Pulses of enhanced continental weathering associated with multiple Late Devonian climate perturbations: Evidence from osmium-isotope compositions

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ABSTRACT

Anomalously high rates of continental weathering have frequently been proposed as a key stimulus for the development of widespread marine anoxia during a number of Late Devonian environmental and biospheric crises, which included a major mass

extinction during the Frasnian–Famennian transition (marked by the Upper and Lower Kellwasser horizons). Here, this model is investigated by presenting the first stratigraphic record of osmium-isotope trends ($^{187}Os/^{188}Os$) in upper Devonian strata from the Kowala Quarry (Holy Cross Mountains, Poland). Changes in reconstructed $^{187}Os/^{188}Os$ seawater values to more radiogenic compositions are documented at the base of both the Lower (~0.42 to ~0.83) and Upper (~0.31 to ~0.81) Kellwasser horizons characteristic of the Frasnian–Famennian transition, and additionally within upper Famennian shales that record a more minor environmental perturbation known as the Annulata Event (~0.20 to ~0.53). These shifts indicate the occurrence of extremely enhanced continental weathering rates at the onsets of the Kellwasser crises and during the later Annulata Event. The similarity of $^{187}Os/^{188}Os$ values in this study from Frasnian–Famennian boundary and lower Famennian strata (between 0.4–0.5) to those from North American stratigraphic equivalents suggests that the $^{187}Os/^{188}Os$ values record global trends. These findings support a causal relationship between increased continental weathering (and thus, nutrient supply to the marine shelf) and the environmental perturbations that occurred during numerous Late Devonian events, including both of the biospherically catastrophic Kellwasser crises as well as other, less severe, oceanic anoxic events.

1. Introduction

The Late Devonian (~383–359 Ma) marked a time of numerous environmental and biotic crises, including one of the 'Big Five' mass extinctions of the Phanerozoic Aeon during the Frasnian–Famennian (F–F) transition (see reviews in Racki, 2005; Bond and Grasby, 2017). Although the magnitude of extinction and/or environmental perturbation appears to have greatly varied between the Late Devonian crises, a common feature of these events was the development of widespread marine anoxia, typically recorded by the appearance of organic-rich laminated shales in the stratigraphic record (e.g., Joachimski and Buggisch, 1993; Walliser, 1996; Bond *et al*., 2004; Racka *et al*., 2010; Becker *et al*., 2016; Bond and Grasby, 2017). Two such anoxic episodes are documented to have occurred during the late Frasnian, widely known as the Lower (LKW) and Upper (UKW) Kellwasser events (~372 Ma), the latter of which coincided with the F–F transition and the associated mass extinction. Subsequent spells of marine anoxia during the Famennian Stage included the Annulata (~363 Ma) and Hangenberg (~359 Ma) events at the end of the Devonian Period, with the Hangenberg Event characterized by another major mass extinction (see reviews by Kaiser *et al*., 2016; and Bond and Grasby, 2017). The ultimate causes of the various Late Devonian environmental perturbations remain debated. Numerous triggers have been postulated for the Kellwasser crises, including extra-terrestrial impacts (e.g., Wang, 1992; Claeys *et al*. 1996; Du *et al*., 2008), large-scale volcanic activity potentially linked to the Viluy Traps in Siberia (e.g., Courtillot *et al*., 2010; Ricci *et al*., 2013; Racki *et al*., 2018), orogenic uplift and erosion (Averbuch *et al*., 2005), and the expansion of vascular-rooted terrestrial flora (Algeo *et al*., 1995; Algeo and Scheckler, 1998). Many of the environmental perturbations also appear to have coincided with climate cooling (e.g., Streel *et al*., 2000; Joachimski and Buggisch, 2002; Balter *et al*., 2008). The Annulata anoxic event was coeval with a major marine transgression (Johnson *et al*., 1985), and may also have coincided with a major pulse of volcanic activity (Percival *et al*., 2018). In contrast, Southern-Hemisphere glaciation, and associated continental weathering and marine regression, has been most frequently proposed as having caused the end-Famennian Hangenberg Event (e.g., Streel *et al*., 2000; Kaiser *et al*., 2016; Lakin *et al*., 2016). Whatever initiated the various Late Devonian crises and caused any associated extinctions, in all cases the development of marine anoxia has been proposed to have been driven by internal triggers. One such postulated trigger is an enhancement of global weathering rates and an associated flux of nutrients to the marine realm, which stimulated increased primary productivity and consumption of oxygen in the water column (e.g., Wilder, 1994; Algeo *et al*., 1995; Algeo and Scheckler, 1998; Averbuch *et al*., 2005; Chen *et al*., 2005; Whalen *et al*., 2015).

This study presents a new long-term stratigraphic record of sedimentary osmium (Os) isotopes (specifically $^{187}Os/^{188}Os$) from rocks that span mid Frasnian up to upper Famennian strata (that represent approximately 20 million years of Late Devonian time). The $^{187}Os/^{188}Os$ composition of sedimentary rocks can track changes in both continental weathering rates and the influx of mantle/meteorite material into the global oceans, due to proportional mixing of inputs to the oceanic inventory from extra-terrestrial and mantle-derived-volcanic osmium ($^{187}Os/^{188}Os$ of 0.13: Allègre *et al*., 1999) and the riverine supply of the element from weathering of the continental crust (average $^{187}Os/^{188}Os$ of ~1.4: Peucker-Ehrenbrink and Jahn, 2001). The marine residence time of Os (10–50 kyr or less; Peucker-Ehrenbrink and Ravizza, 2000; Rooney *et al*., 2016) results in a homogeneous Os-isotope composition throughout the open ocean. Hydrographically restricted basins may have different seawater Os-isotope values, determined by local sources of the element, if their water-mixing time with the global ocean is longer than the lifetime of marine Os (Paquay and Ravizza, 2012; Du Vivier *et al*., 2014; Dickson *et al*., 2015; Percival *et al*., 2016). Past seawater Os-isotope compositions ($Os_{(i)}$) can be calculated from a sedimentary rock after accounting for radiogenic ^{187}Os produced from post-deposition decay of ^{187}Re (rhenium), assuming that the sedimentary system has remained closed with respect to Re and Os, and that the age of the studied sample is known (Cohen *et al*., 1999).

Previous studies of Late Devonian sedimentary records have utilized Re–Os isochrons (based on the known half-life of the decay of ^{187}Re to ^{187}Os) to date organic-rich strata from a number of North American sequences (Figure 1). This technique can also determine the isotopic composition of the sediment at the time of deposition ($Os_{(i)}$), and thus, for an open-marine palaeoenvironment, the Os-isotope signature of the global ocean at that specific time. Following these investigations, the Late Devonian (particularly Famennian) ocean is considered to have had an average $^{187}Os/^{188}Os$ composition of ~0.46 (Figure 2), with values of ~0.45 and 0.42 measured at the Frasnian–Famennian and Devonian–Carboniferous (D–C) boundaries, respectively (Selby and Creaser, 2005; Turgeon *et al*., 2007; Gordon *et al*. 2009; Harris *et al*., 2013). However, trends in Os-isotope values across the stratigraphic sequences of specific Late Devonian events, such as the Kellwasser crises, have not been previously documented. Consequently, it is unknown how the global Os inventory responded to possible influences from any or all of the postulated meteorite impacts, volcanic activity, or enhanced continental weathering rates thought to have occurred during the various Late Devonian environmental perturbations (e.g., Wang, 1992; Claeys *et al*., 1996; Algeo and Scheckler, 1998; Averbuch *et al*., 2005; Chen *et al*., 2005; Courtillot *et al*., 2010; Ricci *et al*., 2013; Whalen *et al*., 2015; Racki *et al*., 2018).

The Kowala Quarry (hereafter termed Kowala), near the town of Kielce in the Holy Cross Mountains, Poland, records a well-known long-term record of the Late Devonian, with strata from the lower Frasnian through to basal Tournasian (Early Carboniferous) series well constrained by conodont biostratigraphy (Szulczewski, 1996; see figure 1 in De Vleeschouwer *et al*., 2013). The sediments were deposited in the Chęciny–Zbrza intra-shelf basin, which was surrounded by more elevated shoal areas that formed part of a very large carbonate platform on the north-eastern part of Laurentia (Figure 1, see also review by Racki *et al*., 2002). The presence of conodont fossils found across Europe, North America, and South China (Szulczewski, 1971, 1996) indicates that marine organisms could certainly migrate between the basin and global ocean, although the degree of connectivity between those two environments in terms of water-mass mixing remains unknown. Organic-rich shales (interbedded with limestones) are prevalent throughout much of the Kowala stratigraphic sequence, ideal for Re–Os analysis due to the uptake of both Re and Os from seawater into organic muds during deposition (Ravizza and Turekian, 1989; Cohen *et al*., 1999). The UKW Horizon has been well documented at Kowala on the basis of conodont biostratigraphy (Szulczewski, 1971, 1996), an elevated total organic carbon (TOC) content, and a positive carbon-isotope (δ^{13}C) excursion of up to 4 ‰ in both carbonates and bulk and compound-specific organic matter (Joachimski *et al*., 2001), which is characteristic of both Kellwasser events in stratigraphic archives across the globe (e.g., Joachimski and Buggisch, 1993; Chen *et al*., 2005; De Vleeschouwer *et al*., 2017). This stratigraphic positioning of the UKW Horizon is supported by several other indications of marine anoxia such as pyrite framboid size populations and trace metal contents (e.g., vanadium/chromium ratios), all of which show perturbations just below the F–F boundary (Joachimski *et al*., 2001; Racki *et al*., 2002; Bond *et al*., 2004). The position of the LKW Horizon has been inferred previously from the appearance of organic-rich shales about 10 metres below the UKW Horizon in the Late *rhenana* conodont Zone, consistent with other western European records and supported by lithological evidence for marine anoxia, although the positive δ^{13}C excursion characteristic of the LKW Horizon is not well defined at Kowala (Joachimski *et al*., 2001; Bond *et al*., 2004). Several Famennian episodes of marine anoxia/euxinia are also well known from the appearance of black shale horizons higher in the Kowala Quarry sequence, with both the Annulata and Hangenberg Events recorded (e.g., Bond and Zatoń, 2003; Racka *et al*., 2010; Marynowski *et al.*, 2012).

For this study, sedimentary rocks from both Kellwasser horizons and the Annulata and Hangenberg shales at Kowala, together with sediments from seven Frasnian and Famennian stratigraphic levels that were deposited between the times of the individual Late Devonian events, were analyzed to determine their $Os_{(i)}$ compositions. New samples were taken from throughout the Kowala stratigraphic sequence in September 2017 (including the Lower Kellwasser, Annulata, and Hangenberg shales), and combined with rocks from an unpublished sample-set spanning the F–F boundary, collected in 2009 by Michal Rakociński and Leszek Marynowski (part of the Global Archive of Devonian System Samples at the University of Silesia, Sosnowiec, Poland). Where possible, the results were compared to $Os_{(i)}$ values in rocks from time-equivalent strata in North America. Because Kowala is an active quarry, it is no longer possible to sample the exact section studied by Joachimski *et al*. (2001); therefore, $\delta^{13}C$, TOC, and trace-metal data were also determined for uppermost Frasnian samples in order to constrain the stratigraphic position of the Kellwasser horizons, particularly the less well defined LKW Level. Finally, in order to better understand the degree of hydrographic connectivity between the Chęciny–Zbrza Basin and the global ocean during the Late Devonian, sedimentary molybdenum and uranium enrichment values were ascertained for a combination of the new samples collected for this study and additional material from a third Kowala sample-set, previously described by Bond *et al*. (2004), which collectively spanned the entire stratigraphic sequence from upper Frasnian to upper Famennian strata.

2. Methods

Preparation of samples for Re–Os analysis was performed in the Laboratory for Source Rock Geochronology and Geochemistry at Durham University (UK), utilising carius-tube digestion with

$Cr^{IV}O_3$-H_2SO_4, and Os purification using solvent extraction (by chloroform) and microdistillation techniques, following the procedure in Selby and Creaser (2003). Re purification was carried out by anion chromatography following treatment with NaOH and acetone (after Cumming *et al*., 2013). Isotope compositions and concentrations of Re and Os were determined by isotope dilution and negative thermal ionisation mass spectrometry (N-TIMS) on a ThermoScientific Triton in the Arthur Holmes Laboratory at Durham University. In-house standards were used to monitor analytical reproducibility (see Nowell *et al*., 2008; and supplementary information in Du Vivier *et al*., 2014). The $^{187}Os/^{188}Os$ and $^{187}Re/^{185}Re$ values generated during sample analysis were 0.16077±0.00032 (1 σ) and 0.59777±0.00147 (1 σ), respectively, consistent with running averages for the laboratory (see Supplementary Tables).

All other accompanying geochemical analyses were undertaken at the University of Lausanne (Switzerland). Total organic carbon (TOC) analyses were performed on bulk rock samples using a Rock Eval 6 (see Behar *et al*., 2001). New $\delta^{13}C$ data were generated as described in Fantasia *et al*. (2018a). Carbonate $\delta^{13}C$ ($\delta^{13}C_{carb}$) compositions were ascertained using a Thermo Fisher Scientific Gas Bench II connected to a Delta Plus XL isotope ratio mass spectrometer, following reaction of precisely weighed aliquots of powdered samples with anhydrous phosphoric acid at 70 ˚C. Bulk organic-matter $\delta^{13}C$ ($\delta^{13}C_{org}$) compositions were determined on aliquots of samples that had been decarbonated using 10% HCl and subsequently rinsed multiple times with deionized water and milli-Q purified water to restore a neutral pH and dried at 40 ˚C, using flash combustion on a Carlo Erba 1108 elemental analyser connected to a Thermo Fisher Scientific Delta V isotope ratio mass spectrometer. Analytical uncertainty was ±0.06 ‰ (1 σ) for $\delta^{13}C_{carb}$, as determined by repeated measurements of a Carrara marble internal standard (7 per 45 unknown samples), and ±0.15 ‰ (1 σ) for $\delta^{13}C_{org}$, based on analyses of internal laboratory and international standards.

Aluminium abundances were established via X-ray fluorescence (XRF) of fused lithium tetraborate glass discs, using a PANalytical PW2400 spectrometer. To create the glass discs, 2.5–3 g (depending on the carbonate content) of powdered bulk sample was measured and its precise mass determined. The weighed samples were baked at 1050 ˚C for 3 hours, weighed again to ascertain the mass lost during calcination, and re-powdered. Exactly 1.2 g of the new powder was mixed with precisely 6 g of $Li_2B_4O_7$ material, and the resultant mixture heated in a platinum crucible at 550 ˚C for 10 minutes to form a fused lithium tetraborate glass disc. The glass was left to cool for at least 5 minutes before being labelled for identification during analysis. The analytical uncertainty of this technique has been shown previously to be lower than ±5% (Fantasia *et al.*, 2018b).

Molybdenum (^{95}Mo) and uranium (^{238}U) contents were determined by laser-ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) on fragments of the glass discs used for XRF analysis (see above). Analysis was conducted using an Element XR sector-field ICP-mass spectrometer interfaced to a NewWave UP-193 ArF excimer ablation system, which fired a 150 μm diameter laser beam with 5 J/cm^2 on-sample energy density at a repetition rate of 10 Hz. A 90 second background was taken before three separate firings of the laser (of 50 seconds duration, with 15–20 seconds between each firing). CaO wt% obtained by XRF analysis (see above) was used as an internal standard, with a sample of NIST-SRM612 glass employed as an external standard. Data reduction was carried out using LAMTRACE software (Longerich *et al.*, 1996), with reproducibility generally within ±5% for Mo and ±1% for U (1 σ). Full geochemical data are presented in the Supplementary Tables.

3. Results

A clear increase in TOC content, correlative with positive excursions in $\delta^{13}C$ values of both carbonates and bulk organic-matter, is recorded 2 m below the F–F boundary (Figure 3). These trends are consistent with previous findings (Joachimski *et al.*, 2001), and, when combined with biostratigraphic information (Racki *et al.*, 2002), are likewise interpreted as indicating the position of the UKW Horizon in the absence of the bituminous shales that typically define the Kellwasser levels in western Europe. An additional set of organic-rich shale layers is also observed 11–12 m below the F–F boundary (~10 m below the base of the UKW Horizon), which is marked by elevated TOC contents and an enrichment in both uranium and molybdenum concentrations (Figure 3). These results indicate that a brief period of marine anoxia occurred in this area prior to, and distinct from, the UKW Event. This level is tentatively interpreted as marking the LKW Horizon. Whilst the absence of biostratigraphic information in the new sample set means that it cannot be verified that this shale layer assumed to be the LKW Horizon occurs within the *Late rhenana* Zone, the position of the level 11–12 m below the base of the F–F boundary matches the biostratigraphic and chemostratigraphic positioning of the LKW at Kowala by Joachimski *et al*. (2001). No positive excursion in either $\delta^{13}C_{carb}$ or $\delta^{13}C_{org}$ is documented at this stratigraphic level, similarly to Joachimski *et al*. (2001) who found only a very minor increase in $\delta^{13}C_{carb}$ values and a single-data-point positive excursion in $\delta^{13}C_{org}$ at their inferred LKW Horizon 12 m below the F–F boundary. In the absence of a positive $\delta^{13}C$ excursion, or detailed conodont biostratigraphy for the new samples, the inferred LKW horizon in this study cannot be stratigraphically correlated with other Late Devonian records, and it cannot be ruled out that this level actually marks a spell of localized anoxia that was unrelated to the LKW Event. Nevertheless, the similarity in geochemical perturbations and stratigraphic position (relative to the F–F boundary) of the layer interpreted as the LKW Horizon here compared to the LKW shale at Kowala established by previous studies (Joachimski *et al*., 2001; Racki *et al*., 2002) means that it is not unreasonable to assume that this episode of marine anoxia prior to the UKW Event was indeed the local manifestation of the LKW crisis. This interpretation is followed hereafter in the results and discussion.

Variations in the enrichment trends of Mo and U throughout upper Frasnian to upper Famennian strata match the patterns expected in a marine basin where the drawdown of molybdenum is dominated by particulate shuttling (Figure 4). This system of molybdenum scavenging relies on a reducing water column. Consequently, it is most prevalent today in marine basins that are at least semi-restricted hydrographically with respect to the global ocean (Algeo and Tribovillard, 2009; see also Algeo and Howe, 2012, and references therein), which has also been proposed for various marine basins from other times in Earth's history (Tribovillard *et al*., 2012), although reducing settings dominated by upwelling have also been shown to feature particulate-shuttle drawdown of molybdenum (Zheng *et al*., 2000).

Stratigraphic trends in $Os_{(i)}$ from Kowala are shown in Figure 2A, where the succession has been split into six divisions (A–F) to aid interpretation. Background $Os_{(i)}$ values of the two lowest Frasnian samples from below the inferred LKW Horizon (division A) and Famennian samples between the UKW and Annulata horizons (division E) are relatively consistent: typically between 0.4–0.5 (mean ~0.52). Contrastingly, there are significant deviations from this background in $Os_{(i)}$ values across the two Kellwasser horizons and the Annulata shales. The base of the LKW Horizon records a very radiogenic $Os_{(i)}$ value of ~0.93, and another peak at ~0.73 just below that level, separated by a return to near background values (division B). The upper part of the LKW Horizon documents a much more unradiogenic $Os_{(i)}$ composition of ~0.21, and a very high content of common osmium (represented as ^{192}Os), albeit based on analysis of just one sample. $Os_{(i)}$ compositions between the two Kellwasser horizons also fluctuate, but to a lesser extent (division C), with both somewhat unradiogenic and a slightly radiogenic value documented, relative to the Late Devonian background. Just below the UKW horizon there is a second increase in $Os_{(i)}$ values from ~0.31 to a peak of ~0.81 (division D). The remainder of samples from the UKW Horizon have a relatively consistent $Os_{(i)}$ composition of ~0.40, comparable to the Late Devonian background (division D), except for the sample closest to the F–F boundary itself, which has an anomalous $Os_{(i)}$ value of -0.25. Above the UKW Horizon, Famennian samples also show relatively consistent $Os_{(i)}$ values of 0.45–0.5 (division E), with only one sample deposited in the *marginifera* Zone recording a more radiogenic $Os_{(i)}$ composition of 0.73. Just below and above the Annulata shales rather unradiogenic $Os_{(i)}$ values of ~0.2 and ~0.35 are documented, respectively, but there is a more radiogenic composition of ~0.53 in the main body of the Annulata shales (division F). A large variability in $Os_{(i)}$ values was also documented in the four samples from the Hangenberg Level, but no clear trend is shown, and two of the four samples recorded compositions well outside the expected range of 0.13 to 1.4 for an open-marine setting (0.06 and -0.91; Supplementary Figure 1).

4. Discussion

4.1. Comparison of Kowala Os-isotope values with North American records

Only one sedimentary horizon from significantly below the Kellwasser horizons at Kowala was investigated for this study, with an $Os_{(i)}$ ratio of 0.61 in the mid Frasnian *punctata* conodont Zone (Figure 2). In contrast, Re–Os isochron data from the only previously studied sedimentary layer that was deposited prior to the LKW Event (from Pecos County Well of the Permian Basin in Texas, USA) recorded a value of 0.29 (Harris *et al.*, 2013). However, this discrepancy in pre-LKW $Os_{(i)}$ values between Kowala and Texas might be because the studied sediments are not time equivalent, as the limited biostratigraphic constraints on the Pecos County Well hinders stratigraphic correlation of that record with those from elsewhere. Therefore, it is currently difficult to constrain a true global-ocean Os-isotope composition for the Frasnian prior to the Kellwasser crises.

North American Os-isotope studies of the F–F boundary and sediments just above (uppermost *linguiformis – marginifera* Zones), across multiple stratigraphic sequences, indicate a global-ocean Os-isotope composition of 0.4–0.5 at the end of the Frasnian Stage and during the earliest Famennian (Figure 2B; see Turgeon *et al.*, 2007; Gordon *et al.*, 2009; Harris *et al.*, 2013). These values are broadly consistent with the results from within UKW and lowermost Famennian strata at Kowala (Figure 2), suggesting that sediments from both Kowala and the North American records were deposited in marine settings where water masses were well mixed with the global ocean. The Late Devonian $Os_{(i)}$ average from North America (~0.46) is also very similar to the Os-isotope compositions recorded in Frasnian–Famennian boundary and lower–mid Famennian strata at Kowala, supporting this hypothesis. An elevated $Os_{(i)}$ value of 0.59 from an upper Famennian level in the Permian Basin might be equivalent to the shift towards more radiogenic compositions recorded at the top of the *marginifera* Zone at Kowala (Figure 2; Harris *et al.*, 2013), although it cannot be conclusively demonstrated that these stratigraphic levels are the same age due to the lack of biostratigraphy in the Permian Basin record. It should be noted that both here, and in previous studies, Famennian $Os_{(i)}$ information is at low resolution, and more detailed studies of early–mid Famennian shales (as done here for the Kellwasser and Annulata beds) are needed to confirm that the global ocean did indeed experience no short-term changes in its Os-isotope composition over millions of years. Nonetheless, the broad agreement in $Os_{(i)}$ trends across the F–F boundary and lower–mid Famennian strata from Kowala and North America is suggestive that the Chęciny–Zbrza Basin was sufficiently hydrographically well connected to the open ocean with respect to osmium to record the global seawater Os-isotope signature during that time interval, despite indications from the trends in sedimentary Mo and U enrichment factors that water-mass exchange into/out of the basin could have been at least semi-restricted (Figure 4). Apparently semi-restricted basins that record $Os_{(i)}$ trends broadly consistent with changes in the global ocean have been previously reported (e.g., the Toarcian record from the Cleveland Basin, UK; see Cohen *et al*., 2004; Percival *et al*., 2016; Them *et al*., 2017); so the possibility of a global ocean $Os_{(i)}$ signature being recorded at Kowala is not inconsistent with the Mo and U evidence of semi-restriction.

Moreover, both of the Kellwasser crises are thought to have featured significant marine transgressions at their onsets, with a large regression following the UKW crisis (e.g., Johnson *et al*., 1985; Bond and Wignall, 2008). If this was the case, then sea levels should have been higher during the transgressions of the two Kellwasser crises than in Famennian times that followed the post-Kellwasser regression. Higher sea levels should have resulted in an increased hydrographic connectivity between marine-shelf basins and the global ocean. Therefore, given that lower–mid Famennian strata at Kowala appear to record the global-ocean $^{187}Os/^{188}Os$ composition, it would be expected that a similarly open-marine signature should also be documented by sediments deposited during the Kellwasser crises, when sea levels were higher than during the Famennian.

The results from the Hangenberg shales and Devonian–Carboniferous boundary interval at Kowala (see Supplementary Figure 1) do not agree with a previously published $Os_{(i)}$ value of 0.42 from the D–C boundary in North America (Selby and Creaser, 2005). Of the four stratigraphic layers that were studied from that interval at Kowala, two document $Os_{(i)}$ compositions outside the expected range for the open ocean (0.13–1.4), and none match the North American value of 0.42. However, there is evidence of potential trace-metal content alteration in strata at the top of the Kowala Quarry (where the Hangenberg shales and D–C boundary are recorded; Marynowski *et al*., 2017) via weathering of those sediments, which could have remobilized the Re and Os in those sediments and caused the anomalous $Os_{(i)}$ values (Peucker-Ehrenbrink and Hanningan, 2000). A similar problem might also be responsible for the single anomalous data point at the F–F boundary, where it has been previously noted that some sediments appear to have been oxidized by groundwater or hydrothermal fluids (see Racki *et al*., 2002; Bond *et al*., 2004). However, the sample in question does not appear to show the same discolouration as mentioned in those studies.

4.2. Globally enhanced weathering rates during the Frasnian–Famennian transition

If the sediments at Kowala are correctly interpreted as recording the $^{187}Os/^{188}Os$ composition of the open ocean, the significant variations observed in $Os_{(i)}$ values from Frasnian–Famennian boundary strata at that location should reflect changes in the inputs of osmium to that inventory. Consequently, whilst $Os_{(i)}$ values from uppermost Frasnian and lower–mid Famennian strata indicate a relatively consistent global-ocean Os-isotope composition, a shift towards more radiogenic signatures just below the UKW Horizon suggests that the marine realm experienced an influx of relatively radiogenic osmium (or a reduction in primitive osmium input) immediately prior to that event. The shifts towards radiogenic $Os_{(i)}$ values in the lower part of and a little below the LKW Horizon may reflect a similar phenomenon taking place before/during the earlier crisis, assuming that the interpreted position of the LKW Horizon is correct. However, because there is also a return to near-background $Os_{(i)}$ within the more radiogenic values below the LKW Horizon, it is not clear whether these data represent two distinct weathering pulses, or a single pulse partially offset by a coeval influx of unradiogenic osmium. However, in either case, the two radiogenic values within/below LKW strata are suggestive of an increased influx of terrigenous material in the lead up to that crisis. It should be noted though that the inferred hypothesis of radiogenic osmium input is based on only two or three data points for both crises, and should be confirmed by additional higher resolution studies, particularly for the LKW Event.

The most plausible explanation for the increases in global-ocean $Os_{(i)}$ seawater values at the onsets of the two Kellwasser events is a large influx of radiogenic Os derived from enhanced continental weathering rates at those times. This hypothesis is consistent with elemental ratios such as titanium/aluminium, silicon/aluminium, and zirconium/rubidium from numerous other F–F marine records that indicate an increased detrital influx from the continents (e.g., Pujol *et al*., 2006; Whalen *et al*., 2015). Alternatively, a shift towards a more radiogenic $^{187}Os/^{188}Os$ signature in the global ocean might signify a large decrease in mid-ocean-ridge volcanism, but such a change would be expected to occur over millions of years, and would be very unlikely to result in the abrupt changes in seawater $Os_{(i)}$ recorded at Kowala, leaving weathering as the more likely cause.

Interestingly, this interpretation suggests that continental weathering rates were extremely elevated just before and during the onsets of the two Kellwasser crises, but then returned to background levels or below throughout the main body of the two events. This finding is in contrast to detrital-influx and strontium-isotope ($^{87}Sr/^{86}Sr$) studies from Europe, North America and South China (Chen *et al*., 2005; Pujol *et al*., 2006; Whalen *et al*., 2015), which suggest that weathering rates were enhanced throughout the entirety of the two Kellwasser crises. However, strontium is less suitable than osmium for recording the precise timing and/or duration of geologically abrupt changes to the marine inventory due to the very long oceanic residence time of that element (1–4 Myr; Palmer and Edmond, 1989). A prolonged input of terrigenous detrital input to some basins might indeed have occurred, but could have been local to those areas, and not reflective of global-scale changes in continental weathering. An alternative possibility is that enhanced terrestrial runoff did continue throughout the entirety of the Kellwasser crises, but that following the initial pulse of continental weathering, the radiogenic seawater $Os_{(i)}$ composition was offset by an influx of primitive osmium related to some form of volcanic/hydrothermal activity or basalt-seawater interaction. Thus, the published Sr-isotope and detrital-influx trends are not necessarily inconsistent with the findings of this study. Consequently, on the basis of the results presented here and in previous studies (Chen *et al*., 2005; Pujol *et al*., 2006; Whalen *et al*., 2015), it is concluded that the most significant pulses of global continental weathering during the Frasnian–Famennian transition began just prior to the two Kellwasser crises, although enhanced terrestrial runoff may have continued in some areas throughout the events.

A significant increase in global-scale continental weathering rates would likely have resulted in a greatly enhanced delivery of nutrients to the marine realm, elevating primary-productivity levels and consequently stimulating widespread marine anoxia and burial of organic carbon (as previously proposed by e.g., Wilder, 1994; Algeo *et al*., 1995; Algeo and Scheckler, 1998; Averbuch *et al*., 2005), which may then have been sustained by remobilization of nutrients from aquatic sediments under those low-oxygen conditions (Murphy *et al*., 2000). Together with this organic-carbon burial, the enhanced silicate weathering could also have resulted in a drawdown of CO_2 and consequential global cooling, which has also been reported for the two Kellwasser crises (e.g., Joachimski and Buggisch, 2002; Balter *et al*., 2008; Xu *et al*., 2012; Le Houedec *et al*., 2013; Huang *et al*., 2018). Thus, the pattern of enhanced continental weathering rates immediately prior to/during the onsets of the two Kellwasser crises is consistent with evidence of several other environmental perturbations in effect during those times, and follows a relationship between climate change, continental weathering, and/or marine anoxia that is similar to scenarios proposed for a number of other major events throughout the Phanerozoic Aeon (e.g., Kaiser *et al*., 2006; Bond and Grasby, 2017; Jenkyns, 2018). Importantly, these findings also support previous proposals that this weathering acted as an important trigger for degradation to the global environment during the Kellwasser events (Algeo and Scheckler, 1998; Averbuch *et al*., 2005).

4.3. Possible causes of the Frasnian–Famennian weathering pulses

What process or processes initially caused the increase in continental weathering rates remains unclear. Mesozoic Oceanic Anoxic Events (OAEs) have been widely linked to large-scale volcanism, with volcanic CO_2 emissions thought to have triggered atmospheric warming and subsequent increased weathering rates (see review by Jenkyns, 2010). Argon–argon (Ar–Ar) dating of Viluy Trap basalts has indicated a major magmatic pulse of late Frasnian age (~374 Ma; Ricci *et al*., 2013; Polyansky *et al*., 2017), with widespread volcanic activity also taking place on several tectonic rift-systems during the Late Devonian (reviewed in Kravchinski, 2012). A precise coincidence between this volcanism and the Upper Kellwasser Event has been inferred on the basis of mercury enrichments within UKW strata (Racki *et al*., 2018). The very high Os concentration and low $Os_{(i)}$ value of 0.21 from the inferred LKW Horizon observed in this study (Figure 3) may also indicate a major input of unradiogenic Os from primitive mantle-derived volcanism during the earlier event; a meteorite impact might also cause these changes in Os concentration and isotopic composition, but evidence for such a phenomenon during the LKW Event is lacking (Claeys *et al*., 1996; Racki, 1999; Percival *et al*., 2018). However, it should be noted that this pulse in primitive osmium appears above the shift to radiogenic $Os_{(i)}$ values, which would imply that any volcanism during the LKW Event occurred after the weathering pulse. Moreover, there is currently limited evidence that surface warming occurred during the Kellwasser events; rather, those times appear to have been associated with global cooling (e.g., Joachimski and Buggisch, 2002; Balter *et al*., 2008; Le Houedec *et al*., 2013; Huang *et al*., 2018). Possible negative excursions in conodont oxygen-isotope compositions just below the two Kellwasser horizons might indicate brief warming spells at the onsets of the two crises (see Joachimski and Buggisch, 2002), but these trends are far more ambiguous than the pronounced positive shifts interpreted as cooling signals, and could also have resulted from local salinity changes rather than warming. Better evidence of significant global warming is required in order to satisfactorily link the weathering and marine anoxia during the Kellwasser events to volcanism, unless Late Devonian volcanic activity triggered enhanced global weathering via a profoundly different causal mechanism to that proposed for the Mesozoic OAEs.

Increased weathering rates related to global cooling events have been recorded as having coincided with the expansion of Cenozoic ice sheets during the Eocene–Oligocene transition and Early–Mid Pliocene (e.g., Blum, 1997; Robert and Kennett, 1997; von Blanckenburg and O'Nions, 1999), as well as throughout the formation of alpine-style glaciers in the Alpine–Himalayan belt (Herman *et al*., 2013). Additionally, continental weathering pulses have been associated with the onset and termination of both the Late Ordovician and Fammenian glaciations, which also occurred broadly coevally with the development of widespread marine anoxia/euxinia and major faunal extinctions (e.g., Finlay *et al*., 2010; Kaiser *et al*., 2016; Lakin *et al*., 2016). However, whilst it is clearly possible to trigger enhanced continental weathering and/or marine anoxia during times of cooling and glacial expansion, conclusively demonstrating such a model for the Kellwasser events is inhibited by the lack of clarity regarding the precise temporal relationship between the two crises and the onset of global cooling associated with each of them. Different sedimentary records individually suggest that cooling may have begun before, synchronous with, or after the commencement of marine anoxia and associated increase in the deposition of organic matter (e.g., Joachimski and Buggisch, 2002; Balter *et al*., 2008; Le Houedec *et al*., 2013; Huang *et al*., 2018). Higher resolution temperature and weathering proxy data are needed to clarify whether the Kellwasser cooling occurred in response to elevated silicate weathering and organic-carbon burial during the two crises, or could have initiated those environmental perturbations. An additional problem with the hypothesis of glacially-induced-weathering is that although both a southern-hemisphere ice sheet and additional alpine-style glaciers of latest Famennian age are well documented by diamictite deposits in numerous South American sedimentary basins and the North American Appalachian Basin (e.g., Caputo *et al*., 1985; Brezinski *et al*., 2008; Isaacson *et al*., 2008; Lakin *et al*., 2016), similar sediments spanning the Frasnian–Famennian boundary are unknown. A F–F glaciation event has been proposed in order to account for sea-level changes and oxygen-isotope perturbations recorded in uppermost Frasnian to lowermost Famennian sedimentary archives (e.g., Streel *et al*., 2000; Joachimski and Buggisch, 2002), but there is currently no direct evidence for the existence of any such ice volumes of that age.

Other possible triggers for enhanced continental weathering at the onset of each of the Kellwasser crises include marine transgression (e.g., Bond and Wignall, 2008), tectonic uplift associated with the formation of numerous Late Devonian orogenic belts (Averbuch *et al*., 2005), evolution of vascular-rooted plants (Algeo and Scheckler, 1998), an acceleration of the hydrological cycle by orbital forcing (De Vleeschouwer *et al*., 2017), and soil erosion related to the extinction of terrestrial plants (Kaiho *et al*., 2013). However, the severity of land-plant extinctions during the F–F extinction remains poorly constrained (see Racki, 2005; and references therein). Marine transgressions could have caused significant subaerial and/or submarine erosion of the new coastline, and also brought increased moisture into the continental interior, intensifying the hydrological cycle and increasing riverine runoff, although a markedly wetter climate is inconsistent with the widespread evidence for cooling at those times. Finally, whilst processes such as mountain building and the evolution of vascular-root systems likely caused a gradual elevation in continental weathering rates throughout the Late Devonian (a hypothesis consistent with long-term strontium isotope trends: van Geldern *et al*., 2006), it less clear whether such processes could have occurred rapidly enough to trigger two distinct, abrupt, and short-lived pulses of increased weathering taking place within a million years of each other. However, long-term volcanism, land-plant expansion, orogenic processes, and repeated marine transgressions could plausibly have increased stress in the global climate system throughout Late Devonian times, leaving it increasingly vulnerable to additional environmental perturbations from more rapid triggers such as orbital forcing (see De Vleeschouwer *et al*., 2017).

4.4 Volcanically stimulated weathering and anoxia during the Annulata Event

As well as appearing across the Kellwasser horizons, significant variations in $Os_{(i)}$ values are also documented in strata spanning the late Famennian Annulata Event at Kowala (Figure 2A). Just below the organic-rich Annulata shales, there is a pronounced shift from Famennian background $Os_{(i)}$ values (between 0.4–0.5) towards a very unradiogenic signature, suggesting an influx of primitive osmium to the global ocean. There is currently no evidence for a meteorite impact at that time; however, the date of the Annulata Event matches the Ar–Ar age of the youngest known pulse of Viluy Trap volcanism (363 Ma; Ricci *et al*., 2013; Polyansky *et al*., 2017; Percival *et al*., 2018), based on a cyclostratigraphic timescale anchored to the precise uranium–lead age of the Devonian–Carboniferous boundary (Myrow *et al*., 2014). A volcanic cause for the shift to primitive $Os_{(i)}$ in strata immediately below the Annulata shales might also be supported by a low $Os_{(i)}$ value in strata just above that unit, which suggests that there may have been a relatively long-lived flux of primitive osmium to the marine realm, a phenomenon more easily explained by prolonged volcanic activity than two distinct inputs of unradiogenic Os from separate, unrecorded, impacts.

In this context, it is likely that the rise in $Os_{(i)}$ values within the Annulata shales signifies an influx of radiogenic osmium to the ocean during a weathering pulse, superimposed upon a previously very unradiogenic seawater Os-isotope composition, rather than a simple return to background Famennian conditions as might also be inferred from the similarity of $Os_{(i)}$ values between the Annulata shales and lower Famennian strata. Such an increase in continental weathering rates related to volcanic activity would likely have stimulated anoxic conditions following the mechanism outlined above for the Kellwasser crises, and marine anoxia has been documented as having occurred in a number of marine basins during the Annulata Event (e.g., Walliser, 1996; Bond and Zatoń, 2003; Becker *et al*., 2004; Racka *et al*., 2010). Establishing palaeotemperature records for the Annulata Event (in particular, whether this late Famennian crisis was associated with climate warming) will be important for further understanding this proposed causal relationship. Regardless of what initiated the enhanced continental weathering during the Annulata Event, its occurrence coincident with widespread marine anoxia highlights the potential similarities between this environmental perturbation and the earlier Kellwasser crises, perhaps supporting previous hypotheses that the Frasnian–Famennian mass extinction may simply have been related to the most severe manifestation of these phenomena (Bond and Grasby, 2017).

5. Conclusions

This study has presented the first stratigraphic osmium-isotope ($^{187}Os/^{188}Os$) dataset spanning a long-term record of Frasnian–Famennian times, including the Kellwasser crises and the later Annulata Event. Seawater $^{187}Os/^{188}Os$ values documented in samples from the Frasnian–Famennian boundary and lower–mid Famennian strata at the Kowala Quarry study area are very similar to previously published results from North America, suggesting that the Os-isotope record presented here reflects the global ocean inventory. A number of variations in reconstructed seawater $^{187}Os/^{188}Os$ values are documented, albeit at low resolution. Significantly radiogenic seawater $^{187}Os/^{188}Os$ compositions recorded just below/at the base of both the Lower and Upper Kellwasser horizons indicate that enhanced continental weathering took place immediately prior to and/or during the onset of both of those crises and potentially caused subsequent environmental degradations such as climate cooling and/or widespread marine anoxia, although alternative interpretations regarding the stratigraphic position of the Lower Kellwasser Horizon at Kowala cannot be discounted. An additional, lower-magnitude, shift in $^{187}Os/^{188}Os$ towards radiogenic values within the Annulata shales suggests that high weathering rates were also a feature of that later event. These results are consistent with enhanced continental weathering and associated nutrient runoff as a key contributor towards the development of widespread marine anoxia during both the most severe and other, comparatively minor, Late Devonian environmental perturbations, although the ultimate trigger of these different weathering pulses remains unclear. Further work is needed to confirm the record of these weathering pulses at other Late Devonian sedimentary archives, and to determine whether they were initiated by volcanism, glaciation, or some other cause.

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Figure Captions

Figure 1: Palaeogeographic reconstruction of the Late Devonian world. The locations of the Late Frasnian Siljan impact crater (X), and the Frasnian–Famennian Viluy Traps (V) and Kola, Vyatka, and Pripyat–Dniepr–Donets volcanic rift systems (K-V-PDD) are indicated. The palaeogeographic position of the Kowala Quarry, Poland (K) investigated in this study is shown (black circle), along with North American sedimentary records where Re–Os isochrons have

been generated previously (black squares): J: Jura Creek (Alberta, Canada; Selby and Creaser, 2005); W: West Valley Core (New York, USA; Turgeon *et al*., 2007); I: Irish Gulf section (New York, USA; Gordon *et al*., 2009); P: Pecos County Well (Texas, USA; Harris *et al*., 2013). Based on Figure 1 in Percival *et al*. (2018).

Figure 2: A: Stratigraphic trends in $Os_{(i)}$ from the Kowala Quarry record, Kielce, Poland. The stratigraphic positions of the Upper Kellwasser and Annulata levels are shown, along with the inferred Lower Kellwasser Horizon, and the Hangenberg Horizon. Lithological and biostratigraphic information after Szulczewski (1996) and De Vleeschouwer *et al*. (2013). All osmium data are from this study (solid circles). The vertical scale is in metres **B:** Stratigraphic composite of previously published Re–Os isochron data from North American records (open circles). $Os_{(i)}$ data are from Selby and Creaser (2005), Turgeon *et al*. (2007), Gordon *et al*. (2009), and Harris *et al*. (2013). CARB. stands for CARBONIFEROUS. The lowest natural terrestrial value of $^{187}Os/^{188}Os$ (0.13; Allègre *et al*., 1999) and Late Devonian average seawater $Os_{(i)}$ value (based on North American isochron data) are shown on both figures.

Figure 3: Stratigraphic trends in geochemical data from upper Frasnian sediments at the Kowala Quarry. The interpreted stratigraphic positions of the Lower (LKW) and Upper (UKW) Kellwasser horizons are indicated by the grey bars. Uranium (U) and molybdenum (Mo) enrichment factors (EF) are calculated with respect to Al, relative to average upper continental crust (UCC) abundances as shown by $[(element/Al)_{sample}/(element/Al)_{UCC}]$, where U/Al_{UCC} and Mo/Al_{UCC} are taken as 0.0000331 and 0.0000135, respectively (Rudnick and Gao, 2003). The lowest natural terrestrial value of $^{187}Os/^{188}Os$ (0.13; Allègre *et al*., 1999) and Late Devonian average seawater $Os_{(i)}$ value (based on North American isochron data) are plotted alongside the $Os_{(i)}$ data from Kowala. Common ^{192}Os contents are presented as the best representation of Os concentrations in sediments at the time of deposition. The vertical scale is in metres. FM. stands for FAMENNIAN. All data are from this study. Unpublished measurements made in 2011 indicate a small enrichment in Mo and U concentrations from samples within the UKW

Horizon, but those data were generated via a different methodology to the samples analysed for this study and without accompanying Al contents; therefore, they are not included in this figure (they are presented in Supplementary Figure 2). The enrichment in Mo and U was also observed on UKW Horizon samples from elsewhere in the Kowala Quarry, based on samples from David Bond's 2004 sample-set analysed by LA-ICP-MS for this study (see Supplementary Figure 2), and in previous works (Joachimski *et al*., 2001; Bond *et al*., 2004).

Figure 4: Comparison of trends in uranium (U) and molybdenum (Mo) enrichment factors (EF) to determine the palaeoenvironmental setting recorded at the Kowala Quarry, following the model of Algeo and Tribovillard (2009). Mo/U_{SW} indicates the modern-day Mo/U ratio of seawater. Mo_{EF} and U_{EF} data are calculated as for Figure 3. All data are from this study.

Figure 1

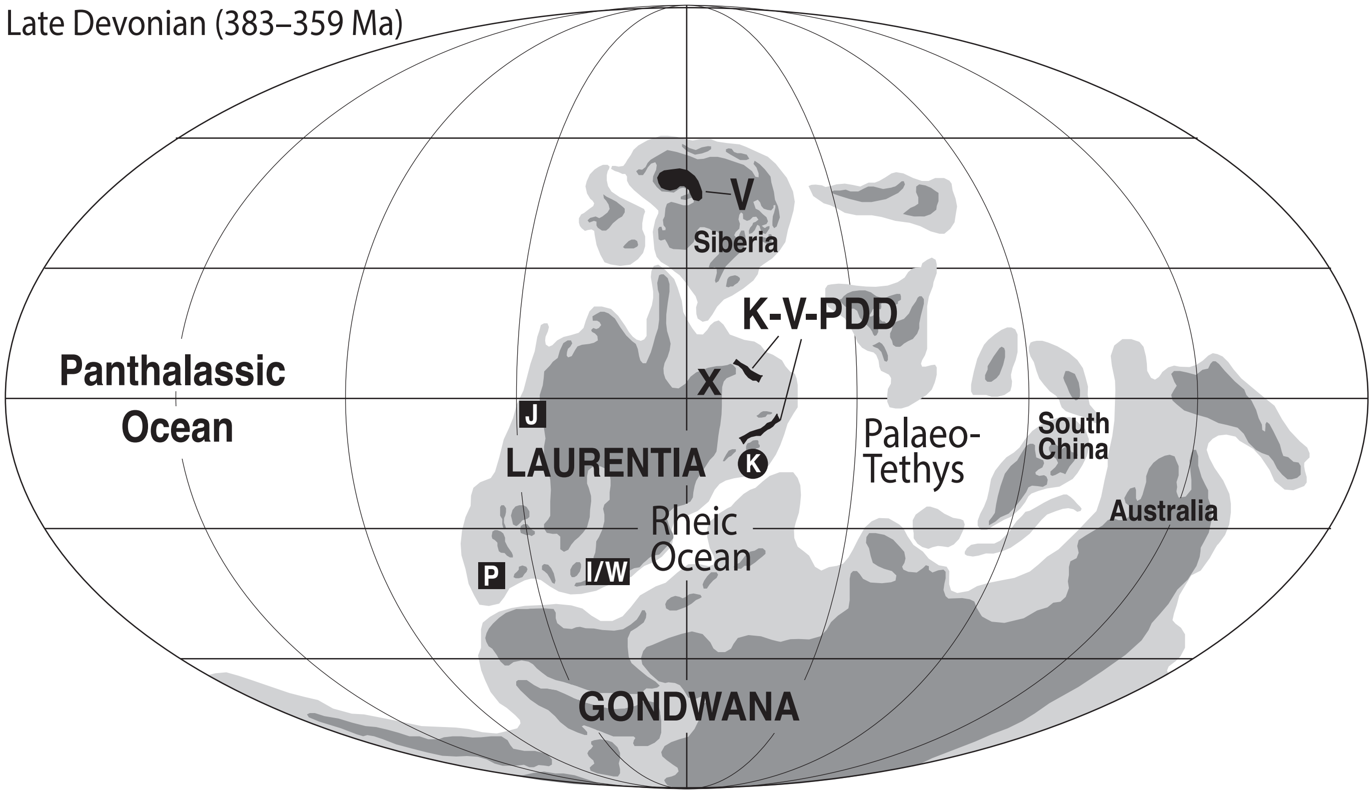

Late Devonian (383–359 Ma)
V
Siberia
K-V-PDD
X
Panthalassic
Ocean
J
LAURENTIA
K
Palaeo-
Tethys
South
China
Australia
Rheic
Ocean
P
I/W
GONDWANA

Figure 2

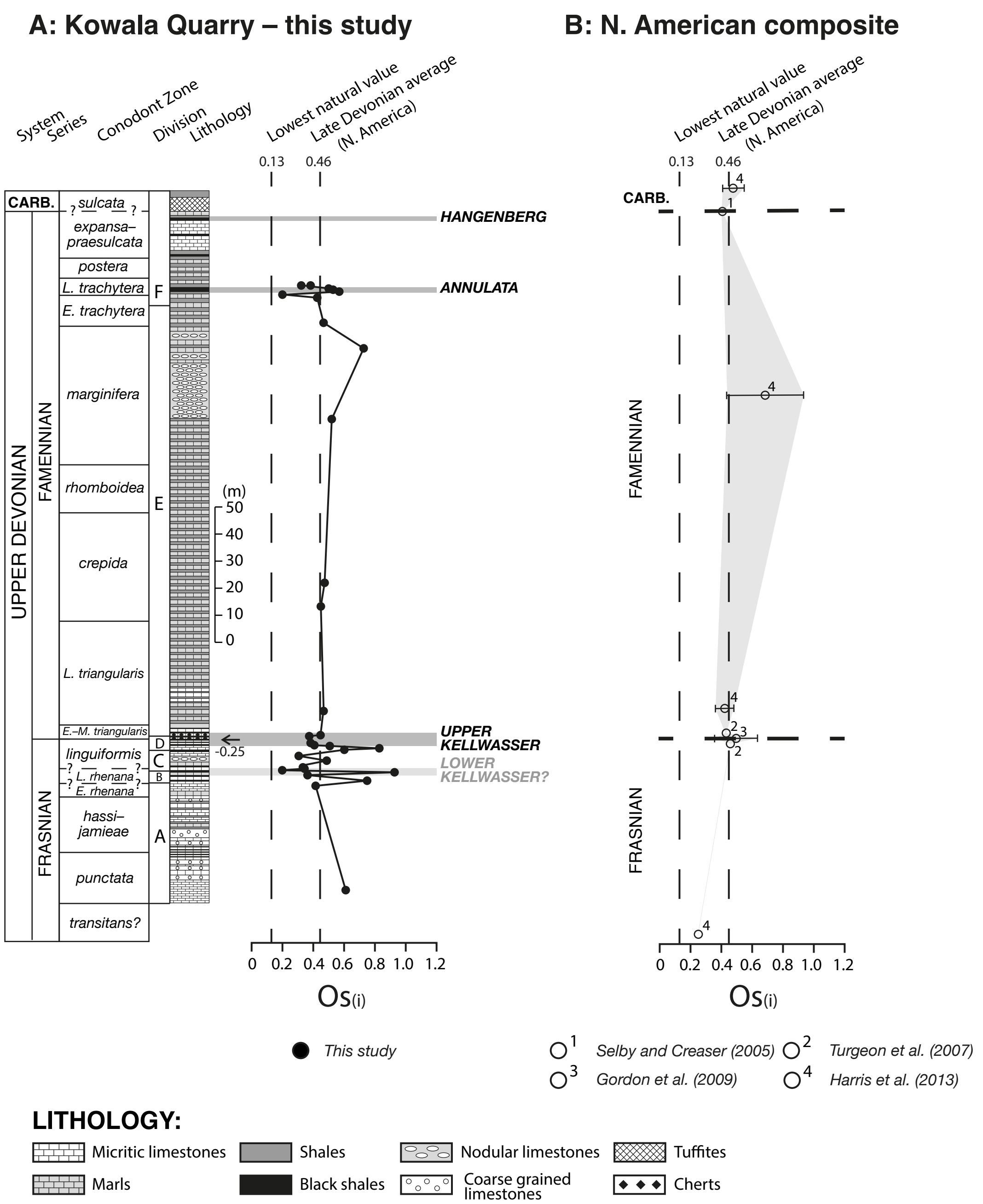

A: Kowala Quarry – this study
B: N. American composite
System
Series
Conodont Zone
Division
Lithology
Lowest natural value
Late Devonian average (N. America)
0.13
0.46
CARB.
UPPER DEVONIAN
FAMENNIAN
FRASNIAN
sulcata
expansa–praesulcata
postera
L. trachytera
E. trachytera
marginifera
rhomboidea
crepida
L. triangularis
E.–M. triangularis
linguiformis
L. rhenana
E. rhenana
hassi–jamieae
punctata
transitans?
A
B
C
D
E
F
(m)
50
40
30
20
10
0
HANGENBERG
ANNULATA
UPPER KELLWASSER
LOWER KELLWASSER?
-0.25
0 0.2 0.4 0.6 0.8 1.0 1.2
Os(i)
This study
Selby and Creaser (2005)
Turgeon et al. (2007)
Gordon et al. (2009)
Harris et al. (2013)
LITHOLOGY:
Micritic limestones
Marls
Shales
Black shales
Nodular limestones
Coarse grained limestones
Tuffites
Cherts

Figure 3

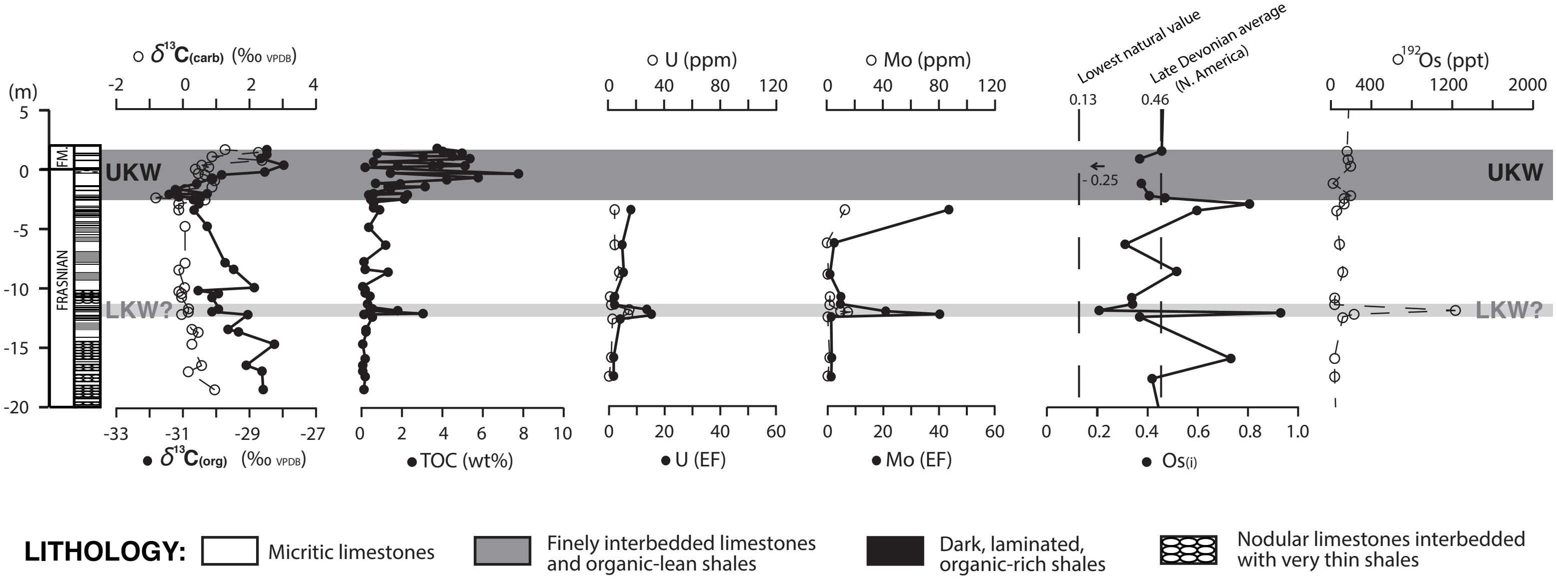
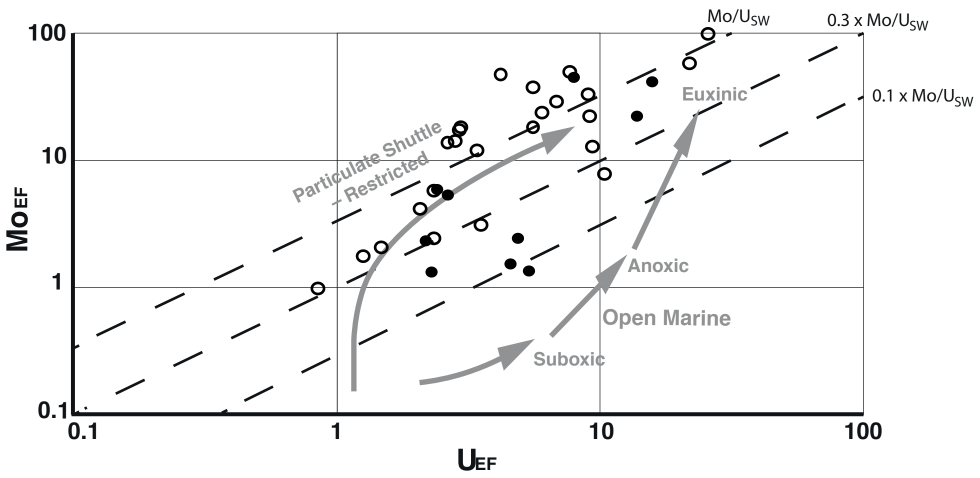

δ13C(carb) (‰ VPDB)
δ13C(org) (‰ VPDB)
TOC (wt%)
U (ppm)
U (EF)
Mo (ppm)
Mo (EF)
Lowest natural value
Late Devonian average (N. America)
Os(i)
192Os (ppt)
(m)
FM.
FRASNIAN
UKW
LKW?
LITHOLOGY:
Micritic limestones
Finely interbedded limestones and organic-lean shales
Dark, laminated, organic-rich shales
Nodular limestones interbedded with very thin shales

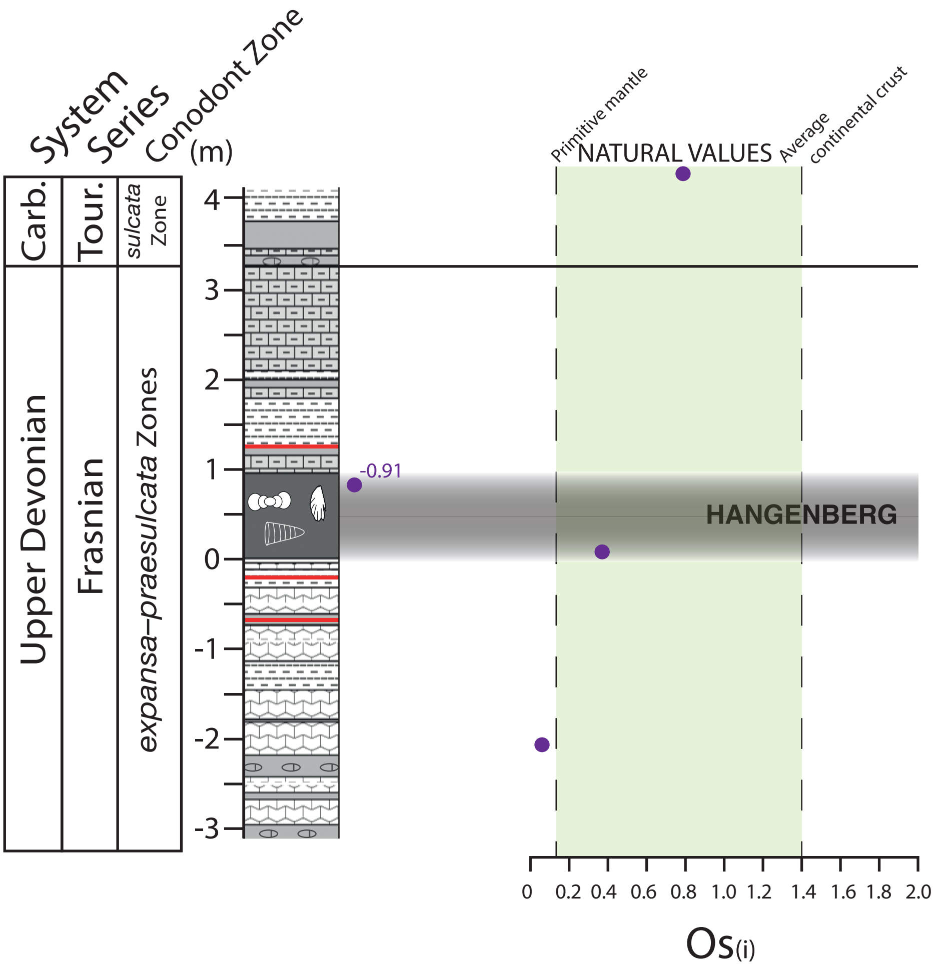
Figure 4



● 2017 Lower Kellwasser Samples ○ Bond *et al*. (2004) Frasnian–Famennian Samples

Supplementary Figure 1

HANGENBERG SHALE, KOWALA QUARRY (POLAND) – OSMIUM ISOTOPE RECORD

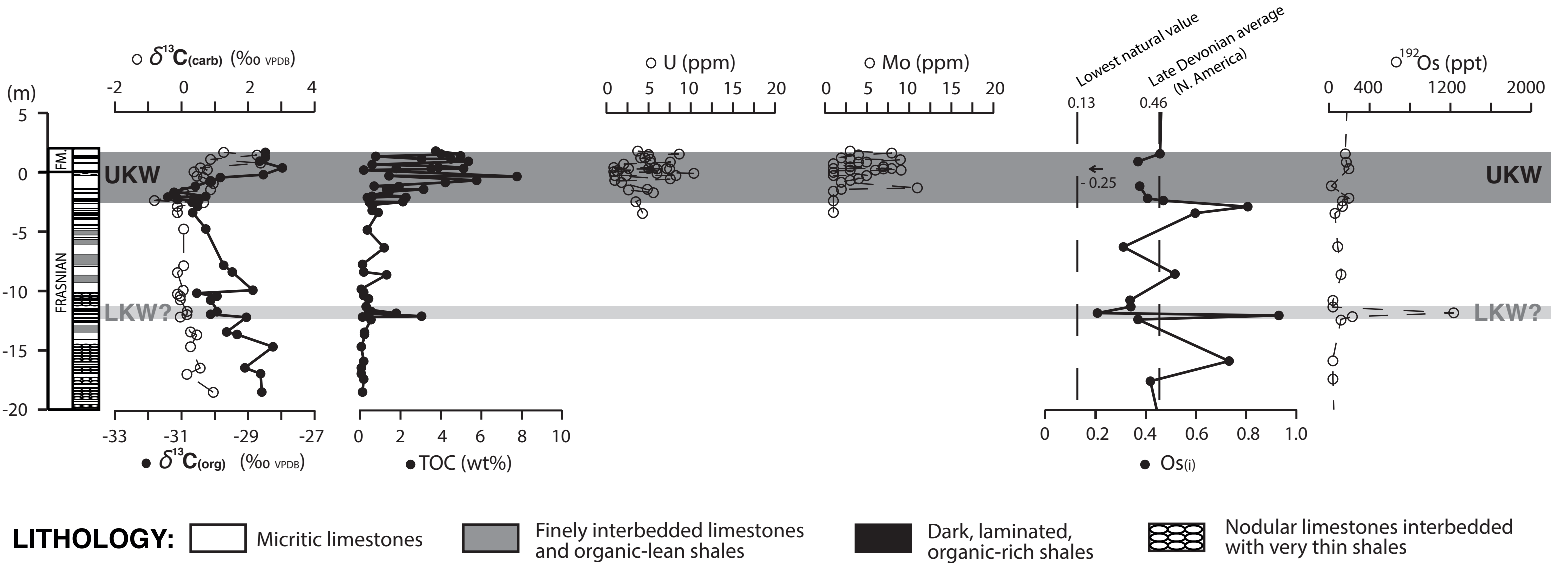


NB. Lithological column and stratigraphic information from Myrow *et al*. (2014). Osmium-isotope data are from this study.
Natural range of values of seawater Os(i) features endmembers of 0.13 (primitive mantle volcanics and extra-terrestrial influx; Allégre *et al*., 1999) and 1.4 (average composition of riverine runoff of upper continental crustal material; Peucker-Ehrenbrink and Jahn, 2001) in the modern, and this range is assumed to have also applied during the Devonian Period.

Supplementary Figure 2

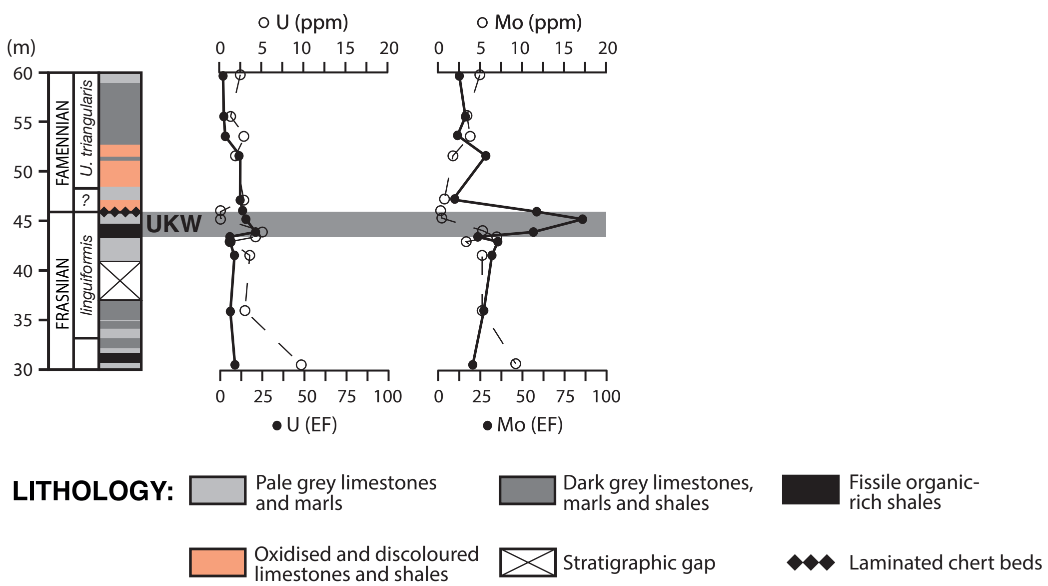
UPPER KELLWASSER HORIZON MOLYBDENUM AND URANIUM RECORDS

University of Sielsia Samples, analysed at Ancaster ACTLabs (Ontario, Canada) in 2011.



Mo and U concentrations were determined by analysis of fused glass discs using a Perkin Elmer Sciex Elemental Analyzer. All other data were generated via the methods described in the main methodology section.

David Bond's 2004 sample set, analysed at the University of Lausanne by LA-ICP-MS (2017).



Samples were collected for Bond et al. (2004). Mo, U, and Al data were generated following the methods outlined in the main methodology section. The samples were taken from a different part of the quarry to the other rocks described in this study, and therefore cannot be easily incorporated on to the same stratigraphic log. Lithological and biostratigraphic information, and the inferred position of the Upper Kellwasser Horizon, are as for Bond et al. (2004).