Strontium and carbon isotopic evidence for decoupling of $\rho$CO$_2$ from continental weathering at the apex of the late Paleozoic glaciation

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**ABSTRACT**

Earth’s penultimate icehouse (ca. 340–285 Ma) was a time of low atmospheric $p$CO$_2$ and high $p$O$_2$, formation of the supercontinent Pangaea, dynamic glaciation in the Southern Hemisphere, and radiation of the oldest tropical rainforests. Although it has been long appreciated that these major tectonic, climatic, and biotic events left their signature on seawater $^{87}$Sr/$^{86}$Sr through their influence on Sr fluxes to the ocean, the temporal resolution and precision of the late Paleozoic seawater $^{87}$Sr/$^{86}$Sr record remain relatively low. Here we present a high-temporal-resolution and high-fidelity record of Carboniferous–early Permian seawater $^{87}$Sr/$^{86}$Sr based on conodont bioapatite from an open-water carbonate slope succession in south China. The new data define a rate of long-term rise in $^{87}$Sr/$^{86}$Sr (0.000035/m.y.) from ca. 334–318 Ma comparable to that of the middle to late Cenozoic. The onset of the rapid decline in $^{87}$Sr/$^{86}$Sr (0.000043/m.y.), following a prolonged plateau (318–303 Ma), is constrained to ca. 303 Ma. A major decoupling of $^{87}$Sr/$^{86}$Sr and $p$CO$_2$ during 303–297 Ma, coincident with the Paleozoic peak in $p$O$_2$, widespread low-latitude aridification, and demise of the pan-tropical wetland forests, suggests a major shift in the dominant influence on $p$CO$_2$ from continental weathering and organic carbon sequestration (as coals) on land to organic carbon burial in the ocean.

**INTRODUCTION**

Seawater $^{87}$Sr/$^{86}$Sr has long been used as a tool for chronostratigraphic correlation (e.g., McArthur et al., 2012), and, in combination with global seawater $\delta^{13}$C, to constrain the timing and magnitude of tectonic events, continental weathering, and paleoclimate change (e.g., Kump and Arthur, 1997; Goddéris et al., 2017). For the middle to late Cenozoic, the high-resolution seawater $^{87}$Sr/$^{86}$Sr curve has provided robust chronostratigraphic constraints and insight into the interlinked processes of the Earth system during our modern icehouse (e.g., Zachos et al., 1999).

The late Paleozoic ice age (LPIA, ca. 340–285 Ma) is one of two major icehouses of the Phanerozoic, and records the only greenhouse gas–forced transition from an icehouse with complex terrestrial ecosystems to a fully greenhouse world (Montañez and Poulson, 2013). The LPIA was a time of very low atmospheric $p$CO$_2$ (Montañez et al., 2016) and high $p$O$_2$ (Glasspool et al., 2015), dynamic glaciation on Gondwana (Isbell et al., 2015), formation of the supercontinent Pangaea (Isbell et al., 2015), global tectonic reconfiguration (Veevers, 2013), and the evolution of the paleo-tropical wetland rainforests on continental weathering and atmospheric $p$CO$_2$ during Earth’s penultimate icehouse.

**GEOLOGIC SETTING AND METHODS**

During the Carboniferous–Permain, the South China Block was a nearly isolated terrain located at the interface of the Paleo-Tethys Ocean (west) and Panthalassic Ocean (east) (Fig. DR1). The Carboniferous–Permain Naqing succession in the Guizhou Province consists of thin-beded lime mudstones intercalated with intraclast-bearing bioclastic wackestones to packstones (Fig. 1), and contains abundant conodonts with complete evolutionary lineages (Qi et al., 2014). The succession records a major shift in the dominant influence on $p$CO$_2$ from continental weathering and organic carbon sequestration (as coals) on land to organic carbon burial in the ocean.

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$^{1}$GSA Data Repository item 2018128, analytical methods, age calibration, revision of $p$CO$_2$ estimates, Figures DR1 and DR2, and Tables DR1 and DR2, is available online at http://www.geosociety.org/datarepository/2018/, or on request from editing@geosociety.org.
44) over the study period. All data are normalized to a SRM 987 value (avg. of 0.000035/m.y.) over a 16 m.y. period (334–318 Ma) to 0.70827.

Figure 1. Conodont and carbonate 87Sr/86Sr (this study) and carbonate δ13C (Buggisch et al., 2011) from the Naqing section, south China, with updated conodont biostratigraphy. Trend lines are locally weighted scatterplot smoothing (LOESS, 0.1 smoothing) regressions with 2.5% and 97.5% bootstrapped errors. M—lime mudstone; W—wackestone; F—fine-grained packstone; C—coarse-grained packstone; FAD—first appearance datum for conodont taxa.

strontium carbonate isotopic standard SRM 987 (avg. of 0.710251; n = 44) over the study period. All data are normalized to a SRM 987 value of 0.710249.

RESULTS AND DISCUSSION

Refined Seawater 87Sr/86Sr

Conodont apatite 87Sr/86Sr values from the Naqing section delineate three phases during the middle Mississippian to early Permian (Fig. 1; Fig. DR2). First, after a brief decline from 0.70780 to 0.70769 during the Middle Mississippian (ca. 336–334 Ma), 87Sr/86Sr values increase rapidly (avg. of 0.00035/m.y.) over a 16 m.y. period (334–318 Ma) to 0.70827. Second, the 87Sr/86Sr values define an ~15 m.y. plateau throughout much of the Pennsylvanian (318–303 Ma). Third, 87Sr/86Sr values decline, at an average rate of 0.000043/m.y., from ca. 303 Ma through to the end of the record in the early Permian (ca. 298 Ma).

The 87Sr/86Sr values of diagenetically screened micrite from the Naqing section are overall higher, by up to 0.00029, than co-existing conodonts and exhibit greater scatter (Fig. 1). The Naqing conodont 87Sr/86Sr record largely agrees with a published first-order 87Sr/86Sr trend (Bruckschen et al., 1999; Korte et al., 2006), but with significantly less scatter and greater continuity (Fig. 2B). The Naqing data, with minimal stratigraphic uncertainty and higher temporal resolution (10^3 yr), refine the trend and fill in existing gaps. Notably, the Naqing 87Sr/86Sr values are comparable, within analytical uncertainty, with those of brachiopods from Panthalassic open-ocean settings (Brand et al., 2009) and of conodonts from the high-precision U-Pb calibrated Russian succession (Henderson et al., 2012).

Seawater 87Sr/86Sr represents a mixture of two main sources: a continent-derived, more-radiogenic weathering flux, and mantle-derived, less-radiogenic volcanic and hydrothermal fluxes. The rise in 87Sr/86Sr during ca. 334–318 Ma likely records the increased 87Sr/86Sr ratio of the riverine flux due to exposure and weathering of uplifted radiogenic basement rocks (Goddéris et al., 2017) driven by the Hercynian orogeny (ca. 340–260 Ma; Hatcher, 2002; Vevers, 2013). The subsequent protracted (15 m.y.) 87Sr/86Sr plateau (318–303 Ma) is interpreted to record sustained high-87Sr/86Sr riverine flux due to westward progression of maximum elevations and subsequent rapid denudation of the highlands in the paleo-tropics. The new 87Sr/86Sr record indicates a rate of rise comparable to that of last 34 m.y. of the Cenozoic icehouse (0.000040/m.y.; McArthur et al., 2012, and references therein), suggesting that increased global weatherability due to orogenic uplift may be a common driver of these icehouses (cf. Kump and Arthur, 1997).

Conversely, the rapid, near-linear decline in 87Sr/86Sr ca. 303–285 Ma likely records decreased continental (silicate) weathering. This raises a paradox, as the potential for tectonically driven weatherability most likely remained unchanged through the early Permian (cf. Goddéris et al., 2017) with continued orogenesis to ca. 260 Ma (Hatcher, 2002). We hypothesize that continental weathering likely decreased during this time based on two other factors. First, the onset of widespread aridification in pan-tropical regions that began in the late Moscovian and intensified with time eastward across Pangaea through to the early Permian (Tabor and Poulsen, 2008; Michel et al., 2015) would have dramatically decreased silicate weathering. Second, the Euramerican tropical wetland forests underwent permanent turnover toward the close of the Carboniferous to dryland forests with less weathering potential (Wilson et al., 2017). Moreover, weathering of less-radiogenic basaltic provinces, which were emplaced initially in the latest Carboniferous and throughout the early Permian opening of the Neo-Tethys (e.g., Liao et al., 2015), may have contributed to declining 87Sr/86Sr. The relative contribution of basalt weathering on global seawater 87Sr/86Sr, however, was likely small in the latest Carboniferous–earliest Permian, as early basaltic province emplacement was limited in volume and occurred primarily in mid-latitude regions (Liao et al., 2015) where weathering rates would have been lower, in particular during the earliest Permian apex of glaciation.

Coupled 87Sr/86Sr and δ13C and Implications for the Evolution of pCO₂ and pO₂

In order to evaluate the relative roles of silicate weathering and organic carbon (Corg) burial in regulating pCO₂, we couple the 87Sr/86Sr and carbon δ13C records and compare them to proxy-based pCO₂ estimates (Fig. 2). We present a consensus seawater δ13C curve for the late Paleozoic (Fig. 2C) developed using published values of diagenetically screened brachiopods from Euramerican epeiric platforms (Grossman et al., 2008) and slope carbonates, argued to be unaltered by meteoric diagenesis (Buggisch et al., 2011).

Integrated isotopic records and published pCO₂ estimates delineate four intervals (Fig. 2). First, the long-term rise (ca. 334–318 Ma) and earlier portion of the 87Sr/86Sr plateau (318–309 Ma) correspond to a long-term decline in pCO₂ (~1200 to ~500 ppm) and to relatively stable δ13C values (~3‰) between 340 Ma and 324 Ma, followed by a subsequent rise to a δ13C maximum (>5‰) at 309 Ma. Second, the later portion of the 87Sr/86Sr plateau (309–303 Ma) corresponds to a decline in δ13C to its nadir (<3‰) at 304 Ma and overall low pCO₂ values (~500–200 ppm), with a short-lived rise in pCO₂ at the end of the 87Sr/86Sr plateau.
Third, a decline in $^{87}\text{Sr}/^{86}\text{Sr}$ from 303 to 297 Ma coincides with a renewed rise in $\delta^{13}\text{C}$ to ~5‰ and a drop in $p\text{CO}_2$ to its nadir (~200 ppm). Fourth, continued decline in $^{87}\text{Sr}/^{86}\text{Sr}$ from 297 to 285 Ma corresponds with the rapid decline in $^{87}\text{Sr}/^{86}\text{Sr}$ between 303 Ma and 297 Ma and a long-term rise in $p\text{CO}_2$.

Perturbations in global carbon cycling and atmospheric $p\text{CO}_2$ are thought to have been the primary driver of the initiation and demise of the LPIA (e.g., Montañez et al., 2007, 2016; Goddéris et al., 2017). Increased tectonically driven weatherability of silicate rocks inferred from the long-term rise in $^{87}\text{Sr}/^{86}\text{Sr}$ would have drawn down $p\text{CO}_2$, and initiated major glaciation (Goddéris et al., 2017). Radiation of the tropical forests in the latest Mississippian to their apex in the Middle Pennsylvanian (Fig. 2A; Cleal and Thomas, 2005; DiMichele, 2014) would have further contributed to lowering $p\text{CO}_2$ through enhanced silicate weathering and $C_{\text{org}}$ sequestration in tropical wetlands (Nelsen et al., 2016). Evidence for this exists in the long-term $\delta^{13}\text{C}$ rise (Fig. 2C) and overall falling $p\text{CO}_2$ (Fig. 2D) through the Early and Middle Pennsylvanian. Major contraction of the Carboniferous tropical wetland rainforests during the Late Pennsylvanian (Kasimovian; Kasimovian; Fig. 2A; Cleal and Thomas, 2005; DiMichele, 2014), however, would have decreased the terrestrial $C_{\text{org}}$ sink (Cleal and Thomas, 2005; Montañez et al., 2016) as recorded in the widespread loss of coals, decreased $\delta^{13}\text{C}$ values (Fig. 2C), and increased $p\text{CO}_2$ (Fig. 2D).

While the coupled $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ records provide support for the collective influence of orogenic uplift and expansion of the terrestrial tropical ecosystems on both accelerated weathering and overall decreasing $p\text{CO}_2$ through the Pennsylvanian, the records also reveal a paradoxical relationship with regard to the driver of the $p\text{CO}_2$ minimum across the Carboniferous–Permian transition. That is, reduced continental weathering driven by the aforementioned climatic and biotic factors and coincident with the rapid decline in $^{87}\text{Sr}/^{86}\text{Sr}$ between 303 Ma and 297 Ma hypothetically should have led to decreased consumption of atmospheric CO$_2$ and a consequent rise in $p\text{CO}_2$ (Goddéris et al., 2017). However, the proxy-based $p\text{CO}_2$ estimates decrease to a nadir across the Carboniferous–Permian transition (Fig. 2). While the low $p\text{CO}_2$ is consistent with the apex of late Paleozoic glaciation (Fig. 2A; Fielding et al., 2008; Isbell et al., 2012; Montañez and Poulsen, 2013) and eustatic fall of ~120 m (Rygel et al., 2008), it requires an additional driver given the aforementioned hypothesized decrease in continental weathering rates at this time.

One mechanism that could account for the $p\text{CO}_2$ minima coincident with peak $p\text{O}_2$ in the earliest Permian (Glasspool et al., 2015) is an increase in the magnitude of the $C_{\text{org}}$ burial flux, which is supported by a return to more positive carbonate $\delta^{13}\text{C}$ values (Fig. 2C). An increase in terrestrial $C_{\text{org}}$ burial precluded by the loss of wetland forests and peat burial throughout Euramerica in the Late Pennsylvanian (Nelsen et al., 2016). We hypothesize that a major shift in the predominant $C_{\text{org}}$ sink from land to the oceans occurred across the Carboniferous–Permian transition. Reconstructed paleo-plant physiology and process-based ecosystem modeling support this hypothesis and suggest a 2- to 6-fold increase in water-use efficiencies (WUE) of early Permian tropical plants relative to the Carboniferous wetland floral dominants (Wilson et al., 2017). This shift in WUE suggests an up to 50% decrease in canopy transpiration and a similar magnitude increase in surface runoff. Increased surface runoff would have resulted in greater delivery of nutrients and organic matter to coastal waterways, increasing the potential for increased primary productivity and $C_{\text{org}}$ burial in the oceans. This hypothesized shift in the loci of late Paleozoic $C_{\text{org}}$ burial sinks requires further evaluation through integrated biogeochemical and ecosystem modeling. It is further possible that hypothesized enhanced eolian delivery of reactive iron during the apex of the LPIA (Sur et al., 2015) would have further stimulated marine primary productivity and increased marine $C_{\text{org}}$ burial.

In summary, coupled conodont apatite $^{87}\text{Sr}/^{86}\text{Sr}$ and carbonate $\delta^{13}\text{C}$ records indicate predominant roles for both continental weathering and $C_{\text{org}}$ burial in regulating LPIA climate. A decoupling of $p\text{CO}_2$ from continental weathering across the Carboniferous–Permian transition (303–297 Ma), however, suggests that the coincident $p\text{CO}_2$ minimum and $p\text{O}_2$ maximum during the earliest Permian apex glaciation may record a previously unrecognized unidirectional shift in the primary loci of $C_{\text{org}}$ burial from the apex of late Paleozoic glaciation.
land to sea. This shift was not a response to tectonically driven changes in weathering intensity or source, but rather to pantropical climate change and major ecosystem restructuring.

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REFERENCES CITED


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