Characteristics of micromorphology and element distribution of iron–manganese cutans in typical soils of subtropical China

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ABSTRACT

The goal of this study was to investigate the characteristics of iron–manganese cutans and to observe information of their pedogenic processes and certain environmental condition changes in the pedogenic process of subtropical Chinese soils. The characteristics of micromorphology of iron–manganese cutans and element distribution with linear microprofiles (i.e., the vertical microprofile from cutan to matrix soil) in Fragiudalfs (FRA), Ferrudalfs (FER) and Hapludult (HAP). Cutans and matrix soils were studied by chemical analyses, optical microscopy (OM) and energy dispersive spectroscopy (EDS). The micromorphological structure of iron–manganese cutan was a thin black film with alternating color of red and brown, and about 1 mm thick of soil particles. The structures of cutan materials were denser, and the boundaries between cutans and matrix soils were clear. EDS analyses of cutans and the plasma phase of the matrix soils, showed that the contents of MnO₂, Fe₂O₃ and CaO in cutans were higher than those in matrix soils, while the content of SiO₂ showed the opposite trend. From the outer to inner, cutans in Fragiudalfs and Ferrudalfs can be easily fractionated into manganese-rich, iron–manganese-rich and iron-rich regions. But there were only iron–manganese-rich and iron-rich regions in cutans in Hapludult, there was no clear manganese-rich region of belt structure in it. These differences were attributed to soil-forming factors. The formation of belt structure in iron–manganese cutans would probably undergo several great change in landscapes and soil environments. It indicated that the growth of cutans was in environments of alternating wetting and drying. They gradually grew in the oxidation–reduction process on the dry or wet condition of whole bulk soils.

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1. Introduction

Soil cutans form gradually in the long-term soil pedogenic processes. They are one of the common fabric features and information carrier of element movement and solid-solution-plant-air interaction in soils (Brewer, 1976; Jongmans et al., 1993, 1994, 1996; Liu et al., 2002b). The shape, structure and elemental composition characteristics of cutan were the products of soil-forming processes and environmental conditions (Buol and Hole, 1959; Chartres, 1987; Hartres, 1987; Feijtel et al., 1989; Sullivan and Koppi, 1991; Payton, 1993; Boulet et al., 1998; McCarthy et al., 1999; Tsatskin and Ronen, 1999). It can serve as an important basis for identifying the pedogenic processes and the environmental variations in different periods (Jongmans et al., 1996; Padmanabhan and Mermut, 1996; Hopkins and Franzen, 2003).

It was reported that the growth complexities of ferri-agillans formed in fossil soils indicated that these soils had undergone basic soil erosion and deposition process from moist to semiarid in ferruginous soil in Indian (Venugopal, 1998). Ferruginous clay cutans

on the surface of Australian podzol particles revealed that the soil had been periodic flooded in the soil soil-forming process (Harris et al., 1987). It could be extrapolated that the forming process of cutans was intermittent through analyzing the relationship between the shapes and oriented types of different cutans (Rebertus and Buol, 1985; Robinson, 1993). The morphology of the clay coating indicated that the vesicles in a desert loam soil (Haplic Durargid) in Australia had considerable durability (Sullivan and Koppi, 1991). Size and frequency of microcrystalline calcite coatings increased from aridic to xeric moisture regime, but decreased again towards the areas with an ustic moisture regime in highly calcareous arid and semiarid soils of the Fars Province, Southern Iran (Khormali et al., 2006). Carbonate coatings in stony soils were stratified into distinct microlamina, which provided a record of local environmental changes. Their growth rates could be employed to evaluate the age of paleograssland of arid and semiarid regions in Germany (Pustovoytov, 2002). These studies had all verified that cutans were the micro-environment recorders for the activity, migration and illuviation of specific components in soils. It also served as information carriers for the soil-forming process, environmental changes and paleoclimatic transitions.

Iron and manganese oxides as well as hydroxide minerals are very active constituents in soils because they are sensitive to environmental

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changes and they move frequently along soil cracks or holes and deposit in peds (McKenzie, 1989; Dixon and Skinner, 1992). As the condition changes from that of reduction to oxidation, iron and manganese may become immobilized (Padmanabhan and Mermut, 1996; Tan et al., 2005). In soils, the reduction and oxidation of iron and manganese, as a result of seasonal changes in soil moisture, contributes to the formation of cutans, forming coatings and concretions (Hartres, 1987; Robinson, 1993; Zhang and Karathanasis, 1997; Liu et al., 2002a,b). Mn(II) possesses higher mobility in soil profile than iron, holding a high oxidation potential compared with Fe(II) (Lindsay, 1979). These differences contribute to the formation of alternate layers with variable distribution of iron and manganese oxides in cutans, reflecting the wetting and drying variations in soil microenvironments that enclose in the cutans.

Iron–manganese cutans are widely distributed in Alfisol and Ultisols in subtropical zone in China. The behavior of chemical elements in these cutans was affected by climatic changes, landforms and land use (Tan et al., 2005; Huang et al., 2007). The migration and deposition of massive iron–manganese oxides in these soils was changed under different micro-environmental situations. Thus, elemental distributions with linear microprofiles in different iron–manganese cutans should have different characteristics in subtropical soils, but related research was extremely limited. The aims of the present study were (i) to determine the microscopic characteristics of iron–manganese cutans through analyzing the shape, microstructure and chemical composition with their linear microprofiles, and (ii) to identify the pedogenic processes, which response for their characteristics, and (iii) to observe information of certain environmental changes in the pedogenic processes of these subtropical Chinese soils.

2. Materials and methods

2.1. Soil sampling and descriptions

Three representative soils with iron–manganese cutans in B horizons from different subtropical regions in central China, were collected for this study. They are Fragiudalfs, Ferrudalfs and Hapludult, according to Key to Soil Taxonomy (Soil Survey Staff, 2006), collected from Xinyang city (32°22'N, 114°39'E) in Henan Province, Wuhan City (30°42'N, 114°24'E) in Hubei Province and Taoyuan City (28°52'N, 111°27'E) in Hunan Province, respectively. Climatic data and description of the studied samples were listed in Table 1. These soils were all from barren lands on the upper part of slopes. The landscapes of these areas are hills with good drainage condition. The B horizons in these soils usually exhibit a coarse polyhedral to columnar structure. The

subangular blocky peds (matrix soils) that contain cutans were collected from the B horizon at the depth about 20–50 cm. The cutans were usually black or brown in color and showed a waxy luster. Six to eight representative reddish-brown iron–manganese cutans (i.e., at least 30 g) were collected from each kind of B horizon soil. The cutan samples only were black or brown materials collected with a sterile blade under a microscope from soil blocks lightly. Matrix soils (i.e., at least 25–30 kg) were collected from adjacent ped interior blocks that scraped off cutans. Cutans were air-dried in original sample phases. The air-dried matrix soils and part of cutans were ground to pass 10-, 20-, 60- and 100-mesh sieves, respectively.

2.2. Soils and cutans chemical and physical analyses

Soil pH was measured by a Thermo Orion pH meter (Model 868) using a combined glass electrode (Model 9165BN) with a 1:2.5 ratio of soil to water. Cation-exchange capacity (CEC) of soils tested was determined according to the method described by Jackson (1979). The contents of organic matter in samples were determined following the $K_2Cr_2O_7$ volumetric methods (Walkley and Black, 1934). The particle-size distribution was determined by the pipette method after hydrogen peroxide treatment (Gee and Bauder, 1986).

The samples were digested with aqua regia ($HNO_3:HCl=1:3$) (125 °C) to extract iron (Fe) and manganese (Mn) (Liu et al., 2002b). Exchangeable K, Na, Ca, Mg were extracted with 1 mol L⁻¹ NH_4OAc . K and Na were measured with a flame photometer (FP-640). Ca, Mg, Fe and Mn were determined using an atomic spectrophotometer (Varian AA240FS). Extractable X-ray noncrystalline Fe (Feo) was dissolved in ammonium oxalate solution (i.e., 0.2 M, pH 3.0, 4 h in dark) (McKeague and Day, 1966), and free Fe-oxide (Fed) was dissolved in dithionite-carbonate-citrate (DCB, free Fe-oxide) (Mehra and Jackson, 1960).

Deferrated clay samples were saturated with Mg and K and mounted as slurries on petrographic slides for X-ray diffraction analysis (Jackson, 1979). The Mg-saturated clays were X-rayed at 25 °C before and after glycerol salivation. The K-saturated clays were X-rayed at 25 °C before and after heating at 110, 250, 350, 450 and 550 °C for 2 h (Jackson, 1979). Part of the clay fractions without DCB treatments were separated into magnetic and non-magnetic fractions (Schulze and Dixon, 1979). Soil clays were quantitatively separated using DCB treatments. Clays were treated by ultrasonic dispersion in pH 9.5 Na_2CO_3 solutions and then passed through the magnetic field of a strong electromagnet. Flow rate for water was 0.05 L min⁻¹. All clay suspensions were fractionated at 0.9 T to separate the non-iron-bearing minerals. After high-gradient magnetic separation (HGMS)

Table 1
Climate data and description of the samples tested

Sample	Location	Parent material	Mean annual rainfall mm	Mean annual temperature °C	Soil moisture and temperature regime	Description
Cutan of FRA ^a Matrix of FRA	Xinyang Henan	Quaternary (Q ₃)	670	12.8–15.5	Udic-mesic	Reddish black moist color (10R 2/1) Strong brown (7.5YR 5/6); light clay; weak/moderate subangular blocky structure; very firm; some cutans
Cutan of FER ^b Matrix of FER	Wuhan Hubei	Quaternary (Q ₃)	1269	15.8–17.5	Udic-thermic	Yellowish black moist color (5Y 2/1) Yellowish red (5YR 5/8); clay; weak/moderate subangular blocky structure; very firm; many cutans
Cutan of HAP ^c Matrix of HAP	Taoyuan Hunan	Quaternary (Q ₂)	1437	16.0–16.5	Udic-thermic	Reddish black moist color (10R 2/1) Reddish yellow (7.5YR 6/8); clay; moderate subangular blocky structure; very firm; many cutans

^a FRA = Fragiudalfs.

^b FER = Ferrudalfs.

^c HAP = Hapludult.

Table 2
Selected soil chemical and physical properties

Sample type	pH ^a	O.M. ^b mg g ⁻¹	Exchangeable cation				B.S. ^c %	CEC cmol kg ⁻¹	Sand g kg ⁻¹	Clay g kg ⁻¹	Texture
			K	Na	Ca	Mg					
			cmol kg ⁻¹	cmol kg ⁻¹	cmol kg ⁻¹	cmol kg ⁻¹					
Cutan of FRA	6.60	10.56	0.66	1.08	6.05	4.50	42.07	29.21	186.1	535.6	C ^d
Matrix of FRA	6.44	8.14	0.23	0.78	4.50	3.50	46.81	19.25	363.8	395.8	CL ^e
Cutan of FER	5.93	3.35	0.38	1.12	4.05	3.66	45.06	20.44	214.6	514.8	C
Matrix of FER	5.81	3.01	0.20	0.51	3.90	3.33	53.65	14.80	208.8	457.7	C
Cutan of HAP	4.41	3.61	0.32	0.15	2.70	2.25	35.85	15.12	250.3	547.8	C
Matrix of HAP	4.25	3.24	0.20	0.09	1.55	1.66	34.15	10.25	141.8	462.5	C

^a Soil:H₂O=1:2.5.

^b O.M. = organic matter.

^c B.S.= base saturation.

^d C = clay.

^e CL = clay loam.

treatments, clay suspensions were flocculated with NaCl, and excess salts were removed by centrifugation, washed by distilled water and freeze-dried. Clay minerals analysis was carried out with XRD techniques (Fe K α radiation generated at 40 kV and 20 mA) using a D/Max-3B diffractometer (JDX-10P3A) on clay fractions of cutan and matrix soil before and after HGMS or DCB treatments.

2.3. Optical microscopy and electron microscopy of sample

Cutans were impregnated with polyester resin (crystic) to solidify, then cut along the vertical direction of cutan surface into impregnated blocks and burnished into several thin sections (FitzPatrick, 1984). Thin section samples were investigated with a polarizing microscope (Opton Universal R Pol) using polarized light. The enlarged multiple was 10 or 40 times.

Selected representative thin section samples were coated with carbon in a vacuum evaporator, and then examined with energy dispersive spectrometer (EDS) (JXA-733) operated in an automated quantitative elemental analysis mode that performed at 15 kV and 20 mA and 2 μ m microtie diameter, using metals of Si, Ti, Al, Fe, Mn, K, Na, Ca and Mg as standard. The measured element contents in cutan with linear microprofiles were converted into oxide contents, and the coefficients of variation for oxide contents were obtained with Excel 2003.

3. Results

3.1. Properties and morphology of iron–manganese cutans

The soil texture of samples ranged from clay to clay loam. From Fragiudalfts, Ferrudalfts to Hapludult, pH decreased obviously while the

contents of Fe₂O₃, clay and kaolinite increased, with gradually decreasing base saturation and vermiculite contents (Tables 2 and 3). The pH, organic matter, exchangeable cations, CEC, clay, Fe₂O₃, MnO₂, Feo contents of the cutans of three soils were all higher than those of matrix soils in B horizon (Tables 2 and 3). The contents of Fed in cutans of Fragiudalfts and Hapludult were lower than those in matrix soils in B horizons. The Feo to Fed molar ratio of cutans was higher than that of matrix soils. This is mainly due to the organic matter contents and moistures of cutans were richer than those in matrix soils, and the source and forming time of Fe-oxide in cutans were shorter than those in matrix soils. The difference in MnO₂ content between cutans and matrix soils was marked. The contents of MnO₂ in cutans were 1.27–19.31 times greater than those in matrix soils. Vermiculite, illite and kaolinite are major clay compositions in both cutans and matrix soils. It had been reported that hydroxy-interlayered vermiculite (HIV) existed in matrix soils of Fragiudalfts and Ferrudalfts (Huang et al., 2007). The type of Fe-oxide was goethite in cutans and matrix soils. The Mn-oxides in cutans of three soils contained low contents of birnessite and lithiophorite, but they could not be detected in corresponding matrix soils.

Fig. 1 showed optical micrographs of iron–manganese cutans under crossed polarized light of three soils. The black films alternating with red and brown in the middle-upper side of the micrographs was cutans. Cutan in Fragiudalfts of Xinyang City (Fig. 1(a)) formed a thin film on the surface of soil block, and was obviously different from the matrix soil. It consisted of black MnO₂ and red Fe₂O₃ from the outer to inner cutan layer, and the transition was obvious on the edge of cutan. After being magnified 40 times (Fig. 1(b)), the cover of MnO₂ on the surface of cutans could be observed and it alternated with red Fe₂O₃, indicating that there was massive deposition of MnO₂ and Fe₂O₃ on the cutans of Fragiudalfts.

Table 3
Soil sesquioxide contents and clay mineralogical compositions

Sample type	Fe ₂ O ₃	MnO ₂	Feo ^a	Fed ^b	Feo/Fed	Clay mineralogical composition ^c	Fe and Mn oxides ^d
	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹			
Cutan of FRA	57.07	9.97	2.95	21.36	0.14	V(++), I(++++), K(+)	G, B, L
Matrix of FRA	45.93	0.86	1.71	22.72	0.08	V(++), H(+), I(++++), K(++)	G
Cutan of FER	62.37	10.04	5.35	36.07	0.15	V(++), I(++++), K(++),	G, B, L
Matrix of FER	45.56	0.52	1.41	31.22	0.05	V(+), H(+), I(++++), K(++)	G
Cutan of HAP	60.76	5.83	6.94	40.28	0.17	V(+), H(+), I(++++), K(++)	G, B, L
Matrix of HAP	56.53	0.66	1.45	46.74	0.03	V(+), H(+), I(++++), K(+++)	G

^a Oxalate-extracted iron.

^b Dithionite–citrate–bicarbonate-extracted iron.

^c V = vermiculite, H = hydroxy-interlayered vermiculite(HIV), I = illite, K = kaolinite. Symbols of +: <10 g kg⁻¹, ++: 10–25 g kg⁻¹, +++: 25–50 g kg⁻¹, ++++: 50–75 g kg⁻¹. The semiquantitative mineralogical compositions were estimated by peak areas of XRD to phyllosilicate.

^d G = goethite, B = birnessite, L = lithiophorite.

Fig. 1. Optical micrographs of soil iron-manganese cutans under crossed polarized light in Fragiudalfs (a and b), Ferrudalfs (c and d), and Hapludult (e and f). The black films alternating with red and brown in the middle-upper side of the micrographs are iron-manganese cutans. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The deposition of MnO_2 was later than that of Fe_2O_3 , but the deposited layer was thicker (about 0.4 mm).

The inner layer of cutans (Fig. 1(c) and (d)) in Ferrudalfs of Wuhan City was mainly composed of thicker reddish-brown Fe_2O_3 , while the outer layer comprised mainly of dense black MnO_2 . The transition of the outer layer and the inner layer was clear. Obviously, there was a gradient of red Fe_2O_3 deposition between the inner layer and the matrix soil, and Fe_2O_3 reduced gradually from the outer to inner layer. These indicated that iron cutan was formed first, followed by manganese cutan in the subsequent formation of cutans, causing MnO_2 to cover Fe_2O_3 . The layer of MnO_2 (about 0.2 mm) on the surface of cutan in Ferrudalfs was thinner than that in Fragiudalfs, but the deposition gradient of Fe_2O_3 was more significant than that in Fragiudalfs of Xinyang City.

The cutans in Hapludult of Taoyuan City (Fig. 1(e) and (f)) were black film mixed with reddish-brown substance, and had a clear black and red belt. The superficial coating was reddish-brown Fe_2O_3 , and the

subsurface stratum was black MnO_2 , then they alternated with the inner layer composed mainly of Fe_2O_3 . The transition zone between cutan and matrix soil was obvious. Compared with the cutans of Fragiudalfs and Ferrudalfs, the Hapludult cutan showed a remarkable characteristic of black belts alternating with red ones, and the thickness of cutan material was beyond 0.4 mm. This indicated that the deposition of Fe_2O_3 was more obvious than that of MnO_2 in the forming process of cutans in Hapludult.

The belt structure of cutan in Hapludult was more complicated compared with that of the other cutans. It presented the multilayered cutan of manganese alternating with iron, revealing that the strong reduced situation caused iron and manganese to emigrate from the matrix soils massively, and gathered in the soil cracks or pores. The cutans of Fragiudalfs and Ferrudalfs were compound cutans composed of thick Fe_2O_3 and MnO_2 . The environmental transition in their forming process possibly was less frequent than that in the Hapludult region. The microstructure of cutans demonstrated that the material

Table 4

The mean values of element contents in the linear profiles of samples tested

Samples	Items	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO ₂	K ₂ O	Na ₂ O	CaO	MgO	Total	Mn/Fe ^a	Si/Al ^b
		wt.%											
Cutan of FRA (<i>n</i> ^c = 16)	Mean	45.60	1.02	21.08	9.79	7.27	2.91	0.17	1.32	1.97	91.14	0.71	17.37
	C.V. ^d	16.43	186.16	16.23	22.67	100.24	63.32	137.63	33.69	69.25	2.41	99.46	29.89
Matrix of FRA (<i>n</i> = 10)	Mean	49.16	0.46	24.16	8.71	0.10	2.84	0.09	0.75	1.99	88.26	0.01	16.12
	C.V.	6.70	52.33	12.84	26.87	89.08	48.12	83.92	57.29	32.49	3.32	100.92	18.35
Cutan of FER (<i>n</i> = 12)	Mean	37.64	0.55	20.84	12.14	11.64	2.47	0.05	0.75	1.05	87.13	0.85	14.58
	C.V.	20.15	45.51	19.80	21.00	91.86	31.30	128.02	27.06	23.00	6.23	88.24	33.42
Matrix of FER (<i>n</i> = 8)	Mean	48.07	0.63	27.35	9.78	0.14	2.07	0.14	0.52	1.10	89.81	0.01	13.86
	C.V.	8.19	28.34	9.48	11.44	39.12	22.15	21.14	27.63	17.85	0.74	34.46	19.82
Cutan of HAP (<i>n</i> = 11)	Mean	36.61	0.88	24.08	13.99	10.04	2.91	0.16	0.64	1.00	90.31	0.60	11.88
	C.V.	27.63	71.52	15.28	25.94	97.36	27.61	65.37	68.49	22.79	1.17	92.48	29.68
Matrix of HAP (<i>n</i> = 7)	Mean	46.45	0.50	27.78	11.08	0.01	1.94	0.09	0.29	1.02	89.15	0.00	13.28
	C.V.	8.89	17.44	12.82	18.34	223.61	47.04	64.01	68.79	25.17	1.94	223.61	22.07

^a Mn/Fe molar ratio.^b Si/Al molar ratio.^c *n* = the number of EDS single point analysis.^d C.V. (coefficient of variation) = standard deviation / mean value × 100.

deposition in cutans transformed mainly from MnO₂ to Fe₂O₃ gradually from Fragiudalfs, Ferrudalfs to Hapludult.

3.2. Element contents in linear profiles of iron–manganese cutans

Table 4 shows soil linear profiles analyzed by EDS. The percentages of TiO₂, K₂O, Na₂O and CaO of sampling spots in the iron–manganese cutans were generally higher than those in the matrix soils. The SiO₂ and Al₂O₃ contents in the cutans were all lower than those in the matrix soils. However, the Si/Al molar ratios in cutans were quite close to those in the matrix soils. This was similar to that of aluminosilicate coatings and groundmass in Guadeloupe Andisol (Jongmans et al., 1994) and that of wall-shaped bridge and coatings in a hard sandy-loam soil from semiarid Northern Cameroon (Lamotte et al., 1997). The Fe₂O₃ and MnO₂ contents in cutan were all higher than those in the matrix soils. In particular, the contents of MnO₂ in the cutans were 73, 83 and 1004 times greater than those in the matrix soils, respectively. The change in Mn/Fe molar ratio reflected the separation and accumulation of iron and manganese along with the change in soil environmental conditions. The Mn/Fe molar ratios of cutans in three soils all were bigger than those in matrix soils. This indicated that manganese, compared with iron, was easier to accumulate in the cutans in the transition from matrix soils to cutans.

The variation coefficients of major elements in cutans were greater than those in the matrix soils. The variation coefficient of MnO₂ in cutans of three soils were 1.13, 2.35 and 0.44 times greater than those in the matrix soils, but the variation coefficient of Fe₂O₃ in cutans were 0.84, 1.84 and 1.41 times greater than that in the matrix soils, respectively.

In addition, even in the spot-position of cutans where the contents of iron and manganese were very high (about 40%), the contents of silicon and aluminum still accounted for a great proportion. This was similar to the element composition in dark reddish void coatings that were dominated by Si, Al and Fe in Lower Cretaceous Paleosols in Canada (McCarthy et al., 1999). The most possible migration form of iron and manganese was the colloidal phases (Dixon and Skinner, 1992). Iron and manganese in tested soils were oxidized to deposit on the soil surface, cracks and channels, and they were often accompanied with migration and deposition of layered aluminosilicate clays, as reported by Lamotte et al. (1997).

3.3. Distribution curves of parts of elements in iron–manganese cutan profile

The changes of elements with linear microprofiles in the cutans and the matrix soils from the outer to inner layers can be examined by EDS analysis.

Fig. 2(a) shows in Fragiudalfs that the thickness of cutan was within 1 mm, as suggested by Sullivan and Koppi (1991) on composite coatings in desert loam soil. The change range of CaO was higher than that of Fe₂O₃, but the change range of MnO₂ content was greater than those of Fe₂O₃ and CaO. The content of SiO₂ increased gradually from outside to inside. Extending from cutans to the interior of matrix soils, MnO₂ trended to reduce gradually, and its content in the matrix approached to zero, the content of Fe₂O₃ and CaO reduced gradually, but SiO₂ increased slightly. In the outer layer of cutan (about 0–0.4 mm), the average MnO₂ content was about 20%, but Fe₂O₃ was less than 10% and CaO approached 2%. Thus, this region was manganese-rich. In the middle layer of cutan (i.e., about 0.4–0.7 mm), the MnO₂ content decreased slightly and the Fe₂O₃ content increased gradually, CaO reduced to approximately 1.2%, so this was an iron–manganese-rich region. In the interior of cutan (about 0.7–1.0 mm), the MnO₂ content was extremely low, but Fe₂O₃ content rose, while CaO decreased slightly, so this was an iron-rich region. In the 1 mm thick cutan from outside to inside, the Mn/Fe molar ratio (Fig. 2(b)) presented three obvious peaks.

The thickness of cutan was within 1 mm in Ferrudalfs (Fig. 2(c)). From the outside to inside of cutans, in a region of 0–0.2 mm, the content of MnO₂ (i.e., about 20% in average) was two times higher than that of Fe₂O₃ (about 10% in average), while the content of CaO was approximately 1.3%. This was manganese-rich region. In the 0.2–0.5 mm region, the MnO₂ content reduced slightly and was close to Fe₂O₃, while CaO reduced to approximately 0.7%. This was an iron–manganese-rich region. In the 0.5–0.9 mm region, the content of MnO₂ reduced rapidly, and the change of Fe₂O₃ was not significant. The content of CaO reduced to approximately 0.5%, so this was an iron-rich region. In the iron–manganese-rich region, the content of Fe₂O₃ was higher than that in Fragiudalfs, and the difference of content between Fe₂O₃ and MnO₂ was smaller than that in Fragiudalfs. The Mn/Fe molar ratio (Fig. 2(d)) had two obvious peaks in cutan, but it approached zero in the matrix soils.

The changes of elements with linear microprofiles in cutan of Hapludult (Fig. 2(e)) were different from other two kinds of soils. In the outer layer of the cutan (approximately 0–0.4 mm), the content of MnO₂ was close to that of Ferrudalfs. The distribution curve of Fe₂O₃ was close to that of MnO₂, indicated that this was an iron–manganese-rich region. In the inner layer of cutan (approximately 0.4–1.0 mm), the MnO₂ content reduced obviously and approached zero. The change of Fe₂O₃ content was not obvious. it was an iron-rich region. This demonstrated that no manganese-rich region existed in the cutan of Hapludult. In the iron–manganese-rich region of cutan, from outside to inside fluctuation of CaO content decreased gradually. In the iron-rich region, the CaO content (approximately 0.5%) was lower than the former two kinds of soils. In the matrix

Fig. 2. Distributions of certain elements and Mn/Fe molar ratio in iron–manganese cutan linear profile in Fragiudalfs (a and b), Ferrudalfs (c and d) and Hapludult (e and f).

region, the content of MnO₂ approached zero, while the content of CaO was approximately 0.3% (lower than Fragiudalfs and Ferrudalfs), and Fe₂O₃ was approximately 11% (higher than Fragiudalfs and Ferrudalfs). The content of SiO₂ in Hapludult was higher than other elements, and was close to that in Fragiudalfs and Ferrudalfs. The change range of Mn/Fe molar ratio (Fig. 2(f)) in cutan had two peaks.

4. Discussion

The formation of belt structures in iron–manganese cutans was correlated with soil moisture, redox condition, pH, material source,

landscape, etc. The standard redox potential (E_h°) of manganese system is generally higher than that of the iron system (Lindsay, 1979), such as E_h° is 1.23 V for MnO₂–Mn(II) system and 0.77 V for Fe(III)–Fe(II) system. Therefore, manganese is generally more easily reduced but more difficult to be oxidized than iron (McKenzie, 1989; Huang, 1991). The range of pH and E_h for Mn(II) to exist in soil is greater than that of Fe(II). Mn(II) would migrate from the matrix soil, which was far away from the microzone of cutan, but the migration distance of Fe(II) was much smaller (Lindsay, 1979; Tan et al., 2005). During iron–manganese cutan forming process, the spatial variation of manganese was higher than that of iron. The contents of MnO₂, Fe₂O₃ and CaO and Mn/Fe molar ratios fluctuated

from the interior to the outside of the cutan profile, all indicating that the soil was under relatively arid or moist environment in different cycle. If the change of wetting and drying is strong, it was advantageous for the separation of manganese and iron oxide, formed the manganese-rich or iron-rich belt structure. If the intensity of soil moisture and aridity was weak and the alternation speed was fast, iron and manganese were not easily separated, thus forming the iron–manganese symbiotic belt structure. Padmanabhan and Mermut (1996) described a similar migration process within the Fe-oxide coatings developed on quartz grains. These belt structures were similar to the layers of Fe- and Mn-rich material observed in many manganese–iron nodules (White and Dixon, 1996; Liu et al., 2002a).

There were iron–manganese-rich and iron-rich regions in cutans of Hapludult, but no manganese-rich region. Compared with Fragiudalfs and Ferrudalfs, Hapludult was in the typical subtropical climate zone of high temperature and rainfall. Here, the soil underwent intensive desilicification and allitization, its pH was lower than that in Fragiudalfs and Ferrudalfs, and the clay and kaolinite contents increased. So, there was a significant amount of transportable Fe (II) and Mn (II) under the moist and low pH condition in Hapludult, and the migration intensity of iron and manganese increased. It was thus easier to form iron–manganese-rich deposits in cutans of Hapludult than the other soils. From Hapludult, Ferrudalfs to Fragiudalfs, the climate became dry, the acidic leaching function weakened, and the base content and pH value increased. Compared with Fe₂O₃, the content of MnO₂ obviously increased, and its function emerged gradually in the cutan forming process.

In summary, soil weathering destroyed phyllosilicate and released massive Fe (II) and Mn (II). The migration of water caused them to emigrate out of the soil interior to reach the surface of the soil body or moved from the surface layer to the alluvial horizon. Then soil environment became dry, which caused the dissolved Fe (II) and Mn (II) to be oxidized and deposited on cracks or surfaces of soil structure bodies. The emigration of base ions also caused pHs in three matrix soils all were lower than those in three cutans, and the results led iron and manganese more easy to dissolve and emigrate from matrix soil to deposit on cutans in the cutan forming processes. The formation of iron–manganese cutan depended much on landscape setting which directly influenced the soil moisture and wet and dry cycles. The tested three soils all located on hills which had good drainage condition, it made the layers of iron and manganese deposition in cutans limited because of the long length of alternation cycle. Further more, the subtropical area had a unique climate that formed an environment of wetting and drying cycles in the soils. The soil properties had the obvious characteristic of transition from north to south in this area in China. Although the base ions were leached out massively, the iron–manganese oxides were still in the stage of frequent migration and deposition, this was also the main reason why the iron–manganese cutans were widely distributed in the subtropical soils. The belt structure character and the distribution of iron–manganese cutans had further instructed the pedogenic process and climatic conditions in the different soils. Therefore, it may be reasonable and significant to regard the material composition and belt characteristic of iron–manganese cutan as the result of soil forming over the long-term evolution. Further research on the formation of soil cutans could gain information of certain historical environmental transformations.

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