

1 **The osmium isotope signature of Phanerozoic Large Igneous Provinces**

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11 **Abstract**

12
13 The emplacement of Large Igneous Provinces (LIPs) throughout the Phanerozoic Eon introduced
14 vast quantities of mafic rocks to the Earth's surface, which were subsequently weathered into the
15 oceans. Osmium isotope data can be used to track these LIP-related weathering fluxes, providing
16 a global fingerprint of the timing and magnitude of LIP emplacement, and guiding assessments of
17 the impact of these events on ocean biogeochemistry and the regulation of the global climate
18 system. Sedimentary Os isotope records spanning late Phanerozoic LIP events are reviewed
19 herein and new observations from Eocene hyperthermal event ETM-2 are presented. While Os
20 isotope stratigraphy can provide major constraints on LIP activity in the geological record, it cannot
21 always distinguish whether the extrusive activity was subaerial or submarine. The utility of osmium
22 isotopes as a global tracer of past volcanism may be enhanced when used alongside proxies such
23 as mercury concentrations, which may be more diagnostic of the style of individual episodes of LIP
24 emplacement. Hitherto, only a few high-resolution Os-isotope records across Phanerozoic LIPs
25 have effectively exploited the short oceanic residence time of Os. Future high-resolution studies
26 across suitable, well-preserved stratigraphic records will significantly improve our understanding of
27 the nature, progression and consequences of LIP emplacement.

28 **Introduction: the episodic nature of LIP emplacement**

29
30 The emplacement of Large Igneous Provinces (LIP) is characterized by anomalously high
31 magmatic fluxes, such that the majority of their volume is emplaced within a relatively short time-
32 period of < 1–2 million years. They comprise massive volumes of mantle-derived igneous material
33 sometimes in excess of 10^6 km³, intruded into the crust as dykes, sills and batholiths, and extruded
34 onto the surface as effusive lava flows or as explosive ejecta together with a cocktail of
35 superheated gases and fluids in either a subaerial or submarine environment (Coffin and Eldholm,
36 1992, 1994; Ernst, 2014). LIPs have often been linked to mantle plumes, which are persistent
37 upwellings of anomalously hot mantle. The rapid eruption rates and huge volumes of material
38 sourced from melting in the plume head during the early stages of LIP emplacement far exceed
39 present-day eruption rates and volumes, and because of this rapidity they are proposed to have

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

44 Several key questions regarding LIP behaviour have been postulated: When did individual
45 LIP events occur? Was volcanic activity continuous or intermittent over the period of
46 emplacement? Did LIP emplacement drive changes in the global climate system? What climatic
47 feedback processes do LIPs perturb? Do all LIPs alter Earth System processes (weathering,
48 ocean chemistry, warming etc) in the same way? Do all LIPs cause biotic extinctions? The
49 approach to answering many of these questions is commonly to undertake rigorous radiometric
50 dating of igneous rocks that can be related to specific episodes of LIP activity. These efforts initially
51 centred on Ar-Ar dating of flood basalts. These Ar-dating approaches have been instrumental in
52 establishing first-order relationships between the timing of LIP events and major extinction and
53 environmental changes across the Phanerozoic and beyond (Wignall et al., 2001), but are
54 sometimes limited by relatively large absolute age uncertainties, which may be on the order of \sim
55 $\pm 10^5$ – 10^6 years. Recent advances in U-Pb dating, with reported age uncertainties of $\pm 10^4$ years,
56 have significantly reduced the age uncertainties on some LIP events, thereby allowing a greater
57 understanding of how individual episodes of LIP activity may proceed within a longer period of
58 emplacement (e.g. Schoene et al., 2010; Svensen et al., 2010; Blackburn et al., 2013; Burgess
59 and Bowring, 2015; Davies et al., 2017; other contributions in this volume). Ultra-high resolution
60 dating of magmatic episodes has greatly improved our understanding of the nature of LIP activity,
61 providing a precise framework to explore the potential of volcanic activity as a trigger for the
62 complex environmental changes and feedbacks leading to mass extinction events. Nonetheless,
63 this approach requires the preservation of datable rocks that can be stratigraphically related to the
64 overall LIP sequence. This requirement inevitably leads to LIP chronologies that can potentially be
65 discontinuous and patchy.

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

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

85

86 **Os isotope stratigraphy**

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

99 Three important aspects of the Os-isotope system in regard to LIPs need to be considered.
100 Firstly, Os isotopes are an indirect tracer for LIP activity. The rapid emplacement of LIPs can result
101 in the intense and rapid weathering of juvenile mafic and ultramafic rocks, either by atmospheric
102 and biogeochemical processes, low-temperature submarine basalt-seawater interaction or by the
103 creation of hydrothermal systems around submarine volcanic centres (Ravizza and Peucker-
104 Ehrenbrink, 2000; Cohen and Coe, 2002; Turgeon and Creaser, 2008). These weathering fluxes
105 release unradiogenic Os into seawater, which lowers the seawater $^{187}\text{Os}/^{188}\text{Os}$ ratio. However, if
106 LIP rocks are not easily susceptible to weathering, or if LIP activity re-mobilizes Os from previously
107 buried sedimentary reservoirs, the $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater might instead record a shift
108 towards radiogenic values. This trend may be amplified if climate feedbacks associated with
109 widespread volcanism are able to increase the congruency of terrestrial rock weathering. In
110 practice, the Os-isotope 'signature' of a LIP might involve swings in seawater $^{187}\text{Os}/^{188}\text{Os}$ in either
111 direction at different times, a feature that is clearly apparent during many LIP events (e.g. the
112 Ontong-Java Plateau and the North Atlantic Igneous Province (Bottini et al., 2012; Dickson et al.,
113 2015). The second important feature of the Os isotope system is the short residence time of Os in
114 the oceans, of ~ 10 – 50 kyrs (Sharma et al., 1997; Levasseur et al., 1998). This feature provides
115 Os-isotope stratigraphy with the potential for tracing the pulsed emplacement of LIPs at timescales

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

122 Osmium is present in seawater only in ultra-trace concentrations, but is strongly enriched in
123 reducing marine sediments. The enrichment of Os (and Re) in low-oxygen depositional settings
124 means that paleo-seawater $^{187}\text{Os}/^{188}\text{Os}$ ratios can be traced by the careful measurement of Re and
125 Os compositions in organic-rich mudrocks, followed by a correction for the post-depositional decay
126 of ^{187}Re (Ravizza and Turekian, 1989; Cohen et al., 1999). The requirement to correct $^{187}\text{Os}/^{188}\text{Os}$
127 ratios in organic-rich rocks for ^{187}Re decay means that so-called initial Os-isotope stratigraphies
128 (Os_i) have been produced mainly for those events where suitable deposits exist with independent
129 age control. Where there is no independent age control, 'initial' $^{187}\text{Os}/^{188}\text{Os}$ ratios can be estimated
130 without independent age control using the isochron approach of measuring samples with different
131 $^{187}\text{Re}/^{188}\text{Os}$ ratios collected from a restricted stratigraphic range (e.g. Cohen et al., 1999). Some
132 Os-isotope records have also been produced from Fe-Mn crusts and oxic metalliferous sediments
133 (e.g. Pegram et al., 1992; Peucker-Ehrenbrink et al., 1995; Ravizza et al., 2001; Klemm et al.,
134 2005, 2008; Burton, 2006; Robinson et al., 2009). These records do not require a significant
135 correction for Re decay, but may be systematically biased due to the partial liberation of detritally-
136 hosted Os phases from the bulk sediment (e.g. Pegram and Turekian, 1999). Furthermore, such
137 records from Fe-Mn crusts have a limited temporal resolution because of their slow accumulation
138 rates. In all types of approach (mudrocks or crusts/sediments), Os_i records spanning early
139 Phanerozoic LIPs (i.e. pre-Permian) have not yet been produced. The LIP record of only the late
140 Phanerozoic will therefore be summarized in the following discussion, and illustrated in Figs 3 and
141 4.

142

143 **The Phanerozoic Os-isotope record of LIPs**

144 *The Columbia River LIP (~17–15 Ma)*

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

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

170

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

172 The Ethiopian-Yemeni LIP has the best-preserved sequence of flood basalts in the Cenozoic
173 geological record. The main phase of flood basalt volcanism began shortly before ~ 30 Ma and
174 lasted for less than ~ 1 million years (Hofmann et al., 1997; Ukstins et al., 2002), before continuing
175 in pulses concomitant with the opening of the Red Sea and the Gulf of Aden (Courtillot and Renne,
176 2003). Magnetostratigraphy of the Ethiopian flood basalts indicate a correlation to magnetochrons
177 C11r to C11n (Hofmann et al., 1997; Touchard et al., 2003), making them younger than the
178 Eocene–Oligocene boundary event, which occurred during chrons C13r–C12r (~ 34 Ma, e.g.
179 Zachos et al., 1996). The effect of the Ethiopian–Yemeni LIP on the osmium chemistry of the
180 oceans is not well understood, with low-resolution data available from only three locations
181 (Peucker-Ehrenbrink and Ravizza, 2012). These records agree in the sense that they all show
182 $^{187}\text{Os}/^{188}\text{Os}$ ratios evolving to less radiogenic values at $\sim 30\text{--}31$ Ma. However, the magnitude and
183 pattern of this decrease varies, from ~ 0.08 in Indian Ocean ODP Site 711, to ~ 0.12 in South
184 Atlantic DSDP Site 522 (Peucker Ehrenbrink and Ravizza, 2012). Os-isotope stratigraphy therefore
185 appears to reveal a signature of basalt weathering on ocean chemistry, though the true size of this
186 weathering flux, and its wider temporal context, are limited by the available data.

187

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

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

192 benthic foraminifera (Thomas and Shackleton, 1996). The NAIP consists of a series of subaerial
193 lava flows and intrusive units (e.g. Svensen et al., 2004, 2010), that are dated to between ~60 and
194 ~53 Ma (Storey et al., 2007; Svensen et al., 2010; Wilkinson et al., 2016). Only two existing Os-
195 isotope records (from Fe-Mn crusts CD-29 and D11-1) cover the entire period of emplacement,
196 (Klemm et al., 2005; Burton, 2006). These records show a shift in seawater $^{187}\text{Os}/^{188}\text{Os}$ to slightly
197 more unradiogenic values, as would be expected as extruded basalts began to weather into the
198 oceans (Fig. 4). A number of high-resolution Os-isotope records span the Paleocene–Eocene
199 boundary (Ravizza et al., 2001; Weiczorek et al., 2013; Dickson et al., 2015), when the
200 accumulation rate of NAIP basalts increased significantly at the commencement of seafloor
201 spreading (Storey et al., 2007b). These records actually show a small change (~0.05) to more
202 radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratios that has been interpreted to reflect enhanced weathering of terrestrial
203 rocks due to elevated atmospheric temperatures and moisture (Ravizza et al., 2001; Dickson et al.
204 2015). The small magnitude of the increase in $^{187}\text{Os}/^{188}\text{Os}$ compared with other Phanerozoic
205 events (e.g. Cohen et al., 2004) may be due to the competing influences of Os being weathered
206 from both radiogenic and unradiogenic sources at the same time. Several of the NAIP datasets
207 also demonstrate a very brief shift to more unradiogenic values in seawater near the Paleocene–
208 Eocene boundary, which likely records a pulse of unradiogenic Os associated with magmatic
209 activity at the commencement of the PETM (Weiczorek et al., 2013; Dickson et al., 2015), or
210 perhaps an extraterrestrial impact event (c.f. Schaller et al., 2017). The stratigraphic
211 correspondence between unradiogenic Os-isotope ratios and a peak in Hg concentrations in pre-
212 PETM deposits in Svalbard tend to support a volcanic origin for this feature (Jones et al., 2019).
213 This observation highlights the potential for Os isotope stratigraphy to reveal very fine-scale detail
214 of volcanic activity that is pertinent to testing hypotheses relating LIP emplacement to rapid climate
215 change.

216 The influence of episodic NAIP activity on brief global warming events ('hyperthermals')
217 that occurred *after* the PETM is largely untested. A new Os-isotope record is shown in Fig. 4 from
218 IODP Site M0004A (Arctic Ocean) spanning one such event, Eocene Thermal Maximum 2 (~53
219 Ma). These data were produced using techniques identical to those of Dickson et al. (2015). Initial
220 Os-isotope ratios increase by ~0.1 (0.38–0.48) shortly before the carbon isotope excursion that
221 marks the start of the event, and again in more dramatic fashion at the termination of the carbon
222 cycle perturbation, from ~0.4–0.8. The data are similar to $^{187}\text{Os}/^{188}\text{Os}$ ratios of metalliferous
223 sediments from DSDP 549 that contain a shift to more radiogenic values (from ~0.44–0.50) across
224 ETM 2 (Peucker-Ehrenbrink and Ravizza, 2012), thus supporting the hypothesis of a rapid
225 increase in continental weathering across the hyperthermal. A single unradiogenic value of 0.18
226 also stratigraphically precedes ETM 2 at Site M0004A (Fig. 4). Given the short duration of the ETM
227 2 (~100 kyrs) the unradiogenic value before the event began is at least consistent with a volcanic
228 trigger. These observations come with the caveat of increasing hydrographic restriction in the
229 Arctic during the Early Eocene (Brinkhuis et al., 2006; Dickson et al., 2015) that may have caused

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

234

235 *The Deccan Traps (~66.3–65.5 Ma)*

236 Ar-Ar age estimates of the timing of LIP emplacement place the Deccan Traps close to the mass-
237 extinction event at the Cretaceous–Paleogene boundary (K–Pg) (Chenet et al., 2007). U–Pb dating
238 of zircons recovered from ashfall and erosive units interbedded with lava flows has recently
239 allowed the chronology of this event to be improved substantially, with an estimate of ~753 kyrs for
240 80–90% of the total eruptive history (Schoene et al., 2015). Os-isotope records from a variety of
241 carbonate successions show reproducible trends in seawater $^{187}\text{Os}/^{188}\text{Os}$ prior to the K–Pg, with a
242 ~20–25% decrease towards unradiogenic values commencing at the C29r/C30n boundary,
243 followed by a second decrease towards even more unradiogenic values occurring much closer to
244 the K–Pg itself (Fig. 5, Ravizza and Peucker-Ehrenbrink, 2003; Robinson et al., 2009). Os data
245 from K–Pg locations in Europe and the US show that seawater $^{187}\text{Os}/^{188}\text{Os}$ decreased nearly to
246 mantle values of ~0.14 at the acme of the unradiogenic shift prior to the K–Pg. This decrease is
247 consistent both with an extraterrestrial impactor (Luck and Turekian, 1983; Esser and Turekian,
248 1989; Geissbühler, 1990; Peucker-Ehrenbrink et al., 1995; Meisel et al., 1995; Yin et al., 1995),
249 and also with the emplacement of the Poldapur Deccan basalts, according to recent U–Pb data
250 (Schoene et al., 2019). Osmium isotope data from latest Cretaceous rocks have been instrumental
251 in testing the hypothesis that the eruption of the Deccan Traps caused the end-Cretaceous mass
252 extinction. The earliest shift in $^{187}\text{Os}/^{188}\text{Os}$ associated with volcanism occurs considerably earlier
253 than the major extinction horizon, an observation that tends to favour an extraterrestrial impactor
254 as the cause of most (though not all) of the major biotic consequences of this time interval
255 (Ravizza and Peucker-Ehrenbrink, 2003).

256 The Deccan Traps illustrate an interesting conundrum in the interpretation of $^{187}\text{Os}/^{188}\text{Os}$
257 data in terms of LIP activity. Ravizza and Peucker-Ehrenbrink (2003) interpreted the decrease in
258 $^{187}\text{Os}/^{188}\text{Os}$ commencing at the C29r/C30n boundary as recording a decrease in the weathering of
259 radiogenic Os as flood basalts were extruded across crystalline basement rocks in the early
260 phases of the Deccan LIP. This argument was in part supported by the low concentration of Os in
261 Deccan basalts (Allègre et al., 1999). Other LIP events featuring a decrease in the $^{187}\text{Os}/^{188}\text{Os}$ of
262 seawater have been interpreted in terms of an increase in the weathering of unradiogenic Os from
263 mafic rocks (Turgeon and Creaser, 2008; Tejada et al., 2009; Bottini et al., 2012; Du Vivier et al.,
264 2014). These differences highlight the fact that the marine $^{187}\text{Os}/^{188}\text{Os}$ ratio is the product of two
265 competing inputs, and that the use of complementary datasets is often required to arrive at a
266 satisfactory interpretation of the observed chemostratigraphic variations.

267

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

269 Volcanism has long been hypothesized as a trigger for one of the most profound episodes of
270 Phanerozoic ocean deoxygenation, at the Cenomanian–Turonian boundary. This event, Oceanic
271 Anoxic Event 2 (OAE 2) took place at a similar time as the emplacement of several LIPs, most
272 notably the Caribbean LIP (CLIP) and the High Arctic LIP (HALIP). Early studies attributed
273 concentration spikes of mafic-derived trace elements in sedimentary rocks to infer volcanism (e.g.
274 Orth et al., 1993), and this approach has continued recently (Eldrett et al., 2014). The publication
275 of the first Os-isotope records for the Cenomanian–Turonian boundary, by Turgeon and Creaser
276 (2008), revealed mantle-like signatures in global seawater that were sustained for hundreds of
277 thousands of years during the acme of the environmental changes associated with OAE 2. These
278 data firmly supported the significant role of voluminous volcanic activity in driving and sustaining
279 widespread environmental change during this event, presumably through volcanism-climate
280 feedbacks. Such feedbacks may have included the delivery of bio-limiting nutrients and sulfate to
281 the oceans, stimulating organic matter production and the consequent consumption of dissolved
282 oxygen in many parts of the oceans (Adams et al., 2010; Jenkyns, 2010). The Os-isotope datasets
283 of Turgeon and Creaser (2008) have since been supplemented by Du Vivier et al. (2014, 2015),
284 who were able to show how abrupt shifts in $^{187}\text{Os}/^{188}\text{Os}_{(t)}$ ratios towards mantle values (~ 0.15)
285 occurred several thousands of years in advance of the positive carbon isotope excursion that
286 defines the event (c.f. Arthur et al., 1987; Tsikos et al., 2004) (Fig. 6). The persistence of
287 unradiogenic Os-isotope values over a period of several hundreds of thousands of years, far in
288 excess of the Os residence time in the oceans, demonstrates the prolonged period of time during
289 which Os was weathered from volcanic rocks on land and/or by submarine basalt-seawater
290 interaction (Turgeon and Creaser, 2008; Du Vivier et al., 2014, 2015). Furthermore, changes in the
291 concentration of Os in sedimentary successions throughout the phase of otherwise unradiogenic
292 Os-isotope ratios within OAE 2 may suggest small changes in the amount of Os being weathering
293 into the oceans (Du Vivier et al., 2014, 2015). However, despite the clear signature of LIP activity
294 afforded by the unradiogenic Os-isotope values that span OAE 2, these data are not able to
295 unambiguously fingerprint the source of the unradiogenic Os flux. Various studies continue to
296 debate the relative importance of volcanism associated with the HALIP (Eldrett et al., 2017) and
297 the CLIP (Kuroda et al., 2007; Holmden et al., 2016; Scaife et al., 2017), while Ar-Ar ages for
298 eruptive events associated with the Madagascan LIP (Cucciniello et al., 2010) also slightly overlap
299 the age of the Cenomanian-Turonian boundary (Meyers et al., 2012). It is possible that these
300 events all contributed in some way to the widespread environmental changes that occurred during
301 OAE 2.

302 OAE 2 provides an interesting case study of hysteresis in Earth-System processes. The
303 lead-lag relationship between Os-isotope and C-isotope changes at the onset of OAE 2 clearly
304 supports the contention of a volcanic trigger with the rapid emplacement of submarine basalts,
305 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 CO₂ 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 $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ values, and exhibit near-identical shifts in $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ 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 $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ 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 $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ 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 $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ 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 nanofossil flora (Erba et al., 2010; Bottini et al., 2012). The existing data
331 resolution is, however, not sufficient to resolve this hypothesis. Thirdly, $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ 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 $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ 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 $^{187}\text{Os}/^{188}\text{Os}_{(i)}$.

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.

344 Duncan et al., 1997; Sell et al., 2014), with a much shorter period of intense activity around the T-
345 OAE itself, including hydrothermal venting, at ~183 Ma (e.g. Svensen et al., 2007, 2012; Burgess
346 et al., 2015). Three marine Os_(i) isotope records span part of the duration of the K-F LIP, from
347 Yorkshire, UK (Cohen et al., 2004); North Wales, UK (Percival et al., 2016); and western Canada
348 (Them et al., 2017). A fourth Os-isotope dataset was recently measured in lacustrine shales of the
349 Chinese D'hanzhai member, which contain distinctly more radiogenic values than the marine
350 sections (Xu et al., 2017). The marine records all retain a similar range of values, which point to a
351 well-mixed ocean inventory of Os in the early Jurassic (Fig. 8). They also all exhibit large increases
352 in ¹⁸⁷Os/¹⁸⁸Os_(i) ratios towards radiogenic values across the T-OAE in the range 0.3–0.8 (Fig. 8),
353 which is somewhat counter-intuitive given the intense volcanic activity that took place at that time.
354 The explanation for this trend may lie partly in the largely sub-aerial nature of the K-F LIP and the
355 associated lack of continental breakup, which inhibited the weathering rate of mafic rocks into the
356 oceans following emplacement (Percival et al., 2016). Also, volcanic-driven climate warming
357 probably contributed to the intense weathering of continental crust that would have caused a large
358 influx of radiogenic Os to the oceans, thereby overwhelming any unradiogenic flux (Cohen et al.,
359 2004). The Os isotope records spanning part of the K-F LIP clearly demonstrate the unique
360 characteristics of the climatic and weathering feedbacks associated with this LIP, certainly in
361 contrast with large LIP events of the Cretaceous (Ontong-Java and Caribbean LIPs) (Figs 6 and
362 7). However, no single Os isotope record has yet been produced that spans the entire estimated
363 K-F duration. Establishing such records in the future will be useful to test hypotheses linking
364 volcanism to early Jurassic climate change, particularly in the light of recent studies that tend to
365 suggest ocean deoxygenation began considerably earlier than the T-OAE, closer to the putative
366 onset of K-F volcanism before ~183 Ma (Them et al., 2018).

367

368 *The Central Atlantic Magmatic Province (201.6–200.9 Ma)*

369 The Central Atlantic Magmatic Province (CAMP) has been the subject of many detailed studies
370 that have established precise chronologies of volcanic pulses from ~201.6–200.9 Ma (e.g.
371 Schoene et al., 2010; Blackburn et al., 2013; Davies et al., 2017). These, and other stratigraphic
372 studies, have shown a close temporal relationship between initial pulses of intrusive volcanism, a
373 first order mass extinction, and a large negative carbon isotope excursion of only a few tens of kyrs
374 duration (Hesselbo et al., 2002; Ruhl et al., 2010; Whiteside et al., 2010). While there are two Os_(i)
375 isotope records that span the duration of the CAMP, from the South West UK (Cohen and Coe,
376 2002), and from Japan (Kuroda et al., 2010), neither of these is presently able to resolve the
377 impact of the CAMP on seawater chemistry with comparable temporal precision to U-Pb
378 chronologies (e.g. Blackburn et al., 2013) or chemostratigraphic studies (e.g. Hesselbo et al.,
379 2002; Ruhl et al., 2011). Both Os records contain evidence for a decrease in the ¹⁸⁷Os/¹⁸⁸Os ratio
380 of seawater between the latest Triassic (Rhaetian) and the early Jurassic (Hettangian) broadly
381 from ~0.3–0.6 to 0.1–0.5. However, the UK record has no data from the critical interval

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

393

394 *The Siberian Traps (~252.2–250.2 Ma)*

395 Zircon U–Pb ages of the Siberian Traps have been used to formulate a model of LIP evolution in
396 relation to the largest mass extinction event of the Phanerozoic Eon. Volcanism began at ~ 252.4
397 Ma and ended before $\sim 250.2 \pm 0.3$ Ma (Kamo et al., 1996; Bowring et al., 1998; Burgess and
398 Bowring, 2015, Burgess et al., 2014, 2017). The mass extinction horizon itself has been tied
399 closely to the first evidence for intrusive volcanism at ~ 251.9 Ma (Burgess et al., 2017). Despite
400 the detailed chronological constraints on the Siberian Traps, osmium isotope stratigraphy has not
401 yet been applied to this event in great detail. $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ values have been estimated from Re–Os
402 isochrons with ages of ~ 252 – 252.5 Ma, to the range 0.56 – 0.62 (Georgiev et al., 2011) (Fig. 10).
403 These data tend to suggest a limited evolution of seawater $^{187}\text{Os}/^{188}\text{Os}$ across the early interval of
404 volcanism, although younger Re–Os datasets (247–234 Ma) have $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ values of ~ 0.8 – 1.4 ,
405 implying a slight evolution of seawater to more radiogenic values by the early Triassic (Yang et al.,
406 2004; Xu et al., 2009; Pašava et al., 2010). Nonetheless, the data are of low-resolution and do not
407 clearly cover the major phase of intrusive volcanism, allowing for the large uncertainties in the Re–
408 Os estimates of depositional ages and $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ (Georgiev et al., 2011). A single stratigraphic
409 record at Opal Creek, Alberta, exhibits a decrease in $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ from 0.54 to 0.35 following the
410 Late Permian extinction level, followed by a return to ~ 0.60 at the Permian–Triassic boundary
411 (Schoepfer et al., 2012) (Fig. 10). These data suggest a transient excursion in seawater Os
412 chemistry towards unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ values during an interval of intrusive volcanism in the
413 Siberian Traps (c.f. Burgess et al., 2017), that is temporally constrained by U–Pb ages to a
414 duration < 60 kyrs (c.f. Burgess et al., 2014). Additional data for this section show a small excursion
415 to an unradiogenic value of ~ 0.20 shortly following the main extinction level (Georgiev et al., 2015).
416 The reasons for this brief excursion are not clear, but may be linked to variations in subaerial
417 basalt weathering and/or the transport of radiogenic or unradiogenic weathering signals from the
418 Siberian LIP to the global ocean. The relatively small magnitude of documented $^{187}\text{Os}/^{188}\text{Os}_{(i)}$
419 variation for the Siberian Traps compared to, e.g. the CAMP or OJP LIPs, may be related to the

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

423

424 **Summary: Os-isotope stratigraphy and LIPs**

425 Os isotope data from a number of marine sedimentary successions has been instrumental in
426 establishing the link between LIP volcanism and major environmental changes in the Early
427 Cretaceous (OAE 1a) and Late Cretaceous (OAE 2), with significant shifts in seawater chemistry to
428 mantle-like values over timescales of 10^4 – 10^5 years (Turgeon and Creaser, 2008; Tejada et al.,
429 2009; Bottini et al., 2012; Du Vivier et al., 2014, 2015). The data have been useful in distinguishing
430 the effect of extraterrestrial impacts and LIP volcanism on major extinction events (Ravizza and
431 Peucker-Ehrenbrink, 2003; Robinson et al., 2009) and in testing hypotheses of Earth-System
432 feedbacks during LIP-inspired intervals of profound global warming (Cohen et al., 2004; Dickson et
433 al., 2015; Percival et al., 2016; Them et al., 2017).

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

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

455 . 8). Additionally, the role of continental rock weathering as a driver of Os-isotope change in
456 the oceans might also be better constrained by pairing these measurements with other emerging
457 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.

465

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Figure captions

Figure 1: Ages of Late Phanerozoic LIPs and the temporal overlap of existing $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ 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 $\sim 10\text{--}30\%$ from unradiogenic (mantle and extraterrestrial dust) fluxes and $\sim 70\text{--}90\%$ 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 $^{187}\text{Os}/^{188}\text{Os}$ 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.

962

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

968

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

975

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

981

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

987

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

992

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

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998

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

1000

Sample (core-section-top depth-lower depth)	Depth (mcd)	Os (ppt)	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}$	\pm	$^{187}\text{Os}/^{188}\text{Os}_i$
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

1001