Biotic Enhancement of Weathering over the Past 3.7 Billion Years
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$_2$:

\[
\begin{align*}
\text{MgO} + 2\text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{Mg}^{2+} + 2\text{HCO}_3^- , \quad (1) \\
\text{CaO} + 2\text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- , \quad (2) \\
\text{Na}_2\text{O} + 2\text{CO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{Na}^+ + 2\text{HCO}_3^- , \quad (3) \\
\text{K}_2\text{O} + 2\text{CO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{K}^+ + 2\text{HCO}_3^- . \quad (4)
\end{align*}
\]

Loses 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:

\[
\text{Ca}_5(\text{PO}_4)_3(\text{OH}) + \text{CO}_2 \rightarrow 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{HCO}_3^- . \quad (5)
\]

This is a simplification of four intermediate apatite 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 by 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):

\[
C = \frac{-0.51 \times 100}{0.49} \left( \frac{\rho}{0.27} \right) - 1 \quad . \quad (6)
\]

Tau analysis of paleosols (Brimhall et al., 1992) calculates mole fraction mass transport ($\tau_{i,w}$) of a mobile element and mole fraction strain ($\varepsilon_{i,w}$) of the profile during soil formation using an immobile element from the parent material (Ti used here). Equations 7–8 for mass transport and strain include bulk density ($\rho$ in g.cm$^{-3}$) and oxide assay (C in wt%) for successive samples (subscripts $i,j$) of weathered material (subscript $w$) and parent material (subscript $p$) of a single paleosol profile:

\[
\varepsilon_{i,w} = \left[ \frac{\rho_{j,p}}{\rho_{j,w}} \right]^{1} - 1 , \quad (7)
\]

\[
\tau_{j,w} = \left[ \frac{\rho_{j,p}}{\rho_{j,w}} \right]^{1} \left[ \varepsilon_{i,w} + 1 \right] - 1 . \quad (8)
\]

Soils and paleosols lose mass with weathering and so have negative strain ($\varepsilon_{i,w} < 0$), and also lose nutrient cations and silica, so have negative mass transfer ($\tau_{j,w} < 0$). In contrast, sediment accumulation and diagenetic alteration add elements and mass, so have positive strain and mass transfer. Moles of CO$_2$ used to displace alkali and alkaline earths during weathering assessed by tau analysis (Equations 7–8) can be used to calculate soil CO$_2$ (ppm) consumed by the whole profile during its formation using Equations 9–11 (modified from Sheldon, 2006). Components of these calculations are areas under the curves of depletion of bases or phosphorus in reconstructed paleosol profiles, calculated for the whole profile for a square centimeter of surface area of the profile (Fig. 2):

\[
p\text{CO}_2 = \frac{F}{A} \left[ \frac{K_{p\text{CO}_2} \rho \alpha}{1000} + \kappa \frac{D_{\text{CO}_2} \alpha}{L} \right] , \quad (9)
\]

\[
F = 2 \sum \rho_{j,p} \int_{Z_{w,0}}^{Z_{w,0}} \tau_{j,w} \alpha j \delta Z , \quad (10)
\]

\[
G = 5 \sum \rho_{j,p} \int_{Z_{w,0}}^{Z_{w,0}} \tau_{j,w} \alpha j \delta Z . \quad (11)
\]

Variables and constants for these calculations besides those needed for Equations 6–8 are $F$ (mol CO$_2$.cm$^{-3}$) = summed molar mass transfer loss of CaO, MgO, Na$_2$O, and K$_2$O using Equation 9; $G$ (mol CO$_2$.cm$^{-3}$) = summed molar mass transfer loss of P using Equation 10; $Z$ (cm) = depth in soil represented by analysis corrected for compaction using Equation 10; $A$ (years) = duration of soil formation using Equations 12 and 13; $K_{p\text{CO}_2}$(mol.kg.bar) = Henry’s Law constant for CO$_2$ (=0.034, range 0.031–0.0045); $\rho$ (cm$^{-1}$) = mean annual precipitation using Equation 13; $\kappa$ (s.cm$^{-1}$.[mol.year]$^{-1}$) = seconds per year divided by volume per mole of gas at standard temperature and pressure (=1430);
Supplemental Material. Table S1. Base and phosphorus depletion and paleoenvironments of 97 well-studied paleosols. Go to GSA Today, 2022, to obtain this table (after decompacted using Equation 6).

Some of the transfer functions used are outlined by Retallack et al. (2021). 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 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 sulfates, 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, revealed 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
The Archean acid-sulfate weathering style was geographically limited by late Archean spread of carbonic acid weathering, which dominated after the 2.45 Ga GOE (Rye and Holland, 1998). The rise of cyanobacteria as part of a largely freshwa
ter and terrestrial clade of “Terrabacteria” (Battistuzzi and Hedges, 2009) maintained soil productivity, promoting perineutral car
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 geo
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 magni
tude 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 mod
er 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 Pre
cambrian 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 (Bernier, 1997; Retallack, 2022a, 2022b).

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 Gelisols and Aridisols have acted as a planetary thermostat. Mollisol-Oxisol expansion curbs greenhouse CO$_2$ spikes, but Gelisol-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).

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.
