Anatomy of a Sub-Cambrian Paleosol in Wisconsin: Mass Fluxes of Chemical Weathering and Climatic Conditions in North America during Formation of the Cambrian Great Unconformity

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ABSTRACT

A paleosol beneath the Upper Cambrian Mount Simon Sandstone in Wisconsin provides an opportunity to evaluate the characteristics of Cambrian weathering in a subtropical climate, having been located at 20°S paleolatitude 500 My ago. The 285-cm-thick paleosol resulted from advanced chemical weathering of a gabbroic protolith, recording a total mass loss of 50%. Weathering of hornblende and plagioclase produced a pedogenic assemblage of quartz, chlorite, kaolinite, goethite, and, in the lowest part of the profile, siderite. Despite the paucity of quartz in the protolith and 40% removal of SiO$_2$ from the profile, quartz constitutes 11%–23% of the pedogenic mineral assemblage. Like many other Precambrian and Cambrian paleosols in the Lake Superior region, the paleosol experienced potassium metasomatism, now containing 10%–25% mixed-layer illite-vermiculite and 5%–44% potassium feldspar. Estimates of mean annual precipitation and mean annual temperature are 1777 mm y$^{-1}$ and 20.1°C, respectively, which are consistent with a paleolatitude of 20°S. For an atmospheric CO$_2$ concentration of 4000–6000 ppm at 550–500 Ma, the duration of weathering is constrained to have been between 20,000 and 100,000 y. When the effects of erosion and influence of protolith composition are considered, the degree, or maturity, of weathering for the Wisconsin paleosol and four other sub-Cambrian paleosols is comparable to that for two modern soils in subtropical and temperate climates, despite the lack of land plants in Cambrian time. Such correspondent degrees of weathering likely result from the effects of elevated levels of atmospheric CO$_2$ and microbial activity on weathering in Cambrian time.

Online enhancements: appendix.

Introduction

The first Phanerozoic continental-scale marine transgression is marked by the Cambrian Great Unconformity, the formation of which was preceded by extensive chemical weathering of continental crust, followed by widespread physical reworking of soil, regolith, and basement rock during the advance of a transgressive shoreface system [Peters and Gaines 2012].

Sub-Cambrian paleosols provide significant insights into the characteristics of chemical weathering and the contribution of labile elements to the hydrosphere and, ultimately, to seawater at 550–500 Ma, but many such paleosols were stripped away by the erosive effect of the transgressive Cambrian ocean.

During exploration by Flambeau Mining in 1996 for volcanogenic massive sulfide deposits in Trempealeau County, Wisconsin, a weathered profile beneath
the Mount Simon Formation (Upper Cambrian) was recovered in drill core TR119, thus providing an exceptional opportunity to investigate the properties of a sub-Cambrian paleosol. We have examined this paleosol in detail, establishing its depth variation in pedogenic features, mineralogy, and whole-rock chemical compositions; calculating mass fluxes of weathering and K-metasomatism; determining past climate using several paleoclimate functions; and evaluating the degree of weathering. We have applied a similar analysis to three other sub-Cambrian paleosols in North America (Driese et al. 2007) and one in Israel (Sandler et al. 2012) to provide a continental-scale comparison of sub-Cambrian weathering during this important episode of Earth history. Finally, mass fluxes of weathering have been calculated for modern subtropical weathering of a granite (Liu et al. 2016) and for modern temperate weathering of diabase and granite (Bazilevskaya et al. 2012) to provide a comparison of weathering characteristics before and after the advent of land plants.

Locality and Overview of Drill Core TR119

Core TR119 was taken from a drill hole located in Trempealeau County, Wisconsin (44.4438°N, 91.3162°W), which in Cambrian time at 500 Ma was located ~20° south of the equator, as were three other North American sub-Cambrian paleosols (fig. 1). All would have been situated in a wind belt of tropical easterlies (trade winds).

Drilling through the Upper Cambrian siliciclastic Mount Simon Formation reached a nonconformity with gabbro basement at a depth of 93 m, passed through the paleosol for 2.85 m, and continued another 10.4 m in unweathered gabbro. The basal Mount Simon is bimodal in grain size and composition, consisting of subangular to subrounded quartz pebbles and granules in an arkosic sandy matrix. The paleosol progresses downward through Bt (~52 cm), Bts (~95 cm), and Bk/Cr (~112 cm) horizons, below which incipient weathering continues for another ~26 cm, where amphibole is partly replaced by siderite but plagioclase remains unweathered.

The degree (maturity) of weathering and possible effects of K-metasomatism in paleosols may be evaluated by application of the familiar A-C'N-K plot (fig. 2; Nesbitt and Young 1984), in which A, C', N, and K are whole-rock molar quantities of Al2O3, CaO [in silicate], Na2O, and K2O, respectively. The TR119 gabbro protolith, being devoid of K-feldspar, plots along the A-C'/C3N-K join, as does the incipiently weathered sample at a depth of 271 cm, in which
plagioclase remains unweathered. In the remaining weathered profile, plagioclase was completely removed by hydrolysis, and the weathering trend effectively reached the A-apex, with weathered samples consisting of kaolinite + quartz + chlorite + goethite ± siderite.

However, the bulk compositions of all weathered samples, except that at a depth of 271 cm, are displaced significantly from the predicted weathering trend toward the K-apex (fig. 2), signifying appreciable postweathering addition of potassium, which is a common phenomenon in sub-Cambrian paleosols and Cambro-Ordovician siliciclastic sediments in the midcontinent region (Bethke and Marshak 1990; Driese et al. 2007). X-ray diffraction (XRD) analysis (see below) reveals that mixed-layer illite and vermiculite is abundant in samples at depths of 3 and 9 cm and that illite-vermiculite and K-feldspar are abundant in deeper samples in the weathered profile, accounting for the relative enrichment in K2O.

Gabbro Protolith

Texture and Mineralogy. The TR119 protolith is a medium-grained subhedral granular gabbro, consisting largely of subequal amounts of plagioclase and amphibole with a subordinate amount of diopside that is partly replaced by amphibole (fig. 3A). Sample 315.7 is slightly silica saturated, containing a small amount of interstitial quartz (fig. 3B), and sample 314.8 is slightly undersaturated, being devoid of quartz. Although igneous texture is generally preserved, the gabbro has locally been recrystallized under low-grade metamorphic conditions; some grains of igneous amphibole have been replaced by a fine-grained assemblage of actinolite and chlorite (fig. 3A), and plagioclase has been partly replaced by saussurite (a fine-grained mixture of clinzoisite and albite; fig. 3A, 3C). Such low-grade metamorphism is widespread in Paleoproterozoic rhyolite, granite, and diorite in southern Wisconsin, where these rocks contain lower greenschist facies mineral assemblages, but igneous textures are preserved (Medaris et al. 2003).

Selected protolith minerals were analyzed by electron microprobe techniques (table A1; analytical methods are given in the appendix [appendix and tables A1–A5 are available online]). Igneous plagioclase is slightly zoned labradorite, ranging in composition from 66 mol% An in cores to 58% An in rims of grains, with a mean value of 60 mol% An. In contrast, recrystallized plagioclase in saussurite is near endmember albite. Igneous clinopyroxene is diopside, with a Ca:Mg:Fe ratio of 44.9:41.1:13.9 and a magnesium number (100 x Mg/(Mg + FeTotal)) of 74.7.
Igneous amphibole ranges in composition from magnesiohornblende to magnesiohastingsite and is commonly zoned with respect to TiO₂, having TiO₂-rich cores (~2.5 wt%) and TiO₂-poor rims (<0.5 wt%). Recrystallized amphibole is actinolite, which contains ~2.2 wt% Al₂O₃ and <0.1 wt% TiO₂, and has a magnesium number of 72.4. Metamorphic chlorite associated with actinolite is the variety ripidolite (Si₅p₄apfu; Fe Total = 3.6 apfu), with a magnesium number of 61.7. Epidote (clinzoisite) in saussurite originated by recrystallization of labradorite to albite and epidote and ranges in Fe₂O₃ content from ~0.74 to ~0.27 wt%, corresponding to Fe₄⁺ numbers [100 × Fe³⁺/[Fe³⁺ + Al]] of 24.5 and 8.9.

**Bulk-Rock Geochemistry.** Whole-rock chemical analyses of two protolith samples were provided by the GeoAnalytical Laboratory at Washington State University, where major and selected trace element concentrations were measured by X-ray fluorescence spectrometry (table A2; analytical details are given in the appendix). The TR119 protolith is a subalkaline, metaluminous gabbro that contains ~50 wt% SiO₂ and ~15 wt% Al₂O₃. The two analyzed samples are closely comparable in major element concentrations, displaying <10% relative standard deviation among the major elements, but are highly variable with respect to minor and trace elements (table A2). Both samples are close to silica saturation, sample 315.7 is slightly saturated (2.95 wt% normative quartz) and contains a small amount of interstitial quartz (fig. 3B), whereas sample 314.8 is slightly undersaturated (2.5 wt% normative olivine) and is devoid of quartz. Samples 315.7 and 314.8 are both relatively magnesian and undifferentiated, having magnesium numbers of 76.6 and 77.7 and differentiation indices [normative orthoclase + albite + quartz] of 21.8 and 19.0, respectively.

**Paleosol Mineralogy and Micromorphology**

The paleosol consists of pedogenic kaolinite, quartz, chlorite, goethite, and siderite and postweathering, metasomatic illite-vermiculite and K-feldspar. Proportions of these minerals were determined by XRD, and all phases except siderite occur throughout the weathered profile (table A3; fig. 4; see the appendix for details on the XRD method).

Pedogenic horizons for the TR119 paleosol profile have been identified on the basis of micromorphological features observed in thin sections of selected samples (table 1). B horizons show evidence for destruction of primary igneous rock texture and development of pedogenic fabrics in clay-rich materials known as “birefringence fabrics” [b-fabrics], which are characterized by domains of clay particles aligned in parallel extinction patterns in response to periodic wetting and drying (Bullock et al. 1985). Such fabric is now largely defined by postweathering illite-vermiculite but is thought to be inherited from the weathering stage. An additional micromorphological feature is a very fine-grained association of goethite, chlorite, quartz, and postweathering illite-vermiculite, termed “sesquioxides,” in some cases occurring as a pseudomorph after original amphibole. Cryptic features include vermiciform tubular shapes that are 10–15 μm in diameter and 40–50 μm long as well as goethite preserved both as spherules with fine fibrous bristles and filaments and as larger colloform aggregates. Pedogenic siderite occurs toward the base of the weathered profile, below a depth of ~185 cm, as both spherulitic and nonspherulitic crystal masses. The “Cr horizon” refers to saprolite formed from decomposed protolith that retained primary igneous textures, despite extensive mineral alteration.

Two different processes in the weathering of plagioclase and amphibole were responsible for generation of the bulk of the pedogenic minerals (fig. 5A). Kaolinite was produced by the hydrolysis of plagioclase and occurs as aggregates of 10–50 μm grains at the site of former plagioclase (fig. 5B). Amphibole was weathered by a combination of hydrolysis and
oxidation, yielding 10–50-μm grains of closely associated quartz and chlorite at the site of former amphibole [fig. 5C; 5D; see “Discussion” for further explanation]. In contrast to metamorphic chlorite, which is ripidolite in protolith, pedogenic chlorite is pincnochlorite, in which Si increases from 5.8 apfu in most of the weathered profile to 6.2 apfu in the uppermost weathered sample and Fe^{total} decreases from 3.2 to 2.4 apfu [table A4].

Siderite first appears in small amounts in incipiently weathered sample 313.9, where it [along with chlorite] partly replaces amphibole [fig. 6A]. In the weathered profile, siderite is confined to the lower ~100 cm of the section, with abundances of 13% and 20% in samples 312.0 and 313.1, respectively. In sample 313.1, siderite occurs in veins, where it is associated with goethite [fig. 6B], and as dispersed euhedral grains ≤50 μm in diameter [fig. 6D]. In sample 312.0, siderite occurs as 100–300-μm rounded aggregates with small, euhedral grains at the rims of the aggregates [fig. 6C]. In both samples, siderite displays discontinuous, sharp compositional zoning, with a core-to-rim increase of ~5 mol% in siderite and rhodochrosite components and an ~5 mol% decrease in magnetite and calcite components [fig. 6C, 6D; table A4].

All weathered samples except one contain 3–5 wt% very fine-grained goethite, which is widely dispersed in general but is locally concentrated in thin diffuse layers or zones in some samples. An exception to this pattern is sample 309.5, which contains 10 wt% goethite concentrated in thin, discrete, subhorizontal layers and veins; goethite in this sample displays a colloform texture that may be microbial in origin [fig. 7; see “Discussion”].

Some samples in the B horizon contain a distinctive vermiculite feature that resembles the microfossil Siphonophycus [fig. 8], based on compa-
ison with examples provided in Anderson et al. (2017, their fig. 8). The vermiform features have been largely replaced by illite, but they retain well-defined walls composed of organic matter, as revealed by UV fluorescence (not shown here). This feature is interpreted to be microbial in origin (see “Discussion”).

Metasomatic, mixed-layer illite-vermiculite is abundant throughout the weathered profile (10–25 wt%), where it forms mats of extremely small grains dispersed through the samples (fig. 9A, 9B, 9D) and locally replaces kaolinite (fig. 9C). This potassic mixed-layer silicate contains 7.3 apfu of Si [based on a total of 22 apfu of oxygen] and significant quantities of FeO (5.0 wt%) and MgO (2.9 wt%; table A4).

Metasomatic K-feldspar is abundant (13–44 wt%) in the midsection of the weathered profile, but it is less so (5–9 wt%) in the uppermost and lower parts [table A3; fig. 4]. K-feldspar occurs as clusters of rounded grains, ranging in diameter from 20 to 50 μm, that display adularia habit [fig. 9A, 9B]. The feldspar is effectively an end-member potassic phase, containing 0.1 wt% of Na₂O and no CaO [table A4]. Transmission electron microscopy and selected area electron diffraction demonstrate that the K-feldspar has triclinic symmetry [microcline]. The cluster texture of microcline, which is characteristic in the TR119 weathered profile [fig. 9A, 9B], has been produced by potassium metasomatism elsewhere [Pirajno 2009].

Chemical Changes in TR119 Paleosol Relative to Protolith

Evaluation of Immobile Elements. Quantitative estimates of compositional changes during weathering can be obtained by comparing the compositions of
Figure 6. Backscattered electron images of pedogenic siderite. A, Sample 313.9: siderite (s) replacing igneous amphibole (a). B, Sample 313.1: cross-cutting siderite vein (s) associated with locally abundant goethite (g). C, Sample 312.0: colloform siderite with compositional zoning, cores = 80 mol% siderite; rims = 86 mol% siderite. D, Sample 313.1: euhedral siderite. Core and rim compositions are the same as in C.

Figure 7. Goethite in sample 309.5 displaying colloform texture. A, Photomicrograph, plane polarized light. B, Backscattered electron image.
Figure 8. Vermiform features in sample 308.7 that are interpreted to be microfossils, possibly *Siphonophycus* species. **A**, Photomicrograph, plane polarized light. **B**, Backscattered electron image. *f* = feldspar; *i* = illite-vermiculite; *q* = quartz.

weathered and unweathered materials while normalizing to an immobile element [or oxide] by means of the equation

\[
\% \text{ change } = 100 \times \left[ \frac{c_{i,w}/c_{i,p}}{c_{i,w}/c_{i,p}} - 1 \right],
\]

where \( c_{i,w} \) is the concentration of element \( j \) in weathered material, \( c_{i,p} \) is the concentration of element \( j \) in protolith, \( c_{i,w} \) is the concentration of immobile element in weathered material, and \( c_{i,p} \) is the concentration of immobile element in protolith.

Likely candidates as immobile elements during weathering are Al, Ti, Zr, and Nb, although Nb is excluded from consideration here because of its extremely low concentration [0.8 ppm] and high relative standard deviation (141%) in the gabbro protolith. Accurate calculation of compositional changes in a weathered profile depends on the protolith being compositionally homogeneous, and this is not the case for TR119 gabbro, where Al, Ti, Fe, and Zr have relative standard deviations of 5%, 46%, and 38%, respectively. In addition, although the concentrations of Al, Ti, and Zr generally increase upward in the TR119 profile, as they should with removal of labile constituents, there are numerous excursions from a smooth trend that are consistent with the existence of compositional heterogeneities in the protolith (fig. 10).

To correct for the variability of immobile elements due to compositional heterogeneity, linear least squares fits have been determined for the depth variations of Al, Ti, Fe, and Zr in regolith, saprolite, and protolith, as illustrated by the dashed lines in figure 10. Samples at depths of 213 and 247 cm were excluded from the least squares fits due to the presence of siderite and high Fe, Ti, and Zr content (~19 wt%), which effectively dilutes the concentration of other oxides, especially Al. These least squares fits for Al, Ti, Fe, and Zr were applied to each sample, whose concentration sums were then normalized to 100% to generate transformed compositions for use in subsequent calculations (table A5).

After accounting for heterogeneity in the immobile element candidates, the question remains, Which elements are truly immobile? This question may be answered by plotting ratios of Al, Ti, Fe, and Zr with depth, as illustrated in figure 11. The ratio of Al/Ti is effectively constant with depth, but the ratios Zr/Al and Zr/Ti increase upward in the weathered profile, demonstrating that Al and Ti were relatively mobile compared with Zr and were removed to some extent by weathering. Consequently, in this instance Zr is the best choice as an immobile element for calculating percent changes in the paleosol.

**Depth Variation in Composition.** CaO, Na2O, and Sr, whose percent changes approach ~100, were effectively completely removed by weathering, and MgO, Ba, SiO2, and Al2O3 were substantially removed (fig. 12). Although not shown, removal of TiO2 was comparable to that for Al2O3, the integrated changes for the two being ~24% and ~27%, respectively.

Fe2O3 and MnO are strongly partitioned in the profile, being enriched at depths of 213 and 247 cm due to the precipitation of siderite and depleted at levels above this. Integrated percent changes for Fe2O3 and MnO are relatively small, as are mass fluxes, indicating that these two constituents were partitioned but not removed by weathering. Percent changes with depth for P2O5 scatter about a value of zero with a negligible mass flux, indicating that P2O5, like Fe2O3 and MnO, was partitioned within but not removed from the profile.

Potassium [K2OMEAS] was added throughout the weathered profile, as predicted by the A-C’-N-K plot (fig. 2), and Rb was added as well. The extremely large values of change, 1000%–2000% for K2OMEAS and 500% for Rb, originate from their low concentrations in protolith, 0.32 wt% and 7 ppm, respectively, compared with their concentrations in the paleosol (table A5). The pretreatment percent change in potassium [K2OCALC] due to weathering can be calculated by judicious application of the A-C’-N-K plot, the method for which is described by Medaris et al. (2015). Following that method, K2O is seen to have been substantially removed by weathering, with an integrated change of ~67% (fig. 12). However, this procedure provides only a minimum value for the integrated percent removal of K2O due to weathering, the value of which is controlled by the position of protolith and weathered sample in the A-C’-N-K plot—that is, the more potassic the protolith, the smaller the calculated percent removal of K2O. Alternatively, an estimate of the maximum integrated percent removal of K2O due to weathering [K2OEST] may be obtained by assigning the percent change of K2O through the weathered profile as equal to that for Na2O. The minimum [K2OCALC] and maximum [K2OEST] percent removals for K2O integrated over the TR119 weathered profile are ~67.1% and ~90.2%, respectively.

**Mass Fluxes**

The mass flux (removal or addition) of material in a weathered profile can be calculated from the equation

\[
m_i = \rho \int_{Z_{i,w}}^{Z} \tau_{i,w} dZ,
\]
where $m_j$ is the mass flux of constituent $j$, $\rho_p$ is the density of the protolith, $c_{j,p}$ is the concentration of constituent $j$ in the protolith, and $\tau_{j,w}$ is the transfer (percent change) of constituent $j$ in the weathered profile integrated over the depth of weathering, $Z$ (Chadwick et al. 1990).

Mass fluxes for the TR119 weathered profile have been calculated accordingly, using the transformed compositions of regolith, saprolite, and average protolith. Total mass flux for the weathered profile is $-6.0 \text{ mol cm}^{-2}$ (table 2), and mass fluxes for individual oxides are included in figure 12. Mass fluxes for individual oxides depend to a large extent on their protolith concentrations; for example, SiO$_2$ is the most abundant oxide in the protolith (50 wt%) and accounts for the greatest mass flux ($-2.7 \text{ mol cm}^{-2}$).

**Figure 10.** Depth variation in Al$_2$O$_3$, TiO$_2$, and Zr concentrations in regolith and saprolite (circles) and in protolith (squares). Dashed lines are linear least squares fits to all data except for samples at depths of 213 and 247 cm (see text for explanation). Relative standard deviations for the three constituents in protolith are given in the insets.

**Figure 11.** Depth variation in ratios of Al$_2$O$_3$, TiO$_2$, and Zr in regolith and saprolite (circles) and in protolith (squares). Dashed lines are linear least squares fits to all data except for samples at depths of 213 and 247 cm (see text for explanation).
in the total, while CaO, which exhibits a greater percent change in the profile than does SiO₂ (fig. 12), contributes less mass flux [−1.5 mol cm⁻²] due to its smaller concentration [11.6 wt%] in the protolith.

Oxides that exhibit negative percent changes through the profile and have small concentrations in the protolith necessarily yield small negative mass fluxes. Such is the case for potassium [K₂Oₙ₉₉₉₀ = 0.32 wt%], with mass fluxes for K₂O₉₉₉₀ and K₂O₀₉₉₀ being −0.018 and −0.024 mol cm⁻², respectively. Although Fe₂O₃ is relatively abundant in the protolith [8.5 wt%], its mass flux is only −0.07 mol cm⁻², which indicates that iron was retained overall in the paleosol during weathering despite partitioning in the profile.

Values of mass flux would be more intuitively meaningful if expressed in terms other than moles per square centimeter. For example, mass flux may be expressed as percentage of mass removed (%MR), which is defined as

\[
\%MR = 100 \times \frac{\text{mass removed}}{\text{complete mass removal}}
\]

where “mass removed” for an oxide is its calculated mass removed from a weathered profile and “complete mass removal” for that oxide is its mass removed for a transfer, \( \tau_{\text{tot}} \), of 100% throughout the profile. Resulting values of %MR for the TR119 profile are as follows: Na₂O, 90.2; CaO, 89.7; MgO,
<table>
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<tr>
<th>Weathered profile</th>
<th>Location</th>
<th>Protolith</th>
<th>Minimum age of weathering</th>
<th>Depth of weathering, mean ± SE [cm]</th>
<th>CIA*</th>
<th>FIW*</th>
<th>CDF</th>
<th>TMF [mol cm⁻²]</th>
<th>%MR*</th>
<th>RMF [10³ × mol cm⁻³]</th>
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<td>Gabbro</td>
<td>Late Cambrian</td>
<td>285 ± 14</td>
<td>97 ≤CIA≤CALC</td>
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<td>50.0, 50.1</td>
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Note. %MR = percentage of mass removed; CDF = chemical depletion fraction (cf. Zr, except Ti for Squaw Creek and Piedmont); FIW = feldspar index of weathering; RMF = reduced mass flux; TMF = total mass flux.

* Chemical index of alteration [CIA], either calculated [CIA≤CALC] or measured [CIA≤MEAS].

Maximum and minimum values for FIW, TMF, %MR, and RMF in K-metasomatized profiles.

¹ Driese et al. (2007).
² Sandler et al. (2012).
³ Liu et al. (2016).
⁴ Pavich et al. (1989).
67.2% K₂O, 67.1% SiO₂, 40.6% and Al₂O₃ 27.1%. Total %MR is simply the sum of calculated mass fluxes for all of the oxides divided by the sum of their mass fluxes, taking τ₁o,w to be 100% for each oxide throughout the profile. The total %MR for the TR119 profile is 50.0, that is, one-half of the protolith mass was removed by weathering. Note, however, that %MR is a relative quantity and that total mass flux is an absolute quantity [see “Discussion”].

**Paleoclimate Functions and Atmospheric P CO₂**

Empirical relations among bulk geochemistry, weathering, and climate of modern soils have been used to develop paleoclimate proxies [a.k.a. climofunctions] and soil characterization proxies [e.g., pH] that allow for interpretations of past climate and soil-forming conditions (Sheldon and Tabor 2009; Lukens et al., forthcoming). However, accurate application of such functions requires that properties of the paleosol in question lie within the range of properties of modern soils on which the climofunctions and characterization proxies are based. The most obvious failure of this requirement is that sub-Cambrian paleosols lacked a vegetative cover, although organic ligands may have been provided by microbial activity. With this caveat in mind and in lieu of acceptable alternatives, proxies developed by Sheldon et al. (2002), Sheldon (2006a), and Stinchcomb et al. (2016) were used to estimate mean annual precipitation [MAP] and mean annual temperature [MAT], and a calibration by Lukens et al. [forthcoming] was used to estimate pH, a master soil variable where water availability is a first-order control (Slessarev et al. 2016). The model developed by Stinchcomb et al. (2016), PPM₁₀, was modified to exclude the element Zr from the analysis, as not all paleosols studied had reported Zr. The PPM without Zr (PPM₁₀) was compared with the original PPM [PPM₁₀], demonstrating that the exclusion of Zr does little to affect the model results [G. E. Stinchcomb, L. C. Nordt, S. G. Driese, W. E. Lukens, and D. J. Peppe, unpub. manuscript]. The residual errors between models are similar, and the root mean squared errors for PPM₁₀, MAP = 223 mm and MAT = 2.52°C, are comparable to those for PPM₁₀, MAP = 228 mm and MAT = 2.46°C.

**Mean Annual Precipitation.** The two uppermost TR119 paleosol samples were selected for application of MAP estimates because the upper part of the profile has characteristics most appropriate for comparison with B horizons of the modern soils used to develop the PPM model (Stinchcomb et al. 2016). Estimates of MAP [Sheldon et al. 2002] and MAPₐ [Stinchcomb et al. 2016], based on the average of the two uppermost paleosol samples, are 1509 and 1777 mm y⁻¹, respectively, which are within error of each other (table 3).

**Mean Annual Temperature.** MAT was estimated by the PPM model of Stinchcomb et al. (2016) and the MATₐ calibration of Sheldon (2006a), which is defined as

\[ \text{MAT}_{\text{a}}{^\circ C} = 46.94C + 3.99, \]

where \( C = \text{mAl}_2\text{O}_3/\text{mSiO}_2 \).

MATₐ for the TR119 paleosol is 20.1°C, which is somewhat higher than the MATₐ value of 16.7°C (table 3). It is worth noting that both MAT estimates are within error of present-day subtropical temperatures.

**pH.** A regression-based bulk geochemical transfer function, AlCa, was developed by Lukens et al. [forthcoming] for estimating the paleo-pH of B horizons of paleosols and is defined as

\[ \text{AlCa} = 100 \times [\text{Al}_2\text{O}_3/\text{[Al}_2\text{O}_3 + \text{CaO}]]. \]

<table>
<thead>
<tr>
<th>Weathered profile</th>
<th>MAP_{\text{CIA-R}} [mm y⁻¹]</th>
<th>MAP_{\text{PPM₁₀}} [mm y⁻¹]</th>
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</table>

Note. MAP = mean annual precipitation; MAT = mean annual temperature.

* After Sheldon et al. (2002), SE = 181 mm y⁻¹.
* After Stinchcomb et al. (2016).
* After Sheldon (2006a), SE = 0.6°C.
* After Lukens et al. [forthcoming], Root mean squared error = 0.83.
* Formation time for atmospheric \( \text{CO}_2 = 5000 \) ppm.
* Driese et al. (2007).
* Sandler et al. (2012).
Regression of second- and third-order polynomial fits of modern soil pH (n = 619) versus AlCa pH yields $R^2$ values of 0.66 and 0.67, respectively, and root mean square errors of 0.86 and 0.84, respectively.

For the upper two paleosol samples, the average pH value is 5.2 (table 3), which is consistent with advanced acid attack on aluminosilicate minerals and the absence of plagioclase and amphibole from the weathered profile. This pH value is maintained within error through the profile to lower depths, where it increases to more basic values of 6.1 and 6.5 at depths of 213 and 247 cm, respectively, which are compatible with the occurrence of siderite at these depths. Such inferred acidic conditions in the upper part of the profile also suggest a net surplus in available moisture, which is consistent with our MAP reconstructions.

Atmospheric $P_{\text{CO}_2}$: Sheldon (2006b) proposed a thermodynamic model for estimating paleoatmospheric $\text{CO}_2$ levels from the mass balance of paleosol weathering. The essential equation is

$$M/t \approx P_{\text{CO}_2}[(K_{\text{CO}_2}, r)/10^3 + \alpha D_{\text{CO}_2}, \alpha/L],$$

where $M/t$ is the time-averaged flux of CO$_2$ required for the observed weathering [mol cm$^{-2}$ y$^{-1}$], $P_{\text{CO}_2}$ is the partial pressure of atmospheric CO$_2$ [atm], $K_{\text{CO}_2}$ is the Henry’s law constant for CO$_2$, $r$ is precipitation [cm y$^{-1}$], $\alpha$ is a constant [1.43 x 10$^8$ cm$^3$ mol$^{-1}$ y$^{-1}$], $D_{\text{CO}_2}$ is the diffusion constant for CO$_2$ in air [0.162 cm$^2$ s$^{-1}$], $\alpha$ is the ratio of the diffusion constant for CO$_2$ in soil divided by that in air, and $L$ is the depth to the water table [cm].

During silicate weathering, 2 mol of CO$_2$ are required for the liberation of 1 mol of the base cations, Mg, Ca, Na, and K. Although Si is not considered in Sheldon’s model, it has been included here because 41% SiO$_2$ has been removed from the TR119 paleosol. In contrast to the MO oxides, 4 mol of CO$_2$ is required for the removal of 1 mol of SiO$_2$. In the TR119 profile, the mass flux removal of MgO, CaO, Na$_2$O, and K$_2$O$_{\text{calc}}$ is a total of 2.9 mol cm$^{-2}$, which requires a CO$_2$ flux of 5.8 mol cm$^{-2}$ to account for the observed magnitude of weathering. When SiO$_2$ is included, these values increase to 5.6 and 16.6 mol cm$^{-2}$, respectively. The effect of including the mass flux of SiO$_2$ is to increase the calculated $P_{\text{CO}_2}$ value by a factor of 2.8, as illustrated in figure 13A.

In calculating $P_{\text{CO}_2}$, depth to the water table ($L$) is a significant parameter, but its former position in the TR119 profile is uncertain. Siderite formation is intricately linked to depth to the water table; most models of pedogenic siderite formation and observations of pedogenic siderite in paleosols indicate that siderite formation requires saturated conditions, along with reducing conditions and available organic matter [Driese et al. 2010; Ludvigson et al. 2013]. This can be achieved by either endosaturation (saturation achieved by rising water table from below) or episaturation (saturation achieved by water table perched on top of paleosol). In this instance, there is no evidence for gley (low-redox) conditions in the upper part of the paleosol, so an endosaturation scenario makes more sense. During siderite precipitation, the water table in the TR119 profile must have been relatively high, certainly higher than the saprolite/protolith interface at 285 cm and, conservatively, at a depth as shallow as the top of the siderite zone at 185 cm. Raising the depth of the water table from 285 to 185 cm decreases the value of $P_{\text{CO}_2}$ by a factor of 1.5 (fig. 13B).

Among variables in the equation, the parameter $T$ (formation time) is the most uncertain and has a large influence on the magnitude of calculated $P_{\text{CO}_2}$; a factor of 10 difference in time yields a factor of 10 difference in calculated $P_{\text{CO}_2}$. However, this strong dependence of calculated $P_{\text{CO}_2}$ on time can be turned into an advantage because if the level of atmospheric CO$_2$ during weathering is known, then the time of weathering can be estimated. According to the GECOCARIII model of Berner and Kothavala (2001), the concentration of CO$_2$ in the atmosphere at 550–500 Ma was between 4000 and 6000 ppm, corresponding to values of 14.4 and 21.5 x PIAL, respectively, where PIAL refers to a preindustrial atmospheric level of 280 ppm. These levels of CO$_2$ constrain weathering times to between 32,000 and 21,000 y for a water table depth of 185 cm (fig. 13B). These values are minima, however, because an unknown portion of the weathered profile may have been removed by erosion. For example, if 50% of the paleosol were eroded, the time of weathering would have been between ~200,000 and ~140,000 y (fig. 13B).

Comparison of Weathering Parameters in Sub-Cambrian Paleosols

To evaluate weathering and climatic conditions in Cambrian time during formation of the Great Unconformity, properties of the TR119 paleosol are compared with those of three other sub-Cambrian paleosols in North America [Driese et al. 2007] and one in Israel [Sandler et al. 2012], including SQ8 (drill core beneath Upper Cambrian Mount Simon Sandstone, southeastern Minnesota), Butler Hill (drill core beneath Upper Cambrian Lamotte Sandstone, southeastern Missouri), Squaw Creek (an outcrop beneath Middle Cambrian Hickory Sandstone, central Texas), and Timna (outcrop beneath Lower Cam-
Transformed whole-rock compositions and values of $K_2O_{\text{CALC}}$ were generated for these four paleosols following the procedure described for TR119, and their resultant salient properties are summarized in table 2. Note that the profile at the Squaw Creek locality escaped K-metasomatism, whereas the other three were metasomatized. In addition, Zr analyses are unavailable for the Squaw Creek profile, so TiO$_2$ was used as the immobile normalizing oxide in this instance. A sub-Cambrian paleosol in South Dakota that developed from a metagabbro protolith (Hordyskyj et al. 2012) was not included for comparison because it experienced Mg- and Ca-metasomatism in addition to K-metasomatism, which precludes an accurate assessment of weathering parameters. Numerous methods have been proposed to evaluate the degree, or maturity, of chemical weathering, including the chemical index of alteration (CIA; Nesbitt and Young 1982), the chemical depletion fraction (CDF; Riebe et al. 2003), the feldspar index

$$s = f_{\text{climate}}(u,t,\ldots),$$

where $s$ varies as a function of climate with other factors being held constant. The term $u$ is an uncertainty factor, recognizing that factors assumed to be constant actually vary.

The paleosols compared here are similar in being overlain by flat-lying, fluvial, or shallow-marine sandstones and thus formed under subdued paleotopography. They are also similar in having formed prior to the advent of land plants in Ordovician time, and organic ligands involved in chemical weathering were derived from microbial activity and simple plant forms, such as algae, rather than more complex plant forms. The major difference among the paleosols is protolith lithology, which varies from gabbro to alkali feldspar granite. They also differ in the minimum age of weathering, which ranges from Late Cambrian to Early Cambrian.

Comparison of the paleosols is based on the fundamental state-factor theory of soils (Jenny 1941, 1980):

$$S \text{ or } s = f(\text{cl, o, r, p, t, \ldots}),$$

where $S$ is soil, $s$ is some soil property, $\text{cl}$ is climate, $o$ is organisms, $r$ is relief, $p$ is parent material, and $t$ is time. The ellipsis represents other possible factors unaccounted for that influence $S$. A property $s$ can

**Figure 13.** Cross plots of $\text{PCO}_2 \times \text{PIAL}$ and formation time of weathering, calculated following Sheldon (2006b). Note the differences in scale for the two panels. A, Comparison of results between including the mass flux of SiO$_2$ in the calculation and excluding it. Both are for a water table depth ($L$) of 185 cm. B, Comparison of results illustrating the effect of groundwater table depth ($L$) at 185 and 285 cm and the effect of 30% and 50% erosion. All calculations include the mass flux of SiO$_2$ and levels of atmospheric $\text{PCO}_2$ (4000 and 6000 ppm) at 550–500 Ma from the GEOCARBIII model of Berner and Kothavala (2001). The stippled area constrains the estimated range in formation time of weathering for the TR119 paleosol.
of weathering (FIW; Medaris et al. 2015), and reduced mass flux (RMF; Medaris et al. 2017). In weathered profiles, one can distinguish between absolute and relative degrees of weathering, where absolute values are given by an element ratio for an individual weathered sample and relative values are given by mass fluxes averaged over an entire weathered profile; among the four functions considered here, CIA and CDF are absolute measures of weathering, and FIW and RMF are relative measures of weathering.

Chemical Index of Alteration. The chemical maturity of weathering may be evaluated quantitatively by means of the CIA (Nesbitt and Young 1982), which is defined as

\[
\text{CIA} = \text{molar} \left( \frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}} \right) \times 100.
\]

A CIA value of 100 corresponds to the end stage of chemical weathering, in which CaO*, Na2O, and K2O are completely removed from the paleosol. Direct calculation of CIA in K-metasomatized samples, however, yields spurious values due to displacement of whole-rock compositions from the predicted weathering trend by the addition of potassium. The effect of K-metasomatism may be corrected by projecting a line from the K-apex through a metasomatized sample to an intersection with the predicted weathering trend to yield a premetasomatic, calculated CIA value \(\text{CIA}_{\text{calc}}\) (Fedo et al. 1995). However, the ultimate value for CIA_{calc} in a weathered profile is controlled by protolith composition and intersection of its predicted weathering trend with the A-K join in the A-C’N-K diagram—that is, the higher the protolith K2O content, the lower the limiting value of CIA_{calc}.

The Squaw Creek paleosol, which is not metasomatized, yields a measured CIA value of 98 (table 2), which reflects complete removal of plagioclase and K-feldspar in the upper part of the profile. TR119, whose gabbroic protolith is devoid of K-feldspar and plots very close to the A-C’N join (fig. 2), yields a CIA_{calc} value of 97, consistent with complete removal of plagioclase throughout the profile. Values of CIA_{calc} for the other three paleosols are 70, 87, and 90 (table 2), which are directly correlated \(R^2 = 0.97\) with their protolith K2O concentrations. Although K-feldspar remains at depth in these three profiles, it was removed from the uppermost levels, and the metasomatic CIA values were most likely ≥95.

Supermature quartz arenites are a conspicuous feature of Cambrian sedimentary rocks in the North American interior and the Arabian-Nubian Shield, resulting from vigorous physical reworking coupled with advanced sub-Cambrian chemical weathering enhanced by subaerial microbial mats and soil crust (Dott 2003). However, K-feldspar is an abundant constituent in silty fractions of the Cambrian sedimentary sequences, revealing its persistence in source regions for Cambrian detritus (Odom 1975; Odom et al. 1976).

Chemical Depletion Fraction. For a soil undergoing steady-state formation, erosion, and weathering, total denudation flux is equal to the sum of chemical weathering flux and physical erosion flux. The function CDF was introduced by Riebe et al. (2003) to express the relation between chemical weathering flux, total denudation flux, and the ratio of an immobile element in soil and protolith, as follows:

\[
\text{CDF} = \left( 1 - \frac{[X]_{\text{protolith}}}{[X]_{\text{soil}}} \right) = \frac{W}{D},
\]

where \(X\) is the concentration of an immobile element, \(W\) is the chemical weathering flux, and \(D\) is the total denudation flux. Although this equation was derived to evaluate the chemical removal rates of CaO, Na2O, and K2O, it can also be used as an estimate of the degree of chemical weathering because CDF values increase as labile elements are removed by weathering and concentrations of immobile elements correspondingly increase.

CDF values for the four granitic paleosols are comparable, 0.32–0.38, but that for TR119 is much larger, 0.61 (table 2), reflecting a greater relative chemical weathering flux and degree of weathering of TR119 gabbro compared with weathering of granitic rocks in the other paleosols.

Feldspar Index of Weathering. Because plagioclase and potassium feldspar are abundant phases in most common igneous rocks (~50–80 vol%), the amount of feldspar removed from paleosols is a good measure of the overall degree of weathering. Accordingly, to evaluate the relative removal of feldspar in a weathered profile, Medaris et al. (2015) introduced the parameter FIW, which is defined as follows:

\[
\text{FIW} = 100 \times \frac{\text{MF}_{\text{CNK}}}{\text{MF}_{100}},
\]

where \(\text{MF}_{\text{CNK}}\) is the mass flux of CaO, Na2O, and K2O removed from a paleosol, either measured directly in unmetasomatized paleosol or calculated in K-metasomatized paleosol, and \(\text{MF}_{100}\) is the mass flux calculated for complete removal of CaO, Na2O, and K2O over an entire weathered profile—that is, complete removal of both plagioclase and K-feldspar.
Although the extent of feldspar removal from individual samples is effectively illustrated by a CIA plot, the FIW has the advantage of quantitatively evaluating the removal of feldspar over an entire paleoweathering profile. FIW values range from 0 in unweathered protolith to $>90$ in mature paleosols. FIW values never reach 100 because even though feldspar may be completely removed from the upper levels of mature paleosols, some feldspar commonly remains at deeper levels. In addition, even in paleosol domains from which feldspar has been completely removed, small amounts of CaO, Na$_2$O, and K$_2$O remain (on the order of 1 wt% total).

The minimum and maximum FIW values for TR119, whose protolith is devoid of K-feldspar, are 89.5 and 89.8, respectively (table 2), indicating that plagioclase was removed by weathering through most of the paleosol, as illustrated by the depth distribution of CaO and Na$_2$O in the weathered profile (fig. 12). Similar plots (not shown) for the other four granitic paleosols reveal that plagioclase was largely removed through the profiles in each. In contrast to plagioclase, significant amounts of K-feldspar remain at depth. The FIW value for the unmetasomatized Squaw Creek paleosol is 79, and minimum and maximum FIW values for the other three metasomatized granitic paleosols are 48 and 83, 62 and 72, and 73 and 76. The different ranges and averages of FIW values for the three metasomatized paleosols reflect the different K$_2$O contents of their granitic protoliths and represent not different magnitudes of weathering but rather different protolith compositions.

**Reduced Mass Flux.** In a given catchment basin, depths of weathering and total mass fluxes vary with topographic position, that is, being different on ridge lines, hill slopes, and valley floors (Bazilevskaya et al. 2012). Thus, direct comparison of total mass fluxes is useless for distinguishing different degrees of chemical weathering among paleosols that may have formed at different topographic positions from different protoliths. However, mass flux can be used as a basis for comparison by dividing total mass flux (mol cm$^{-2}$) by depth of weathering (cm) to provide an average mass flux (mol cm$^{-2}$ cm$^{-1}$) over the depth of weathering, which is designated as the RMF (Medaris et al. 2017):

$$\text{RMF} = 1000 \times \frac{\text{total mass flux}}{\text{depth of weathering}},$$

where the factor 1000 is introduced for convenience of scale.

The RMF values are $-21.1$ for TR119, $-11.6$ for the unmetasomatized Squaw Creek paleosol, and $-5.0$, $-9.4$, and $-9.6$ for the other three paleosols (table 2).

**K-metasomatism.** As was done for TR119 (fig. 12), the depth variations of K$_2$O$_{\text{MEAS}}$ and K$_2$O$_{\text{CALC}}$ were determined for the three metasomatized granitic paleosols, and the total mass flux of K$_2$O added to each of the four metasomatized profiles has been calculated (table 2). Remarkably, the total mass fluxes of K$_2$O for the three metasomatized North American paleosols are essentially the same (0.30–0.33 mol cm$^{-2}$) regardless of protolith composition. In contrast, the mass flux of K$_2$O for the Timna paleosol in Israel is twice as large, at 0.68 mol cm$^{-2}$, but note that the preserved depth of weathering for the Timna paleosol is also approximately twice that of the others.

**Discussion**

**Pedogenic Minerals.** A remarkable feature of the TR119 paleosol is the abundance of quartz (11%–23%, table 3) when little quartz occurs in the gabbro protolith and 40% SiO$_2$ was removed from the weathered profile ($-2.7$ mol cm$^{-2}$; fig. 12). This apparently anomalous situation arises from weathering of amphibole, the reaction for which is expressed qualitatively as

$$\text{amphibole} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{quartz} + \text{chlorite} + \text{goethite} + \text{Mg}^{2+} + \text{Ca}^{2+} + \text{Na}^+ + \text{K}^+ + \text{HCO}_3^-,\,$$

where SiO$_2$ is precipitated as quartz rather than being removed in solution, as in the case for hydrolysis of feldspar. The labile elements in amphibole, Ca, Na, and K, are removed in solution, as is some Mg, with the remaining Mg being transferred to chlorite. Through the entire profile, the mass flux of MgO is $-1.2$ mol cm$^{-2}$ (fig. 12), which corresponds to 67% bulk removal. Iron is both precipitated as goethite and incorporated in chlorite rather than being removed from the profile, which is consistent with its negligible total mass flux, $-0.07$ cm$^{-2}$ (fig. 12).

The stability fields for quartz, Fe-chlorite, and goethite in terms of Eh and pH in the system, Fe-Al-Si-O-H, were calculated by means of the Geochemist’s Workbench (GWB 11) software package with the thermos database. Figure 14 was generated using the following input parameters: $T = 20^\circ$C, $P_{\text{Total}} = 1$ atm, $\alpha(\text{Fe}) = 10^{-4} \text{M}$, $\alpha(\text{Al}) = 10^{-3} \text{M}$, and $\alpha(\text{Si}) = 2 \times 10^{-4} \text{M}$ (note that quartz is stable in the system at $\alpha(\text{Si}) \geq 1.58 \times 10^{-4} \text{M}$). These parameters were chosen when considering the mineral assemblage of the paleosol and potential surface water.
conditions, following Driscoll (1985) and Lee and Wilkin (2010). Quartz is in equilibrium with goethite and Fe-chlorite at $\text{Eh} \approx 0.1 \text{ V}$ and $\text{pH} \approx 5.6$. This latter value is in good agreement with the estimated pH (5.2) determined by the method of Lukens et al. (forthcoming).

The stability range of siderite was evaluated by adding C to the system, using the input parameters above, and setting $a(\text{HCO}_3^-) = 10^{-5} \text{ M}$ (fig. 14). Siderite is in equilibrium with quartz, goethite, and Fe-chlorite at $\text{Eh} \approx 0.1 \text{ V}$ and $\text{pH} \approx 6.0$. As expected, this pH value is greater than that for the siderite-free assemblage, and it is in good agreement with the pH range (6.1–6.5) estimated for the siderite-bearing samples by the method of Lukens et al. (forthcoming). Note that allowing for a variation in $a(\text{Al})$ between $10^{-4}$ and $10^{-6} \text{ M}$ yields an even closer correspondence between the pH values calculated here and those determined by the method of Lukens et al. (forthcoming).

Triangular plots of Si-Fe$_\text{Total}$-Al and Si-Mg-Al (fig. 15) illustrate the topological relations among amphibole, quartz, chlorite, and goethite and allow proportions of pedogenic phases to be estimated through application of the lever rule. In the Fe-bearing system the proportion of quartz to goethite is 48:47:5, and in the Mg-bearing system the proportion of quartz to chlorite to Mg is 40:52:8, with 8% Mg being removed in solution.

The weathering of plagioclase was responsible for precipitation of kaolinite and loss of SiO$_2$ in the form of soluble silicic acid, according to the reaction

$$\text{plagioclase + H}_2\text{O + CO}_2 \rightarrow \text{kaolinite + Ca}^{2+} + \text{Na}^+ + \text{HCO}_3^- + \text{H}_4\text{SiO}_4,$$

which resulted in a total loss of 40% SiO$_2$ from the profile. The paradox originating from the bulk removal of SiO$_2$ and concurrent precipitation of pedogenic quartz is resolved by recognizing that pedogenic quartz was produced by the weathering of hornblende while SiO$_2$ was removed in solution in the form of silicic acid due to hydrolysis of plagioclase, resulting in a net negative mass flux of SiO$_2$ in the profile.

**Mass Flux of Weathering.** To provide perspective on the degree of sub-Cambrian weathering and the influence of protolith composition, we compared mass flux parameters of the investigated sub-Cambrian paleosols, which formed at $\sim 207^\circ$ paleolatitude, and three modern weathered profiles (table 2), one of which formed from monzogranite in a subtropical setting in China (latitude, 25°N; Liu et al. 2016) and two of which formed from diabase and syenogranite in a temperate climate in the Piedmont of Virginia (latitude, 39°N; Bazilevskaya et al. 2012). Because plagioclase is more susceptible to weathering than K-feldspar and quartz, one would expect to find greater depths and total mass fluxes of weathering in mafic rocks than felsic rocks. However, the reverse is found in modern weathered profiles worldwide, and
in the Piedmont syenogranite exhibits a greater depth of weathering and total mass flux than diabase (2050 cm and $26.8 \text{ mol cm}^{-2}$ vs. 95 cm and $2.4 \text{ mol cm}^{-2}$, respectively; table 2; Bazilevskaya et al. 2012). This phenomenon is attributed to differences in the distribution and densities of micron-sized pores and microfractures that control fluid ingress in the two types of protolith.

Thus, it appears that physical properties of protolith may override the influence of mineral composition with respect to depth of weathering and total mass flux. Indeed, depths of weathering and total mass fluxes in the five sub-Cambrian paleosols and three modern weathered profiles are not correlated with composition, regardless of the choice of compositional parameter, such as mineral modes, weight percent oxides, or normative differentiation index. Direct comparison of depths of weathering and total mass fluxes among sub-Cambrian paleosols and those in modern profiles (table 2) is problematic because of the likely removal of some portions of the sub-Cambrian profiles by erosion. Although depths of weathering and total mass fluxes of sub-Cambrian profiles derived from felsic protoliths are less than those in the modern profiles, the depth of weathering and total mass flux for the TR119 gabbro are significantly greater than those for the Piedmont diabase (285 cm and $-6.0 \text{ mol cm}^{-2}$ vs. 95 cm and $-2.4 \text{ mol cm}^{-2}$) despite the possibility that some portion of the TR119 paleosol may have been removed by erosion.

Although protolith composition is not correlated with the absolute parameters, depth of weathering and total mass flux, it is correlated with the relative parameters, RMF and %MR. As illustrated in figure 16, there is a perfect correlation between RMF and %MF, which is not surprising because both are functions of total mass flux. The utility of this cross plot is the demonstration that both RMF and %MR increase from felsic to mafic protolith compositions (compare the results for the most felsic protolith, Butler Hill granite, with those for the two most mafic protoliths, TR119 gabbro and Piedmont diabase). The effects of possible erosion on values of RMF and %MR are shown for the two extreme sub-Cambrian protolith compositions, Butler Hill and TR119, which are calculated for 50% erosion.

The correlation of protolith compositions with relative weathering parameters is further illustrated in figure 17, where RMF and %MR are plotted against the differentiation index, which is the sum of normative quartz, orthoclase, and albite in protolith. For the three modern profiles, values of $R^2$ for RMF and %MF are 0.99 and 0.97, respectively, although these high values are dictated by the large gap in data points. For the sub-Cambrian paleosols, values of $R^2$ for RMF and %MR are 0.78 and 0.79, respectively, but some of the scatter in these data undoubtedly arises from some unknown degree of erosion of the profiles. Assuming 50% erosion of each of the sub-Cambrian profiles, values of $R^2$ for both RMF and

\[ \text{Figure 15. Molar plots of mineral compositions in the TR119 paleosol. A, Molar plot of Si-Fe_{Total}-Al. In this compositional space, igneous amphibole weathers to a pedogenic assemblage of quartz (48%), chlorite (47%), and goethite (5%). B, Molar plot of Si-Mg-Al. In this compositional space, amphibole weathers to an assemblage of quartz (40%) and chlorite (52%), and 8% Mg is removed in solution. Am = amphibole; Chl = chlorite; Qtz = quartz.} \]
%MR increase to 0.88, and the resulting least squares fits are in close agreement with those for the modern profiles. Thus, in terms of RMF and %MR, the relative degree of weathering in the sub-Cambrian paleosols is comparable to that in modern soils in subtropical to temperate settings. Such correspondence may originate from a fortuitous combination of an elevated level of atmospheric CO₂ ([15–20 × PIAL]) and a reduced influence of organic ligands (absence of vegetative cover) in the sub-Cambrian paleosols compared with that in modern soils.

Although Fe is partitioned with depth in the TR119 (fig. 12), Butler Hill, Squaw Creek, and Timna profiles, its total mass flux in each is negligible. The negligible mass flux for Fe in the TR119 profile is similar to that calculated for the 1700 Ma Baraboo profile in south-central Wisconsin, for which variations in percent changes of Fe with depth are attributed to activities of various microbes utilizing either reduction or oxidation reactions as part of their metabolism (Medaris et al. 2017). In contrast, Fe was substantially removed (71%) from the existing SQ8 profile, but the preserved thickness of this profile is relatively small for a felsic protolith (230 cm), and it is possible that erosion destroyed what may have been an original partitioned distribution of Fe.

Phosphorus net flux in TR119 is likewise very small, and P is partitioned with depth (fig. 12), although not coinciding with Fe partitioning. Phosphorus distribution in the Timna profile is the most unusual among the studied profiles, with extensive net gains in the upper 150 cm that resemble the ef-

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**Figure 16.** Cross plot of averages of reduced mass flux (RMF) and percentage of mass removed (%MR) in sub-Cambrian paleosols and the Longnan and Piedmont modern weathered profiles. White circles show observed values for sub-Cambrian paleosols, and gray circles show values prior to 50% erosion for Butler Hill and TR119. RMF and %MR values for the modern Longnan and Piedmont weathered profiles are indicated by square and diamond symbols, respectively.

**Figure 17.** Cross plots of averages of reduced mass flux (RMF) and percentage of mass removed (%MR) in sub-Cambrian paleosols versus differentiation index in protoliths. White circles show observed values for sub-Cambrian paleosols, and gray circles show values prior to 50% erosion for sub-Cambrian paleosols. RMF and %MR values for the modern Longnan and Piedmont weathered profiles are indicated by square and diamond symbols, respectively.
fects of P bioconcentration in modern weathered profiles (not shown). Horodyskyj et al. (2012) found geochemical evidence for P biocycling by mycorrhizal fungi in the upper 30 cm of a 3-m-thick red paleosol profile, the Elk Point paleosol (overlain by the Mount Simon Sandstone of Middle Cambrian age), formed on 1.73 Ga metagabbro in South Dakota. However, because minerals containing P are commonly variably distributed in protoliths, bulk geochemical analyses for P can be sample biased, and this may explain the noise observed for P in many of the profiles examined.

**Metasomatism.** Potassium metasomatism is a common phenomenon in sub-Cambrian paleosols and Cambro-Ordovician sedimentary rocks in the midcontinent region of North America, and such metasomatism has been attributed to continental-scale brine migration related to the Pennsylvanian-Permian Allegheny and Ouachita orogenies (Bethke and Marshak 1990, Fedo et al. 1995). In the TR119 drill core, evidence for metasomatism is provided by K-feldspar overgrowths on silt-size detrital K-feldspar in the Mount Simon Sandstone and an abundance of fine-grained illite-vermiculite (10%–25%) and K-feldspar (5%–44%) in the weathered profile (table A3; figs. 4, 9). The age of K-metasomatism in drill core TR119 is yet to be determined, due to the analytical difficulties in dating the extremely fine-grained associated potassic phases, illite and K-feldspar. However, Liu et al. (2003) obtained 40Ar/39Ar ages for different textural varieties of metasomatic K-feldspar in weathered granite located in west-central Wisconsin in the vicinity of TR119. Coarse-grained K-feldspar yielded plateau ages of 446–427 Ma (Silurian), and fine-grained K-feldspar, which in some respects is texturally similar to that in TR119, gave integrated ages of 365–359 Ma (Late Devonian). However, these latter ages should be viewed with caution, due to the possible effects of recoil in such fine-grained material.

**Paleoclimate Functions.** Consistent with the approach taken with TR119, we excluded all but the upper two samples in each of the four sub-Cambrian paleosols from North America and Israel for calculating paleoclimate functions, the logic being the same as with TR119. For example, such samples most likely represent the uppermost subsoil horizons and thus more closely reflect those subsoil samples used to develop the PPM (Stinchcomb et al. 2016). Values of MAP_{ppm} (1777 mm y⁻¹) and MAT_{ppm} (20.1 °C) for TR119 are the highest paleoclimate estimates compared with those for SQ8, Butler Hill, Squaw Creek, and Timna (table 3). The MAP_{ppm} estimates for Butler Hill are significantly lower than the corresponding MAP_{calc} estimates, which are independent of potassium, and we attribute these differences to the high K₂O_{calc} value throughout the saprolite, which is similar to K₂O_{meas} values in the protolith. The obvious limitation of using the PPM for reconstructing climate in this case is the inclusion of K₂O, where this oxide has been modified by metasomatism. Even when K₂O values are adjusted (K₂O_{calc}), the MAP_{ppm} estimates remain lower than those from MAP_{calc}, except for TR119.

The best estimates of MAT_{ppm} are all consistently higher than those predicted by MAT_{calc}, with only SQ8, Squaw Creek, and Timna MAT_{calc} predictions being within error of MAT_{ppm} ranges. Overall, the range of MAT_{ppm} estimates approach values more in line with modern-day subtropical temperatures than do the MAT_{calc} estimates.

As described above, the level of atmospheric CO₂ at 550–500 Ma is estimated to have been between 4000 and 6000 ppm (Berner and Kothavala 2001). For a concentration of 5000-ppm CO₂ in the atmosphere, the formation times of weathering for the TR119, SQ8, Butler Hill, Squaw Creek, and Timna paleosols are thus 38,000, 16,000, 33,000, 17,000, and 128,000 y, respectively (table 3). These results were obtained by including the mass flux of SiO₂ in each paleosol and, because of the uncertainty in water table depth, setting the water table depth at the saprolite/protolith contact in each case. Consequently, the differences among the results for the times of weathering arise largely from different depths of weathering. For example, the depth of weathering in the Timna paleosol is 760 cm, but if the water table is assigned a depth of 250 cm, similar to that in the North American paleosols, the time of weathering is reduced from 128,000 to 46,000 y. Regardless, the time required for a steady-state weathered profile to be established in the paleosols was between 10⁴ and 10⁵ y. These estimates of formation times for the sub-Cambrian paleosol are in the same range as those for modern soils in subtropical environments, which range widely (from 10⁴ to 10⁶ y) and which are highly dependent on other soil-forming factors, such as climate, organisms, relief, and parent materials (Birkeland 1999). The most extreme case for long duration of soil formation in the tropics and subtropics is the deeply weathered Oxisols soil order, which today forms on very old landscapes with formation times of 10⁶ to 10⁷ y and from parent materials that have undergone multiple cycles of weathering, erosion, redeposition, and renewed weathering (Soil Survey Staff 2014).

**Microfossils.** Previous authors have reported microbial features in Precambrian marine rocks, now going back to as old as 3.7 Ga, preserved in stromatolites in the Isua supracrustal belt in Greenland.
Vermiform features occur in Precambrian sedimentary successions, many of which are of a larger size than what we observe in TR119 [e.g., Donaldson 1967; Seilacher et al. 2000]. The vermiform features in the TR119 profile are composed of vermiculite-illite (fig. 8) but are not the same size and shape as the Archaeoscilla species and Primaevifilium species recently reexamined in the species microfossils illustrated in Knoll et al. [85x235]

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