The osmium isotope signature of Phanerozoic Large Igneous Provinces

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Abstract

The emplacement of Large Igneous Provinces (LIPs) throughout the Phanerozoic Eon introduced vast quantities of mafic rocks to the Earth's surface, which were subsequently weathered into the oceans. Osmium isotope data can be used to track these LIP-related weathering fluxes, providing a global fingerprint of the timing and magnitude of LIP emplacement, and guiding assessments of the impact of these events on ocean biogeochemistry and the regulation of the global climate system. Sedimentary Os isotope records spanning late Phanerozoic LIP events are reviewed herein and new observations from Eocene hyperthermal event ETM-2 are presented. While Os isotope stratigraphy can provide major constraints on LIP activity in the geological record, it cannot always distinguish whether the extrusive activity was subaerial or submarine. The utility of osmium isotopes as a global tracer of past volcanism may be enhanced when used alongside proxies such as mercury concentrations, which may be more diagnostic of the style of individual episodes of LIP emplacement. Hitherto, only a few high-resolution Os-isotope records across Phanerozoic LIPs have effectively exploited the short oceanic residence time of Os. Future high-resolution studies across suitable, well-preserved stratigraphic records will significantly improve our understanding of the nature, progression and consequences of LIP emplacement.

Introduction: the episodic nature of LIP emplacement

The emplacement of Large Igneous Provinces (LIP) is characterized by anomalously high magmatic fluxes, such that the majority of their volume is emplaced within a relatively short time-period of < 1–2 million years. They comprise massive volumes of mantle-derived igneous material sometimes in excess of 10^6 km^3, intruded into the crust as dykes, sills and batholiths, and extruded onto the surface as effusive lava flows or as explosive ejecta together with a cocktail of superheated gases and fluids in either a subaerial or submarine environment (Coffin and Eldholm, 1992, 1994; Ernst, 2014). LIPs have often been linked to mantle plumes, which are persistent upwellings of anomalously hot mantle. The rapid eruption rates and huge volumes of material sourced from melting in the plume head during the early stages of LIP emplacement far exceed present-day eruption rates and volumes, and because of this rapidity they are proposed to have

had a deleterious impact on the global environment. LIPs occurred periodically throughout Earth's history, at approximate intervals of a few tens of millions of years (Prokoph et al., 2013) and have been associated with episodes of extreme global climate change and biotic extinction (Ernst and Youbi, 2017) (Fig. 1).

Several key questions regarding LIP behaviour have been postulated: When did individual LIP events occur? Was volcanic activity continuous or intermittent over the period of emplacement? Did LIP emplacement drive changes in the global climate system? What climatic feedback processes do LIPs perturb? Do all LIPs alter Earth System processes (weathering, ocean chemistry, warming etc) in the same way? Do all LIPs cause biotic extinctions? The approach to answering many of these questions is commonly to undertake rigorous radiometric dating of igneous rocks that can be related to specific episodes of LIP activity. These efforts initially centred on Ar-Ar dating of flood basalts. These Ar-dating approaches have been instrumental in establishing first-order relationships between the timing of LIP events and major extinction and environmental changes across the Phanerozoic and beyond (Wignall et al., 2001), but are sometimes limited by relatively large absolute age uncertainties, which may be on the order of ~ $\pm 10^5$–10^6 years. Recent advances in U-Pb dating, with reported age uncertainties of $\pm 10^4$ years, have significantly reduced the age uncertainties on some LIP events, thereby allowing a greater understanding of how individual episodes of LIP activity may proceed within a longer period of emplacement (e.g. Schoene et al., 2010; Svensen et al., 2010; Blackburn et al., 2013; Burgess and Bowring, 2015; Davies et al., 2017; other contributions in this volume). Ultra-high resolution dating of magmatic episodes has greatly improved our understanding of the nature of LIP activity, providing a precise framework to explore the potential of volcanic activity as a trigger for the complex environmental changes and feedbacks leading to mass extinction events. Nonetheless, this approach requires the preservation of datable rocks that can be stratigraphically related to the overall LIP sequence. This requirement inevitably leads to LIP chronologies that can potentially be discontinuous and patchy.

Despite these limitations, recent advances in radiometric dating have shown that the catastrophic environmental changes potentially driven by LIP volcanism are triggered by intense short-lived volcanic episodes rather than persistent volcanism spanning the entire period of emplacement. Similarly, the associated feedback processes set in motion (including carbon cycle reorganization, climatic warming, weathering, ocean anoxia and biotic extinction) operate on comparable centennial–millennial timescales. Therefore, in order to constrain the magnitude and duration of these perturbations and establish an order of events it is necessary generate proxy data with age constraints precise enough to resolve the environmental changes in the stratigraphic record. Strontium isotopes have been used to constrain the source and duration of weathering during extended warming events, but the long oceanic residence time of Sr (> 4 million years; Veizer, 1989) limits its ability to resolve very short-term weathering events. The very much shorter ocean residence time of Os (~ 10–50 Kyr, Sharma et al., 1997; Levasseur et al., 1998) makes its

isotope system a more effective tracer of relatively rapid changes in the temporal evolution of global seawater chemistry as it continually adjusts to the input of Os weathered from newly emplaced volcanic rocks. This feature gives Os-isotope stratigraphy the almost unique quality of being able to trace the temporal progression of LIP events at fine levels of detail (potentially $<10^4$ years) at far-field sites that are not affected by the erosion or thermal alteration processes that can disturb sedimentary succession in more proximal settings. It is this utility of Os isotopes that will form the focus of this contribution.

Os isotope stratigraphy

Rhenium and Os readily partition into metal, sulfide and organic phases, and because of this behaviour the Re-Os isotope system provides a complementary record of geological processes compared to silicate-hosted isotopic systems such as Rb-Sr, Sm-Nd, Lu-Hf and U-Pb. Rhenium and Os show differences in compatibility which give rise to contrasting low and high Re/Os ratios for the mantle and crust respectively. This marked parent-daughter fractionation and the subsequent radiogenic ingrowth of ^{187}Os as a result of β-decay of ^{187}Re produces orders of magnitude variations in the $^{187}Os/^{188}Os$ of geological reservoirs. In crustal rocks, where the Re/Os ratio is relatively high, the in-situ production of ^{187}Os leads to high (radiogenic) $^{187}Os/^{188}Os$ ratios that average ~1.4 (Peucker-Ehrenbrink and Jahn, 2001). In mantle and ultramafic rocks, where Re/Os ratios are low, $^{187}Os/^{188}Os$ ratios are lower (unradiogenic) with a value that is more chondritic in nature, ~0.12 (Luck and Allegré, 1983). The oceans record the proportional mixing of the two Os isotope end-members (Peucker-Ehrenbrink and Ravizza, 2000) (Fig. 2).

Three important aspects of the Os-isotope system in regard to LIPs need to be considered. Firstly, Os isotopes are an indirect tracer for LIP activity. The rapid emplacement of LIPs can result in the intense and rapid weathering of juvenile mafic and ultramafic rocks, either by atmospheric and biogeochemical processes, low-temperature submarine basalt-seawater interaction or by the creation of hydrothermal systems around submarine volcanic centres (Ravizza and Peucker-Ehrenbrink, 2000; Cohen and Coe, 2002; Turgeon and Creaser, 2008). These weathering fluxes release unradiogenic Os into seawater, which lowers the seawater $^{187}Os/^{188}Os$ ratio. However, if LIP rocks are not easily susceptible to weathering, or if LIP activity re-mobilizes Os from previously buried sedimentary reservoirs, the $^{187}Os/^{188}Os$ ratio of seawater might instead record a shift towards radiogenic values. This trend may be amplified if climate feedbacks associated with widespread volcanism are able to increase the congruency of terrestrial rock weathering. In practice, the Os-isotope 'signature' of a LIP might involve swings in seawater $^{187}Os/^{188}Os$ in either direction at different times, a feature that is clearly apparent during many LIP events (e.g. the Ontong-Java Plateau and the North Atlantic Igneous Province (Bottini et al., 2012; Dickson et al., 2015). The second important feature of the Os isotope system is the short residence time of Os in the oceans, of ~10–50 kyrs (Sharma et al., 1997; Levasseur et al., 1998). This feature provides Os-isotope stratigraphy with the potential for tracing the pulsed emplacement of LIPs at timescales

of 10^3–10^4 years, and the nature of the associated climate/weathering feedbacks. As will be discussed, this utility has rarely been fully exploited for any individual LIP to date. Finally, the Os-isotope composition of the oceans can also be influenced by extraterrestrial fluxes, such as from impactor events (e.g. Sato et al., 2013) or cosmogenic particles (Ravizza, 2007). Extraterrestrial impacts have been suggested for several intervals bracketed by LIPs, and these must be borne in mind when examining the reconstructed temporal evolution of seawater chemistry.

Osmium is present in seawater only in ultra-trace concentrations, but is strongly enriched in reducing marine sediments. The enrichment of Os (and Re) in low-oxygen depositional settings means that paleo-seawater $^{187}Os/^{188}Os$ ratios can be traced by the careful measurement of Re and Os compositions in organic-rich mudrocks, followed by a correction for the post-depositional decay of ^{187}Re (Ravizza and Turekian, 1989; Cohen et al., 1999). The requirement to correct $^{187}Os/^{188}Os$ ratios in organic-rich rocks for ^{187}Re decay means that so-called initial Os-isotope stratigraphies (Os_i) have been produced mainly for those events where suitable deposits exist with independent age control. Where there is no independent age control, 'initial' $^{187}Os/^{188}Os$ ratios can be estimated without independent age control using the isochron approach of measuring samples with different $^{187}Re/^{188}Os$ ratios collected from a restricted stratigraphic range (e.g. Cohen et al., 1999). Some Os-isotope records have also been produced from Fe-Mn crusts and oxic metalliferous sediments (e.g. Pegram et al., 1992; Peucker-Ehrenbrink et al., 1995; Ravizza et al., 2001; Klemm et al., 2005, 2008; Burton, 2006; Robinson et al., 2009). These records do not require a significant correction for Re decay, but may be systematically biased due to the partial liberation of detritally-hosted Os phases from the bulk sediment (e.g. Pegram and Turekian, 1999). Furthermore, such records from Fe-Mn crusts have a limited temporal resolution because of their slow accumulation rates. In all types of approach (mudrocks or crusts/sediments), Os_i records spanning early Phanerozoic LIPs (i.e. pre-Permian) have not yet been produced. The LIP record of only the late Phanerozoic will therefore be summarized in the following discussion, and illustrated in Figs 3 and 4.

The Phanerozoic Os-isotope record of LIPs

The Columbia River LIP (~17–15 Ma)

As the youngest LIP of the Phanerozoic, the Columbia River (CR) event has a very well defined chronology and stratigraphic framework (Barry et al., 2013; Riedel et al., 2013). $^{40}Ar/^{39}Ar$ and K-Ar age determinations of the CR eruptive history suggested that activity occurred across a total interval of ~16.9–6 Ma, with most activity occurring during emplacement of the Grande Ronde Basalt, from ~16–15.6 Ma (Barry et al., 2013). Recent zircon U-Pb ages of CR ashes have refined this chronology to constrain ~95% of the eruptive history to the interval 16.7–15.9 Ma (Kasbohn and Schoene, 2018). There are few Os-isotope data that record the impact of the CR LIP on ocean chemistry. The records that exist are from oceanic ferromanganese crusts, which record changes in seawater $^{187}Os/^{188}Os$ at multi-million year timescales that are far in excess of the oceanic

residence time of Os (Klemm et al., 2005, 2008; Burton et al., 2006). These records (illustrated in Fig. 3) do suggest a small $^{187}Os/^{188}Os$ shift of ~0.1 towards more unradiogenic ratios in seawater during the Miocene, as would be expected from an enhanced weathering flux of unradiogenic Os from CR basalts (Klemm et al., 2008). However, the timing of this shift depends on the age-model applied to the crust records. Even revised age-models based on Os-isotope stratigraphy imply an unradiogenic shift in $^{187}Os/^{188}Os$ between ~15–12 Ma, a pattern that significantly post-dates radiometric ages of most of the CR eruptive episodes. For a LIP to have had a discernable impact on Os ocean chemistry it must have been volumetrically large, the constituent lavas and intrusive rocks must have contained high Os concentrations, and the rocks must have been weathered rapidly following emplacement. Although effusion rates in individual pulses of CR volcanism may have been comparable to larger LIPs in the geological record, the CR river event was volumetrically small compared to many earlier Phanerozoic LIPs, and the amount of basalt weathered was orders of magnitude smaller than, for example, the CAMP event at the Triassic–Jurassic boundary (Cohen and Coe, 2002). Thus it is possible that the putative unradiogenic signal observed by Klemm et al. (2008) is actually unrelated to the CR LIP and records a different perturbation to Os ocean chemistry in the Miocene.

Ethiopian-Yemeni Flood basalts (~31–29 Ma)

The Ethiopian-Yemeni LIP has the best-preserved sequence of flood basalts in the Cenozoic geological record. The main phase of flood basalt volcanism began shortly before ~30 Ma and lasted for less than ~1 million years (Hofmann et al., 1997; Ukstins et al., 2002), before continuing in pulses concomitant with the opening of the Red Sea and the Gulf of Aden (Courtillot and Renne, 2003). Magnetostratigraphy of the Ethiopian flood basalts indicate a correlation to magnetochrons C11r to C11n (Hofmann et al., 1997; Touchard et al., 2003), making them younger than the Eocene–Oligocene boundary event, which occurred during chrons C13r–C12r (~34 Ma, e.g. Zachos et al., 1996). The effect of the Ethiopian–Yemeni LIP on the osmium chemistry of the oceans is not well understood, with low-resolution data available from only three locations (Peucker-Ehrenbrink and Ravizza, 2012). These records agree in the sense that they all show $^{187}Os/^{188}Os$ ratios evolving to less radiogenic values at ~30–31 Ma. However, the magnitude and pattern of this decrease varies, from ~0.08 in Indian Ocean ODP Site 711, to ~0.12 in South Atlantic DSDP Site 522 (Peucker Ehrenbrink and Ravizza, 2012). Os-isotope stratigraphy therefore appears to reveal a signature of basalt weathering on ocean chemistry, though the true size of this weathering flux, and its wider temporal context, are limited by the available data.

The North Atlantic Igneous Province (NAIP) (~61–54 Ma)

The emplacement of the NAIP near the Paleocene–Eocene boundary has been suggested to have influenced the genesis of rapid global warming during the Paleocene-Eocene Thermal Maximum (PETM: Storey et al., 2007; Frieling et al., 2016), an event that also includes an extinction of

benthic foraminifera (Thomas and Shackleton, 1996). The NAIP consists of a series of subaerial lava flows and intrusive units (e.g. Svensen et al., 2004, 2010), that are dated to between ~60 and ~53 Ma (Storey et al., 2007; Svensen et al., 2010; Wilkinson et al., 2016). Only two existing Os-isotope records (from Fe-Mn crusts CD-29 and D11-1) cover the entire period of emplacement, (Klemm et al., 2005; Burton, 2006). These records show a shift in seawater $^{187}Os/^{188}Os$ to slightly more unradiogenic values, as would be expected as extruded basalts began to weather into the oceans (Fig. 4). A number of high-resolution Os-isotope records span the Paleocene–Eocene boundary (Ravizza et al., 2001; Weiczorek et al., 2013; Dickson et al., 2015), when the accumulation rate of NAIP basalts increased significantly at the commencement of seafloor spreading (Storey et al., 2007b). These records actually show a small change (~0.05) to more radiogenic $^{187}Os/^{188}Os$ ratios that has been interpreted to reflect enhanced weathering of terrestrial rocks due to elevated atmospheric temperatures and moisture (Ravizza et al., 2001; Dickson et al. 2015). The small magnitude of the increase in $^{187}Os/^{188}Os$ compared with other Phanerozoic events (e.g. Cohen et al., 2004) may be due to the competing influences of Os being weathered from both radiogenic and unradiogenic sources at the same time. Several of the NAIP datasets also demonstrate a very brief shift to more unradiogenic values in seawater near the Paleocene–Eocene boundary, which likely records a pulse of unradiogenic Os associated with magmatic activity at the commencement of the PETM (Weiczorek et al., 2013; Dickson et al., 2015), or perhaps an extraterrestrial impact event (c.f. Schaller et al., 2017). The stratigraphic correspondence between unradiogenic Os-isotope ratios and a peak in Hg concentrations in pre-PETM deposits in Svalbard tend to support a volcanic origin for this feature (Jones et al., 2019). This observation highlights the potential for Os isotope stratigraphy to reveal very fine-scale detail of volcanic activity that is pertinent to testing hypotheses relating LIP emplacement to rapid climate change.

The influence of episodic NAIP activity on brief global warming events ('hyperthermals') that occurred *after* the PETM is largely untested. A new Os-isotope record is shown in Fig. 4 from IODP Site M0004A (Arctic Ocean) spanning one such event, Eocene Thermal Maximum 2 (~53 Ma). These data were produced using techniques identical to those of Dickson et al. (2015). Initial Os-isotope ratios increase by ~0.1 (0.38–0.48) shortly before the carbon isotope excursion that marks the start of the event, and again in more dramatic fashion at the termination of the carbon cycle perturbation, from ~0.4–0.8. The data are similar to $^{187}Os/^{188}Os$ ratios of metalliferous sediments from DSDP 549 that contain a shift to more radiogenic values (from ~0.44–0.50) across ETM 2 (Peucker-Ehrenbrink and Ravizza, 2012), thus supporting the hypothesis of a rapid increase in continental weathering across the hyperthermal. A single unradiogenic value of 0.18 also stratigraphically precedes ETM 2 at Site M0004A (Fig. 4). Given the short duration of the ETM 2 (~100 kyrs) the unradiogenic value before the event began is at least consistent with a volcanic trigger. These observations come with the caveat of increasing hydrographic restriction in the Arctic during the Early Eocene (Brinkhuis et al., 2006; Dickson et al., 2015) that may have caused

the $^{187}Os/^{188}Os$ ratio of Arctic Ocean seawater to deviate from the global value – although the comparison of ETM 2 data from Site M0004A and Site 549 suggest that this effect was small. The NAIP is a clear candidate for future high-resolution Os-isotope studies that seek to unravel the interaction of volcanism and climate change in the early Cenozoic.

The Deccan Traps (~66.3–65.5 Ma)

Ar-Ar age estimates of the timing of LIP emplacement place the Deccan Traps close to the mass-extinction event at the Cretaceous–Paleogene boundary (K–Pg) (Chenet et al., 2007). U–Pb dating of zircons recovered from ashfall and erosive units interbedded with lava flows has recently allowed the chronology of this event to be improved substantially, with an estimate of ~753 kyrs for 80–90% of the total eruptive history (Schoene et al., 2015). Os-isotope records from a variety of carbonate successions show reproducible trends in seawater $^{187}Os/^{188}Os$ prior to the K–Pg, with a ~20–25% decrease towards unradiogenic values commencing at the C29r/C30n boundary, followed by a second decrease towards even more unradiogenic values occurring much closer to the K–Pg itself (Fig. 5, Ravizza and Peucker-Ehrenbrink, 2003; Robinson et al., 2009). Os data from K–Pg locations in Europe and the US show that seawater $^{187}Os/^{188}Os$ decreased nearly to mantle values of ~0.14 at the acme of the unradiogenic shift prior to the K–Pg. This decrease is consistent both with an extraterrestrial impactor (Luck and Turekian, 1983; Esser and Turekian, 1989; Geissbühler, 1990; Peucker-Ehrenbrink et al., 1995; Meisel et al., 1995; Yin et al., 1995), and also with the emplacement of the Poldapur Deccan basalts, according to recent U-Pb data (Schoene et al., 2019). Osmium isotope data from latest Cretaceous rocks have been instrumental in testing the hypothesis that the eruption of the Deccan Traps caused the end-Cretaceous mass extinction. The earliest shift in $^{187}Os/^{188}Os$ associated with volcanism occurs considerably earlier than the major extinction horizon, an observation that tends to favour an extraterrestrial impactor as the cause of most (though not all) of the major biotic consequences of this time interval (Ravizza and Peucker-Ehrenbrink, 2003).

The Deccan Traps illustrate an interesting conundrum in the interpretation of $^{187}Os/^{188}Os$ data in terms of LIP activity. Ravizza and Peucker-Ehrenbrink (2003) interpreted the decrease in $^{187}Os/^{188}Os$ commencing at the C29r/C30n boundary as recording a decrease in the weathering of radiogenic Os as flood basalts were extruded across crystalline basement rocks in the early phases of the Deccan LIP. This argument was in part supported by the low concentration of Os in Deccan basalts (Allègre et al., 1999). Other LIP events featuring a decrease in the $^{187}Os/^{188}Os$ of seawater have been interpreted in terms of an increase in the weathering of unradiogenic Os from mafic rocks (Turgeon and Creaser, 2008; Tejada et al., 2009, Bottini et al., 2012; Du Vivier et al., 2014). These differences highlight the fact that the marine $^{187}Os/^{188}Os$ ratio is the product of two competing inputs, and that the use of complementary datasets is often required to arrive at a satisfactory interpretation of the observed chemostratigraphic variations.

The Caribbean (~95–60 Ma), High Arctic (127–81 Ma) and Madagascan (~84–95 Ma) LIPs

Volcanism has long been hypothesized as a trigger for one of the most profound episodes of Phanerozoic ocean deoxygenation, at the Cenomanian–Turonian boundary. This event, Oceanic Anoxic Event 2 (OAE 2) took place at a similar time as the emplacement of several LIPs, most notably the Caribbean LIP (CLIP) and the High Arctic LIP (HALIP). Early studies attributed concentration spikes of mafic-derived trace elements in sedimentary rocks to infer volcanism (e.g. Orth et al., 1993), and this approach has continued recently (Eldrett et al., 2014). The publication of the first Os-isotope records for the Cenomanian–Turonian boundary, by Turgeon and Creaser (2008), revealed mantle-like signatures in global seawater that were sustained for hundreds of thousands of years during the acme of the environmental changes associated with OAE 2. These data firmly supported the significant role of voluminous volcanic activity in driving and sustaining widespread environmental change during this event, presumably through volcanism-climate feedbacks. Such feedbacks may have included the delivery of bio-limiting nutrients and sulfate to the oceans, stimulating organic matter production and the consequent consumption of dissolved oxygen in many parts of the oceans (Adams et al., 2010; Jenkyns, 2010). The Os-isotope datasets of Turgeon and Creaser (2008) have since been supplemented by Du Vivier et al. (2014, 2015), who were able to show how abrupt shifts in $^{187}Os/^{188}Os_{(i)}$ ratios towards mantle values (~0.15) occurred several thousands of years in advance of the positive carbon isotope excursion that defines the event (c.f. Arthur et al., 1987; Tsikos et al., 2004) (Fig. 6). The persistence of unradiogenic Os-isotope values over a period of several hundreds of thousands of years, far in excess of the Os residence time in the oceans, demonstrates the prolonged period of time during which Os was weathered from volcanic rocks on land and/or by submarine basalt-seawater interaction (Turgeon and Creaser, 2008; Du Vivier et al., 2014, 2015). Furthermore, changes in the concentration of Os in sedimentary successions throughout the phase of otherwise unradiogenic Os-isotope ratios within OAE 2 may suggest small changes in the amount of Os being weathering into the oceans (Du Vivier et al., 2014, 2015). However, despite the clear signature of LIP activity afforded by the unradiogenic Os-isotope values that span OAE 2, these data are not able to unambiguously fingerprint the source of the unradiogenic Os flux. Various studies continue to debate the relative importance of volcanism associated with the HALIP (Eldrett et al., 2017) and the CLIP (Kuroda et al., 2007; Holmden et al., 2016; Scaife et al., 2017), while Ar-Ar ages for eruptive events associated with the Madagascan LIP (Cucciniello et al., 2010) also slightly overlap the age of the Cenomanian-Turonian boundary (Meyers et al., 2012). It is possible that these events all contributed in some way to the widespread environmental changes that occurred during OAE 2.

OAE 2 provides an interesting case study of hysteresis in Earth-System processes. The lead-lag relationship between Os-isotope and C-isotope changes at the onset of OAE 2 clearly supports the contention of a volcanic trigger with the rapid emplacement of submarine basalts, probably associated with the CLIP, being rapidly weathered into seawater. However, the shift to

306 more radiogenic Os-isotope ratios in marine sediments before the end of OAE 2 does not clearly
307 link to a decrease in global temperatures, as would be expected if volcanic CO_2 emissions slowed
308 and were further reduced by silicate weathering and organic-carbon burial feedbacks (Robinson et
309 al., 2019). As well as driving transient environmental changes, LIP volcanism may also drive
310 Earth's climate system into new, quasi-stable states.
311
312 *The Ontong-Java Plateau (~126–117 Ma)*
313 Os-isotope stratigraphy has been instrumental in demonstrating that the emplacement of the
314 Ontong-Java LIP in the ancestral Pacific Ocean occurred at precisely the same time as an episode
315 of major environmental change, during Oceanic Anoxic Event 1a (Tejada et al., 2009; Bottini et al.,
316 2012). These Os-isotope records, from locations in two different ocean basins, have strikingly
317 similar $^{187}Os/^{188}Os_{(i)}$ values, and exhibit near-identical shifts in $^{187}Os/^{188}Os_{(i)}$ ratios when compared
318 to the carbon- and bio-stratigraphic frameworks for each locality (Malinverno et al., 2010) (example
319 in Fig. 7). The Os-isotope records clearly support three major findings. Firstly, the major phase of
320 environmental change during OAE-1a (the 'Selli' level; c.f. Coccioni et al., 1987) coincided with
321 almost mantle-like $^{187}Os/^{188}Os_{(i)}$ ratios of ~0.15–0.2 (Bottini et al., 2012). These unradiogenic
322 values must have been maintained for almost 900,000 years by the continual hydrothermal
323 weathering of very large quantities of mafic and ultramafic rocks during a major phase of
324 submarine LIP emplacement. Secondly, the $^{187}Os/^{188}Os_{(i)}$ records bear some similarity to events
325 surrounding Late Cretaceous OAE 2 because the influence of LIP weathering on ocean chemistry
326 began prior to the onset of OAE-1a (Bottini et al., 2012). This lead-lag relationship implies a causal
327 relationship between the O-J LIP and major environmental change during OAE-1a. Somewhat
328 enigmatic, less radiogenic $^{187}Os/^{188}Os_{(i)}$ ratios in Upper Barremian strata of the Cismon core, Italy,
329 hint at an even earlier, less intense phase of volcanism that may have been linked to a bio-
330 calcification crisis in nannofossil flora (Erba et al., 2010; Bottini et al., 2012). The existing data
331 resolution is, however, not sufficient to resolve this hypothesis. Thirdly, $^{187}Os/^{188}Os_{(i)}$ ratios exhibit
332 significant shifts throughout OAE-1a, with radiogenic values occurring at the base of the Selli level
333 at Gorgo a Cerbara (Italy, Tejada et al., 2009) and Cismon (Bottini et al., 2012). As with all
334 $^{187}Os/^{188}Os_{(i)}$ records, such shifts cannot be uniquely interpreted as a reflection of continental
335 weathering because of the interplay between the weathering of *both* mafic and continental rocks.
336 Circumstantial reasoning based on coeval proxy data, however, can assist with qualitative
337 interpretations of such stratigraphic fluctuations in $^{187}Os/^{188}Os_{(i)}$.
338
339 *The Karoo-Ferrar LIP (189–178 Ma)*
340 Volcanism in the Karoo and Ferrar (K-F) provinces, in present day South Africa, South America
341 and Antarctica, has been linked to episodes of rapid environmental change in the Early Toarcian,
342 particularly the Toarcian Oceanic Anoxic Event (T-OAE). Radiometric dating of rocks attributable to
343 the Karoo and Ferrar provinces indicate an overall duration of several millions of years (e.g.

Duncan et al., 1997; Sell et al., 2014), with a much shorter period of intense activity around the T-OAE itself, including hydrothermal venting, at ~183 Ma (e.g. Svensen et al., 2007, 2012; Burgess et al., 2015). Three marine $Os_{(i)}$ isotope records span part of the duration of the K-F LIP, from Yorkshire, UK (Cohen et al., 2004); North Wales, UK (Percival et al., 2016); and western Canada (Them et al., 2017). A fourth Os-isotope dataset was recently measured in lacustrine shales of the Chinese D'hanzhai member, which contain distinctly more radiogenic values than the marine sections (Xu et al., 2017). The marine records all retain a similar range of values, which point to a well-mixed ocean inventory of Os in the early Jurassic (Fig. 8). They also all exhibit large increases in $^{187}Os/^{188}Os_{(i)}$ ratios towards radiogenic values across the T-OAE in the range 0.3–0.8 (Fig. 8), which is somewhat counter-intuitive given the intense volcanic activity that took place at that time. The explanation for this trend may lie partly in the largely sub-aerial nature of the K-F LIP and the associated lack of continental breakup, which inhibited the weathering rate of mafic rocks into the oceans following emplacement (Percival et al., 2016). Also, volcanic-driven climate warming probably contributed to the intense weathering of continental crust that would have caused a large influx of radiogenic Os to the oceans, thereby overwhelming any unradiogenic flux (Cohen et al., 2004). The Os isotope records spanning part of the K-F LIP clearly demonstrate the unique characteristics of the climatic and weathering feedbacks associated with this LIP, certainly in contrast with large LIP events of the Cretaceous (Ontong-Java and Caribbean LIPs) (Figs 6 and 7). However, no single Os isotope record has yet been produced that spans the entire estimated K-F duration. Establishing such records in the future will be useful to test hypotheses linking volcanism to early Jurassic climate change, particularly in the light of recent studies that tend to suggest ocean deoxygenation began considerably earlier than the T-OAE, closer to the putative onset of K-F volcanism before ~183 Ma (Them et al., 2018).

The Central Atlantic Magmatic Province (201.6–200.9 Ma)

The Central Atlantic Magmatic Province (CAMP) has been the subject of many detailed studies that have established precise chronologies of volcanic pulses from ~201.6–200.9 Ma (e.g. Schoene et al., 2010; Blackburn et al., 2013; Davies et al., 2017). These, and other stratigraphic studies, have shown a close temporal relationship between initial pulses of intrusive volcanism, a first order mass extinction, and a large negative carbon isotope excursion of only a few tens of kyrs duration (Hesselbo et al., 2002; Ruhl et al., 2010; Whiteside et al., 2010). While there are two $Os_{(i)}$ isotope records that span the duration of the CAMP, from the South West UK (Cohen and Coe, 2002), and from Japan (Kuroda et al., 2010), neither of these is presently able to resolve the impact of the CAMP on seawater chemistry with comparable temporal precision to U-Pb chronologies (e.g. Blackburn et al., 2013) or chemostratigraphic studies (e.g. Hesselbo et al., 2002; Ruhl et al., 2011). Both Os records contain evidence for a decrease in the $^{187}Os/^{188}Os$ ratio of seawater between the latest Triassic (Rhaetian) and the early Jurassic (Hettangian) broadly from ~0.3–0.6 to 0.1–0.5. However, the UK record has no data from the critical interval

encompassing the earliest emplacement of intrusive magmas and the end-Triassic mass extinction, corresponding to the upper Westbury and Lilstock Formations (Cohen and Coe, 2002) (Fig. 9). The Japanese record, in contrast, has a higher stratigraphic resolution, but differs from the UK record in two respects: firstly, minimum $^{187}Os/^{188}Os_{(i)}$ ratios of ~0.2 occur in late Triassic deposits in Japan, but in early Jurassic deposits in the UK; and secondly, $^{187}Os/^{188}Os_{(i)}$ ratios are slightly more radiogenic throughout the Japanese section than in the UK. The stratigraphic differences between the sections may be due to the difficulty of correlating the Japanese locality with the northern European biostratigraphic scheme (Kuroda et al., 2010), or to heterogeneity in late Triassic – early Jurassic seawater $^{187}Os/^{188}Os$ ratios. As with the K-F LIP, the potential for Os-isotope chemostratigraphy to unravel the impact of the CAMP on global seawater chemistry at a resolution comparable to the U-Pb geochronology has not yet been fully realized.

The Siberian Traps (~252.2–250.2 Ma)

Zircon U–Pb ages of the Siberian Traps have been used to formulate a model of LIP evolution in relation to the largest mass extinction event of the Phanerozoic Eon. Volcanism began at ~252.4 Ma and ended before ~250.2 ± 0.3 Ma (Kamo et al., 1996; Bowring et al., 1998; Burgess and Bowring, 2015, Burgess et al., 2014, 2017). The mass extinction horizon itself has been tied closely to the first evidence for intrusive volcanism at ~ 251.9 Ma (Burgess et al., 2017). Despite the detailed chronological constraints on the Siberian Traps, osmium isotope stratigraphy has not yet been applied to this event in great detail. $^{187}Os/^{188}Os_{(i)}$ values have been estimated from Re–Os isochrons with ages of ~252–252.5 Ma, to the range 0.56–0.62 (Georgiev et al., 2011) (Fig. 10). These data tend to suggest a limited evolution of seawater $^{187}Os/^{188}Os$ across the early interval of volcanism, although younger Re–Os datasets (247–234 Ma) have $^{187}Os/^{188}Os_{(i)}$ values of ~0.8–1.4, implying a slight evolution of seawater to more radiogenic values by the early Triassic (Yang et al., 2004; Xu et al., 2009; Pašava et al., 2010). Nonetheless, the data are of low-resolution and do not clearly cover the major phase of intrusive volcanism, allowing for the large uncertainties in the Re–Os estimates of depositional ages and $^{187}Os/^{188}Os_{(i)}$ (Georgiev et al., 2011). A single stratigraphic record at Opal Creek, Alberta, exhibits a decrease in $^{187}Os/^{188}Os_{(i)}$ from 0.54 to 0.35 following the Late Permian extinction level, followed by a return to ~0.60 at the Permian–Triassic boundary (Schoepfer et al., 2012) (Fig. 10). These data suggest a transient excursion in seawater Os chemistry towards unradiogenic $^{187}Os/^{188}Os$ values during an interval of intrusive volcanism in the Siberian Traps (c.f. Burgess et al., 2017), that is temporally constrained by U–Pb ages to a duration <60 kyrs (c.f. Burgess et al., 2014). Additional data for this section show a small excursion to an unradiogenic value of ~0.20 shortly following the main extinction level (Georgiev et al., 2015). The reasons for this brief excursion are not clear, but may be linked to variations in subaerial basalt weathering and/or the transport of radiogenic or unradiogenic weathering signals from the Siberian LIP to the global ocean. The relatively small magnitude of documented $^{187}Os/^{188}Os_{(i)}$ variation for the Siberian Traps compared to, e.g. the CAMP or OJP LIPs, may be related to the

high latitude of their emplacement, which would have resulted in a low weathering rate. Thus, the impact of the Siberian Traps on ocean Os chemistry may have been disproportionate to their considerable environmental impact.

Summary: Os-isotope stratigraphy and LIPs

Os isotope data from a number of marine sedimentary successions has been instrumental in establishing the link between LIP volcanism and major environmental changes in the Early Cretaceous (OAE 1a) and Late Cretaceous (OAE 2), with significant shifts in seawater chemistry to mantle-like values over timescales of 10^4–10^5 years (Turgeon and Creaser, 2008; Tejada et al., 2009; Bottini et al., 2012; Du Vivier et al., 2014, 2015). The data have been useful in distinguishing the effect of extraterrestrial impacts and LIP volcanism on major extinction events (Ravizza and Peucker-Ehrenbrink, 2003; Robinson et al., 2009) and in testing hypotheses of Earth-System feedbacks during LIP-inspired intervals of profound global warming (Cohen et al., 2004; Dickson et al., 2015; Percival et al., 2016; Them et al., 2017).

Nonetheless, the usefulness of Os-isotope stratigraphy to understand the timing and effects of LIP volcanism is capable of further refinement. Os isotopes have most commonly been used to investigate the effects of volcanism on stratigraphically well-defined episodes of environmental change, thus testing putative links between volcanism and climate. While these groundbreaking studies established the fundamental basis for this approach, the resulting data do not often span the full interval of LIP activity. Additionally, the fundamental drivers of the Os-isotope budget of the oceans - the weathering of continental and oceanic rocks - make it difficult to uniquely disentangle the effects of basalt and continental rock weathering on seawater $^{187}Os/^{188}Os$ ratios. Many different factors may cause the balance of the weathering products of these sources to vary over time, in addition to the simple presence of a LIP. Such factors include the prevalence of intrusive or extrusive volcanism; the amount and composition of Os liberated from igneous and sedimentary rocks during intrusive events; the latitude of LIP emplacement (and thus proximity to regions of intense physical or chemical weathering); the association of LIP emplacement with continental breakup (i.e. the CAMP); and the effects of volcanism-climate feedbacks on the intensity and/or congruency of global weathering regimes. The heterogeneous Os isotope signatures of Phanerozoic LIPs reflect the many ways in which these factors can combine in both time and space.

The recent emergence of mercury (Hg) concentrations as a proxy for volcanism (e.g. Sanei et al., 2008; Percival et al., 2015; Charbonnier et al., 2017; Scaife et al., 2017, among others), opens the possibility of pairing Os-isotopes with Hg analyses to help interpret stratigraphic variations in $^{187}Os/^{188}Os_{(i)}$ (e.g. Percival et al., 2016, 2018) (Fig

. 8). Additionally, the role of continental rock weathering as a driver of Os-isotope change in the oceans might also be better constrained by pairing these measurements with other emerging proxies for silicate weathering, such as Li isotopes. One such application of Os and Li isotopes, to

458 OAE 2, has been used to calculate the mass of basalts weathered into the oceans during that
459 event (Pogge van Strandmann et al., 2013). Paired applications of Os and Li may yield fruitful
460 insights into global weathering patterns related to other LIP events.

461 Os-isotope stratigraphy holds a crucial place in the compendium of approaches used to
462 investigate the effect of LIPs on the Earth's environment. Future applications of this technique at
463 even finer temporal scales will offer further insights into the timing and environmental
464 consequences of LIPs.

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Figure captions

Figure 1: Ages of Late Phanerozoic LIPs and the temporal overlap of existing $^{187}Os/^{188}Os_{(i)}$ records with these volcanic events. Ages for each LIP are taken from Barry et al. (2013), Schoene et al. (2015), Duncan et al. (1997), Hofmann et al. (1997), Duncan (2002), Storey et al. (2007), Timm et al. (2011), Blackburn et al. (2013), Loewen et al. (2013), Burgess and Bowring (2015), Davies et al. (2017), and Kingsbury et al. (2018). Dashed lines indicate approximate periods of reduced activity within the overall duration of a LIP.

Figure 2: The modern mass balance of osmium. Osmium isotope ratios for different geological materials are shown along with key literature references. The modern seawater value of ~1.06 represents a contribution of ~10–30% from unradiogenic (mantle and extraterrestrial dust) fluxes and ~70–90% from radiogenic sources in the continental crust.

Figure 3: Miocene Os-isotope data spanning the emplacement of the Columbia River LIP. Data are from Klemm et al. (2008). The grey shaded region denotes a shift towards more unradiogenic seawater $^{187}Os/^{188}Os$ ratios that are taken to record the rapid weathering of basalts associated with LIP emplacement and/or a reduction in the weathering rate of continental rocks.

Figure 4: Paleocene–Eocene Os-isotope data spanning the emplacement of the North Atlantic Igneous Province. Fe-Mn crust data are from Klemm et al. (2005); all PETM data are from Dickson et al. (2015); ETM-2 Os isotope data are presented in this paper; ETM-2 C-isotope data for IODP Site M0004A are compiled from Sluijs et al. (2009) and Dickson and Cohen (2012). Grey shaded regions denote the main phases of the PETM and ETM-2.

Figure 5: Maastrichtian–Paleocene Os-isotope data spanning the emplacement of the Deccan Traps and the K-Pg boundary. Data are from Robinson et al. (2009). The grey shaded region denotes a shift towards more unradiogenic seawater $^{187}Os/^{188}Os$ ratios that are taken to record the rapid weathering of basalts associated with LIP emplacement and/or a reduction in the weathering rate of continental rocks.

Figure 6: Cenomanian–Turonian Os-isotope data spanning Oceanic Anoxic Event 2, and a putative magmatic episode linked to the Caribbean LIP and/or the High Arctic LIP. C-isotope data are from Erbacher et al. (2006) and Os-isotope data are from Turgeon and Creaser (2008). The grey shaded region denotes a shift towards more unradiogenic seawater $^{187}Os/^{188}Os$ ratios that are taken to record the rapid weathering of basalts associated with LIP emplacement and/or a reduction in the weathering rate of continental rocks.

Figure 7: Early Cretaceous Os-isotope data spanning part of the emplacement of the Ontong-Java Plateau LIP and Oceanic Anoxic Event 1a. Data are from Tejada et al. (2009). The grey shaded region denotes a shift towards more unradiogenic seawater $^{187}Os/^{188}Os$ ratios that are taken to record the rapid weathering of basalts associated with LIP emplacement and/or a reduction in the weathering rate of continental rocks.

Figure 8: Pliensbachian–Toarcian (Early Jurassic) Os-isotope and Hg concentration data spanning the emplacement of the Karoo-Ferrar LIP and the Toarcian Oceanic Anoxic Event. C-isotope data are from Xu et al. (2018), and Os-isotope and Hg concentration data are from Percival et al. (2016). The grey shaded region denotes the main phase of emplacement of the Karoo-Ferrar LIP.

Figure 9: Triassic–Jurassic Os-isotope data spanning the emplacement of the Central Atlantic Magmatic Province and the end-Triassic extinction event. Data are from Cohen and Coe (2002). The grey shaded region denotes the main period of CAMP emplacement. Note that the existing Somerset Os-isotope record does not contain data from within this zone.

Figure 10: End-Permian Os-isotope data spanning the emplacement of the Siberian Traps LIP. Circles for the Siberian Traps are for three $^{187}Os/^{188}Os_{(i)}$ estimates (Georgiev et al., 2011) whose age uncertainties span the entire duration of LIP emplacement (c.f. Burgess and Bowring, 2014). Additional data (squares) are from Schoepfer et al. (2013).

Table 1: ETM-2 osmium data for IODP Site M0004A

Sample (core-section-top depth-lower depth)	Depth (mcd)	Os (ppt)	$^{187}Re/^{188}Os$	$^{187}Os/^{188}Os$	±	$^{187}Os/^{188}Osi$
27-1-76-77	368.16	280.60	1354.76	1.741	0.002	0.529
27-1-94-95	368.34	671.36	4021.20	4.419	0.017	0.820
27-1-110-111	368.50	641.05	1468.63	1.759	0.003	0.444
27-1 (120-121)	368.60	330.35	1335.92	1.670	0.002	0.475
27-1-129-130	368.69	523.74	1076.04	1.463	0.004	0.500
27-1-137-138	368.77	428.68	2171.30	2.490	0.005	0.546
27-1-149-150	368.89	514.71	1304.16	1.650	0.003	0.483
27-2-4-5	368.94	213.45	389.80	0.901	0.002	0.552
27-2-15-16	369.05	630.75	2096.88	2.256	0.003	0.379
27-2-25-26	369.15	179.95	974.19	1.250	0.001	0.378
27-2-60-61	369.50	370.05	1324.71	1.366	0.002	0.180
27-2-131-132	370.21	261.81	512.49	0.906	0.002	0.447
27-3-22-23	370.62	334.44	1130.95	1.370	0.001	0.358