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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

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Abstract—Re-Os isotopic analyses of a single organic-rich sedimentary rock unit (ORS) of known depositional age, and at three levels of regional hydrocarbon maturity, show that hydrocarbon maturation does not affect the ability the ^{187}Re - ^{187}Os chronometer to yield a depositional age for such rocks. We present Re-Os isotope analyses from the Late Devonian Exshaw Formation in the subsurface of the Western Canada Sedimentary Basin, Alberta, and obtain a Re-Os isochron age of 358 ± 10 Ma (2σ , Model 3, $\lambda = 1.666 \times 10^{-11} \text{ a}^{-1}$) for samples ranging from hydrocarbon immature to overmature. This age is within uncertainty of the established absolute age for the Exshaw Formation. Hydrocarbon immature, and mature plus overmature samples show no significant age differences if regressed individually, indicating that hydrocarbon maturation did not greatly disturb the Re-Os isotope system in the Exshaw Formation. As such, we propose that the Re-Os geochronometer may be used as a reliable tool for measuring the depositional ages of ORS regardless of their level of hydrocarbon maturity. We find that minimizing natural variation in the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio is more important than avoiding hydrocarbon maturation in obtaining precise Re-Os ages. In particular, the Exshaw Formation appears to contain a nonhydrogenous component of unradiogenic Os, in addition to the hydrogenous Os load. A subset of Exshaw Formation samples with $>5\%$ total organic carbon (TOC), which should best reflect the hydrogenous Os load alone, yields a very well-fitted isochron having a depositional age of 358 ± 9 Ma (2σ , $\lambda = 1.666 \times 10^{-11} \text{ a}^{-1}$) with an initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.59 ± 0.05 (Model 3, Mean Square of Weighted Deviates (MSWD) = 1.8). The initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of this regression may provide an estimate of the Os isotopic composition of local seawater at the time of deposition. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

Determination of the absolute depositional ages of clastic sedimentary rocks using radioactive isotope methods is exceptionally difficult, and unambiguous depositional age estimates cannot usually be obtained using the common long-lived isotope systems such as U-Pb, Sm-Nd, and Rb-Sr. Problems are varied, and include inheritance of provenance isotopic characteristics and diagenetic effects. For example, an 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 (Morton, 1985). In contrast, the Re-Os radioactive isotope system in organic-rich sedimentary rocks (ORS) such as black shale has been shown to be a viable chronometer for dating clastic sedimentary sequences containing these rocks. The conceptual basis for this method was developed by Ravizza and Turekian (1989), and further evaluated by Ravizza et al. (1991) and Cohen et al. (1999). ORS are a significant crustal reservoir of Re and Os with concentrations of up to 300 ppb Re and 3 ppb Os, more than two orders of magnitude higher than average continental crust (Esser and Turekian, 1993), and they are major contributors of radiogenic Os to the oceans (Peucker-Ehrenbrink and Ravizza, 2000). Most of the

Re and Os in ORS is hydrogenous in origin; i.e., the elements were largely sequestered from seawater at the time of deposition (Ravizza and Turekian, 1989).

Despite the geochemical significance of ORS as a crustal reservoir for Re and Os and the potential of these rocks for geochronology, there are few detailed Re-Os isotopic studies. Pioneering work in this field by Ravizza and Turekian (1989) on the upper Mississippian Bakken Formation, North Dakota, yielded a Re-Os isochron age of 354 ± 49 Ma (using $\lambda = 1.52 \times 10^{-11} \text{ a}^{-1}$) or 336 Ma (using $\lambda = 1.666 \times 10^{-11} \text{ a}^{-1}$) which is within uncertainty of the known stratigraphic age of ~ 350 Ma. The samples analyzed by Ravizza and Turekian (1989) originate from an area of the Williston basin in which the Bakken Formation has undergone hydrocarbon maturation (Hunt, 1996). Considerable scatter was observed both between and within localities, which was attributed mainly to hydrocarbon maturation and migration, together with minor effects due to analytical uncertainty and initial Os isotope heterogeneity. Using improved analytical techniques, Cohen et al. (1999) obtained Re-Os isochron ages of 155 ± 4.3 Ma, 181 ± 13 Ma, and 207 ± 12 Ma ($\lambda = 1.666 \times 10^{-11} \text{ a}^{-1}$) from outcrops of Jurassic ORS in England. These isochron ages agree within uncertainty to the respective stratigraphic ages of 149 ± 3 Ma, 187 ± 4 Ma, and 198 ± 4 Ma (Gradstein et al., 1994). The samples used by Cohen et al. (1999) were ORS that had not undergone hydrocarbon maturation, one factor cited by Cohen et al. (1999) as contributing to the improvements made over previous studies. Other studies involving the Re-Os system in

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ORS such as black shales have focused on the weathering of these rocks and their importance in contributing a radiogenic Os flux to the oceans (Singh et al., 1999; Pierson-Wickman et al., 2000; Peucker-Ehrenbrink and Hannigan, 2000).

Although the potential for widespread application of the Re-Os isotope system in ORS is high, the effects of postdepositional processes such as weathering, hydrocarbon maturation, and metamorphism remain poorly understood. The effect of these processes must be investigated in detail before the Re-Os chronometer can be applied on a routine basis. Surface weathering and oxidation is the only postdepositional process that has been recently studied in detail, and has been shown to result in the loss of up to 64% Re and 90% of the Os coupled with substantial loss of organic matter (Peucker-Ehrenbrink and Hannigan, 2000).

This study aims to evaluate further the applicability of the Re-Os isotope system as a geochronometer for ORS such as black shales, and to investigate the effects of hydrocarbon maturation on the Re-Os isotope systematics of these rocks. This study is the first to concentrate on the aspect of hydrocarbon maturation, tests whether hydrocarbon maturation perturbs the Re-Os systematics of ORS, and aims to provide accurate, precise geochronologic data for a Paleozoic ORS unit. The hydrocarbon maturation process could potentially have a large effect, as significant Re and Os contents (hundreds of ppt to tens of ppb) have been reported in some oils, asphaltenes, and bitumens that are typically generated from ORS source rocks (Poplavko et al., 1974; Barre et al., 1995; Creaser and Selby, unpublished data). This implies that some Re and Os migrate with hydrocarbons produced from ORS. If the Re/Os ratios of the matured source rocks are changed during this process, then the Re-Os geochronometer may be useful for determination of depositional ages only in ORS that have not undergone hydrocarbon maturation. We show in this study that hydrocarbon maturation does not impair the utility of the Re-Os isotope system to determine depositional ages from ORS. We also show that samples of the Exshaw Formation likely contain a component of nonhydrogenous, unradiogenic Os, which may be detrital or extraterrestrial in origin.

2. THE EXSHAW FORMATION, WESTERN CANADA SEDIMENTARY BASIN

The Exshaw Formation is an important stratigraphic marker horizon and hydrocarbon source rock in the Western Canada Sedimentary Basin (WCSB), (Leenheer, 1984; Creaney and Allan, 1991). It is a thin but continuous unit ranging from 2 to 12 meters in thickness, averaging ~6 meters thickness, comprising a lower member of organic-rich, black shale and an upper member of siltstone (Fig. 1). All samples analyzed in this study originate from the lower black shale member, the depositional age of which is well-constrained biostratigraphically. Initial deposition occurred as a result of transgression onto the Alberta cratonic platform during Late Devonian (Famennian) time (Caplan and Bustin, 1998), and the Exshaw Formation mostly rests with minor disconformity upon the underlying Upper Devonian strata (Richards et al., 1999). In the Peace River area specifically, where our samples originate (Fig. 1), deposition of the lower black shale member during the Lower *expansa* and *praesulcata* conodont zones of latest Famennian

time is reported (Johnston and Meijer Drees, 1993). Identical biostratigraphic constraints for the lower black shale member are also reported from southwestern Alberta at the type section, and elsewhere (Savoy and Harris, 1993; Richards et al., 1999). A significant change in depositional regime from the anoxic, low-energy conditions of the lower black shale member, to oxygenated marine conditions of the overlying siltstone member of the Exshaw Formation is interpreted to have occurred as early as the Middle *praesulcata* Zone of the Famennian (Fig. 1) (Caplan and Bustin, 1998). However, in southwestern Alberta, faunal evidence that the uppermost part of the lower black shale member extends into Early Tournasian time also exists with the identification of *Siphonodella cooperi* (MacQueen and Sandberg, 1970; Savoy and Harris, 1993), which first appears in the Upper *duplicata* Zone (Richards et al., 1999). The conodont *S. duplicata* has been recovered from the upper siltstone member of the Exshaw Formation, deposition of which likely continued to the *crenulata* Zone of Tournasian time, followed by deposition of the overlying Banff Formation (Savoy and Harris, 1993; Caplan and Bustin, 1998). Thus, the known depositional interval for the lower black shale member of the Exshaw Formation is the period between the *expansa* and *duplicata* zones, of Late Famennian to Early Tournasian time.

The absolute depositional age of the lower black shale member is constrained directly by a U-Pb monazite age of 363.4 ± 0.4 Ma from a tuff horizon close to the base of the black shale member (Richards et al., in press). This age is identical within uncertainty to the composite U-Pb zircon age of 363.6 ± 1.6 Ma for volcanic rocks within the Upper *expansa* Zone from New Brunswick, Canada (Tucker et al., 1998). Tucker et al. (1998) also determined that the Devonian-Carboniferous System boundary (base of *sulcata* Zone) lies close to 362 Ma, and using their time-scale, the Early Tournasian *duplicata* Zone would start at ~360 Ma. Thus, in terms of absolute age, the depositional interval of the lower black shale member of the Exshaw Formation spans a maximum period of time from ~363 to ~360 Ma.

The lower member of the Exshaw Formation contains high organic carbon content (up to 20%) and is also highly enriched in the suite of metals characteristically associated with black shales such as Ni, V, Mo, and U (Duke, 1983). In the westernmost WCSB, the Exshaw Formation has been buried to temperatures necessary for hydrocarbon maturation, increasing in maturation level westward in zones roughly parallel to the Cordilleran orogenic front (Fig. 2) (Piggott and Lines, 1992). Hydrocarbon maturation of WCSB strata is interpreted to have occurred at around 60 Ma, during the time of Laramide orogeny (Issler et al., 1999). Apatite fission track analyses suggest that the strata attained maximum burial and peak temperature at this time. Thus, hydrocarbon maturation in the Exshaw Formation occurred ~300 Ma after deposition.

The widespread occurrence, well-constrained biostratigraphic and absolute age, well-defined hydrocarbon maturation zones, the large time interval between deposition and hydrocarbon maturation, together with the high total organic carbon (TOC) and metal contents of the Exshaw Formation make it an ideal candidate for further evaluating the Re-Os geochronometer in ORS.

3. SAMPLES AND ANALYTICAL METHODS

Samples of ORS from the basal member of the Exshaw Formation were collected from the Alberta Energy and Utilities Board, Core

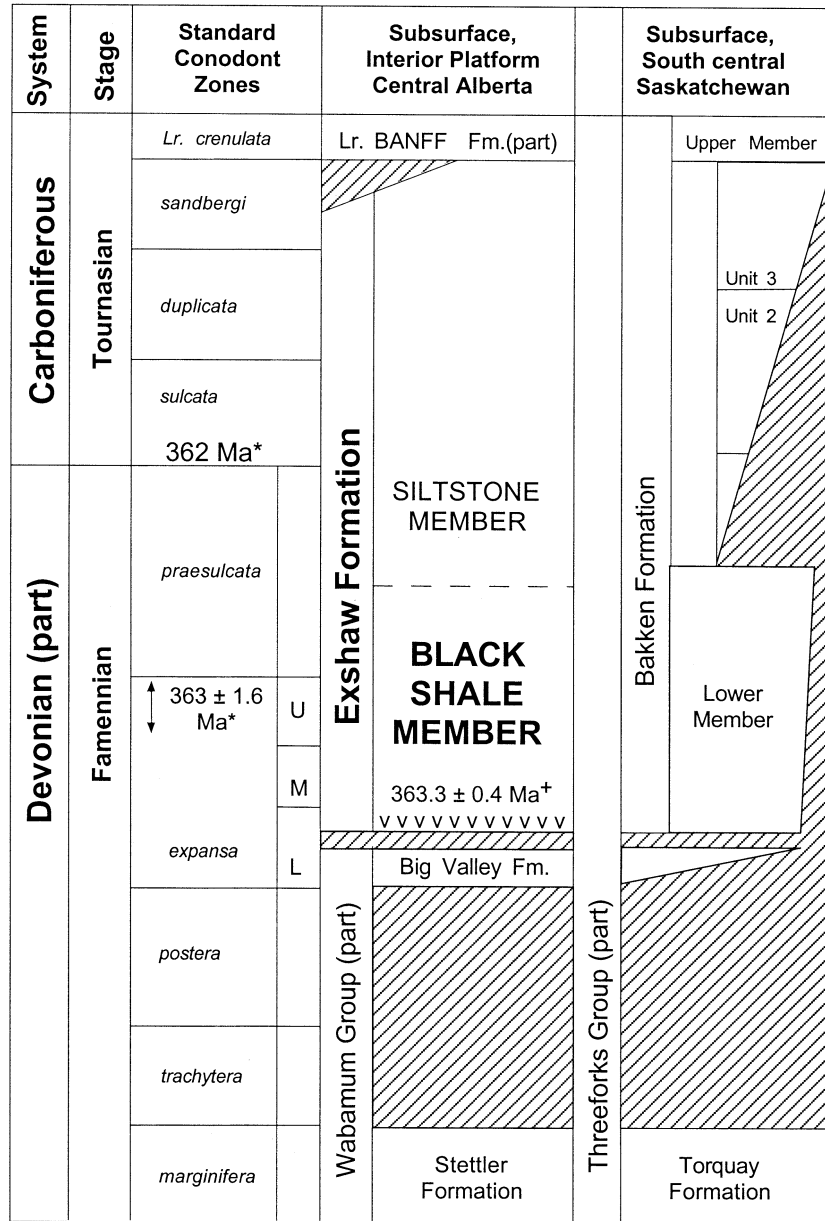


Fig. 1. Devonian–Carboniferous stratigraphic column for the Western Canada Sedimentary Basin of central Alberta and south central Saskatchewan, modified from the compilation of Caplan and Bustin (1998). All samples analyzed in this study originate from the lower black shale member of the Exshaw Formation. Deposition of the black shale member commenced in the *expansa* Zone of Late Famennian time, and locally may have continued to the *duplicata* Zone of Early Tournasian time. Absolute ages designated “*” are from the Devonian timescale calibration study of Tucker et al (1998). The age of a tuff unit (shown as “v v v”) in the basal part of the Exshaw Formation black shale member designated “+” is from Richards et al (in press). Diagonal hatching represents time of depositional hiatus.

Research Center, Calgary. Drill core samples were used in order to avoid possible loss of Re and Os and subsequent disturbance to the Re-Os isotope system relating to surface weathering (Peucker-Ehrenbrink and Hannigan, 2000). Multiple samples were taken from each well from different depths, in order to cover the entire depositional interval of the lower Exshaw Formation member. Also, coverage of different hydrocarbon maturity levels required sampling at a lateral scale of >150 km (Fig. 2). The edges of the core samples were ground to remove drilling marks, and samples were taken from the inner part of the core, broken to chips without metal contact, and were further crushed using a jaw crusher equipped with ceramic plates. Final crushing into fine powder was performed using an agate mill. All Re-Os

isotope analyses were carried out in the Radiogenic Isotope Facility of the Department of Earth and Atmospheric Sciences, University of Alberta using analytical procedure for chemical separation of Re and Os modified from methods described by Shirey and Walker (1995), Cohen and Waters (1996), and Birck et al. (1997), as described by Selby and Creaser (2001); specific information relevant for this study follows.

Approximately 0.8 gram of powdered sample was accurately weighed and transferred to a thick-walled, borosilicate glass Carius tube. An accurately weighed amount of a mixed ¹⁸⁵Re + ¹⁹⁰Os spike was added to each sample and dissolved at 240°C for 48 h, followed by

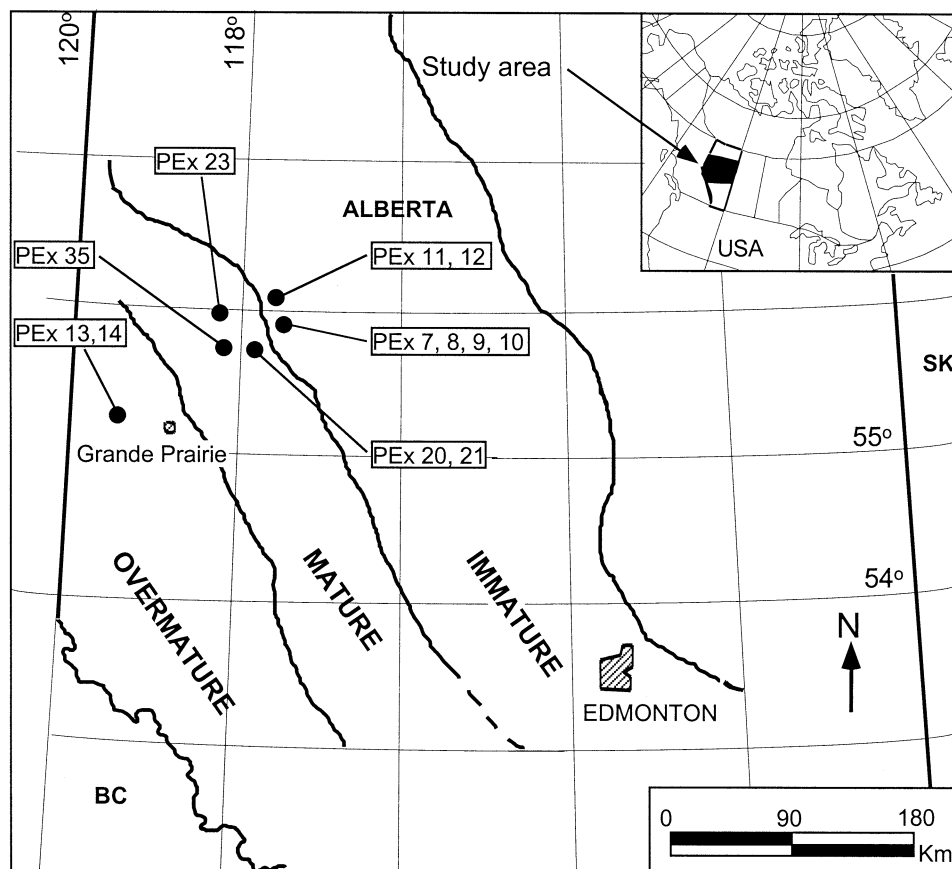


Fig. 2. Map showing the well locations containing Exshaw Formation samples analyzed in this study, together with the regional hydrocarbon maturity levels for the Exshaw Formation. (After Piggott and Lines, 1992.)

separation of Os and Re (Selby and Creaser, 2001). Osmium was loaded onto Pt filaments in 9N HBr, covered with a NaOH-Ba(OH)₂ mixture and analyzed by negative thermal ion mass spectrometry (NTIMS) (Creaser et al., 1991; Volkening et al., 1991) using a Micro-mass Sector 54 mass spectrometer. During the course of this study, improvements in the quality of the separated Os meant that samples containing more than ~200 picograms (pg) of Os (assuming 100% chemical yield) could usually be analyzed by static Faraday collector analysis. Analyses conducted early in the course of the study were made by single collector peak-hopping using an ETP electron multiplier operating in pulse-counting mode. The Re fraction was loaded to either a Pt or a Ni filament together with Ba(NO₃)₂ and analyzed using Faraday collectors. Measured oxide ratios for Os and Re were corrected for isobaric oxygen interferences to obtain metal ratios, which were then corrected for mass fractionation using $^{192}\text{Os}/^{188}\text{Os} = 3.08761$ and $^{185}\text{Re}/^{187}\text{Re} = 0.59738$, spike contributions and blank. Total procedural blanks ranged from 50 to 3 pg Re and 1.5 to 4 pg Os, with an average $^{187}\text{Os}/^{188}\text{Os}$ value of 0.21. The Re blanks decreased significantly during the study as a result of: (1) using Ni rather than Pt for analysis, (2) using disposable polymethylpentene (PMP) beakers for sample dry down and collection, (3) using disposable polyethylene columns for chromatography, and (4) using Eichrom rather than Bio-Rad anion exchange resin. The ^{185}Re and ^{190}Os abundances in the mixed spike were calibrated using Re and Os standard solutions made from 99.9999% pure Re metal and 99.999% (metals basis) ammonium hexachlorosmate. Yin et al. (2001) have shown that ammonium hexachlorosmate can be nonstoichiometric in terms of its Os content, and thus can introduce uncertainties into absolute spike calibrations if stoichiometry is assumed. However, Selby and Creaser (2001) showed that precise, reproducible determination of the Os content of this compound could be made directly by gravimetric reduction in a gas furnace. This gravimetric determination of Os content is lower than the

stoichiometric Os content of this compound, as was also found by Yin et al. (2001), and the gravimetrically determined value of Os is used for spike calibration calculations. Triplicate calibrations of the ^{185}Re abundance agree to $\pm 0.13\%$, and duplicate calibrations of the ^{190}Os abundance agree to within $\pm 0.03\%$. To assess long-term instrument reproducibility, an in-house Os solution has been repeatedly analyzed over the course of this study and yields an $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.106855 ± 0.000015 (1 SD, $n = 9$) by static Faraday collector analysis. The Os standard used at the University of Maryland (Brandon et al., 1999) has yielded an average $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.113809 ± 0.000009 (1 SD, $n = 4$) for analysis of nanogram-sized Os runs by Faraday collector, identical to the value of 0.113807 ± 0.00002 ($n = 21$) reported by Brandon et al. (1999). The same Os standard analyzed by peak-hopping using the electron multiplier yields an average value of 0.11389 ± 0.00018 (1 SD, $n = 24$) for 100 pg Os loads. A standard solution of Re is used to monitor $^{185}\text{Re}/^{187}\text{Re}$, which was determined to be 0.59751 ± 0.00027 (1 SD, $n = 14$) using a Pt filament and 0.59874 ± 0.00051 (1 SD, $n = 16$) using a Ni filament, compared with a value of 0.59738 ± 0.00039 determined by Gramlich et al. (1973). Re samples analyzed with a Ni filament were corrected for the difference observed between standard Re analyses on Ni and the value of Gramlich et al. (1973); samples run on Pt had no correction applied.

All regressions are calculated using the program *Isoplot* (Ludwig, 1998), and all uncertainties are quoted at the 2σ level as produced by *Isoplot*. Regression uses uncertainties of $\pm 1\%$ for $^{187}\text{Re}/^{188}\text{Os}$, the measured $2\sigma_m$ uncertainty in $^{187}\text{Os}/^{188}\text{Os}$, and a value of $\lambda = 1.666 \times 10^{-11} \text{ a}^{-1}$ (Smoliar et al., 1996).

The N and S contents of the samples were determined using a Carlo Erba 1108 elemental analyzer and by the Schoniger method, respectively, at the Micro-Analytical Laboratory of the Department of Chemistry, University of Alberta. Accuracy and reproducibility for N analyses are monitored using an acetanilide standard, which typically yields

better than $\pm 1.5\%$ reproducibility (2 SD) in any given analytical session and an average value within 0.3% of accepted. For S analyses, a thiophene standard is used and shows reproducibility of better than $\pm 4\%$ (2 SD) and an average value within 3% of accepted over a period of several months. TOC content and hydrocarbon maturity level were determined by Rock-Eval pyrolysis (Peters, 1986; Hunt, 1996) at the Geological Survey of Canada, Calgary. For Rock-Eval pyrolysis, samples are progressively heated in a stream of helium to 550°C and the emitted vapors analyzed. At $\sim 300^\circ\text{C}$, free hydrocarbons are distilled from the sample and are detected as the peak P_1 . Between 300°C and $\sim 390^\circ\text{C}$ carboxyl groups are released from kerogen as CO_2 (peak P_2), and from $\sim 350^\circ\text{C}$ to 550°C hydrocarbons are released by cracking kerogen and detected as P_3 . The parameter T_{max} is a laboratory temperature used to evaluate sample hydrocarbon maturity level; it represents the temperature of peak hydrocarbon release by kerogen cracking in the Rock-Eval pyrolyzer (P_3). Samples with T_{max} values of $< 435^\circ\text{C}$ are immature, those with values between 435°C and 465°C are mature, and those with values $> 465^\circ\text{C}$ are overmature (Peters, 1986). The uncertainty in this parameter is $\pm 2\text{--}3^\circ\text{C}$, based upon replicate analysis of both samples analyzed here and laboratory standards (K. Osadetz, personal communication, 2002).

4. RESULTS

4.1. Hydrocarbon Maturity

The Rock-Eval pyrolysis determination of hydrocarbon maturity level for the samples of the Exshaw Formation studied here generally agrees well with that expected from their known maturity relative to geographic distribution, with two exceptions (Table 1) (Piggott and Lines, 1992). Sample PEx-9 failed to yield a meaningful value for T_{max} , and replicate analyses did not reproduce within expected limits ($\pm 2\text{--}3^\circ\text{C}$). The organic material in this sample was found to be partly oxidized, which accounts for its anomalous T_{max} value, and which results in an erroneous indication for thermal maturity (K. Osadetz, personal communication, 2002). The thermal maturity of PEx9 is best described by the three other samples from this well (all immature). Samples PEx-20 originates from a well in the mature zone of the Exshaw Formation (Table 1) (Piggott and Lines, 1992), but yielded a T_{max} value of 432°C, slightly below the hydrocarbon mature-immature transition of 435°C. However, samples PEx-20 and PEx-21 are separated by only 10 cm in this well, and the latter sample yielded a T_{max} value of 435°C. Thus, given the known uncertainties of $\pm 2\text{--}3^\circ\text{C}$ in the determination of T_{max} , the geographic distribution of this well and the T_{max} value for sample PEx-21, sample PEx-20 is designated as hydrocarbon mature.

4.2. Elemental Variations

The measured TOC, sulfur and nitrogen contents, together with the measured Re and Os abundances and isotopic compositions are shown in Table 1 and Fig. 3A–F. Samples of the Exshaw Formation show a range in TOC from ~ 1.6 to 12%, but most samples contain ~ 2 to 4% TOC. These values are generally lower than the ORS samples investigated by Ravizza and Turekian (1989), Cohen et al. (1999), and Peucker-Ehrenbrink and Hannigan (2000). The TOC abundances show a strong positive correlation with the abundance of nitrogen (Fig. 3A) but a much weaker correlation with sulfur abundance (Fig. 3B). Re and ^{192}Os concentrations range from 23 to 130 ppb and 0.07 to 0.55 ppb, respectively, and are comparable with those determined from other ORS (Ravizza and Turekian, 1989;

Cohen et al., 1999; Peucker-Ehrenbrink and Hannigan, 2000). As found in these previous studies, there is a general positive correlation between both Re and ^{192}Os contents in ORS and carbon and nitrogen content, which can be used to infer the predominantly hydrogenous origin of these elements in ORS. However, covariations of ^{192}Os with TOC and N in the Exshaw Formation are consistently better correlated than variations involving Re (Fig. 3C–F). Possible reasons for these elemental variations are discussed later.

4.3. Re-Os Isotopic Results

Measured $^{187}\text{Re}/^{188}\text{Os}$ ratios range from ~ 147 to 905 and $^{187}\text{Os}/^{188}\text{Os}$ ratios range from ~ 1.4 to 5.9. Several samples were chosen for replicate analysis to assess reproducibility. In most cases, such as sample PEx-10, both the Re and Os abundances replicated very well (better than $\pm 1\%$). In other cases such as PEx-14 and -23, Re abundances replicated to better than $\pm 0.5\%$, but the Os abundance variation was considerably larger; up to $\pm 10\%$. In these cases, the resulting variation in $^{187}\text{Re}/^{188}\text{Os}$ between the replicate analyses is positively coupled to variation in $^{187}\text{Os}/^{188}\text{Os}$, such that the initial $^{187}\text{Os}/^{188}\text{Os}$ values determined at the known stratigraphic age of 364 Ma (hereafter, I_{Os}) are very similar. This implies that, for these samples, complete homogenization of the sample powder was not achieved despite grinding in an automated agate mill. It is also notable that the $^{187}\text{Re}/^{188}\text{Os}$ ratio can vary by up to factors of ~ 3 over very short vertical distances (< 0.1 m) in the same drill core, such as samples PEx-20 and -21. Similar variations have also been reported by Cohen et al. (1999).

Regression of all Re-Os isotopic data yields an age of 368 ± 14 Ma and a value for I_{Os} of 0.44 ± 0.10 (Model 3). Although the derived age is within uncertainty of the known absolute age (~ 364 Ma), the scatter of these data around the regression line is large (MSWD = 103). However, much of this scatter can be attributed to a single sample PEx-23, two analyses of which plot well below the regression line (Fig. 4A). This sample also has one of the lowest TOC abundances (1.58%) and has a markedly lower I_{Os} value than other samples (Table 1), the importance of which will be discussed below. Omitting sample PEx-23 and regressing all remaining data results in an age of 358 ± 10 Ma with an I_{Os} value of 0.53 ± 0.07 (Model 3, Fig. 4B). The MSWD value of this regression is reduced to 19, which is similar to the best-fitted isochrons produced by Cohen et al. (1999) from Jurassic ORS that have not undergone hydrocarbon maturation (range of MSWD from 11 to 88 for three regressions). The resulting age of 358 ± 10 Ma is within uncertainty of the Exshaw Formation's known depositional age.

Further evaluation of any effects of hydrocarbon maturation on these samples can be made by separate regression of those samples that are immature, versus those that are mature or overmature. Regression of nine analyses of six samples that have not undergone hydrocarbon maturation yields an age of 351 ± 23 Ma and an I_{Os} value of 0.57 ± 0.17 (Model 3, MSWD = 19; samples PEx-7, -8, -9, -10, -11, and -12). Considering only the remaining five mature and overmature samples produces a regression with an age of 360 ± 13 Ma with an I_{Os} value of 0.53 ± 0.10 (Model 3, MSWD = 22; samples PEx-13, -14, -20, -21, and -35). The ages produced by these two regressions are not significantly different at 2σ un-

Table 1. Location and analytical data for Exshaw Formation samples, Alberta, Canada.

Sample # ^a	Well ^b	Depth ^c	Above base ^d	Maturity ^e	T_{\max} (°C) ^f	Maturity ^g	Re (ppb)	Os (ppb) ^h	¹⁹² Os (ppb)	¹⁸⁷ Re/ ¹⁸⁸ Os	¹⁸⁷ Os/ ¹⁸⁸ Os ⁱ	I_{Os} ^j	TOC (%) ^k	N (%)	S (%)
PEX 7	3-19-80-23W5	1752.0	4.5	I	431	I	72.17	1.020	0.296	485.6	3.4307 (14)	0.48	3.14	0.13	nd
PEX 8	3-19-80-23W5	1753.0	3.5	I	430	I	89.45	1.658	0.516	344.5	2.6619 (8)	0.57	11.99	0.42	4.12
PEX 9	3-19-80-23W5	1754.0	2.5	I	<i>[456]</i>	<i>[M]</i>	22.81	0.496	0.163	279.8	2.1951 (15)	0.49	2.31	0.24	nd
PEX 9 rpt							25.03	0.539	0.177	281.6	2.1533 (17)	0.44			
PEX 10	3-19-80-23W5	1756.5	0	I	431	I	32.39	0.495	0.149	437.9	3.180 (12)*	0.52	3.02	0.13	2.06
PEX 10 rpt							32.10	0.495	0.148	433.5	3.153 (9)*	0.52			
PEX 11	13-18-80-23W5	1748.8	2.2	I	432	I	50.89	0.664	0.189	538.9	3.677 (4)	0.43	2.10	0.15	2.34
PEX 11 rpt							48.33	0.634	0.179	538.0	3.7428 (9)	0.47			
PEX 11 rpt							48.08	0.635	0.181	529.0	3.6363 (7)	0.42			
PEX 12	13-18-80-23W5	1750.9	0.1	I	421	I	71.18	1.148	0.347	408.5	3.0085 (6)	0.51	7.92	0.26	6.73
PEX 20	8-29-78-01W6	2099.1	0.9	M	432	<i>I</i>	129.0	1.725	0.485	528.6	3.7541 (16)	0.54	12.62	0.48	4.15
PEX 20 rpt							128.6	1.702	0.476	536.5	3.7998 (7)	0.54			
PEX 21	8-29-78-01W6	2099.2	0.8	M	435	M	19.98	0.698	0.244	163.2	1.5611 (6)	0.57	8.11	0.29	nd
PEX 23	14-22-80-02W6	2058.3	1.7	M	435	M	32.78	0.897	0.315	207.5	1.527 (4)*	0.27	1.58	0.18	nd
PEX 23 rpt							32.15	0.743	0.252	254.6	1.868 (5)*	0.32			
PEX 35	6-19-78-25W5	2006.2	1.8	M	441	M	52.97	0.831	0.252	419.4	2.9794 (15)	0.43	2.23	0.15	nd
PEX 13	4-23-72-10W6	3570.4	0.1	O	485	O	31.28	0.290	0.070	904.6	5.955 (3)	0.45	1.42	0.11	0.38
PEX 14	4-23-72-10W6	3567.7	2.7	O	465	O	42.35	0.856	0.276	306.4	2.363 (5)*	0.50	3.26	0.15	0.85
PEX 14 rpt							42.19	0.787	0.249	337.2	2.516 (3)	0.46			
PEX 14 rpt							42.24	0.789	0.250	337.1	2.522 (5)	0.47			

^a "rpt" denotes replicate analysis. Samples ordered in table by increasing hydrocarbon maturity (e).

^b In township-range notation which is conventional in Alberta.

^c Depth from the surface in meters.

^d Depth above the logged base of the Exshaw Formation in meters.

^e Hydrocarbon maturity expected based on location of well, from Piggott and Lines (1992); I = immature; M = mature; O = overmature.

^f The parameter T_{\max} as determined by Rock-Eval pyrolysis; sample PEX-9 failed to yield a meaning value (see text for explanation). Italicized data indicate discrepancy between maturity expected based on Piggott and Lines (1992), and maturity determined by Rock-Eval pyrolysis (see text).

^g Hydrocarbon maturity determined by Rock-Eval pyrolysis (see text for explanation). I= immature; M= mature; O= overmature.

^h Os ppb calculated from the measured Os isotopic composition and includes radiogenic ¹⁸⁷Os.

ⁱ Number in parentheses indicates the uncertainty as $2\sigma_m$ in the measured ratio. * Denotes analysis by electron multiplier; others by Faraday collector.

^j I_{Os} is the initial ¹⁸⁷Os/¹⁸⁸Os ratio calculated at 364 Ma using $\lambda = 1.666e^{-11}a^{-1}$.

^k TOC is the total organic carbon content determined by Rock-Eval pyrolysis.

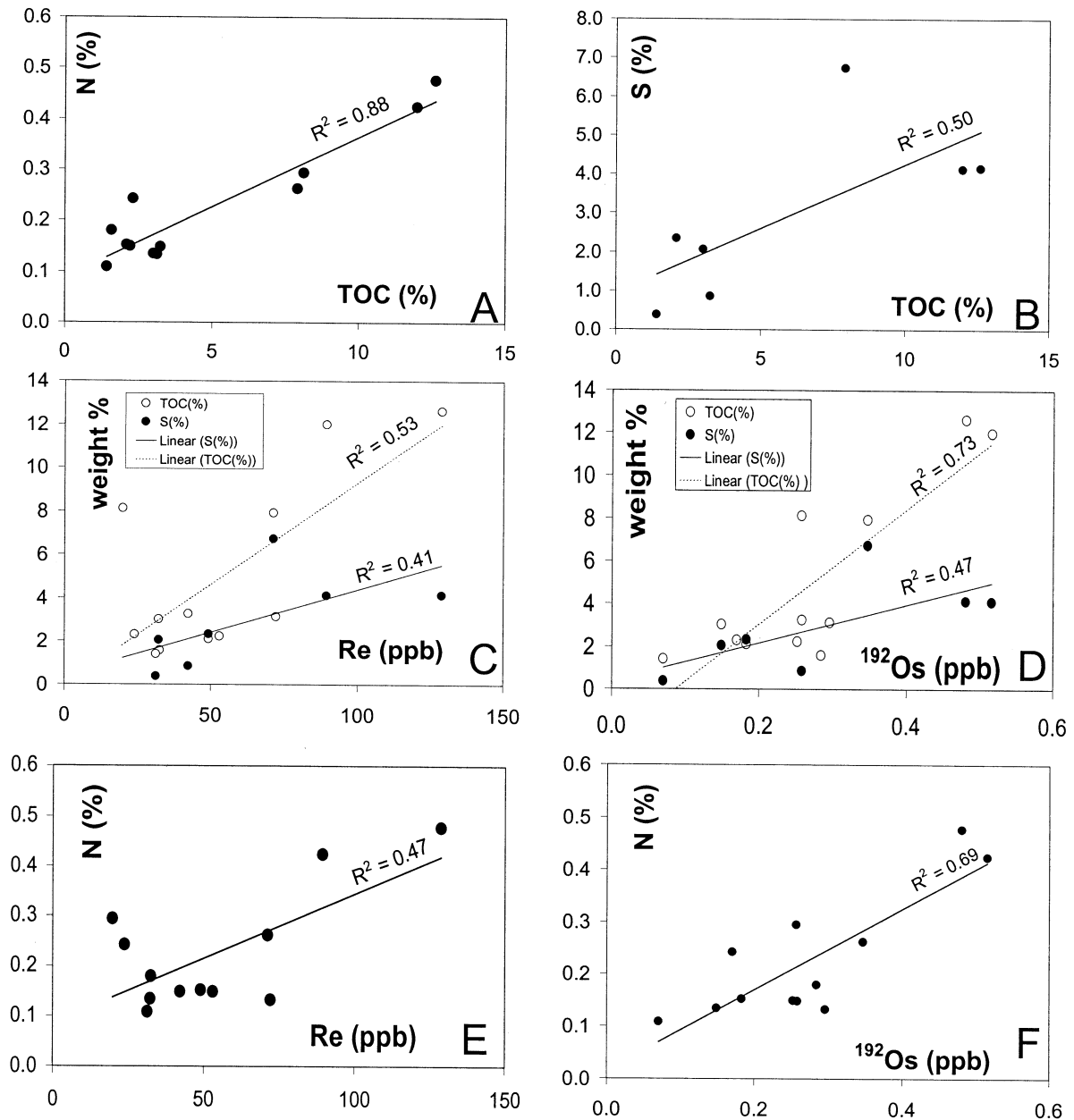


Fig. 3. Geochemical diagrams showing the variation in Re and Os abundance for the Exshaw Formation as a function of total organic carbon (TOC %), nitrogen and sulfur contents. Samples from which replicate analyses were made for Re and Os analysis, the average abundances of Re and ^{192}Os are plotted.

certainty levels, which suggests that the process of hydrocarbon maturation does not negatively affect the ability of the Re-Os system to record depositional ages in ORS.

5. DISCUSSION

5.1. Minimal Effects of Hydrocarbon Maturation on Re-Os Isotope Systematics in ORS

The depositional age obtained here of 358 ± 10 Ma from Re-Os geochronology of the Exshaw Formation agrees within uncertainty to that of the Upper *expansa* conodont zone, dated by the U-Pb zircon method in volcanic ashes (363.6 ± 1.6 Ma;

Tucker et al., 1998). This Re-Os age is derived from samples having a range of hydrocarbon maturity levels spanning immature to overmature (T_{max} values of 421–485 °C). To first order then, we conclude that the degree of hydrocarbon maturation for the Exshaw Formation does not impede the ability of the Re-Os isotope system to record depositional ages for this ORS. This finding is reinforced by the observation that ages determined from separate regressions of immature, and mature plus over mature samples, are not significantly different at the 2σ level of confidence. The importance of this finding reaches beyond the realm of ORS geochronology, into the nature of metal incorporation into hydrocarbons generated from ORS.

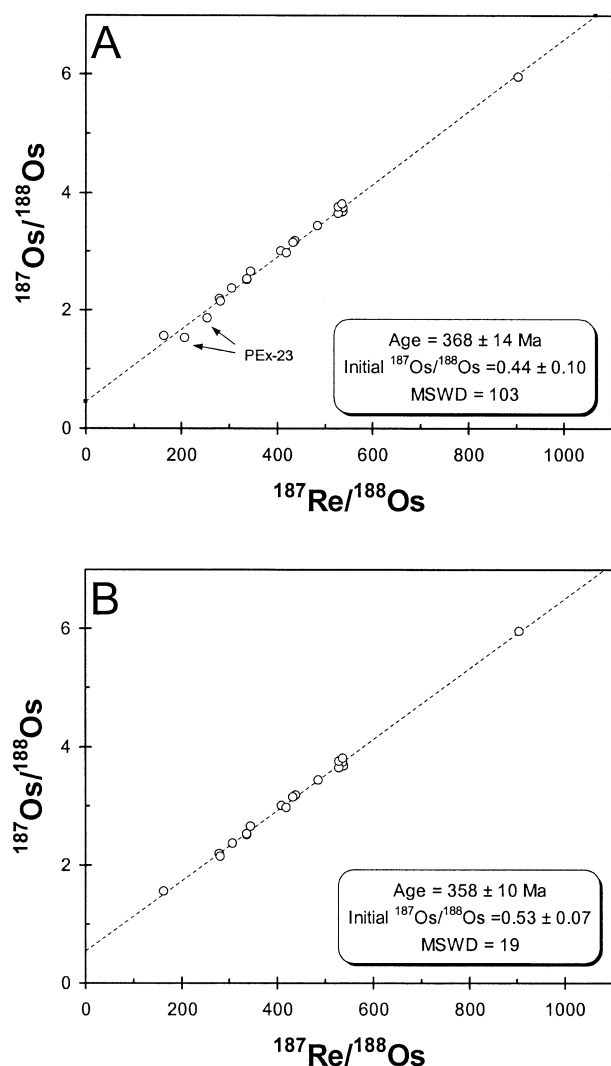


Fig. 4. Re-Os isochron diagrams for the Exshaw Formation. All regressions are calculated using the program *Isoplot* (Ludwig, 1998) and all uncertainties are quoted at the 2σ level. (A) All Exshaw Formation samples. (B) All samples less PEx-23.

Some evidence exists that Re and Os are present in natural hydrocarbons (Poplavko et al., 1974; Barre et al., 1995; Creaser and Selby, unpublished data); elements with broadly similar geochemical characteristics such as Pt and Mo also have high stability indices for metalloporphyrin formation, which are important metal complexing agents in natural hydrocarbons (Manning and Gize, 1993 and references therein). If then, to first order, the process of hydrocarbon maturation has not greatly altered the Re/Os ratio of a matured ORS, the same may be true of the Re/Os ratio in the generated hydrocarbons if the Re and Os mass balance between matured shale and generated hydrocarbons is not completely dominated by the matured shale. It is also reasonable to assume that the Os isotopic composition of the hydrocarbon will mirror that of its parent ORS, and these putative relationships may prove useful in future application of the Re-Os isotope system in organic and petroleum geochemistry.

The MSWD value of 19 for the regression of all Re-Os data

from the Exshaw Formation (except PEx-23), although similar to those produced from nonmatured ORS using similar analytical techniques (Cohen et al., 1999), clearly indicates that some cause of scatter of the data about the regression line exists beyond that ascribed to analytical uncertainty. Therefore, we suggest that two factors could result in data scatter about the isochron: (1) minor postdepositional mobility of Re and Os by hydrocarbon maturation, and (2) variations in the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio during the depositional interval for the samples involved. The first factor has been identified or cited as a major cause of scatter in earlier studies (Ravizza and Turekian, 1989; Cohen et al., 1999), but appears not to be a major cause of scatter in this study. To examine the possibility of minor Re-Os disturbance as a result of hydrocarbon maturation, the value of I_{Os} is plotted versus the parameter T_{max} (Fig. 5A). If hydrocarbon maturation caused a minor systematic variation in Re/Os, then a correlation between the degree of maturation (T_{max}) and I_{Os} might be expected, but none is evident (Fig. 5A). Thus, we conclude it likely that minor primary variations in I_{Os} are controlling the scatter seen in the Exshaw Formation data, which is now discussed.

5.2. Possible Causes of Variation in I_{Os} for the Exshaw Formation

If the scatter of the Exshaw Formation data around the regression lines is being caused by variation of the isotopic composition of Os incorporated into the ORS at the time of deposition, then the origin of this variation has to be evaluated in two different ways. Firstly, consideration has to be given to oceanic Os isotopic variations over timescales shorter than those over which the Exshaw Formation was deposited. Secondly, evaluation of possible Os fluxes into the Exshaw Formation other than Os derived hydrogenously has to be considered. It is also possible that both of these processes are important during the deposition of any ORS.

The residence time of Os in the modern oceans is not fully constrained, but is known to be intermediate between those of the isotope tracers Sr and Nd (Oxburgh, 2001; Levasseur et al., 1998; Sharma et al., 1997). Thus, the modern oceans are relatively uniform in their Os isotopic composition but variations with time over the last few thousand years are reported (Oxburgh, 2001). Given that deposition of ORS such as black shales may be as slow as 2 m/Ma (Cohen et al., 1999), if major changes to the Os ocean fluxes occurred during ORS deposition, then variations in I_{Os} are to be expected, as the time duration over which the basal member of the Exshaw Formation was deposited may extend over a few million years (Section 2). In addition, the residence time of Os should decrease and further promote short-term variation in I_{Os} if the proportion of anoxic bottom sediments, which are important Os sinks, increases during periods of extensive black shale deposition, such as at the Devonian–Carboniferous boundary. The importance of minimizing variation in I_{Os} has been previously recognized for Re-Os ORS studies, and is typically countered by detailed sampling strategies over very short stratigraphic intervals (Cohen et al., 1999).

However, the primary aim of this study, to test hydrocarbon maturation effects, requires sampling over large distances (~ 150 km) in order to encounter the regional maturation zones,

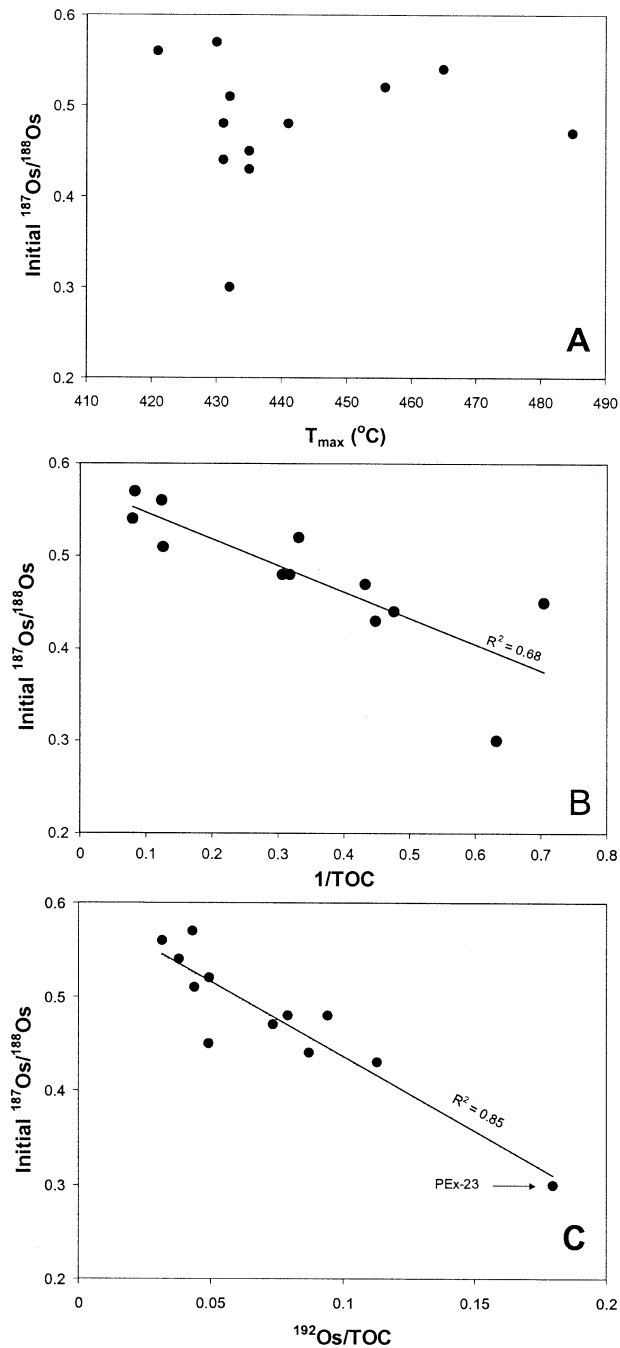


Fig. 5. Variations of the initial $^{187}\text{Os}/^{188}\text{Os}$ for Exshaw Formation samples with: (A) the degree of hydrocarbon maturation shown as the parameter T_{max} , (B) $1/\text{TOC}$ content, and (C) the index $^{192}\text{Os}/\text{TOC}$. The initial $^{187}\text{Os}/^{188}\text{Os}$ ratio was calculated using measured $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$, together with an absolute age of 364 Ma and a value of $\lambda = 1.666 \times 10^{-11} \text{ a}^{-1}$. In cases where duplicate analyses were conducted, the average value of initial $^{187}\text{Os}/^{188}\text{Os}$ is plotted.

and this unavoidable sampling strategy could not precisely correlate individual layers between widely spaced drillholes in a lithologically uniform ORS; it is thus not optimal for minimizing time-dependent variation in oceanic I_{Os} . An assessment of the importance of time-dependent I_{Os} variation can be made by considering only those samples from the lowermost strati-

graphic levels of the basal zone, rather than the entire basal zone, thereby minimizing the time duration of deposition. These data are shown in Figure 6A, which yield an age of $356 \pm 3 \text{ Ma}$ with an I_{Os} value of 0.59 ± 0.02 (Model 1, MSWD = 1.3). The very well-fitted nature of this regression suggests that variation in I_{Os} over the period of deposition for the entire lower black shale member of the Exshaw Formation may be an important cause of scatter in the Re-Os data, but is discussed further below.

The source of Os in sedimentary rocks like ORS is dominated by hydrogenous sources (Ravizza and Turekian, 1989; Cohen et al., 1999), but lower I_{Os} values in marine sediments compared with Os dissolved in overlying sea water column can result from the extraterrestrial Os flux to the ocean floor (Sharma et al., 1997). In addition, Ravizza et al. (1991) have shown that in one case, detrital Os fluxes can influence the Os isotopic composition of modern ORS. If any of these fluxes were important during deposition of the Exshaw Formation, then they could provide an explanation for the variation in I_{Os} values observed. These effects should be evident in samples where the hydrogenous Os load is lowest, which should be in the samples with the lowest TOC and N contents. Indeed, a relationship exists between the TOC content of the samples and the value of I_{Os} , with high TOC samples recording higher I_{Os} values and low TOC samples recording lower I_{Os} values, with sample PEx-23 recording the lowest I_{Os} value (Fig. 5B, Table 1). These data suggest a component of unradiogenic Os is present in the Exshaw Formation sedimentary rocks, which, because it is revealed at low TOC contents, is most probably nonhydrogenous in origin. This is also evident if the amount of "common osmium" (^{192}Os) is normalized to TOC content (Fig. 5C), which shows that as the I_{Os} value decreases, the common Os content of the samples actually increases on a TOC-normalized basis. However, with the available data, it is not possible to discern whether this effect is a result of an extraterrestrial or detrital component, as both could increase ^{192}Os relative to TOC and decrease bulk sediment I_{Os} value if the detrital component is less radiogenic than hydrogenous Os. Cohen et al. (1999) have tried to quantify the influence of extraterrestrial Os input for Jurassic ORS, and found that for sediment accumulation rates of 50 m/Ma and assuming a meteorite flux of $3.7 \times 10^4 \text{ t/A}$ (the average Cenozoic flux), the extraterrestrial Os contribution is exceptionally small (0.01–0.1%) and can be ignored. Given that the bulk Os contents of the Exshaw Formation samples are broadly similar to the Jurassic ORS studied by Cohen et al. (1999), this suggests that if the unradiogenic Os component identified above results from extraterrestrial Os, either the sediment accumulation rate was much lower or the meteorite flux much higher than the parameters used by Cohen et al. (1999) during deposition of the Exshaw Formation.

The identification of systematic variation in I_{Os} in the Exshaw Formation has importance for Re-Os geochronology, because invariant I_{Os} is one criterion required for establishing an isochron. Using only the samples with $>5\%$ TOC as proxies for the hydrogenous Os, a regression having an age of $358 \pm 9 \text{ Ma}$ with an I_{Os} value of 0.59 ± 0.05 (Model 3, MSWD = 1.8) is calculated (Fig. 6B). It is worthwhile noting that this regression of high TOC samples shares many of the same samples as that in Fig. 6A, where only samples from the basal

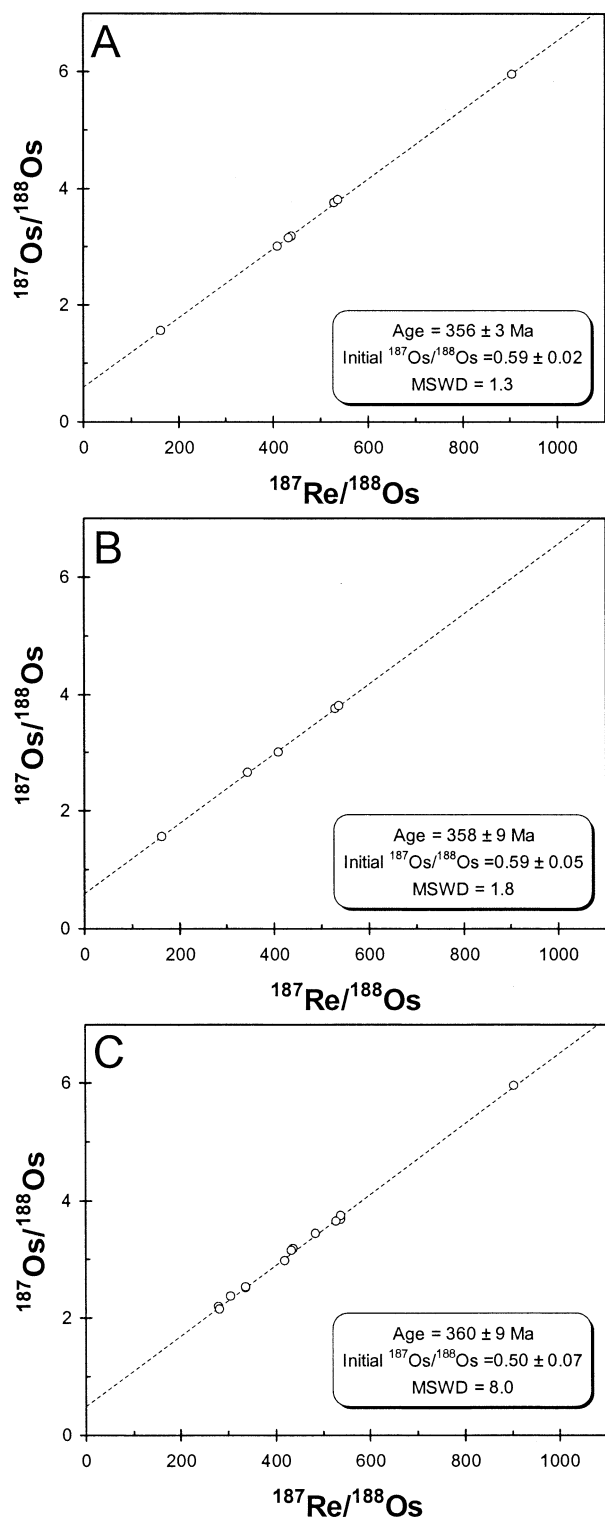


Fig. 6. Subset Re-Os isochron diagrams for the Exshaw Formation. All regressions are calculated using the program *Isoplot* (Ludwig, 1998) and all uncertainties are quoted at the 2σ level. (A) Exshaw Formation samples within 1.0 meter of the base of the basal black shale member (samples PEx-10, -12, -13, -20, and -21). (B) Exshaw Formation samples with TOC values $>5\%$ (samples PEx-8, -12, -20, and -21). (C) Exshaw Formation samples with TOC values $<5\%$ (samples PEx-7, -9, -10, -11, -13, -14, and -35).

1 meter were considered. Given the variation in I_{Os} is clearly related to TOC (Figs. 5B, C), we suggest that the “high TOC subset” regression of Fig. 6B is the most precise determination of both the Re-Os age and I_{Os} value for the black shale member of the Exshaw Formation. Fig. 6C shows the Re-Os regression for the remaining Exshaw Formation samples (except PEx-23) with TOC $<5\%$, and illustrates that the derived ages and I_{Os} values overlap the high TOC regression within 2σ uncertainty, although the scatter around the regression is significantly greater.

5.3. Re-Os Systematics Beyond Hydrocarbon Maturation Temperatures

The integrity of the Re-Os isotope system in ORS beyond the temperatures required for hydrocarbon generation and maturation, i.e., above $\sim 150^\circ\text{C}$, remains speculative. Systematic studies are required in order to better understand and constrain the robustness of the Re-Os geochronometer during higher temperature processes such as regional metamorphism. Moreover, the phases within ORS which host Re and Os are not known with certainty. Because 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 phases, it is important to determine their physical association within these rocks. Organic material and sulfides are possible candidates. The Re and Os contents of diagenetic pyrite nodules associated with ORS were found to be much lower than that of the sedimentary rocks, thus ruling out the possibility of sulfide phases as the dominant hosts for these elements (Cohen et al., 1999). It is therefore probable that Re and Os are associated directly with organic matter, and comparison of Re-Os analyses of separated organic matter from ORS with those from the corresponding whole rock samples may be useful in this regard. Ripley et al. (2001) have reported that kerogen and graphite from metasedimentary rocks are highly enriched in Re and Os in a contact aureole environment, illustrating the importance of organic matter as a potential host for Re and Os in metasedimentary rocks.

5.4. Re-Os Abundance Variations in ORS

The observation that replicate aliquots of some samples yield similar Re but different Os abundances indicates that, in these cases, Re and Os are unlikely to be bound in the same phase. If both Re and Os were totally bound by a single phase such as organic carbon (hereafter C_{org}) for example, Re and Os abundances in different aliquots of an inhomogeneous powder should both vary similarly, as a function of C_{org} in each aliquot. Peucker-Ehrenbrink and Hannigan (2000) also found that Os and other platinum group elements were very well correlated with C_{org} in unweathered Ordovician ORS from Quebec, but that Re was not well correlated with C_{org} . Thus there is a possibility that Re and Os are not coupled to the same phases in ORS such as black shales that are at very low metamorphic grade. If this is a primary feature of sedimentary accumulation of Re and Os in ORS, it may indicate differing mechanisms of accumulation in ORS for the two elements. It may be suggestive of a more direct association of marine Os with organic matter as a concentration mechanism for Os in ORS than for

Re. Rhenium is known not to be scavenged onto particles in the oceans, but rather is removed by reduction at or below the sediment/water interface from pore waters in suboxic and anoxic environments (Colodner et al., 1993; Crusius et al., 1996). The specific mechanisms of Os transfer to sediments like ORS are not fully understood, but have been assumed to be reductive capture (Koide et al., 1991). Cohen et al. (1999) invoke this mechanism for Os removal in Jurassic ORS because of a lack of clear correlation between Os abundance and TOC in these rocks. However, for the Exshaw Formation, Os abundance is positively correlated with TOC (Fig. 3D). In addition, Oxburgh (2001) has outlined evidence for the presence of Os in recent Cariaco Basin sediments coupled to an organic matter flux, and Levasseur et al. (1998) have suggested the existence of osmium organocomplexes in seawater. Thus, both reductive capture and, in some cases, a direct association with organic matter flux may be important for Os accumulation in ORS. If it is correct that Re and Os can accumulate in ORS by differing mechanisms, then this may offer an explanation for observations of rapidly varying Re/Os ratio, by factors of 3 or more, over very short stratigraphic intervals in some ORS (Cohen et al., 1999; this study), because Re and Os accumulation to any ORS will thus reflect a balance between sediment redox conditions and organic matter flux.

6. CONCLUSIONS

Re-Os dating of ORS from the Exshaw Formation, WCSB, yields an age of 358 ± 10 Ma (2σ , Model 3, $\lambda = 1.666 \times 10^{-11} \text{ a}^{-1}$), which agrees well with the known depositional age.

There is no significant difference in the Re-Os ages derived from hydrocarbon immature, versus hydrocarbon mature plus overmature samples, implying that hydrocarbon maturation has no major impact on the Re-Os isotope system in ORS. This indicates that obtaining Re-Os depositional ages from ORS should be viable regardless of the level of hydrocarbon maturity.

Exshaw Formation samples contain evidence for a component of unradiogenic Os. A subset of samples containing high TOC (>5%) yields a well-fitted isochron having an age of 358 ± 9 Ma (2σ , $\lambda = 1.666 \times 10^{-11} \text{ a}^{-1}$) with an initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.59 ± 0.05 (Model 3, MSWD = 1.8). This value for the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio likely is the best estimate for local seawater at the time of sediment deposition. The source of the unradiogenic Os load cannot be directly constrained with the data presented here, but may be meteoritic or detrital in origin.

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