ABSTRACT
Over the past four billion years, our sun became 30% brighter, yet Earth’s water has neither completely frozen nor boiled off during that time. A theoretical solution to this paradox is a carbon dioxide greenhouse planetary thermostat regulated by evolutionary advances in biologically mediated silicate and apatite weathering. This carbon sequestration history can now be quantified using paleosols. Calculations of precipitation-normalized nutrient depletion rates (µmol mm⁻¹ a⁻¹) in paleosols ranging in age back to 3.7 Ga show discrete order of magnitude increases in carbon consumption by silicate and apatite weathering due to evolutionary advances in life on land at around the Great Oxidation Event (2.45 Ga) and Neoproterozoic Oxidation Event (0.8 Ga). This biological weathering countered increased solar luminosity and continued emission of volcanic greenhouse gases.

INTRODUCTION
The faint young sun paradox arises from stellar evolution of increased solar luminosity through time (Ribas, 2009), which predicts frigid temperatures on early Earth, with or without present atmosphere (Fig. 1). However, moderate Archean temperatures are inferred from salt stability, water-lain sedimentary structures, and glacial episodes (Walker, 1982). Paleotemperatures from paleosols (Fig. 1) are evidence of long-term stability (Retallack, 2013, 2018; Retallack et al., 2016), averting terminal freezing, apparent from Mars, as well as the other extreme of an uninhabitable inferno, apparent from Venus (Lovelock and Margulis, 1974). Both freezing and steaming may have been prevented by greenhouse gases such as CH₄ and CO₂ regulated by the biological carbon cycle (Schwartzmann, 2017). Continued volcanic degassing of CO₂ prevented a terminal icehouse, whereas building of biomass and consumption of carbonic acid by biotically enhanced silicate and apatite weathering prevented a terminal greenhouse (Retallack, 2022a). Consumption of CO₂ by abiotic silicate weathering in lifeless Precambrian landscapes was modeled by Rye and Holland (1998), but a role for life on land enhancing weathering is indicated as far back as 3.7 Ga by paleosol salts, stable isotopic compositions, and phosphorus depletion (Retallack, 2022b). Thus, theoretical concepts of biotic planetary temperature regulation can now be assessed from the record of fossil soils back to 3.7 Ga. Generally declining atmospheric CO₂ over time (Kasting, 2010) is not the only issue involved, because soil CO₂ increased with increased productivity of terrestrial vegetation (Retallack, 2022b). Paleosols are not only evidence of carbon sequestration by silicate and apatite weathering, but also include fossils as evidence of the evolution of life on land.

PALEOSOLS AS PROXIES FOR CARBON SEQUESTRATION
Paleosols are soils of the past, buried in sedimentary or volcanic sequences, and interpretable by comparison with modern soils. Release of soluble alkali and alkaline earth cations and bicarbonate into soil solution by carbonic acid from CO₂ in solution...
can be simplified to Equations 1–4, showing that each mole of oxide consumed 2 moles of CO$_2$:

\[
\begin{align*}
\text{MgO} + 2\text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{Mg}^{2+} + 2\text{HCO}_3^- , \\
\text{CaO} + 2\text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- , \\
\text{Na}_2\text{O} + 2\text{CO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{Na}^+ + 2\text{HCO}_3^- , \\
\text{K}_2\text{O} + 2\text{CO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{K}^+ + 2\text{HCO}_3^- .
\end{align*}
\]

(1)\(\text{Ca}_4(\text{PO}_4)_3(\text{OH}) + \text{CO}_2 \rightarrow \text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{HCO}_3^- .(5)\)

This is a simplification of four intermediateapatite dissolution reactions and other intermediate reactions producing carbonic acid from CO$_2$ in solution (Dorozhkin, 2012). Actual phosphate procurement in soils from relatively insoluble apatite is catalyzed by a variety of carbon-based acid moieties, such as acetic and oxalic acid with higher mole fractions of carbon (Neaman et al., 2005). Another complication is that Archean apatite dissolution also may have been partly achieved by strong sulfuric acid, rather than weak carbonic acid (Retallack, 2022c). Again, this is based on mass transfer, including volume loss during soil formation with depth in reconstructed soils as they would have been before burial compaction and metamorphism (Sheldon, 2006).

Original soils can be reconstructed from paleosols by estimating compaction due to burial overburden (C as %) from total depth of burial (B in km) and suitable physical constants, in this case taken from Aridisols (Sheldon and Retallack, 2001):

\[
\begin{align*}
C = \frac{-0.51 \times 10^3}{0.49} \left[ \frac{2}{0.27} \right]^{-1} .
\end{align*}
\]

(6)

Losses of these elements from soils on a molar basis is a proxy for moles of CO$_2$ consumed by soil over its time of formation (Sheldon, 2006). Whole profile loss can be envisaged as the area under the curves in mole fraction alkali and alkaline earth depletion for decompacted paleosols (Fig. 2).

Dissolution of apatite as a source of P can be reduced to Equation 5, in which 1 mol of CO$_2$ in aqueous solution liberates 3 moles of soluble phosphate from apatite:

\[
5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{HCO}_3^- .
\]

(5)

Variables and constants for these calculations besides those needed for Equations 6–8 are F (mol CO$_2$·cm$^{-2}$·yr$^{-1}$) = summed molar mass transfer loss of CaO, MgO, Na$_2$O, and K$_2$O using Equation 9; G (mol CO$_2$·cm$^{-2}$·yr$^{-1}$) = summed molar mass transfer loss of P using Equation 10; Z (cm) = depth in soil represented by analysis corrected for compaction using Equation 10; $\tau$ (years) = duration of soil formation using Equations 12 and 13; $K_{CO_2}$ (mol/kg·bar) = Henry’s Law constant for CO$_2$ (=0.034, range 0.031–0.0045); $P$ (cm) = mean annual precipitation using Equation 13; $\kappa$ (s·cm$^{-3}$·[mol·year]$^{-1}$) = seconds per year divided by volume per mole of gas at standard temperature and pressure (=1430);
$D_{CO_2}$ (cm²·s⁻¹) = diffusion constant for CO₂ in air (=0.162); α (fraction) = ratio of diffusion constant for CO₂ in soil divided by diffusion constant for CO₂ in air (=0.1, range 0.08–0.12); $L$ (cm) = original depth to water table (after decompacted using Equation 6).

The duration of soil formation in years ($A$ in k.y.) can be calculated from carbonate nodule diameter ($D$ in cm: $r^2 = 0.57$, s.e. = 1.8, $p = <0.001$) for calcareous soils (Retallack, 2005), or thickness of profile ($T$ in cm: $r = 0.79$, s.e. = 140, $p = 0.01$) for non-calcareous unconformity paleosols (Markewich et al., 1990):

$$A = 3.92D^{0.34},$$

$$A = 4.915T – 343.4.$$

Mean annual precipitation ($P$ in mm) can be obtained by the CIA-K proxy, effectively a chemical index of alteration without diagenetically problematic K ($I$ as mole fraction: $r^2 = 0.72$, s.e. = 182, $p = <0.0001$; Sheldon et al., 2002), or compaction-corrected depth to calcic horizon ($D$ in cm: $r = 0.52$, s.e. = 147, $p = <0.0001$; Retallack, 2005):

$$P = 221.1e^{0.007I},$$

$$P = 137.24 + 6.45D – 0.0132^2.$$

The normalized value of μmol $F$·cm⁻², mm⁻¹·a⁻¹, where $F$ is the sum of the four alkaline and alkaline earth bases, or μmol $G$·cm⁻²·mm⁻¹·a⁻¹, where $G$ is the sum of phosphorous depletions, become proxies for global CO₂ consumption if multiplied by modal mean annual precipitation, which is 764 mm in the modern world, with a standard error of 704 mm (Beck et al., 2005). This modal mean annual precipitation may have changed in deep time, but the current understanding of paleoprecipitation from paleosols shows mainly arid to subhumid estimates (Retallack, 2013, 2018; Retallack et al., 2016), comparable with today (Beck et al., 2005). Estimates of exposed land area in deep time are from published areas of continental crust and hypsometric curves (Cawood and Hawkesworth, 2019). These changing land areas were proportionally scaled to a modern land area of 148,429,000 km², and carbon consumption to modern global silicate weathering (Ciais et al., 2013) of 0.3 PgC·a⁻¹ (Pg = 10¹² g). Carbon consumption by silicate weathering can be calculated from stoichiometry of Equations 1–4 and carbon consumption by apatite weathering from stoichiometry of Equation 5.

**DATABASE, ERROR CALCULATIONS, AND ALTERNATIVES**

Detailed accounts of each of the paleosols used in the compilation for these calculations have all been published elsewhere: citations and component data, including error estimates for individual profiles, are listed in the supplemental material1. Criteria for quality of data outlined by Rye and Holland (1998) were used to select paleosols for the compilation. Full petrographic and geochemical data, as well as bulk density determinations, were essential for all horizons (Equations 7 and 8). Also needed was evidence of at least moderate development, such as argillic, calcic, or gypsic horizons (Retallack, 2013, 2018, 2022b). To be included, paleosols had to have chemical weathering demonstrated by tau analysis (Brimhall et al., 1992). Weakly developed, gleyed, and inadequately documented paleosols were not included. The paleosol database includes profiles on bedrock unconformities (Rye and Holland, 1998), as well as within sedimentary sequences (Retallack, 2013, 2018, 2022b). Virtually all suitable Precambrian paleosols are included in the database, along with most suitable Phanerozoic paleosols for which data was available. Errors for the calculations were based on standard errors of transfer functions (Equations 12–15) and Gaussian error propagation from partial derivatives of transfer equations summed in quadrature as outlined by Retallack et al. (2021).

Some of the transfer functions used are compromised by other variables: Equations 14 and 15 for paleoprecipitation include components of temperature (Sheldon et al., 2002) and paleoproductivity, respectively (Breecker and Retallack, 2014), which contribute to cited standard errors. Warmth and high precipitation can also compromise age estimates of paleosols using nodule size (Retallack, 2005) and depth of weathering (Markewich et al., 1990), again within standard error of the data used for the transfer function. Although individual paleosol depletion rate standard deviations were small, the variance of estimated depletion rates is large, so rates were pooled by 500-m.y. increments to calculate standard deviations as the height of the open box (Fig. 3).

**STEPWISE BIOTIC ENHANCEMENT OF WEATHERING**

The results of mass transfer calculations of paleosols ranging back in age to 3700 Ma show three orders of magnitude increases in nutrient depletion of both phosphorus and alkali and alkaline earths, but on different time scales (Figs. 3A–3B). Most of the range of alkali and alkaline earth depletion was achieved by the Great Oxidation Event (GOE) of 2.45 Ga, but phosphorus depletion rose markedly at both the GOE and the Neoproterozoic Oxidation Event (NOE) of 0.8 Ga. These changes may reflect increased rates of nutrient procurement due to increased biological productivity at those times.

Alkali and alkaline earth depletion rose steadily from 3.5 to 2.4 Ga under acid-sulfate weathering by anaerobic bacterial soil microorganisms (Retallack, 2018; Retallack et al., 2016), now restricted to waterlogged soils and playa lakes (Benison and Bowen, 2015). Alluvial paleosols from 3.5 to 3.0 Ga contain desert roses of sulfate minerals, such as barite and gypsum, as evidence for weathering by strong sulfuric acid rather than weak carbonic acid (Retallack, 2018; Retallack et al., 2016). The microbiome of desert rose paleosols dated to 3.0 Ga is permineralized with silica, and its microfossils, analyzed for cell-specific carbon-isotopic-composition, reveal an anaerobic community of purple sulfur bacteria, actinobacteria, and methanogens (Retallack et al., 2016).

Other paleosols in the data set formed in humid climates on bedrock (supplemental material [see footnote 1]) and were thick, clayey profiles, with little evidence of soluble salts (Rye and Holland, 1998). These do not stand out as anomalies in Figure 3 compared with paleosols with soluble salts (Retallack, 2022c) because they were normalized for mean annual precipitation (Equations 12–13) and duration of formation (Equations 14–15). CO₂ consumption rates of Paleoproterozoic and Archean paleosols are too low (Fig. 4) to explain paleotemperatures under a faint young sun (Kasting, 2010). Likely sulfur bacteria and methanogens in paleosols support the idea that other greenhouses gases, such as methane, ethane, and SO₂, formed a greenhouse

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1Supplemental Material. Table S1. Base and phosphorus depletion and paleoenvironments of 97 well-studied paleosols. Go to https://doi.org/10.1130/GSAT.S.20126417 to access the supplemental material; contact editing@geosociety.org with any questions.
haze (Haqq-Misra et al., 2008). Modeling of methane production rates from a P-limited and SO$_4$-poor Archean ocean would not have produced enough methane for a significant CH$_4$-greenhouse (Laakso and Schrag, 2019), but anaerobic methanogenesis would have been more widespread in well-drained Archean soils than its current geographic limitation to waterlogged wetlands (Benison and Bowen, 2015). Another Archean warming possibility is three times the current mass of atmospheric N$_2$ and a H$_2$O$_2$ mixing ratio (Wordsworth and Pierrehumbert, 2013). This seems unlikely because N$_2$ in the atmosphere was limited to 1.1–0.5 bars judging from nitrogen and argon isotopic ratios in fluid inclusions dated to 3500 Ma (Marty et al., 2013), and total atmospheric pressure at 2700 Ma may have been only half modern judging from the size of lava vesicles and raindrop impressions (Som et al., 2016).

The Archean acid-sulfate weathering style was geographically limited by late Archean spread of carbonic acid weathering, which dominated after the 2.45 Ga (Rye and Holland, 1998). The rise of cyanobacteria as part of a largely fresh-water and terrestrial clade of “Terrabacteria” (Battistuzzi and Hedges, 2009) maintained soil productivity, promoting perineutral carbonic acid hydrolysis and free oxygen in both soil and air (Fig. 4). Perineutral pH in soils by 2.4 Ga is indicated by pedogenic carbonate in paleosols of that age and in aridland soils ever since (Pekkarinen, 1979). Thus, hydrolytic weathering systems geographically displaced archaic acid-sulfate weathering, now limited to areas of sulfide ore weathering and anaerobic parts of waterlogged soils and lakes (Benison and Bowen, 2015).

Phosphorus depletion of paleosols rose during the GOE, and again during the NOE (Fig. 3B). The Neoproterozoic does not signify a fundamental change in style of weathering, but rather the evolution of more effective biologically produced ligands, which were mainly bacterial during the GOE, but supplemented by more effective ligands of fungi and lichens during the Neoproterozoic (Neaman et al., 2005; Retallack, 2013; Kump 2014). Both increases in terrestrial productivity coincide in time with Snowball Earth cooling events (Walker, 1982; Kasting, 2010).

**IMPLICATIONS FOR SOIL GASES IN DEEP TIME**

Some of these same paleosols also have been used to calculate CO$_2$ consumption as a guide to atmospheric evolution (Sheldon, 2006; Retallack et al., 2021), but they are imperfect guides to the atmosphere. Today, soils may have up to three orders of magnitude more CO$_2$ than the atmosphere because of soil respiration, and three orders of magnitude less O$_2$ due to waterlogging (Elberling et al., 2011). The differences in CO$_2$ and O$_2$ from the atmosphere are less marked in well-drained soils with open-soil structure (Kyaw Tha Paw et al., 2006). Calculations of gas consumption from paleosols (Sheldon, 2006; Retallack et al., 2021), combined with modern soil gas measurements (Elberling et al., 2011; Kyaw Tha Paw et al., 2006), allow idealized hypotheses for gas concentrations within well-drained alluvial soils over the past 3.7 billion years (Fig. 4). Both O$_2$ and CO$_2$ are higher in modern than in Precambrian soils, and geologically younger
soils show more variable concentrations with seasons, within profiles, and geographically (Breecker and Retallack, 2014). Thus, biotic enhancement of weathering was not just a matter of changing the atmosphere (Kasting, 2010), because soil gases at the site of silicate and apatite weathering were critical (Kump, 2014). Neoproterozoic consumption of CO$_2$ was less by increased silicate weathering than by increased apatite weathering (Fig. 3), suggesting a role for ligands from life on land (Neaman et al., 2005). With later evolution of land plants, soil CO$_2$ rose orders of magnitude higher than in the atmosphere, supplying carbonic acid for both silicate and apatite weathering (Berner, 1997; Retallack, 2013; Kump, 2014). The advent of land plants did draw down atmospheric CO$_2$ (Berner, 1997) but did not appreciably alter rates of CO$_2$ consumption by either silicate or apatite weathering at the coarse 500-m.y. scale of this investigation (Fig. 3). During the past 16 million years, range expansion and contraction of carbon-hungry soils such as Mollisols and Oxisols, with reciprocal adjustment of carbon-lean soils such as Gelsisols and Aridisols have acted as a planetary thermostat. Mollisol-Oxisol expansion curbs greenhouse CO$_2$ spikes, but Gelsisol-Aridisol expansion cannot override continued volcanic degassing of CO$_2$ (Retallack, 2022a). Too few Archean paleosols are now known to demonstrate such counterbalancing carbon sequestration, but biotic enhancement of weathering is suspected then as well. The record of paleosols reveals that atmospheric and soil CO$_2$ show considerable temporal and presumably also geographic variation (Fig. 3) but not a monotonic increase (Fig. 4). Nevertheless, carbon sequestration by silicate weathering and phosphorus depletion did rise (Fig. 4), as predicted in theory (Schwartzmann, 2017).

The estimates of CO$_2$ consumption by Paleoproterozoic and Archean soils do not show expected (Kasting, 2010) high amounts of soil or atmospheric CO$_2$ (Sheldon, 2006; Retallack, 2018; Retallack et al., 2016, 2021). Common sulfates formed in Archean paleosols despite low atmospheric O$_2$, suggest that strong sulfuric acid produced by anaerobic sulfur oxidizing bacteria, creating more amorphous colloids such as imogolite than clay, may have been more important than weak carbonic acid in Archean silicate weathering (Retallack, 2018; Retallack et al., 2016). Paleoproterozoic atmospheric oxidation raised rates of atmospheric CO$_2$ consumption by both oxidative silicate and apatite weathering from aerobic cyanobacteria and actinobacteria, but increases in apatite, not silicate, weathering rates are seen in the Neoproterozoic (Fig. 3), perhaps from newly evolved fungal-lichen microbial earths (Retallack, 2013; Kump, 2014). The advent of land plants did draw down atmospheric CO$_2$ (Berner, 1997) but did not appreciably alter rates of CO$_2$ consumption by either silicate or apatite weathering at the coarse 500-m.y. scale of this investigation (Fig. 3). During the past 16 million years, range expansion and contraction of carbon-hungry soils such as Mollisols and Oxisols, with reciprocal adjustment of carbon-lean soils such as Gelsisols and Aridisols have acted as a planetary thermostat. Mollisol-Oxisol expansion curbs greenhouse CO$_2$ spikes, but Gelsisol-Aridisol expansion cannot override continued volcanic degassing of CO$_2$ (Retallack, 2022a). Too few Archean paleosols are now known to demonstrate such counterbalancing carbon sequestration, but biotic enhancement of weathering is suspected then as well. The record of paleosols reveals that atmospheric and soil CO$_2$ show considerable temporal and presumably also geographic variation (Fig. 3) but not a monotonic increase (Fig. 4). Nevertheless, carbon sequestration by silicate weathering and phosphorus depletion did rise (Fig. 4), as predicted in theory (Schwartzmann, 2017).

### COMPARISON WITH EXPERIMENTS

Increases of three orders of magnitude in nutrient depletion of individual paleosols (Fig. 3A) and global carbon sequestration (Fig. 3C) is greater than an estimate of two orders of magnitude of biotic enhancement of weathering derived from compilation of experimental studies (Schwartzmann, 2017) for three reasons. First, experimental studies reveal enhancement factors of major steps in terrestrial productivity, such as the evolution of trees (Retallack, 2022b), and does not consider the origin of microbial life in soils and prokaryotic evolutionary advances in microbiome weathering. Second, global carbon sequestration has been aided by the growth of land area through time. The estimates of land-area increase used here are based on estimates of continental area and paleohypsometry (Cawood and Hawkesworth, 2019), which are relatively conservative, but show a factor of three, rather than a factor of 100 increase through time (Fig. 3C). Third, nutrient depletion fuels biomass carbon sequestration increases of about the same magnitude (Retallack, 2022a).

### CONCLUSIONS

Paleosols are now evidence for progressive CO$_2$ and CH$_4$ greenhouse reduction by biologically enhanced weathering to offset increased stellar luminosity and continued volcanic greenhouse gas emission. Biological regulation of soil and atmospheric gases may have maintained habitable surface conditions on Earth for the past 3.7 Ga.
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Manuscript received 15 Apr. 2022
Revised manuscript received 10 June 2022
Manuscript accepted 17 June 2022