STUDIES ON MANGANESE AND IRON OXIDES IN SOME EGYPTIAN SIOLS

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A THESIS

SUBMITTED IN PARTIAL FULFILMENT

OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

IN

Agriculture (Soil Science)

Soils Department

FACULTY OF AGRICULTURE

AIN SHAMS UNIVERSITY

1988

APPROVAL SHEET

Title : STUDIES ON MANGANESE AND IRON OXIDES IN SOME EGYPTIAN SOILS.

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Date : / /1988.

بسم الله الرحمن الرحيم

ACKNOWLEDGEMENT.

The author wishes to express his deep thanks and gratitude to Prof. Dr. F.M. Abdou, Professor of Soils, Faculty of Agriculture, Ain Shams Univ. and Prof. Dr. S. El-Demerdashe, Professor of Soils and Head of Soil Chemistry and Mineralogy Unit, Desert Research Inst. for suggesting the problem, supervision, sincere guidance and constructive criticism throughout the course of study and preparation of the manuscript.

Thanks are also extended to Dr. A.S.N. Sheta, Ass. Professor of Soils, Fac. Agric., Ain Shams Univ., and Dr. I.W. Hafez, Ass. Professor of Soils, Desert Research Inst. for their co-operation, sincere help and guidance during this work.

The author is also indebted to the staff members and colleagues of Soils Dept., Desert Research Institute whose co-operation is deeply appreciated.

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1. INTRODUCTION.

Iron and manganese oxides are among the important constituents in soils since they are sources of the micro-nutrients Fe and Mn. Their reversible oxidation-reduction controls their behaviour in soils and, to a great extent, the available amount of those micronutrients.

From the pedological view point, iron-rich concretions, nodules, mottles, plinthites, bog iron ores and coatings are common features of some soils. Iron oxides have a high pig-menting power that determines soil colour. Thus, soil colour as determined by the type and distribution of iron oxides within a soil profile is helpful in explaining soil genesis, and is considered as an important criterion for naming and classifying soils.

Black manganese-rich concretions, nodules, mottles and glaebules are also common in some soils, and their presence as dominant features in seasonally-saturated horizons, is taken as morphological evidence of a fluctuating water-table.

Considering soil mineralogy, Fe and Mn are involved in the crystal structures of some clay and non-clay minerals, and may also be incorporated or entrapped into such structures during soil formation and development. Moreover, the chemical nature of both Fe and Mn oxides and their high specific sur-face area allow iron oxides to be an efficient sink for anions such as phosphate, molybdate and silicate in addition to the trace elements Cu, Pb, V, Zn, Co, Cr and Ni while lead to a high sorption capacity for heavy metals in case of manganese oxides.

The aim of the current study is to characterize the mineralogy and chemistry of Fe and Mn oxides in a collection of profiles representing soils of Nile and desert alluvium and those derived from lacustrine, sandy and calcareous deposits. Therefore, the study includes an evaluation of Fe and Mn bearing minerals in the clay fraction together with their forms in soils. Furthermore, sequential extraction was applied to distinguish the fractions of Fe and Mn associated with soil components.

2. REVIEW OF LITERATURE.

2.1. Iron.

Iron is one of the metallic constituents of soils. It exists in ferrous and ferric forms either in primary or secondary minerals. The primary iron-bearing minerals are mainly olivines, pyroxenes and amphiboles which are collectively termed ferromagnesium silicates that are usually associated with igneous rocks. The biotite micas with a Trimorphic clay structure and the iron ores comprise hematite, ilmenite and magnetite. The iron containing secondary minerals cannot be defined clearly owing to their heterogenity, Ahmed (1976). Biogenic products and chemical constituents such as calcite and dolomite formed at the place of deposition usually contain less than 1 % iron except where the deposition has occurred in shallow seas when calcites and perhaps iron minerals, as for example chamosite and/or siderite, may be found, Ahmed (1976).

Iron occurs in the weathering sequence perhaps as hematite and/or goethite through the alteration of Fe, Mg-bearing silicate minerals such as biotite, hornblende, and illite clay minerals,... etc.

Clay and primary minerals containing iron as an essential element are "hydromicas" illite, nontronite, chlorite, vermiculite, chamosite, glauconite, griffithite, cronsteolite and greenalite, Brindley (1961).

In soils, Fauck (1970) found that during pedogenic processes a great amount of silica being dissolved from quartz and leached out the ferrolitic profile, in red soils developed on parent material containing 50-95 % quartz, 5-40 % kaolinite and 1-6 % iron oxides under tropic condition with annual precipitation of 1-2m and one or two dry seasons. The main characteristics of soil development were rubification by accumulation of Fe oxides in the quartz skeletons.

Various iron minerals in different colours may be found in soils, namely; goethite with a yellowish brown colour (7.5 YR-10 YR); hematite with a bright red colour (5R-[illegible] 5YR), lepidocrocite with an orange colour (5YR-7.5Y); maghemite (reddish brown); magnetite (black) and also ferrihydrite with a reddish brown colour (5YR-7.5YR), Chukov (1973).

According to Schwertmann and Taylor (1977), there are other types of iron minerals like limonite, akaganeite and green rust. These minerals, although of less importance, may appear in the earth due to special environmental conditions that favour their formation. Generally, hematite is responsible for the red colour of many Oxisols (Laterite) and goethite may give the yellow colour of some Alfisols and other types of soils, Celso de Castro Fitho (1984).

2.1.1. Forms of iron in soils.

Iron occurs in soils in different forms of oxides, hydroxides and amorphous inorganic materials as reported by several investigators. The various crystalline iron oxides and their properties are briefly summarized by Schwertmann and Taylor (1977). They mentioned that with the exception of magnetite, all have been identified as products of pedogenesis. The properties of these oxides can differ markedly due mainly to adsorption or incorporation of foreign ions present in the soil environment into their structure, (Taylor and Graky, (1967), this can affect crystal development. Particle size and degree of isomorphous substitution can affect line width and position in the X-ray diffraction pattern as well as the temperature of the reaction during thermal analysis, Norrish and Taylor (1961) and Pawluk (1972).

a) Goethite (α-FeooH).

Goethite is the most frequently occurring form of iron oxides in soils. Thermodynamically, it has the greatest stability under most soil conditions, Berner (1969) and

Langmuir and Whittemore (1971). It occurs in almost every soil type and climate region and is responsible for the yellowish brown colour of many soils, while the high concentration of goethite may assume dark brown and even black colours, but it generally gives the yellow-brown streak typical of goethite, Schwertmann and Taylor (1977).

Goethite in soils may possibly be formed by any of the following three processes, Tamura and Jackson (1953).

I. Slow precipitation of ferric ions in solution at low pH.

II. Aging of ferric hydroxide gel at high temperature and pH.

III. Oxidation of ferrous carbonate ions.

According to these authors, the process (I) is perhaps the most feasible. According to Murphy et al.(1975), goethite is formed in solution under various conditions. The rate and amount of precipitate formation were dependent on the degree of anion penetration for the polycations and precipitates and the total anion concentration.

b) Hematite (α-Fe_2O_3).

In many reddish soils, goethite is associated with hematite which is the second most frequent soil iron oxide, Schwertmann and Taylor (1977). Hematite appears to be absent in soils recently formed under a humid temperate climate. It gives the soil a red colour and has a greater pigmenting effect particularly when it occurs in finely dispersed form.

According to Tamura and Jackson (1953), hematite can be formed as follows.

1- Transformation of all iron oxides to hematite when heated to sufficiently high temperature.

2- Ageing of ferric-hydroxide gel at high temperature in very dilute alkaline solution.

3- Rapid drying of $FeCO_3$ films.

c) Lepidocrocite (γ-FeOOH).

Lepidocrocite occurs in soils less frequently than goethite or hematite, Van der Marel (1951), Brown (1953) and Schwertmann (1959). Goethite and lepidocrocite are often associated. Lepidocrocite is usually formed from the oxidation of precipitated Fe^{2+} hydroxy compounds, and appears to be restricted hydromorphic soils where Fe^{2+} is generated due to oxygen deficiency. Therefore, its occurrence is indicative of hydromorphic conditions (water-logged soils). Accordingly, it is found commonly in gleys and pseudogleys, particularly those high in clay, Fischer (1972). Nevertheless, it is not found in calcareous hydromorphic soils where goethite forms instead, Schwertmann and Taylor (1973). Macroscopically, lepidocrocite occurs as bright orange mottles or bands. Lepidocrocite does not originate directly from ferric iron. The possible pathways being through ferrous iron as follows, Tamura and Jackson (1953).

(1) Oxidation of ferrous hydroxide at pH 4-8 in the absence of carbonate ions. (2) Oxidation of ferrous bicarbonate or sulphide. Lepidocrocite is more likely to occur under conditions of low carbonate and oxygen concentration. This being the reason for its presence only in the lower horizons of water-water-logged soils. Schwertmann and Taylor(1977)studied the occurrence of lepidocrocite and its association with goethite in Natal soils (South Africa). They found that hydromorphic soils (pseudogleys) in high land mountain climate of Natal contain appreciable amounts of lepidocrocite. Its occurrence appears to be restricted to imperfectly drained lower positions on southern (cooler) slopes at an altitude between 1,300-1,900 m. In these positions, Fe is reduced under anaerobic conditions leading to lepidocrocite formation on reoxidation. Goethite is closely associated with lepidocrocite and increases on approaching better aerated microzones such as root channels and textural boundaries where it usually forms crusts. Ross and Wang (1982) found that lepidocrocite occurred in B and C horizons of several poorly drained acid soils.

d) Maghemite ($\gamma-Fe_2O_3$).

Maghemite is especially common in highly weathered soils of tropical and subtropical climates and also occurs in soils of temperate regions, Taylor and Schwertmann (1974). Occurrences in soils formed from basic igneous rocks seem to prevail in all these regions. The mineral is reddish brown and ferromagnetic. It may be finely dispersed or concretions, frequently in association with hematite.

The formation of maghemite in nature may occur by oxidation of magnetite, Bonifas and Legoux (1957), and by ignition of amorphous oxides in presence of organic materials. There is also evidence for the formation of maghemite pedologically through the agency of soil organic matter.

e) Magnetite (Fe_3O_4).

Magnetite is a ubiquitous oxide mineral in igneous, metamorphic and sedimentary rocks. It is present in the heavy fraction of soils developed on very diverse parent materials, Oades (1963), including showers of volcanic ash, Mizota et al. (1975).

Magnetite may be formed by the following methods, Tamura and Jackson (1953).

1- Precipitation of a mixture of ferrous and ferric ions.
2- Slow oxidation of ferrous ions in solution.
3- Oxidation of ferrous hydroxide at low temperature using