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Calcium carbonate pendants in semiarid soils of Rashakan region (Urmia, Iran) and their paleoclimatic significance

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Abstract

Accumulation of secondary calcium carbonates in arid and semiarid regions is a valuable tool for evaluating the degree of soil evolution, soil age, palaeoenvironmental reconstruction, and soil classification. In particular, laminated pedogenic carbonate pendants are able to provide evidence regarding local environmental and climatic changes. In this study, calcitic pendants from semiarid soils of Rashakan region (West Azerbaijan province, Iran) were investigated. Rashakan region is composed of four physiographic units, including mountains, hills, plateaus, and piedmont plains. A transect of four soil profiles was studied micromorphologically. Based on micromorphic observations, carbonatic pendants are present as mammillary to botryoidally stalactite-like masses, growing downwards from the bottom of coarse fragments. They are multilayered and comprised several light and dark-colored layers, indicating the differences in calcite precipitation conditions. Sequences of light and dark-colored lamina of pendants probably represent climatic changes. We propose that light-colored lamina with relatively pure calcite are precipitated in dry periods that climatic conditions are not favorable for biological activities. However, dark-colored lamina, consisting of calcite mixed with clay and organic impurities, are formed in relatively wet periods with better conditions for biological activities. Therefore, the sequence of light and dark-colored laminae can reflect climatic variations and be employed as a tool for palaeoclimatical and palaeoenvironmental studies. In the structure of some pendants, there exist some fractures and voids between pendant and skeletal grains. Accordingly, these pendants must be considered for palaeoclimatical and palaeoenvironmental reconstructions.

Key words: Micrite, Micromorphology, Semiarid, West Azerbaijan

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1. Introduction

Pedogenic calcium carbonate accumulations are valuable indicators in recognizing the evolution of soils and sediments because they are strongly affected by environmental conditions such as temperature and moisture regimes (Pustovoytov, 2002; Shankar and Achyuthan, 2007; Durand *et al*., 2010; Zamanian *et al*., 2016; Silva *et al*., 2017). In arid and semiarid climates, the dissolution and accumulation of carbonates are very important processes, to the point that the quantity and quality of carbonatic features have been included in most of the researchs conducted in these environments. Secondary carbonates (frequently termed pedogenic carbonates) represent one of the most characteristic morphological pedofeatures of soils in arid and semiarid regions. The depth and intensity of carbonate accumulation and shape of secondary carbonates allow inferences to be drawn about the genesis of soil horizons and sometimes about the stages of soil development under different past climatic conditions (Shankar and Achyuthan, 2007; Zamanian *et al*., 2016).

Different forms of pedogenic carbonate were summarized by Zamanian *et al*. (2016) in 10 main forms. They classified pedogenic carbonate accumulations according to their morphology, properties, formation mechanisms, contribution of biotic and abiotic processes to their formation, and the rates of pedogenic carbonate formation. The mentioned forms are earthworm biospheroliths, calcified root cells, rhizoliths, needle fiber calcite, pseudomorph calcite after

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gypsum, soft masses, hypocoatings, nodules, clast coatings, calcrete, and laminar caps.

Calcium carbonate pendants are among the most important forms of calcium carbonate accumulation in soils of arid and semiarid regions and the size, shape, and basic distribution of carbonate crystals in their composition vary in different soils (Durand *et al*., 2010; Zamanian *et al*., 2016). They are usually concentrated in the Bk/Bkk horizons of exposed soil profiles and tend to lie at deeper depths below the soil surface with the increase in mean annual precipitation (Shankar and Achyuthan, 2007; Durand *et al*., 2010). As pedogenesis proceeds, carbonates dissolved in soil solution (derived from calcareous dust, limestone alluvium, or weathering of Ca-bearing silicates) are deposited on gravels as the water is depleted via evapotranspiration. The deposition depth is associated with the balance of precipitation and evapotranspiration and the soil water-holding capacity (Durand *et al*., 2010; Zamanian *et al*., 2016; Silva *et al.*, 2017). The rates at which pendants thickness increases might be utilized as a chronological information source for interpretations of palaeoenvironmental history. If the pendant growth rate is known, its thickness can be used as an indicator of the pendant formation duration. However, the thickness of pendants has been observed to be a function of soil age (Courty *et al*., 1994; Treadwell-Seitz and McFadden, 2000; Badia *et al*., 2009).

An overview of research on pedogenic carbonate pendants on clasts in soils shows that these coatings have a potential for use as environmental records (Courty *et al*., 1994; Shankar and Achyuthan, 2007; Durand *et al*., 2010). Pedogenic carbonate pendants manifest themselves as a widespread phenomenon in the soils of every temperature zone; therefore, they can be useful tools in palaeoenvironmental research.

Rashakan region is located south of Urmia city (West Azerbaijan Province) on the western side of Urmia Lake with consequative variations in topography. According to the geological map of Urmia region (Soltani Sisi, 2005), the parent material of this area is composed of white-grey limestone; previous studies (Manafi, 2014) have also revealed the presence of different forms of carbonatic accumulations in this area. Therefore, given the capability of calcium carbonate coatings based on palaeoclimatical studies (as mentioned earlier) and their presence in the soils of this area, the objective of the present study was to investigate the micromorphology of secondary calcium pendants and their mechanisms of formation. We further aimed to examine the possibility of their use for palaeoclimate reconstruction in Rashakan region of West Azerbaijan, Iran.

2. Materials and Methods

2.1. Study area

This study was conducted in Rashakan region, located approximately 40 km south of Urmia city and west of Urmia Lake; this region is in the central part of West Azerbaijan Province, Iran, from 37° 16' 15'' to 37° 20' 00'' N latitude and 45° 15' 00'' to 45° 18' 30'' E longitude (Fig. 1a). The elevation of the study area varies from 1233 to 1585 m above sea level. A transect composed of four soil profiles was studied physico-chemically and micromorphologically (Fig. 1b). As shown in Fig. 1b, in this transect, the approximate distance between consequative soil profiles 1 and 2 is 2000 meter, soil profiles 2 and 3 is 1000 meter, and soil profiles 3 and 4 is 1500 meter.

Physiographically, Rashakan region is composed of four land units, including mountains, hills, plateaus, and piedmont plains. Rashakan region is limited to the north by Urmia city, to the west by the Alborz mountain range, to the east by the Urmia Lake, and to the south by Naghadeh city. Geologically, this area is located on Qom formation equivalent in quaternary era and composed of white-grey limestone. Lithologically, this formation is composed of fine grained limestone and micrite and calcareous white-grey to pink marl with medium to thick lamination (Soltani Sisi, 2005). The mean annual precipitation and temperature of Rashakan region are 295 mm and 10.8 °C, respectively. According to the soil moisture and temperature regimes map of Iran (Banaei, 1998), the soil moisture and temperature regimes of this area are Dry Xeric and Mesic, respectively. The native vegetation of this area comprises *ephorbiaceae*, *geramineae*, *poaceae*, *composite*, and *rosaceae* species. Agricultural crops in this area are rainfed cereals in the upper parts of the transect (soil profiles 1, 2 and 3) and alfaalfa, apple trees, and vineyards in the lower parts of the transect (soil profile 4).

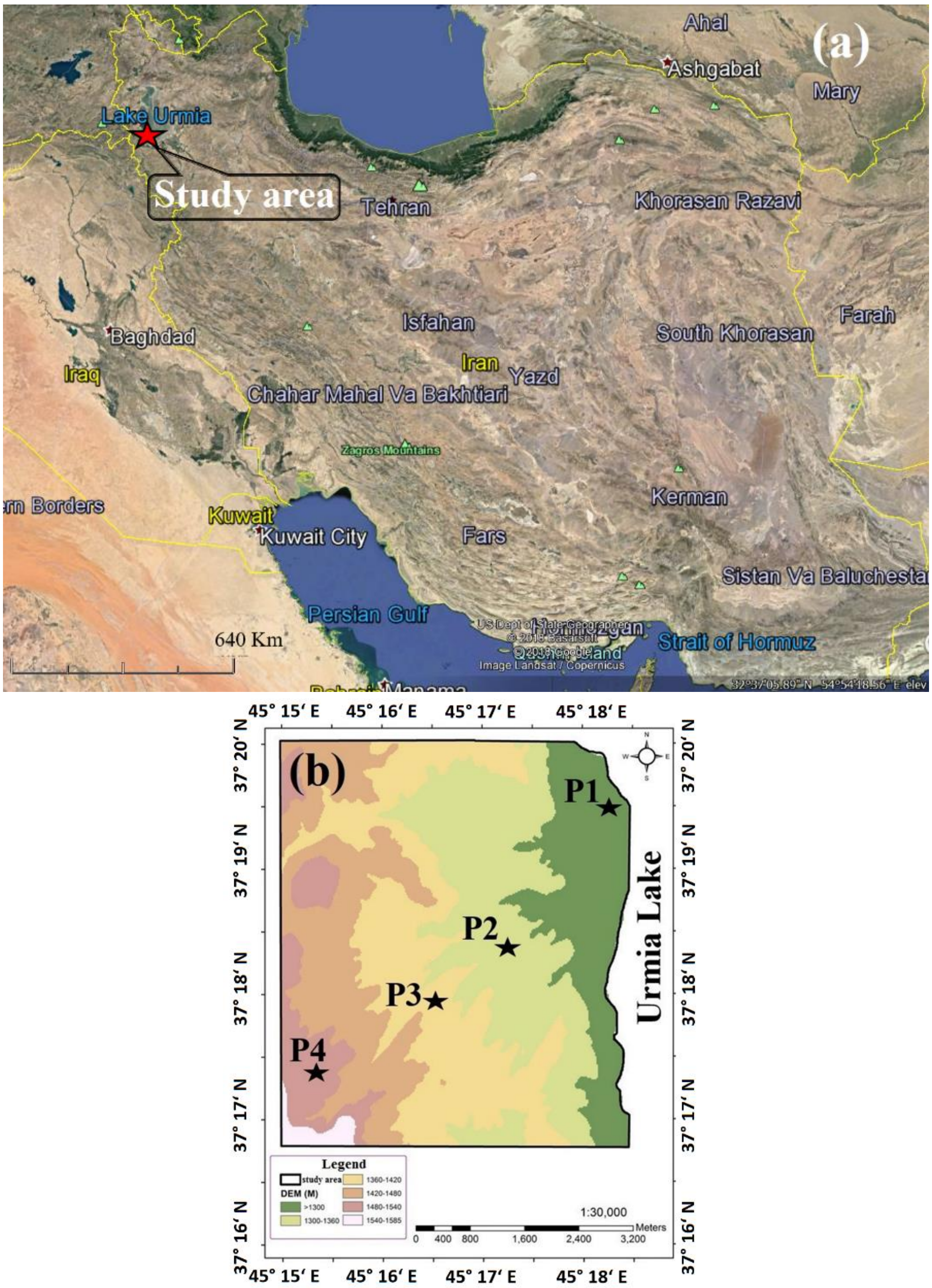

Fig. 1. The position of the study area and the location of the representative soil profiles in each land type. Soil profiles 1 to 4 are located in piedmont plain, plateau, hills, and mountain land types, respectively

2.2. Field and laboratory studies

Based on reconnaissance survey (Manafi, 2014) and previous field observations, a soil transect composed of four physiographic units was selected to indicate the variations in the topography of Rashakam region (Fig. 1b). In each physiographic unit, three soil profiles were studied, and the results of one representative soil profile for each land type were reported. The location of the representative soil profiles in different physiographic units is in the following order: soil profile 1 on the piedmont plains, soil profile 2 on the plateaus, soil profile 3 on the hills, and soil profile 4 on the mountains.

These soil profiles were described and sampled using standard techniques (Soil Survey Staff, 2012) and classified according to Soil Taxonomy (Soil Survey Staff, 2014). Prior to soil analysis, all soil samples were air dried, crushed, and passed over a 2mm sieve in order to remove coarse fragments. Particle size analyses were performed on the samples of each genetic horizon using the hydrometer method and soil organic carbon was measured by oxidation with chromic acid and back titration with ferrous ammonium; furthermore, calcium carbonate equivalent was measured by the acid neutralization method, the electrical conductivity (ECe) and pH of the saturated extract were determined by use of an EC-meter and a pH-meter, respectively, and cation exchange capacity (CEC) was determined by the ammonium acetate method (NH_4OAc) at pH = 8.2 (USDA-NRCS, 2004). Soil thin sections were prepared using techniques proposed by Benyarku and Stoops (2005). The oriented thin sections were described through the use of a POL-MIC polarizing microscope with magnification of 2.5X to 40X for the analysis of the micromass (s-matrix) and pedofeatures. Scanning Electron Microscope (SEM) analyses were performed with a ZEISS DSM 940A microscope.

3. Results and Discussion

Table 1 shows some of the selected macromorphological and physico-chemical properties of the representative soil profiles. All of the studied soil profiles were calcareous, and calcic horizons were observed in all of them except for soil profile 4 in the mountain land type. Several macromorphological carbonatic features were identified in the field, including soft powdery masses, pendants, phillaments and treades. Micromorphological carbonatic features were further identified in the thin sections of the studied soils. Table 2 summarizes the micromorphic properties for the referred soil profiles of the studied transect. According to Table 2, the c/f related distribution pattern pertaining to most of the studied soils, except for soil profile 4, was porphyric. In this soil profile, the c/f related distribution pattern was enaulic in Ap and C horizons and single grain in Cr horizons, corresponding to the original structure of the detrital parent material. The common microstructures of these soils were weakly to highly separated granular and sbangular blocky in A horizons, moderately to highly separated angular blocky with vughy microstructures in B horizons, and massive and single grain microstructures in C horizons of soil profile 4. Due to the presence of high amounts of micrite, the b-fabric of the studied soils was mainly crystallitic; however, some horizons showed monostriated and granostriated b-fabrics, particularly in calcite-depleted zones, where the absence of micrite allows for the observation of argilloturbation effects. Indeed, calcite depleted zones had the main pedofeatures in lower depths and deeper horizons. Cytomorphic calcite was present in profile 2 along with needle fiber calcite and depleted zones (Table 2).

In microscopic studies, calcitic pedofeatures were identified in all soil profiles except for soil profile 4. These pedofeatures consist in nodules, pendants, calcite depleted zones, needle fiber calcite, and cytomorphic calcite (Table 2).

Table 1. Selected morphological, physico-chemical properties and classification of representative profiles in studied soils

Horizon	Depth (cm)	Color (Dry)	Clay	Silt	Sand	fc/tc	Structure	OC (%)	pH	CCE (%)	CEC (cmol/kg)
Profile 1 (Piedmont plain): *Fine, mixed, superactive, mesic Calcic Haploxeralfs*											
Ap	0-22	10YR 6/4	38.9	39.9	21.2	0.24	1,2; f; gr 2;m;sbk	0.96	7.6	33.88	28.56
Bw	22-47	10YR 5/4	40.9	35.5	23.6	0.27	2; c; abk 1; m;sbk	0.69	7.6	37.11	26.6
Bk	47-86	10YR 5/6	42.7	31.9	25.4	0.27	2; vc;abk	0.46	7.8	41.74	28.44
Btk1	86-156	10YR 4/4	53.6	27.5	18.9	0.45	2; vc;abk	0.32	7.8	43.32	28.73
Btk2	156-217	10YR 4/3	56.1	23	20.9	0.41	2; vc;abk	0.26	7.5	44.52	30.6
Profile 2 (Plateaux): *Fine loamy, mixed, superactive, mesic Calcic Haploxeralfs*											
Ap	0-19	10YR 6/4	41.6	40.6	17.8	0.26	1,2; s; gr	0.92	7.7	30.86	26.27
Bw	19-57	10YR 5/4	41.8	46.6	11.6	0.25	2; m;sbk	0.72	7.6	29.17	24.55
Bk	57-91	10YR 5/4	45.4	38.8	15.8	0.28	3; c; abk	0.53	7.8	36.37	27.64
Btk	91-159	10YR 4/4	54.6	28.6	16.8	0.39	3; c; abk	0.36	7.8	37.25	29.46
Profile 3 (Hill): *Fine, mixed, active, mesic Typic Calcixerepts*											
Ap	0-17	10YR 5/4	36.2	41.4	22.4	0.23	2; s, m;gr	1.07	7.5	23.52	26.18
Bw	17-55	10YR 5/4	37.4	41.8	20.8	0.23	2; c; abk	1.12	7.8	22.08	26.18
Bk1	55-71	10YR 4/4	41.6	39.4	19	0.26	3; c; abk	0.78	7.8	29.83	24.11
Bk2	71-126	10YR 5/4	41.6	31.6	26.8	0.24	3; c; abk	0.44	7.5	34.21	25.04
Profile 4 (Mountain): *Fine, mixed, superactive, calcareous, mesic Lithic Xerorthents*											
Ap	0-14	10YR 5/4	35.6	32.8	31.6	0.25	2; m; gr	1.76	7.1	10.64	21.9
C	14-47	10YR 5/4	22.2	28.6	49.2	0.22	m	1.12	7.2	27.38	17.5
Cr	47-59	10YR 7/4	11.7	37.3	51	0.21	-	0.98	7.5	31.49	14.83

*Structure: gr: granular, sbk: subanglar blocky, abk: angular blocky, m: massive; 1: weak, 2: moderate, 3: strong; f: fine, m: medium, c: coarse, vc: very coarse

fc/tc: the ratio of fine clay to total clay, OC: organic carbon, pH: soil reaction, CCE: calcium carbonate equivalent, CEC: cation exchange capacity.

Table 2. Selected micromorphological properties of representative profiles in studied soils

Horizon	Depth (cm)	b-fabric	c/f R.D	Microstructure	Voids	Pedofeatures
Profile 1 (Piedmont plain): *Fine, mixed, superactive, mesic Calcic Haploxeralfs*						
Ap	0-22	Cr	Po (open)	Sb	Cdp	-
Bk	47-86	Cr, Gs	Po (open)	Ab	Pn, Ch	Nodules (5%) and pendants (2%) of calcite
Btk1	86-156	Cr, Gs	Po (open)	Ab	Pn	Nodules (10%), pendants (2%) and typic coatings (5%) of calcite, calcite depleted zones (10%), and clay coatings (2%)
Btk2	156-217	Cr, Gs	Po (open)	Ab (%90), Vu (%10)	Vu, Pn	Nodules (15%), pendants (3%) and typic coatings (5%) of calcite, and clay coatings (7%)
Profile 2 (Plateaux): *Fine loamy, mixed, superactive, mesic Calcic Haploxeralfs*						
Ap	0-19	Cr	Po (open)	Sb	Cdp	-
Bw	19-57	Cr	Po (Double spaced)	Sb (%20), Ab (%80)	Pn	-
Bk	57-91	Cr	Po (Double spaced)	Ab	Pn	Nodules (10%), pendants (2%) and typic coatings (2%) of calcite, and calcite depleted zones (5%)
Btk	91-159	Cr, Gs	Po (Double spaced)	Ab (%85), Vu (%15)	Pn, Vu	Nodules (15%), pendants (4%) and typic coatings (5%) of calcite, and clay coatings (3%)
Profile 3 (Hill): *Fine, mixed, active, mesic Typic Calcixerepts*						
Ap	0-17	Cr	Po(open)	Sb	Cdp, Pn	-
Bw	17-55	Cr	Po (Double spaced)	Sb (%40), Ab (%60)	Pn	-
Bk1	55-71	Cr	Po (Double spaced)	Ab (%80), Vu (%20)	Pn, Vu, Ch	Nodules (5%), pendants (2%) and typic coatings (5%) of calcite, calcite depleted zones (2%), cytoporphic calcite (3%), and needle fiber calcite (5%)
Bk2	71-126	Cr	Po (Single spaced)	Ab (%75), Vu (%25)	Pn, Vu, Ch	Nodules (10%) and pendants (2%) of calcite, calcite depleted zones (5%), cytoporphic calcite (3%), and needle fiber calcite (2%)
Profile 4 (Mountain): *Fine, mixed, superactive, calcareous, mesic Lithic Xerorthents*						
Ap	0-14	Cr	En	Gr	Cdp	-
C	14-47	Cr	En, Sg	Ab (%20), Ma (%80)	Pn, Vu	-
Cr	47-59	Cr	Sg	Sg	Sp	-

Remarks: Cdp: compound packing void, Vu: vugh, Pn: planar void, Ch: channel, Sp: Simple packing, Ma: massive, Gr: granular, Ab: angularblocky, Sb: subangularblocky, Sg: Single grain, c/f R. D: Related distribution, Po: porphyric, En: Enaulic, Cr: crystallitic, Gs: Grano-striated. Numbers in parenthesis show the relative abundance of each feature.

The most common calcitic pedofeatures were nodules and pendants. Pendants of calcium carbonate are of the main carbonatic features discussed in this paper (Figs 2 and 3).

In the studied soils, pendants of calcium carbonate were detected in soil profiles 1, 2 and 3; however, they were still absent in soil profile 4 (Table 2). The thickness of pendants ranged from 220 µm to 8.32 mm. Their thickness and frequency increased with soil depth (Table 2). There are different reports on the thickness of pendants. Based on the reports of Durand *et al.* (2010) and Zamanian *et al.* (2016), pendants range in thickness from approximately a millimeter to a centimeter; however, according to some other reports, the thickness of pendants in older desert soils could reach as thick as 10-30 mm (Treadwell-Steitz and McFadden, 2000; Zamanian *et al.*, 2016). The thickness of these pendants increased with soil depth and was higher under limestone fragments. Such a trend was reported by Treadwell-Steitz and McFadden (2000) in the soils of New Mexico, Badia *et al.* (2009) in Spain, and Silva *et al.* (2017) in Brazilian paleosols.

Figure 2 shows the pendants of calcium carbonte on the underside of coarse fragments. As shown in Fig. 3, there are certain voids in the underside of the pendants (between pendant and soil micromass) caused by the decomposition of dead roots, faunal remains, or mechanical disturbances in the soil (Fig. 3). Blank and Fosberg (1990) and Durand *et al.* (2010) supposed that the presence of void space is necessary for unrestricted precipitation of calcium carbonate and, consequently, pendant development. It seems that such spaces provide the space required for evaporation and the subsequent precipitation of carbonates and development of pendants.

In general, pendants occur where the downward growth of calcium carbonate bearing water is not hindered by the groundmass of soil. Because percolating water is restricted in contact with impervious limestone or coarse fragments, the concentration of Ca^{2+} and CO_3^{2-} ions exceeds the solubility product of $CaCO_3$ due to the evaporation or absorption of water by plant roots or microorganisms. This results in the supersaturation of soil solution with respect to carbonate and pendant formation.

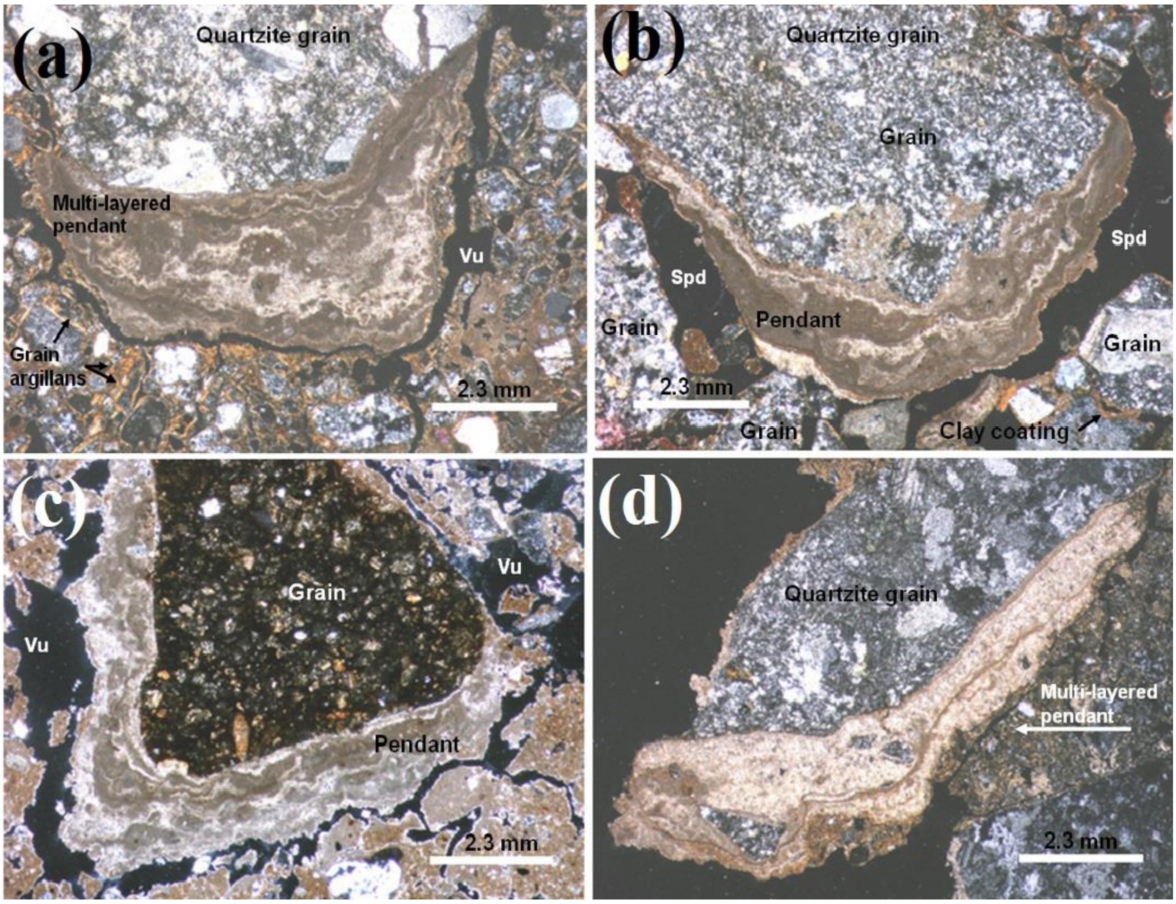

Fig. 2. Laminated pendants of calcite on the underside of coarse grains. Figures (a) and (b) are related to the Btk2 horizon of soil profile 1, Figure (c) belongs to the Bk2 horizon of soil profile 3, and Figure (d) is associated with the Btk horizon of soil profile 2. Photos are in XPL light

SEM observations and EDAX analyses of the pendants confirmed that they are calcium carbonate crystals (Figs. 3b and 3d; Table 3). As shown in Figs. 2 and 3a, pendants are composed of dark- and light-colored laminae. SEM observations showed that calcite crystals in the composition of light-colored laminae were relatively loose with void spaces between crystals; however, calcite crystals in dark-colored laminae were densely packed with minimal void spaces between them (Fig. 3b).

The differences in the composition of dark- and light-colored laminae reflect their formation in different conditions. Table 3 shows the elemental percent of elements such as O, Al, Si, P, Ca, Mg, and Na in light and dark laminae based on EDAX analyses. EDAX analyses of the laminae (Table 3) showed that the dark bands were more clayey and had some P, while, light bands were almost pure calcium carbonate (Table 3).

Micromorphic observations confirmed that nearly all the pendants in these semiarid soils were laminated and comprised of micritic and microsparitic calcite. Lamination was generally parallel to the bottoms of the host coarse fragments and the number of laminae differed from 2 to 5 in each pendant (Fig. 2).

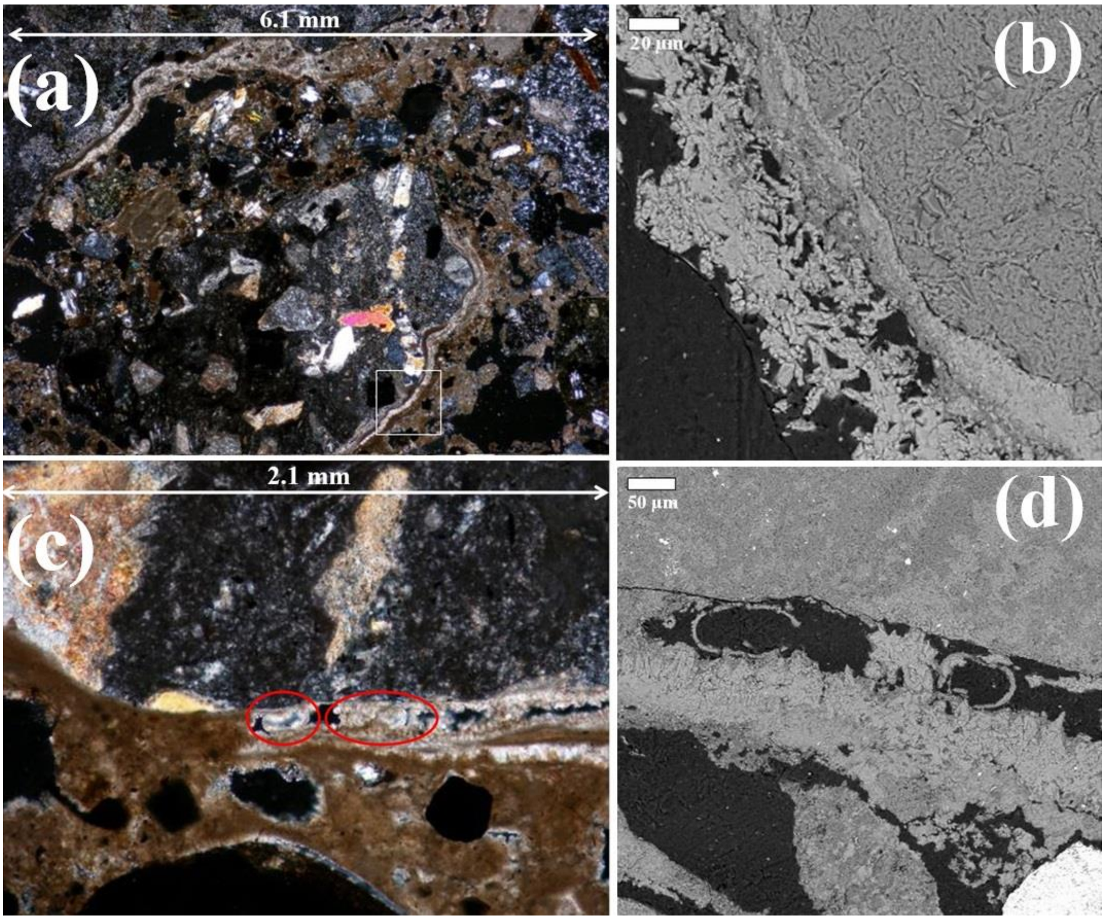

Fig. 3. (a) a laminated pendant of calcium carbonate in the Bk2 horizon of soil profile 3 selected for X-ray point analysis; (b) shows the loose and dense packing of calcite crystals in the light- and dark-colored layers of pendant, respectively; (c) shows rounded structures in the interface of pendant-pebble in the Bk2 horizon of the soil profile; (d) the SEM micrograph of rounded structures in Figure (c). The linear void between pendant and pebble is clearly observed

Table 3. Elemental analysis of elements in dark and light colored layers of studied pendant in Fig. 3a

Element percentage	O	Al	Si	P	Ca	Mg	Na
Dark layers	70.59	0.55	1.99	0.40	26.48	-	-
	68.84	2.63	6.22	0.29	20.77	0.51	0.74
Light layers	70.55	0.10*	0.30	0.15*	28.90	-	-
	69.88	-	0.81	-	28.72	0.58	-

*: values under detection limit; -: not determined

The lamination of pendants and their dark- and light-colored laminae has been summarized in the reviews of Brock and Buck (2005), Durand *et al*. (2010), and Zamanian *et al*. (2016). They stated that the calcitic pendants display a complex layering which could result from sequential aggradation. According to Durand *et al*. (2010), the major factor causing the lamination of pendants is the changes created in the crystal size by alternating the micritic and microsparitic laminae. Blank and Fosberg (1990) identified changes in crystal morphology as a factor leading to the lamination of pendants.

Zamanian *et al*. (2016) proposed that the variations in the hydrological and chemical regimes of the soil account for the differences in crystal morphology. They further showed that the rate of crystal growth in each phase of precipitation depends on the desiccation rate and presumed that the calcite coatings might have recorded the fluctuations in Quaternary climates. Courty *et al*. (1994), in their micromorphological studies on the carbonate coatings in Spitsbergen, observed that the lightest and most limpid microlaminae of the coatings consist of relatively pure microsparitic calcite whereas the dark ones are built up from micrite and include abundant detrital particles and traces of biological remnants such as fungi hyphae. They stated that the dark microlaminae reflect suitable conditions for biological activities and ameliorated climatic conditions. Pustovoytov (2002) stated that light coating microlayers, formed by pure calcium carbonate with better formed and parallel oriented crystals, seem to be indicative of drier periods that are less favorable for biological activity (hotter in warm climates and colder in cool climates). The high content of admixtures, with poorer formed and more randomly oriented calcite crystals, presumably mark wetter periods characterized by climatic warming (Pustovoytov, 2002). Therefore, we propose that in these studied pendants, light-colored laminae with relatively pure calcite (Table 3) was precipitated in dry periods in which climatic conditions were not favorable for biological or faunal activities. Nonetheless, the dark-colored laminae, composed of calcite and some organic silicate clay impurities (Table 3), were formed in relatively wet periods with better conditions for biological and faunal activities. Therefore, the sequence of light- and dark-colored laminae in the composition of calcium carbonate pendants can reflect climatic variations in the studied semiarid area; finally, these features can be employed as a tool for paleoclimate and paleoenvironmental research as suggested by (Courty *et al*., 1994; Pustovoytov, 2002; Brock and Buck, 2005; Durand *et al*., 2010; Zamanian *et al*., 2016).

The formation processes of pendants are similar to the development of stalactite, where the initial accumulation of carbonate rich material occurs on the underside of the host clasts followed by later laminae below each successive lamina (or layer). This results in a set of laminae varying from the oldest to the youngest with the increase in the distance from the clast in which the innermost laminae is the oldest and the outermost laminae is the youngestas reported by many researchers (Courty *et al*., 1994; Treadwell-Seitz and McFadden, 2000; Brock and Buck, 2005). This is the relevant model for the formation of pendants. Based on the formation trend of successive laminae in the composition of pendants, many researchers (Kuzyakov *et al*., 2006; Brock and Buck, 2005) have dated their microlaminae using U/Th and ^{14}C so as to determine the minimum ages of landforms. However, this technique has not been entirely successful. Literature review shows that the formation mechanism of pendants under clasts is not always similar to that of stalactites. Brock and Buck (2005), Owliaei *et al*. (2006 and 2018), Durand *et al*. (2010), and Zamanian *et al*. (2016) have reported the presence of cracks between the coating and the clast surface, creating a free space for the precipitation of new carbonates. Brock and Buck (2005) reported that in these conditions, the dating of “inner” and “outer” laminae revealed certain inconsistencies. We found some of our studied pendants to be more recent based on the evidence in the interfaces of pendants and host grains. As shown in Figs. 3c and 3d, there exist some spaces and fractures between pendant and host clast and some rounded structures of biological origin at the contact surface between the pendant and the coarse fragment. The SEM observations and EDAX analyses confirmed that these rounded structures were calcium carbonate. These rounded structures were found in an accommodated planar void whose origin could be a physical detachment of the first layer of the pendant due to pedoturbation. There were also calcitic regrowths at the contact between the coarse fragment and the pendant, implying a recent dissolution-reprecipitation process. Perhaps the microenvironment at this interface, with preferential water circulation along the fragment walls, favors the establishment of biological activity. Accordingly, it seems that these "inner" laminae may be the youngest ones in contrast to the normal mode of pendant formation. Therefore, the rounded structures observed between pendants and host clasts indicate that these pendant-clast systems are not close, and it be might that the pendant growth takes place not only in the outer laminae, but also in the inner laminae. Under such conditions, the formation process of pendants can be very complicated. Based on their observations, Brock and Buck (2005) concluded that these processes would impact both the dating of the carbonate and its isotopic composition for use in paleoclimatic interpretations. It is necessary to have a thorough understanding of the processes occuring in pendants prior to their use in these studies.

3.1. Calcium carbonate pendants and paleoenvironment reconstruction

The literature review and results of this study revealed that depending on the crystal form, crystal packing, and lamina morphology, it is possible to link the formation of the calcitic pendants to climatic variations. Light microlaminae, composed of purer calcium carbonate with better-formed and parallel oriented crystals, seem to be indicative of drier periods less favorable for biological activity (hotter in warm climates and colder in cool climates). The dark microlaminae with high content of detrital particles, clay, and organic impurities, composed of less well-developed and more randomly oriented calcite crystals, presumably show wetter periods characterized by the activation of soil biota and ameliorated climatic conditions. Therefore, the light laminae might be of physico-chemical origin and the dark laminae of biological origin. The successive sequence of light- and dark-colored calcitic micro layers in the composition of pendants represents a useful tool for dating soils and landforms (Blank and Fosberg, 1990; Pustovoytov, 2002; Kuzyakov *et al*., 2006) and reconstruct palaeoenvironmental conditions (Courty *et al*., 1994; Pustovoytov, 2002). However, our findings and the reports of Brock and Buck (2005) indicate that in certain pendants, the inner most lamineae is the youngest one; therefore, the dating of "inner" and "outer" lamianae has some inconsistencies. Such an uncertainty has been reported by Durand *et al*. (2010) and Zamanian *et al*. (2016). They found that several of their samples had inner laminae (believed to be the oldest) younger than the outer laminae (believed to be the youngest). Thus, it might be problematic to use laminae in pendants in order to date the ages of landforms or for paleoenvironmental reconstruction. As discussed earlier, we detected new microlaminae in the contact of pendants and grain surface, resulting from biological origin and subsequent recrystallization of calcite in the interface of pendant and coarse fragments. The recrystallization of calcite under conditions different from the environment during the formation of calcium carbonate coatings (such as changes in local vegetation or environmental temperature) will strongly complicate the application of laminated pendants for paleo-reconstruction studies.

4. Conclusions

The detailed study of calcitic pendants revealed that their genesis is convoluted and can be the product of one or more formation cycles in different environments. In particular, calcitic pendants consisting of dark- and light-colored lamina indicate several palaeoclimatic cycles. Light-colored layers with micritic calcite precipitated in dry periods. However, dark-colored layers were formed in more humid periods, promoting a higher biological activity; the presence of organic impurities in their composition could further confirm the better conditions during the precipitation of these dark laminae of pendants. In addition, SEM observations revealed certain open spaces and micro-voids between pendants and host pebbles and some rounded structures therein. These open spaces in the contact of calcitic pendants and the host coarse fragments, along with biogenic structures, indicated that these interfaces are more recent and can be the youngest laminae of the pendants. These findings show that pendants may undergo chemical and physical changes after formation, complicating and affecting their suitability for dating and palaeoenvironmental reconstruction. Therefore, despite the potential ability of calcium carbonate pendants for dating and palaeoenvironmental reconstruction, the reliability of pedogenic carbonate features as proxies for paleoenvironment reconstructions and dating purposes can be questionable. Accordingly, more attention must be paid to the use of these features for palaeoenvironmental reconstruction.

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