



SOME ASPECTS OF THE NATURE OF IRON OXIDES
IN SOILS.

A Thesis for the Degree of Master of Science

by

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Table of Contents.

	<u>Page No.</u>
Statement .	1
Summary	2
Chapter I Introduction	
1. The role of Iron Oxides in Soils.	5
2. Forms of the Iron Oxides.	7
3. Scope of this Thesis.	9
Chapter II The origin of Iron Oxides in Soils.	
1. Introduction.	11
2. Experimental Data.	20
3. Results and Discussion.	22
Chapter III Quantitative Estimation of Iron Oxides by X-ray Diffraction Techniques.	
1. Introduction.	29
2. Experimental Data.	34
3. Results and Discussion.	44
4. Summary.	57
Chapter IV Amorphous Iron Oxides in Soils.	
1. Introduction.	59
2. Apparatus and Methods.	61
3. Results and Discussion.	63

Continued over....

	<u>Page No.</u>
Chapter V The Chemistry of Soil Goethites.	
1. Introduction.	75
2. Choice of Samples.	77
3. Methods.	80
4. Results.	87
5. Discussion.	94
Acknowledgements.	104
Bibliography.	110



STATEMENT.

This thesis contains no material which has been submitted for the award of any degree or diploma in any University.

To the best of my knowledge and belief, this thesis does not contain any material previously published or written by any other person, except where due acknowledgement is made either in the text, or in the bibliography.

(R.M. Taylor.)

SUMMARY.

Soil classification, which is essential for efficient land usage, is often influenced by the colour or zones of accumulation or depletion of iron oxides. These minerals are also of practical importance, as they provide the nutrient iron needed by plants and may affect the fixation of phosphate. Iron oxides occur in soils in many forms, and each variety may be indicative of the dominance of certain soil forming factors.

Synthetic preparations of many of these minerals have suggested possible methods of formation in soils. Some of these suggested methods, however, utilise conditions not generally realised in soils. Recent experiments have shown that three of the most common forms, viz. goethite, haematite and lepidocrocite, can all be synthesised from the same initial material by changes in environmental conditions of the order and in the range that could be expected in soils.

For much of the work in this project it was necessary to have a satisfactory method for quantitatively estimating the various mineral forms present in a soil. X-ray diffraction techniques have previously been used but these methods generally have some inherent limitation or require elaborate sample preparation. Using a Norelco high angle diffractometer

to measure both the diffracted intensities and the mass absorption coefficients, determinations at least as accurate as more tedious methods can be made. The limitations to the accuracy of this proposed method are imposed by such parameters as orientation, particle size, concentration and composition; but these factors also limit the accuracy of most other methods of quantitative X-ray diffractometry.

The presence of amorphous iron oxides has often been invoked to establish a mineralogical balance sheet between the measured total Fe_2O_3 and the detected crystalline forms. Because of the difficulty, not only of determining, but also of detecting, minor quantities of crystalline iron oxide minerals, it is likely that many soils have been incorrectly described as containing this amorphous form. An exothermic peak on D.T.A. records at about $330^\circ\text{C}.$, has often been used for the identification and confirmation of the presence of amorphous iron oxides in soils. However, it is shown that this diagnostic exotherm can be due to the oxidation of difficultly removed organic matter.

Goethite is a very common iron oxide in soils and has been observed to display quite anomalous properties. It is shown that the majority of soil goethites contain aluminium, which has isomorphously replaced some of the iron. This substitution affects

both the spacing and intensity of diffracted lines, but the reduction in cell dimensions is not uniform in the direction of each crystallographic axis. Substitution also limits crystal growth and is greatest in the smallest particle sizes, where aluminium contents of up to 25 mole per cent have been measured. The ease of removal by sodium dithionite reduction techniques is also affected; the higher the substitution the more difficult is the extraction.