Calcium isotope constraints on the end-Permian mass extinction

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The end-Permian mass extinction horizon is marked by an abrupt shift in style of carbonate sedimentation and a negative excursion in the carbon isotope ($\delta^{13}$C) composition of carbonate minerals. Several extinction scenarios consistent with these observations have been formulated. Secular variation in the calcium isotope ($\delta^{44}$/40Ca) composition of marine sediments provides a tool for distinguishing among these possibilities and thereby constraining the causes of mass extinction. Here we report $\delta^{44}$/40Ca across the Permian-Triassic boundary from marine limestone in south China. The $\delta^{44}$/40Ca exhibits a transient negative excursion of ~0.3‰ over a few hundred thousand years or less, which we interpret to reflect a change in the global $\delta^{44}$/40Ca composition of seawater. CO2-driven ocean acidification best explains the coincidence of the $\delta^{44}$/40Ca excursion with negative excursions in the $\delta^{13}$C of carbonates and organic matter and the preferential extinction of heavily calcified marine animals. Calcium isotope constraints on carbon cycle calculations suggest that the average $\delta^{13}$C of CO2 released was heavier than ~28‰ and more likely near ~15‰; these values indicate a source containing substantial amounts of mantle- or carbonate-derived carbon. Collectively, the results point toward Siberian Trap volcanism as the trigger of mass extinction.

An abrupt shift in style of carbonate sedimentation occurs across the end-Permian extinction horizon. Microbialites and oolites overlie diverse, fossiliferous limestones of the latest Permian age in carbonate strata deposited across the tropical Tethys (1–8) and in the Panthalassa Ocean (8, 9) (Fig. S1). The mass extinction and facies shift are associated with a large negative excursion in the carbon isotope ($\delta^{13}$C) composition of carbonate minerals.

Geochemical and sedimentary observations have been used to support various causal mechanisms for the mass extinction. Three different scenarios have been put forth. First, the “Strangelove Ocean” scenario links mass extinction to collapse of the biological pump—the vertical separation in the water column of carbon fixation and respiration, which results from the sinking of organic matter out of the surface ocean (10). Under this scenario, an initial decrease in carbonate deposition would occur because of mixing of surface waters with CaCO3-underseasndered deeper waters (assuming an oxygenated deep ocean); subsequent increase in alkalinity because of continental weathering would lead to enhanced carbonate deposition, explaining the deposition of microbialites and oolites (10). Second, the ocean overturn model proposes that extensive sulfate reduction in anoxic deep waters of the Permian oceans resulted in a buildup of carbonate alkalinity and hydrogen sulfide in deep water prior to the extinction event (11–14). Upwelling of these alkaline deep waters would have triggered carbonate precipitation on the shelves (2, 5, 15, 16) and caused mass extinction through combined stresses of hypercapnia, anoxia, and hydrogen sulfide poisoning (14, 15, 17). Third, the ocean acidification model proposes that massive release of $^{13}$C-depleted carbon from a reservoir in the crust (e.g., methane clathrates, coal, and magma) (18–22) acidified the ocean, reducing carbonate sedimentation and potentially leading to dissolution of carbonate sediments (8). Subsequently enhanced continental weathering and consequent delivery of carbonate alkalinity to the oceans would account for the widespread deposition of microbialites and oolites above the extinction horizon (8).

One avenue for distinguishing among these hypotheses lies in their differing implications for the global cycling of calcium, an element with a residence time of approximately 600–1,000 ky and uniform isotope composition in the modern oceans (23, 24). Isotopes of calcium are fractionated during the precipitation of carbonate (25–27): $^{40}$Ca is preferentially incorporated into the solid phase, leaving seawater enriched in $^{44}$Ca at steady state relative to the delivery and burial fluxes (24, 28). Consequently, scenarios that require imbalances between the delivery and burial fluxes of calcium in the oceans should impart changes in the calcium isotope composition in the oceans and associated sediments.

We constructed a one-box, isotope mass-balance model of the global calcium cycle (see Methods and SI Discussion) to generate quantitative predictions for marine calcium isotopes and concentrations associated with the various Permian-Triassic (P/T) boundary scenarios. Fig. 1 illustrates the predictions for these scenarios as well as two alternative possibilities requiring a shift in calcium isotopes only. Both the Strangelove Ocean and acidification scenarios predict an initial decrease in the carbonate depositional flux followed by an increase in carbonate deposition to return the system to steady state, but the perturbation is potentially much larger under the acidification scenario. In contrast, under the ocean overturn scenario one would expect a positive excursion in $\delta^{44}$/40Ca because of the stimulation of carbonate precipitation by upwelling of alkaline deep water (2, 5, 15). Oceanographic mechanisms allowing for the overturn scenario have been debated (29–31); here we consider its implications for calcium isotopes irrespective of its feasibility from an oceanographic standpoint. A permanent global shift from calcite- to aragonite-dominated carbonate deposition across the extinction horizon is capable of producing $\delta^{44}$/40Ca variation similar to that predicted under the acidification scenario; it causes no change in the calcium concentration of the ocean. A global shift in the isotope composition of the calcium delivery flux within the range of likely values would cause a much smaller and more gradual change in
Results
Fig. 2 illustrates the P/T δ44/40Ca and δ13C records from the Dajiang section, along with age constraints from conodont bios-

tratigraphy and geochronology and model output for the acidification scenario (our preferred scenario; see Discussion below) and a scenario involving a global shift from calcite- to aragonite-dominated carbonate deposition. The δ44/40Ca values are significantly correlated with the δ13C values (Pearson’s r = 0.62; p = 0.002) but not with indicators of precipitation rate or diagenesis such as Sr/Ca, Mn/Sr, or δ44/40Ca versus SRM-915a) is in agreement with Permian values from a Phanerozoic compilation of δ44/40Ca values for carbonate rocks and well-preserved shell calcite (39).

Several lines of evidence suggest that the δ44/40Ca measurements are primary. The δ44/40Ca shift coincides with the globally recognized negative δ13C excursion (38), and the δ44/40Ca values are significantly correlated with the δ13C values (Pearson’s r = 0.62; p = 0.002) but not with indicators of precipitation rate or diagenesis such as Sr/Ca, Mn/Sr, or δ44/40Ca versus SRM-915a) is in agreement with Permian values from a Phanerozoic compilation of δ44/40Ca values for carbonate rocks and well-preserved shell calcite (39).

The light values in δ44/40Ca continue from the microbialite facies into overlying micritic limestones before trending back toward preexcursion values (Fig. 2), suggesting that variation in δ44/40Ca does not simply reflect differences among facies in either primary fractionation of calcium isotopes or later diagenetic alteration. Finally, similar to the δ13C of carbonate rocks, there is far more calcium in the mineral than the pore fluids, helping buffer the δ44/40Ca of carbonate minerals against alteration during burial diagenesis (40).

Discussion
The P/T boundary δ44/40Ca excursion is inconsistent in direction with the prediction for ocean overturn and is larger in magnitude than the excursion predicted under the Strangelove Ocean or through a change in the isotope composition of weathered calcium. The δ44/40Ca excursion is consistent in direction, magnitude, and
time scale with ocean acidification or a large shift in the proportional deposition of aragonite versus calcite. The $\delta^{44/40}$Ca excursion could also result from a local (not global) change in isotope fractionation during carbonate precipitation or a change in the local $\delta^{44/40}$Ca composition of seawater. Below, we consider the support for these local factors before addressing the global scenarios.

One possibility is that there is a temperature component to the $\delta^{44/40}$Ca excursion. Calcium isotope fractionation decreases with increasing temperature (41). Because temperatures increased across the P/T boundary (42), the temperature effect tends in the opposite direction from the observed excursion, reducing its apparent magnitude. The amount of warming across the boundary is poorly constrained, but an increase of 5–10°C (43, 44) could reduce the fractionation by as much as 0.1–0.2‰ (26, 41). Thus, the negative excursion in seawater $\delta^{44/40}$Ca may be somewhat larger than reflected in the raw data.

An alternative mechanism for locally changing the $\delta^{44/40}$Ca of carbonate minerals is through a change in the local precipitation rate. Sr/Ca can serve as a proxy for precipitation rate (41); it is not larger than reflected in the raw data. The isotope excursion could also reflect a change in the local, and not global, $\delta^{44/40}$Ca composition of seawater. There is no evidence for a significant $\delta^{44/40}$Ca gradient in the modern oceans (23), but stratigraphic variability in the isotope composition of ancient carbonates has been suggested to result from limited mixing between the open ocean and tectonic basins or epeiric seaways (45). The $\delta^{44}$Ca excursion on the GGB, however, has been observed in carbonate sections across the globe (46, 47) and appears to be representative in terms of relative change in isotope composition as well as in absolute value. Any oceanographic gradient in $\delta^{44/40}$Ca would therefore need to have existed in the absence of a similar gradient in $\delta^{44}$Ca. Consequently, we view a changing local $\delta^{44/40}$Ca gradient as unlikely.

A shift in mineralogy of carbonate sediment from calcite to aragonite could produce a negative excursion in $\delta^{44/40}$Ca of carbonate rocks because aragonite is ~0.6‰ lighter than calcite relative to source fluid (26). The observed $\delta^{44/40}$Ca excursion of 0.3‰ would thus require that half of the sediment pool in the ocean switched from calcite to aragonite across the extinction horizon. If the shift in mineralogy was only local, then the isotope recovery would require a local return to calcite-dominated sedimentation; if it was global and permanent, then the excursion decays because the global ocean approached a new steady state with a heavier $\delta^{44/40}$Ca of seawater because of the globally lighter $\delta^{44/40}$Ca in carbonate sediments (Fig. S2). The global scenario is consistent with the greater relative abundance of aragonite versus calcite-producing skeletal animals globally in the Lower Triassic (48), with petrographic evidence for an originally aragonitic mineralogy for Early Triassic ooids and carbonate crystal fans (5), and with the similarity of Lower Triassic carbonate strata across the global tropics (8).

Finally, the excursion could reflect a decrease in the global $\delta^{44/40}$Ca of seawater. Such a decrease is most plausibly generated by ocean acidification (Fig. 1), which would reduce the carbonate ion concentration and carbonate saturation level of seawater and therefore allow calcium to accumulate. The calcium delivery flux is coupled to the dominant burial flux of carbonate sedimentation ($F_{\text{calcite}}$) through the carbonate saturation state of seawater:

$$F_{\text{calcite}} = k(\Omega - 1)^{\eta}$$

where $k$ is a scaling constant, $\eta$ is the order of the reaction [approximately 2 (refs. 10 and 49)], $\Omega$ is the saturation state with respect to calcite or aragonite ($\Omega = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] / K_{sp}$), and $K_{sp}$ is the solubility product of the relevant carbonate mineral (50). Therefore, the effect of elevated calcium delivery via rivers, for example, is mitigated by an increase in $\Omega$, which causes $F_{\text{calcite}}$ to increase concomitantly. An increase in seawater $[\text{Ca}^{2+}]$ is most likely to result from decreases in $k$ and/or $[\text{CO}_3^{2-}]$. The loss of skeletal carbonate sinks following the end-Permian mass extinction (34) may have caused $k$ to decrease because skeletal animals and algae had been expending metabolic energy to drive carbonate precipitation prior to the extinction. A decrease in $[\text{CO}_3^{2-}]$ and an increase in the calcium river flux are expected under scenarios of CO$_2$ or methane release previously proposed to account for the negative excursion in $\delta^{44}$Ca (51–53): Because CO$_2$ is a weak acid (and methane oxidizes to CO$_2$ within years), rapid CO$_2$ input would lower ocean pH and $[\text{CO}_3^{2-}]$, reduce $\Omega$ and $F_{\text{calcite}}$, and thereby allow calcium to accumulate in seawater while simultaneously warming the climate and accelerating the weathering of calcium-bearing rocks. If acidification caused the oceans to become undersaturated with respect to calcite, calcium could also have been released into seawater through dissolution of marine carbonate sediments.

The magnitude of excess calcium delivery required to explain our measured $\delta^{44/40}$Ca excursion under this acidification scenario can be calculated by mass balance, assuming a known isotopic composition of the calcium input and the starting size of the marine calcium reservoir. Because the mass extinction event occurred over less than 500 ky and likely less than 150 ky (54), we can approximate the event as instantaneous (see SI Discussion, Tables S1 and S2, and Fig. S4). Assuming that the input $\delta^{44/40}$Ca is isotopically similar to the river calcium flux and that the ocean $\delta^{44/40}$Ca was 1.4‰ heavier than our measured preextinction $\delta^{44/40}$Ca (i.e., fractionation similar to modern), we calculate an increase in seawater $[\text{Ca}^{2+}]$ of 21.2% (2.15 mM) for a 0.2‰ excursion or 36% (5.6 mM) for a 0.3‰ excursion (see SI Discussion). Here we have ignored the potential effects of changing temperature and mineralogy in order to investigate the effects of acidification alone. Because expected effects of temperature and mineralogy work in opposing directions (given increases in temperature and prevalence of aragonite) and the likely magnitudes of their effects are similar, in aggregate they may have mostly offset one another.

We favor the ocean acidification scenario over a change in sediment mineralogy as the explanation for the calcium isotope excursion because it also explains a wide range of geochemical, sedimentological, and paleontological observations associated with the P/T boundary not predicted by a shift in carbonate mineralogy alone. First, the synchronous deposition of microbialsites and oolites across the global tropics within the H. parvus conodont zone (7, 8) could reflect rapid carbonate deposition resulting from enhanced silicate and carbonate weathering in the aftermath of a CO$_2$ release event. The weathering hypothesis can explain why synchronous, widespread deposition of these facies is confined to the earliest Triassic, despite the persistence of ocean anoxia (55) and skeleton-poor carbonate sediments (34) through much of Early Triassic time. Moreover, removing the calculated 2.2–3.6 $\times$ 10$^{18}$ mol of calcium from the oceans as calcium carbonate would have translated to roughly 8–13 m of carbonate sediment on the 10$^5$ km$^2$ of Late Permian carbonate shelves (56), which is broadly consistent with the thickness of the microbialite and oolite deposits within the H. parvus zone (Table S3). Second, acidification can explain observations of submarine carbonate dissolution of beds immediately underlying the microbialite (8). Third, rapid CO$_2$ release can account for the negative excursion in $\delta^{43}$C at the P/T boundary (46). Finally, ocean acidification can account for the preferential extinction of heavily calcified marine animals with limited ability to buffer calcifying fluids against changes in ambient water chemistry (17).

If the primary acid added to the oceans was CO$_2$, then the $\delta^{44/40}$Ca excursion can provide first-order constraints on the magnitude and C-isotope composition of carbon released because
each mole of CO₂ released would allow approximately 1 mol of calcium to be stored in the oceans (57). Assessing the source, magnitude, and isotope composition of carbon released at the P/T boundary has been challenging because the δ^{13}C excursion can potentially result from a smaller release from a 10^{13}C-depleted source (e.g., biogenic methane) or a larger release from a less depleted reservoir (e.g., coal and basaltic magma). Berner (51) argued that only biogenic methane could account for the magnitude of the δ^{13}C excursion, but more recent studies of Siberian Traps intrusions suggest that the magnitude of carbon release may have been larger than previously suspected (22), opening the possibility of carbon release from less depleted reservoirs. One can estimate the δ^{13}C of the carbon source as a function of the initial total carbon given the estimated excess calcium delivery (2.2–3.6 × 10^{18} mol) and the excursion in δ^{13}C_{carb} (−3.6‰; cf. Fig. 2). The likely δ^{13}C composition of the CO₂ added on the basis of the above calculation is between −5 and −13‰ (Fig. 3). This calculation assumes that all acidifying power comes from CO₂. However, if emplacement of the Siberian Traps played a significant role (22), then sulfur release could account for as much as half of the acidification [volatile fluxes from flood basalts suggest a molar role (22), then sulfur release could account for as much as half of the acidification]. Because H₂SO₄ can acidify the ocean without contributing to the decrease in δ^{13}C, including its effects in the calculation requires a smaller, and thus isotopically lighter, carbon source. In the more conservative case, only 1.1–1.8 × 10^{18} mol of CO₂ release would account for the δ^{13}C excursion and the δ^{13}C of the CO₂ would be between −11 and −28‰ (Fig. 3). Even under this more conservative scenario, the δ^{13}C of methane clathrates (−60‰) is far too negative to have been the primary source of carbon; the range of likely values instead points toward a mixture of carbon sources, which appear to have included a substantial component from carbonate rocks and/or mantle-derived volatiles.

Intrusion of Siberian Traps magmas through a thick sequence of carbonate sediments and coal (22) coeval with mass extinction (59) provides a mechanism for releasing sufficient quantities of CO₂ with the appropriate δ^{13}C composition through the production of thermogenic methane during the heating of coal (22) and CO₂-rich volatile phases during the incorporation of carbonate rocks into basaltic magma (60). Although previous studies have emphasized the release of carbon from methane clathrates or coal (51–53), δ^{44/40}Ca constraints instead suggest that carbon release associated with the end-Permian extinction may have included a substantial contribution from the incorporation of carbonate rock into Siberian Traps magmas.

The ocean acidification scenario that we favor for the P/T boundary is similar to that proposed for the Paleocene-Eocene Thermal Maximum (PETM), where there is abundant evidence of a global decrease in the δ^{13}C and dissolution of deep-marine carbonate sediments (61) and possibly a negative excursion in δ^{13/44}Ca (62). Unlike the end-Permian event, however, the PETM is not associated with global mass extinction—only deep-sea benthic foraminifera were severely affected (63). Differences in the distribution of carbonate sediments between 250 and 55 million years ago may account for much of the contrast. At the PETM, as today, the oceans were buffered against acidification by extensive, fine-grained, un lithified carbonate sediments on the deep-sea floor, which could relatively rapidly dissolve to counter acidification (64). By contrast, the Late Permian deep sea contained no such carbonate buffer because Permian oceans lacked abundant pelagic carbonate producers such as coccolithophors and planktonic foraminifera. Consequently, any buffering against acidification via dissolution of carbonate sediments could only have occurred more slowly in the less extensive, coarse-grained, mostly lithified, shallow-marine carbonate platform sediments or via chemical weathering of silicate and carbonate rocks on land. Thus, carbonate sediments may not only record critical information constraining the causes of end-Permian mass extinction; their spatial distribution in the oceans may also have been a key control on its severity.

Methods

Notation. Calculation of δ^{44/40}Ca follows standard delta notation:

$$\delta^{44/40}Ca = \left[ \frac{^{44}Ca/^{40}Ca_{sample}}{^{44}Ca/^{40}Ca_{std}} - 1 \right] \times 1,000.$$  

In this study, δ^{44/40}Ca values are referenced to a bulk Earth standard. To compare our numbers to those referenced to the SRM915a scale, our measured value of SRM915a (−1.2‰) can be added to the numbers reported in this work.

Sample Preparation. Samples collected from the outcrop were cut on a rock saw and subsequently ground and polished on a vibrating lapidary tray. The polished face was then drilled with a 1-mm dental bur to produce powder for analysis. Areas of micrite were selected for drilling in samples exhibiting macroscopic variation in carbonate phases. Early and late diageneric cements, especially fracture-filling vein calcite, were avoided.

Calcium Isotope Analysis. Carbonates were dissolved in SEASTAR acetic acid. Calcium concentrations were determined, and 30–μg Ca aliquots were removed. A 42–48 calcium double spike was added to the aliquots and equilibrated in 5–8 mL of 2N nitric acid. The samples were loaded in 1N nitric acid onto ion separation columns filled with DOWEX® AG 50W-X8 resin. The samples were eluted in 2N nitric acid and dried down. These chemically separated, spiked samples were loaded onto Re filaments with phosphoric acid and measured on a multicollector thermal ionization mass spectrometer. Two replicates of each sample were run, and the standard deviation between replicate measurements is presented.

Trace Metal Analysis. For trace metal analysis, ~2 mg of dried, powdered limestone was dissolved in 1M acetic acid. After centrifugation, the supernatant was removed and subjected to trace metal analysis (Mn and Sr) as well as Ca and Mg analysis using a Thermo Jarrell Ash IRIS Advantage/1000 Radial Inductively Coupled Argon Plasma Spectrometer with a solid state charge induction device detector.

Oxygen Isotope Analysis. For oxygen isotope analysis, samples were reacted with concentrated phosphoric acid at 90 °C in a common acid bath and then measured on a dual inlet mass spectrometer (VG Optima). Isotopic composition is reported in standard delta notation relative to the Vienna Pee Dee belemnite (VPDB) standard. Analytical precision was ±0.1‰ (2σ) on the basis of replicate measurements of a laboratory standard.
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Geochemical Model.


Supporting Information

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SI Text

SI Discussion. Ca isotope mass balance—The "instantaneous" calculation. We perform a mass balance calculation to determine how much calcium must be added to the ocean at a specified isotopic composition to decrease the global seawater δ44/40Ca by 0.1‰ to 0.3‰. This is done by using a simple mass balance and approximates the event as instantaneous. The mass balance equations used in this calculation are

\[ M_f \delta^{44/40}Ca_f = M_i \delta^{44/40}Ca_i + M_p \delta^{44/40}Ca_p \]  

[S1]

and

\[ M_f = M_i + M_p. \]  

[2]

where \( M_f \) is the final mass of calcium, \( \delta^{44/40}Ca_f \) is the final isotope composition of Ca, \( M_i \) is the initial mass of Ca, \( \delta^{44/40}Ca_i \) is the initial isotope composition, \( M_p \) is the mass of calcium added in the perturbation, and \( \delta^{44/40}Ca_p \) is the isotope composition of the Ca added. Fluid inclusion data suggest that the calcium concentration in the Permian ocean was approximately 10 mM [1]. We further estimate \( \delta^{44/40}Ca \) of 0.9‰ by assuming that our youngest Permian carbonates are 1.4‰ lighter than coeval seawater values. We assume that calcium added during the perturbation was similar in isotope composition to the river calcium flux and thus estimate \( \delta^{44/40}Ca_p \) of ~0.6‰.

In the absence of better constraints, we assume that Late Permian delivery and burial fluxes were similar to the modern (2), implying a residence time of Ca in the oceans similar to today, around 1 My (2, 3).

Calcium cycle box model—A time-dependent approach to test the assumptions of the instantaneous calculation. The calcium isotope model was built by following the previous work by DePaolo (2) and Fantle and DePaolo (3). The ocean is treated as a single box with the main fluxes of calcium to the ocean being river input, hydrothermal alteration, and diffusion/dewatering from pore fluid (2, 4), and the main sink is the deposition of carbonate minerals. The equation for the change in calcium concentration with time is

\[ \frac{dM_{Ca}}{dt} = \text{Flux}_{in} - \text{Flux}_{out} = F_{riv} + F_{hyd} + F_{pw} - F_{carb}. \]  

[3]

The river, hydrothermal, and pore water fluxes are prescribed \( (F_{riv}, F_{hyd}, \text{and } F_{pw}, \text{respectively}) \), and the carbonate sink is prescribed as proportional to the square of the ratio between the current concentration of calcium in the ocean and the steady-state (equilibrium) value (5, 6). Each of these fluxes can be assigned a calcium isotope composition \( (\delta^{44/40}Ca) \) such that the changes in calcium concentration and \( \delta^{44/40}Ca \) can be modeled simultaneously. The revised equation is

\[ \frac{d(M_{Ca}\delta_{sw})}{dt} = F_{riv}\delta_{riv} + F_{hyd}\delta_{hyd} + F_{pw}\delta_{pw} - F_{carb}(\delta_{SW} - \epsilon_{carb}). \]  

[4]

where \( \delta_{SW} \) is the \( \delta^{44/40}Ca \) of seawater, \( \delta_{riv}, \delta_{hyd}, \text{and } \delta_{pw} \) are the \( \delta^{44/40}Ca \) of rivers, hydrothermal input, and pore waters, respectively, and \( \epsilon_{carb} \) is the fractionation factor between seawater and carbonate minerals. The values used for each of these fluxes in the latest Permian are listed in Table S1.

We solve Eq.4 above by using finite difference with a time step of 1,000 years and run the model for 5 million years to study the response of the system to prescribed perturbations. Because the objective here is to probe the response of the calcium cycle to the perturbation at the Permian-Triassic (P/T) boundary, it is less important that the absolute values used are accurate than that they are correct relative to one another. This modeling approach allows us to simulate the system in steady state and examine how the various fluxes respond after a prescribed change.

To examine the predicted consequences for marine calcium concentrations and the \( \delta^{44/40}Ca \) of carbonate sediments under scenarios proposed to account for variation in \( \delta^{13}C \) and carbonate facies across the P/T boundary, we ran the model under a variety of perturbation scenarios. These scenarios are described below. Model output for \( \delta^{44/40}Ca \) and \([Ca^{2+}] \) is presented in Fig. 1. Weathering and burial fluxes of Ca and various sensitivity tests to duration and magnitude of the excursion are presented in Fig. S2.

1. Strangelove Ocean: Carbonate sedimentation initially decreases due to collapse of the biological pump and then subsequently increases to slightly exceed steady-state values prior to returning to steady state (7). To simulate this scenario, we reduced carbonate sedimentation by a factor of 24 for 30 ky, the duration of reduced sedimentation under the model of Rampino and Caldeira (7), and then allowed the model to return to its normal dynamics.

2. Ocean overturn: Carbonate sedimentation increases due to the mixing of anoxic, alkaline deep waters with oxygenated shallow waters (8). To simulate this scenario, we increased the scaling between calcium concentrations and the carbonate burial flux by a factor 2.06 for 100 ky. The magnitude of forcing was selected such that the marine calcium concentrations decreased by 2 mM over the course of the perturbation. Sensitivity tests were conducted to achieve a similar reduction in \([Ca^{2+}] \) over different time scales. As discussed in the main text, such a reduction in calcium concentrations corresponds approximately to the amount of calcium stored in microbialite and oolite deposits immediately overlying the end-Permian extinction horizon and thus provides a constraint on the magnitude for this effect.

3. Ocean acidification: Carbonate deposition decreases due to ocean acidification and then subsequently increases due to weathering feedbacks. To simulate this scenario, we reduced the carbonate burial flux by 17.7% and increased the calcium weathering flux as much as necessary to produce the magnitude and duration of the desired excursion. We explored durations between 10 and 500 ky for the excursion and magnitudes between 0.1 and 0.5‰. The scenario for a 0.3‰ excursion over 100 ky is presented as the preferred scenario in the main text (Figs. 1 and 2). The results from sensitivity analyses are presented in Fig. S2 and Table S2. Note that this model does not assume any dissolution of existing seafloor carbonate sediments. It merely assumes greatly reduced burial and increased weathering through the river flux. Because the isotope composition of the river flux is similar to that of carbonate sediments (Table S1), we do not explicitly resolve the terrestrial and (possible) marine components of calcium delivery.

4. Shift from calcite- to aragonite-dominated carbonate deposition: Calcium isotope composition of sediments (and the ocean) changed due to a change in the ratio of calcite to aragonite production and a consequent global change in the fractionation between seawater and sediments. To simulate this scenar-
io, we assumed an increase of 0.3‰ in the fractionation between seawater and carbonate sediments, as would be predicted if half of the carbonate sediments shifted from calcite to aragonite across the extinction horizon. Under this scenario, seawater calcium concentrations do not change, but seawater δ^{44}/δ^{40}Ca increases while sediment δ^{44}/δ^{40}Ca decreases (temporarily).

5. Shift in the δ^{44}/δ^{40}Ca composition of the global weathering flux: Calcium isotope composition of seawater changes due to a change in the isotope composition of the calcium weathering flux. To simulate this scenario, we decreased the δ^{44}/δ^{40}Ca of the river calcium flux by 0.3‰ for time scales of 100 and 500 ky, before returning it to its preexcursion value. We also determined the magnitude of change in the δ^{44}/δ^{40}Ca of the weathering flux to account for a −0.3‰ excursion over 100 and 500 ky. The calculated values (reductions by 3.0 and 0.85‰, respectively) require a global average isotope composition of weathered calcium outside of the range of measured values for igneous and carbonate rocks (2), indicating that the weathering flux cannot plausibly account for the observed isotope excursion.

Calculating excess calcium weathering flux. As discussed in the main text, model-data comparison suggests ocean acidification is the scenario that can best account for the calcium isotope, carbon isotope, sedimentological, and paleobiological observations. The change in the calcium isotope composition of seawater depends primarily on the net imbalance between calcium delivery and calcium burial in the ocean. As discussed in the main text, we couple the carbon cycle model to the calcium cycle model through the calcium weathering flux from rivers and the calcium burial flux. The excess carbon input (in moles) is assumed to be equivalent to the calcium burial flux. Results are described here and in presented in Fig. S4. If all excess calcium is buffered by CO$_2$ and the excursion is 0.3‰, then the δ$^{44}$C of the CO$_2$ released must have been close to mantle values. If the excursion was partially buffered by other acids (e.g., SO$_2$), then the implied δ$^{44}$C of the CO$_2$ released was more negative. For example, if CO$_2$ release accounted for only 0.2‰ of the calcium isotope excursion, then its δ$^{43}$C would have been near −14‰, and if CO$_2$ release accounted for only 0.1‰ of the calcium isotope excursion, then its δ$^{43}$C would have been near −25‰. Thus, model calculations indicate that the δ$^{43}$C of carbon released only approaches organic carbon values if the calcium isotope excursion was very small or if carbon only accounted for a small fraction of the acidification event. The nonmonotonic behavior of δ$^{43}$C as a function of excursion time scale in Fig. S4 results from the change in equilibrium δ$^{43}$C incorporated into the model across

Following an approach analogous to the one described above in relation to δ$^{44}$/δ$^{40}$Ca, we can perform a simple mass balance calculation to determine how much carbon must be added to the ocean at a specified isotopic composition to decrease the global seawater δ$^{13}$C from +3.6‰ to 0‰ (5). This calculation requires an estimate of the Late Permain dissolved inorganic carbon (DIC) reservoir size. Although there are few direct constraints on this value, Earth system models provide an estimate of the likely range of DIC reservoir sizes. Ridgwell’s (10) modeling of Phanerozoic seawater carbonate chemistry suggests a likely DIC concentration of 4,000–5,000 μmol and thus a total reservoir size of 5.5–6.9 × 10$^{15}$ mol (66,000 to 82,000 GT, where 1 GT = 10$^{15}$ g). The entire range of DIC concentrations over the past 500 My in Ridgwell’s model varies between 2,000 (slightly less than modern) and 7,000 μmol (approximately three and a half times modern). These values provide plausible upper and lower bounds. Consistent with Ridgwell’s model, previous studies of the P/T δ$^{44}$C record have used estimates between the modern and up to two and a half times the modern for the Late Permain DIC reservoir (8, 11, 12).

The mass balance equations are Eq. 4 from above and

$$ M_f δ^{13}C_f = M_i δ^{13}C_i + M_p δ^{13}C_p. $$

where $M_f$ is the final DIC reservoir size, δ$^{13}$C$_f$ is the final isotope composition of DIC (‰) (Fig. 2), $M_i$ is the initial DIC reservoir size, δ$^{13}$C$_i$ is the initial isotope composition of the DIC reservoir (-3.6‰) (Fig. 3), $M_p$ is the mass of carbon added in the perturbation, and δ$^{13}$C$_p$ is the isotope composition of the carbon added.

Carbon cycle box model—A time-dependent approach to test the assumptions of the instantaneous calculation. The isotope model used for the carbon cycle is a standard one-box model, with a weathering flux of mantle composition (−4.9‰) in these calculations, though the absolute value has little effect within the narrow range of likely values) and separate carbonate and organic carbon burial fluxes. By using Ridgwell’s (10) model of Phanerozoic carbonate chemistry in seawater, we assume DIC of 4,500 μM, more than two times modern values. Organic carbon is assumed to be 25‰ lighter than carbonate, with carbonate approximating the bulk seawater average value. We further assume a decrease in the proportion of carbon burial in the organic form (rather than in carbonate minerals) across the P/T boundary (Permian = 0.34, Triassic = 0.275) to be faithful to a change from background values of δ$^{13}$C in the Permian near +4‰ and in the Early Triassic closer to +2‰ (13). Thus, the equilibrium (steady-state) δ$^{43}$C value for the ocean (and carbonate rocks) prior to the excursion is 3.6‰ and postexcursion is +2‰.

We couple the carbon cycle model to the calcium cycle model through the calcium weathering flux from rivers and the calcium burial flux. The excess carbon input (in moles) is assumed to be equal to the imbalance between calcium delivery and calcium burial (5). The burial of carbon in carbonate sediments is assumed to be equivalent to the calcium burial flux. Results are described here and in presented in Fig. S4. If all excess calcium is buffered by CO$_2$ and the excursion is 0.3‰, then the δ$^{44}$C of the CO$_2$ released must have been close to mantle values. If the excursion was partially buffered by other acids (e.g., SO$_2$), then the implied δ$^{44}$C of the CO$_2$ released was more negative. For example, if CO$_2$ release accounted for only 0.2‰ of the calcium isotope excursion, then its δ$^{43}$C would have been near −14‰, and if CO$_2$ release accounted for only 0.1‰ of the calcium isotope excursion, then its δ$^{43}$C would have been near −25‰. Thus, model calculations indicate that the δ$^{43}$C of carbon released only approaches organic carbon values if the calcium isotope excursion was very small or if carbon only accounted for a small fraction of the acidification event. The nonmonotonic behavior of δ$^{43}$C as a function of excursion time scale in Fig. S4 results from the change in equilibrium δ$^{43}$C incorporated into the model across
the P/T boundary and the response time of C to this shift. More realistic coupling of the calcium and carbon cycles is desirable but would require explicit calculations of not only dissolved inorganic carbon concentrations but also alkalinity and silicate weathering. Given the existing uncertainties in the magnitude of the \( \delta^{44/40}\text{Ca} \) excursion and the amount of the excursion accounted for through \( \text{CO}_2 \)-driven acidification, such additional specificity is not justified by existing data and is beyond the scope of the current study.

In summary, if carbon release buffered the increased calcium concentration in seawater, then that carbon likely had an isotope composition between mantle values and those of organic carbon. However, only under the scenarios involving the least amount of carbon and the shortest time scales do implied \( \delta^{44/40}\text{C} \) values approach those of organic matter (near ~25\%). Thus, our results indicate a substantial contribution of carbon heavier in \( \delta^{44/40}\text{C} \) than organic carbon or methane sources. Such carbon was likely derived from the mantle or carbonate rocks.

11. Payne JL, Kump LR (2007) Evidence for recurrent Early Triassic massive volcanism and the P/T boundary and the response time of C to this shift. More realistic coupling of the calcium and carbon cycles is desirable but would require explicit calculations of not only dissolved inorganic carbon concentrations but also alkalinity and silicate weathering. Given the existing uncertainties in the magnitude of the \( \delta^{44/40}\text{Ca} \) excursion and the amount of the excursion accounted for through \( \text{CO}_2 \)-driven acidification, such additional specificity is not justified by existing data and is beyond the scope of the current study.

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Fig. S1. P/T boundary facies on the Great Bank of Guizhou. (A, B, and E) P/T boundary contact near Dajiang. (C and D) Micritic limestone facies near Dajiang. (F) Polished slab of the P/T boundary contact, illustrating contact between fossiliferous Wuchiaping Formation (Bottom) and microbialite (Top). (G) Photomicrograph of sponge-bearing packstone from the Wuchiaping Formation. (H) Photomicrograph of the contact between the Wuchiaping Formation and microbialite. (I) Photomicrograph of the micritic limestone facies.
Fig. S2. Additional model results and sensitivity analyses for the acidification and overturn scenarios as well as changes in weathering and mineralogy. All perturbations begin at 252.6 My and end after the specified interval. (A) Calcium isotope history for a 0.3‰ excursion over time scales from 10 to 500 ky. (B) Histories of calcium weathering flux from rivers and burial flux in carbonate sediments and ocean calcium concentrations under the 100 ky acidification scenario. (C) Calcium isotope history for a 2-mM reduction in ocean calcium concentration under the overturn scenario over time scales between 10 and 500 ky. (D) Histories of calcium weathering flux from rivers and burial flux in carbonate sediments and ocean calcium concentrations under the 100 ky overturn scenario. (E) Calcium isotope histories predicted under a change in the isotope composition of the river calcium flux; 100 and 500 ky shifts in the river flux of 0.3‰ do not produce excursions of the observed magnitude. Shifts in the isotope composition of the weathering flux required to produce the observed excursion over 100 or 500 ky are much larger than geological constraints permit (0.85‰ under the 500 ky scenario and 3.0‰ under the 100 ky scenario). Weathering and burial flux magnitudes and ocean calcium concentrations are not presented because they do not vary under these scenarios. (F) Calcium isotope histories of carbonate sediments and seawater predicted due to a shift from calcite-dominated to aragonite-dominated sedimentation. Also depicted is the resulting change in the fractionation between seawater and carbonate sediments. Weathering and burial flux magnitudes and ocean calcium concentrations are not presented because they do not vary under this scenario. (G) Sensitivity analysis of the calcium weathering flux under excursion magnitudes between 0.1‰ and 0.3‰ and durations between 100 and 500 ky. (H) Sensitivity analysis of calcium concentrations in the ocean under excursion magnitudes between 0.1‰ and 0.3‰ and durations between 100 and 500 ky. All acidification models assume the same reduction in the calcium burial flux for the duration of the perturbation.
Fig. S3. Comparison of $\frac{\delta^{44}}{\delta^{40}}$Ca to other geochemical proxies. $\frac{\delta^{44}}{\delta^{40}}$Ca is only significantly correlated with $\delta^{13}$C, which records a globally recognized negative excursion across the end-Permian extinction horizon. These findings suggest that the $\frac{\delta^{44}}{\delta^{40}}$Ca are also primary and reflect a global calcium cycle disturbance.

(A–E) Stratigraphic plots. (F–I) Cross-plots of $\frac{\delta^{44}}{\delta^{40}}$Ca versus other proxies. (A) Stratigraphic distribution of $\frac{\delta^{44}}{\delta^{40}}$Ca. (B) Stratigraphic distribution of $\delta^{13}$C. (C) Stratigraphic distribution of $\delta^{18}$O. (D) Stratigraphic distribution of Sr/Ca. (E) Stratigraphic distribution of Mn/Sr. (F) Cross-plot of $\frac{\delta^{44}}{\delta^{40}}$Ca versus $\delta^{13}$C (Pearson’s $r = 0.6$, $p = 0.005$). (G) Cross-plot of $\frac{\delta^{44}}{\delta^{40}}$Ca versus $\delta^{18}$O (Pearson’s $r = -0.01$, $p = 0.96$). (H) Cross-plot of $\frac{\delta^{44}}{\delta^{40}}$Ca versus Sr/Ca (Pearson’s $r = -0.22$, $p = 0.30$). (I) $\frac{\delta^{44}}{\delta^{40}}$Ca versus Sr/Ca (Pearson’s $r = -0.37$, $p = 0.07$). See Table S4 for raw data.
Fig. S4. Contour plot of $\delta^{13}C$ for carbon released at the P/T boundary versus the time scale over which it was released and the magnitude of the $\delta^{44/40}Ca$ excursion accommodated by CO$_2$-driven acidification. The nonmonotonic relationship between $\delta^{13}C$ and time scale results from the modeled shift in the fraction of carbon buried as organic matter in the model, which also imposes a negative shift from $+3.6\%$ to $+2.0\%$ on the steady-state value for the $\delta^{13}C$ of carbonate rocks between the Permian and Triassic and its associated response time.

Table S1. Parameter values used in calcium cycle box model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value and unit</th>
<th>Source (see SI References)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[Ca]_i$</td>
<td>10 mM</td>
<td>(1)</td>
</tr>
<tr>
<td>$F_{riv}$</td>
<td>$14 \times 10^{12}$ mol/yr</td>
<td>(14)</td>
</tr>
<tr>
<td>$F_{hyd}$</td>
<td>$4.0 \times 10^{12}$ mol/yr</td>
<td>(15)</td>
</tr>
<tr>
<td>$F_{pw}$</td>
<td>$6.3 \times 10^{12}$ mol/yr</td>
<td>(14)</td>
</tr>
<tr>
<td>$k_{carb}$</td>
<td>$24.3 \times 10^{12}$ mol/yr</td>
<td>Feedback on calcium concentrations via carbonate saturation state (5, 6)</td>
</tr>
<tr>
<td>$\delta_{iv}$</td>
<td>$-0.6%$</td>
<td>Assumes majority of calcium from carbonate weathering</td>
</tr>
<tr>
<td>$\delta_{hyd}$</td>
<td>$-0.25%$</td>
<td>(16)</td>
</tr>
<tr>
<td>$\delta_{pw}$</td>
<td>$-0.45%$</td>
<td>Approximation assuming pore fluids are only slightly heavier isotopically than carbonates</td>
</tr>
<tr>
<td>$\varepsilon_{carb}$</td>
<td>$1.4%$</td>
<td>(17) and references therein</td>
</tr>
</tbody>
</table>

Table S2. Amount of excess calcium weathering above background rate required to account for the calcium isotope excursion as a function of excursion time scale

<table>
<thead>
<tr>
<th>Excursion</th>
<th>Instantaneous approximation</th>
<th>10 ky</th>
<th>100 ky</th>
<th>500 ky</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.1%$</td>
<td>$0.93 \times 10^{18}$</td>
<td>$0.93 \times 10^{18}$</td>
<td>$1.03 \times 10^{18}$</td>
<td>$1.35 \times 10^{18}$</td>
</tr>
<tr>
<td>$0.2%$</td>
<td>$2.00 \times 10^{18}$</td>
<td>$2.00 \times 10^{18}$</td>
<td>$2.13 \times 10^{18}$</td>
<td>$3.00 \times 10^{18}$</td>
</tr>
<tr>
<td>$0.3%$</td>
<td>$3.25 \times 10^{18}$</td>
<td>$3.25 \times 10^{18}$</td>
<td>$3.53 \times 10^{18}$</td>
<td>$4.90 \times 10^{18}$</td>
</tr>
</tbody>
</table>

Table S3. Localities and thickness of microbialite and oolite deposits immediately overlying the end-Permian extinction horizon

<table>
<thead>
<tr>
<th>Locality</th>
<th>Region</th>
<th>Lithology</th>
<th>Thickness</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Takachiho, Kyushu Island, Japan</td>
<td>Panthalassa Ocean</td>
<td>Microbialite</td>
<td>5.5 m</td>
<td>(18)</td>
</tr>
<tr>
<td>Nanpanjiang Basin, China and northern Vietnam</td>
<td>Eastern Tethys</td>
<td>Microbialite</td>
<td>5–15 m</td>
<td>(19–24)</td>
</tr>
<tr>
<td>Sichuan Basin, China</td>
<td>Eastern Tethys</td>
<td>Microbialite</td>
<td>3 m</td>
<td>(25–28)</td>
</tr>
<tr>
<td>Hambast Mountains, Iran</td>
<td>Eastern Tethys</td>
<td>Microbialite, Crystal Fans</td>
<td>3 m</td>
<td>(29)</td>
</tr>
<tr>
<td>Arabian Platform, Saudi Arabia</td>
<td>Western Tethys</td>
<td>Microbialite</td>
<td>3 m</td>
<td>(30)</td>
</tr>
<tr>
<td>Antalya Nappes, Turkey</td>
<td>Western Tethys</td>
<td>Microbialite, Oolite</td>
<td>5–40 m</td>
<td>(31, 32)</td>
</tr>
<tr>
<td>Transcaucases, Armenia</td>
<td>Western Tethys</td>
<td>Microbialite</td>
<td>2 m</td>
<td>(33)</td>
</tr>
<tr>
<td>Bukk Mountains, Hungary</td>
<td>Western Tethys</td>
<td>Microbialite</td>
<td>8 m</td>
<td>(34)</td>
</tr>
<tr>
<td>Southern Alps, Italy</td>
<td>Western Tethys</td>
<td>Oolite</td>
<td>5–7 m</td>
<td>(35, 36)</td>
</tr>
</tbody>
</table>
Table S4. Calcium isotope compositions of analyzed samples illustrated in Fig. 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stratigraphic elevation (m)</th>
<th>$\delta^{44}$Ca</th>
<th>Standard deviation</th>
<th>$\delta^{13}$C (VPDB)</th>
<th>$\delta^{18}$O (VPDB)</th>
<th>Sr/Ca</th>
<th>Mn/Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDJ-001</td>
<td>0</td>
<td>−0.50</td>
<td>0.11</td>
<td>3.18</td>
<td>−3.77</td>
<td>0.001781</td>
<td>0.112452</td>
</tr>
<tr>
<td>PDJ-009</td>
<td>9</td>
<td>−0.56</td>
<td>0.16</td>
<td>3.53</td>
<td>−2.68</td>
<td>0.001345</td>
<td>0.118056</td>
</tr>
<tr>
<td>PDJ-017</td>
<td>17</td>
<td>−0.39</td>
<td>0.02</td>
<td>3.23</td>
<td>−4.78</td>
<td>0.001278</td>
<td>0.17529</td>
</tr>
<tr>
<td>PDJ-026</td>
<td>26</td>
<td>−0.26</td>
<td>0.08</td>
<td>3.02</td>
<td>−4.05</td>
<td>0.001085</td>
<td>0.186127</td>
</tr>
<tr>
<td>PDJ-030</td>
<td>30</td>
<td>−0.68</td>
<td>0.11</td>
<td>2.52</td>
<td>−5.15</td>
<td>0.001156</td>
<td>0.312711</td>
</tr>
<tr>
<td>PDJ-033</td>
<td>33</td>
<td>−0.52</td>
<td>0.09</td>
<td>2.88</td>
<td>−3.44</td>
<td>0.001262</td>
<td>0.333708</td>
</tr>
<tr>
<td>PDJ-040</td>
<td>39.7</td>
<td>−0.62</td>
<td>0.04</td>
<td>2.22</td>
<td>−5.31</td>
<td>0.002186</td>
<td>0.109726</td>
</tr>
<tr>
<td>PDJ-044</td>
<td>43</td>
<td>−0.74</td>
<td>0.11</td>
<td>0.95</td>
<td>−4.01</td>
<td>0.001261</td>
<td>0.614865</td>
</tr>
<tr>
<td>PDJ-046</td>
<td>44.5</td>
<td>−0.78</td>
<td>0.08</td>
<td>2.07</td>
<td>−2.70</td>
<td>0.001243</td>
<td>0.579677</td>
</tr>
<tr>
<td>PDJ-050</td>
<td>47</td>
<td>−0.84</td>
<td>0.10</td>
<td>0.37</td>
<td>−4.48</td>
<td>0.001383</td>
<td>0.425197</td>
</tr>
<tr>
<td>PDJ-053</td>
<td>50</td>
<td>−0.89</td>
<td>0.14</td>
<td>0.03</td>
<td>−4.22</td>
<td>0.001280</td>
<td>2.563522</td>
</tr>
<tr>
<td>PDJ-055</td>
<td>51.6</td>
<td>−0.84</td>
<td>0.09</td>
<td>−0.03</td>
<td>−6.00</td>
<td>0.001288</td>
<td>2.014563</td>
</tr>
<tr>
<td>PDJ-058</td>
<td>54</td>
<td>−0.71</td>
<td>0.04</td>
<td>0.54</td>
<td>−3.94</td>
<td>0.001546</td>
<td>0.725183</td>
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<tr>
<td>PDJ-061</td>
<td>56.4</td>
<td>−0.73</td>
<td>0.01</td>
<td>0.66</td>
<td>−4.04</td>
<td>0.001705</td>
<td>0.095718</td>
</tr>
<tr>
<td>PDJ-064</td>
<td>57.4</td>
<td>−0.52</td>
<td>0.02</td>
<td>1.43</td>
<td>−4.71</td>
<td>0.001956</td>
<td>0.196133</td>
</tr>
<tr>
<td>PDJ-068</td>
<td>60</td>
<td>−0.84</td>
<td>0.12</td>
<td>1.87</td>
<td>−5.32</td>
<td>0.002685</td>
<td>0.034841</td>
</tr>
<tr>
<td>PDJ-072</td>
<td>64</td>
<td>−0.72</td>
<td>0.13</td>
<td>1.70</td>
<td>−4.40</td>
<td>0.004116</td>
<td>0.068886</td>
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<tr>
<td>PDJ-075</td>
<td>66</td>
<td>−0.80</td>
<td>0.10</td>
<td>2.31</td>
<td>−4.47</td>
<td>0.001596</td>
<td>0.020517</td>
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<tr>
<td>PDJ-080</td>
<td>70.1</td>
<td>−0.74</td>
<td>0.18</td>
<td>2.19</td>
<td>−4.92</td>
<td>0.003823</td>
<td>0.075784</td>
</tr>
<tr>
<td>PDJ-081</td>
<td>71</td>
<td>−0.76</td>
<td>0.05</td>
<td>No data</td>
<td>No data</td>
<td>0.000860</td>
<td>0.251981</td>
</tr>
<tr>
<td>PDJ-090</td>
<td>80</td>
<td>−0.75</td>
<td>0.05</td>
<td>2.29</td>
<td>−4.40</td>
<td>0.000768</td>
<td>0.343173</td>
</tr>
<tr>
<td>PDJ-100</td>
<td>87.6</td>
<td>−0.85</td>
<td>0.13</td>
<td>2.43</td>
<td>−2.82</td>
<td>0.001781</td>
<td>0.112452</td>
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<tr>
<td>PDJ-115</td>
<td>100.4</td>
<td>−0.48</td>
<td>0.09</td>
<td>1.96</td>
<td>−6.08</td>
<td>0.001345</td>
<td>0.118056</td>
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<tr>
<td>PDJ-140</td>
<td>156.2</td>
<td>−0.36</td>
<td>0.02</td>
<td>1.71</td>
<td>−4.43</td>
<td>0.000700</td>
<td>0.355482</td>
</tr>
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</table>