INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI®

University of Alberta

Re-Os systematics of the Exshaw Formation: An evaluation of the effects of hydrocarbon maturation on the Re-Os geochronometer in black shales

By

Poulomi Sannigrahi ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

Department of Earth and Atmospheric Sciences

Edmonton, Alberta

Fall 2000

National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-59873-X

Canada

University of Alberta

Library Release Form

Name of Author: Poulomi Sannigrahi

Title of Thesis: Re-Os systematics of the Exshaw Formation: An evaluation of the effects of hydrocarbon maturation on the Re-Os geochronometer in black shales.

Degree: Master of Science

Year this Degree Granted: 2000

Permission is hereby granted to the University of Alberta Library to reproduce single copies of this thesis and to lend or sell such copies for private, scholarly or scientific research purposes only.

The author reserves all other publication and other rights in association with the copyright in the thesis, and except as herein before provided, neither the thesis nor any substantial portion thereof may be printed or otherwise reproduced in any material form without the authors prior written permission.

P. Sannigrahi

Poulomi Sannigrahi
Plot 407-D1
Hijli Co-op Society
Kharagpur, W.B. 721306
India.

Date 9 August, 2000

Abstract

Re-Os isotope analyses of drill core samples of black shales from the Exshaw Formation, Alberta have been carried out in order to determine their depositional age. I obtained a Re-Os isochron age of 358 ± 12 Ma, which is within error of the established stratigraphic age of 363.6 ± 1.6 Ma. The initial $^{187}Os/^{188}Os$ ratio of 0.524 ± 0.094 is an estimate of the Os isotopic composition of local water at the time of deposition of these sediments. The effects of hydrocarbon maturation and migration on the Re-Os system in black shales have also been evaluated by analyzing samples from all levels of hydrocarbon maturity. Hydrocarbon immature, mature and overmature samples all plot directly on the Re-Os isochron, implying that hydrocarbon maturation has no significant effect on the Re-Os isotope system in these rocks. The Re-Os geochronometer can, therefore, be used as a reliable tool for measuring the depositional ages of organic-rich shales regardless of their level of hydrocarbon maturity.

University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Re-Os isotope systematics of the Exshaw Formation: An evaluation of the effects of hydrocarbon maturation on the Re-Os geochronometer in black shales** submitted by Poulomi Sannigrahi in partial fulfillment of the requirements for the degree of Master of Science.

Dr. R. A. Creaser (Co-Supervisor)

Dr. T. Chacko (Co-Supervisor)

Dr. K. Muehlenbachs (Committee Member)

Dr. A. Meldrum (Committee Member)

Date: 9 AUGUST 2000

Acknowledgements

This project was funded by NSERC grants to Dr. Creaser and Dr. Chacko and University of Alberta graduate teaching assistantships to the author.

I would like to thank Dr. Robert Creaser for his guidance, help, and above all for introducing me to the fascinating science of Re-Os isotope geochemistry. I am indebted to Dr. Thomas Chacko for his support, wisdom and help at every stage of my work. I also thank the other members of the examining committee for their insightful comments that helped improve the quality of my thesis.

Sincere thanks go out to the following people without whom this work would not have been possible:

Dave Selby for being such a great help at every stage especially with the analytical work and mass spectrometry.

Cathy Skilliter for teaching me to use the invaluable Accumap database and initiating me to the core lab.

Stacey Hagen for her help in the mass spectrometry lab, Judith Enarson for patiently and readily solving all my registration and administrative problems.

I thank Jen Unterschutz for her friendship and all the great times we had together. Rajeev, Elizabeth and Elspeth were also great friends and colleagues.

Finally, I would like to thank my family for their love, encouragement and for always being there for me.

List of Figures

List of tables

Abbreviations

ICPMS	Inductively coupled plasma mass spectrometry
Ma	Mega anos (million years)
MSWD	Mean square of weighted deviates
NAA	Neutron activation analysis
nmol/g	nano moles per gram
NTIMS	Negative thermal ionization mass spectrometry
PGE	Platinum group elements
ppb	parts per billion
ppt	parts per trillion
RIMS	Resonance ionization mass spectrometry
SIMS	Secondary ionization mass spectrometry
TOC	Total organic content
WCSB	Western Canada sedimentary basin

Table of Contents

Exshaw Formation

Analytical Procedures

INTRODUCTION:

Determination of the depositional ages of sedimentary rocks is a direct method of calibrating the geological time scale. However, an unambiguous depositional age estimate cannot be obtained for most clastic sedimentary rocks with the common long-lived isotope systems such as U-Pb, Sm-Nd, and Rb-Sr. For example, a Rb-Sr study on fine and coarse illite fractions from the Upper Devonian Woodford Shale (360 Ma) of West Texas, gave diagenetic (302 Ma) and source (539 Ma) ages, respectively, but no estimate of the depositional age of the formation (Morton, 1985).

In contrast to the standard radiogenic isotope systems, recent studies suggest that the Re-Os system in organic-rich (black) shales may be a useful chronometer for dating clastic sedimentary sequences. However, there have only been a few studies using the Re-Os system to determine the depositional age of black shales (Ravizza and Turekian, 1989; Cohen et al., 1999; Singh et al., 1999). To date, the modern methods of Re-Os isotope analysis have not yet been applied to organic rich sediments older than the Jurassic (150 to 205 Ma).

Black shales are a significant crustal reservoir of Re and Os with concentrations of up to 300 ppb Re and 3 ppb Os, which is more than an order of magnitude higher than that of average continental crust. Re and Os concentrations of the upper continental crust have been estimated at 0.4-0.6 ppb Re and 0.05 ppb Os (Esser and Turekian, 1993). Most of the Re and Os in black shales is associated with organic matter and has been inferred to be hydrogenous in origin i.e., the elements were largely sequestered from the seawater at the time of deposition with negligible detrital and extra-terrestrial contributions (Ravizza and Turekian, 1989). Therefore, the Re and Os isotope composition of black shales should not be strongly influenced by the age of the sedimentary source rocks. Furthermore, the reducing nature of black shales renders them extremely retentive of both Re and Os. Taken together, the above-mentioned properties potentially make the Re-Os isotope system a useful tool for determining the depositional ages of organic-rich shales.

Despite the geochemical significance of black shales as a crustal reservoir for Re and Os, the number of detailed isotopic studies on these rocks are few. In particular, the robustness of the Re-Os isotope system during post-depositional processes such as hydrocarbon maturation and metamorphism remains poorly understood. The effect of these processes must be investigated before the Re-Os chronometer can be applied on a routine basis.

The present study aims to evaluate further the applicability of the Re-Os isotope system as a geochronometer for black shales, and to investigate the effects of hydrocarbon maturation on the Re-Os systematics of these rocks. This study is the first to concentrate on the aspect of hydrocarbon maturation. The maturation process may have a profound effect as significant Re and Os contents (hundreds of ppt to tens of ppb) have been measured in oils, asphaltenes and bitumens generated from black shale source rocks (Poplavko et al., 1974; Barre et al., 1995). This indicates that Re and Os migrate with hydrocarbons produced from organic rich shales. If the isotopic ratios are altered during this process, then the Re-Os geochronometer may be applicable to hydrocarbon immature shales only.

This study focuses on the Re-Os isotope systematics of the Exshaw Formation, an important stratigraphic marker horizon and hydrocarbon source rock in the Western Canada Sedimentary Basin (WCSB), (Creaney and Allan, 1991; Leenheer, 1984). The lower Exshaw shale member has been well dated stratigraphically (Savoy and Harris, 1993), and is therefore an ideal candidate for checking the depositional age obtained using the Re-Os isotope system. Additionally, the Exshaw Formation extends over hydrocarbon immature, mature and overmature regions (Piggott and Lines, 1992), which permits a test as to whether hydrocarbon maturation perturbs the Re-Os systematics of black shales. Finally, comparison of Re-Os isotope data for the Exshaw Formation with that reported previously for the stratigraphically equivalent Bakken Formation (Ravizza and Turekian, 1989) enables an assessment of the impact of improved analytical techniques on the precision of isochrons obtained with the Re-Os system.

History and Challenges of Re-Os isotope analysis:

The Re-Os geochronometer is based on the β-decay of ^{187}Re to ^{187}Os. The equation used for age calculations is given by:

$$({}^{187}\mathrm{Os}/{}^{188}\mathrm{Os})_{\mathrm{present}} = ({}^{187}\mathrm{Os}/{}^{188}\mathrm{Os})_{\mathrm{initial}} + ({}^{187}\mathrm{Re}/{}^{188}\mathrm{Os})\,(e^{\lambda t} - 1)$$

The currently used value of the decay constant λ is $1.666*10^{-11}a^{-1}$ (Shen et al., 1996; Smoliar et al., 1996).

A major hindrance in the full utilization of the Re-Os system for its various possible applications has been the lack of suitable analytical techniques. This is particularly important in view of the extremely low concentration of these elements in many crustal rocks. Mass spectrometric techniques for the Re–Os system have evolved sporadically over the last two decades. The earliest studies on Re-Os were carried out using electron-bombardment mass spectrometry (Nier, 1937). Later techniques included secondary ionization mass spectrometry or SIMS (Luck and Allegre, 1983); resonance ionization mass spectrometry or RIMS (Walker and Fassett, 1986); and inductively coupled plasma mass spectrometry or ICPMS (Russ et al., 1987). All of the above techniques suffered from relatively low sensitivity and precision of no better than ±1-2% (2σ) for $^{187}Os/^{188}Os$.

In 1991, the development of the high-precision negative thermal ionization mass spectrometry (NTIMS) technique by Creaser et al. (1991) and Völkening et al. (1991), provided the necessary analytical precision (of > ± 0.1% 2σ) to exploit fully the potential of the Re-Os system. In this method, Re and Os salts are loaded onto separate Pt filaments along with an electron emitter such as $Ba(NO_3)_2$. They are ionized as the OsO_3^- and ReO_4^- molecular species with ionization efficiencies as high as 10-20% in some cases. Creaser et al. (1991) demonstrated that NTIMS could determine the $^{187}Os/^{188}Os$ ratio with a precision of better than ± 1‰ for 4 ng Os. The precision attainable using SIMS ranged from 3-10‰ whereas that using RIMS and ICPMS was ± 10‰. Since these studies were published, effectively all Re-Os studies including the present have used NTIMS to measure isotope ratios and concentrations.

The analytical procedures used to separate Re and Os from geological samples by early workers involved large amounts of samples as well as reagents, thus increasing the procedural blanks and decreasing data precision. However, major developments have taken place in this field over the last ten years, a few of which are outlined below.

Shirey and Walker (1995) developed the Carius tube digestion method that can be applied to <0.1 g to 5 g size samples, which involves high temperature oxidizing digestion in sealed Pyrex glass tubes using aqua regia. This technique is capable of dissolving platinum-group element (PGE) minerals, metals and sulfides and also enables sufficient reaction with silicates so as to liberate most of the Re and Os from a silicate matrix. An added advantage of this procedure is that it leads to the oxidation of both Re and Os to their highest valences, thus promoting the complete chemical equilibration of these elements in the sample with their enriched isotopes in the spike. Os is subsequently separated by double distillation in sulfuric acid and Re by anion exchange chromatography.

Cohen and Waters (1996) further improved upon this technique and devised an elegant method of Os separation following sample digestion in aqua regia. Their method involved the partitioning of OsO_4 directly from aqua regia digest solution into an organic phase (CCl_4), and then its recovery by back extraction into concentrated HBr. This is followed by a simple micro-distillation step after which the purified sample is ready for mass spectrometry. This approach reduces blank contributions through the use of small reagent volumes and simple handling procedures. The procedures given by Shirey and Walker (1995) and Cohen and Waters (1996) are used in this study.

Previous studies on the Re-Os systematics of black shales:

Pioneering work on the Re-Os geochronometry of black shales was done by Ravizza and Turekian (1989). They studied drill core samples from the Devono-Missippian Bakken Formation, North Dakota. Their study yielded a Re-Os isochron age of 354 ± 49 Ma ($\lambda = 1.52*10^{-11}a^{-1}$) or 336 ± 46 Ma ($\lambda = 1.666*10^{-11}a^{-1}$), which is within error of the known stratigraphic age (~352 Ma, Tucker et al., 1998). However, considerable scatter was observed both between and within localities, which the authors attributed mainly to hydrocarbon maturation and migration, as all samples were from maturated strata. Analytical error and initial Os isotope heterogeneity were also held partly responsible for the scatter in the data. That study also inferred that because most of the Os in black shales was sequestered from seawater at the time of deposition, the initial Os isotopic composition of black shales and organic-rich sediments reflects that of contemporaneous local seawater. It has been established that the Os isotopic ratio of seawater shows fluctuations similar to that observed in the $^{87}Sr/^{86}Sr$ ratio. The seawater residence time of Os, however, is about two orders of magnitude shorter than that of Sr, which enables it to record changes in marine chemistry that have occurred on a smaller time scale.

More recently, Cohen et al. (1999) studied the Re-Os systematics for three suites of organic-rich mudrocks from Jurassic coastal outcrops in England. They used the latest analytical techniques, similar to those used in the present study, and obtained precise Re-Os isochron ages of 155 ± 4.3 Ma; 181 ± 13 Ma and 207 ± 12 Ma (λ=1.666*$10^{-11}a^{-1}$). These isochron ages agreed within error to the respective stratigraphic ages of 149 ± 3 Ma; 187 ± 4 Ma and 198 ± 4 Ma (Gradstein et al., 1995). The significant improvement in the precision of data compared to the Ravizza and Turekian (1989) study was ascribed to better analytical techniques, sampling strategies and the use of non-hydrocarbon maturated samples. This study also provided the first estimate of the $^{187}Os/^{188}Os$ ratio of Jurassic seawater as a range from 0.15 at the start of the Jurassic, to 0.80 after 20 Ma and then 0.59 during the late Jurassic. The extremely unradiogenic Os isotope composition of early Jurassic seawater was inferred to be the result of a relatively high unradiogenic Os flux from the hydrothermal alteration of oceanic crust. This dominated over the small radiogenic Os flux to the oceans from continental weathering. These results demonstrate that the Os isotope composition of seawater can vary extensively over a short period of time.

Among the post-depositional processes affecting black shales, surface weathering and oxidation is the only one which has been studied in some detail. Peucker-Ehrenbrink and Hannigan (2000) reported that the Re-Os system in black shales is severely affected by surface oxidation and weathering with Re and Os contents decreasing by as much as 30-64% and 45-90%, respectively. This can be correlated with the heavy loss of organic matter (almost 90%) from the shales as a result of weathering because Re and the PGE are thought to be associated with organic material.

Most other studies involving the Re-Os system in black shales and sediments have focussed on the weathering of these rocks and their contribution of radiogenic Os to the oceanic $^{187}Os/^{188}Os$ ratio (Singh et al., 1999; Pierson-Wickman et al., 2000). These studies dealt with the role of weathering of black shales from the Himalayas in influencing the temporal variations in $^{187}Os/^{188}Os$ ratio of oceans. Most of the river bedrocks and sediments other than black shales were found to have an Os isotope composition similar to the average continental crust. Weathered black shales carried by rivers were found to be responsible for the major flux of radiogenic Os to the oceans.

EXSHAW FORMATION:

Regional geology and stratigraphy:

The Exshaw Formation was named after the town of Exshaw, Alberta, which is near its type locality of Jura Creek. It is a thin, but extremely persistent unit, stretching from the Wapiti Lake near Jasper, southwards to the Crowsnest Pass – a total distance of about 670 Km. The unit has also been reported from boreholes in the central and southern plains of Alberta and the southwestern part of Saskatchewan (Mountjoy, 1954). The thickness of the Exshaw formation is quite uniform in the Rockies. It ranges between 2 and 12 m, with an average thickness of around 6 m. The type section at Jura Creek is about 10 m thick. Macqueen and Sandberg (1970) interpreted this thin, widespread and uniform nature of the Exshaw shale as an indication of accumulation in a series of extremely shallow, stagnant, marine or brackish lagoons along the shoreline of a transgressive sea.

Figure 1 is a Devonian-Carboniferous stratigraphic column of central Alberta and south central Saskatchewan, modified from Caplan and Bustin (1998). The Exshaw Formation is marine in nature and consists of two units in Alberta. The lower unit mainly comprises jet black, fissile, pyritic shale, most of which is non-calcareous. The upper unit is made up of tan, silty, dolomitic limestone. The topmost part of the Exshaw Formation is massive, calcareous mudstone (Mountjoy, 1954; Macqueen and Sandberg, 1970).

The Exshaw overlies the Wabamun formation in the plains and the Palliser formation in the Rocky Mountains and the foothills. The Banff Formation, comprising calcareous shales and shaly limestone, underlies the Exshaw. Together, they are a part of the spectacular Palliser-Banff-Rundle "sandwich" in the Canadian Rockies. The contact of the Exshaw formation with the underlying Palliser limestone is distinct and abrupt and most workers have termed it an unconformity. The upper contact, however, is a more gradual change from non-calcareous black Exshaw shale to the lighter, more calcareous shales and argillaceous limestone of the Banff formation.

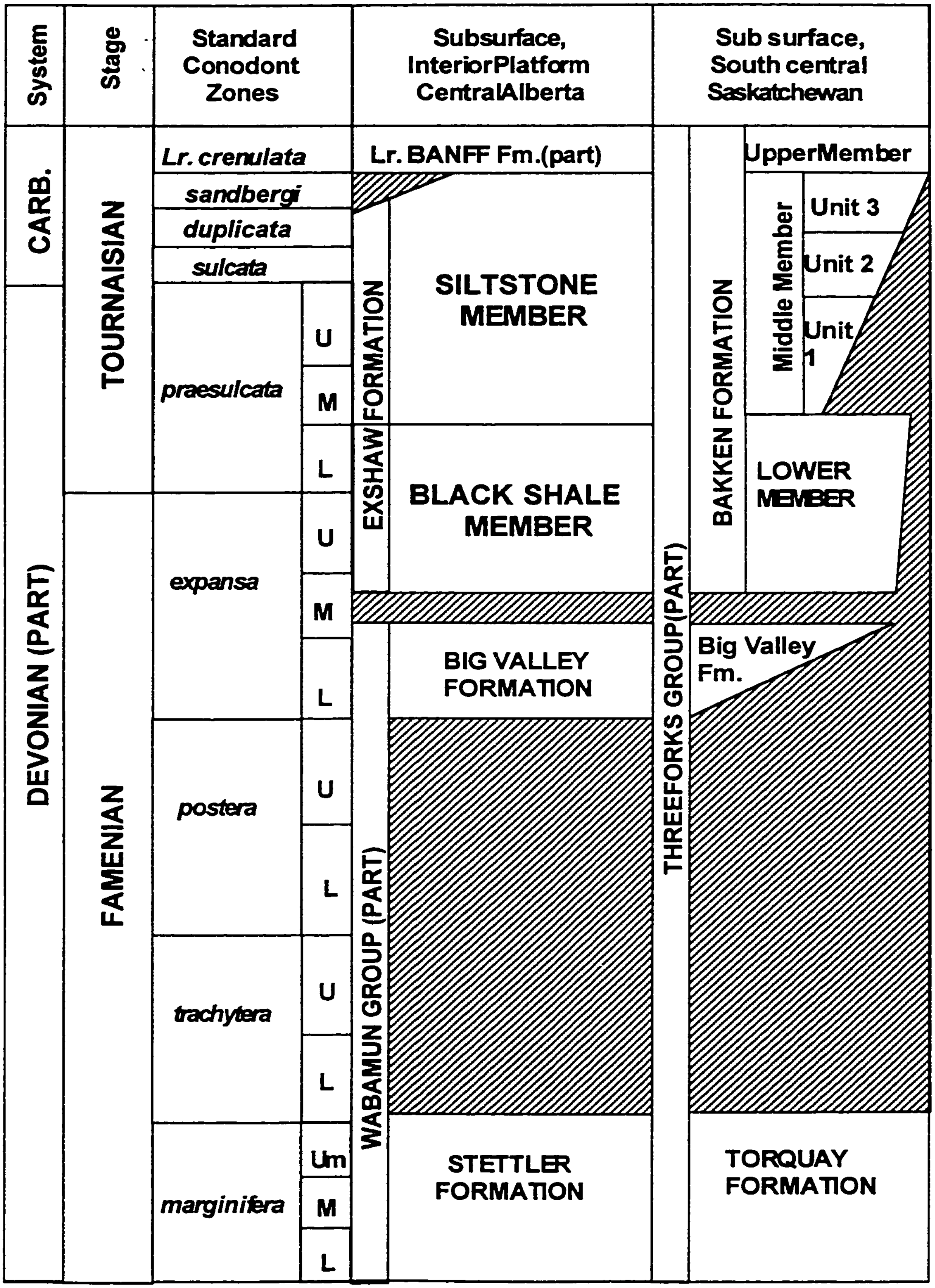

FIGURE 1. Devonian-Carboniferous Stratigraphic column of central Alberta and south-central Saskatchewan (Modified from Caplan and Bustin, 1998)

On a regional scale, the Exshaw formation is a part of a continent-wide Devono-Missippian black shale event. It is stratigraphically correlated with other prominent black shale sequences of North America, such as, the Bakken Shale in Saskatchewan, North Dakota and Montana; the Chattanooga Shale in the Mississippi Valley and mid-continent United States; the Woodford Shale in Texas etc. Ettensohn and Barron (1981) proposed that this continent-wide black shale sequence formed on the leeward side of the Acadian Mountains, a north-south trending barrier across the equator on the eastern part of the continent. This barrier served as an obstruction for moisture-laden trade winds, thus producing rain shadow conditions west of the mountains. As a consequence of being in this rain shadow area, the reduced clastic influx and restricted circulation within the basin led to the deposition of black, euxinic, organic-rich muds.

Previous work on the Exshaw Formation:

Comprehensive geochemical analyses of the Exshaw shale was carried out by Duke (1983) using Neutron Activation Analysis (NAA) and other allied techniques. This study indicated a very high concentration of U (up to 92 ppm), Mo and V in the Exshaw shales as compared to average shale values. This is relevant for applying the Re-Os chronometer to these shales, as Re has a geochemical behavior similar to Mo and V. Also, the concentrations of these elements were found to be directly proportional to the total organic carbon content (TOC values). X-ray diffraction studies carried out to determine the mineralogy of the Exshaw shale showed that quartz, calcite, dolomite and clays were the major minerals, along with minor amounts of orthoclase and muscovite. Illite was inferred to be the main clay mineral.

Most other geochemical studies on the Exshaw Formation have concentrated on its potential as a hydrocarbon source rock. Leenheer (1984) studied source rocks and hydrocarbons from the Bakken/Exshaw formations of the Williston and Western Canada basins in order to evaluate their source-rock potential and oil-source correlations. This study used TOC values and type of kerogens in the source rocks as determined by Rock-Eval pyrolysis to examine the hydrocarbon source rock potential of the shales. Carbon isotope ratios of the rocks and hydrocarbons were compared to each other in order to correlate the two. The biomarker data, together with the carbon isotope ratios, supported a strong correlation between Exshaw/Bakken shales and Mississippian oils from the Western Canada and Williston basins.

Creaney and Allan (1990) carried out an extensive study on the source rocks and migration histories of the different hydrocarbon systems of the WCSB. The Exshaw/Bakken shales were inferred to be one of the most prolific source rocks in the region. Piggott and Lines (1992), used Rock-Eval pyrolysis and gas source - mass spectrometry (GC-MS) to characterize source-rock extracts and oils and make oil-oil and oil-source rock correlations. This study also provided a hydrocarbon maturity map of the Exshaw sources rocks, in which hydrocarbon immature, mature and overmature regions have been delineated.

The earliest age estimates of the Exshaw Formation were on the basis of faunal evidence. Warren (1937) dated it as Upper Devonian based on the presence of the cephalopod fauna, *Tornoceras uniangulare.* However, Clark (1949) argued that the cephalopod fauna used by Warren was probably from the black argillaceous limestones belonging to the overlying Banff formation. Fox (1948) called the formation Devono-Missippian due to conflicting field and faunal evidence. Most workers later accepted a Mississippian age for the Exshaw Formation but agreed that the faunal evidence was not really conclusive and that the exact age was still doubtful (Fox, 1951; Crickmay, 1952). However, Warren (1956) and Warren and Stelck (1956) maintained that the Exshaw was Devonian. Radiometric dating using the K-Ar system on samples from a bentonite bed within the Exshaw formation gave a upper Carboniferous age of 267 ± 14 Ma (Folinsbee and Baadsgaard, 1958). This was considerably younger than the known stratigraphic age of the formation and the discrepancy was likely the result of Ar loss from the samples. The age conflict was resolved when Savoy and Harris (1993) reported conodonts belonging to the late Fammenian *expansa* condont zone from the lower Exshaw black shale member, thus providing a firm faunal basis to date the formation. Recently, the *expansa* zone has been precisely dated at 363.6 ± 1.6 Ma using the U-Pb system on volcanic ashes from New Brunswick, Canada (Tucker et al., 1998), which confirms the Exshaw shale as being uppermost Devonian in age.

Hydrocarbon maturation of the Exshaw Formation occurred at around 60 Ma, during the time of the Laramide orogeny (Issler et al., 1999). Apatite fission track analyses suggest that the strata attained maximum burial and peak temperature at this time. This is considerably younger than the stratigraphic age (~363 Ma) of the Exshaw Formation.

ANALYTICAL PROCEDURES:

Sample acquisition:

Drill core samples of shales from the Exshaw Formation were collected from the Alberta Energy and Utilities Board, Core Research Center, Calgary. Multiple samples were taken from each well from different depths, in order to cover the entire depositional interval of the Exshaw shale. Also, the three different hydrocarbon maturity zones were multiply analyzed so as to obtain regional sampling coverage. Figure 2 is a map showing the well locations of the samples analyzed and Table 1 gives their depth and hydrocarbon maturity levels (after Piggott and Lines, 1992).

Re-Os isotope analyses:

The edges of the core samples were ground on a diamond plate to remove saw marks. The samples were first broken into small chunks using a rock hammer (with its head wrapped in thick plastic) and then fed to a ceramic jaw crusher for further downsizing. Final crushing into fine powder was done using an agate

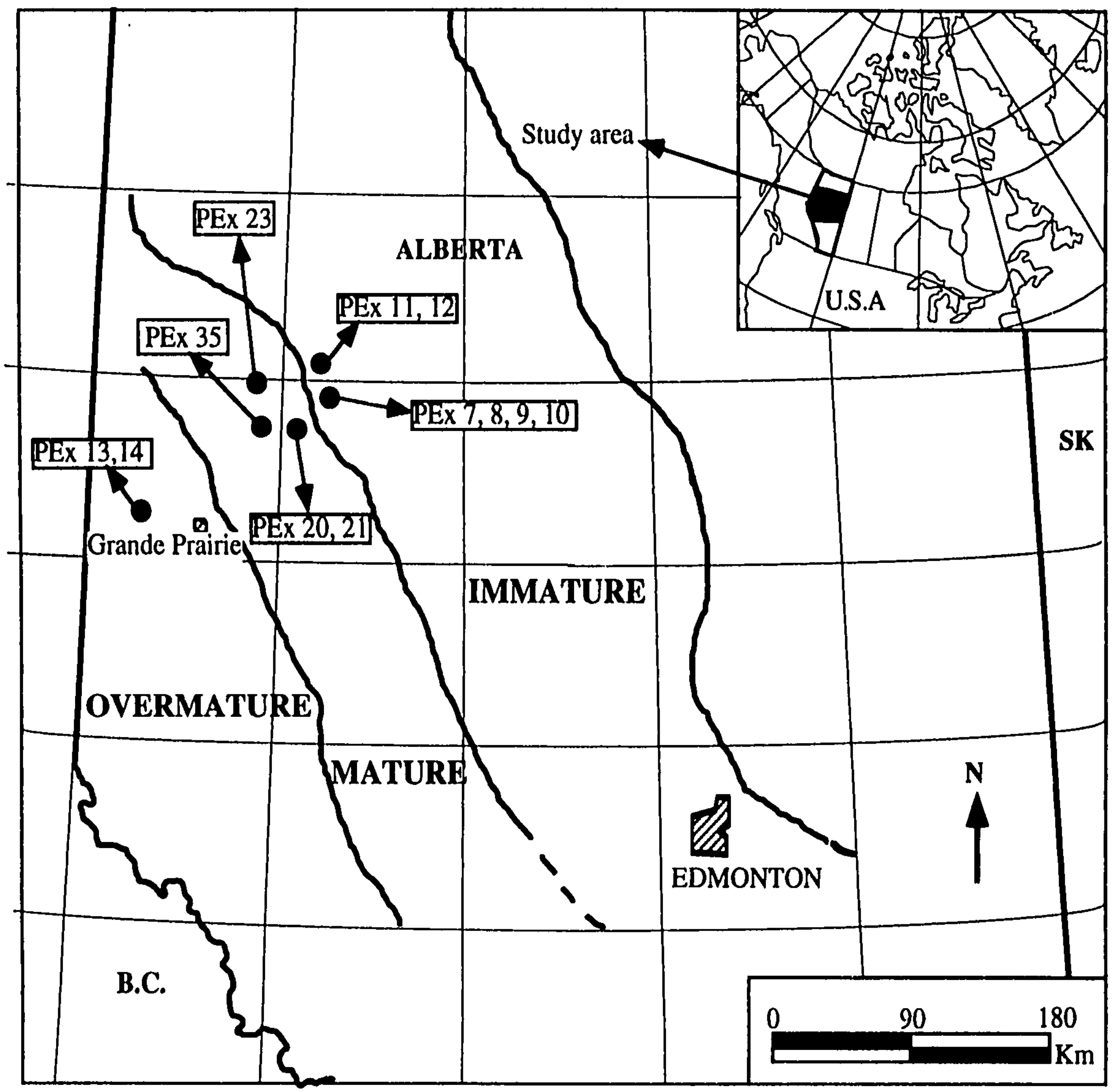

FIGURE 2. Map showing well locations of samples (B.C., British Columbia; SK., Saskatchewan) Hydrocarbon maturity regions after Piggott and Lines (1992).

TABLE 1. Well locations, depth and hydrocarbon maturity level of samples.

Sample #	Well Location*	Depth (m)†	Hydrocarbon Maturity level
PEx 7	3-19-80-23W5	1752.0	Immature
PEx 8	3-19-80-23W5	1753.0	Immature
PEX 9	3-19-80-23W5	1754.0	Immature
PEx 10	3-19-80-23W5	1756.5	Immature
PEx 11	13-18-80-23W5	1748.8	Immature
PEx 12	13-18-80-23W5	1750.9	Immature
PEx 13	4-23-72-10W6	3570.4	Overmature
PEx 14	4-23-72-10W6	3567.7	Overmature
PEx 20	8-29-78-01W6	2099.1	Mature
PEx 21	8-29-78-01W6	2099.2	Mature
PEx 23	14-22-80-02W6	2058.3	Mature
PEx 35	6-19-78-25W5	2006.2	Mature

* In township-range notation which is conventional in Alberta

† Depth from the surface

mill. Extreme care was taken at each step to avoid any contact of the samples with metal surfaces, which is known to contaminate samples with trace amounts of Re and Os.

All Re-Os isotope analyses were carried out at the geochemistry and mass spectrometry labs of the Department of Earth and Atmospheric Sciences, University of Alberta.

A new high Re/Os spike (Dilute Mixed #3 Re-Os) was prepared for use in this study and future work on black shales, tar sands, etc. Tracer solutions of isotopically enriched ^{185}Re and ^{190}Os were combined together in 6N HCl to make up the spike. The ^{185}Re and ^{190}Os abundances of the spike were then calibrated directly against gravimetric Re and Os standard solutions ALB-1 and ALB-2 respectively. For ^{185}Re calibration, 0.2g ALB-1 standard was added to 0.1g of the spike in a quartz vial and weighed. 3ml 16N HNO_3 was added to the resulting solution which was then left to dry down on a hot plate. The isotopic ratios of Re were measured on the mass spectrometer and the ^{185}Re concentration of the spike calculated from those values. Three replicate calibrations carried out using the above procedure, gave an average value for the ^{185}Re concentration in the spike (Dilute Mixed #3) as 2.9408 nmol/g with a standard deviation of 0.13%. For ^{190}Os calibration, 0.35g ALB-2 standard was added to 3g of the prepared spike in a Carius tube and weighed. 2ml 16N HNO_3 was added and the contents of the tube were frozen by placing them in methanol-dry ice slurry. The tubes were then sealed, placed in steel jackets and kept in the oven at 240°C for 24 hours. The procedure used for Os extraction after taking the tubes out is the same as that used for the samples and is described later in this section. ^{190}Os concentration of the spike was calculated from the measured Os isotope ratios as obtained from mass spectrometry. Two separate calibrations gave ^{190}Os concentration of the spike as 0.00459991 nmol/g and 0.00460260 nmol/g with an average value of 0.004625 nmol/g.

The analytical procedure followed for the separation of Re and Os from the samples was modified from Shirey and Walker (1995), Cohen and Waters (1996) and Birck et al. (1997) and is as described below.

About 0.8 g of sample powder was carefully weighed, transferred to a Carius tube and then spiked with 0.1 g of the mixed^{190}Os - ^{185}Re spike in HCl. The sample and spike were accurately weighed to ± 0.0004 g. The tubes containing the spiked samples were immediately placed in a Dewar flask containing methanol-dry ice slurry and frozen to prevent volatile loss of Re or Os prior to sealing. 3ml 6N HCl and 6ml 16N HNO_3 forming (reverse) aqua regia were then carefully added to the samples and the tubes covered with parafilm. Care was taken to ensure that the contents of the tubes were completely frozen before sealing, as freezing reduces the vapor pressure of the reagents, thus making it easier to seal the tubes. The Carius tubes were carefully sealed by drawing in the neck using an oxygen-propane flame. The sealed tubes were then placed in steel jackets and kept in the oven at 240°C for about 48 hours. This step is essential for the release of all Os from the samples along with the complete equilibration of sample Re and Os with the ^{185}Re and ^{190}Os from the spike. It results in the oxidation of the Os in the spike-sample mixture to OsO_4.

After taking out from the oven, the Carius tubes were cooled to room temperature and then frozen in liquid nitrogen to prevent any loss of the volatile OsO_4 upon opening. For opening the tubes, a hole was first vented in the neck to release the internal gas pressure and the upper portion then broken off by scoring and touching the score with a hot glass rod. 3.5 ml of Carbon Tetrachloride (CCl_4) was added to the contents of the tube, which were then left to thaw to 0°C. This is necessary to ensure that no Os remains frozen to the walls of the Carius tubes when the contents are transferred to the polypropylene centrifuge tubes. The centrifuge tubes with the sample and CCl_4 were kept in a water bath for around 15 minutes before proceeding further. The tubes were then centrifuged to separate the CCl_4 and aqua regia components, before transferring the former to Teflon vials containing 3ml 9N HBr. The previous step was repeated twice, after adding 3.5 ml CCl_4 each time and the Teflon vials were capped and left overnight under a heat lamp at 50°C. The material left behind in the centrifuge tube was transferred to a 15ml Teflon vial, dried down on a hot plate and kept aside for Re separation by anion exchange chromatography.

The CCl_4 component of the Os fraction, which typically settles down to the base of the vial was then pipetted out to waste, and the HBr left to dry overnight on a hotplate at 60°C. This dried Os fraction was dissolved in 30μl 9N HBr, transferred to the cap of a "Tristar" (3 ml conical Savillex, PFA Teflon) vial, and kept on the hotplate for an hour. 20µl 9N HBr was added to the tip of the "Tristar" vial, which was then placed upside down. 30µl CrO_3 solution was added to the sample and the vial carefully capped so as not to disturb the HBr at the tip. The sealed vials were kept upside down on a heating block at 80°C for around 3 hours. In doing this, the Os is volatilized to OsO_4 by the CrO_3 and then reduced to $OsBr^{2-}_6$ by the HBr in the tip. After 3 hours, the vials were taken out from the heating block and the lids washed to removed all the dried CrO_3. Special lids, which enabled a constant flow of nitrogen, were then attached and the vials left on a hotplate at 60°C to dry down the Os fraction. This method of micro solvent extraction serves as a final purification step before loading the Os fraction for mass spectrometry.

The dried Re cut was dissolved in 3 ml 6N HNO_3 and then purified by anion-exchange chromatography using Biorad AG 1-X8 200-400 mesh resin in heat-shrink TFE columns. Re was purified by eluting with HNO_3 and HCl of varying strengths and collected as 6N HNO_3. The Re obtained from chromatography was then dried down overnight on a hot plate inside a laminar flow fumehood.

The dried Re fraction was dissolved in 0.5µl 16N HNO_3 and the Os fraction in 0.5µl 9N HBr before loading onto the Pt filaments for mass spectrometry. Ba $(NO_3)_2$ was used as activator for Re and Ba, $Na(OH)_2$ for Os. Re and Os isotope ratios were analyzed by NTIMS on a Micromass Sector 54 mass spectrometer equipped with nine Faraday collectors. Some samples were measured on the Faraday collectors in static mode, and the others on the electron multiplier in peak hopping mode. From the measured oxide ratios as obtained from the mass spectrometer, atomic ratios were calculated after making the necessary corrections for instrumental mass fractionation, oxygen isotopes and spike and blank contributions. Total procedural blank values ranged from 42-130 ppt Re and 2-3 ppt Os.

Total C, N and S analyses:

Total C, N and S contents of the samples were analyzed using a Carlo Erba 1108 elemental analyzer at the Micro-analytical laboratory of the Department of Chemistry, University of Alberta. The samples were combusted in the presence of catalysts and oxygen in a sealed chamber to convert the carbon to CO_2 and the nitrogen to N_2 gases. The gases were then passed into a chromatographic column and their concentrations determined using a thermal conductivity detector. Sulfur was analyzed by the Schöniger method in which the sample powder is burnt in an oxygen filled flask at around 1200°C to destroy the organic matter and the remaining oxides of sulfur are absorbed and finally converted to sulfuric acid.

RESULTS:

Table 2 lists the total carbon, nitrogen and sulfur contents of the samples. The total carbon content varies from 2.25% to 14.97%, whereas the total nitrogen content is between 0.10% to 0.47% and sulfur between 0.38% to 4.2%. The

TABLE 2. Re, Os concentrations and isotope ratios; total C, N and S abundances

Sample #	Re(ppb)	Os(ppb)	187Re/188Os	187Os/188Os	± 2 sigma	Total C(%)	N(%)	S(%)
PEx 7(a)	73.8	0.72	493.3	3.463	0.028	2.80	0.13	–
PEx 8(b)	90.06	1.25	344.4	2.645	0.015	13.07	0.42	4.12
PEx 8(c)	92.27	1.31	337.8	2.653	0.005	13.57	0.45	4.12
PEx 9(b)	22.96	0.39	281.6	2.195	0.002	6.26	0.24	–
PEx 9(c)	24.64	0.49	241.3	1.846	0.002	6.26	0.24	–
PEx 10(a)	32.51	0.36	432.8	3.157	0.012	6.35	0.13	2.06
PEx 10(b)	31.88	0.36	430.4	3.153	0.009	6.35	0.13	2.06
PEx 11(a)	41.3	0.36	551.6	3.742	0.010	2.50	0.15	2.34
PEx 11(b)	52.29	0.45	553.5	3.704	0.002	2.50	0.15	2.34
PEx 11(c)	48.33	0.43	537.8	3.743	0.001	2.50	0.15	2.34
PEx 12(a)	70.82	0.84	406.3	2.991	0.001	8.93	0.26	6.73
PEx 13(a)	32.9	0.17	903.2	5.939	0.033	3.79	0.11	0.38
PEx 13(b)	32.09	0.22	699.3	4.801	0.026	3.79	0.11	0.38
PEx 14(a)	41.96	0.66	303.5	2.362	0.005	4.82	0.15	0.85
PEx 14(c)	41.93	0.60	335.0	2.516	0.003	4.82	0.15	0.85
PEx 20(a)	131.22	1.25	503.0	3.506	0.018	14.97	0.48	4.15
PEx 20(b)	128.93	1.17	528.4	3.745	0.002	14.97	0.48	4.15
PEx 21(b)	19.74	0.65	146.4	1.434	0.013	9.54	0.29	–
PEx 23(a)	32.7	0.76	207.0	1.527	0.004	2.25	0.18	–
PEx 23(c)	32.07	0.61	245.0	1.868	0.005	2.25	0.18	–
PEx 35(b)	52.98	0.61	419.2	2.979	0.001	3.15	0.15	–

Note: The suffix a,b or c in parentheses after the sample number indicates replicate analyses of sample powder from the same vial .

organic carbon contents for the Exshaw Formation as reported in Duke (1983) ranged from 1.2 to 14.5 %. Figures 3 and 4 are plots of the total Re and Os concentrations of the samples versus their total C and N contents. An overall positive correlation (as indicated by the R^2 values) is observed between both Re and Os and the total C and N contents of the Exshaw shales. The covariations between Os and total C and N (Figure 4) are stronger when compared to those between Re and total C and N (Figure 3).

Re and Os concentrations and isotopic ratios are also presented in Table 2. The $^{187}Re/^{188}Os$ ratio ranges from 146.11 to 903.21 while the $^{187}Os/^{188}Os$ ratio ranges from 1.434 to 5.939. Total Re concentrations are between 19.70 to 131.19 ppb and total Os concentrations between 0.17 to 1.87 ppb. Absolute errors (presented as $\pm 2\sigma$) in the $^{187}Os/^{188}Os$ ratio measurements range from 0.0008 to 0.033. No systematic variations are observed between the Re and Os concentrations and isotopic ratios. When studied in conjunction with the sample depths (Table 1), the $^{187}Re/^{188}Os$ ratio in some cases (e.g. samples 20 and 21) is seen to vary by up to factors of ~3 over short vertical distances. Similar variations have also been reported by Cohen et al. (1999). This ratio, however, is quite similar for laterally adjacent samples from the same stratigraphic level e.g., samples 7 and 11.

Almost all the replicate analyses agree within limits of analytical error, both in terms of isotopic ratios and element concentrations (Table 2). The only samples in which significant differences in isotopic ratios are observed between

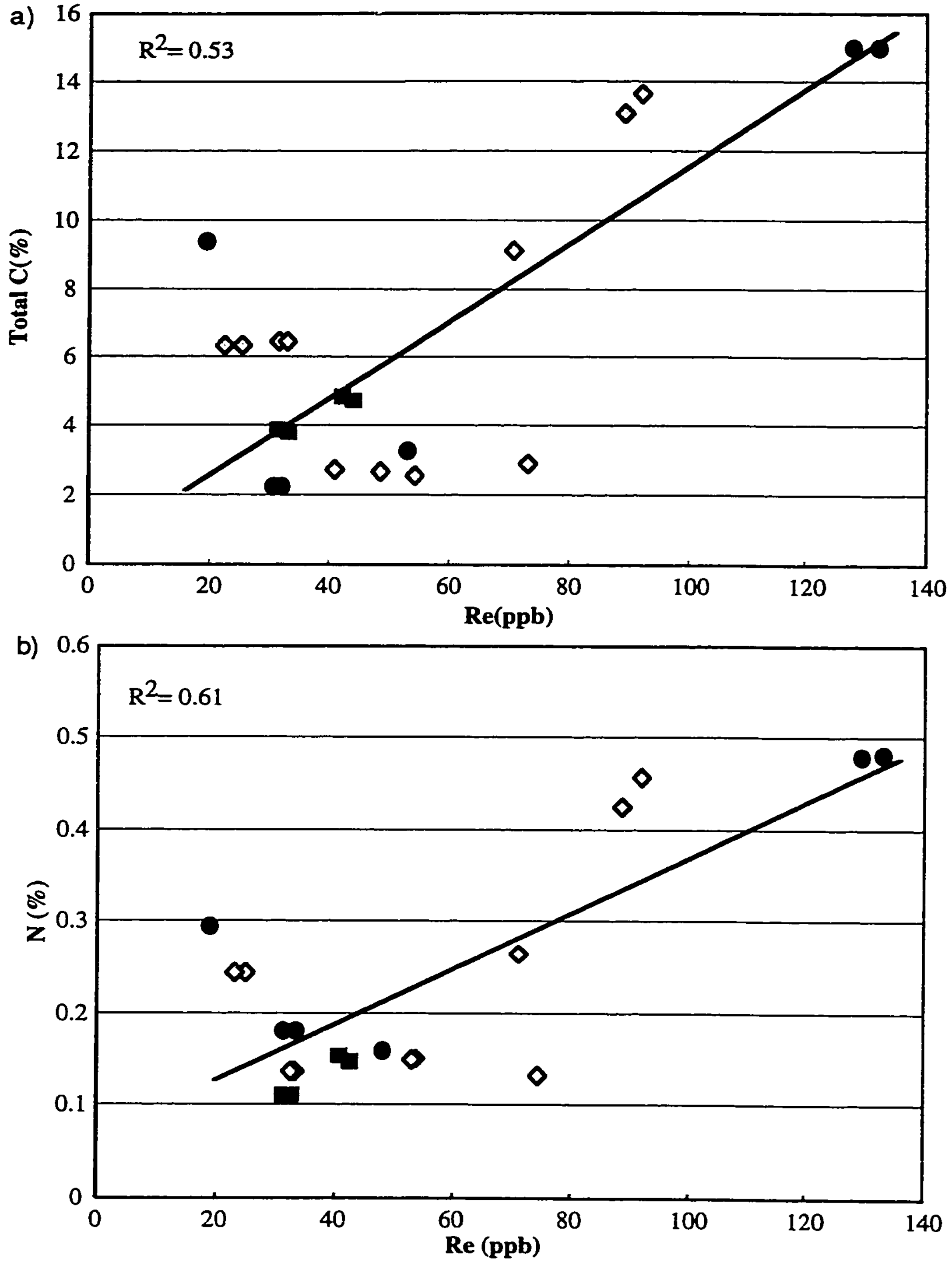

Figure 3. Variation diagrams showing the relationship between the abundances of Re, Total C and N for samples analyzed in this study.
◇: Hydrocarbon immature; ●: Hydrocarbon mature; ■: Hydrocarbon overmature

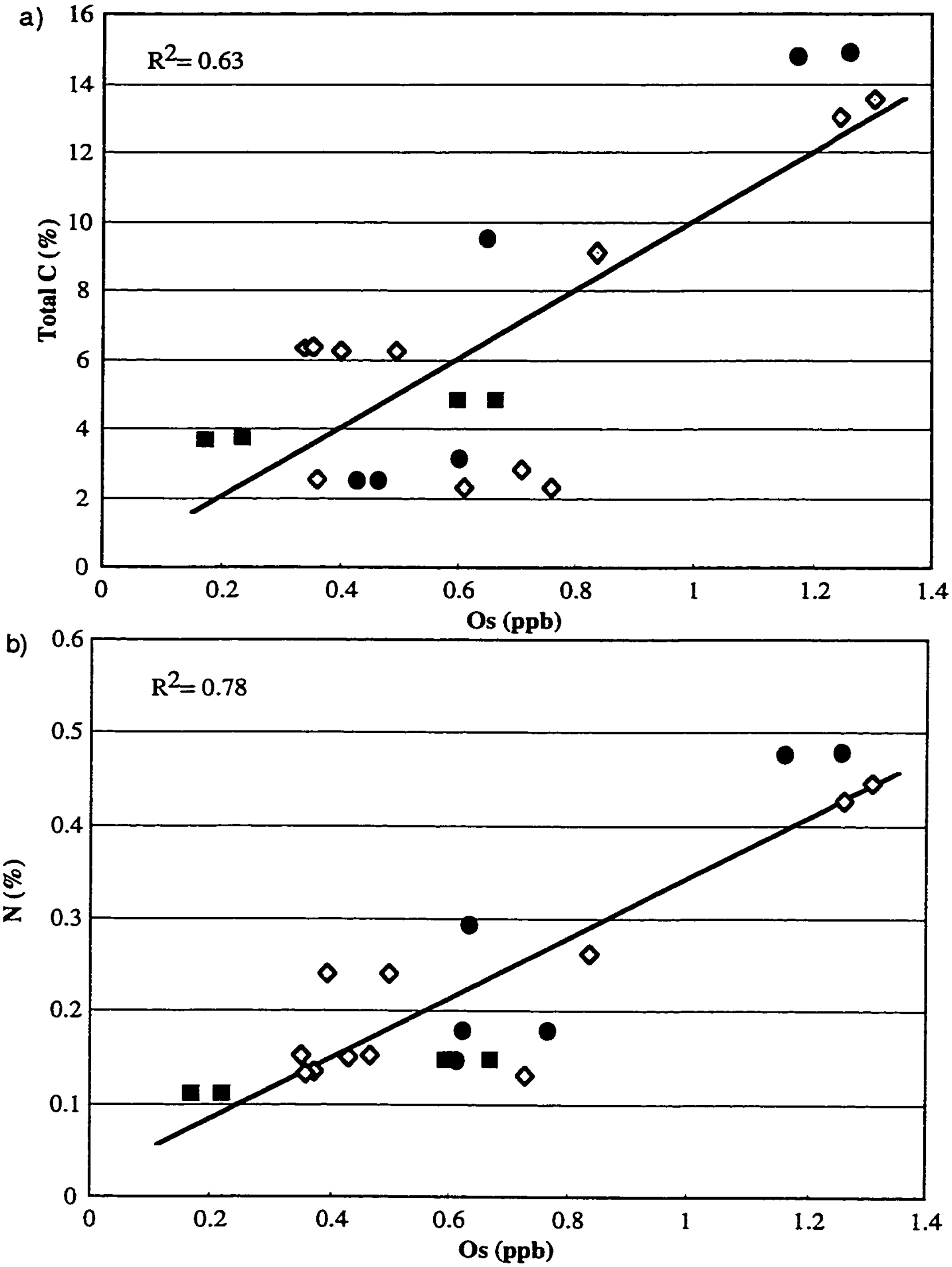

Figure 4. Variation diagrams showing the relationship between the abundances of Os, Total C and N for samples analyzed in this study.

◇ : Hydrocarbon immature; ● : Hydrocarbon mature; ■ : Hydrocarbon overmature replicate analyses are 13(a) and 13(b). The ^{187}Re/^{188}Os of sample 13(b) is about 30% lower than that of sample 13(a), but this value is still higher than any of the other samples. Sample 11(a) shows less Re and Os content than its repeat analyses 11(b) and 11(c).

DISCUSSION:

The positive correlations between Re, Os and total C and N contents observed in Figures 3 and 4 indicate an association of Re and Os with the organic matter in the black shales. Thus it can be concluded that almost all of the Re and Os must have been scavenged from seawater at the time of deposition of these sediments (Ravizza and Turekian, 1989). The abundances of Re and Os as reported in Table 2 are much higher than the average crustal abundances of 0.39 ppb Re and 0.05 ppb Os, which further rules out a significant detrital contribution of these elements. The initial ^{187}Os/^{188}Os ratio as obtained from the geochronology of the shales, therefore, reflects the Os isotopic composition of local seawater at the time of deposition.

As mentioned in the previous section, the replicate analyses agree well with each other for almost all the samples, with the exception of samples PEx 13(a) and PEx 13(b). Both these data points however, plot well on the isochron (Figure 6). The differences in isotopic ratios may thus be attributed to an isotopic inhomogeneity in different aliquots of the sample powder. Longer grinding times on the agate mill may be required to ensure complete homogenization of the sample powder and improve data reproducibility. However, this sample needs to be analyzed at least once more before the cause of isotopic variation can be stated with certainty.

When all the data presented in Table 2 are plotted on a Re-Os isochron diagram using ISOPLOT (Appendix A), the age obtained is 367 ± 14 Ma with an MSWD value of 81 (Figure 5). From this plot we see that data points corresponding to analyses 23(a) and 23(c) plot well off the isochron. The deviation of these analyses may be related to the position of sample 23 towards the top of the Exshaw Formation. Thus this sample likely belongs in part to the Upper Exshaw siltstone member. This is also suggested by the low total carbon content (2.25%) of this sample. Removing samples 23(a) and 23(c) brings the MSWD value down to 35 (Figure 6). Figure 6 is our final isochron for the Exshaw Formation. The age obtained is 358 ± 12 Ma along with an initial $^{187}Os/^{188}Os$ ratio of 0.524 ± 0.094.

Further scrutiny of Figure 6 reveals the slight deviation of analyses 9(c), 11(a) and 11(b) from the isochron. However, no inherrent problems are evident with these samples unlike the earlier case of sample PEx 23. Analysis 9(b), which is a replicate analysis of 9(c), plots on the isochron. Therefore the deviation of 9(c) may be the result of variable blanks in different sets of analyses or slight changes introduced in the analytical procedure over the course of work. The case of data points 11(a) and 11 (b) is also similar in that their replicate analysis 11(c) plots on the isochron. This may be as a result of the fact that 1ml

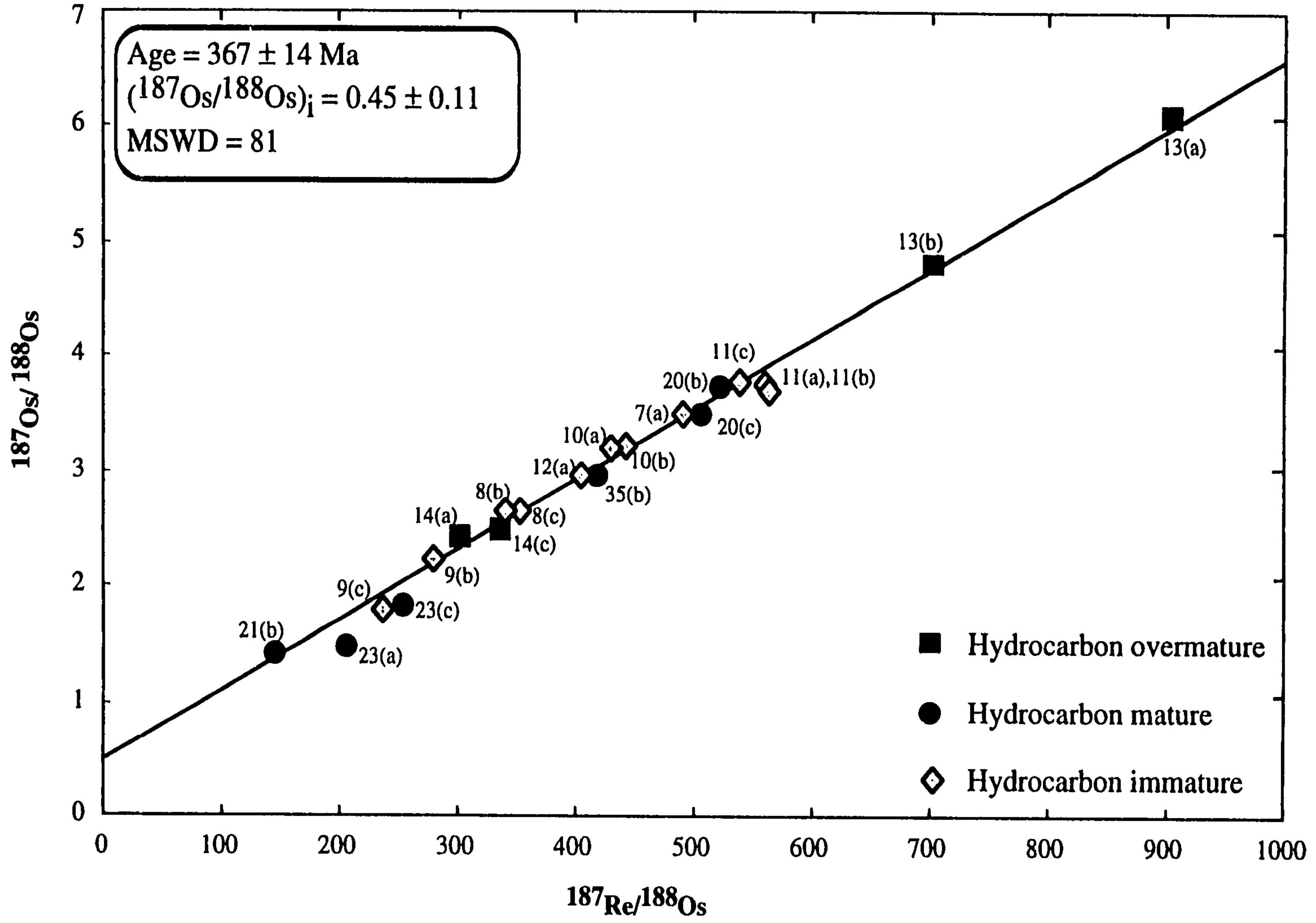

Figure 5. Re-Os isochron plot of all data given in Table 2.

(the numbers beside the data points indicate sample numbers as given in Tables 1 and 2).

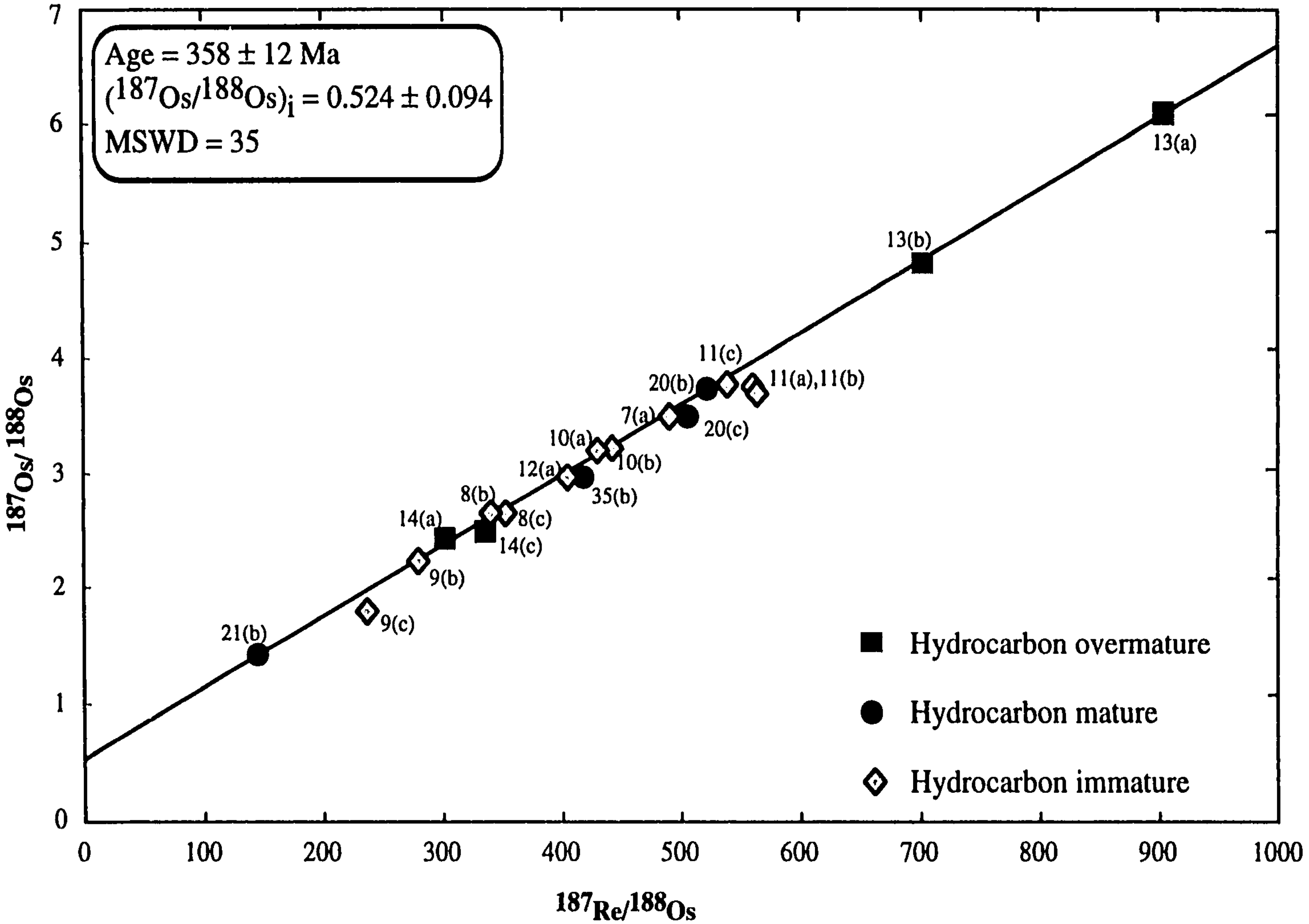

Figure 6. Re-Os isochron plot of the Exshaw Formation.

(the numbers beside the data points indicate sample numbers as given in Tables 1 and 2).

H_2O_2 was added to this sample during digestion in the Carius tube which probably aided in better oxidation and sample-spike equilibration. The removal of the data points discussed above slightly improves the precision in the age data (358 ± 9 Ma) and brings the MSWD value down to 13. However, since there is no apparent geological problem with these samples and their replicates plot well, Figure 6 is treated as the final isochron plot for the Exshaw Formation.

The age obtained (358 ± 12 Ma) from Re-Os geochronology of the Exshaw shales agrees within error to that of the *expansa* conodont zone (363.6 ± 1.6 Ma) which has been dated using the U-Pb system on zircons separated from volcanic ashes (Tucker et al., 1998). The initial $^{187}Os/^{188}Os$ ratio of 0.524 ± 0.094 is the first estimate of the Os isotopic composition of local seawater at the time of deposition of the Exshaw shale. This is considerably lower than the present day seawater $^{187}Os/^{188}Os$ ratio of ~1.03. The more radiogenic present day value may be due to the high levels of continental weathering (Cohen et al., 1999). The initial $^{187}Os/^{188}Os$ value for the Bakken shale (Ravizza and Turekian, 1989), was 0.74 ± 0.4, which is within error of our value.

The MSWD value of 35 obtained in the present study is typical for Re-Os geochronology of black shales, but is still considerably greater than 1, the upper limit of values for which data scatter can solely be attributed to analytical errors. Apart from analytical errors, two factors that could result in data scatter about the isochron are: 1) post-depositional mobility of Re and Os from the shales, which in this case may be caused by hydrocarbon maturation and migration from these rocks. Because the Exshaw Formation is relatively impermeable, the effect of other kinds of fluid activity may be ruled out; and 2) variations in the initial $^{187}Os/^{188}Os$ ratio.

The first factor, has been ascribed as the main cause of scatter in earlier studies (Ravizza and Turekian, 1989; Cohen et al., 1999). However, in my study, hydrocarbon mature, immature and overmature samples all plot directly on the isochron (Figure 6), which implies that the Re-Os geochronometer in black shales is not significantly affected by hydrocarbon maturation and migration. The scatter about the isochron, which is represented by the MSWD value, is in the range of values obtained by Cohen et al. (1999) using hydrocarbon immature samples only. Plotting of hydrocarbon immature, mature and overmature samples on separate isochron diagrams (Figures 7 a, b, and c) yields the same age within error and similar MSWD values as in Figure 6.

In order to assess whether there is any heterogeneity in the initial $^{187}O/^{188}Os$ ratio of the Exshaw shales, all samples which were from within 1 m of the base of the Exshaw Formation (i.e., at the same stratigraphic level), were plotted on an isochron diagram (Figure 8). One meter of a black shale sequence represents approximately 20,000 years of deposition (Cohen et al., 1999), which is a relatively small interval of time. The MSWD value in Figure 8 is 9, but there was no improvement in the age data when compared to Figure 6. The initial $^{187}O/^{188}Os$ ratio is also quite similar in both cases. The reduced MSWD value of 9 is still significantly greater than unity, suggesting a slight spatial heterogeneity in the initial $^{187}Os/^{188}Os$ ratio within the Exshaw Formation. This heterogeneity likely reflects fluctuations in the local seawater $^{187}Os/^{188}Os$ during

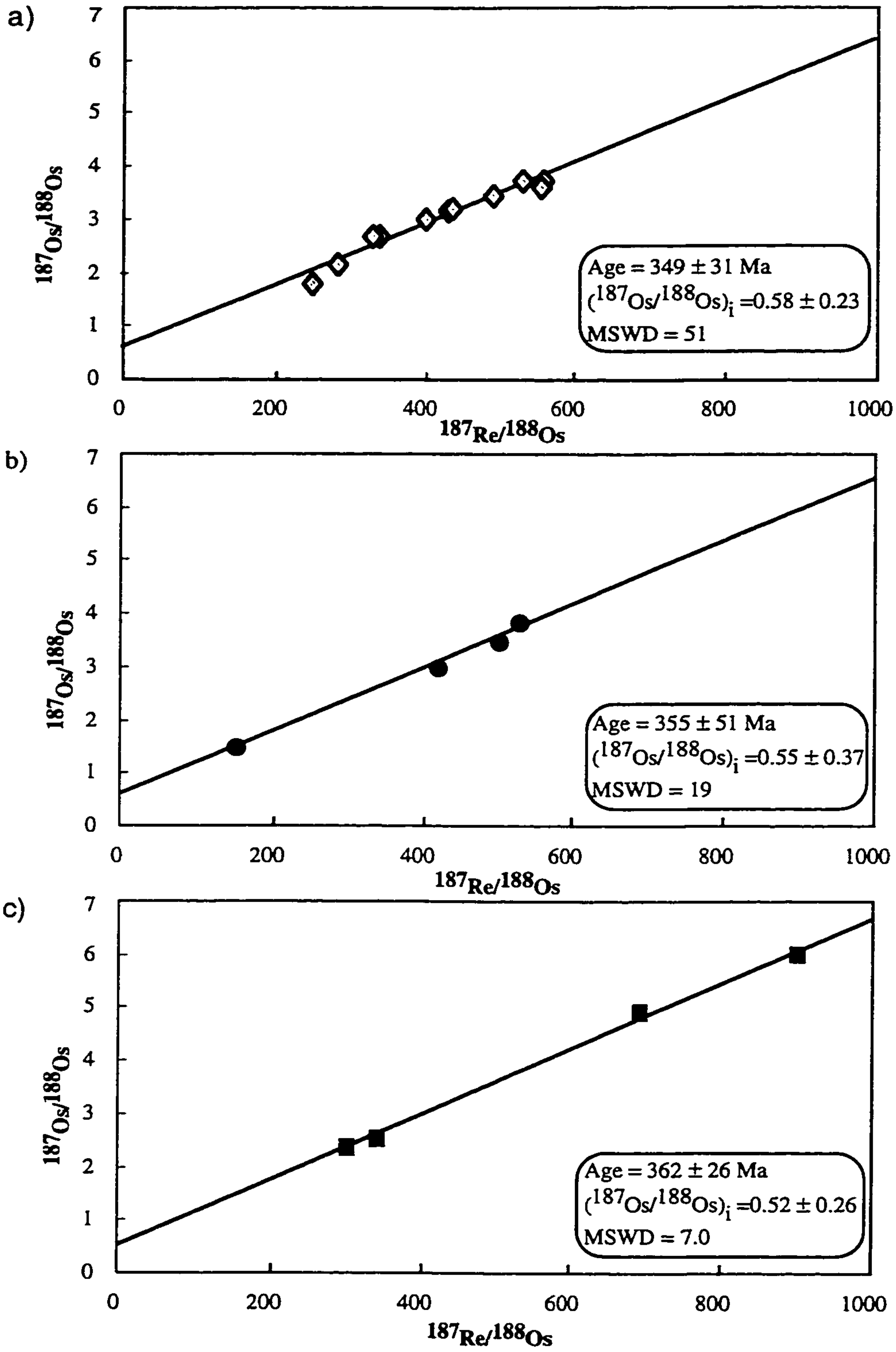

Figure 7. Separate isochron plots for a) hydrocarbon immature, b) hydrocarbon mature and c) hydrocarbon overmature samples

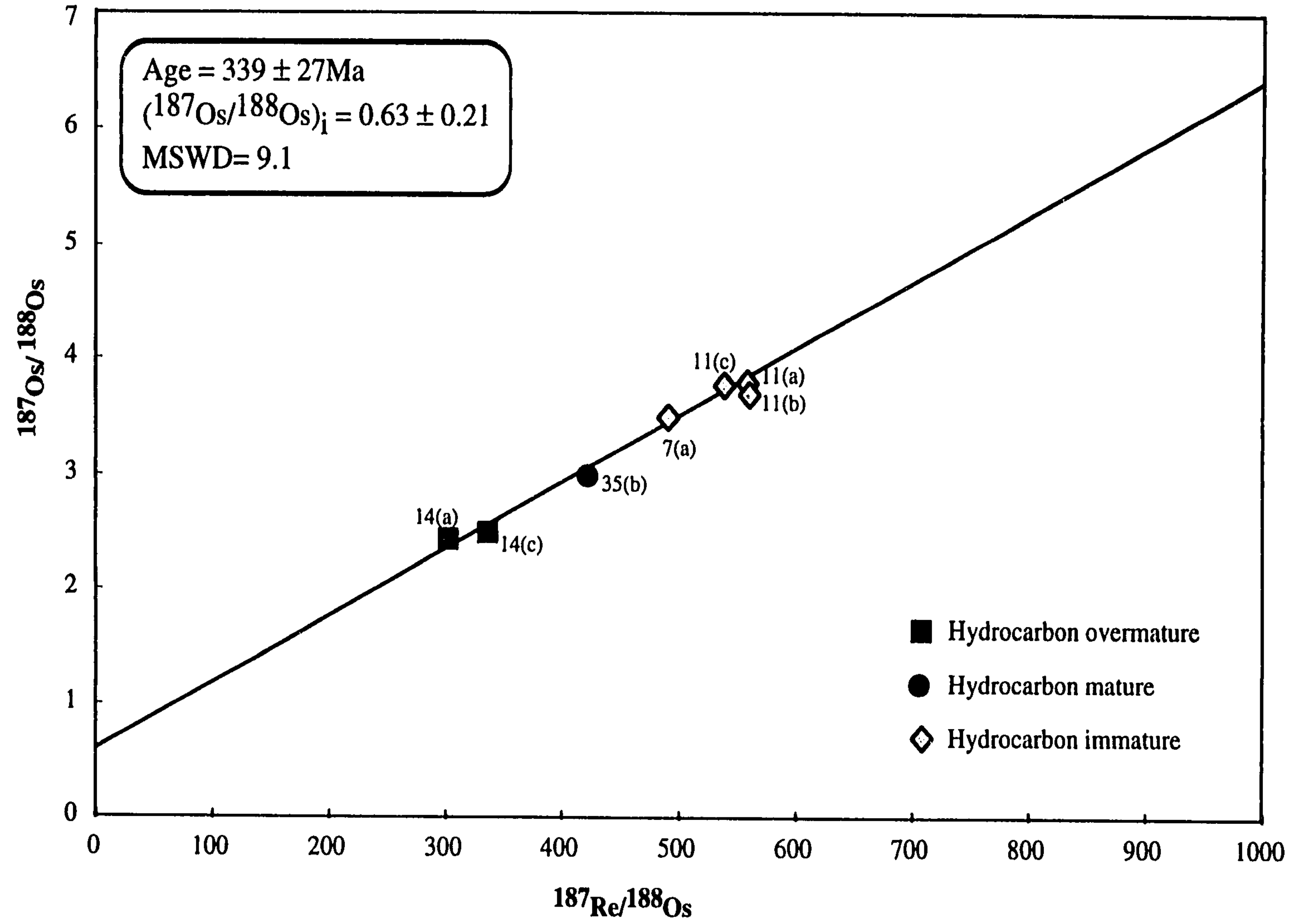

Figure 8. Re-Os isochron plot of samples from up to 1meter of the base of the Exshaw Formation.

the Upper Devonian. Other possible reasons may be small detrital contributions of Re and Os to the Exshaw shales. Initial $^{187}Os/^{188}Os$ ratios were calculated for each of the samples using the equation given on page 3 and assuming an age of 363 Ma. When these values are plotted geographically along a SW-NE transect (Figure 9), no systematic variation is observed. Sample 23 has a much lower initial $^{187}Os/^{188}Os$ ratio and has been excluded from Figure 9b.

CONCLUSIONS AND SCOPE FOR FUTURE WORK:

1) Re-Os dating of black shales from the Exshaw Formation yields an age of 358 ± 12 Ma, which agrees well with the accepted stratigraphic age of 363.6 ± 1.6 Ma.
2) Hydrocarbon mature, immature and overmature samples all plot well on the Re-Os isochron implying that hydrocarbon generation and migration has no significant impact on the Re-Os isotope system in black shales.

Taken together, the above points indicate that the Re-Os geochronometer can be used to determine the depositional age of organic rich shales with good precision regardless of age and level of hydrocarbon maturity.

However, the behavior of this system beyond the temperatures required for hydrocarbon generation and maturation i.e., above ~150°C remains speculative. Systematic studies are required in order to better understand and constrain the robustness of the Re-Os geochronometer during higher temperature processes like metamorphism. Moreover, the phases within black

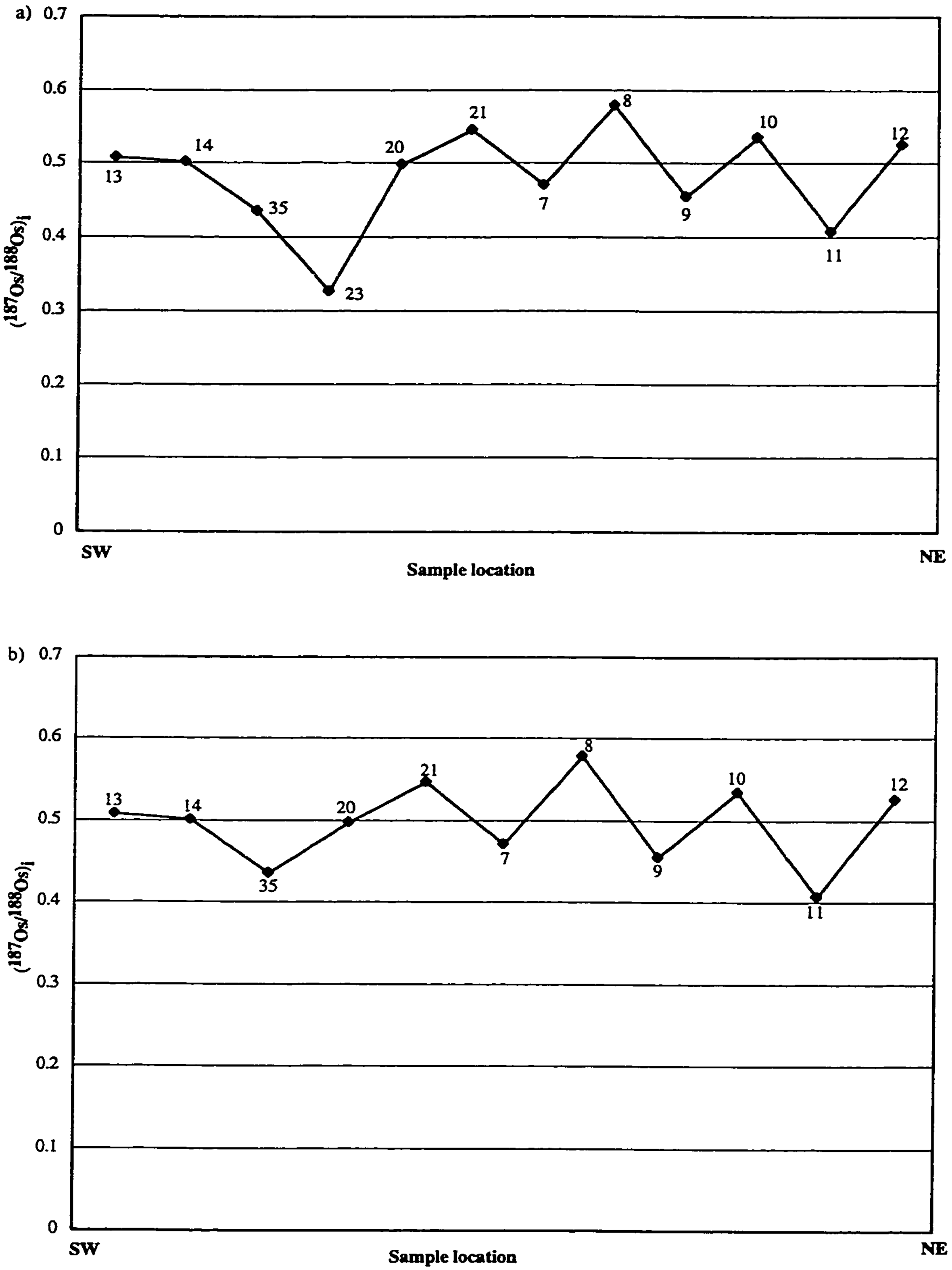

Figure 9. Variations in the $(^{187}Os/^{188}Os)_i$ ratios along the SW-NE transect a) for all samples, b) all samples excluding 23. $(^{187}Os/^{188}Os)_i$ values have been calculated assuming t = 363 Ma.

shales which host Re, Os and the PGE are not known with certainty. Since the behavior of the Re and Os in black shales, under high temperature and pressure conditions will be largely governed by the reaction history of their host phase it is important to determine their association within these rocks. Organic material and sulfides are possible candidates. The Re and Os contents of diagenetic pyrite nodules associated with organic rich sediments were found to be much lower than that of the sediments, thus ruling out the possibility of sulfide phases as the dominant hosts for these elements (Cohen et al., 1999). It is therefore believed that these elements are associated with the organic matter. Comparison of Re-Os analyses of separated organic matter from black shales with those from the corresponding whole rock samples may be useful in this regard.

REFERENCES:

Barre, A.B., Prinzhofer, A., and Allegre, C.J. 1995. Osmium isotopes in the organic matter of crude oil and asphaltenes. *Terra Abstracts* **7**, 199.

Birck, J.L., Roy Barman, M., and Capmas, F. 1997. Re-Os isotopic measurements at the femtomole level in natural samples. *Geostandards Newsletter* **20**, 19-27.

Caplan, M.L., and Bustin, R.M. 1998. Sedimentology and sequence stratigraphy of Devonian-Carboniferous strata, southern Alberta. *Bulletin of Canadian Petroleum Geology* **46**, 487-514.

Clark, L.M. 1949. Geology of the Rocky Mountain Front Ranges near Bow River, Alberta. *Bulletin American Association of Petroleum Geologists* **33**, 614-633.

Cohen, A.S., and Waters, F.G. 1996. Separation of osmium from geological materials by solvent extraction for analysis by thermal ionization mass spectrometry. *Analytica Chimica Acta* **332**, 269-275.

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* **167**, 159-173.

Creaney, S., and Allan, J. 1990. Hydrocarbon generation and migration in the Western Canada Sedimentary Basin. In Brooks, J.(ed.) Classic Petroleum provinces. *Geological Society Special Publication No. 50,* 189-202.

Creaser, R.A., Papanastassiou, D.A., and Wasserburg, G.J. 1991. Negative thermal ion mass spectrometry of osmium, rhenium and irridium. *Geochimica et Cosmochimica Acta* **55**, 397-401.

Crickmay, C.H. 1952. Discrimination of late Upper Devonian. *Journal of Paleontology* **26**, 585-609.

Duke, M.J.M. 1983. Geochemistry of the Exshaw Shale of Alberta-an application of neutron activation analysis and related techniques. Unpub. M.Sc. thesis, University of Alberta. 168p.

Esser, B.E., and Turekian, K.K. 1993. The osmium isotopic composition of the continental crust. *Geochimica et Cosmochimica Acta* **57**, 3093-3104.

Ettensohn, F.R., and Barron, L.S. 1981. Depositional model for the Devonian-Missippian black shale sequence of North America: a tectono – climatic approach. Prepared for U.S. Department of Energy. Contract No. DE-AC21-76ET12040.

Folinsbee, R.E., and Baadsgaard, H. 1958. An absolute age for the Exshaw Shale. *Alberta Society of Petroleum Geology 8th Annual field conference guide book.* 69-73.

Fox, F.G. 1948. The stratigraphy of the Devonian and Mississpian rocks in the foothills of Southern Alberta. Unpub. PhD thesis, University of Oklahoma.

Fox, F.G. 1951. Devonian stratigraphy of Rocky Mountains and Foothills between Crowsnest Pass and Athabasca River. *Bulletin American Association of Petroleum Geologists* **35**, 822-843.

Gradstein, F.M., Agterberg, F.P., Ogg, J.G., Hardenbol, J., van Veen, P., Thierry, J. and Huang, Z. 1994. A Mesozoic time scale. *Journal of Geophysical Research* **99**, No. B12, 24,051-24,074.

Issler, D.R., Willett, S.D., Beaumont, C., Donelick, R.A. and Grist, A.M. 1999. Paleotemperature history of two transects across the Western Canada Sedimentary Basin: Constraints from apatite fission track analysis. *Bulletin of Canadian Petroleum Geology* **47**, 475-486.

Leenheer, M.J. 1984. Missippian Bakken and other equivalent formations as source rocks in the Western Canada basin. *Organic Geochemistry* **6**, 521-533.

Ludwig, K.R. 1992. ISOPLOT: A plotting and regression program for radiogenic isotope data, version 2.57. *U.S. Geological Survey Open File Report 91-445.* 40p.

Luck, J.M., and Allegre, C.J. 1983. Rhenium and osmium systematics in meteorites and cosmochemical consequences. *Nature* **302**, 130-132.

Macqueen, R.W., and Sandberg, C.A. 1970. Stratigraphy, age and interregional correlation of the Exshaw formation, Alberta Rocky Mountains. *Bulletin of Canadian Petroleum Geology* **18**, 32-66.

Morton, J.P. 1985. Rb-Sr dating of diagenesis and source age of clays in Upper Devonian black shales of Texas. *Geological Society of America Bulletin* **96**, 1043-1049.

Mountjoy, E.W. 1956. The Exshaw Formation, Alberta. *Transactions Canadian Institute of Mining and Metallurgy* **59,** 376-380.

Nier, A.O. 1937. The isotopic constitution of Osmium. *Physics Reviews* **52,** 885.

Peucker-Ehrenbrink, B., and Hannigan, R.E. 2000. Effects of weathering on the mobility of rhenium and platinum group elements. *Geology* **28**, 475-478.

Pierson-Wickman, A.C, Reisberg, L., and France-Lanord, C. 2000. The Os isotopic composition of Himalayan river bedloads and bedrocks: importance of black shales. *Earth and Planetary Science Letters* **176**, 203-218.

Piggott, N., and Lines, M.D. 1992. A case study of migration from the West Canada Basin. In England, W.A., and Fleet, A.J. (eds.), Petroleum Migration. *Geological Society Special Publication No.59*, 207-225.

Poplavko, Ye.M., Ivanov, V.V., Longinova, L.G., Orekhov, V.S., Miller, A.D., Nazarenko, I.I., Nishankhodzhayev, R.N., Razenkova, N.I., and Tarkhov, Yu.A. 1977. Behavior of rhenium and other metals in combustible central Asian shales. *Geokhimiya* **2**, 273-283.

Ravizza, G., and Turekian, K.K. 1989. Application of the ^{187}Re - ^{187}Os system to black shale geochronometry. *Geochimica et. Cosmochimica Acta* **55**, 3257-3262.

Russ, G.P., Bazan, J.M., and Date, A.R. 1987. Osmium isotopic ratio measurements by inductively coupled plasma source mass spectrometry. *Analytical chemistry* **59**, 984-989.

Savoy, L.E., and Harris, A.G. 1993. Conodont biofacies and taphonomy along a carbonate ramp to black shale basin (latest Devonian and earliest Carboniferous), southernmost Canadian Cordillera and adjacent Montana. *Canadian Journal of Earth Sciences* **30**, 2404-2422.

Shen, J.J., Papanastassiou, D.A., and Wasserburg, G.J. 1996. Precise Re-Os determinations and systematics of iron meteorites. *Geochimica et. Cosmochimica Acta* **60**, 2887-2900.

Shirey, S.B., and Walker, R.J. 1995. Carius tube digestion for low blank Re-Os analysis. *Analytical Chemistry* **67**, 2136-2141.

Singh, S.K., Trivedi, J.R., and Krishnaswami, S. 1999. Re-Os isotope systematics in black shales from the Lesser Himalaya: Their chronology and role in the $^{187}Os/^{188}Os$ evolution of seawater. *Geochimica et. Cosmochimica Acta* **63**, 2381-2392.

Smoliar, M.I., Walker, R.J., and Morgan, J.W. 1996. Re-Os isotopic constraints on the crystallization history of group IIA, IIIA, IVA and IVB iron meteorites. *Science* **271**, 1099-1102.

Tucker, R.D., Bradley, D.C., Ver Straeten, C.A., Harris, A.G., Erbert, J.R., and McCutcheon, S.R. 1998. New U-Pb zircon ages and the duration and division of Devonian time. *Earth and Planetary Science Letters* **158**, 175-186.

Völkening, J., Walzcyk, T. and Heumann, K.G. 1991. Osmium isotope ratio determination by negative thermal ionization mass spectrometry. *International Journal of Mass Spectrometry and Ion Processes.* **105**, 147-159.

Walker, R.J., and Fassett, J.D. 1989. Isotopic measurement of sub-nanogram quantities of rhenium and osmium by resonance ionization mass spectrometry. *Analytical chemistry* **58**, 2923-2927.

Warren, P.S. 1937. Age of the Exshaw Shale in the Canadian Rockies. *American Journal of Science* **33**, 454-457.

Warren, P.S. 1956. The Exshaw Shale. *Journal of Alberta Society of Petroleum Geologists* **4**, 141.

Warren, P.S., and Stelck, C.R. 1956. Devonian faunas of western Canada. *Geological Association of Canada Special Publication No. 1* **15**, 29pp.

Appendix A.

ISOPLOT (Ludwig, 1992) is a plotting and regression program for radiogenic isotope data, developed by K.R. Ludwig of the Berkeley Geochronology Center. It is in the form of a plugin for the Microsoft Excel software and is widely used by geochronologists for isochron age calculations. Isotope ratios as obtained after making the necessary corrections from the oxide ratios measured on the mass spectrometer are entered in the form of a spreadsheet. Percentage or absolute external error values in the form of 1σ or 2σ are also entered along with the data. The program regresses the data points on a best fit line and calculates the age from the slope of the line, and the initial isotope ratio from its y-intercept for the isotope system specified by the user. It also gives an estimate of the degree of scatter around the isochron in the form of the MSWD value.