Magnetic minerals as recorders of weathering, diagenesis, and paleoclimate: a core-outcrop comparison of Paleocene-Eocene paleosols in the Bighorn Basin, WY, U.S.A.

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Abstract

Magnetic minerals in paleosols hold important clues to the environmental conditions in which the original soil formed. However, efforts to quantify parameters such as mean annual precipitation (MAP) using magnetic properties are still in their infancy. Here, we test the idea that diagenetic processes and surficial weathering affect the magnetic minerals preserved in paleosols, particularly in pre-Quaternary systems that have received far less attention compared to more recent soils and paleosols. We evaluate the magnetic properties of non-loessic paleosols across the Paleocene-Eocene Thermal Maximum (a short-term global warming episode that occurred at 55.5 Ma) in the Bighorn Basin, WY. We compare data from nine paleosol layers sampled from outcrop, each of which has been exposed to surficial weathering, to the equivalent paleosols sampled from drill core, all of which are preserved below a pervasive surficial weathering front and are presumed to be unweathered. Comparisons reveal an increase in magnetization in outcrops compared with core equivalents, which is principally driven by secondary hematite production. Authigenic hematite production in outcrops presents a complication for goethite-hematite based paleoprecipitation proxies where estimates will be biased toward drier climate regimes. The occurrence of low coercivity minerals is more consistent between core and outcrop. However, we propose an

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alteration process for pedogenic magnetite that is observed in both core and outcrop, where pedogenic magnetite becomes progressively oxidized leading to higher mean coercivities and broader coercivity distributions compared to modern pedogenic magnetite. This combination of diagenetic processes and surface weathering influences the magnetic properties of paleosols. Despite these changes, magnetic enhancement ratios from B-horizons correlate with independent MAP estimates from geochemical proxies, which suggests that paleoprecipitation information is preserved. Future work should continue to address these complications by developing useful protocols that isolate the magnetic properties that are most resistant to alteration and remain strong indicators of MAP and climate.

Keywords: weathering, diagenesis, environmental magnetism, paleosol, paleoprecipitation

1. Introduction

The magnetic properties of soils and paleosols are often used to make environmental and climatic interpretations throughout the geologic record (see reviews by Maher, 1998; Maxbauer et al., 2016). This is possible largely because magnetic minerals such as goethite (FeOOH), hematite ($\alpha\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4), and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) form through a combination of processes that are often critically dependent on soil moisture (Maxbauer et al., 2016, and references therein). Many studies have established empirical, quantitative relationships between pedogenic iron oxide minerals and the mean annual precipitation (MAP) under which the soil formed (e.g., Maher and Thompson, 1995; Geiss et al., 2008; Long et al., 2011; Hyland et al., 2015). These quantitative methods, along with earlier more qualitative interpretations, hold enormous potential for understanding environmental vari-

14 ability in the deep past. Two recent studies have highlighted the potential
 15 for methods based on the ratio of goethite-to-hematite (G/H ; Hyland et al.,
 16 2015) and direct estimates of pedogenically produced magnetite (Geiss et al.,
 17 2008). The G/H method presented by Hyland et al. (2015) was calibrated
 18 using modern soils that formed over a wide range of MAP values (200 - 3000
 19 mm yr⁻¹). In contrast, the calibrations of Geiss et al. (2008) are similar
 20 to other pedogenic magnetic susceptibility based proxies (e.g., Maher and
 21 Thompson, 1995) in that they only range up to ~ 1000 mm yr⁻¹. However,
 22 Geiss et al. (2008) offered calibrations between MAP and magnetic enhance-
 23 ment ratios (M_B/M_C , where M is the mean value of a generic magnetic
 24 property for the B and C soil horizons) or direct measures of pedogenic mag-
 25 netite (e.g., ratio of anhysteretic to isothermal remanence) that may prove
 26 useful in expanding methods developed on loessic soils into other soil types
 27 and climatic regimes.

28 Most paleosol studies are based on observations from Quaternary or
 29 younger loess-paleosol sequences (e.g., Geiss et al., 2008; Maher and Thomp-
 30 son, 1995; Maher et al., 2003) so little is known about the magnetic properties
 31 of more ancient paleosols as paleoclimatic indicators. The few studies that
 32 examine this topic report low magnetic susceptibility (χ) in ancient paleosols
 33 compared to modern soils (Rankey and Farr, 1997; Cogoini et al., 2001; Re-
 34 tallack et al., 2003; Tramp et al., 2004). However, in some ancient systems

35 there is evidence for preservation of pedogenic magnetic mineral assemblages
36 that may be useful for reconstructing past environmental conditions (Rankey
37 and Farr, 1997; Cogoini et al., 2001; Tramp et al., 2004; Morón et al., 2013;
38 Hyland et al., 2015). Despite these exciting suggestions, there remains a
39 general lack of information regarding the role of diagenesis and weathering
40 in altering the original magnetic mineral assemblages in ancient paleosols,
41 which limits our ability to interpret environmental conditions from ancient
42 paleosol sequences with confidence. We must learn more about the diage-
43 netic changes that affect soil magnetic mineral assemblages throughout their
44 transformation into paleosols, throughout the subsequent burial history and
45 exposure to chemically variable groundwater, and throughout their weather-
46 ing history (for a recent review on magnetic mineral diagenesis, see Roberts,
47 2015).

48 Here, we examine these processes in paleosols preserved at the Polecat
49 Bench locality in the Bighorn Basin, Wyoming (Figure 1). The Bighorn
50 Basin Coring Project (BBCP; Clyde et al., 2013) recovered nearly 900 me-
51 ters of sediment core from three localities in the Bighorn Basin, including
52 Polecat Bench. Core scan images (Figure 2A) clearly indicate that oxidative
53 weathering has altered sediment color to depths of up to 25 meters below
54 the ground surface (Clyde et al., 2013). This observation calls into ques-
55 tion whether magnetic mineral assemblages in paleosol outcrops reflect the

56 original pedogenic assemblage and the environmental conditions in which
57 they formed. This question has important implications for applying most
58 magnetic-based paleoprecipitation proxies to ancient systems since they as-
59 sume that the magnetic minerals preserved in paleosols are pedogenic and are
60 not significantly altered by subsequent diagenesis and late-stage weathering.

61 The presence of the same paleosols in both BBCP cores and nearby out-
62 crops presents an opportunity to test whether surficial weathering of outcrops
63 significantly affects magnetic mineral preservation. We present magnetic data
64 from nine marker bed paleosols, which were sampled from both core and out-
65 crop (Figure 3). All paleosols occur well below the oxidative weathering front
66 in the sediment core and we assume that these sediments are largely unweath-
67 ered compared to equivalent outcrop exposures (see Figure 2). Both core and
68 outcrop paleosols have likely been subjected to various long-term diagenetic
69 processes (for example, interaction with fluids and elevated temperatures
70 post-burial and before exposure of the basin). We compare magnetic proper-
71 ties of the Bighorn Basin paleosols to those of some modern soils to evaluate
72 the effects that diagenesis can have on magnetic mineral preservation, inde-
73 pendent from weathering.

74 Our record spans the Paleocene-Eocene Thermal Maximum (PETM, 55.5
75 Ma), which was a rapid global warming event driven by a massive release of
76 isotopically light carbon into the mixed atmosphere/ocean system (see re-

Figure 1: Maps of the study site at Polecat Bench in the Bighorn Basin, WY. **A.** Map of the northern Bighorn Basin. The highlighted and labeled box indicates the study area at Polecat Bench. The location of the study site in Wyoming is indicated in the inset of panel A. **B.** Polecat Bench locality with sampling locations indicated for outcrop paleosols (black circles) and coring location (red square). Color guide: darkest brown = Paleocene Fort Union Formation, dark tan = Paleocene-Eocene Willwood Formation, light tan = Quaternary gravels, and green = Cretaceous units.

77 view by McInerney and Wing, 2011). In the Bighorn Basin, the PETM was
78 associated with a transient precipitation decrease that has been well docu-
79 mented in qualitative and quantitative paleoflora records (Wing et al., 2005)
80 and from paleosol geochemistry and morphology (Kraus and Riggins, 2007;
81 Adams et al., 2011; Kraus et al., 2015). We compare our rock magnetic record
82 to a recent study of MAP estimates derived from geochemical weathering in-
83 dices (Kraus et al., 2015) to evaluate whether magnetic mineral assemblages
84 in these paleosols record paleoprecipitation changes during the PETM.

85 **2. Geological Setting**

86 The Bighorn Basin in northwestern Wyoming is a NW-to-SE trending
87 intermontane basin that formed in response to local subsidence and regional
88 uplift during the Laramide orogeny throughout late Cretaceous to Paleogene
89 time (Figure 1; Gingerich, 2001). Paleocene and Eocene sediments of the
90 Willwood Formation are well exposed at the Polecat Bench locality in the
91 northern reaches of the basin (Gingerich, 2001; Kraus, 2001). These sedi-
92 ments have been the focus of extensive research due to interest in biotic and
93 climatic changes associated with the PETM (Clyde et al., 2013; Bowen et al.,
94 2015).

95 Paleosols within the Willwood Formation, including the marker bed pa-
96 leosols studied here, have all been described extensively by previous workers

Figure 2: **A.** Line scan images from sediment cores recovered by the Bighorn Basin Coring Project (BBCP; Clyde et al., 2013). The approximate thickness of the weathering zone in sediment cores, as determined by color changes, is highlighted by the red box around the upper 25 meters of core. The asterisk in the red box highlights the Polecat Bench sediment core that is the focus of this study. **B.** Schematic illustration of how the weathering front (indicated with brighter, hashed colors) has affected outcrop exposures. Colored horizons indicate laterally continuous paleosols that are preserved in both core and outcrop. The drilling rig and black vertical line approximates a core location. Paleosols in the sediment core below the weathered zone are presumably relatively unweathered compared to their laterally equivalent exposure in outcrop.

97 (Kraus, 2001; Kraus and Hasiotis, 2006; Kraus and Riggins, 2007; Smith
 98 et al., 2008; Kraus et al., 2013, 2015). At Polecat Bench, paleosols are sorted
 99 into two general categories based on their B-horizon color. Red paleosols are
 100 characterized by a main red mudstone to silty mudstone B-horizon that is
 101 sometimes overlain by a grey or yellow-brown A horizon. Calcium carbonate
 102 nodules, slickensides, and grey mottles with red or purple rims are common
 103 in red paleosols and have been interpreted to represent generally well-drained

104 and oxidizing conditions (Kraus and Hasiotis, 2006). In contrast, the purple
105 paleosols are characterized by a purple mudstone B-horizon with abundant
106 yellow-brown mottling and nodules, a lack of calcium carbonate nodules,
107 abundant grey mottles with red rims, and slickensides (Kraus and Hasiotis,
108 2006).

109 Red paleosols are associated with generally dry climatic conditions where
110 seasonal wetting and drying drove nucleation and growth of calcium carbon-
111 ate nodules as well as the shrink-swell slickenside structures (Kraus and Hasi-
112 otis, 2006). Purple paleosols are interpreted to represent more poorly drained
113 conditions likely reflecting increased moisture and precipitation (Kraus and
114 Hasiotis, 2006; Kraus and Riggins, 2007). These qualitative interpretations
115 of paleosol color and climatic conditions are reinforced by a semi-quantitative
116 morphology index (Adams et al., 2011) and quantitative geochemical weath-
117 ering indices (Kraus and Riggins, 2007; Kraus et al., 2013, 2015) that produce
118 similar reconstructions for paleoprecipitation within the Bighorn Basin.

119 **3. Methods**

120 *3.1. Sampling*

121 All outcrop marker bed profiles were identified within the stratigraphic
122 framework of Gingerich (2001) (also used by Abdul Aziz et al., 2008). Previ-
123 ous work has established correlations between the Gingerich (2001) outcrop

124 section and the sediment cores recovered by the BBCP (see Bowen et al.,
125 2015). We utilized these correlations and confirmed all relationships using
126 line scan images prior to sampling of core sediments (see Figure 3). Depth
127 below the surface for the Polecat Bench core studied here (core 2B) was
128 converted to meters composite depth (mcd) following Bowen et al. (2015)
129 using standards determined by the BBCP science team. All outcrop profiles
130 were projected onto the mcd scale using either the top or base of paleosol
131 B-horizons to anchor correlations.

132 In an effort to collect the freshest outcrop samples possible, and thus to
133 mimic the sampling routine normally used in outcrop settings, the upper-
134 most 0.5 to 1 m of rock was removed before paleosol samples were collected
135 in the field. For each marker bed, samples were taken at 5 cm intervals
136 through B-horizons and at 10 cm intervals through C (parent material) and
137 A-horizons (when present). In order to assess the reproducibility of magnetic
138 properties in individual paleosols, we collected additional profiles (with the
139 number of profiles collected in parentheses) for four marker beds at lateral
140 distances ranging from ~10's of meters to nearly a kilometer from the orig-
141 inal profile (see Figure 1): Purple-Red Mudstone (3), Red Mudstone (2),
142 Purple-2 (3), and Top Red A (3). All designations for the studied paleosols
143 and their stratigraphic order are indicated in Figure 3. This approach allows
144 us to quantify magnetic variability in soils that were originally developed in

Figure 3: Correlations between outcrop stratigraphy (following Gingerich, 2001) and core stratigraphy. All correlations follow those of Bowen et al. (2015) and were independently confirmed from line scan images and during core sampling for this study. Marker paleosols in outcrop stratigraphy are denoted with red and purple. Marker bed abbreviations are as follows: TRB = Top Red B, TRA = Top Red A, P4 = Purple 4, UDRB = Upper Double Red B, P2 = Purple 2, LDRA = Lower Double Red A, P0 = Purple 0, RM = Red Mudstone, and PRM = Purple Red Mudstone.

145 subtly different settings across a landscape. These additional lateral profiles
 146 were sampled at 10 cm intervals through all horizons. Notably, no additional
 147 detail was derived from the 5 cm sampling resolution in the original pro-
 148 files compared with the 10 cm sampling resolution in the additional profiles,
 149 which suggests that 10 cm resolution is sufficient to capture the important
 150 magnetic variability in these paleosols. Samples from correlative paleosols

151 in the core were acquired at roughly 10 cm intervals, with occasional minor
152 adjustments to accomodate the availability of sediment core remaining after
153 previous sampling.

154 Sample preparation and magnetic measurements were performed at the
155 Institute for Rock Magnetism, University of Minnesota. Core and outcrop
156 samples were placed into diamagnetic plastic cubes and were secured using a
157 non-magnetic potassium silicate adhesive. Samples were neither crushed nor
158 homogenized in order to avoid altering the natural grain size distribution of
159 the paleosols, which can significantly impact grain size dependent magnetic
160 properties (for example, anhysteretic remanent magnetization). However,
161 multiple individual mudstone pieces were included in each cube and highly
162 mottled and/or depleted rhizosphere zones were avoided during sampling.
163 Each specimen underwent all of the magnetic measurements described below
164 unless otherwise indicated. All B-horizon mean values come from individual
165 paleosol profiles and are a mean of all B-horizon specimens measured for
166 a particular profile and measurement. Comparisons between core and out-
167 crop are between core profiles and individual outcrop profiles, even where an
168 individual paleosol layer was collected from multiple outcrop profiles.

169 *3.2. Magnetic Susceptibility*

170 In-phase magnetic susceptibility (χ) was measured on all specimens (n
171 = 376 outcrop, n = 169 core) at low (465 Hz) and high frequency (4650

172 Hz) using a Magnon variable frequency susceptibility meter in an alternating
 173 current (AC) field of 300 Am⁻¹. Reported values for individual specimens
 174 represent the mean of 4 replicate low frequency measurements. The fre-
 175 quency dependence of χ is commonly used in environmental magnetic stud-
 176 ies of soils and paleosols as an indicator of the presence of ultrafine grained
 177 magnetite/maghemite that is close to the grain size threshold of stable sin-
 178 gle domain (SSD) and superparamagnetic (SP) magnetite (Dearing et al.,
 179 1996). Frequency dependence of susceptibility ($\chi_{fd}\%$) was calculated, where
 180 $\chi_{fd}\% = [(\chi_{465Hz} - \chi_{4650Hz})/\chi_{465Hz}] \times 100\%$.

181 3.3. *IRM and ARM*

182 An isothermal remanent magnetization (*IRM*) and an anhysteretic rema-
 183 nent magnetization (*ARM*) were imparted to all specimens (n = 376 outcrop,
 184 n = 169 core). For each specimen, *ARM* was imparted in a peak alternating
 185 field (AF) of 100 mT in the presence of a weak direct current (DC) bias field
 186 of 50 μ T. The *ARM* susceptibility (χ_{ARM}), was calculated by dividing the
 187 measured *ARM* by the bias field. *IRMs* were imparted using three pulses
 188 of a 100 mT direct current field in a pulse magnetizer. *IRM* and *ARM* re-
 189 manences were measured immediately using a 2G Enterprises 760-R SQUID
 190 magnetometer within a shielded room with a background field of less than
 191 100 nT.

192 3.4. *Hysteresis Properties*

193 Hysteresis loops and backfield remanence curves were measured on a sub-
194 set of samples from each paleosol profile ($n = 170$ outcrop, $n = 70$ core) using
195 a Princeton Measurements Corporation Micromag vibrating sample magne-
196 tometer (VSM) at room temperature in fields up to 1 Tesla. Saturation
197 magnetization (M_s), saturation remanent magnetization (M_{rs} ; equivalent
198 to saturation IRM , or $SIRM$), coercivity (B_c), and coercivity of rema-
199 nence (B_{cr}) are all derived from hysteresis and backfield measurements (see
200 overview in Maxbauer et al., 2016). The remanence held by magnetic min-
201 erals between 100 mT and 1 T is referred to as the "hard" IRM , or $HIRM$,
202 where $HIRM = 0.5 \times (SIRM + IRM_{-100mT})$.

203 3.5. *Coercivity Unmixing*

204 For all B-horizon specimens where backfield curves were collected, we cal-
205 culated coercivity distributions using the absolute value of the first derivative
206 of backfield remanence. In order to identify the individual components that
207 contribute to remanence at various field strengths up to 1 T we used a curve-
208 fitting program developed in the R programming language (available on-line
209 at <http://www.irm.umn.edu/maxunmix>), which is based on similar methods
210 to those of Kruiver et al. (2001), Heslop et al. (2002), and Egli (2003). Our
211 method uses skew-normal distributions that can be described with a mean
212 coercivity (B_h), a dispersion parameter (DP , equivalent to one standard

213 deviation in log-space), and a skewness factor (S). Modeled distributions
214 for each component can be added linearly to approximate the measured co-
215 ercivity distribution (on a coercivity versus log-field diagram). The total
216 contribution of each component to the *SIRM* is calculated as the integrated
217 area under each model component divided by the total integrated area un-
218 derneath the coercivity distribution across the range of field values covered
219 by the magnetization data (i.e., there is no extrapolation for unsaturated
220 backfield curves).

221 Initial optimization of user-defined fitting was automated to minimize
222 the residual sum squared (RSS) between the measured and modeled coer-
223 civity distributions. Error in the model is accounted for by a Monte Carlo
224 style resampling routine. For each iteration, the program randomly drops
225 5% of the original magnetization data prior to deriving coercivity distribu-
226 tions. The resampled coercivity distributions are then fitted using the initial
227 optimized fits (achieved using the entire magnetization dataset), which are
228 resampled assuming a 2% error in their initial value. Optimization is again
229 automated for each resampled coercivity distribution and the reported mod-
230 els for coercivity distributions and individual components are the mean of
231 100 resamples with error envelopes representing the 2.5 and 97.5 percentiles
232 (95% confidence interval).

233 3.6. Temperature dependent measurements

234 Temperature dependent measurements were conducted on a small subset
235 of specimens in order to more definitively identify magnetic minerals within
236 the studied paleosols. Room temperature saturation *IRM* (RT-*SIRM*) was
237 measured using a Quantum Design Magnetic Properties Measurement Sys-
238 tems (MPMS). Specimens were first given an *IRM* of 5 T at room temper-
239 ature (300 K; followed by a smaller *IRM* of 2.5 T along the same axis to
240 minimize recoil within the MPMS system). Remanence was then measured
241 during cooling to 20 K and subsequent warming back to room temperature.
242 RT-*SIRM* curves reveal remanence loss at diagnostic transition tempera-
243 tures (e.g., the Verwey and Morin transitions for magnetite and hematite,
244 respectively). However, the Morin transition of hematite is often suppressed
245 in natural soils and sediments due to defects and aluminum substitution
246 (e.g., Maher et al., 2004). In order to confirm the presence of hematite, we
247 measured backfield remanence curves with saturating fields of 1.5 T at 25
248 °C (298 K) and 130 °C (403 K). The high temperature backfield curve was
249 measured above the Néel temperature of goethite (125 °C) and all high-field
250 remanence in this experiment is attributed to hematite.

251 4. Results

252 4.1. Magnetic Susceptibility, *ARM*, and *IRM*

253 Bulk χ within core and outcrop paleosol profiles range from 5×10^{-8} to
254 $25 \times 10^{-8} \text{ m}^3 \text{kg}^{-1}$, which is consistent with values reported for ancient pale-
255 osols (Figure 4A and Figure S1; Rankey and Farr, 1997; Cogoini et al., 2001;
256 Retallack et al., 2003; Tramp et al., 2004; Morón et al., 2013). Frequency
257 dependence of susceptibility for the paleosols studied here was low ($< 2\%$)
258 and inconsistent, which suggests either the absence of ferrimagnetic minerals
259 in the SP state in these soils prior to fossilization, or their poor preservation.
260 *ARM* (Figure 4C and Figure S2) and *IRM* (Figure 4E and Figure S3) both
261 have similar trends within and amongst paleosol profiles in core and outcrop.
262 *ARM* ranges from 3×10^{-6} to $30 \times 10^{-6} \text{ Am}^2 \text{kg}^{-1}$ and *IRM* values are between
263 1×10^{-4} and $15 \times 10^{-4} \text{ Am}^2 \text{kg}^{-1}$ (Figure S2 and S3, respectively). Vertical pro-
264 files of χ , *ARM*, and *IRM* variations within paleosols generally do not have
265 systematic magnetic parameter increases within the upper B-horizon, as is
266 commonly observed in modern soils (see Figures S1-S3; Maher, 1998; Geiss
267 et al., 2008; Lindquist et al., 2011). We note that the A-horizon for these pa-
268 leosols has been mostly stripped off, which likely contributes, in part, to the
269 lack of an enhanced magnetic signature. In nearly all instances, *ARM* and
270 *IRM* values for B-horizons are greater than the underlying C-horizons upon
271 which the soil developed (Figures S1-S3). Notably, the χ , *ARM*, and *IRM*

272 data are not offset systematically between core and outcrop for equivalent
273 paleosol B-horizons (Figure 4A, C, and E; $p > 0.25$ for all paired t-tests and
274 Wilcoxon Signed-Rank Tests, which supports no difference between core and
275 outcrop records).

276 4.2. Hysteresis Properties

277 Example hysteresis loops and backfield curves for both low and high co-
278 ercivity end member specimens are shown in Figure 5. All hysteresis loops
279 are wasp-waisted to varying extents, which indicates mixed magnetic mineral
280 assemblages (Roberts et al., 1995; Tauxe et al., 1996). Mean B-horizon B_c
281 varies between 10 and 160 mT with B_{cr} values ranging from 80 to 500 mT.
282 Both B_c and B_{cr} are considerably higher in paleosol B-horizons compared
283 with underlying C-horizons (Figures S6 and S7). Similar to the patterns ob-
284 served for the χ , ARM , and IRM data, despite variations amongst various
285 outcrop and core profiles (Figures S6 and S7) for equivalent paleosol layers,
286 there is no consistent difference in bulk B_c or B_{cr} between core and outcrop
287 (Figure 4D and 4F; $p > 0.3$ for all paired t-tests and Wilcoxon Signed-
288 Rank Tests). By contrast, M_r and $HIRM$ for B-horizons sampled from core
289 sediments are consistently lower than those observed in equivalent outcrop
290 B-horizons (Figure 6; $p < 0.05$ for all paired t-tests and Wilcoxon Signed-
291 Rank Tests, which indicate that outcrop values are significantly greater than
292 core values). On average mean B-horizon M_r increases by 23% in outcrops

Figure 4: Comparison of magnetic parameters for equivalent B-horizons preserved in core and outcrop. The data are expected to fall on 1-to-1 lines (dashed lines in all plots) if there is no difference between core and outcrop data. All data points represent mean B-horizon values with error bars at ± 1 standard deviation. For all parameters there is high variability, but no significant difference between outcrop and core values (all p-values > 0.25 for a paired t-test and Wilcoxon Signed-Rank Test).

and *HIRM* increases by 41% in equivalent outcrop profiles. B-horizon values of M_s within both cores and outcrop profiles range between 4×10^{-3} and $12 \times 10^{-3} \text{ Am}^2\text{kg}^{-1}$. Although there is mostly a similar trend of increased M_s in outcrops relative to core equivalents, this effect is not as consistent as M_r and *HIRM* observations (compare Figure 4B with Figure 6C and 6D).

4.3. Coercivity Unmixing

Analysis of coercivity distributions of B-horizon samples revealed that the remanent magnetization is principally held by two components (e.g., Figure 7A). The low-coercivity component (*LCC*) is characterized by average B_h values between 1.3 and 2.1 (20 – 126 mT) and *DP* between 0.3 and 0.8 (Figure 7B). The average B_h and *DP* observed for the *LCC* in both core and outcrop paleosols are generally higher than values typically reported in the literature for pedogenic magnetite (green squares in Figure 7B; Egli, 2004; Geiss et al., 2008; Lindquist et al., 2011). The degree of skewness for the *LCC* is pronounced (0.46 – 0.76; upper and lower quartiles; note that $S = 1$ is equivalent a normal distribution; see Table S5), with a consistent low-field tail observed. There is generally no consistent deviation between the *LCC* preserved in the core compared to the *LCC* preserved in equivalent outcrops (consistent B_h and contribution to remanence, all p-values ≥ 0.05).

The *HCC* in both core and outcrops is characterized by B_h values between 2.4 and 3.0 (251 – 1000 mT) with *DP* consistently between 0.2 and 0.7

Figure 5: **A-B.** Example hysteresis loops (A) and backfield demagnetization curves (B). The solid line is from specimen PCB-01-LDRA-070 and represents a relatively low-coercivity but strongly magnetic end member (common in the large red paleosols LDRA and UDRB). The wasp-waistedness of this loop is likely due to a mixed magnetic assemblage of ‘hard’ and ‘soft’ magnetic minerals. The dashed line for specimen P2-155 represents an example of a more weakly magnetic, but higher-coercivity specimen more commonly observed in purple paleosols. **C.** A room-temperature *SIRM* for specimen PCB-03-PRM-100 undergoes a loss of magnetization across the Verwey transition of magnetite (110 K for pure magnetite) and an overall remanence increase on cooling that indicates likely contributions from goethite (Maher et al., 2004). **D.** Backfield curves measured on specimen PCB-01-UDRB-145 at room temperature (solid line) and at 403 K (130 °C; dashed line), above the Néel temperature of goethite. The high temperature backfield curve still carries a majority of the room temperature remanence, which suggests that hematite and not goethite is the primary high field remanence carrier in these specimen.

Figure 6: **A-B.** Mean B-horizon remanent magnetization (M_r , A) and 'hard' isothermal remanent magnetization (HIRM, B) for equivalent paleosol layers in the core (closed symbols, solid line) and outcrop (open symbols, dashed line). **C-D.** Cross plots of M_r (C) and HIRM (D) highlight the observed increase in both magnetic parameters within outcrops compared with the equivalent paleosol preserved in the core. All error bars are ± 1 standard deviation. For both HIRM and M_r , there is a significant ($p < 0.05$; for both paired t-test and paired Wilcoxon Signed-Rank Test) increase observed in outcrops relative to the equivalent core.

(Figure 7B). Skewness in the *HCC* is less pronounced, with a median value for *S* of 1.01 (0.96, 1.04; upper and lower quartiles). The remanence held by the *HCC* is consistently higher in outcrops ($\sim 46\%$ increase in outcrop relative to core) and has a consistent pattern with observations made from *HIRM* and M_r values. The observed B_p and DP of the *HCC* reported here are consistent with work from a previous study that identified high-coercivity components with similar B_h and DP as hematite (Hyland et al., 2015, note that they used non-skewed normal distributions).

4.4. Temperature Dependent Measurements

RT-*SIRM* undergoes a characteristic decrease just prior to 110 K, which is diagnostic of the Verwey transition of magnetite (or partially oxidized magnetite), and a nearly 2-fold increase in remanence on cooling, which indicates contribution from goethite and/or fine-grained hematite (Figure 5C; Maher et al., 2004). Previous work has shown that both hematite and goethite are present in Bighorn Basin paleosols based on XRD data (note that magnetite is too scarce volumetrically to be detected by XRD; Kraus and Hasiotis, 2006). The Morin transition is absent from the RT-*SIRM* measured in this study (similar to some modern red soils; Maher et al., 2004). However, the presence of hematite as the dominant high-field remanence carrier is inferred by comparison of backfield demagnetization curves measured at room temperature (25 °C; 298 K) and at 130 °C (403 K). The majority of high-field

335 remanence (> 100 mT) in specimen PCB-01-UDRB-145 remains when back-
336 field remanence is monitored above the Néel temperature of goethite (125 °C;
337 above which goethite carries no remanence), which indicates that hematite
338 is the dominant ‘so-called’ antiferromagnetic phase in these paleosols (Figure
339 5D).

340 5. Discussion

341 Our results comprise arguably the most complete magnetic dataset for
342 an ancient (pre-Quaternary) non-loessic paleosol sequence. Furthermore, de-
343 tailed correlations between core and outcrop, for the first time, allow direct
344 comparison of the magnetic properties of weathered and unweathered sec-
345 tions of the same paleosols. Our dataset allows us to directly address two
346 fundamental assumptions that must be made when applying magnetic paleo-
347 precipitation proxies to ancient paleosols: (1) surficial weathering of outcrops
348 does not impact magnetic mineral preservation, and (2) magnetic minerals
349 retain information about paleoprecipitation. We address these two assump-
350 tions below.

351 5.1. Magnetic mineral resistance to surficial weathering

352 The observed increase in M_r , $HIRM$, and the remanence held by the
353 HCC all indicate that there is a consistent remanence increase for high coer-
354 civity minerals in outcrop paleosols relative to their core equivalents (Figure

Figure 7: **A.** Example of backfield coercivity spectra (data shown in grey symbols) with the modeled best fit (orange). Data were fitted using a two-component model with a high (blue) and low (purple) coercivity component. Shaded envelopes for component distributions and model indicate an approximate 95% confidence interval. Data shown are from core specimen UDRB-100. **B.** Cross plot of the dispersion parameter (DP) and mean coercivity (B_h). Examples of modern pedogenic magnetite (green squares) are displayed with data from Egli (2004), Geiss and Zanner (2006), Lindquist et al. (2011), and Bourne et al. (2015). Note that Bourne et al. (2015) presented data recovered from a speleothem, but were interpreted to represent partially oxidized pedogenic magnetite. Data for B-horizon specimen from core and outcrop are shown in purple (low-coercivity component; LCC) and blue (high-coercivity component; HCC).

6). Notably, this increase is not observed in *HIRM* if calculated using a back-field of 300 mT instead of 100 mT. This indicates that the principal increase in remanence is acquired in magnetic fields of 100 – 300 mT. Remanence acquired at these field strengths is most likely held by either partially oxidized magnetite/maghemite or by low-coercivity, ultrafine-grained hematite (Liu et al., 2002, 2007; Özdemir and Dunlop, 2014). We propose that the increase in both M_r and *HIRM* that is observed in outcrops is due to formation of ultrafine (25 – 100 nm) pigmentary hematite within outcrops that formed via oxidation associated with surficial weathering.

Similar to observed color changes in the upper 25 meters of sediment cores recovered by the BBCP, visual inspection suggests that the outcrop paleosols have a more intense red coloration. Comparison of the semi-quantitative redness index (a^* ; calculated from reflectance spectral data; Abdul Aziz et al., 2008; Bowen et al., 2015) for outcrop marker bed paleosols compared with their core counterparts indicates a consistent and significant redness increase within outcrops (Figure 8; $p < 0.003$ for both paired t-test and Wilcoxon Signed-Rank Test). Fine-grained hematite acts as a red pigment in a variety of sedimentary settings (Chen et al., 2010). Furthermore, the magnetic properties of ultrafine pigmentary hematite are consistent with the observed variations noted here between core and outcrop paleosols. Grain sizes associated with pigmentary hematite in paleosols on the Chinese Loess Plateau are

roughly 50 – 100 nm (Chen et al., 2010), which corresponds roughly to B_c values on the order of 10 – 200 mT (Özdemir and Dunlop, 2014). This suggests that ultrafine grained hematite, if present, would acquire M_r beginning at low fields (100 mT) and could be the primary source of the anomalously high M_r and $HIRM$ in outcrops.

Figure 8: Redness Index (a^*) data from paleosol B-horizons at Polecat Bench. The dashed line indicates the 1:1 relationship. Note that in each paleosol, the mean a^* value of the outcrop is higher than the equivalent paleosol layer sampled from core. Redness data for the core are from Bowen et al. (2015) and are from Abdul Aziz et al. (2008) for the outcrop.

Pigmentary hematite formation within outcrops could result from either transformation of low-coercivity magnetite/maghemite, alteration of pre-existing clay minerals, or dehydration of goethite to hematite. Transformation of low-coercivity ferrimagnets into ultrafine hematite would likely be associated with a paired decrease in χ , ARM , and IRM values for outcrops.

386 This is not consistent with our data (Figure 4), where despite deterioration
387 of the low-coercivity minerals, their contribution to remanence is not signifi-
388 cantly different between core and outcrop (e.g., remanence held by the *LCC*,
389 $p \geq 0.38$ for paired t-test and paired Wilcoxon Signed-Rank Test). Alter-
390 ation of iron-bearing clay minerals is associated with pigmentary hematite
391 formation within paleosols on the Chinese Loess Plateau (Chen et al., 2010)
392 and remains a possibility in the Bighorn Basin sequence, where clay minerals
393 are abundant within B horizons (~ 30 weight %; Kraus et al., 2015).

394 Dehydration of goethite to hematite is a proposed mechanism for the
395 post-burial reddening of red beds and paleosols (Retallack, 1991). Previous
396 work mostly discounted this mechanism for paleosols in the Bighorn Basin
397 on the basis that the effect should be pervasive and would erase the complex
398 color assemblages that preserve pedogenic mottling in these deposits (Kraus
399 and Hasiotis, 2006). Dehydration of fine-grained goethite in these paleosols
400 into hematite would be consistent with observed increases in M_r , *HIRM*,
401 and increased remanence held by *HCC* in outcrops. Secondary hematite for-
402 mation in this system may also explain the strong normal polarity overprint
403 that has been observed in paleomagnetic studies from the Bighorn Basin
404 (e.g., Clyde et al., 2007). However, we cannot make a definitive conclusion
405 about the dehydration mechanism because our saturating fields (1 T) were
406 far too low to efficiently magnetize goethite within these sediments (Rochette

et al., 2005). The production of secondary hematite as a weathering product in outcrop paleosols, regardless of the exact geochemical pathway, challenges the assumption that magnetic minerals within paleosols, and outcrops of sedimentary rocks in general, remain unaffected by surface weathering.

5.2. Relationships between magnetic minerals and precipitation

Whether pedogenic magnetic mineral assemblages are preserved in ancient paleosols remains a fundamental question when applying magnetic oprecipitation proxies to ancient systems. As discussed above, it appears that surficial weathering of outcrops results in authigenic pigmentary hematite formation. The presence of non-pedogenic hematite in outcrop paleosols has considerable implications for the application of G/H proxies (Hyland et al., 2015; Long et al., 2011). Additional hematite will act to decrease the G/H ratio and cause MAP estimates to be biased to lower values. Authigenic hematite formed via surficial weathering may help to explain G/H based MAP estimates that are drier than other geochemical and paleobotanical methods (Hyland et al., 2015; Hyland and Sheldon, 2016). Accordingly, we suggest that G/H MAP estimates be viewed as minimum constraints.

Parameters that remain unaffected by weathering (e.g., χ , ARM , IRM) are generally controlled by low coercivity ferrimagnetic minerals (magnetite and maghemite). However, these parameters have considerable variability and lack characteristics of a magnetically enhanced profile similar to modern

soils (Maher, 1998; Geiss and Zanner, 2006; Geiss et al., 2008; Lindquist et al., 2011). This suggests that diagenetic processes, independent of weathering, have altered the low coercivity ferrimagnetic mineral population. However, relative enhancement ratios (as used in modern calibrations with MAP; Geiss et al., 2008) for the Polecat Bench section are comparable with those of some modern soils and appear to correlate with independent MAP estimates from the CALMAG geochemical weathering index (Figure 9 and Table 1; Geiss et al., 2008; Kraus et al., 2015). Correlations between MAP and enhancement ratios are generally higher for the core sediments compared with outcrop correlations, which may suggest that more variability is introduced via surficial weathering to outcrops that are not observed in core sediments (Table 1). However, significant ($p < 0.05$) and moderately strong ($R^2 \geq 0.46$; Table 1) correlations still exist in the outcrop section, which suggest that despite small influences from surficial weathering qualitative climatic information will still be preserved by the magnetic mineral assemblage.

Using empirical transfer functions to produce quantitative MAP estimates from the enhancement ratios shown in Figure 9 requires the assumption that the ratio has remained unchanged throughout the geologic history of a paleosol (from burial of the original soil to exposure as outcrop or recovery from core). Magnetic enhancement in modern soils is principally driven by pedogenic production of SSD and SP magnetite/maghemite in the upper

Figure 9: Mean B-horizon magnetic enhancement parameters for marker bed paleosols at Polecat Bench. **A.** Line-scan image of core stratigraphy and location of marker paleosols in the core. **B.** Carbon isotopic composition of pedogenic carbonates is shown to highlight the onset, main body, and recovery of the PETM (data from Bowen et al., 2015). **C-D.** B-horizon enhancement ratios for magnetic susceptibility (χ , C) and isothermal remanent magnetization (IRM , D). For each magnetic parameter the mean B-horizon value was normalized to the mean value of the C-horizon. B-horizon means for enhancement ratios were calculated using “enhanced” specimen, indicated in bold in Tables S1 and S3, similar to the approach taken by Geiss et al. (2008). Error bars approximate the 95% confidence interval and were calculated as the 2.5 and 97.5 percentiles of a Monte Carlo style resampling using B and C horizon means and standard deviations assuming a normal distribution. **E.** B-horizon mean ratio of susceptibility of anhysteretic remanent magnetization to IRM (χ_{ARM}/IRM). **F.** CALMAG mean annual precipitation (MAP) data are from Kraus et al. (2015) and represent independent estimates of MAP derived from the bulk geochemistry of the same marker bed paleosols (both core and outcrop). Note that in cases where arrows are on the ends of error bars the error bars were reduced to avoid overlap with adjacent panels.

Table 1: Correlation of magnetic parameters with mean annual precipitation (MAP) and B-horizon thickness.^a

Parameter	Core		Outcrop	
	MAP	Thickness	MAP	Thickness
χ_B/χ_C	0.79 (0.0014)	0.02 (0.72)	0.64 (0.0002)	0.21 (0.08)
IRM_B/IRM_C	0.79 (0.0014)	0.04 (0.60)	0.46 (0.0040)	0.30 (0.03)
ARM_B/ARM_C	0.55 (0.0227)	0.05 (0.57)	0.46 (0.0037)	0.30 (0.03)
χ_{ARM}/IRM	0.03 (0.68)	0.23 (0.19)	0.12 (0.20)	0.07 (0.31)
$HIRM$	0.08 (0.46)	0.03 (0.65)	0.001 (0.90)	0.05 (0.41)

^aMean B-horizon values are used for each indicated magnetic parameter. MAP data are derived from the geochemical weathering index CALMAG and come from Kraus et al. (2015). R^2 values are reported with p-values in parentheses. Significant correlations are highlighted with bold and italics.

soil horizons (Maher, 1998; Geiss et al., 2008; Orgeira et al., 2011). Coercivity spectra (from *ARM* and *IRM* experiments) from many modern soils have identified a low-coercivity component that is often referred to as pedogenic magnetite (Figure 7B; Egli, 2004; Geiss et al., 2008; Lindquist et al., 2011). Recovery of a similar low-coercivity component within ancient paleosols would increase confidence in the assumption that observable magnetic enhancement in paleosols is driven by similar processes as in modern soils.

The *LCC* recovered from analysis of B horizons in the Bighorn Basin paleosols suggests either a lack of pedogenic magnetite in these soils or alteration of pedogenic magnetite via diagenesis and weathering (Figure 7B). Assuming that magnetite was produced in the original soils during pedogenesis, it is feasible that diagenetic processes increased B_p (via partial or complete maghemitization; e.g., van Velzen and Dekkers, 1999; Chen et al., 2005) and *DP* (by increasing the range of coercivities within the original population of

463 grains) of the pedogenic magnetite component. Notably, the average *LCC*
464 of Bighorn Basin paleosols has this trend for pedogenic magnetite (Figure
465 7B) and, therefore, we suggest that the *LCC* represents partially oxidized
466 pedogenic magnetite.

467 Magnetic paleoprecipitation proxies based on properties such as χ , *ARM*,
468 and *IRM* (likely to be dominated by pedogenic magnetite/maghemite) in
469 empirical relationships with MAP are likely to be compromised by the pro-
470 gressive oxidation of pedogenic magnetite during weathering and diagenesis.
471 For example, the χ_{ARM}/IRM ratio is used as a direct indicator for pedo-
472 genic magnetite in the methods of Geiss et al. (2008); our data indicate no
473 correlation between independent estimates of MAP and χ_{ARM}/IRM (Table
474 1; Figure 9E). Enhancement ratios may provide a means to normalize the
475 effects of magnetic mineral oxidation, principally under the assumption that
476 any magnetic minerals present in the parent material experience similar pro-
477 cesses. It is encouraging that the magnetic enhancement ratios preserved in
478 the studied Bighorn Basin paleosols are of a similar magnitude to those of
479 modern soils (Geiss et al., 2008). We urge caution in assuming that a similar
480 degree of enhancement in a particular magnetic property suggests equivalence
481 between modern and fossil soils. However, the good agreement between mag-
482 netic enhancement ratios and geochemical proxies highlights that magnetic
483 minerals do record at least qualitative information about paleoclimate in the

484 geologic record.

485 6. Conclusions

486 Our core-to-outcrop comparison of the magnetic properties of paleosols
487 preserved in the Paleocene-Eocene Willwood Formation of the Bighorn Basin
488 allows us to address two fundamental questions related to the application of
489 magnetic paleoprecipitation proxies in ancient systems. First, we evaluated
490 the effects of surficial weathering on the magnetic minerals preserved in out-
491 crops. Outcrop samples have a consistent and significant increase of $\sim 23\%$
492 in M_r and $\sim 41\%$ for *HIRM* compared with equivalent core samples (Fig-
493 ure 6). This increase is interpreted to be caused by secondary pigmentary
494 hematite ($\sim 25 - 100$ nm) production in outcrops and is supported by similar
495 increases in redness index (a^*) within outcrops compared to the studied core
496 (Figure 8). The increase in magnetic remanence within outcrops complicates
497 application of magnetic paleoprecipitation proxies that use the proportion of
498 total remanence held by hematite and goethite to estimate magnetic mineral
499 abundance ratios (Long et al., 2011; Hyland et al., 2015). It may be possible
500 with future work to address this complication by more detailed unmixing
501 analysis to differentiate primary pedogenic hematite from the secondary au-
502 thigenic hematite that forms in subaerial weathering regimes. In this way it
503 may be possible to remove, or at least account for, this non-pedogenic mag-

netic mineral phase when applying methods based on high-field magnetic properties (e.g., Long et al., 2011; Hyland et al., 2015). At minimum, the observed increase in *HIRM* and M_r increases the uncertainty in applying these methods and the associated error in MAP estimates derived from them. Attempts to address this uncertainty should be included in future work based on these methods.

Second, we evaluated the possibility that magnetic minerals in ancient paleosols record changes in paleoprecipitation across the PETM. Magnetic enhancement ratios of parameters such as χ and *IRM* correlate with independent MAP estimates from geochemical proxies (Figure 9, Table 1; Kraus et al., 2015). However, applications of magnetic enhancement proxies are complicated by the fact that the pedogenic magnetite recovered from the Bighorn Basin appears to have been altered during diagenesis (in both core and outcrop), which results in higher mean coercivities and broader coercivity distributions. Additionally, current magnetic precipitation proxies have large uncertainties (Heslop and Roberts, 2013; Maher and Possolo, 2013) even when applied in systems where pedogenic magnetite is not altered by diagenesis. So, while the magnetic mineral assemblage preserves qualitative information about paleoprecipitation, quantitative estimates from empirically derived transfer functions may prove difficult to defend if pedogenic magnetite commonly undergoes alteration during diagenesis.

Our analysis presents some challenging obstacles for quantitative application of soil magnetism to paleoclimate problems in deep time. However, environmental magnetic information is still preserved in these ancient paleosols (e.g., magnetic enhancement ratios, Figure 9), which suggests their continued promise for magnetic assessment of ancient MAP. In future studies, degradation of pedogenic magnetite should be possible to identify based on comparison of coercivity components to magnetites observed in modern soils as done here. Unfortunately, there is currently no obvious way to identify the presence of non-pedogenic, authigenic hematite in outcrops where comparison to equivalent core sediments is not possible. More detailed studies on pre-Quaternary paleosol sequences combined with expanded studies on modern soils could provide solutions to these complications and allow soil magnetism to become an important tool for reconstructing past climates.

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