Strontium and carbon isotopic evidence for decoupling of $p$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 $^8$Sr/$^6$Sr through their influence on Sr fluxes to the ocean, the temporal resolution and precision of the late Paleozoic seawater $^8$Sr/$^6$Sr record remain relatively low. Here we present a high-temporal-resolution and high-fidelity record of Carboniferous–early Permian seawater $^8$Sr/$^6$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 $^8$Sr/$^6$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 $^8$Sr/$^6$Sr (0.000043/m.y.), following a prolonged plateau (318–303 Ma), is constrained to ca. 303 Ma. A major decoupling of $^8$Sr/$^6$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 $^8$Sr/$^6$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 $^8$Sr/$^6$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., 1995).

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 Poulsen, 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., 2012), global tectonic reconfiguration (Veevers, 2013), and the evolution and radiation of the oldest tropical rainforests (DiMichele, 2014). The fingerprints of these events should have been recorded in seawater $^8$Sr/$^6$Sr given they collectively influenced continental weathering, and thus Sr flux to the late Paleozoic oceans. The existing Carboniferous–early Permian seawater $^8$Sr/$^6$Sr record derived using calcitic brachiopods (Bruckschen et al., 1999; Korte et al., 2006) remains only moderately resolved, reflecting stratigraphic uncertainties, relatively low temporal resolution, and possible diagenetic alteration.

Here, we present a $^8$Sr/$^6$Sr record of unprecedented temporal resolution (10$^3$ yr) for ~38 m.y. of the LPIA, built using conodont bioapatite from an open-water carbonate slope succession (Naqing, south China) of the eastern Paleo-Tethys Ocean (Fig. DR1 in the GSA Data Repository$^*$). Our record refines the structure of the middle Mississippian to early Permian seawater $^8$Sr/$^6$Sr curve and places more precise temporal constraints on the timing of major shifts and rates of change. Integrated conodont apatite $^8$Sr/$^6$Sr and carbonate $\delta^{13}$C records provide insight into the relative roles of orogenic uplift, pan-tropical aridification, 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–Permian, 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–Permian Naqing succession in the Guizhou Province consists of thin-bedded 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 near-continuous, hemipelagic deposition on a carbonate slope episodically punctuated by turbidity currents and debris flows in the Qian-Gui Basin that defined an open-water seaway to the Paleo-Tethys Ocean (Buggisch et al., 2011; Chen et al., 2016).

Sr was isolated from conodonts (n = 99) and carbonates (n = 22), collected from the Naqing section, using Eichrom exchange resin (50–100 μm) in pipette-tip columns attached to a Watson Marlow 205U Peristaltic pump (detailed methods are provided in the Data Repository). The $^8$Sr/$^6$Sr ratios were measured on a Nu Plasma HR (Nu032) multicollector–inductively coupled plasma–mass spectrometer (MC-ICPMS) at the University of California–Davis (USA). Analytical precision (2 standard deviations [SD] = ±0.000026) is based on repeated $^8$Sr/$^6$Sr analysis of

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$^*$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.
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 $^{87}$Sr/$^{86}$Sr

Conodont apatite $^{87}$Sr/$^{86}$Sr 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), $^{87}$Sr/$^{86}$Sr values increase rapidly (avg. of 0.00035/m.y.) over a 16 m.y. period (334–318 Ma) to 0.70827. Second, the $^{87}$Sr/$^{86}$Sr values define an ~15 m.y. plateau throughout much of the Pennsylvanian (318–303 Ma). Third, $^{87}$Sr/$^{86}$Sr 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 $^{87}$Sr/$^{86}$Sr 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 $^{87}$Sr/$^{86}$Sr record largely agrees with a published first-order $^{87}$Sr/$^{86}$Sr 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 $^{87}$Sr/$^{86}$Sr 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 $^{87}$Sr/$^{86}$Sr 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 $^{87}$Sr/$^{86}$Sr during ca. 334–318 Ma likely records the increased $^{87}$Sr/$^{86}$Sr ratio of the riverine flux due to exposure and weathering of uplifted radiogenic basement rocks (Godderis et al., 2017) driven by the Hercynian orogeny (ca. 340–260 Ma; Hatcher, 2002; Vevers, 2013). The subsequent protracted (15 m.y.) $^{87}$Sr/$^{86}$Sr plateau (318–303 Ma) is interpreted to record sustained high-$^{87}$Sr/$^{86}$Sr riverine flux due to westward progression of maximum elevations and subsequent rapid denudation of the highlands in the paleo-tropics. The new $^{87}$Sr/$^{86}$Sr 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 $^{87}$Sr/$^{86}$Sr 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. Godderis 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 forested areas 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 $^{87}$Sr/$^{86}$Sr. The relative contribution of basalt weathering on global seawater $^{87}$Sr/$^{86}$Sr, 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 $^{87}$Sr/$^{86}$Sr and $\delta^{13}$C and Implications for the Evolution of pCO$_2$ and pO$_2$

In order to evaluate the relative roles of silicate weathering and organic carbon (C$_{org}$) burial in regulating pCO$_2$, we couple the $^{87}$Sr/$^{86}$Sr and carbon $\delta^{13}$C records and compare them to proxy-based pCO$_2$ estimates (Fig. 2). We present a consensus seawater $\delta^{13}$C curve for the late Paleozoic (Fig. 2C) developed using published values of diagenetically screened brachiopods from Euramerican epicontinental platforms (Grossman et al., 2008) and slope carbonates, argued to be unaltered by meteoric diagenesis (Buggisch et al., 2011).

Integrated isotopic records and published pCO$_2$ estimates delineate four intervals (Fig. 2). First, the long-term rise (ca. 334–318 Ma) and earlier portion of the $^{87}$Sr/$^{86}$Sr plateau (318–309 Ma) correspond to a long-term decline in pCO$_2$ (~1200 to ~500 ppm) and to relatively stable $\delta^{13}$C values (~3‰) between 340 Ma and 324 Ma, followed by a subsequent rise to a $\delta^{13}$C maximum (>5‰) at ca. 309 Ma. Second, the later portion of the $^{87}$Sr/$^{86}$Sr plateau (309–303 Ma) corresponds to a decline in $\delta^{13}$C to its nadir (<3‰) at ca. 304 Ma and overall low pCO$_2$ values (~500–200 ppm), with a short-lived rise in pCO$_2$ at the end of the $^{87}$Sr/$^{86}$Sr plateau.
Third, a decline in $^{87}\text{Sr}/^{86}\text{Sr}$ from 303 to 297 Ma is coincident with a widespread loss of coals, decreased $^{13}\text{C}$, and overall falling $p\text{CO}_2$ (Fig. 2C). This suggests a decrease in the $\delta^{13}\text{C}$ of carbonates and a long-term rise in $p\text{CO}_2$. Perurbations 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; Fig. 2A), 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 rates is 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...
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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