minerals

MDPI

Article

A Mottled, Non-Lithified Paleosol in Brazil: Diagnosis by Morphological and Mineralogical Features

Yuri Lopes Zinn [1,*] and Camila Fernandes Miranda [2]

[1] Department of Soil Science, Federal University of Lavras, Lavras 37200-900, MG, Brazil
[2] Department of Forestry, Federal University of Lavras, Lavras 37200-900, MG, Brazil; cfmiranda@estudante.ufla.br
* Correspondence: ylzinn@ufla.br

Abstract: The identification of paleosols is difficult when no buried horizons or lithification occur. Here, we described the identification of a possible paleosol, its characterization, and which features supported its positive diagnosis. In a construction site, a vertical cut exposed an unusual red–yellow mottling with massive structure and channels (probably faunal), in contrast with the overlying homogeneous red Oxisol with fine granular structure. A similar but more deferrified section with white–yellow mottling also occurred nearby, and both were sampled as large clods. In thin sections, many oriented clay coatings occur along channel voids, suggesting illuviation, as well as dissolving Fe nodules and Mn coatings along planar and channel voids. X-ray diffraction showed a clay dominated by kaolinite, traces of illite, and absence of gibbsite, again contrasting with the gibsitic-kaolinitic clay of the Oxisol. We confirmed the diagnosis of a Paleoultisol due to the following incompatibilities with the overlying Oxisol: (1) massive, apedal structure, and higher bulk density; (2) clay coatings indicative of illuviation as key soil-forming process; (3) low clay contents in particle-size analysis due to cementation; (4) very low organic carbon consistent with long-term inhumation; and (5) kaolinitic–illitic clay. The unusual granular microstructure of the B horizon of the Oxisol is partly derived from disintegration and desilication of the Paleoultisol.

Keywords: pedology; tropical soils; soil micromorphology; soil mineralogy

Citation: Zinn, Y.L.; Miranda, C.F. A Mottled, Non-Lithified Paleosol in Brazil: Diagnosis by Morphological and Mineralogical Features. *Minerals* **2021**, *11*, 616. https://doi.org/10.3390/min11060616

Academic Editor: Yul Roh

Received: 29 April 2021
Accepted: 6 June 2021
Published: 8 June 2021

1. Introduction

Paleosols are defined as soils with distinctive morphology formed on a landscape of the past, i.e., a soil-forming environment that no longer exists at that particular site, although the paleosol persists without major alteration [1]. A paleosol classification was proposed [2] based on its burial (inhumation) or erosive exposure (exhumation), enduring properties relative to formative processes, and lithification, among other criteria. Many paleosol studies focus on the field identification and description of an A horizon or A/B sequences buried by other soils or lithified strata, especially in the latter case when a geochronological dating is possible [3]. In non-lithified soil settings without buried horizons, paleosols can be identified by carbon-dated age of organic matter or other morphological contrast with the overlying current soil, since their preservation can be as precarious as a "thin basal stump" [4]. However, such contrast can be highly variable and not always evident, and thus paleosol diagnosis is subject to a debate, in which soil micromorphology is a critical tool.

Paleosols can be separated from sedimentary strata by features such as root marks, structure, gleying, structure and clay illuviation or eluviation [5], although the latter are not always visible to the naked eye. However, the study of soils with undisturbed structure in thin sections, with use of a petrographic microscope, provides a powerful means of analysis, visualization, and even quantification of soil components and formative processes, and on parent materials [6], and thus has been a tool of choice for paleosol study for decades [4]. These authors state that paleosols can be identified by one or more of the following micromorphological aspects: undisturbed biological features, pedogenic *b*-fabrics, and one or more pedofeatures, especially when in contrast with a current soil cover or reference.

Here, we aimed to describe and confirm the diagnosis of a non-lithified paleosol underneath a deep (1 m to >5 m), red, very clayey gibbsitic Oxisol of granular structure in Brazil. Our main hypothesis is that the vertical section of the terrain exposes a remnant of a buried paleosol, identifiable due to the presence of mottling unlikely to reflect current redoximorphism, and other features posing a sharp contrast with the surrounding soil. Our rationale is to provide researchers and field pedologists with useful information to identify possible paleosols, in the absence of the more obvious and conventional indicators, such as buried A horizon and lithification.

2. Materials and Methods

2.1. Site Description, Sampling, and Sample Preparation

A large excavation for a truck parking lot, near Ijaci, Minas Gerais, Brazil, (Figure 1a, at an altitude of 889 a.s.l.) exposed a vertical section of a small, hill-shaped (Figure 1b) truncated soil matrix lying in complete non-conformity with the terrain surface and soil horizons, and marked by a red–yellow mottling. Although this mottling pattern is not unusual in the region, its current drainage conditions suggested it was probably not caused by current redoximorphism, and lacked any conformity with the current terrain surface and soil horizons (Figure 1b,c). Such mottled section lacked a dark-colored buried A horizon and was not lithified, i.e., had the consistency of a lightly cemented soil and not of a rock, which are the most known hints of a paleosol. However, the mottled section presented: (1) a massive structure (Figures 1c and 2b); (2) many unusual, centimetric masses of clear quartz (Figure 2a,b); and (3) multiple faunal channels infilled by red granular soil (Figure 2b–d), which are unusual in current soils. In some parts, channels with much denser infillings with deferrified material around an irregular axis, suggestive of former roots, were also visible (Figure 2e). About ca. 30 m southeast in the same vertical cut, another mottled section very similar in morphology, except for a more pronounced deferrification that resulted in a white–yellow mottling, was also exposed (Figures 1d and 2g,h). The two mottled sections pose a very stark contrast with the surrounding and overlying soil, marked by homogeneous reddish colors and granular structure (Figure 1b,c). The morphological ensemble of the mottled sections and their sharp contrast with the surrounding soil suggested that this situation could be a little known type of paleosol and raised the motivation for this study.

The surrounding soil has been described in detail [7,8] and correlated in Soil Taxonomy [9] as a well-drained, acidic Anionic Acrudox, currently under a moist, warm temperate climate, with mean annual temperature and precipitation of 19.3 and 1530 mm, respectively. The clay fraction of this soil is predominantly gibbsitic (ca. 58% of the total soil mass is composed by Al_2O_3), also containing highly-crystalline kaolinite, hematite, and goethite (ca. 20% total Fe_2O_3). This Oxisol overlies a Proterozoic meta-limestone that lies perhaps >10 m, or much more, below the soil surface. However, this Oxisol no longer has any carbonates, and its composition was believed to derive from the accumulation of silicate impurities of the carbonate rock [7].

Sampling of large clods from the red–yellow and white–yellow mottled zones were done directly from the vertical exposures with help of hoes and shovels. The clods were air-dried for months, and some sub-samples were disrupted with use of a spatula to separate the red and yellow (Figure 2f), but not the white–yellow, matrices for analyses. Other clod subsamples with undisturbed structure and containing the red–yellow and white–yellow matrices were impregnated with epoxy resin under vacuum, hardened, and cured at 100 °C–140 °C, cut with diamond saw, and mounted on glass slides for micromorphological description [6].

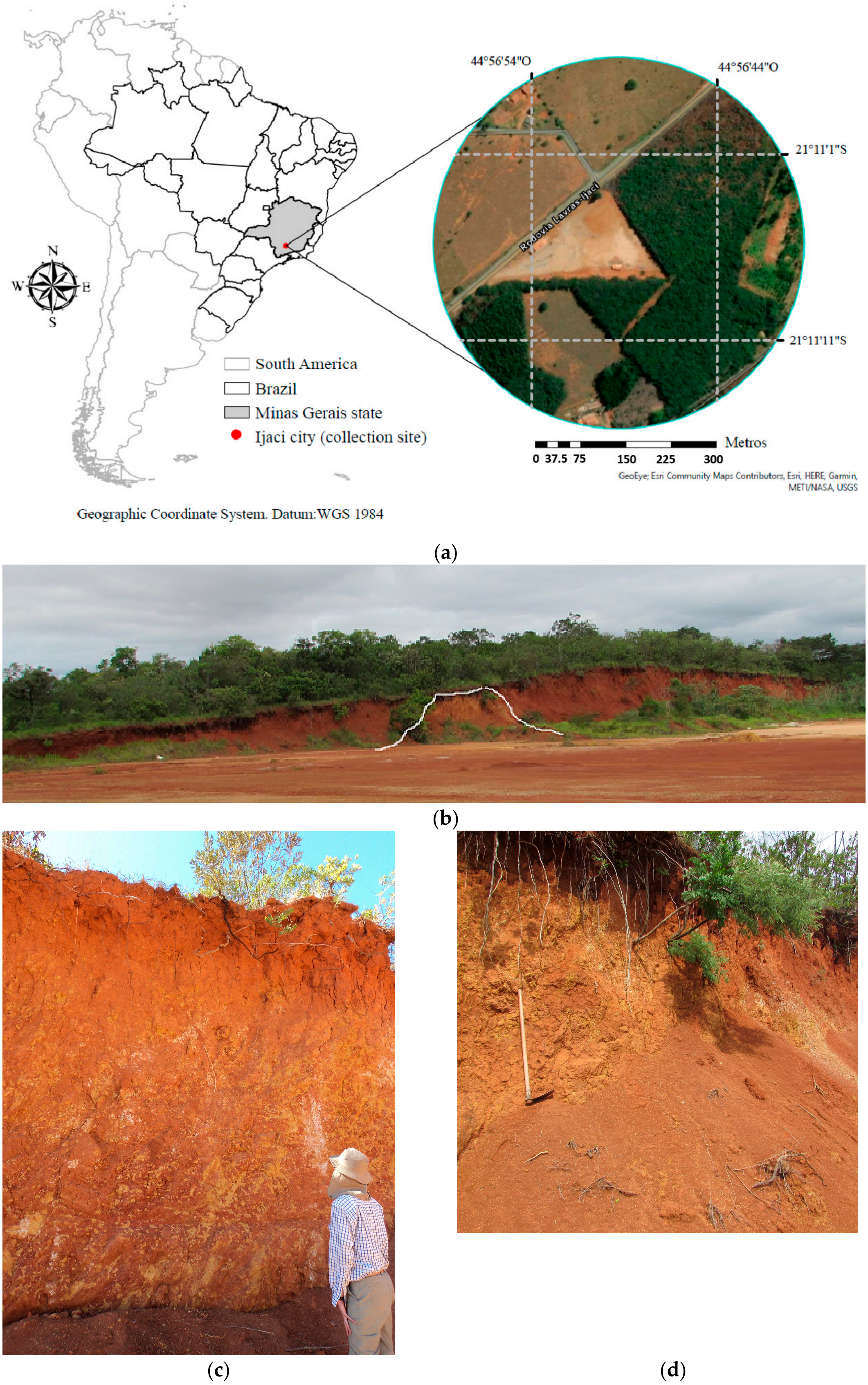
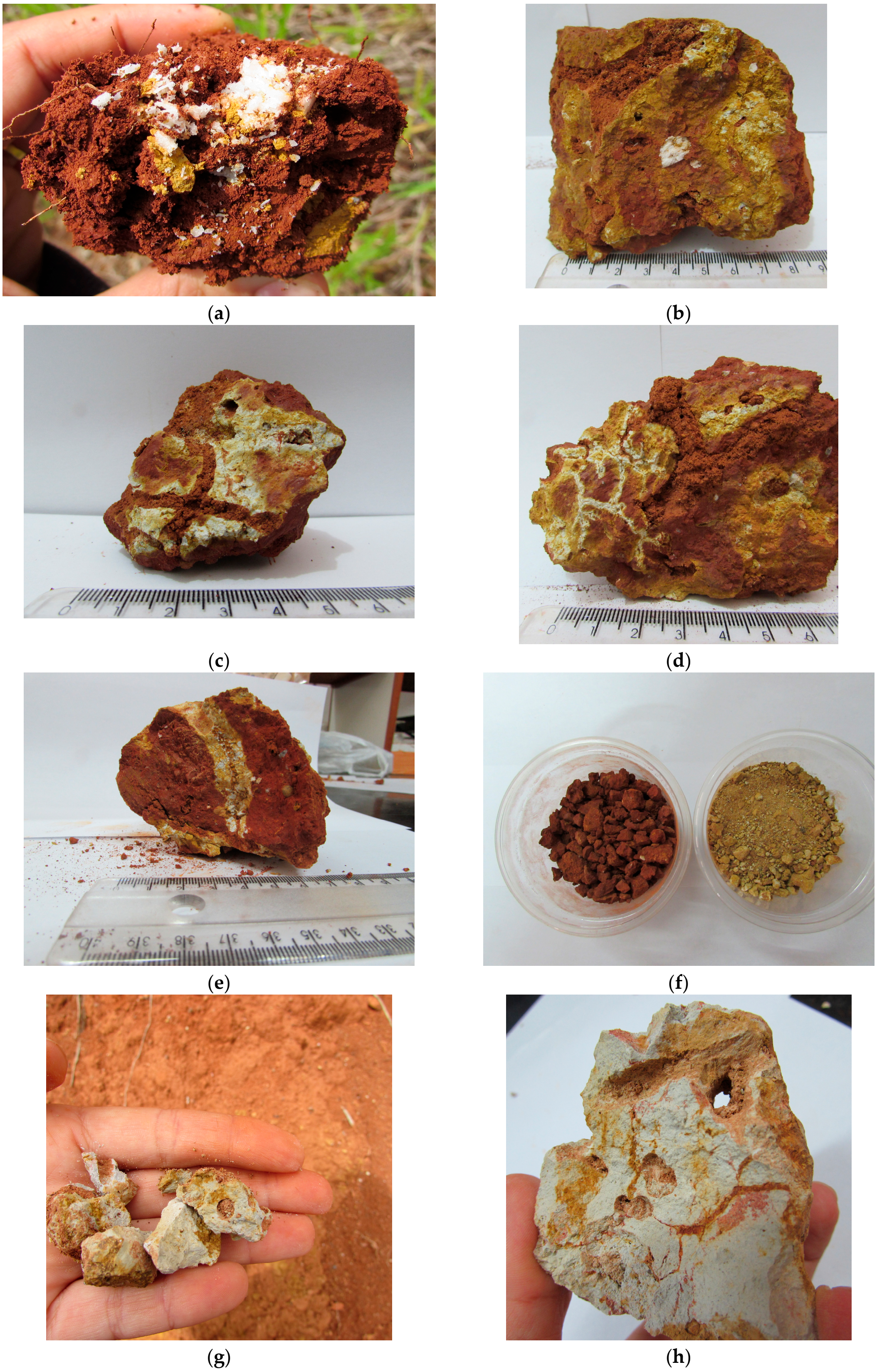


Figure 1. (**a**) Map with location of study site and the triangular-shaped mechanized cut from the air; (**b**) ground view showing the hill-shaped mottling intersecting non-conformably the red Oxisol and land surface; (**c**) red–yellow mottling; and (**d**) mostly deferrified, white–yellow mottling. Note the deferrified, mostly white colors of the white–yellow mottled section on the right corners of (**a**,**b**,**d**).



(**a**) (**b**) (**c**) (**d**) (**e**) (**f**) (**g**) (**h**)

Figure 2. (**a**,**b**) clods of red–yellow mottles containing masses of clear (with no clay impregnations) quartz, which break with gentle finger pressure into gravel and sand particles; (**c**) crossing channels intersecting a clod surface with varying deferrification; (**d**) partial and total deferrification along clod or ped surfaces, aside from large channels; (**e**) root channel; (**f**) hand-separated matrices; (**g**,**h**) yellow–white clod with infilled faunal channels.

2.2. Sample Characterization

Bulk density was determined by the clod method in a sub-sample of the red–yellow mottling with undisturbed structure. Particle-size distribution was determined by the Boyoucos method after dispersion of red–yellow and white–yellow matrices in NaOH 0.1 Mol L^{-1} and 16 h agitation and sand sieving. The mineral composition was assessed by X-ray powder diffraction of clay separates for the red, yellow, and white matrices, obtained after dispersion in NaOH 1 mol L^{-1}, slow shaking, sieving, and siphoning. The apparatus used was a Bruker D2 Phaser, using Cuκα radiation (λ = 1.5418 Å) at 30 kV and 10 mA, in the 5–40 °2θ interval, in angle steps of 0.02 °2θ, and dwelling time of 0.5 s.

Soil pH in water was determined for the red, yellow, and white–yellow matrices, using a 1:2.5 soil:water suspension. Exchangeable Ca^{2+}, Mg^{2+}, and Al^{3+} were extracted with 1 mol L^{-1} KCl; Ca^{2+} and Mg^{2+} were determined by atomic absorption, and Al^{3+} contents by titration with NaOH solution 0.025 mol L^{-1} and indicator blue of bromothymol. Mehlich−1 available K^+ and P were extracted with 0.05 mol L^{-1} HCl and 0.0125 mol L^{-1} H_2SO_4 solution; K was determined by flame photometry and P by colorimetry. Potential or total acidity (H^++Al^{3+}) was assessed by extraction with Ca-acetate buffered at pH 7.0 and determined by titration with 0.06 mol L^{-1} NaOH, with phenolphthalein as indicator [10]. With these data, the following indicators were calculated: cation exchange capacity (CEC pH 7.0 = Ca^{2+} + Mg^{2+} + K^+ + H^+ + Al^{3+}); clay activity (CFA = CEC pH 7.0 × 1000/clay content g kg^{-1}); base saturation (BS = (Ca^{2+} + Mg^{2+} + K^+ + Na^+) × 100/CEC pH 7.0). Soil organic carbon content was determined by Walkley–Black wet combustion with potassium dichromate 0.07 mol L^{-1} in concentrated sulfuric acid.

3. Results and Discussion

3.1. Macro- and Micromorphological Description

The morphological description of the Oxisol and mottled sections of the suspected paleosol are summarized in Table 1. The red–yellow and white–yellow mottled sections did not show pedality in the field, i.e., they did not form naturally occurring peds of any kind, and their soil materials have much higher dry and moist consistence than the Oxisol, and slight cementation compatible with incipient (or residual) lithification (see also particle-size distribution in Section 3.2). An apedal or massive microstructure or the packing of rounded aggregates has been interpreted as an indicator of a pedosediment [4], i.e., transported soil materials, which are often difficult to distinguish from some relict Oxisol [11]. In any case, the presence of this massive structure, mottled soil body, non-conformably situated within the overlying Anionic Acrudox, was the initial hint of a paleosol in the present study. In fact, such massive structure, and the ensuing limited soil porosity, resulted in a bulk density of 1.15 g cm^{-3} as determined by the clod method. This value was considerably higher than those reported for the overlying Oxisol at a depth of 1 m, which were 0.77 g cm^{-3}, a low but common value for Oxisol, ascribed to the fine granular structure and large packing void volume [8]. At a depth of 5 m, bulk density in this Oxisol was only ca. 0.85 g cm^{-3} [12], suggesting that the granular structure pattern was constant through its profile, and much less dense than the mottled sections.

Soil structure patterns in the field and lab were evident under the microscope. The A horizon of the Oxisol is marked by a fine to mid-sized granular microstructure in which peds are mostly spherical granules with sharp outlines, either isolated or welded into clusters (Figure 3a). This pattern was ascribed to intense faunal activity and gibbsitic clay [8], and contrasts sharply with the B horizon of the same Oxisol, marked also by fine granular microstructure, but comprising much smaller angular peds that are mostly accordant with the surrounding peds (Figure 3b). To the best of our knowledge, this unusual pattern of granular microstructure has seldom been reported in the literature, and was ascribed [13] to the disintegration of the spheroid peds in the A horizon, as suggested by features like those seen in the upper left corner of Figure 3b. However, the majority of these small angular granules more probably resulted from the disjointing or cracking of larger angular peds or clods with an apedal or blocky microstructure, which can be originated from the underlying mottled sections, as described below.

Table 1. Morphological description of the Oxisol and mottled sections.

Soil	Morphological Description	Micromorphological Description
Oxisol A horizon (depth 0–15 cm)	*Structure*: granular, small- to medium-sized, strong, mostly coalescing into apparent subangular blocks; *Consistency*: dry-hard, moist-friable. Plastic, slightly sticky. *Dry Munsell color* 5YR 4/6.	*Microstructure*: granular, spheroidal peds (24 µm to 1000 µm diameter) often coalesced reaching cm-sized clusters. *Voids*: complex packing, random distribution pattern. *c/f limit and related distribution*: 15 µm, open porphyric. *Coarse material*: subangular quartz (<400 µm dia.), often Fe-impregnated, opaque nodules (<400 µm dia.). *Organic material*: roots, charcoal. *Micromass*: reddish brown, b-fabrics: undifferentiated to stipple-speckled and granostriated. *Pedofeatures*: nodules, excrements (often infilling coalesced peds).
Oxisol B horizon (depth 50–100+ cm)	*Structure*: granular, very small to medium-sized, moderate, in parts coalescing into apparent subangular blocks. *Consistency*: dry-slightly hard, moist-friable. Slightly plastic, slightly sticky. *Dry Munsell color* 5YR 5/8.	*Microstructure*: granular, mostly angular peds from apparent block disruption, less frequently spheroids disrupted into “onion-skin” (24 µm to 1000 µm diameter). *Voids*: complex packing, random distribution pattern. *c/f limit and related distribution*: 15 µm, open porphyric. *Coarse material*: subangular quartz (<1000 µm dia.), often Fe-impregnated, opaque nodules (<400 µm dia.). *Organic material*: charcoal. *Micromass*: red to reddish brown, b-fabrics: undifferentiated to stipple-speckled and circular-striated in parts. *Pedofeatures*: nodules, excrements (often infilling coalesced peds).
Red-yellow mottle section	*Structure*: massive. *Consistency*: dry-extremely hard, moist-very firm. Slightly plastic, slightly sticky. Weakly cemented. Coarse, white brittle quartz masses (Figure 2a,b). Abundant faunal channels infilled with red (2.5YR 4/9) fine granular soil material (Figure 2b–d). Evidences of root channels with yellow to white colors (Figure 2e). Clod interior mostly red (2.5YR 4/9) with surfaces yellow (10YR 7/6) to light pink (7.5YR 8/2); in parts white (7.5YR 9.5/1).	*Microstructure*: massive or apedal. Voids: planar, vughs, vesicles, large faunal channels, random distribution pattern. *c/f limit and related distribution*: 15 µm, open porphyric. *Coarse material*: subangular quartz (<400 µm dia.) grains, quartz fragmented into splinters, opaque nodules (<400 µm dia.). *Organic material*: not observed. *Micromass*: mottled colors, b-fabrics: undifferentiated to stipple-speckled, grano- and circular-striated in parts. *Pedofeatures*: laminated, concentric, and relict clay coatings, Mn coatings, dissolving nodules, loose discontinuous infillings within faunal channels
White-yellow mottle section	*Structure*: massive. *Consistency*: dry-very hard, moist-very firm. Slightly plastic, slightly sticky. Weakly cemented. Abundant faunal channels infilled with pink (5YR 7/4) fine granular soil material (Figure 2g,h). Coarse, white brittle quartz masses. Clod interior mostly white (7.5YR 9.5/1) with surfaces yellow (10YR 7/6) to light pink 7.5YR 8/2), in parts pink (5YR 7/4).	The same as for red–yellow mottle section, but with lighter colors. Greater expression of grano- and circular-striated b-fabrics due to general Fe depletion.

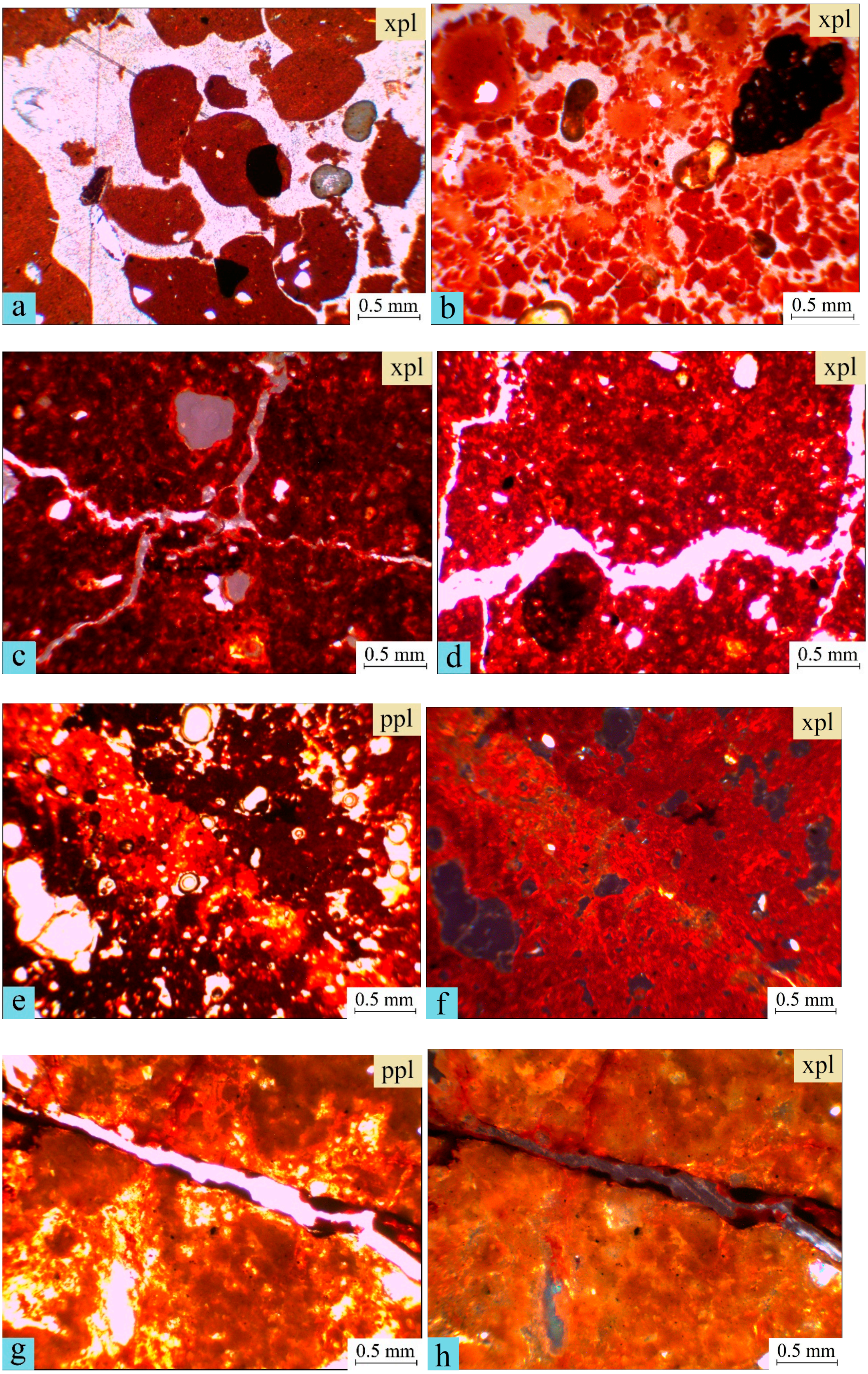


Figure 3. Soil microstructure patterns: (**a**) overlying Oxisol, A horizon; (**b**) Oxisol, B horizon; (**c**–**f**) red-yellow matrix; (**g**,**h**) white-yellow matrix. Note residual Mn oxide deposits along planar void in (**g**,**h**). ppl: plane polarized light; xpl—cross-polarized light.

Both the red–yellow and white–yellow mottles showed a massive or apedal microstructure tending to fragment into weakly separated, accordant angular blocks, as delimited by linear or irregular planar voids (Figure 3c,d,g,h) or fissures. However, vughs (Figure 3c,e–h) and vesicle (Figure 3c,e,f) pore types also occur, some with apparent clay coatings and pore striations (Figure 3c). The c/f distribution was open-spaced porphyric due to the very low amounts of coarse material (sand-sized quartz and opaque nodules), which is also the case for the Oxisol, reflecting a similar texture of both mottling and soil materials. The *b*-fabrics was undifferentiated in the Oxisol and most parts of the red mottling (Figure 3a–d), but with increasing deferrification, poro- and granostriations become visible (Figures 3e–h and 4a,b), as well as circular striations (Figure 5g,i). In other words, the fine material (mostly clay since silt and humus were sparse) of the mottled sections shows signals of orientation due to compressive or contractive stresses, whereas Fe oxides tend to mask these striations in the non- or less-deferrified matrices, and the Oxisol mostly lacked such features. Coarse material comprised angular to sub-rounded quartz (Figure 3a), and less frequently opaque nodules (Figures 3a,b and 4a,b), but the largest and most remarkable coarse material was the unusual brittle, colorless gravel-sized quartz (Figure 2a,b). In thin section, these quartz masses showed continuous optical orientation (Figures 4c,d and 5d,e) indicating that they are fractured phenocrysts, i.e., large crystals that broke up, but were nonetheless preserved as an undisturbed cluster. These quartz masses occurred sometimes along pores (Figure 4c,d) from which clay was apparently removed, but mostly occurred within the soil matrix (Figures 2a,b and 5d,e). The absence of fine material (namely clay or organic matter) among the shards is responsible for their clear, white color (Figure 2a,b), although they break easily with gentle finger pressure. When these quartz masses were naturally disturbed during soil development, angular shards became scattered in the soil matrix (Figures 3a and 5d,e). Although quartz splinters have been reported in many paleosols [4], to the best of our knowledge, this unusual pattern of coarse, clear brittle quartz was never reported in tropical or other soils, current or relict, and can be regarded as an indicator of paleosols in similar settings.

Pedofeatures in the overlying Oxisol were restricted to opaque Fe nodules and excrements (Table 1). However, there were multiple pedofeatures in the mottled sections, including (in order of occurrence and relevance):

(1) Fe segregation, which varies from local to nearly complete depletion, and actually define the very mottled zones, which were the most evident hint of a paleosol. Most Fe depletions in the red–yellow mottling form along preferential-flow paleochannels and planar voids, but can also be unrelated to evident or current large voids (Figures 3e,f and 4a,b). A moderate deferrification resulted in yellow colors, indicative of hematite dissolution or hydration into goethite, and when more advanced, resulted in the white matrices of the white–yellow mottles (Figures 2g,h and 5). However, the deferrification cycle that formed the white–yellow mottling occurred after the formation of faunal channels and infillings (see next), since red infillings were also partly deferrified into a pinkish color. Thus, the red–yellow and white–yellow mottles are probably different "pedogenic facies" [4], since, despite differing morphologically only in the degree of deferrification, they do represent different cycles of soil formation;

(2) Infillings—these are soil materials filling faunal channels that intersect the red–yellow mottles along planar voids and clod surfaces (Figure 2c,d) and, thus, were necessarily formed after this mottling cycle. The infillings were mostly loose and discontinuous, and comprised granular material of redder colors in either the red–yellow and white–yellow mottling (Figure 2c,d,g,h). The pinkish infillings in Figure 2g,h indicate that the white–yellow mottled section result from further and nearly complete deferrification of the red–yellow mottled section after the burrowing and infilling (see above). In thin section, the granules are mostly rounded and spherical, although often welded into clusters (Figures 4g and 5i), with a *b*-fabrics contrasting with that of the surroundings, which aside from the different colors suggests different formation times [4]. It is

possible that this granular material comes from the overlying Oxisol, although the granules are much smaller than those in the A horizon of the Oxisol (Figure 3a), suggesting the work of burrowing fauna rather than abiotic infilling of abandoned channels, which would result, most likely, in irregularly-shaped granules;

(3) Clay coatings—features of clay illuviation are often considered one of the most reliable indicators of soil-forming processes. However, we considered clay coatings third in the ranking of pedofeatures, since they are much less abundant in volume than Fe depletions and infillings, and were perceived only in thin section. However, the apparent little abundance of clay coatings is less important than their occurrence: as little as a 5% clay coating area in a thin section suggests extreme illuviation [6]. In addition, it is possible that clay coatings were not as frequent due to very clayey texture of the soil material, in contrast to what typically occurs in coarser soils, where coatings are more evident. Here, they are most often lining vesicle or channel voids as laminated coatings (Figure 4e,f) with concentric deposition (Figure 5a–c). However, clay coatings with poor lamination also appear as relicts unrelated to current ped or clod surfaces, in yet another hint of a paleosol [4].

(4) Opaque Fe oxide nodules, similar to those in the overlying Oxisol, were also described, although they can be inherited [4]. However, in the mottled sections, they showed evidences of instability due to Fe hydration or deferrification resulting in partial dissolution (Figure 4a,b), in contrast with their apparent stability in the well-drained Oxisol matrix (Figure 3a).

(5) Opaque Mn oxide coatings along planar and channel voids (Figures 3g,h and 5f–h), in the white-yellow matrix. The fact that these Mn coatings apparently occur only in the more deferrified mottling suggest that they only formed in the more poorly drained locations, where redoximorphism was or is more active. The cracking of these Mn coatings along planar voids in some parts is suggestive of their relict character, although they are the probably among the more recent features to be formed.

Pedofeatures are useful indications of soil formation. However, pedofeatures 1, 2, 4, and 5 can also occur in sediments, which is not the case of clay coatings. Aside from the root mark evidence (Figure 2e), these clay coatings suffice the usual requisite by of two out of three features to a paleosol diagnosis, the other being pedogenetic horizons [2], the latter missing in the present study.

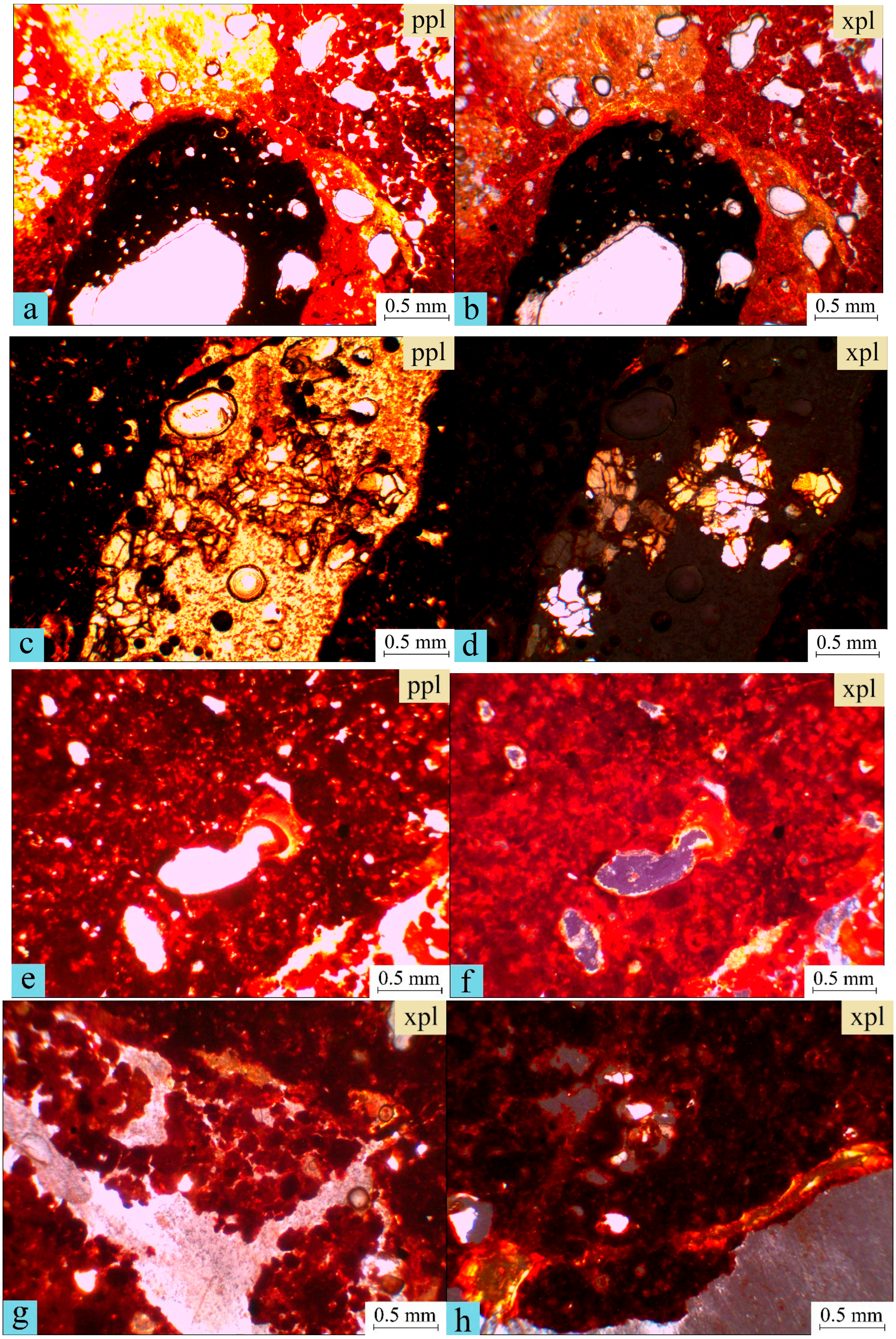


Figure 4. Pedological features in the red–yellow mottling: (**a**,**b**) dissolving Fe nodule surrounded by hydration halo; (**c**,**d**) clear, fissured quartz crystal within channel void showing continuous optical orientation and absence of clay impregnation; (**e**,**f**) laminated clay coating; (**g**) loose discontinuous infilling of spherical granules on faunal channel; (**h**) laminated coating probably formed on relict clod surface. ppl: plane polarized light; xpl—cross-polarized light.

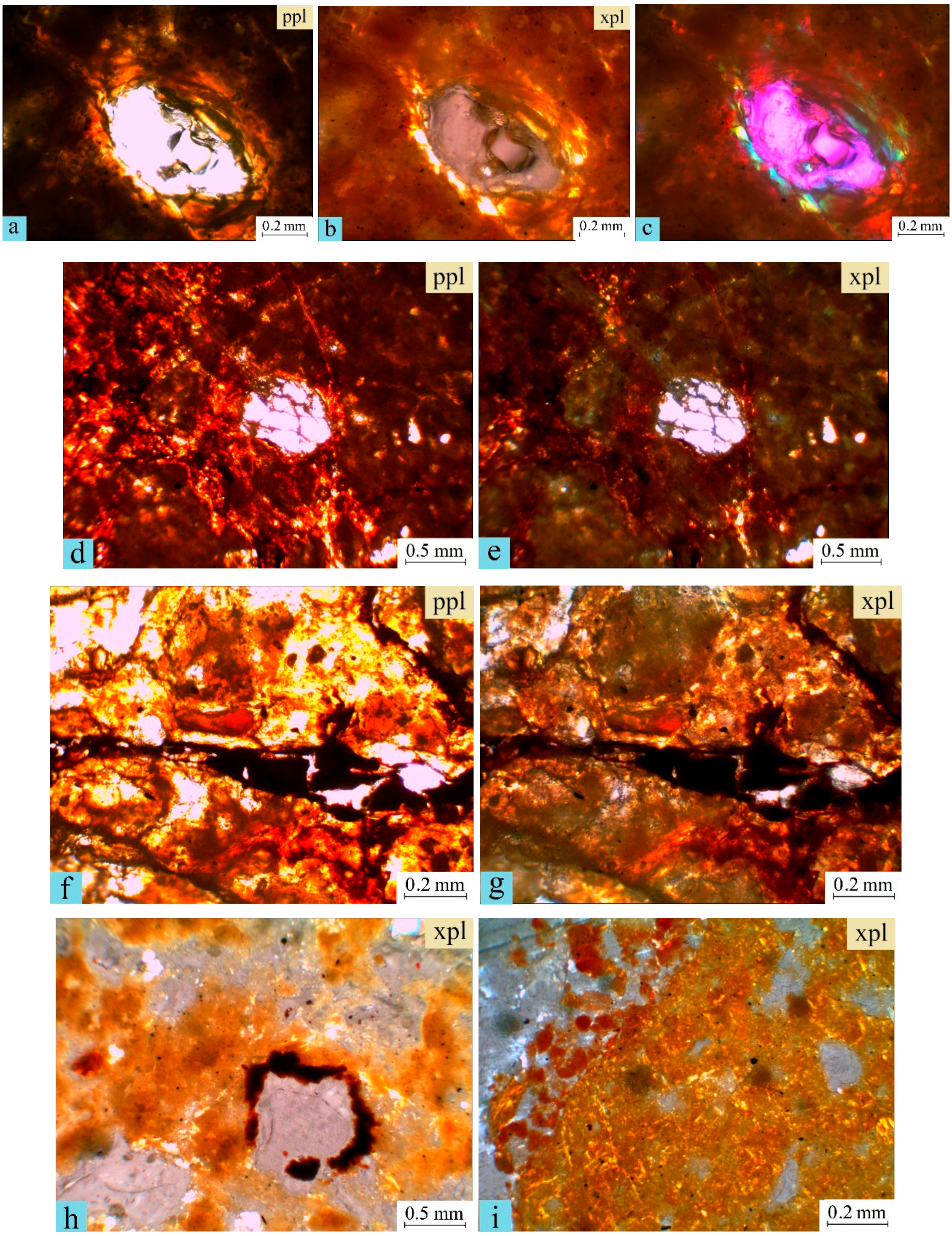


Figure 5. Pedological features in the white–yellow mottling: (**a**,**b**) laminated clay coating along pore wall, with gypsum plate (**c**) showing concentric deposition; (**d**,**e**) clear, jointed quartz crystal showing crystalline continuity and absence of clay impregnation; (**f**,**g**) Mn oxide coating along planar and channel; (**h**) voids of preferential water flow; (**i**) loose discontinuous infilling of redder, spherical granules on faunal channel. Note different types of *b*-fabrics. ppl: plane polarized light; xpl—cross-polarized light.

3.2. Chemical, Particle-Size and Mineralogical Characterization

Table 2 presents soil chemical characterization data of the red, yellow, and white matrices of the sampled clods, and similar data from the A and B horizon (0–15 and

50–100 cm depth, respectively) of the overlying Anionic Acrudox for comparison. Soil pH is acidic and similar across each soil material, as well as Mehlich-P. Exchangeable Al^{3+} is higher in the A horizon of the Acrudox, and increases with deferrification of the mottled matrices, reaching a considerably high value of 90% Al saturation in the white matrix. Exchangeable bases were low in all samples, although the yellow matrix showed slight higher levels, and thus the highest base saturation. The most contrasting property was organic carbon, which reached high levels in the Acrudox, but almost negligible values in the mottled matrices, especially the most deferrified white one (Figure 2g,h). The decay of organic matter is a common feature of the "palimpsest-like soil memory" of buried paleosols [4]. Thus, the negligible carbon contents in Table 1 are another strong hint for the diagnosis of a paleosol, which can be interpreted as indication of a very long time for burial, during which C would be decomposed or leached away. For comparison, at a depth of 5 m, and sampled ca. 50 m from the mottled zones, the Anionic Acrudox presented a much higher soil organic carbon of 0.66% [12], suggesting that the mottled sections indeed present a much older age of formation.

A remarkable contrast between the Oxisol and the mottled sections is noted for particle-size distribution: the Oxisol has >70% clay and <20% silt (Table 2), whereas for the red–yellow section clay was 56% and silt 21%. For the white–yellow section, clay content was only 17%, whereas silt was 78%. These results are striking since thin sections showed beyond any doubt that most of the mottled sections matrices were composed of fine material, i.e., clay, and the much lower clay contents in Table 2 could only be interpreted as resulting from poor dispersion in NaOH resulting from relict clay cementation. In other words, the much coarser particle-size distribution upon Na dispersion in comparison with thin section analysis is another evidence strongly suggesting that the mottled sections are indeed a paleosol.

The mineralogical composition of the clay fraction of the three basic mottled areas is shown in Figure 6. The most remarkable feature is the predominance of kaolinite peaks, from which the main 0.72 nm is very symmetric and with a fair height/width relation, indicative of highly crystalline structure, especially in the white matrix, devoid of hematite and goethite, which increased the diffraction background for the red and yellow matrices. In addition, traces of a 2:1 phyllosilicate, most likely illite (clay mica) exist in the yellow and especially the white matrices, with an apparent asymmetry to the left (low 2 angles), consistent with a interstratified phase. Anatase, a secondary Ti oxide indicative of advanced weathering [14], is also present, especially in the white matrix, which also presented quartz, unlike the red and yellow ones. Finally, gibbsite peaks were absent, which is a striking and unexpected contrast with the most gibbsitic clay of the surrounding Oxisol [7]. Although this mineralogical contrast between the mottled matrices and the Oxisol is, per se, a strong argument for the paleosol hypothesis, it also helps explain the contrasts between the structure types. Gibbsitic clay suites are mostly associated with fine granular microstructures in current Oxisols in the study area, developed from silica-poor parent materials [7,8], whereas kaolinitic and kaolinitic—2:1 suites are typically associated with Ultisols and Inceptisols developed from silica-richer rocks [15]. Although it is not possible to ascertain whether the paleosol is actually developed from the meta-limestone underneath, it is most likely that it derives from residual accumulation of the weathering of layers more rich in silicate impurities or calci-phyllites [16].

Table 2. Chemical and particle-size characterization of the B horizon of the overlying Anionic Acrudox and the different-colored matrices of the Paleosol.

Soil Matrix/Texture	pH	K^+	P	Ca^{2+}	Mg^{2+}	Al^{3+}	H^+ + Al^{3+}	SB	CEC pH 7.0	Base sat.	Al^{3+} sat.	OC	Sand	Silt	Clay
		–mg kg^{-1}–		———— Cmol$_c$ kg^{-1} ————						———— % ————					
Acrudox (A) Clay	4.8	50	1.90	0.5	0.1	0.9	9.0	0.7	9.70	6.6	58.9	2.32	10	17	73
Acrudox (B) Clay	5.4	4.0	0.90	0.1	0.1	0.2	5.9	0.20	6.30	3.9	49.5	0.81	8	13	79
Red Clay	4.9	12.0	0.84	0.2	0.1	0.5	3.6	0.33	3.91	8.5	60.2	0.08	23	21	56
Yellow clay	5.0	12.0	0.56	0.5	0.3	0.7	3.5	0.83	4.37	19.0	45.7	0.14	-	-	-
White–yellow Silt loam	5.3	6.1	0.64	0.1	0.1	2.2	8.6	0.25	8.85	2.8	89.7	0.01	5	78	17

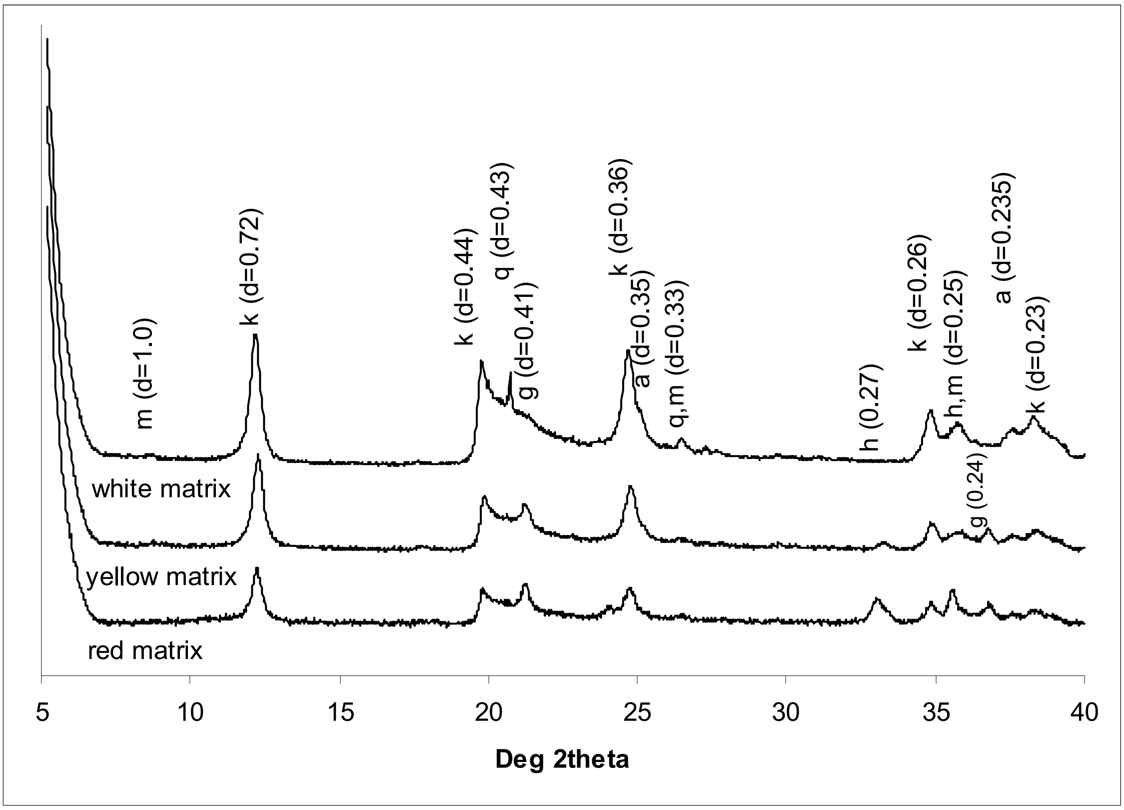


Figure 6. X-ray powder diffraction pattern of different soil matrixes with *d*-spacings (nm) and minerals: m—mica, k—kaolinite, g—goethite, h—hematite, a—anatase.

3.3. Integrative Perspective

From all the morphological, chemical, and mineralogical evidence presented here, we propose that the most compelling to confirm the diagnosis of a paleosol are the following contrasts with the surrounding Oxisol: (1) massive, apedal structure with moderate bulk density vs. fine granular structure with low density; (2) clay illuviation as a soil-forming process vs. advanced silica leaching in Oxisol; (3) low clay contents after Na dispersion due to clay cementation in the paleosol; (4) very low vs. high soil organic carbon contents; and (5) kaolinitic-illitic vs. gibbsitic-kaolinitic clay. These features were listed in order of importance for our diagnosis, although only (1), (3), and (4) can be easily identified in the field, or with simple laboratory analysis and, thus, can be more widely used by other workers. Therefore, we can accept our hypothesis that the mottled sections exposed as a vertical cut in the terrain are indeed remnants of a paleosol.

A further step would be trying to identify which type of paleosol it was. The combination of clay coatings, aside from the >2 m thickness, massive structure, and a clay mineral suite typical of advanced, but not extreme, weathering, suggests that the paleosol can probably be better described as a Paleoultisol. In fact, many current Udults in the area have high clay contents, red kaolinitic clay, and are very deep [7,15], and we prefer to use here the term "Paleoultisol" instead of the unyielding, non-suggestive term "Paleoeldisol" [2]. Another possibility is that it was once a Paleoalfisol, but this is much less likely due to its overall red colors resulting from considerable Fe oxides and, thus, more desilicated clay mineral suites.

A probable evolution sequence of the landscape (Paleoultisol + Oxisol) can be attempted as follows:

(1) Formation of a pedosediment from the accumulation of materials in silicate-rich layers within the limestone after its gradual dissolution. The homogeneous, massive structure suggests it could have formed in a suspension, or more likely in a thixotropic flow (mudslide or moving groundwater) [4];
(2) Partial cementation and erosion/weathering of the upper part of the pedosediment, preserving a small hill (Figure 1a) or truncated stump, which was probably simultaneous with the development of the current Oxisol from desilication and dismantling of the cemented pedosediment, forming the unusual granular structure in Figure 3b, and gibbsite from desilication of the kaolinitic clay;
(3) Jointing and cracking of the massive structure of the inhumed pedosediment or paleosol, resulting in hydration of hematite into goethite (xanthization), and deferrification forming white areas, along the resulting preferential flow pore network, forming the red–yellow mottled section, which is currently the highest part of the Paleoultisol, and most of the hill-shaped section in Figure 1b;
(4) Formation of faunal channels in the Paleoultisol and their infilling with granular material coming in part from the Oxisol;
(5) Further deferrification of the Paleoultisol, turning the burrowed red–yellow mottles into the white–yellow mottled section, which now greatly predominates in palimpsest area (Figure 1).

It is not clear in which step the clay mobilization and deposition forming the clay coatings and the transformation of the pedosediment into an Ultisol occurred, but it must have occurred between steps 2 and 4. The processes, which currently proceed in the area, are the formation of the Oxisol from the dismantling and desilication of the Paleoultisol, and the redoximorphism and total deferrification of the Paleoultisol leading to the white–yellow mottle facies. We cannot explain the formation of the brittle, clear quartz aggregates among the Paleoultisol matrix, although this unusual feature can be noted as a further indicator of the existence of a paleosol in a similar soil environment.

4. Conclusions

We concluded that the mottled sections currently underneath a red Oxisol are actually parts of a Paleoultisol, due to a set of morphological (soil structure, clay coatings), chemical (very low organic carbon), and mineralogical (kaolinitic clay) differences with the overlying Oxisol. Furthermore, we identified the Paleoultisol as the most likely parent material from which the Oxisol developed, and not the underlying meta-limestone previously believed [7,13], which we believe is a novel idea. Finally, the unusual feature of brittle, clear quartz phenocrysts, although not a commonly reported feature can also be a hint for paleosol detection. We hope that this paper will be useful in efforts towards the identification and study of non-lithified paleosols in Brazil and other tropical humid countries.

Author Contributions: C.F.M. performed field and lab work, the micromorphological analysis, and helped choose the analytical procedures. Y.L.Z. prepared the soil thin sections and wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: The Minas Gerais Research Foundation funded this work (grant#CAG-APQ778-15) and sponsored a research scholarship to C.F. Miranda. Y.L. Zinn holds a research productivity grant from the Brazilian National Research Council (CNPq).

Acknowledgments: The authors are indebted to Luis F. Silva and A. V. Inda (UFRGS, Brazil) for the X-ray diffractions.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Soil Science Society of America. *Glossary of Soil Science Terms*; Soil Science Society of America: Madison, WI, USA, 2001.
2. Nettleton. W.D.; Olson, C.G.; Wysocki, D.A. Paleosol classification: Problems and solutions. *Catena* **2000**, *41*, 61–92. [CrossRef]
3. Nascimento, D.L.; Ladeira, F.S.B.; Batezelli, A. Pedodiagenetic characterization of Cretaceous Paleosols in Southwest Minas Gerais, Brazil. *Rev. Bras. Ciênc. Solo* **2017**, *41*, e0160065. [CrossRef]
4. Fedoroff, N.; Courty, M.-A.; Guo, Z. Palaeosols and Relict Soils. In *Interpretation of Micromorphological Features of Soils and Regoliths*, 1st ed.; Stoops, G., Marcelino, V., Mees, F., Eds.; Elsevier: Amsterdam, The Netherlands, 2010; pp. 623–662.
5. Wright, V.P. Paleosol Recognition: A Guide to Early Diagenesis in Terrestrial Settings. In *Diagenesis III. Developments in Sedimentology*; Wolf, K.H., Chilingarian, G.V., Eds.; Elsevier: Amsterdam, The Netherlands, 1992; Volume 47, pp. 591–619.
6. Stoops, G. *Guidelines for Analysis and Description of Soil and Regolith Thin Sections*; Soil Science Society of America: Madison, WI, USA, 2003.
7. Araujo, M.A.; Pedroso, A.V.; Amaral, D.C.; Zinn, Y.L. Paragênese mineral de solos desenvolvidos de diferentes litologias na região sul de Minas Gerais. *Rev. Bras. Ciênc. Solo* **2014**, *38*, 11–25. [CrossRef]
8. Araujo, M.A.; Zinn, Y.L.; Lal, R. Soil parent material, texture and oxide contents have little effect on soil organic carbon retention in tropical highlands. *Geoderma* **2017**, *300*, 1–10. [CrossRef]
9. Soil Survey Staff. *Keys to Soil Taxonomy*; NRCS: WA, USA, 2010; p. 337.
10. Teixeira, P.C.; Donagemma, G.K.; Fontana, A.; Teixeira, W.G. (Eds.) *Manual de Métodos e Análise de Solo*, 3rd ed.; Embrapa: Rio de Janeiro, Brazil, 2017.
11. Ladeira, F.S.B. Solos do passado: Origem e identificação. *Rev. Bras. Ciênc. Solo* **2010**, *34*, 1773–1786. [CrossRef]
12. Silva, T.A.C.; Pádua, E.J.; Faria, J.A.; Araújo, M.A.; Zinn, Y.L. Densidade do solo e carbono orgânico do solo ao longo do perfil de um Latossolo Vermelho-Amarelo sob vegetação nativa. In Proceedings of the 26th Congresso de Iniciação Científica da UFLA-CIUFLA (Annals), Universidade Federal de Lavras, Lavras, Brazil, 2–3 December 2013.
13. Zinn, Y.L.; Faria, J.A.; Araujo, M.A.; Skorupa, A.L.A. Soil parent material is the main control on heavy metal concentrations in tropical highlands of Brazil. *Catena* **2020**, *185*, 104319. [CrossRef]
14. Fitzpatrick, R.W.; Chittleborough, D.J. Titanium and Zirconium Minerals. In *Soil Mineralogy with Environmental Applications*; Dixon, J.B., Schulze, D.G., Eds.; Soil Science Society of America: Madison, WI, USA, 2002; pp. 667–690.
15. Zinn, Y.L.; Guerra, A.R.; Silva, C.A.; Faria, J.A.; Silva, T.A.C. Soil organic carbon and morphology as affected by pine plantation establishment in Minas Gerais. *For. Ecol. Manag.* **2014**, *318*, 261–269. [CrossRef]
16. Quéméneur, J.J.G.; Ribeiro, A.; Paciullo, F.V.P.; Heilbron, M.; Trouw, R.A.J.; Valença, J.G.; Noce, C.M. *Mapa Geológico—Folha Lavras SF 23-X-C-I. 1:100.000*; COMIG: Belo Horizonte, Brazil, 2002.