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Iron oxides forms quantification in relation with soil genesis in soil parent materials

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Abstract

Soil of iron oxides forms are important parameters for the proper understanding of soil genesis. Triplicate soil profiles were selected at three different development stages in each of loess, alluvium, shale residuum, and sandstone residuum. It hypothesized that iron oxides forms differed with soil parent material, soil genesis causes redistribution of iron oxides phases in profile within a parent material. The objectives of this study were to quantify various Fe oxide forms in selected parent materials and their relationship with soil genesis within a parent material. Beside, basic analysis, each soil sample was characterized for free iron oxides, amorphous and crystalline iron oxides. The shale derived soils had higher dithionite extractable as well as crystalline iron oxides followed by alluvium, loess and sandstone derived soils. The study concludes that the iron oxides forms vary with the soil parent material and soil genesis results in an increase in crystalline iron oxides with soil development.

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Introduction

Iron (Fe) oxides are naturally occur as goethite, hematite, lepidocrocite and ferrihydrite minerals in soils and sediments (Cornell and Schwertmann, 1996) and directly affect adsorption of plant nutrients (Hinsinger, 2001; Yuji and Sparks, 2001) and contaminants retention (McBride, 1994). Iron oxides presence in soil serves as important parameters in understanding development which influence soil properties. Iron oxides interact strongly with plant nutrients, especially phosphorus *via* ligand exchange and anion exchange and adsorbed in the form of a bidentate complex (Rhoton and Bigham, 2005). Physical behavior of iron oxides is size and crystallography dependant (Guyodo and Valet, 1999). Among iron oxides, ferrihydrite, is poorly ordered mineral and have a specific surface area up to 700 m² g⁻¹ (Jambor and Dutrizac, 1998; Cornell and Schwertmann, 2003). Nutrient adsorption, especially of phosphorus is related to the surface area of ferrihydrite (Rhoton and Bigham 2005; Mehmood *et al.*, 2015). The lepidocrocite (iron oxyhydroxides) has lower surface area than ferrihydrite and low adsorption capacity. The specific surface area of lepidocrocite may be up to 260 m² g⁻¹ (Cornell and Schwertmann, 2003). Hematite (iron oxide) is highly crystalline mineral with very low surface area ranges from 10 to 90 m² g⁻¹ (Cornell and Schwertmann, 2003).

The origin of free iron oxides in soils is due release of iron from rock weathering (Walker, 1983). Free iron oxides then precipitated as poorly crystalline ferrihydrite followed by formation highly crystalline hematite/goethite (Mehmood, 2014). Iron oxides are usually identified using X-Ray diffraction technique but iron oxides in calcareous soils are minor fraction of soil mineral. Differential thermal analysis, infrared, transmission electron microscopy examination of silicate clays minerals also produce sharper peaks and shapes of minerals which help in their identification. Several methods have been proposed for the removal of free iron oxides. The most widely used methods are the ammonium oxalate method and reduction of

ferric by dithionate. The dithionate-citrate-bicarbonate (Fed) extracts organic matter iron oxide plus the non-crystalline oxides and finely crystalline oxides. The ammonium oxalate extraction method (Feo) extracts the organic matter iron oxides and the non-crystalline iron oxides in the soil. From the above statement, the amount of (Fed) extracted should be equal to or greater than the amount of (Feo). The differences between the dithionite extractable and oxalate extractable Fe represents the amount of iron present in definite crystalline forms (Mehmood *et al.*, 2010; Akinbola *et al.*, 2013).

Indus River tributaries alluvium, loess deposits, and residuum of sandstone and shale are the four morphological units that host 90 % soils of Pothwar plateau (Pakistan). These morphological units can be taken as different soil parent materials as different source rocks, having variation in mineralogy, have contributed sediments for soil formation (Mian and Syal, 1985; Mehmood, 2014). Much of the work has been done either on synthetic samples or on acidic soils, which have more Fe oxide as compared to calcareous soils. It hypothesized that different parent materials and different iron oxides content and within a parent material soil genesis control iron oxide distribution in soil profile. The objectives of this study were to quantify various Fe oxide phases in selected parent materials and their relationship with soil genesis within a parent material.

Materials and methods

Site and Soil Description

Soils were taken from the Pothwar area having different parent material at different stages of development. In loess soils weathering depends on the toposequence, soils on level plains are more weathered than the soils on slopes and loess deposited during Late Pleistocene period. The Chakwal series consist of deep, well-drained, non-calcareous, moderately fine to fine texture soil with structural B horizon, occupies very gently sloping sites to level loess plains in a sub-humid subtropical continental climate. The Rawalpindi series consist of

moderately deep, well-drained, calcareous, fine texture soil with structural B horizon, occupies level to nearly level to gently sloping Sub-recent erosional surfaces in level loess plains while the Rajar is least weathered soil with no cambic B horizon (Gullied land). Alluvial soils development depends upon the time of deposition. The Gujranwala soil is fine textured, non-calcareous and is developed in mixed calcareous clayey alluvium derived from Himalayas and deposited probably during the late Pleistocene period, and the Argan soil is calcareous medium textured developed in mixed alluvium derived from Himalayas and Pothwar uplands during sub recent epoch while the Shahdra is calcareous, coarse textured soils formed in Recent mixed alluvium derived from Himalayas. Among residual soils, residuum which may be sandstone derived (Siwalik formation in Pliocene period) or shale admixture of sandstone derived (Muree formation in Miocene period). In Siwalik sandstone, the Kahuta series consist of very deep, well-drained, non-calcareous, moderately fine and medium texture soil with argillic B horizon. It is developed in material derived from underlying tertiary sandstones, the Balkasar soil is moderately fine textured, calcareous developed in calcareous, white and grey residual materials derived from lower and middle Siwalik sandstone and the Qazian soil is developed in lower and middle Siwalik white and grey sandstone with no B horizon. In Murree formation, the Murree soil is developed in red Murree's shale with admixture of sandstone and is decalcified due to high rainfall, the Tirnul soil is also developed in red Murree's shale which is calcareous soil which shows is less developed from the Murree soil, and the Ghoragali soil less weathered, with no cambic B horizon.

Soil Sampling

Triplicate soil profiles at three different stages of development in each of loess alluvium, residuum derived from shale, and residuum derived from sandstone were taken (Table 1). At each site soil profile was exposed and described. Soil samples were taken from each genetic horizon of each profile. The

samples were air dried and pass through 2 mm sieve.

Iron Oxides Phases

Total extractable Fe including crystalline and amorphous iron oxides were determined for each soil sample by extracting soil Fe and Al in $C_6H_5Na_3O_4 \cdot 2H_2O$, $NaHCO_3$ and $Na_2S_2O_4$ (Mehra and Jackson, 1960). One g soil was added to 40 mL of 0.3 M $C_6H_5Na_3O_4 \cdot 2H_2O$ solution in 50 mL centrifuge tubes, and 5 mL of 1 M $NaHCO_3$ solution was added. The soil suspension was heated at 80 °C adding 1 g $Na_2S_2O_4$. Soil suspension was centrifuged for 30 mins at 3000 rpm. Amorphous Fe was determined for each soil sample by extracting soil in acidified $(NH_4)_2C_2O_4 \cdot H_2O$ solution (Jackson *et al.*, 1986). The 0.25 g soil was added in 10 mL of 0.2 M acidified $(NH_4)_2C_2O_4 \cdot H_2O$ solution in 50 mL centrifuge tubes, shaken for 4 h on an end to end shaker and centrifuged for 30 min at 3000 rpm. Iron concentration in the extract was determined by Atomic Absorption Spectrometer (AAS) using air-C₂H₂ flame. The crystalline iron oxides content was calculated by subtracting amorphous iron from dithionite extractable iron.

Statistical Analysis

The variance in the iron oxides phases at horizons level was analyzed using multivariate analysis of variance (MANOVA) in GLM procedure of SAS version 9.4 (SAS Institute, 2014). Class variable was 'parent material' and the measurements at various depths were multiple dependent variables.

Results and discussion

Soil Characteristics

The salient morphological features observed in the field including soil color, texture, pH and calcium carbonate are presented in Table 2 and 3. Most soils were dark brown to yellowish brown in color except that the shale derived soils being reddish to reddish brown. The young soils were calcareous without a zone of lime accumulation while soils at relatively higher development stage were decalcified to variable depths with a distinct zone of lime accumulation.

Most soils had pH greater than 7.0, and the surface of relatively highly developed soil had low pH while the young soils had uniform pH throughout the profile depth.

Table 1. Selected soils with USDA soil classification in selected parent materials.

Parent Material	Soil Series	USDA Soil Classification
Alluvium	Shahdra	Typic Ustifluvents
	Argan	Fluventic Haplustepts
	Gujranwala	Typic Haplustalfs
Loess	Rajar	Typic Ustorthents
	Rawalpindi	Udic Haplustepts
	Chakwal	Typic Haplustafls
Sandstone	Qazian	Lithic Ustipsamments
	Balkassar	Typic Haplustalfs
	Kahuta	Udic Haplustalfs
Shale	Ghoragalli	Typic udorthents
	Tirnul	Typic Haplustepts
	Murree	Typic Hapludolls

Table 2. Salient characteristics of soils developed in alluvial and loess soils.

PM@	Soil series	Description of salient features
Alluvium	Shahdra	Dark yellowish brown* (10YR 4/4), silt loam, calcareous, pH 7.6 surface, and yellowish brown (10YR 4/6), silt loam to loamy sand, calcareous, pH 8.0 subsurface, with frequent lithological discontinuity.
	Argan	Dark brown (10YR4/3), silt loam, calcareous, pH 7.7 surface and dark brown (10YR4/3), silty clay loam to sandy loam, calcareous, pH 7.8 subsurface, soft Mn concretions, with lithological discontinuity.
	Gujranwala	Dark yellowish brown (10YR 4/4), loam to sandy loam, noncalcareous, pH 7.3 surface and dark brown (10YR4/3), clay loam, clay cutanes on ped surfaces, noncalcareous, pH 8.0 subsurface.
Loess	Rajar	Yellowish brown (10YR 5/4), silt loam, strongly calcareous, pH 7.9 surface, and yellowish brown (10YR 5/4), silt loam strongly calcareous, pH 8.2 subsurface
	Rawalpindi	Dark yellowish brown (10YR4/4), silt loam, noncalcareous, pH 7.1 surface and dark yellowish brown (10YR4/4), silty clay loam to silt loam, yellow iron oxides mottles, calcareous, pH 7.8 subsurface.
	Chakwal	Dark brown (10YR4/3), silt clay loam, noncalcareous, pH 7.5 surface and dark brown (10YR4/3), silty clay to silt loam, slightly to strongly calcareous with CaCO ₃ mycelia, pH 7.8 subsurface.

Table 3. Salient characteristics of soils developed in shale and sandstone derived soils.

PM@	Soil series	Description of salient features
Shale	Ghoragali	Dark brown (7.5 YR 3/3), silt loam to silty clay loam, strongly calcareous, pH 7.2 surface and dark reddish brown (7.5 YR 4/4), silty clay loam to silty clay, calcareous, pH 7.6 subsurface.
	Tirnul	Reddish brown (7.5 YR 4/6), loam to clay loam, calcareous, pH 7.6 surface and dark reddish brown (7.5 YR 4/6), silty clay loam to silty clay, calcareous, pH 7.9 subsurface.
	Murree	Dark brown (7.5 YR 3/3), sandy loam to silty clay loam, noncalcareous, pH 6.5 surface and dark reddish brown (5YR 4/4), silty clay loam to clay, noncalcareous to calcareous, pH 7.5 subsurface.
Sandstone	Qazian	Dark yellowish brown (10YR 4/4), sandy loam, calcareous, pH 7.6 surface and light olive brown (5Y 6/4), sandy loam to loamy sand, calcareous, pH 7.7 subsurface.
	Balkassar	Dark brown (10YR4/3), sandy loam to sandy clay loam, noncalcareous, pH 7.6 surface and dark brown (10YR4/3), clay loam to silty clay, slightly calcareous to calcareous, pH 8.0 subsurface.
	Kahuta	Dark brown (10YR 4/3), sandy loam to sandy clay loam, noncalcareous, pH 6.9 surface and dark brown (10YR 4/3) sandy loam to clay loam, slightly calcareous to calcareous, pH 7.7 subsurface.

*Moist soil color was recorded; @ parent material; sequence of soils under parent material is from soil at early stage of development to soils at relatively higher stage of development

Iron Oxides Distribution

The vertical distribution pattern of dithionite extractable iron (Fe_d), which includes amorphous and

crystalline iron oxides, in profile varied with parent material as the hypothesis of non-significant depth × PM effect was rejected through MANOVA test criteria

Wilks' λ ($p \geq 0.05$), and the difference remained statistically significant ($p \geq 0.05$) at most of the horizons level (Fig. 1c). Shale derived soils had significantly higher Fe_a followed by the group of soils derived from alluvium, loess and sandstone. High Fe_a content in shale derived soils is due to lithogenic

hematite (Memon *et al.*, 2009; Mehmood *et al.*, 2015). Memon *et al.* (2009) also reported higher Fe_d content in alluvial soils than sandstone derived soils. Dithionite extractable iron content also increased with soil development in all the soil parent materials (Fig. 2).

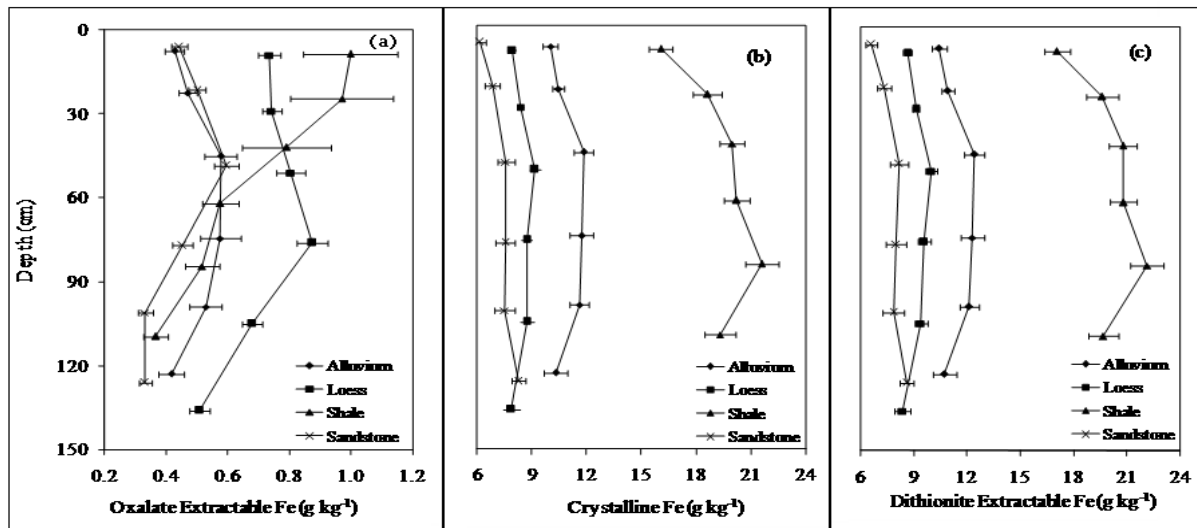


Fig. 1. Iron distribution variation with soil depth in parent materials: (a) Distribution of amorphous iron oxides, (b) distribution of crystalline iron oxides and (c) distribution of dithionite extractable iron oxides, error bars show one standard error.

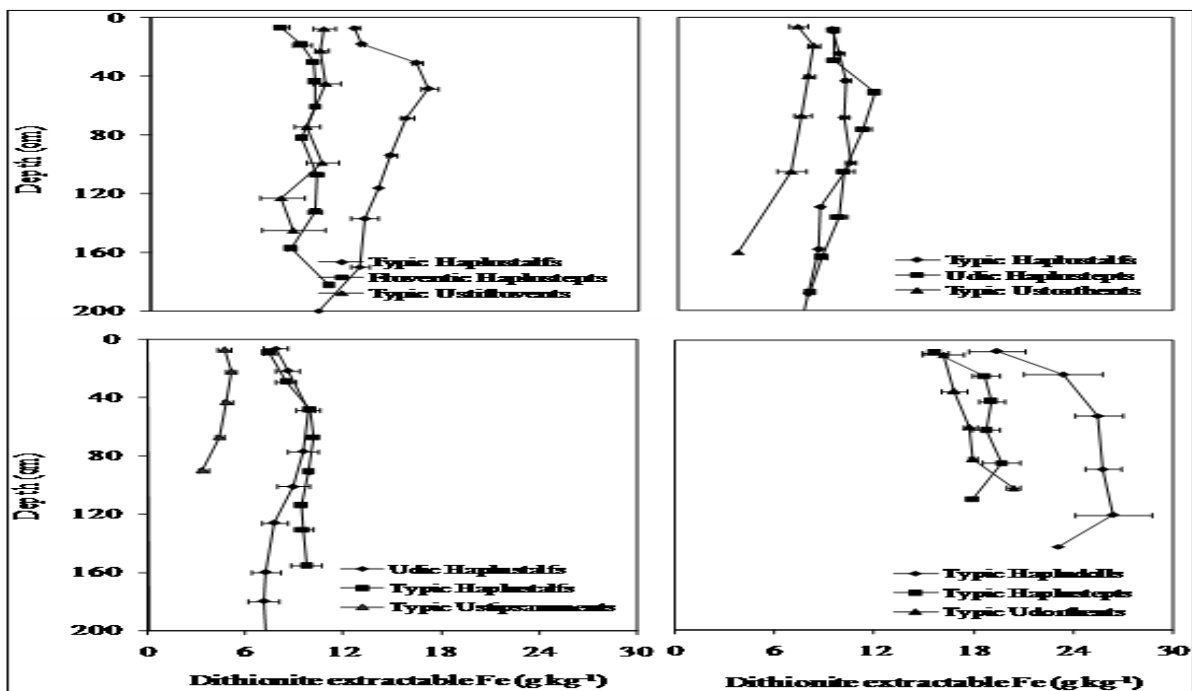


Fig. 2. Dithionite extractable iron distribution the soil series at different level of development separately in each parent material: (a) alluvium, (b) loess, (c) sandstone, and (d) shale, (Mean $n = 3$ and error bars show one standard error).

The Fe_d content increased with soil development was due to release of iron from primary mineral. High Fe_d content at Bt horizon level was due to weathering at surface releases iron which leached down and accumulate at Bt horizon level. Dithionite extractable iron accumulated in Bt horizon of soils relatively at

higher stage of development while uniformly distributed in young soils. Dithionite extractable iron correlated significantly with Fe_o ($r = 0.42$) as amorphous iron oxides is the fraction of dithionite extractable iron (Memon, 2008).

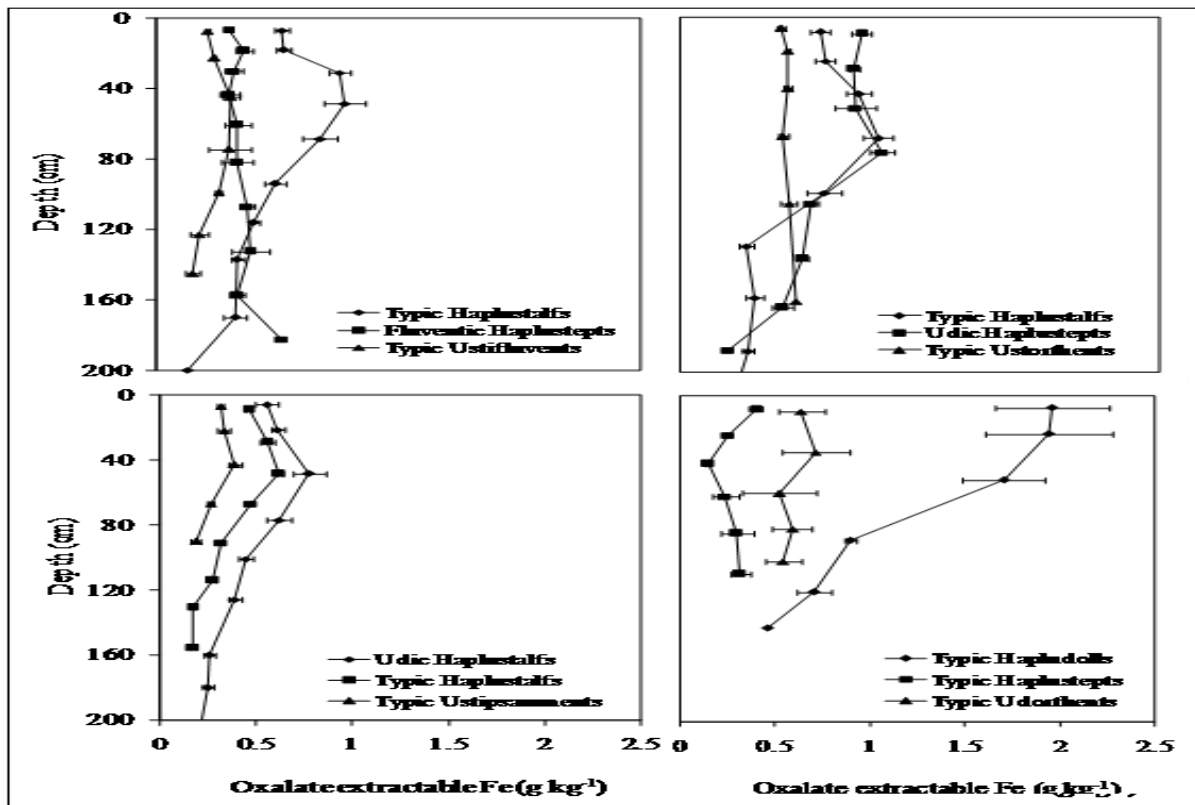


Fig. 3. Oxalate extractable iron distribution the soil series at different level of development separately in each parent material: (a) alluvium, (b) loess, (c) sandstone, and (d) shale, (Mean $n = 3$ and error bars show one standard error).

The vertical distribution pattern of oxalate extractable iron (Fe_d) represents the amorphous iron oxides and Fe_o in soil profile also varied with parent material as the hypothesis of non-significant depth \times PM effect was rejected through MANOVA test criteria Wilks' λ ($p \geq 0.05$), and the difference remained statistically significant ($p \geq 0.05$) at most of the horizons level (Fig. 1c). Amorphous iron oxides at surface of shale derived soils was higher may be attributed to high rainfall which restrict iron oxides crystallization and low concentration at lower depth may be due to restricted leaching of clayey material (Mehmood, 2014). Amorphous iron oxides increased with soil

development in each parent material (Fig. 3). Soils at relatively higher stage of development had high Fe_o due to weathering and increased towards surface when averaged over soil parent materials and development stages. Oxalate extractable iron was accumulated at Bt horizon level in soils at relatively higher stage of development in all parent materials except shale derived Murree soil series. Impeded infiltration of water due to clayey texture of shale, the iron oxide leaching is minimal (Jenny, 1941). Oxalate extractable iron correlated significantly with soil pH ($r = -0.65$) as amorphous iron oxides are common under humid conditions which result in decrease in pH due to decalcification.

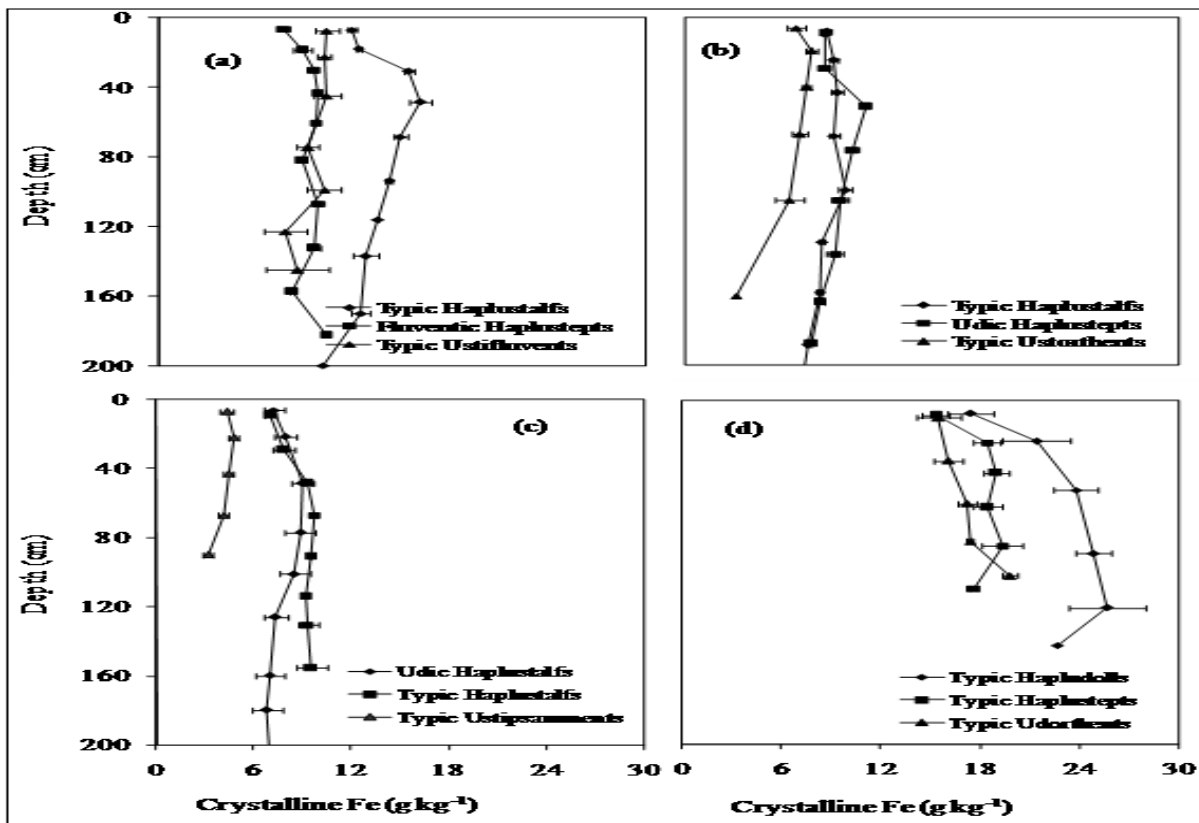


Fig. 4. Crystalline iron oxides distribution the soil series at different level of development separately in each parent material: (a) alluvium, (b) loess, (c) sandstone, and (d) shale, (Mean n = 3 and error bars show one standard error).

The distribution with soil depth of crystalline iron oxides, which is calculated by subtracting amorphous iron oxides from dithionite extractable iron, in profile varied with parent material as the hypothesis of non-significant depth × PM effect was rejected through MANOVA test criteria Wilks' λ ($p \geq 0.05$), and the difference remained statistically significant ($p \geq 0.05$) at most of the horizons level (Fig. 1b). Shale derived soils had significantly higher crystalline iron oxides followed by the group of soils derived from alluvium, loess and sandstone. High crystalline iron oxides content in shale derived soils is due to lithogenic hematite (Memon *et al.*, 2011; Mehmood *et al.*, 2015). Crystalline iron oxides had the similar trend with soil depth as of dithionite extractable iron oxides. Crystalline iron oxides also increased with soil development in all the soil parent materials (Fig. 4). The crystalline iron oxides content increased with soil development and concentrated at Bt horizon level in weathered soils while crystalline iron oxides were

uniformly distributed in young soils. High crystalline iron oxides content at Bt horizon level was due to weathering at surface releases iron which leached down and accumulate at Bt horizon level.

Conclusion

It is concluded from the present study that the iron oxides forms vary with soil parent material and within a soil parent material, soil genesis control the redistribution of iron oxides phases in the soil profile. Shale derived soils contained the highest iron oxides extractable using dithionite as well as crystalline and amorphous iron oxides. The soils at higher level of development contained significantly greater crystalline and amorphous iron oxides content.

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