

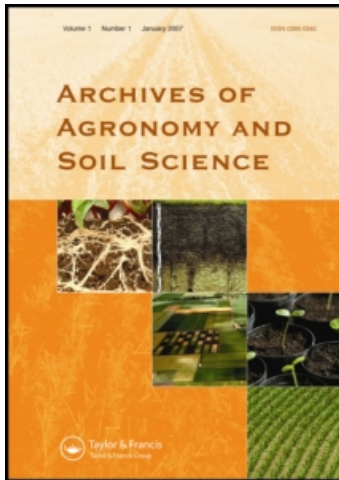
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## Distribution of iron oxides forms on a transect of calcareous soils, north-west of Iran

Salar Rezapour<sup>a\*</sup>, A.A. Jafarzadeh<sup>a</sup>, Abbas Samadi<sup>a</sup> and Sh. Oustan<sup>a</sup>

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The iron oxides fractions of four major physiographic units obtained from a transect of calcareous materials were studied to assess the effects of key pedogenic processes and local hydrology conditions as well as physiographic units in controlling iron oxides forms in the north-west of Iran. Samples from different horizons belonging to six pedons were selected and analyzed for soil physicochemical properties, clay minerals, and Fe oxides forms ( $Fe_d$ ,  $Fe_o$ ,  $Fe_p$ ). In general, the soils indicated some variation in the concentration of iron oxides that could be related to rate of weathering, pedogenic accumulations, geomorphologic conditions (as results of different in physiographic units), wet and dry cycle, and organic matter. A wide relative variation in mean values of  $Fe_d$  ( $6.4\text{--}9.9\text{ g kg}^{-1}$ ),  $Fe_o$  ( $2.9\text{--}4\text{ g kg}^{-1}$ ), and  $Fe_p$  ( $0.68\text{--}1.3\text{ g kg}^{-1}$ ) was observed among physiographic units. On the plateau unit, the presence of the most stable geomorphologic conditions and high rate *in situ* weathering (reflected in clay content), coupled with minor deposition of sediment suggest that the soils have more dynamic conditions than other units, reflecting in the greatest amount  $Fe_d$  and the lowest  $Fe_o/Fe_d$  ratio.  $Fe_d$  content of the soils containing less clay content (15–25%) was significantly different from those with greater clay content (25–35%).

**Keywords:** physiographic units; iron oxides forms; weathering; pedogenic processes

### Introduction

Studies on the distribution and occurrence of iron oxides and their influence on soil properties as a logical tool to help understand soil and pedogenetic environments in Iran are almost unknown. Iron oxides of soils are found as a component of several iron-bearing minerals that release those to poorly crystalline and crystalline pools or other forms by weathering at different rates. The rate of these alteration products generally increase with soil development (Ogunsola et al. 1989). Three basic types of iron hydroxides, oxyhydroxides, and oxides are commonly known as the most abundant of the metallic oxides in most soils and all climatic regions (Schwertmann and Taylor 1989). Under earth surface conditions, iron oxides exist in several mineral forms consisting of ferrihydrite, goethite, hematite, lepidocrocite, maghemite, and magnetite (Schwertmann 1988; Schwertmann and Taylor 1989). Goethite and hematite are the dominant minerals

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in well-oxidized or arid and semi-arid environments. Lepidocrocite is found predominantly in hydromorphic environments (Kämpf et al. 1999). Magnetite occurring predominantly in the silt and sand-size fractions is most common in reduced or slightly-weathered soils, and maghemite is common in many different soils, especially in the tropics and subtropics (Schulze and Dixon 1979). Ferrihydrite is likely to exist in most soils, although usually in small quantities, but is frequently a major component in soils exhibiting fluctuating redox potential (Schwertmann 1991). Each of the soil iron oxide minerals exists in relatively well-ordered crystalline form (such as magnetite) to short-range (e.g., ferrihydrite) or poorly crystalline (Thomasson and Bullock 1975). Commonly, decomposition of the soil matrix followed by selective dissolution techniques, prior to chemical analysis, is applied to quantify the relative proportion of iron oxides. Poorly crystalline Fe oxides (often called non-crystalline, poorly ordered, short-range ordered, active or amorphous iron oxides) can be measured by acid oxalate extraction ( $Fe_o$ ). Free or pedogenic Fe compounds may be estimated by citrate-bicarbonate-dithionite (CBD) extraction ( $Fe_d$ ), and Na-pyrophosphate-extraction is utilized for determination of organically bound Fe ( $Fe_p$ ). The amount of crystalline secondary oxides, inorganic Fe, i.e., the Fe sequestered in crystalline oxides, can be estimated with the difference between  $Fe_d$  and  $Fe_o$  (Birkeland 1999). The  $Fe_o/Fe_d$  ratio, as an active Fe ratio, quantifies the proportion of the more and less active fractions (Kämpf et al. 1999). This ratio is related to the degree of crystallinity of the Fe-oxides, and it has been found that a low  $Fe_o/Fe_d$  ratio reflects the higher degree of soil development (McKeague and Day 1966; Blume and Schwertmann 1969).

Primary Fe-bearing minerals (biotite, feldspars, amphiboles, pyroxenes, pyrite etc.) are thermodynamically unstable in soils, eventually being transformed to secondary minerals (Owliaie et al. 2005). The weathering of phyllosilicates mainly micaceous minerals is known as one of the important sources of Fe release by several studies. Stolt et al. (1993) emphasized that although some Fe may be lost during the degradation of silt and sand to clay-size particles, most is probably released during the oxidation and weathering of biotite. Ghabru et al. (1990) found that the high extractability of  $Fe_d$  is as a result of release from phyllosilicates, mainly micaceous minerals, without complete destruction of the mineral structure. Douglas (1967) ranked similar observations for biotite that had been ground to clay size. On the other hand, since soil Fe is present predominantly in the form of iron oxides, relative increase or decrease in the content of Fe forms can occur due to gains and losses (Blume and Schwertmann 1969). Such conditions are usually related to climate, landscape, landscape associated with drainage, and soil depth (Motta and Kämpf 1991; Peterschmitt et al. 1996). Nevertheless, local hydrological and landscape conditions often lead to redistribution of Fe in the profile and absolute gains or losses are less common. Therefore, the distribution of iron forms in relation to landscape can be a useful parameter for investigating soil formation and development processes as well as the influence of the soil ecosystem on them.

Investigated transect and profiles site (as one of the intermountain plains of the Zagros region) which have occurred along a slope with diverse physiographic units and local hydrological condition, provide a suitable case to assess the nature, concentration, and distribution of iron oxides. The objectives of this study were: (i) To identify iron oxides forms and determine their contents and relative distribution

in relation to local hydrological conditions and pedogenic processes; and (ii) to interpret the relationship between the iron oxides and physiographic units.

## Material and methods

### *Environmental setting*

The study site was selected on the Urmia area, in western Azerbaijan Province, north-west of Iran (Figure 1). This transect, about 20 km in length, is part of the Zagros orogenic zone ranging in elevation from 1220–1330 m a.s.l. As represented in Figure 2, the main rock units were made up during different periods of geology in the area. During the upper Cretaceous (about 50 million years BP), the Urmia area occurred through sediments in the type of limestone and shale which also exposed in the mountains of the area (Figure 2). White grey limestone, marl and calcareous sandstone formations took place during the upper Cretaceous to Tertiary (about 30 million years BP) in the form of alternate layers. These formations, which contacted with the Quaternary deposits, are characterized by a clear boundary and variety thick of materials. The Quaternary formations consisting of alluvium and recent deposits were formed during the different unstable phases of this period about 10,000 years BP. In this period, the irregular distribution of rainfall led to much runoff and subsequently erosion episodes, followed by the great sediments, so that this area filled with alluvial deposits coming from surrounding mountains. The mean annual rainfall is 330 mm and most of it falls from December to April. The mean annual temperature is 11°C and varies about 14–20°C between winter and summer. Soil moisture and temperature regimes are xeric and mesic, respectively.

### *Soils transect and field observation*

The study area and profiles sites were selected in a long vertical transect from NE to NW (Figure 2). Six profiles were chosen: P2 on piedmont plain (P.P), P3 and P4 on plateau (Plat), P5 on river alluvial plain (R.A.P) and P1 and P6 on the colluvial alluvial plain (C.A.P). C.A.P and R.A.P units are typically influenced colluvial

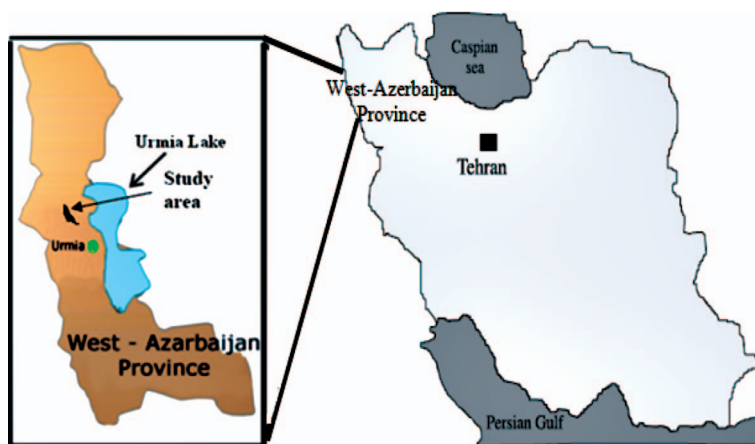


Figure 1. Situation map of study area.

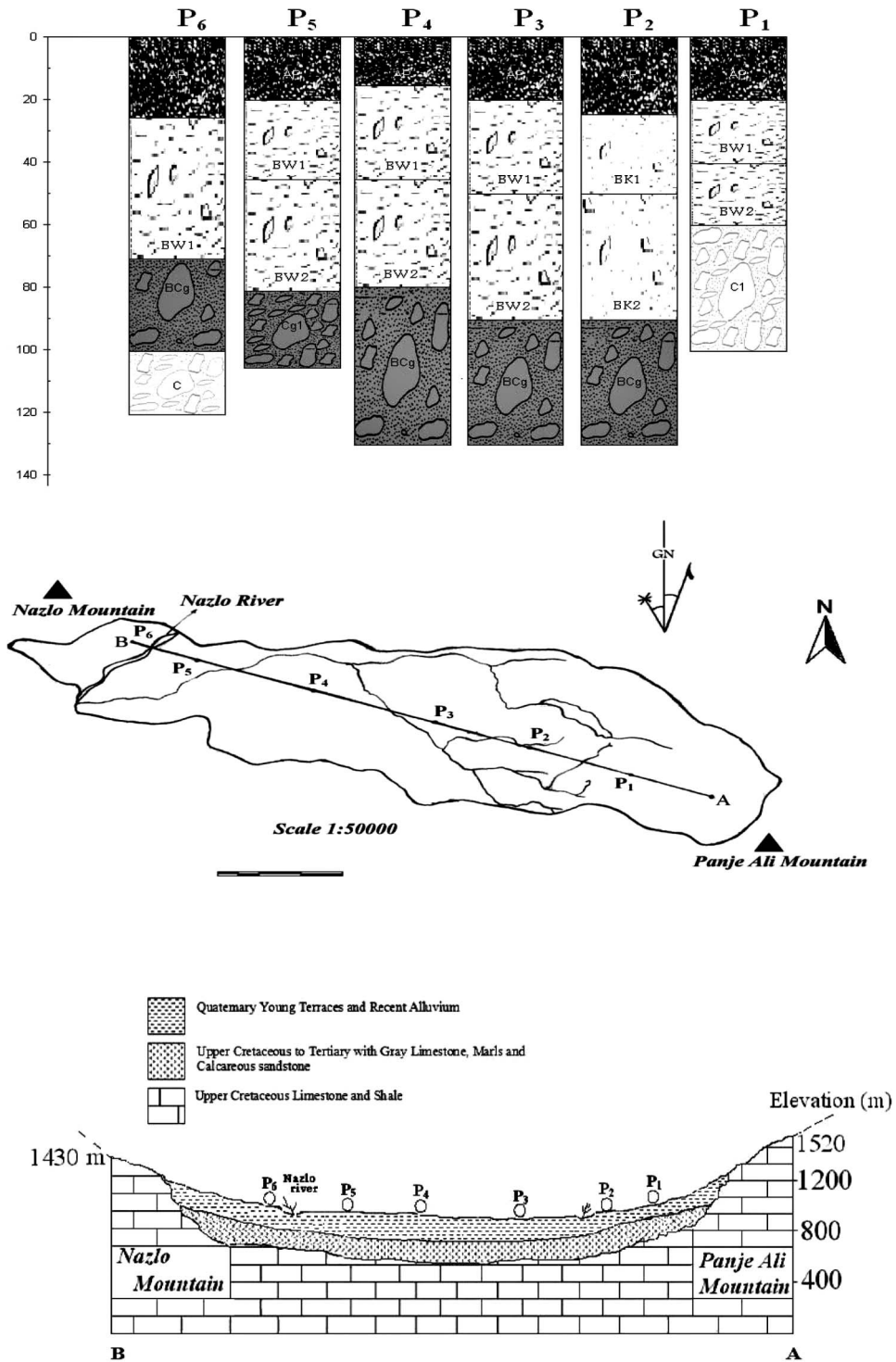


Figure 2. Map and cross-section of study area showing the location of studied profiles and the sedimentary petrology and different landforms, respectively.

deposition from upslope and cycle of alluvial sediments, respectively. Plat unit, which is less indicative of deposition of sediments and episodes of erosion, reflects higher stable geomorphic condition whereas P.P unit is impacted periodic alluvial and colluvial depositions. Samples were taken from observed horizons, air-dried, crushed, passed into a 2-mm sieve, and the fine fractions saved for analysis.

### ***Physicochemical analyses***

Particle-size distribution was determined according to the pipette methods (Day 1965). Alkaline-earth carbonates were measured by acid neutralization and back titration (Nelson 1982). Organic carbon (OC) was determined using the wet digestion method (Nelson 1982). PH and electrical conductivity were estimated in saturated paste and saturated extract, respectively (Salinity Laboratory Staff 1954). Cation exchange capacity was obtained by saturation with 1 M  $\text{NH}_4\text{OAc}$  at pH 8.2 for the soils and clay fraction (Chapman 1965). Acid ammonium oxalate extraction, during 4-h shaking at pH 3 in darkness, was used to analysis poorly crystalline Fe oxides and organically bound iron ( $\text{Fe}_o$ ) (McKeague and Day 1966). The Fe extracted by the dithionite-citrate-bicarbonate (DCB) was attributed to crystalline, poorly crystalline and organically bound Fe ( $\text{Fe}_d$ ) (Holmgren 1976). In addition, Fe was extracted by 0.1 M Na-pyrophosphate at pH 10 for determination of organically bound Fe ( $\text{Fe}_p$ ) (Loveland and Digby 1984). The differences between CBD-Fe and ammonium oxalate-Fe and between ammonium oxalate-Fe and pyrophosphate-Fe were considered as an estimation of crystalline secondary oxides and non-crystalline oxides, respectively (Birkeland 1999). Statistical analyses were carried out in three replications using MSTATC software.

### ***Mineralogy analysis***

The clay fraction was separated after destruction of chemical cementing agents according to Mehra and Jackson (1960) and Kunze (1965). Clay minerals were analyzed on glass slides by X-ray diffraction using Shimadzu XRD 6000 and  $\text{CuK}\alpha$  radiation source. The (001) reflections were obtained following Mg-saturation, glycerol salivation, K-saturation, and K-saturation plus heating at 550°C. Clay minerals were estimated semi-quantitatively, employing Biscaye method (1965). Powdered samples were used for record of random powder diffraction patterns.

## **Result and discussion**

### ***Soil morphological characteristics***

Soil morphological data, as a useful tool in the description of weathering process and pedogenesis, are presented in Table 1. Soils' color ranges are with the Munsell color index of (moist) 10YR and value and chroma of 3–5 and 2–4, respectively. In general, soils exhibited evidence of gleying conditions underlying the sola except P1 soils. The presence of these conditions is indicated by gray zones and distinct mottles as a result of Fe depletion (Thompson and Bell 1998). The disappearance of these properties in P1 can be attributed to the deep groundwater table, followed by the lack of wetting and drying cycles. The soils have relatively high levels of OC in  $A_p$  horizons (5.2–15.4  $\text{g kg}^{-1}$ ), which regularly decrease with depth in P1, P5, and P6, but P2, P3, and P4 have an irregular pattern of OC of decreasing with depth due to

Table 1. Morphology and description of the investigated soils.

Horizon	Depth (cm)	Color (Moist)	Structure <sup>a</sup>	Consistence <sup>a</sup> (Moist)	Boundary <sup>a</sup>	Notes
<b>P1<sup>b</sup> – Typic Haploxerepts</b>						
Ap	0–20	10YR 4/2	clabk	mvfr	gs	Coarse and medium roots
Bw1	20–42	10YR 4/3	f2abk	mfr	ds	Many fine and medium roots
Bw2	42–75	10YR 4/4	f2abk	mfi	ds	Many fine and medium roots
C1	75–100	10YR 4/4	m	mfi	–	Few fine roots, many lime concretion
<b>P2 – Typic Calcixerepts</b>						
Ap	0–24	10YR 4/5	m2abk	mvfr	gs	Many medium roots
Bk1	24–50	10YR 4/3	m2abk	mfi	cs	many fine and medium roots, fine lime powdery pockets, medium snail shells
Bk2	50–90	10YR 4/4	labk	mfi	cs	Many fine irregular lime powdery pockets and concretion, medium snail shells
BCg	90–130	10YR 4/2	flabk	mfi	–	Common medium distinct dark yellowish brown (10YR 4/3) mottles, medium snail shells
<b>P3 – Fluventic Haploxerepts</b>						
Ap	0–20	10YR 3/2	m2gr	mvfr	gs	Many fine and medium roots
Bw1	20–50	10YR 4/5	m2abk	mfi	cs	Many fine roots
Bw2	50–90	10YR 4/4	m2abk	mvfi	cs	Few fine roots, medium snail shells
BCg	90–130	10YR 6/1	a1bk	mvfi	–	Common medium to coarse very dark grayish brown (10YR 3/4) mottles, medium snail shells
<b>P4 – Fluventic Haploxerepts</b>						
Ap	0–15	10YR 3/3	m1abk	mvfr	gs	Many fine and medium roots
Bw1	15–45	10YR 4/5	m2abk	mvfi	cs	Common medium roots
Bw2	45–80	10YR 4/6	m1abk	mfi	gs	Common medium roots in horizontal zone, snail shells
BCg	80–130	10YR 4/2	m1abk	mfi	–	Many fine faint mottles, snail shells, few fine roots, few lime concretion

(continued)

Table 1. (Continued).

Horizon	Depth (cm)	Color (Moist)	Structure <sup>a</sup>	Consistence <sup>a</sup> (Moist)	Boundary <sup>a</sup>	Notes
<b>P5 – Aquic Haploxerepts</b>						
Ap	0–20	10YR 4/3	m1gr	mfr	gs	Many fine and medium roots
Bw1	20–45	10YR 4/4	m2abk	mfi	cs	Few to common fine roots, few fine lime powdery pockets
Bw2	45–80	10YR 4/6	m2abk	mfi	cs	Few fine roots, few fine lime powdery pockets
Cg1	80–105	10YR 5/2	m	mfi	–	Common medium distinct dark yellowish brown (10YR 4/3) mottles, few lime concretion
<b>P6 – Aquic Haploxerepts</b>						
Ap	0–25	10YR 4/4	m1abk	mfr	gs	Many fine and medium roots
Bw	25–70	10YR 5/4	f2abk	mfi	cs	Many fine roots, few fine lime powdery
BCg	70–100	10YR 4/2	f1abk	mvfi	cs	Common medium distinct dark yellowish brown (10YR 4/3) mottles
C	100–120	10YR 5/4	m	mvfi	–	–

<sup>a</sup>Symbols applied according to Soil Survey Manual, USDA. Hand book no. 18; <sup>b</sup>Profile number.



repeated cycles of sediment deposition. The presence of a significant correlation between OC and clay content ( $r = 0.48$   $p \leq 0.05$ ) reflected the fact that clay protects soil organic matter from decomposition. Accumulation of organic carbon of the soils is reflected in their structure. Weakly medium granular or moderate medium granular to weak or moderate medium angular blocky were generally found in topsoil, whereas mainly moderate fine angular blocky or moderate medium angular blocky to massive could be observed in subsoil. The soils do not show clear evidence of clay movement in the field but their structure developments, mainly as a result of high organic C, as well as development of soil color, lead to form cambic horizons (Soil Survey Staff 2006). Although the content of calcium carbonates was relatively high in these soils, only P2 met the criteria of a calcic horizon (Soil Survey Staff 2006). The active pedogenic processes which influence the degree of soil development seem to be weathering, gleization, humification, the occurrence of pedogenic Fe oxides and calcification. These processes, which are followed or coupled with the development of color and soil structure, lead to the formation of Inceptisols.

### ***Physicochemical characteristics***

In general, the soils exhibit a wide range in texture classes, including clay loam, silty loam, and loamy sand in light-texture profiles to silty clay in heavy-texture soils (Table 2). Commonly the clay content of the soils varied from 20–30% in the upper horizons, increasing through a smooth boundary into cambic horizons (Bw). However, clay skins were not observed in lower horizons. This implies that clay illuviation was absent and the higher clay value of Bw horizons is as a result of *in situ* weathering of the bedrock. The pH value was alkaline and varied from 7.5–8.3 with an average of 8.0 in all the soil profiles. All of the soils were non-saline and  $EC_e$  varied from 0.18 (P1) to 1.4 (P2)  $dS\ m^{-1}$  with a mean of 0.65  $dS\ m^{-1}$ . The CEC of the soils characterized by the type and the amount of clay minerals and organic matter, ranges from 5.2 (P6) to 14 (P3)  $cmol_c\ kg^{-1}$  with a maximum 42  $cmol_c\ kg^{-1}$  in clay fraction of Bw (P3).

### ***Distribution of minerals of soils***

The semi-quantitative estimates of relative clay minerals revealed that the minerals were almost uniform in the type but differ in the relative abundance as results of different in physiographic units (Figure 3 and Table 3,  $1\ \text{Å} = 0.1\ \text{nm}$ ). The occurrence of micaeous minerals/illite (1 nm) and chlorite (1.4 nm), as predominant clay minerals, is largely due to their inheritance from parent material (Khormali and Abtahi 2003). Smectite that is reflected by the basal *d*-spacing of 1.82 nm in the glycerol-treated samples typically was greater in Plat followed by P.P, R.A.P and C.A.P units in abundance. Transformation of micaeous minerals (illite) mainly in surface horizons, as indicated by the presence of interstratified clay minerals, and *in situ* synthesis particular mainly in Bw horizons with poor drainage, seems to be the main pathway for the formation of smectite (Khormali and Abtahi 2003). Nevertheless, inheritance origin for the occurrence of smectite in semi-arid regions such as Iran is not ruled out as was highlighted by Khormali and Abtahi (2003). The reflectance of a broad peak (2.2–2.8 nm) with glycerol salvation and its collapse to 1.0 and 1.4 nm in K-saturation and heating of 550°C treatments, respectively, exhibited the presence of randomly interstratified illite-smectite. Random powder

Table 2. Some physicochemical properties of studied profiles.

Horizon	Depth cm	Clay %	Textural Class	pH	OC CCE		CEC cmol <sub>c</sub> kg <sup>-1</sup>	EC dS m <sup>-1</sup>	Fe <sub>d</sub> g kg <sup>-1</sup>	Fe <sub>o</sub> g kg <sup>-1</sup>	Fe <sub>p</sub> g kg <sup>-1</sup>
					%	%					
P1											
Ap	0–20	20	1	7.6	0.52	18.6	9.5	0.18	6.5	3.8	1.0
Bw1	20–42	23	1	7.7	0.42	23.5	10.4	0.2	7.6	2.7	0.4
Bw2	42–75	21	1	7.9	0.31	24.4	10.1	0.4	7.8	2.5	0.0
C1	75–100	18	1	7.8	0.11	26.2	8.3	0.45	3.5	1.8	0.0
P2											
Ap	0–24	25	1	7.5	0.69	26.4	10.7	0.9	7.1	4.3	3.1
Bk1	24–50	30	c11	7.8	0.33	32.1	10.2	1.1	7.9	3.1	0.2
Bk2	50–90	27	1	8.0	0.45	38.3	9.9	1.4	8.5	2.8	0.5
BCg	90–130	21	1	8.1	0.28	45.6	10.5	1.4	4.0	2.2	0.0
P3											
Ap	0–20	23	1	7.8	1.34	25.4	13	0.35	8.9	5.1	1.6
Bw1	20–50	30	c11	8.1	0.52	26.8	13.5	0.33	11.0	4.5	1.1
Bw2	50–90	30	si11	8.0	0.61	28.2	13.2	0.65	12.2	3.9	1.2
BCg	90–130	28	c11	7.9	0.3	30.6	12.7	0.7	12.0	2.5	0.0
P4											
Ap	0–15	27	1	7.9	0.96	17.5	12.1	1.1	8.0	4.8	1.5
Bw1	15–45	31	c11	8.0	0.63	18.3	12.6	0.65	10.4	4.2	1.2
Bw2	45–80	29	c11	8.0	0.27	21.7	12.1	0.45	10.2	4.1	0.2
BCg	80–130	33	si11	8.1	0.4	19.1	9.2	0.5	6.5	3.2	0.0
P5											
Ap	0–20	22	1	7.9	1.54	16.5	9.8	0.76	7.3	5.3	2.2
Bw1	20–45	28	1	7.9	0.86	18.2	11.2	0.85	9.2	4.1	1.1
Bw2	45–70	28	c11	8.0	0.22	19.6	10.9	0.62	9.5	3.9	0.1
Cg1	70–105	8	ls	8.2	0.11	9.3	4.5	0.43	4.2	2.5	0.0
P6											
Ap	0–25	18	1	8.0	0.77	14.9	8.6	0.45	6.7	4.0	1.2
Bw	25–70	26	sil	8.2	0.56	17.8	9.7	0.69	8.4	3.8	1.1
BCg	70–100	19	sil	8.3	0.33	15	8.8	0.53	7.0	2.5	0.0
C	100–120	7	ls	8.0	0.09	9.2	4.1	0.35	3.5	2.3	0.0

OC, Organic Carbon; CCE, Calcium Carbonate Equivalent; CEC, Cation Exchange Capacity; EC, Electrical Conductivity; Fe<sub>d</sub>, citrate-bicarbonate-dithionite extraction of Fe; Fe<sub>o</sub>, acid oxalate extraction of Fe; Fe<sub>p</sub>, Na-pyrophosphate-extraction of Fe.

XRD patterns reflected the presence of quartz, feldspars, mica, chlorite, and kaolinite as the major minerals in all samples (not shown data).

Figure 4 summarizes the researcher's idea on main pathways for the formation of clay minerals in studied area. Inheritance from bedrock is the major pathway for the occurrence of chlorite, illite, interstratified mineral and kaolinite. The presence of smectite may be as a consequence of the neosynthesis from soil solution and transformation of illite. Likewise, relatively low content of this mineral in bedrock suggests that inheritance may be a minor mechanism in formation of smectite in this area (Khormali and Abtahi 2003).

### *Evolution of nature and distribution of iron compounds*

In general, soils of the study area indicated some differences in the concentrations of iron oxides and their vertical distribution within profiles (Figure 5 and Table 2) that

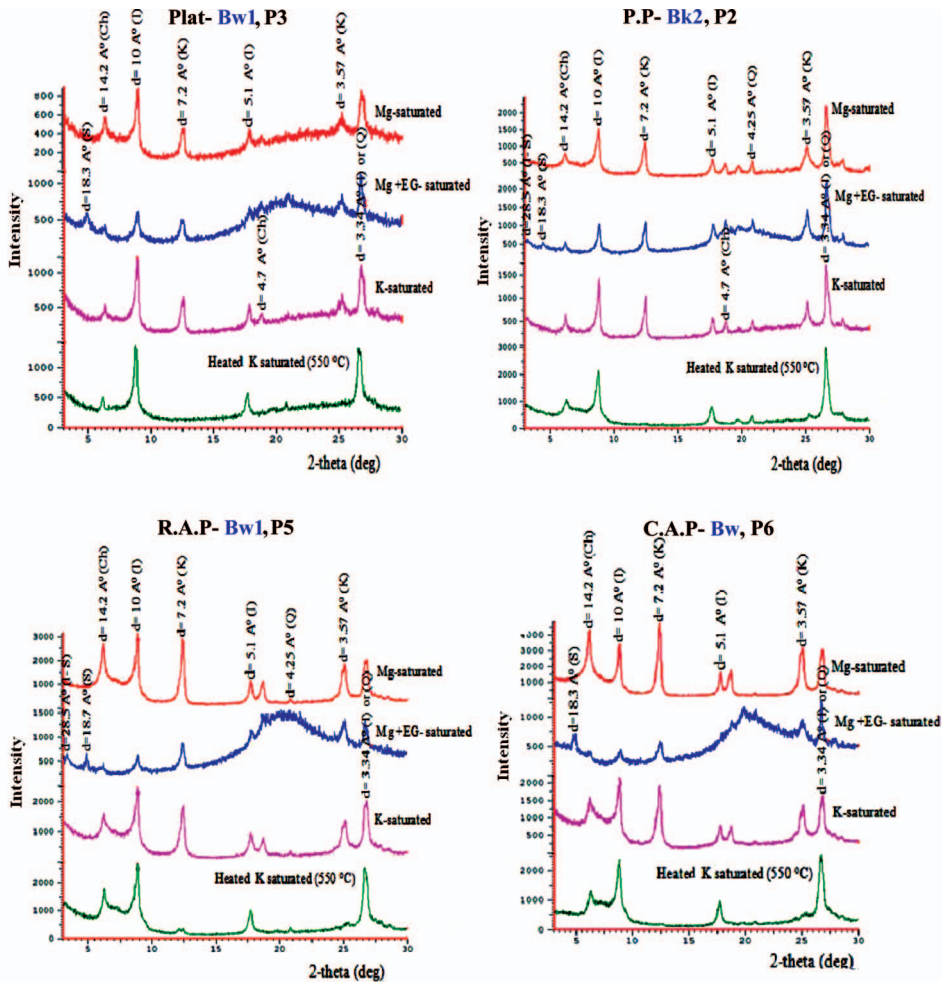


Figure 3. XRD pattern of clay from different horizons of Plat, P3 (plateau, profile 3); P.P, P2 (piedmont plain, profile 2); R.A.P, P5 (river alluvial plain, profile 5); C.A.P, P6 (colluvial alluvial plain, profile 6); Ch, chlorite; I, illite (micaeous minerals); S, smectite; K, kaolinite; Q, quartz; Is, interstratified mineral. 1 Å = 0.1 nm.

might be related to the degree of weathering, pedogenic accumulation, seasonal fluctuations in water table, and organic matter. Tite and Linington (1975) have suggested that environmental conditions, such as distinct wetting-drying cycles and associated alternation among reduction-oxidation, provide the best conditions for the pedogenic formation of iron oxides in Mediterranean climates such as those of the soils being studied. The values of  $Fe_d$  in these soils were commonly quite low, ranging between 3 and 12 g kg<sup>-1</sup>, reflecting low weathering of primary Fe-bearing minerals and formation of Fe oxides. Similar results have been reported for soils with Mediterranean climate (Singer 1977; Pena and Torrent 1984). The vertical distribution of  $Fe_d$  indicated an increasing trend towards the lower B horizons and the largest amount of  $Fe_d$  was associated with cambic horizons. This pattern may be explained in two ways: The first interpretation is related to the high rate of *in situ* weathering, as a result of wetting-drying cycle and activity of roots, and the great

presence of micaceous minerals at B horizons (Table 3). The occurrence of high rates of mica (illite) along with parallel increase of  $Fe_d$  in Bw horizons suggests that large amount of  $Fe_d$  are released from micaceous minerals by weathering. Aniku and Singer (1990) indicated that high  $Fe_d$  value (reflected in increase of  $Fe_d/Fe_{total}$  ratio) was a result of the progressive transformation of silicate-bound Fe into Fe oxides. However, the presence of partial swelling of chlorite after glycerolation (Figure 3) suggests that the release of some Fe from chlorite could also be possible. According to the second interpretation, the accumulation of  $Fe_d$  in subsurface horizons can be attributed to migration of iron oxide-coated clay from upper to lower horizons. The determination of association of  $Fe_d$  with translocation of clay fraction was calculated by the  $Fe_d/clay$  ratio (Blume and Schwertmann 1969; Rebertus and Buol 1985). With the exception of P1, this ratio increased from soil surface to lower solum in all of the profiles (Figure 5). Accordingly, the high proportion of  $Fe_d$  is independent of clay fraction; therefore, most of its content is a product of *in situ* pedogenic processes and seems not necessarily to be the redeposition of clay with  $Fe_d$ . Additionally, lack of evidence of clay movement within the profiles along with the weak relationship of  $Fe_d$  and clay ( $R^2 = 0.34$ ,  $p < 0.01$ ) supports this assessment. Within the soils with more restricted drainage, exhibiting typically Fe depletion processes with repeated cycles of wet and dry as distinctive grey zones and mottles in subsoil (P3, P4 and P5), horizons of Bw had higher concentration of  $Fe_d$  as well as greater part of Fe oxides in the crystalline form ( $Fe_{cryst.}$ ). These results suggest the degree of more development of those soils in comparison with other soils because  $Fe_d$  provides an estimate of the total pedogenic Fe (Blume and Schwertmann 1969; Birkeland 1999).

Table 3. Relative abundance of clay minerals and CEC of clay fraction for selected studied soils.<sup>a</sup>

Profile	Horizon	Ch	Il	Sm	Ka	Q	Is	CEC of clay cmol <sub>c</sub> kg <sup>-1</sup>
		%						
1	Ap	20.0	26	11	31	12	–	28.0
1	Bw1	17.0	30	12.0	29	12	–	30.5
1	C1	20.0	35	Tr	31	13	–	21.0
2	Ap	19.0	20	13.5	30	13	<5	25.0
2	Bk2	14.0	27	9.0	28	17	<5	26.5
2	Cg	18.0	34	Tr	30	17	–	20.5
3	Ap	13.0	23	19.2	26	10	<10	35.0
3	Bw1	10.5	28	22.5	24	10	<5	41.8
3	BC	15.5	36	8.0	27	12	tr	28.5
4	Ap	17.5	23	12.0	32	11	<5	32.0
4	Bw2	12.5	25	18.0	28	15	tr	36.9
4	BCg	18.0	32	<5	33	13	–	22.2
5	Ap	16.0	24	10.0	35	11	<5	28.5
5	Bw1	13.0	26	15.0	29	9	<10	34.2
5	Cg	20.0	34	<5	29	12	tr	15.5
6	Ap	16.0	31	8.0	27	15	<5	27.0
6	Bw	11.0	27	14.0	28	18	tr	32.1
6	BCg	15.0	35	<5	29	18	–	23.0
6	C	18.0	39	–	32	11	–	14.0

<sup>a</sup>Ch, chlorite; Il, illite (micaceous minerals); Sm, smectite; Ka, kaolinite; Q, quartz; Is, Interstratified minerals.

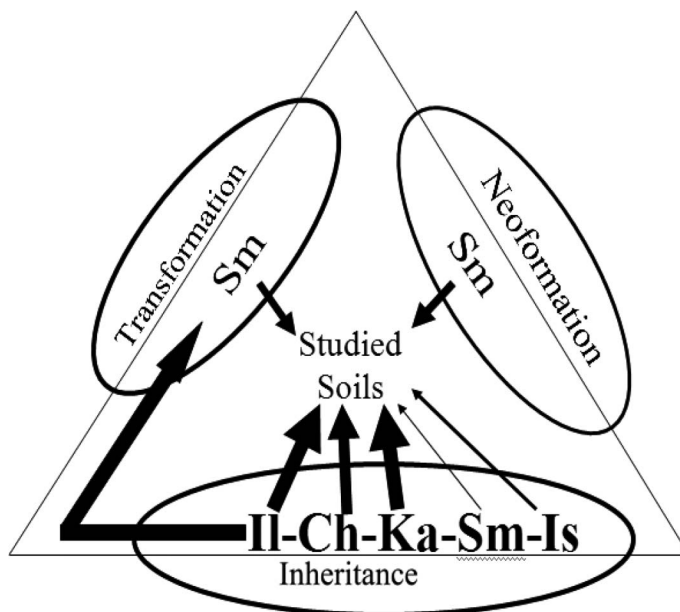


Figure 4. Main scheme for the formation of clay minerals in studied profiles. The thickness of arrows exhibits the importance of the scheme. II = illite; Ch = chlorite; Sm = smectite; Ka = kaolinite; Is = interstratified minerals.

The vertical distribution pattern of oxalate extractable Fe ( $Fe_o$ ) and part of Fe oxides in organic-complex form as  $Fe_p$  showed a decreasing trend with depth (Figure 5). Within the profiles of P3, P4 and P5, where the anaerobic conditions were more prevalent than other soils, the amount of  $Fe_o$  was greater. This is probably attributed to a great extent by the change of oxidation-reduction conditions in these zones (Schwertmann and Taylor 1989). The  $Fe_o$  content ranged from 1.8–5.3 g kg<sup>-1</sup>. The presence of a considerable amount of organic matter in the topsoils and some decline in content of  $Fe_o$  with depth revealed that the proportion of  $Fe_o$  forms complexes with organic matter, especially in A<sub>p</sub> horizons. This was confirmed by the high significant relationship of  $Fe_p$  and organic carbon content ( $R^2 = 0.61$ ,  $p < 0.001$ ).

The  $Fe_o/Fe_d$  ratio, as active Fe ratio, almost varied in all soils (Figure 5). Several authors (Schwertmann and Taylor 1989; Thomas and Munn 1991; Singer et al. 1998) remarked that the amount of pedogenic iron oxides and their crystallinity were increased with an increase in weathering rate and soil age leading to a decline in the pattern of the  $Fe_o/Fe_d$  ratio, while higher active Fe ratio typically associated with a lower amount of secondary Fe oxides in the crystalline form. As is shown in Figure 5, the  $Fe_o/Fe_d$  ratio generally was high for A horizons than B horizons, which may be interpreted as follows: Firstly, organic matter impeded crystallization of Fe oxides in surface horizons, as represented by Schwertmann and Taylor (1989). For example, P5 with the highest organic matter as a key for inhibition of crystallization of Fe oxides exhibited the highest  $Fe_o/Fe_d$  ratio. This assertion was highlighted by evidence from Blume and Schwertmann (1969), who suggested that the crystallization of amorphous Fe oxides might be promoted by low organic matter content, and their ageing speeded up by relatively high pH. Secondly, the occurrence of frequent

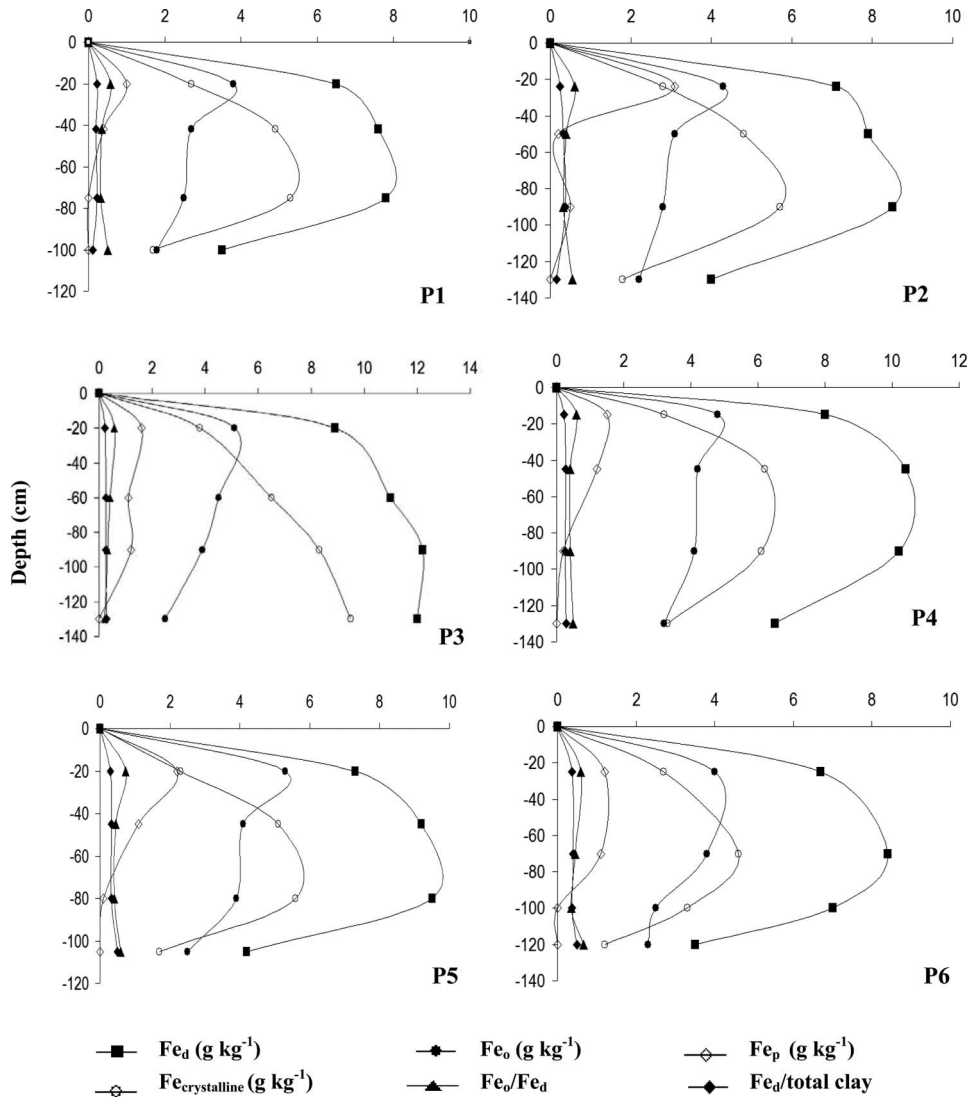


Figure 5. Distribution of iron forms with depth in studied profiles.

wetting-drying cycles along with high content of micaceous minerals in lower solum (with exception of P1), followed by *in situ* weathering, exhibited a larger proportion of crystalline Fe minerals that is reflected by a decrease in the  $\text{Fe}_o/\text{Fe}_d$  ratio. In the Bw2 horizon of P3 that shows the least active Fe ratio (0.25) and the greatest  $\text{Fe}_{\text{crys.}}$  ( $9.5 \text{ g kg}^{-1}$ ) presented suitable condition for the formation of secondary Fe oxides: low organic matter, relative high pH and micaceous minerals, distinctive wetting-drying cycles, alternative oxidation-reduction and suitable *in situ* weathering. Schwertmann and Kämpf (1983) observed that crystalline iron forms are widely distributed in all climatic conditions and prevail in alternating reducing and oxidizing environments similar to that in the area in the current study. With the exception of P3, an increase of active Fe ratio underlying the B horizons (which are widely associated

with redoximorphic features), followed by the same pattern of  $Fe_o$  suggests that poorly crystalline iron oxides are more abundant in these zones (Kämpf et al. 1999). The poor crystalline Fe oxides in these soils were likely ferrihydrite and ferrihydritelike minerals, common iron oxides in soils with restricted drainage under repeated cycles of oxidation-reduction (Pattil and Dasog 1997; Kämpf et al. 1999).

Some authors (McKeague and Day 1966; Moore 1973) employed the active Fe ratio to recognize well-drained from poorly drained soils; soils containing ratio of more than 0.35 were classified as well-drained, while poorly drained soils have content less than 0.35. In this study, this interpretation cannot separate well-drained soils from their poorly drained counterparts, which is according to Oguniola et al. (1989).

Correlation coefficients ( $r$ ) among iron forms, clay and organic-C are given in Table 4. As can be seen,  $Fe_d$  showed positive correlation with  $Fe_{crist.}$  and negative correlation with  $Fe_o/Fe_d$  ratio, which is consistent with the findings of other workers (Blume and Schwertmann 1969; Oguniola et al. 1989; Kämpf et al. 1999). The recorded correlation between  $Fe_d$  and  $Fe_o$  may have implied that both are characterized by the similar pedological processes or both extracts remove essentially the same form of iron (Oguniola et al. 1989). There was also positive significant correlation between  $Fe_o$  and  $Fe_d$  forms and clay content. The trend may be corroborated by the fact that the release and synthesis rate of  $Fe_o$  and  $Fe_d$  are associated with clay synthesis. The high rate of  $Fe_o$  and mainly  $Fe_d$  occur in horizons with high synthesis in clay and micaceous minerals. Indeed,  $Fe_d$  was generally found in close association with clay and micaceous minerals that is in agreement with others (Stolt et al. 1993). Statistical analysis showed (Figure 6) that  $Fe_d$  content of the soil containing less clay (15–25%) was significantly different from those with greater clay (25–35%) and this may confirm the results reported by Stolt et al. (1993) and Igwe et al. (2005). He and Tang (2008) described that increasing trend of soil clay in Sichuan China could be attributed to the fast weathering of Fe-rich biotite during the early stages of weathering. In spite of an increase in the content of  $Fe_o$  in soils with more clay (25–35%) in comparisons with lesser clay (15–25%), this increase was not significant (Figure 6).

In respect of the fact that the  $Fe_d$  and  $Fe_o/Fe_d$  ratios are useful indicators in the relative estimate of the degree of soil development (Blume and Schwertmann 1969; Oguniola et al. 1989; Tsai et al. 2006), we applied  $Fe_d$  and active Fe ratio along with CEC/clay and smectite/illite + chlorite ratio (S/I + Ch) as aids in determining the relative degree of development of subsurface horizons (Table 5). Accordingly, the

Table 4. Correlation coefficients for linear relationships between iron oxides forms, clay content and organic carbon.

	$Fe_o$	$Fe_d$	$Fe_o/Fe_d$	$Fe_p$	$Fe_{crist.}$	Clay
$Fe_o$						
$Fe_d$	0.49*					
$Fe_o/Fe_d$	0.33	0.63**				
$Fe_p$	0.63**	-0.26	0.71**			
$Fe_{crist.}$	0.13	0.92**	-0.84**	-0.5*		
Clay	0.63**	0.59**	-0.09	0.43	0.39	
OC	0.8**	0.26	0.4	0.64**	-0.04	0.48*

\* and \*\*, significant at the 0.05 and 0.01 levels, respectively.

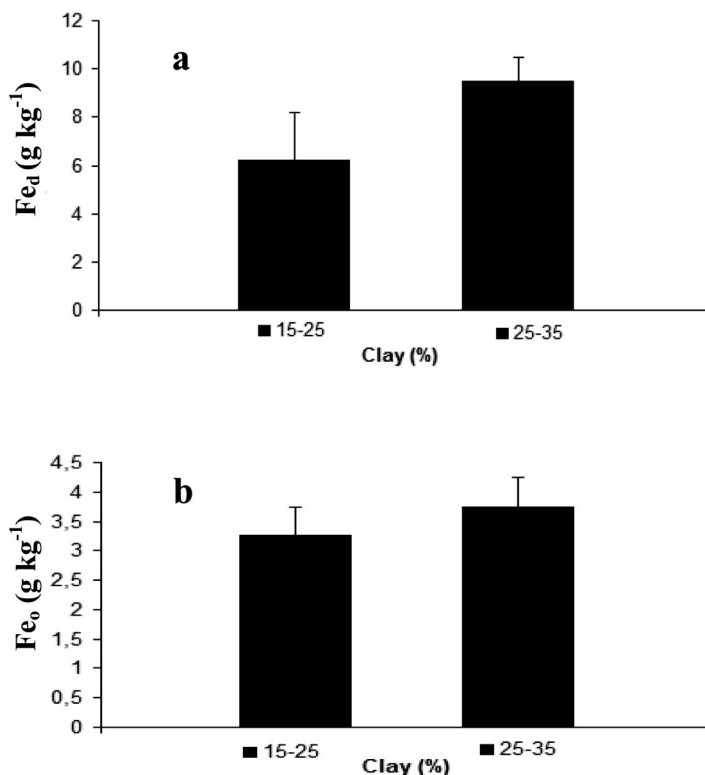


Figure 6. Analysis of variance of (a) mean  $Fe_d$  and (b)  $Fe_o$  content of soils with different amounts of clay.

Table 5. Smectite/illite + chlorite ratio, free iron, active Fe ratio and CEC of clay for selected studied soils.

Profile	Horizon	S/I + Ch <sup>a</sup>	$Fe_d$ <sup>b</sup>	$Fe_o/Fe_d$ <sup>c</sup>	CEC of clay $cmol_c\ kg^{-1}$
1	Bw1	0.25	7.6	0.36	30.5
2	Bk2	0.22	8.5	0.39	26.5
3	Bw1	0.57	11.0	0.25	41.8
4	Bw2	0.48	10.2	0.40	36.9
5	Bw1	0.38	9.5	0.45	34.2
6	Bw	0.37	8.4	0.45	32.1

<sup>a</sup>Smectite/illite + chlorite ratio; <sup>b</sup>Free iron; <sup>c</sup>Active Fe ratio.

degree of development of cambic horizons as well as the development degree of studied soils can be ranked in the following order: P3 > P4 > P5 > P6 > P1.

#### *Iron oxides forms and physiographic units*

The soils studied were divided into two groups with regard to the relationship between  $Fe_d$  and physiographic units: First group Plat unit and the second group consisting of P.P, R.A.P and C.A.P units. Differences in  $Fe_d$  form and clay content



Table 6. Grouping of studied soils in physiographic units according to different forms of Fe oxides, clay content and OC.

	Plat.	P.P	R.A.P	C.A.P
Fe <sub>o</sub> (g kg <sup>-1</sup> )	4.03 <sup>a</sup>	3.1 <sup>a</sup>	3.95 <sup>a</sup>	2.92 <sup>a</sup>
Fe <sub>d</sub> (g kg <sup>-1</sup> )	9.88 <sup>a</sup>	6.87 <sup>b</sup>	7.55 <sup>ab</sup>	6.37 <sup>b</sup>
Fe <sub>p</sub> (g kg <sup>-1</sup> )	0.85 <sup>a</sup>	0.95 <sup>a</sup>	0.85 <sup>a</sup>	0.46 <sup>a</sup>
Clay (%)	28.88 <sup>a</sup>	25.75 <sup>ab</sup>	21.5 <sup>ab</sup>	18.38 <sup>b</sup>
OC (%)	0.61 <sup>a</sup>	0.43 <sup>a</sup>	0.68 <sup>a</sup>	0.38 <sup>a</sup>

Plat. = plateau; P.P = piedmont plain; R.A.P = river alluvial plain; C.A.P = colluvial alluvial plain; Fe<sub>d</sub> = citrate-bicarbonate-dithionite extraction of Fe; Fe<sub>o</sub> = acid oxalate extraction of Fe; Fe<sub>p</sub> = Na-pyrophosphate-extraction of Fe; OC = organic carbon; Mean followed by the same small of capital letter in each row are not significantly different by Duncan's test ( $p \leq 0.05$ ).

were present in greater amount in Plat unit than in the other physiographic units (Table 6). These differences may be due to the diversity of degree of soil development or weathering rate, reflecting in clay percentage and type of clay minerals, variation in stability geomorphologic condition and pedogenic processes as well as variability in abundance of micaceous minerals. Igwe et al. (2005) reported that the dominance of Fe<sub>d</sub> over Fe<sub>o</sub> may have been due to the age of these soils or the age of the sediments in which these soils formed. In the Plat unit, the presence of the most stability geomorphologic condition and highest rate of weathering was confirmed by the highest content of smectite and S/I + Ch ratio coupled with minor deposition of sediments, leading to significant different in its Fe<sub>d</sub> content in comparison with other units. Despite 28% apparent differences between Plat and C.A.P units, there was no significant differences among Plat, P.P, R.A.P and C.A.P units with respect to Fe<sub>o</sub> content (Table 6). There also was no significant difference between physiographic units with respect to Fe<sub>p</sub> and OC content. As stated earlier, Fe<sub>p</sub> fraction is function of OC; therefore, similarity in distribution of OC between physiographic units can be responsible for the insignificant different in Fe<sub>p</sub> content of these soils.

## Conclusion

Variation in weathering of primary Fe-bearing minerals, geomorphologic conditions, and pedogenic processes (as results of diversity in physiographic units) resulted from a noticeable difference in contents, forms, and distribution of pedogenic Fe oxides. The presence of the highest Fe<sub>d</sub> content, clay content, S/I + Ch ratio and the lowest Fe<sub>o</sub>/Fe<sub>d</sub> ratio in Plat unit suggested dynamic conditions in this unit in comparison with other units and were matured irrespective of the presence of sediment deposition. Whereas, in R.A.P and C.A.P units which are subject to episodes of sediment deposition, transformation of recent sediments from the Nazlo river and upland to the units explain the occurrence of incipient weathering products such as increase of poorly crystalline Fe minerals, and high rate of Fe<sub>o</sub>/Fe<sub>d</sub> ratio as well as the abundance of clay mineral inheritance such as kaolinite and chlorite. The synthesis of pedogenic Fe oxides in conjunction with the occurrence of smectite, as results of *in situ* synthesis and micaceous minerals weathering, showed that chemical weathering, and in particular *in situ* chemical weathering, is one of the most important agents of pedogenesis in studied soils. Those processes, coupled with the wetting-drying cycle and humification process, had created differences in solum

thicknesses, colors, structure, and distribution of iron oxides, so that cambic horizons have formed with diversity degrees of development. Because of the presence of fluventic properties, an important criterion in soil taxonomy (Soil Survey Staff 2006), new subgroups Haploxerepts and Calcixerepts are suggested for inclusion in soil taxonomy: (i) Fluventic Calcixerepts for Calcixerepts that have fluventic origin (pedon 2), and (ii) Fluventic Humic Haploxerepts for Haploxerepts that have both fluventic and humic properties (pedon 3).

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