
Supplementary information

Transient ocean oxygenation at end-Permian mass extinction onset shown by thallium isotopes

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Supplementary Information for:

**Transient ocean oxygenation at end-Permian mass extinction onset
shown by thallium isotopes**

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Supplementary Methods:

Geochemical box model

A forward geochemical box model using the modern marine Tl isotope mass balance (Extended Data Figure 2) was employed to recreate the major isotopic excursions observed but specifically the short-lived negative excursion, during the Permo-Triassic transition (see Figures 2 and 4). The model duration is 2 million years (Myr), with an integration time of 1 thousand years. As all the sources have nearly the same isotopic composition, this box model is primarily controlled by the alteration of oceanic crust (AOC) and Mn-oxide burial fluxes which follows previously published Tl models¹. However, given the long timescales of AOC, only Mn-oxide burial changes are perturbed to drive short-term changes observed in the data, which is utilized in this geochemical box model. The following equation is used to determine the change isotope composition of Tl in the ocean from an initial steady-state, here δ^{Tl}_0 is the seawater Tl isotopic composition at a given time, F^{Tl}_{flux} indicates the size of a certain flux (in moles per year), δ^{Tl}_{flux} is the isotopic composition of the flux, and M^{Tl}_0 is the mass of Tl in the oceanic reservoir (in moles):

$$\delta^{Tl}_0/dt = ((F^{Tl}_{source}(\delta^{Tl}_{source} - \delta^{Tl}_0)) - ((F^{Tl}_{AOC}/M^{Tl}_0)(\delta^{Tl}_{AOC}/M^{Tl}_0) + ((F^{Tl}_{Mn}/M^{Tl}_0)(\delta^{Tl}_{Mn}/M^{Tl}_0))) / M^{Tl}_0$$

Initial parameters used were based on the modern marine isotopic mass balance^{1,2} and are summarized in Supplementary Table 1. This creates a steady-state oceanic reservoir at $\epsilon^{205}\text{Tl} = -6.0$. Starting at 0.2 Myr, Mn-oxide burial flux is steadily decreased over ~1.3 Myr to 20% of the starting Mn-oxide burial flux (30.3×10^4 moles/year), causing a perturbation in the marine Tl isotopic value to ~-2.0 by 1.5 Myr. It should be noted that due to analytical error and the sensitivity of the Tl proxy there could be less Mn-oxide burial, but this represents a conservative estimation of burial flux change. This resulting steady increase in $\epsilon^{205}\text{Tl}$ values is approximately

equivalent to the rate of change seen in the data (see Figure 2). At 1.5 Myr, a range of increases in Mn-oxide burial flux is induced that result in an $\epsilon^{205}\text{Tl}$ excursion back to ~ -6.0 as the observed magnitude of Tl perturbation (see Figure 2), compared to an initial run without an induced increase in oxic seafloor. These sensitivity tests examine the large and rapid perturbation using a range of Mn oxide fluxes from 1400% to 100% of the modern values over a respective duration of 0.001 to 0.050 Myr (1,000 to 50,000 years; see Extended Data Figure 2). Each test results in an isotopic perturbation of ~ 4 epsilon units. Following the oxygenation interval, all model runs the Mn-oxide burial flux returns to the pre-event value of 20% modern flux to maintain a steady-state near $\epsilon^{205}\text{Tl} = -2.0$. The minimum value and duration of the Tl excursion can also be determined using this model. The duration was found using the length of time from 1.5 Myr to when Tl isotopic values return to less negative than -2.3 (the average isotopic values of sources minus the instrument's analytical error).

Supplementary Discussion:

Duration of Tl excursion at Japanese sections

The approximate duration of the oxygenation interval was determined to be ~ 60 kyr based on previous astrochronologic data for the Japanese sections³. An age-depth relationship was determined in the original publication through the comparison of lithology and total organic carbon deposition with orbital cycles, which was then compared using two different age-depth models³. The amount of time that passed between the bottom and top of the excursion at both Gujo-Hachiman and Ubara was then determined. Only a rough estimate of the duration of the excursion was taken at both sections due to the uncertainties intrinsic with astrochronologic dating and generally slow sedimentation rates making age estimates more difficult. Additionally, a few tens of thousands of years difference between models at Gujo-Hachiman during this

interval as well as the excursion being a smaller portion of the entire section cause the estimates to be weighted more favorably to the Ubara. Importantly, though, both sections using either model indicate the approximate passage of $\sim 60 \pm 20$ kyr during the excursion interval. The Gujo-Hachiman age model was also utilized to determine the extent of time prior to the EPME at this section, which can be roughly estimated at 1 million years.

Interpretations of geochemical model

Using a geochemical Tl isotope mass balance box model across the EPME shows that it is possible to recreate the notable trends, especially the short duration event, observed for Tl isotopes during this interval through influencing the burial of Mn-oxides alone (Extended Data Figure 2). Importantly, across all excursion tests, an increase in Mn-oxide burial at or above modern fluxes can induce a negative Tl isotopic excursion of the observed magnitude in the data (see Figure 2) over relatively short timescales. The duration of the oxidation event and degree of Mn-oxide burial is modulated across the different tests so that all excursions have the same magnitude, with longer durations of oxidation associated with lower Mn-oxide burial fluxes and vice versa. It should be noted that the duration of the Tl excursion across all tests is ~ 57 kyr longer than the duration of the oxic seafloor event that initiates the excursion, as can be expected for renewal time of Tl to the new baseline ($\epsilon^{205}\text{Tl} = -2.0$) compared to its residence time (~ 18.5 kyr), indicating that only a short interval of oxic seafloor is necessary to drive a much longer Tl excursion. Additionally, this information indicates that most modeled excursions, except the longest duration test, are within the range of the estimated duration of the negative Tl excursion in the geologic record ($\sim 60 \pm 20$ kyr).

In terms of Mn-oxide burial flux increases, there is a large range of values, between modern flux rates and 1400% of the modern fluxes. As there is little previous work to derive

global Mn fluxes under rapidly altering oceanic redox conditions^{4,5}. Thus, we explore a range of values in modeling space as there are limited constraints but not all may be realistic as discussed below. The higher fluxes, especially 1400%, are extremely high and would require both a large marine Mn reservoir that accumulated due to the lack of Mn-oxide burial in the previous 1 Myr and/or was delivered during weathering events as well as rapidly precipitate high burial flux of Mn-oxides in the oxic portions of the seafloor. As discussed in the text, Mn is likely accumulating within the marine realm, but the oxygenation of the seafloor may not be sufficient to match such a large increase in Mn-oxide burial fluxes. Other modeled fluxes of Mn-oxide burial, from 325% to 100%, are far more reasonable with Mn enriched seawater, becoming more amenable as these fluxes get closer to modern values. However, these lower Mn-oxide burial fluxes also require greater durations of oxic seafloor, which is also less tenable.

As a result of the above considerations, it seems likely that a moderately increased Mn-oxide burial rate from increased oxic seafloor over an intermediate amount of time (325% to 130% increase in Mn-oxide burial for 5,000 to 20,000 years, respectively) is reasonable. These moderate Mn-oxide burial and moderate duration models also require an increased Mn reservoir in the oceans due to anoxia and weathering, but not nearly to the degree expected from the far greater flux model^{6,7}. Additionally, they show a relatively short interval of Mn-oxide burial can induce a large negative Tl excursion that lasts several times longer than the initial oxygenation event. Therefore, short intervals of oxygenation via volcanism-induced cooling^{8,9} is viable for many of these modeled scenarios and could explain the Tl record. However, the duration of oxygenation for most of these models is still longer than individual eruptive phases^{10,11} and may indicate a more cumulative effect on the ocean redox state across several eruptive phases and its effects on global temperature, ocean circulation, and gas solubility⁸.

Supplementary Tables:

Supplementary Table 1: Initial parameters for Tl geochemical box model.

Initial parameters used in the Tl model (Extended Data Figure 2) based on previously published Tl geochemical box models³⁵. Mn-oxide burial flux is the only parameter that is modulated in this box model to account for changes observed in the geochemical record across the EPME.

Initial Parameters		
	Tl (moles)	$\epsilon^{205}\text{Tl}$
Marine reservoir	8.6×10^{10}	-6.00
	Tl flux (moles/year)	$\epsilon^{205}\text{Tl}$
All Sources	484.3×10^4	-1.77
Mn-oxide burial	151.7×10^4	16.00
(range of tested values)	30.3×10^4 to $2,123.8 \times 10^4$	–
Altered oceanic crust	332.7×10^4	-7.14

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