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Valanginian climate cooling and environmental change driven by Paraná-Etendeka basalt erosion

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ABSTRACT

The Valanginian Weissert Event (ca. 134 Ma) has long been linked to emplacement of the Paraná-Etendeka large igneous province (LIP). Although several Mesozoic crises were triggered by volcanic CO_2 emissions and global warming, causing oceanic oxygen depletion, the Weissert Event featured climate cooling and limited marine anoxia. Here, the impact of silicate weathering on environmental change during the Weissert Event is investigated by presenting the first osmium isotope ($^{187}Os/^{188}Os$) data sets for the late Berriasian–Valanginian interval. These records document a possible rise in weathering and nutrient runoff during the latest Berriasian, followed by a switch to Paraná-Etendeka basalt erosion during the Valanginian. The high weatherability of LIP basalts enhanced global silicate weathering despite limited coeval climate warming. This weathering triggered the documented cooling, with consequent micronutrient runoff potentially aiding ocean fertilization, highlighting a mechanism linking LIP formation with environmental change that was uniquely different than that of other Mesozoic crises.

INTRODUCTION

The Early Cretaceous was marked by several pronounced disturbances to the global carbon cycle (e.g., Weissert et al., 1998), many of which were associated with global climate change, oceanic anoxia, and large igneous province (LIP) volcanism (e.g., Weissert and Erba, 2004; Jenkyns, 2010). The Valanginian Weissert Event (ca. 134 Ma; Cavalheiro et al., 2021; Martinez et al., 2023) was the first such Cretaceous environmental perturbation. This time interval is marked globally by a positive carbon isotope ($\delta^{13}C$) excursion of ∼2‰ in carbonate and up to 4‰ in organic material across Valanginian–Hauterivian strata (e.g., Weissert et al., 1998; Erba et al., 2004; Bornemann and Mutterlose, 2008; Littler et al., 2011; Price et al., 2018).

Extrusive volcanism and degassing during formation of the Paraná-Etendeka LIP are widely thought to have triggered the Weissert Event (e.g., Dodd et al., 2015; Charbonnier et al., 2020a; Rocha et al., 2020; Martinez et al., 2023). While LIPs are typically thought to have caused Mesozoic environmental change through CO_2 emissions and consequent climate warming (Bond and Sun, 2021), evidence of increased temperatures at the onset of the Weissert Event has been reported from only a few NW Tethys sites (see Charbonnier et al., 2020b; Cavalheiro et al., 2021). Rather, strata recording the peak of the $\delta^{13}C$ excursion typically document climate cooling, particularly in mid- to high-latitude archives, suggesting a steepening of latitudinal temperature gradients that contrasted with the preceding Berriasian–early Valanginian warm world (McArthur et al., 2007; Littler et al., 2011; Meissner et al., 2015; Price et al., 2018; Charbonnier et al., 2020b; Cavalheiro et al., 2021). Moreover, Paraná-Etendeka magmas were extruded at a slow rate over 4–5 m.y., were potentially volatile depleted, did not intrude carbon-rich sediments to produce thermogenic CO_2 emissions, and at least some intense eruptions postdated the onset of the Weissert Event (Callegaro et al., 2014; Dodd et al., 2015; Jones et al., 2016; Rocha et al., 2020). Thus, there is little evidence that Paraná-Etendeka volcanism caused global climate warming, leaving the link between Valanginian environmental change and this LIP unclear.

This study presents the first Berriasian–Valanginian osmium (Os) isotope records to investigate the role played by weathering of newly formed Paraná-Etendeka basalts in driving environmental change during the Weissert Event. Enhanced silicate weathering has been linked with numerous environmental crises in Earth's history, increasing nutrient runoff to seawater and stimulating marine anoxia while promoting carbon sequestration to lower atmospheric CO_2 and global temperatures (e.g., Cohen et al., 2004; Jenkyns, 2010; Cox et al., 2016). The innate weatherability of newly formed LIP basalts supports silicate weathering as a potential key driver of environmental change (Dessert et al., 2003).

Erosion of Paraná-Etendeka basalts ($^{187}Os/^{188}Os$ ∼0.13; Rocha-Júnior et al., 2012) and/or changes in continental weathering and runoff as a whole (modern average $^{187}Os/^{188}Os$ ∼1.4; Peucker-Ehrenbrink and Ravizza, 2000) would have been two of the main sources of osmium to the Valanginian global ocean. Mid-ocean-ridge activity, submarine basalt alteration, and the influx of extraterrestrial material also supply unradiogenic Os ($^{187}Os/^{188}Os$ ∼0.13) to seawater (Peucker-Ehrenbrink and Ravizza, 2000). However, on geologically short time scales, mid-ocean-ridge and extraterrestrial Os fluxes remain relatively constant, except during a bolide impact or oceanic plateau formation, for which no evidence exists in Valanginian records. Thus, a rise in LIP basalt erosion or change in global net continental weathering would have been the likely driver of any variation in seawater $^{187}Os/^{188}Os$ at that time. Such changes would have been recorded throughout the open ocean due to a seawater residence time of tens of thousands of years for Os, except in hydrographically restricted basins, where local sources may have dominated (e.g., Dickson et al., 2015).

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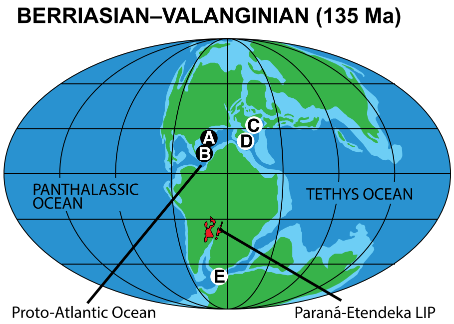

Figure 1. Paleogeographic map of Berriasian–Valanginian world, adapted from Charbonnier et al. (2020a). Paraná-Etendeka large igneous province (LIP) is shown in red. Locations of Valanginian archives are as follows: A—Deep Sea Drilling Project (DSDP) Site 603; B—DSDP Site 534; C—Vocontian Basin (SW France); D—Subbetic Domain, Betic Cordillera (SE Spain); E—Ocean Drilling Program (ODP) Site 692 (Weddell Sea, East Antarctica).

MATERIALS AND METHODS

Berriasian–Valanginian strata at Deep Sea Drilling Project (DSDP) Site 603 Hole B (lower continental rise off Cape Hatteras) and DSDP Site 534 Hole A (Blake Bahama Basin) record two low-latitude, open-marine proto–Atlantic Ocean settings (Fig. 1; see Appendix S1-1 in the Supplemental Material[1]). The Atlantic Basin became hydrographically connected with the Panthalassic and Tethyan realms in the Late Jurassic (Riccardi, 1991); thus, recorded trends in $^{187}Os/^{188}Os$ should reflect variations in the global ocean isotopic composition. These data were integrated with a stratigraphic age model based on biostratigraphic, magnetostratigraphic, and $\delta^{13}C$ records from each site (revised from Littler et al., 2011; see Appendix S1-1). Concentrations and isotopic compositions of rhenium (Re) and osmium were determined by isotope dilution and negative thermal ionization mass spectrometry (N-TIMS) using a Thermo Scientific Triton at Durham University, UK (see Appendix S1-2). Past seawater Os isotope compositions at the time of deposition [$^{187}Os/^{188}Os_{(i)}$] were determined using the age and measured $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ ratios of a sample to account for postdepositional decay of ^{187}Re to ^{187}Os (Cohen et al., 1999). Procedural blanks were 11.3 ± 3.8 pg for Re and 0.096 ± 0.081 pg for Os, with a $^{187}Os/^{188}Os$ ratio of 0.206 ± 0.017 (1σ; n = 9). Analytical precision was monitored through repeated analysis of 50 pg DROsS and 125 pg ReSTD solution standards, yielding mean $^{187}Os/^{188}Os$ and $^{187}Re/^{185}Re$ ratios of 0.16087 ± 0.00014 (1σ; n = 11) and 0.59832 ± 0.00075 (1σ; n = 7) over the course of the study, consistent with long-term averages for the laboratory (Appendix S2-1).

RESULTS AND DISCUSSION

Uppermost Berriasian strata at Site 603 show a rise in $^{187}Os/^{188}Os_{(i)}$ values from a background of ∼0.60 to a maximum of ∼0.73 between 1555 and 1545 m below seafloor (mbsf; Fig. 2). There is a sharper increase in $^{187}Os/^{188}Os_{(i)}$ from ∼0.54 to ∼0.74 in the upper part of nannofossil zone NK2B at Site 534 (∼1250 mbsf). This acute shift may have resulted from a hiatus (see Appendix S1-1) and/or the data resolution. At both sites, $^{187}Os/^{188}Os_{(i)}$ values decline across the NK3A-NK3B boundary, reaching a minimum of 0.40–0.45 in the NK3B zone (chron M11), correlative with the $\delta^{13}C$ peak (1515–1505 mbsf at Site 603 and 1200–1185 mbsf at Site 534; Fig. 2). The topmost studied samples return to higher $^{187}Os/^{188}Os_{(i)}$ (0.55–0.67). By contrast, there is no stratigraphic trend in Re contents (0.15–17.5 ppb) or calculated initial osmium concentrations (12–654 ppt [$Os_{(i)}$]) for either core (Fig. S1). The $^{187}Os/^{188}Os_{(i)}$ trends do not result from lithological changes, as there is no relationship between sediment type and isotope ratio (Appendix S2-1), and stratigraphic archives reflecting variable sedimentary facies and redox settings can still record open-ocean Os isotope trends (see Appendix S1-2). Yet, minor differences in the recorded $^{187}Os/^{188}Os_{(i)}$ trends across the two sites may reflect local factors superimposed on the global signal, such as variable input of terrestrial material due to the differing proximity of the two sites to the paleoshoreline (see Jones et al., 2021), or uncertainties in the constructed age model. Future study of Tethyan and Panthalassic sites will aid in reconstruction of these global versus local influences.

The data highlight two changes in the input of osmium to the global ocean during Berriasian–Valanginian times. First, riverine Os derived from continental weathering potentially rose by ∼60%–70% during the late Berriasian (assuming an average $^{187}Os/^{188}Os$ of 1.4 at that time, as for today; Appendix S1-3). This process would have elevated nutrient runoff to the ocean and promoted primary productivity, consistent with evidence of increased nutrient levels coeval with the Berriasian shift in oceanic Os isotope

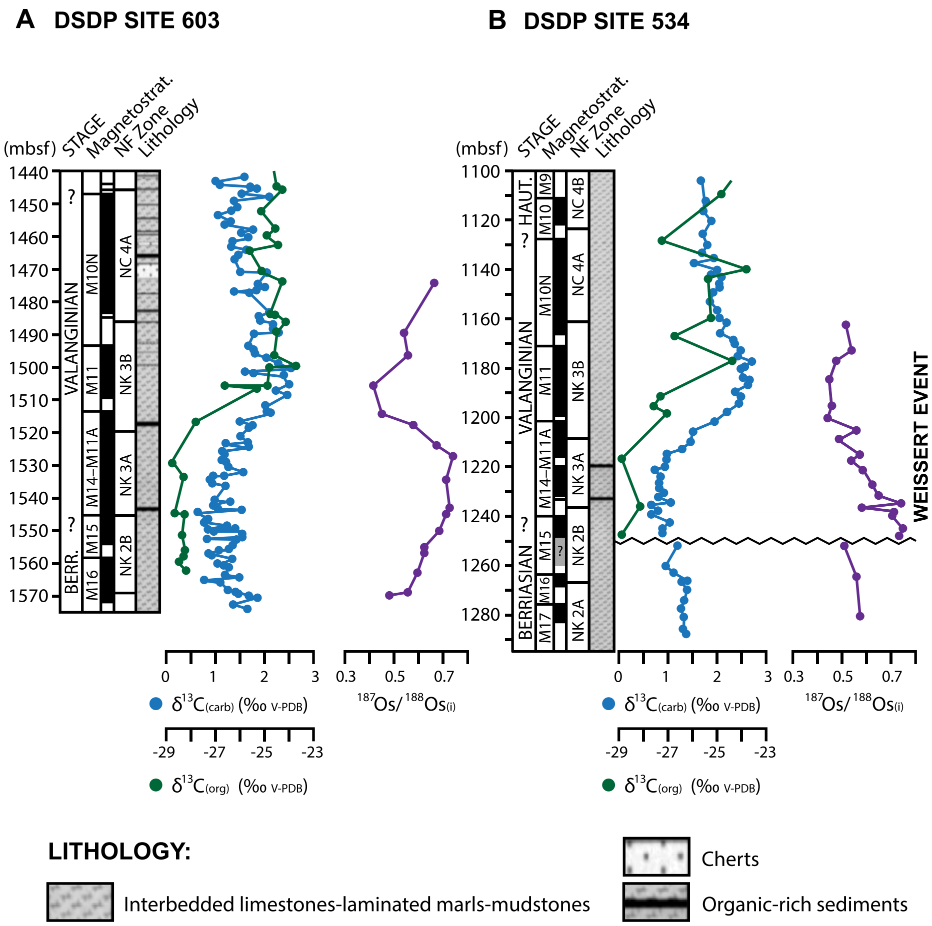

Figure 2. Stratigraphic trends in $\delta^{13}C$ and $^{187}Os/^{188}Os_{(i)}$ from Deep Sea Drilling Project (DSDP) Sites 603 and 534. Lithology, biostratigraphy, and carbonate $\delta^{13}C$ data are from Bornemann and Mutterlose (2008); organic $\delta^{13}C$ data are from Littler et al. (2011); magnetostratigraphy is from Ogg (1987). Os isotope data are from this study. Uppermost Berriasian hiatus at Site 534 (∼1250 mbsf) is shown. NF—nannofossil; V-PDB—Vienna Peedee belemnite; mbsf—m below seafloor.

[1]Supplemental Material. Appendices S1–S2, Figure S1, and Tables S1–S2. Please visit https://doi.org/10.1130/GEOL.S.23061098 to access the supplemental material, and contact editing@geosociety.org with any questions.

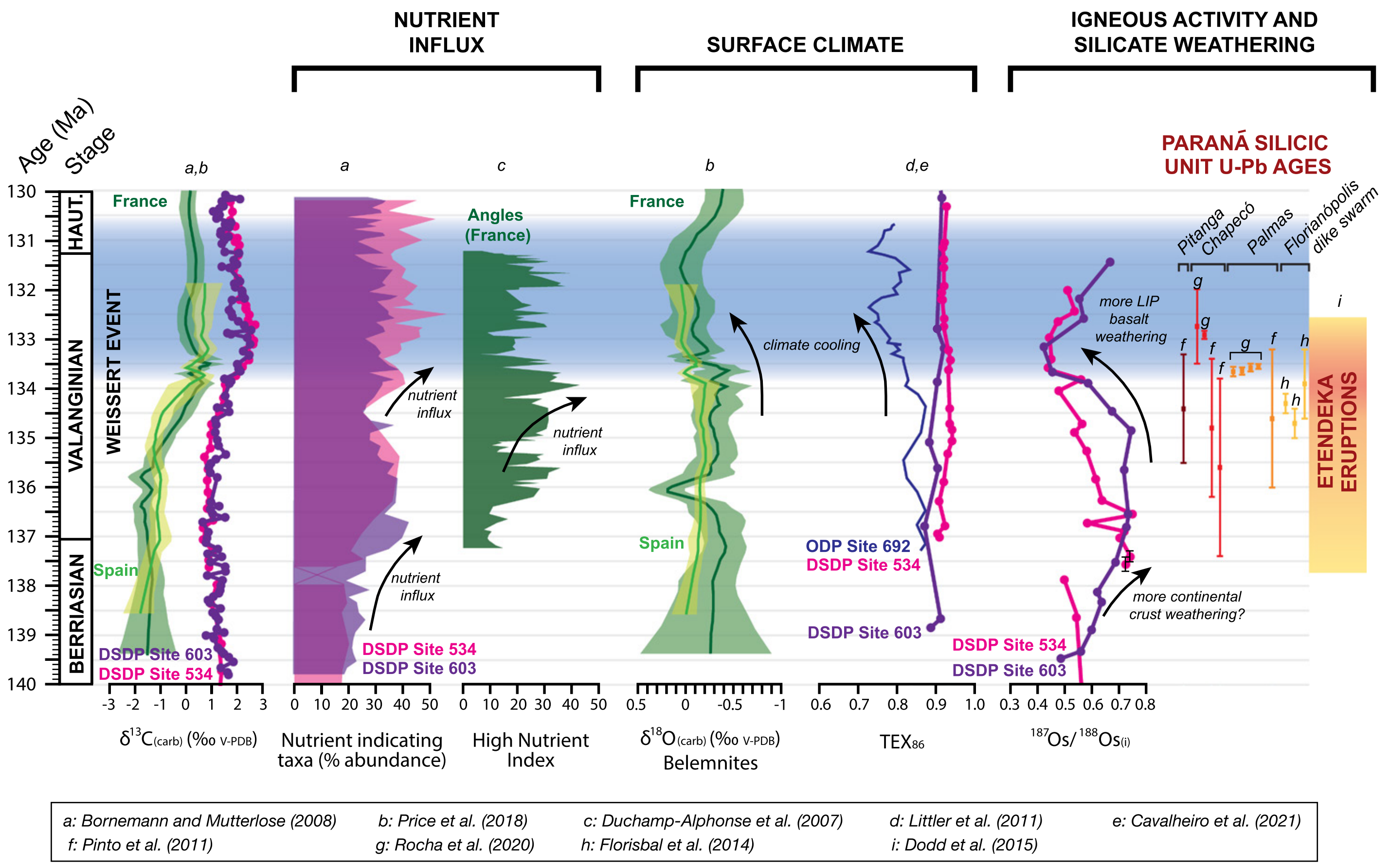

Figure 3. Trends in Berriasian–Valanginian carbonate δ^{13}C, nutrient-indicating nannofossil taxa abundance, nannofossil-derived high nutrient index data, belemnite δ^{18}O, TEX$_{86}$ temperature records, ^{187}Os/^{188}Os$_{(i)}$ (this study), and Paraná-Etendeka volcanism vs. time. Time scale is based on cyclostratigraphically determined Valanginian biozone ages and Berriasian magnetic chron (Appendix S1-1 [see text footnote 1]). To minimize uncertainty in age comparison with U-Pb–anchored time scale of Martinez et al. (2023), only Paraná igneous units dated using that method are presented. Etendeka lavas are assumed to have formed between chrons M11 and M15 (Dodd et al., 2015). Timing of cooling at Ocean Drilling Program (ODP) Site 692 is approximated due to imprecise nannofossil zone boundaries at that site. Haut—Hauterivian; V-PDB—Vienna Peedee belemnite; DSDP—Deep Sea Drilling Project; LIP—large igneous province.

composition (Fig. 3; Bornemann and Mutterlose, 2008). However, weathering increases are typically associated with warming events (e.g., Cohen et al., 2004; Dickson et al., 2015), but there is no evidence for global temperature rise in late Berriasian strata (Weissert and Erba, 2004; McArthur et al., 2007). Alternatively, the change in seawater ^{187}Os/^{188}Os may have been unrelated to continental runoff and instead been caused by an ~40% reduction in the flux of unradiogenic Os from mantle sources. Modeling of ocean spreading suggests that this flux did decrease slightly during the earliest Cretaceous, but only by ~10%–15% (e.g., Marcilly et al., 2021). Further work is needed to determine what caused the late Berriasian change in seawater ^{187}Os/^{188}Os composition. Regardless, whatever process triggered this isotopic shift, it occurred ~2–3 m.y. before the Weissert Event—too early to have been the sole trigger (Fig. 3).

The transient shift to lower (more unradiogenic) Os isotope values in early Valanginian strata likely reflects a switch from weathering of radiogenic lithologies to erosion of Paraná-Etendeka basalts as the latter were extruded onto Earth's surface. Additionally, a transient peak in seafloor-spreading and subduction rates thought to have occurred ca. 130 Ma (Marcilly et al., 2021) could also have contributed unradiogenic osmium to the global ocean. The relative inputs of radiogenic versus unradiogenic Os to seawater may also have been altered by the hydrographic isolation of the Arctic Ocean following tectonic closure of the Pacific-Arctic gateway (Lunt et al., 2016), or reduced weathering of felsic continental material. However, the ages of the postulated gateway closure and change in spreading rates are poorly constrained, and their temporal relationship with the Weissert Event is unclear. Higher mid-ocean-ridge activity should also have raised volcanic CO_2 emissions and global temperatures, for which there is little evidence in Valanginian strata (Price et al., 2018). While these other processes cannot be excluded completely, the overlap in age between strata that record the unradiogenic Os isotope shift, precisely dated Paraná igneous units, and the high-volume late-stage Etendeka eruptions suggests erosion of newly formed LIP basalts as the most likely cause (Fig. 3).

To cause the unradiogenic shift, preferential weathering of LIP rocks would have lowered the ^{187}Os/^{188}Os ratio of riverine runoff from 1.4 to 0.81, assuming that the net flux of Os remained unchanged (Appendix S1-4). It should be noted that while LIP basalts are typically eroded more easily than felsic silicate rocks, Paraná-Etendeka lavas were erupted in an arid desert environment, where weathering rates would have been lower than in a warm, wet climate (Dessert et al., 2003). However, the shift in seawater ^{187}Os/^{188}Os composition during the Valanginian (over ~1 m.y.; Fig. 3) was much slower than for other intervals marked by LIP basalt weathering, such as the latest Maastrichtian (~100 k.y.; Sinnesael et al., 2016). This relatively gradual change in seawater ^{187}Os/^{188}Os may reflect the muted weatherability of Paraná-Etendeka basalts compared to other LIPs. Nonetheless, the rise in mafic material runoff would have increased the supply of micronutrients to parts of the marine realm, potentially elevating primary productivity levels, particularly in areas that had been nutrient limited previously. High productivity in at least some areas during the Valanginian is

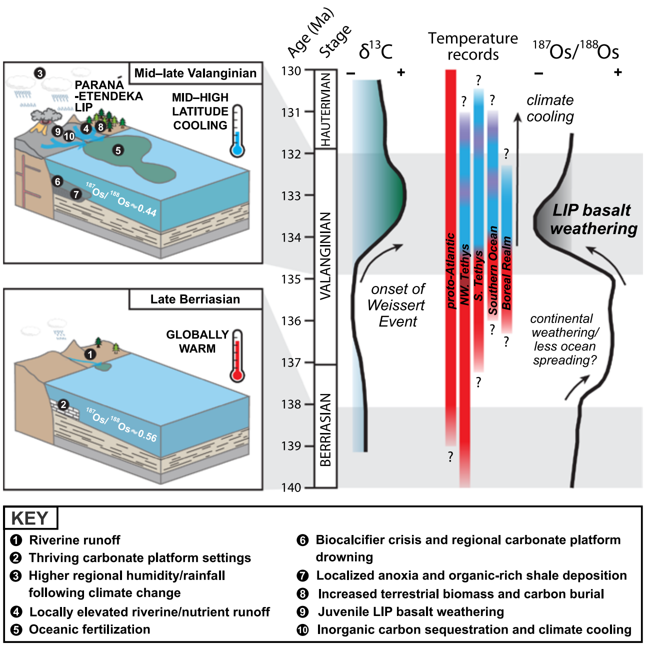

Figure 4. Simplified schematic of surface phenomena during late Berriasian to late Valanginian. Idealized δ13C trend is based on Bornemann and Mutterlose (2008); summaries of regional temperature variation are adapted from Cavalheiro et al. (2021); Os isotope data are from this study. LIP—large igneous province.

consistent with a recorded spike in oceanic fertilization at NW Tethys and Pacific sites (Erba et al., 2004; Duchamp-Alphonse et al., 2007), and it may have helped trigger localized anoxia and biocalcification crises during the Weissert Event (Fig. 4).

The $^{187}Os/^{188}Os_{(i)}$ minimum in zone NK3B/chron M11 likely marks the height of LIP basalt erosion; strata of the same age record the onset of Valanginian climate cooling at several mid- to high-latitude sites (Erba et al., 2004; McArthur et al., 2007; Meissner et al., 2015; Price et al., 2018; Cavalheiro et al., 2021). This pattern highlights carbon sequestration during basalt weathering as a driver of Valanginian cooling and latitudinal temperature-gradient steepening (Fig. 4; Erba et al., 2004; Charbonnier et al., 2020b; Cavalheiro et al., 2021). If basalt erosion rates were indeed relatively slow, this cooling may have been aided by localized organic-carbon burial, potentially on land, given the paucity of preserved organic-rich marine shales from that time compared to the later Cretaceous oceanic anoxic events (Jenkyns, 2010; Westermann et al., 2010). Volcanic SO_2 output can also lower surface temperatures, but while the Valanginian cooling was broadly coeval with intense/voluminous LIP eruptions (Fig. 3), the short atmospheric residence time of sulfate aerosols and low sulfur content of Paraná-Etendeka magmas do not support such a link (Callegaro et al., 2014).

Crucially, enhanced nutrient runoff and carbon drawdown due to the high weatherability of newly erupted basalts reconciles the Paraná-Etendeka LIP as a key trigger for the Weissert Event with the relatively limited evidence for rising temperatures at that time (Price et al., 2018; Cavalheiro et al., 2021). This model highlights a causal link between these phenomena that differed from the canonical LIP-warming model proposed for most climate events in the past 300 m.y. Intriguingly, LIP basalt weathering has been proposed as a trigger of some Paleozoic and Neoproterozoic cooling events, such as the Sturtian glaciation (Cox et al., 2016). Thus, the Weissert Event may have represented a rare Mesozoic example of how LIPs influenced the global environment earlier in Earth's history.

CONCLUSIONS

This study presents the first data sets for global ocean osmium isotope ($^{187}Os/^{188}Os$) trends during the late Berriasian to Valanginian time interval, encompassing the Weissert Event. Osmium isotope values increase in uppermost Berriasian strata, although the cause of this change is not clear, and it was too early to trigger the Weissert Event. A shift to a more unradiogenic composition in early Valanginian marine strata highlights a switch to preferential weathering of Paraná-Etendeka basalts that had newly erupted on the continental surface. Basalt erosion and nutrient runoff may have aided in triggering the Weissert Event, while also promoting carbon sequestration and climate cooling. The highly weatherable nature of LIP basalts enabled this rise in silicate weathering without any prerequisite carbon emissions or climate warming, consistent with the limited evidence for Valanginian temperature increase. This causal mechanism linking the Paraná-Etendeka LIP and Weissert Event is distinct from the volcanic–CO_2-warming model proposed for other Mesozoic crises and LIPs.

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