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Iron Oxides Minerals in Soils Derived from Different Parent Materials

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Authors' contribution

The research work was carried out in collaboration among all authors. All authors read and approved the manuscript.

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Short Research Article

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ABSTRACT

The knowledge on soil iron oxides morphology and crystallization is important for the management of nutrients especially phosphorus. The objectives of the study were to determine the iron oxides minerals in Pothwar uplands. In the study one soil from each parent material (loess, alluvium, sandstone and shale) was selected. Selected clay samples suspensions were observed under transmission electron microscope. Ferrihydrite was common iron oxide mineral observed in all selected parent material soils at different level of crystallinity. Ferrihydrite was observed in scattered granules and also as aggregates or clusters. Crystalline iron oxides hematite and lepidocrocite was observed only in shale derived Murree soil. Mica and Rutile were the inorganic crystalline material on which masses of ferrihydrite was scattered. Energy dispersive spectra of scattered ferrihydrite masses show it has more phosphorus than lepidocrocite and hematite.
The study concludes that ferrihydrite was the major iron oxides mineral in all selected parent material soils while shale derived soil also had lithogenic hematite and lepidocrocite.

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1. INTRODUCTION

Naturally, iron oxides in soil occur as mixtures ferrihydrite, lepidocrocite, goethite and hematite. These iron oxides have different physical characteristics such as specific surface area, morphology, and stability [1,2]. Ferrihydrite is poorly ordered mineral consist of aggregates and granules with diameter of 2 to 6 nm. Goethite is an oxy-hydroxide, an abundant mineral in tropical as well as subtropical soils, and gives yellowish brown color to soils [3]. Hematite is well-developed crystalline iron oxide is wide spread in soils and has high stability and it is responsible for rich red color of soils [4].

Ferrihydrite is more active for P adsorption in soils due to its small particle size, high specific surface area, and gel-like structure. Ferrihydrite formation is favored by soil solution rich in ferrous ion which exposed to rapid oxidation in presence of organic matter and considered a transient phase in the Fe oxide crystallization sequence unless its surfaces are contaminated by compounds such as phosphate and organic acids [5,6]. Ferrihydrite is metastable and often associated with lepidocrocite and goethite [7].

Iron oxides limits the bioavailability of nutrients especially phosphorus [8]. Iron oxides interact strongly with phosphate ions via ligand exchange and anion exchange. It is often adsorbed in the form of a bidentate complex. Studies on iron oxides mineralogy in Pothwar uplands of Pakistan are scarce. This article describes types of iron oxides in different parent material soils especially less crystalline ferrihydrite at different crystallinity levels. Specific objectives of study are to know the dispersion of ferrihydrite granules and aggregates on inorganic substrates and formation of crystalline iron oxides (lepidocrocite and hematite).

2. MATERIALS AND METHODS

2.1 Soil Sampling and Size Fractionation

One soil profile from each parent material (loess, alluvium, shale residue, and sandstone residue) in Pothwar uplands of Pakistan were dug and sampled at each genetic horizon. The USDA soil classification and sampling location is given in Table 1. One sample from each soil was selected for transmission electron microscope analysis. Soils were fractioned into sand silt and clay after removal of calcite using pH 5.0 NaOAc and dispersion in high pH sodium carbonate [9]. Soil suspension was dispersed and the sand was separated by wet sieving through a 53 µm sieve. Silt and clay fractions were separated by centrifugation and decantation using 0.1 M Na_2CO_3 pH 10 as a dispersant. The clay suspension was made free of salt by dialysis [9].

2.2 Transmission Electron Microscopy

Sample was prepared by diluting a well-dispersed suspension in water until it is only slightly turbid. A drop was taken with a disposable pipette and it was placed and dried on a copper grid coated with a holey carbon film. The grid was studied with a transmission electron microscope (FEI Tecnai F20) with an energy dispersive spectrum (EDS) for chemical analyses.

3. RESULTS AND DISCUSSION

3.1 Basic Characteristics of Selected Samples

Basic properties of the soils are given in Table 2. Rawalpindi soil is silty clay loam and Kahuta and Gujranwala are clay loam while Murree soil is silty clay in texture. Murree soil has higher dithionite and oxalate extractable iron (Fed and Feo) than Gujranwala while Kahuta and Rawalpindi has lowest Fed and Feo. All selected samples are deficient in available P and noncalcareous. Murree soil is acidic in nature and Kahuta and Rawalpindi are almost neutral pH while Gujranwala soil is slightly alkaline pH [16].

3.2 Ferrihydrite Formation on Inorganic Substrate

Ferrihydrite is amorphous or poorly crystalline iron oxide which observed in almost all samples. The transmission electron microscope (TEM) image (Fig. 1a) suggests that large crystals are the substrate on which ferrihydrite form in Gujranwala soil. The layer silicates are large enough to support the diverse small and large aggregate. This TEM image showed two types of ferrihydrite. One was opaque and dispersed on whole silicate crystal having higher surface area due its amorphous nature. This amorphous material should be more active in adsorption of nutrients e.g. phosphorus [8]. The second one was clusters of ferrihydrite aggregates having less surface area as compared to opaque particles and less important in adsorption of nutrients. Their morphology suggests that these are ferrihydrite particles at early stage of crystallinity. In image 1b the left particle is the excellent example of porous aggregate with numerous granular Fe-oxides particles in Gujranwala soil. Image 1c shows that cluster of ferrihydrite aggregates that are wrapped in highly crystalline material in Kahuta soil. The wrapped crystalline material d-spacing shows it is Rutile particle. Image 1d is higher magnification of Fig. 1c showing the ferrihydrite granules. Image 1e showed the ferrihydrite granules forming aggregates (lower side of the image) the scattered ferrihydrite masses on the layers silicates (upper side of the image) in Rawalpindi soil. Fig. 1f showed the masses of ferrihydrite on crystalline material. These masses were at early stages of crystallinity towards lepidocrocite, which was shown on left side of the image.

Mica and rutile were observed in all soils. Ferrihydrite was scattered on mica and rutile particles (Fig. 2) Mica and rutile both has measurable fringes. The d-spacing of mica was 10 Å. Mica is abundant mineral in all Pakistani soils [17] and it is large enough it can support ferrihydrite masses and clusters.

3.3 Crystalline Iron Oxides Soils

Lepidocrocite and hematite are the crystalline minerals observed in Murree soil. Murree soil has also ferrihydrite but it has mainly hematite. Image 3a depicted the lepidocrocite laths because d-spacing was 6.26 Å. The Murree soil is noncalcareous and has humid climate and is saturated and these condition favored the formation of lepidocrocite in soil [18]. Under cool temperature and low evaporation rates, ferrous iron is mobilized and lepidocrocite is formed by the oxidation. Lepidocrocite was also observed by Wang et al. [19] in Paddy soils of Texas. Fig. (3c) shows the crystalline hematite. Image 3d showed the fringes of hematite (d= 2.70 Å). Hematite is widespread in soils and sediments and is a highly stable mineral. Pedogenic hematite is abundant in arid and semiarid as well as humid soil [7]. In Murree soil hematite may be lithogenic because Murree is developed in red shale parent material which is hematite rich [20].

3.4 Phosphorus Adsorption and Iron Oxides from Energy Dispersive Spectra

The Fig. 3 describes the relationship between iron oxides and phosphorus adsorption by energy dispersive spectra (EDS). The EDS showed high content of P and Fe in opaque ferrihydrite dispersed on layer silicates. As these particles have greater specific surface area, they could adsorb more P. Ferrihydrite has a specific surface area up to 700 $m^2\ g^{-1}$ [21,2]. Phosphorus adsorption is related to the surface area of ferrihydrite [8]. Fig. 4b showed lower P/Fe ratio than that in Fig. 4a. This spectrum is of cluster of ferrihydrite aggregates. Ferrihydrite aggregate have less surface area than single granules (opaque) so less P is adsorbed on the Ferrihydrite. Fig. 4c also showed little P and Fe in EDS, this relates to the lepidocrocite mineral. As ferrihydrite and lepidocrocite mixture was observed in that image, so there is little P. The lepidocrocite has lower surface area than ferrihydrite and low adsorption capacity. The specific surface area of lepidocrocite can be up to 260 $m^2\ g^{-1}$ [2]. Energy dispersive spectrum of hematite mineral shows only Fe and no P was observed in that spectrum. Hematite is highly crystalline mineral with very low surface area ranges from 10 to 90 $m^2\ g^{-1}$ [2].

Table 1. Selected soil series with USDA classification and GPS locations

Parent material	Soil series	USDA classification	GPS location
Loess	Rawalpindi	Udic Haplustepts	33° 29.65" N 73° 12.87" E
Alluvium	Gujranwala	Typic Haplustalfs	33° 24.74" N 72° 31.22" E
Sandstone residuum	Kahuta	Udic Haplustalfs	32° 12.07" N 73° 05.53" E
Shale residuum	Murree	Typic Hapludolls	33° 54.85" N 73° 25.51" E

Table 2. Selected parent material soils and basic characteristics

PM	Soil	Olsen-P	DOC	TOC	Fed	Feo	pH	CaCO3	Clay
		-------mg kg $^{-1}$------		g kg $^{-1}$	----mg kg $^{-1}$--			----------%----------	
Loess	Rawalpindi	2.76	27	2.40	12.0	0.68	6.86	1.31	32
Alluvium	Gujranwala	3.73	43	2.80	17.4	1.03	7.46	0.77	32
Shale	Murree	4.02	44	2.23	30.5	2.46	4.85	0.66	46
Sandstone	Kahuta	2.20	27	3.47	12.1	0.78	6.7	0.61	31

Olsen-P: Phosphorus extracted by 8.5 pH 0.5 M $NaHCO_3$ [10], DOC: Dissolved organic carbon [11], TOC: Total organic carbon [12], Fed: dithionite extractable iron [13], Feo: Oxalate extractable iron [14], $CaCO_3$ [15]

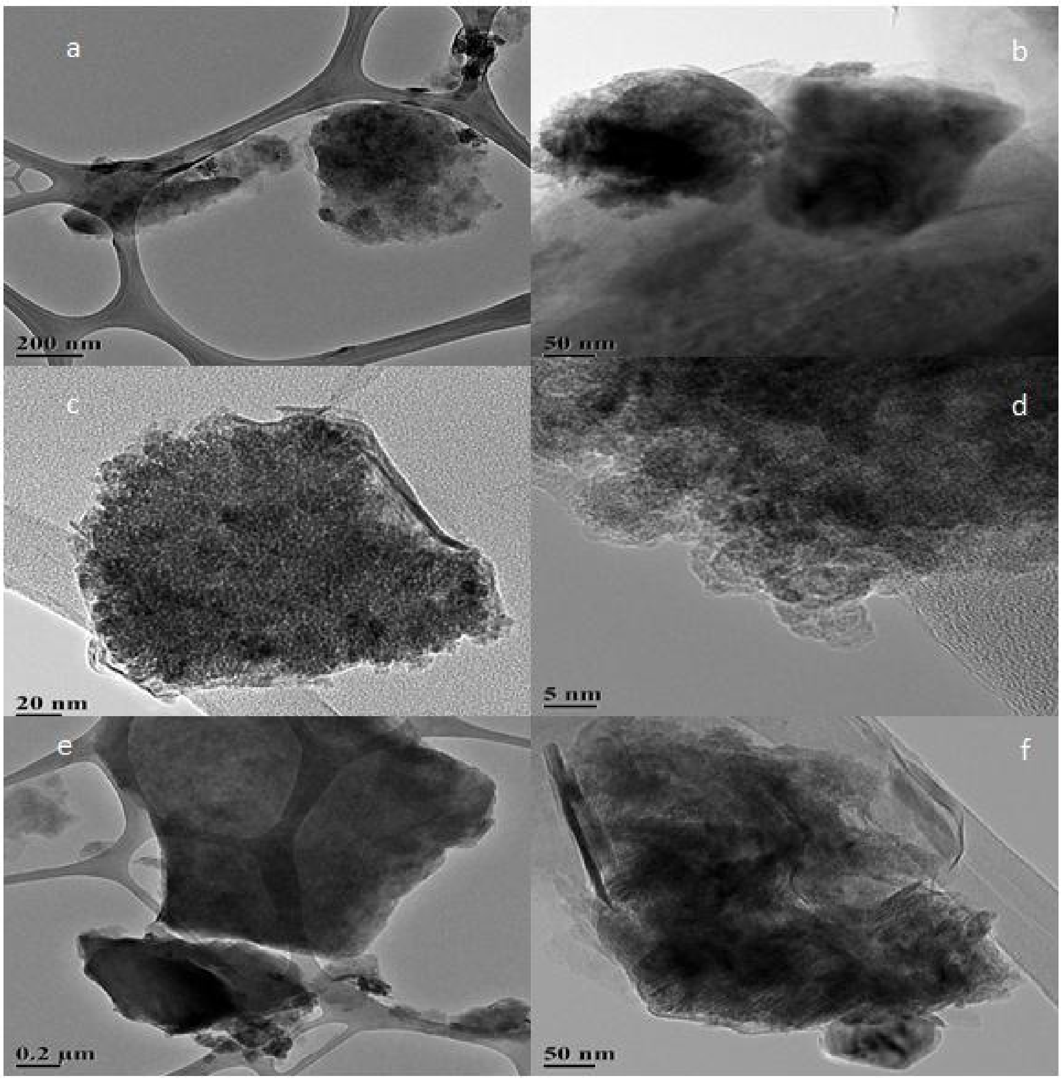

Fig. 1. Ferrihydrite formation on layer silicates: (a) opaque grains of ferrihydrite and clusters of tiny granules (Gujranwala soil), (b) ferrihydrite on porous crystalline material (c) is Ferihydrite agregates wrapped in thin crystalline material (Kahuta soil), (d) is enlargement of (1c), (e) in the lower part there are clusters of ferrihydrite at early stage of crystallinity and upper mica particle has dispersed masses of ferrihydrite (Rawalpindi soil), (f) showing scattered ferrihydrite and on left sides laths of lepidocrocite (Murree Soil) and it shows the transformation of ferrihydrite into lepidocrocite

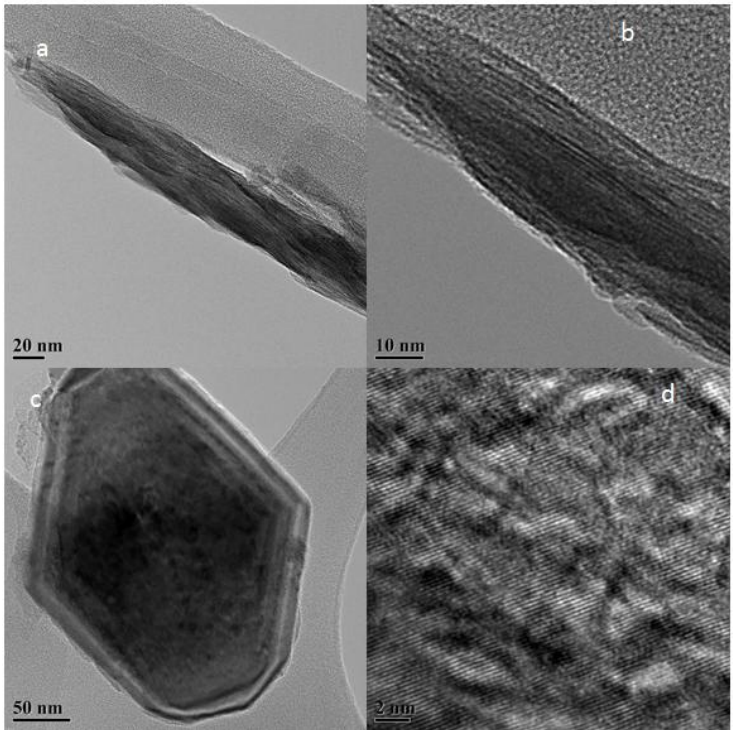

Fig. 2. (a) Mica (b) mica fringes with d spacing of 10 Ǻ (c) Rutile and (d) Rutile fringes: Rutile is very stable mineral at 1.05 mX

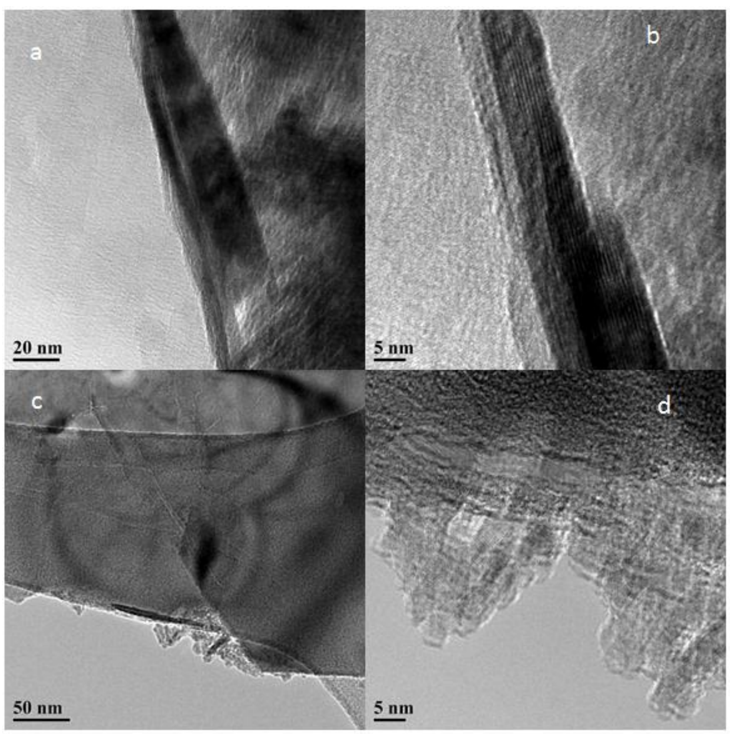

Fig. 3. (a) Lepidocrocite (b) lepidocrocite laths having d spacing 6.26 Ǻ in Murree soil (c) hematite at lower tip and (d) hematite fringes d spacing of 2.67 Ǻ confirm it hematite mineral

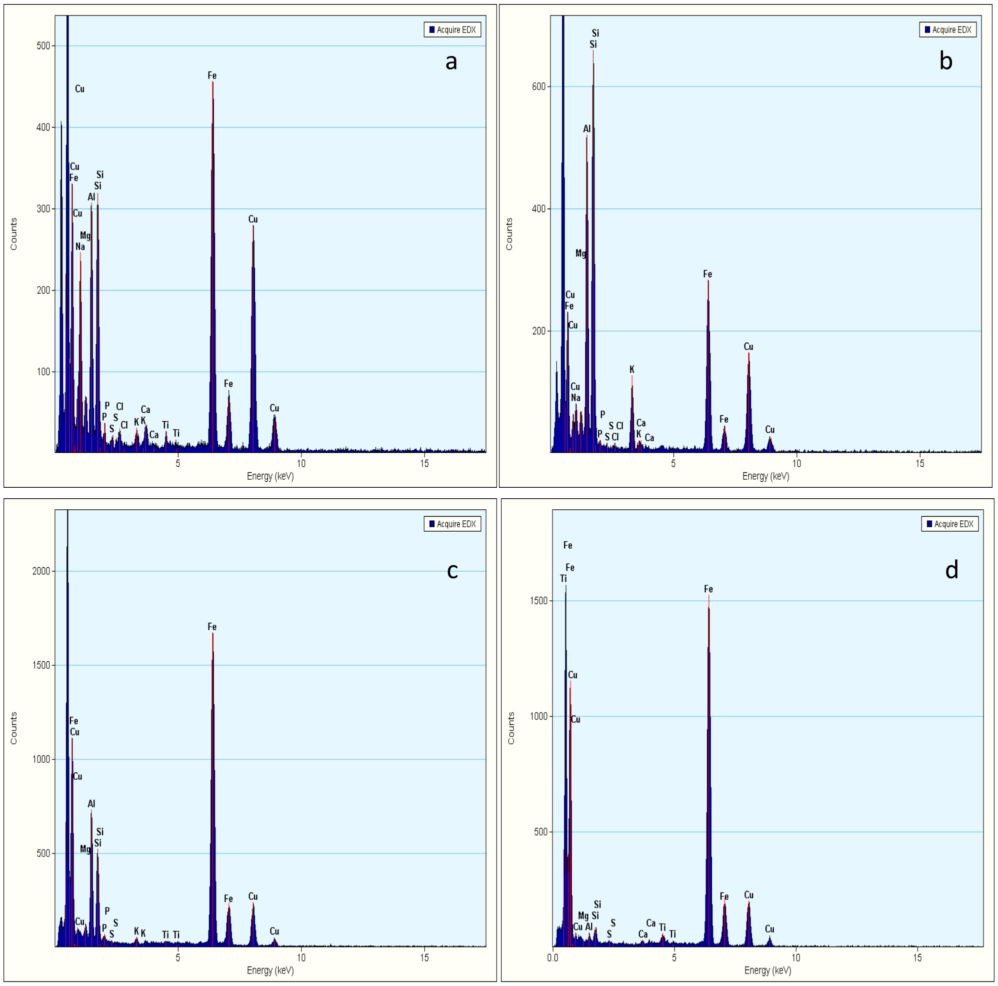

Fig. 4. EDS relationship of iron oxides surface area and P (a) ferrihydrite scattered (surface area can be up to 700 m^2g^{-1}) (b) ferrihydrite cluster of aggregates (c) lepidocrocite (surface area up to 260 m^2g^{-1}) (d) hematite (surface area 10-90 m^2g^{-1}) (Cornell and Schwertmann [2]

4. CONCLUSIONS

It is concluded from study that ferrihydrite is dominant iron oxides mineral in Pothwar uplands soils of Pakistan as soils are at early stage of development. Due its higher specific surface area it can be a main adsorbent of P in soils. From energy dispersive spectrum (EDS), it is concluded that ferrihydrite had more P than hematite and lepidocrocite. Hematite and lepidocrocite are observed only in shale derived Murree soil.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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