Direct radiometric dating of the Devonian-Mississippian time-scale boundary using the Re-Os black shale geochronometer

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ABSTRACT

Many Phanerozoic time-scale boundaries are characterized by oceanic anoxia and mass extinction events with the deposition of black shale. The Re-Os isotope system in black shale can be used to provide depositional ages for these rocks, thus yielding direct radiometric ages for time-scale boundaries. We demonstrate that the Re-Os black shale geochronometer can yield precise ages useful for time-scale research through study of the Devonian-Mississippian boundary within the Exshaw Formation, Canada. The Re-Os date determined places the Devonian-Mississippian boundary at 361.3 ± 2.4 Ma (2σ including λ uncertainty, model 1, mean square of weighted deviates = 1.2), in accord with recent calibration interpolated from U-Pb zircon dates (360.7 ± 0.7 Ma) for the Hasselbachtal section, Germany.

Keywords: Re-Os, black shale, geochronology, Devonian-Mississippian boundary.

INTRODUCTION

There is a continuous effort to conjoin the stratigraphic and chronometric geologic time scales, whereby units defined biostratigraphically are linked to an absolute chronometric value of time (cf. Gradstein et al., 2005; Harland et al., 1990). The previous and new 2004 geologic time-scale boundary ages, especially for the Paleozoic and Mesozoic, are primarily derived from U-Pb zircon dating of volcanic units (Gradstein et al., 2005; Harland et al., 1990) because the U-Pb zircon chronometer is widely accepted as the most robust and well-calibrated geologic chronometer (Gradstein et al., 2005). However, volcanic units are rarely found directly at stratigraphic boundaries, and thus absolute ages for specific interval boundaries are derived by interpolation of U-Pb zircon dates above and below any boundary, sometimes over considerable distances (Gradstein et al., 2005). Many Phanerozoic system, epoch, and stage boundaries are marked by the deposition of black shale units, several of which are coincident with mass extinction events (Barnes et al., 1996). The depositional age of these rocks can be determined by the Re-Os geochronometer (Ravizza and Turekian, 1989; Cohen et al., 1999), and more recent studies have indicated that the Re-Os isotope systematics in black shale remain undisturbed by hydrocarbon maturation and chlorite-grade metamorphism (Creaser et al., 2002; Kendall et al., 2004; Selby and Creaser, 2003b). With improved analytical methodologies, Re-Os age precision better than ±1% (2σ) has been obtained on black shale (e.g., Kendall et al., 2004). As such, the Re-Os black shale geochronometer potentially holds the novel ability to directly yield absolute dates for some stratigraphic boundaries (Cohen et al., 1999), thus eliminating the requirement for mathematical fitting of chronometric data to boundary points (Gradstein et al., 2005).

The Exshaw Formation black shale from western Canada includes the Devonian-Mississippian period boundary and is correlated with the Hangenberg mass extinction event from Europe (Caplan and Bustin, 1999; Richards and Higgins, 1988). This period boundary at the Hasselbachtal section, Germany, has been the focus of a numerical calibration study by U-Pb zircon dating (Trapp et al., 2004) in order to reconcile a debate surrounding the true age of the Devonian-Mississippian boundary (Compston, 2000). We present here the first utilization of the Re-Os black shale geochronometer for time-scale boundary age determination, and demonstrate its potential by production of a Re-Os age of 361.3 ± 2.4 Ma (2σ). This age is in accord with most recent numerical calibration of the Devonian-Mississippian boundary determined by interpolation of U-Pb zircon dates (360.7 ± 0.7 Ma; Trapp et al., 2004).

STRATIGRAPHY

The type section for the Exshaw Formation is located at Jura Creek, ~80 km west of Calgary, Alberta, Canada (Fig. 1). Here, the Exshaw Formation is ~47 m thick, comprises a lower (9.3 m) and upper member (37.4 m), and overlies the Palliser Formation. The lower member consists of a 1–6 cm basal sandstone-conglomerate, 6.9 m of noncalcareous to slightly calcareous black shale, and an upper 2.4 m of calcareous black shale (Fig. 1) (Richards and Higgins, 1988). The upper member is predominantly siltstone. An ~5-cm-thick bentonitic tuff occurs in the black shale ~2 m above its basal contact at Jura Creek (Richards et al., 2002). The Exshaw Formation contains two types of volcaniclastics (ash-fall crystal tuff and arkosic sandstone to conglomerate), but only in the lower member has the former been identified (Richards et al., 2002). The crystal tuff at the same stratigraphic position, with a mineralogy similar to that of the Jura Creek tuff, has yielded a $^{207}Pb/^{235}U$ monazite age of 363.3 ± 0.4 Ma from the Exshaw Formation at Nordegg, ~120 km north of Jura Creek (Richards et al., 2002). Organic geochemical analyses indicate that the Exshaw Formation black shale is overmature with respect to hydrocarbon generation at Jura Creek (Barson et al., 2000).

Uppermost Devonian and lowermost Mississippian conodonts have been identified from the Exshaw Formation black shale member at the Jura Creek section. At 90 cm above the basal contact, *Bispathodus costatus* morphotype 1 and *Apatognathus* sp. indicate middle *expansa* to lower middle *praesulcata* biozones (Fig. 1). At 3.1 and 5.6 m *Palmatolepis gracilis sigmoidalis* is found, which in relation to the conodonts at 90 cm indicate biozones no older than middle *expansa* and no younger than upper *praesulcata* of latest Devonian age (Richards and Higgins, 1988). The next conodont found here is *Siphonodella cooperi*, in the upper 76 cm of the calcareous black shale (Fig. 1) (Macqueen and Sandberg, 1970). This conodont species represents the upper *duplicata* and upper *crenulata-isosticha* biozones (Sandberg et al., 1978), indicating an earliest Mississippian age.

The conodont *Siphonodella sulcata*, the first presence of which defines the Devonian-Mississippian boundary (Paproth, 1980), and conodonts within the *sulcata* and lower *duplicata* biozones have not been identified at the Exshaw type section and might either be absent or in a condensed sequence (Richards and Higgins, 1988). However, conodont species at the type section indicate that the Devonian-Mississippian boundary is present and is restricted to an interval of ~2.9 m, 1.64 m above the base of the upper calcareous black shale and 1.3 m below the top of the lower noncalcareous black shale (Fig. 1). The

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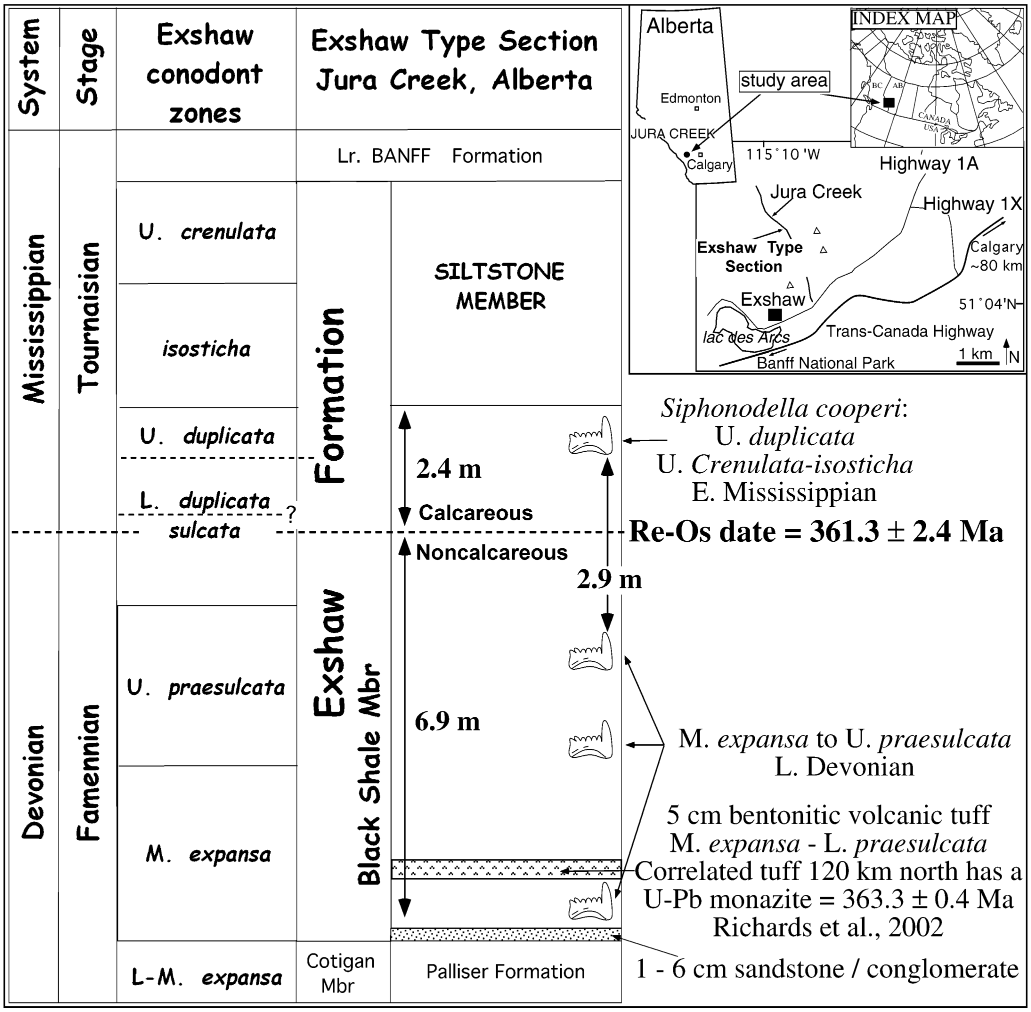

Figure 1. Stratigraphic column for Devonian-Mississippian Exshaw Formation, Jura Creek, Alberta, Canada (see text for discussion).

Devonian-Mississippian boundary at Jura Creek has thus been placed at the contact of the two units (Richards and Higgins, 1988) (Fig. 1).

ANALYTICAL PROTOCOL

Six Exshaw Formation black shale samples were collected in October 2003 over an ~4 m lateral interval along the Devonian-Mississippian boundary at the contact between the lower calcareous and upper noncalcareous black shale units (51°05′29″N 115°09′29″W: NTS 82 O/3) (Fig. 1). Surface weathered material was removed from the outcrop prior to sampling fresh material. No more than 10 cm of vertical stratigraphy was sampled for this sample set. Based on the correlation of the Exshaw Formation conodont zones with those from other localities and associated U-Pb dates (e.g., Tucker et al., 1998; Compston, 2000; Richards et al., 2002; Trapp et al., 2004), the 9.3 m of black shale of the lower Exshaw Formation may represent ~4 m.y. of time, implying that the 10 cm of vertically sampled shale could represent ~43,100 yr of sedimentation, assuming uniform sedimentation rates. Four samples were treated individually (DS53, DS54, DS56, DS57), and larger samples DS55 and DS58 were subdivided (Table 1). All samples were cut and ground to expose fresh surfaces, and 15–100 g of rock was milled to a fine powder in a ceramic mill.

TABLE 1. Re AND Os DATA FOR EXSHAW FORMATION BLACK SHALE AND THE DEVONIAN-MISSISSIPPIAN BOUNDARY

Sample	^{187}Re/^{188}Os	^{187}Os/^{188}Os	Re (ppb)	Os (ppt)	rho
DS53	253.49 ± 94	1.9475 ± 55	15.63 ± 0.05	367.8 ± 1.3	0.312
DS54	283.84 ± 105	2.1405 ± 56	17.54 ± 0.06	375.9 ± 1.3	0.321
DS55A	273.73 ± 97	2.0725 ± 36	15.47 ± 0.05	341.4 ± 0.9	0.301
DS55B	277.30 ± 101	2.1001 ± 49	16.36 ± 0.05	363.5 ± 1.2	0.325
DS55C	306.14 ± 119	2.2650 ± 75	21.18 ± 0.07	426.3 ± 1.7	0.366
DS56	190.35 ± 69	1.5704 ± 35	16.40 ± 0.05	493.3 ± 1.4	0.294
DS57	391.83 ± 138	2.7866 ± 58	35.97 ± 0.12	595.8 ± 2.0	0.265
DS58A	189.33 ± 68	1.5632 ± 35	15.18 ± 0.05	458.7 ± 1.3	0.283
DS58B	194.46 ± 68	1.5971 ± 31	16.61 ± 0.05	490.6 ± 1.3	0.273

Note: Total procedural blanks were ~12 pg for Re and 0.25 pg for Os. Uncertainties are given as 2σ for ^{187}Re/^{188}Os and ^{187}Os/^{188}Os. For the latter the uncertainty includes the 2 SE uncertainty for mass spectrometer analysis plus uncertainties for Os blank abundance and isotopic composition. rho is the associated error correlation (Ludwig, 1980). Sample powders are held by D. Selby.

The Re and Os isotopic compositions and abundances for black shale powders were determined following procedures detailed by Kendall et al. (2004) at the University of Alberta Radiogenic Isotope Facility using the Cr^{VI}-H_2SO_4 dissolution method. Total procedural blanks for Re and Os are ~12 and <0.2 pg, respectively, with an average ^{187}Os/^{188}Os value of ~0.15. Uncertainties for ^{187}Re/^{188}Os and ^{187}Os/^{188}Os are determined by error propagation of uncertainties in Re and Os mass spectrometer measurements, blank abundances and isotopic compositions, spike calibrations, and reproducibility of standard Re and Os isotopic values.

Re-Os isotopic data are regressed to yield age information using Isoplot/Ex version 3 (Ludwig, 2003), with λ ^{187}Re = $1.666 \times 10^{-11} \cdot yr^{-1}$ (Smoliar et al., 1996), 2σ input uncertainties for ^{187}Re/^{188}Os and ^{187}Os/^{188}Os, and

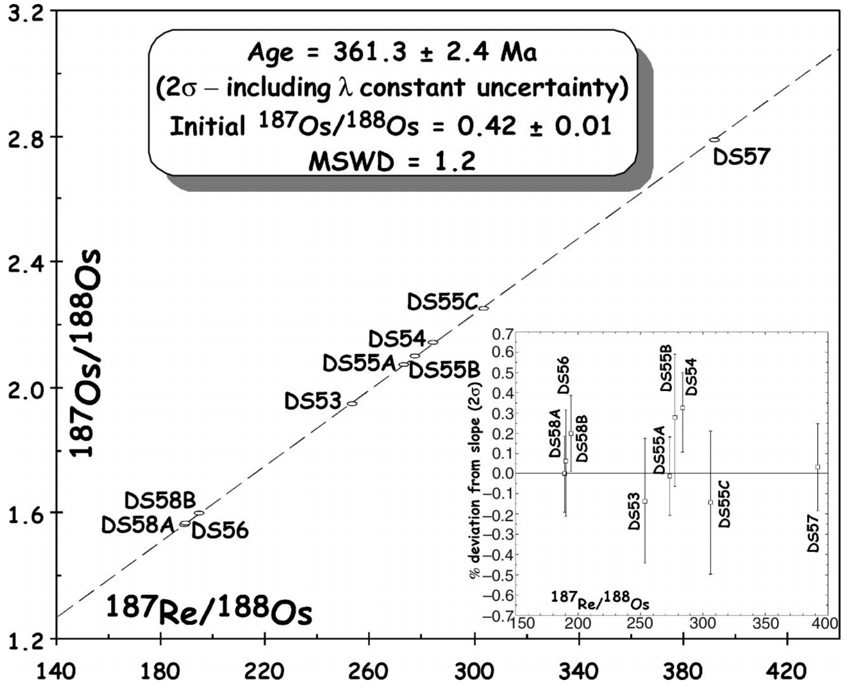

Figure 2. Re-Os isochron for Exshaw Formation black shale from Devonian-Mississippian boundary.

the associated error correlation function rho (Ludwig, 1980).

RESULTS

The abundances of Re and Os are between 15 and 36 ppb and 341 and 596 ppt, respectively, with ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios ranging from 189 to 391, and 1.56 to 2.8, respectively (Table 1). These values are slightly lower than those for the Exshaw black shale in the Peace River region (Creaser et al., 2002; Selby and Creaser, 2003b). Regression of the Re-Os data ($n = 9$) yields a model 1 date of 361.3 ± 2.1 Ma (±0.6% age uncertainty 2σ, mean square of weighted deviates [MSWD] = 1.2, probability = 0.28), with an initial ^{187}Os/^{188}Os value of 0.42 ± 0.01 (Fig. 2). On this basis the 2σ model 1 age uncertainties are reported here as calculated by Isoplot, and have not been multiplied by $(\mathrm{MSWD})^{0.5}$. The initial Os ratio likely represents only the local Os seawater composition of the Prophet trough at the Devonian-Mississippian transition as it was a marginal basin at that time (Richards et al., 2002). The inset in Figure 1 illustrates the fit of data points about the regression line as a percent deviation from the regression line; all deviations are <0.35%. This result further demonstrates that the Re-Os systematics in black shales are undisturbed by hydrocarbon maturation, in accord with the findings of Creaser et al. (2002) and Selby and Creaser (2003b).

DISCUSSION

The accuracy and precision of the ^{187}Re decay constant ($\lambda = 1.666 \times 10^{-11}\cdot\mathrm{yr}^{-1} \pm$ 0.31%; Smoliar et al., 1996) and cross-calibration to the U-Pb chronometer are important considerations for use of the Re-Os system for any time-scale research. Smoliar et al. (1996) established a λ value, with a factor of 10 better uncertainty than that experimentally determined (Lindner et al., 1989) from Re-Os data for Group IIIA meteorites of known Pb-Pb age, using an Os tracer calibrated against an Os standard solution that may include a systematic uncertainty of ∼±1.2%, from nonstoichiometry effects of the Os compound used for the standard. Thus, for laboratories not calibrating Os spike solutions against this particular Os standard solution, an absolute uncertainty of ∼1% remains for the ^{187}Re decay constant. We have overcome this limitation by obtaining precise reproducible gravimetric determinations for the Os content of our Os standard solution (Selby and Creaser, 2001). In addition, by intercalibrating the Re-Os molybdenite and U-Pb zircon chronometers from magmatic ore systems utilizing the same Os standard solution used in this study for spike calibration, λ ^{187}Re of $1.666 \times 10^{-11}\cdot\mathrm{yr}^{-1}$ was found to be within ±0.35% (2σ) of the decay constants used for U-Pb geochronology (Selby and Creaser, 2003a), almost identical to the uncertainty determined by Smoliar et al. (1996) by different methods. Propagating the uncertainty in the slope of the regression determined from Isoplot, together with a 0.35% uncertainty for λ, the Re-Os Exshaw black shale date for the Devonian-Mississippian boundary is 361.3 ± 2.4 Ma.

During the past 40 yr there have been nearly 20 determinations for the age of the Devonian-Mississippian boundary (Compston, 2000; Gradstein et al., 2005; Jie-dong et al., 1988; Trapp et al., 2004; Williams et al., 2000). The majority of these determinations are based on interpolation of geochronologic data through tie points and pseudo tie points (Harland et al., 1990), splines (Gradstein et al., 2005), and best-fit lines (Tucker et al., 1998). Several studies relied entirely on a sensitive high resolution ion microprobe (SHRIMP) U-Pb zircon age of 353.7 ± 4.2 Ma from a bed 79 tuff unit 35 cm above the biostratigraphically defined Devonian-Mississippian boundary at the Hasselbachtal section, Germany (Claoue-Long et al., 1995, 1992). Other determinations are based on time-fitted lines of U-Pb zircon data of 362 Ma (Tucker et al., 1998), which have been reinterpreted based on reassessment of the Tucker et al. U-Pb data to 359.6 Ma (Compston, 2000) and 359.2 ± 2.5 Ma (Gradstein et al., 2005). To date, the only direct determination of the boundary is a Rb-Sr illite date of 361.0 ± 4.1 Ma (^{87}Sr/^{86}Sr = 0.7079 ± 0.0002; York, 1969) from bed 58 of the stratotype section at Nanbiancun, China (Jie-dong et al., 1988). Only by using the robust regression method of Isoplot (Ludwig, 2003) can an age similar to that reported by Jie-dong et al. (1988) be obtained; including the ^{87}Rb decay constant (Neumann and Huster, 1976) uncertainty, this method yields an age of 360.5 ± 9.2 Ma.

The accuracy of SHRIMP U-Pb zircon date from the Hasselbachtal section was reassessed and subsequently increased by 1.6% to 359.1 ± 1.0 Ma (Compston, 2000). In accord with this recalculation, a study of bed 79 zircons by U-Pb isotope dilution thermal ionization mass spectrometry (ID-TIMS) methodology gave an age of 360.5 ± 0.8 Ma, and from bed 70, 57 cm above bed 79, an age of 360.2 ± 0.7 Ma was determined (including decay constant uncertainties) (Trapp et al., 2004). These new ID-TIMS data were used together with U-Pb zircon ages from tuff horizons in the *expansa* to *praesulcuta* biozones of the Piskahegan Group, New Brunswick (363.6 ± 1.6 Ma; Tucker et al., 1998) and Exshaw Formation (363.3 ± 0.4 Ma; Richards et al., 2002) to interpolate the age of the Devonian-Mississippian boundary to be 360.7 ± 0.7 Ma (Trapp et al., 2004). The Re-Os isochron age from the Devonian-Mississippian period boundary determined here (361.3 ± 2.4 Ma) matches the 360.7 Ma U-Pb interpolated boundary age to within ∼0.2% of the nominal age values.

This study clearly demonstrates that the Re-Os black shale geochronometer is useful for direct absolute dating of some biostratigraphically defined boundaries, thus producing an improved chronometric framework to aid in establishing the timing of events and rates of processes through geologic time. The precision of the age determination (±2.4 m.y., or ±~0.7%, including decay constant uncertainty) at the Devonian-Mississippian boundary, and its accurate cross-calibration to the U-Pb chronometer, makes the geochronometer a valuable tool, in addition to the widely used U-Pb and Ar-Ar chronometers, for Phanerozoic time-scale research. The Re-Os black shale geochronometer may be particularly useful in time periods with a paucity of volcanic beds, and might aid in resolving current controversies for the age of the Permian-Triassic and Anisian-Ladinian boundaries (Bowring et al., 1998; Mundil et al., 1996, 2004; Palfy et al., 2003). Furthermore, black shale Re-Os dating could improve the time-scale calibrations of certain intervals of the Cretaceous, Jurassic, Triassic, Permian, and Mississippian that are devoid of detailed radiometric dates (Gradstein et al., 2005).

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