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Climate change during the Early Paleogene in the Bogotá Basin (Colombia) inferred from paleosol carbon isotope stratigraphy, major oxides, and environmental magnetism



Sara Morón ^{a,c,*}, David L. Fox ^a, Joshua M. Feinberg ^{a,b}, Carlos Jaramillo ^c, German Bayona ^d, Camilo Montes ^e, Jonathan I. Bloch ^f

^a Department of Earth Sciences, University of Minnesota, 310 Pillsbury Drive SE, Minneapolis, MN, 55455-0231, USA

^b Institute for Rock Magnetism, University of Minnesota, 100 Union Street SE, Minneapolis, MN, 55455, USA

^c Smithsonian Tropical Research Institute, Box 0843-03092, Balboa, Ancon, Panama

^d Corporación Geológica Ares, Calle 44a # 53-96, Bogotá D.C., Colombia

^e Geociencias, Universidad de los Andes, Calle 1A # 18A-10, Edificio IP, Bogotá D.C., Colombia

^f Florida Museum of Natural History, University of Florida, Gainesville, FL 32611-7800, USA

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ABSTRACT

Paleosols in the Bogotá Basin, Colombia, record an increase in chemical weathering across the Paleocene–Eocene (P–E) transition. Rock magnetic properties and major element geochemistry exhibit an abrupt change in an interval identified as including the P–E boundary, as established by previously published biostratigraphy and a U/Pb date on volcanic zircons (56.2 ± 1.6 Ma). During the stratigraphic interval that contains the P–E transition, magnetic susceptibility increases significantly, with an order of magnitude higher concentration of magnetite/maghemite and hematite. The preponderance of pure stoichiometric magnetite in the paleosols of this interval indicates that the increase in magnetic susceptibility is due to changes in the rate of pedogenesis, rather than an increase in the erosion of nearby volcanic rocks, which would contribute titanomagnetite. Pedogenic structures preserved within the paleosols, a lack of iron oxides as cement, friability of the sand-stones, and previously published thermochronologic data are not consistent with burial diagenesis as an explanation for the origin of the magnetic mineral assemblage. These enhanced pedogenesis and related chemical weathering is also confirmed by increases in the erosen of Fe₂O₃ and Al₂O₃ and loss on ignition values. An increase in mean precipitation across this interval is inferred by the lack of carbonate nodules and a decrease in SiO₂ in paleosols. Thus, we hypothesize that there was an intensification of chemical weathering the interval that contains the P–E transition.

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1. Introduction

The Late Paleocene and Early Eocene record a series of short-lived hyperthermal events including the Paleocene–Eocene Thermal Maximum (PETM), the Eocene Thermal Maximum 2 and the Eocene Thermal Maximum 3, with the PETM displaying the highest temperature changes in the Cenozoic (Zachos et al., 2001; Cramer et al., 2009; Gradstein et al., 2012). All of these events are associated with negative carbon isotope excursions that reflect large injections of isotopically light carbon either as CO₂ or in a form that would be rapidly oxidized to CO₂ (Zachos et al., 2001; Lourens et al., 2005; Pagani et al., 2006; McInerney and Wing, 2011). The release of isotopically light carbon into the ocean–atmosphere–terrestrial carbon reservoirs is coincident with changes in climate, oceanic and terrestrial geochemistry, as well

E-mail address: sara.moronpolanco@adelaide.edu.au (S. Morón).

as marine and terrestrial ecosystems (Zachos et al., 2005; Cramer et al., 2009; McInerney and Wing, 2011; D'haenens et al., 2012; Secord et al., 2012). The primary climate change of these hyperthermal events is an intense period of global warming (Zachos et al., 2003; Lourens et al., 2005; Tripati and Elderfield, 2005; Sluijs et al., 2006; Charles et al., 2011; McInerney and Wing, 2011).

The effect of these global warming events in the hydrologic cycle and the mechanisms for temperature stabilization, such as weathering, on the other hand, are controversial (Bowen et al., 2004; Wing et al., 2005; Clechenko et al., 2007; Kraus and Riggins, 2007; Schmitz and Pujalte, 2007; Bowen and Bowen, 2008; Bowen, 2011; Clementz and Sewall, 2011; McInerney and Wing, 2011; Foreman et al., 2012). Precipitation rates are highly variable for sites from similar latitudes, and estimates from tropical latitudes are still poorly constrained. Existing empirical estimates of paleoprecipitation use paleosol elemental ratios that have been specifically calibrated for soils in temperate climates where mean annual precipitation rarely exceeds 1500 mm/yr (Sheldon et al., 2002; Nordt and Driese, 2010). However, wet tropical

^{*} Corresponding author at: Australian School of Petroleum, The University of Adelaide, SA 5005, Australia. Tel.: $+61\,8\,83138044$.

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regions receive much greater precipitation (up to 12,000 mm/yr, Burnham and Johnson, 2004) and models derived from temperate soils cannot be extrapolated to wet tropical zones (Sheldon et al., 2002). Wet tropical soils are typically more highly weathered than soils forming in temperate regions, and concentrations of refractory elements (e.g. Fe, Si and Al) and the magnetic minerals that incorporate these elements may be more suitable proxies for understanding the potential effects of hyperthermal events on tropical terrestrial environments. In wet tropical soils, metal cations, such as iron, aluminum, and silica are leached from the uppermost horizons, and then reprecipitated as iron oxides, aluminosilicates, and oxy-hydroxides lower in the soil profile (Kronberg et al., 1982; Simas et al., 2005; Muggler et al., 2007; Burak et al., 2010).

In this paper, we present geochemical and environmental magnetic proxies of environmental change in a P-E paleosol sequence in the Bogotá Basin, Colombia. Use of carbon isotope stratigraphy to identify carbon isotopic excursions during the P-E is common (Wing et al., 2005; Jaramillo et al., 2010), and several previous studies have used both magnetic minerals (Villasante-Marcos et al., 2009; Dallanave et al., 2010) and paleosol geochemistry (Clechenko et al., 2007; Kraus and Riggins, 2007) to examine environmental changes across the P-E boundary associated with hyperthermal events. The proxies we use include: i) carbon isotope composition of bulk paleosol organic matter; ii) magnetic susceptibility and magnetic mineral concentration (magnetite/maghemite, goethite, and hematite); and iii) major oxides in bulk paleosol samples. In this paper, we provide environmental information from a low latitude site that will contribute towards i) a better understanding of regional climatic patterns across the P-E, particularly changes in precipitation, and the impact of those changes on chemical weathering and ii) to investigate the hypothesis that a negative feedback of silicate weathering could have been the primary mechanism for stabilization of global surface temperatures as proposed by earlier workers (Walker et al., 1981; Kump et al., 2000; Dallanave et al., 2010).

2. Geological setting

The Paleogene upper Guaduas, Cacho, Bogotá, and Regadera formations represent the terminal, youngest sedimentation episode during a regressive cycle in the Andes of northwestern South America that started in the Late Cretaceous (Julivert, 1970; Gomez et al., 2005; Bayona et al., 2010) and culminated with continental deposits during the early Paleogene. Paleogene strata are preserved in the axes of north- to northeast trending synclines in the Colombian Eastern Cordillera. The Usme Syncline (Fig. 1) is one of these north-plunging structures, it exposes Upper Cretaceous to Oligocene units and preserves the most complete lower Eocene record of the Eastern Cordillera (Julivert, 1970; Bayona et al., 2010; Ochoa et al., 2012). The total thickness of the Paleogene units in the Usme Syncline is approximately 2000 m.

The paleosols studied here, although now exposed along the crest of the Eastern Cordillera at nearly 2800 m a.s.l., represent a Paleocene– Eocene lowland accumulation environment not influenced by orographic effects. These paleosols were formed long before the surface uplift of the Eastern Cordillera, which occurred between the Miocene and the Pliocene (Van der Hammen et al., 1973; Mora et al., 2008; Parra et al., 2009; Horton et al., 2010; Ochoa et al., 2012).

An age model for the stratigraphic section was compiled (Fig. 2) using published palynological zones and U/Pb dates (Bayona et al., 2010, 2012). Bayona et al. (2010) processed 95 samples for palynological analysis following standard procedures (Traverse, 2007). Pollen grains were classified by comparing morphological features with descriptions and illustrations from local palynological literature (Hoorn, 1988; Jaramillo and Dilcher, 2001; Jaramillo et al., 2009; Jaramillo and Rueda, 2008; Santos et al., 2008; Jaramillo et al., 2009). Counting of

2462 grains and determination of 192 species allowed establishing palvnological assemblages and four important biostratigraphic events (First appearance datum (FAD) of Monocolpopollenites ovatus, Last appearance datum (LAD) of Psilamonocolpites operculatus, FAD of Corsinipollenites psilatus, and FAD of Cicatricosisporites dorogensis). In this age model, the Guaduas and Cacho formations in the Usme Syncline are assigned Paleocene ages (Bayona et al., 2010). A middle-late Paleocene to early Eocene age is assigned to the Bogotá Formation. A single fossil dentary of a primitive xenungulate mammal (Etayoa bacatensis) was previously identified within the upper Bogotá Formation (Mochuelo Creek section), suggesting a middle Paleocene age (Villaroel, 1987). However, the age of the Bogotá Formation has been more recently constrained as Early Eocene by U/Pb ages of volcanic zircons recovered from an interbedded tuff (56.2 \pm 1.6 Ma, n = 98, Bayona et al., 2012). The margin of error of this tuff encompasses the P–E boundary, which is defined as 55.85 \pm 0.10 Ma by Gradstein et al. (2012). We present also all the zircon ages previously reported (Fig. 2), as well as the average depositional ages reported in Bayona et al. (2012). Our interpretation of these data is that the Bogotá Formation includes the P-E boundary. Three of these U/Pb ages were extracted from detrital volcanic zircons recovered from fluvial sandstone beds and therefore provide only maximum depositional ages (60.96 \pm 0.7 Ma, n = 89 at 937 m, 55.72 \pm 1.1 Ma, n = 79 at 1190 m and 53.6 \pm 1.1 Ma, n = 108 at 1650 m, Bayona et al., 2012). It is important to note that the depositional age of the sediment is likely to be younger than these U/Pb ages, in agreement with the palynological data. A late Eocene age is assigned to the Regadera Formation in the Usme Syncline based on the FAD C. dorogensis in the fossil pollen assemblage (Bayona et al., 2010) and the palynological zonation for the region (Jaramillo et al., 2011).

3. Materials and methods

3.1. Measurement of stratigraphic section and paleosol description

We measured and described a 2 km thick stratigraphic section along Mochuelo Creek (4.51773°N, 74.14980°W) south of Bogotá, Colombia. The zero meter datum of the section was set within the Guaduas Formation, at the bottom of the exposures near the brick factories of the Mochuelo area (McLaughlin and Arce, 1975).

Samples were taken from trenched paleosols along the stratigraphic sequence for carbon isotope, magnetic, elemental, and X-ray diffraction (XRD) analyses. Ninety samples were analyzed for the stable carbon isotope composition of bulk organic matter, 112 for magnetic mineralogy, 15 for X-ray fluorescence, and three for XRD using methods described in the following sections.

Paleosol descriptions and classifications provide a context for the geochemical and magnetic data; however, it is beyond the scope of this paper to present detailed descriptions of all the paleosols. Paleosols were described in the field following the guidelines of the Soil Survey Staff (1999). Matrix color change and grain size were used as criteria to define the paleosol horizons in the field. Matrix and mottling color were determined using the Munsell color classification. The presence of nodules (carbonate), redoximorphic features (mottling), and pedoturbation were also noted in the field. Subsequently, paleosol types were classified based on the paleosol-specific taxonomic scheme (Mack et al., 1993; Sheldon and Tabor, 2009).

The stratigraphic positions of bulk samples of paleosols for carbon isotope analyses were measured relative to the upper contact of the sampled paleosol horizon (e.g., Wing et al., 2005; Foreman et al., 2012).

3.2. Magnetic properties

All magnetic properties were measured at the Institute for Rock Magnetism at UMN using measurements of low-field susceptibility and various forms of laboratory-induced magnetization.



Fig. 1. Geologic map showing the location of the Usme Syncline and the Mochuelo Creek section (black rectangle). Modified from (Bayona et al., 2010). Index map shows location of the Mochuelo Creek section in northwestern South America.

In-phase magnetic susceptibility was measured using a Geofyzika KLY-2 KappaBridge AC susceptibility bridge with a nominal sensitivity of 4×10^{-8} SI (AC field of 300 Am⁻¹ and frequency of 920 Hz). Laboratory induced magnetizations were measured in a shielded room with a background field less than 100 nT using a 2G Enterprises 760-R cryogenic SQUID magnetometer with a nominal sensitivity of 2×10^{-11} Am².

Measurements of in-phase magnetic susceptibility act as a proxy for the concentration of magnetic minerals in a sample. To estimate the concentrations of remanence carrying magnetic minerals, we used a combination of isothermal remanent magnetizations (IRMs) and thermal demagnetization steps. We used S-ratios to quantify the remanence held by low-coercivity minerals, such as magnetite and maghemite, versus high-coercivity minerals, such as hematite and goethite (Bloemendal et al., 1992). A complete description of the S-ratio and magnetic mineral concentration calculations can be found in the Supplementary material.

Low-temperature magnetic measurements were conducted on select samples to further test for the presence of goethite, hematite, and magnetite–maghemite. All low temperature measurements were conducted using a Quantum Designs Magnetic Property Measurement system. The presence of a magnetic mineral can often be verified by identifying mineral-specific magnetic transitions while cycling a sample from 300 K (room temperature) to 10 K and back to 300 K. To increase



Fig. 2. Chronology showing the extent of the four palynological events (gray horizontal lines), the U/Pb ages of zircons, and the approximate location of the *Etayoa bacatensis*. Ages for detrital zircons (black solid circles) are from Bayona et al. (2010, 2012), and gray error bars indicate their 1σ error. The depositional age of a volcanic tuff (asterisk) and the average age of fluvial sandstone beds (non-solid circle) are from Bayona et al. (2012). Stages and epoch boundaries are based on Gradstein et al. (2012).

the magnetic signal during these measurements, samples are typically given a 2.5 T IRM at 300 K immediately prior to cooling, and for this reason the experiments are called 'room-temperature saturation isothermal remanent magnetization (RT-SIRM) measurements'. A more detailed list of the procedures used to detect the presence of each mineral can be found in the Supplementary material.

Low temperature magnetic measurements can also be used to test for the presence of siderite, which has a diagnostic magnetic transition at 38 K. Samples were cooled from room temperature to 10 K in a zero field environment or in the presence of a 2.5 T DC field. At 10 K samples were given a 2.5 T IRM and the resulting remanence was measured on warming back to room temperature. These experiments are typically referred to as "zero-field-cooled" (ZFC) or "field-cooled" (FC) low temperature saturation isothermal remanent magnetization (LT-SIRM) measurements. In this study, the in-phase and quadrature AC susceptibilities were measured using the Quantum Designs MPMS2 at frequencies of 1, 6, 32, 178, and 997 Hz, in a field of 200 A/m.

Magnetic extracts were obtained from select samples in order to determine their Curie temperatures. Differences in Curie temperatures were used to determine the degree of Ti and/or Al substitution within the magnetite and to ultimately determine whether the magnetite in the Bogotá Formation originated as a product of pedogenesis (Ti-free magnetite/maghemite) or as erosional detritus from nearby volcanics (Ti-rich magnetite/maghemite). Major hysteresis loops were collected before and after each thermomagnetic experiment using a MicroMag Princeton Measurements vibrating sample magnetometer with a nominal sensitivity of 5×10^{-9} Am². Samples' induced (1 T) magnetizations were measured at 1 °C increments while cycling the temperature from 23 °C to 700 °C to 23 °C in a continuous stream of helium gas (used to inhibit oxidation of samples). Curie temperatures and inversion temperatures were calculated by identifying peaks in the second derivative of the measured data. A detailed description of the magnetic separation can be found in the Supplementary materials.

3.3. X-ray diffraction

To test for the presence of pedogenic siderite in the samples, XRD was carried out before 6 N HCl treatment on three samples (13.5, 547, 909.7) using a Rigaku Miniflex XRD unit with a copper target and a scintillation detector. XRD spectra were analyzed using the Jade software package.

3.4. Carbon isotopes

We measured the carbon isotope (δ^{13} C) composition of bulk organic matter to determine if any of the carbon isotope excursions associated with the P–E are preserved in the Mochuelo Creek section. Samples were decarbonated with 0.5 M HCl for 24 h and then rinsed with distilled water to neutral pH. Afterwards, samples were oven dried at 50 °C and then pulverized with a mortar and a pestle. Decarbonated samples were combusted in a Carlo Erba Elemental Analyzer, and the δ^{13} C of the resulting CO₂ was measured with a Finnigan MAT Delta V gas source isotope ratio mass spectrometer in the Department of Earth Sciences at the University of Minnesota (UMN). Multiple samples of NIST 2711a (Montana soil) were analyzed in parallel with each set of samples to normalize sample values, and Costech acetanilide was also analyzed as a standard with each set of samples for quality control. Since δ^{13} C values of bulk organic matter can be affected by the total organic carbon (TOC) of a sample, we examine the stratigraphic pattern of the residuals of a regression of δ^{13} C values on TOC for each sample as done previously by Wing et al. (2005). Results are expressed in conventional δ^{13} C notation relative to Vienna Pee Dee Belemnite (VPDB).

Repeated analyses revealed poor reproducibility for individual Mochuelo Creek samples, with standard deviations larger than 0.5‰. Three approaches were undertaken to address this problem: 1) splits from the same samples were analyzed at University of Florida (UF) to exclude the possibility of instrumental error; 2) results from UMN were compared and samples with low reproducibility were removed; and 3) samples were pre-treated with 6 N HCl to dissolve any trace concentrations of pedogenic siderite (FeCO₃), in case isotopically distinct C from siderite was contaminating the organic matter isotope measurements. Each of these methods is further discussed below.

Samples analyzed at UF were pre-treated with 1 N HCl overnight and rinsed three times with deionized water. Acidification and rinsing was repeated for samples that still reacted with HCl. Subsequently, samples were dried at 60 °C and re-pulverized and combusted in a Carlo Erba NA1500 CNS. The CO₂ released in the combustion was measured in a Finnigan-MAT DeltaPlus. USGS40 was used as a standard to normalize sample δ^{13} C values and to determine analytical precision.

Results from UMN were used exclusively to obtain a carbon isotopic record with an intra-sample variability of less than 0.5‰. Thus, the difference between the maximum and the minimum of each sample was calculated and compared among runs. Samples analyzed multiple times that had differences in δ^{13} C values with larger than 0.5‰ were excluded from the record.

The 6 N HCl pre-treatment followed the method proposed by Larson et al. (2008) to remove pedogenic siderite that may contaminate the carbon signal from the organic matter. Samples were acidified in situ each day for three days with 100 μ L of 6 N HCl in silver capsules and oven dried at 50 °C overnight every day. Then, the silver capsules containing the acidified samples were enclosed in tin capsules and analyzed at UMN using the Finnigan MAT Delta V gas source isotope ratio mass spectrometer.

3.5. X-ray fluorescence

Major oxide concentrations were measured for 15 samples using X-ray fluorescence (XRF) at a commercial laboratory (ALS Minerals) with a PANalytical AXIOS X-ray spectrometer with a detection limit of 0.01%. Samples were ground and sieved to 75 μ m (200 mesh) and then homogenized in a tungsten carbide ball mill. STSD-4 and SY-4 were used as standards. Loss on ignition (LOI) was determined by combusting 3 g of the powdered sample at 1000 °C for 1 h, and then the sample was weighed to determine the mass difference for LOI. Subsequently 0.9 g of sample was used for fusion for the whole rock analysis.

3.6. Statistics

Iron oxides are often responsible for soil coloration in low organic content soils (Torrent and Schwertmann, 1987). Thus, soil and paleosol colors have been used to infer iron oxide phases and environmental changes in time (Kraus and Riggins, 2007). We investigated the

difference in frequencies of paleosol colors before, during, and after the P-E interval (828-1009 m) by calculating the ratio of the number of gray horizons to the sum of red and purple horizons for each zone (i.e., before, during, and after the P–E) so that the lowest ratio indicates the lowest frequency of gray paleosols and more intensely weathered paleosols (Kraus and Riggins, 2007). To establish a confidence interval for the empirical differences we produced a null hypothesis (e.g. no differences in paleosol color before, during and after the P-E) by randomizing the paleosol colors then calculating the ratio of each zone and by iterating this algorithm 10,000 times. We then compared the empirical ratios with the randomized distribution of the ratios. We also conducted a goodness-of-fit test to determine difference in the distribution of paleosol colors before, during and, after the assumed P-E for the entire stratigraphic sequence. An unpaired t-test was performed to test the differences in the carbon isotopic record and in magnetic properties before, during and, after the P-E interval. All statistical analyses were carried out using the R Project for statistical computing (R Development Core Team, 2011).

4. Results

4.1. Pedogenic features and paleosol classification

4.1.1. Oxisols

These paleosols appear as persistent alternations of red and purple beds that exhibit red, gray or yellow redoximorphic features. Identification of magnetic minerals (see Section 4.2.1) confirmed the presence of hematite and goethite, and these minerals are likely the origin of the coloration. The XRD spectrum of sample 909.7 m displays a peak at ~12° (20) and a shoulder at 20° (20) suggesting the presence of kaolinite (see Supplementary materials). The low total organic carbon (TOC) content in these samples excludes the possibility that these paleosols are Spodosols.

4.1.2. Argillisols

These paleosol horizons display interbedded gray, red and purple mottled mudstone beds. Clay coats were observed on angular to subangular blocky peds. The claying ratio (Si/Al) in the paleosol horizon 201 m-205.5 m displays an increase in the intermediate horizon suggesting that clay formation occurred due to eluviation/illuviation (Supplementary materials). Other diagnostic horizons were observed in Argillisols, and their modifiers are described below. We identified both vertic and calcic Argillisols. Argillisols identified as vertic had slickensides but retained well defined horizons and did not exhibit homogenization of the profile by pedoturbation and so are not identified as Vertisols. Calcic Argillisols with carbonate nodules and rhizoliths filled with carbonate occur at eight stratigraphic levels. These calcic horizons are present in red, purple and gray mudstone. Carbonate nodules are generally ~4 cm in diameter while rhizoliths range in diameter from 2 mm to 3 cm, although some of them do not have well defined boundaries and are pervasive.

4.1.3. Protosols

These paleosols contain gray, weakly developed horizons with very few redoximorphic features and platy peds. The presence of platy peds could be related to relict bedding and confirms that poor horizonation of the soil profile is not related to homogenization by pedoturbation. Thus, paleosols with these features are classified as Protosols.

4.2. Rock magnetic record

The rock magnetic record around stratigraphic meters 829–1009 displays persistently large values, with sample 839 m marking the start of the abrupt increase in both magnetic susceptibility and concentration of magnetic minerals (Fig. 3B). The termination of this zone is



Fig. 3. Paleosol color, carbon isotope stratigraphy, and rock magnetic results of the Paleocene–Eocene Mochuelo section. From left to right: (A) for the entire section U/Pb age in zircon from the volcanic tuff reported by Bayona et al. (2012); lithostratigraphy of the section; paleosol color; redoximorphic feature color (R = red, P = purple, G = gray. Y = yellow); δ^{13} C bulk organic matter record from UMN (0.5 M HCl pre-treatment), dashed curve is a 5-point moving average; rock magnetic results (magnetic susceptibility, concentration of magnetite/ maghemite (Mag/Magh), goethite, and hematite). The horizontal dashed lines identify the limits for Zones 1, 2 and 3. (B) detailed view of Zone 2.

more gradual than sudden, with values becoming progressively lower until 1009 m when they remain more or less constant.

These changes in rock magnetic properties are coincident with changes in lithology and are used to separate the stratigraphic section into three zones. Zone 2 refers to section described above (829–1009 m), and the intervals below and above are Zones 1 and 3, respectively. Zone 2 also shows a statistically significant lower number of gray paleosol horizons (goodness-of-fit test, $p = 5.51 \times 10^{-7}$, p < 0.01) than in Zones 1 and 3. The gray to red and purple ratios indicate that the number of gray paleosol horizons in Zone 2 (0.26) is lower than in Zones 1 (0.47) and 3 (0.56) within the Bogotá Formation. Results from the bootstrapping analysis showed that the probability of generating the frequency of paleosol colors Zone 2 (bootstrapped mean ratio = 0.45, observed ratio = 0.26) by chance is small (p < 0.08), but not statistically significant. Additionally, Zone 2 does not contain any paleosols with carbonate nodules (Bk horizons), while Zone 1 has two Bk horizons and Zone 3 has six.

4.2.1. Magnetic susceptibility and magnetic mineral concentrations

Magnetic susceptibility values in Zone 2 (mean = 1.8×10^{-7} m³/kg) are significantly higher than those in Zones 1 (mean =

 $7.1 \times 10^{-8} \text{ m}^3/\text{kg}$, *t*-test $p = 9.9 \times 10^{-8}$, df = 31.886) and 3 (mean = $1.2 \times 10^{-7} \text{ m}^3/\text{kg}$, *t*-test $p = 3.0 \times 10^{-4}$, df = 34.096). Additionally, Zone 1 exhibits values significantly lower than Zone 3 (*t*-test $p = 2.9 \times 10^{-7}$, df = 76.108).

Hematite is the predominant iron-bearing magnetic phase in the samples (Fig. 3A). Goethite and magnetite/maghemite are also present in all samples; magnetite/maghemite concentrations are generally an order of magnitude lower than the other minerals (Table 1). Magnetite/ maghemite have significantly higher concentrations in Zone 2 (mean = 17.81 ppm) relative to Zones 1 (mean = 7.07 ppm, *t*-test, p = 0.006, df = 29.936) and 3 (mean = 8.87 ppm, *t*-test, p = 0.019, df = 28.995). Hematite is also substantially more abundant in Zone 2 (mean = 11,151 ppm) compared both to Zone 3 (mean = 7065, t-test, t)p = 0.007, df = 32.151) and to Zones 1 and 3 combined. The latter value is referred to hereafter as background (mean = 7605 ppm, *t*-test, p = 0.026, df = 42.896). Additionally, an order of magnitude increase is observed in the concentration of magnetite/maghemite (101 ppm) and hematite (39,421 ppm) at the base of Zone 2. This dramatic increase begins with the sample at meter 839, and replicate magnetic measurements on separate splits from this sample all yielded similarly high concentrations of magnetic minerals. Even if this sample is removed from

Table 1

Summary of values from the rock magnetic record discriminated by the described zones in the text.

	Magnetic susceptibility (m ³ /kg)	Magnetite/maghemite (ppm)	Goethite (ppm)	Hematite (ppm)
Zone 1 (0–828)				
Max	1.2E-07	23.00	3762	43,960
Min	2.9E-08	1.00	124	758
Mean	7.1E-08	7.07	1386	8704
Zone 2 (828–1009)				
Max	4.8E-07	101.00	5380	39,420
Min	7.3E-08	5.00	162	3110
Mean	1.8E-07	17.28	1577	11,150
Zone 3 (1009–2020.5)				
Max	3.2E-07	31.00	4005	18,310
Min	3.5E-08	0.10	29	87
Mean	1.2E-07	9.019	1378	7065

our analysis, the differences between the magnetic properties of Zone 2 compared to both Zones 1 and 3 remain statistically significant. Magnetic susceptibility values of Zone 2 (excluding sample 839 m) are higher than those of both Zone 1 (*t*-test, $p = 7.2 \times 10^{-10}$, df = 36.008) and Zone 3 (*t*-test, $p = 6.6 \times 10^{-5}$, df = 40.779). Magnetite/maghemite concentrations in Zone 2 (without sample 839 m) are still significantly different than Zones 1 (*t*-test, $p = 1.0 \times 10^{-4}$, df = 43.260) and 3 (*t*-test, $p = 1.0 \times 10^{-3}$, df = 41.462), and hematite concentrations in Zone 2 (removing sample 839 m) are still higher than background (*t*-test, p = 0.03, df = 67.525). That the results remain statistically significant demonstrates not only that the sample at 839 m marks the start of the abrupt increase in magnetic minerals, but also that the sample at 839 m is not solely responsible for the high values of Zone 2.

4.2.2. Room-temperature saturation isothermal remanent magnetization (RT-SIRM)

Results from low temperature RT-SIRM measurements corroborate the presence of magnetite/maghemite, hematite, and goethite in the paleosol samples (Fig. 4). Three main features were identified in the measurements: 1) a gentle decrease in magnetization during warming attributed to the presence of both goethite and oxidized magnetite; 2) a divergence between the cooling and warming curves at 110 K, attributed to the Verwey transition in pure magnetite (Kasama et al., 2010); and 3) a sharp deviation in the first derivative of the magnetization curve on warming between 265 and 270 K, attributed to the Morin transition of hematite (Lascu and Feinberg, 2011).

4.2.3. Testing for the presence of siderite

The XRD analyses did not indicate the presence of siderite in any samples analyzed. However, XRD is usually only sensitive to siderite concentrations >2% and smaller concentrations could still affect bulk sediment δ^{13} C values. Therefore, we analyzed sample 947.4 m, one of the samples with a standard deviation for replicate δ^{13} C values of >1‰, using FC-LT-SIRM (Fig. 5). The sample shows a gradual decrease in remanent magnetization during warming to 300 K. For comparison, we include data from previously published experiments on a siderite standard and a siderite bearing marine sediment from Housen et al. (1996). These two datasets show a dramatic loss in magnetization between 35 and 40 K associated with the Néel temperature of siderite (Martin-Hernandez and García-Hernández, 2010). The siderite-bearing marine sediment also shows evidence of the Verwey transition in pure magnetite near 110 K. The paleosol sample from the Bogotá Formation shows neither the remanence loss at 35 to 40 K, nor the Verwey transition. Given that these rock magnetic methods are sensitive to siderite at ppm concentrations, we find no evidence for the presence of siderite in the samples analyzed.

4.2.4. Magnetic extracts

Strong-field thermomagnetic measurements for representative samples within and outside Zone 2 display two fundamentally different behaviors (Fig. 6). The sample from Zone 3 (1292.5 m) is a Ti-rich maghemite (volcanic origin) whereas the sample from Zone 2 (839 m) contains Ti-free maghemite (non-volcanic). Magnetic extracts collected from outside the P–E interval display thermomagnetic curves that are characteristic of the inversion of partially oxidized, cation-deficient titanomaghemite (Fig. 6A). Such cation (<300 °C), such as might be expected in soils forming in tropical latitudes receiving elevated levels of precipitation. Titanomaghemite is



Fig. 4. Room-temperature saturation isothermal remanent magnetization (RT-SIRM) data for sample 947.4 m and magnetic standards. (A) The upper two data sets were measured after the sample had acquired a thermal remanence while cooling from 400 K to 300 K in a 300 mT field. The middle data sets were measured after cooling from 400 K to 300 K in zero field (thereby demagnetizing the goethite). The lower data sets show the remanence held by goethite (uppermost data minus middle data). (B) RT-SIRM cooling and warming curves for synthetic magnetite (solid line) and goethite (dashed line). Synthetic goethite was normalized to its 10 K remanence, whereas the magnetite was normalized to its initial 300 K remanence (Modified from Lascu and Feinberg, 2011) (C) Expanded view of the middle data sets in (A). The cooling curve is shown by the arrow pointing up whereas the warming curve is shown by the pointing downwards arrow and the difference between these curves has been rescaled and is indicated by the dots. The two curves deviate at approximately 110 K, which is the expected temperature for the Verwey transition in magnetite. (D) First derivative of the uppermost warming data from (A). The solid line shows a third-order polynomial fit to the derivative data. The largest deviations from this best fit occur at 265 and 270 K (biggest points), which is consistent with the Morin transition of hematite.



Fig. 5. Field cooled magnetic remanence measured on warming from 5 K to 300 K. The upper curve shows the magnetic moment of sample 947.4 m. The middle curve shows the behavior of a siderite powder standard reported by Housen et al. (1996). The dramatic decrease in remanence at 30 to 40 K is the effect of the Néel temperature of siderite. The lower curve shows the behavior of a natural marine sediment from Barbados (156-948C-19X-5). The marine sediment also shows a trace concentration of pure magnetite as evidenced by the Verwey transition at 110 to 120 K. Note that the sample 947.4 m from this study shows absolutely no indication of the siderite transition at 30 to 40 K.

a metastable phase that, upon heating, inverts into stoichiometric intergrowths of titanomagnetite (Fe₃ – $_x$ Ti_xO₄) and hemoilmenite (Fe₂ – $_y$ Ti_yO₃). The inversion temperature (T₁) of titanomaghemite may range from 250 to 460 °C depending on the initial degree of oxidation (Ozdemir, 1987). The inversion temperature of the Bogotá Formation sample shown in Fig. 6A is 430 °C, and the Curie temperature of the resulting titanomagnetite is 552 °C, corresponding to an unoxidized composition of Fe_{2.96}Ti_{0.04}O₄ using the relationship of Bleil and Petersen (1982). This inversion process often results in a

significantly stronger induced magnetization on cooling than was observed on warming. An example of titanomaghemite inversion ($T_1 = 390$ °C) reported by Sanver and O'Reilly (1970) for a basaltic andesite sample is included in Fig. 6A and is a reference for the kind of behavior that is expected from an oxidized titanomaghemite of volcanic origin.

In contrast, magnetic extracts from within Zone 2 display markedly different thermomagnetic behavior. We see no evidence of titanomaghemite inversion and a Curie temperature at 527 °C, which is substantially lower than the Curie temperature expected for pure magnetite (580 °C). The heating and cooling curves are semi-reversible, with the cooling curve showing a 9% decrease in induced magnetization. This thermomagnetic behavior is consistent with a population of stable maghemite (γ -Fe₂O₃) grains that experiences minor oxidation to hematite (α -Fe₂O₃) during the high temperature portion of the experiment.

4.3. Carbon isotopes in organic matter

The δ^{13} C in bulk organic matter of the samples analyzed at UMN range from -28.91% to -22.18% (Fig. 3A). The δ^{13} C values do not show a notable correlation with the TOC values (r = 0.32, p = 0.004, df = 75) and the residual pattern did not differ significantly from the original data (Supplementary materials).

Despite the intra-sample variability of the δ^{13} C values pretreated with 0.5 M HCl, stratigraphic changes in the carbon record can be recognized. Using the three stratigraphic zones based on the magnetic minerals and lithologies (Section 4.2), Zone 1 (0–828 m, mean δ^{13} C = – 25.24‰) has a mean value slightly less depleted than that for Zone 2 (829–1009 m, mean = – 25.86‰, *t*-test, p-value = 0.178, df = 31.428), but the difference is not statistically significant. However, the mean value in Zone 2 is significantly more depleted than that in Zone 3 (1009–2020.5 m, mean = –24.11‰, *t*-test, p = 0.0007, df = 38.143). The mean δ^{13} C value in Zone 1 is also significantly more depleted than in Zone 3 (*t*-test, p = 0.0008, df = 52.554). The dated volcanic horizon at 928 m (56.2 ± 1.0 Ma, Bayona et al., 2012) is located in Zone 2 and it is coincident with the ages of several hyperthermals associated with the P–E transition (McInerney and Wing, 2011).



Fig. 6. Representative strong-field thermomagnetic curves for magnetic extracts collected from (A) Zone 3 and (B) Zone 2. Solid lines show the induced magnetization measured during heating (arrows pointing down) and cooling (arrows pointing up). The points in (a) are thermomagnetic data from a basaltic andesite reported by Sanver and O'Reilly (1970), and are included here as a reference for the behavior expected from a partially oxidized titanomagnetite of volcanic origin. (C) and (D) show hysteresis loops measured before (solid) and after (dashed) each thermomagnetic experiment.

After the intra-sample variability filter was applied, 41% of the UMN analyses were excluded from the record. Only the mean δ^{13} C value of Zone 3 (-23.65%) remained significantly less depleted than that of Zone 1 (-25.24%, *t*-test, p-value = 0.00042, df = 18.96). In order to test whether the 6 N HCl treatment improved the reproducibility, five replicates from two samples with low reproducibility (sampled at 909.7 and 979.7 m) were analyzed, yielding standard deviations for the treated replicates of 0.16‰ and 0.37‰, respectively, whereas the standard deviations for these samples after the 0.5 M HCl treatment were 1.97‰ and 2.24‰, respectively. The entire 6 N HCl record displays values between -22.16% and -26.38% (Supplementary materials).

Recent studies have shown that δ^{13} C values vary from A to B horizons due to changes in carbon isotope fractionation during decomposition of organic matter (Wynn, 2007). These changes can be observed by comparing the δ^{13} C values obtained from different depths in the soil horizon. To investigate if this could explain some of the scatter in the carbon isotopic record, we explored the relationship between depth from the top horizon and δ^{13} C value. We did not find any significant relationship between depth and δ^{13} C (r = 0.015, p-value: 0.89, df = 76), nor among the depth of samples grouped by color, and likely reflecting horizon type (red r = 0.07, p-value: 0.78, df = 15; purple r = 0.06, p-value: 0.81, df = 19; gray r = 0.18, p-value: 0.26, df = 38) (Supplementary materials).

4.4. Major element geochemistry

A systematic change occurs for all major oxides at the base of Zone 2. Fig. 7 focuses on the behavior of Fe₂O₃, Al₂O₃, and SiO₂, since those elements are important components of the elemental flux in tropical soils, and also loss on ignition (LOI). At the base of Zone 2, Fe₂O₃ increases by 48%, Al₂O₃ by 25%, and LOI by 10%, and SiO₂ decreases by 17%.

The elemental abundance of Fe₂O₃ does have significant correlations with the concentrations of goethite (r = 0.49, p-value = 3.7×10^{-3}) and hematite (r = 0.42, p-value = 8.4×10^{-3}) throughout the entire record as expected.



Fig. 7. Rock geochemistry showing major oxides (Fe_2O_3 , Al_2O_3 , SiO_2) and LOI; dotted vertical lines show the average for each interval. The horizontal dashed lines identify Zone 2.

5. Discussion

5.1. Climatic implications

The increase of magnetic susceptibility, magnetic mineral concentrations (magnetite/maghemite, hematite, and goethite), Al₂O₃, Fe₂O₃, and LOI, as well as the decrease in the number of gray paleosol horizons and in the concentration of SiO₂ in Zone 2, suggests enhanced chemical weathering and pedogenesis during the P–E boundary interval. All proxies are in agreement with the characteristics of heavily weathered modern surface soils in regions with intense precipitation (Simas et al., 2005; Kleber et al., 2007; Muggler et al., 2007; Anda et al., 2008; Burak et al., 2010). In such soils, silica is depleted because of intense leaching, leaving iron and aluminum cations in the soil profile from which hematite and goethite are then precipitated (Schaetzl and Anderson, 2005).

The characteristically high pCO₂ levels of hyperthermal events should generally lead to higher chemical weathering by enhanced formation of carbonic acid, particularly in humid tropical regions (Archer et al., 2009). Therefore, enhanced chemical weathering may result from the combination of high CO₂ levels and a perturbation of the hydrological cycle during green house events (Kump et al., 2000; Bowen et al., 2004; Archer et al., 2009). Carbonic acid allows intense weathering of Fe-bearing silicate rocks and increased rainfall fosters additional runoff and severe leaching of soils (Fig. 8A). The suggested



Fig. 8. Conceptual model of climatic conditions and soil geochemical and mineralogical behavior during: (A) Zone 2; and (B) Zones 1 and 3. Provenance analysis from Bayona et al. (2010) reports detritus from the Central Cordillera of Colombia (CCC) in the Bogotá Basin. See text Section 5.1 for discussion.

increase in chemical weathering and pedogenesis in the Bogotá Formation is consistent with high rates of precipitation that had have been identified in another P-E section about 700 km north of the Bogotá basin using deuterium isotopes (Jaramillo et al., 2010). Evidence of increased runoff has also been identified in marine records at different latitudes using magnetic techniques (Villasante-Marcos et al., 2009; Dallanave et al., 2010), concentrations in clay minerals (Robert and Kennett, 1994; Gibson et al., 2000; Bolle and Adatte, 2001; Dypvik et al., 2011) and abrupt changes to high-energy depositional settings (Schmitz and Pujalte, 2003; Foreman et al., 2012). Villasante-Marcos et al. (2009) also found a strong negative correlation between various magnetic parameters (bulk magnetic susceptibility, hysteresis properties, isothermal remanent magnetization) and the $\delta^{13}\text{C}$ record in a marine section in New Zealand. Villasante-Marcos et al. (2009) suggest an increase in clastic discharge associated with the intensification of the hydrological and weathering cycles. Dallanave et al. (2010) also found an increase in magnetic susceptibility at the same level as the P-E in a section in NE Italy. The inferred increase in weathering is also consistent with the presence of a kaolinite-rich layer in marine sections along the East Antarctic (Robert and Kennett, 1994) and Mediterranean coasts (Bolle and Adatte, 2001; Dypvik et al., 2011). In addition, previous studies on the east coast of the United States have suggested that the strong changes in weathering and sedimentation patterns during the P-E drove diversification of magnetite-generating marine organisms (Kopp et al., 2007; Lippert and Zachos, 2007; Schumann et al., 2008; Kopp et al., 2009).

The increase in LOI identified in this study may be related to the presence of hydroxyl groups in the mineral structures of gibbsite, goethite, and kaolinite. The hydroxyls in these minerals are volatilized to water vapor during heating (Alexander and Cady, 1962; Schaetzl and Anderson, 2005). Thus, the increase in LOI could also reflect the increment of kaolinite in the samples, but further investigation is required to test this hypothesis since quantitative powder XRD analysis was not conducted in this study.

Our model of enhanced weathering occurring within the P-E transition is consistent with many of the magnetic, geochemical, and lithologic observations made on paleosols from the Bogotá Formation; however it is important to assess alternative models. The heavy leaching observed in the paleosols of Bogotá Basin section does not appear to be due to prolonged exposure during a period of low deposition or non-deposition. The pollen record indicates the presence of tropical vegetation (Bayona et al., 2010; Ochoa et al., 2012) and δ^{13} C values less than -20% are consistent with exclusively C3 plants (Diefendorf et al., 2010), confirming that the paleosols were formed in tropical conditions and that the leaching of elements is not due to long term exposure. Sediments of the Bogotá Formation were deposited along an active margin, with sedimentation rates ranging from 115 to 131 m/my (Bayona et al., 2013). Furthermore, the observed iron oxides and iron oxyhydroxides were not formed as a result of diagenesis after burial. Pedogenic structures such as redoximorphic features and burrows with depletion zones are still preserved within the paleosols of this section, and extreme diagenesis after burial would have removed these redoximorphic features (PiPujol and Buurman, 1994; Théveniaut and Freyssinet, 2002; Kraus and Hasiotis, 2006). Moreover, (i) burial was less than 500 m (vitrinite reflectance Ro = 0.27, Ochoa et al., 2012); (ii) thermochronologic data suggests that exhumation occurred since the Oligocene, which is consistent with burial only for a short interval (Bayona et al., 2012); and (iii) the interbedded sandstones in the section are friable and do not contain iron oxides as cement (Bayona et al., 2010). Thus, several lines of evidence are consistent with the interpretation that the iron oxides primarily reflect accelerated chemical weathering and pedogenic processes.

Changes in the source of sediment deposited in the Bogotá Basin during late Paleocene–middle Eocene are also unlikely to be the cause of the observed magnetic anomalies. Igneous and metamorphic rocks

exposed in the Central Cordillera supplied sediments to the Bogotá Basin since the late Cretaceous to middle Eocene (Bayona et al., 2010, 2012). Additionally, studies in Brazil (Muggler et al., 2007) and Thailand (Wiriyakitnateekul et al., 2007) have demonstrated that hematite and goethite occur in soils originating from different parent materials. Thermomagnetic measurements of the paleosol sample showing the most dramatic enrichment in magnetic susceptibility and magnetic mineral concentration (839 m, Zone 2) contain no evidence of volcanic titanomagnetite, and instead are dominated by maghemite. The Ti-free nature of magnetic minerals in Zone 2 is corroborated by low temperature remanence experiments (sample 947.4 m) that show evidence of the Verwey transition (Fig. 5). Trace concentrations of Ti-substitution are known to suppress the Verwey transition in magnetite (Kakol et al., 1994), and so the recovery of a clear Verwey transition is usually interpreted as a sign that pure stoichiometric magnetite is present. Thus, the paleosols within Zone 2 contain enriched concentrations of Ti-free magnetite, which we believe was produced during pedogenesis. In contrast, thermomagnetic measurements show that paleosols outside of Zone 2 (e.g., sample 1292.5 m) contain detrital volcanic titanomagnetite that has been oxidized to form cation-deficient titanomaghemite. Magnetic susceptibility $(1.82 \times 10^{-07} \text{ m}^3/\text{kg})$ values and magnetic mineral concentrations of this sample are smaller than average values in Zone 2 ($1.82 \times 10^{-7} \text{ m}^3/\text{kg}$). This indicates that paleosols containing detrital volcanic components do not necessarily exhibit elevated magnetic susceptibility values and magnetic mineral concentrations.

5.2. Low reproducibility of the carbon isotope data

Despite the improvement of intra-sample variability in the results from the 6 N HCl pretreatment, we consider that the method is not appropriate for the Bogotá Basin samples because the absence of siderite in both the XRD and magnetic measurements confirms that the low reproducibility of the bulk organic δ^{13} C experiments is not due to contamination by pedogenic siderite. Results from UF also showed low reproducibility of δ^{13} C values, eliminating the possibility of instrumental error.

Another explanation for a scatter δ^{13} C record is that degradation of organic matter occurred heterogeneously throughout the stratigraphic section. This hypothesis could be tested using compound specific isotope analyses of long-chain leaf waxes (n-alkanes), which are only produced by terrestrial higher plants. A second explanation is related to the analytical limitations of conducting an accurate carbon isotope measurement on samples with very low organic matter content, such as those from the Bogotá Formation, where the mean TOC is 0.05%. A third alternative is that carbon isotope excursions are simply not recorded in the section; however this theory is unlikely as there is an indication of a possible δ^{13} C excursion recorded in Zone 2. Yet, as previously mentioned, the noisy isotopic record does not allow us to determine which particular hyperthermal event this excursion is associated with across the P–E transition. Interestingly, a section about 700 km north of the Bogotá basin, where the carbon isotopic excursion associated with the Paleocene-Eocene Thermal Maximum was identified also contains a dated volcanic tuff at 56.09 \pm 0.03 Ma (Jaramillo et al., 2010). However, until these questions are resolved, the observed fluctuations in the carbon isotopic record of the Bogotá Formation cannot be ascribed to a single or a particular hyperthermal event.

6. Conclusions

Lithologic, magnetic, and geochemical observations collected as part of this study allow us to identify three distinct zones in the Bogotá Basin section:

- i) Zone 1 (late Paleocene) shows the lowest magnetic susceptibilities and lowest concentrations of magnetic minerals. This section has low concentrations of Fe₂O₃, Al₂O₃, and LOI; while SiO₂ concentrations are high. All of these proxies establish a baseline for chemical weathering that is lower than the overlying sediments. Additionally, carbonate nodules are present within the upper part of this zone.
- ii) Zone 2 (P–E transition) contains heavily weathered paleosols. There is a significant increase in magnetic susceptibility accompanied by an order of magnitude increase in the concentration of magnetite/maghemite and hematite at the base of this zone. Increased concentrations of Fe₂O₃ and Al₂O₃, and LOI are also consistent with an increase in chemical weathering, as are the concomitant decrease in the frequency of gray paleosol horizons and SiO₂ concentrations. The absence of carbonate nodules could also imply that effective precipitation values increased during this interval. We suggest that the enhanced chemical weathering may have been related to the hyperthermal events occurring across the P–E. However, our chronology is still not precise enough to test this hypothesis. The carbon isotope record needs to be improved as well as the biostratigraphic and geochronological dating of the section.
- iii) Zone 3 (early Eocene) exhibits a decrease in magnetic susceptibility and in concentrations of magnetic minerals and refractory elements; however values are not as low as in the first zone. Carbonate nodules reappear in this section and all proxies suggest a decrease in the rate of chemical weathering.

This study represents a first step in the study of the climatic response of tropical terrestrial ecosystems in the Bogotá Basin during the Paleocene–Eocene. Additional work, such as a high resolution magnetostratigraphic study and compound specific stable isotope analyses of *n*-alkanes to isolate the terrestrial plant record in the paleosols are required to provide an improved age model and a less scatter carbon isotopic record. More detailed analyses of paleosol micromorphology, soil textures, and mineral composition would also allow workers to refine the pedotypes and physical changes related to the climatic forcing of sedimentation and pedogenesis during the P–E.

Our results of enhanced chemical weathering during the P–E transition in the Bogotá Basin seem to be consistent with the hypothesis that chemical weathering of silicates was a negative feedback mechanism for the long-term stabilization of Earth's surface temperature following perturbation to the global carbon cycle during the Early Eocene hyperthermals (Walker et al., 1981; Kump et al., 2000; Ravizza et al., 2001; Dallanave et al., 2010).

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Appendix A. Supplementary data

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