

Direct Rhenium-Osmium age of the Oxfordian-Kimmeridgian boundary, Staffin bay, Isle of Skye, U.K., and the Late Jurassic time scale

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Rhenium-Osmium (Re-Os) dating of black shale of the proposed Global Stratotype Section and Point (GSSP) for the Oxfordian-Kimmeridgian boundary, at Staffin Bay, Isle of Skye, U.K., yields an age of 154.1 ± 2.2 Ma. This Re-Os age presents a 45 % (1.8 m.y.) improvement in precision for the basal Kimmeridgian. It demonstrates that the duration of the Kimmeridgian is nominally 3.3 m.y. and thus is 1.6 m.y. shorter than previously indicated. The new Re-Os age together with a recently determined ^{40}Ar - ^{39}Ar age for the basal Berriasian suggest that the duration of the Kimmeridgian and Tithonian were nominally ~650 k.y. shorter than previously determined.

The Re-Os data for the Staffin black shale indicates that the seawater Os isotope composition at the Oxfordian/Kimmeridgian boundary was radiogenic ($^{187}\text{Os}/^{188}\text{Os} = 0.53$), similar to that for the Early Tithonian, but much higher than the Late Callovian ($^{187}\text{Os}/^{188}\text{Os} = 0.27$). These Os isotope compositions suggest that the rate of continental weathering had increased from the Callovian to Kimmeridgian/Tithonian.

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Introduction

The extensive study of the Jurassic period to calibrate the chronostratigraphic scale with chronometric dates during the past twenty years has resulted in more than a dozen time scales (cf. Gradstein et al. 2005). Pre-1996 Jurassic time scales disagree considerably and possess large uncertainties. This was largely the result of the extrapolation of limited geochronology databases, the scarcity of biostratigraphy with well constrained isotopic ages, and the use of K-Ar ages, which may reflect a younger age due to isotopic disturbance and/or reflect slow cooling due to low closure temperature (Gradstein et al. 1994, Pálffy 1995).

Typically, sedimentary units are not directly amenable to radiometric dating. Therefore, defining the absolute age of a biostratigraphic boundary is rarely possible. However, volcanic units are often interbedded in a sedimentary package and can be dated using U-Pb zircon geochronology. The U-Pb zircon chronometer is widely accepted as the most robust and well-calibrated dating method. Thus the age of a stratigraphic boundary can be derived from the interpolation of U-Pb zircon ages from interbedded volcanic units. The integration of U-Pb zircon ages and ammonite biostratigraphy for the Jurassic strata of the Canadian Cordillera has resulted in considerable improvements to the Early and Late Jurassic time scale (Pálffy et al. 1995, 1997, 1999, 2000).

Direct stratigraphic boundary dating is inherently difficult throughout much of the geologic time scale. In the current Jurassic time scale, it is only the base of the Hettangian that

is constrained by a U-Pb zircon age (199.6 ± 0.3 Ma, 2σ) from a tuff unit that lies directly below the Triassic-Jurassic boundary (Pálffy et al. 2000). Because of the rare association of volcanic units with stratigraphic boundaries, absolute ages for the Jurassic Period and stage boundaries are derived mainly by mathematical fitting of U-Pb zircon ages (and a few Ar-Ar ages) from above and below any of the stage boundaries (Gradstein et al. 2004). Mathematical scaling of the Jurassic timescale combines radiometric dates, constraints on durations from cyclic stratigraphy, linear trends in Sr isotopic variations, proportional scaling of ammonite zones, and magnetic polarity (M-sequence) time scale derived from estimates of Pacific sea floor spreading (Gradstein et al. 2004). The stage boundaries of the Late Jurassic are the least accurate and most imprecise (± 4 my) of any section in the Phanerozoic, because of a dearth of precise radiometric ages for the Late Jurassic and assumptions based on the spreading-rate model for M-sequence magnetic anomalies (Gradstein et al. 2004). As a result, the uncertainty for the boundary ages is similar to the duration for some of the stages.

To eliminate the assumptions that surround mathematical scaling of the time scale, direct dating of the stratigraphic boundary is required. The Re-Os black shale geochronometer has been demonstrated to be a powerful tool for time scale boundary age determination by defining the age of the Devonian-Mississippian boundary at 361.3 ± 2.4 Ma (2σ) (Selby & Creaser 2005). In addition, several recent

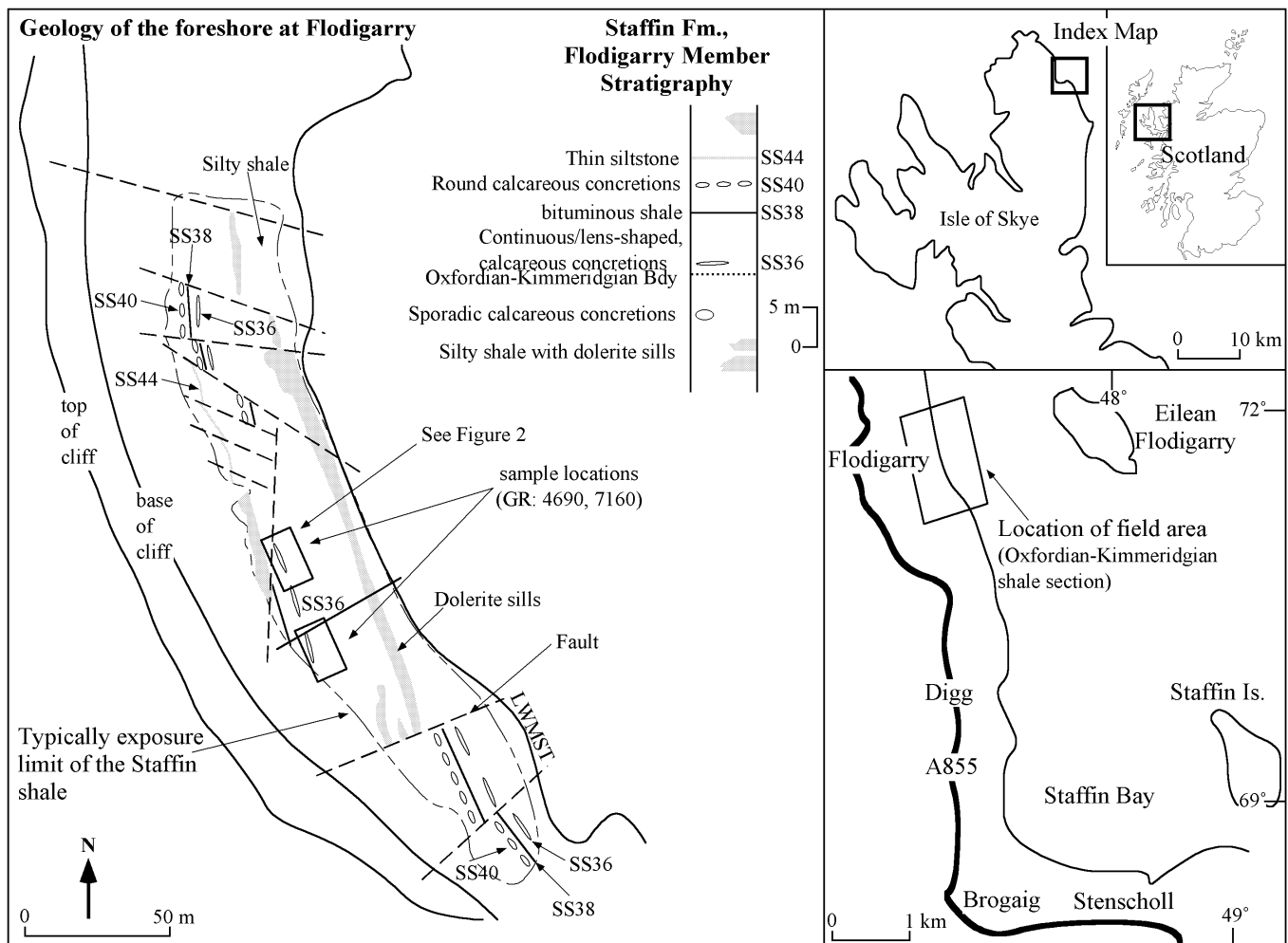


Fig. 1. Location of the Oxfordian-Kimmeridgian Staffin black shale, Isle of Skye, UK.

studies have shown age precision better than $\pm 1\%$ (2σ) (Kendall et al. 2004, Selby & Creaser 2005, Kendall et al. 2006). Organic-bearing units (e.g., black shales) are common in many stratigraphic sequences and often mark stratigraphic boundaries. These units are amenable to the rhenium-osmium (Re-Os) geochronological method (Ravizza & Turekian 1989, Cohen et al. 1999), and recent studies have shown that the Re-Os systematics in black shales remain undisturbed by hydrocarbon maturation and chlorite-grade metamorphism (Creaser et al. 2002; Kendall et al. 2004, Selby & Creaser 2003b). To further the development of the Jurassic time scale this study presents a precise Re-Os age for the base of the Kimmeridgian from the Oxfordian-Kimmeridgian sequence of the Staffin Shale Formation, Isle of Skye - the proposed Global Stratotype Section and Point (GSSP) for this stratigraphic time.

Stratigraphy

The Oxfordian-Kimmeridgian boundary succession lies within the Flodigarry Member of the Staffin Formation, Isle of Skye, UK (Fig. 1). The exposed member comprises a 25 m continuous sequence of silty and bituminous black shale interbedded with limestone, minor sandstone

and layers of limestone concretions. The unit is moderately condensed with 3 to 4 ammonite zones within the exposed section. Tertiary dolerite dykes and sills intrude the sequence. However, metamorphism and strong diagenetic alteration of the shale is restricted to the contact margins. The section is contained within eight slipped blocks, as part of the Quirang landslip (Wright 1989), resulting in the section having an almost vertical dip.

The Staffin Formation east of Flodigarry (Fig. 1-2), hosts diverse, abundant and well-preserved boreal and subboreal ammonite faunas (Sykes & Callomom 1979, Birkeland & Callomom 1985, Matyja et al. 2004, 2006). These provide a means for defining the Oxfordian-Kimmeridgian boundary (Matyja et al. 2004, 2006). The location of this boundary has recently been established to be at the base of the *Bauhini* (boreal) / *Baylei* (subboreal) zones. The boundary is characterised by the first appearance of *Pictonia* with *Prorasenia* replacing *Ringsteadia* and *Microbiplices* (subboreal), as well as the first occurrence of *Amoeboceras* (*Plasmatites* - *A. praebauhini*, boreal) (Salfeld 1913, Matyja et al. 2004, 2006) (Fig. 2).

At Flodigarry, the subboreal Oxfordian-Kimmeridgian (Pseudocordata/Baylei zones) boundary is placed between 1.65 - 1.47 m and 1.08 m below bed 36 - the last occur-

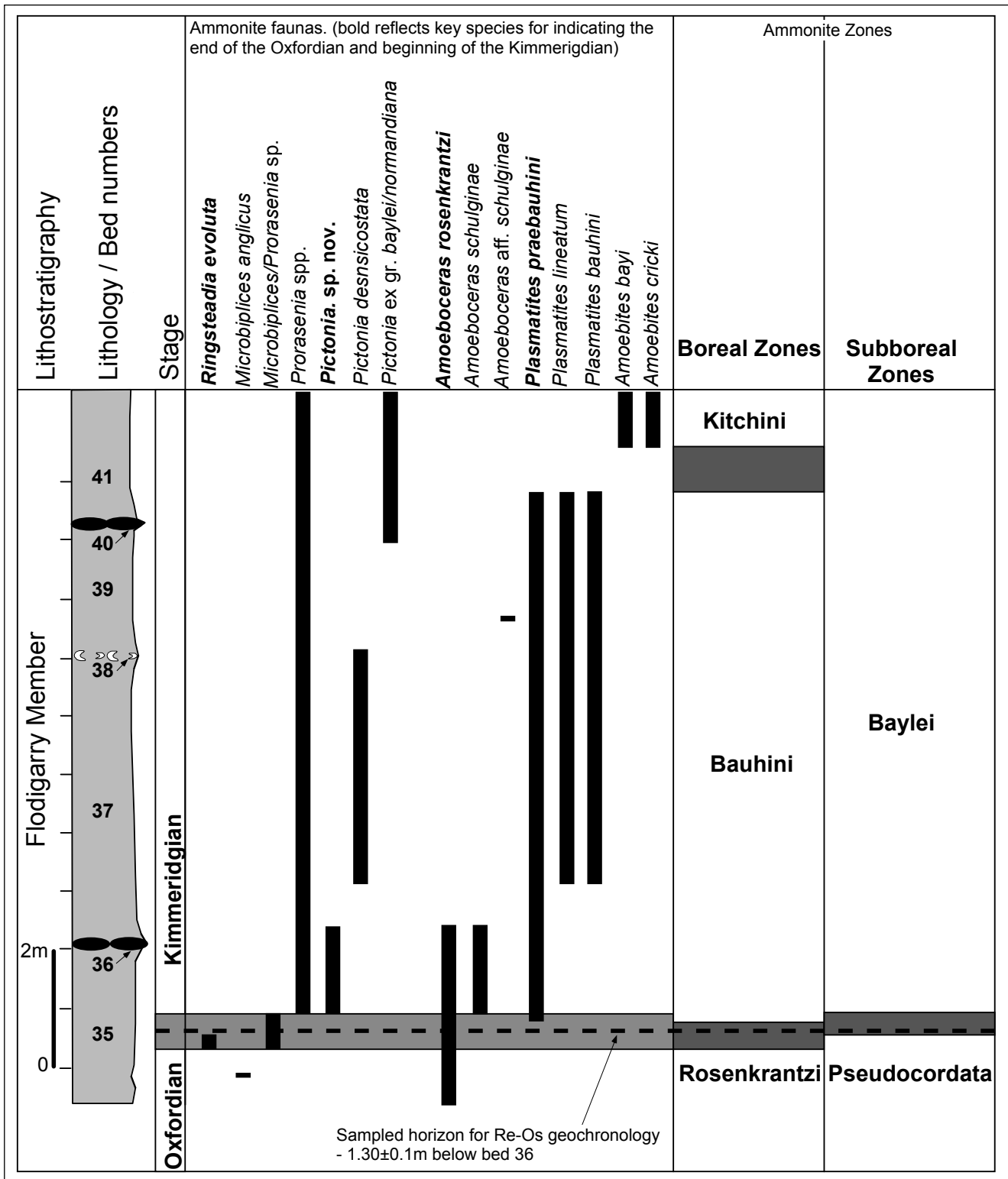


Fig. 2. Ammonite biostratigraphy of the Staffin Shale Member, Flodigarry, Isle of Skye, UK showing the sampled horizon for Re-Os geochronology that encompasses both the boreal and subboreal Zones that define the Oxfordian/Kimmeridgian boundary. The lithology between beds 35 and 41 is a silty black shale. Bed 36 and 40 are concretionary limestone units. Bed 35 is *Pictonian densicostata*-rich. Modified after Matyja et al. 2004, 2006). Fig. 2. Ammonite biostratigraphy of the Staffin Shale Member, Flodigarry, Isle of Skye, UK showing the sampled horizon for Re-Os geochronology that encompasses both the boreal and subboreal Zones that define the Oxfordian/Kimmeridgian boundary. The lithology between beds 35 and 41 is a silty black shale. Bed 36 and 40 are concretionary limestone units. Bed 35 is *Pictonian densicostata*-rich. Modified after Matyja et al. 2004, 2006).

rence of *Ringsteadia* and the first occurrence of *Pictonia*, respectively (Fig. 2). At almost the same interval, the boreal Oxfordian-Kimmeridgian boundary (Rosenkrantzi/Bauhini zones) is placed between 1.65 m and 1.17 m below

bed 36 - the last occurrence of *A. rosenkrantzi* and the first appearance of *A. (P.) praebauhini* (Fig. 2). Additionally, the boreal and subboreal zone ammonite faunas have been correlated with the sub-Mediterranean zonal scheme

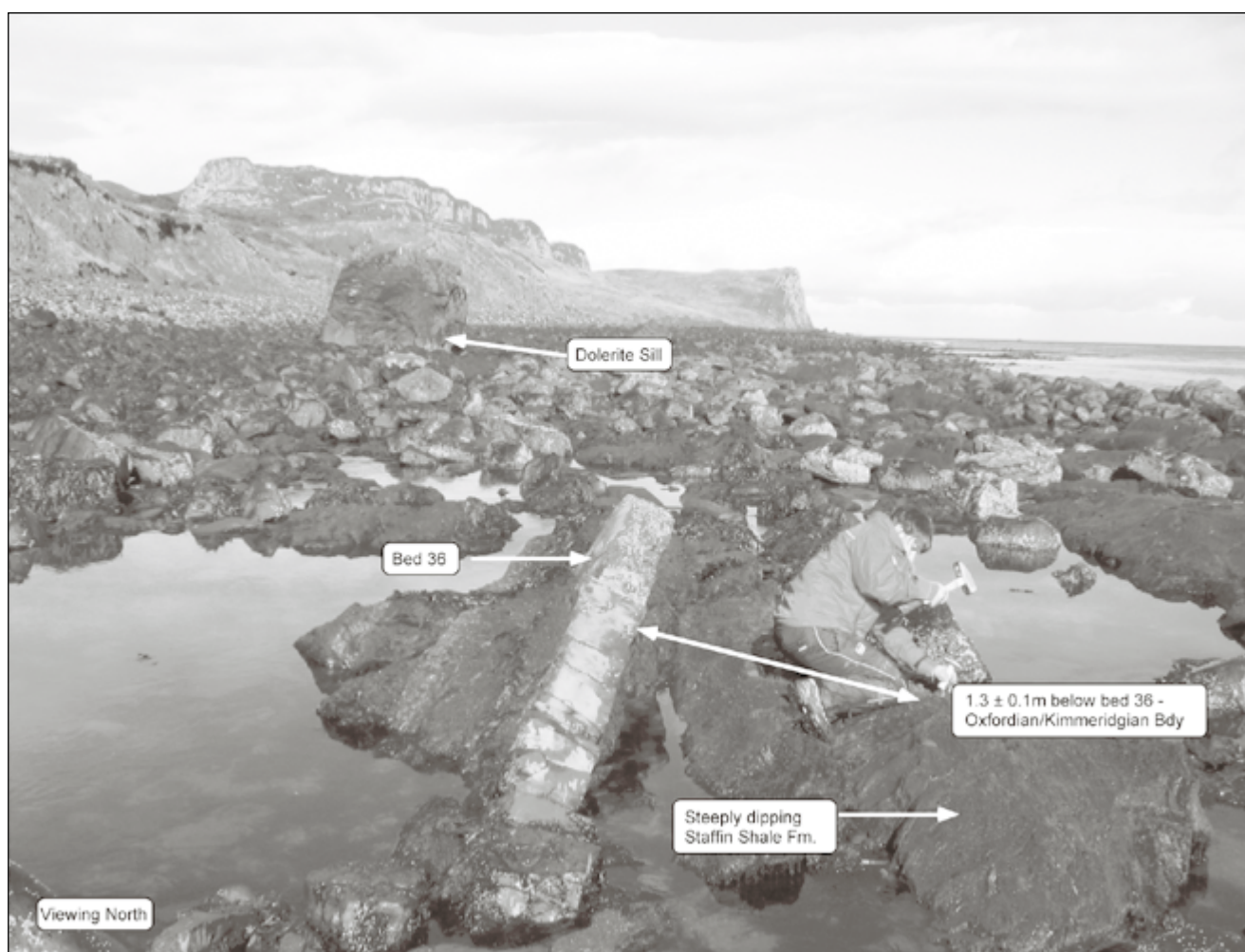


Fig. 3. Sample location of the Oxfordian-Kimmeridgian Staffin black shale, Isle of Skye, UK

using the secondary standard parallel zonation, placing the Oxfordian-Kimmeridgian boundary between the Rosenkrantzi/ Pseudocordata and Bauhini/Baylei zones (Callomon 2004, Matyja et al. 2004, 2006). As a result of the well-constrained ammonite stratigraphy and the completeness and undisturbed nature of the Staffin Shale section at Flodigaray, it is currently proposed to place the Global Stratotype Section and Point for the base of the Kimmeridgian stage here (Wierzbowski 2005).

Methodology

Sampling

The boreal and subboreal ammonite biostratigraphy place the Oxfordian-Kimmeridgian boundary between 1.08 m and 1.65 m below an almost continuous limestone concretion (bed 36) (Fig. 1-3). Black shale samples for Re-Os geochronology were collected at 1.30 ± 0.1 m below bed 36 to encompass the Oxfordian-Kimmeridgian boundary of both ammonite zonal schemes that coincide over 0.5 m. At this stratigraphic level, samples were collected laterally at one metre intervals over 10

m ($57^{\circ}39'42.00''\text{N}$, $6^{\circ}14'45.26''\text{W}$) (Figs. 1-3). Surface weathered material was removed from the outcrop prior to sampling fresh material. All samples were cut and ground to expose fresh surfaces and 55 - 100 g of rock were milled to a fine powder in a ceramic mill. Sample powders are held by Selby at Durham University.

Analytical protocols

The Re and Os isotopic compositions and abundances for black shale powders were determined at the Arthur Holmes Isotope Laboratory, Durham University following procedures detailed by Selby & Creaser (2003b) and Kendall et al. (2004). Approximately 1g of sample powder was digested with a ^{190}Os and ^{185}Re mixed tracer (spike) solution in a $\text{Cr}^{\text{VI}}\text{-H}_2\text{SO}_4$ solution at 240°C for ~ 48 h. The Re and Os were purified from the acid solution using solvent extraction, micro-distillation and anion chromatography methods. The purified Re and Os were loaded onto Ni and Pt filaments, respectively (Selby et al. 2007), the isotopic measurements being conducted using negative thermal ionisation mass spectrometry (Creaser et al. 1991) on a Thermo Electron TRITON mass spectrometer via ion-counting using a secondary electron multiplier in

Table 1: Re and Os data for the Staffin Shale and the Oxfordian-Kimmeridgian Boundary

Sample	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}$	Re (ppb)	Os (ppt)	rho
DS96-05	393.42 ± 2.31	1.5438 ± 39	13.36 ± 0.08	193.9 ± 0.6	0.169
DS98-05	376.41 ± 1.69	1.4904 ± 64	13.20 ± 0.04	199.1 ± 0.8	0.470
DS102-05	374.16 ± 1.85	1.4856 ± 28	16.98 ± 0.08	257.5 ± 0.7	0.167
DS103-05	705.70 ± 3.58	2.3252 ± 54	32.70 ± 0.16	287.3 ± 1.0	0.204
DS105-05	616.05 ± 4.9	2.1120 ± 221	49.81 ± 0.24	490.3 ± 3.5	0.487
DS107-05	807.64 ± 2.85	2.6146 ± 46	44.25 ± 0.14	349.6 ± 1.0	0.322
DS108-2-05	901.63 ± 3.34	2.8436 ± 72	47.09 ± 0.15	340.9 ± 1.3	0.352
DS108-05	899.52 ± 4.48	2.8319 ± 52	47.16 ± 0.23	341.8 ± 1.1	0.166

Note: Total procedural blanks were ~ 15 pg for Re and 0.16 pg for Os, with a $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1960 ± 0.010 . Uncertainties are given as 2σ for $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$. 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

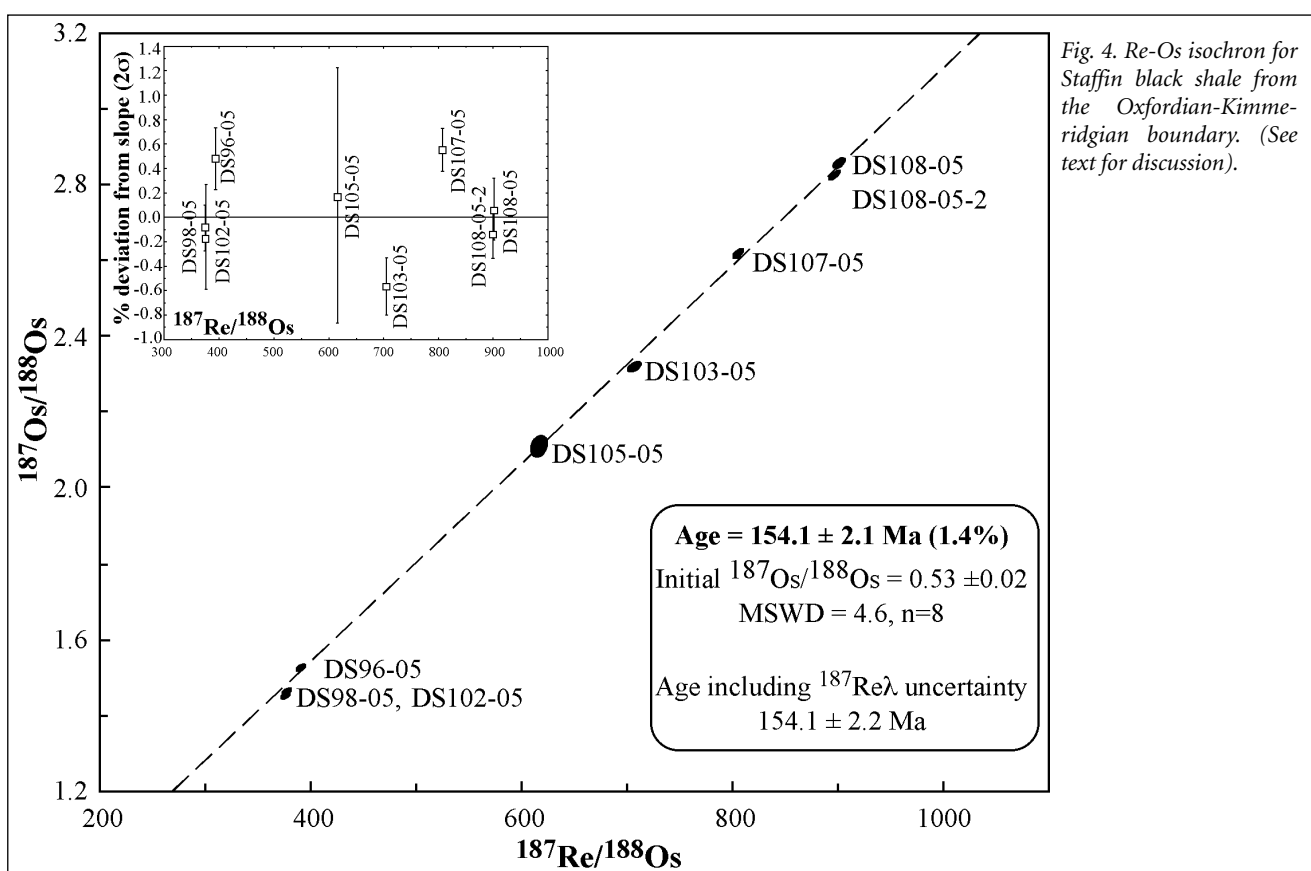


Fig. 4. Re-Os isochron for Staffin black shale from the Oxfordian-Kimmeridgian boundary. (See text for discussion).

peak-hopping mode for Os, and static Faraday collection for Re. Total procedural blanks for Re and Os are ~ 15 and < 0.16 pg, respectively, with an average $^{187}\text{Os}/^{188}\text{Os}$ value of ~ 0.19. Uncertainties for $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ (Table 1) 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. Rhenium-Os isotopic data are regressed to yield age information using *Isoplot V. 3.0* (Ludwig, 2003), with λ $^{187}\text{Re} = 1.666 \times 10^{-11} \text{ a}^{-1}$ (Smoliar et al. 1996), 2σ calculated uncertainties for $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$, and the associated error correlation function rho (Ludwig, 1980) (Table 1).

During the course of this study, an in-house Re and Os solution (AB2) was analyzed as a monitor of long-term instrument reproducibility. The Re solution, made from zone-refined Re ribbon, yields an average $^{185}\text{Re}/^{187}\text{Re}$ ratio of 0.5977 ± 0.0012 (1SD, n = 8). The measured difference in $^{185}\text{Re}/^{187}\text{Re}$ for this solution and the accepted $^{185}\text{Re}/^{187}\text{Re}$ ratio (0.5974; Gramlich et al. 1974) is used for correcting sample Re data. The Os standard (AB2), made from ammonium hexachloro-osmate, yields an $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.10679 ± 0.00007 (1SD, n = 6), using an electron multiplier. This value is identical to that reported by Selby et al. (2006).

Results

The abundances of Re and Os for the Staffin black shale at the Oxfordian-Kimmeridgian boundary are between 13 - 50 ppb and 194 - 490 ppt, respectively. The $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios range from 374 - 902, and 1.4856 - 2.8436, respectively (Table 1). Isotope geochronology requires the use of the most accurate and precise decay constants (Begemann et al. 2001). The $\lambda^{187}\text{Re}$ of $1.666 \times 10^{-11} \text{ a}^{-1} \pm 0.005$ ($\pm 0.35\%$) (Smoliar et al. 1996) is the value most widely applied in Re-Os geochronology. However, other studies have suggested different values for $\lambda^{187}\text{Re}$ (Shukolyukov & Lugmair 1997, Birck & Allègre 1998). An important test of the $\lambda^{187}\text{Re}$ value has recently been provided by the inter-calibration of the Re-Os molybdenite and U-Pb zircon chronometers from magmatic ore systems (Selby et al. 2007). This study obtained a $\lambda^{187}\text{Re}$ value ($1.6668 \times 10^{-11} \text{ a}^{-1} \pm 0.20\%$) almost identical (within 2σ uncertainty) with that of Smoliar et al. (1996) by different methods.

Regression of the Re-Os data ($n = 9$) yields a Model 3 isochron age of 154.1 ± 2.1 Ma (95% conf., ± 1.4 % age uncertainty 2σ , Mean Squared Weighted Deviate [MSWD] = 4.6), with an initial $^{187}\text{Os}/^{188}\text{Os}$ value of 0.53 ± 0.02 (Fig. 4). The 2σ Model 3 age uncertainties determined by *Isoplot* assume that the scatter about the linear regression is

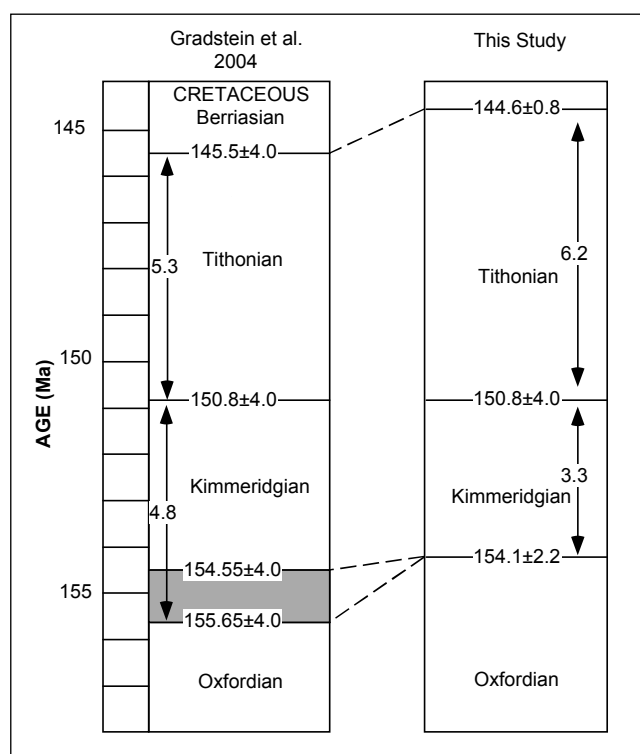


Fig. 5. Shows the Late Jurassic time scale of Gradstein et al. (2004) and the new time scale based on the Re-Os age for the Oxfordian/Kimmeridgian Staffin Shale Member and the Early Berriasian Ar-Ar age (Mahoney et al. 2005). The new ages suggest, based on the age for the Kimmeridgian/Tithonian boundary (150.8 ± 4.0 Ma), that the Kimmeridgian and the Tithonian are nominally 1.6 m.y. shorter and 0.9 m.y. longer, respectively.

a combination of assigned uncertainties, including an unknown initial $^{187}\text{Os}/^{188}\text{Os}$ ratio variation. The inset plot in Figure 4 illustrates the fit of data points as a percent deviation from the regression line, which are all < 0.6 %.

Propagating the uncertainty for the slope of the regression determined from *Isoplot*, together with a 0.31% uncertainty for $\lambda^{187}\text{Re}$ (Smoliar et al. 1996), the Re-Os age for the Oxfordian-Kimmeridgian boundary is 154.1 ± 2.2 Ma. The initial Os ratio (0.53 ± 0.02) is interpreted to represent the local Os seawater composition during the Oxfordian-Kimmeridgian transition.

Discussion

Basal Kimmeridgian Re-Os black shale dating

The absence of high-precision radiometric ages for the Late Jurassic has resulted in the present time scale being determined by correlation of ammonite zones with the M-sequence polarity scale, established using the Hawaiian anomalies in the Pacific. The spreading rate used for the M-sequence polarity scale is constrained only by two radiometric ages. These are a K-Ar age of 155.3 ± 6.8 Ma (2σ) for a celadonite vein in a basalt, which is assigned to the middle of Chron M26n (Ludden 1992) and an ^{40}Ar - ^{39}Ar plateau age of 167.7 ± 3.4 Ma (2σ), correlated to Chron M41 (Koppers et al. 2003). A second age for Chron 26n is given by a total fusion ^{40}Ar - ^{39}Ar basalt age of 155 ± 6 Ma (2σ). Though the latter age is considered unreliable (Pálffy et al. 2000), Gradstein et al. (2004) applied a 155 Ma age for scaling the Late Jurassic M-sequence because both ages for Chron 26n are nominally identical.

The Boreal realm correlates the base of the *baylei* Zone to the lower part of polarity Chron 26r, which is dated at 155.7 ± 4.0 Ma (2σ). The Tethyan environment correlates the *platynota* Zone to Chron M25r at 154.6 ± 4.0 Ma (2σ). Calibration of the magnetostratigraphy to Boreal and Tethyan (Sub-Mediterranean) ammonite stratigraphy presently yields two ages that are within uncertainty for the base of the Kimmeridgian (Gradstein et al. 2004) (Fig. 5). Though the Tethyan Kimmeridgian is nominally 1 m.y. younger than the Boreal realm, both ages are in agreement with the statistically determined age for the basal Kimmeridgian of $154.7^{+3.8}_{-3.3}$ Ma (2σ) (Pálffy et al. 2000).

Direct Re-Os dating for the basal Kimmeridgian of the Staffin Shale Formation, which is based on boreal and subboreal ammonite biostratigraphy, and can be correlated with the Sub-Mediterranean zonal scheme using the secondary standard parallel zonation (Callomon 2004, Matyja et al. 2004, 2006), constrains the boundary to 154.1 ± 2.2 Ma (2σ). This age, including its uncertainty, is identical to the mathematically determined values for the base of the Kimmeridgian. However, the Re-Os age eliminates the assumptions and uncertainties used in the

magnetostratigraphy (Pálffy et al. 2000, Gradstein et al. 2004). In addition, the direct Re-Os age determination is ~ 45% (1.8 m.y.) more precise than current boundary estimates.

Since the formulation of the Geologic Time scale 2004 (Gradstein et al. 2004) a direct age for the basal Berriasian (Jurassic-Cretaceous boundary) has been reported (mean ^{40}Ar - ^{39}Ar age 144.6 ± 0.8 Ma, Mahoney et al. 2005). This age is from volcanic sills in the Pacific Ocean present in the lowermost Berriasian sediments established by both calcareous nanofossils (Zone NK1, Bralower et al. 1989) and radiolaria (*Pseudodictyomitra carpatica* Zone, Matsuoka & Yang 2005). The ^{40}Ar - ^{39}Ar age is nominally 1 m.y. younger than the statistically determined value for the 2004 time scale (145.5 ± 4.0 Ma; Gradstein et al. 2004). The Ar-Ar age for the Early Berriasian and the Re-Os age for the basal Kimmeridgian suggest that the nominal duration for the Kimmeridgian and Tithonian stages is 9.5 m.y. (Fig. 5). This duration is 650 k.y. shorter than previously determined using the boreal biostratigraphic scheme (chron 26r) and M-sequence polarity scale (Gradstein et al. 2004, Fig. 5). Using the new Re-Os age (this study), together with the statistical estimate for the basal Tithonian (150.8 ± 4.0 Ma; Gradstein et al. 2004) and the ^{40}Ar - ^{39}Ar age (Mahoney et al. 2005) the nominal durations for the Kimmeridgian and Tithonian are 1.6 m.y. shorter and 0.9 m.y. longer, respectively, than previously determined (Gradstein et al. 2004, Fig. 5). The latter suggests that the rates of processes of the Late Jurassic were significantly different than previously thought. Future research to establish the age of the basal Tithonian will further benefit in defining the absolute duration(s) of the last two stages of the Late Jurassic and, in turn, the rate of processes (e.g., flora and fauna evolution, plate tectonics) during this geologic interval.

Late Jurassic Os seawater composition and evolution

In addition to yielding an age for the base of the Kimmeridgian, the Re-Os isochron approach determines the initial Os isotopic composition of the Staffin Shale Fm. (Fig. 4), which is interpreted to represent the hydrogenous Os isotopic composition of seawater during the time of deposition (Ravizza & Turekian 1989, Cohen et al. 1999). The residence time (10 and 40 ka) for Os in the ocean allows for short-term changes in the ancient seawater Os isotope composition to be established from the Re-Os black shale data (cf. Peucker-Ehrenbrink & Ravizza 2000 and references therein). Hydrogenous Os in seawater is dominantly controlled by the dissolution of weathered upper crust material (Esser & Turekian 1993). Analyses of continental shelf sediments and loess have been used to estimate an upper crust average Os abundance of 50 ppt, with $^{187}\text{Os}/^{188}\text{Os}$ values between ~1.4 and 2.0 (Esser & Turekian 1993 – values recalculated using $\lambda^{187}\text{Re}$ of Smoliar et al. 1996). The $^{187}\text{Os}/^{188}\text{Os}$ compositions are determined using model ages for upper continental crust (1.46 and 2.20 Ga). Therefore, less radiogenic $^{187}\text{Os}/^{188}\text{Os}$ compositions may

result from the weathering of younger crust (e.g., 1 Ga = 1.0, 0.5 Ga = 0.6, 0.1 Ga = 0.2). The seawater Os isotope composition can also be affected by the Os contribution of weathered ultramafic/mafic rock units, hydrothermal activity and extraterrestrial material that will have non-radiogenic values (~0.12-0.13, Allégre & Luck 1980, Meisler et al. 1996, Cohen & Coe 2002). Given the likely Os input characteristics (abundance and isotope composition) to the ocean, the $^{187}\text{Os}/^{188}\text{Os}$ value (0.53 ± 0.02) determined from the Staffin Shale Formation suggests that the Oxfordian-Kimmeridgian seawater reflects a predominantly (80%) radiogenic Os composition derived from weathering of the upper crust of ≥ 0.5 Ga.

A Re-Os isochron for the Lower Tithonian (*P. wheatleyensis* Subzone) Kimmeridge Clay Formation, Dorset, UK, gave a very similar initial $^{187}\text{Os}/^{188}\text{Os}$ value (0.59 ± 0.07 , Cohen et al. 1999) to the Oxfordian/Kimmeridgian Staffin Shale reported here. However, the determined Re-Os age for the Kimmeridge Clay is 155 ± 4.3 Ma (2σ) (Cohen et al. 1999). This age, including its uncertainty, overlaps the age for the Lower Tithonian *P. wheatleyensis* Subzone (150 ± 4 Ma, Gradstein et al. 2004). The Re-Os data for the Kimmeridge Clay were determined by an *aqua regia* digestion method. This protocol is now known to liberate exotic detrital Re and Os that can affect the accuracy and precision of Re-Os black shale geochronology and will also off-set initial Os isotope compositions (Selby & Creaser 2003, Kendall et al. 2004). Regardless, the $^{187}\text{Os}/^{188}\text{Os}$ value of 0.59 ± 0.07 is likely a good approximation of the seawater Os isotope composition (Selby & Creaser 2003b, Kendall et al. 2004) and is within the uncertainty of the value determined here.

In contrast, to the lower Tithonian and basal Kimmeridgian, the Callovian seawater determined from the Oxford Clay Formation (162.2 ± 4.0 – 164.7 ± 4.0 Ma, Gradstein et al. 2004), also using the *aqua regia* method, has an Os isotope composition of 0.25 to 0.27 (mean value of 0.26 ± 0.01 , 1SD) (Cohen 2004). The duration between the Late Callovian and Early Kimmeridgian and basal Early Kimmeridgian and Early Tithonian is nominally 7 and 4 m.y., respectively (Gradstein et al. 2004, this study). During this time, short-term variations in the seawater Os isotope composition could have occurred as shown during the Early and mid Jurassic (Cohen & Coe 2002, 2007, Cohen et al. 2004).

The reconstruction of the Phanerozoic Os marine isotope record is poor (Cambrian, Mao et al. 2002, Devonian-Mississippian, Selby & Creaser 2005), with the exception of the Late Triassic and Jurassic (Cohen & Coe 2002, 2007, Cohen 2004, Cohen et al. 2004, this study). These studies show that the $^{187}\text{Os}/^{188}\text{Os}$ values for seawater are typically between 0.4 and 0.8. Fluctuations to non-radiogenic Os isotope values (~0.1 to 0.3) are interpreted to reflect low levels of contribution from the upper crust (Callovian, Cohen 2004) and weathering of basalt lavas (Cohen & Coe 2002, 2007).

In the absence of data between the Callovian and Kimmeridgian, evidence from the Kimmeridgian (this study) and the Tithonian (Cohen et al. 1999) suggests that the Os isotope composition of seawater returned to a more common radiogenic signature during the Late Jurassic. The contrast in the Os isotope composition of seawater for the Callovian to the Kimmeridgian and Tithonian may reflect an increase in the continental weathering rates since the Callovian.

The observation of significantly more radiogenic Os isotope compositions for Late Jurassic seawater is also mirrored by $^{87}\text{Sr}/^{86}\text{Sr}$ values, which show an increase from 0.7067 (Callovian/Oxfordian boundary), the lowest value recorded for the Phanerozoic, to values of 0.7069 (Oxfordian/Kimmeridgian boundary) to 0.7071 for the mid-Lower Tithonian (Jones et al. 1994). The Sr and Os isotope data record the seawater (NW European seaway) geochemical characteristics of the boreal/subboreal province (Sykes & Callomon 1979). This is a relatively small area, which includes, in addition to areas of the UK, parts of central and northern Europe, areas of Greenland and the area west of the Urals. However, similar trends shown by $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}_{\text{org}}/\text{carb}$ values between the Kimmeridgian to Tithonian from the Tethyan realm (Switzerland, New Zealand) suggest that the geochemical trends reflect the global characteristics of the Late Jurassic seawater (Jenkyns et al. 2002, Gröcke et al. 2003). As a result, the return towards more radiogenic Os and Sr isotope values between the Callovian and Tithonian may reflect a quiescence in hydrothermal activity, and/or a change in the flux of radiogenic Os and Sr to the global Jurassic ocean due to an increase in the continental weathering rate (Jones et al. 2001, Cohen 2004). The large change in the seawater $^{187}\text{Os}/^{188}\text{Os}$ composition between the Callovian and Kimmeridgian in comparison to $^{87}\text{Sr}/^{86}\text{Sr}$ values, coupled with the low Os abundance of the crust, makes the Os isotopic compositions determined from black shale a potential ideal tracer for the source of Os to the ocean.

Conclusion

The proposed GSSP for the basal Kimmeridgian exposed at Staffin bay, Isle of Skye, U.K., has been directly dated at 154.1 ± 2.2 Ma (2σ) using the Re-Os isotope system. The Re-Os age is in excellent agreement with previous statistical estimates, but is $\sim 45\%$ (1.8 m.y.) more precise and thus allows a confident re-evaluation of the duration of the Kimmeridgian and Tithonian stages to be made. The Re-Os data also indicates that the Oxfordian-Kimmeridgian ocean had a $^{187}\text{Os}/^{188}\text{Os}$ composition of 0.53 ± 0.02 (2σ). This value is within uncertainty of that for the lower Tithonian ($^{187}\text{Os}/^{188}\text{Os} = 0.59 \pm 0.07$ (2σ)), but contrasts with the Late Callovian seawater ($^{187}\text{Os}/^{188}\text{Os} = 0.26 \pm 0.01$ (1SD)). These data may suggest an increase in the rate of continental weathering since the Late Callovian. The Re-Os data of this study support the excellent

potential of the Re-Os black shale geochronometer for improving the geologic time scale (Selby & Creaser 2005). Further, large variations in $^{187}\text{Os}/^{188}\text{Os}$ compositions over short time periods in comparison to other isotope systems (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$) highlight the potential for Os isotopic compositions in tracking ancient oceanic chemical evolution (Cohen 2004, Cohen & Coe 2007, this study)

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