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

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ABSTRACT

Large igneous provinces (LIPs) are proposed to have caused a number of episodes of abrupt environmental change by increasing atmospheric CO2 levels, which were subsequently alleviated by drawdown of CO2 via enhanced continental weathering and burial of organic matter. Here the sedimentary records of two such episodes of environmental change, the Toarcian anoxic event (T-OAE) and preceding Pliensbachian–Toarcian (Pi-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 (187Os/188Os) records are compared with those of mercury (Hg) and carbon isotopes (δ13C) 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 Pi-To boundary, when seawater 187Os/188Os increased from ~0.4 to ~0.53, in addition to new data that show elevated 187Os/188Os (from ~0.42 to ~0.68) during the T-OAE. Both increases in 187Os/188Os 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 CO2 proposed to result, at least partially, from the emplacement of large igneous provinces (LIPs), and alleviated by the subsequent draw down of excess CO2 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 (Pi-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 (δ13C) 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 (Sanelli 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 (187Os/188Os of ~1.4) and the alteration and weathering of juvenile basaltic (187Os/188Os of ~0.12). Past seawater 187Os/188Os ratios calculated from a sedimentary sample are expressed as 187Os/188Os @_Os, after accounting for additional radiogenic Os produced via decay of 187Re to 187Os after deposition (for further details of the Re-Os proxy, see Appendix DR1 in the GSA Data Repository1). Strata recording the T-OAE in Yorkshire, England, show an increase in 187Os/188Os 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...
METHODS

Samples were prepared for Re-Os analysis at The Open University (Milton Keynes, UK) using procedures adapted from Cohen and Waters (1996) and Birk 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 δ¹³C 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, δ¹⁸⁷Os/¹⁸⁸Os trends recorded in Mochras samples are likely representative of worldwide trends in the seawater Os isotope composition. The δ¹³Corg and Hg/TOC data for the Mochras samples are presented stratigraphically in Figure 3, alongside δ¹³Corg and Hg/TOC data from the same sediments, and published δ¹³Corg and δ¹⁸⁷Os/¹⁸⁸Os data from Yorkshire. Although there is notable variation in δ¹³Corg and δ¹⁸⁷Os/¹⁸⁸Os values of the Pliensbachian samples, only 1 value exceeds 0.44. The average δ¹⁸⁷Os/¹⁸⁸Os of ~0.4 for Pliensbachian samples is therefore taken as a reasonable baseline against which to compare the Toranian values. An increase in δ¹⁸⁷Os/¹⁸⁸Os from ~0.53 occurs at the Pl-To boundary and persists through the lower half of the tenacostatum ammonite zone, suggesting an increased influx of radiogenic Os to the ocean resulting from enhanced weathering of continental material. An increase in seawater δ¹⁸⁷Os/¹⁸⁸Os at the Pl-To boundary has not been previously documented, and such an abrupt and significant rise in seawater δ¹⁸⁷Os/¹⁸⁸Os is difficult to explain without invoking rapid changes in continental weathering rates. The return of seawater δ¹⁸⁷Os/¹⁸⁸Os to background values (~0.42) throughout the upper half of the tenacostatum 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 δ¹⁸⁷Os/¹⁸⁸Os 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 δ¹⁸⁷Os/¹⁸⁸Os 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 δ¹⁸⁷Os/¹⁸⁸Os 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 δ¹⁸⁷Os/¹⁸⁸Os 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 δ¹⁸⁷Os/¹⁸⁸Os 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 δ¹⁸⁷Os/¹⁸⁸Os can be calculated, assuming that mid-ocean ridge activity is constant on geologically short time scales (Appendix DR4). The increase in seawater δ¹⁸⁷Os/¹⁸⁸Os 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
MOCHRAS

YORKSHIRE

Figure 3. δ13Corg and 187Os/188Os 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 δ13C negative excursion; line C marks the end of the δ13C negative excursion. The gray shaded area marks the stratigraphic width of the δ13C 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. Pns.—Pliensbachian; spin.—spinatum. For δ13C and Hg/TOC data from Mochras, closed circles illustrate published data and open circles illustrate new data. The δ13Corg Yorkshire data are at too high a resolution to include individual data points. Published data sources: Mochras δ13Corg data are from Jenkyns et al. (2001); Yorkshire δ13Corg data are from Cohen et al. (2004), Littler et al. (2010), and Kemp et al. (2011); Yorkshire Os isotopic data are from Cohen et al. (2004); Mochras Hg/TOC data are from Percival et al. (2015). Preliminary 187Os/188Os(i) data from the Toarcian of western North America show broadly similar patterns (Them et al., 2015).

The two intervals of perturbed 187Os/188Os, Hg/TOC and δ13Corg, are separated by the latter part of the tenoncostatum 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 187Os/188Os 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 187Os/188Os, due to the rapid weathering of LIP basalts at low latitudes (Cohen and Coe, 2007), or direct release of uradiogenic Os into the oceans (Bottni 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 187Os/188Os record, as shown here for Mochras and previously for Yorkshire (Cohen et al., 2004). Similar signals of predominantly increased seawater 187Os/188Os 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 $^{87}$C/$^{84}$Corg, 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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