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Osmium isotope evidence for two pulses of increased continental weathering linked to Early Jurassic volcanism and climate change

L.M.E. Percival[1]*, A.S. Cohen[2], M.K. Davies[2†], A.J. Dickson[1], S.P. Hesselbo[3], H.C. Jenkyns[1], M.J. Leng[4,5], T.A. Mather[1], M.S. Storm[1], and W. Xu[1]

[1]Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, UK

[2]Department of Environment, Earth and Ecosystems, Faculty of Science, The Open University, Walton Hall, Milton Keynes MK 7 6AA, UK

[3]Camborne School of Mines and Environment and Sustainability Institute, University of Exeter, Penryn Campus, Penryn, Cornwall TR10 9FE, UK

[4]British Geological Survey, Keyworth, Nottingham NG12 5GG, UK

[5]School of Geography, University of Nottingham, Nottingham, NG7 2RD, UK

ABSTRACT

Large igneous provinces (LIPs) are proposed to have caused a number of episodes of abrupt environmental change by increasing atmospheric CO_2 levels, which were subsequently alleviated by drawdown of CO_2 via enhanced continental weathering and burial of organic matter. Here the sedimentary records of two such episodes of environmental change, the Toarcian oceanic anoxic event (T-OAE) and preceding Pliensbachian–Toarcian (Pl-To) event (both possibly linked to the Karoo-Ferrar LIP), are investigated using a new suite of geochemical proxies that have not been previously compared. Stratigraphic variations in osmium isotope ($^{187}Os/^{188}Os$) records are compared with those of mercury (Hg) and carbon isotopes ($\delta^{13}C$) in samples from the Mochras core, Llanbedr Farm, Cardigan Bay Basin, Wales. These sedimentary rocks are confirmed as recording an open-marine setting by analysis of molybdenum/uranium enrichment trends, indicating that the Os isotope record in these samples reflects the isotopic composition of the global ocean. The Os isotope data include the first results across the Pl-To boundary, when seawater $^{187}Os/^{188}Os$ increased from ~0.40 to ~0.53, in addition to new data that show elevated $^{187}Os/^{188}Os$ (from ~0.42 to ~0.68) during the T-OAE. Both increases in $^{187}Os/^{188}Os$ correlate with negative carbon isotope excursions and increased mercury concentrations, supporting an interplay between terrestrial volcanism, weathering, and climate that was instrumental in driving these distinct episodes of global environmental change. These observations also indicate that the environmental impact of the Karoo-Ferrar LIP was not limited solely to the T-OAE.

INTRODUCTION

Oceanic anoxic events (OAEs) were times of abrupt carbon-cycle perturbations, driven by increases in atmospheric CO_2 proposed to result, at least partially, from the emplacement of large igneous provinces (LIPs), and alleviated by the subsequent draw down of excess CO_2 through enhanced continental weathering and widespread burial of organic matter (Jenkyns, 2010). The Early Jurassic Toarcian OAE (T-OAE, 183 Ma) was one such event: geochemical evidence for LIP volcanism, oceanic anoxia, release of carbon to the atmosphere, and increased continental weathering rates are found in a number of sedimentary sections (reviewed in Jenkyns, 2010; see also Brazier et al., 2015; Percival et al., 2015). However, there remains no single sedimentary record where evidence for volcanic activity, carbon-cycle perturbation, and enhanced weathering rates are compared using proxy data from the same succession. This situation is also the case for a preceding event during the Pliensbachian–Toarcian (Pl-To) transition, which took place <1 m.y. prior to the T-OAE and has also been associated with a carbon-cycle perturbation and an episode of LIP volcanism (Littler et al., 2010; Percival et al., 2015). Thus, the relationship between such processes during the T-OAE is based upon comparisons of geochemical proxies across multiple sedimentary sections which may not be precisely synchronous.

This study integrates new osmium (Os) isotope data with both new and previously published results recording mercury (Hg) concentrations and carbon isotopes ($\delta^{13}C$) from a single record to investigate the relationships between volcanism, weathering, and the carbon cycle during Pliensbachian–Toarcian time. Large-scale volcanism during the T-OAE has previously been inferred from elevated concentrations of sedimentary Hg of assumed volcanogenic origin (Percival et al., 2015), and attributed to the Karoo-Ferrar LIP, which is radiometrically dated as ca. 183 Ma and therefore Toarcian in age (e.g., Rampino and Strothers, 1988; Duncan et al., 1997; Svensen et al., 2012; Burgess et al., 2015). Volcanism is known to release gaseous Hg, which has an atmospheric residence time of 1–2 yr, allowing global distribution before it is deposited in sediments. Thus, volcanic activity may be recorded as enrichments in sedimentary Hg, typically normalized against total organic carbon (TOC) to account for its strong association with organic matter (Sanei et al., 2012, and references therein).

Changes in continental weathering rates can be estimated from the records of seawater Os isotope composition (Cohen et al., 1999), which is controlled by proportional mixing of radiogenic fluxes from both fluvial input ($^{187}Os/^{188}Os$ of ~1.4) and the alteration and weathering of juvenile basalts ($^{187}Os/^{188}Os$ of ~0.12). Past seawater $^{187}Os/^{188}Os$ ratios calculated from a sedimentary sample are expressed as $^{187}Os/^{188}Os_{(i)}$, after accounting for additional radiogenic Os produced via decay of ^{187}Re to ^{187}Os after deposition (for further details of the Re-Os proxy, see Appendix DR1 in the GSA Data Repository[1]). Strata recording the T-OAE in Yorkshire, England, show an increase in $^{187}Os/^{188}Os$ from ~0.3 to ~0.9, from which a major (400%–800%) increase in continental weathering rates was inferred (Cohen et al., 2004). However, the degree to which this record is representative of the global ocean has been questioned because of the hydrographic nature of that setting (McArthur et al., 2008).

The Mochras borehole (Llanbedr Farm, Cardigan Bay, Wales, UK; Fig. 1) cored a

*E-mail: lawrence.percival@earth.ox.ac.uk

†Current address: School of Geography, Earth and Environmental Sciences, Fitzroy Building, Plymouth University, Drake Circus, Plymouth, Devon PL4 8AA, UK.

[1]GSA Data Repository item 2016248, Appendices DR1–DR4, and Table DR1, is available online at www.geosociety.org/pubs/ft2016.htm, or on request from editing@geosociety.org.

stratigraphically expanded section of lower Jurassic calcareous mudrock, containing terrigenous and marine organic matter (0.5–2 wt% TOC in the interval of interest), and detrital clastics likely derived from the Welsh Massif (O'Sullivan et al., 1972). Both organic carbon and carbonate document negative excursions in $\delta^{13}C$ at the Pl-To boundary and T-OAE level (Jenkyns and Clayton, 1997; this study). Paleogeographic reconstructions indicate a hydrographically open setting (Sellwood and Jenkyns, 1975), which would have allowed Os to be well mixed within the global ocean. This model is tested here by analysis of molybdenum (Mo) and uranium (U) sedimentary enrichments, which have been shown to vary depending on redox conditions and levels of hydrographic restriction in recent marine sediments (Algeo and Tribovillard, 2009).

METHODS

Samples were prepared for Re-Os analysis at The Open University (Milton Keynes, UK) using procedures adapted from Cohen and Waters (1996) and Birck et al. (1997) (see Appendix DR1). Os isotope compositions and concentrations were determined by isotope dilution and negative thermal ionization mass spectrometry on a Thermo Finnigan Triton, and Re concentrations were determined by isotope dilution and multicollector–inductively coupled plasma–mass spectrometry (ICP-MS) on a Thermo Finnigan Neptune.

Mo, U, and Al abundances were determined using a Thermo-Finnigan Element 2 magnetic-sector ICP-MS at the University of Oxford. New Hg and TOC data were generated using a RA-915 portable mercury analyzer with PYRO-915 Pyrolyzer (Lumex), and Rock Eval 6, respectively, at the University of Oxford, using the methods given in Percival et al. (2015). New $\delta^{13}C_{org}$ data were generated by combustion in a Costech elemental analyzer online to a VG TripleTrap and Optima dual-inlet mass spectrometer at the British Geological Survey (Keyworth), as in Riding et al. (2013) (Appendix DR2).

RESULTS AND DISCUSSION

Variations in Mo and U enrichment trends for samples from Mochras and Yorkshire are shown in Figure 2. The Mochras data show a trend of initial U enrichment, followed by increasing Mo enrichment, indicative of an unrestricted open-marine setting (Algeo and Tribovillard, 2009). Therefore, $^{187}Os/^{188}Os_{(i)}$ trends recorded in Mochras samples are likely representative of worldwide trends in the seawater Os isotope composition. The $^{187}Os/^{188}Os_{(i)}$ data for the Mochras samples are presented stratigraphically in Figure 3, alongside $\delta^{13}C_{org}$ and Hg/TOC data from the same sediments, and published $\delta^{13}C_{org}$ and $^{187}Os/^{188}Os_{(i)}$ data from Yorkshire. Although there is notable variation in $^{187}Os/^{188}Os_{(i)}$ values of the Pliensbachian samples, only 1 value

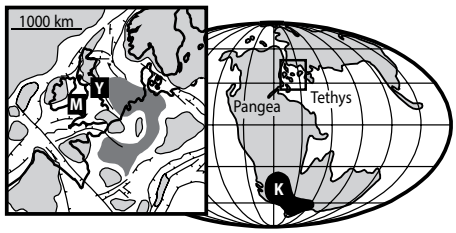

Figure 1. Global paleogeography during the Toarcian, modified from Hesselbo et al. (2007). The dark gray area represents marine areas of Europe thought to have been hydrographically restricted during the Toarcian. The three marked locations are Mochras (M), Yorkshire (Y), and the Karoo-Ferrar (K) large igneous province.

exceeds 0.44. The average $^{187}Os/^{188}Os_{(i)}$ of ~0.4 for Pliensbachian samples is therefore taken as a reasonable baseline against which to compare the Toarcian values. An increase in $^{187}Os/^{188}Os_{(i)}$ to ~0.53 occurs at the Pl-To boundary and persists through the lower half of the *tenuicostatum* ammonite zone, suggesting an increased flux of radiogenic Os to the ocean resulting from enhanced weathering of continental material. An increase in seawater $^{187}Os/^{188}Os$ at the Pl-To boundary has not been previously documented, and such an abrupt and significant rise in seawater $^{187}Os/^{188}Os$ is difficult to explain without invoking rapid changes in continental weathering rates. The return of seawater $^{187}Os/^{188}Os$ to background values (~0.42) throughout the upper half of the *tenuicostatum* Zone further indicates that the transient increase in continental weathering during the Pl-To transition was part of a distinct climate-weathering feedback, rather than the beginning of a long-term increase in weathering rates leading up to the T-OAE.

The lower part of the *falciferum* Zone records a second increase in $^{187}Os/^{188}Os_{(i)}$ values to an average of ~0.68 at the base of the T-OAE level, indicating that, during the T-OAE, a second increase in continental weathering took place, appreciably greater than the one that occurred during the Pl-To transition. The onset of this increase correlates well with the similar pattern of increased $^{187}Os/^{188}Os_{(i)}$ in Yorkshire, supporting the previous inferences of globally elevated continental weathering rates during the T-OAE (Cohen et al., 2004). In addition, both the Pl-To and T-OAE increases in $^{187}Os/^{188}Os$ correlate with perturbations observed in Toarcian Sr and Ca isotope records from Yorkshire and Portugal that have previously been used to infer increases in continental weathering rates (Pálfy and Smith, 2000; Cohen et al., 2004; Brazier et al., 2015). However, the new $^{187}Os/^{188}Os$ trends are a better indication of geologically abrupt increases in continental weathering rates due to the much shorter residence time of Os in the ocean (~10–50 k.y.; Peucker-Ehrenbrink and Ravizza, 2000) compared with that of Ca or Sr.

These two increases in seawater $^{187}Os/^{188}Os$ document two separate pulses of increased global weathering rates during the Pl-To transition and T-OAE, respectively. If the ocean is considered as a single well-mixed reservoir, with continental weathering as the only input of radiogenic Os and alteration of juvenile basalts as the main input of unradiogenic Os, the changes in weathering flux of continental crust required to bring about the observed increases in $^{187}Os/^{188}Os$ can be calculated, assuming that mid-ocean ridge activity is constant on geologically short time scales (Appendix DR4). The increase in seawater $^{187}Os/^{188}Os$ from ~0.4 in the latest Pliensbachian to ~0.53 during the Pl-To transition would require a near doubling of continental weathering rates, increasing by a

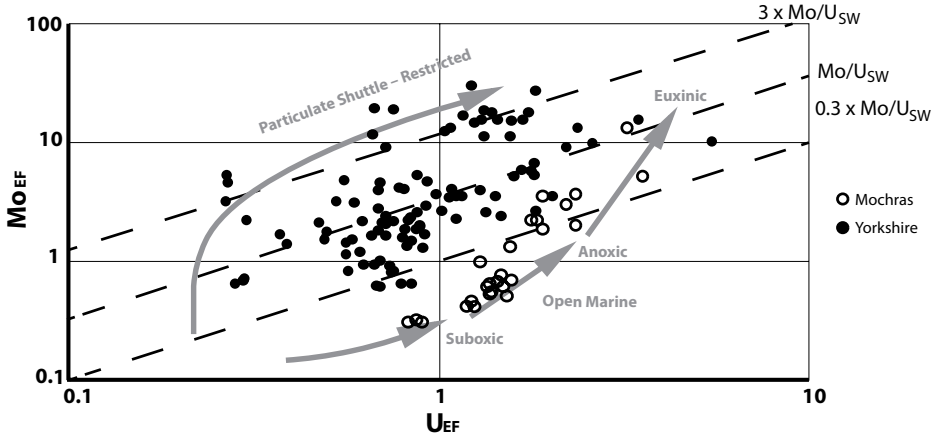

Figure 2. Comparison of the paleoenvironmental settings at Yorkshire and Mochras (UK) using Mo/U enrichment ratios, following the model of Algeo and Tribovillard (2009). Yorkshire data are from the supplementary data of McArthur et al. (2008). Mo/U_{SW} indicates the modern-day Mo/U ratio of seawater. Mo_{EF} and U_{EF} indicate the calculated enrichment factor of molybdenum and uranium, respectively, relative to average upper continental crust (UCC) abundances (Rudnick and Gao, 2003), using $[(element/Al)_{sample}/(element/Al)_{UCC}]$.

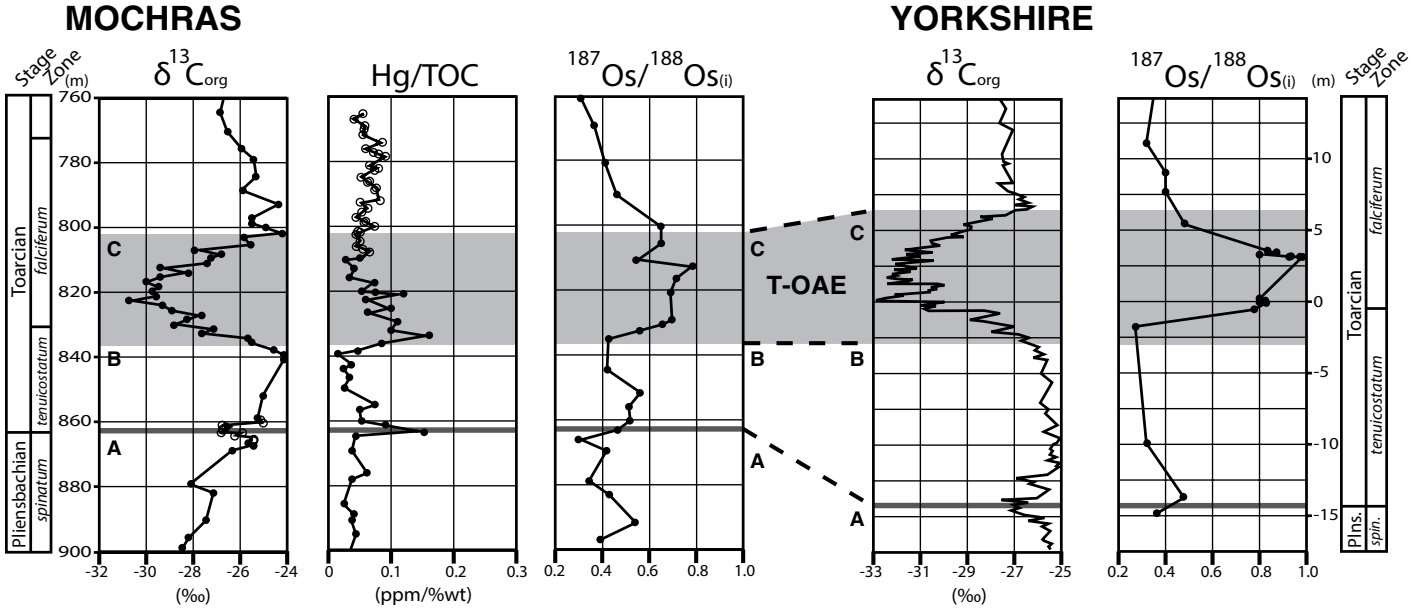

Figure 3. $\delta^{13}C_{org}$ and $^{187}Os/^{188}Os_{(i)}$ data from Mochras and Yorkshire (UK) and Hg/total organic carbon (TOC) ratios from Mochras. Line A marks the Pliensbachian-Toarcian (Pl-To) boundary; line B marks the onset of the Toarcian oceanic anoxic event (T-OAE) as defined by the lowest appearance of organic-rich shales in Yorkshire, which is broadly coincident with the onset of the $\delta^{13}C$ negative excursion; line C marks the end of the $\delta^{13}C$ negative excursion. The gray shaded area marks the stratigraphic width of the $\delta^{13}C$ negative excursion. Stratigraphic heights are in meters; stage refers to the stage in geological time; zone refers to biostratigraphic ammonite zones that subdivide that stage. Plns.—Pliensbachian; *spin.*—*spinatum*. For $\delta^{13}C$ and Hg/TOC data from Mochras, closed circles illustrate published data and open circles illustrate new data. The $\delta^{13}C_{org}$ Yorkshire data are at too high a resolution to include individual data points. Published data sources: Mochras $\delta^{13}C_{org}$ data are from Jenkyns et al. (2001); Yorkshire $\delta^{13}C_{org}$ data are from Cohen et al. (2004), Littler et al. (2010), and Kemp et al. (2011); Yorkshire Os isotope data are from Cohen et al. (2004); Mochras Hg/TOC data are from Percival et al. (2015). Preliminary $^{187}Os/^{188}Os_{(i)}$ data from the Toarcian of western North America show broadly similar patterns (Them et al., 2015).

factor of ~1.69. The subsequent rise in seawater $^{187}Os/^{188}Os$, from ~0.42 to ~0.68, during the T-OAE demands a near tripling of continental weathering rates, increasing by a factor of ~2.58. Moreover, these values are minimum estimates because subaerial weathering of the coevally emplaced Karoo-Ferrar LIP would have contributed additional unradiogenic Os to the oceans, although the impact of such LIP-derived Os is ambiguous.

The estimates here of weathering rate increases are lower than the 400%–800% estimate of Cohen et al. (2004). However, the pattern of Mo/U enrichment in samples from Yorkshire indicates particulate shuttling of Mo in a hydrographically restricted basin, in contrast to the more open-marine environment preserved in the Mochras core (Fig. 2). Consequently, the Os-isotope composition at Yorkshire may have evolved away from the global composition toward that of local input fluxes, potentially exaggerating the increase in seawater $^{187}Os/^{188}Os$ at that location. Nonetheless, the two records in tandem confirm that a pronounced and abrupt increase in continental weathering rates coincided precisely with the environmental perturbations that occurred during the T-OAE.

The increases in seawater $^{187}Os/^{188}Os$ also correlate with changes in Hg/TOC and $\delta^{13}C_{org}$ recorded in the same samples at both the Pl-To boundary and the base of the T-OAE level. Negative $\delta^{13}C$ and positive Hg/TOC excursions have been previously hypothesized to indicate increased output of isotopically light carbon to the atmosphere and large-scale volcanic activity, respectively (Hesselbo et al., 2000; Percival et al., 2015). The correlation of all three proxies suggests that volcanism and carbon-cycle perturbations were accompanied by increased rates of continental weathering. This conclusion supports previous hypotheses that volcanism triggered a carbon-cycle perturbation, which was eventually alleviated through a feedback of increased silicate weathering as well as organic-carbon burial (summarized in Jenkyns, 2010). Although such a mechanism has previously been proposed for the T-OAE (Cohen et al., 2004), the data presented here indicate that similar processes operated during the Pl-To transition.

The two intervals of perturbed $^{187}Os/^{188}Os$, Hg/TOC and $\delta^{13}C_{org}$ are separated by the latter part of the *tenuicostatum* Zone, which is thought to have lasted hundreds of thousands of years (Kemp et al., 2011). Consequently, any volcanically related trigger of these perturbations would need to have operated on at least two separate occasions. Burgess et al. (2015) recorded a 600 k.y. age difference between Karoo and Ferrar basalts, which could support the notion of episodic LIP volcanism. However, the uncertainties in such measurements, as well as their similarity with the ages of many Karoo basalts (Svensen et al., 2012), means that there is no unambiguous evidence for episodic emplacement of the Karoo-Ferrar LIP. An alternative hypothesis could involve sporadic interaction of LIP basalts with organic-rich sediments, causing output of thermogenic carbon and mercury (McElwain et al., 2005; Svensen et al., 2007; Percival et al., 2015).

The increase in seawater $^{187}Os/^{188}Os$ recorded during both the Pl-To transition and T-OAE may have been aided by the high-latitude, subaerial emplacement of the Karoo-Ferrar LIP. Intervals associated with low-latitude subaerial LIPs such as the Central Atlantic or Deccan provinces, or submarine LIPs such as the Ontong-Java Plateau or Caribbean plateau, tend to record predominantly decreased seawater $^{187}Os/^{188}Os$, due to the rapid weathering of LIP basalts at low latitudes (Cohen and Coe, 2007), or direct release of unradiogenic Os into the oceans (Bottini et al. 2012; Du Vivier et al., 2014). In contrast, a high-latitude LIP would have undergone less intense weathering compared to lower latitude crust, resulting in an increased flux of radiogenic Os from continental material dominating the seawater $^{187}Os/^{188}Os$ record, as shown here for Mochras and previously for Yorkshire (Cohen et al., 2004). Similar signals of predominantly increased seawater $^{187}Os/^{188}Os$ are also recorded from Paleocene–Eocene sediments that formed contemporaneously with the high-latitude North Atlantic LIP (Dickson et al., 2015; summary in Table DR1). Thus, comparison of Os isotope records highlights the importance of the setting

of LIP emplacement, as well as the magnitude and tempo of volcanism, in controlling the nature of subsequent environmental change.

CONCLUSIONS

This study documents two relatively rapid and transitory increases in the $^{187}Os/^{188}Os$ of seawater during latest Pliensbachian–early Toarcian time. The $^{187}Os/^{188}Os$ increases correlate well with excursions in Hg/TOC and $\delta^{13}C_{org}$, thus demonstrating a close coupling between volcanism, weathering, and carbon-cycle perturbations in two distinct Early Jurassic events. The similarity of these events, separated by only a few hundred thousand years, is consistent with a repeating trigger for the cascade of environmental responses, postulated as linked to sequential emplacement of the Karoo-Ferrar LIP or sporadic release of thermogenic volatiles. The new observations demonstrate that major environmental perturbations in the Early Jurassic were episodic, and not solely restricted to the T-OAE.

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