

# **Stony Brook University**



OFFICIAL COPY

**The official electronic file of this thesis or dissertation is maintained by the University Libraries on behalf of The Graduate School at Stony Brook University.**

**© All Rights Reserved by Author.**

**The Upper Pennsylvanian Hushpuckney “Core” Black Shale Member from the Swope  
Formation in Kansas: Rhenium – Osmium Isotope Systematics, and the Highly Siderophile**

**Elements**

A Thesis Presented

by

**Lynnette L. Pitcher**

to

The Graduate School

in Partial Fulfillment of the

Requirements

for the Degree of

**Master of Science**

in

**Geosciences**

**(Earth and Space Sciences)**

Stony Brook University

**December 2011**

**Stony Brook University**

The Graduate School

**Lynnette L. Pitcher**

We, the thesis committee for the above candidate for the  
Master of Science degree, hereby recommend  
acceptance of this thesis.

**Troy Rasbury - Thesis Advisor**  
**Associate Professor (Department of Geosciences)**

**Scott McLennan – Second Reader**  
**Professor (Department of Geoscience)**

**Martin Schoonen (chair)**  
**Professor (Department of Geosciences)**

This thesis is accepted by the Graduate School

Lawrence Martin  
Dean of the Graduate School

Abstract of the Thesis

**The Upper Pennsylvanian Hushpuckney “Core” Black Shale Member from the Swope Formation in Kansas: Rhenium – Osmium Isotope Systematics, and the Highly Siderophile**

**Elements**

by

**Lynnette L. Pitcher**

**Master of Science**

in

**Geosciences**

**(Earth and Space Sciences)**

Stony Brook University

**2011**

This thesis presents Rhenium – Osmium (Re-Os) systematics and Highly Siderophile Element (HSE) data from the (otherwise) geochemically and stratigraphically well studied Hushpuckney black shale from the Swope Formation in Kansas. Rhenium concentrations and the Re/Os ratios have a large spread that surpasses all published work on Re-Os. While the Re-Os data show significant scatter, the slope gives the expected age of 306 Ma. I use HSE's and Mo to consider geological processes that might have influenced the Re-Os systematics. The chondrite normalized HSE patterns are remarkably similar to that of seawater and supports the interpretation that the Midcontinent Seaway had an unrestricted opening to the open sea. Based on a comparison of the chondrite normalized HSE patterns to other sulfides, as well as a comparison of Mo and Re, the Hushpuckney black shale samples are most consistent with a mix of hydrogenous Re and molybdenite.

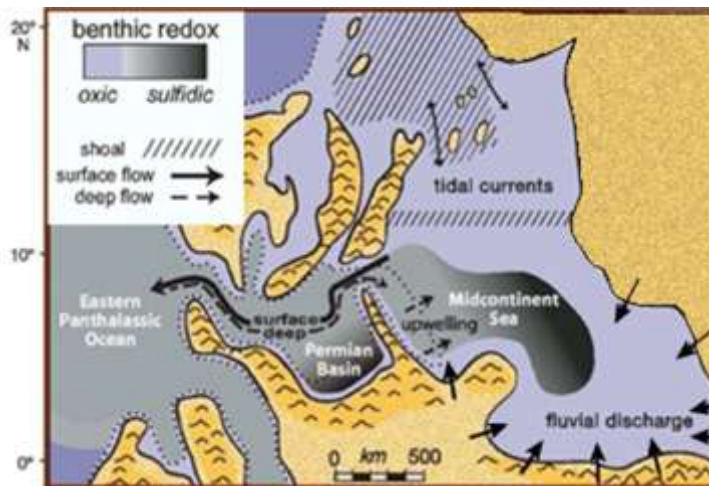
## Table of Contents

Chapter 1 Introduction	1
1.1 Re – Os, the Highly Siderophile Elements, and the Geochemistry of Black Shales	2
Chapter 2 Geological Background	4
Chapter 3 Methods	9
3.1 Sampling	9
3.2 Chemical Separation Method	11
3.3 Trace Element (TE)	13
3.4 Scanning Electron Microscope (SEM)	14
Chapter 4 Results	15
4.1 Rhenium – Osmium	15
4.2 HSE	17
4.3 Major and Trace Elements (XRF)	19
4.4 SEM	19
Chapter 5 Discussion	21
5.1 Analytical Techniques	24
5.2 Sulfide nuggets	29
5.3 Water Mass Restriction	34
Chapter 6 Conclusions	39
Chapter 7 Future Work	40
Work Cited	41

## Chapter 1 Introduction

$^{187}\text{Re}$ - $^{187}\text{Os}$  dating of black shales has been shown to have tremendous potential for providing the age of sedimentation [Creaser *et al.*, 2002, Selby *et al.*, 2003, Cohen *et al.*, 2004, and Kendall *et al.*, 2006], but not all black shales have well behaved Re-Os systematics [e.g. McArthur *et al.*, 2008]. Based on studies of recent sediments there are clear links to redox processes, including the production of  $\text{H}_2\text{S}$ , for fixation of Re, Mo, and U in organic sediments in euxinic basins [Colodner *et al.*, 1993; Crusius *et al.*, 1996]. There are also clear relationships for euxinia in the rock record, with the well-established proxies being the occurrence of sulfides, elevations in sulfur loving metals, and absence of evidence for bioturbation [e.g. Algeo and Maynard, 2004]. It is clear that Re and Os enrichments in black shales relative to crustal values are positively correlated to Total Organic Carbon (TOC), but there is a similarly close relationship to sulfide minerals. For example, euxinic conditions favor sulfide precipitation, which should be favorable for elevated Re concentrations. Models are emerging that water mass restricted basins are not favorable for Re-Os isochrons because the initial Os isotope ratio cannot be expected to be constant through time due to the drawdown from the water so that the reservoir is highly sensitive to changes in Os inputs. The purpose of this study is to examine Re-Os systematics and associated Highly Siderophile Element (HSE) patterns in the context of models for the behavior of Re-Os in black shales. The Hushpuckney core black shale from the Midcontinent Basin of North America (Fig. 1) is ideal for this study because there are detailed studies of the geochemistry in the context of proxies for oxygen levels and euxinia [Algeo *et al.*, 2004] and Algeo and Maynard [2004] have a predictive model for the behavior of sulfur loving and redox sensitive elements in this context. The Hushpuckney core black shale is one of many Pennsylvanian aged black shales from the Midcontinent Basin that represent maximum marine

transgressions with the waning of Carboniferous-Early Permian southern continent glaciers. These black shales vary in thickness, TOC, and type, presence or absence of biota, and in trace element behavior. These changes can occur laterally [e.g., Mo and other trace metals *Coveney et al.*, 1991] and through the interval of deposition of one black shale [e.g., *Hatch and Leventhal*, 1992;



**Figure 1:** Paleogeographic map showing inferred oxygen gradients in the Late Pennsylvanian. High frequency / high amplitude changes in sea level resulting from waxing and waning of Gondwana glaciers created cyclothems with core black shales signaling the maximum transgressions and conditions shown in this cartoon map. Figure from *Algeo and Maynard* [2008].

*Algeo et al.*, 2004; *Algeo and Maynard*, 2004; *Cruse and Lyons*, 2004; *Schultz*, 2004; *Algeo and Heckel*, 2008]. Based on the comparison of the enrichment factors of U and Mo in the Hushpuckney core black shale to modern low oxygen settings, it is suggested that deep water oxygen levels during deposition of the Hushpuckney shifted on rapid timescales [*Algeo and Tribovillard*, 2009]. This framework provides an excellent background to consider the sources and sinks of the HSE to the black shales of the Midcontinent Basin and the impact of these factors to the Re-Os system.

### 1.1 Re – Os, the Highly Siderophile Elements, and the Geochemistry of Black Shales

Due to the short residence time of Os in the oceans, *Cohen et al.* [1999] suggested that for Re-Os isochron work it is important to sample intervals representing less than 0.5 Ma so that possible complications from temporal changes in Os isotope compositions can be avoided. *McArthur et*

*al.* [2008] further suggested that if euxinic conditions persist without replenishment of seawater, the trace-element inventory may be drawn down such that there is a strong influence on initial Os isotope ratios, limiting the potential for high precision Re-Os isochron ages. Besides the degree of isolation of the water column from normal marine water or level of oxygenation, other conditions have been suggested to explain gradients in metal concentration, including rates of siliciclastic input, variations in organic reservoirs, sub-pycnoclinal water mass restriction and reduced microbial consumption, sorting of organic matter, post syngenetic alteration, and other sources of metals such as epigenetic enrichment [Coveney *et al.*, 1991; Cruse and Lyons, 2004; Rowe *et al.*, 2008]. The impact of these varying conditions may cause an “impressive array of geochemical complexity” [Schultz, 2004]. High levels of organic matter accumulated in core black shales due to a combination of sediment starved conditions and oxygen depleted waters resulting from a stratified water column [Heckel, 1977; Algeo and Heckel, 2008]. Stratification of the water column was facilitated by freshwater runoff from the north and eastern portion of the Midcontinent Basin (Fig. 1); and a thermocline developed to the south and west [Hatch and Leventhal, 1992].

The main source of Re and Os in the Midcontinent Basin is the influx of freshwater into the basin via rivers and their tributaries. On the Earth’s continents Re and Os are tied up in organic sediments, ultramafic rocks, and sulfides [Miller *et al.*, 2011]; therefore the influx of freshwater could carry some of this material as weathered byproducts of the surrounding mountain belts and from the low lying swamp areas. In oxic water, Re is highly mobile as the perrhenate anion( $ReO_4^-$ ), which is stable over a wide range of pH in rivers [Miller *et al.*, 2011; Cohen, 2004]. The consensus is that Os is transported to the open ocean via rivers as a byproduct of weathered material (e.g. Peridotites, komatiites, mafic rocks, and organic rich sediments)

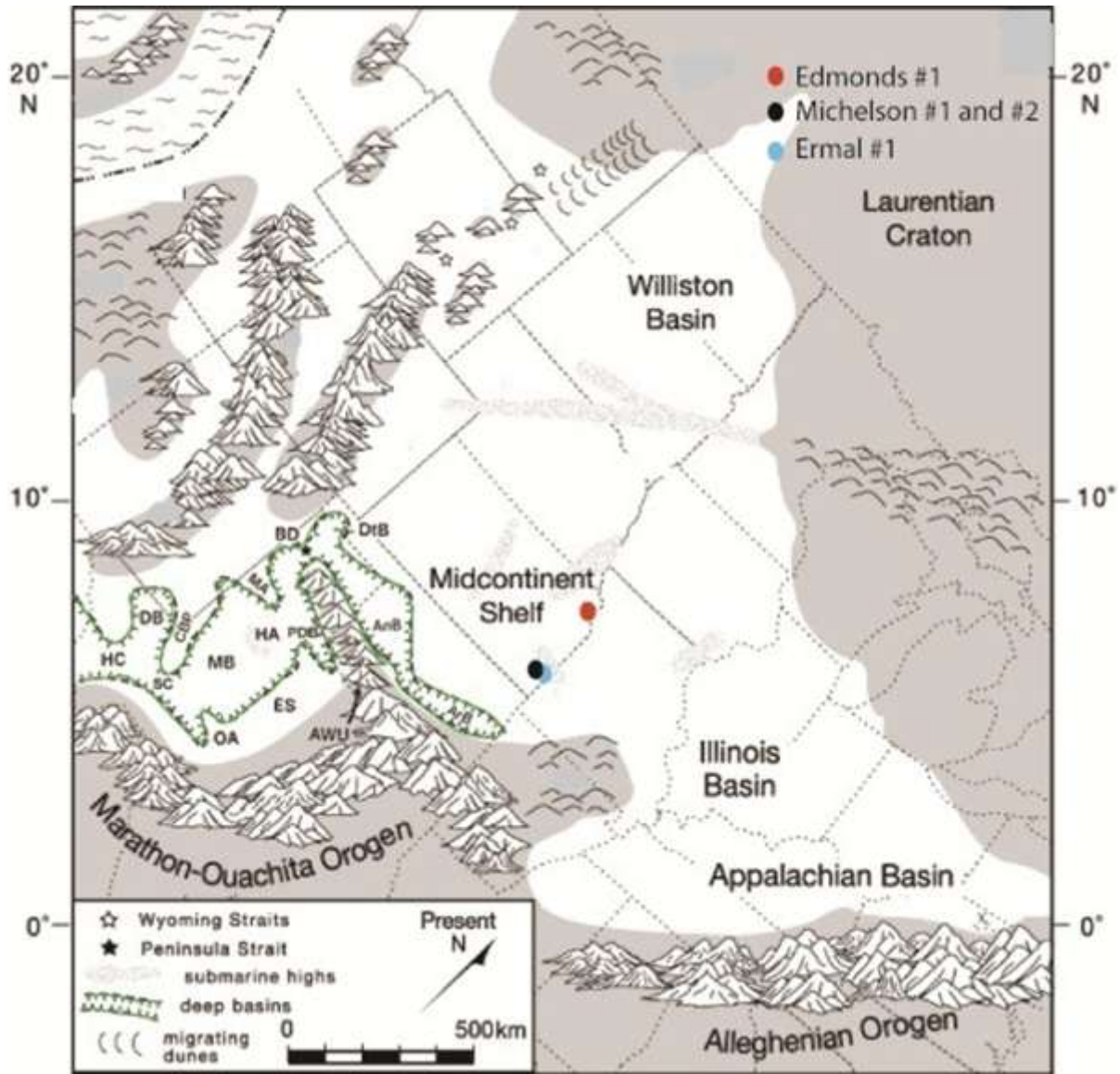


[*McDaniel et al.*, 2004]. Weathered organic material has high Re/Os ratios and is considered the main source of Re to seawater [*Colodner et al.*, 1993]. Based on inorganic speciation calculations for fully oxygenated seawater, Os should be at its highest valence state, which is consistent with the high affinity for organics [*Ravizza*, 2010]. Since Re is readily complexed with sulfides, it is removed from the water column under reducing conditions and should become even more enriched in the euxinic sediments where  $^{187}\text{Re}$  decays to the stable  $^{187}\text{Os}$ . It is anticipated that sulfide minerals would be enriched in the black shales where the conditions are euxinic and the concentration of sulfur is elevated [*Algeo et al.*, 2004]. It is expected that the concentration of Re will surpass Os in chondrite normalized HSE plots because relative to the mantle (0.25 – 0.30 ppb Re; 2.8 – 3.4 ppb Os), crust materials are extremely depleted in Os (< 0.05 ppb) and somewhat enriched in Re (< 1 ppb) [*Shirey and Walker* 1998]. This is due to the fact that Re readily partitions into the melt phase during mantle melting, because it is moderately incompatible element while Os is highly compatible [*Shirey and Walker* 1998]. Like Os, the remaining Platinum Group Elements (PGE; Ir, Ru, Pt, and Pd) behave compatibly during mantle melting, but Pt and Pd are less so than Os, Ir, and Ru [*Shirey and Walker* 1998] and are consequently extremely depleted in the crust.

## Chapter 2 Geological Background

Major climate changes occurred with the merging of the continents to form Pangea in the Late Paleozoic. Prolonged glaciation with associated cyclothemic sedimentation began in the late Mississippian (Serpukhovian Stage) as an equatorial seaway closed when Gondwana encountered North America [*Crowell*, 1978; *Rygel, et al.*, 2008]. Conodont apatite  $\delta^{18}\text{O}$  values show two major positive shifts of +2‰ and +1.5‰ V-SMOW in the late Tournaisian and

Serpukhovian Stages, respectively. These shifts are interpreted to reflect climatic cooling and increases in ice volume [Buggisch *et al.*, 2008]. During the Carboniferous and Permian Periods, the North American continent was rotated clockwise relative to its present-day position and located near equatorial latitudes, with the Midcontinent shifting from about 20° S in the Mississippian to near equatorial latitudes in the Pennsylvanian. It moved northward, shifting into the trade-winds belt by the middle to late Permian [Scotese, 2004]. In the late Serpukhovian, sea level fell due to the buildup of glaciers on Gondwana [Miller *et al.*, 2005; Haq and Schutter, 2008], thus a major unconformity separates the Mississippian and Pennsylvanian Systems in North America [Sloss, 1963]. Throughout the Carboniferous, the convergence of Gondwana into Laurentia from the paleo-east initiated orogenic activity along the convergent margin with a foreland basin developed in the early Carboniferous and early late Carboniferous along the margin. This led to drowning of the late Mississippian carbonate platform. Rising relative sea level [Miller *et al.* 2005; Haq and Schutter, 2008] created an inland sea in the Midcontinent bounded by the Ancestral Rockies to the paleo-north and the Appalachian-Ouachita Mountains to the paleo-south (Fig. 2). The Midcontinent Seaway opened westward into the Panthalassa Ocean through a narrow seaway (Hovey Channel, Delaware Basin, and Midland Basin) between the Ancestral Rockies and the Marathon – Ouachita Orogeny (Fig. 2). It is through this opening that the Panthalassa seawater floods in and out of the Midcontinent Basin as the global sea level rose and fall.



**Figure 2:** Paleogeography of the Late Pennsylvanian Midcontinent Basin of North America. Edmonds #1, Michelson #1 and #2 and Ermal #1 are the four cores that were sampled for this study of the Missourian Hushpuckney core black shale. Note that the Edmonds core is closer to the influx from rivers delivering freshwater from the east and north. Figure from *Algeo and Heckel* [2008]. Abbreviations: AnB = Anadarko Basin, ArB = Arkoma Basin, AWU = Amarillo–Wichita Uplift, BD = Bravo Dome, CBP = Central Basin Platform, DtB = Dalhart Basin, ES = Eastern Shelf, HA = Horseshoe Atoll, HC, Hovey Channel, MA = Matador Arch, MB = Midland Basin, MRA = Mississippi River Arch, OA = Ozona Arch, PDB = Palo Duro Basin, SC = Sheffield Channel.

Estimated maximum water depths on the shelf range upwards of 80 m and deeper in basinal areas leading to condensed marine sections, often expressed by reduced, black, laminated shales characteristically high in TOC, redox sensitive elements, rare-earth elements, and pelagic fauna [Coveney *et al.*, 1987; Hatch and Leventhal, 1992; Kidder *et al.*, 2003; Cruse and Lyons, 2004; Feldman *et al.*, 2005]. Benthic anoxia appears to have been amplified by a replenishing of deep oceanic water and freshwater influx from the surrounding landmass [Algeo *et al.*, 2004] leading to a complex and often punctuated succession of short-lived dysaerobic and near-oxic events [Schultz, 2004]. During the Pennsylvanian, the portions of the continent that were in the rain belt developed major swamps resulting in

burial of terrestrial organic matter. Economic coal deposits in Kansas occur in the Desmoinesian and are attributed to wetter climate and peat accumulation, which was particularly widespread during the initial stages of marine transgression during cyclothem sedimentation [Peppers,

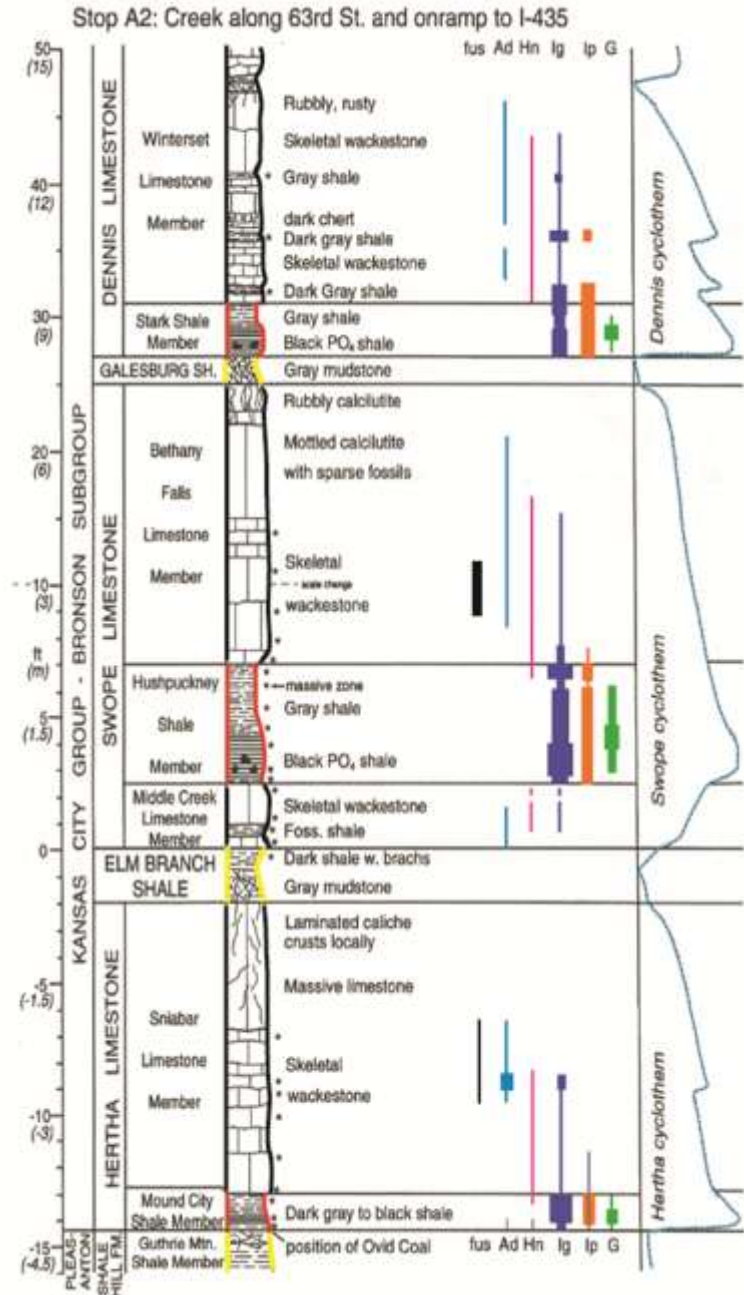
1996; West *et al.*, 1997]. In the drier areas of the Midcontinent, distant from

tectonic activity, the depositional sequences are represented by major limestone-dominated cyclothem, and far fewer coals. These drier times are exemplified by the Upper Pennsylvanian Hushpuckney Shale which is the focus of this study (Fig. 3).



**Figure 3:** The Swope formation in an outcrop alongside a creek beside 63rd street at I-435 in Jackson County, Missouri. The Hushpuckney “core” shale member is between two limestone members; Bethany Falls (regressive) and Middle Creek (transgressive).

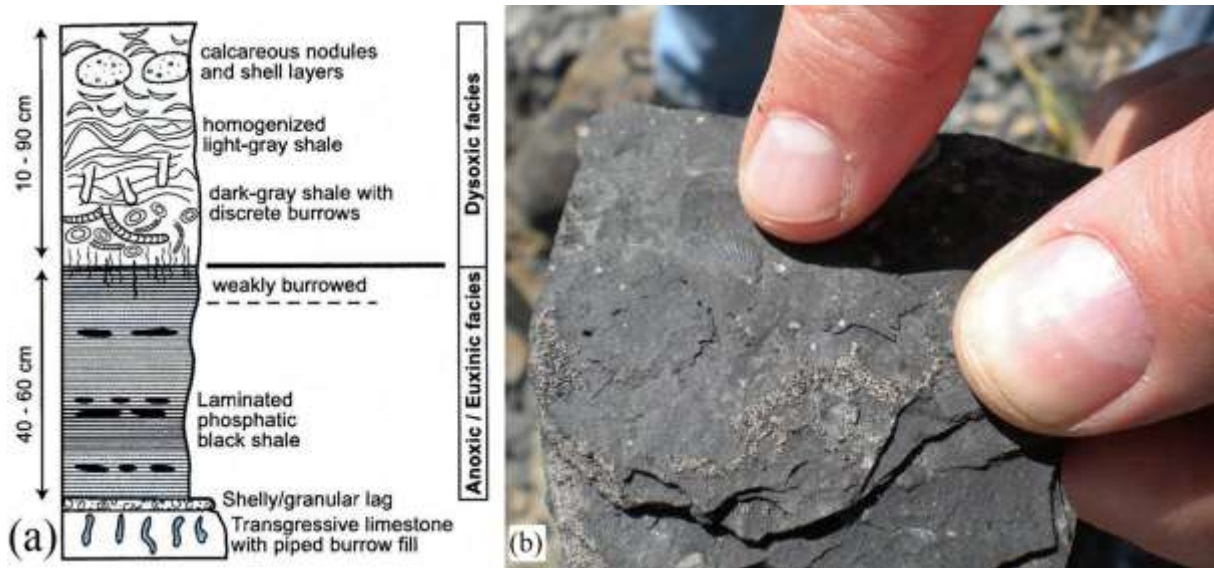
The Hushpuckney core black shale is a member of the early Missourian Swope Formation. Black shales such as this represent high stands of sea level and are characterized by high total organic carbon (TOC) and associated trace metals, and cosmopolitan fauna. The Hushpuckney member is between the thin transgressive Middle Creek Limestone Member at the base and the thick regressive Bethany Fall Limestone Member at the top (Fig. 3 and 4). The black shales represent a sediment starved, low oxygen environment based on their fine grain size, high concentrations of organic carbon and authigenic phosphate, enrichment in redox – sensitive



**Figure 4:** Stratigraphic position of the Hushpuckney shale in the Upper Pennsylvanian rocks of Kansas. Diagram from *Heckel, [1999]*

trace elements and sulfides, the absence of biota other than rare pelagic organisms, and <sup>34</sup>S depletion of authigenic Fe – sulfides [*Algeo et al., 2004*].

The lower portion of the Hushpuckney Shale member has a 40 – 60 cm thick laminated black shale sub member that is sparsely to non – fossiliferous and has a high TOC content > 2.5 wt.%. The top portion of the shale member is bioturbated, fossiliferous gray shale sub member ~10 – 90 cm thick with TOC content < 2.5 wt.% (Fig. 5).



**Figure 5:** (a) A model of core shale from the Upper Pennsylvanian “Kansas” cyclothems showing lower black shale and upper gray shale sub members [Algeo *et al.*, 2004]. (b) A brachiopod fossil I found in the Heebner “core” shale which is the one directly below the Hushpuckney during a field outing to a limestone quarry (Hamm Quarry) north of Lawrence, Kansas.

## Chapter 3 Methods

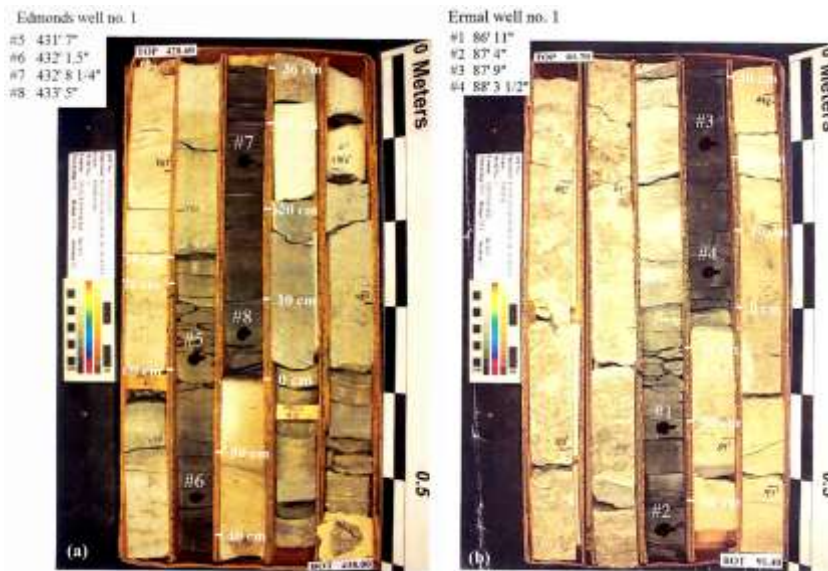
### 3.1 Sampling

Sample selections were made from four drill cores containing the Hushpuckney black shale member which were drilled in different locations in the state of Kansas; Edmonds Well no.1, Mitchelson Well no.1 and 2, and Ermal Well no.1 (Table 1, Fig. 2). These cores are curated by the Kansas Geological Survey (KSG). The Edmonds core is located in the northeastern corner of Kansas, on the “upper shelf” bordering the Arkoma basin. Algeo [2004] refer to Edmonds Well

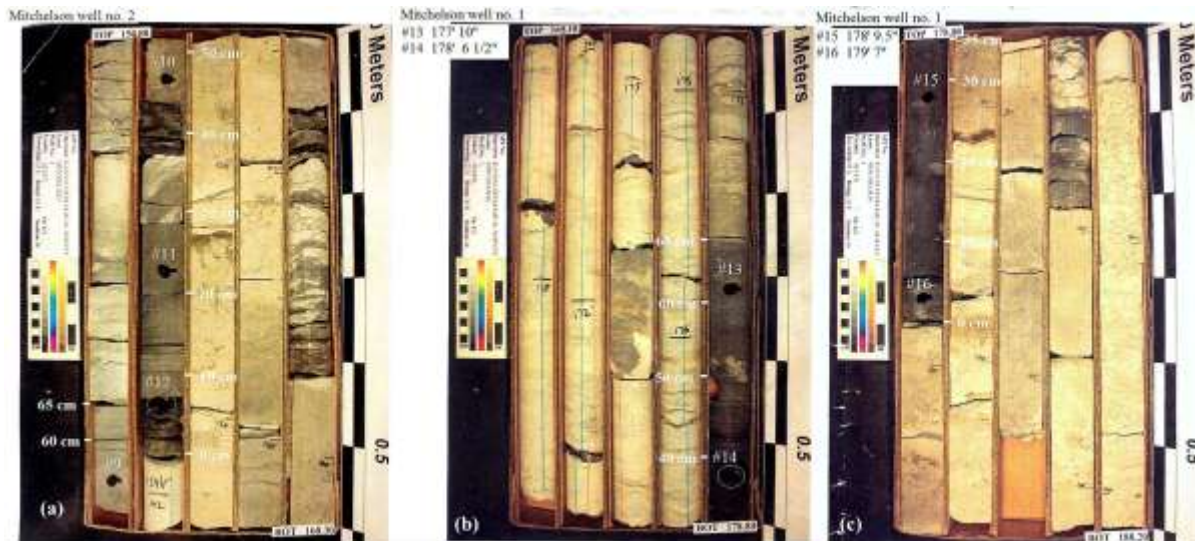
no. 1 as the open marine facies belt. The Ermal and Mitchelson cores are located on the lower shelf, more proximal to the Arkoma basin. Selections of cores were facilitated by our collaborator, W. Lynn Watney of the KGS and were selected based on their black color and the absence of phosphate nodules. Once selected, the lengths of the drill cores were measured, recorded, photographed, and sampled intervals were marked (Fig. 6-7).

Table 1. List of samples analyzed.

Sample Number	Core Name	Well No.	Well Depth	Redox Zone	Drill Location
#11	Mitchelson	2	152' 11"	Decreasing Euxinia	Allen County, Kansas
#12	Mitchelson	2	154' 5"	Increasing Euxinia	
#14	Mitchelson	1	178' 6 1/2"	Fluctuating Anoxia	
#15	Mitchelson	1	178' 9 1/2"	Decreasing Euxinia	
#16	Mitchelson	1	179' 7"	Increasing Euxinia	
#3	Ermal	1	187' 9"	Decreasing Euxinia	Crawford County, Kansas
#4	Ermal	1	188' 3 1/2"	Increasing Euxinia	Kansas
#5	Edmonds	1		Dysoxia (Gray Shale)	Leavenworth County, Kansas
#6	Edmonds	1	432' 1 1/2"	Fluctuating Anoxia	
#7	Edmonds	1	432' 8 1/4"	Decreasing Euxinia	
#8	Edmonds	1	433' 5"	Increasing Euxinia	



**Figure 6:** (a) The Edmonds Well no.1 drill core. The length of the drill core was measured, recorded, photographed, and sample sites were marked (#5-8). (b) . The Ermal Well no.1 drill core. The length of the drill core was measured, recorded, photographed, and sample sites were marked (# 1 – 4).



**Figure 7:** The Mitchelson Well no.2 and 1 drill core (a-c). The length of the drill core was measured, recorded, photographed, and sample sites were marked (# 10 – 16).

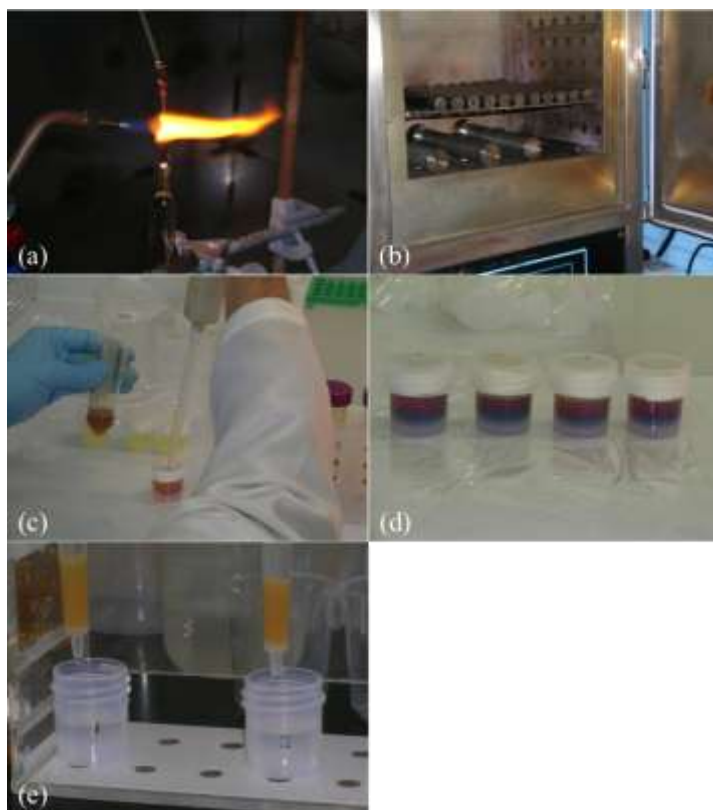
### 3.2 Chemical Separation Method

Approximately four grams of each sample were ground to a fine powder using an agate mortar and pestle. Inverse aqua regia was used to dissolve samples for Re, Os, and the other PGE chemistry because this technique is well established at the University of Maryland where the work was done under the supervision of Dr. Richard Walker. We recognize that the Re and Os in black shales are found in the hydrogenous component and it is considered that this complexation occurs at a time of sedimentation, whereas detritus is something to avoid because it does not represent the time of sedimentation. There is an additional complexity in that sulfide minerals form at the time of sedimentation in euxinic environments but additional sulfide minerals may form later. Due to the very high concentration of Re in the Hushpuckney samples and the very radiogenic nature of the Os isotopes, we felt that the problems encountered in other studies using the inverse aqua regia method, which suggest that some detrital Os might cause scatter in the Re – Os system [Selby and Creaser, 2003] should not be a problem here.



A more detailed description of the reverse aqua regia chemistry used in this study can be found in *Shirley and Walker* [1995], but briefly ~500 milligrams of finely powdered sample is sealed in Pyrex™ Carius tubes along with a mixed  $^{191}\text{Ir}$ ,  $^{99}\text{Ru}$ ,  $^{194}\text{Pt}$ , and  $^{106}\text{Pd}$  spike and individual  $^{185}\text{Re}$ ,  $^{190}\text{Os}$  spikes for isotope dilution; and concentrated nitric (5g) and hydrochloric (3g) acid. The Carius tubes were heated in steel jackets in steel jackets at 240°C for 48 hours to obtain complete sample spike equilibration (Fig. 8a – b). Osmium was purified using a carbon tetrachloride solvent extraction technique [Cohen and Waters, 1996] followed by microdistillation purification [Birck *et al.*,

1997; Fig. 8c – d]. Rhenium, Ir, Ru and Pd were separated and purified from the residual acid using ion exchange columns with 200–400 mesh resin (Fig. 8e). Osmium was analyzed via Negative Thermal Ionization Mass Spectrometer (NTIMS) with an ion counter [Creaser *et al.*, 1991] on the NBS designed 68 degree sector, 12 inch radius of curvature TIMS at the University of Maryland. The multiplier



**Figure 8:** (a – b) Sealed Pyrex™ Carius tubes in steel jackets heated to 240°C in oven. (c – d) The carbon tetrachloride solvent extraction technique followed by osmium microdistillation. (e) Ion exchange columns with 200–400 mesh resin.

was calibrated and tested for accuracy using a 3ng Os standard. The measured 68 degree sector, 12 inch radius of curvature  $^{188}\text{Os}/^{188}\text{Os}$ ,  $^{186}\text{Os}/^{188}\text{Os}$ , and  $^{189}\text{Os}/^{188}\text{Os}$  ratios are 0.1138, 0.1120, and 1.221 respectively. Rhenium, Ir, Ru, Pt, and Pd analyses were conducted using a Nu Plasma multicollector

Inductively Coupled Plasma Mass Spectrometer (ICP-MS) coupled with a Cetac Aridus™ desolvating nebulizer. Isotopic ratios from standard runs (300ppt Pd, 200ppt Pt, 500ppt Ru, 200ppt Ir, and a 100ppb Re – 50ppb W mix) were used to make fractionation corrections to the measured Re, Ru, Pt, Ir, and Pd ratios.

### 3.3 *Trace Element (TE)*

The sample powders were analyzed for Trace Elements (TE) using a Wavelength Dispersive X-ray Fluorescence (WDXRF) spectrometer at Stony Brook University's Department of Geosciences, under the supervision of Dr. Martin Schoonen. Approximately one gram of powdered sample was deposited into a sample vessel, which was then screwed into a steel container; the steel jackets for each sample analyzed were placed into the spectrometer and their positions recorded (Fig 9). Because we wanted to use the powders for additional analyses, they



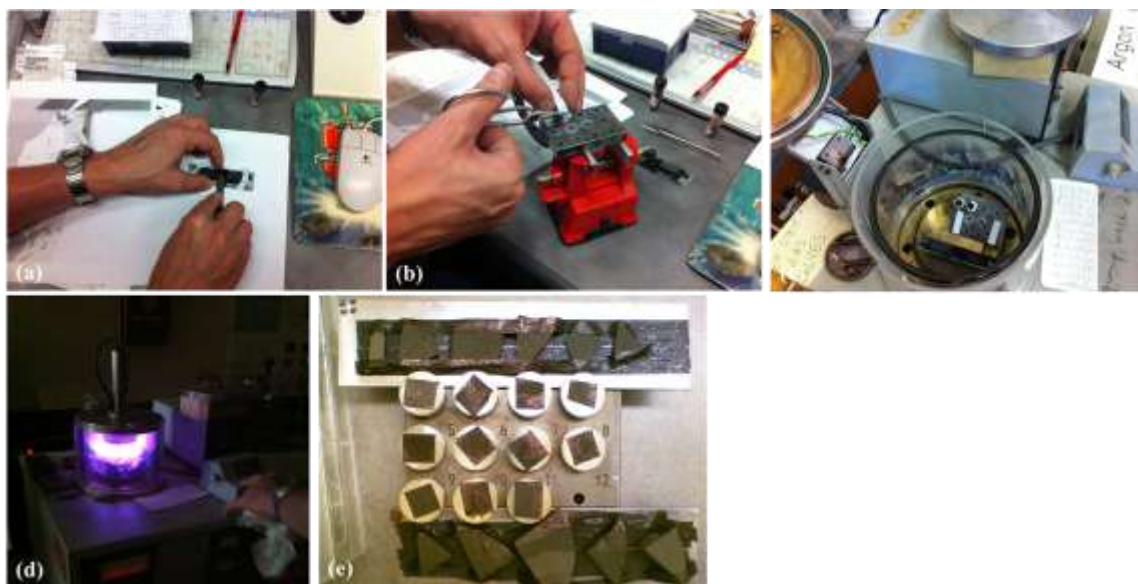
**Figure 9:** (a – b) Sample preparation for trace element analysis, using the Wavelength Dispersive X – ray Fluorescence spectrometer with the aid of Dr. Martin Schoonen at Stony Brook University.

were not made into pellets. We used a He atmosphere program for liquids to avoid disturbing the powder during analyses. The ‘Eval’ Bruker XRF program was used which gives major and trace element data that is detectable in weight percent. The reproducibility of the data was checked by measuring several of the samples more than one time and as a separate measurement. The

reproducibility uncertainty is ~10%. A black shale standard was not used, therefore it may be difficult to compare directly to other studies from black shales, but the comparison of results from this study provides an important look at the relative changes in redox sensitive elements with respect to the behavior of the Re-Os system.

### 3.4 Scanning Electron Microscope (SEM)

Samples (powders and whole rock) were examined with a Schottky Field – Emission Scanning Electron Microscope (SEM – model LEO1550) in the Material Sciences Department at Stony Brook University with the guidance of Dr. Jim Quinn. Whole rock samples from the cores were cleaved to produce fresh surfaces and strapped down with carbon double – sided tape onto the loading plate (Fig. 10a-b). A sputter coater was used to make the samples electrically conductive



**Figure 10:** (a –e) Sample preparation for Scanning Electron Microscope (SEM) analysis.

by covering the surfaces with gold (Fig. 10c). Argon gas and a high voltage were introduced in order to make a plasma which chemically eroded the gold (Fig. 10d) and prepared the samples to go into a vacuum (Fig. 10e). Samples were examined for anything that stood out, such as sulfides

which have heavy elements relative to silicates and are much brighter in the electron beam. We scanned the sample at relatively low magnification (120x) and when we encountered bright spots we went to higher magnification and got major element abundances with the EDAX for approximately 500 – 1000 counts per second.

## Chapter 4 Results

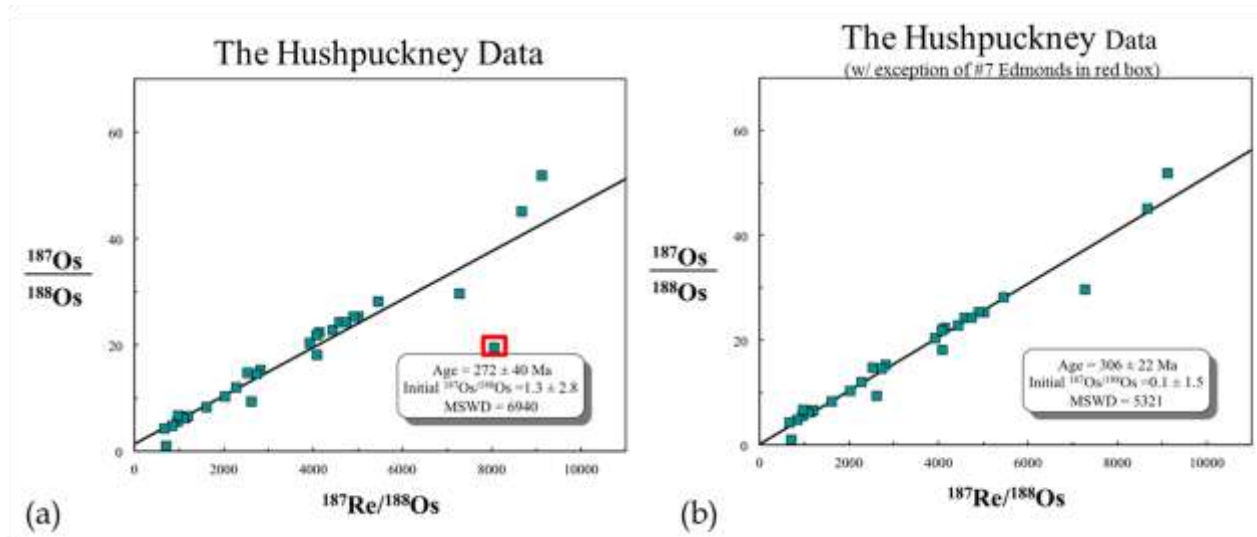
### 4.1 *Rhenium – Osmium*

Eleven samples were analyzed for Re and Os with a few replicates (Table 2). The analyses were done in five batches in January 2010, June 2010, July 2010, January 2011 and June 2011. The Re and Os concentrations,  $^{187}\text{Re}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  ratios ranges from 46.3 – 2,480 ppb, 0.27 – 11.6 ppb, 713 – 9,122 and 1 – 52 respectively. Model ages were calculated assuming an initial  $^{187}\text{Os}/^{188}\text{Os}$  of 0.1271 and they range from 143-347 Ma (Table 2). A linear regression of all of the analytically reliable data points give a calculated age of  $272 \pm 40$  Ma with a MSWD of 6940 (Fig. 11) using IsoExcel [Ludwig,2003].

**Table 2.** Rhenium and Osmium data for the Hushpuckney "core" black shales analyzed for this study.

Core Name and Well #	Depth	Re (ppb)	Os (ppb)	<sup>192</sup> Os (ppb) Common Os	<sup>187</sup> Re/ <sup>188</sup> Os	<sup>187</sup> Os/ <sup>188</sup> Os (corrected)	Model Age
#11 Michelson Well 2	152' 11"						
7/6/2010		1498.2 ± 3.6	6.033 ± 0.116	1.006	2621 ± 0.13	9.334 ± 0.02	2.09E+08
5/6/2011		1513.1 ± 0.8	9.353 ± 1.319	1.331	1610 ± 0.15	8.301 ± 0.12	3.04E+08
#12 Michelson Well 2	154' 5"						
<sup>a</sup> 6/7/2010		1450.7 ± 0.1	6.038 ± 0.313	0.1716	4401 ± 0.13	21.92 ± 0.04	2.92E+08
7/6/2010		1108.0 ± 2.7	4.872 ± 0.303	0.1338	3929 ± 0.13	20.37 ± 0.05	3.02E+08
6/6/2011		1103.8 ± 0.6	4.799 ± 0.313	0.1849	4134 ± 0.13	22.38 ± 0.05	3.03E+08
#14 Mitchelson Well no. 1	178' 6 1/2"						
<sup>a</sup> 7/6/2010		229.1 ± 1.3	1.726 ± 0.136	0.08822	1136 ± 0.13	6.255 ± 0.07	3.14E+08
<sup>a</sup> 1/25/2011		222.8 ± 0.8	1.720 ± 0.088	0.02902	1130 ± 0.13	6.494 ± 0.04	3.29E+08
<sup>a</sup> 5/6/2011		222.1 ± 0.3	1.655 ± 0.073	0.1743	1194 ± 0.13	6.640 ± 0.04	3.26E+08
#15 Mitchelson Well no. 1	178' 9 1/2"						
7/6/2010		2682 ± 6	10.98 ± 1.05	0.4603	5010 ± 0.14	25.31 ± 0.08	2.99E+08
<sup>a</sup> 1/25/2011		2784 ± 2	11.65 ± 0.51	0.3493	4902 ± 0.13	25.35 ± 0.04	3.05E+08
<sup>a</sup> 6/6/2011		2524 ± 2	9.803 ± 0.749	0.6133	4094 ± 0.13	18.17 ± 0.07	2.58E+08
#16 Mitchelson Well no. 1	179' 7"						
<sup>b</sup> 1/1/2010		46.29 ± 0.01	0.3960 ± 0.0015	0.1683	960.7 ± 0.13	5.567 ± 0.02	3.37E+08
<sup>a</sup> 6/7/2010		93.74 ± 0.08	0.7366 ± 0.0433	0.02319	999.2 ± 0.13	5.245 ± 0.06	2.89E+08
<sup>ab</sup> 6/6/2011		34.62 ± 0.17	0.2698 ± 0.0031	0.03375	979.3 ± 0.13	6.728 ± 0.07	2.74E+08
#3 Ermal Well no. 1	187' 9"						
1/1/2010		1221.2 ± 0.2	5.298 ± 0.026	1.0284	4596 ± 0.13	24.21 ± 0.012	3.13E+08
6/7/2010		2479.8 ± 0.2	10.26 ± 1.08	0.1110	4722 ± 0.14	23.74 ± 0.09	2.97E+08
7/6/2010		1069 ± 3	5.232 ± 0.226	0.05571	2822 ± 0.13	15.24 ± 0.04	3.04E+08
<sup>a</sup> 1/25/2011		1053 ± 1	5.630 ± 0.005	0.1213	2282 ± 0.14	12.01 ± 0.11	3.08E+08
<sup>ab</sup> 6/6/2011		1048 ± 1	5.186 ± 0.035	0.6363	2730 ± 0.13	14.55 ± 0.011	3.03E+08
#4 Ermal Well no. 1	188' 3 1/2"						
6/6/2011		1006.5 ± 0.5	4.361 ± 0.046	0.3870	4071 ± 0.04	21.78 ± 0.005	3.00E+08
#5 Edmonds well no. 1 ( <i>gray shale</i> )							
5/6/2011		64.94 ± 0.03	0.4882 ± 0.10	0.1633	713.0 ± 0.17	0.9903 ± 0.17	
#6 Edmonds Well no.1	432' 1 1/2"						
7/6/2010		354.7 ± 0.9	1.919 ± 0.030	0.2519	2031 ± 0.13	10.33 ± 0.02	2.89E+08
6/6/2011		320.5 ± 0.2	1.622 ± 0.041	0.1188	2527 ± 0.13	14.78 ± 0.02	3.01E+08
#7 Edmonds Well no.1	432' 8 1/4"						
<sup>b</sup> 1/1/2010		332.23 ± 0.05	0.6977 ± 0.011	0.1548	8060 ± 0.13	19.51 ± 0.02	1.43E+08
7/6/2010		1391 ± 3	5.613 ± 0.350	0.1606	5454 ± 0.13	28.16 ± 0.05	3.00E+08
6/6/2011		1827 ± 1	5.570 ± 0.512	0.2169	7280 ± 0.14	29.69 ± 0.08	2.28E+08
#8 Edmonds Well no.1	433' 5"						
7/6/2010		1103 ± 3	4.074 ± 0.416	0.05788	8674 ± 0.14	45.11 ± 0.09	2.99E+08
6/6/2011		1127 ± 1	4.108 ± 0.267	0.04829	9122 ± 0.13	51.88 ± 0.05	2.97E+08

Uncertainties are 2 sigma. Re and Os concentration uncertainties are from the Re standard bias [the fractionation correction uncertainty] and Os in - run precision (w/ exception to a = Re in - run precision and b = Os blank uncertainty). <sup>187</sup>Re/<sup>188</sup>Os and <sup>187</sup>Os/<sup>188</sup>Os uncertainties are the sum of (1) Re and Os blank uncertainty, (2) Re and Os spike calibration uncertainty, (3) Re and Os spike weight uncertainty, (4) sample weight uncertainty, (5) Re/Re and Os/Os internal error of mass spectrometer, and (6) the Re standard bias [the fractionation correction uncertainty]. <sup>190</sup>Os/<sup>192</sup>Os and <sup>185</sup>Re/<sup>187</sup>Re uncertainties were calculated based on the in - run precision of the mass spectrometers.



**Figure 11:** (a – b) Rhenium – Osmium errorchrons for the Hushpuckney black shales. The calculated Rho is 0.1 – 0.2. (a) All of the data that are considered reliable based on in run precision and appropriate spike addition for the concentrations. (b) All of the reliable data except for the data point from #7 Edmonds well no. 1 which has such an extreme range of ratios and concentrations that we feel something in the sample is making it difficult to obtain proper sample-spike equilibration

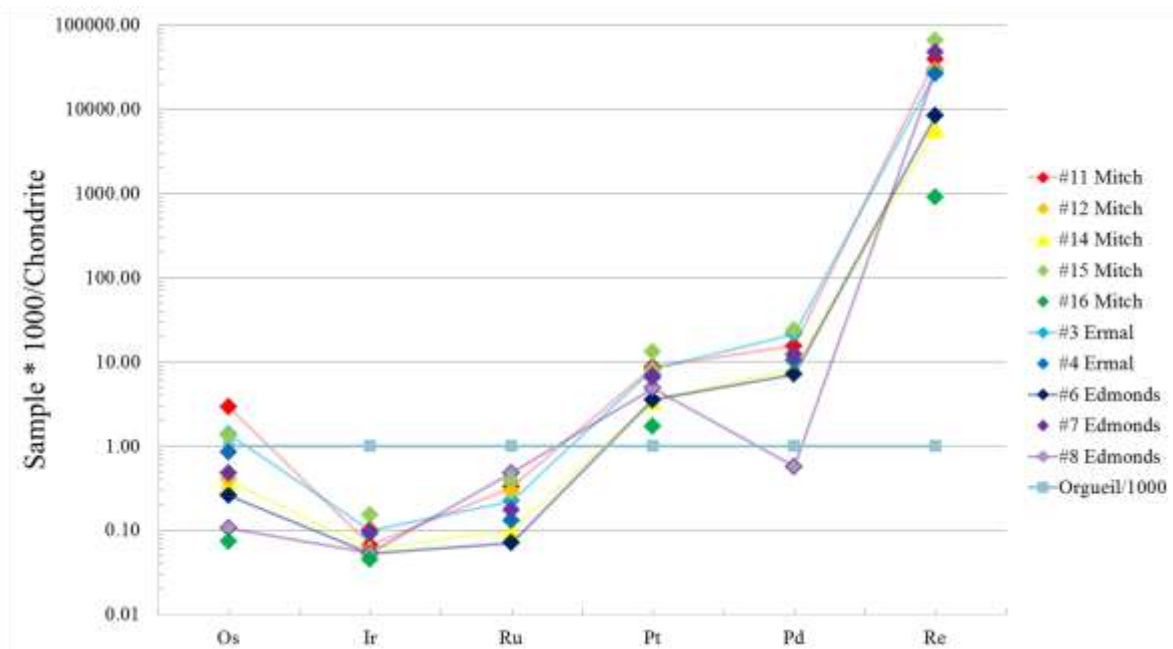
#### 4.2 HSE

The HSE were analyzed in the black shales only during the May and June 2011 lab visits and the data are listed in Table 3 along with their 2 sigma uncertainties. The concentrations are as follows; Os (0.27 – 9.8), Ir (0.02 – 0.07), Ru (0.04 – 0.31), Pt (3.0 – 11.3), Pd (0.32 – 13.3), and Re (34.6 – 1,827) in parts per billion. The data in Table 3 were used to make a HSE plot that is normalized relative to the chondrite Orgueil. The Hushpuckney samples have moderate enrichment to depletion of Os, extreme enrichment in Re, and are depleted in Ir and Ru and enriched in Pt and Pd relative to this chondrite (Fig. 12).

**Table 3.** Platinum Group Elements Data for the Hushpuckney "core" black shales analyzed for this study.

Core Name and Well #	Depth	Os	Ir	Ru	Pt	Pd	Re
#11 Michelson Well 2 5/6/2011	152' 11"	9.353 ± 1.319	0.0301 ± 0.005	0.2109 ± 0.0902	7.447 ± 0.001	8.699 ± 0.045	1513 ± 1
#12 Michelson Well 2 6/6/2011	154' 5"	4.799 ± 0.31	0.0476 ± 0.006	0.1892 ± 0.0969	6.615 ± 0.002	5.825 ± 0.049	1104 ± 1
#14 Michelson Well no. 1 5/6/2011	178' 6 1/2"	5.570 ± 0.073	0.0274 ± 0.006	0.0645 ± 0.0945	2.929 ± 0.003	4.750 ± 0.047	222.1 ± 0.3
#15 Michelson Well no. 1 6/6/2011	178' 9 1/2"	9.803 ± 0.749	0.0688 ± 0.005	0.2482 ± 0.0850	11.35 ± 0.001	13.37 ± 0.043	2524 ± 2
#16 Michelson Well no. 1 6/6/2011	179' 7"	0.270 ± 0.00	0.0203 ± 0.005		1.473 ± 0.007		34.62 ± 0.17
#3 Ermal Well no. 1 6/6/2011	187' 9"	5.186 ± 0.035	0.0452 ± 0.006	0.1444 ± 0.0958	7.020 ± 0.001	12.05 ± 0.048	1048 ± 1
#4 Ermal Well no. 1 6/6/2011	188' 3 1/2"	4.361 ± 0.046	0.0417 ± 0.005	0.0855 ± 0.1000	5.913 ± 0.002	5.873 ± 0.044	1006 ± 1
#6 Edmonds Well no.1 5/6/2011	432' 1 1/2"		0.0243 ± 0.006	0.1274 ± 0.0988	3.121 ± 0.003	3.972 ± 0.049	313.7 ± 0.9
#6 Edmonds Well no.1 6/6/2011	432' 1 1/2"	1.622 ± 0.041	0.0243 ± 0.006	0.0460 ± 0.1069	3.035 ± 0.003	3.996 ± 0.053	320.5 ± 0.2
#7 Edmonds Well no.1 5/6/2011	432' 8 1/4"		0.0345 ± 0.006	0.1923 ± 0.0934	5.595 ± 0.002	7.285 ± 0.047	
#7 Edmonds Well no.1 6/6/2011	432' 8 1/4"	5.570 ± 0.512	0.0451 ± 0.006	0.1123 ± 0.0990	5.574 ± 0.002	6.831 ± 0.050	1827 ± 1
#8 Edmonds Well no.1 6/6/2011	433' 5"	4.108 ± 0.267	0.0244 ± 0.006	0.3107 ± 0.0944	4.156 ± 0.002	0.3209 ± 0.047	1127 ± 1

Uncertainties are from the blank (2 sigma).



**Figure 12:** Iridium, Os, Ru, Pt, Pd, and Re normalized plot. Data normalized to the chondrite Orueuil.

#### 4.3 Major and Trace Elements (XRF)

The XRF program used a semi quantitative algorithm to generate concentrations for the detectable elements. The main focus here is on elements that are known to be controlled by redox and H<sub>2</sub>S such as Mo [2,980 – 230 ppm], V [4,260 – 628 ppm], Zn [12,340 – 100 ppm] , and Cr [418 – 2,600 ppm]. This enrichment and variability in the black shales is expected based on the work of *Algeo and Maynard* [2004] which shows enrichments of these elements in intervals of eunxina which were targeted for this study.

**Table 4.** XRF data in ppm

Formula	Na wt. %	Mg wt. %	Al wt. %	Si wt. %	P ppm	S ppm	Cl ppm	K wt. %	Ca wt. %	Ti ppm	V ppm	Cr ppm	Mn ppm
#11 Michelson Well no. 2	0.038	0.613	3.38	11.96	15400	10000	790	1.96	13.4	3610	3310	1330	260
#12 Michelson Well no. 2	0.117	0.907	4.84	15.30	5410	7820		2.84	7.13	4840	3550	418	330
#14 Michelson Well no. 1	0.192	0.643	5.42	16.85	8680	6550		2.62	7.33	4370	628	1090	240
#15 Michelson Well no. 1	0.075	0.855	4.09	15.06	4810	14400	1300	2.53	6.65	4350	4260	2600	330
#16 Michelson Well no. 1	0.220	2.345	4.56	12.63	2495	3680		2.2	17.8	3870		425	1340
#3 Ermal Well no. 1	0.135	0.691	4.63	15.34	5160	9693	847	2.74	4.73	4577	2510	2057	217
#4 Ermal Well no. 1	0.074	0.961	4.70	14.69	7680	7030		2.76	8.82	4830	2650	524	280
#5 Edmonds Well no. 1	0.453	0.833	6.10	19.72	240	6540		3.41	1.49	6460		350	341
#6 Edmonds Well no.1	0.376	0.923	5.95	18.32	628	6480	970	3.4	1.88	5930	820	859	355
#7 Edmonds Well no.1	0.155	0.986	4.48	13.99	6230	8840	1100	2.8	7.86	5080	2830	845	300
#8 Edmonds Well no.1	0.109	1.210	4.51	13.51	13400	5390	820	2.467	14.5	4260	1320	440	360

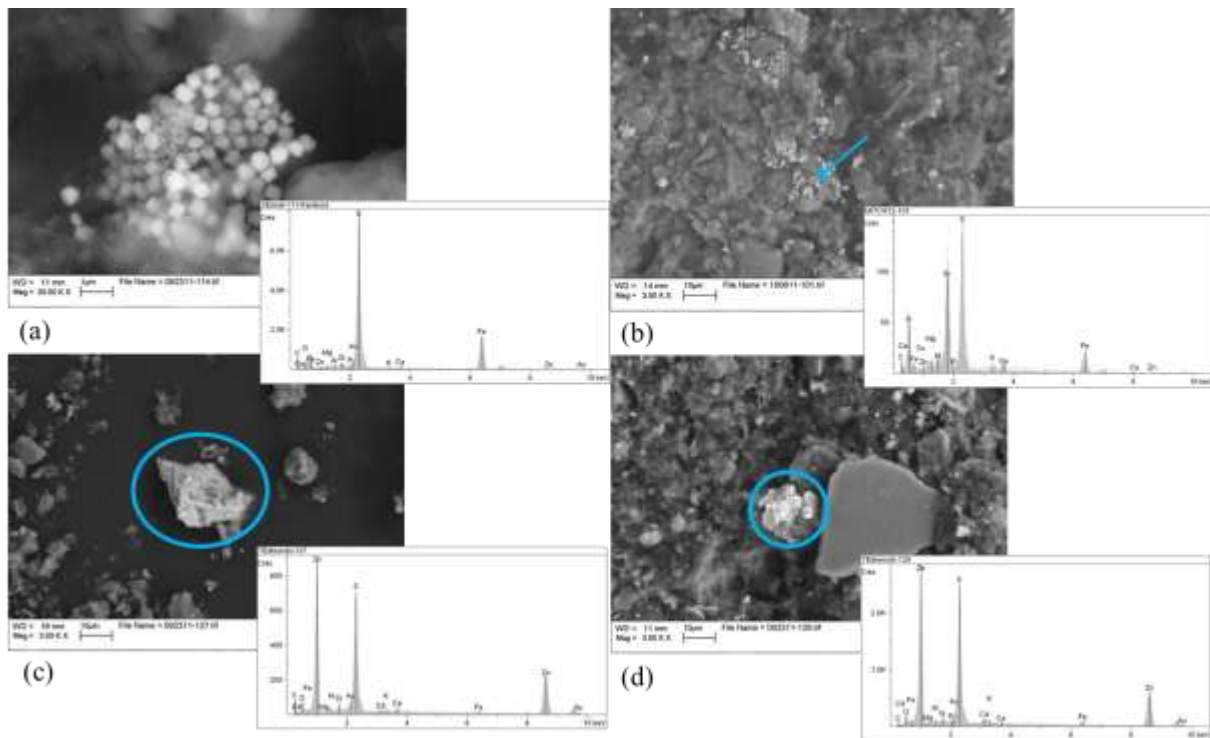
Formula	Fe wt. %	Ni wt. %	Ni ppm	Cu ppm	Zn ppm	Se ppm	Rb ppm	Sr ppm	Zr ppm	Mo ppm	Cd ppm	Pb ppm	U ppm
#11 Michelson Well no. 2	4.43	0.097	973	220	8489	194	182	3180		745			
#12 Michelson Well no. 2	4.78	0.072	719	229	6530	166	366	2460		2980	870	940	800
#14 Michelson Well no. 1	4.03	0.058	576	180	4320	90	324	2950		230			
#15 Michelson Well no. 1	6.02	0.141	1410	337	7260	216	298	1740		1430		940	660
#16 Michelson Well no. 1	3.92	0.024	240	155	185		103	3140					
#3 Ermal Well no. 1	4.40	0.100	997	303	4290	311	351	2370		759			
#4 Ermal Well no. 1	4.28	0.073	726	216	5510	142	331	2880		2150		940	800
#5 Edmonds Well no. 1	4.90	0.021	210		100	472		552	351				
#6 Edmonds Well no.1	5.25	0.052	516	180	1030		477	548	284	229			
#7 Edmonds Well no.1	5.61	0.088	881	285	6990	158	354	1100		1460	640	1140	750
#8 Edmonds Well no.1	3.80	0.048	480	170	12340	110	740	1430		470			

#### 4.4 SEM

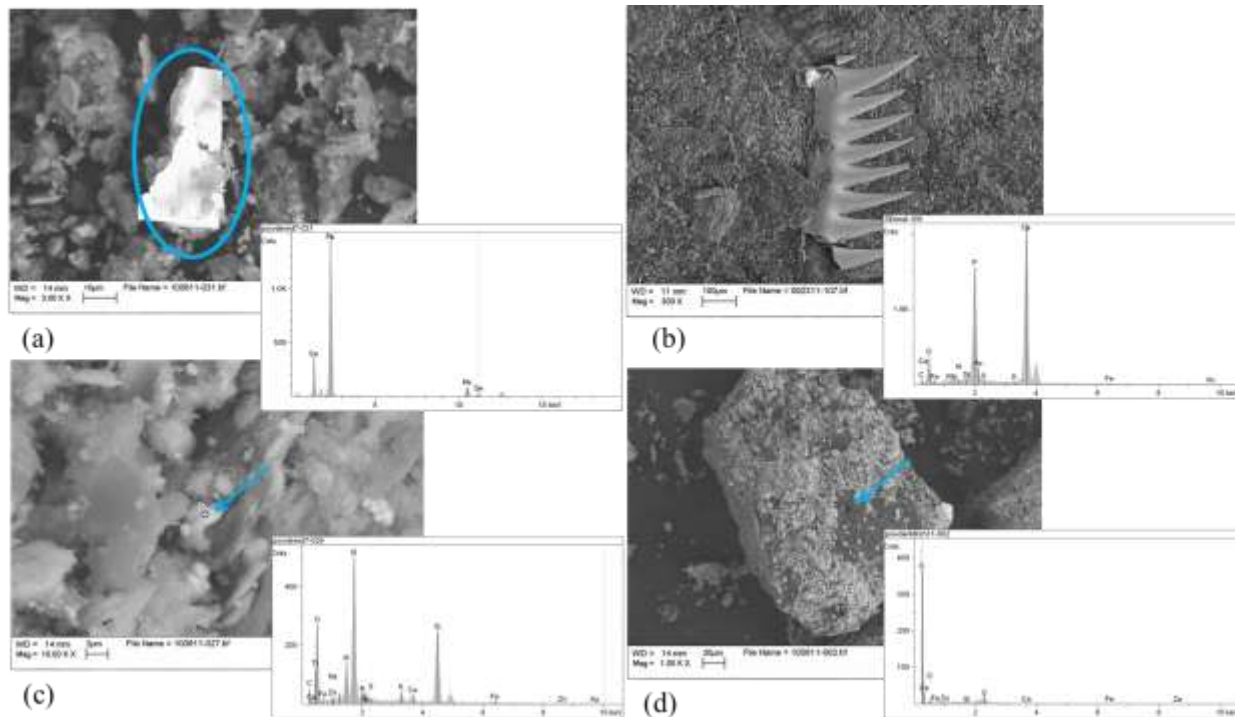
The SEM is an excellent way to examine shales for sulfides because their greater density makes them very easy to find. Sulfides can be a major sink for Re and it is important to try to understand how this influences the Re-Os results. The dominant sulfides in the Hushpuckney



black shales are sphalerite ( $ZnS$ ) – which often has  $Cd$  – and pyrite ( $FeS_2$ ) (Fig. 13a-d). Unusual minerals with notable element enrichments found in the Hushpuckney black shales are clausthalite ( $PbSe$ ),  $Sr$  with pyrite (Fig. 14a and 13b). Additionally we found conodont fossils, organic carbon, phosphate and calcium, silica,  $Ti$  (Fig. 14b-d).



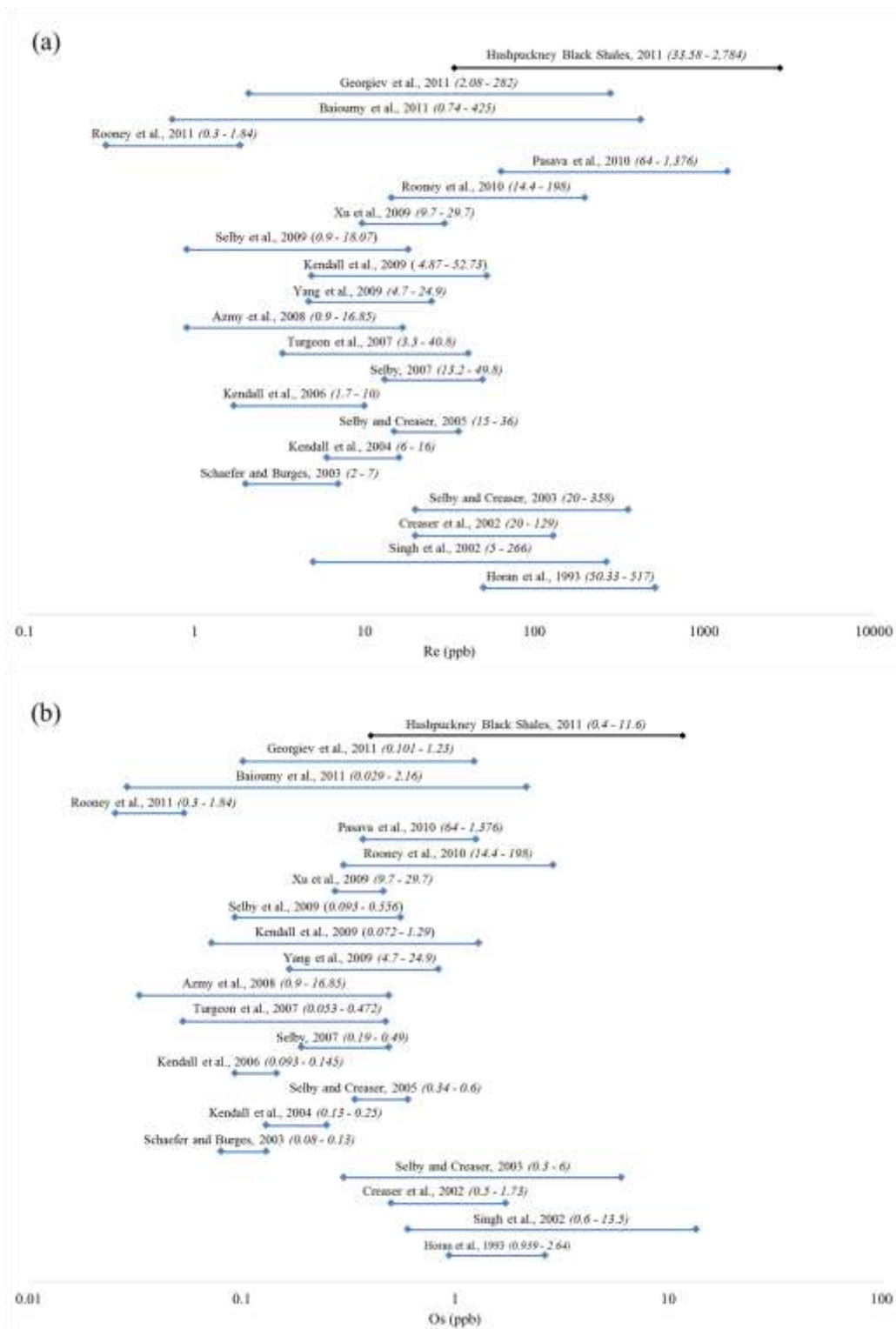
**Figure 13:** SEM images of (a) pyrite framboids, (b) strontium with pyrite, (c) sphalerite, and (d) cadmium + sphalerite next to a aluminum silicate (flat disk).



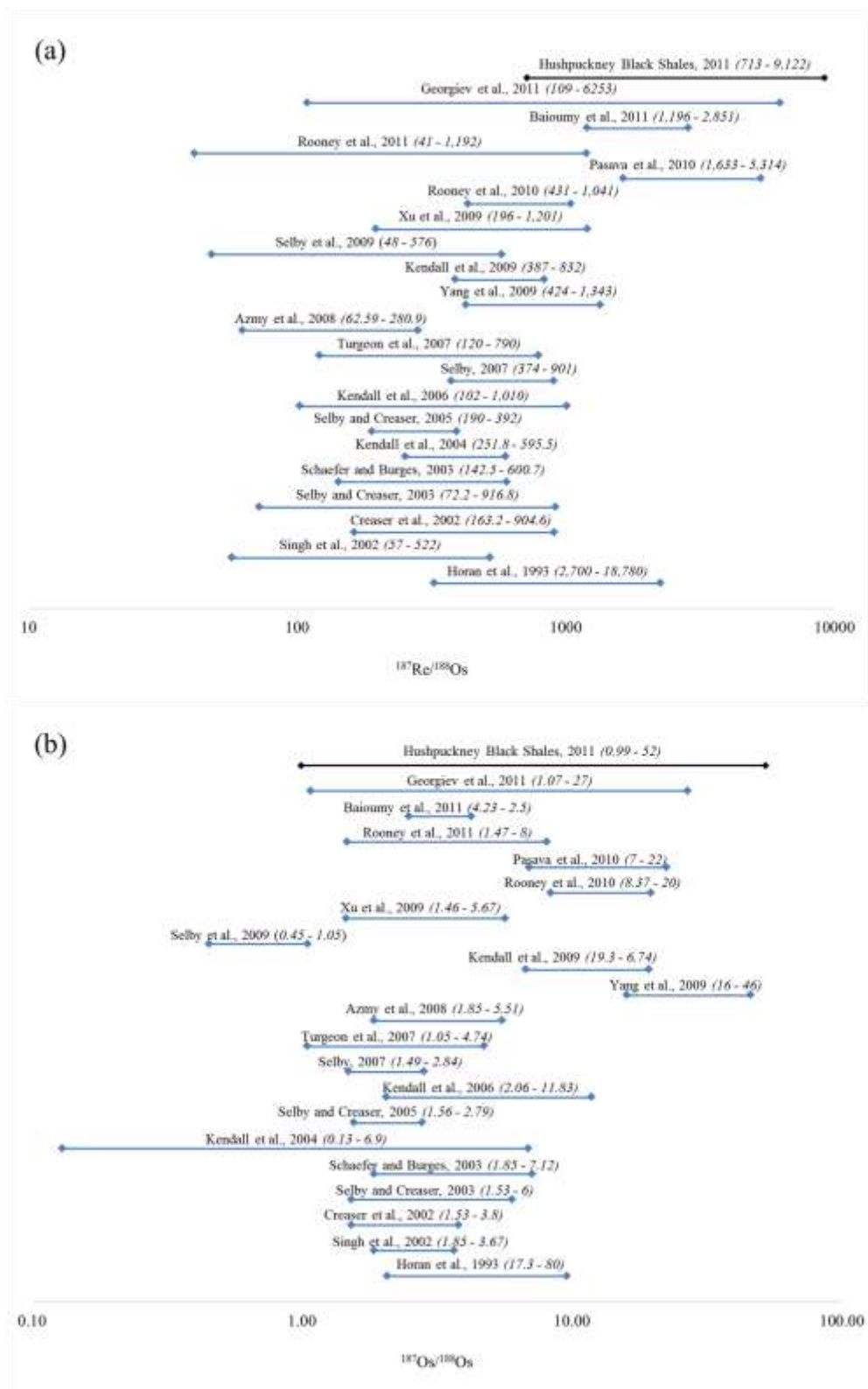
**Figure 14:** SEM images of (a) Calusthalite, (b) fossilized conodont, (c) silica + titanium, and (d) organic carbon.

## Chapter 5 Discussion

The Re concentrations from the Hushpuckney core black shale samples are quite variable and range from typical black shale enrichments of a few hundred ppb to values that are much higher to nearly 3,000 ppb; whereas Os concentrations have a similar range to published work (Fig.15). Due to the contrast in the behavior of Re and Os, the  $^{187}\text{Re}/^{188}\text{Os}$  ratio ranges from typical published values for black shales of less than 1000, to extreme values that are near 10,000 (Fig. 16a). Due to the extraordinary  $^{187}\text{Re}/^{188}\text{Os}$  ratios, the  $^{187}\text{Os}/^{188}\text{Os}$  ratios are also higher than published work even for much older samples (Fig. 16b).



**Figure 15:** Range of Re (a) and Os (b) in this study (in black) relative to published work on black shales. The extreme range of Re – relative to the typical Os concentrations – produces the highest  $^{187}\text{Re}/^{188}\text{Os}$  values that have been reported in the black shale literature.



**Figure 16:** The range of (a)  $^{187}\text{Re}/^{188}\text{Os}$  and (b)  $^{187}\text{Os}/^{188}\text{Os}$  in this study relative to published work on black shales.

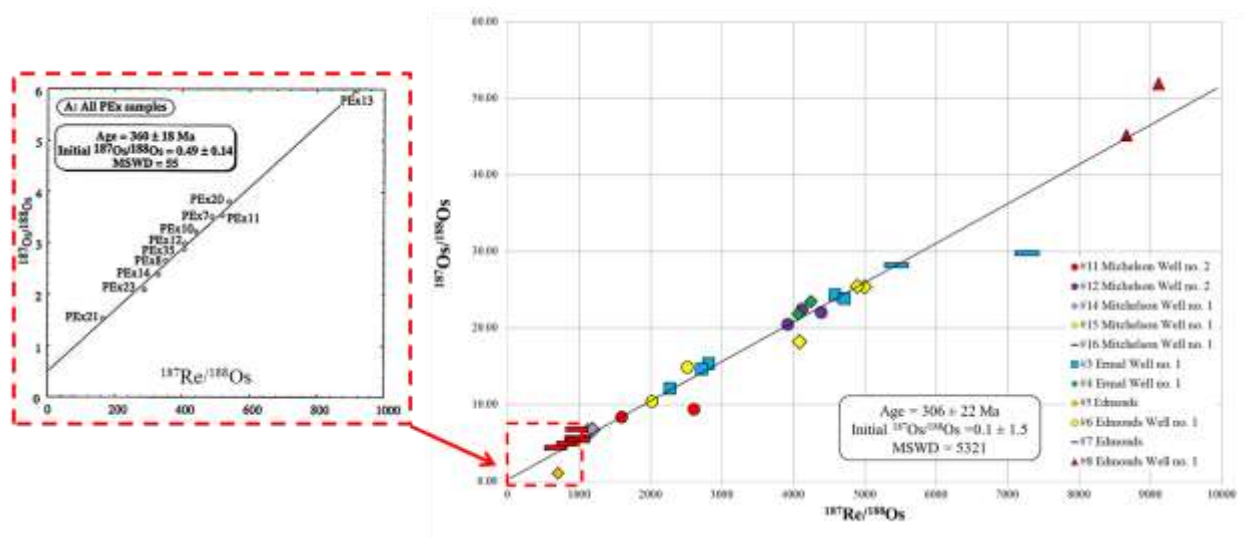
In spite of the impressive  $^{187}\text{Re}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  ratios, the Hushpuckney Re – Os results produce an errorchron with a MSWD of over 5000 (Fig. 11b). The data included in the errorchron calculation are considered reliable analytically because they have reasonable in run precision and are well spiked, and therefore there is no *a priori* justification for throwing them out. The boundaries of the Kasimovian (essentially the Missourian stage of North American nomenclature) is fairly well known from U – Pb zircon dating of ashes from the type section in the Urals [Ramezani *et al.*, 2007] that have been used with Milankovitch cycles to extrapolate to boundaries with uncertainties [Peterson, 2011], and are estimated at  $306.17 \pm 0.49$  to  $302.38 \pm 0.61$  Ma. Thus, the Swope Formation should be approximately 306 Ma – Early Missourian. The calculated age from the Hushpuckney black shale (excluding the #7 Edmonds sample, which has multiple lines of evidence for analytical complexities) is  $306 \pm 23$  Ma (Fig. 11b). While the age uncertainty is more than the duration of the Pennsylvanian, the close fit to the known age suggests that very little has changed the Re-Os system since the time of sedimentation.

Here I will consider several possible reasons for the scatter including, analytical technique, the presences of sulfides, and initial Os isotope heterogeneity due to water mass restriction. I will use the petrographic evidence for sulfides, XRF data showing high and variable redox sensitive elements such as Mo, and the HSE patterns to attempt to address the question of scatter in the Re/Os data.

### 5.1 Analytical Techniques

Selby and Creaser [2003] compared  $\text{CrO}_3 - \text{H}_2\text{SO}_4$  chemistry to the inverse aqua regia method for Re-Os analyses of the Devonian Exshaw black shale unit and found the  $\text{CrO}_3 - \text{H}_2\text{SO}_4$  produced far less scatter in the data. The reduction in scatter is due to the fact that  $\text{CrO}_3 - \text{H}_2\text{SO}_4$

targets only the hydrogenous (organic) portion of a whole rock sample and not the detrital and/or extraterrestrial phases [Selby and Creaser, 2003]. In the Hushpuckney study the inverse aqua regia method was used because this is a pilot study and the chemistry is well established at the University of Maryland where the work was done. Our starting justification for using the older technique, is based on the much higher concentrations of Re and to a certain degree Os than had been reported in previous studies (Exshaw Re: 20 – 358 ppb versus Hushpuckney Re: 33.5-2480 ppb; Exshaw Os: 0.3 – 6 ppb versus Hushpuckney Os:0.26-11.6 ppb). Because the Exshaw black shales had lower concentrations of Re and much lower  $^{187}\text{Re}/^{188}\text{Os}$ , any non – hydrogenous Re and Os could have more of an impact on the precision of data obtained. In the case of the Hushpuckney black shales, the large spread in the  $^{187}\text{Re}/^{188}\text{Os}$  means that the small amount of Re and Os contributed from detritus should have little impact on the isochron (Fig.17).



**Figure 17:** Comparison of isochrons from Selby and Creaser [2003] on the Exshaw black shale unit (red box) and the Hushpuckney black shale.

Multiple aliquots were run on most of the Hushpuckney samples and these were run in four different batches from January 2010 to June 2011. The reproducibility of the replicate analyses was used to assess the reliability of the data. In addition to the reproducibility, the in run precision and how well spiked the samples were for the isotope dilution method were criteria used for accepting or rejecting data. Taking a look back at figure 17, some samples such as #11 Mitchelson, #7 and 8 Edmonds, and #15 Mitchelson, shows the most extreme differences in the  $^{187}\text{Re}/^{188}\text{Os}$  ratios from the same samples. Some data points correlates well and plot on the reference line while others plot to the right – with the exception of #8 Edmonds which has the highest  $^{187}\text{Os}/^{188}\text{Os}$  ratio at 51.88 (Table 2), is the only sample to plot to the left of the reference line. It could be argued that the scatter in the data points is due to variability in the  $^{187}\text{Os}/^{188}\text{Os}$  initial ratio. However, it seems the most likely reason is lab problems during inverse aqua regia chemistry such as insufficient sample – spike equilibration, incomplete Os purification during the Carbon Tetrachloride ( $\text{CCl}_4$ ) extraction and micro – distillation, and bad ion exchange column chemistry hygiene

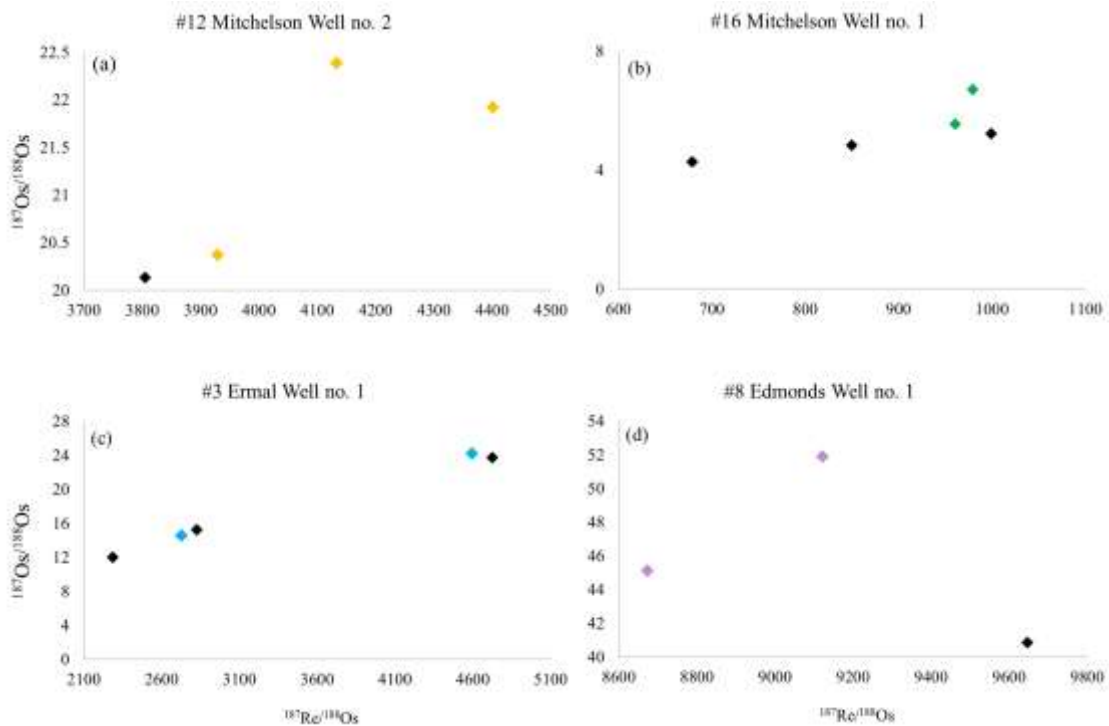
Erroneous spike weights due to evaporation before weighing, which would lead to lower calculated sample concentrations, or not washing all the spike solution into the Carius tube, which would lead to higher calculated concentrations could account for some of the scatter in the Re/Os. Insufficient time in the oven might only partially dissolve the sample, such that lower concentrations and erroneous Re/Os could be generated. Additionally, incorrect Re – Os spike weights, which are vital for isotope dilution method, also impact isotopic compositions. Correct Os spike quantity (ng) needs to be entered into the reduction program of the TIMS because the spike is subtracted from the measured ratios; incorrect quantities can lead to inaccurate ratio measurements.

Osmium can be lost if not enough  $\text{CCl}_4$  was added to and extracted from the Carius tube medium after digestion in the oven; but the most likely error is the incompleteness of the Os micro – distillation, where the dichromate did not have enough time to volatilize all the Os in the sample before this solvent was discarded. Completion of Os micro – distillation is normally determined based on the color of the dichromate. A red color indicates that all the Os in the sample has been volatilized. A green color indicates that more dichromate needs to be added to the sample for complete Os volatilization. If there was a misjudgment in color, then the dichromate could have been discarded before the collection of all of the sample's Os.

Bad column chemistry hygiene during the collection of Re could include inefficient cleaning and incorrect acid molarities. Cleaning the resin mesh is very important but keeping the walls of the columns above the resin clean is a common mistake often made during ion exchange chemistry. A residue of unwanted acids or unclean sample could have been left behind as droplets stuck on the walls of the columns due to adhesion. If these unwanted droplets are not washed away before Re collection, it is possible to collect unwanted elements which could have an isobaric interference on Re signal during mass spectrometry; leading to incorrect  $^{185}\text{Re}/^{187}\text{Re}$  ratios. The recovery of Re due to incorrect acid molarities could be compromising because the sample's Re could either remain in the resin or was accidentally washed out before collection. If insufficient spike – sample equilibration, Carbon Tetrachloride ( $\text{CCl}_4$ ) extraction, Os micro – distillation, and unhealthy ion exchange hygiene – or combination of the four – took place in lab chemistry there would be impact on the accuracy of the Re – Os data. There is no way to determine if some or none of these factors resulted in the scatter to this data, but incomplete sample to spike equilibration is the most obvious culprit for the huge differences in the Re/Os of the same samples with similar  $^{187}\text{Os}/^{188}\text{Os}$ , that are notable in #7 Edmonds (Table 2; Fig. 17).



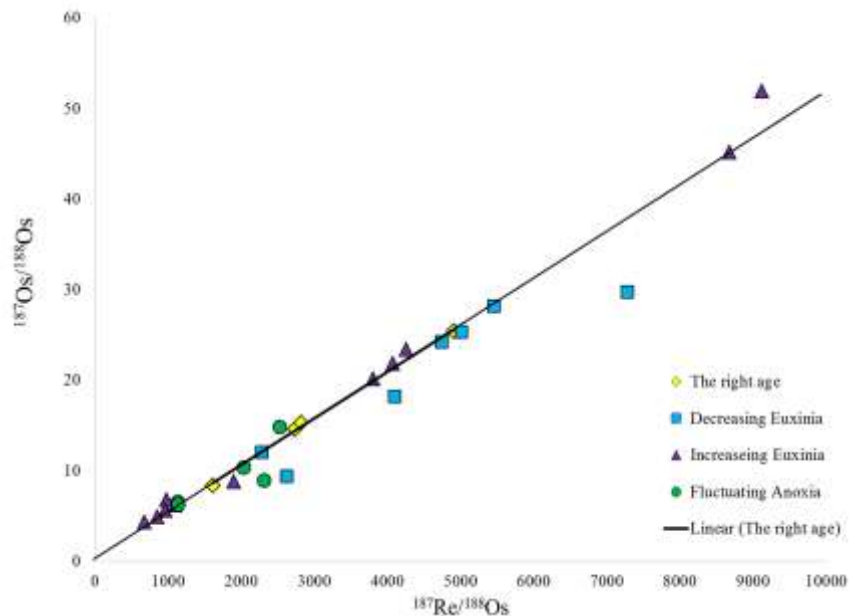
Under and over spiking the samples could perhaps contribute to the scatter of the Re – Os data. In order to determine the concentration of an element through the isotope dilution method it is imperative to have a well calibrated spikes (separate  $^{185}\text{Re}$  and  $^{190}\text{Os}$  spikes were calibrated and used for this study). Grossly over and under spiking a sample creates a large error magnification, producing not only a large uncertainty, but also reducing the reliability of the data. To test this theory Re – Os isochrons of samples that were ran in multiple aliquots, including data from the runs that were greatly over spiked, were made (Fig. 18). The figures do not reveal much scatter in the  $^{187}\text{Re}/^{188}\text{Os}$  results, therefore indicating that spiking issues are not a likely reason for the significant scatter. We must turn to other possible reasons such as the potential lab problems as described above and or sulfide nuggets which is discussed below.



**Figure 18.** Multiple runs of samples from the #12 Mitchelson, #16 Mitchelson, #3 Ermal and #8 Edmonds Wells no.1 plotted on a Re – Os isochron. The black diamonds are analyses that were over and under spiked while the others were equitably spiked. It is clear that the main scatter in the Re-Os data is not due to over spiking.

## 5.2 *Sulfide nuggets*

It is clear that the scatter in the Re/Os data is not simply from lab complexity because there are differences in the  $^{187}\text{Os}/^{188}\text{Os}$  ratios from aliquots of the same samples. For all of the samples that exhibit this behavior, there is a positive correlation of  $^{187}\text{Re}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$ . The most notable example is the #3 Ermal Well no. 1 sample (Table 2; Fig. 18) which appears to be two populations of data (Fig. 17). This behavior suggests that there are nuggets with high Re/Os, but because the two populations plot on the reference isochron, it seems unlikely that nuggets are responsible for creating the scatter. To further consider this, a reference isochron was created by taking only the data points that give the ‘correct’ model age (Table 2 samples that give model ages of about 304 Ma; Fig. 19). Interestingly some samples that plot off the regression line are from intervals that were interpreted as having been deposited during decreasing euxinia and one from a zone of alternating anoxia. However, many of the samples that were deposited during the same conditions plot on the regression line. It is possible an authigenic phase (such as a sulfide mineral) is favored during decreasing euxinia and that this mineral resists sample spike equilibration, making it a geologically

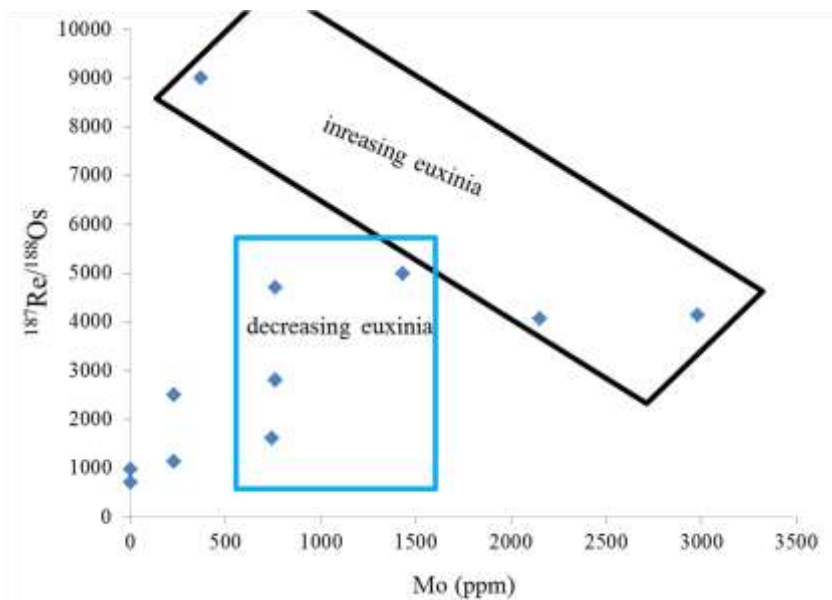


**Figure 19.** A reference isochron was constructed from samples that give the ‘correct’ model age. The rest of the data are plotted on the same graph and grouped by the redox facies based on previous studies and summarized in Table 1

controlled lab issue. This is to say, whatever mineral or phases that formed during the conditions of decreasing euxinia is problematic for dissolving and equilibrating with the spike.

Samples # 7 and 8 from the Edmonds core have the highest  $^{187}\text{Re}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  ratios (Fig 17). One difference between the Edmonds and the three other wells is that the Edmonds is further into the continent than the other wells (Fig. 2), and it was also deposited in shallower waters because the other wells are influenced by the subsidence of the Arkoma Basin. Thus geographically the Edmonds is further from the flux of seawater into this basin, and closer to the flux of freshwater that produces the pycnocline and euxinic conditions during maximum transgression. This is a setting where more sulfides could be expected. However, the trace element data (Table 4) does not show profound enrichments in Mo relative to samples from the

other wells. Nevertheless, if one examines Mo contents relative to the  $^{187}\text{Re}/^{188}\text{Os}$ , samples that were deposited during increasing euxinia appear to have a negative correlation with Mo (Fig. 20).



**Figure 20:** Mo concentrations plotted against  $^{187}\text{Re}/^{188}\text{Os}$  to examine potential controls on these ratios. The blue diamonds that are not enclosed are from fluctuating anoxia, while samples from intervals of increasing and decreasing euxinia are boxed.

Chondrite normalized HSE plots of published ore

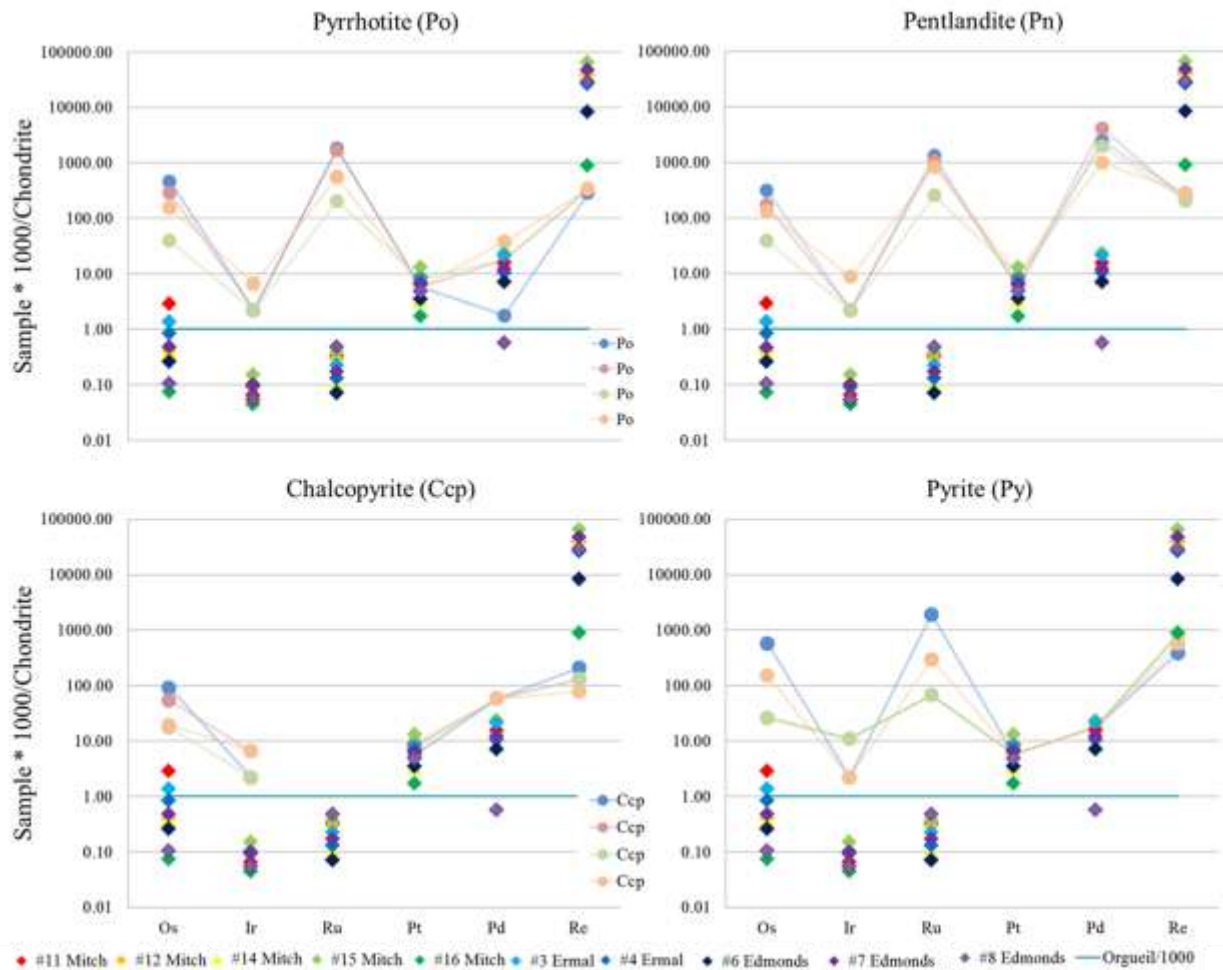
sulfides (which may not be a good proxy for sulfides that formed in seawater) pyrite ( $\text{FeS}_2$ ), pentlandite ( $\text{Fe, Ni}_9\text{S}_8$ , pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) and chalcopyrite ( $\text{CuFeS}_2$ ) all have distinctly less Re

compared to Os than the Hushpuckney black shales, and thus sulfides such as these could not be responsible for the nugget effect seen in some of the Hushpuckney samples (Fig. 21). Molybdenite ( $\text{MoS}_2$ ) is the most likely sulfide nugget because molybdenite has the highest concentration of Re (63,860 ppb) and  $^{186}\text{Os}$  (912 ppb) of all the Re – Os bearing sulfides and minerals (Table 5). This is because  $\text{MoS}_2$  is a Re – bearing mineral;  $\text{Re}^{4+}$  and  $\text{Mo}^{4+}$  have similar chemical and physical properties such as their ionic radius (0.71 Å Re and 0.68 Å Mo),  $4^+$  valance state, and electronegativity (1.9 Re and 1.8 Mo). According to the Goldschmidt rules of element substitution,  $\text{Re}^{4+}$  is ideal for  $\text{MoS}_2$  mineral structure. Although I did not observe  $\text{MoS}_2$  in my SEM study of these samples, I did find abundant framboidal pyrite (Fig. 13a) and *Coveney et al.* [1991] found that Mo occurs largely on the fringes of pyrite framboids. Additionally the XRF Mo data for this study ranges from below detection to 3000 ppm.

Table (5). Concentrations of Re and Os in minerals

Material	Concentration, ppb		Re/Os
	Re	Os	
Minerals			
Molybdenite	63,860	912 ( $^{187}\text{Os}$ )	Very Large
Native Gold	15.8	2890	0.0055
Pyrite	2.32	0.385	6
Pentlandite	146	9.1	16
Chalcopyrite	137	6.21	22
Pyrrhotite	168	11.1	15.1
Gersdorffite ( $\text{NiAsS}$ )	53.4	10,468	0.0051
Sulfide Cu - Ni - PGE	112	554	0.2
Olivine Sulfide Cumulate	1.93	70.6	0.027
Magnetite	10.8	0.51	21.2
Ilmenite	3.68	0.182	20.2
Chromite	0.478	50.7	0.0094
Garnet	12.6	--	--

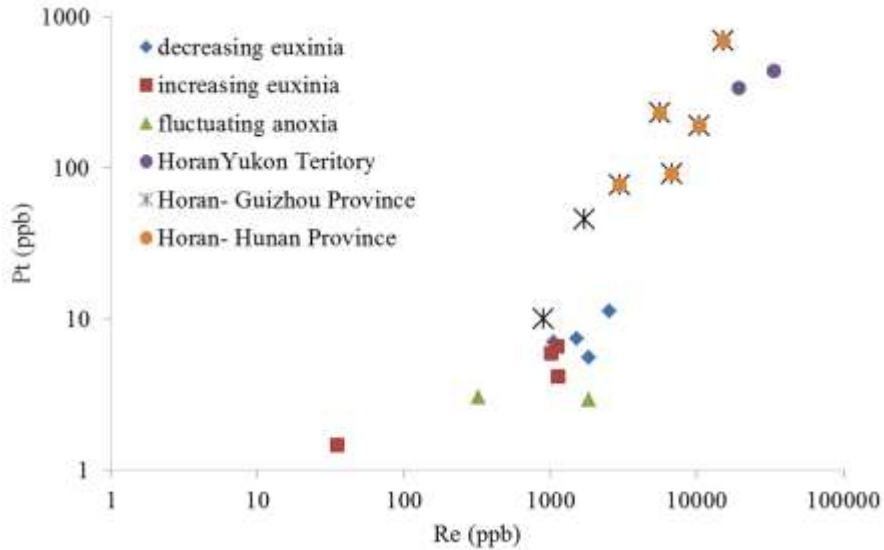
(Faure and Mensing, 2005)



**Figure 21** Highly Siderophile Elements from the Hushpuckney black shales and Fe – Ni – Cu – sulfides [Pyrrhotite (Po), Pentlandite (Pn), and Pyrite (Py), and Chalcopyrite (Ccp)] from *Dare et al.*, 2010. Normalized to the Orgueil chondrite.

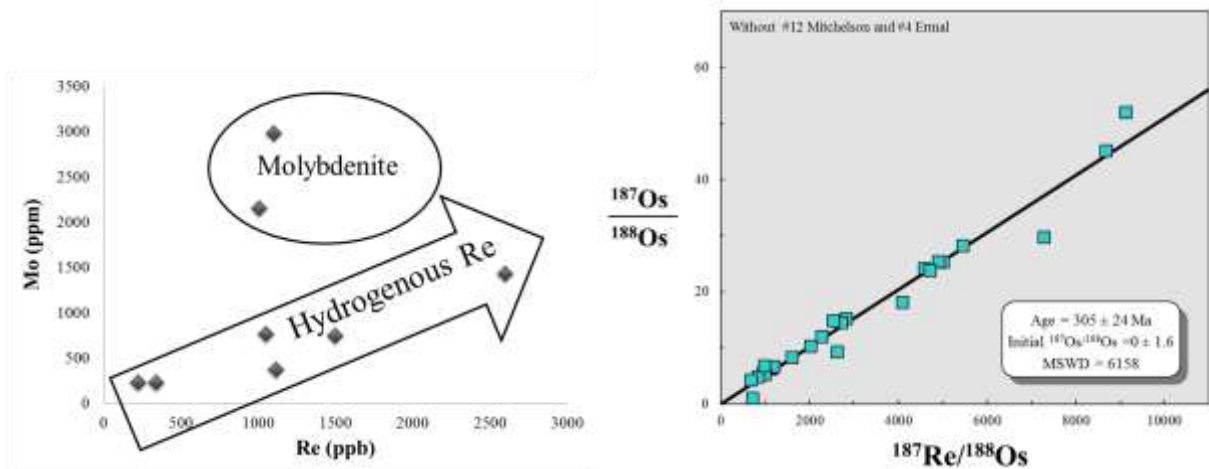
Unfortunately there are no published HSE patterns for molybdenite, but in addition to the Re and Os concentrations, *Horan et al.* [1994] studied ore grade Ni and Ni-Mo sulfides and black shales hosted in the sulfide layers from two localities in China and one in the Yukon Territory and this study provides a framework for considering the control of sulfides in the Hushpuckney black shale, because this study focused on sulfides associated with black shales and also presented Pt concentrations (Fig. 22). These ore grade Ni and Ni-Mo sulfides appear to have more Pt relative

to Re than the Hushpuckney samples and would thus have HSE patterns that are more like the sulfides from *Dare et al.* (2011). Based on the comparison of Re-Os data from the black shale and separated sulfides, it is clear that the sulfides must have formed within a few tens of millions of years of the time of sedimentation [*Horan et al.*, 1994].



**Figure 22.** Pt and Re data from ore grade sulfide deposits hosted in black shales from the Yukon Territory and from the Hunon and Guizhou Provinces of China [*Horan et al.*, 1994] show steeper slopes than the Hushpuckney samples or this study.

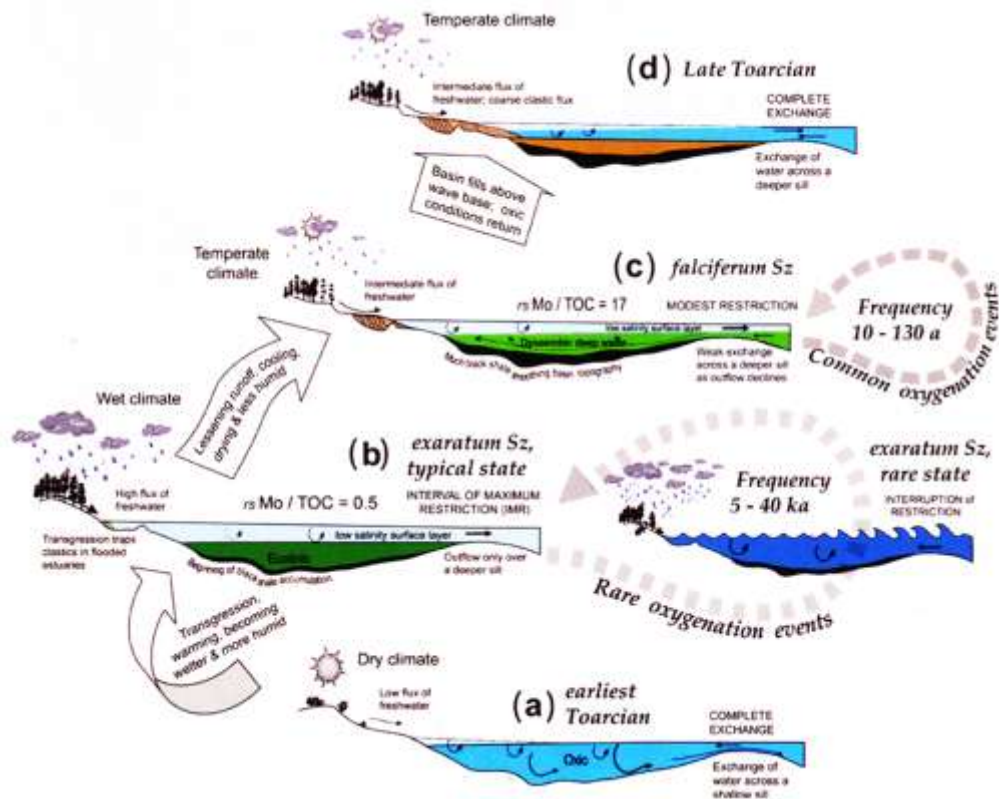
As an attempt to better understand the relationship between Mo and the Re-Os systematics and to filter out sulfides of  $\text{MoS}_2$ , I plotted Mo versus Re (Fig. 23). The data are quite scattered, but there appears to be a general positive trend of low Mo for the Re samples which may represent the hydrogenous Mo and Re, and two samples with much higher Mo concentrations relative to Re which might be representing a mixing trend towards molybdenite. An isochron plot excluding the samples with high Mo content (#12 Mitchelson and #4 Ermal Wells) does not improve the age uncertainty or MSWD (Fig. 23), suggesting that although  $\text{MoS}_2$  is likely present, it is not responsible for the scatter in the Re-Os data.



**Figure 23:** The plot of Mo versus Re reveals a lot of scatter. The data points that fall off the line designated as hydrogenous Re comes from the #12 Michelson and #4 Ermal which were excluded from the errorchron plot to the right, but made no difference in the age or uncertainty.

### 5.3 Water Mass Restriction

Water restriction in the Midcontinent Basin could have impact on dating organic rich sediments with Re – Os geochronology. *McArthur et al*, [2008] demonstrated that organic rich black shales with evidence for extended water mass restriction could not be dated by Re – Os because the initial Os/Os ratio was not constant over time (Fig. 24). Water mass restriction occurs when excess precipitation causes an increased flux of freshwater into a basin that acts as a cap, preventing the deeper water from mixing with the open ocean. This causes euxinia which draws down Re, perhaps preferentially over Os into the euxinic sediments. Something refreshes normal marine water into the basin basin (tropical storm or a regression) and makes the whole system oxic again. If the basin becomes restricted again, any new Re and Os introduced to the system will be drawn down and these changes from the marine Os isotope values to the freshwater flux which can be significantly different, establishes a heterogeneous initial Os isotope ratio.

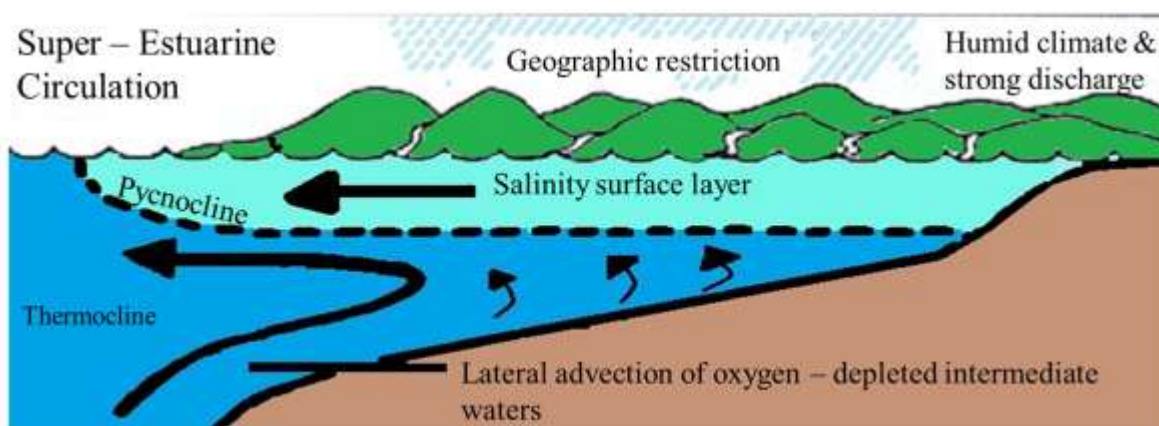


**Figure 24:** Model for how restricting a basin and limiting the exchange of seawater can draw down trace metals and produce a water column that is so dilute in Os that changes in the flux to the basin will cause significant heterogeneity in the initial Os isotope ratios [McArthur *et al.*, 2008].

Algeo and Heckel [2008] show that extended water restriction was not important in the Midcontinent Basin during the formation of the cyclothems although freshwater flux into the Midcontinent Basin from continental runoff produced a salinity surface water layer which extended from the eastern region to Midcontinent Shelf and possibly into the Great Permian Basin. This salinity surface water layer did not prevent the deep basin water from mixing with the open ocean because the subpycnocline water mass of the Midcontinent Basin was close to normal marine salinity, which could only be accomplished if there was frequent exchange with the open ocean waters. It was proposed that the Midcontinent Basin had super – estuarine like circulation (Fig. 25); unrestricted influx of cold deep waters with normal marine salinity circulating below via the narrow seaway (Hovey Channel, Delaware Basin, and Midland Basin)



between the Ancestral Rockies and the Marathon – Ouachita Orogeny and above the pycnocline, surface waters are also circulating unrestricted. Supporting the unrestricted influx of seawater theory, Mo and U data from the Hushpuckney shales plot at enrichment factors of about 0.3 to 1 suggest that replenishment to the Midcontinent Basin was frequent [Algeo and Tribovillard, 2009]. Further, the extreme Re/Os ratios of the Hushpuckney shale make small differences in the initial  $^{187}\text{Os}/^{188}\text{Os}$  unlikely to have much of an impact on the isochron.

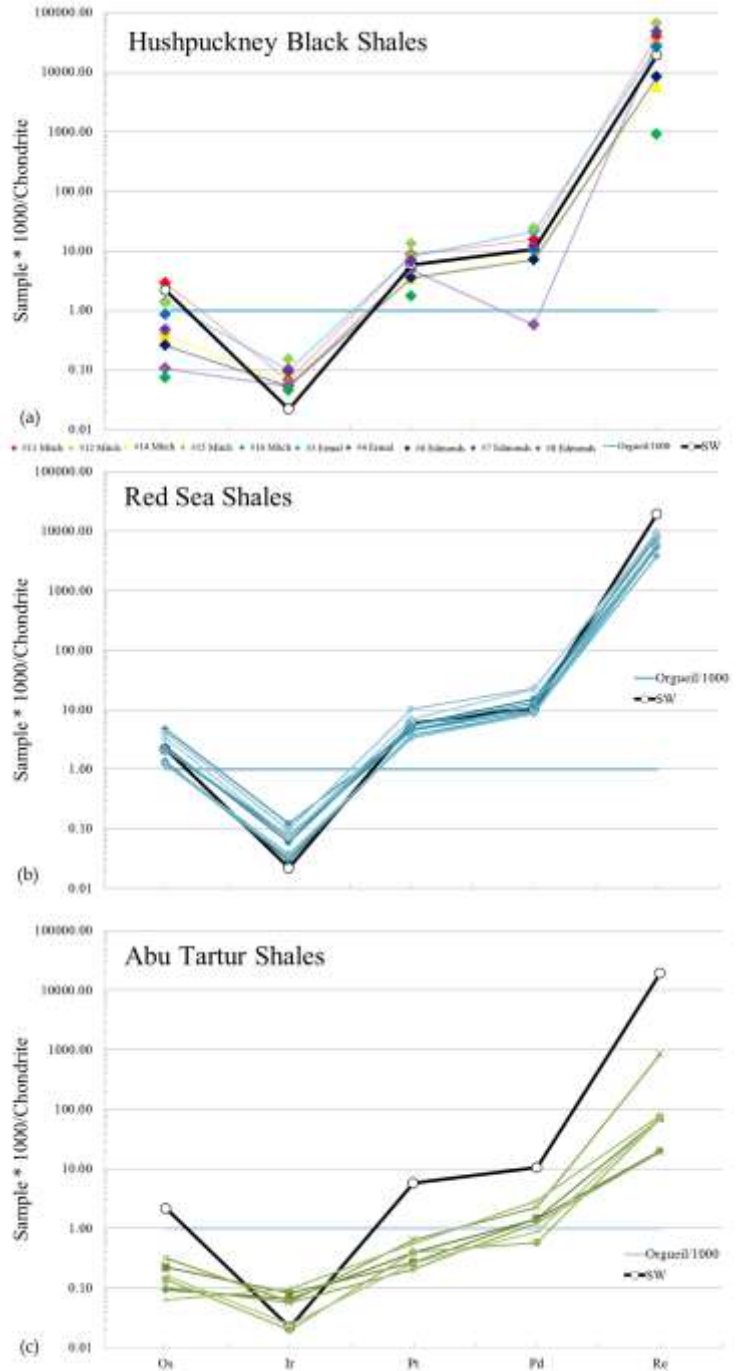


**Figure 25:** Super – estuarine circulation in the Midcontinent Basin. [Algeo et al., 2008].

Algeo and Heckel [2008] also demonstrate that the Midcontinent Basin was unrestricted based on the trace metal concentration patterns. Redox sensitive trace elements such as Mo and Zn tend to become depleted in the subpycnocline water mass of restricted silled anoxic basins due to drawdown into the sediment without adequate resupply. The Hushpuckney black shale units are the opposite; Mo remains elevated in the black shale, but drops off in the gray shale unit which was deposited above the organic rich sediment.

To further strengthen the idea that the Midcontinent Basin was unrestricted, the Hushpuckney HSE patterns are remarkably similar to seawater (Fig. 26a) and to Cretaceous marine black shales from the Red Sea region (Fig. 26b) which is considered to represent a unrestricted marine

setting [Baïoumy *et al.*, 2011]. Like the Hushpuckney black shale, the Red Sea black shale unit has elevated Re and Os concentrations (113 – 425ppb Re; 2.16 – 0.47ppb Os) and  $^{187}\text{Re}/^{188}\text{Os}$  ratios (2,590 – 1,190). Baïoumy *et al.* [2011] argue that organic rich marine sediments are characterized by unique HSE patterns that mimic that of average seawater, and the similarity of the Pennsylvanian Hushpuckney shales suggests a remarkable stability in the pattern through time. Baïoumy *et al.* [2011] also present HSE patterns for Abu Tartur shales that were deposited in restricted marine settings (Fig. 26c). Their HSE patterns are much less steep than seawater, further supporting the interpretation that the

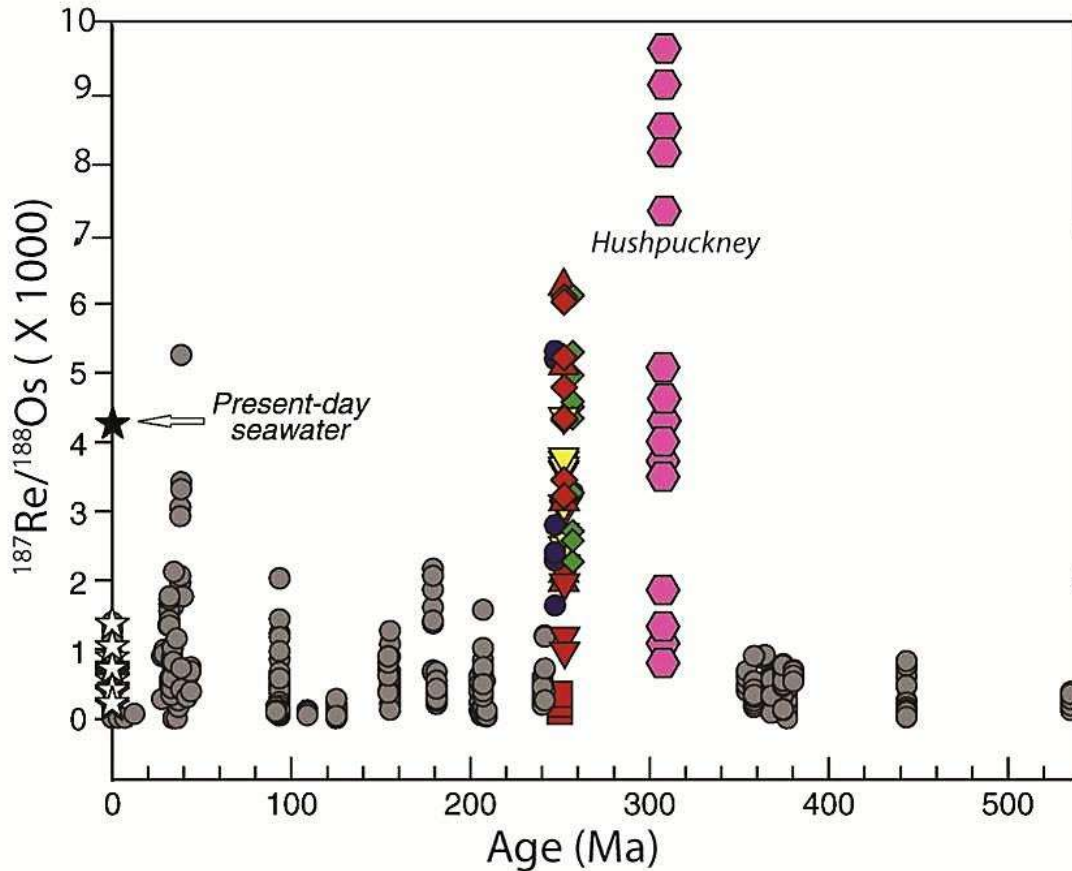


**Figure 26:** Highly Siderophile Element (HSE) data for (a) the Hushpuckney black shales; (b) the Red Sea black shales and (c) the Abu Tartur Shales from Baïoumy *et al.*, 2011. All data was normalized by the chondrite Orgueil. The average seawater (SW) concentrations (Ravizza, 2001; 10fg Os/g, 0.1 fg Ir/g, 50 fg Pt/g, 60 fg Pd/g, and 7.45 pg Re/g) multiplied by E+11, are shown for comparison as black line with open white circles.

Midcontinent Basin was unrestricted during Hushpuckney core black shale deposition. The difference in the HSE patterns between marine and terrestrial settings, also allows us to consider the *Coveney et al.* [1991] model that high Mo concentrations in the Midcontinent core black shales result in the input of terrestrial organic matter, where lower pH due to the near shore input of freshwater facilitates Mo uptake. The HSE patterns of the Hushpuckney core black shale are unlike those from coals and terrestrial black shales in the *Baioumy et al.* [2011] study. Further the compelling fit of the HSE with seawater argues strongly that Mississippi Valley Type (MVT) mineralization is not likely responsible for the Re and Os enrichment in the Hushpuckney, which we expect would be more like the Pt/Re ratios obtained in the *Horan et al.* [1994].

On the other hand, the large Re/Os ratios and concentrations could be viewed as the beginning of environmental changes in Panathassa. *Georgiev et al.* [2011] found similarly high  $^{187}\text{Re}/^{188}\text{Os}$  values from late Permian deposits of Greenland and Norway (Fig. 27). They used the Re – Os data as evidence that the late Permian oceans bordering the Pangea supercontinent experienced warming deep – water temperatures and increasing ocean acidity that they link to the deterioration of environmental conditions at the end of the Permian that led to the greatest extinction event in the Phanerozoic. *Georgiev et al.*[2011] reasoned that the high temperatures would strain biotic metabolisms and lower dissolved oxygen in seawater thereby promoting anoxia and H<sub>2</sub>S poisoning, thus interpreting the Re/Os as a syndepositional enrichment. On the other hand, *Pasava et al.* [2010] also found high  $^{187}\text{Re}/^{188}\text{Os}$  in the Permian Kupferschiefer, but attributed this to later diagenetic addition of the elements related to the ore mineralization found elsewhere in the Kupferschiefer. The Hushpuckney predates the Permian Triassic boundary by 55 million years and has even greater Re/Os ratios and Re enrichments. The Late Pennsylvanian is a time of glaciations with evidence of cool conditions even at equatorial latitudes [*Soreghan et al.*,

2008]. Obviously more work is necessary to understand the conditions that promoted anomalous Re/Os in the latest Paleozoic, but it is unlikely to be related to the factors that caused the mass extinctions.



**Figure27:** Re–Os isotopes in shales through the Phanerozoic.  $^{187}\text{Re}/^{188}\text{Os}$  from organic-rich rocks, showing extraordinarily high  $^{187}\text{Re}/^{188}\text{Os}$  for Upper Permian shales from four localities (East Greenland and Norway from the *Georgiev et al.* [2011] study; Poland (blue circles, Pasava et al., 2010), China (green diamonds, Yang et al., 2004), and the Hushpuckney black shales (pink hexagons). The gray circles are from published Re–Os shale data from multiple literature sources. Present-day  $^{187}\text{Re}/^{188}\text{Os}$  for seawater (black star, Peucker – Ehrenbrink and Ravizza, 2000) and Black Sea–Saanich inlet sediments (white stars, Poirier, 2006; Ravizza et al., 1991) are specified. Figure from *Georgiev et al.* [2011].

## Chapter 6 Conclusions

The Hushpuckney black shales of the Swope Formation in Kansas have highly variable  $^{187}\text{Re}/^{188}\text{Os}$  ratios and Re concentrations that exceed that of all published work on black shales.

These  $^{187}\text{Re}/^{188}\text{Os}$  ratios produce one of the widest ranges of  $^{187}\text{Os}/^{188}\text{Os}$  ratios published, and include some of the highest measured in black shales, even from the Archean. The only studies that have comparable  $^{187}\text{Re}/^{188}\text{Os}$  are from the Permian, leading us to speculate that unique conditions were associated with the initial amalgamation of Pangea that strongly influenced ocean chemistry. HSE patterns from the eleven Hushpuckney samples are remarkable similar to each other, although the range in concentrations is more than a factor of ten. The patterns are like present day seawater, which suggests that the basin had a good connection to the open ocean and that the enrichment was syndepositional, not from later mineralizing fluids.

## Chapter 7 Future Work

For future work it is suggested to take a closer look for molybdenite in the cores using heavy mineral separation techniques and analyze for Re-Os and HSE to compare with the data presented in this thesis. The impact of shale diagenesis should be considered as well, particularly to understand if the formation and dissolution of sulfides could affect the mobility of the HSE; similar to how phosphates played a role in the redistribution of REE (Rare Earth Elements) in *Lev et al.* [1998] study of shales. Total organic carbon and trace elements of the samples would provide insight into the Re-Os system with respect to the redox models of *Algeo and Maynard* [2004]. Additional gray shale submember samples from the cores should be sampled and processed for Re and Os and HSE to provide insight into the detrital background patterns.

## Work Cited

- Algeo, T. J., and Heckel, P. H., 2008, The Late Pennsylvanian Midcontinent Sea of North America: A review: *Palaeogeography Palaeoclimatology Palaeoecology*, v. 268, no. 3-4, p. 205-221.
- Algeo, T. J., and Maynard, J. B., 2004, Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems: *Chemical Geology*, v. 206, no. 3-4, p. 289-318.
- Algeo, T. J., Schwark, L., and Hower, J. C., 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, no. 3-4, p. 259-288.
- Algeo, T. J., and Tribouillard, N., 2009, Environmental analysis of paleoceanographic systems based on molybdenum-uranium covariation: *Chemical Geology*, v. 268, no. 3-4, p. 211-225.
- Azmy, K., Kendall, B., Creaser, R. A., Heaman, L., and de Oliveira, T. F., 2008, Global correlation of the Vazante Group, Sao Francisco Basin, Brazil: Re-Os and U-Pb radiometric age constraints: *Precambrian Research*, v. 164, no. 3-4, p. 160-172.
- Baioumy, H. M., Eglinton, L. B., and Peucker-Ehrenbrink, B., 2011, Rhenium-osmium isotope and platinum group element systematics of marine vs. non-marine organic-rich sediments and coals from Egypt: *Chemical Geology*, v. 285, no. 1-4, p. 70-81.
- Boardman, D.R., II, 1999. Virgilian and lowermost Permian sea – level curve and cyclothems; in, Middle and Upper Pennsylvanian (Upper Carboniferous) Cyclothems Succession in Midcontinent Basin, U.S.A., P.H. Heckel, ed.: XIV International Congress on the Carboniferous – Permian, Field Trip #8 Guidebook; Kansas Geological Survey, Open – file Report 99-27, p. 103-118
- Birck, J. L., RoyBarman, M., and Capmas, F., 1997, Re-Os isotopic measurements at the femtomole level in natural samples: *Geostandards Newsletter-the Journal of Geostandards and Geoanalysis*, v. 21, no. 1, p. 19-27.
- Buggisch, W., Joachimski, M. M., Sevastopulo, G., and Morrow, J. R., 2008, Mississippian delta C-13(carb) and conodont apatite delta O-18 records - Their relation to the Late Palaeozoic Glaciation: *Palaeogeography Palaeoclimatology Palaeoecology*, v. 268, no. 3-4, p. 273-292.

- Cohen, A. S., 2004, The rhenium-osmium isotope system: applications to geochronological and palaeoenvironmental problems: *Journal of the Geological Society*, v. 161, p. 729-734.
- Cohen, A. S., Coe, A. L., Bartlett, J. M., and Hawkesworth, C. J., 1999, Precise Re-Os ages of organic-rich mudrocks and the Os isotope composition of Jurassic seawater: *Earth and Planetary Science Letters*, v. 167, no. 3-4, p. 159-173.
- Cohen, A. S., and Waters, F. G., 1996, Separation of osmium from geological materials by solvent extraction for analysis by thermal ionisation mass spectrometry: *Analytica Chimica Acta*, v. 332, no. 2-3, p. 269-275.
- Colodner, D., Edmond, J., and Boyle, E., 1995, RHENIUM IN THE BLACK-SEA - COMPARISON WITH MOLYBDENUM AND URANIUM: *Earth and Planetary Science Letters*, v. 131, no. 1-2, p. 1-15.
- Colodner, D., Sachs, J., Ravizza, G., Turekian, K., Edmond, J., and Boyle, E., 1993, THE GEOCHEMICAL CYCLE OF RHENIUM - A RECONNAISSANCE: *Earth and Planetary Science Letters*, v. 117, no. 1-2, p. 205-221.
- Coveney, R. M., Leventhal, J. S., Glascock, M. D., and Hatch, J. R., 1987, ORIGINS OF METALS AND ORGANIC-MATTER IN THE MECCA QUARRY SHALE MEMBER AND STRATIGRAPHICALLY EQUIVALENT BEDS ACROSS THE MIDWEST: *Economic Geology*, v. 82, no. 4, p. 915-933.
- Coveney, R. M., Watney, W. L., and Maples, C. G., 1991, CONTRASTING DEPOSITIONAL MODELS FOR PENNSYLVANIAN BLACK SHALE DISCERNED FROM MOLYBDENUM ABUNDANCES: *Geology*, v. 19, no. 2, p. 147-150.
- Creaser, R. A., Sannigrahi, P., Chacko, T., and Selby, D., 2002, Further evaluation of the Re-Os geochronometer in organic-rich sedimentary rocks: A test of hydrocarbon maturation effects in the Exshaw Formation, Western Canada Sedimentary Basin: *Geochimica Et Cosmochimica Acta*, v. 66, no. 19, p. 3441-3452.
- Crowell, J. C., 1978, GONDWANAN GLACIATION, CYCLOTHEMS, CONTINENTAL POSITIONING, AND CLIMATE CHANGE: *American Journal of Science*, v. 278, no. 10, p. 1345-1372.
- Cruse, A. M., and Lyons, T. W., 2004, Trace metal records of regional paleoenvironmental variability in Pennsylvanian (Upper Carboniferous) black shales: *Chemical Geology*, v. 206, no. 3-4, p. 319-345.
- Crusius, J., Calvert, S., Pedersen, T., and Sage, D., 1996, Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition: *Earth and Planetary Science Letters*, v. 145, no. 1-4, p. 65-78.

- Dare, S. A. S., Barnes, S. J., and Prichard, H. M., 2010, The distribution of platinum group elements (PGE) and other chalcophile elements among sulfides from the Creighton Ni-Cu-PGE sulfide deposit, Sudbury, Canada, and the origin of palladium in pentlandite: *Mineralium Deposita*, v. 45, no. 8, p. 765-793.
- Doveton, J. H., and Merriam, D. F., 2004, Borehole petrophysical chernostratigraphy of Pennsylvanian black shales in the Kansas subsurface: *Chemical Geology*, v. 206, no. 3-4, p. 249-258.
- Faure, Gunter and Mensing, Teresa M. *Isotopes Principles and Applications* 3<sup>rd</sup> Edition. New Jersey: John Wiley & Sons, INC., 2005
- Feldman, H.R., Franseen, E.K., Joeckel, R.M., and Heckel, P.H., 2005, Impact of longerterm modest climate shifts on architecture of high-frequency sequences (cyclothems), Pennsylvanian of Midcontinent U.S.A., *JSR*, v., 75, no. 3, p. 350-368.
- Haq, B. U., and Schutter, S. R., 2008, A chronology of Paleozoic sea-level changes: *Science*, v. 322, no. 5898, p. 64-68.
- Hatch, J. R., and Leventhal, J. S., 1992, RELATIONSHIP BETWEEN INFERRED REDOX POTENTIAL OF THE DEPOSITIONAL ENVIRONMENT AND GEOCHEMISTRY OF THE UPPER PENNSYLVANIAN (MISSOURIAN) STARK SHALE MEMBER OF THE DENNIS LIMESTONE, WABAUNSEE COUNTRY, KANSAS, USA: *Chemical Geology*, v. 99, no. 1-3, p. 65-82.
- Heckel, P.H., 1999. Overview of Pennsylvanian (Upper Carboniferous) stratigraphy in midcontinent region of North America; in, *Middle and Upper Pennsylvanian (Upper Carboniferous) Cyclothems Succession in Midcontinent Basin, U.S.A.*, P.H. Heckel, ed.: XIV International Congress on the Carboniferous – Permian, Field Trip #8 Guidebook; Kansas Geological Survey, Open – file Report 99-27, p. 68-102.
- Heckel, P.H., Boardman, D.R., and Barrick, J.E., 1999. Proposed Desmoinesian – Missourian Stage boundary stratotype; in, *Middle and Upper Pennsylvanian (Upper Carboniferous) Cyclothems Succession in Midcontinent Basin, U.S.A.*, P.H. Heckel, ed.: XIV International Congress on the Carboniferous – Permian, Field Trip #8 Guidebook; Kansas Geological Survey, Open – file Report 99-27, p. 186-198.
- Heckel, P.H., 1999. Geologic, stratigraphic, and geographic context of stops; ; in, *Middle and Upper Pennsylvanian (Upper Carboniferous) Cyclothems Succession in Midcontinent Basin, U.S.A.*, P.H. Heckel, ed.: XIV International Congress on the Carboniferous – Permian, Field Trip #8 Guidebook; Kansas Geological Survey, Open – file Report 99-27, p 10 – 12..
- Heckel, P. H., 1977, ORIGIN OF PHOSPHATIC BLACK SHALE FACIES IN PENNSYLVANIAN CYCLOTHEMS OF MID-CONTINENT NORTH-AMERICA: *Aapg Bulletin-American Association of Petroleum Geologists*, v. 61, no. 7, p. 1045-1068.



- Horan, M. F., Morgan, J. W., Grauch, R. I., Coveney, R. M., Murowchick, J. B., and Hulbert, L. J., 1994, RHENIUM AND OSMIUM ISOTOPES IN BLACK SHALES AND NI-MO-PGE-RICH SULFIDE LAYERS, YUKON-TERRITORY, CANADA, AND HUNAN AND GUIZHOU PROVINCES, CHINA: *Geochimica Et Cosmochimica Acta*, v. 58, no. 1, p. 257-265.
- Jaffe, L. A., Peucker-Ehrenbrink, B., and Petsch, S. T., 2002, Mobility of rhenium, platinum group elements and organic carbon during black shale weathering: *Earth and Planetary Science Letters*, v. 198, no. 3-4, p. 339-353.
- Joachimski, M. M., von Bitter, P. H., and Buggisch, W., 2006, Constraints on Pennsylvanian glacioeustatic sea-level changes using oxygen isotopes of conodont apatite: *Geology*, v. 34, no. 4, p. 277-280.
- Kawasaki, K., Symons, D. T. A., and Coveney, R. M., 2006, Preliminary paleomagnetic dating of the metalliferous (Zn-Pb rich), Stark black shale, Kansas City region, USA: *Journal of Geochemical Exploration*, v. 89, no. 1-3, p. 174-178.
- Kendall, B., Creaser, R. A., Calver, C. R., Raub, T. D., and Evans, D. A. D., 2009a, Correlation of Sturtian diamictite successions in southern Australia and northwestern Tasmania by Re-Os black shale geochronology and the ambiguity of "Sturtian"-type diamictite-cap carbonate pairs as chronostratigraphic marker horizons: *Precambrian Research*, v. 172, no. 3-4, p. 301-310.
- Kendall, B., Creaser, R. A., Gordon, G. W., and Anbar, A. D., 2009b, Re-Os and Mo isotope systematics of black shales from the Middle Proterozoic Velkerri and Wollongorang Formations, McArthur Basin, northern Australia: *Geochimica Et Cosmochimica Acta*, v. 73, no. 9, p. 2534-2558.
- Kendall, B., Creaser, R. A., and Selby, D., 2006, Re-Os geochronology of postglacial black shales in Australia: Constraints on the timing of "Sturtian" glaciation: *Geology*, v. 34, no. 9, p. 729-732.
- Kendall, B. S., Creaser, R. A., Ross, G. M., and Selby, D., 2004, Constraints on the timing of Marinoan "Snowball Earth" glaciation by Re-187-Os-187 dating of a Neoproterozoic, post-glacial black shale in Western Canada: *Earth and Planetary Science Letters*, v. 222, no. 3-4, p. 729-740.
- Kidder, D. L., Krishnaswamy, R., and Mapes, R. H., 2003, Elemental mobility in phosphatic shales during concretion growth and implications for provenance analysis: *Chemical Geology*, v. 198, no. 3-4, p. 335-353.
- Lee, C. T. A., Wasserburg, G. J., and Kyte, F. T., 2003, Platinum-group elements (PGE) and rhenium in marine sediments across the Cretaceous-Tertiary boundary: Constraints on Re-PGE transport in the marine environment: *Geochimica Et Cosmochimica Acta*, v. 67, no. 4, p. 655-670.

- Lev, S. M., McLennan, S. M., and Hanson, G. N., 1999, Mineralogic controls on REE mobility during black-shale diagenesis: *Journal of Sedimentary Research*, v. 69, no. 5, p. 1071-1082.
- Lev, S. M., McLennan, S. M., and Hanson, G. N., 2000, Late diagenetic redistribution of uranium and disturbance of the U-Pb whole rock isotope system in a black shale: *Journal of Sedimentary Research*, v. 70, no. 5, p. 1234-1245.
- Lev, S. M., McLennan, S. M., Meyers, W. J., and Hanson, G. N., 1998, A petrographic approach for evaluating trace-element mobility in a black shale: *Journal of Sedimentary Research*, v. 68, no. 5, p. 970-980.
- Ludwig, K.R., 2003, User's Manual for Isoplot 3.00: A Geochronological Toolkit for Microsoft Excel: Berkeley Geochronological Center Special Publication No. 4, 70 p.
- McArthur, J. M., Algeo, T. J., van de Schootbrugge, B., Li, Q., and Howarth, R. J., 2008, Basinal restriction, black shales, Re-Os dating, and the Early Toarcian (Jurassic) oceanic anoxic event: *Paleoceanography*, v. 23, no. 4.
- McDaniel, D. K., Walker, R. J., Hemming, S. R., Horan, M. F., Becker, H., and Grauch, R. I., 2004, Sources of osmium to the modern oceans: New evidence from the Pt-190-(OS)-O-186 system: *Geochimica Et Cosmochimica Acta*, v. 68, no. 6, p. 1243-1252.
- Miller, C. A., Peucker-Ehrenbrink, B., Walker, B. D., and Marcantonio, F., 2011, Re-assessing the surface cycling of molybdenum and rhenium: *Geochimica Et Cosmochimica Acta*, v. 75, no. 22, p. 7146-7179.
- Morford, J. L., Martin, W. R., Francois, R., and Carney, C. M., 2009, A model for uranium, rhenium, and molybdenum diagenesis in marine sediments based on results from coastal locations: *Geochimica Et Cosmochimica Acta*, v. 73, no. 10, p. 2938-2960.
- Orberger, B., Pasava, J., Gallien, J. P., Daudin, L., and Trocellier, P., 2003, Se, As, Mo, Ag, Cd, In, Sb, Pt, Au, Tl, Re traces in biogenic and abiogenic sulfides from Black Shales (Selwyn Basin, Yukon Territories, Canada): A nuclear microprobe study: *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, v. 210, p. 441-448.
- Pasava, J., Oszczepalski, S., and Du, A. D., 2010, Re-Os age of non-mineralized black shale from the Kupferschiefer, Poland, and implications for metal enrichment: *Mineralium Deposita*, v. 45, no. 2, p. 189-199.
- Pearce, C. R., Coe, A. L., and Cohen, A. S., 2010, Seawater redox variations during the deposition of the Kimmeridge Clay Formation, United Kingdom (Upper Jurassic): Evidence from molybdenum isotopes and trace metal ratios: *Paleoceanography*, v. 25.

- Peppers, R.A., 1996, Palynological Correlation of Major Pennsylvanian (Middle and Upper Carboniferous) Chronostratigraphic Boundaries in the Illinois and Other Coal basins: Geological Society of America, Memoir 188, 111 p.
- Peterson, J. A., 2011, Better mathematical constraints on ages of Carboniferous stage boundaries using radiometric tuff dates and cyclostratigraphy: *Geochemistry Geophysics Geosystems*, v. 12.
- Peucker-Ehrenbrink, B., and Hannigan, R. E., 2000, Effects of black shale weathering on the mobility of rhenium and platinum group elements: *Geology*, v. 28, no. 5, p. 475-478.
- Ramezani, J., Hoke, G. D., Fastovsky, D. E., Bowring, S. A., Therrien, F., Dworkin, S. I., Atchley, S. C., and Nordt, L. C., 2011, High-precision U-Pb zircon geochronology of the Late Triassic Chinle Formation, Petrified Forest National Park (Arizona, USA): Temporal constraints on the early evolution of dinosaurs: *Geological Society of America Bulletin*, v. 123, no. 11-12, p. 2142-2159.
- Ravizza, G. E., 2010, Platinum Group Elements and Their Isotopes in the Ocean: in Steele, J. H., Thorpe, S. A., and Turekian, K. K., eds, *Marine Chemistry and Geochemistry: A Derivative of the Encyclopedia of Ocean Sciences*, 2nd ed., p. 29-39.
- Rooney, A. D., Chew, D. M., and Selby, D., 2011, Re-Os geochronology of the Neoproterozoic-Cambrian Dalradian Supergroup of Scotland and Ireland: Implications for Neoproterozoic stratigraphy, glaciations and Re-Os systematics: *Precambrian Research*, v. 185, no. 3-4, p. 202-214.
- Rooney, A. D., Selby, D., Houzay, J. P., and Renne, P. R., 2010, Re-Os geochronology of a Mesoproterozoic sedimentary succession, Taoudeni basin, Mauritania: Implications for basin-wide correlations and Re-Os organic-rich sediments systematics: *Earth and Planetary Science Letters*, v. 289, no. 3-4, p. 486-496.
- Rowe, H. D., Loucks, R. G., Ruppel, S. C., and Rimmer, S. M., 2008, Mississippian Barnett Formation, Fort Worth Basin, Texas: Bulk geochemical inferences and Mo-TOC constraints on the severity of hydrographic restriction: *Chemical Geology*, v. 257, no. 1-2, p. 16-25.
- Rygel, M. C., Fielding, C. R., Frank, T. D., and Birgenheier, L. P., 2008, The magnitude of late Paleozoic glacioeustatic fluctuations: a synthesis: *Journal of Sedimentary Research*, v. 78, no. 7-8, p. 500-511.
- Schultz, R. B., 2004, Geochemical relationships of Late Paleozoic carbon-rich shales of the Midcontinent, USA: a compendium of results advocating changeable geochemical conditions: *Chemical Geology*, v. 206, no. 3-4, p. 347-372.

- Scotese, C. R., 2004, A continental drift flipbook: *Journal of Geology*, v. 112, no. 6, p. 729-741.
- Selby, D., 2007, Direct Rhenium-Osmium age of the Oxfordian-Kimmeridgian boundary, Staffin bay, Isle of Skye, UK, and the Late Jurassic time scale: *Norwegian Journal of Geology*, v. 87, no. 3, p. 291-299.
- Selby, D., and Creaser, R. A., 2003, Re-Os geochronology of organic rich sediments: an evaluation of organic matter analysis methods: *Chemical Geology*, v. 200, no. 3-4, p. 225-240.
- Selby, D., and Creaser, R. A., 2005, Direct radiometric dating of the Devonian-Mississippian time-scale boundary using the Re-Os black shale geochronometer: *Geology*, v. 33, no. 7, p. 545-548.
- Selby, D., Mutterlose, J., and Condon, D. J., 2009, U-Pb and Re-Os geochronology of the Aptian/Albian and Cenomanian/Turonian stage boundaries: Implications for timescale calibration, osmium isotope seawater composition and Re-Os systematics in organic-rich sediments: *Chemical Geology*, v. 265, no. 3-4, p. 394-409.
- Shirey, S. B., and Walker, R. J., 1998, The Re-Os isotope system in cosmochemistry and high-temperature geochemistry: *Annual Review of Earth and Planetary Sciences*, v. 26, p. 423-500.
- Sloss, L. L., 1963, Sequences in the Cratonic Interior of North America: *Geological Society of America Bulletin*, v. 74, no. 2, p. 93-93.
- Soreghan, G. S., Soreghan, M. J., Poulsen, C. J., Young, R. A., Ebel, C. F., Sweet, D. E., Davogusto, O. C., 2008, Anomalous Cold in the Pangean Tropics: *Geology*, v. 36, p. 659-662.
- Tribovillard, N., Algeo, T. J., Lyons, T., and Riboulleau, A., 2006, Trace metals as paleoredox and paleoproductivity proxies: An update: *Chemical Geology*, v. 232, no. 1-2, p. 12-32.
- Turgeon, S. C., Creaser, R. A., and Algeo, T. J., 2007, Re-Os depositional ages and seawater Os estimates for the Frasnian-Famennian boundary: Implications for weathering rates, land plant evolution, and extinction mechanisms: *Earth and Planetary Science Letters*, v. 261, no. 3-4, p. 649-661.
- West, R. R., Archer, A. W., and Miller, K. B., 1997, The role of climate in stratigraphic patterns exhibited by late Palaeozoic rocks exposed in Kansas: *Palaeogeography Palaeoclimatology Palaeoecology*, v. 128, no. 1-4, p. 1-16.
- Wilkinson, B. H., Merrill, G. K., and Kivett, S. J., 2003, Stratal order in Pennsylvanian cyclothems: *Geological Society of America Bulletin*, v. 115, no. 9, p. 1068-1087.

Xu, G. P., Hannah, J. L., Stein, H. J., Bingen, B., Yang, G., Zimmerman, A., Weitschat, W., Mork, A., and Weiss, H. M., 2009, Re-Os geochronology of Arctic black shales to evaluate the Anisian-Ladinian boundary and global faunal correlations: *Earth and Planetary Science Letters*, v. 288, no. 3-4, p. 581-587.

Yamashita, Y., Takahashi, Y., Haba, H., Enomoto, S., and Shimizu, H., 2007, Comparison of reductive accumulation of Re and Os in seawater - sediment systems: *Geochimica Et Cosmochimica Acta*, v. 71, no. 14, p. 3458-3475.