Re–Os age for the Lower–Middle Pennsylvanian Boundary and comparison with associated palynoflora

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ABSTRACT

The Betsie Shale Member is a relatively thick and continuous unit that serves as a marker bed across the central Appalachian basin, in part because it includes an organic-rich shale unit at its base that is observable in drill logs. Deposited during a marine transgression, the Betsie Shale Member has been correlated to units in both Wales and Germany and has been proposed to mark the boundary between the Lower and Middle Pennsylvanian Series within North America. This investigation assigns a new Re–Os date to the base of the Betsie and examines the palynoflora and maceral composition of the underlying Matewan coal bed in the context of that date. The Matewan coal bed contains abundant lycopsid tree spores along its base with assemblage diversity and inertinite content increasing upsection, as sulfur content and ash yield decrease. Taken together, these palynologic and organic petrographic results suggest a submerged paleomire that transitioned to an exposed peat surface. Notably, separating the lower and upper benches of the Matewan is a parting with very high sulfur content (28 wt.%), perhaps representing an early marine pulse prior to the full on transgression responsible for depositing the Betsie. Results from Re–Os geochronology date the base of the Betsie at 323 ± 7.8 Ma, consistent with previously determined age constraints as well as the palynoflora assemblage presented herein. The Betsie Shale Member is also highly enriched in Re (ranging from 319.7 to 1213 ng/g), with high $^{187}Re/^{188}Os$ values ranging from 3644 to 5737 likely resultant from varying redox conditions between the pore water and overlying water column during deposition and early condensing of the section.

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1. Introduction

The Pennsylvanian (Upper Carboniferous) System of the Appalachian basin is dominated by economically important, coal-bearing sedimentary packages. Generally lacking tonsteins (kaolinized volcanic ash deposited in mires) or igneous units, palynology and macrofloral paleobotany have been used to determine relative ages for coals and associated horizons within the basin. However, plant micro- and macrofossils as geochronologic tools generally lack precision and, often, independent verification of assigned ages. Although these bio-stratigraphic methods cannot assign absolute dates to sedimentary successions, Re–Os geochronology can provide radiometric depositional ages of organic-rich sedimentary units. During subaqueous deposition, redox reactions at or below the sediment–water interface sequester Re and Os into organic-rich material and, with time, ^{187}Re undergoes β-decay to ^{187}Os, providing a radiometric geochronometer that directly yields the depositional age for the organic-rich sediment (Ravizza and Turekian, 1989). The Re–Os system has been successfully used to date organic-rich sedimentary units ranging in age from *ca.* 155 Ma (Cohen et al., 1999) to *ca.* 2695 Ma (Yang et al., 2009) and provide dates that refine the geologic time scale (Tripathy et al., 2014; Xu et al., 2009, 2014). Although not strictly for use in marine deposits (cf. Cumming et al., 2012), most freshwater systems do not provide initial reservoirs that are both homogenous with respect to Re and Os and large enough to provide detectable amounts of these very rare trace elements (with global mean concentrations in rivers of 428 and ~9 fg/g, respectively; Peucker-Ehrenbrink and Ravizza, 2000; Sharma and Wasserburg, 1997). This limitation may affect the usefulness of Re–Os geochronometry in the field of coal geology. Most well-studied coal beds (i.e., those of economic significance) developed in nonmarine environments; because marine-influenced coals tend toward higher S concentrations (Cecil et al., 1985), their viability as an economic resource is limited.

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The Betsie Shale Member is a heterolithic sequence of beds deposited in shallow marine environments. The basal part of the Betsie is composed of an organic-rich layer that exhibits a distinctive gamma-ray log signature that serves as an important marker horizon in the central Appalachian basin (CAB). In some areas, it is also the roof-rock for the underlying Matewan coal bed. The Betsie Shale Member is of particular significance because its base has been proposed as the stage boundary between the Lower and Middle Pennsylvanian in North America (Blake et al., 2002). This study (1) applies Re–Os geochronometry directly to the lowermost bed of the Betsie Shale Member and (2) compares those results to palynological analyses from the underlying Matewan coal bed to better understand palynology's accuracy as a geochronologic tool. As the relative age of the Betsie is fairly well constrained, it is an ideal horizon to test the usefulness of the Re–Os geochronometer to coal-associated systems, which are unique compared to the more commonly studied organic-rich shale deposited under relatively deeper marine conditions.

1.1. The Betsie Shale Member

The CAB is a globally important coal-producing region that has been actively mined for over 200 years (Chesnut, 1996) and covers areas of West Virginia, Virginia, Kentucky and Tennessee in the eastern United States (Fig. 1). Although the geology of the CAB has been studied in detail because of the presence of economic coal deposits, correlation of units across the basin has been problematic. Early geologic studies began in various states and separate nomenclatures were developed in each area. As a result, there is no unified nomenclature scheme; each State geological survey has developed its own preferred names for the same units. Although Chesnut (1996) attempted to clarify the situation by introducing a unified nomenclature scheme for the coal-bearing strata of the CAB, it has not gained widespread usage. Problematic nomenclature aside, the geology of the CAB is complicated. The stratigraphy of the basin consists of alternating coal, shale, siltstone, and sandstone units that are generally similar but vary laterally and vertically, making them difficult to correlate. Proper correlation therefore depends on recognizing a select few index horizons that possess diagnostic features and are laterally extensive in drill holes and outcrops across the region. Due to its vast aerial expanse, the unique lithology and characteristic gamma-ray signature (kick), the Betsie Shale Member is commonly used as one of these key index horizons (Blake, 1997, 1998; Rice et al., 1987).

The Betsie Shale Member is located within the Kanawha Formation of southern West Virginia and the Pikeville Formation of the Breathitt Group of eastern Kentucky, USA, in the CAB. The base of the Betsie Shale Member is an about 1-m-thick, sparsely fossiliferous black shale, easily identified in outcrop and by gamma-ray logs (Blake, 1997; Rice et al., 1987). It was deposited during a marine transgression onto the high shelf and low-lying coastal plain. The transgression flooded widespread mires that were precursors to the underlying Matewan coal bed of West Virginia (investigated herein) and Manchester coal bed of eastern Kentucky. Because apparently contemporaneous and correlative stratigraphic sequences are observed in Europe, previous researchers have proposed a glacioeustatic origin to account for such a widespread transgression over multiple continents (e.g., Blake, 1997, 1998; Blake et al., 1994; Chesnut, 1993). In this model, Milankovitch cycles forced changes in Gondwanan ice volumes and thus affected global sea levels, resulting in laterally extensive marine bands across the Euramerican Paleoequatorial Belt (Blake, 1997; Chesnut, 1993; Martino, 1996; Maynard and Leeder, 1992).

Given the presence of similar units in Europe, the Betsie Shale Member is not only significant as a marker horizon within the CAB, but potentially across the Carboniferous world (Blake et al., 2002). Within North America, the Betsie Shale member has been assigned to the upper Morrowan (a North American regional stage of the Lower Pennsylvanian) based on the finding of a fragment of the goniatite *Gastrioceras* in an outcrop near the town of Whitesburg, Kentucky (unpublished finding discussed in Rice et al., 1987). In Europe, Riley and Turner (1995) similarly used goniatites biostratigraphy to suggest a correlation between the Betsie Shale Member and the Katharina Marine Band in Germany, the base of which defines the Western European regional substage boundary between the Langsettian and Duckmantian
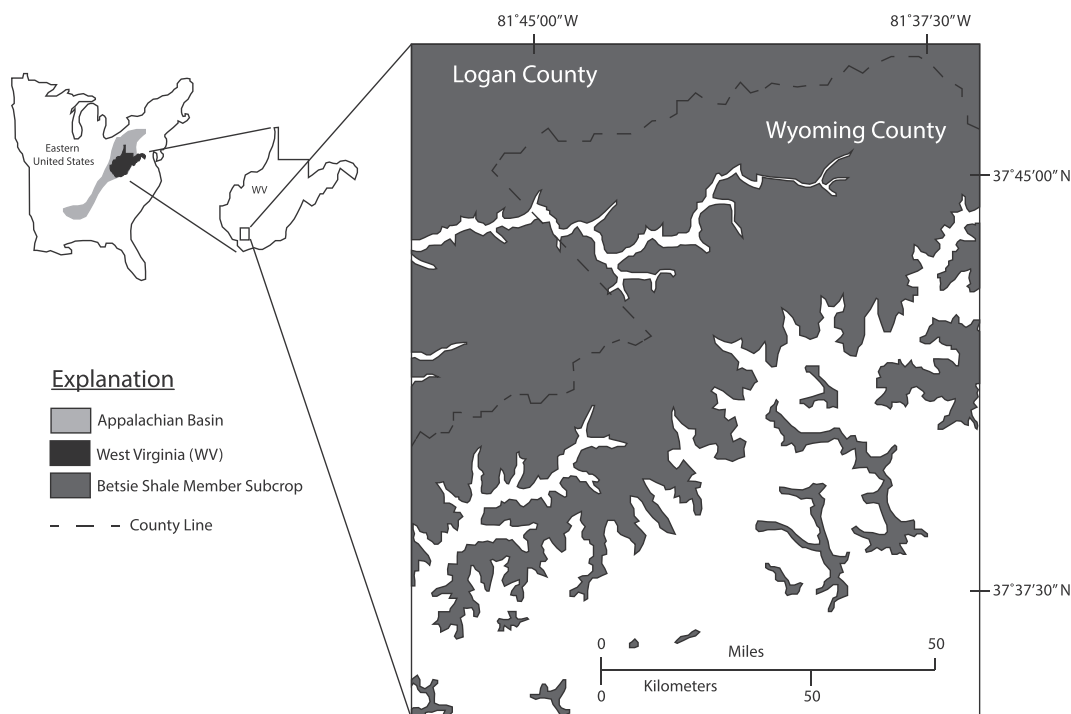

Fig. 1. Location map for this study. The Appalachian basin is located in the eastern United States. Samples for this study come from Wyoming County within the state of West Virginia.

stages in the Ruhr coal field. Paleofloral assemblages above and below the base of the Betsie Shale are consistent with this substage boundary, leading Blake (1997, 1998) and Blake et al. (2002) to correlate the Betsie Shale Member with the Vanderbekei and Amman Marine Bands that mark the same chronostratigraphic horizon in Great Britain (Gayer et al., 1999). Miospore palynology further supports this correlation as the top of the *Schulzospora rara* (VII) miospore zone (as identified in Smith and Butterworth, 1967), which coincides with both the Langsettian–Duckmantian boundary in Great Britain and the base of the Betsie Shale Member in the United States (Blake et al., 2002; Eble, 1996). A detailed investigation of the Manchester coal bed, which underlies the Betsie Shale Member in eastern Kentucky, shows it to contain *Schulzospora rara*, though in very minor amounts (Eble and Hower, 1995).

2. Methods

Samples from a drill core intersecting the Betsie Shale Member and Matewan coal bed in Wyoming County, West Virginia, were obtained from Cliffs Natural Resources exploration company (Fig. 1). The core samples were wrapped in plastic and boxed immediately to protect them from weathering. In this drill core, the Matewan coal is largely friable but coherent stratigraphically due to intercalation with shaly partings. Nine intervals within the coal were subsampled for geochemical and palynological analyses. Seven pristine samples were taken from the basal Betsie Shale Member within 30 cm of the contact with the underlying coal for Re–Os and ancillary organic analyses. All analyzed samples were subsampled from the same drill core.

2.1. Palynology, coal petrology and coal quality of the Matewan coal Bed

Samples were prepared according to ASTM International standard practice D-2013-07 (ASTM D2013-07, 2007). Approximately 50 g of −20-mesh coal (850-micron screen openings) was used for palynology and coal petrographic analyses. Another split was further reduced in size to −60 mesh (25-micron screen openings) for geochemical analyses.

Coal petrographic pellets were constructed from the −20-mesh material by mixing 5 g of shale or coal with epoxy resin in a 3.8-cm diameter ring mold. Upon hardening, samples were ground using 320-, 400-, and 600-grit papers, and polished using 1-micron, 0.3-micron, 0.05-micron alumina suspensions, and <0.05-micron colloidal silica. Samples were point counted using a Zeiss UMSP reflecting/transmitting light microscope equipped with both white and fluorescent (UV) light sources. Point counts of organic matter (macerals) were performed for each sample using a Zeiss epiplan 40× oil immersion objective, in conjunction with a 1.6× magnification changer (final magnification of 640×). Fluorescent light was used to assist with identification of liptinite components. A Zeiss 09 fluorescence filter set with a 450- to 490-nm excitation filter, a 510-nm beam splitter, and a 520-nm emission filter was used in conjunction with a high-intensity metal halide light source for all of the samples. Vitrinite reflectance analysis was done by first calibrating the system using a 0.94% reflectance standard with monochromatic white light (546 nm). Following this step, 50 random reflectance measurements were taken on particles of collotelinite for each sample.

Spores and pollen (palynomorphs) were separated from coal using Schulze's solution (concentrated nitric acid saturated with potassium chlorate) to oxidize the coal, followed by digestion with 5% potassium hydroxide. Organic residues were concentrated with zinc chloride (specific gravity of 1.9) and washed with cellosolve (2-ethoxyethanol), in conjunction with ultrasonic treatment, to remove fine organic debris. Cover glass strew mounts were made using a water-soluble adhesive and were attached to standard microscope slides using Canada balsam.

2.2. Re–Os and ancillary data for the Betsie Shale Member

Re and Os concentrations and isotopic ratios of the Betsie Shale Member samples were measured by isotope dilution-negative thermal ionization mass spectrometry following established analytical protocols of the AIRIE Program, Colorado State University (Georgiev et al., 2011; Xu et al., 2009; Yang et al., 2009). Approximately 0.1–0.2 g of well-homogenized shale sample, along with known amounts of ^{185}Re and ^{190}Os spikes, was digested using a CrO_3–H_2SO_4 solution in sealed Carius tubes at 240 °C for 48 h. This digestion approach leaches only the authigenic component of Re and Os from the samples (Selby and Creaser, 2003). A combination of solvent (CCl_4) extraction and microdistillation techniques was used for further purification of the Os present in the solution, whereas Re was purified through conventional anion-exchange chromatography (Yang et al., 2009). Purified Re and Os were loaded on Pt filaments and their isotopic ratios were measured using negative thermal ionization mass spectrometry. Measured Re and Os isotopic data were subsequently corrected for instrumental mass fractionation, oxygen isobaric interferences and blank contributions; the corrected Re and Os abundance and the, ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios are reported in this study. Further details on the Re–Os isotopic measurements are given in Georgiev et al. (2011).

Pyrolysis and total organic carbon (TOC) measurements were conducted at GeoMark Research labs in Humble, Tex., following established methods. Rock-Eval pyrolysis reveals details of the quantity, type and maturity of organic matter in the shale (Peters, 1986) with data including T_{max}, S_1, S_2, S_3, hydrogen index (HI), and oxygen index (OI). T_{max} represents the temperature at which the maximum amount of hydrocarbons are degraded from and generated by the kerogen and therefore represents a relative level of thermal maturity. From an initial mass of 1 g of rock, the S_1 value represents the milligrams of hydrocarbons distilled during burial (fixed temperature of 300 °C), S_2 represents the milligrams of hydrocarbons generated from degrading the kerogen (at temperatures between 300 °C and T_{max}) and S_3 represents the quantity of CO_2 (in mg) that is generated during combustion. From these measured parameters, other proxy values can be calculated, including HI and OI, which are indirect measurements of the ratios of hydrogen and oxygen to carbon, respectively, and can be used to evaluate the type of organic matter present.

3. Results

3.1. Palynology, petrography, and geochemistry of the Matewan coal bed

Of the nine Matewan samples, five benches are coal (<50% ash yield, by weight) and four are shale (>50% ash yield, by weight; Schopf, 1956), representing a total bed thickness of 0.75 m. The five coal benches can be broken into two groups based on results presented below, where the lower three benches are similar to one another but different from the upper two benches, which also appear similar to one another. Percent vitrinite reflectance (%R_o) values obtained from two of the coal samples showed maximum values of 0.92 and 0.93% R_o, indicating a high volatile A bituminous rank. The coal samples are moderate in ash yield, averaging 13.3% on a dry basis, and moderate to high in total sulfur content, averaging 2.7% on a dry basis. Shale samples average 65.4% ash on a dry basis and are extremely variable in total sulfur content, ranging from 0.5 to 28.2% (Table 1).

Petrographic results for both the coal and shale benches are shown in Table 1. Vitrinite is the most common maceral group within the coal samples, with telovitrinite (TV) occurring more frequently than either detrovitrinite (DV) or gelovitrinite (GV) (TV/(DV + GV) values are given in Table 1). Shale samples are also strongly vitrinite dominant but with proportionally more detrovitrinite and gelovitrinite than the coal samples (Table 1). Liptinite maceral content varied little within either the coal or shale sample sets in contrast to inertinite content, which varied much more widely in both lithologies.

Table 1

Petrography, palynology and geochemistry data from the Matewan coal bed, including partings. [TV = telovitrinite; DV = dendrovitrinite; GV = gelovitrinite; mmf = mineral-matter free basis].

	All Matewan coal (n = 5)			All shale partings in Matewan coal bed (n = 4)			Upper two Matewan coal benches	Lower three Matewan coal benches
Parameter	Mean	Max.	Min.	Mean	Min.	Max.	Mean	Mean
Vitrinite (mmf)	79.1	87.6	59.2	87.3	78	92	66.6	87.5
TV/(DV + GV)	3.3	1.6	6.3	1.7	1.3	2.2	–	–
Liptinite (mmf)	6.2	8.4	4.4	5.6	4.8	6.4	7.2	5.5
Inertinite (mmf)	14.7	32.4	6.4	7.1	1.6	17.2	26.2	7
Ash yield (%, dry basis)	13.3	17.7	9	66.1	52.3	79.5	10.4	15.3
Fixed carbon (%, dry basis)	51.3	54.8	46.3	16.8	10.2	23.9	–	–
Moisture (%, as-received basis)	0.6	0.6	0.5	0.4	0.3	0.6	–	–
Volatile matter (%, dry basis)	34.8	35.6	33.6	16.7	10	23.5	–	–
Chlorine (ppm)	1103.4	1462	848	192	176	200	–	–
Total sulfur (%, dry basis)	2.7	5.3	1.4	11.3	0.5	28.2	1.5	3.5
Mineral matter (%, dry basis)	15.9	20.5	10.6	74.4	63.6	86.2	–	–
Lycopod trees (%)	–	–	–	–	–	–	48.2	73.5
Small lycopods (%)	–	–	–	–	–	–	3.2	2
Tree ferns (%)	–	–	–	–	–	–	3.4	8
Small ferns (%)	–	–	–	–	–	–	12	2.9
Calamites (%)	–	–	–	–	–	–	22.4	10
Cordaites (%)	–	–	–	–	–	–	10.2	3.2

Palynomorph data, grouped according to parent plant affinity, are also shown in Table 1. Most of the coal and shale palynomorph assemblages are dominated by *Lycospora*, which is typical of Langsettian coal beds in the Appalachian basin (Eble, 1996). However, the top two coal benches contain more diverse assemblages, less sulfur and less ash compared to the three lower coal benches.

3.2. Re–Os, TOC and Rock-Eval data from the Betsie Shale Member

Table 2 shows results from Re and Os analyses of Betsie Shale Member samples. Rhenium and Osmium concentrations range from approximately 320 to 1200 ng/g and 1.5 to 5.3 ng/g, respectively (Table 2). Like most black shale, the basal Betsie is enriched in both Re and Os relative to typical crustal material, but the Re values observed here are particularly high. These highly enriched Re values result in notably high parent:daughter ratios (^{187}Re/^{188}Os ~3644–5737). The data show an isochronous relationship yielding a Model 1 age of 323 ± 7.8 Ma ($n = 7$; MSWD = 0.63) with an initial ^{187}Os/^{188}Os (Os$_i$), signature of 0.08 ± 0.64 (Fig. 2). The Os$_i$ value is considered to be representative of the ancient seawater in which the Betsie was deposited. The large uncertainty on the Os$_i$ value is likely resultant of minor variability in the isotopic composition of the coeval seawater during the period of deposition. These subtle changes may have led to the less precise Re–Os age.

Rock-Eval results for the Betsie show little variation among the seven shale samples (Table 3). TOC values range from 3.05 to 4.89 wt.%. The Betsie Shale Member is mature, with consistent T_{max} values of 433–442 °C. Both OI and HI values are uniformly low within the Betsie samples, generally ranging from 7 to 11 and 81 to 112, respectively. The relationship between T_{max} and HI values shows the Betsie contains type-III kerogen, despite being deposited in a marine setting where type-I may be more expected. Marine shale units in the CAB are generally coarsening up sequences that contain marine fossiliferous zones and terrestrially sourced type-III kerogen.

4. Discussion

4.1. Radiometric constraints within the Kanawha Formation

The Re–Os age assignment of 323 ± 7.8 Ma for the most basal part of the Betsie Shale Member is consistent with other radiometric dates from within the CAB. Currently, the International Commission on Stratigraphy (ICS) places the boundary between the Early and Middle Pennsylvanian at 315.2 ± 0.2 Ma (Gradstein et al., 2012), an age that statistically overlaps with the one presented in this study. The ICS date is based on the midway point between two radiometric dates derived from tonsteins located on either side of the boundary. The Upper Banner (Gilbert "A" in West Virginia) tonstein, located ~150 m below the Betsie Shale Member in the study area (Fig. 3), has been dated at 316.1 ± 0.8 Ma (uranium–lead (U–Pb) technique on zircons; Lyons et al., 1997) with a paleofloral assemblage indicative of a late Langesettian age (Blake et al., 2002). The younger Fire Clay tonstein, ~200 m above the base of the Betsie (Fig. 3), was dated at 314.6 ± 0.9 Ma by Lyons et al. (2006), again using U–Pb (single crystal, zircon technique). Argon–argon (Ar–Ar) ages from sanidines from the Fire Clay tonstein are slightly younger at 312.1 ± 2.0 Ma (Hess and Lippolt, 1986) and 310.9 ± 0.6 Ma (Kunk and Rice, 1994), but a recent push to use these sanidine crystals as a date standard produced ages of 315.3 ± 0.7 Ma or 314.6 ± 1.1 Ma, depending on the calibration used (Hemming et al., 2012). In addition, the roof shale of the Fire Clay coal bed contains a typical Duckmantian paleoflora, providing a relative age constraint (Blake, 1998). The Re–Os date reported here has a larger uncertainty

Table 2

Re–Os results from the Betsie Shale Member.

| AIRIE run #	Sample ID	Re (ng/g)	2σ	Os (ng/g)	2σ	Common Os (ng/g)	^{187}Re/^{188}Os	2σ	^{187}Os/^{188}Os	2σ	rho
ORG-1025	Betsie_33.20-34.60_A	559.0	3.799	2.524	0.0069	0.6073	4304.1	30.4	23.379	0.057	0.146
ORG-1026	Betsie_33.20-34.60_B	811.6	8.190	3.541	0.0091	0.7566	5012.9	51.5	27.256	0.061	0.104
ORG-1027	Betsie_33.20-34.60_C	1213.2	7.835	5.281	0.0149	1.1371	4986.1	33.7	26.994	0.066	0.168
ORG-1028	Betsie_33.20-34.60_D	1018.6	5.367	4.381	0.0114	0.9111	5224.0	29.3	28.206	0.063	0.185
ORG-1029	Betsie_33.20-34.60_E	958.8	5.854	4.056	0.0118	0.7807	5737.1	36.8	31.068	0.078	0.166
ORG-1030	Betsie_33.20-34.60_F	495.1	2.619	2.204	0.0061	0.5169	4477.4	25.2	24.178	0.059	0.185
ORG-1015	Betsie_33.20-34.60_G	319.7	5.680	1.504	0.0032	0.4105	3644.0	65.0	19.740	0.041	0.052
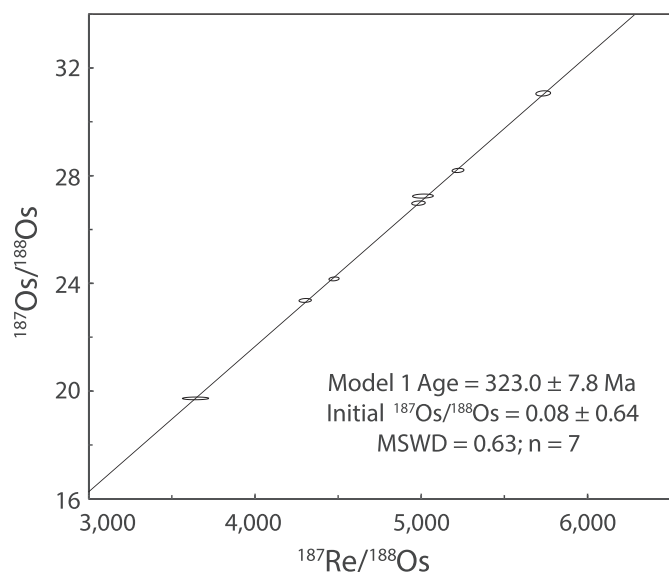
Fig. 2. Re–Os isochron for the Betsie Shale Member, constructed with Isoplot/Ex v. 3.75 (Ludwig, 2012, Model 1 defined therein) using a ^{187}Re decay constant of 1.666×10^{-11} (Smoliar et al., 1996). The y-intercept represents the initial osmium composition and MSWD = mean square weighted deviation, a measure of the line fit.

than the previously reported Ar–Ar or U–Pb dates. This is likely due to small changes in the initial osmium isotopic composition sequestered during deposition of the Betsie Shale Member. Although subtle changes to the Os reservoir during deposition have affected the precision of the date presented here, the fact that the Re–Os data define an isochron within the expected age of the Betsie suggests that the isotopic system has not been disturbed enough to affect the accuracy.

4.2. Palynology and plant paleontology of the Matewan coal bed and Betsie Shale Member

The Matewan coal bed, conformably underlying the Betsie Shale Member, is thin and laterally discrete. In the examined core, the coal bed is ~0.75 m thick and consists of five coal benches intercalated with four carbonaceous shale benches. As such, the Matewan paleomire in this area was clearly prone to inundation by water external to the mire, and thus carried a significant sediment load throughout its accumulation history. Of the five coal benches, the lowermost three are similar in that they are moderate in ash yield, moderate to high in total sulfur content, and high in vitrinite and lycopsid tree spore content. The uppermost two benches, however, are lower in ash yield and total sulfur content and contain proportionally more inertinite. The amounts of small fern and calamite spores and cordaite pollen are also much higher in the top two benches (Table 1).

During the Early and Middle Pennsylvanian, lycopsid trees (e.g., *Lepidodendron*, *Lepidophloios*) were dominant elements of coal-forming floras across Euramerica. As a group, they are indicative of very wet areas, and, in fact, had developed reproductive and

physiological features that allowed for growth and proliferation in consistently flooded areas (DiMichele and Phillips, 1994). When found in abundance, they are almost always associated with high vitrinite-content coal. The same conditions that favored lycopsid dominance (i.e., water-covered areas that were acidic and anoxic) are also known to promote the formation of vitrinite (Teichmüller, 1989).

The higher inertinite content and more diverse palynoflora seen in the top two coal benches suggest more surficial peat exposure, which would allow for increased inertinite formation through both microbial (mainly fungal) activity (Hower et al., 2011) and charring from wildfire (Scott and Jones, 1994). An exposed peat surface would also curtail the proliferation of lycopsid trees and allow other plant groups to become established. The cause of this change appears to be decreased moisture and a subsequently lower water table, which affected changes in mire flora and resulting coal maceral composition in the latter stages of paleomire development. The top two coal benches are separated by a carbonaceous shale that is extremely high in total sulfur (28.2%, dry basis with sulfate flouring visible in hand sample), which might signal the beginning of the marine transgression that ultimately resulted in the deposition of the overlying Betsie Shale Member.

Within the Kanawha Formation of West Virginia, there is a small but documented paleoflora divide at the base of the Betsie Shale Member. Below the Betsie, palynomorphs and plant megafossils are largely similar to the underlying New River Formation (Blake et al., 2002). However, several taxa such as *Neuralethopteris schlehanii*, *Karinopteris acuta* and *Lyginopterus hoeninghausii* become extinct within the part of the Kanawha Formation below the Betsie (Blake, 1997; Blake et al., 2002). These disappearances are consistent with the top of the Langsettian stage of Great Britain (Blake et al., 2002; Smith and Butterworth, 1967; Wagner, 1984). Above the Betsie Shale Member, Langsettian indices are replaced by a typical Duckmantian paleoflora (Blake, 1998). These observed changes in plant macrofossils seen in the CAB and correlated in similar lithologies throughout Euramerica (Thomas and Cleal, 1994; Wagner, 1984), led Blake (1997) to suggest and Blake et al. (2002) to synonymize the Lower to Middle Pennsylvanian boundary with the Langsettian–Duckmantian stage boundary and place them at the base of the Betsie Shale Member in the CAB. This boundary assignment is proposed solely on the stratigraphy and paleofloral assemblages, regardless of absolute age.

4.3. Re–Os fractionation in the Betsie Shale Member

The Re–Os data suggest a strong preferential uptake of Re over Os into the Betsie Shale Member during deposition. Although elevated Os concentrations are observed (over 5 ng/g), they are not remarkable in that they are within the range of values observed in other black shale; the Re concentrations of up to 1.2 µg/g, however, are unusual. Previous work on similar coal-associated, marine black shale has shown Re concentrations reaching no higher than ~0.42 µg/g (Baioumy et al., 2011). This extreme enrichment of Re results in the unusually high ^{187}Re/^{188}Os ratios observed in Table 2 and Fig. 2.

Currently, the uptake and binding mechanisms of Re and Os to organic phases are poorly understood, making these data difficult to interpret. Previous studies have suggested that sedimentation rates may

Table 3
Rock-Eval and total organic carbon (TOC) results from the Betsie Shale Member. [mmf = mineral matter free; HI = (100 ∗ S$_2$) / TOC, or hydrogen index; OI = (100 ∗ S$_3$) / TOC, or oxygen index].

| Sample ID	Carbonate (wt.%)	TOC (wt.%)	S1 (mg HC/g)	S2 (mg HC/g)	S3 (mg CO$_2$/g)	TMAX (°C)	HI	OI
Betsie_33.20-34.60_A	3.71	4.56	1.20	3.71	0.380	435	81.4	8.33
Betsie_33.20-34.60_B	6.06	3.05	0.980	2.89	0.260	438	94.8	8.52
Betsie_33.20-34.60_C	3.88	4.89	1.80	5.12	0.360	433	105	7.36
Betsie_33.20-34.60_D	3.49	4.69	1.69	5.23	0.400	442	112	8.53
Betsie_33.20-34.60_E	3.05	4.56	1.45	4.37	0.420	441	95.8	9.21
Betsie_33.20-34.60_F	4.19	4.02	1.16	2.83	0.460	436	70.4	11.4
Betsie_33.20-34.60_G	1.20	3.79	1.29	3.54	0.380	437	93.4	10.0
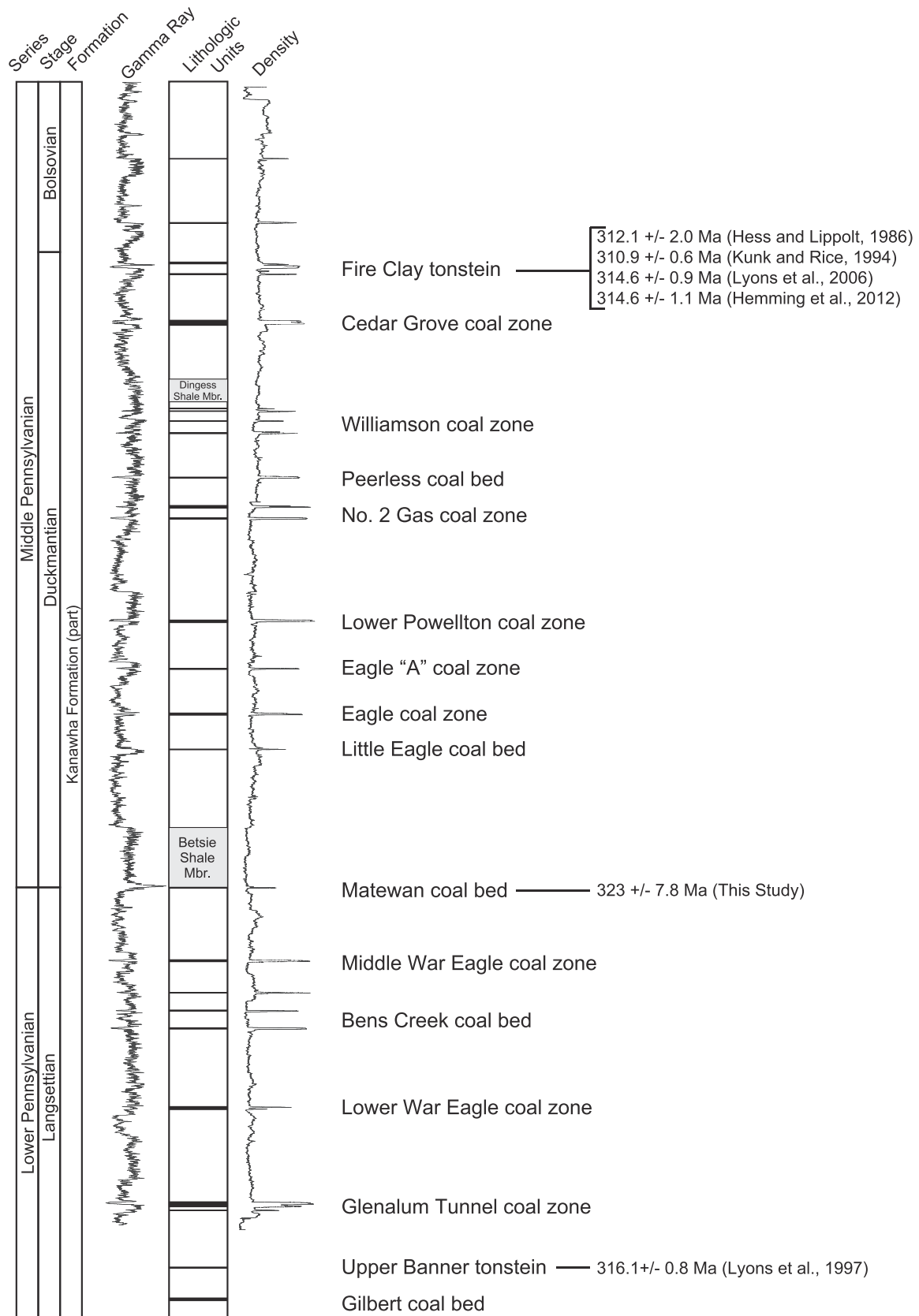
Fig. 3. Schematic stratigraphic column for the Kanawha Formation in West Virginia, USA. The generalized gamma-ray log illustrates the "kicks" observed in the Betsie Shale Member and other shale-rich units. Existing radiometric age constraints are included. The Kanawha Formation can range in thickness from 60 to 600 m, so no vertical scale is implied.

control the binding and preservation of Re and Os into organic-rich sediments (Rooney et al., 2012; Selby et al., 2009); however, although while reduced sedimentation rate may correlate with elevated Re/Os, it is not the principal cause. Water column conditions, including pH and temperature (Georgiev et al., 2011) and salinity (Martin et al., 2001), have been proposed as influential in the regulation of uptake and fractionation of Re and Os; however, there are no proxy data available for these parameters within the Betsie Shale Member. Rooney et al. (2012) evaluated a similar type-III-kerogen-bearing shale, the Jurassic Staffin Bay Formation in Scotland. Although their study supported the finding that Re and Os are bound within the kerogen of an organic-rich shale, they did not observe the strong preferential inclusion of Re over Os seen in the Betsie Shale Member. Ultimately, redox conditions at the sediment–water interface may best explain the observed high Re content. The Betsie samples all display very low OI values, indicating there was very low oxygen content within the kerogen. Under highly reducing conditions, Re may be more readily incorporated into organic-rich material (Yamashita et al., 2007). The shale parting near the Matewan–Betsie contact is marked by high sulfur content (28 wt.%) and Re is enriched relative to Os in the presence of highly sulfidic waters (Helz and Dolor, 2012; Tripathy et al., 2014). Molybdenum, which is geochemically similar to Re, is effectively precipitated under euxinic conditions by conversion to thiomolybdates (Helz et al., 1996), which may also contribute to the enriched Re values observed in the Betsie. Finally, the conditions below the sediment–water interface may be critical controls on relative uptake of Re and Os may be conditions below the sediment–water interface. More strongly anoxic or euxinic conditions may exist in pore waters compared to the overlying water column, which may enhance higher uptake of Re provided that the pathway to the overlying water column remains open (Lewan and Maynard, 1982; Rooney et al., 2012). This effect could be enhanced if condensed sections promote diffusion rates from the water column to pore waters (Lewan and Maynard, 1982).

5. Conclusions

Previous studies marking subdivisions within the Carboniferous have relied on palynology and plant macrofossils within coal beds and other organic-rich strata. Rhenium–osmium geochronology, however, allows for direct radiometric dates to which palynology may be compared. The palynology of the Matewan coal bed observed in this study is dominated by lycopsid tree spores at its base with increasing calamites spores and cordaites pollen toward the top. The diminution of lycopsids, increased diversity, reduced sulfur content, and reduced ash yield suggests greater surface exposure of the paleomire toward the end of its development. A shale parting with a very high sulfur content (28 wt.%) separating the lower and upper benches of the Matewan may represent the first pulse of a marine transgression that ultimately deposited the Betsie Shale Member ca. 316 Ma. This depositional age for the Betsie Shale Member may also be extended to correlative units in Germany (Katharina Marine Band) and the United Kingdom (Vanderbekei and Amman Marine Bands). The Betsie Shale Member is also significant as its base marks an important stage boundary within the Carboniferous between the Lower and Middle Pennsylvanian Series in North America and the Langsettian and Duckmantian stages in Western Europe. Although the Re–Os age of 323 ± 7.8 Ma is imprecise, it is statistically within the expected age of ~316 Ma. The Betsie Shale Member is highly enriched in Re (over 1 μg/g in some samples), which led to the evolution of very high parent:daughter ratios (up to 5737), which are among the highest ratios documented in organic–rich sediments. Variable redox conditions between the pore waters within the Betsie Shale Member and the overlying water column likely contributed to the efficient sequestration of Re into the system.

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