Journal homepage www.jzs.uos.edu.krd
**Journal of Zankoi Sulaimani**
Part-A- (Pure and Applied Sciences)

# Iron Oxide Mineralogy of Asnawa Soils, Sulaimani Province, Kurdistan region

Sherwan Kafoor & Carman Q. Maulood

*Department of Soil Science, College of Agriculture, University of Salahaddin, KRG,*
email: sherwan53@gmail.com

---

**Article info**

Original: 14 Oct. 2014
Revised: 21 Jan. 2015
Accepted: 22 Feb. 2015
Published online:
20 June 2015

***Key Words:***
*Asnawa,*
*aqua regia,*
*citrate dithionite*
*magnetite*
*wustite*

## Abstract

Forty soil samples from three different zones (A, B and C) in Asnawa area were studied to identify and characterize the forms of Fe oxides in the <2 mm soil fractions using chemical extractions and XRDA technique. Neither citrate dithionite nor aqua regia solution were not effective enough to extract free Fe oxides in the soil samples. The maximum amounts of Fe oxides obtained were when five successive treatments with aqua regia solution had done. Soils of the quarry area (zone A) contained the highest amount of Fe oxides followed by soils from zone B and C. They were ranged from 52.1%, 38.6% and 15.1% respectively. XRD traces of the studied soils showed peaks characteristics of magnetite at 0.297, 0.256, 0.210, 0.161 and 0.147 nm. Other peaks of hematite at 0.271 nm, and wustite (Fe(1-X)O at 0.88 were also present. Diffraction peaks of magnetite after a single treatment with citrate dithionite and aqua regia were still evident on the X-ray chart whereas the diffraction peaks of hematite and wustite were disappeared.

## Introduction

In Kurdish vocabulary Asnawa means the "village of Iron" or a place where iron is rich in the area. Asnawa is a small village near the Iraq-Iran border, located about 3km to the east of Penjween – a town belongs to Sulaimany province (Fig. 1).

The iron ore of Asnawa is located to the south east of Penjween town. A difficult unpaved road; from Penjween climbs through the Bilkian valley leads to the area of the iron ore which can be visited only by means of four wheel drive vehicles. The road is 1350 meters high in elevation and takes only half an hour to reach to the quarry. The areas surrounding the road and the iron ore are dangerous as being full of remnants of weapons especially mine fields and different kinds of unexploded shells.

With the exception of a limited number of reports and scientific papers which are mainly geological reviews (Jassim and Goff, 2006), little information is available on soil mineralogy of the area.

McCarthy (1956) was the first researcher who investigated the occurrence of iron ore in Asnawa. He reported that the iron occurrence is situated in a complex zone of igneous and metamorphic rocks of uncertain age. Bolton (1958) mentioned in his report that the iron ore was found within metamorphic rocks in the Qandil series. In 1957-1959, the Site Investigations Company resumed its work on the Asnawa iron ore and estimated it's quantity as around 250 thousand tons of iron (Teretenko and Khadikov, 1961).

Kafoor (2014) studied the colours of Asnawa soils in relation to iron oxide content. He derived an equation from which he concluded that colour of the studied area can be measured as a parameter to identify and quantify soil Fe oxides.

Fig. 1: Map of Kurdistan Region showing the studied area

## Materials and Methods:

According to the visible differences in soil's colour, the studied area was divided to three zones (A,B and C). Forty surface soil samples were randomly collected; five samples from zone A (quarry zone), fifteen samples from zone B (downhill zone) and twenty samples from zone C (Penjween suburb zone). For each location GPS coordination was measured (Fig. 2). Bulk surface samples of 2-3 kg were placed in plastic bags. The soil samples of zone A were numbered as $S_1$, $S_2$….to $S_5$ whereas the samples of zone B were numbered as $S_6$ to $S_{20}$ and the samples of zone C were numbered as $S_{21}$, $S_{22}$ ….$S_{40}$.

In the laboratory, the soil samples were dried at room temperature, grounded and passed through 2.0 mm sieve. The colours of air dried soils were measured using Munsell colour chart book. Extraction of Fe oxides was carried out using citrate dithionite (Mehra and Jackson 1960; Coffin 1963), acidified ammonium oxalate AAO (McKeague and Day, 1966), potassium pyrophosphate (Bascomb, 1968) and aqua regia solution. (ISO, 2002). The solutions of the digested samples with the use of prepared standards were analysed by (AAS-UNICAM model 929). XRDA were performed on samples of fine earth (< 0.5 mm) using the X-ray machine model HUBER G670 and analysed for minerals identification (Stahl, 2000).

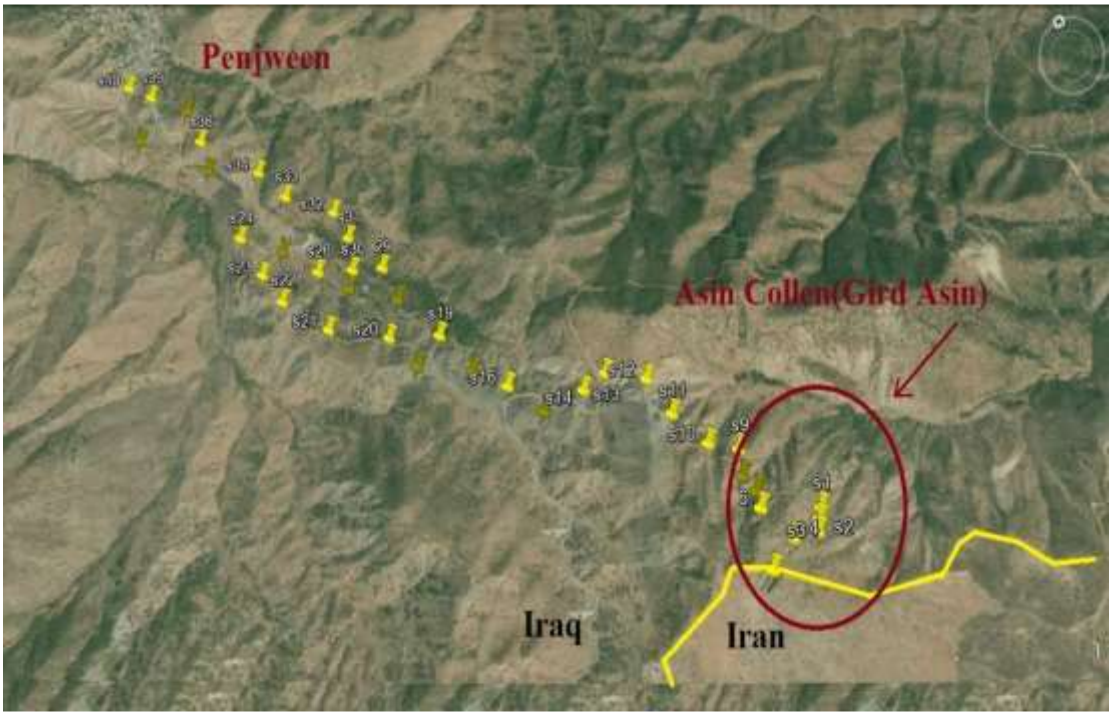

Fig. 2: Locations where soil samples taken according to GPS coordination’s

## Results and Discussion:

The colours of the soils of the studied area were compared against colours available in the Mansell colour chart; they ranged between hue of 5YR and value/chroma of 2.5/1 to 5/8 suggesting presence of iron oxides. Soils of zone A had a much darker colour compared to soils of zone B and C (Kafoor, 2014). Other researchers reported that oxides of iron determine soil colour and have a major influence on physical and chemical characteristics of soils (Schwertmann, 1993). Another indication in the field, which established presence of Fe oxide minerals (magnetite in particular), was the phenomenon of magnetic force that pulled other ferromagnetic materials such as iron (Mawlud, 2014). Fontes et al (2000) studied magnetic measurements of five different soils and reported that soils containing iron-rich with spinel structure such as magnetite and maghemite that impart soil magnetization are considered magnetic.

Potassium pyrophosphate, acidified ammonium oxalate, citrate dithionite and aqua regia solution have been frequently applied by many researchers to determine amounts and forms of Fe oxides in soils (Schwertman, 1964, 1982, 1985, 1993; Torrent et. al., 1980; Golden et. al., 1994, Bascom, 1968).

The amounts of Fe oxides extracted independently by citrate dithionite ($Fe_d$), ammonium oxalate ($Fe_o$), potassium pyrophosphate ($Fe_p$) and aqua regia ($Fe_{aq}$) expressed as percentage in the air dry fine earth are shown in (Table 1).

The amount of Fe dissolved by aqua regia solution $Fe_{aq}$ was higher than other extractant which ranged between 9.45% and 32.96% with an average value of 18.36% ± 8.3. The average value of $Fe_{aq}$ in the soils of zones A, B, and C were 30.84%, 24.66%, and 10.51 respectively indicating higher amounts of Fe oxides in the soils of zone A compared to the soils of zone B and C. Whereas the lowest values obtained was when the soils were extracted with potassium pyrophosphate ($Fe_p$). They were ranged between 0.029 and 0.106% with an average value of 0.06% ± 0.03. In fact the average value of 0.06 % can be considered negligible, therefore it can be suggested that no Fe oxides in the studied area have been complexed yet by organic matter through the pedogenic processes (Bascomb et al, 1968).

Table 1: Amounts of $Fe_p$, $Fe_o$, $Fe_d$, and $Fe_{aq}$ in the studied forty soil samples

| Zones | Sample No. | $Fe_p$ % | $Fe_o$ % | $Fe_d$ % | $Fe_{aq}$ % |
|---|---|---|---|---|---|
| A | 1 | 0.029 | 11.47 | 31.08 | 32.96 |
| A | 2 | 0.030 | 10.31 | 27.18 | 30.31 |
| A | 3 | 0.030 | 10.85 | 25.41 | 29.62 |
| A | 4 | 0.030 | 11.38 | 27.71 | 29.83 |
| A | 5 | 0.030 | 10.93 | 30.02 | 31.46 |
| B | 6 | 0.031 | 10.49 | 24.17 | 27.81 |
| B | 7 | 0.029 | 9.25 | 21.86 | 27.23 |
| B | 8 | 0.030 | 9.25 | 22.40 | 27.95 |
| B | 9 | 0.031 | 8.54 | 21.16 | 25.59 |
| B | 10 | 0.033 | 9.43 | 22.75 | 24.21 |
| B | 11 | 0.035 | 8.19 | 21.51 | 23.82 |
| B | 12 | 0.033 | 8.98 | 22.40 | 22.92 |
| B | 13 | 0.035 | 9.43 | 21.16 | 23.69 |
| B | 14 | 0.035 | 8.9 | 19.38 | 23.17 |
| B | 15 | 0.035 | 9.07 | 19.56 | 23.43 |
| B | 16 | 0.036 | 8.54 | 19.91 | 23.52 |
| B | 17 | 0.035 | 8.36 | 19.56 | 23.72 |
| B | 18 | 0.035 | 7.92 | 19.56 | 24.15 |
| B | 19 | 0.035 | 7.39 | 18.14 | 24.18 |
| B | 20 | 0.037 | 7.92 | 18.85 | 24.55 |
| C | 21 | 0.064 | 3.22 | 13.00 | 15.37 |
| C | 22 | 0.067 | 2.96 | 10.34 | 12.46 |
| C | 23 | 0.070 | 2.96 | 9.63 | 11.37 |
| C | 24 | 0.073 | 2.96 | 8.22 | 9.85 |
| C | 25 | 0.077 | 2.87 | 8.57 | 10.09 |
| C | 26 | 0.079 | 2.16 | 7.86 | 10.41 |
| C | 27 | 0.081 | 2.43 | 8.75 | 10.34 |
| C | 28 | 0.084 | 2.6 | 6.97 | 10.65 |
| C | 29 | 0.086 | 2.07 | 8.22 | 10.86 |
| C | 30 | 0.106 | 3.49 | 10.70 | 11.29 |
| C | 31 | 0.105 | 3.05 | 9.99 | 10.23 |
| C | 32 | 0.087 | 1.98 | 8.75 | 9.83 |
| C | 33 | 0.089 | 2.51 | 8.04 | 9.92 |
| C | 34 | 0.088 | 2.69 | 8.75 | 9.65 |
| C | 35 | 0.088 | 2.34 | 6.97 | 9.72 |
| C | 36 | 0.088 | 1.72 | 6.44 | 9.54 |
| C | 37 | 0.087 | 2.07 | 7.15 | 9.45 |
| C | 38 | 0.087 | 1.81 | 6.09 | 9.67 |
| C | 39 | 0.088 | 1.81 | 5.20 | 9.88 |
| C | 40 | 0.088 | 1.98 | 5.91 | 9.69 |
| Average | | 0.06 | 5.9 | 15.48 | 18.36 |
| SD | | 0.03 | 3.59 | 7.86 | 8.3 |

Amounts of Fe oxides extracted by citrate dithionite ($Fe_d$) ranged between 5.20% to 31.1% with an average value of 15.5% ± 7.86. $Fe_d$ was higher in the soils of zone A compared to soils of zone B and soils of zone C with an average value of (28.3%, 20.8%, and 8.3%) respectively.

Values of Fe oxides extracted by ammonium oxalate ($Fe_o$) covered similar trend but with less amount of Fe; it ranged between 1.72% and 11.47% with an average value of 5.90% ± 3.59. The average value of $Fe_o$ in the soils of zones A, B, and C were 11%, 8.8%, and 2.5% respectively.

Acidified ammonium oxalate AAO has been frequently applied in soil science as well as in some environmental magnetism studies to determine the poorly crystalline iron oxide content of soils (Torrent et al. 1980; Schwertmann et al. 1982, 1985; Golden et al. 1994; Rozan et al. 1997). However, several studies have shown that some crystalline iron oxides can be dissolved with the AAO method (McKeague et al. 1971; Schwertmann 1973); other researchers reported that oxalate method can be applied to dissolve specific minerals such as magnetite, and that differentiation on the basis of mineralogy would be possible with this method (Golden et al., 1994). These results contrast with the original observation that AAO only dissolves amorphous iron oxides. In this study, on average AAO extracted 33% of the total free Fe oxides extracted by citrate dithionite (CD) and 20.8% of total Fe oxides dissolved by aqua regia (AQ).

Citrate dithionite (CD) is well known as a reagent that extracts crystalline free Fe oxides which are found in soils but are not part of the crystal lattice of other minerals. Mehra and Jackson (1960) followed by Coffin (1963) and Bascomb (1968) were first to test a series of methods for the extraction of iron oxides from soils and found that CD was the most effective reagent in the removal of free iron oxides. Pansu (2006) reported that sodium dithionite ($Na_2S_2O_4$) is a strong reducing component that reduces and solubilizes iron oxides, including goethite, hematite and magnetite when the pH for reduction is between 7 and 8. This reagent dissolves crystalline iron oxides, non-crystalline iron oxides, iron and aluminium organic complexes as well as exchangeable iron and manganese oxides ((Hunt, 1994).

Chandra et al, (2006) studied reaction conditions of the CD method and found several inconsistencies in the selection of procedures such as pH and time of extractions. Other researchers also reported that CD is not effective enough to extract magnetic particles of Fe such as magnetite unless successive treatments with citrate dithionite were employed. Seven successive extractions were reported by (Santana et al, 2001).

In this investigation, unexpectedly the soil residues in the containers after treatment with citrate dithionite and aqua regia solution still had magnetic attraction force indicating that there were yet residues of non-extracted Fe oxides leftover in the soil samples. Therefore it was inevitable to carry on with a number of successive extractions until total solubility had achieved.

Successive treatments were planned in order to achieve maximum extraction. Five successive treatments were carried out on each sample. In each extraction the residual sample was washed with distilled water, centrifuged then treated again with citrate dithionite. The amount of $Fe_d$ in the first, second, third, fourth and fifth extractions for all samples are shown in Table 2. The sum of the extracted $Fe_d$ after five treatments was supposed to represent total free Fe oxides. Assuming that citrate dithionite extracted all Fe oxide in five successive treatments, this would give the average value of 17.91% ± 9.30 of free Fe oxide. The average value of Fe after five successive extractions in the soils of zone A, B, and C were 33.8%, 23.9% and 9.4% respectively. The residues after five treatments were analysed by XRD analyses and showed diffraction peaks of magnetite still present in the samples. This evidently indicated that citrate dithionite was not effective enough to extract well crystallized magnetite.

Table 2: Percentages of $Fe_d$ after five treatments of extractions

| Zone | Sample | 1st extraction | 2nd extraction | 3rd extraction | 4th extraction | 5th extraction | Total extraction |
|---|---|---|---|---|---|---|---|
| A | S1 | 31.08 | 3.12 | 1.25 | 0.85 | 0.35 | 36.65 |
| | S2 | 27.18 | 2.95 | 1.45 | 0.75 | 0.45 | 32.78 |
| | S3 | 25.41 | 2.99 | 1.82 | 1.25 | 0.84 | 32.31 |
| | S4 | 27.71 | 2.15 | 1.64 | 0.97 | 0.67 | 33.14 |
| | S5 | 30.02 | 1.95 | 1.11 | 0.55 | 0.35 | 33.98 |
| B | S6 | 24.17 | 2.83 | 1.23 | 0.84 | 0.33 | 29.40 |
| | S7 | 21.86 | 2.09 | 0.87 | 0.52 | 0.30 | 25.63 |
| | S8 | 22.40 | 1.81 | 0.66 | 0.49 | 0.24 | 25.59 |
| | S9 | 21.16 | 1.45 | 0.50 | 0.34 | 0.20 | 23.64 |
| | S10 | 22.75 | 1.30 | 0.44 | 0.33 | 0.13 | 24.94 |
| | S11 | 21.51 | 3.28 | 1.37 | 0.88 | 0.29 | 27.33 |
| | S12 | 22.40 | 2.32 | 0.74 | 0.62 | 0.13 | 26.21 |
| | S13 | 21.16 | 2.13 | 0.63 | 0.44 | 0.10 | 24.46 |
| | S14 | 19.38 | 1.33 | 0.51 | 0.34 | 0.08 | 21.65 |
| | S15 | 19.56 | 1.12 | 0.40 | 0.25 | 0.07 | 21.39 |
| | S16 | 19.91 | 1.75 | 0.95 | 0.66 | 0.16 | 23.43 |
| | S17 | 19.56 | 1.73 | 0.87 | 0.48 | 0.10 | 22.73 |
| | S18 | 19.56 | 1.30 | 0.83 | 0.38 | 0.08 | 22.14 |
| | S19 | 18.14 | 1.11 | 0.55 | 0.33 | 0.04 | 20.18 |
| | S20 | 18.85 | 0.93 | 0.43 | 0.25 | 0.03 | 20.50 |
| C | S21 | 13.00 | 1.47 | 0.82 | 0.37 | 0.00 | 15.66 |
| | S22 | 10.34 | 1.11 | 0.60 | 0.27 | 0.00 | 12.32 |
| | S23 | 9.63 | 0.71 | 0.43 | 0.15 | 0.00 | 10.93 |
| | S24 | 8.22 | 0.51 | 0.33 | 0.11 | 0.00 | 9.17 |
| | S25 | 8.57 | 0.60 | 0.28 | 0.13 | 0.00 | 9.58 |
| | S26 | 7.86 | 1.34 | 0.65 | 0.43 | 0.00 | 10.28 |
| | S27 | 8.75 | 0.87 | 0.40 | 0.24 | 0.00 | 10.26 |
| | S28 | 6.97 | 0.77 | 0.32 | 0.15 | 0.00 | 8.20 |
| | S29 | 8.22 | 0.52 | 0.28 | 0.07 | 0.00 | 9.09 |
| | S30 | 10.70 | 0.38 | 0.21 | 0.07 | 0.00 | 11.35 |
| | S31 | 9.99 | 0.88 | 0.52 | 0.13 | 0.00 | 11.52 |
| | S32 | 8.75 | 0.55 | 0.46 | 0.08 | 0.00 | 9.83 |
| | S33 | 8.04 | 0.50 | 0.44 | 0.05 | 0.00 | 9.03 |
| | S34 | 8.75 | 0.38 | 0.20 | 0.04 | 0.00 | 9.37 |
| | S35 | 6.97 | 0.39 | 0.17 | 0.03 | 0.00 | 7.56 |
| | S36 | 6.44 | 0.88 | 0.34 | 0.00 | 0.00 | 7.66 |
| | S37 | 7.15 | 0.70 | 0.26 | 0.00 | 0.00 | 8.10 |
| | S38 | 6.09 | 0.45 | 0.10 | 0.00 | 0.00 | 6.63 |
| | S39 | 5.20 | 0.35 | 0.07 | 0.00 | 0.00 | 5.63 |
| | S40 | 5.91 | 0.25 | 0.06 | 0.00 | 0.00 | 6.22 |
| | mean | 15.48 | 1.33 | 0.63 | 0.35 | 0.12 | 17.91 |
| | SD | 7.77 | 0.86 | 0.43 | 0.31 | 0.19 | 9.30 |

Originally the dissolution of Fe oxides by aqua regia solution was designed to dissolve all components of the sample except quartz. In this study, as happened with CD the soil residues in the containers still had magnetic attraction force suggesting that there were yet residues of non-dissolved Fe oxides leftover in the soil samples. Therefore additional treatments were carried out to achieve total solubility. For comparison with CD, five successive extractions were carried out on all soil samples (Table 4).

Table 3: Total amounts of ($Fe_{aq}$) after five successive extractions

| Zone | Sample No | 1st extraction | 2nd extraction | 3rd extraction | 4th extraction | 5th extraction | Total Extraction |
|---|---|---|---|---|---|---|---|
| **A** | S1 | 32.96 | 14.27 | 6.59 | 1.96 | 0.40 | 56.19 |
|  | S2 | 30.31 | 13.82 | 6.20 | 2.05 | 0.42 | 52.80 |
|  | S3 | 29.62 | 12.45 | 6.11 | 1.95 | 0.43 | 50.56 |
|  | S4 | 29.83 | 11.88 | 6.05 | 1.88 | 0.44 | 50.08 |
|  | S5 | 31.46 | 11.50 | 5.75 | 1.55 | 0.41 | 50.67 |
| **B** | S6 | 27.81 | 11.91 | 4.11 | 1.53 | 0.39 | 45.74 |
|  | S7 | 27.23 | 10.24 | 3.95 | 1.22 | 0.35 | 42.99 |
|  | S8 | 27.95 | 10.65 | 3.66 | 1.35 | 0.33 | 43.94 |
|  | S9 | 25.59 | 9.81 | 3.55 | 1.32 | 0.26 | 40.52 |
|  | S10 | 24.21 | 9.75 | 3.95 | 1.11 | 0.34 | 39.36 |
|  | S11 | 23.82 | 9.45 | 3.23 | 1.09 | 0.34 | 37.93 |
|  | S12 | 22.92 | 9.22 | 3.12 | 1.05 | 0.32 | 36.63 |
|  | S13 | 23.69 | 9.15 | 2.95 | 0.99 | 0.31 | 37.09 |
|  | S14 | 23.17 | 9.02 | 2.87 | 0.91 | 0.26 | 36.22 |
|  | S15 | 23.43 | 8.95 | 2.77 | 0.88 | 0.25 | 36.28 |
|  | S16 | 23.52 | 8.75 | 2.85 | 0.95 | 0.22 | 36.29 |
|  | S17 | 23.72 | 9.11 | 2.89 | 1.25 | 0.24 | 37.21 |
|  | S18 | 24.15 | 9.21 | 2.85 | 0.88 | 0.28 | 37.37 |
|  | S19 | 24.18 | 9.28 | 2.99 | 0.79 | 0.30 | 37.54 |
|  | S20 | 24.55 | 6.56 | 2.45 | 0.75 | 0.15 | 34.46 |
| **C** | S21 | 15.37 | 6.87 | 2.33 | 0.55 | 0.12 | 25.24 |
|  | S22 | 12.46 | 5.45 | 2.35 | 0.45 | 0.16 | 20.87 |
|  | S23 | 11.37 | 4.43 | 2.12 | 0.33 | 0.19 | 18.44 |
|  | S24 | 9.85 | 4.50 | 1.85 | 0.25 | 0.11 | 16.56 |
|  | S25 | 10.09 | 3.83 | 1.24 | 0.30 | 0.05 | 15.50 |
|  | S26 | 10.41 | 3.45 | 1.11 | 0.25 | 0.00 | 15.22 |
|  | S27 | 10.34 | 3.25 | 0.95 | 0.11 | 0.00 | 14.65 |
|  | S28 | 10.65 | 2.88 | 0.99 | 0.09 | 0.00 | 14.61 |
|  | S29 | 10.86 | 2.95 | 1.11 | 0.05 | 0.00 | 14.97 |
|  | S30 | 11.29 | 2.88 | 0.97 | 0.12 | 0.00 | 15.26 |
|  | S31 | 10.23 | 2.58 | 0.95 | 0.15 | 0.00 | 13.91 |
|  | S32 | 9.83 | 2.98 | 0.88 | 0.08 | 0.00 | 13.77 |
|  | S33 | 9.92 | 2.45 | 0.85 | 0.10 | 0.00 | 13.32 |
|  | S34 | 9.65 | 2.33 | 0.82 | 0.12 | 0.00 | 12.92 |
|  | S35 | 9.72 | 2.35 | 0.78 | 0.08 | 0.00 | 12.93 |
|  | S36 | 9.54 | 2.25 | 0.75 | 0.10 | 0.00 | 12.64 |
|  | S37 | 9.45 | 2.23 | 0.77 | 0.10 | 0.00 | 12.55 |
|  | S38 | 9.67 | 2.12 | 0.84 | 0.10 | 0.00 | 12.73 |
|  | S39 | 9.88 | 1.90 | 0.88 | 0.10 | 0.00 | 12.76 |
|  | S40 | 9.69 | 1.91 | 0.66 | 0.10 | 0.00 | 12.35 |
|  | mean | 18.360 | 6.714 | 2.552 | 0.725 | 0.177 | 28.527 |
|  | STDV | 8.302 | 3.915 | 1.748 | 0.634 | 0.163 | 14.589 |

The average sum of $Fe_{aq}$ after five successive extractions were 52.1%, 38.6% and 15.1% for the soils of zone A, B and C respectively. The residues after five treatments were analysed by XRD and showed no diffraction peaks of any form of Fe oxides indicating that all Fe oxides were dissolved after five treatments and considered as final total Fe oxides in the studied soils. Therefore it can be concluded that the known conventional procedure of aqua regia was not well effective enough to dissolve magnetite in the soils of Asnawa. Natalia Oliver (2012) in her thesis suggested a modified method for aqua regia for magnetite extraction by allowing the components to react overnight at $90^0$C, placing lids on the vials to prevent evaporation.

Very close correlations were found between ($Fe_o$ and $Fe_{d)}$, ($Fe_o$ and $Fe_{aq}$) and ($Fe_d$ and $Fe_{aq)}$ are shown in (Table 4) indicating that these reagents were extracted same or fractional entities of Fe oxides in the soils. From the gradient of the relationship and the regression line that passes near the origin, it can be concluded that the amounts of Fe oxides which were extracted by AAO were within the fine-grained free Fe oxides in the soils extracted by CD and aqua regia (Figs. 3, 4 and 5). It also indicates that these reagents were extracted same or fractional entities of Fe oxides in the studied soils. However, the results of the AAO method gave information about the type of iron oxides that are dissolved. The most important parameter in the CD method is the extraction temperature but in the AAO method light and pH can influence the extraction. The dissolution mechanism in the AAO method was less aggressive and the results gave more aspects than the CD method (Cornell and Schindler, 1997), therefore, this procedure is recommended for use in further studies.

Suggestion for future studies is that the AAO extraction method has good potential as a tool in environmental magnetism. It may be suitable to dissolve all fine-grained pedogenic iron oxides samples in one extraction, while leaving the lithogenic iron oxides virtually untouched.

Table 4: Regression equations between $Fe_o$ and $Fe_d$, $Fe_o$ and $Fe_{aq}$, $Fe_d$ and $Fe_{aq}$.

| Y | X | Correlation (r) | Regression equation |
|---|---|---|---|
| $Fe_d$ | $Fe_o$ | 0.974*** | Y= 0.3713x – 0.744 |
| $Fe_{aq}$ | $Fe_d$ | 0.986*** | Y= 0.6367x – 0.252 |
| $Fe_{aq}$ | $Fe_o$ | 0.979*** | Y = 0.2414x – 0.961 |

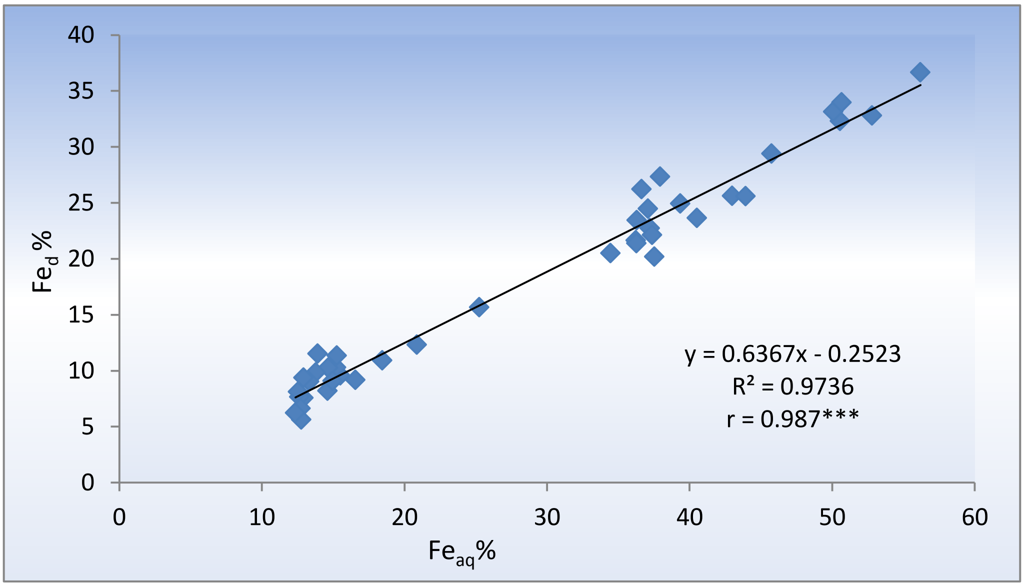

Fig. 3: Correlation coefficients and regression equations between Fe oxide extracted by aqua regia and citrate dithionite

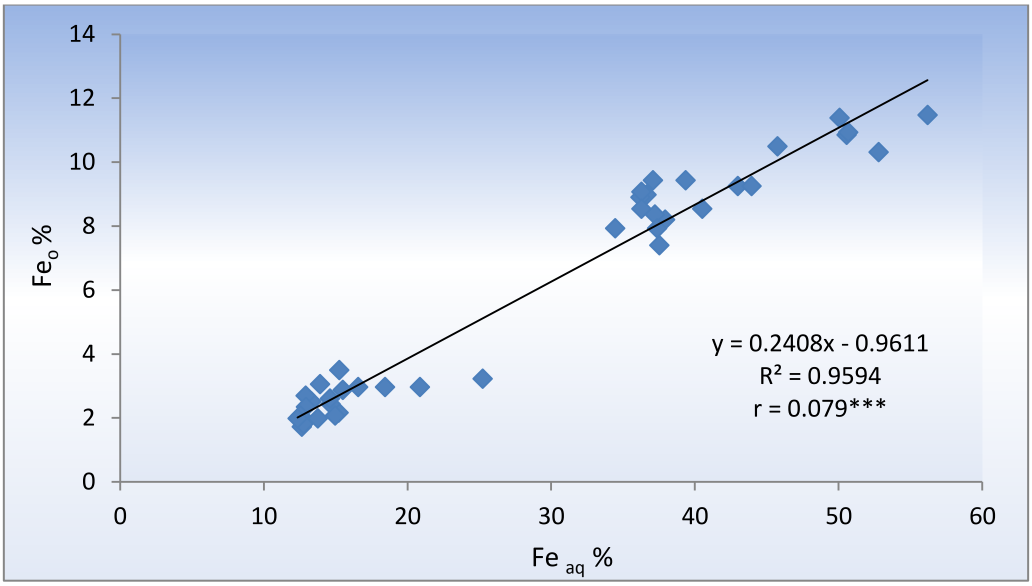

Fig. 4: Correlation coefficients and regression equations between Fe oxide extracted by aqua regia and ammonium oxalate.

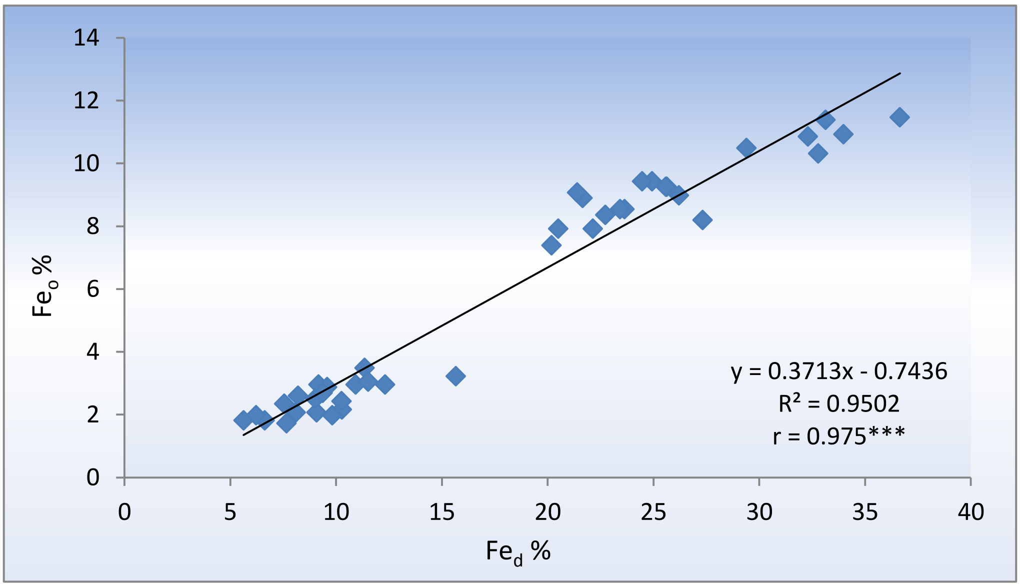

Fig. 5: Correlation coefficients and regression equations between Fe oxide extracted by citrate dithionite and ammonium oxalate.

XRD analyses were carried out on a number of soil samples, all traces showed similar trends of diffraction peaks indicating presence of same type of iron oxides. As there were similarity in the positions and shapes of the peaks, only few figures are shown in this paper.

The XRD analyses showed diffraction peaks at position similar to those given by synthetic magnetite. The highest Peak at 0.256 nm then smaller peaks at 0.297, 0.210, 0.161 and 0.147 nm which are characteristic of magnetite were clearly evident (Fig. 6). However other diffraction peaks at 0.257, 0.271 and 0.386 nm were also evident indicating presence of hematite in the soil samples. Although the peak at 0.257 nm of hematite overlaps with 0.256 nm of magnetite, the other peaks at 0.271 and 0.386 nm were indications of the presence of hematite. Another peak at 0.884nm was also present which was characteristic of pure iron oxides wustite Fe(1-x)O.

XRD were carried out on the soil samples after magnetite were pulled out magnetically using a magnet rod. The diffraction peaks of hematite and wustite in the examined soils became more evident (Fig. 7 & 8).

Peaks which were initially evident in the samples and characteristics of hematite and wustite were removed after the first extraction with citrate dithionite and aqua regia indication the effect of these extractant on the dissolution on various Fe oxides but not magnetite (Figs. 9 & 10).

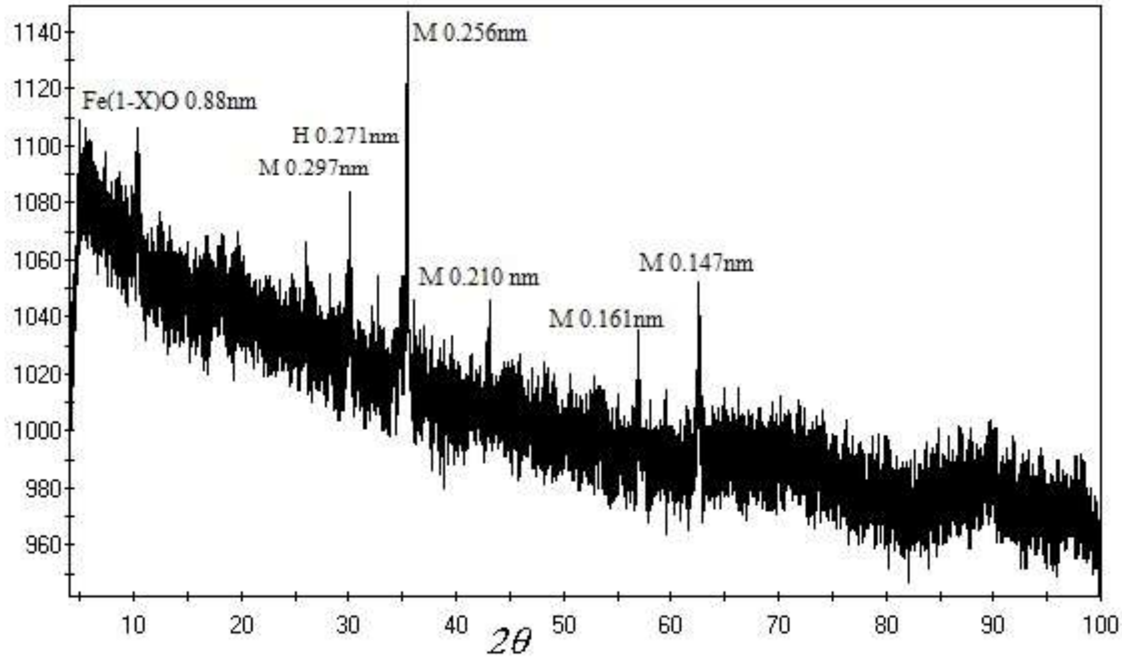

Fig. 6: X- ray diffraction peaks of the studied soil samples of zone A before treating with any extractants (M is magnetite, H is hematite and Fe(1-X)O is wustite.

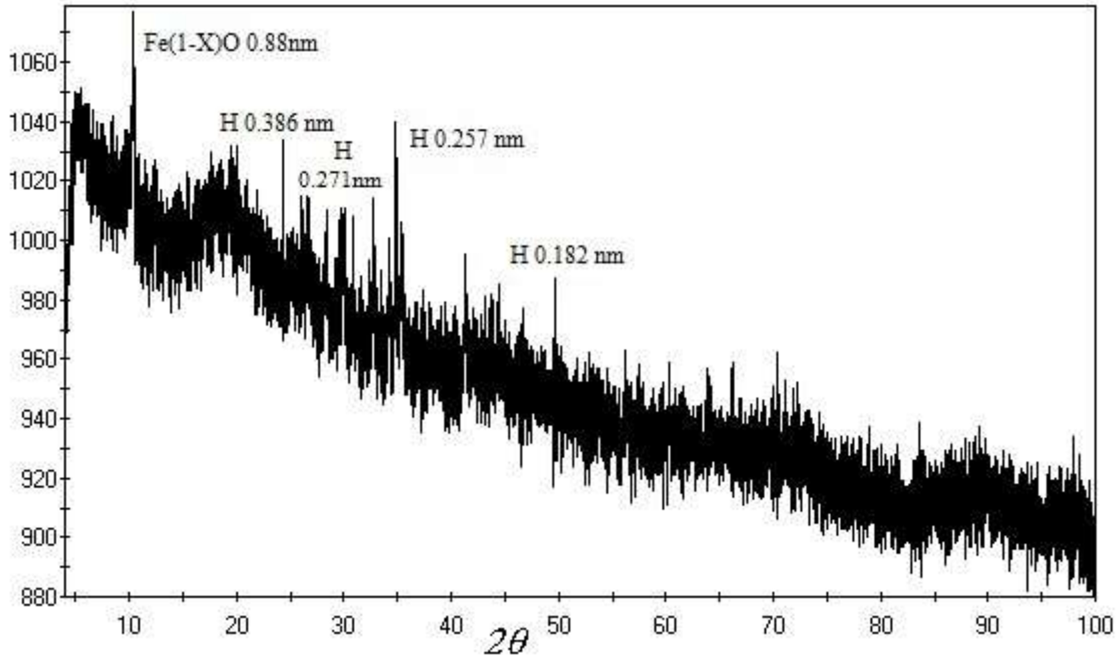

Fig. 7: X-ray diffraction peaks of the studied soil sample of zone A showing peaks of hematite and wustite after Fe oxides have pulled out magnetically

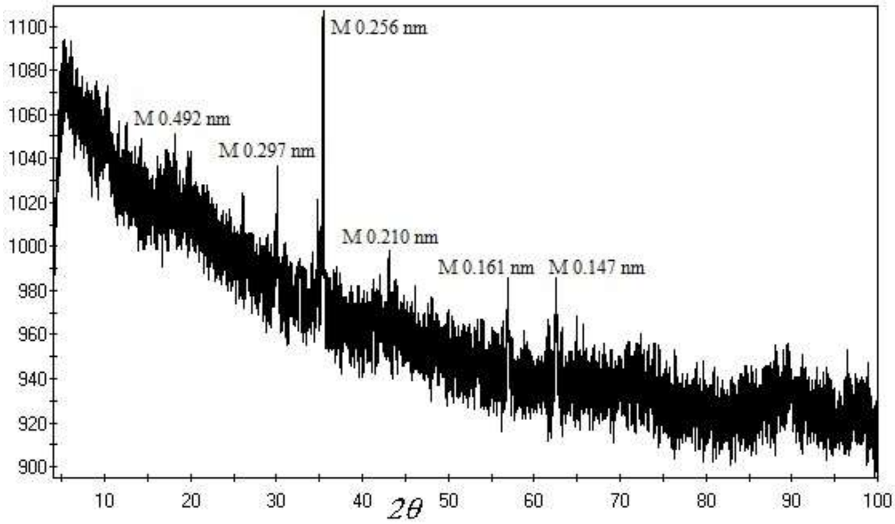

Fig 8: X-ray diffraction peaks of Fe oxide (magnetite) after had pulled out magnetically from soil

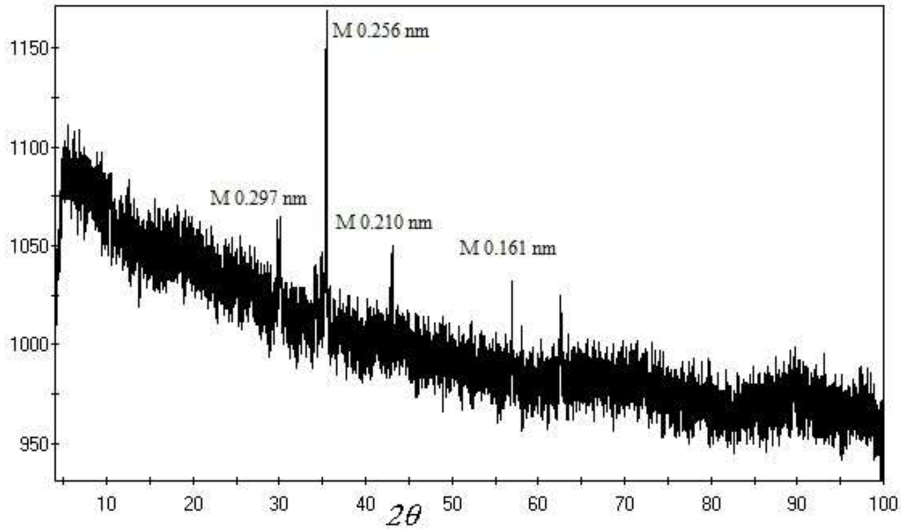

Fig. 9: X-ray diffraction peaks of Fe oxides after 1st treatment with citrate dithionite and aqua regia showing disappearance of hematite and wustite peaks

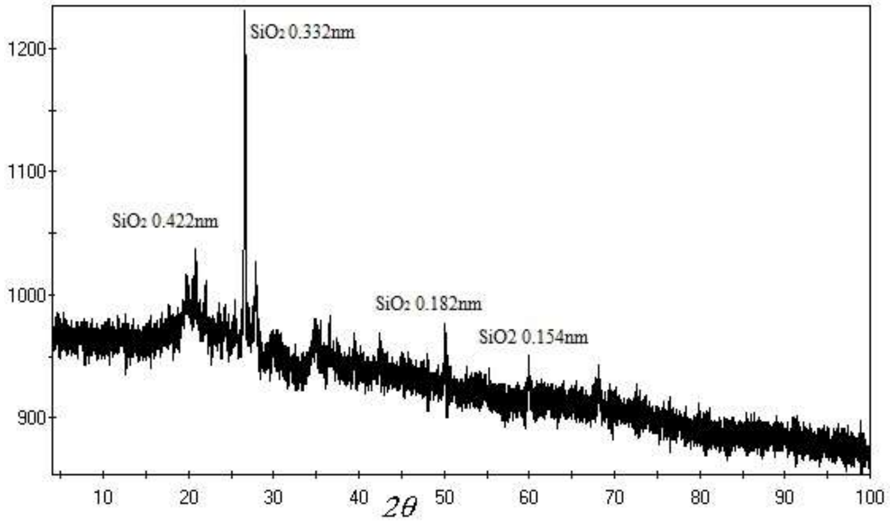

Fig 10: X-ray diffraction peaks of Fe oxide after five treatments of using aqua regia solution

## Conclusions

This study on the identification of the forms of Fe oxides in soils of Asnawa has shown that:

1. X-ray diffraction analyses showed that Magnetite $F_3O_4$ was the dominant Fe oxide mineral in Asnawa soils followed by hematite $Fe_2O_3$ and wustite Fe(1-x)O.
2. A fair amount of poorly ordered Fe oxides were also present; this may have been occurred through pedogenic processes.
3. Citrate-dithionite extraction method by Mehra and Jackson, and Coffin were not effective methods to extract forms of magnetite in Asnawa soils.
4. Extraction of magnetite by aqua regia solution was a better method but required five successive treatments to reach maximum dissolution.
5. Potassium pyrophosphate reagent at pH 10 extracted very low Fe oxides compared to $Fe_d$ and $Fe_o$ suggesting that no Fe oxides in the studied area have been complexed by organic matter through the pedogenic processes.

## References

[1] Bascomb, C. L., "Distribution of pyrophosphate – extractable iron and organic carbon in soils of various groups" J. of soil Sci. 19: 251-268, (1968).

[2] Bolton, C. M. G., "The geology of Ronia area" Site. Inv. Co. report, SOM Library, No. 271 Baghdad (1958).

[3] Chandra, V. G. and Andkunal G. GHOSH2 Clay Research, Dissolution of Iron Oxides Vol. 25, pp. 1-19, (2006).

[4] Coffin, D. E. "A method for determination of free iron in the soil and clay". Can. J. Soil Sci. 43: 7-17, (1963).

[5] Cornell R. M. and P. W. Schindler. "Photochemical dissolution of goethite in acid oxalate solution", Clays Clay Min. 35: 347-352, (1997).

[6] Hunt, C.P., Singer M. J., Kletetschka G., Tenpas J. and Verosub K. L., "Effect of citrate-bicarbonate-dithionite treatment on fine-grained magnetite and maghemite", Earth and Planetary Science Letters, issue 130, pp. 87-94, (1995).

[7] Jassim, Z. and Goff S.C., "Geology of Iraq", Published by Dolin, Prague and Moravian Museum, Brno, (2006).

[8] Natalia Oliver, S.D. World Economic outlook and Financial Surveys Coping with high debt and sluggish growth, international monetary fund. ISBN-13: 978-988, (2012).

[9] Pansu, M. and Gautheyrou J., "Handbook of Soil Analysis Mineralogical, Organic and Inorganic methods", XIX, 993 pp. 183, (2006).

[10] Rozan, T. F., Benait G., and April R. H., "A selective dissolution analysis optimized for measurement of weathering products in soil", J. Soil Sci. Soc. Am. 61: 949-958, (1997).

[11] Fontes, M.P.F., Oliveira, T. S., Costa, L.M. & Campos, A.A.G. "Magnetic separation and evaluation of magnetization of Brazilian soils from different parent materials", Geoderma, Vol. 96: 81-99, (2000).

[12] Golden, D. C. D., W. Ming., L. H. Bowen., R. V. Morris, and Jr. H. V. Lauer, "Acidified oxalate and dithionite solubility and colour of synthetic, partially oxidized Al magnetites and their thermal oxidation products. Clays Clay Min. 42:58-64 (1994).

[13] International Organisation for Standardisation (ISO), Soil Quality, "Extraction of trace elements soluble in aqua regia", ISO 11, 466, (2002b).

[14] Kafoor, S. N., "Iron oxide contents in relation to the colour of Asnawa soils", unpublished paper, (20014).

[15] Mawlud, Q. K., "Iron oxide mineralogy of Asnawa area using different techniques", MSc thesis, University of Salahaddin, Arbil, (2014).

[16] Mckeague, J. A., Brydone J. E. and N. M. Miles, "Differentiation of forms of extractable iron and aluminum in soils". Soil Sci. Soc. Amer. Proc. 35: 33-38, (1971).

[17] Mckeague, J.A. and J.H. Day, "Dithionite and Oxalate extractable Fe and Al as aids in differentiating various classes of soil", Can. J. Soil Sci. 46: 13-22, (1966).

[18] McCarthy, M.J., "Geology of Penjwin area", A report by State Company of Geological Survey and miming, Baghdad-Iraq, (1956).

[19] Mehra, O. P. and M. L. Jackson, "Iron oxide removal from soils and clays by a dithionite–citrate system buffered with sodium bicarbonate", Clays & Clay miner. 7: 317-327, (1960).

[20] Santana, G. P., J. D. Fabris and A. T. Goulart, "Magnetite and its transformation to hematite in soil derived from steatite", R. Bras. Ci. Solo, 25: 33-42, (2001).

[21] Schwertmann, U., "Relations between iron oxides, soil colour and soil formation. SSSA. Special edition", Vol 31. Soil colour, 51-69, (1993).

[22] Schwertmann, U. "Differenzierung der Eisenoxide des Bodens durch photochemische Extraktion mit saurer Ammonium oxalate" Losung, Z. Pflanzenerna¨hrung, Du¨ngung Bodenkunde, 105, 194–202, (1964).

[23] Schwertmann, U., "Use of oxalate for Fe extraction from soils". Canad. J. Soil Sci.53: 244-246, (1973).

[24] Schwertmann, U., "The effect of pedogenic environments on iron oxide minerals", Soil Sci. 1, 172-200, (1985).

[25] Stahl, K. J. "The Huber G670 imaging-plate Guinier camera tested on beam line I711 at the MAX II synchrotron", J. Appl. Crystallogr. 33- 394, (2000).

[26] Terentenko N.A. and B.B. Khadikov, "Exploration of Asnawa iron ore Deposit and Mishau iron ore occurrence:, Report on Prospecting Vol. 1, state company of geological survey and mining, Baghdad–Iraq. (1961).

[27] Torrent, J., U. Schwertmann, and D. G. Schulze, "Iron oxide mineralogy of some soils of two river terrace sequence in Spain", Goederma, 23: 191-208, (1980).