}\text{U}/^{238}\text{U}$	U ppm	Pb ppm	μ
WLT-02	142.2m	18.5454	15.7571	37.7502	0.0356	14.0668	52.2372	16.9997
	145.9m	19.4645	15.8532	39.0573	0.0237	18.9937	40.3005	30.6981
	146.4m	18.8268	15.8073	37.9122	0.0237	19.3483	41.4752	29.6482
	147.5m	19.0226	15.8367	37.8925	0.0999	3.6203	43.3058	5.3279
	148.0m	19.1275	15.8380	38.1080	0.1002	3.4680	41.6143	5.3344
	148.1m	19.4367	15.8677	38.4826	0.1268	3.2094	49.1744	4.2179

ka values for Maximum, Minimum, and Average Ranges

		Ka		
		Maximum	Average	Minimum
WLT-02	Depth (m)	Depositional Age=2509	Depositional Age=2501	Depositional Age=2493
	142.2	2.91	2.91	2.91
	145.9	2.20	2.20	2.19
	146.4	2.72	2.72	2.72
	147.3	2.56	2.55	2.55
	147.5	2.78	2.78	2.77
	148.0	2.98	2.98	2.98
	148.1	2.95	2.95	2.95
WLT-10	379.9	2.26	2.26	2.25
	381.0	2.31	2.30	2.30
	383.8	3.45	3.45	3.45
	387.4	2.75	2.75	2.75
Mean		2.72	2.71	2.71