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Quaternary Research 67 (2007) 275–285
QUATERNARY RESEARCH
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# Evidence for the silicate source of relict soils on the Edwards Plateau, central Texas ☆

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Received 30 August 2005
Available online 7 February 2007

**Abstract**

Relict soils provide insights into Quaternary soil formation and erosion on the Edwards Plateau of central Texas and into soil-forming processes in karst terranes. Late Quaternary climate-driven soil erosion produced a mosaic of thick and thin soils on the Edwards Plateau landscape. Thick soils on uplands of the Edwards Plateau are interpreted to be relicts of a formerly more extensive soil cover that was eroded during the late Pleistocene to middle Holocene. The relict, thick soils are silicate-rich and most commonly overlie the relatively silicate-poor Cretaceous Edwards Limestone, which supports the idea that the thick soils did not form from weathering of the underlying limestone. Other potential sources of silicates for the relict soils include dust, alluvial sediments, and the Del Rio Clay, a stratigraphically higher but locally eroded clay-rich unit. Here we investigate the geographic distribution, texture, clay-sized mineralogy, rare earth element geochemistry, and neodymium isotope composition of the relict soils. We have found that the relict, thick soils are deeply weathered soils that occur dominantly over the Edwards Limestone and have a high clay content and a neodymium isotope composition that is similar to that of the Del Rio Clay. Thus, we propose that *in situ* weathering of the Del Rio Clay, along with partial weathering of the upper portion of the underlying Edwards Limestone produced thick chert- and clay-rich soils over resistant limestone. In areas like the Edwards Plateau, where pure limestones are interbedded with clay-rich strata, the overlying clay-rich strata must be considered as a possible silicate source to soils on pure limestone bedrock.


*Keywords:* Soil; Relict; Edwards Plateau; Texas; Limestone; Del Rio Clay; Neodymium

## Introduction

### *Objective*

The occurrence of thick, clay-rich soils on the Cretaceous limestone bedrock of the Edwards Plateau region of central Texas (Fig. 1A) is enigmatic because the underlying limestone has a low abundance of silicate minerals, which may weather to form clays. The goal of this research is to identify the silicate parent material of the relict, central Texas soils by integrating the following approaches: (1) determining the spatial distribution of the relict, thick soils in relation to geomorphic position and underlying rock type; (2) comparing the texture and mineralogy of the modern, thin, and relict, thick soils to potential silicate sources; and (3) applying variations in the neodymium isotope composition, depleted-mantle model age, and rare earth element concentrations of the soil as a constraint on the provenance of the silicates. Possible silicate sources include: (1) the underlying Edwards Limestone bedrock, (2) a stratigraphically higher formation as proposed by Rabenhorst and Wilding (1986) and specified here as the Del Rio Clay, (3) eolian sediments, or (4) ancient alluvial sediments.

### *Edwards Plateau soils*

The Edwards Plateau is an exposed Cretaceous limestone upland that has been locally dissected by streams (Fig. 1). The southern and eastern margins of the plateau are bounded by the

☆ Portions of this manuscript were previously published in the Ph.D. dissertation of the corresponding author (Cooke, 2005).

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0033-5894/$ - see front matter 
doi:10.1016/j.yqres.2006.11.007

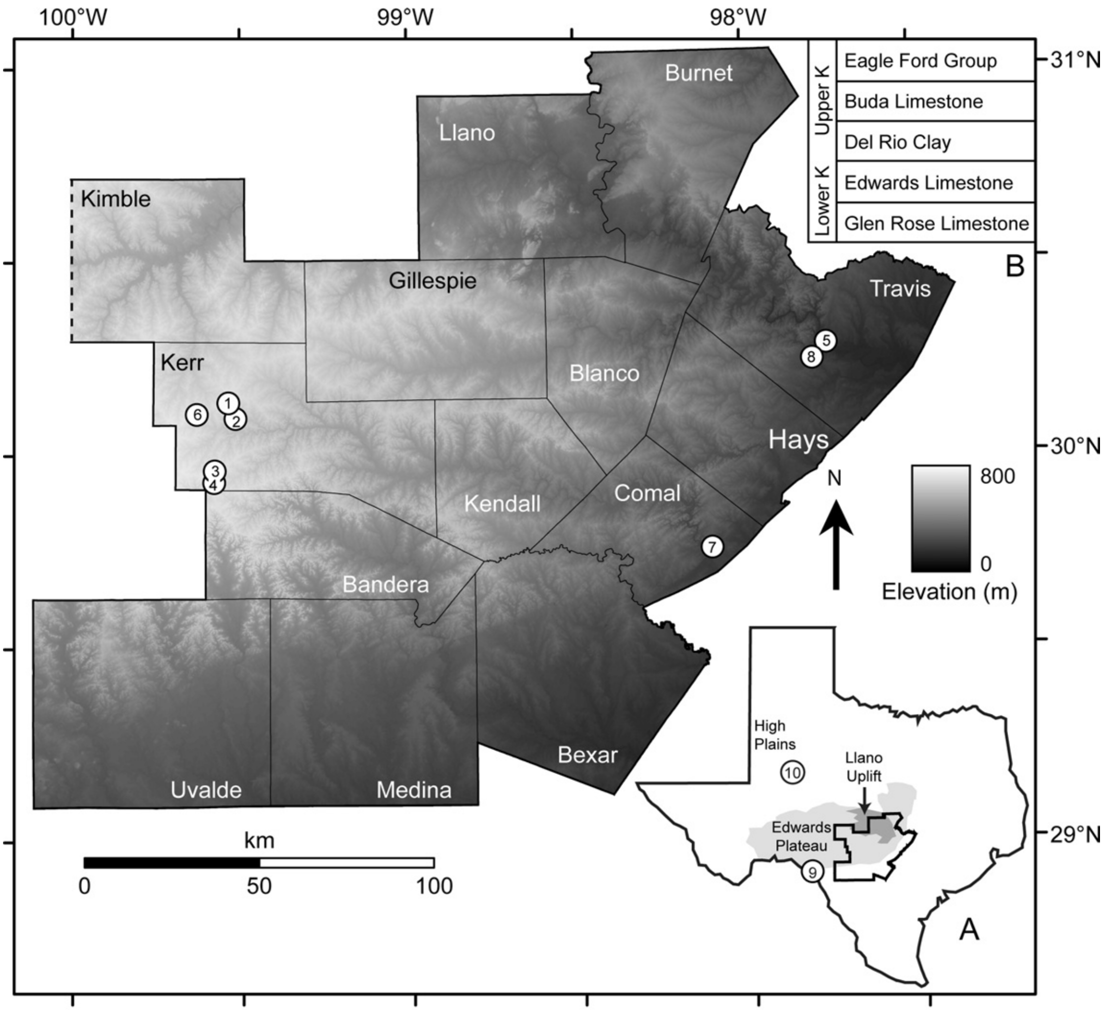


Figure 1. Study area location, elevation, and stratigraphy. Shaded relief map (National Elevation Dataset) (Data available from the U.S. Geological Survey Eros Data Center, Sioux Falls, SD) of the geology and soil map area in Figure 2. The dashed line indicates that Kimble County continues to the west. Inset A shows the location of the map area in Texas as well as the locations of the Edwards Plateau, Llano Uplift, and High Plains physiographic regions. Inset B is a simplified stratigraphy of Cretaceous rocks in the study area.

Miocene-age normal fault system of the Balcones Fault Zone (Weeks, 1945; Young, 1972). To the north, the Edwards Plateau merges with the High Plains, an abandoned alluvial surface capped by Tertiary fluvial deposits (Reeves and Reeves, 1996).

As one would expect of soils forming from pure limestone parent material in a semiarid environment, most of the soils on the Edwards Plateau are thin and rocky. These thin soils (typically <30 cm) of the Edwards Plateau are dark brown, clay-rich mollisols that support live oak and juniper savanna and woodlands and are often relegated to ranchland. However, in isolated areas of the Edwards Plateau, there are thick, red to brown, chert- and clay-rich soils that are classified as alfisols and vertisols. Descriptions of a typical thin soil profile and several thick soil profiles are provided in Appendix A. The thick soils are described as Redland range sites due to their unusual texture, thickness (~0.5 to 2 m), and atypical vegetation such as black jack oaks and post oaks (Dittemore and Coburn, 1986). Some Redland soils have an abrupt enrichment of clays below the A/B-horizon boundary, providing evidence for truncation of the upper soil horizon (Dittemore and Coburn, 1986). These thick, Redland range soil types occur in upland areas over hard, indurated limestone and compose only <1 to 15% of the total soils in several counties spanning the Edwards Plateau region (Figs. 1 and 2; Table 1).

The thick soils are interpreted to be relicts of a former thick soil cover that was once more extensive on the Edwards Plateau. This interpretation is supported by the presence of red clay sediments and fossils of burrowing mammals in central Texas cave-fill deposits in areas that currently lack thick soils (Toomey, 1993; Toomey et al., 1993). Other evidence for a more widespread, thick soil cover in the past includes "terra rossa" karst-fill features and silicified fossils in Cretaceous limestone (Young, 1986). Reddened and silicified portions of the Edwards Limestone that lack soil today may have been produced by silicate leaching from a former soil cover (Young, 1986). While the age of the relict soils is not well constrained, they were at least formed by the late Pleistocene because several central Texas caves contain sediments from the eroded soils (Toomey et al., 1993; Cooke et al., 2003). Sedimentological variations and changes in faunal assemblages in central Texas

https://doi.org/10.1016/j.yqres.2006.11.007 Published online by Cambridge University Press

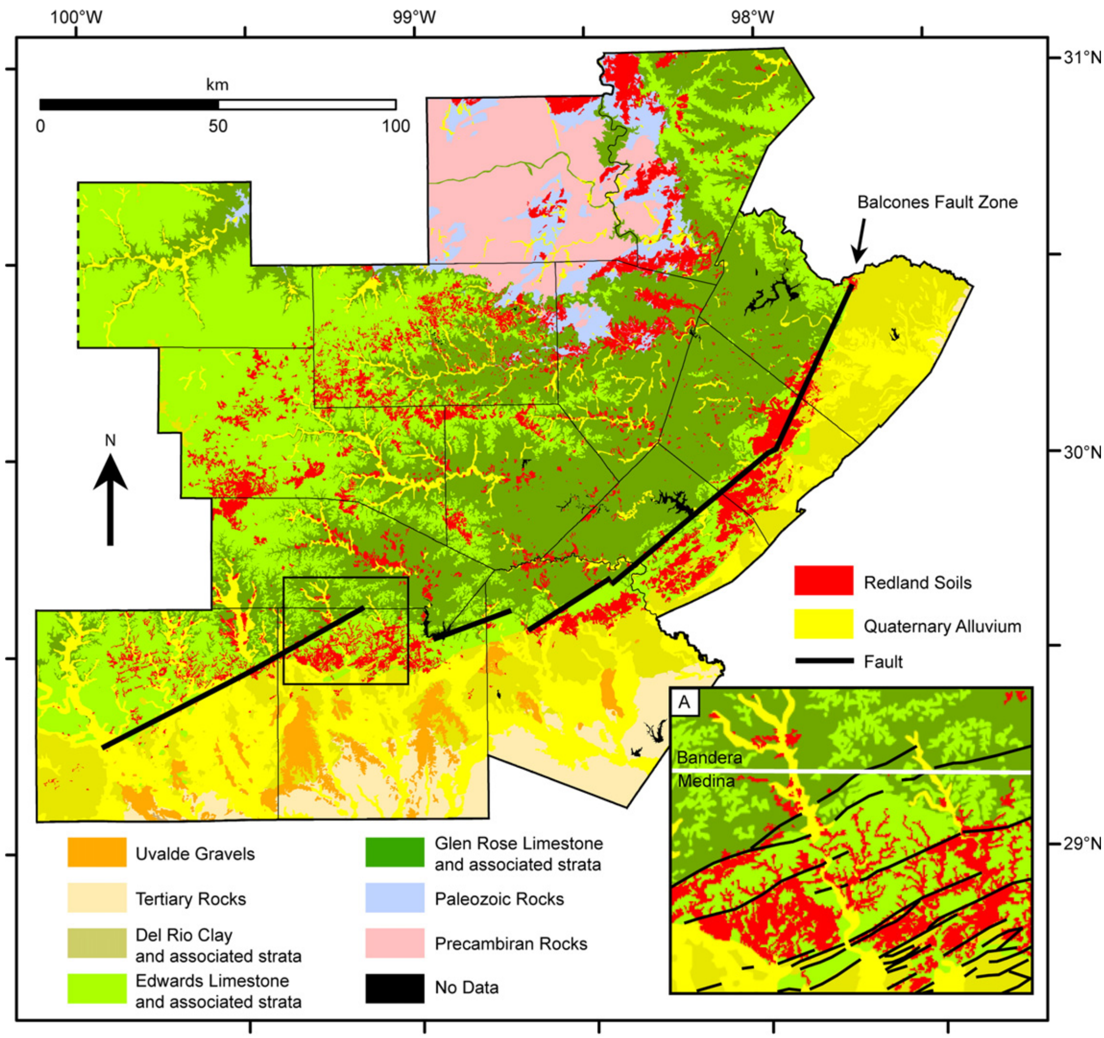


Figure 2. Redland range site soil distribution with underlying rock type. Map shows only those soils classified as Redland range-type soils in red (Appendix B) superimposed on the underlying geology (see Methods). Refer to Appendix C for a detailed listing of the lithologic units included in each simplified map unit. Heavy lines indicate the approximate north-easterly trends of faults on the northern edge of the Balcones Fault Zone, which marks the southern and eastern margins of the Edwards Plateau and the abrupt transition where the relict soils are dominantly absent on the Glen Rose Limestone and present on the Edwards Limestone. Inset A is an enlargement of the area in the black box in the larger map. In inset A, normal faults are indicated as heavy black lines and the white line denotes the boundary between northern Medina and southern Bandera counties.

cave-fill deposits support the hypothesis that climate changes toward greater aridity and/or increased seasonality of precipitation facilitated massive soil erosion on the Edwards Plateau in the late Pleistocene to early Holocene (Toomey et al., 1993; Blum et al., 1994). Strontium isotope variations through a sequence of fossils contained in one of these cave-fill deposits record progressive thinning of the Edwards Plateau soil mantle between 18 and 4 $^{14}$C yr BP (Cooke et al., 2003; Cooke, 2005). Here we build on these previous studies to address the origin of the former thick soil cover.

## *Research problem and hypothesis*

The occurrence of thick clay-rich soils on relatively pure limestone indicates, by mass balance, that the soils did not form solely from silicate minerals within the underlying limestone. For example, the Segovia Member of the Edwards Limestone, which is found underlying the thick soils in central and western areas of the Edwards Plateau, has a low insoluble residue content of ~1% (determined in this study for one sample of the Segovia Member). Thus, ~50 to 200 m of Edwards Limestone would have to dissolve to produce the observed 0.5- to 2-m-thick soils. This required thickness of dissolved limestone is, in places, greater than or approximately equal to the entire thickness of the Segovia Member of the Edwards Limestone. Some of the thick soils are found near the top of the Segovia Member, as inferred by their proximity to the contact of the Segovia Member with the overlying Del Rio Clay. Dissolution of only a portion of the Segovia Member would be insufficient to form the observed soils.

Rabenhorst and Wilding (1986) studied the mineralogy, texture, and quartz grain morphology of soils of variable character and thickness that occur over resistant Cretaceous limestones (like the Edwards Limestone) on the Edwards Plateau. They concluded that neither the underlying bedrock nor eolian fall-out could be the dominant parent material for these

Table 1
Distribution of Redland soils by central Texas county with underlying rock type

| | County | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Bandera | Bexar | Comal and Hays | Gillespie | Kendall | Kerr | Kimble | Medina | Travis | Uvalde |
| *Redlands over rock type (%)* | | | | | | | | | | |
| Edwards Limestone and associated strata | 38 | 66 | 82 | 69 | 60 | 92 | 100 | 84 | 74 | 57 |
| Glen Rose Limestone and associated strata | 57 | 20 | 11 | 21 | 38 | 7 | 0 | 6 | 12 | 13 |
| Del Rio Clay and associated strata | 0 | 11 | 6 | 0 | 0 | 0 | 0 | 4 | 9 | 6 |
| *Area Redlands over rock type/area rock type (%)* | | | | | | | | | | |
| Edwards Limestone and associated strata | 9 | 28 | 44 | 16 | 21 | 13 | 0.2 | 29 | 17 | 7 |
| Glen Rose Limestone and associated strata | 6 | 7 | 3 | 6 | 3 | 4 | 0.0 | 6 | 1 | 5 |
| Del Rio Clay and associated strata | – | 2 | 6 | – | – | 0.3 | 0.0 | 2 | 1 | 1 |
| % Redland soils | 7 | 4 | 15 | 11 | 7 | 10 | 0.1 | 6 | 3 | 3 |

Percent of Redland soil area (of total Redland soil area) over different rock types on the Edwards Plateau, percent of the area of Redland soils over a rock type relative to the total area of that rock type, and percent of Redland soil area (of total soil area) in given counties are provided. Percentages were quantified from the map in Figure 2 using ArcMap. A detailed description of the formations included in each rock type is included in Appendix C. For some counties, a small percentage of Redland soils occurs over non-Cretaceous rock types and thus, the sum of the percentages of Redland soils over the Edwards Limestone, Glen Rose Limestone, and the Del Rio Clay and associated strata in a given county is less than 100%. Redland soil distributions are mapped in Blanco, Burnet, and Llano counties (Fig. 2), but are not included in this table because these counties include large areas outside the Edwards Plateau in the Llano Uplift region.

central Texas soils. The soils lack euhedral quartz grains that are found in the underlying limestone residue, and the soils also lack smooth, conchoidally fractured, silt-sized grains that are found in modern dust. Thus, they suggested that a stratum previously overlying the resistant limestone may have been the dominant parent material.

If the underlying limestone did not contribute significant amounts of silicate material to the soil, the formation of thick soils requires another (or multiple) silicate source(s). Alternative sources of silicates include: dust, sediments deposited on a former high alluvial surface, or insoluble residue from a stratigraphically higher unit. We will test the hypothesis that the Del Rio Clay, an Upper Cretaceous marly limestone that locally overlies the Edwards Limestone (Fig. 1B), is the dominant silicate source of these soils. The Del Rio Clay is gray to tan and contains pyrite, marcasite, gypsum, and localized siltstone facies and concentrations of *Ilmatogyra* oyster fossils. The Del Rio Clay was deposited in a shallow-water, near-shore marine environment such as a lagoon or bay (Kruger, 1983) and has been eroded off most areas in the Edwards Plateau. For the remainder of this paper, the term *relict* will refer to thick and potentially much older soils of the Edwards Plateau landscape, and the term *modern* will refer to typical thin soils of the Edwards Plateau landscape.

## Methods

A map was constructed in ArcGIS using (1) geologic map shape files of the Geologic Atlas of Texas (published by The University of Texas Bureau of Economic Geology) that were digitized by the U.S. Army Corps of Engineers and projected to the Texas Water Development Board Texas State Plane Projection (unpublished data available on CD-ROM) and (2) soil maps from the Soil Survey Geographic Database (SSURGO) published by the U.S. Department of Agriculture Natural Resources Conservation Service (http://www.ncgc.nrcs.usda.gov/products/datasets/ssurgo/). Soil types described as Redland, Deep Redland, and Gravelly Redland range sites (listed in Appendix B) in central and eastern portions of the Edwards Plateau were included in Figure 2.

Soil and limestone bedrock samples were collected from the Kerr Wildlife Management Area (KWMA) and Hall's Ranch in the vicinity of Mountain Home in Kerr County, Texas and from southwestern Kerr County. The Del Rio Clay was sampled from Shoal Creek and the Barton Creek Greenbelt in Travis County, road cuts in central-western Kerr County and New Braunfels in Comal County, and at the base of soil profiles of the Felipe series in Val Verde County. Dust samples provided by the USDA are from attics of two historic buildings that have collected dust since the early 1900's in Big Spring, Howard County (where the Edwards Plateau merges with the High Plains). Figure 1, Table 2, and Appendix D describe the sample material and/or sample locations.

Limestone residue was isolated from the Segovia Member of the Edwards Limestone and the Del Rio Clay by dissolution in ~9% sodium acetate- or ammonium acetate-buffered acetic acid (pH 6). Insoluble residue was Ca-saturated with 0.1 M calcium chloride, and rinsed in deionized water and 50% ethanol prior to X-ray diffraction (XRD) analysis. XRD patterns were determined for the clay size fraction (<2 μm) of oriented samples, prepared on glass slides, by scanning with CuKα radiation between 3 and 40° (2θ). The presence of smectite and smectite layers in mixed-layer clays was determined by XRD analysis of samples in both the ethylene glycol-solvated and air-dried state. Particle-size separation and measurement of the silt and clay size-fraction (<63 μm) was completed by the pipette method described by Folk (1980). The particle-size distribution of the >63 μm fraction was determined by dry sieving.

Soil and rock samples for neodymium (Nd) and samarium (Sm) isotope measurements were completely digested with hydrofluoric, nitric, and hydrochloric acids using a combination of hotplate and high-pressure vessel dissolution. Dissolved

Table 2
Sample names and locations

| Sample | Depth (cm) | Map number (Fig. 1) | County | Location |
|---|---|---|---|---|
| *Modern soils* | | | | |
| $Thin1_A$ | 0–5 | 1 | Kerr | Hall's Cave vicinity |
| $Thin1_{B1}$ | 5–14 | 1 | Kerr | Hall's Cave vicinity |
| $Thin1_{B2}$ | 14–18 | 1 | Kerr | Hall's Cave vicinity |
| $Thin2_A$ | 0–12 | 1 | Kerr | Hall's Cave vicinity |
| $Thin3_A$ | 0–12 | 2 | Kerr | Kerr Wildlife Management Area |
| *Relict soils* | | | | |
| $Thick4_{B4}$ | 39–52 | 2 | Kerr | Kerr Wildlife Management Area |
| $Thick5_A$ | 0–9 | 2 | Kerr | Kerr Wildlife Management Area |
| $Thick5_{B1}$ | 9–35 | 2 | Kerr | Kerr Wildlife Management Area |
| $Thick5_{B2}$ | 35–52 | 2 | Kerr | Kerr Wildlife Management Area |
| $Thick5_{B3}$ | 52–70 | 2 | Kerr | Kerr Wildlife Management Area |
| $Thick6_B$ | 43–47 | 2 | Kerr | road cut Highway 39 |
| $Thick7_A$ | 0–13 | 3 | Kerr | road cut Highway 187 |
| $Thick7_B$ | 13–45 | 4 | Kerr | road cut Highway 187 |
| *Del Rio Clay* | | | | |
| DRC-1 | – | 5 | Travis | Shoal Creek |
| DRC-2 | – | 6 | Kerr | road cut Highway 41 |
| DRC-3 | – | 7 | Comal | road cut Highway 306 |
| DRC-4 | – | 8 | Travis | Barton Creek Greenbelt |
| DRC-5 | – | 9 | Val Verde | road cut Highway 277 |
| DRC-6 | – | 9 | Val Verde | road cut Highway 277 |
| *Edwards Limestone (Segovia Member)* | | | | |
| LS-1 | – | 1 | Kerr | Hall's Cave vicinity |
| LS-2 | – | 2 | Kerr | Kerr Wildlife Management Area |
| *Dust* | | | | |
| Dust-1 | – | 10 | Howard | building attic, Big Spring |
| Dust-2 | – | 10 | Howard | building attic, Big Spring |

samples were spiked with a mixed $^{150}Nd$–$^{149}Sm$ tracer. Rare earth elements (REEs) were collected by cation exchange chromatography using rare-earth-element-specific resin (RE-Spec). Sm and Nd were further separated from the eluted rare earth elements by cation exchange chromatography using HDEHP resin. Combined measurements of Nd isotope ratios and concentrations were performed at The University of Texas at Austin on a Finnigan-MAT 261 thermal ionization mass spectrometer operated in dynamic multi-collection mode; Sm concentrations were determined by static multi-collection. $\varepsilon_{Nd}(0)$ values presented in this paper are calculated using a chondritic uniform reservoir (CHUR) $^{143}Nd/^{144}Nd$ ratio of 0.512638. Depleted-mantle model ages were calculated using the method described by DePaolo (1981). Major and trace element concentrations for aliquots of samples that were prepared for Sm and Nd isotope analysis were measured by ICP-MS. Appendix E provides details of the Nd and Sm sample preparation and measurement methods.

## Results

### *Soil distribution*

The distribution of Redland range soil types on the Edwards Plateau was used as a proxy for the distribution of the relict soils. Although the distribution of Redland range-type soils is the best available proxy for the distribution of the relict soils, there are associated caveats. For example, some dark-colored relict soils, or relict soils truncated from their original thickness, may not be identified as Redland range-type soils. Furthermore, soil map units identified as dominantly Redland range-type soils may include a lesser abundance of non-Redland soil types.

On the Edwards Plateau, the resistant Edwards Limestone caps the relatively flat-lying Cretaceous strata and therefore is preserved on uplands. Across several central Texas counties, Redland soils occur most commonly in broad, upland areas greater than ~700 m in elevation and less frequently at lower elevations (Figs. 1 and 2). In most of the counties on the Edwards Plateau that were included in this study, the distribution of the Redland soils correlates well with the distribution of the Lower Cretaceous Edwards Limestone and its stratigraphic equivalents (Fig. 2; Table 1). For example, in Kerr County, the percent area of Redland soils over the Edwards Limestone is approximately four times greater than the percent area of Redland soils over the Glen Rose Limestone (Table 1). Where Redland soils are common over the Glen Rose Limestone, there are dominantly in and surrounding drainages (Figs. 1 and 2), as is the case for most of the Redland soil occurrences in Bandera and Uvalde counties. The sharp fault contact and topographic discontinuity that juxtaposes the Glen Rose and Edwards limestones in the Balcones Fault Zone is also the boundary for the absence/presence of Redland range soils (Fig. 2A). Redland soils occur over Edwards Limestone uplands north of the Balcones Fault Zone but also at relatively lower elevations within the Balcones Fault Zone.

North of the Edwards Plateau, Redland soils occur dominantly over Paleozoic sedimentary rocks and Precambrian igneous and metamorphic rocks exposed in the Llano Uplift region (Figs. 1A and 2). Some of the silicate-rich Paleozoic and Precambrian lithologies may weather to form soils similar to Redland soils over the limestones of the Edwards Plateau. Thus, Redland soil types can only be used as a proxy for the distribution of relict soils in the Edwards Plateau and not in the Llano Uplift.

### *Texture and color*

Soil texture varies with the parent material and weathering history (Birkeland, 1984) and thus, may be a useful provenance indicator, provided that no subsequent processes (e.g. dissolution, recrystallization, or selective transport) have biased or altered the grain-size distribution. The amount of material in the clay (<2 μm), fine silt (2 to 20 μm), and coarser (>20 μm) grain-size fractions varies between the relict and modern soils of the Edwards Plateau (Fig. 3). Although coarse gravel-sized chert occurs in some horizons of the relict soils, it was excluded from

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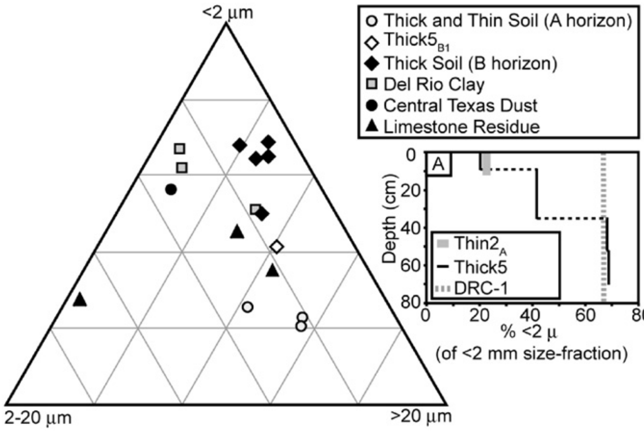


Figure 3. Grain-size distribution of soils and potential silicate sources. Soil A horizons of modern ($Thin2_A$) and relict ($Thick5_A$) soils include samples from this study (Appendix F) as well as an average value of A horizons from central Texas soils on resistant limestone reported by Rabenhorst and Wilding (1986). Relict soil samples include Thick5 (B1, B2, and B3 horizons), $Thick4_{B4}$, $Thick7_B$, and $Thick6_B$ (Appendix F). Del Rio Clay samples are the insoluble residue of DRC-1, DRC-5, and DRC-3. The central Texas dust value is an average of modern dust measurements reported by Rabenhorst et al. (1984). Limestone values represent the carbonate-free-fraction of bedrock at the base of soil profiles over resistant limestone reported by Rabenhorst and Wilding (1986). Inset A shows variation in clay content with depth in the soil profile of a relict soil in Kerr County. The clay content of a modern soil and the Del Rio Clay are also provided for comparison.

the particle-size analysis. The B horizons of relict soil profiles from Kerr County are very clay-rich and are depleted in fine silt. The clay content decreases towards the surface of the relict soil profile (Fig. 3A). The A horizons of relict and modern soils have approximately equal amounts of clay and fine silt and are enriched in the coarse (>20 μm) size fraction. Resembling the B horizons of the relict soils, the Del Rio Clay (this study) and modern dust (reported by Rabenhorst et al., 1984) both contain large amounts of clay, with the Del Rio Clay being most similar in clay content to the relict soils (Fig. 3). The insoluble residue samples from the underlying pure limestone (reported by Rabenhorst and Wilding, 1986) contain varying amounts of fine silt and coarse material, and have clay contents that are more similar to those of the soil A horizons than the relict soil B horizons.

It is important to note that most soils overlying the Del Rio Clay display tan to olive hues. However, the olive (2.5Y) and red (2.5YR) colors and clay texture of relict soil sample Thick5 is similar to the olive and red colors and clay texture of weathered Del Rio Clay (DRC-5 and DRC-6) from Felipe series soils near Del Rio in Val Verde County, Texas (Appendix A; Golden et al., 1982).

*Clay mineralogy*

The mineralogy of the clay size fraction may provide information about the different silicate sources (e.g., Rabenhorst and Wilding, 1986) or weathering history of the relict and modern soils. Most samples of relict and modern soils contain illite, kaolinite and smectite as mixed-layer illite/smectite or kaolinite/smectite (Fig. 4). Quartz and feldspar are present in some of the modern soils as well as in the relict soil A and B1 horizons but quartz and feldspar are absent in all other relict soil B horizons. The Del Rio Clay also lacks quartz (one sample) and feldspar (all samples). Excluding the more surficial B1 horizon, the B horizons of the relict soils are most similar mineralogically to the Del Rio Clay compared with other possible silicate sources such as central Texas dust and residue of the Edwards Limestone (Fig. 4). One exception is the lack of smectite and mixed-layer kaolinite/smectite in the Del Rio Clay and the presence of smectite and mixed-layer kaolinite smectite in at least some of the relict soil B horizons. The lack of smectite in the Del Rio Clay (Fig. 4) is suspect because the Del Rio Clay commonly contains abundant shrink-swell clays (Harpster, 1957; Kruger, 1983). Even though smectite may not appear as a discrete phase, there may be a significant amount of smectite in mixed-layer clays, yielding a high shrink-swell potential (Wilding, L.P. and White, N., personal communication, 2005). Thus, the absence of smectite in the Del Rio Clay samples analyzed in this study cannot be used to dismiss the Del Rio Clay as a potential silicate source. Furthermore, smectite is a

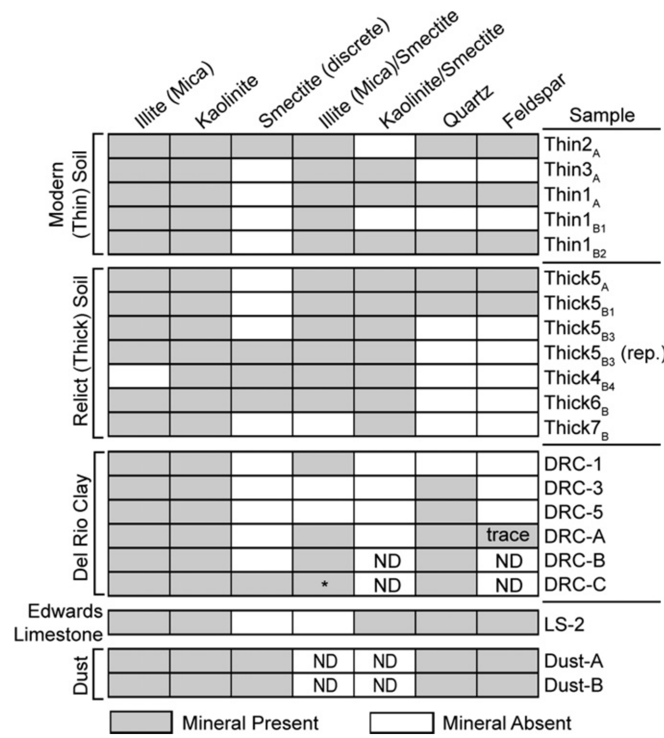


Figure 4. Mineralogy of the <2 μm size fraction of soils and potential sources. ND indicates the previous study did not provide information on the presence or absence of a mineral. Insoluble residue of the Edwards Limestone (LS-2) and the Del Rio Clay (DRC-1, DRC-3, and DRC-5) was calcium-saturated prior to X-ray diffraction (XRD) analysis. Additional Del Rio Clay samples include: DRC-A (Wilding, L.P. and White, N., personal communication, 2005) (unpublished laboratory data provided by J. Dixon's laboratory courtesy of L.P. Wilding and N. White, Soil Mineralogy Laboratory, Soil and Crop Sciences Department, Texas A&M University), DRC-B (Harpster, 1957), and DRC-C (Kruger, 1953). Dust-A represents the mineralogy of modern central Texas dust as reported by Rabenhorst et al. (1984) and Dust-B represents the mineralogy of historic dust from north-central Texas (Gill et al., 2000). *Kruger (1953) reported the presence of mixed-layer clays (not illite/smectite, specifically). Refer to Appendix G for details of XRD methods.

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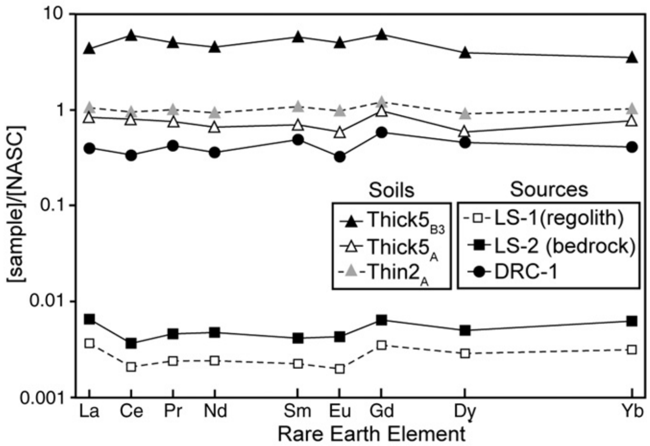


Figure 5. Rare earth element concentrations of soils and potential sources. REE concentrations determined by ICP-MS are normalized to values for the North American Shale Composite (NASC). Concentrations are reported in Appendix H.

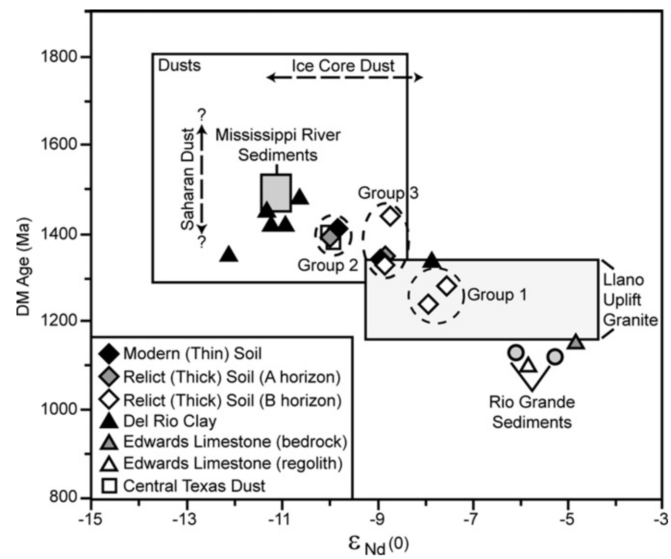


Figure 6. $\varepsilon_{Nd}(0)$ values of soils and potential sources. $\varepsilon_{Nd}(0)$ and depleted-mantle model ages (DM) provided for modern and relict soils in Kerr County and potential silicate sources including: historic central Texas dust, and bulk rock analyses of the Del Rio Clay and Edwards Limestone (Appendix I). Range of values of Precambrian Llano Uplift granite (light grey box) is from $^{143}Nd/^{144}Nd$ ratios and Sm and Nd concentrations for the Enchanted Rock Batholith reported by Smith et al. (1997) and from $^{143}Nd/^{144}Nd$ ratios, Sm and Nd concentrations, and DM ages for the Enchanted Rock Batholith and Town Mountain Granite reported by Patchett and Ruiz (1989). Range of values of Atlantic and Pacific dust (white box) is from $^{143}Nd/^{144}Nd$ ratios, $\varepsilon_{Nd}(0)$ values, and Sm and Nd concentrations reported by Goldstein et al. (1984). Horizontal dashed line indicates the range of $\varepsilon_{Nd}(0)$ values for Pleistocene dust deposited over the last 45,000 yr in a Greenland ice core (model ages not available; Svensson et al., 2000). Vertical dashed line shows the average $\varepsilon_{Nd}(0)$ value for modern Saharan dust (summarized by Borg and Banner, 1996); arrows indicate DM ages not available. $\varepsilon_{Nd}(0)$ values and DM ages for sediments from the Mississippi River (dark grey square) and Rio Grande (grey circles) from Goldstein et al. (1984) and Awwiller and Mack (1991). Local and regional volcanics are much more radiogenic than the modern and relict soils. Cretaceous volcanics of the Balcones Igneous Province have $\varepsilon_{Nd}(0)$ values from +5 to +7 (Wittke and Mack, 1993) and West Texas volcanics have $\varepsilon_{Nd}(0)$ values from −2 to +2 (Cameron et al., 1996).

common weathering product in semi-arid environments and may be neo-formed in the relict soils.

### *Rare earth element variations and Nd isotope compositions*

Because rare earth elements such as Sm and Nd are relatively immobile during weathering and diagenesis (McCulloch and Wasserburg, 1978; Banner et al., 1988; Borg and Banner, 1996), REE patterns and Nd isotope systematics of soils may be applicable to identifying the provenance of the silicate components. There is a higher concentration of both heavy and light REEs in the relict soil B horizon than in the A horizons of the modern and relict soils and potential bedrock sources (Fig. 5). The lowest ratio of mobile to immobile elements (i.e., K:Al, K:Fe, and K:Nd) is also found in the relict soil B horizon (Table 3). Ce anomalies are noted by Ce/Ce* values <1, where Ce/Ce* is the shale-normalized (NASC) ratio of the measured Ce concentration to the Ce concentration interpolated from lanthanum (La) and neodymium (Nd) concentrations. All samples, except the relict soil A and B horizons, have a Ce/Ce* values <1 (Fig. 5; Table 3).

Nd isotope compositions (expressed here as $\varepsilon_{Nd}(0)$ values), Sm/Nd ratios, and depleted-mantle model ages (the time that the Nd in a rock was separated from the upper mantle;

Table 3
Elemental indicators of chemical weathering

| Sample | Modern soil | Relict soil (A horizon) | Relict soil (B horizon) | Del Rio Clay | Edwards Limestone (regolith) | Edwards Limestone (bedrock) |
|---|---|---|---|---|---|---|
| | $Thin2_A$ | $Thick5_A$ | $Thick5_{B3}$ | DRC-1 | LS-1 | LS-2 |
| *Mobile/immobile elements* | | | | | | |
| K/Al | 0.17 | 0.18 | 0.05 | 0.27 | 0.47 | 0.85 |
| K/Fe | 0.40 | 0.43 | 0.12 | 0.53 | 1.5 | 1.5 |
| K/Nd | 320 | 370 | 39 | 710 | 500 | 920 |
| *REE fractionation* | | | | | | |
| Ce/Ce* | 0.94 | 1.0 | 1.4 | 0.87 | 0.64 | 0.61 |
| Eu/Eu* | 0.86 | 0.71 | 0.85 | 0.61 | 0.71 | 0.83 |

Ratios of mobile to immobile elements (i.e., K:Al, K:Fe, and K:Nd) serve as an index of weathering, where lower ratios of mobile to immobile elements indicate more intense weathering. The following calculations use the REE concentrations for the North American Shale Composite (NASC).
Cerium (Ce) anomalies are denoted by: $Ce/Ce^* = (3^*Ce_{sample}/Ce_{NASC})/(2^*La_{sample}/La_{NASC} + Nd_{sample}/Nd_{NASC})$.
Europium (Eu) anomalies are denoted by: $Eu/Eu^* = (Eu_{sample}/Eu_{NASC})/\sqrt{((Sm_{sample}/Sm_{NASC})^*(Gd_{sample}/Gd_{NASC}))}$.

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DePaolo, 1981) of relict and modern soils and potential silicate sources show several important results. First, the relict soils and the modern soils on the Edwards Plateau have $\varepsilon_{Nd}(0)$ values that are much lower than those of the underlying Edwards Limestone (Fig. 6). $\varepsilon_{Nd}(0)$ values for the Edwards Limestone were measured on the bulk limestone, wherein the Sm and Nd were most probably concentrated in the insoluble residue. The underlying limestone has a much younger depleted-mantle (DM) model age and higher $\varepsilon_{Nd}(0)$ value (1100 to 1150 Ma; −5.8 to −4.8) than the soils (1240 to 1440 Ma; −10.0 to −7.5) and Del Rio Clay samples (1340 to 1480 Ma; −12.1 to −7.8).

The Kerr County soils analyzed in this study can be divided into the following three groups based on their $\varepsilon_{Nd}(0)$ values: Group 1 comprises relict soil B horizons from soil profiles in the Kerr Wildlife Management Area (KWMA) with $\varepsilon_{Nd}(0)$ values that are very similar to the Del Rio Clay sample DRC-1 from Shoal Creek in Travis County; Group 2 comprises A horizons from modern and relict soils in the KWMA that have the lowest $\varepsilon_{Nd}(0)$ values; and Group 3 comprises a modern soil from the vicinity of Hall's Cave and B horizons of relict soils from southwestern Kerr County that have $\varepsilon_{Nd}(0)$ values intermediate between Groups 1 and 2 (Fig. 6).

## Discussion

### *Soil distribution*

The Redland soil distribution is controlled not only by physiography but also by bedrock stratigraphy. This result is contrary to the hypothesis of soil formation solely from dust deposition or from alluvial deposits, unless those deposits predate the Miocene faulting. The presence of Redland soil types over the Del Rio Clay and the Edwards Limestone is consistent with the hypothesis that the Del Rio Clay is a likely silicate source. In the Balcones Fault Zone, where faulting has exposed Upper Cretaceous strata, there are areas where the Redland soils overlie the Del Rio Clay, Buda Limestone, and Eagle Ford Group (Fig. 1B). The Eagle Ford Group — an Upper Cretaceous, clay-rich unit that overlies the more resistant Buda Limestone and is lithologically similar to the Del Rio Clay — may be a source of silicates to those Redland soils found over the limited exposures of the Buda Limestone and Eagle Ford Group (Fig. 2).

### *Texture, clay mineralogy, and Nd isotope compositions*

The high clay content of the relict soil B horizons (Fig. 3) is consistent with soil development by weathering of a clay-rich silicate source such as the Del Rio Clay. However, the high clay content of the relict soil B horizons is not solely related to the source material. Instead, the high clay content may result from illuviation and concentration of the clay-size fraction in the B horizon. The similarity of the model ages and $\varepsilon_{Nd}(0)$ values of the Del Rio Clay sample DRC-1 (1340 Ma; −7.8) and the B horizons of relict soils from Kerr Wildlife Management Area in Group 1 (1240 to 1280 Ma; −7.9 to −7.5) is consistent with a Del Rio Clay source for the B horizons of the relict soils in Group 1.

The textural and Nd isotopic differences between the limestone residue and the B horizons of the relict soils support the hypothesis that the underlying limestone residue is not a significant source of silicate material to the relict soils. Mixing of a minor proportion of silicates from the underlying limestone with the dominant source of silicates from the Del Rio Clay is supported by the model ages and $\varepsilon_{Nd}(0)$ values of the soils in Group 1, which are between end member values for the Edwards Limestone and the Del Rio Clay (Fig. 6). Although most of the clay in the relict soil may not be sourced from the underlying limestone, the gravel-sized chert in the relict soils may be derived from weathering of the underlying Edwards Limestone. Vertical transport of Edwards Limestone chert within the soil profile by shrink–swell processes related to wet/dry and freeze/thaw cycles may account for the presence of chert throughout the soil profile.

Recent eolian additions to central Texas soils probably produced the relatively coarse texture of and the presence of quartz and feldspar in the modern and relict soil A horizons (Figs. 3 and 4). These additions overprint the original texture and may have followed truncation of the relict soils. Although relatively clay-rich, the modern central Texas dust analyzed by Rabenhorst et al. (1984) has a silt-sized composition that is similar to those of the modern and relict soil A horizons (Fig. 3), supporting the interpretation that an eolian component is likely present in the A horizons. Furthermore, the A horizons of the modern and relict soils from the KWMA in Group 2 have DM ages and $\varepsilon_{Nd}(0)$ values (1390 to 1410 Ma; −10.0 to −9.8) that are almost identical to north-central Texas dust samples (1380 to 1400 Ma; −10.0 to −9.9). Although the similar Nd isotope composition of the dust and soil samples may reflect eolian contribution to the soils, it may also reflect dust derivation from erosion of the local soils. Modern and relict soils in Groups 2 and 3 have DM ages and $\varepsilon_{Nd}(0)$ values that are also within the range of modern Atlantic and Pacific dust (1300 to 1790 Ma; −13.6 to −8.5; Goldstein et al., 1984) and have $\varepsilon_{Nd}(0)$ values similar to late Quaternary dust from a Greenland ice core (−11.2 to −8.3; Fig. 6; Svensson et al., 2000). Thus, one cannot discount the possibility of either local or far-traveled dust input to these soils. The DM ages and $\varepsilon_{Nd}(0)$ values of the soils in Group 1 support the interpretation that these soils could not have formed solely from dust deposition.

Even though there is a lack of sand and silt-sized material in the relict soils, the possibility of alluvial and/or eolian contribution to the soils cannot be dismissed. The bimodal texture of clays and gravel-sized chert observed in the relict soils may be explained by (1) selective transport of alluvial clay and gravel, and/or (2) dissolution of silt- and sand-sized grains from eolian or alluvial sediments in an environment of intense weathering. The DM ages and $\varepsilon_{Nd}(0)$ values of Group 3 soils (1330 to 1440 Ma; −8.9 to −8.7) are intermediate between soils from Groups 1 and 2. Thus, we infer that Group 3 soils may have formed from the Del Rio Clay with possible contributions from eolian and/or alluvial materials. Alluvial sediments from a former drainage system would likely have model ages and

$\varepsilon_{Nd}(0)$ values within the range of sediments from the Mississippi River (1460 to 1520 Ma; −11.3 to −10.9) and the Rio Grande (1120 to 1130 Ma; −6.1 to −5.3; Fig. 6; Goldstein et al., 1984; Awwiller and Mack, 1991). Thus, alluvial sediments cannot be eliminated as a possible silicate source to soils in Groups 1, 2, or 3 on the basis of Nd isotope composition.

*Weathering history*

The rare earth element (REE) concentrations and patterns for the soils may provide information about the degree of weathering of soils as well as the provenance of the silicate parent material (Borg and Banner, 1996). Rare earth elements and elements such as Fe, Al, and Ti are relatively immobile in weathering environments compared to elements such as K, Na, Ca, and Mg. Thus, the concentrations of REEs and the ratios of mobile to immobile elements can be used as an index for the degree of weathering (Middelburg et al., 1988). The high concentration of REEs and low ratio of mobile to immobile elements in the relict soil B horizon is evidence for intense weathering (Fig. 5; Table 3; Appendix H). Intense weathering is also supported by the lack of quartz and feldspar in the B horizons of the relict soils (Fig. 4).

Negative Ce anomalies are typical of marine sediments because in oxidizing ocean environments, Ce occurs as $Ce^{4+}$, which preferentially partitions into iron and manganese nodule oxides and hydroxides, while other REEs in the $3^{+}$ oxidation state remain in solution (as summarized by Banner, 2004). Thus, marine sediments, such as the Edwards Limestone, are commonly depleted in Ce relative to other REEs. The relict soil B horizon is the only sample with a Ce/Ce* value >1 (Fig. 5; Table 3), which may reflect intense weathering of the relict soils.

Braun et al. (1990) and Marsh (1991) demonstrated that deeply weathered laterite soils can exhibit a positive Ce anomaly. Marsh (1991) attributed this anomaly to the oxidation of $Ce^{3+}$ to the more immobile $Ce^{4+}$ combined with the slow leaching of the trivalent REE in the weathering environment. Therefore, the positive Ce anomaly of the relict soil B horizon may be evidence for oxidation of Ce and selective leaching of the other REEs during intense weathering. This inverse weathering pattern, whereby the B horizon is more intensely weathered than the A horizon, is in agreement with the hypothesis that the relict soils did not form from weathering of the underlying limestone. Furthermore, this substantiates the idea that the relict, thick soils formed earlier and have experienced more intense weathering than the modern, thin soils.

## Summary and implications

A combination of geographic, textural, mineralogical, and geochemical evidence provides important constraints on the silicate source of the relict soils on the Edwards Plateau. Possible sources investigated include: (1) the underlying limestone bedrock, (2) dust, and (3) the Del Rio Clay, a stratigraphically higher unit that has been subsequently eroded away. Another potential silicate source that should be further investigated is sediment from a former, high alluvial surface.

Textural, mineralogical and geochemical differences between the soils and Edwards Limestone bedrock support the interpretation that the underlying limestone is not contributing a significant amount of silicate material to either the relict or modern soils in Kerr County. This conclusion is in agreement with previous observations of Rabenhorst and Wilding (1986), and is not unexpected given the low insoluble residue content of the Edwards Limestone. Some contribution of silicates from the underlying chert-rich limestone to the relict soils is supported by the presence of chert pebbles and cobbles in the relict soils.

Textural, mineralogical, and Nd isotope differences between the B horizons of the relict soils and modern dust support the interpretation that dust is not the dominant silicate source to the B horizons of the relict soils but is a silicate source to the modern soils and the A horizons of the relict soils. However, the possibility of multiple and changing dust sources and dust deposition rates through time limits our ability to accurately characterize and evaluate the potential of an eolian parent material.

The possibility of alluvial sediment contribution to the relict soils is difficult to assess, because if a former alluvial surface extended over the Edwards Plateau it has since been eroded away. Woodruff and Abbott (1986, 2004) suggested that ancient alluvial deposits on high terraces and erosion scars along modern drainage divides are evidence for the former existence of fluvial systems in the Edwards Plateau region prior to the development of modern drainage systems. This hypothesis of Miocene or Pliocene alluvial-blanket deposits over central Texas is also supported by the occurrence of ancient alluvial deposits along the Balcones Fault Zone and on the Coastal Plains (i.e., the Reynosa and Goliad formations) that are interpreted to be derived from a similar source area in New Mexico as the Ogallala sediments of the High Plains (Price, 1933, 1949; Byrd, 1971; Woodruff and Abbott, 2004). The distribution of Redland soils over the Edwards Limestone within and north of the Balcones Fault Zone is consistent with an alluvial silicate source if the alluvial deposition occurred after exposure of the Edwards Limestone. We recommend analyses of the texture, mineralogy, and Nd isotope composition of potential alluvial sources (i.e., sediments from the Ogallala Formation on the High Plains and the Goliad Formation on the Coastal Plains) to further assess the potential of an ancient alluvial silicate component in the relict soils.

The texture, mineralogy, Nd isotope composition, and distribution of the relict soils are all consistent with a Del Rio Clay silicate source. The high clay content of the Del Rio Clay (~70%, determined for one sample in this study), requires only ~1.4 m of the Del Rio Clay (which is locally 10 to 40 m thick) to weather to produce a 1-m-thick soil. This thickness is much more reasonable than the 100 to 900 m of Edwards Limestone that would have to dissolve to yield a 1-m-thick soil (estimated on the basis of the 1% insoluble residue content of the limestone and the concentrations of Nd in the Edwards Limestone bedrock and the relict soil). We propose that *in-situ* weathering of the pyrite-rich Del Rio Clay, in combination with some weathering

https://doi.org/10.1016/j.yqres.2006.11.007 Published online by Cambridge University Press

of the underlying chert-rich Edwards Limestone, would produce the thick, red, clay- and chert-rich soils that ultimately rest on the pure limestone bedrock of the Edwards Plateau.

Exotic sediments, such as those from volcanic, fluvial, and eolian deposition, have been found to be the parent material for soils over resistant limestones in other karst terranes, such as those in the Mediterranean (Genova et al., 2001), Croatia (Durn et al., 1999), Barbados (Borg and Banner, 1996), and the midwestern United States (Hall, 1976; Olson et al., 1980; Frolking et al., 1983). In this study we have found that the formerly overlying, but now-eroded strata served as a local parent material for the soil. Similarly, overlying strata were important silicate sources to clays overlying chalks in France (Laignel et al., 2002), a paleosol overlying dolomite in Tennessee (Driese et al., 2003), and likely sources to vertisols overlying Upper Cretaceous chalks in east-central Texas (Driese et al., 2003). These and our results suggest silicate sources external to the underlying limestone may be the parent material for karst soils more often than is recognized. Our conclusion that relict soils were derived from a now-exhausted silicate source has implications for understanding soil-development processes in central Texas where the bedrock is composed of inter-layered resistant and non-resistant limestone, but also for other karst terranes with similar stratigraphic relationships.

The relict soils on the Edwards Plateau provide insights into the Quaternary evolution of the Edwards Plateau landscape and insights into soil management. The mosaic landscape of thin sand thick soil types has resulted from at least two stages of soil formation, from distinct parent materials and late Quaternary, climate-driven soil erosion. Furthermore, relict soils above silicate-poor limestone may have been derived from a now-exhausted silicate source, and therefore may be nonrenewable resources.

## Acknowledgments

The National Science Foundation Geology and Paleontology Program, the Geological Society of America, The University of Texas, and The University of Texas Geology Foundation and Environmental Science Institute provided generous support for the completion of this work. This study also benefited from discussions with C. Woodruff, E. Lundelius, W. Gabriel, and P. Rose and the technical assistance of J. Lansdown, T. Housh, and M. Helper. We appreciate the helpful reviews of E. Taylor and an anonymous reviewer. We would like to acknowledge T.D. and B. Hall and B. Armstrong for providing access to the study locations and S. Van Pelt from the USDA office at Big Spring, Texas for providing dust samples. Thanks also for the assistance of P. Mickler, A. Townshend-Small, A. McCole, A. Guilfoyle, J. Ruddy, C. Caran, and D. Schuchmann.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.yqres.2006.11.007.

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