Radiometric dating of marine-influenced coal using Re-Os geochronology

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28 Abstract

29 Coal deposits are integral to understanding the structural evolution and thermal history of
30 sedimentary basins and correlating contemporaneous estuarine and fluvial deltaic strata with
31 marine sections. While marine shales may readily lend themselves to Re-Os dating due to the
32 dominance of hydrogenous Re and Os, the lack of a chronometer for near-shore sedimentary
33 environments hampers basinwide correlations in absolute time. Here, we employ the Re-Os
34 geochronometer, along with total organic carbon (TOC) and Rock-Eval data, to determine the
35 timing and conditions of a marine incursion at the top of the Matewan coal bed, Kanawha
36 Formation, Pottsville Group, West Virginia, USA. The observed range for hydrogen index (HI:
37 267-290 mg hydrocarbon/gram total organic carbon) for these coal samples suggests dominance
38 of aliphatic hydrocarbons with low carbon ($<C_{19}$) chain length. Average Re (107.6 ± 16.4 ng/g)
39 and Os (0.52 ± 0.09 ng/g) concentrations of the marine-influenced Matewan coal are higher by
40 few orders of magnitude than published data for terrestrial coal. A Re-Os isochron for the
41 Matewan coal provides an age of 325 ± 14 Ma (Model 3; MSWD = 12; $n = 19$; 2σ). This is the
42 first Re-Os age derived from coal samples; the age overlaps a new composite Re-Os age of $317 \pm$
43 2 Ma for the immediately overlying Betsie Shale Member.

44 External precision for replicate Os analyses carried out for several Matewan coal samples
45 shows a positive correlation with their HI. The HI, which is low in terrestrial organic matter,
46 reflects the degree of marine influence. Thus, samples with the most profound marine influence
47 also have the best analytical reproducibility. Equilibration of Os isotopes with seawater under
48 marine conditions overwhelms variability inherited from terrestrial plant debris, decreasing
49 scatter on the isochron. The $^{187}\text{Re}/^{188}\text{Os}$ ratios of the Matewan coal (~ 3300 -5135) are higher than
50 most of those previously published for Phanerozoic black shale (mostly <2000). Mass balance

calculations based on Re/TOC and Os/TOC ratios for the Matewan coal indicate that both Re and Os are primarily marine in origin, and their high $^{187}\text{Re}/^{188}\text{Os}$ ratios confirm efficient removal of both elements from a sulphidic water column into the coal. We show that Re-Os geochronology of marine-influenced coal can be a viable tool for constraining depositional ages.

Keywords: *Re-Os geochronology; marine-influenced coal; hydrogen index (HI); Matewan coal, Betsie Shale Member.*

1. Introduction

Coal is an organic sedimentary rock that forms through biochemical degradation and subsequent metamorphism of plant debris, usually deposited in anoxic waterlogged environments. This important energy resource is part of the rock record since the development of vascular plants in the Ordovician, and is present in mineable quantities since the Devonian (Thomas, 2002; Petersen, 2006). The depositional age of coal is essential in reconstructing the evolution and thermal history of these sedimentary deposits, and for correlating time-equivalent facies at the regional to global scale. Direct age assignment for coal is challenging, however. In this regard, radiometric dating of tonsteins (ash beds within coals) and other igneous units have been used for geochronology (e.g. Lyons et al., 2006; Fildani et al., 2009); absence of these units in basins or, depositional disturbance by erosion and redeposition (e.g., turbidites) limits their employment to provide age limits for coal beds. Similarly, success of palynology of coal, another frequently used geochronological tool, is limited by microfloristic provinces, and variable preservation of palynomorph assemblages (Cirilli, 2010 and references therein). In this context, we, through this study, establish the potential of Re-Os geochronometry to provide reliable age constraints for marine-influenced coal beds.

Re-Os geochronology provides direct depositional ages for organic-rich sediments (Ravizza and Turekian, 1989; Kendall et al., 2009). Re and Os in reducing sediments have a strong association with organic matter and sulfides, and are mostly hydrogenous. Given the long half-life of ^{187}Re (41.6 Ga) and typically high Re/Os ratios in marine sediments, the ^{187}Re - ^{187}Os geochronology can provide depositional ages for marine and lacustrine organic-rich shale of widely ranging age, from Archean to Mesozoic (e.g., Selby and Creaser, 2005; Yang et al., 2009; Xu et al., 2009; Georgiev et al., 2011; Tripathy et al., 2014). A recent study of PGE (platinum

group element) patterns for shale and coal samples (Baïoumy et al., 2011) has established that Re and PGEs in terrestrial organic-rich sediments remain unaltered during diagenesis and the coalification processes. In the present study, we present the Re-Os isotopic, Rock-Eval and TOC data for coal samples from the Matewan coal bed (Kanawha Formation, USA) to evaluate the potential of Re-Os systematics in yielding chronological information on coal. We compare these data to a new and highly precise Re-Os isochron age for the overlying Betsie Shale Member. We show that the Re and Os in marine-influenced coal are primarily marine in origin and in this geological setting, the Re-Os clock can provide reliable time constraints for the marine incursion into the peat bog that ultimately produced the coal.

2. Geological details

The central Appalachian basin (CAB) is an elongated foreland basin created during the Alleghenian orogeny by collision between southern Laurentia and Gondwana. This basin received siliciclastic sediments predominantly from the Appalachian Mountains and Canadian cratons throughout the Pennsylvanian (Ruppert et al., 2010), with fluvio-deltaic sedimentation regulated by glacial eustasy, tectonics and climate (Cecil, 1990; Greb and Chesnut, 1996; Jerrett et al., 2011). The CAB was positioned south of the equator at 5-20° and rotated 35-45° clockwise from its present position (Scotese and McKerrow, 1990); it drifted through paleo-ITCZ (intertropical convergence zone) from wet to dry tropical latitudes during the Pennsylvanian (Cecil, 1990). The CAB is one of the largest Pennsylvanian bituminous coal-producing regions in the world and its sedimentary section is composed mainly of sandstone, siltstone, shale, mudstone, and coal. Despite geologic and economic interests, the CAB lacks unified stratigraphic names for its geological units and boundaries, making regional and/or global correlations challenging (Ruppert et al., 2010). In this context, the Betsie Shale Member situated

at the Lower-Middle Pennsylvanian stage boundary serves as an important horizon for correlation due to its distinctive basal high radioactivity and vast aerial exposure (Rice et al., 1987). The Betsie Shale Member is part of the Kanawha Formation of the Pottsville Group (Fig. 1). This dark shale and siltstone unit is an upward-coarsening bay-fill sequence deposited during upstream retreat of fluvial systems and a subsequent marine incursion (Rice et al., 1987). The Betsie Shale Member directly overlies the Matewan coal bed investigated here (Fig. 1). The Matewan coal bed, with vitrinite bands (~5-10 mm thick) throughout, is highly volatile bituminous A in rank (ASTM rank (D-388) standard; Ruppert et al., 2010), with high sulfur content (~2.7 %, dry basis; Geboy et al., 2015).

3. Previous geochronological constraints

The base of the Betsie Shale Member is the proposed stage boundary for Lower-Middle Pennsylvanian in North America (Geboy et al., 2015 and references therein) and the proposed age for this boundary is 315.2 ± 0.2 Ma (Gradstein et al., 2012). Earlier reported radiometric ages for the sedimentary sequences bracketing the Matewan coal bed and Betsie Shale Member are consistent with each other (Geboy et al., 2015; Hemming et al., 2012; Lyons et al., 1997, 2006) and confirm an age of ~315 Ma for the Betsie shale (Fig. 2). Specifically, a U-Pb zircon age for the underlying Upper Banner tonstein (316 ± 1 Ma; Lyons et al., 1997), and concordant single zircon age for the overlying Fire Clay tonstein (314.6 ± 0.9 Ma; Lyons et al., 2006) provide age constraint for the Betsie Shale Member. Further, reported ^{40}Ar - ^{39}Ar ages for sanidine range from ~311 to ~315 Ma (summarized in Geboy et al., 2015), with recent inter-laboratory comparisons yielding ages of 314.6 ± 1.1 or 315.3 ± 0.7 Ma, depending on the calibration used (Hemming et al., 2012). More recently, we reported a Model 1 Re-Os age of 323 ± 8 Ma for the Betsie Shale Member (Geboy et al., 2015), which overlaps with its expected age of ~315 Ma.

4. Material and Methods

A suite of coal samples belonging to the Matewan coal bed, underlying the Betsie Shale Member (Fig. 2), was analyzed in this study for total organic carbon (TOC), Rock-Eval pyrolysis data, and Re-Os isotope ratios. These coal samples were obtained from a core drilled in Wyoming County, West Virginia, USA (precise location proprietary). The core is characterized by sandstones and shales with interbedded coal horizons. Geboy et al. (2015) identified five coal facies within the Matewan coal bed (total bed thickness of 0.75 m). These five coal facies can be sub-divided into two groups: (i) the lowermost three facies are similar with moderate to high sulfur concentrations and high vitrinite content, whereas (ii) the uppermost two facies contain lower sulfur and proportionally higher inertinite. These two groups are separated by a sulfur-rich, carbonaceous shale layer which might signal the onset of flooding with a marine transgression into the basin. The coal facies immediately below the shale layer is investigated herein.

Seven discrete samples were extracted from the inner portion of the core within a stratigraphic interval of 0.4 feet (~12 cm). The samples are mostly shiny, friable and clarain-rich. Seven black shale samples from the Betsie Shale Member were also analyzed in an effort to improve the precision of the Re-Os age reported in our earlier study (Geboy et al., 2015). These shale samples were collected within a stratigraphic interval of ~3 inches (7.6 cm) and are ~2 ft (~61 cm) above the shale layer studied by Geboy et al. (2015). For each of the coal and shale samples, several grams were finely ground using an agate ball mill; aliquots of the same sample powders were used for Rock-Eval and Re-Os isotopic analyses. TOC and Rock-Eval data for these samples were acquired from GeoMark Research Ltd., Texas. Rock-Eval pyrolysis (Peters, 1986) yields data on S1 (mg of free hydrocarbon per gram of the sample), S2 (mg of hydrocarbon generated by pyrolytic degradation per gram of sample), S3 (mg of CO₂ generated

per gram of sample), and $T_{\max}$ (temperature at which maximum S2 is measured). These data are used to calculate the hydrogen index (HI: S2/TOC), and oxygen index (OI: S3/TOC) of the samples (Peters, 1986; Langford and Blanc-Valleron, 1990).

Re-Os isotopic analyses of the samples were carried out following established analytical methods for shale at the AIRIE (Center for Applied Isotope Research for Industry and Environment) Program, Colorado State University (Yang et al., 2009; Georgiev et al., 2011; Tripathy et al., 2014)). About 0.1-0.2 gm of sample, together with known amounts of ^{185}Re and ^{190}Os tracers, was treated with a $\text{CrO}_3\text{-H}_2\text{SO}_4$ solution in a sealed Carius tube for 48 hours at 240°C . This partial leaching of samples using a $\text{CrO}_3\text{-H}_2\text{SO}_4$ solution extracts mostly the authigenic Re and Os components of the samples (e.g. Selby and Creaser, 2003). Osmium from this solution was purified following a combination of solvent (CCl_4) extraction and micro-distillation methods, whereas pure Re was extracted using conventional chromatography. Purified Re and Os fractions were loaded onto Pt ribbons and analyzed for their isotopic compositions using a thermal ionization mass spectrometer (TIMS) in negative ionization mode. The measured isotopic data were further corrected for procedural blank contributions, instrumental mass fractionation and isobaric interferences. Accuracy of the Re and Os isotopic measurements was monitored through repeated analyses of in-house Re and Os standards during this study. The Re-Os isochron line is constructed in this study through a bidirectional-uncertainty weighted regression analysis using a statistical software package, Isoplot/Ex v. 3.75 (Ludwig, 2012). The Isoplot software, depending on the goodness of fit, provides either a Model 1 age (which assumes that the observed data scatter is only due to assigned errors), or a Model 3 age (which assumes that the deviation of data points from the best-fit line is not only linked to assigned errors, but also to variation in the initial $^{187}\text{Os}/^{188}\text{Os}$). The errors on the Re-Os age

reported in this study include the uncertainties associated with the regression slope and decay constant. Output also includes the Mean Square of Weighted Deviates (MSWD), a rough measure of the deviation of the data points from the regression line that is strongly controlled by calculated errors and error correlations.

5. Results

TOC, Rock-Eval and Re-Os isotopic data for Matewan coal samples are provided in Table 1 and those for the Betsie shale samples are listed in Table 2. The TOC concentrations of the Matewan coal samples vary from 73.8 to 76.3 wt%. The average $T_{\max}$ value of the Matewan coal samples ($443 \pm 1^{\circ}\text{C}$) falls within the lower part of the oil generation window for organic matter (435° - 460°C ; Peters, 1986 and references therein). The observed HI range (267-290; Table 1) for the Matewan coal samples points to dominance of aliphatic hydrocarbons with lower carbon ($<C_{19}$) chain length (Petersen and Nytoft, 2006). These HI values are higher by 2-3 times than those of the Betsie shale samples (Geboy et al., 2015; Table 2), an observation attributable to high energy (retention of heat) potential of the coal. A plot of HI vs. OI (modified van Krevelen diagram; not shown here) suggests that the Matewan coal samples contain Type I organic matter. However, characterization of organic matter in coal samples through modified van Krevelen plot remains problematic (Peters, 1986). In this regard, S₂ vs. TOC plot (Langford and Blanc-Valleron, 1990) is an effective approach to characterization of organic matter. The S₂ vs. TOC plot for the Matewan coal samples (Fig. 3) indicates their mixed (Type II/III) oil-gas potential.

Table 3 compares Re and Os concentrations and $^{187}\text{Os}/^{188}\text{Os}$ ratios for Matewan coal samples with corresponding data compiled for terrestrial coal, river sediments, and Phanerozoic black shale. Average Re and Os concentrations of the Matewan coal samples are 108 ng/g and 0.52 ng/g respectively, significantly higher than average Re (198 pg/g) and Os (31 pg/g)

concentrations of upper continental crust (Peucker-Ehrenbrink and Jahn, 2001). Again, Re and Os concentrations for the marine-influenced Matewan coal samples are higher by about two orders of magnitude than those for terrestrial coal (data from Baioumy et al., 2011) and tree plants (data from Rodushkin et al., 2007; Table 2). The $^{187}\text{Re}/^{188}\text{Os}$ ratios of the Matewan coal samples are higher than those reported earlier for most of the Phanerozoic organic-rich shale (c.f. Table 2 for data source). The $^{187}\text{Re}/^{188}\text{Os}$ ratios of the coal range from 3299 to 5134, and show a linear co-variation with their corresponding $^{187}\text{Os}/^{188}\text{Os}$ ratios (range: 18.52-28.97; Table 1). The linear regression (Isoplot/Ex v. 3.75; Ludwig, 2012) of $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ ratios yields an age of 325 ± 14 Ma (2σ ; Model 3; MSWD = 12; $n = 12$) for the Matewan coal samples with an initial $^{187}\text{Os}/^{188}\text{Os}$ ratio (Os_i) of 0.86 ± 0.88 (Fig. 4A). Importantly, the Re-Os isochron for coal samples with higher HI values (>270) provides a stratigraphic age (321 ± 15 Ma; MSWD = 9.3; $n = 12$; Fig. 4B) for the coal bed, which is statistically indistinguishable from its expected age (~ 315 Ma; cf. section 3). Although the Re-Os isochron for low-HI samples yields statistically similar age (338 ± 21 Ma; MSWD = 2.4; $n = 7$; Fig. 4C) with a lower MSWD value, the nominal value of this age is found to be older than its expected age and it is marginally older outside of uncertainties than the expected age of ~ 315 Ma based on U-Pb zircon ages from stratigraphically higher and lower tonsteins (Fig. 2). The significance of these age variations with respect to HI ranges of the samples is linked to the extent of marine influence on coal horizons, as discussed in a following section.

More recently, Geboy et al. (2015) reported a Re-Os (Model 1) age of 323 ± 8 Ma for a shale section immediately above the herein investigated coal bed. In this study, we also analyzed Re-Os isotopic systematics of a few additional shale samples from core 60 cm higher in the section (Table 2; Fig. 5) to improve the chronological information for the Betsie Shale Member.

The Re-Os isochron for these shale samples yielded an imprecise age of 346 ± 24 Ma (2σ ; Model 3; MSWD = 4.2; $n = 7$). However, by excluding one outlier with distinctly lower $^{187}\text{Re}/^{188}\text{Os}$ and model initial Os isotopic ratio (Table 2), the shale isochron yields an age of 329 ± 34 Ma (2σ ; Model 3; MSWD = 3.6; $n = 6$) with an Os_i ratio of 0.40 ± 0.41 (Fig. 5A). This age obtained for the shale section (329 ± 34 Ma; $n = 6$) overlaps the Re-Os age reported earlier for an underlying shale section (323 ± 8 Ma; Geboy et al., 2015). Despite the small stratigraphic separation, the observed ranges for $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios for these two sections are distinctly different. Regressing all shale data (excluding the one outlier; Fig. 5A) on a single Re-Os isochron yields a much more precise Re-Os age for the Betsie Shale Member. This improved isochron, with large spread in $^{187}\text{Re}/^{188}\text{Os}$ (range: 722-5134) and $^{187}\text{Os}/^{188}\text{Os}$ (range: 4.35-28.92) ratios, provides a precise Model 3 age of 317 ± 2 Ma (MSWD= 1.5; $n = 13$; Fig. 5B) with an Os_i ratio of 0.55 ± 0.02 , overlapping the expected age of ~ 315 Ma for Betsie Shale Member (Fig. 2).

6. Discussion

6.1. Re-Os age of the Matewan coal

Earlier studies have demonstrated that the Re-Os chronometer can yield reliable depositional ages for organic-rich sediments (Ravizza and Turekian, 1989; Selby and Creaser, 2005; Georgiev et al., 2011; Xu et al., 2014; Tripathy et al., 2014), provided they have not been influenced by oxidative weathering or hydrothermal fluid interactions (Kendall et al., 2009). Intact Re-Os systematics for coal with several tens of percent of TOC has not been demonstrated thus far.

Regression of Re-Os isotopic data for coal samples from the Pennsylvanian Matewan coal bed in West Virginia, USA yields an isochron age of 325 ± 14 Ma (Fig. 4A). This age agrees well with the Re-Os ages obtained for shale sequences immediately overlying the Matewan Coal

bed (317 ± 2 Ma; this study, 323 ± 8 Ma; Geboy et al., 2015). Further, these Re-Os ages derived from coal and shale samples are consistent with available chronological information in literature (Fig. 2) for this sedimentary sequence, indicating that the Re-Os age for these coal samples is an accurate depositional despite lower than desired precision ($\sim 0.5\%$; Georgiev et al., 2011).

The MSWD value derived from the regression line in the Re-Os isochron plot (Isoplot/Ex v. 3.75; Ludwig, 2012) is higher for the Matewan coal samples (~ 12 ; Fig. 4A) than the ideal value of ~ 1 . This elevated MSWD value indicates deviation of the data points from the regression line is not only linked to assigned errors, but also controlled by geological factors. Previous studies have demonstrated that large MSWD values in Re-Os geochronology are mostly due to (1) large-scale and/or small-scale post-depositional disturbances and/or (2) heterogeneity in initial $^{187}\text{Os}/^{188}\text{Os}$ ratios (Yang et al., 2009; Rooney et al., 2010; Tripathy et al., 2014). As demonstrated above, the Re-Os age of the Matewan coal samples overlaps its expected age and hence, is accurate. This age accuracy hints at insignificant influence of large-scale post-depositional processes (e.g. hydrothermal fluid interaction and/or metasomatic processes) on the Re-Os systematics of the Matewan coal samples. The apparent accuracy of the Re-Os isochron, however, does not rule out chemical disturbance. For instance, negative initial $^{187}\text{Os}/^{188}\text{Os}$ ratio observed for an Archean shale led Yang et al. (2009) to invoke impact of small-scale element exchange by mobilization of Re from intercalated mafic tuffs in perturbing the Re-Os systematics of the shales. Although heterogeneity in initial $^{187}\text{Os}/^{188}\text{Os}$ ratios seems to the prime cause for the observed higher MSWD value for the Matewan coal isochron, possible influence of small-scale post-depositional disturbances, such as preferential mobilization of Re/Os during local oxidation and/or regional thermal events, in perturbing the Re-Os systematics cannot be ruled out.

Another possible explanation for the observed high MSWD is heterogeneity in initial Os isotopic composition during the deposition period. To evaluate this, Os_i ratios of the Matewan coal samples are calculated for an age of 315 Ma (Table 1). Calculated Os_i ratios show significant variation between 1.12 and 1.97 (Table 1), suggesting that variation in Os_i may explain the elevated MSWD for the Matewan coal Re-Os isochron (Fig. 4A). This is not unexpected for coal, given the heterogeneity of plant debris that fixes Os. Further, McArthur et al. (2008) demonstrate that a minor change in hydrological flux can alter the Os_i ratio of a restricted basin. Coal mires are restricted basins with highly variable hydrologic input through time – a recipe for fluctuations in Os_i through time. In sum, a demonstrably accurate age for the Matewan coal bed carries with it an increased uncertainty, reflecting the coastal geological setting and/or small-scale post-depositional alteration of the samples.

6.2. Sources of Re and Os in coal

Average Re (108 ng/g) and Os (0.52 ng/g) concentrations for the Matewan coal samples are of the same order in magnitude as those observed for Phanerozoic black shale (Table 3). Re and Os preserved in black shale are often found to be marine in origin. Comparable Re and Os concentration levels in the Matewan coal and the black shale (Table 3) hint at a similar source and/or paleo-environment; that is, some or all of the Re and Os may be of marine origin. In order to evaluate this, the contributions of seawater to the Re (Re_{sw}) and Os (Os_{sw}) contents of the coal samples are estimated. For this calculation, it is assumed that Re and Os in the Matewan coal samples are mainly derived from terrestrial and marine sources. The available data for terrestrial coal samples constrains the Re/TOC ($\sim 18 \times 10^{-10}$) and Os/TOC ($\sim 0.52 \times 10^{-10}$) ratios for terrestrial sources (Table 3; Baioumy et al., 2011). These ratios for terrestrial coals, excluding an outlier sample with an order of magnitude higher Re concentration, are comparable to those for

terrestrial plant leaves (Table 3). The Re_{sw} and Os_{sw} for the Matewan coal samples can be calculated using Re/TOC and $^{188}Os/TOC$ ratios of non-marine coals (Table 3), and the following equations. For Os_{sw} estimation, TOC-normalized ratio of ^{188}Os (instead of total Os) is used to avoid effect of radiogenic ^{187}Os on total Os .

$$Re_{sw} = Re_{sample} - \left[\left(\frac{Re}{TOC} \right)_{terrestrial} \times TOC_{sample} \right] \quad \text{-----} \quad (1)$$

$$Os_{sw} = ^{188}Os_{sample} - \left[\left(\frac{^{188}Os}{TOC} \right)_{terrestrial} \times TOC_{sample} \right] \quad \text{-----} \quad (2)$$

The estimated contribution from marine sources to the Re in the Matewan coal samples vary from 98.2 % to 98.9 % (average: $98.7 \pm 0.2\%$) and that of the Os vary from 61.2 % to 81.1 % (average: $92.1 \pm 1.7\%$). The present estimates both for Re and Os in the Matewan coal samples clearly shows that these elements are mainly from marine sources. Paleomires can receive significant seawater sulfate during marine incursions and these sulfates interact with available iron in oxygen-poor environments to ultimately form pyrite (Kolker, 2012). Assuming, *a priori*, that the Matewan paleomire contained limited terrestrial Re and Os , it must have received significant amounts of seawater Re and Os during marine incursion(s) into the mire; the Re and Os , along with seawater sulfate, were subsequently adsorbed or fixed by reduction in bottom sediments in association with organic matter and/or pyrite.

The Re and Os concentrations observed for marine-influenced Matewan coal samples are higher by ~2 orders of magnitude than previously reported terrestrial coal samples (Table 3; Baioumy et al., 2011). However, the Re and Os concentrations for terrestrial coal (Baioumy et al., 2011) are observed to be comparable to those reported for terrestrial plants and leaves (Table 3; Rodushkin et al., 2007). This is expected, given the origin of terrestrial coals from terrestrial

plant debris. In contrast, the high Re and Os concentrations in the Matewan coal indicate derivation from seawater during marine incursion(s) into the paleomire. This study, therefore, establishes that Re-Os geochronology can provide useful age information for marine-influenced coal deposits. Re-Os isochroneity for terrestrial coal remains untested. Baïoumy et al. (2011) analyzed the elemental and isotopic composition of Re and Os for *terrestrial* coal samples in separately powdered aliquots and hence, isochroneity of these samples cannot be evaluated. Recent studies have successfully demonstrated that Re-Os geochronology can yield accurate age information for lacustrine sedimentary deposits (Cumming et al., 2012) and hence, it will also be interesting to evaluate the possibility of dating a terrestrial coal deposit using Re-Os geochronology.

6.3. Impact of marine-influence on Re-Os age of coal

Our results (Fig. 4A) demonstrate that the Matewan coal samples, with dominance of marine-derived Re and Os in them, could be successfully dated. The Re-Os age is interpreted as the timing of marine incursion into the basin. To test the hypothesis that Re-Os isochroneity and resulting age uncertainties depend on the degree of marine-influence on the coal samples, we investigate here the sensitivity of Re-Os age with respect to the HI value of the samples (Fig. 4B, 4C). The HI value for marine-influenced coal serves as a proxy for the degree of marine-influence on the coal samples (Petersen, 2006 and references therein). Further, a relationship between HI and sulfur content of coal worldwide shows that HI values and the hydrogen content of coals are also associated with marine influence during peat accumulation (Petersen, 2006). Interestingly, we note that the HI values for coal samples show a statistically significant correlation ($r = -0.81$; $p < 0.02$, $n = 8$) with the external (replicate analysis of single powder) precision, or analytical reproducibility of Os measurements (Fig. 6), indicating a relationship

between degree of marine influence and heterogeneity in the Os isotopic composition of the Matewan coal samples. The co-variation of HI with Os precision indicates that samples with profound marine influence are relatively homogenous in initial osmium isotopic composition and hence, provide better analytical reproducibility leading to better Re-Os isochrons. In other words, for terrestrial coal, the Os isotopic variability inherited from terrestrial plant debris destroys isochroneity, whereas for marine coal, a proportionally larger Re and Os supply from seawater overwhelms initial Os isotopic heterogeneity delivered in plant material and improves isochroneity. The result is increased accuracy and precision using samples with higher HI (Fig. 4B).

The external precision of Os measurements for samples with HI>270 are similar to those reported earlier by the AIRIE Program (Xu et al., 2009); the Re-Os isochron for samples with high HI values (>270) provides a Re-Os age of 321 ± 15 Ma (Model 3; MSWD = 9.3; $n = 12$; 2σ) with an Os_i ratio of 1.24 ± 0.95 (Fig. 4B). This Re-Os age for the Matewan coal samples is statistically indistinguishable from its expected age of ~315 Ma (cf. section 3) and the recent Re-Os ages reported for the immediately and conformably overlying Betsie Shale Member (Fig. 5; Geboy et al., 2015). The Re-Os isochron for coal samples with low HI values (i.e. reduced marine influence) yield a statistically similar age (338 ± 21 Ma, MSWD = 2.4; $n = 7$; Fig. 4C), but the nominal age for these samples is older than expected. This Re-Os age derived for low-HI samples (338 ± 21 Ma) marginally overlap with the new Re-Os age of the Betsie Shales (317 ± 2 Ma; Fig. 5B) within quoted uncertainties. Further, the Re-Os age of the low-HI samples is significantly older than the previously reported U-Pb ages for Upper Banner and Fire Clay tonsteins (~315 Ma; Fig. 2). Relatively older ages for low-HI samples may result from different macerals or proportionately more terrestrial debris supplying appreciable Re and Os from detrital

organic matter with older ages. Further, the initial Os isotopic (Os_i) ratios for the coal samples are calculated for the expected depositional age (~315 Ma; Table 1) to determine if samples with profound marine influence have more homogenous $^{187}Os/^{188}Os$ ratios. Indeed, the estimated Os_i ratios for high HI samples are relatively homogenous (~12% spread), whereas low-HI samples are more heterogeneous (~23% spread; Table 1). Thus, coal samples with higher HI values (i.e., with profound marine influence) apparently acquire a relatively homogenous Os isotopic composition, thereby providing improved chronological information. This proposition is based on comparison of nominal Re-Os ages and estimated Os_i ratios for the low and high-HI samples from the Matewan coal bed; clearly, more thorough work is needed to be carried out in terrestrial basins to test this hypothesis.

Assuming samples with profound marine influence equilibrate with the relatively homogenous seawater $^{187}Os/^{188}Os$ ratio, the high-HI samples are expected to yield a well-constrained Re-Os regression with a lower MSWD. Surprisingly, the goodness of fit for the Re-Os isochron is better for the low-HI samples (MSWD~2.4) than the high-HI samples (MSWD~9.3; Fig. 4). Although the exact cause for this discrepancy is unknown, this difference may arise from relatively higher average uncertainties associated with $^{187}Re/^{188}Os$ ratios for the low HI samples. The average uncertainty (internal precision) on $^{187}Re/^{188}Os$ ratio for the low HI samples is 0.92%, which is lower than that observed for high HI samples (0.66%). The MSWD value represents deviation of data from the regression line; data with higher uncertainty has larger spread in the isochron plot and hence, are likely to be relatively closer to the regression line, which in turn can reduce the MSWD values. Along with the data spread, distribution of data points in the isochron plot may also contribute to the MSWD values of the isochron lines. The Re-Os data of the low-HI samples are evenly distributed across the full range of isotopic ratios in

the isochron plot (Fig. 4C). Evenly distributed data points are likely to yield a well-constrained regression line and hence, a lower MSWD value. On the contrary, the Re-Os regression line for the high-HI samples is based on two clusters (at around $^{187}\text{Os}/^{188}\text{Os}$ ratios of 22 and 30) of datasets, resulting in relatively higher MSWD values (Fig. 4B). This clearly demonstrates that the MSWD value of the Re-Os isochron depends on both scatter and distribution of data points across the regression line.

The initial $^{187}\text{Os}/^{188}\text{Os}$ (Os_i) ratio in organic-rich sediments provides clues about paleo-environmental conditions. The Os_i obtained from the isochron for all Matewan coal samples (0.86 ± 0.88 ; Fig. 4A) has too large an uncertainty to be useful. In contrast, the Betsie shale samples yield a well-constrained Os_i (0.55 ± 0.02 ; Fig. 5B). This ratio for the Lower-Middle Pennsylvanian boundary is not unusual for pre-Cenozoic units, but is significantly lower than present-day seawater. A major oceanic large igneous province or substantial increase in rifting might increase hydrothermal input of non-radiogenic Os. Such activity during the Lower-Middle Pennsylvanian has not been recognized; rather this Period was ruled by two large land masses – Gondwanaland and Laurasia – and likely less ridge length than at present (Bryan and Ernst, 2008). While it is beyond the scope of this paper to address causes of temporal variations in seawater $^{187}\text{Os}/^{188}\text{Os}$, we suggest that 3 factors may have contributed to higher ratios after the Paleozoic: (1) increased continental weathering because of increased dominance of vascular land plants, which in turn enhances the soil CO_2 inventory – the primary agent for chemical weathering (Algeo and Scheckler, 1998) (2) increased input of radiogenic Os tied to greatly increased length of convergent margins and dramatic mountain building after continental break-up in the Mesozoic; (3) increased input of radiogenic Os as Re-rich organic material stored in

sedimentary section contribute increasingly radiogenic Os with age (Peucker-Ehrenbrink and Ravizza, 2000; Georgiev et al., 2011).

6.4. Redox-dependent removal of Re and Os during coal deposition

The $^{187}\text{Re}/^{188}\text{Os}$ ratios of organic-rich shales are, in general, observed to be lower than that of the present-day seawater (Fig. 7). The lower $^{187}\text{Re}/^{188}\text{Os}$ ratios of the shale are commonly linked to preferential reductive removal of Os over Re into the sediments (Yamashita et al., 2007; Georgiev et al., 2011; Tripathy et al., 2014). This preferential removal is due to differences in the principal conditions (e.g. Eh-pH conditions, temperature and salinity) required to remove Re and Os from the water column (Georgiev et al., 2011). In contrast to these observations, the $^{187}\text{Re}/^{188}\text{Os}$ ratios of the Matewan coal samples are found to be significantly higher than most Phanerozoic shales reported in the literature (Fig. 7). The depositional environment for the euxinic shales compiled here was previously inferred through enrichment of key redox-sensitive elements in them (e.g. S, Mo, Re; Georgiev et al., 2011; Geboy et al., 2015). The average ($\pm 2\sigma_{\mu}$) $^{187}\text{Re}/^{188}\text{Os}$ ratio of the coal samples (3954 ± 252) is higher by about an order of magnitude than that of the anoxic shales (461 ± 35), but of similar to that of the euxinic shales (2964 ± 565 ; Table 3). Clearly, these ratios for the Matewan coal samples are higher than those of the anoxic shales at a confidence level better than 99% ($p < 0.01$). The higher $^{187}\text{Re}/^{188}\text{Os}$ ratios of the Matewan coal samples (Fig. 7), therefore, is attributable to efficient removal of Re and Os from the water column onto the underlying organic-rich sediments in a sulfidic depositional environment. Sulfidic depositional conditions for the Matewan coal samples are further supported by their high sulfur content and abundant pyrite.

Another possible explanation for higher $^{187}\text{Re}/^{188}\text{Os}$ ratios of the Matewan coal (Fig. 7) is the relatively low salinity (relative to seawater) in the Matewan paleomire. The distribution coefficient (D_s) for a trace element defines its preference for the solid phase over the aqueous solution. The D_s value depends on the ionic strength of the aqueous solution and hence, the D_s value for a given element is significantly different for seawater and fresh water system. Uptake of Re from aqueous solutions by microorganisms varies significantly depending on the ionic strength of the solution, decreasing with increasing NaCl concentration (Mashkani et al. (2009). Thus, the Re uptake was likely higher in the low-salinity environment of the marine-influenced Matewan coal basin than in an open ocean. Although this geochemical process can partly explain the higher $^{187}\text{Re}/^{188}\text{Os}$ ratio of the Matewan coal, understanding the dependence of Os uptake on ionic strength is required to ascertain the role of electrolyte concentrations on the biosorption/sequestration of both Re and Os, and therefore the resulting Re/Os ratio, under different aqueous conditions.

7. Conclusions

This study presents the first Re-Os age derived from marine-influenced coals. A Re-Os isochron for samples from the Matewan coal bed (Kanawha Formation of the Pottsville Group, West Virginia, USA) provides an age of 325 ± 14 Ma, in agreement with the Re-Os depositional age of the overlying Betsie Shale Member (317 ± 2 Ma). The Re and Os contents of the coal are predominantly marine in origin, making Re-Os geochronology viable for constraining the timing of marine incursion at the top of the coal bed. A statistically-significant positive correlation between external precision of the Os measurements, and HI values (a measure of marine influence) indicates that samples with profound marine influence are characterized by well-equilibrated Os isotopic compositions and hence, can provide accurate age information. The

447 $^{187}\text{Re}/^{188}\text{Os}$ ratios of the coal samples are mostly higher than those observed for Phanerozoic
448 black shales. These $^{187}\text{Re}/^{188}\text{Os}$ ratios indicate efficient removal of Re over Os from seawater
449 into the coals from an overlying sulfidic water column.

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Figure Captions:

Figure 1: Geologic details of the Pennsylvanian rocks in West Virginia, USA. Scale is not implied for the stratigraphic column. Figure modified from Ruppert et al., 2010; <http://www.wvgenweb.org/wvcoal/red3t.htm>.

Figure 2: Stratigraphic section of the Kanawha Formation, showing the position of coal beds, the Betsie Shale Member, stage boundaries, and radiometric ages from the literature and this study.

Figure 3: Characterization of organic matter in the Matewan coal bed and overlying Betsie Shale Member using S₂-TOC diagram. General trends for different types of organic matter are from Peters (1986) and Langford and Blanc-Valleron (1990).

Figure 4: Re-Os isochron plot (A) for coal samples from the Matewan coal bed, Kanawha Formation, Pottsville Group, USA, (B) for coal samples with high HI (>270) values, i.e. with profound marine influence, and (C) for samples with relatively low HI values. All isochrons include the ¹⁸⁷Re decay constant uncertainty.

Figure 5: Re-Os isochron plot for shale samples from Geboy et al. (2015) and this study (Table 2; excluding one outlier with lower ¹⁸⁷Re/¹⁸⁸Os ratio). The ¹⁸⁷Os/¹⁸⁸Os and ¹⁸⁷Re/¹⁸⁸Os ratios of the samples vary by 2-3 orders of magnitude (e.g. Fig. 5B); data are shown in squares (and not as error ellipses) to clearly locate them in the plot.

Figure 6: Co-variation of analytical reproducibility of Os for replicate measurements of coal samples and their hydrogen index (HI) values (n = 8; This study). HI is a proxy for degree of marine-influence. The statistically significant correlation between HI and Os reproducibility

620 shows that samples with profound marine influence are well-homogenized in Os and yield better
621 external precision.

622 **Figure 7:** Comparison of $^{187}\text{Re}/^{188}\text{Os}$ ratios in marine-influenced versus terrestrial coals. Ratios
623 for Phanerozoic black shale, river sediments and present-day seawater are also shown. Relatively
624 higher $^{187}\text{Re}/^{188}\text{Os}$ ratios for Matewan coal samples, but comparable to present-day seawater,
625 indicate efficient removal of Re and Os under intense sulfidic aquatic conditions. See Table 3 for
626 data sources.

627

628 **Table 1:** TOC, Rock-eval and Re-Os isotopic data for the Matewan coal samples, Kanawha Formation, central Appalachian basin, USA.

AIRIE Run	Sample ID*	TOC (wt%)	Re	Os	¹⁸⁷ Re/ ¹⁸⁸ Os	¹⁸⁷ Os/ ¹⁸⁸ Os	rho	Os _i	S1	S2	S3	Tmax	HI	OI
			(ng/g)					(for 315 Ma)	mg HC/g	mg CO ₂ /g	°C	(=S2/TOC)	(=S3/TOC)	
ORG-1031	34.67-35.06 (A)	73.8	109.9 ± 1.2	0.521 ± 0.002	3795 ± 42	21.09 ± 0.07	0.105	1.12	11.76	199.08	1.54	443	270	2
ORG-1049	34.67-35.06 (A) rept	-	110.0 ± 0.6	0.546 ± 0.002	3299 ± 20	18.52 ± 0.07	0.289	1.16	-	-	-	-	-	-
ORG-1041	34.67-35.06 (B)	74.5	104.3 ± 0.7	0.487 ± 0.002	4148 ± 30	23.23 ± 0.09	0.254	1.40	12.83	198.62	1.82	442	267	2
ORG-1057	34.67-35.06 (B) rept	-	106.0 ± 0.4	0.513 ± 0.002	3579 ± 16	20.01 ± 0.07	0.397	1.18	-	-	-	-	-	-
ORG-1042	34.67-35.06 (C)	75.3	108.4 ± 0.7	0.521 ± 0.004	3816 ± 31	21.66 ± 0.15	0.342	1.58	14.21	209.45	1.39	444	278	2
ORG-1058	34.67-35.06 (C) rept	-	110.0 ± 0.3	0.530 ± 0.002	3723 ± 15	21.00 ± 0.07	0.393	1.41	-	-	-	-	-	-
ORG-1043	34.67-35.06 (D)	74.3	117.1 ± 0.7	0.568 ± 0.004	3749 ± 29	21.38 ± 0.16	0.341	1.65	13.48	215.55	1.68	444	290	2
ORG-1051	34.67-35.06 (D) rept	-	119.0 ± 1.0	0.576 ± 0.002	3663 ± 31	20.65 ± 0.07	0.141	1.38	-	-	-	-	-	-
ORG-1059	34.67-35.06 (D) rept	-	117.1 ± 0.5	0.573 ± 0.002	3635 ± 18	20.76 ± 0.08	0.364	1.63	-	-	-	-	-	-
ORG-1044	34.67-35.06 (E)	76.3	78.2 ± 0.7	0.363 ± 0.009	4484 ± 85	25.52 ± 0.60	0.651	1.93	17.90	204.98	1.27	443	269	2
ORG-1052	34.67-35.06 (E) rept	-	78.3 ± 0.9	0.358 ± 0.003	4682 ± 55	26.47 ± 0.19	0.230	1.83	-	-	-	-	-	-
ORG-1060	34.67-35.06 (E) rept	-	78.3 ± 0.3	0.353 ± 0.002	4687 ± 22	26.10 ± 0.12	0.453	1.44	-	-	-	-	-	-
ORG-1045	34.67-35.06 (F)	74.9	91.2 ± 0.6	0.408 ± 0.004	5134 ± 48	28.98 ± 0.29	0.512	1.97	15.46	206.90	1.18	445	276	2
ORG-1061	34.67-35.06 (F) rept	-	93.1 ± 0.3	0.415 ± 0.002	4940 ± 22	27.54 ± 0.11	0.360	1.55	-	-	-	-	-	-
ORG-1046	34.67-35.06 (G)	74.0	124.2 ± 0.8	0.616 ± 0.004	3616 ± 29	20.99 ± 0.14	0.332	1.96	13.09	210.84	1.60	441	285	2
ORG-1054	34.67-35.06 (G) rept	-	124.3 ± 0.9	0.615 ± 0.002	3521 ± 27	20.17 ± 0.06	0.159	1.64	-	-	-	-	-	-
ORG-1062	34.67-35.06 (G) rept	-	124.0 ± 0.4	0.614 ± 0.002	3537 ± 14	20.33 ± 0.06	0.394	1.72	-	-	-	-	-	-
ORG-1047	34.67-35.06 (H)	74.3	125.4 ± 1.0	0.616 ± 0.002	3586 ± 31	20.46 ± 0.07	0.183	1.59	14.41	214.00	1.41	442	288	2
ORG-1063	34.67-35.06 (H) rept	-	125.3 ± 0.4	0.613 ± 0.002	3538 ± 14	20.00 ± 0.06	0.367	1.38	-	-	-	-	-	-

*Labels (A)-(H) stand for separate powdered aliquot of the coal samples, whereas “rept” represents replicate analysis of the same powder.

629 **Table 2:** TOC, Rock-eval and Re-Os isotopic data for black shale samples, Betsie Shale Member, Kanawha Formation, central Appalachian basin, USA.

630

AIRIE Run	Sample ID	TOC (wt%)	Re	Os	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}$	ρ	Os _i	S1	S2	S3	Tmax	HI	OI
			(ng/g)					(for 315 Ma)	mg HC/g	mg CO ₂ /g	°C	(=S2/TOC)	(=S3/TOC)	
ORG-1055	31.89-32.09 (A)	1.75	36.7 ± 0.7	0.360 ± 0.001	785 ± 16	4.70 ± 0.01	0.053	0.57	2.03	2.38	0.39	441	136	22
ORG-1065	31.89-32.09 (B)	1.94	42.4 ± 0.2	0.476 ± 0.001	637 ± 3	3.85 ± 0.01	0.367	0.50	2.16	2.66	0.31	441	137	16
ORG-1066	31.89-32.09 (C)	2.04	48.3 ± 0.3	0.453 ± 0.001	842 ± 5	5.03 ± 0.02	0.259	0.60	2.11	2.66	0.36	443	130	18
ORG-1067	31.89-32.09 (D)	1.95	38.3 ± 0.1	0.397 ± 0.001	722 ± 3	4.35 ± 0.01	0.338	0.55	2.12	2.62	0.38	443	134	19
ORG-1068	31.89-32.09 (E)	1.91	37.2 ± 0.2	0.381 ± 0.001	737 ± 4	4.47 ± 0.01	0.254	0.59	2.13	2.13	0.36	442	112	19
ORG-1069	31.89-32.09 (F)	1.83	36.3 ± 0.1	0.373 ± 0.001	733 ± 3	4.45 ± 0.01	0.372	0.59	2.03	2.29	0.29	443	125	16
ORG-1070	31.89-32.09 (G)	1.85	36.9 ± 0.1	0.373 ± 0.001	751 ± 3	4.53 ± 0.01	0.317	0.58	2.02	2.25	0.32	444	122	17

631 **Table 3:** Comparison of average Re and Os concentrations and their isotopic ratios for various geological samples.

Sample Type	Re, ng/g	Os, ng/g	Re/Os (wt. ratio)	$^{187}\text{Re}/^{188}\text{Os}$	Re/TOC ($\times 10^{-10}$)	Os/TOC ($\times 10^{-10}$)	Reference
Marine-influenced coal	108 (78.2-125.4; n=19)	0.52 (0.35-0.62; n=19)	210 (201-224; n=19)	3,954 (3,299-5,134; n=19)	1,439 (1025-1,688; n=8)	6.87 (4.57-8.32; n=8)	[1]
Terrestrial Coal	1.21 (0.10-4.82; n=5)	0.036 (0.018-0.047; n=5)	33.7 (4.8-138; n=5)	231 (26.0-977; n=5)	18.0 (1.3-72.9; n=5)	0.52 (0.24-0.68; n=5)	[2]
Tree Leaves[#]	~0.2	~0.006 (<0.02)	~33	-	2.0 ^{\$}	0.06 ^{\$}	[3]
River sediments*	0.81 (0.007-7.89; n=96)	0.048 (0.003-0.223; n=113)	15.0 (0.9-144; n=95)	89.6 (5.6-902; n=95)	906 (95-16,060; n=62)	116 (14.92-360; n=62)	[4-8]
Lacustrine sediments	28.3 (10.5-83.5; n=39)	0.32 (0.11-0.56; n=39)	89 (51-279; n=39)	538 (297-1831; n=39)	3471 (1034-11,513; n=35)	37.3 (14.0-74.5; n=35)	[9]
Phanerozoic Black shales*	68.0 (0.14-1376; n=387)	0.73 (0.02-20.9; n=387)	83 (2.8-1,100; n=387)	717 (14.2-6,253; n=380)	20,662 (638-258,668; n=246)	243 (15.77-5,114; n=246)	[1, 10-17]
Phanerozoic shales (Anoxic)*	56.1 (0.14-1,376; n=341)	0.73 (0.02-20.9; n=341)	68 (2.8-1,100; n=341)	461 (14.2-5,314; n=334)	16,034 (638-133,333; n=200)	242 (15.77-5,114; n=200)	[1, 10-15]
Phanerozoic shales (Euxinic)	203 (2.08-1,213; n=46)	0.88 (0.09-5.3; n=46)	189 (20.4-289; n=46)	2,964 (109-6,253; n=46)	53,958 (2,701-258,668; n=46)	258 (39.46-1,126; n=46)	[16-17]

*Average values are calculated after rejecting a few outliers; ^{\$}TOC-normalized ratios are estimated assuming 100% organic matter in tree leave samples; [#]Excluding Lichen and humus samples with relatively higher Os (0.06-0.70 ng/g) and lower Re (~0.07 ng/g) concentrations [3]. [1]: Present study; [2]: Baioumy et al., 2011; [3]: Rodushkin et al., 2007; [4]: Singh et al., 2003; [5]: Paul, 2008; [6]: Galy et al., 2008 (used for TOC data of [4-5]); [7]: Huh et al., 2004; [8]: Chen et al., 2006; [9]: Cumming et al., 2012; [10]: Selby, 2007; [11]: Selby et al., 2009; [12]: Pasava et al., 2010; [13]: Tripathy et al., 2014 and references therein; [14]: Xu et al., 2014; [15]: Georgiev et al., 2015; [16]: Georgiev et al., 2011; [17]: Geboy et al., 2015.

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Figure 2

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