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Persistent late Permian to Early Triassic warmth linked to enhanced reverse weathering

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In the Precambrian, reverse weathering—a process consuming oceanic silica, metal cations and alkalinity to form marine clays—was a key control of the long-term carbon cycle. However, the appearance of marine silicifiers decreased the importance of this process in regulating climate in the Phanerozoic eon. Here, we present seawater lithium and strontium isotope records derived from bulk carbonates and fossil brachiopods spanning the Permian to Early Triassic, an interval of pronounced climatic fluctuations and widespread extinctions. We show that the lithium isotope composition of seawater remained constant for most of the Permian until a sharp decrease in the late Permian (~254 Myr ago) with low seawater Li isotope values (~10‰) persisting throughout the Early Triassic. Based on box modelling, changes in chemical weathering and hydrothermal fluxes are unable to explain the abrupt decline in seawater Li isotopes. Rather, increased lithium output fluxes through enhanced reverse weathering are required to produce the low Li isotope values of the late Permian and Early Triassic (253-247 Myr ago). Increased reverse weathering rates could explain the failure of chemical weathering to draw down atmospheric CO₂ levels during the Early Triassic, leading to protracted biotic recovery from the Permian-Triassic mass extinction.

or most of the Phanerozoic eon, chemical weathering has maintained Earth's habitability by regulating atmospheric CO₂ levels and by controlling marine chemistry^{1,2}. However, earlier in Earth's history, reverse weathering probably played a key role in regulating climate and ocean chemistry³⁻⁶. Reverse weathering is classically expressed as a backward reaction of silicate weathering³, forming new clays through interactions of seawater and ocean crust, as well as transformation of pre-existing cation-poor clay minerals^{5,7}. Reverse weathering plays a negligible role in modern biogeochemical cycles because the biogenic silica pump (that is, silicifiers) remove most of the dissolved silica from the modern ocean, limiting the reverse weathering reactions^{8,9}. However, reverse weathering rates were much higher before the appearance of silicifiers^{4,8,10,11}. By consuming alkalinity and increasing seawater acidity, reverse weathering exerts a key control on marine pH and atmospheric CO₂ levels over geological times⁴.

The Permian to Early Triassic interval witnessed large changes in the marine silica cycle coupled with large climate fluctuations, with a transition from icehouse in the Early Permian to greenhouse in the Early Triassic^{12–14}. Chemical weathering rates varied during this interval, as evidenced by fluctuations in the seawater strontium isotope ratios (87 Sr/ 86 Sr_{sw})^{15,16}. However, these fluctuations cannot explain the persistently hot conditions of the Early Triassic^{17,18}. Additionally, the interpretation of chemical weathering changes during the Permian to Early Triassic interval suffers from the limitations of the strontium isotope weathering proxy. Many alternative scenarios could explain the 87 Sr/ 86 Sr_{sw} trends without invoking changes in chemical weathering, including an enhanced hydrothermal flux during the opening of the Neotethys Ocean¹⁵, changes in continental arc weathering¹⁹ or changes in low-temperature seafloor alteration²⁰. ⁸⁷Sr/⁸⁶Sr_{sw} is also insensitive to changes in reverse weathering, hampering the possibility to test if this process might have played a role in regulating climate²¹.

Seawater lithium isotope compositions ($\delta^7 \text{Li}_{sw}$) are controlled by both chemical weathering and reverse weathering, thus could complement the ${}^{87}\text{Sr}/{}^{86}\text{Sr}_{sw}$ record because these elements have similar residence time in the modern ocean, ~1 Myr for Li and ~2.5 Myr for Sr, respectively^{22,23}. The modern marine Li isotope budget has two main sources, the chemical weathering (riverine) flux and the high-temperature hydrothermal flux, each accounting for approximately 50% of the total Li flux with their combined $\delta^7\text{Li}$ averaging 15% $e^{22,24,25}$). The marine Li isotope budget is also controlled by low-temperature hydrothermal alteration and reverse weathering that remove Li from seawater and fractionate Li isotopes ($\Delta_{\text{Seawater}-\text{Sediment}} = +16\% e$), leading to modern seawater $\delta^7\text{Li}$ of 31% e^{25} .

Sample screening and evaluation of diagenetic alteration

Here we reconstructed a record of $\delta^7 \text{Li}_{sw}$ and ${}^{s_7}\text{Sr}/{}^{s_6}\text{Sr}_{sw}$ from marine carbonates spanning from the Permian boundary and Early Triassic (300–247 Myr ago (Ma)). The $\delta^7 \text{Li}_{sw}$ reconstructed from bulk carbonates is sensitive to carbonate mineralogy, detrital contamination and diagenesis^{26,27}. To limit these issues, we gathered a large collection of shallow marine carbonates from five stratigraphic sections with similar depositional environments (Fig. 1). We then used X-ray diffractometer (XRD) to determine semi-quantitative mineralogy and only selected samples with >75% calcite (Supplementary Fig. 1 and Supplementary Data Table 4). We polished and micro-drilled each sample carefully, avoiding secondary veins,

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Fig. 1 Palaeogeographic maps of study areas. a, Palaeomap reconfiguration⁷⁴ of the late Permian period indicating the position of Ninemile Canyon and South China. **b**, Map of Ninemile Canyon and Rockland Ridge in the Pequop Mountains, Nevada, USA³⁶. **c**, Enlarged map of South China (adapted from ref. ³⁴) showing the study sites including Shanggang section, Shangsi section and Tieqiao section (red stars). Panel **a** reproduced with permission from ref. ⁷⁴, PALEOMAP Project. Panels **b** and **c** adapted with permission from ref. ^{34,36}, Springer Nature Ltd.

recrystallization and cherty nodules (Supplementary Fig. 2). Using the drilled powder, we sequentially leached the samples to further minimize diagenetic carbonate phases and non-carbonate contamination²⁸ (Methods).

For each sample, we analysed elemental concentrations and 87Sr/86Sr. First, we only selected samples with typical elemental diagenetic indices well below accepted thresholds (Mn/Sr < 3 mol mol⁻¹, $Rb/Sr < 1 \text{ mol mol}^{-1}$ and $Mg/Ca < 0.5 \text{ mol mol}^{-1}$; Supplementary Fig. 3). We excluded samples exceeding these thresholds from Li isotope measurements. Second, 87Sr/86Sr record in bulk carbonates fit the well-preserved reference 87Sr/86Sr record in brachiopods and conodonts, supporting a minimal impact of diagenetic impact and contamination (Fig. 2). Six samples from the Shanggang section showed more radiogenic ⁸⁷Sr/⁸⁶Sr values (0.709224-0.710453) than those recorded in concomitant well-preserved conodonts²⁹. These samples may have been diagenetically altered but displayed similar 87Li values to the Early Triassic average. Third, we observed no correlations between δ^7 Li and elemental ratios such as Li/Ca, Al/Ca, Sr/Ca (indices for detrital contamination), Mg/Ca (index for dolomitization), Mn/Sr and Rb/Sr (indices for post-depositional diagenesis; Supplementary Fig. 3). Fourth, we analysed δ^7 Li in overlapping stratigraphic intervals and showed that absolute δ^7 Li values were consistent between sections. Using this screened dataset, we calculated the $\delta^7 Li_{sw}$ by subtracting 5.5% from the measured 87Li of bulk carbonates to correct for isotopic fractionation associated with mineralogical and vital effects^{26,27,30}. Modern bulk core-top sediments that only contain calcite display a constant $\Delta_{sw\text{-}carb}$ of 5.5±1.3% (excluding one outlier in ref. 30). We also analysed $\delta^7\text{Li}$ in six well-preserved brachiopod shells (Supplementary Information) because brachiopods were suggested as the most reliable substrate to obtain $\delta^7\text{Li}_{sw}$ and modern brachiopods show a consistent $\Delta_{sw\text{-}brachiopod}$ of 4.2–4.4% $e^{27,31,32}$. We used the average offset of 4.3% from the measured brachiopod $\delta^7\text{Li}$ values to calculate $\delta^7\text{Li}_{sw}$ from brachiopods. We found that the six $\delta^7\text{Li}_{sw}$ values derived from brachiopods are consistent in both absolute values and trends with those derived from bulk carbonates. This observation combined with petrographic and geochemical screening data supports the robustness of our reconstructed $\delta^7\text{Li}_{sw}$ record with minimal influence from diagenetic alteration, contamination or mixing of isotopically distinct fossil assemblages in the bulk carbonate record.

Lithium isotope records

The reconstructed $\delta^7 \text{Li}_{sw}$ values range from 3.1 to 21.8% during the Permian with most values around 20%, similar to other Palaeozoic records³³ but lower than the modern ocean (31%). Between 300 and ~290 Ma, $\delta^7 \text{Li}_{sw}$ progressively decreases from 21.8 to 13.7%, followed by a negative excursion between 290 and 265 Ma. The $\delta^7 \text{Li}_{sw}$ recovers to Early Permian levels in the Capitanian (up to 19.4%) and remains constant for about 10 Myr, dropping abruptly and reaching a minimum in the Changhsingian (~5%). After the Permian–Triassic boundary (PTB), $\delta^7 \text{Li}_{sw}$ records a minor increase in the Early Triassic but $\delta^7 \text{Li}_{sw}$ values remain low, ranging from 4.7 to 13% (*n*=12, mean ± 1 σ :10±2.2%).



Fig. 2 | Strontium and lithium isotope compositions in seawater reconstructed in this study and compiled from the literature with chronology of tectonic, climatic and biological events occurring during the Permian and Early Triassic. **a**, $\delta^7 Li_{sw}$ reconstructed from bulk carbonate samples and brachiopod samples in this study. $\delta^7 Li_{sw}$ is obtained by subtracting 5.5% for bulk carbonate samples and 4.3% for brachiopod samples^{27,30,31,32}. The shaded area represents the 95% confidence interval of locally weighted polynomial smoothing function smoothing. Vertical error bars represent long-term precision (2 σ) of 1.1% for $\delta^7 Li$ measurements and calculated 2 σ for repeatedly measured $\delta^7 Li$ values. **b**, Measured and compiled ⁸⁷Sr/⁸⁶Sr ratios through time (Supplementary Data Tables 1 and 2)^{15,6,29,62,75}. **c**, Major events during the Permian and the Early Triassic (details about the age model and duration of the tectonic, climatic, biological and stratigraphic events are provided in the Supplementary Information with references). Skull and crossbone silhouette in panel c extracted from www.flaticon.com.

The prominent decline in $\delta^7 \text{Li}_{sw}$ is mainly recorded in the Tieqiao, Shangsi and Shanggang sections (Extended Data Fig. 1). In the Tieqiao section, $\delta^7 \text{Li}_{sw}$ values decrease from 18.2 to 9.7% in the late Wuchiapingian (259.8–254.14 Ma). However, the age model of Tieqiao has a high uncertainty (± 2 Myr) because it is based on limited conodont and foraminifera biostratigraphy with refs. ^{34,35}. At the Shangsi, a section with a robust age model based on high-resolution biostratigraphy anchored on U–Pb ages and cyclostratigraphy³⁶, two samples at 259.19 and 259.03 Ma (Wuchiapingian) display $\delta^7 \text{Li}_{sw} > 15\%$. By contrast, two samples

collected at 253.35 and 252.32 Ma (Changhsingian) have $\delta^7 Li_{sw}$ values <5%. At Shanggang, we exclusively analyse samples in the Changhsingian starting at 252.43 Ma, all showing persistently low $\delta^7 Li_{sw}$ values. Similar trends in the three sections suggest that the $\delta^7 Li_{sw}$ decline initiates in the late Wuchiapingian or early Changhsingian and reaches a minimum in the Changhsingian. The $\delta^7 Li_{sw}$ decline occurs about 2 Myr before the main eruption interval (sill emplacement) of the Siberian Traps, which starts 300 kyr before the PTB and continues for more than 500 kyr after the PTB^{37,38}.

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Fig. 3 | Conceptual reconstruction of the marine Li isotope budget during five critical time periods when large δ^7 Li fluctuations occurred. The representative Li box models are shown and the size of the arrow is proportional to the flux. Detailed model construction and discussion are presented in the Supplementary Information. **a**, Earliest Permian (δ^7 Li_{sw} $\approx 20\%_0$), **b**, late Kungurian (δ^7 Li_{sw} $\approx 10\%_0$), **c**, Capitanian (δ^7 Li_{sw} $\approx 20\%_0$), **d**, Changhsingian (δ^7 Li_{sw} $\approx 5\%_0$), **e**, Early Triassic (δ^7 Li_{sw} $\approx 10\%_0$) and **f**, Present. The trees, grass and mountains are extracted from www.flaticon.com.

Steady-state Li box models

Despite our thorough screening for mineralogy and diagenesis, we prefer to take a conservative approach and focus on interpreting large $\delta^7 \text{Li}_{sw}$ variations (>5 % $_{o}$). Consequently, we build a series of steady-state Li isotope box models for a few critical $\delta^7 \text{Li}_{sw}$ periods: earliest Permian ($\delta^7 \text{Li}_{sw} \approx 20\%_o$), Kungurian ($\delta^7 \text{Li}_{sw} \approx 10\%_o$), Capitanian ($\delta^7 \text{Li}_{sw} \approx 20\%_o$), Changhsingian ($\delta^7 \text{Li}_{sw} \approx 5\%_o$) and Early Triassic ($\delta^7 \text{Li}_{sw} \approx 10\%_o$; Fig. 3). For each of these periods, we solve the Li isotope mass balance by varying fluxes in 0.5 × 10⁹ mol yr⁻¹ increments and varying isotope compositions in 0.5% $_o$ increments within a predetermined set of ranges (Table 1, Methods and Supplementary Information). Next, we discuss plausible scenarios that explain our $\delta^7 \text{Li}_{sw}$ record in combination with ${}^{87}\text{Sr}/{}^{86}\text{Sr}_{sw}$ data (Fig. 2b) and other geologic records (Fig. 2c).

Chemical weathering and hydrothermal flux variations

The Permian constitutes the terminal phase of the supercontinent Pangea assembly, with most active orogens ending during the Early to Middle Permian^{39,40}. During the Early Permian, a relatively high Li flux from chemical weathering (F_{riv}) coupled with high $\delta^7 \text{Li}_{riv}$ could explain the high $\delta^7 \text{Li}_{sw}$ values of this interval (Supplementary Fig. 5), as expected in a world with high topography and rapid glacial erosion^{41,42}. As orogens subside and aridity persists throughout the Permian, limited erosion and sediment transport would have facilitated the formation of a thick regolith globally⁴³⁻⁴⁵. This increased regolith thickness leads to a progressive decrease in the continental weathering flux evidenced by decreasing ⁸⁷Sr/⁸⁶Sr_{sw} and increasing greenhouse conditions^{16,46,47}.

The low $\delta^7 \text{Li}_{sw}$ values of the Changhsingian (~5%) require extremely low δ⁷Li_{riv} values (Supplementary Fig. 9), reflecting either: (1) a weathering-limited regime (high erosion rate and short water residence time in regoliths) with congruent weathering of primary minerals and limited secondary mineral formation; or (2) a supply-limited weathering regime (low erosion rate and long water residence time in regoliths) with dissolution of secondary minerals from highly weathered soils⁴³⁻⁴⁵. During the Changhsingian, most mountain belts have been eroded and Pangea is characterized by a flat topography and arid continental interior. Additionally, climate warms further as evidenced by conodont oxygen isotopes⁴⁸. These conditions would have favoured very low 87Liriv values by preferential release of 6Li accumulated in secondary minerals, similar to what is observed today in the Amazon basin floodplains^{43,49}. The decline in $\delta^7 Li_{riv}$ values during the Changhsingian coincides with slightly increasing ⁸⁷Sr/⁸⁶Sr_{sw} potentially associated with an increase in continental weathering¹⁶. However, increasing continental weathering alone cannot explain the sudden and steep $\delta^7 Li_{sw}$ decline in the late Permian (Supplementary Figs. 9-11).

Our box model results also indicate that the chemical weathering rate would have had to increase after the PTB to explain the 5% $\delta^7 \text{Li}_{sw}$ increase in the Early Triassic (Supplementary Fig. 12). Approximately 8,800 × 10¹⁵ mol CO₂ was released during the sill emplacement interval of Siberian volcanism⁵⁰, creating hot greenhouse conditions⁵¹ and triggering a rapid increase in chemical weathering rates during the Early Triassic^{29,52}. Such an increase in the continental weathering rate is evidenced by the steep increase in ⁸⁷Sr/⁸⁶Sr_{sw}^{16,29,52}. Despite increasing weathering rates, $\delta^7 \text{Li}_{sw}$ values

Table 1 | Description of parameters in the Li box model

Symbol	Description	Value
$\delta^7 Li_{sw}$	Li isotope composition of seawater	31‰ (ref. ²⁵)
F _{riv}	Li flux of continental weathering	10 × 10 ⁹ mol yr ⁻¹ (ref. ²⁵)
$\delta^7 Li_{riv}$	Li isotope of continental runoff	23‰ (ref. ^{25,71})
F _{MOR}	Hydrothermal Li flux	13 × 10 ⁹ mol yr ⁻¹ (ref. ²⁵)
$\delta^7 Li_{MOR}$	Li isotope ratio of hydrothermal flux	8.3‰ (refs. ^{25,72})
F _{alt}	Li flux associated with alteration of oceanic crust	$12 \times 10^9 \mathrm{mol} \mathrm{yr}^{-1}$ (ref. ²⁴)
Δ_{alt}	Isotopic fractionation associated with alteration of oceanic crust	13‰ (refs. ^{24,73})
F _{sed}	Li flux associated with secondary mineral formation during reverse weathering	11 × 10 ⁹ mol yr ⁻¹ (ref. ²⁴)
Δ_{sed}	Isotopic fractionation associated with removal of Li into secondary mineral during reverse weathering	20‰ (ref. ²⁴)

only increase to 10% in the Early Triassic and remain low relative to the Early Permian and other periods of Earth's history³³. Therefore, chemical weathering alone is not sufficient to explain the very low $\delta^7 \text{Li}_{sw}$ values of the Early Triassic.

Some of the observed variations in $\delta^7 \text{Li}_{sw}$ during the studied interval could be influenced by changes in hydrothermal activity. To explain the ${}^{87}\text{Sr}/{}^{86}\text{Sr}_{sw}$ decrease in the Guadalupian, it has been proposed that hydrothermal Sr flux may have doubled due to the opening the Neotethys Ocean¹⁵. We observe a negative $\delta^7 \text{Li}_{sw}$ excursion between 290 and 265 Ma coinciding with the Neotethys opening and the ${}^{87}\text{Sr}/{}^{86}\text{Sr}_{sw}$ decrease (Fig. 2). An increased hydrothermal flux during this interval could explain the observed $\delta^7 \text{Li}_{sw}$ excursion (Supplementary Fig. 8). Conversely, the $\delta^7 \text{Li}_{sw}$ drawdown in the Changhsingian is accompanied by a slight increase in ${}^{87}\text{Sr}/{}^{86}\text{Sr}_{sw}$ and, therefore, cannot be attributed to an increase in hydrothermal activity. We conclude that neither changes in chemical weathering rate nor changes in hydrothermal activity can fully explain the observed $\delta^7 \text{Li}_{sw}$ variations during the Permian to Early Triassic.

Changes in reverse weathering

Most of the Permian period falls within the Permian Chert Event (290–260 Ma), characterized by widespread and intense chert deposition^{12,13}. During this interval, the active biogenic silica pump probably forces low dissolved silica concentration limiting reverse weathering rates^{7,9}. These conditions are similar to those of the modern ocean and could explain the high $\delta^7 Li_{sw}$ values of the Permian^{4,33}. However, as suggested in previous studies³³, the baseline $\delta^7 Li_{sw}$ in the Permian (~20%o) is consistently ~10%o lower than those of the modern ocean (~30%o). Radiolarians, the dominant silicifiers in the Permian Ocean, are less efficient in uptaking silica than diatoms⁵³. Thus, we argue that the 10%o offset between the Permian and the modern ocean $\delta^7 Li_{sw}$ reflects higher reverse weathering rates in the Permian associated with less-efficient silicifiers and higher dissolved silica concentrations^{7,8,53}.

Our box model results indicate that the very low $\delta^7 Li_{sw}$ values in the Changhsingian and Early Triassic require increasing reverse weathering combined with minimal Li isotopic fractionation between seawater and authigenic clays ($\Delta_{Seawater - Sediment}$; Supplementary Fig. 9). High reverse weathering rates would only be possible with high dissolved silica concentrations in the ocean associated with decreased silica uptake by silicifiers. Stratigraphic sections globally support

this idea displaying a progressive decrease in chert deposition in the Wuchiapingian until a complete cessation of chert deposition at the PTB^{12,54-57} (Supplementary Information). The causes for the progressive decline in chert deposition are unclear, but ocean transgression, warming, changes in thermohaline circulation and deep ocean anoxia might have all contributed to a progressive decline of the silica biogenic pump before the Permian–Triassic mass extinction^{12,47,48,58}. We argue that the demise of the Permian Chert Event coincides with the massive $\delta^7 Li_{sw}$ decrease in the Changhsingian (Fig. 2 and Extended Data Fig. 1).

The absence of chert deposition (that is, the chert gap) occurs globally through the Early Triassic^{12,55}. The timing of this chert gap coincides well with the persistently low $\delta^7 Li_{sw}$ values from the late Permian to the Early Triassic (Fig. 1). Thus, we speculate that during the chert gap, dissolved silica in the ocean was high, facilitating an enhanced reverse weathering rate. High rates of reverse weathering would have consumed alkalinity, maintaining high partial pressure of CO_2 (*p*CO₂) and creating oceanic conditions similar to those of the Precambrian oceans when silicifiers had not yet evolved^{11,33}. The purported increase in reverse weathering rates coincides with the persistently high pCO_2 in the Early Triassic, with low pCO_2 only returning in the Anisian when chert deposition resumes with the recovery of radiolarians^{17,18,59,60}. While this high pCO_2 could be due to extremely high degassing rates⁶⁰, the timing of Siberian volcanism and other volcanic indicators do not support this hypothesis^{37,61}. Additionally, there is some evidences for increased continental silicate weathering during the Early Triassic, which should have reduced $pCO_2^{52,62}$. The failure of the chemical weathering feedback to regulate pCO₂ for several million years is particularly puzzling considering the abundance of highly weatherable volcanic rocks from Siberian volcanism63. Low continental fragmentation, limited uplift and high continentality in Pangea's interiors might have limited CO₂ uptake by silicate weathering⁶³. However, this interpretation is not supported by our box model simulations (Supplementary Fig. 12) or by strontium and osmium isotopes records, which suggest higher chemical weathering rates^{29,64}. Lastly, it cannot explain the increase in clay-rich sediment accumulation throughout the chert gap^{54,65}. Several sections globally display a transition from chert to claystone deposition in the Changhsingian coinciding with the initiation of the $\delta^7 \text{Li}_{sw}$ decline^{10,12,54}. Additionally, the global bulk accumulation rate of clay-rich sediments in continental margin and platform settings increased by up to seven times in the Early Triassic relative to the Permian⁶⁵. This increase in clay-rich sediment accumulation has been invoked to support enhanced chemical weathering and erosion from the continents, but it fails to explain the concomitant high pCO_2 . High reverse weathering rates in the Early Triassic, however, can reconciliate those seemingly contradictory observations.

Box model results also suggest that the Li isotope fractionation associated with reverse weathering must be negligible to explain the low $\delta^7 \text{Li}_{\text{sw}}$. The $\Delta_{\text{Seawater - Sediment}}$ value can vary with Li concentrations, pH, temperature and clay mineralogy in the ocean^{24,66}. We hypothesize that during the late Permian and Early Triassic, when the rate of reverse weathering was high, cations with high affinity for clay minerals, such as Li, would be rapidly taken up from seawater to form authigenic clays and lower their seawater concentrations. As Li is taken by clay minerals, the seawater Li isotope composition becomes heavier. However, the near complete removal of Li from seawater through high rates of reverse weathering could have led to very limited isotopic difference between seawater and clay minerals³³. Other possible mechanisms could have further decreased $\Delta_{\text{Seawater - Sediment}}$ in the late Permian and Early Triassic, including: (1) reduced isotope fractionation associated with increased bottom temperature in greenhouse conditions^{66,67}; and (2) limited isotope fractionation during the formation of some types of marine clay (for example, the synthetic saponite and steven site has $\Delta_{\text{Seawater - Sediment}}$ as low as 4.4% o^{68} , the interlayer complexation in smectite barely causes any Li isotope fractionation⁶⁹).

anced rates 21. Bataille, C. P., Willis, A., Yang, X. & Liu, X. Continental igneous rock composition: a major control of past global chemical weathering. *Sci. Adv.* 3, e1602183 (2017).

- Penniston-Dorland, S., Liu, X.-M. & Rudnick, R. L. Lithium isotope geochemistry. *Rev. Mineral. Geochem.* 82, 165–217 (2017).
- Vollstaedt, H. et al. The Phanerozoic δ⁸⁸/⁸⁶Sr record of seawater: new constraints on past changes in oceanic carbonate fluxes. *Geochim. Cosmochim. Acta* 128, 249–265 (2014).
- Li, G. & West, A. J. Evolution of Cenozoic seawater lithium isotopes: coupling of global denudation regime and shifting seawater sinks. *Earth Planet. Sci. Lett.* **401**, 284–293 (2014).
- Misra, S. & Froelich, P. N. Lithium isotope history of Cenozoic seawater: changes in silicate weathering and reverse weathering. *Science* 335, 818–823 (2012).
- Dellinger, M. et al. The effects of diagenesis on lithium isotope ratios of shallow marine carbonates. *Am. J. Sci.* 320, 150–184 (2020).
- Dellinger, M. et al. The Li isotope composition of marine biogenic carbonates: patterns and Mechanisms. *Geochim. Cosmochim. Acta* 236, 315–335 (2018).
- Cao, C., Liu, X.-M., Bataille, C. P. & Liu, C. What do Ce anomalies in marine carbonates really mean? A perspective from leaching experiments. *Chem. Geol.* 532, 119413 (2020).
- Song, H. et al. Integrated Sr isotope variations and global environmental changes through the Late Permian to early Late Triassic. *Earth Planet. Sci. Lett.* 424, 140–147 (2015).
- Pogge von Strandmann, P. A. E. et al. Assessing bulk carbonates as archives for seawater Li isotope ratios. *Chem. Geol.* 530, 119338 (2019).
- 31. Washington, K. E. et al. Lithium isotope composition of modern and fossil Cenozoic brachiopods. *Geology* **48**, 1058–1601 (2020).
- 32. Gaspers, N. et al. Lithium elemental and isotope systematics of modern and cultured brachiopods: implications for seawater evolution. *Chem. Geol.* **586**, 120566 (2021).
- Kalderon-Asael, B. et al. A lithium-isotope perspective on the evolution of carbon and silicon cycles. *Nature* 595, 394–398 (2021).
- Tierney, K. E. & Saltzman, M. R. Carbon and Strontium Isotope Stratigraphy of the Permian from Nevada and China: Implications from an Icehouse to Greenhouse Transition. PhD thesis, Ohio State Univ. (2010).
- Sun, Y. D. et al. Permian (Artinskian to Wuchapingian) conodont biostratigraphy in the Tieqiao section, Laibin area, South China. Palaeogeogr. Palaeoclimatol. Palaeoecol. 465, 42–63 (2017).
- Wu, H. et al. Time-calibrated Milankovitch cycles for the Late Permian. Nat. Commun. 4, 2452 (2013).
- Burgess, S. D. & Bowring, S. A. High-precision geochronology confirms voluminous magmatism before, during, and after Earth's most severe extinction. *Sci. Adv.* 1, e1500470 (2015).
- Burgess, S. D., Muirhead, J. D. & Bowring, S. A. Initial pulse of Siberian Traps sills as the trigger of the end-Permian mass extinction. *Nat. Commun.* 8, 164 (2017).
- Miall, A. D.(ed.) The Sedimentary Basins of the United States and Canada 1–29 (Sedimentary Basins of the World Vol. 5, Elsevier, 2008).
- Blakey, R. C. in *Resolving the Late Paleozoic Ice Age in Time and Space* (eds Fielding, C. R. et al.) 1–28 (Geological Society of America, 2008).
- Goddéris, Y. et al. Onset and ending of the late Palaeozoic ice age triggered by tectonically paced rock weathering. *Nat. Geosci.* 10, 382–386 (2017).
- West, A. J. Thickness of the chemical weathering zone and implications for erosional and climatic drivers of weathering and for carbon-cycle feedbacks. *Geology* 40, 811–814 (2012).
- Foelich, F. & Misra, S. Was the late Paleocene-early Eocene hot because Earth was flat? An ocean lithium view of mountain building, continental weathering, carbon dioxide and Earth's Cenozoic climate. *Oceanography* 27, 36–49 (2014).
- Gabet, E. J. & Mudd, S. M. A theoretical model coupling chemical weathering rates with denudation rates. *Geology* 37, 151–154 (2009).
- Goddéris, Y., Donnadieu, Y., le Hir, G., Lefebvre, V. & Nardin, E. The role of palaeogeography in the Phanerozoic history of atmospheric CO₂ and climate. *Earth Sci. Rev.* 128, 122–138 (2014).
- Berner, R. A. The carbon and sulfur cycles and atmospheric oxygen from Middle Permian to Middle Triassic. *Geochim. Cosmochim. Acta* 69, 3211–3217 (2005).
- Chen, B. et al. Permian ice volume and palaeoclimate history: oxygen isotope proxies revisited. *Gondwana Res.* 24, 77–89 (2013).
- Wang, W. et al. A high-resolution Middle to Late Permian paleotemperature curve reconstructed using oxygen isotopes of well-preserved brachiopod shells. *Earth Planet. Sci. Lett.* 540, 116245 (2020).
- Dellinger, M. et al. Riverine Li isotope fractionation in the Amazon River basin controlled by the weathering regimes. *Geochim. Cosmochim. Acta* 164, 71–93 (2015).
- Jurikova, H. et al. Permian–Triassic mass extinction pulses driven by major marine carbon cycle perturbations. *Nat. Geosci.* 13, 745–750 (2020).

Our $\delta^7 \text{Li}_{sw}$ record provides strong evidence for enhanced rates of reverse weathering in the late Permian and Early Triassic. The persistence of high reverse weathering rates could explain the long-term greenhouse conditions occurring throughout the Early Triassic and the failure of terrestrial weathering rates to rebalance the carbon cycle⁶³. The greenhouse conditions would have reduced the thermohaline circulation and oxygen solubility, facilitating the recurrence of anoxia throughout the Early Triassic⁷⁰ and complicating the biotic recovery during this period⁵⁹.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/ s41561-022-01009-x.

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References

- Berner, R. A., Lasaga, A. C. & Garrels, R. M. The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci.* 283, 641–683 (1983).
- Walker, J. C. G., Hays, P. B. & Kasting, J. F. A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. *J. Geophys. Res.* 86, 9776–9782 (1981).
- Urey, H. C. On the early chemical history of the Earth and the origin of life. Proc. Natl Acad. Sci. USA 38, 351–363 (1952).
- Isson, T. T. & Planavsky, N. J. Reverse weathering as a long-term stabilizer of marine pH and planetary climate. *Nature* 560, 471–475 (2018).
- Mackenzie, F. T., Kump, L. R., Kovacs, J. A., Shoner, S. C. & Ellison, J. J. Reverse weathering, clay mineral formation, and oceanic element cycles metal-carbon bonds in nature. *Science* 270, 586 (1995).
- Aller, R. C. in *Treatise on Geochemistry* 2nd edn, Vol. 8 (ed. Turekian, H.D.H.K.) 293–334 (Elsevier, 2014).
- Michalopoulos, P. & Aller, R. C. Early diagenesis of biogenic silica in the Amazon delta: alteration, authigenic clay formation, and storage. *Geochim. Cosmochim. Acta* 68, 1061–1085 (2004).
- Tréguer, P. J. & de La Rocha, C. L. The world ocean silica cycle. Annu. Rev. Mar. Sci. 5, 477–501 (2013).
- Michalopoulos, P. & Aller, R. C. Rapid clay mineral formation in Amazon delta sediments: reverse weathering and oceanic elemental cycles. *Science* 270, 614–617 (1995).
- Maliva, R. G., Knoll, A. H. & Siever, R. Secular change in chert distribution: a reflection of evolving biological participation in the silica cycle. *Palaios* 4, 519 (1989).
- Siever, R. The silica cycle in the Precambrian. *Geochim. Cosmochim. Acta* 56, 3265–3272 (1992).
- Beauchamp, B. & Baud, A. Growth and demise of Permian biogenic chert along northwest Pangea: evidence for end-Permian collapse of thermohaline circulation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 184, 37–63 (2002).
- Beauchamp, B. & Grasby, S. E. Permian lysocline shoaling and ocean acidification along NW Pangea led to carbonate eradication and chert expansion. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 350–352, 73–90 (2012).
- 14. Frakes, L. A., Francis, J. E. & Syktus, J. I. *Climate Modes of the Phanerozoic* (Cambridge Univ. Press, 1992).
- Wang, W. et al. Revisiting the Permian seawater ⁸⁷Sr/⁸⁶Sr record: new perspectives from brachiopod proxy data and stochastic oceanic box models. *Earth Sci. Rev.* 218, 103679 (2021).
- Korte, C., Kozur, H. W., Bruckschen, P. & Veizer, J. Strontium isotope evolution of Late Permian and Triassic seawater. *Geochim. Cosmochim. Acta* 67, 47–62 (2003).
- Joachimski, M. M. et al. Five million years of high atmospheric CO₂ in the aftermath of the Permian–Triassic mass extinction. *Geology* 50, 650–654 (2022).
- 18. Sun, Y. et al. Lethally hot temperatures during the Early Triassic greenhouse. *Science* **338**, 366–370 (2012).
- Gernon, T. M. et al. Global chemical weathering dominated by continental arcs since the mid-Palaeozoic. *Nat. Geosci.* 14, 690–696 (2021).
- Coogan, L. A. & Dosso, S. E. Alteration of ocean crust provides a strong temperature dependent feedback on the geological carbon cycle and is a primary driver of the Sr-isotopic composition of seawater. *Earth Planet. Sci. Lett.* 415, 38–46 (2015).

ARTICLES

ARTICLES

NATURE GEOSCIENCE

- Payne, J. L. et al. in Large Perturbations of the Carbon Cycle During Recovery from the End-Permian Extinction. *Science* 305, 506–509 (2004).
- Sedlacek, A. R. C. et al. ⁸⁷Sr/⁸⁶Sr stratigraphy from the Early Triassic of Zal, Iran: linking temperature to weathering rates and the tempo of ecosystem recovery. *Geology* 42, 779–782 (2014).
- Conley, D. J. et al. Biosilicification drives a decline of dissolved Si in the oceans through geologic time. *Front. Mar. Sci.* 4, 397 (2017).
- 54. Isozaki, Y. Permo-Triassic boundary superanoxia and stratified superocean: records from lost deep sea. *Science* **276**, 235-238 (1997).
- Sperling, E. A. & Ingle, J. C. A Permian–Triassic boundary section at Quinn River crossing, northwestern Nevada, and implications for the cause of the Early Triassic chert gap on the western Pangean margin. *Bull. Geol. Soc. Am.* 118, 733–746 (2006).
- Grasby, S. E., Beauchamp, B., Embry, A. & Sanei, H. Recurrent Early Triassic ocean anoxia. *Geology* 41, 175–178 (2013).
- Grasby, S. E. & Beauchamp, B. Latest Permian to Early Triassic basin-to-shelf anoxia in the Sverdrup Basin, Arctic Canada. *Chem. Geol.* 264, 232-246 (2009).
- Haq, B. U. & Schutter, S. R. A chronology of Paleozoic sea-level changes. Science 322, 64–68 (2008).
- Chen, Z. Q. & Benton, M. J. The timing and pattern of biotic recovery following the end-Permian mass extinction. *Nat. Geosci.* 5, 375–383 (2012).
- 60. Payne, J. & Kump, L. Evidence for recurrent Early Triassic massive volcanism from quantitative interpretation of carbon isotope fluctuations. *Earth Planet. Sci. Lett.* **256**, 264–277 (2007).
- 61. Wang, X. et al. Mercury anomalies across the end Permian mass extinction in South China from shallow and deep water depositional environments. *Earth Planet. Sci. Lett.* **496**, 159–167 (2018).
- Korte, C., Jasper, T., Kozur, H. W. & Veizer, J. ⁸⁷Sr/⁸⁶Sr record of Permian seawater. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 240, 89–107 (2006).
- 63. Kump, L. R. Prolonged Late Permian–Early Triassic hyperthermal: failure of climate regulation? *Phil. Trans. R. Soc. A* **376**, 20170078 (2018).
- Liu, Z., Selby, D., Zhang, H. & Shen, S. Evidence for volcanism and weathering during the Permian–Triassic mass extinction from Meishan (South China) osmium isotope record. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 553, 109790 (2020).
- Algeo, T. J. & Twitchett, R. J. Anomalous Early Triassic sediment fluxes due to elevated weathering rates and their biological consequences. *Geology* 38, 1023–1026 (2010).

- Coogan, L. A., Gillis, K. M., Pope, M. & Spence, J. The role of low-temperature (off-axis) alteration of the oceanic crust in the global Li-cycle: insights from the Troodos ophiolite. *Geochim. Cosmochim. Acta* 203, 201–215 (2017).
- 67. Pogge von Strandmann, P. A. E. et al. Lithium isotope evidence for enhanced weathering and erosion during the Paleocene–Eocene Thermal Maximum. *Sci. Adv.* 7, eabh4224 (2021).
- Hindshaw, R. S. et al. Experimental constraints on Li isotope fractionation during clay formation. *Geochim. Cosmochim. Acta* 250, 219–237 (2019).
- Pistiner, J. S. et al. Lithium-isotope fractionation during continental weathering processes. *Earth Planet. Sci. Lett.* 214, 327–339 (2003).
- 70. Zhang, F. et al. Multiple episodes of extensive marine anoxia linked to global warming and continental weathering following the latest Permian mass extinction. *Sci. Adv.* **4**, e1602921 (2018).
- Huh, Y., Chan, L. H., Zhang, L. & Edmond, J. M. Lithium and its isotopes in major world rivers: implications for weathering and the oceanic budget. *Geochim. Cosmochim. Acta* 62, 2039–2051 (1998).
- Chan, L. H., Gieskes, J. M., Chen-Feng, Y. & Edmond, J. M. Lithium isotope geochemistry of sediments and hydrothermal fluids of the Guaymas Basin, Gulf of California. *Geochim. Cosmochim. Acta* 58, 4443–4454 (1994).
- Chan, L. H., Alt, J. C. & Teagle, D. A. H. Lithium and lithium isotope profiles through the upper oceanic crust: a study of seawater-basalt exchange at ODP Sites 504B and 896A. *Earth Planet. Sci. Lett.* 201, 187–201 (2002).
- 74. Scotese, C. R. Atlas of Earth History: Volume 1, Paleogeography (PALEOMAP Project, 2001).
- Needham, L., Schmitz, M. D. & Davydov, V. I. A precise and accurate seawater Sr curve from Late Carboniferous–Early Permian conodonts. In *GSA Abstracts with Programs* Vol. 38, 184 (Geological Society of America, 2006).

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Methods

Sample sites and geologic setting. A collection of 101 bulk marine carbonate rocks from the United States and China were selected for this study (Ninemile Canyon: $n = 14^{34}$; Rockland Ridge: $n = 18^{34}$; Tieqiao: $n = 24^{35}$; Shangsi: $n = 12^{36}$; Shanggang: $n = 33^{36}$). The Ninemile and Rockland Ridge sections are currently located in northeastern Nevada (United States) and were deposited on the western margin of Laurentia in a shallow shelf setting. The Shangsi, Tieqiao and Shanggang sections are located in South China, and were deposited in a slope setting (Fig. 1). All selected sections have well-constrained biostratigraphic age models^{77–84} (Extended Fig. 1). These sections are among the thickest and most continuous marine carbonate successions in the world encompassing Permian to Early Triassic periods.

Samples from Ninemile Canyon and Rockland Ridge were collected in the Pequop Mountains, Nevada, as part of K.T.C.'s PhD thesis¹⁴. These sediments were deposited on the western margin of Laurentia in a shallow shelf of a shallow epeiric sea that had open communication with the ocean¹⁵. Samples were collected in measured and correlated sections in conjunction with conodont samples starting in the Gzhelian (latest Pennsylvanian) through the lowest Kungurian Stage (Permian) with high-resolution conodont biostratigraphy, continuous faunal successions and little evidence for major sedimentation hiatuses⁶⁶. Sampling continued upward through the lower Artinskian before switching over to Rockland Ridge approximately 20 km north starting in the upper Sakmarian through the lower-most Kungurian³⁴. This interval of time is represented by two main formations, the Riepe Spring Limestone and the Rib Hill Formation^{78,87,88}. Both of these formations are dominated by a wide range of fine- and coarser-grained limestone lithologies interrupted by occasional chert-rich intervals and conglomeratic channelization (Extended Data Fig. 1).

Samples from the uppermost Artinskian through the lower-most Changhsingian were collected from the Tieqiao section in Guangxi province, 5 km southeast of Laibin city (China) as part of K.T.C.'s PhD thesis¹⁴. The Tieqiao section was located on the eastern palaeomargin of the Yangtze Platform, in the Jiangnan basin³⁵, between the Cathaysian and Yangtze cratons⁸⁶. This section had open communication with the ocean and because it was continuously subsiding, a thick sediment wedge accumulated⁸⁶. The section contains a continuous and conformable sequence of carbonate-dominated marine sediments deposited on the slope of an isolated carbonate platform⁸⁹. The section records continuous deposition from the Guadalupian to the Lopingian^{88,90}, in which a complete succession of pelagic conodont zones was preserved across the Guadalupian-Lopingian boundary^{35,79,81,86,90}. The section naity in the composite section and can also be tied to global biostratigraphic zones³⁵. Detailed stratigraphic sections and biostratigraphy are provided in Extended Data Fig. 1.

The Shangsi section is also located in South China near Guangyuan city, Sichuan province, and was deposited on the lower slope of the ramp on the western palaeomargin of the Yangtze Platform⁷⁹. This section consists of the Wujiaping, Dalong and Feixianguan formations, and displays continuous carbonate-dominated marine sediment from the Wuchiapingian (Upper Permian) to Lower Triassic^{91,92}. The Wujiaping Formation is composed of thick-bedded limestone with chert nodules. The Dalong Formation contains mainly medium-bedded siliceous limestone, along with thin beds of organic-rich limestone and shale. The Feixianguan Formation straddles the PTB but mainly covers the Induan stage of the Triassic. This formation mainly consists of finely laminated micritic limestone, marl and organic-rich shale⁸¹. The age model for the Shangsi section is well constrained by magnetostratigraphy, conodont biozones, cyclostratigraphy and U–Pb ages³⁶. Part of the Shangsi section overlaps with the Tieqaio section; detailed stratigraphy and biostratigraphy are provided in Extended Data Fig. 1.

The Shanggang section is also currently in Guangxi province, but in the Early Triassic it was located south of the Yangtze carbonate platform isolated in the Nanpanjiang basin, in an inner- to mid-shelf setting^{80,93}. This section contains the Changhsingian Heshan Formation and the Lower Triassic Luolou Formation. The Heshan Formation is mainly characterized by skeletal limestone deposition and overlain by microbial limestone and interbedded with limestone⁷⁷. The age model for the Shanggang section is constructed using condont biozones. The rich and abundant condont fauna allows precise biostratigraphy age determination and correlation to other sections in South China that spans the late Permian and Early Triassic, such as the Shangsi section, Meishan section—the Global Boundary Stratotype Section and Point for the PTB, Jinya section and Guandao section^{29,77}.

We constructed a composite stratigraphic section for the Permian to Early Triassic interval by combining the records from the five studied sections, tying age models using existing biostratigraphic constraints and, when available, magnetostratigraphy and U–Pb dating (Supplementary Data Table 1). The original ages were calculated based on Geologic Time Scale 2004 and were recalculated according to Geologic Time Scale 2002 for consistency among the five sections.

Sequential leaching and elemental concentration. The sample preparation for the majority of Sr isotope and Li isotope measurements was performed at the University of North Carolina at Chapel Hill (UNC-Chapel Hill). Before chemical preparation, samples were analysed using a Rigaku Miniflex II X-ray diffractometer to determine semi-quantitative mineralogy and only samples with >75% calcite were selected for chemical analysis (see also Supplementary Information). Rock chips were first cut using a water-based diamond-bladed saw to produce thin-section billets, then cleaned using ultrapure water (deionized, 18 MΩ) in an ultrasonic bath to remove excess sediment. Fine-grained micritic components were preferentially micro-drilled for analysis (Supplementary Information). For each sample, about 200 mg of powder was sequentially leached to minimize contamination from non-carbonate phases such as silicates. The leaching procedure was refined after ref.²⁸.

Sr isotope analysis. A split of the leachate solution (n = 99) was separated for Sr analysis. The aliquot was dried down and re-dissolved in 6 M HNO3. The separation of Sr was processed in 100 µl microcolumns loaded with Sr-spec Resin (100-150 µm; Eichrom Technologies). The matrix was rinsed out using 6 M HNO3. The Sr was collected with 0.05 M HNO3. After separation, the eluates were dried and re-dissolved in 200 µl 2% v/v HNO3 for 87Sr/86Sr analysis. For the Shanggang section, Sr isotopic compositions were measured using a Triton TIMS (Thermo Scientific) at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry. 87Sr/86Sr was corrected for instrumental mass fractionation by normalizing to 88 Sr/ 86 Sr = 8.375209. 87 Sr/ 86 Sr of the Sr reference material NBS-987 and BCR-2 were 0.710235 ± 0.000066 and 0.704986 ± 0.000030, respectively. External reproducibility (1 σ external reproducibility) was 0.000095 (n=7). The Sr isotope values for the rest of the samples were determined using a VG Sector 54 TIMS (Thermal Scientific) with dynamic multicollection at UNC-Chapel Hill. The laboratory value for the SRM 987 standard is (87Sr/86Sr) = 0.710242 ± 0.000010 (1 σ external reproducibility). The NBS-987 analysed along with the samples is 0.710250 (1σ external reproducibility) at UNC-Chapel Hill, which is consistent with the measured value at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry. For the 87Sr/86Sr values the associated uncertainties given are for 2σ mean internal reproducibility, typically based on 100 measured ratios. The 87Sr/86Sr reported ratios are normalized for instrumental fractionation using a normal Sr ratio of 87Sr/88Sr = 0.119400.

Li isotope analysis. A total of 51 samples (Ninemile: n = 10; Rockland Ridge: n = 4; Tieqiao: n = 16; Shangsi: n = 6; Shanggang: n = 15) were further selected for Li isotopes analysis. Based on the Li concentration in the leachate, a percentage of leachate calculated to ensure isotope analysis was dried down on a hotplate and treated with a two-step cation exchange chromatography procedure following methods in ref.⁹⁴. To assess the complete recovery of Li, splits of the solution were collected before and after the collected bracket, and were analysed for Li concentrations. Pre- and post cuts of the bracket contain <0.1% of Li mass relative to the initial sample Li mass. A blank was prepared following the same leaching and column protocol as the samples. The final measurement of Li content in the blank was lower than 10 ppt.

As listed in Supplementary Data Table 1, some Li isotope ratios were measured by a Thermo Scientific Neptune Plus MC-ICP-MS in the Department of Earth and Planetary Sciences at Rutgers University using the method described in ref. 94. Most analyses were conducted using an Agilent 7900 Q-ICP-MS at UNC-Chapel Hill. For seven samples, we used both MC-ICP-MS and Q-ICP-MS instruments (Supplementary Data Table 1). We also repeated all chemical prep and analysis for a few samples to confirm the reproducibility of isotope values between the two methods. The final δ⁷Li values were calculated by averaging all measurements for the same sample. Routine runs of the IRMM-016 gave reproducibility ≤0.6‰ for the MC-ICP-MS measurement⁹⁴ and long-term precision $2\sigma = \pm 1.1\%$ for the Q-ICP-MS method95. We measured JG-2 (granite) and JCP-1 at both UNC-Chapel Hill and Rutgers. UNC-Chapel Hill reports δ^7 Li 0.2 ± 0.3‰ (n=4) for JG-2, in good agreement with the reported value at Rutgers University $(0.32 \pm 0.32\%)$; Supplementary Data Table 4)95. UNC-Chapel Hill reports δ7Li 19.8 ± 1.07% for JCP-1 and Rutgers reports δ^7 Li 18.6 \pm 0.06%. We also ran NIST-SRM 1d (limestone) at UNC-Chapel Hill and obtained values of $4.9 \pm 1.0\%$ (NIST-SRM 1d, n = 20), consistent with the published data⁹⁴.

To validate the robustness of bulk marine carbonate $\delta^7 \text{Li}$ values, six brachiopods from different periods of the record were also analysed for $\delta^7 \text{Li}$. These brachiopods were selected from the collection of C.K. and included six 'pristine' samples used in ref. ⁶² to define the ⁸⁷Sr/⁸⁶Sr seawater curve. The secondary shell layers of these samples (used for the isotope investigations) were inspected by scanning electronic microscope and classified as excellently preserved because of their smooth surfaces^{16,36}. In addition, the concentrations of Mn were less than 250 ppm, whereas those of Sr were more than 400 ppm indicating that these brachiopods are pristine³⁶. Compared with bulk carbonate rocks, brachiopods are more resistant to diagenetic alteration. Thus, isotope values of pristine brachiopods are frequently utilized to reconstruct palaeoseawater chemistry^{16,96,97} and potentially represent robust archives for tracing past $\delta^7 \text{Li}_{sw}$. In addition, $\delta^7 \text{Li}$ is homogeneous in brachiopod shells and vital effects as well as inter-species variations are negligible^{11,32}.

Box model simulations for $\delta^7 \text{Li}_{sw}$. *The oceanic Li isotope budget.* To better understand the controlling factors of the major $\delta^7 \text{Li}_{sw}$ fluctuations over the studied period, we used a Li box model to constrain the potential changes in Li fluxes and isotope compositions. The model was constructed based on a steady state of

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Table 2 | Model parameter presets and results

		Continental runoff		Hydrothermal		Basalt alteration		Authigenic clay formation	
δ ⁷ Li _{sw} (‰)		F _{riv} (10 ⁹ mol yr ⁻¹)	δ ⁷ Li _{riv} (‰)	F _{MOR} (10 ⁹ mol yr ⁻¹)	δ ⁷ Li _{MOR} (‰)	F _{alt} (10 ⁹ mol yr ⁻¹)	Δ_{alt} (‰)	F _{sed} (10 ⁹ mol yr ⁻¹)	Δ_{sed} (‰)
20	Model parameters	5-15	3-23	4-17	8	5-15	5-15	10-20	10-20
	Simulation result	5-15	3-23	4-17	8	5-14	5-15	10-20	10-20
10	Model parameters	0-30	0-44	4-17	8	0-25	0-25	0-30	0-20
	Simulation result	0-30	0-23	4-17	8	8-14	0-24	0-30	0-20
5	Model parameters	0-30	0-44	4-17	8	5-15	0-25	0-30	0-30
	Simulation result	4-20	0-4	4-17	8	5-14.5	0-10	5-30	0-10

the Li seawater reservoir of the modern ocean. The model represents two major Li sources in the modern ocean, including continental weathering ($F_{\rm riv}$) and high-temperature hydrothermal fluids ($F_{\rm MOR}$), which were initially set at 10 × 10⁹ mol yr⁻¹ and 13 × 10⁹ mol yr⁻¹, respectively²⁵. Li isotope compositions of riverine and hydrothermal inputs were initially set at $\delta^7 {\rm Li}_{\rm riv} = 23\% {\rm e}^{71}$ and $\delta^7 {\rm Li}_{\rm MOR} = 8\% {\rm e}^{55/72}$. The model also represents the two main sinks of oceanic Li including basalt alteration ($F_{\rm atl}$)²⁴ and authigenic clay formation or reverse weathering ($F_{\rm seal}$), which were initially set at 12 × 10⁹ mol yr⁻¹ and 11 × 10⁹ mol yr⁻¹, respectively²⁴. Li isotope fractionation during the output processes is expressed as $\Delta_x = \delta^7 {\rm Li}_{\rm sw} - \delta^7 {\rm Li}_{\rm s}$, where *x* means the fraction of Li burial by basalt alteration or reverse weathering. Based on the isotope balance, the output processes are responsible for an additional fractionation of 16% to drive modern $\delta^7 {\rm Li}_{\rm sw}$ of 31% with estimated $\Delta_{\rm att} = 13\% {\rm o}$ and $\Delta_{\rm sed} = 20\% {\rm e}^{24}$.

The mass balance equation was set as:

$$F_{\rm riv} + F_{\rm MOR} = F_{\rm alt} + F_{\rm sed} \tag{1}$$

The isotope balance was set as:

$$\delta^{7}\text{Li}_{riv}F_{riv} + \delta^{7}\text{Li}_{MOR}F_{MOR} = \left(\delta^{7}\text{Li}_{sw} - \Delta_{sed}\right)F_{sed} + \left(\delta^{7}\text{Li}_{sw} - \Delta_{alt}\right)F_{alt} \quad (2)$$

Model parameter justification. The model parameters were chosen based on variations of Li fluxes and isotope values constrained by natural observations, laboratory experiments and theoretical calculations (Table 2). The δ^7 Li values of the present-day river dissolved loads range from 1.3%c to 43.7%c, but are mostly higher than $3\%c^{12,49,69,1,98-103}$. Low δ^7 Li values (1 to -2%c) are only found in cation-poor, organic-rich rivers, such as the Rio Negro in the Amazon floodplains where congruent weathering effectively removes cations⁴⁹. Therefore, δ^7 Li_{riv} values were allowed to vary between 0%c and 44%c for the simulations. The Li riverine flux varies as a function of chemical weathering rate and weathering intensity, and the model simulation for the 87 Sr/ 86 Sr_{sw} variations across the PTB suggest a twofold increase in the ratio of the Sr riverine to the hydrothermal flux¹⁵. Assuming the hydrothermal input could be decreased by 50%, the model allows the Li riverine flux to vary by a factor of 0-4.

The hydrothermal fluid serves as both source and sink of oceanic Li, as the hydrothermal fluids of high temperature (>200 °C) leach Li from the oceanic crust, leading to significantly enriched Li concentration (411–1,322 µmol kg⁻¹) compared with seawater. At a temperature under 150 °C, seawater loses Li to the oceanic crust by incorporation into alteration minerals. Large uncertainties lie in the Li fluxes during low-temperature oceanic crust alteration⁶⁶, varying from 2 to 4×10^9 mol yr⁻¹ (ref. ⁷²) and 11 to 17×10^9 mol yr⁻¹ (ref. ¹⁰⁴). δ^7 Li compositions of hydrothermal fluids at different locations do not vary largely and were calculated to be $7.8\%e^{72}$ and $8.3\%e^{25}$. In this study, the sampling pool for F_{MOR} is allowed to vary between 4 and 17×10^9 mol yr⁻¹, while the δ^7 Li_{MOR} is held constant at 8%e.

 $F_{\rm alt}$ also has a large potential range, from 1.44 to 21 \times 10° mol yr⁻¹ (refs. ^{24,25,6,105,106,73}). We adopted a value of 12 \times 10° mol yr⁻¹ at present-day $F_{\rm alt}$ ²⁴. $\Delta_{\rm alt}$ and $\Delta_{\rm sed}$ are determined mainly by two approaches, natural observations and laboratory experiments. The alteration of oceanic crust under 150 °C causes Li enrichment in altered minerals. However, δ^{2} Li of bulk altered basalts depends on bottom water temperature, water–rock ratio and strongly on mineralogy⁶⁶. Extrapolated $\Delta_{\rm alt}$ have a large range of 8–22% $o^{66,272,7106,107}$. We adopted an initial value of 13% at present day for $\Delta_{\rm alt}$ and allowed the value to range between 0 and 22% during model simulations.

So far, no $\delta^7 {\rm Li}$ measurements in authigenic clay in the ocean exist. However, a limited number of $\Delta_{\rm sed}$ values have been reported by clay synthesis and seawater–basalt interaction experiments 66,69,108 . These data suggest that the level of fractionation significantly varies among minerals. Even within the same mineral, the fractionation can be as small as -0.2% for outer-sphere complexation and up to 20% for inner-sphere incorporation 68 . Therefore, a range of 0--20% was set for the $\Delta_{\rm sed}$ sampling range and a factor of 0--3 was set for $F_{\rm sed}$ in the Monte Carlo simulations.

For a given $\delta^7 Li_{sw}$ the model took one value for each variable from the preset range in Table 2. Then it used equations (1) and (2) to find solutions to the observed $\delta^7 Li_{sw}$ with an uncertainty of $\pm 0.1\%$. When a solution was found it was recorded and the model repeated the process by shifting one variable at a time by 0.1 until the whole preset range is covered. The simulation generated a range of solutions for each tested period. We then evaluated the most common and plausible trends in the potential solutions.

References

- Hautmann, M. et al. Competition in slow motion: the unusual case of benthic marine communities in the wake of the end-Permian mass extinction. *Palaeontology* 58, 871–901 (2015).
- Shen, S. Z., Wang, Y., Henderson, C. M., Cao, C. Q. & Wang, W. Biostratigraphy and lithofacies of the Permian system in the Laibin-Heshan area of Guangxi, South China. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 465, 42–63 (2007).
- Sweet, D. The Late Paleozoic Tectonostratigraphy of the Central Pequop Mountains, Elko County, Nevada. MSc thesis, Biose State Univ. (2003).
- Mei, S., Jin, Y. & Wardlaw, B. R. Conodont succession of the Guadalupian– Lopingian boundary strata in Laibin of Guangxi, China and west Texas, USA. *Palaeoworld* 9, 53–76 (1998).
- Galfetti, T. et al. Late Early Triassic climate change: insights from carbonate carbon isotopes, sedimentary evolution and ammonoid paleobiogeography. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 243, 394–411 (2007).
- Huang, Y. et al. Restoration of reef ecosystems following the Guadalupian– Lopingian boundary mass extinction: evidence from the Laibin area, South China. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 519, 8–22 (2019).
- Shen, S. Z. et al. Calibrating the end-Permian mass extinction. Science 334, 1367-1372 (2011).
- Ovtcharova, M. et al. New Early to Middle Triassic U–Pb ages from South China: calibration with ammonoid biochronozones and implications for the timing of the Triassic biotic recovery. *Earth Planet. Sci. Lett.* 243, 463–475 (2006).
- Lehrmann, D. J. et al. Timing of recovery from the end-Permian extinction: geochronologic and biostratigraphi constraints from South China. *Geology* 34, 1053–1056 (2006).
- Stevens, C. H. Fasciculate rugose corals from Gzhelian and Lower Permian strata, Pequop Mountains, northeast Nevada. *J. Paleontol.* 82, 1190–1200 (2008).
- Shen, S. et al. A comparison of the biological, geological events and environmental backgrounds between the Neoproterozoic–Cambrian and Permian–Triassic transitions. *Sci. China Earth Sci.* 53, 1873–1884 (2010).
- Sweet, D. & Snyder, W. S. Middle Pennsylvanian through Early Permian tectonically controlled basins: evidence from the central Pequop Mountains, northeast Nevada: Late Paleozoic tectonics and hydrocarbon systems of western North America-The greater Ancestral Rocky Mountains: Tulsa. In AAPG Search and Discovery Article; AAPG Hedberg Research Conference 74–77 (2002).
- Wang, W., Cao, C. & Wang, Y. The carbon isotope excursion on GSSP candidate section of Lopingian–Guadalupian boundary. *Earth Planet. Sci. Lett.* 220, 57–67 (2004).
- Qiu, Z., Wang, Q., Zou, C., Yan, D. & Wei, H. Transgressive-regressive sequences on the slope of an isolated carbonate platform (Middle–Late Permian, Laibin, South China). *Facies* 60, 327–345 (2014).
- Jin, Y. et al. The Global Stratotype Section and Point (GSSP) for the boundary between the Capitanian and Wuchiapingian Stage (Permian). *Episodes* 29, 253–262 (2006).
- Xiang, L. et al. Oceanic redox evolution across the end-Permian mass extinction at Shangsi, South China. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 448, 59–71 (2016).

ARTICLES

- 92. Li, Z.-S. et al. Mass extinction and geological events between Paleozoic and Mesozoic era. *Acta Geol. Sin.* **60**, 1 (1986).
- 93. Galfetti, T. et al. Evolution of Early Triassic outer platform paleoenvironments in the Nanpanjiang basin (South China) and their significance for the biotic recovery. *Sediment. Geol.* **204**, 36–60 (2008).
- Li, W., Liu, X. & Godfrey, L. V. Optimisation of lithium chromatography for isotopic analysis in geological reference materials by MC-ICP- MS. *Geostand. Geoanal. Res.* 43, 261–276 (2019).
- Liu, X.-M. & Li, W. Optimization of lithium isotope analysis in geological materials by quadrupole ICP-MS. J. Anal. At. Spectrom. 34, 1708–1717 (2019).
- Korte, C., Kozur, H. W. & Veizer, J. δ¹³C and δ¹⁸O values of Triassic brachiopods and carbonate rocks as proxies for coeval seawater and palaeotemperature. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 226, 287–306 (2005).
- 97. Veizer, J. et al. $^{87}\text{Sr}/^{86}\text{Sr}, \, \delta^{13}\text{C}$ and $\delta^{18}\text{O}$ evolution of Phanerozoic seawater. Chem. Geol. 161, 59–88 (1999).
- Huh, Y., Chan, L. H. & Edmond, J. M. Lithium isotopes as a probe of weathering processes: Orinoco River. *Earth Planet. Sci. Lett.* 194, 189–199 (2001).
- Pogge von Strandmann, P. A. E. et al. Riverine behaviour of uranium and lithium isotopes in an actively glaciated basaltic terrain. *Earth Planet. Sci. Lett.* 251, 134–147 (2006).
- Witherow, R. A., Lyons, W. B. & Henderson, G. M. Lithium isotopic composition of the McMurdo Dry Valleys aquatic systems. *Chem. Geol.* 275, 139–147 (2010).
- Lemarchand, E., Chabaux, F., Vigier, N., Millot, R. & Pierret, M. C. Lithium isotope systematics in a forested granitic catchment (Strengbach, Vosges Mountains, France). *Geochim. Cosmochim. Acta* 74, 4612–4628 (2010).
- Liu, X.-M. & Rudnick, R. L. Constraints on continental crustal mass loss via chemical weathering using lithium and its isotopes. *Proc. Natl Acad. Sci.* USA 108, 20873–20880 (2011).
- Dellinger, M. et al. Lithium isotopes in large rivers reveal the cannibalistic nature of modern continental weathering and erosion. *Earth Planet. Sci. Lett.* 401, 359–372 (2014).
- Elderfield, H. & Schultz, A. Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean. *Annu. Rev. Earth Planet. Sci.* 24, 191–224 (1996).
- Stoffyn-Egli, P. & Mackenzie, F. T. Mass balance of dissolved lithium in the oceans. *Geochim. Cosmochim. Acta* 48, 859–872 (1984).

- Seyfried, W. E., Janecky, D. R. & Mottl, M. J. Alteration of the oceanic crust: implications for geochemical cycles of lithium and boron. *Geochim. Cosmochim. Acta* 48, 557–569 (1984).
- 107. Gao, Y. et al. Downhole variation of lithium and oxygen isotopic compositions of oceanic crust at East Pacific Rise, ODP Site 1256. Geochem. Geophys. Geosyst. 13 (2012).
- Vigier, N. et al. Quantifying Li isotope fractionation during smectite formation and implications for the Li cycle. *Geochim. Cosmochim. Acta* 72, 780–792 (2008).

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Author contributions

X-M.L. and C.P.B. designed the research; H.S., H.W, K.T.C., C.K. and M.R.S. provided rock samples; C.C., C.P.B. and Z. Z. performed geochemical analysis; C.C., X-M. L. and C.P.B. wrote the paper with contributions from all co-authors.

Competing interests

The authors declare no competing interests.

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Extended Data Fig. 1 | Stratigraphic record of the five studied sections with associated age model and geochemical records (δ^{7} Li, δ^{13} C). The stratigraphy and biozones in the sections Ninemile, Rockland Ridge, Tieqiao are from^{34,35,81}. Stratigraphy, U-Pb ages and carbon isotope record in the Shangsi section are from³⁶. Stratigraphy of the Shanggang section are unpublished data from²⁹. Error bars represent long term precision (2 SD) of 1.1‰ for δ^{7} Li measurements at UNC-Chapel Hill and calculated 2 SD for repeatedly measured δ^{7} Li values (Supplementary Data Table 1). Skull and crossbone silhouette extracted from www.flaticon.com.