ARTICLES

A Proxy for Humidity and Floral Province from Paleosols

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ABSTRACT

We develop a proxy to infer humidity from the geochemistry of paleosols in order to enhance reconstructions of ancient paleoclimate beyond trends in mean annual precipitation. Geochemical transfer functions, developed herein, are used to estimate net primary production and evapotranspiration along three latitudinal transects of modern soils in the coterminous United States. Mean annual precipitation and the degree of chemical weathering are estimated from the major element concentrations in soils. The ratio of evapotranspiration, estimated from our proxy, and mean annual precipitation provides a method of determining the humidity province of ancient climates that is more robust and meaningful than previous methods, and our approach differs from existing methods since both the influx and efflux of moisture are explicitly determined. The required input parameters for application of this proxy are (1) the soil morphology, (2) accurate and complete major element concentration data for the active soil and parent material, and (3) the latitude or mean annual temperature (±5°C) of the soil or paleosol. The correlation coefficient between the measured climate and the modeled climate regime using only the latitude, morphologic, and major element data of soils is r = 0.95. We conclude that this proxy provides a refined determination of humidity and floral regimes that can be applied to paleosols.

Online enhancements: supplementary data tables.

We cannot tell whether a climate is moist or dry by knowing the precipitation alone. (C. W. Thornthwaite 1948)

Introduction

How can we determine the moisture state of ancient climates? A technique that has been widely used in deep-time studies of paleoclimate involves using the value of mean annual precipitation as a proxy for the moisture state of paleoclimate [Prochnow et al. 2006; Retallack 2007, 2009], where mean annual precipitation can be estimated from leaf physiognomy of angiosperms [Wilf et al. 1998] or paleosols [table 1; Driese et al. 2005]. One key complication in using mean annual precipitation to make inferences about the moisture content of the atmosphere is that only the influx of water is considered. Here we explore a method to determine humidity provinces that also considers the efflux of water via evapotranspiration and in so doing provides a more accurate description of climate.

Attempts have been made to quantify the seasonality of precipitation from paleosols, such as the thickness of carbonate nodule–bearing soil horizons as a proxy for the difference between the months of highest and lowest precipitation [the value $M; Retallack 2005$. Mean annual precipitation [MAP] has also been used as an index to classify climate moisture regimes [Bull 1991], and studies of paleosols [Prochnow et al. 2006] have inferred changes in climate moisture regimes by utilizing this MAP-based climate index via a geochemical proxy for MAP[CIA – K; Sheldon et al. 2002]. However, these approaches are equally limited in their accuracy by not accounting for (1) the temporal relationship between rainfall and annual evapotranspiration and (2) the annual variability of monthly average precipitation [Fujita 2008]. For example,
rainfall patterns in dryland environments are governed by seasonal storm events [Franz et al. 2010], which in turn are controlled by variability of atmospheric circulation phenomena [Fu et al. 2006], characteristics that are not reflected in the value of MAP. Both the M value [Retallack 2005] and the MAP index [Bull 1991] tend to underestimate the climatic moisture regime [fig. 1] when compared against the ratio of evapotranspiration to MAP [Holdridge 1947]. This underestimation of the moisture state of a climate is in part related to the presumption that MAP and aridity inversely and linearly covary, which can lead to erroneous climate determinations for environments where MAP is between 300 and 1000 mm [fig. 1].

We present a new proxy for constraining humidity, using paleosol morphology and major element geochemistry. Our hypothesis is that chemical weathering within soils will increase with greater production of organic matter by terrestrial vegetation and that net primary production is positively correlated to relative humidity and temperature. This proxy was developed using a pedogenic energy model [Rasmussen et al. 2005] to link evapotranspiration, net primary production [NPP], and MAP to soil major element concentrations and soil morphology. The pedogenic energy model converts influxes of precipitation and organic matter (approximated by NPP) to soils into terms of energy. The importance of this method is that the disparate physical measurements of NPP and precipitation [e.g., g biomass m⁻² and mm rainfall yr⁻¹, respectively] can be directly compared on the basis of their contributions to an energy balance for soils.

The significance of this work is in providing a method to quantify NPP and relative humidity from paleosols preserved in the rock record, thus allowing for a refined examination of paleoecologic and paleoclimatic change in deep-time stratigraphic successions. Vegetation changes are being recognized as an important forcing in deep-time global climate change [Horton et al. 2010] and quantitative reconstructions of NPP and relative humidity can serve as boundary conditions for numerical climate simulations. While this requires knowledge of ancient ecosystems, which is limited at the global scale, it is unlikely that plant responses to climate change in the rock record were markedly dissimilar from modern responses [DiMichele et al. 2009]. For example, for pre-Cenozoic environments, it is necessary to remove grasslands from the possible ecosystem niches that occupied the land surface. However, the net effect on climate vegetation feedbacks with or without grasslands is negligible [Horton et al. 2010]. Nevertheless, our model significantly reproduces modern relative humidity and floral regimes from modern soils, and thus, its applicability can extend to ancient environments.

### Table 1. Proxies for Mean Annual Precipitation (MAP)

<table>
<thead>
<tr>
<th>Proxy</th>
<th>Method</th>
<th>Notes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIA – K¹</td>
<td>MAP = 221.1 e⁻²CIA – K</td>
<td>CIA – K = 100 AlO₃ / (CaO + Na₂O)</td>
<td>Sheldon et al. 2002</td>
</tr>
<tr>
<td>Fe nodulesᵇ</td>
<td>MAP = 654.4 + 31.5 Fe₉₆₅TOT</td>
<td>Fe₉₆₅TOT = %Fe content in vertisol nodules</td>
<td>Stiles et al. 2001</td>
</tr>
<tr>
<td>Leaf physiognomyᶜ</td>
<td>ln MAP = .548M ln A – .768</td>
<td>MlnA = mean natural log of leaf area</td>
<td>Wilf et al. 1998</td>
</tr>
<tr>
<td>Depth to Bk</td>
<td>MAP = –.013D³ + 6.45D + 137.2</td>
<td>D = depth (cm) to Bk horizon (corrected for compaction)</td>
<td>Retallack 1994, 2005</td>
</tr>
<tr>
<td>CALMAGᵈ</td>
<td>MAP = 22.69[CALMAG] – 435.8</td>
<td>CALMAG = 100 AlO₃ / (Al₂O₃ + CaO + MgO)</td>
<td>Nordt and Driese 2010</td>
</tr>
</tbody>
</table>

¹ CIA – K = chemical index of alteration minus potash. Generally restricted to upland soils on shallow sloping to level terrain; oxides are in units of moles. CALMAG = calcium-magnesium index.
² Restricted to Fe-Mn nodules in vertisols.
³ Restricted to angiosperms, woody dicots in particular.
⁴ Restricted to vertisols. Oxides are in units of moles.

Major element concentrations of paleosols and sedimentary rocks have been used to reconstruct patterns in the long-term chemical weathering of the land surface through the use of the chemical index of alteration [CIA; Nesbitt and Young 1982], the chemical index of weathering [CIW; Harnois 1988], and the chemical index of alteration minus potash [CIA – K; Maynard 1992; Fedo et al. 1995]. As weathering progresses, the value of CIA, CIW, or CIA – K of soil B horizons will increase relative to the unaltered parent material. We use the major element concentrations of modern soils and their
corresponding CIA values to assess the degree of chemical weathering and link CIA values to external climatic and biologic factors.

Geochemical data for modern soils were selected from the compilation of Marbut [1935], based on the spatial extent and continuity of coverage on a continental scale to ensure representation of a large range of climate regimes [fig. 2; Gulbranson 2011]. This geochemical data set is unique in that it covers the coterminous United States and the data was obtained using similar laboratory conditions, thereby minimizing complications of interlaboratory biases [see supplementary data table S1, available online or from the Journal of Geology office]. Major element concentration data sets from soils of similar spatial scale and control of analytical procedure have yet to be reproduced elsewhere. A wide range of soils in the United States was studied, and this included major element analyses from the active soil and parent material. It is important to stress that the data and analysis here are for soil individuals [e.g., the smallest spatial unit used for soil mapping] over different landscapes; hence, palesols interpreted as polycyclic paleosols or composite paleosol profiles are probably inappropriate for deploying the methods developed here. The data are grouped into three east-west transects across the United States [42° ± 1.5°N, 38° ± 1.5°N, and 33° ± 1°N] to attain the widest possible coverage while systematically characterizing regional-scale climate trends [fig. 2]. The choice of these transects, however, limits the application of the proxy, developed herein, to the midlatitudes. Geochemical, mineralogic, and morphologic data are needed from modern tropical and polar soils in order to increase the applicability of this approach to paleosols that occur at tropical and polar latitudes; however, to our knowledge, such data are unavailable at the continental scale. Between 60% and 78% of soil analyses in the longitudinal coverage (75°W to 123°W) occur east of the 90°W meridian. For this soil data set, complete major element data are available for C horizons and horizons of the active soil (A and B horizons). In addition, soils were chosen that have a B horizon with a CIA value at least 5 units greater than the associated C horizon either by an absolute difference or by a weighted average.

The use of CIA to evaluate weathering in soils implies a unidirectional weathering trajectory from the parent material. CIA values of B horizons in soil profiles are strongly influenced by the mineralogy of the parent material [Eberl and Smith 2009] and the effects on the geochemical composition of the active soil by nutrient recycling from organic matter [van Breemen et al. 1983]. Additions of material with different mineralogy, particle size, or organometal complexes to the soil can further confound the use of this index as the cation concentrations of the active soil may not reflect the outcome of pedogenic alteration from the parent material [Maynard 1992]. Therefore, we chose to use B horizons that have CIA values at least 5 units greater than the associated parent material in order to overcome the aforementioned effects.

Major element data, reported in weight percent of the oxide [e.g., Al2O3] represents bulk analyses of well-mixed material for each soil horizon. Utilizing this data to compare trends in accumulation or loss of elements requires the conversion of weight percent oxide to moles for every cation in order to eliminate atomic mass bias. Molar CIA and CIA - K values were calculated for each horizon in a soil (see supplementary data table S2, available online or from the Journal of Geology office), where CIA = 100[Al2O3/[Al2O3 + CaO + Na2O + K2O]] and CIA - K = 100[Al2O3/[Al2O3 + CaO + Na2O + K2O]], with CaO indicating Ca concentrations derived from noncarbonate materials. CIA and CIA - K
proxies were used in order to assess the degree of weathering in the soils studied herein, as these proxies are well established for paleosols and likely preserve the original geochemical signature of ancient soils (Sheldon and Tabor 2009).

Climate data for the three transects were extracted from the database of the Parameter-Regression Independent Slope Model (PRISM) Climate Group (Daly et al. 1994). This data set permits estimation of precipitation and temperature for any location within the contiguous United States by way of interpolation between measured values, using climate relationships between topography, elevation, temperature, and precipitation (Daly et al. 1994). Monthly data were extracted from this data set spanning 30 years (1971–2000) to average out climate variation on the decadal or shorter time-scale (e.g., Pacific Decadal Oscillation, North Atlantic Oscillation, El Niño Southern Oscillation). Statistical analyses were performed using PSPP software.

**Pedogenic Energy Model.** A pedogenic energy model consists of a description of the influxes and efflux of energy through a soil. As an open system, soils consume energy during the soil-forming process via chemical weathering (Smeck et al. 1983). The influx of energy to a soil consists of climate variables such as rainfall and temperature; hence, a pedogenic energy model provides a logical way to generalize these variables in order to establish a link between net primary productivity and rainfall to the degree of chemical weathering in soils.

Meteoric precipitation is a principal component of energy influx to the land surface (Runge 1973; Rasmussen et al. 2005; Rasmussen and Tabor 2007). Terrestrial NPP, however, imparts one of the largest energy subsidies to the land surface (Phillips 2009). Annual energy fixation by NPP for the global land surface is approximately $180 \times 10^6$ kJ yr$^{-1}$ (Leith 1975a). This is equivalent to approximately 0.2% of incoming solar irradiance and is a factor of 4 greater than marine NPP. Furthermore, global NPP is expected to vary as climate changes (Nemani et al. 2003), with precipitation exerting the greatest limitation to increases in NPP at the global scale. The combination of NPP and precipitation influxes forms the basis for pedogenic energy models (Runge 1973; Volobuyev 1975; Rasmussen et al. 2005). To date, these models have been utilized toward the prediction of soil orders, soil development, argillic (clay-rich) horizons, MAP, and mean annual air temperature (MAAT; Brye 2004; Rasmussen et al. 2005; Rasmussen and Tabor 2007).

Here we expand upon these applications to define a proxy for humidity and floral regime (sensu Holdridge 1947) that requires knowledge of only the major element geochemistry and taxonomic classification of a paleosol. We develop this proxy by first utilizing the pedogenic energy model to define two transfer functions that allow for the estimation of the energy influx from precipitation [$E_{\text{PP}}$] from the magnitude of NPP, and evapotranspiration [$ET$] from MAP. In turn, ET and the $E_{\text{PP}}$ are linked to climate regimes through the relative humidity index ET/MAP (Holdridge 1947), where MAP is estimated using the CIA – K precipitation proxy (Sheldon et al. 2002).

**Soil Energy Flux and Mass Transfer.** Soil primarily receives energy from solar radiation, which is converted to plant biomass and is locked, as latent heat, within water percolating through the soil. Therefore, the total energy passing through a pedogenic system is the sum of the energy flux from precipitation and net primary productivity (Ras-
mussen et al. 2005; Rasmussen and Tabor 2007]. This approximation does not include kinetic energy from the flow of water within the soil [Brye 2004] or sensible heat flux related to the soil moisture content. The total energy estimated from precipitation \(E_{\text{PPT}}\) and from net primary productivity \(E_{\text{NPP}}\) is termed the effective energy and mass transfer rate \(E_{\text{EEMT}}\) [kJ m\(^{-2}\) yr\(^{-1}\)], where

\[
E_{\text{EEMT}} = E_{\text{NPP}} + E_{\text{PPT}}.
\]

In the subsequent sections we overview the approach to estimate \(E_{\text{NPP}}\) and \(E_{\text{PPT}}\) from climate data.

**Energy from Precipitation \(E_{\text{PPT}}\).** Energy from precipitation \(E_{\text{PPT}}\) for modern locations can be calculated from (1) the air temperature and (2) the effective precipitation \(P_{\text{eff}}\), which represents the water balance of the soil [Arkley 1963] and is the difference between MAP and evapotranspiration, where

\[
P_{\text{eff}} = P_m - \text{ET} \left[ \text{cm}^3 \text{H}_2\text{O cm}^{-2} \text{soil} \text{ mo}^{-1} \right].
\]

The \(P_m\) is the monthly average precipitation, and \(\text{ET}\) is calculated using the relationship of Thornthwaite (1948):

\[
\text{ET} = 1.6 \left( \frac{10^{\frac{\text{MAT}}{I}}} \right)^a,
\]

where \(I = \sum \left( \frac{T}{5} \right)^{1.514}\) for average monthly temperature, \(T\) [°C], summed over 1 year, \(\text{MAT}\) is mean annual temperature, and \(a\) is a third-order polynomial function of \(I\). The energy flux from precipitation \(E_{\text{PPT}}\) is calculated from the equation

\[
E_{\text{PPT}} = 4.18(\Delta T \times P_{\text{eff}}),
\]

where 4.18 is the specific heat capacity of water [kJ kg\(^{-1}\) K\(^{-1}\)] and \(\Delta T\) is the temperature difference between 273.16K and \(\text{MAT}\) [K]. For estimates of \(E_{\text{PPT}}\) in paleosols we replace monthly averages with annual averages for precipitation (MAP) and evapotranspiration. This is justified as estimates of \(E_{\text{PPT}}\) based on monthly averages (per year for 30 yr), and annual averages differ minimally [Rasmussen and Tabor 2007].

**Energy from NPP \(E_{\text{NPP}}\).** We calculate NPP using the relationship of Leith [1975a] to estimate biomass production rate [g biomass m\(^{-2}\) yr\(^{-1}\)] using \(\text{MAT}\) as a proxy for solar irradiance. This estimate is used only for months of positive \(P_{\text{eff}}\) such that water is available for plant growth and is summed to provide annual rates of NPP. This approach may reflect minimum values for NPP as stored water in a soil profile may be used for primary production during months where \(P_{\text{eff}} = 0\). The resulting relationship is

Figure 3. A, Holdridge life zones [Holdridge 1947] adapted from Lugo et al. [1999, their fig. 1]. The shaded area corresponds to the latitudinal range represented in this study, which excludes the tropics and polar regions. B, Evapotranspiration [ET, cm] versus energy influx from precipitation \(E_{\text{PPT}}\) [kJ m\(^{-2}\) yr\(^{-1}\)] diagram. Data points were derived from parameter-regression independent slope model [PRISM] climate data that correspond to a latitudinal range of 30°N to 42°N and a longitudinal transect from 93°W to 113°W. PRISM data were classified using the Köppen-Geiger climate classification system [Kottek et al. 2006] to verify the accuracy of our model for both relative humidity and floral province. The numbers in parentheses correspond to the following humidity provinces defined by the ET/MAP (mean annual precipitation) ratio: (5) arid/semiarid ET/MAP = 4, (4) semiarid/subhumid ET/MAP = 2, (3) subhumid/humid ET/MAP = 1, (2) humid/perhumid ET/MAP = 0.5, and (1) perhumid/superhumid ET/MAP = 0.25 [Holdridge 1947]. The gray shaded region corresponds to the area that would exceed the maximum ET/MAP ratio of Holdridge (1947).
Figure 4. Climate moisture regime determinations. A, Evapotranspiration (ET; cm) versus energy influx from precipitation ($E_{\text{PPT}}$; kJ m$^{-2}$ yr$^{-1}$) for B-horizon geochemical data of Marbut (1935). Bold symbols denote soils that are misclassified by this approach, and their correct moisture regime is indicated next to the symbol.

B, Parameter-regression independent slope model (PRISM) climate data plotted on the ET versus $E_{\text{PPT}}$ diagram. Data points (inset) are shaded or hachured to denote the climate regime classified in Marbut (1935).

Relative Humidity Proxy. We hypothesize that NPP will positively correlate to the chemical index of alteration as NPP is the dominant influx energy to the land surface (Phillips 2009) and is influenced by the precipitation and temperature. The link between NPP and relative humidity needs to be established, and our approach to this end is to describe humidity by $E_{\text{PPT}}$ and ET (fig. 3A). Energy from precipitation [$E_{\text{PPT}}$] is estimated from the magnitude of NPP (eqqs. [1], [7]), and evapotranspiration is estimated from the difference between MAP and effective precipitation (eq. [2]). The result is a proxy that provides quantitative estimates of NPP, evapotranspiration, and humidity.

In order to describe humidity via $E_{\text{PPT}}$ and ET, we rearranged equation (5) ($E_{\text{PPT}} = [4.18 \times \Delta T] \times [\text{MAP} - \text{ET}]$) to be expressed as

$$\text{ET} = \frac{\text{MAP} - E_{\text{PPT}}[4.18(\Delta T)]^{-1}}{1 + e^{3.15 - 0.199\text{MAT}}}.$$  \hspace{1cm} \text{[6]}

Equation (6) is in the form of a line and as such allows for the “boundaries” of humidity provinces to be plotted on a diagram of ET versus $E_{\text{PPT}}$ (fig. 3B). For a given value of MAP the value of ET corresponding to a humidity province boundary is given by the following ET/MAP ratios (Holdridge 1947; UNEP 1997): arid (8 to 4), semiarid (4 to 2), dry subhumid (2 to $\sim$1.5), subhumid ($\sim$1.5 to 1), humid (1 to 0.5), perhumid (0.5 to 0.25), and superhumid (<0.25).

In order to apply this equation to paleosols we derived transfer functions to solve for the two unknown variables of equation [6], $E_{\text{PPT}}$ and ET. One transfer function is developed to link CIA to NPP, which is used to solve for $E_{\text{PPT}}$ using equation [1]. A second transfer function is developed to solve for ET using MAP that is quantified from existing geochemical proxies (Sheldon et al. 2002). In this way, it is possible to plot the variables ET and $E_{\text{PPT}}$ estimated from soil or paleosol major element chemistry and taxonomic classification onto an ET versus $E_{\text{PPT}}$ diagram to infer climatic seasonality (figs.
Table 2. Pedogenic Energy Contributions by Soil Order and Calculated Climate Variables

<table>
<thead>
<tr>
<th>Soil order</th>
<th>%E_{ppt}a</th>
<th>E_{ppt}b [kJ/m² yr]</th>
<th>MAP (CIA – K)c [cm]</th>
<th>E_{ppt}d [kJ/m² yr]</th>
<th>ETe [cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfisol</td>
<td>23.2 (.744)</td>
<td>23,166–43,304</td>
<td>70–136</td>
<td>8108–15,156</td>
<td>20–30</td>
</tr>
<tr>
<td>Aridisol</td>
<td>5</td>
<td>9889–40,836</td>
<td>40–59</td>
<td>494–2042</td>
<td>19–27</td>
</tr>
<tr>
<td>Entisol</td>
<td>17</td>
<td>13,969</td>
<td>35</td>
<td>2375</td>
<td>22</td>
</tr>
<tr>
<td>Mollisol</td>
<td>10</td>
<td>24,687–42,630</td>
<td>36–89</td>
<td>2469–4263</td>
<td>19–28</td>
</tr>
</tbody>
</table>

a %E_{ppt} (energy from precipitation) for aridisols, entisols, and mollisols from Rasmussen et al. (2005); all others are averages calculated using the parameter-regression independent slope model data set [standard deviation in parentheses].

b E_{ppt} (energy from net primary productivity) calculated using transfer functions [presented in “Estimating E_{ppt} from CIA and NPP”].

c Mean annual precipitation [MAP] calculated using CIA – K [chemical index of alteration minus potash] precipitation proxy [Sheldon et al. 2002].

d E_{ppt} calculated on the basis of [(1 – %E_{ppt}) – 1] × E_{ppt} for the PRISM data set was plotted on the ET versus E_{ppt} diagram to assess the accuracy of this approach [3B, 4B].

e Evapotranspiration (ET) calculated using transfer function [presented in “Calculation of ET”].

3B, 4A]. The long-term climate record culled from the PRISM data set was plotted on the ET versus E_{ppt} diagram to assess the accuracy of this approach [3B, 4B]. A potential solution to estimating E_{ppt}, for paleosols where a priori climate information is unavailable, is derived from the equation EEMT = E_{ppt} + E_{ppt}. Rasmussen et al. (2005) indicated that soil orders (i.e., USDA taxonomic classification) partition energy from precipitation [E_{ppt}] and NPP in predictable quantities [%E_{ppt} table 2], consistent with the steady state thermodynamics concepts of Smek et al. (1983). Weakly developed soils (e.g., entisols and inceptisols), however, have poorly defined E_{ppt}/E_{ppt} ratios. If it is possible to accurately estimate E_{ppt}, then E_{ppt} can be calculated according to the type of paleosol since we relate the percentage of E_{ppt} to soil order through the equation

\[ E_{ppt} = E_{ppt} \left( \frac{1}{1 - \%E_{ppt} \text{SoilOrder}} - 1 \right) \, (7) \]

We utilize the aforementioned positive correlation between EEMT and CIA to develop a transfer function that permits E_{ppt} to be estimated from CIA.

In order to estimate ET, we develop a transfer function that correlates MAP to P_{ppt} as P_{ppt} = MAP – ET. For example, if MAP is known from the modern or inferred for a paleosol using the CIA – K proxy (Sheldon et al. 2002), then the expression 1 – ET/MAP, can be used to estimate ET.

Results

In order to link major element concentrations of soils and soil morphology to the climatic variables ET and E_{ppt} it is necessary to develop transfer functions that relate the degree of chemical weathering in soils to climate. The transfer functions defined here are based on soil-forming factors intimately associated with climate (e.g., NPP and precipitation that can control the extent of humification) and that can be inferred for modern soil properties (Buol et al. 2003).

\[
\text{Estimating } E_{ppt} \text{ from CIA and NPP.} \] NPP has an indirect positive relationship to chemical weathering through the production of H₂CO₃ in A horizons, via humification, for proton attack, catalysis, and removal of reaction products by competition of organic ligands for the complexation of solutes (van Breemen et al. 1983; Chadwick and Chorover 2001). Therefore, it is expected that the E_{ppt} influx to soils should correlate to the extent of weathering in soils.

A plot of E_{ppt} values, which were calculated from the PRISM data set, versus CIA values calculated using the major element concentrations of soil B horizons of the Marbut (1935) data set (fig. 5A) reveals a set of parabolic relationships for the three latitudinal transects. The separation of the data by latitude is consistent with the large (>5°C) variation in MAT between the different transects (table 3), suggesting a temperature control on the relationship between E_{ppt} and CIA. In order to calculate transfer functions for E_{ppt} using CIA of soils, a regression analysis was conducted for all CIA data from B horizons and from a subset of soils with a CIA value for B horizons that was ≥5% of the C horizon value. Polynomial regression analysis produced second-order relationships between E_{ppt} and CIA for all latitudes (fig. 5A) with good coefficients of determination [R² = 0.76, 0.87, and 0.77 for transects 33°N, 38°N, and 42°N]. This indicates that CIA is a reasonable proxy of E_{ppt}, a result that is further supported by the good correlation [r = 0.9] between PRISM-based and CIA-based esti-
Figure 5. A, Plot of energy from net primary productivity (\(E_{\text{NPP}}\)) estimated from the parameter-regression independent slope model (PRISM) climate data set versus the chemical index of alteration (CIA) of B horizons from the Marbut (1935) soil chemical data set. Data are organized by latitudinal transect, and lines through the data correspond to polynomial regressions for each transect. B, Calculated \(E_{\text{NPP}}\) (Calc. \(E_{\text{NPP}}\)) versus PRISM-estimated \(E_{\text{NPP}}\). The ordinate axis was calculated using the regressions presented in figure 5A. The bold line indicates 1 : 1 agreement between the ordinate and abscissa axes. Lightly shaded symbols in A and B indicate soil data where the B-horizon CIA value was ≤5% of the C-horizon CIA value.

Estimates of \(E_{\text{NPP}}\) [fig. 5B]. NPP results from transect 33°N are distinguishable from the 42°N and 38°N transects [one-way ANOVA, \(P < .001\)]; however, the difference in NPP between the 42°N and 38°N transects is not statistically significant \((t\text{-test}, P > .2\), suggesting that temperature

may be determining factor separating NPP for latitudinal transects separated by at least 5° of latitude [table 3, fig. 5A]. Performing the regression analysis for all soils in each of the three transects yields correlation coefficients of \(r \leq 0.7\). The statistical correlation is notably improved \(|0.8 < r < 0.93; \text{fig. 5A}\) when only those soils that record a B horizon CIA value (or weighted average) that is >5% of the corresponding C horizon CIA value are used.

These transfer functions are grouped by present-day latitudinal transects, but for ancient soils it is more appropriate to consider these regressions as grouped by temperature since mean annual air temperature is distinguishable between each transect at standard error. Additionally, a dependence on temperature is expected for the CIA to \(E_{\text{NPP}}\) correlation, related in part to van’t Hoff’s law that mathematically relates the change in biochemical productivity as a factor per 10°C change in temperature \([i.e., Q_{10}]\). As latitudinal temperature gradients have varied with mean global temperature throughout Earth history, it is possible that mean soil temperatures for a given latitudinal belt could have been higher during past warm periods. Given that the transfer functions presented here were developed using soils and climate parameters of the modern icehouse state it is possible that anomalous surface and soil temperatures could lead to nonlinearity in the relationship between \(E_{\text{NPP}}\) and CIA.

Based on the aforementioned considerations, we suggest the following transfer functions as proxies of \(E_{\text{NPP}}\) for the following ranges of MAT:

- \(E_{\text{NPP}} = -1.943(CIA)^2 + 352.41(CIA) + 28,197\) for 17°–20°C,
- \(E_{\text{NPP}} = -8.17(CIA)^2 + 1,263.3(CIA) + 11,238\) for 10°–13°C, and
- \(E_{\text{NPP}} = -41.8(CIA)^2 + 5,423(CIA) + 142,635\) for 7°–9°C.

The \(E_{\text{NPP}}\) values for each soil were converted to \(E_{\text{PTT}}\) using equation (7) and the \(\%E_{\text{PTT}}\) values for taxonomic soil orders [table 2]. For paleosols, soil temperatures are inferred from single-mineral paleothermometers and are interpreted as recording MATs [Yapp 2000; Tabor 2007]. These temperature estimates often exceed the range of temperatures developed for these transfer functions. Long-term comparisons of air temperature and ground temperature, however, suggest soil temperatures do exhibit strong seasonal temperature variations [Bartlett et al. 2006] due to variations in soil moisture content at depths <50 cm [Soil Survey Staff 2010]. Thus, the interpretations of crystallization tem-
peratures of soil-formed minerals at temperate latitudes likely reflect seasonal temperature extremes of soils during the time window in which the mineral formed [Breecker et al. 2009; Passey et al. 2010].

**Calculation of ET.** An estimation of evapotranspiration is required to infer relative humidity and floral regime in relation to the Holdridge life zones. Therefore, we sought to calculate ET from the relationship, \( P_{\text{eff}} = \text{MAP} - \text{ET} \). The latter presents an intuitive correlation where, if \( P_{\text{eff}} \) is plotted on the ordinate axis and MAP on the abscissa, the slope of a line \([m]\) on this diagram is equivalent to \( m = 1 - \frac{\text{ET}}{\text{MAP}} \) [fig. 6]. PRISM climate data for the three latitudinal transects of soil used in this study were used to develop transfer functions that estimate \( P_{\text{eff}} \) from MAP, given that paleo-MAP (over the range of 200–1600 mm) can be estimated using the CIA – K proxy (Sheldon et al. 2002; Sheldon and Tabor 2009). The transfer functions are organized by temperature as follows:

\[
P_{\text{eff}} = 0.908[\text{MAP}] - 21.403 \quad (11)
\]

\([R^2 = 0.99]\) for an MAT range of 17°–20°C,

\[
P_{\text{eff}} = 0.924[\text{MAP}] - 19.221 \quad (12)
\]

\([R^2 = 0.98]\) for an MAT range of 10°–13°C, and

\[
P_{\text{eff}} = 0.959[\text{MAP}] - 17.243 \quad (13)
\]

\([R^2 = 0.99]\) for an MAT range of 7°–9°C.

Conceptually, the slope \([m]\) is equivalent to the annual average water balance for a soil and should have values of \( m \leq 1 \). We hypothesize that when \( m \) approaches negative values the linear relationship corresponds to an annually averaged water deficit such as in dryland systems. Slopes approaching unity will correspond to annually averaged water surpluses, and when \( m = 0 \) this implies annual water balance. However, such trends are not apparent for the selected transects [fig. 6], perhaps reflecting the continental scale of the latitudinal transects; these anticipated trends thus may be more important at the watershed scale. ET was subsequently estimated by applying \( P_{\text{eff}} \) calculated using these transfer functions and the relationship \( P_{\text{eff}} = \text{MAP} - \text{ET} \), where MAP was inferred from the CIA – K values of the soils [table 2]. For post-Jurassic periods, an independent check of MAP estimates could be obtained by leaf area analysis of woody dicots (table 1; Wilf et al. 1998; Royer et al. 2005).

**Discussion**

**Accuracy of the Inferred Climate Regimes.** The \( E_{\text{ppt}} \) and ET inferred from the major element geochemistry of active soils [fig. 4A] results in climate inferences in good agreement with humidity provinces defined by measured precipitation, temperature, and seasonality for the sites [figs. 3, 4B; table 3]. Of the 77 soils utilized in this study,
three yield estimated $E_{PPT}$ values that imply inaccurate climatic seasonality. For these three soils, the ET estimates are consistent with PRISM climate data that indicate our approach has overestimated $E_{PPT}$ for these soils. A single aridisol (e.g., aridic soil moisture regime), however, plots in a subhumid regime (fig. 4A). The underestimation of ET may reflect that this aridisol receives <200 mm yr⁻¹ MAP, which is below the limits of the CIA – K proxy for MAP (Sheldon et al. 2002). Furthermore, aridisols are defined as existing in an aridic soil moisture regime (Soil Survey Staff 2010), but the inferred relative humidity for this aridisol is subhumid suggesting that this soil could contain relict properties that formed under a climate with greater relative humidity. The erroneous climate moisture regime indicated by the other two anomalous soils could reflect several factors: (1) the local ecology of these soils is not well represented by the biomass caloric value of 22 kJ g⁻¹, thus leading to an overestimation of $E_{NPP}$ and hence $E_{PPT}$; (2) the climate regime was improperly classified in the Marbut (1935) data set; or (3) other factors contribute to the measured CIA of these soils, and thus, the relationship between CIA and NPP is not well defined by our transfer functions. Notably, for 96% of the soil database utilized in this study, the estimates of ET and $E_{PPT}$ accurately plot within the humidity province indicated independently by the PRISM-based climate classification for these soils (cf. fig. 4A, 4B).

**Paleoecologic Considerations.** For geologic applications it may be essential to accurately distinguish energy influxes for specific floral types given documented large ecologic change throughout the last ~400 m.yr., such as the appearance of vascular plants in the mid-Silurian (Kenrick and Crane 1997), the early Cretaceous radiation of angiosperms (Sun et al. 2002), and the Oligocene expansion of C₄ grassland ecosystems (Edwards et al. 2010). Here we amend our estimation of $E_{NPP}$ to account for these floral changes by incorporating into our calculations caloric values for biomaterials that may be representative of gymnosperms (22 kJ g⁻¹ biomass), angiosperms (19.7 kJ g⁻¹ biomass), and grasses/sedges (17.8 kJ g⁻¹ biomass; fig. 7). This approach yields successively lower $E_{PPT}$ estimates for angiosperms and grasses, respectively, relative to the calculations presented in “Estimating $E_{PPT}$ from CIA and NPP” (fig. 7), highlighting the need to use appropriate caloric values for different soil ecosystems in order to accurately estimate $E_{PPT}$.

**Application to Paleosols**

Paleosols from the Early Permian Abo Formation of New Mexico (Mack et al. 2010), latest Carboniferous Markley Formation, and Early Permian Archer City, Nocona, Petrolia, Waggoner Ranch, and Clear Fork formations of north-central Texas (Tabor and Montañez 2004, 2005) were selected to illustrate the utility of the paleoseasonality proxy. The depositional basin for the Abo Formation was situated within 5°N of the equator during the Sakmarian, whereas the stratigraphic succession from north-central Texas was deposited on the eastern shelf of the Midland Basin that straddled the equator during this time. Preliminary paleotemperature estimates from phyllosilicate oxygen and hydrogen isotope geochemistry suggest soil temperatures of ~22° ± 3°C for the Abo Formation (N. J. Tabor, pers. obs.), whereas paleotemperatures were estimated to range from 26° to 34° ± 3°C for the north-central Texas paleosols (Tabor and Montañez 2005). Atmospheric CO₂ reconstructions for the Early Permian indicate variable partial pressures of CO₂ ranging from the preindustrial atmospheric level (PAL; 270 ppmv) in the earliest Permian up to ~2500 [9 × PAL] ± 500 ppmv in the late Early Permian (Montañez et al. 2007).

The stratigraphic architecture of the Abo Formation indicates that paleosols formed on dissected marine terraces and adjacent interfluve land surfaces. Paleosols of the Abo Formation are ver-
value at least 5 units greater than that of the associated C horizon. The high levels of paleoatmospheric \( pCO_2 \) for the latter half of the Early Permian (Montañez et al. 2007) suggest a decrease in the Northern Hemispheric latitudinal temperature gradient that is corroborated by numerical climate models for the time interval (Horton et al. 2007; Peyser and Poulsen 2008) and the relatively high soil temperatures inferred from the stable isotope compositions of phyllosilicates and goethites from these soils. Thus, the transfer functions developed for the 33\(^\circ\)N [modern latitude] transect are most applicable to this paleoenvironment due to the larger MAATs of that latitude relative to the 38\(^\circ\)N and 42\(^\circ\)N transects and the fact that mean modern summer air temperatures [25.5\(^\circ\)-32.2\(^\circ\)C] for 33\(^\circ\)N are consistent with the estimated paleosol temperatures [22\(^\circ\)-34\(^\circ\)C]. Floral restructuring from “evangel” lycopsid-dominated forests to conifer and tree fern-dominated ecosystems during the Early Permian in this region were coincident with changes in inferred paleoatmospheric \( pCO_2 \) (Montañez et al. 2007). If we consider the effects of increasing solar irradiance and greater variability in soil moisture content related to this floral restructuring, then it is possible that these paleoequatorial soils experienced seasonality in ambient temperatures consistent with applying transfer functions developed for modern midlatitudes.

We applied the major element concentration data from the paleosol B horizons to the 33\(^\circ\)N transfer functions to estimate \( E_{\text{ppt}} \) from the CIA (eq. [8]). In turn, \( E_{\text{ppt}} \) was calculated using equation (7) and the %\( E_{\text{ppt}} \) for vertisols, alfisols, and mollisols (table 2). Mollisol %\( E_{\text{ppt}} \) was used to represent calcic vertisols and alfisol %\( E_{\text{ppt}} \) was used to represent argillisols [i.e., equivalent to alfisols] given that their Na + Ca + K + Mg/Al ratio is >0.5 is above the taxonomic cutoff for alfisols relative to ultisols (Sheldon and Tabor 2009). ET was estimated from \( P_{\text{eff}} \) using the 33\(^\circ\)N transfer function [eq. [11]] for MAP. A plot of the estimated \( E_{\text{ppt}} \) and ET values (fig. 8) illustrates their position within climate moisture regimes.

A relative humidity classification of humid to perhumid estimated for the Abo Formation vertisols is consistent for all samples [n = 9]. The estimated ET and \( E_{\text{ppt}} \) values for the Early Permian paleosols of north-central Texas, in contrast, indicate greater variability in climatic seasonality. The oldest, latest Pennsylvanian samples plot in the perhumid moisture regime and wet forest floral regime, whereas the earliest Permian paleosol indicates a pronounced shift to less humid conditions.
and a transition from wet to moist forest biomes. This shift is consistent with an interpretation of an abrupt increase in aridity and associated change in floral composition inferred independently from paleosol morphology [Tabor and Montañez 2004] and paleobotanical data [Montañez et al. 2007; DiMichele et al. 2009].

Superimposed on a long-term decline in MAP during the Early Permian (fig. 8B), inferred from CIA – K values, are several high-frequency shifts in inferred relative humidity and floral regime (e.g., b to c and d to e in fig. 8). These shifts in relative humidity are delineated by the $E_{\text{ppt}}$ and ET parameters, which were estimated using the new transfer functions defined here, and correspond to a general decrease in MAP values of $\sim 300 \pm 182$ mm. This highlights how MAP is not diagnostic of relative humidity but is rather a homogenization of precipitation throughout the year and likely underrepresents the climatic regime.

The relative humidity and floral regime proxy presented herein allows, for the first time, inferences on the balance between MAP and evapotranspiration to be made from paleosol morphology and major element geochemistry. This proxy reveals climatic variability that is undetectable solely from estimates of MAP from CIA – K values of paleosols. Furthermore, the agreement of our climate and floral regime inferences with existing paleobotanical reconstructions [Montañez et al. 2007; DiMichele et al. 2009] indicates that this relative humidity and floral regime proxy is robust and is sensitive to long-term fluctuations in climate and ecosystems.

**Figure 8.** Climate regimes for Permo-Carboniferous paleosols. A, Proxy estimates of evapotranspiration ET (cm) versus energy influx from precipitation $E_{\text{ppt}}$ for the latest Pennsylvanian (Virgilian) through Early Permian (Wolfcampian-Leonardian) paleosols of north-central Texas are presented as shaded diamond symbols. Proxy estimates for the Early Permian (mid-Wolfcampian) Abo Formation (Formation) paleosols are presented as circles; shaded triangles correspond to the same Abo Formation paleosol data, but mean annual precipitation (MAP) estimates are based on the depth to carbonate precipitation proxy. B, Temporal distribution of MAP estimates for the north-central Texas paleosols. Arrows connecting the shaded diamond symbols (north-central Texas paleosols) indicate the trajectory of climate shifts through time [i.e., Carboniferous [point a] through Permian [point g]], and correspond to the MAP values to the right.
Conclusions

We estimate for a select set of published modern soils, using a pedogenic energy model, the total energy influx to soils based on the NPP and monthly precipitation trends, both of which are sensitive to air temperature. Considering the import of large energy quantities to soils via NPP, a series of highly correlated transfer functions were generated that relate the extent of silicate weathering in a soil (CIA) to NPP, and ET to MAP, of which MAP can be estimated using the CIA – K proxy. These transfer functions allow for the estimation of the energy of precipitation ($E_{PPT}$) and ET by applying the major element concentration and morphology of modern and ancient soils to the aforementioned transfer functions. This, in turn, defines a climate classification scheme from the relationship, $ET_p = \frac{[4.18(DT)]}{MAP^2}$. Our approach faithfully reconstructs modern seasonality from the soil chemical data of Marbut (1935).

The utility of this proxy is demonstrated by its application to published paleosol geochemical and morphologic data sets. We show that relative humidity and floral regime can be reconstructed from the combination of paleosol geochemistry, morphology, and a general sense of paleolatitude and/or paleotemperature. In comparison to climate reconstructions based on MAP, the proxy developed herein reconstructs relative humidity to a degree that is undetectable from solely MAP reconstructions. The addition of floral regime inferences derived from this climate proxy further strengthens its applicability to multidisciplinary studies of terrestrial environments that incorporate paleobotanical techniques.

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