

Direct coupling between carbon release and weathering during the Toarcian oceanic anoxic event

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ABSTRACT

Silicate weathering represents a major feedback mechanism in the Earth's climate system, helping to stabilize atmospheric CO₂ levels and temperature on million-year time scales. On shorter time scales of greater relevance to understanding the fate of anthropogenic CO₂, the efficacy and responsiveness of weathering is less clear. Here, we present high-resolution osmium-isotope data that reflect global chemical weathering from a stratigraphically thick record of the early Toarcian oceanic anoxic event (T-OAE; ca. 182 Ma). A pronounced decrease in the carbon-isotope composition of exogenic carbon reservoirs during this event has been linked to the large-scale release of ¹²C-enriched carbon. Our data indicate that the flux of radiogenic osmium to the oceans increased in lockstep with the decrease in carbon-isotope values, demonstrating a geologically synchronous coupling between massive carbon release and enhanced global continental crust weathering. We show that abrupt shifts in carbon isotopes, previously interpreted as millennial-scale methane hydrate melting or terrestrial carbon-release events, are coeval with rapid increases in weathering. Global weathering may have increased by >40% across each of these intervals of rapid carbon injection. Our results help to reconcile previous estimates of weathering change during the T-OAE, and support the view that, overall, global weathering rates may have increased six-fold through the entire event.

INTRODUCTION

Determining the response time and mechanistic links between rapid, large-scale climate change and weathering in deep time is challenging because of the typically low temporal resolution of geological records of climate change and the need for proxies that can unambiguously track globally significant changes in weathering on short time scales. The early Toarcian oceanic anoxic event (T-OAE; ca. 182 Ma) represents an ideal interval for studying weathering responses to inferred large-scale atmospheric CO₂ and temperature change. A pronounced decrease in the carbon-isotope ($\delta^{13}\text{C}$) composition of exogenic reservoirs through this event, coupled with associated evidence for seawater warming and atmospheric CO₂ increase, has been linked to the release of thousands of gigatons of ¹²C-rich carbon to the biosphere (Hesselbo

et al., 2000; McElwain et al., 2005; Kemp et al., 2005; Ruebsam et al., 2019).

Osmium-isotope (¹⁸⁷Os/¹⁸⁸Os) data from a handful of previous studies have demonstrated that the flux of radiogenic ¹⁸⁷Os derived from continental crust weathering increased significantly during the T-OAE (Cohen et al., 2004; Percival et al., 2016; Them et al., 2017a; van Acken et al., 2019). Nevertheless, the precise timing and pattern of this increase, and its exact relationship to inferred carbon release, are uncertain. In particular, the decrease to minimum $\delta^{13}\text{C}$ values has been shown to comprise a series of abrupt shifts, each likely reflecting millennial-scale carbon injection from methane hydrate or terrestrial wetland and/or permafrost sources (Kemp et al., 2005; Hesselbo and Pieńkowski, 2011; Them et al., 2017b; Izumi et al., 2018a; Ruebsam et al., 2019). The weathering response to these rapid injections is

unclear. Furthermore, the overall magnitude of weathering change across the T-OAE is uncertain because Os-isotope values presented in the previous studies differ. In this study, we address these issues with a new high-resolution Os-isotope record through an expanded sedimentary succession of the T-OAE from Japan.

MATERIALS AND METHODS

To reconstruct the Os-isotope composition of contemporaneous seawater through the T-OAE (¹⁸⁷Os/¹⁸⁸Os_i; i—initial), we analyzed lower Toarcian organic-rich mudrocks exposed at Sakuraguchi-dani, Japan (34°08'N, 131°03'E), that were deposited on the margin of Panthalassa (Fig. 1). Previous organic carbon-isotope ($\delta^{13}\text{C}_{\text{org}}$) analysis at Sakuraguchi-dani has revealed a >35 m record of the T-OAE negative carbon-isotope excursion (CIE; Izumi et al., 2012, 2018a; Kemp and Izumi, 2014; Fig. 2). We selected 24 samples for Os-isotope analysis spanning the T-OAE and extending into the Pliensbachian. Abundances of detrital elements Al, Ti, and Zr were also quantified on these samples using X-ray fluorescence (XRF) analysis. For 11 samples, $\delta^{13}\text{C}_{\text{org}}$ was measured to supplement previously published data. Full details of the methods used for rhenium and osmium extraction, purification, and analysis and XRF and $\delta^{13}\text{C}$ analysis, and all data, are in the Supplemental Material¹.

RESULTS

The lower part of the Sakuraguchi-dani succession (−27.12 m to −9.47 m) is below the T-OAE negative CIE, and is characterized by extremely unradiogenic (¹⁸⁸Os-enriched) ¹⁸⁷Os/¹⁸⁸Os_i (~0.17), except for the lowermost

¹Supplemental Material. Description of methods, Table S1, and Figures S1 and S2. Please visit <https://doi.org/10.1130/G47509.1> to access the supplemental material, and contact editing@geosociety.org with any questions.

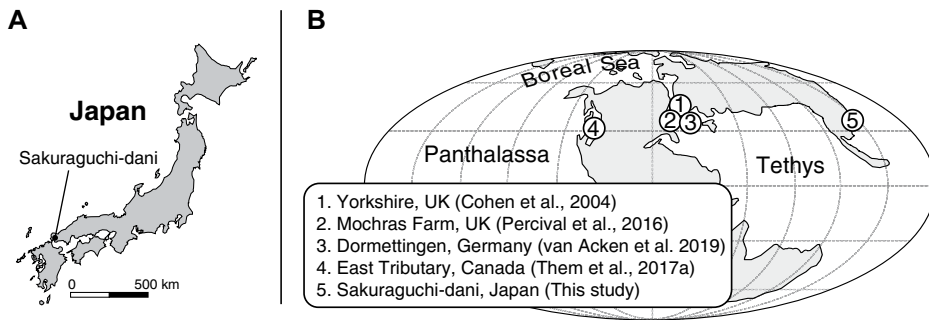


Figure 1. Maps showing modern location (A; 34°08'N, 131°03'E) and paleogeographic (B; ca. 182 Ma) location of the Sakuraguchi-dani site, Japan, and locations of previous early Toarcian Os-isotope studies (see Fig. 3). East Tributary refers to the East Tributary of Bighorn Creek. Redrawn from Izumi et al. (2012).

sample ($^{187}\text{Os}/^{188}\text{Os}_i = 0.47$; Fig. 2A). Above -9.47 m and through the onset of the CIE, $^{187}\text{Os}/^{188}\text{Os}_i$ increases, reaching a maximum of 0.58 at 1.45 m height (Fig. 2A). Above this level, $^{187}\text{Os}/^{188}\text{Os}_i$ varies between 0.34 and 0.53 over the rest of the CIE (to ~ 30 m; Fig. 2A). Between ~ 40 m and 90 m, $^{187}\text{Os}/^{188}\text{Os}_i$ is broadly constant at ~ 0.34 (Fig. 2A). In detail, the increase in $^{187}\text{Os}/^{188}\text{Os}_i$ from unradiogenic values close to the CIE onset (-14.5 m) to the highest (more

radiogenic) values at 1.45 m closely mirrors changes in $\delta^{13}\text{C}_{\text{org}}$ (Fig. 2B). Notably, $\delta^{13}\text{C}_{\text{org}}$ and $^{187}\text{Os}/^{188}\text{Os}_i$ strongly negatively correlate over this interval ($r^2 = 0.93$, p -value < 0.0001 ; Fig. 2C). Below and above this interval, there is no correlation between $\delta^{13}\text{C}_{\text{org}}$ and $^{187}\text{Os}/^{188}\text{Os}_i$ (Fig. 2C).

The overall decrease in $\delta^{13}\text{C}_{\text{org}}$ between -14.5 m and 1.45 m comprises two abrupt shifts in $\delta^{13}\text{C}_{\text{org}}$ of -2.3‰ and -2.9‰ that each

occur over a few centimeters of strata (*a* and *b* in Fig. 2B). These two shifts are associated with pronounced increases in $^{187}\text{Os}/^{188}\text{Os}_i$ of 0.09 (0.31 to 0.40) and 0.15 (0.40 to 0.55), respectively (Fig. 2B). Shift *a* is coincident with a thin (~ 18 cm) brecciated interval likely associated with a minor fault (strata on either side of the interval belong to the same ammonite zone; Izumi et al., 2018a). Shift *b* spans ~ 5 cm, and there is no sedimentological evidence for a fault or hiatus. Previous work has demonstrated that both shift *b* and the stratigraphic interval encompassed by shift *a* can be correlated with abrupt shifts through the CIE onset recognized globally (Izumi et al., 2018a).

DISCUSSION AND CONCLUSIONS

The $^{187}\text{Os}/^{188}\text{Os}_i$ record at Sakuraguchi-dani is similar to the record from the East Tributary of Bighorn Creek, Canada (hereafter 'East Tributary'; Them et al., 2017a; Fig. 3), which was situated on the opposite margin of Panthalassa (Fig. 1). There is no evidence for water-mass restriction in either succession, and the close match in the pattern and magnitude of large-scale $^{187}\text{Os}/^{188}\text{Os}_i$ changes in both sections strongly

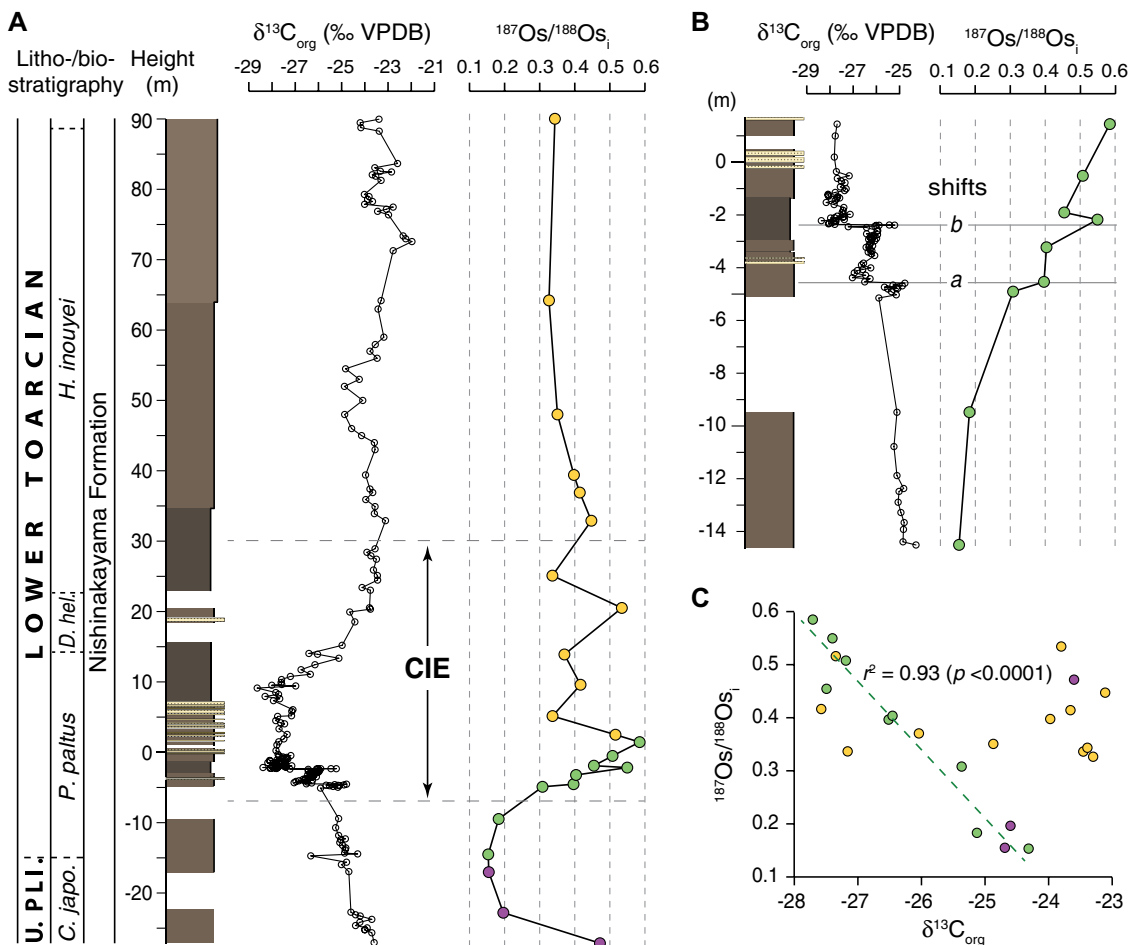


Figure 2. Os-isotope and organic $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{org}}$) through the Sakuraguchi-dani succession, Japan. (A) Sedimentary log with $^{187}\text{Os}/^{188}\text{Os}_i$ (i—initial) and $\delta^{13}\text{C}_{\text{org}}$ variations against lithostratigraphy and ammonite zones (*C. japo.*—*Canavaria japonica*; *P. paltus*—*Paltarpites paltus*; *D. hel.*—*Dactylioceras helianthoides*; *H. inouyei*—*Harpoceras inouyei*). Color-coding divides $^{187}\text{Os}/^{188}\text{Os}_i$ data into pre-carbon-isotope excursion (CIE) data (purple), data primarily through onset of the CIE (minimum to maximum $^{187}\text{Os}/^{188}\text{Os}_i$, green), and data above these (orange). Log is from Izumi et al. (2012, 2018a) and field observations. $\delta^{13}\text{C}_{\text{org}}$ is from Izumi et al. (2012, 2018a, 2018b), Kemp and Izumi (2014), and this study. PLI.—Pliensbachian; VPDB—Vienna Pee Dee belemnite. (B) Close-up of the CIE onset, showing abrupt shifts in $^{187}\text{Os}/^{188}\text{Os}_i$ across $\delta^{13}\text{C}_{\text{org}}$ shifts *a* and *b*. (C) Cross-plot of $^{187}\text{Os}/^{188}\text{Os}_i$ and $\delta^{13}\text{C}_{\text{org}}$ showing the negative correlation between $^{187}\text{Os}/^{188}\text{Os}_i$ and $\delta^{13}\text{C}_{\text{org}}$ across the onset of the CIE/ $^{187}\text{Os}/^{188}\text{Os}_i$ excursion, and no correlation below and above this interval.

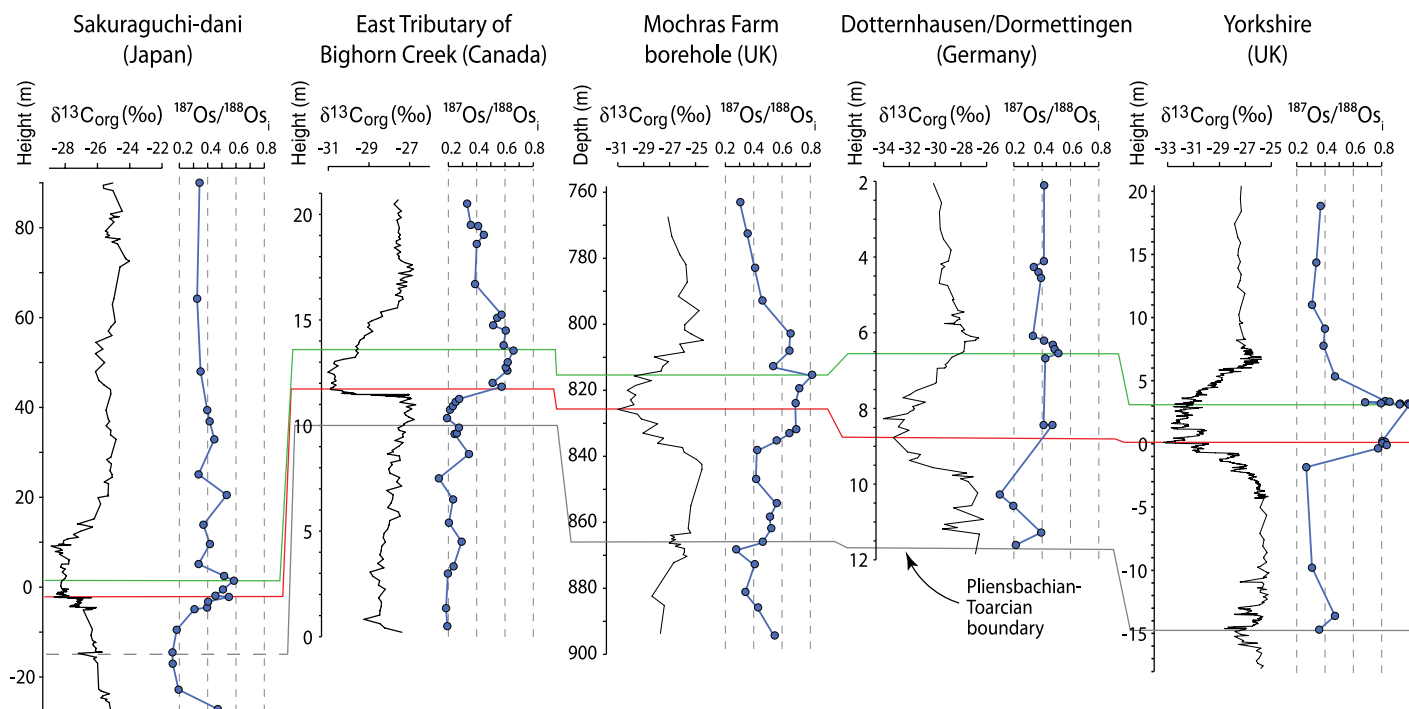


Figure 3. Toarcian organic $\delta^{13}\text{C}_{\text{org}}$ and $^{187}\text{Os}/^{188}\text{Os}_i$ (i—initial) records. Tie lines correlate the Pliensbachian-Toarcian boundary (black line), the end of carbon-isotope excursion (CIE) onset (red line), and the $^{187}\text{Os}/^{188}\text{Os}_i$ maxima (green line) in each section. Heights/depths in each section are taken from the published sources. For Sakuraguchi-dani (Japan), $^{187}\text{Os}/^{188}\text{Os}_i$ data are from this study, and $\delta^{13}\text{C}_{\text{org}}$ data are from Izumi et al. (2012, 2018a, 2018b), Kemp and Izumi (2014), and this study (see Table S1 [see footnote 1]). For East Tributary, Canada, $^{187}\text{Os}/^{188}\text{Os}_i$ data are from Them et al. (2017a) and $\delta^{13}\text{C}_{\text{org}}$ data are from Them et al. (2017b). For Mochras Farm (UK), $^{187}\text{Os}/^{188}\text{Os}_i$ and $\delta^{13}\text{C}_{\text{org}}$ data are from Percival et al. (2016). For Germany, $^{187}\text{Os}/^{188}\text{Os}_i$ data are from van Acken et al. (2019) (Dormettingen quarry), and $\delta^{13}\text{C}_{\text{org}}$ data are from Röhl et al. (2001) (Dotternhausen quarry); Dormettingen-Dotternhausen correlation is from van Acken et al. (2019). For Yorkshire (UK), $^{187}\text{Os}/^{188}\text{Os}_i$ data are from Cohen et al. (2004), and $\delta^{13}\text{C}_{\text{org}}$ data are from Cohen et al. (2004), Kemp et al. (2005), and Littler et al. (2010). All $\delta^{13}\text{C}_{\text{org}}$ data are relative to Vienna Pee Dee belemnite (VPDB).

suggests that these variations reflect changes in the composition of global seawater Os. No correlation exists between detrital proxies (Zr, Al, Ti) and $^{187}\text{Os}/^{188}\text{Os}_i$ at Sakuraguchi-dani, further emphasizing the predominantly hydrogenous nature of the measured Os (Fig. S1 in the Supplemental Material). Nevertheless, the occurrence of volcanic ashes at Sakuraguchi-dani (Izumi et al., 2012) means that we cannot rule out possible local influence of dissolved unradiogenic Os entering the basin, perhaps accounting for the intermittent low $^{187}\text{Os}/^{188}\text{Os}_i$ values between 5.15 m and 25.1 m that are not apparent in the East Tributary data (Them et al., 2017a; Fig. 3). This possibility notwithstanding, our data and the data from East Tributary are only weakly similar to $^{187}\text{Os}/^{188}\text{Os}_i$ data from Europe (Cohen et al., 2004; Percival et al., 2016; van Acken et al., 2019; Fig. 3). Post-CIE $^{187}\text{Os}/^{188}\text{Os}_i$ values of ~ 0.3 – 0.4 occur in all sections, but variable hydrographic restriction in European epicontinental basins may have caused $^{187}\text{Os}/^{188}\text{Os}_i$ to evolve to values partly reflective of local Os inputs, particularly during the CIE (McArthur et al., 2008; Them et al., 2017a).

The high resolution of our sampling and the thickness of the Sakuraguchi-dani section allows us to infer a geologically synchronous coupling between carbon release and weathering. Through the onset of the CIE, which may

have spanned ~ 200 k.y. (e.g., Ruebsam et al., 2019), $\sim 93\%$ of the variance in $^{187}\text{Os}/^{188}\text{Os}_i$ can be explained by changes in $\delta^{13}\text{C}_{\text{org}}$ driven by carbon release (Fig. 2C). As noted above, abrupt negative shifts in $\delta^{13}\text{C}_{\text{org}}$ during the CIE onset at Sakuraguchi-dani (shifts *a* and *b* in Fig. 2B) and recognized globally have been interpreted as being due to astronomically controlled hydrate melting or terrestrial carbon-release events that occurred over just a few thousand years each (Kemp et al., 2005; Them et al., 2017b; Izumi et al., 2018a; Ruebsam et al., 2019). The tight correlation and direct correspondence between these carbon-release events and increases in $^{187}\text{Os}/^{188}\text{Os}_i$ suggest that global weathering responded to carbon inputs on similar time scales. The rapid response of seawater $^{187}\text{Os}/^{188}\text{Os}$ to flux changes suggests that the seawater residence time of Os was comparable to the time scale of carbon release. Modern Os residence-time estimates are variable (10^3 – 10^4 yr; e.g., Georg et al., 2013; Rooney et al., 2016); we note that a short Toarcian residence time is consistent with an increase in the burial flux of Os related to expansion of anoxia during the T-OAE (Them et al., 2017a).

Quantifying the magnitude of the weathering increase through the T-OAE, both overall and across abrupt $\delta^{13}\text{C}$ shifts *a* and *b*, is complicated because the change in $^{187}\text{Os}/^{188}\text{Os}_i$ (as controlled

by changes in the flux and/or isotopic value of Os delivered to the ocean) has no unique solution. Mass-balance calculations based purely on Os fluxes by Them et al. (2017a) indicated that a 500% increase in continental crust weathering rate would have been required to drive the overall $^{187}\text{Os}/^{188}\text{Os}_i$ shift at East Tributary (0.25–0.6), assuming modern mantle and continental crust $^{187}\text{Os}/^{188}\text{Os}$ values of 0.12 and 1.4, respectively. Our pre-CIE $^{187}\text{Os}/^{188}\text{Os}_i$ value of ~ 0.2 (Fig. 2), which is also consistent with the lowest pre-CIE values in East Tributary (Fig. 3), adjusts this estimate to $\sim 800\%$ (scenario 1 in Fig. 4A). An increase of this magnitude is unlikely (Percival et al., 2016; Them et al., 2017a) and conflicts with an independent estimate of a $\sim 500\%$ increase in global weathering rate based on Ca isotopes (Brazier et al., 2015).

Smaller weathering-rate increases can be invoked if unradiogenic Os fluxes decreased or if crustal $^{187}\text{Os}/^{188}\text{Os}$ increased (e.g., Them et al., 2017a). A pre-CIE $^{187}\text{Os}/^{188}\text{Os}_i$ value of ~ 0.2 indicates that the flux of mantle-derived unradiogenic Os overwhelmed any radiogenic Os flux. Some of this unradiogenic Os could have derived from basalts erupted as part of the Karoo large igneous province (present-day southern Africa) across the Pliensbachian-Toarcian boundary and leading up to the CIE (Moulin et al., 2017; Ruebsam et al., 2019; Xu

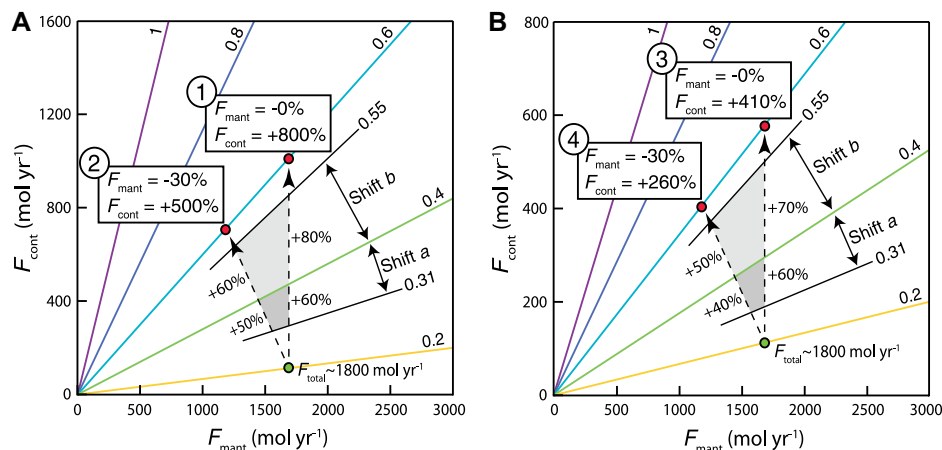


Figure 4. Parameter-space plots illustrating possible changes in radiogenic (F_{cont} , continental crust) and unradiogenic (F_{mant} , mantle) fluxes that could account for the 0.2–0.6 rise in $^{187}\text{Os}/^{188}\text{Os}_i$ (i—initial) at Sakuraguchi-dani, Japan (Fig. 2). $^{187}\text{Os}/^{188}\text{Os}_i$ contours (colored lines) are based on the mass balance of seawater $^{187}\text{Os}/^{188}\text{Os}$; i.e., $^{187}\text{Os}/^{188}\text{Os} = [(F_{\text{cont}} \times N_{\text{cont}}) + (F_{\text{mant}} \times N_{\text{mant}})]/F_{\text{total}}$, where N_{cont} and N_{mant} are end-member $^{187}\text{Os}/^{188}\text{Os}$ compositions of 1.4 (rising to 2 in case of scenarios 3 and 4; scenarios indicated by circled numbers) and 0.12, respectively. The pre-carbon-isotope excursion value (0.2) is, for convenience, based on modern total Os flux (F_{total}) of 1800 mol yr^{-1} (e.g., Georg et al., 2013). (A) Scenario 1 assumes that the overall 0.2–0.6 shift in $^{187}\text{Os}/^{188}\text{Os}_i$ across the early Toarcian oceanic anoxic event results solely from an increase in F_{cont} (i.e., continental crust weathering) with a modern $^{187}\text{Os}/^{188}\text{Os}$ value (N_{cont}) of 1.4. Scenario 2 assumes a concomitant ~30% decrease in F_{mant} . (B) Scenarios 3 and 4 assume an instantaneous increase in N_{cont} from 1.4 to 2 at the start of the $^{187}\text{Os}/^{188}\text{Os}_i$ rise. Gray shaded areas show the changes in F_{mant} and F_{cont} (or just F_{cont}) required to drive abrupt 0.09 and 0.15 changes in $^{187}\text{Os}/^{188}\text{Os}_i$ across the $\delta^{13}\text{C}_{\text{org}}$ shifts a and b, respectively (Fig. 2B). All scenarios require F_{cont} increases of between ~40% and ~80% across these shifts. Calculations assume instantaneous equilibration of Os in seawater, based on the assumed short residence time (see text for details). Mass balance ignores likely minor and invariant Os inputs from other sources, such as cosmic dust.

et al., 2018a; Fig. S2). Karoo volcanism was multi-phased and pulsed (Moulin et al., 2017), and basalts weather rapidly after eruption (e.g., Li et al., 2016). It is thus possible that a decrease in basalt weathering-derived unradiogenic Os flux contributed to the overall $^{187}\text{Os}/^{188}\text{Os}_i$ rise through the T-OAE. Any decrease was likely only modest given the persistence of Karoo and Ferrar (present-day Antarctica) volcanism through the T-OAE (e.g., Moulin et al., 2017) and the low weatherability of these high-latitude basalts (Them et al., 2017a). Nevertheless, an overall decrease in unradiogenic Os flux across the T-OAE is consistent with data from all sections indicating that $^{187}\text{Os}/^{188}\text{Os}_i$ remains high after the event, and maxima in $^{187}\text{Os}/^{188}\text{Os}_i$ occur after the end of the CIE onset, and thus perhaps after cessation of carbon release (Fig. 3). A ~30% decrease in unradiogenic Os flux would be needed to reconcile the Sakuraguchi-dani $^{187}\text{Os}/^{188}\text{Os}_i$ record with the ~500% weathering-increase estimate of Brazier et al. (2015) (scenario 2 in Fig. 4A). A smaller or negligible decrease in unradiogenic flux, and smaller weathering increases, can be invoked if the onset of the T-OAE was accompanied by weathering of ^{187}Os -enriched organic-rich rocks and/or sulfides (e.g., Them et al., 2017a). A rise in crustal $^{187}\text{Os}/^{188}\text{Os}$ from 1.4 to 2 at the start of the CIE would necessitate an ~410% increase in continental weathering to explain the Sakura-

guchi-dani data, or ~260% if a coeval decrease in unradiogenic Os flux occurred (scenarios 3 and 4, respectively, in Fig. 4B). A value of ~2 is a probable upper limit on global continental crust $^{187}\text{Os}/^{188}\text{Os}$ (Cohen et al., 2004; Them et al., 2017a).

Regardless of the overall magnitude of the weathering increase across the T-OAE, the marked increases in $^{187}\text{Os}/^{188}\text{Os}_i$ across the inferred rapid carbon-release events at $\delta^{13}\text{C}_{\text{org}}$ shifts a and b imply abrupt increases in weathering. The broad mass-balance constraints explored above suggest that these carbon-release events were associated with increases in radiogenic Os inputs of between ~40% (shift a, scenario 4) and ~80% (shift b, scenario 1), assuming instantaneous equilibration of seawater $^{187}\text{Os}/^{188}\text{Os}$ and no change in mantle or crust $^{187}\text{Os}/^{188}\text{Os}$ across the shifts themselves (Fig. 4). The larger of the two $\delta^{13}\text{C}_{\text{org}}$ shifts (shift b) spans 5 cm of strata and has been attributed to a carbon-release event with an estimated time scale of <2 k.y. (Izumi et al., 2018a). The maximum of the coeval $^{187}\text{Os}/^{188}\text{Os}_i$ increase (0.55) occurs 16 cm above the end of this $\delta^{13}\text{C}_{\text{org}}$ shift. This suggests that the weathering increase associated with this carbon-release event (~50% to ~80%; Fig. 4) occurred over a comparable time scale (an inference also supported by the short residence time of seawater Os relative to carbon). On such short time scales, runoff may be a key limiting

factor controlling rapid and large-scale Os flux to the ocean (Dosseto et al., 2015; Eiriksdottir et al., 2011; Bastian et al., 2017), and there is widespread evidence that tropical precipitation, runoff, and fluvial power all increased contemporaneously with carbon release and/or warming during the T-OAE (Izumi et al., 2018a; Xu et al., 2018b; Kemp et al., 2019).

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