SOME ASPECTS OF THE NATURE OF IRON OXIDES IN SOILS.

A Thesis for the Degree of Master of Science
by
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Thesis submitted ....

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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.

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(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 inherrent 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°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.

CHAPTER 1.

INTRODUCTION.

1. The Role of Iron Oxides in Soils.

Soil classification and behaviour is often largely affected by the presence and mode of occurrence of the free iron oxides. The various colours imparted by these oxides (Lippi-Boncambi et al. 1955, Norrish and Rogers 1956) can often be used as a broad index to great soil group, for example red and yellow podzolic; while their accumulation in, or removal from, certain horizons is often used for further differentiation, as in a podzol or a laterite. In some soils various morphological and genetic features are so intimately connected with the iron cycle that the designated soil forming processes are actually describing the behaviour and state of the iron in the profile. Podzolisation, gleying and laterisation are good examples of these processes. Large amounts of free ferric oxides can also minimise profile development due to flocculation effects, for example in a kraznozem. (Stephens 1956.)

The presence of iron in the profile may also influence the soil structure. Iron organic complexes have been suggested (McIntyre 1956) to be responsible for this effect, although Lutz (1936) considers that both iron in solution and the crystallisation of freshly precipitated hydroxides influence structure with their respective flocculation and cementation effects. On the other hand Prebble and Stirk (1959) suggest that the structure and presence of iron oxides in a profile both reflect the weathering conditions rather than the former being dependent on the latter. Continued deposition in certain horizons may have an adverse effect on structure due to the formation of hardpans. (Russell 1950).

Since the most important function of a soil is as a medium for plant growth, any influence of the iron oxides on the fertility of a soil will be important. In this regard their ability to fix phosphate, either by adsorption, exchange or precipitation (Dean 1949, Hemwall 1957, Kittrick and Jackson 1956), has been the subject of much experimental work and speculation. The anion exchange capacity (Schofield 1949) at pH values normally found in soils may also be the source of some anions, apart from phosphate. For most plants iron is a necessary nutrient element and its availability from the various forms in soils has also received some attention. Iron acts as a catalyst in all cellular respiration, and is necessary for certain animal tissues and enzymes (Rankama and Sahama, 1949). Where easily weatherable iron oxide minerals are not present, the free ferric oxides in the soil must supply the necessary amounts of iron, and their form and degree of crystallinity are the main factors determining availability (Tsyrupa 1958).

Another aspect in which the iron oxides may exert a slight influence on fertility is through their effect on soil temperature since the colour of a soil can control the amount of heat absorbed. (Russell 1950).

2. Forms of Iron Oxides.

The term "iron oxides" when applied refers not only to true oxides of the type Fe_xO_y but also to the hydroxide form having the formula FeOOH. Haematite, maghemite and magnetite are minerals of the true oxide form, and goethite and lepidocrocite represent the hydroxide. (Double oxides e.g. ilmenite, $FeTio_3$, are not classed as iron oxides because of their stability and relative inactivity). Haematite and maghemite are dimorphous as are goethite and lepidocrocite (see Table 1.) Other polymorphs can be made synthetically but as yet they have not been detected in nature. Most of these naturally occurring "iron oxides" are isostructural with an aluminium analogue; the inferences and importance of this will be discussed in Chapter V. Each of these oxides mentioned above are crystalline, but in young soils or bogs a non-crystalline form containing variable amounts of absorbed water may also be found. (Schwertmann 1959b).

TABLE 1A.

Mineral Name	Composition	Crystal System	Colour	Form
Haematite	Fe_2O_3	Hexagonal	Brick red purple	α
Maghemite ^{x}	Fe_2O_3	Cubic	Black to dark brown	γ
Magnetite ^{x}	Fe_3O_4	Cubic	Black	—
Goethite^x	FeOOH	Orthorhombic	Yellow to Yellow brown	α
Lepidocrocite^x	FeOOH	Orthorhombic	Orange	γ

TABLE 1B.

Iron Oxide	Aluminium Analogue
Haematite	Corundum
Maghemite	-
Magnetite	γ Alumina
Goethite	Diaspore
Lepidocrocite	Boehmite

x Goethite and Lepidocrocite although having the same composition and crystal system differ in their space groups and thus exhibit dissimilar diffraction patterns.

x Maghemite is an imperfect spinel and has a few extra lines which do not appear in the otherwise similar magnetite diffraction pattern.

3. The Scope of this Thesis.

Iron oxides are clearly important minerals in soils so that a better understanding of their origin, composition and properties could lead to a better understanding of the soils themselves. The experimental work recorded in this Thesis, which is part of a broader investigation, will include the following topics:--

(a) A review of proposed methods of formation of iron oxides. Generally, these methods are based on laboratory syntheses which often employ conditions not generally realised in soils. A more probable method of formation is proposed based on the results of some recent experiments by the author.

(b) An X-ray diffraction method for quantitative estimation of some of the different mineral forms included in the expression "free iron oxides."

(c) The occurrence of amorphous iron oxide in soils. It is pointed out that this form is not quite as prevalent as has been previously suggested.

(d) The isomorphous replacement of iron by aluminium in soil goethites. As distinct from mineral goethites the majority of soil goethites examined have been found to contain structural aluminium. This replacement is shown to affect:--

  (1) the X-ray diffraction pattern,
  (2) the ease of removal by conventional "free iron" removal techniques, and,
  (3) the crystal growth of these minerals.

The above topics are discussed separately in Chapters II - V.

CHAPTER 11.

THE ORIGIN OF IRON OXIDES IN SOILS.

1. Introduction.

Before an iron mineral impresses its character on and becomes an integral part of a soil element in equilibrium with its present environment, it existed, possibly in a very different form, in a primary or unweathered rock, or possibly in a buried soil presently exposed to a new regime of weathering.

Iron is the fourth most abundant element in the earth's crust - 5% by weight (Mason 1958), and its major primary occurrences are either of igneous or sedimentary origin. The acidity or basicity of the igneous magma influences the nature of the iron minerals formed during the subsequent crystallisation. For example, in acid magmas, the earliest products of differentiation are the oxides and sulphides of iron, and such minerals as magnetite, ilmenite, haematite, pyrrhotite and pyrite are formed. Ramdohr (1940) believes that haematite in such deposits is an alteration product rather than an original primary mineral. With an alkalic magma, iron tends to remain in the melt during the early stages of crystallisation, and is precipitated later in the iron rich amphiboles and pyroxenes.

The haematite, magnetite and ilmenite deposits, both sedimentary and igneous, are often so massive and pure that they are mined as economic sources of iron. Because of their massive nature and their relative resistance to weathering, (Jackson et al. 1948), these deposits would contribute very little to the iron status of soils. The sulphides, however, are easily oxidised to the sulphate and, on solution may be transported via the soil water to a new environment.

The amphiboles and pyroxenes are also very easily weathered and in fact occupy the lowest positions of stability in the weathering sequence of rocks. (Jackson et al. 1948). The presence of ferrous iron in many of these minerals may actually be a contributing cause to their instability, as is the case in biotites.

It is reasonable to assume therefore that minerals belonging to these latter groups are the main source of the iron which forms the common soil oxides, whereas the former group may exist in a soil as residuals or unweathered primary minerals.

Even if the primary mineral origin of the soil iron oxides is known, the manner in which the common iron minerals form within a soil has been the subject of much speculation. It is obvious, though, that the soil forming factors responsible for the weathering of the primary iron minerals must be the same factors which control the subsequent precipitation and formation of the soil iron oxides.

The less resistant primary minerals are solubilised and the products either transported or redeposited in situ. Whether or not this transportation occurs, the form the iron assumes will depend on a combination of the following factors:

(a) The ionic composition of the environment,

(b) The prevalence of oxidation or reduction conditions,

(c) pH,

(d) Nature and extent of the organic material and micro-organisms present,

(e) The temperature and climatic conditions, and

(f) Time.

Many experimenters have produced synthetic iron oxides, and have shown that variations in either one or more of the above factors produces variations in the end product. Such workers as Weiser and Milligan, (1935) Kulp and Trites, (1951) Gheith, (1952) Scheffer et al., (1957) have carried out many syntheses and have suggested that natural iron oxides form in soils under conditions similar to those maintained during their experiments. However, some of the most important of the above factors were either ignored or given unrealistic values; for example, neglecting the influence of ionic environment or utilising pH values greater than 11. Many results therefore appear contradictory, both in terms of the end product obtained in a particular synthesis, and in the emphasis placed on the various soil forming factors.

Recent work by Schellmann (1959) and Schwertmann (1959) has done much to clarify the discrepancies arising out of earlier results. From his own work and from the results of others, Schwertmann (1959b) suggests that the formation of well defined iron oxides may proceed along two lines;

1. By the ageing of brown, X-ray amorphous ferric oxide gel, produced by the rapid precipitation of ferric ions with an alkali; or
2. By the oxidation and subsequent hydrolysis of divalent iron, or the precipitation and subsequent oxidation of a ferrous compound.

Since both these methods are essentially hydrolysis, and since both have been used to synthesise iron oxides, it is necessary to examine carefully the results and implications of each before deciding which method is the more probable under soil conditions. In each technique, it is necessary for the hydrolysis product to age under moist conditions. This ageing is synonomous with crystal growth; it involves a decrease in surface area and water content and an increase in atomic order.

The ageing of the brown gel produced by method 1 will serve to illustrate the contradiction in results obtained by various workers. The freshly precipitated gel gives an electron diffraction pattern resembling haematite according to Weiser and Milligan (1940), whereas MacKenzie (1952) finds a closer resemblance to β FeOOH. Gheith (1952) found that the washed gel aged to goethite, whereas Weiser and Milligan (1935) observed haematite to be the final product. MacKenzie (1957) produced both goethite and haematite by ageing. In some of these experiments no detail of the extent of washing or the pH of the ageing medium is given, whereas recent work of Schellmann (1959) and Schwertmann (1959b) has shown that the final product is greatly dependent on these factors.

The effect of temperatures on the ageing of this "brown gel" (prepared by the rapid precipitation of ferric ions with an alkali) also seems uncertain; Schellmann (1959) showed that temperatures up to 50 or 60° C. only accelerated ageing and did not influence the direction. Contrary to this Schwertmann (1959b) found an interdependence of temperature and pH effects on the direction of ageing - the higher the temperature the higher the pH necessary to form goethite. From this relationship he postulates that goethite probably forms at a low temperature from the "brown gel" even in the presence of a low hydroxyl concentration.

Schellmann's (1959) investigation is most comprehensive, examining the combined and individual effects of the most important of the soil forming factors. He found that the direction of ageing is influenced most by pH and ionic environment. An increase in pH also accelerated crystallisation, as did the presence of an already crystalline material. This latter factor however had no effect on the end product. The effect of ionic environment had been noted previously by Weiser and Milligan (1935) who found that the presence of an added electrolyte can retard or prevent transformation of the "brown gel" to haematite. Schellmann investigated this effect in a series of experiments in which he aged the gels in the presence of anions and cations which are known to occur in soil solutions. Depending on the isoelectric point of the precipitated gel and the pH of the medium, either anions or cations are adsorbed.

These adsorbed ions influence the direction of ageing to varying degrees. For example, below the isoelectric point, the gel is predominantly negatively charged and cations are adsorbed. Whereas Ca^{++} or Mg^{++} ions direct the ageing towards haematite, the presence or absence of Na^{+}, K^{+} and Ba^{+} ions does not affect the final product either quantitatively or qualitatively. Anions such as HCO_3^{-}, OH^{-} and SO_4^{--} enhance the formation of goethite while $H_2PO_4^{-}$ and $HPO4^{--}$ ions completely inhibit crystallisation. In a region where both anions and cations are adsorbed, say Ca^{++} and OH^{-}, the preferential adsorbtion of the hydroxyl would favour the formation of goethite.

Since the isoelectric point of the "brown gel" prepared by the rapid precipitation of ferric ions with an alkali is 8.6 (Schuylenborgh 1950, Schellmann 1959), a small variation in the pH of the ageing medium near pH7 would be expected to have little effect, and the direction of ageing would be influenced only by the chemical nature of the ions present. Gels prepared by the slow oxidation-hydrolysis method have lower isoelectric values, (Schuylenborgh 1950), and would therefore be more susceptable to pH changes near neutrality. The ageing of these preparations with lower isoelectric points can help explain the occurrence of intimate mixtures of goethite and haematite, as seasonal changes in pH could be sufficient to cause anions and cations to be alternatively adsorbed.

Where a gel ages in an electrolyte free medium, a pH of 11 or higher is necessary to produce pure goethite at room temperatures. (Schwertmann 1959b, Schellmann 1959). As the pH decreases a mixture of goethite and haematite and finally pure haematite results. It is evident therefore that methods of formation suggested by such syntheses are unrealistic, as haematite free goethite is more common in soils than pH values of 11 and greater. It seems reasonable to assume that haematite once formed will not transform to goethite except by subsequent solution and precipitation under a changed environment. The necessity of pH values greater than 11 for the production of pure goethite cannot be used as an argument against the "brown gel" as a likely origin of the iron oxides because it is most improbable that soil solutions are ever free of electrolyte.

There are, however, two important factors, as well as the one already mentioned concerning the isoelectric point, which suggest that this rapidly precipitated gel is an unlikely, or, at least, not a very common origin of the iron oxides in soils. These two factors are:--

(1) This gel has not definitely been found in normal soils* (Schwertmann 1959b); Tamura and Jackson (1953) believe this is due to the absence of resonant co-valent bonds that are present in the analogous and stable $Al(OH)_3$ compounds. However, since ageing is not instantaneous, it is probable that this gel would have been detected at least in some soils if it was common as a source of the iron oxides.

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* This subject is dealt with more fully in Chapter IV.

(2) Lepidocrocite, which commonly occurs with goethite, has not been reported to form from this gel.

The second suggested method of formation that based on the slow oxidation-hydrolysis of a ferrous compound, therefore seems more probable. The ageing of this gel is also subject to the influence of ionic environment, and, because of the lower isoelectric point pH variations near pH 7 are more significant.

This gel also ages to lepidocrocite, and according to Schwertmann (1959b), the production of either goethite or lepidocrocite at room temperatures and neutral pH values depends on the partial pressures of oxygen and carbon dioxide. Schwertmann's assumption that haematite is derived from this gel only via the dehydration of goethite is quite untenable. To accomplish this dehydration minimum temperatures of 140°C. (Posnjak and Merwin 1919), 150-160°C (Schellmann 1959) would be necessary. Schmalz (1958) has calculated from thermodynamic considerations that goethite should be stable in an aqueous medium up to 100°C, while Smith and Kidd (1949) found that goethite can exist in a neutral aqueous medium up to 125± 15°C. Scheffer et al (1957) state that such a transition is not only improbable but that it is practically impossible in soils.

It may be argued therefore, that if this gel cannot age to haematite, the slow hydrolysis method could not satisfactorily explain the adjacent formations of goethite and haematite which are so prevalent in soils. This is not the case, as the present author has produced haematite from such a gel in a recent series of syntheses.

The syntheses reported here were actually commenced in connection with another aspect of this thesis. The occurrence in soils of goethites with some of their iron replaced by aluminium led to the attempted syntheses of such compounds. (See Chapter V) During the preliminary experiments pertaining to these syntheses it was noticed that haematite, goethite and lepidocrocite were each formed from the same slow hydrolysis gel by slightly varying environmental conditions. Because the variations were of the order that could be expected in soils, the results appeared interesting enough to warrant inclusion in this thesis.

2. Experimental Data.

Fixed volumes of ferrous sulphate and/or ferrous chloride solutions of known concentration were mixed with separate solutions of sodium bicarbonate. (See Table 1.) The pH was then adjusted with HCl or NaOH to values within the range 4-7. Aliquots of each mixture were allowed to stand either at room temperature or at 40 or 50°C. for various periods.

The divalent form of iron was chosen rather than the ferric for the following reasons:--

(a) Fe^{++} ions are continually being formed in soils by the action of micro-organisms and localliesed reducing conditions.

(b) The divalent ion is more soluble than the trivalent and can remain in solution over a larger range of pH values. The precipitation of ferric ions begins at pH 3.0 whereas ferrous ions can remain in solution to pH 5.1. Precipitation of ferrous salts is still incomplete at pH7. (Atkins 1930).

(c) Many easily weathered primary minerals contain divalent iron which may be dissolved and distributed throughout a soil profile.

The only anions in these systems were HCO_3^-, SO_4^{--}, Cl^- and OH^- while the cations were Na^+, H^+ and $Fe^{++(+)}$. At the time of these syntheses Schellmann's work on the effect of ionic environment had not been reported and the influence of such ion as Ca^{++} and Mg^{++} was not investigated.

After a period of ageing, any precipitates were washed with water and ethyl alcohol and dried from the latter at 100°C. The precipitates were then examined by X-ray powder diffraction techniques. Using Co $k\alpha$ radiation and a 5.73 cm diameter camera, the powder specimen was rotated and exposed for 40 minutes at 30 kV 10 mA.

3. Results and Discussion.

The most important observation arising out of these syntheses is that goethite, haematite and lepidocrocite are each formed from the same starting materials when the environmental conditions are slightly altered (Table 1). All the X-ray diffraction photographs of the precipitates could not be reproduced for inclusion in this discussion because of the broad and diffuse character of many diffraction lines. This feature is common in very fine grained or poorly crystalline materials. In Table 2 the term "Well Crystalline" would signify a degree of crystallinity comparable to that of naturally occurring soil oxides. In Plate 1 are given three powder diffraction photographs of synthetic preparations, to indicate the extent of line broadening and also the difference between the patterns of haematite and goethite.

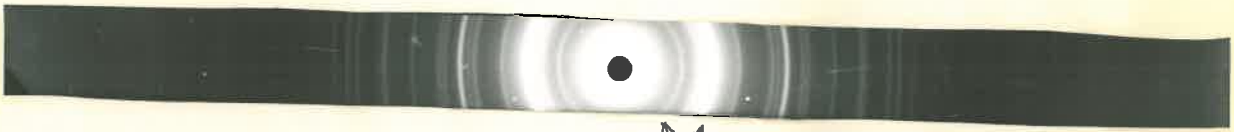
In these syntheses, although goethite-haematite and goethite-lepidocrocite mixtures were readily formed, no haematite-lepidocrocite mixture was produced; furthermore no reference to such a mixture has been noted in the syntheses of other workers. Goethite-haematite and goethite-lepidocrocite mixtures are very common in soils, but only one reference has been noted to a natural occurrence of a haematite-lepidocrocite mixture. Kulp and Trites (1951) report a limonite from Terra do Curral,

TABLE 1.

Exp. No.	Reagents			Initial pH	Ageing Period	Temp.	Results	Remarks
	$FeCl_2$	$FeSO_4$	$NaHCO_3$				(X-ray Diffraction)	
1.	20ml .02N	-	20ml .02N	7	7 days	R.T.	Very fine grained lepidocrocite	Air blown through solution for 7 days
2.	"	-	"	7	"	"	Fine grained lepidocrocite + goethite	Approx. equal amounts
3.	"	-	"	7	"	50° C.	More crystalline lepido. + goethite	Approx equal amounts. Less amorphous material than in 2.
4.	"	-	"	6	"	R.T.	Fine grained lepidocrocite + little goethite	
5.	"	-	"	6	"	50° C.	Fine grained goethite + little lepidocrocite	
6.	"	-	60ml .02N	4	"	R.T.	No precipitate	
7.	"	-	"	4	"	50° C.	Well crystalline haematite + trace goethite	
8.	20ml .01N	-	"	3.9	3 days	50° C.	Well crystalline haematite + trace goethite	
9.	-	10ml .014N	10ml .025N	7	9 mths.	R.T.	Goethite + moderate amount lepidocrocite	More crystalline & less lepid. than 2.
10.	10ml .02N	-	10ml .025N	6	"	"	Well crystalline goethite + little lepidocrocite	More crystalline and less lepid. than 4.
11.	5 ml .02N	5ml .014N	10ml .025N	6	"	"	As above	As above
12.	5 ml .04N	5ml .028N	10ml .025N	6	"	"	Goethite	Well crystalline
13.	-	10ml .014N	-	5	"	"	Goethite	Well crystalline
14.	-	10ml .006N	-	6	"	"	Goethite	Well crystalline

PLATE 1.

X-RAY DIFFRACTION PATTERNS OF SYNTHETIC PREPARATIONS.



SAMPLE 5

F.G. Goethite
little lepidocrocite.

SAMPLE 8

Haematite .
Trace Goethite

SAMPLE 12

Goethite

Brazil, which from X-ray diffraction and differential thermal analysis appears to contain only these two oxides. The simultaneous occurrence of all three forms seems more common and several such formations are listed in the above paper.

The limited data of these syntheses does not permit the derivation of a range of conditions in which a particular oxide is formed. However it seems probable that there is a transition in the formation of these three oxides from pure haematite through haematite-goethite, pure goethite, goethite-lepidocrocite to pure lepidocrocite as environmental conditions change. To account for the natural occurrence of a haematite-lepidocrocite mixture such as that quoted, would therefore require a rapid and marked change in conditions.

Comparison of the precipitates formed in syntheses 10 and 4 and in syntheses 9 and 2 confirms the observations Schwertmann (1959), in which he notes that lepidocrocite may recrystallise to goethite providing that it is not highly crystalline. If conditions, however, favour the continued crystallisation of lepidocrocite, reversion to goethite is unlikely.

Unfortunately in these syntheses, the state of oxidation of the ferrous chloride prior to the addition of the bicarbonate was not known, and it is probable that a large percentage of ferric material was present.[x] Further parameters that need be controlled in the syntheses of iron oxides are the solution-air interfacial area and the $\frac{\text{volume of air}}{\text{volume of solution}}$ ratio. The importance of these parameters was demonstrated in a further set of syntheses in which aliquots of the solutions used in Table 1 were allowed to age either in stoppered test tubes or in stoppered 300 ml conical flasks. The $\frac{\text{volume of air}}{\text{volume of solution}}$ ratios were approximately 1:1 and 7:1 in the respective cases. The resultant precipitates were not examined by X-ray diffraction, but the variation in conditions produced obvious differences.

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[x] Even in a stoppered jar of AR grade of $FeCl_2$ degradation occurs. An insoluble material which is probably an oxidation-hydrolysis product is often found with this reagent. This insoluble material has been identified as β FeOOH which exhibited no tendency to recrystallise to a more common form even after 9 months in water at room temperature. The fact that FeOOH does not occur in nature suggests that soil systems are generally more complex than just Fe^{++} and Cl^- ions.

It was found that in the case of the test tubes, many of the precipitates were black or brown-black and showed ferro-magnetic properties. Identical solutions aged in the flasks gave yellow to yellow-red precipitates. In each case ageing was carried out at 40°C. The only explanation that can be offered is that in the test tubes the reduced amount of air was not sufficient to completely oxidise all the Fe^{++} ions and that some magnetite was formed. Maghemite was not suspected because this is usually formed by the oxidation of magnetite or the recrystallisation of lepidocrocite at about 300°C. (Schwertmann 1959b).

As a point of interest, a naturally occurring gel has recently been examined. The sample occurred as a thin surface coating on the recently drained Clybucca swamp in the Kempsey area of New South Wales. X-ray diffraction showed that this material exhibited bands identical with those given by the amorphous gel precipitated by the hydrolysis of a ferric sulphate solution. By removing much of the amorphous material with a 0.1N HCl wash a diffraction pattern of a fine grained goethite was obtained. On ageing this residue for one week at 60°C. the material became more crystalline.

The origin of this material can be explained by reference to the rest of the profile. Sub surface horizons included marine muds containing ferrous sulphide

(P. Walker, Private communication 1960). Partial oxidation and combination with potassium led to the formation of jarosite ($KFe_3(SO_4)_2(OH)_6$) in root channels. Complete oxidation to ferric sulphate at the surface and subsequent hydrolysis gave this thin amorphous coating.

As stated before the syntheses described here were commenced in relation to aluminiferous goethites (see Chapter V). The important observation that arose out of these syntheses was the formation of each of the common soil iron oxides from the same slow hydrolysis gel by subtle variations in conditions.

It appears that this gel is the most probable source of the iron oxides, and more detailed work, defining the ranges of formation of each mineral form in terms of pH, temperature ionic environment and oxidation-reduction conditions, should be carried out.

CHAPTER III.

QUANTITATIVE ESTIMATION OF IRON OXIDES BY X-RAY DIFFRACTION TECHNIQUES.

1. Introduction.

The determination of the elemental composition of soils, rocks, etc. by chemical and instrumental methods has been developed to such a high degree of accuracy that it is surprising to see an analysis in which the tally is not 100%. Qualitative X-ray diffraction and microscopy provide the tools for taking an analysis a further step, by providing information on how the elements are combined. The only remaining problem is the quantitative estimation of these compounds.

Microscopy cannot provide the solution to this problem in most soil analyses because of two serious limitations. Firstly, the number of particles that have to be examined to ensure a truly reasonable accuracy would render the method tedious and, secondly the clay size fraction, which constitutes the active part of a soil, is too small for accurate observations with normal optical microscopes. X-ray diffraction is not subject to these limitations and techniques have been developed and employed by some workers, with some success, to estimate certain crystalline components present in mixtures.

Generally these methods have used calibration charts or internal standards, both of which depend on the comparison of the diffracted intensities of the sample and a standard. Since the intensity of diffraction from any atomic plane in a crystallite can be seriously influenced by the composition of the surrounding matrix, the above methods would be accurate only over a limited range of samples.

Because iron oxides in soils are found in association with many other minerals it was necessary to develop a method which is independent of the matrix. This necessity arose when a project concerning amorphous iron oxides in soils was commenced. (See Chapter IV.) As will be shown in the next chapter, being able to account for all the measured Fe_2O_3 by the crystalline forms, eliminates the possibility of the presence of an amorphous form.

The method which was developed for the estimation of the iron oxides is not new in principle, but the experimental techniques, reported by Norrish and Taylor (1958), present certain advantages over existing methods. The following derivation of the equations used in the estimation is reproduced in part from the above report.

If the incident and diffracted X-ray beam enter and emerge symmetrically on the same side of a "thick" flat powder specimen, it is easily demonstrated that, (Klug and Alexander 1954, p.412)

$$I_x = \frac{KV}{\mu} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where I_x is the measured intensity of a diffraction line of a crystalline component of the sample:--

V is the volume fraction of the component;

μ is the linear absorption of the specimen and

K is a constant for any particular line of a particular mineral.

This constant depends on the incident X-ray intensity, the diffracting power of the crystal planes giving rise to the spacing being measured and the geometry of the instrument. In deriving this equation it is assumed that the crystallites of the specimen are small enough not to give microabsorption effects. (Brindley, 1945).

If ρ is the apparent density of the specimen and ρ_x the true density of the component being analysed, then

$$I_x = \frac{KX}{\rho_x A_x} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where $X = \frac{\rho_x . V}{\rho}$ is the weight fraction of the component being analysed, and

$A_x = \frac{\mu}{\rho}$ is the mass absorption coefficient of the specimen.

If now the same diffraction line is measured on a standard sample for which X is known and equal to S

$$I_S = KS/\rho_s A_s \quad \ldots\ldots\ldots\ldots(3)$$

combining equations (2) and (3)

$$X = \frac{A_x \; I_x \; S}{A_s \; I_s} \quad \ldots\ldots\ldots\ldots\ldots(4)$$

since $\rho_s = \rho_x$

Generally a pure material can be selected as the standard, in which case $S = 1$.

Most commercial diffractometers have a geometry such that the above equations are satisfied and the measurements of I_x and I_s with them presents no problem in principle. The use of internal standards (Ballard et al 1943, Klug 1953) and calibration curves are essentially methods of allowing for A_x/A_s and direct measurement of these quantities would both eliminate the difficulties and reduce the time associated with the above techniques.

Leroux et al (1953) used equation 4 to analyse for quartz in various mixtures, using a diffractometer to measure I_x and I_s. A_x and A_s were calculated from the measured absorption coefficient of the samples to shorter "white" radiation. In principle this method cannot be used to obtain absorption coefficients with high accuracy for two reasons:--

(a) Since the beam is not monochromatic the mass absorption coefficient is not constant.

(b) If the absorption coefficient is measured for any other wave length than that used in measuring diffracted intensities, the presence of any element with an absorption edge between the two wave lengths would give rise to serious errors.

Shorter wavelength radiation such as $MoK\alpha$ is more satisfactory for absorption measurements because much thicker samples can be used, but this wavelength does not give sufficient dispersion for most diffraction studies of minerals. Leroux (1957) used monochromatic $MoK\alpha$ radiation (reflected from quartz 101 plane) instead of the white radiation of the direct incident beam from a Mo target. Using this technique in quartz estimations he obtained a standard deviation of 2% from the nominal values.

For most estimations, a method in which A_x and A_s are measured eliminates the need of any sample pretreatment other than that necessary to obtain a suitable diffraction record. An obvious advantage is that the diffraction peak from which I_x is measured can be selected from any peak due to the mineral. Thus any peak in a routine diffraction trace could be chosen, but naturally one with a high line/background ratio and with little or no interference from neighbouring peaks would increase the accuracy of the determination. This factor is important in the analysis of rocks and soils. Because of the large number of minerals (often with complex diffraction patterns) there is a high probability that any preselected line of a mineral may suffer interference from coincident or adjacent lines.

From a routine trace a suitable line is selected and its intensity is measured. The intensity of the same line of a standard is then measured. If due to low concentrations a suitable line cannot be selected, it is necessary to concentrate the component being estimated.

This method of quantitative estimation was successfully used with a number of iron oxide/kaolin mixtures as well as with naturally occurring soils. Its applicability was also tested on minerals other than the iron oxides and the results obtained in these cases will also be discussed.

2. Experimental Data.

(a) Instrumentation.

In preliminary experiments a Norelco high angle diffractometer utilising a geiger-counter detector in conjunction with a ratemeter and recorder was used to estimate I_x and I_s. This equipment has since been modified by the addition of a linear amplifier, and a pulse height analyser, and the geiger counter has been replaced by a scintillation detector. With this arrangement non monochromatic radiation, can be partially eliminated and the line to background ratio was increased over that obtained using Geiger counter instrumentation.

The coefficients A_x and A_s were at first measured using a fluorescent X-ray spectrograph. Later using samples which gave a high intensity reflected beam as a source of monochromatic radiation, the diffractometer was used to measure these quantities, using the same radiation as that used to measure I_x and I_s.

In measuring the absorption coefficients it is preferable to use as a source of the monochromatic radiation, a reflecting plane with a weak second order. Crystals slabs, (e.g. quartz, lithium fluoride, or sodium chloride) or highly oriented powder specimens (e.g. graphite) give suitably high intensities of monochromatic radiation to which the absorption coefficients of the minerals to be estimated can be measured.

(b) Sample Preparation.

In general the samples analysed were $<5\mu$ fractions. In the case of the various artificial mixtures the individual components were ground and this fraction separated before mixing. The soil samples were dispersed before the $<5\mu$ (or $<2\mu$) fraction were separated. Specimens for diffractometry were prepared by lightly pressing the powder into rectangular metal holders, 2 cm X 1 cm (Klug and Alexander 1954). Sometimes during this treatment minerals with a pronounced fibrous or platy habit become preferentially oriented, in which case, the diffracted intensity of a peak is no longer linearly related to the amount of the mineral present. It was found that orientation effects could be reduced, if, during the sample preparation, the front surface was pressed against finely ground glass or against paper rather than a polished surface, as this restored some degree of randomness in the packing.

Mass absorption coefficients were calculated from the amount of attenuation experienced by a monochromatic beam of X-rays in passing through a parallel sided sample of known mass. (See Section c.) The samples for this measurement were prepared by pressing the powder into a ½" (1.27 cm) diameter hole in a "Perspex" holder. Pressures varying between 200 and 2000 Kg./cm^2 were found necessary to ensure self supporting specimens of some samples. (Preferred orientation does not influence this determination.) Uniform thickness of individual samples was obtained with the aid of jigs. The mass of the samples was obtained by weighing the holders before and after loading. Difficulty was experienced in making samples weighing less than 0.03 gm, and generally 0.07-0.10gm was used.

Since the attenuation of a beam of monochromatic X-rays generally increases with an increase in atomic weight, very thin samples are sometimes required to prevent complete absorption, which precludes the measurement of the absorption coefficient. When sufficiently thin samples cannot be made, materials with high absorption coefficients may be diluted. The measured coefficients must then be corrected for the amount of diluent added. When there is a large difference in absorption coefficients between the sample and the diluent, it is important that the particle sizes are small enough to prevent micro-absorption effects. (Brindley, 1945).

(c) Measurement of Mass Absorption Coefficient.

If a sample of thickness is inserted in a monochromatic X-ray beam the intensity, I, of the attenuated beam is related to the incident beam intensity, Io, by the relation

$$I = I_o \exp(-\mu l)$$

so that measurement of I and Io determine μl. The weight of the sample and its area (1.27 cm^2) gives its mass/cm^2 and

$$A \text{ (the mass absorption coefficient)} = \mu/\rho = \mu l/\rho l$$

Ratios of I/I_o as low as 3×10^{-5} ($\mu l = 10$) could be measured to give accurate measurements of A. Table 1 shows some mass absorption measurements compared with those calculated from standard tables.

In these tables the mass absorption coefficients for each element are given for various wavelengths of the incident radiation. The mass absorption coefficient of a compound, e.g. SiO_2, could then be calculated from the following relation:--

TABLE 1.

Comparison of measured and calculated Mass Absorption Coefficients.

Sample	CuK		CoK		FeK	
	Measured.	Calculated.	Measured.	Calculated.	Measured.	Calculated.
Al[1]	48.7	48.9	75.0	73.4	94.5	93.8
Quartz, SiO_2[1]	36.1	35.0	55.1	54.8	69.2	67.6
Haematite, Fe_2O_3[1]		230	44.7	47.7	56.4	56.3
Goethite[2]	187	200	43.4	43.7	53.0	51.4
Kaolin[3]	32.0	31.6	48.0	47.0		
Dolomite, $CaMg(CO_3)2$[1]			69	71		
Calcite, $CaCo_3$[1]			108	106		

1. Chemical composition assumed to correspond to formula.
2. Analysis, 86.7% Fe_2O_3; 13.2% H_2O; 0.15% SiO_2
3. Assumed, 45% SiO_2; 40.5% Al_2O_3; 14.5% H_2O.

$$A_{SiO_2} = \frac{M_{Si} \cdot A_{Si}}{M_{SiO_2}} \qquad \frac{M_{O_2} \cdot A_{O_2}}{M_{SiO_2}}$$

where A_{SiO_2} is the mass absorption coefficient of SiO_2 to a wavelength λ,

A_{Si} and A_{O_2} are the mass absorption coefficients of Si and O_2 to the same wavelength.

M_{SiO_2} is the molecular weight of SiO_2, and

M_{Si} and M_{O_2} are the weights of Si and O_2 present in the molecular weight of the compound.

The deviations between calculated and experimental absorption coefficients are, in most cases, less than the uncertainty in published mass absorption coefficients of the elements. The data available on experimentally determined absorption coefficients (Compton and Allison 1935, Hodgman et al 1956) are very incomplete, so that calculated coefficients (Henry et al 1953), had to be used, and, for low atomic number elements the latter often disagree seriously with the former. Mass absorption coefficients could generally be measured with a reproducibility of about 1%. The counting errors in any observation $= \frac{\sqrt{N}}{N}$ (where N is the number of counts) and were reduced to 1% by counting for a sufficiently long time. The main source of error in the determination of the mass absorption coefficient is the deviation from a uniform parallel sided slab. This error is introduced in the factor ρl which is determined by the measured values M/a where M is the mass of the sample and a is the sample area. Sample preparation and the measurement of mass absorption coefficients requires only a few minutes. Usually duplicate samples are made and measured for this determination.

(d) Measurement of Line Intensities.

The selection of a suitable line on which to measure I_x, the intensity of a diffraction line in the sample, can be made from a routine diffraction record. A line free of interference and of suitable intensity is selected and the same line of the standard is then measured. Usually in this laboratory, powder diffraction photographs rather than diffractometer traces, are made for routine qualitative analysis, and from these photographs a suitable line is selected. A powder photograph, although having a lower resolution on a small camera, has a greater sensitivity than a diffractometer trace.

When a suitable line has been chosen, its intensity is measured either by scanning the peak and recording the trace with a recorder, or by measuring the count rate at the position of maximum intensity with a ratemeter or scaler. This latter method is the most accurate for determining I_x when the crystallite size is not small enough to give line broadening, and when the peak tails on either side to a uniform flat background. Determinations of I_x by either method, however, require the background intensity to be deducted from the measured or recorded peak intensity.

Because of the line broadening, associated with small crystallite size, in many soils, the count rate at the position of maximum intensity is reduced, and unless the intensity of the line of the standard is measured on a sample of identical particle size, any estimation will be in error. Also, if the crystallite size is not sufficiently small (say $< 5\mu$) relatively large variations can occur in the peak height due to the small number of particles contributing to diffraction at a particular angle. Because of these difficulties, the intensity of the selected line is obtained by measuring the integrated intensity of a recorded trace over a small angular region.

The integrated intensity can itself be measured by two methods; either by measuring the area enclosed by the peak and the estimated background, or by taking the product of the maximum peak height and the peak width at half maximum height. However there are further problems associated with the accurate measurement of peak areas. A diffraction line has the profile of a tailed triangle, (see Fig. 1) for which the level of the base (background) is the most uncertain feature whilst the area changes markedly with small changes in background because of the width of the line in this region. To overcome the large

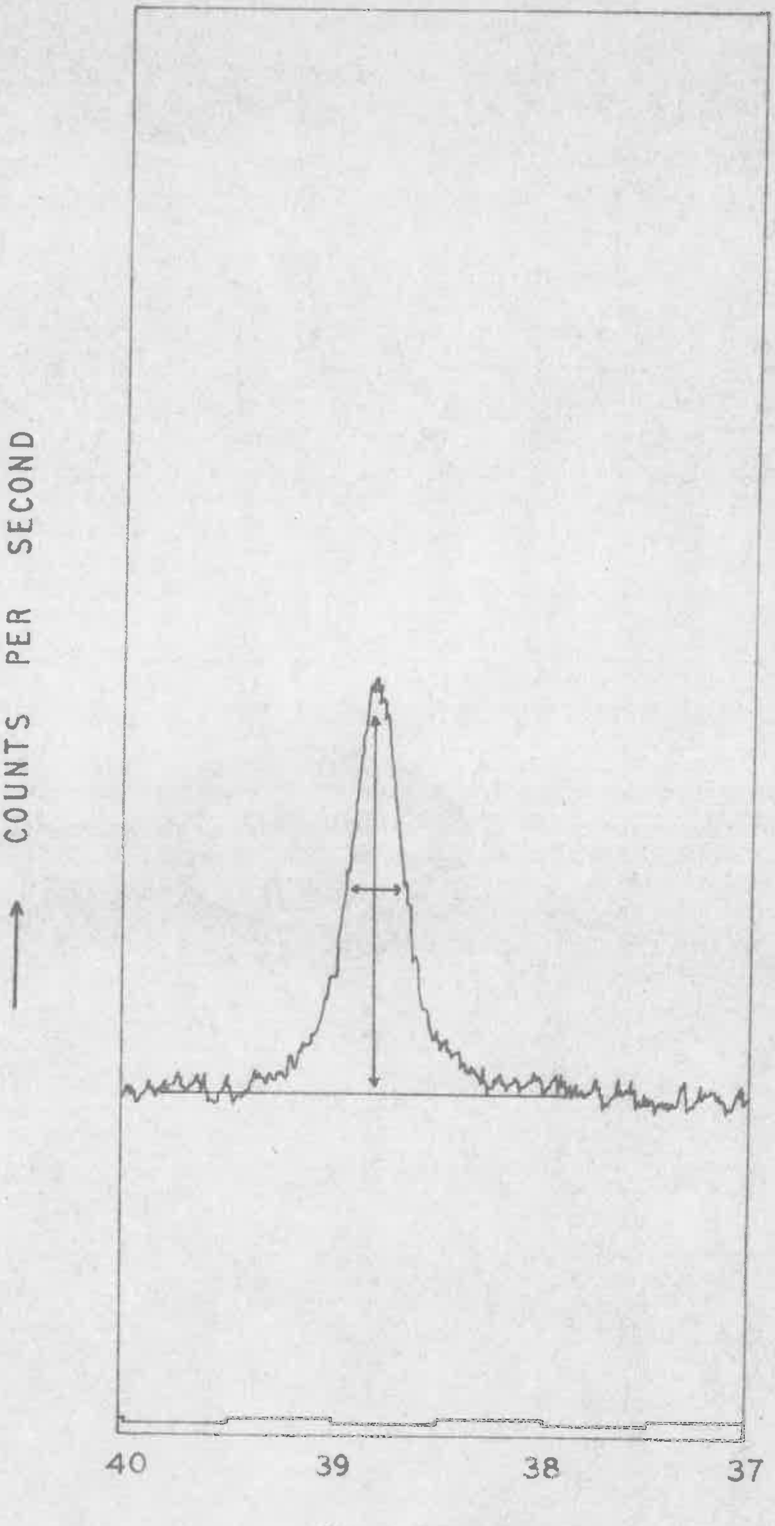

Fig. I Profile of a typical X-ray diffraction line, the (130) line of goethite.

errors which might thus occur, and to take cognisance of the line width, the product of the peak height and the width at half peak height was chosen as the most satisfactory measurement of I. Table 2 shows the errors introduced into the various measures of line intensity by purposeful errors in background.

Table 2.

Variations in Line Intensity due to Background Uncertainty (Assumed ± 5% of Peak Height).

Sample	Peak Height Variation	Width at ½ Height	Line Intensity	
			Area	Width x ½ Hght.
Goethite (130) Line	+ 5%	0.3°	+22.4%	+12.2%
	-5%	0.3°	-15.8%	- 8.8%
Quartz (101)	-5%	0.175°	-16.1%	-13.2%

The diffracted intensities of the peaks used in the estimation of the iron oxides were generally obtained using CoKα radiation.

For convenience, values of chart speed and goniometer speed were chosen to rationalise the chart graduations with values of 2θ. The time constant of the ancillary equipment was chosen so that there was no peak distortion.

Co Kα radiation was chosen for two reasons:--

(1) The wavelength of the radiation (1.7902 Å)

is sufficiently long to give adequate resolution of most soil mineral diffraction peaks, and

(2) Co radiation does not cause fluorescence of the iron samples as would Cu radiation and hence gives a higher line to background ratio.

3. <u>Results and Discussion</u>.

Fig. 2 shows the experimental values of I_x/I_s for CoKα and CuKα radiations, for artificial mixtures of goethite and kaolinite, and it is seen that these values lie close to the curves predicted by equation 4. The two curves are quite different because the mass absorption coefficients of kaolinite and goethite for CuKα differ widely (32 and 187 respectively) whereas for CoKα radiation they are almost the same. Hence there is almost a linear relation between I_x/I_s and goethite concentration for CoKα.

In obtaining the theoretical curves of Fig. 2., A_x was calculated from the relation,

$$A_x = XA_g + (1-X)\ A_k$$

where A_g and A_k are the mass absorption coefficients of goethite and kaolin, and X is the proportion of goethite present.

Table 3 shows the results obtained by the application of equation 4 to some artifical mixtures, the quantities A_s, I_s A_x and I_x being determined experimentally. The agreement between the actual and the

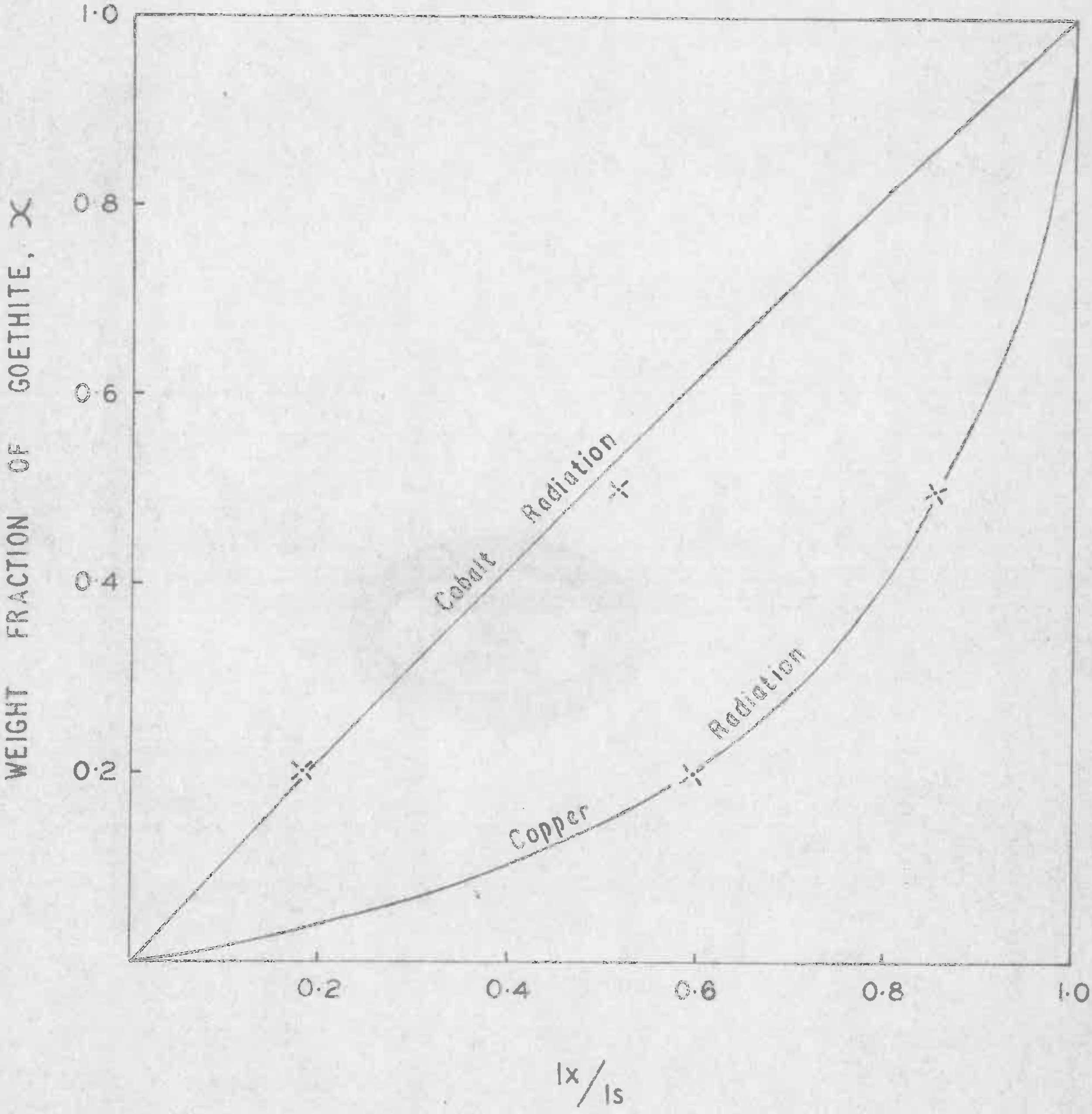

Fig. 2 Variation of I_x/I_s with goethite content for Co and Cu radiations. Continuous lines show the predicted relationship. ✕ experimental points.

determined quantities is satisfactory in that the errors are of the same order as errors in A and I. Analyses made using different lines of a diffraction pattern gave good agreement, even when the lines have a large angular separation.

Table 3.

Calculated and Nominal Compositions for Various Synthetic Mixtures.

Mixtures in Kaolin	Nominal Composition %	Calculated Comp. %		Line
		Using Areas	Using Products	
Sample 1	50 Goethite	47	49.2	(130)
		50.5	--	(111)
Sample 2	5 Haematite	-	4.25	(102)
Sample 3	50 Quartz	47	50.1	(101)
		49.5	49.4	(112)
Sample 4	20 Quartz	20.2	21.5	(101)
		22	20.4	(112)
Sample 5	50 Goethite	50.1[x]	--	(130)
		48.2	50.5	(111)
	25 Haematite	23.2	--	(102)
Sample 6	50 Goethite	24.6[ø]	--	(130)
		22.2	27.5	(111)
	37.5 Haematite	37.5	--	(102)
	25 Quartz	21	20.7	(101)

x, ø - Calculated from the intensity of the compound peak at 2.69 Å by subtracting the intensity due to the (102) line of the haematite component.

Table 4a.

X-ray Diffraction Estimations of Iron Oxide Minerals in Soils.

Sample	Diffraction Results %	Free Fe_2O_3 %	%Fe_2O_3 accounted for.
Cook Is.[1] Whole Soil	Goethite 42	49.5	76
W.A. $< 2\mu$ Lateritic	Goethite 30	29.6	91
W.A. $< 2\mu$ Lateritic	Goethite 39	37.8	93
W.A.[2] $< 2\mu$ Lateritic	Goethite 60	55.8	97
Victoria Kraznozem $< 5\mu$	Haematite 6 Goethite 3	9.5	92
Tasmania Med. Podz. $< .5\mu$	Goethite 3.5	4	79
Barbados Red Soil $< 2\mu$	Goethite 6.2	7.5	74
W.A. $< 2\mu$ Lateritic	Haematite 1.2 Goethite 2	4.6	65

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[1] A small amount of ilmenite or haematite was identified from diffraction photographs.

[2] This sample had been concentrated in iron oxides by digestion in 5N NaOH. (See Chapter V.)

Table 4a presents the analysis of some soils and clays for goethite and haematite, these particular results being given for comparison with independent chemical estimates.

Table 4b compares the percentages of gorceixite and crandallite measured by diffraction methods, with these calculated from the chemically estimated P content. These calculations were made assuming that the minerals were constituted according to their ideal formula.

Table 4b.

Estimation of Gorceixite and Crandallite in Soils.

Sample	Results by Diffraction %	Calculated from P content	Ratio of Estimations.
Queensland			
Whole soil	Gorceixite 3.2	2.6	1.23
0.5 - 5	Gorceixite 12.5	11.5	1.10
Cook Is.	Crandallite 7	8.5	.83

Although reasonable agreement was obtained in the results listed, there are limitations to the accurate estimate of most minerals in soils by this method. By their nature, these limitations would also affect other methods of quantitative estimation by X-ray diffraction. These limitations will be discussed only in regards to the iron oxide determinations, although most would apply to other minerals.

Preferred orientation gives rise to such a limitation. Suppose a mineral to be estimated had a pronounced platy habit, with cleavage faces parallel to the (hk0) set of lattice planes, then any pressure during sample preparation would tend to allign these particles with their cleavage faces parallel. If a surface parallel to these faces is now presented to the incident X-ray beam the 001 reflections will be inhibited. Thus preferred orientation can cause either the enhancement or dimunition in diffracted intensity of a peak, and if cognisance is not taken of this effect, any estimation is liable to serious error. This effect was particularly noticeable with a standard mineral goethite on which the values of I_s and A_s were at first measured. This goethite was a fibrous variety from Mt. Searle, S.A., whose pronounced crystalline habit made it exceedingly prone to orientation. Fig. 3 shows the variation in intensity of two neighbouring goethite lines, the (130) at 2.67 Å and the (111) at 2.44 Å when the sample is oriented to different extents.

Fig. 3a shews the height of the two peaks when the sample was prepared under a slight pressure on a filter paper surface, which tends to eliminate orientation. Fig. 3b demonstrates the increase in intensity of the (130) and an associated decrease in the (111) peaks after pressing the sample on a flat surface to a pressure of 4000 lbs./sq. in.

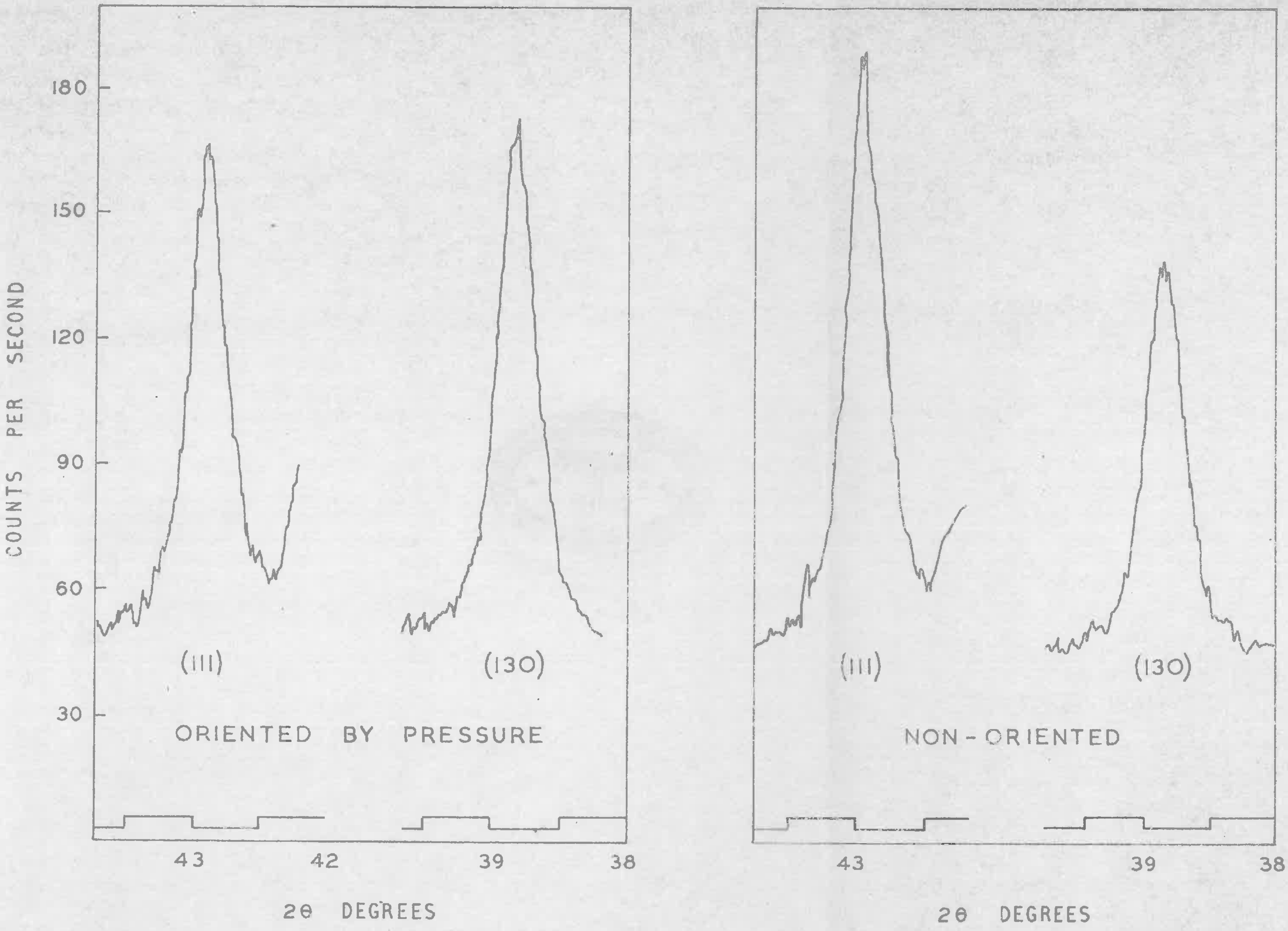

Fig. 3 The effect of orientation on the relative intensities of geothite (130) and (111) diffraction peaks.

From various well crystalline synthetic goethites and from non-oriented mineral forms, a ratio of the intensities of the (111)/(130) peaks has been calculated. This value has been measured many times during a period of three years and has been found to be reasonably constant, 1.43. The intensity ratio for these two lines has also been calculated from structural factor considerations, and was found to be 1.38. It has been assumed in these determinations, that the crystalline habit of the soil goethites is such that preferred orientation of the constituent particles is unlikely. Electron micrographs of goethites extracted from soils, Plate 1, justify this assumption, as the particles appear quite irregular or rounded in shape. These micrographs will be discussed more fully in Chapter V, since they apply to the soils discussed in that chapter.

A second limitation could be introduced by lattice replacements in a mineral. As will be shown in Chapter V. most soil goethites in the clay size fraction have some of their iron isomorphously replaced by aluminium. Since the absolute intensities as well as intensity ratios for diaspore differ from those of goethite, (see Table 5) the presence of aluminium within the goethite lattice should change the values of I_x whether calculated from peak heights or from integrated intensities. This effect is demonstrated in Table 6 in which the peak intensities of a normal goethite are compared with those of a highly aluminiferous one, in which (FeAl) OOH constitutes 71% of the sample.

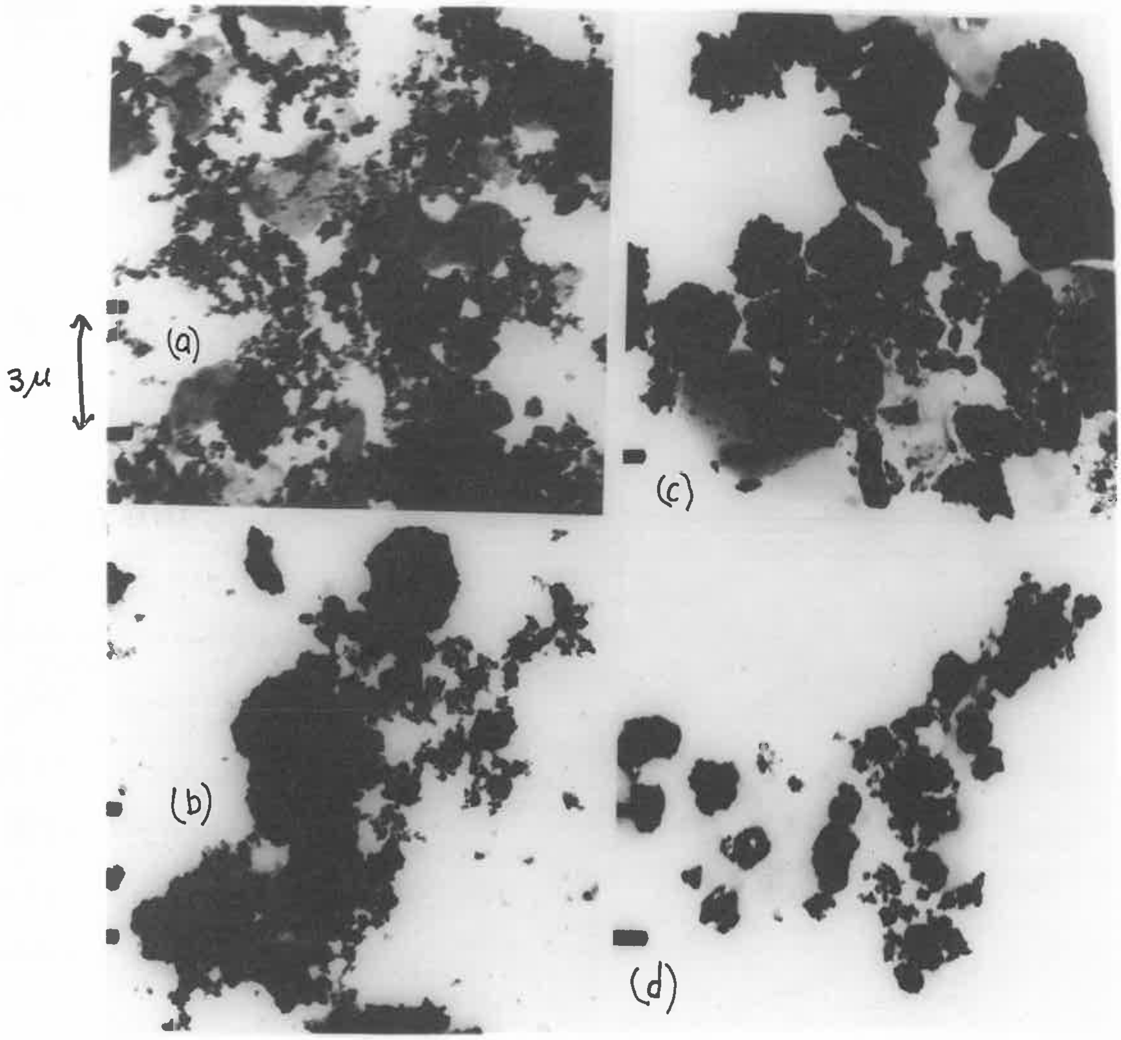

PLATE I.

Electron Micrographs of Soil Goethites.

(a) Bs 29 $<.5^{*}$ μ

(b) H165/10 <2 μ

(c) Bs 29 2-.5 μ

(d) H165/10 $<.5$ μ

* These are nominal particle sizes only. See Page

Table 5.

Integrated Intensities of Goethite and Diaspore

(111) Lines.

Sample	Integrated Intensity *	
	(130) Line	(111) Line
Diaspore	2.84	3.65
Goethite	8.45	12.05

* The integrated intensity here is the product of the line height, minus background, and the width at ½ peak height.

The use of the equation 4 for this sample gives a goethite estimate of 57%, unless the reduction in integrated intensity due to the presence of aluminium is taken into consideration.

Assuming a linear change in intensity in passing from 100% FeOOH to 100% AlOOH, a corrected intensity for a sample wholly containing substituted goethite can be derived. For this derivation, however, it was necessary to know the actual composition of the goethite. As can be seen from Table 6 the estimation based on the corrected intensity gave a result accurate to two per cent. The assumption of a linear change in intensity in passing from 100% goethite to 100% diaspore was subsequently justified by calculation of the expected relative intensities from structural considerations.

It can be seen from Table 7 that there is a linear change in $|F_{111}|$, the structure factor of the (111) reflection in passing from (100%Fe)OOH to (100%Al)OOH, and the intensity of any reflection is proportional to $/F/^2$.

Table 6.

Estimation of Goethite with a High Aluminium Content.

Sample	Integrated Intensity		% Goethite
Standard Goethite	$I_s = 12.05$	$A_s = 43.4$	$S = I$
Goethite (Fe,Al)OOH .75, .25	I_s'[ø] $= 9.96$	$A_s' = 43.7$	$S' = I$
H165/10[x]	$I_x = 6.65$	$A_x = 47.5$	$X = I_xA_x/I_sA_s \simeq 57$
			$= I_xA_x/I_s'A_s' = 73$

[ø] I_s' is calculated from the I_s values of pure diaspore and goethite.

[x] The nominal composition of sample H165/10 was 71.15% Goethite. This was calculated from the results of chemical analysis.

Table 7.

Variation in $|F|$ with Aluminium Content in Goethite.

Composition	$\|F\|_{111}$
$(Fe_{1.0})OOH$	-118
$(Fe_{0.75},Al_{0.25})OOH$	-103
$(Fe_{0.50},Al_{0.50})OOH$	-88
$(Fe_{0.25},Al_{0.75})OOH$	-74
$(Al_{1.0})OOH$	-59

A further limitation to the estimation of Soil iron oxides arises from having too low a total content of free Fe_2O_3 present. If only a few per cent (say 5-10%) are present there is a possibility that all the crystalline forms present may not be detected. In such a case, the use of equation 4 will lead to an underestimate of the crystalline forms. On concentration, however, accurate estimations can be made. Reference to this procedure is made in Chapter IV.

Because other lines of suitable intensity cannot be satisfactorily resolved from neighbouring clay lines, the goethite (130) line at 2.67 A° and the haematite (104) line at 2.69 A° are generally chosen for the measurement of I_x. Because of their proximity, further difficulties are introduced when a clay contains both these mineral forms, and in such systems the technique for estimating I_x has to be modified. On concentration, the haematite (102) line at 3.68 A°. should be capable of being estimated. Knowing the intensity ratio of the (102)/(104) lines, the value of the integrated intensity due to the haematite component at 2.69 A°. can be derived. The difference between the total intensity of the 2.69 A° line and the calculated intensity will give the intensity due to the (130) line of the Goethite component. This method has been used for some of the estimations of the synthetic mixtures given in Table 3. (The intensity ratios must be derived from a non-oriented standard under the same conditions.) This method of calculation using intensity ratios may be applied to any lines of either component to find the contributions of each form to the total intensity of a compounded peak.

4. Summary.

An X-ray diffraction technique has been developed for quantitative estimation of crystalline materials. In the application of this method to synthetic mixtures of iron oxides, close agreement was obtained between nominal and estimated values. Moreover, most of the free iron oxides in many soils examined could be accounted for satisfactorily by the goethite and haematite determined by the method described.

A quantitative determination may be subject to certain limitations which, however, would be imposed on any diffraction method of analysis. These limitations will be more important in unknown samples since they are imposed by such factors as the composition, concentration and crystalline habit of the component being measured as well as the nature of the matrix.

The method described nevertheless produces an accuracy as good as other diffraction techniques without the necessity for calibration curves or internal standards.

CHAPTER IV.

AMORPHOUS IRON OXIDES IN SOILS.[*]

1. Introduction.

The first stage in the chemical analysis of a soil is the estimation of its component elemental oxides or groups of oxides. The next stage is to determine the manner of combination of these groups, assessing what minerals are present, and the third step is the quantitative estimation of these minerals.

Correlation of the results of these three analytical stages can give rise to errors. To successfully account for 100% of a sample, the difference between the measured concentration of a certain element and the amount that can be ascribed to the estimated minerals that contain it, is often relegated to a compound that is difficult to detect or estimate. For example, if the $Al_2O_3 : SiO_2$ ratio is between 1 and 2, and no mineral is detected to account for this surplus of aluminium, the presence of allophane may be suggested.

Similarly with the iron oxides, the difference between the estimated Fe_2O_3 and that which can be allocated to the detected mineral forms, is often attributed to the presence of an amorphous form. The presence of an exothermic reaction at about 330°C. on the Differential Thermal Analysis (D.T.A.) records has been regarded by

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[*] Published by the author in J. Soil Sci. Vol. 10 No. 2 P.309-315, September, 1959.

MacKenzie (1949) as confirmation of the suspected presence of amorphous iron oxide.

The "brown gel" (See Chapter II) was assumed to be the amorphous oxide present because of the similar exothermic reaction it also exhibits at about 330°C., as it crystallises to haematite. (Since the internal energy of the crystalline material is lower than that of the amorphous form, there is an accompanying evolution of heat during crystallisation. The temperature at which this crystallisation and exothermic reaction take place depends on the method of preparation of the gel. (Mackenzie 1957, Gheith 1952, Kulp and Trites 1951.) The appearance of haematite in X-ray diffraction patterns after heating (to 330°C.) further supports the interpretation of this exotherm as due to the "brown gel".

These "diagnostic" exotherms were observed on the D.T.A. records during routine examination of many soils and clays in this laboratory. These samples were obtained from various locations and were of various soil types. The current interpretation of this exothermic reaction was first doubted when it was observed in a soil from Barbados. Initially, the presence of amorphous iron oxide was accepted, and it was decided to estimate the quantity of Fe_2O_3 present in this form. The total and free Fe_2O_3 contents were measured and the crystalline goethite, detected in routine diffraction photographs, was estimated by the X-ray diffraction technique described in Chapter III.

When it was found that the estimated goethite accounted for nearly all the measured free iron oxide, the previous identification of amorphous iron was placed in doubt. This balance of the iron oxides suggested that in the case of the Barbados soil the exothermic reaction was not due to amorphous iron and other soils on which it had been observed were re-examined.

When it was found that the measured free iron oxide in these other soils could be satisfactorily allocated to the estimated crystalline forms, it was decided to investigate further the nature and origin of the exothermic reaction, since its current interpretation was not consistent with the present results.

2. Apparatus and Methods.

The Differential Thermal apparatus used has a horizontal furnace based on the design of Norton (1939). A heating rate of 10°C per minute was maintained by a programmed Kent controller-recorder from room temperature to 1030°C. The differential temperature was measured with Pt-Pt 13% Rh/thermocouples in opposition, connected to a galvanometer with a mirror attached to the moving coil assembly. The galvanometer deflection due to any net emf was continuously recorded by a Beckman photopen recorder via a light lever focussed on the mirror. The sensitivity of the recorder is controlled by the length of the light throw and the shunt galvanometer resistance. For this work a sensitivity of 3μV per mm was chosen and at 330°C this corresponds to a sensitivity of 30 mm per 1°C of differential temperature. Because of this high sensitivity a stainless steel sample holder could be used. (A metal block tends to lower the differential temperature between sample and inert material, but has the compensating advantage of maintaining both sides at a constant temperature close to the furnace temperature, while no exothermic and endothermic reactions are occurring.) The sample block was encased within a cylindrical casing of the same material; the sample, however, was exposed quite freely to the furnace atmosphere. Calcined alumina was used as the inert material and also as a 1:1 diluent with the sample to give it approximately similar thermal properties. Generally 0.15 gm of alumina was mixed with 0.15 gm of sample to fill completely the specimen hole in the block.

As there was no interest in the low temperature (130°C) endothermic reaction due to the vaporisation of absorbed water, no attempt was made to bring all the samples to a humidity equilibrium before analysis.

The $< 2\mu$ fractions were obtained by dispersing 10 gm. of the soil in 200 ml of water in the presence of 10 ml of 10% "calgon" and 2 ml N sodium hydroxide. A representative sample of the $< 2\mu$ fraction was subsequently obtained by repeated decantation.

X-ray powder diffraction photographs were obtained on 5.73 and 19 cm diameter cameras using CoKα

radiation. Quantitative estimations of goethite and haematite were made by a modification of the method of Leroux et al.(1953) as discussed in Chapter III. For these estimations the absorption coefficients were measured on an X-ray fluorescent spectrograph rather than on the diffractometer.

Fluorescent X-ray spectroscopy was also used to measure the free iron oxide contents by estimating the total iron in the clay before and after free iron removal. The free iron was removed from the clay by treatment with sodium dithionite (Mitchell and MacKenzie 1954). In this method no citrate buffer was used although recent work (Mehra and Jackson, 1960) has shown this greatly facilitates the removal of the iron oxides.

Carbon estimates were carried out on the Barbados soil by the Chemistry Section of the Division of Soils. The results of these analysis, obtained using the dry combustion method of Piper (1942), are considered accurate to two significant figures and are given in Table 1 together with Fe_2O_3 contents.

3. Results and Discussion.

The interpretation of the exothermic reaction at about 330°C. on the D.T.A. records of the Barbados soil (Hardy 1950) was first queried when the estimated goethite was found to account for the measured free iron oxide in the sample. The clay fraction, ($< 2\mu$) which had been treated with 6% H_2O_2 to remove the organic matter, was submitted to this laboratory for routine D.T.A., and the record of its reactions appear in Fig. 1, curve 2. Besides the exothermic reaction at 330°C. there were two endothermic and one further exothermic reaction in the temperature range examined. The first endotherm is due to the loss of absorbed water while the second arises from the loss of structural OH from halloysite. The high temperature exotherm is due to the recrystallisation of the decomposition products of the halloysite to mullite.

When the origin of the 330°C. exotherm was first in doubt a D.T.A. was made on the whole soil, to see if the reaction was due to an artefact, introduced during sample preparation. The record of this analysis is given in curve 1 of Fig. 1. The only variations between the results of the whole soil and its clay fraction are the broad low temperature exothermic reaction extending from 200-450°C., and an endothermic peak at about 750°C. The broad exotherm is indicative of the oxidation of organic matter, which was removed by peroxidation of the clay sample, while the endotherm arose from the decomposition of calcium carbonate, also removed during the separation of the clay.

Goethite was estimated at 6% by X-ray diffraction and accounted for 80% of the free iron oxide content of the clay fraction, (See Table 2). Since at

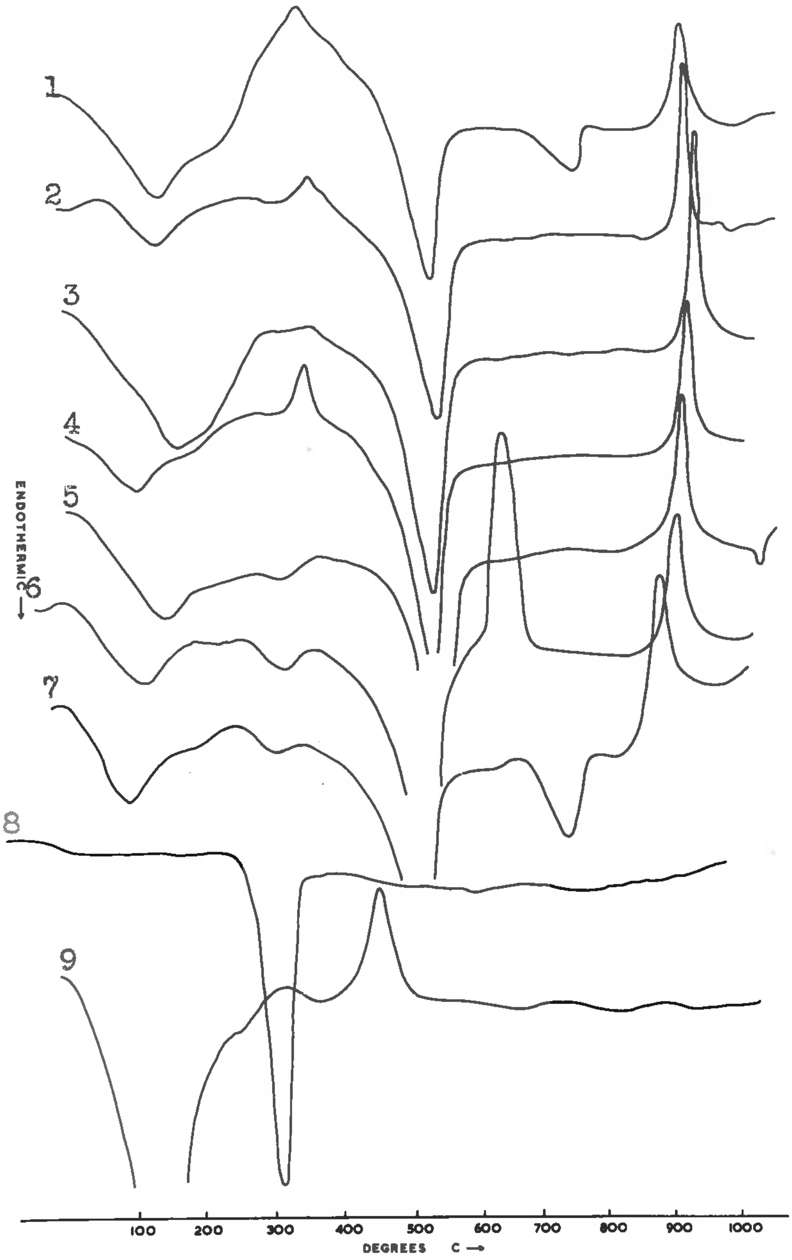

FIG.1.

Curve 1. Red Soil Barbados, Whole Soil.
2. $<2\mu$ fraction.
3. $<2\mu$ free iron removed.
4. $<2\mu$ after boiling for 1½ hours in 1 M citric acid.
5. $<2\mu$ after 120 hours in 30% H_2O_2.
6. $<2\mu$ in nitrogen atmosphere. (Air readmitted 610°C).
7. Whole soil in nitrogen atmosphere.
8. Goethite (Mt. Searle, S.A.)
9. Freshly precipitated ferric hydroxide.

the time of this investigation the effect of aluminium within the goethite lattice was not considered, it is possible that a further estimate, taking account of the composition of the goethite, may account for even more of the free iron content. (See Chapter III.)

Goethite loses structural water and crystallises to haematite at about 320°C when subjected to differential thermal analysis. This loss of water produces an endothermic reaction which is not apparent in Curve 2, although 6% goethite is quite sufficient to produce a noticeable reaction on the sensitive equipment used. Presumably its absence is due to the masking effect of the coincident exothermic reaction at 330°C.

TABLE 1.

Fe_2O_3 and C contents of Barbados Soil after various treatments.

Sample: Red Barbados Soil Treatment.	Total iron content $Fe_2O_3\%$	Carbon content %
Whole soil (270 mesh)	9.6	1.9
<2μ With 6% H_2O_2 treatment	10.5	1.2
<2μ free Fe_2O_3 removed by dithionite extraction	3.0	1.0
<2μ boiled for 1½ hours in 1M citric acid	3.9	1.2
<2μ after 120 hours in 30% H_2O_2	10.3	0.42

Curve 3 shows the effect of the free iron removal on the clay. The elimination of this exothermic peak at 330°C by this treatment would strongly support the view that the peak was due to some form of free iron oxide. However, only a little, if any, of the free iron oxide present can be amorphous. (Table 2.) By comparing the energies involved in both the crystallisation of ferric hydroxide gel to haematite (Curve 8) and the dehydration of goethite to haematite (Curve 9) it is obvious that the latter reaction is far more energetic.

Therefore it appears unlikely if, say, 20% of amorphous iron oxide could cause an exothermic reaction sufficiently vigorous to mask the endothermic peak due to 80% goethite!

If amorphous iron oxide is present in a soil it is reasonable to assume that it would be more readily removed by an iron complexing agent than more crystalline forms. (Schwertman (1959A) treated soils with amonium oxalate and employed the amount of iron extracted under fixed conditions as an index of the crystallinity of the iron oxides present.) Curve 4 was obtained after boiling the clay in molar citric acid for 1½ hours. It is seen from Table 1 that this treatment removed 80% of the estimated total free iron oxides. If the above reasoning is correct the residual iron oxides after this treatment should be the most crystalline, and, since goethite was the only crystalline oxide identified an endothermic reaction should now be recorded on the trace. However, the 330°C exothermic reaction appears enhanced. The partial or complete elimination of the coincident endothermic reaction by the removal of some or all the crystalline goethite appears to be the only explanation of this behaviour.

After treatment of the clay with 30% H_2O_2 for 120 hours, the D.T.A. record (curve 5) showed that the 330°C exothermic peak had been replaced by an endothermic reaction arising from the structural breakdown of goethite. The iron oxide content decreased by 0.2% with this treatment, whereas the carbon content decreased by 0.8%. Conversely, The D.T.A. curves below were aligned at 300°C and the temperature scale is the average derived from the individual curves.

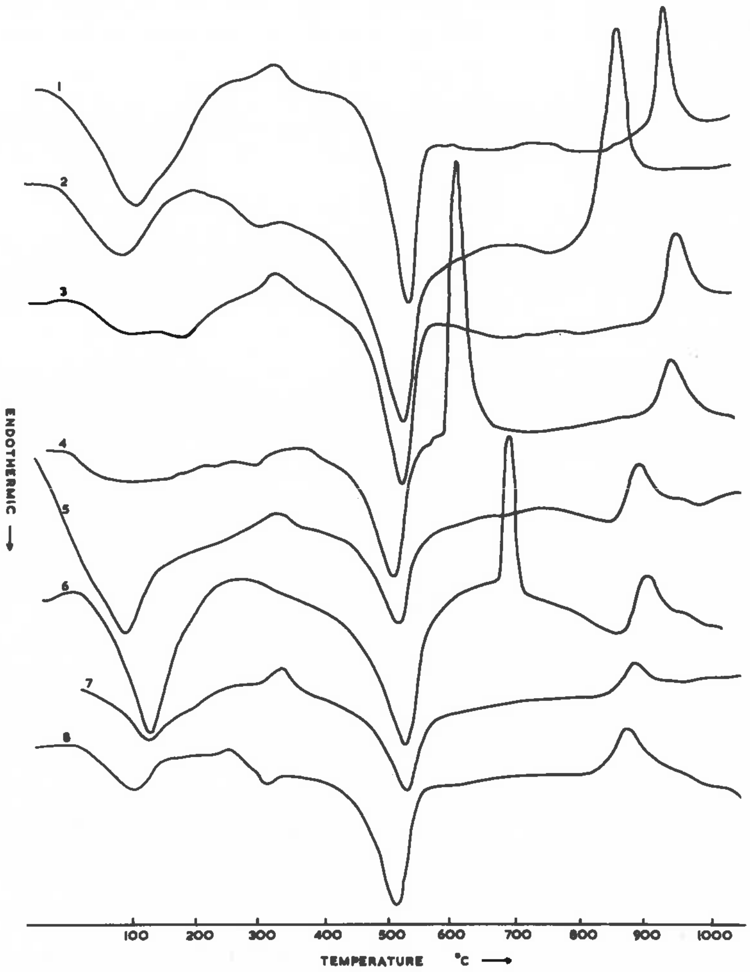

FIG. 2.

Curve 1. 2042 (Victoria) $< 5\mu$.
2. As above in nitrogen atmosphere.
3. 2087 (Victoria) $< 5\mu$ (after 96 hours H_2O_2)
4. As above in nitrogen atmosphere. (Air readmitted 580°C).
5. 16061 (S. Aus.) $< 2\mu$.
6. As above in nitrogen atmosphere (Air readmitted 680°)
7. H53/4 (Tasmania) $< 0.5\mu$.
8. As above after 8 days in H_2O_2.

the carbon content was not affected by the citric acid treatment which removed most of the free iron (Table 1).

These results suggest that the exotherm is due to organic matter. To support this the $<2\mu$ material used in curve 2 was again subjected to D.T.A., this time in a nitrogen atmosphere. This technique prevents an exothermic reaction from organic matter by inhibiting oxidation. Curve 6 shows that under these conditions the exothermic peak is completely suppressed and is replaced by the goethite endotherm. On readmitting air at a higher temperature, 610°C, the organic matter is vigorously oxidised and causes a much more pronounced exothermic reaction.

In view of the rapidity with which amorphous ferric oxide gels crystallise (Gheith 1952), it was necessary to demonstrate that none of the treatments used was responsible for the transformation of existing amorphous material into goethite. This was accomplished by analysing the whole soil in a nitrogen atmosphere (curve 7) when the same reactions were recorded as with the $<2\mu$ (curve 6).

Other soils whose D.T.A. records featured this exothermic peak were examined to ensure that the Barbados soil was not an isolated case where the exotherm was of organic origin. The D.T.A. records of these soils with various treatments are given in Fig. 2, and their free iron and estimated mineralogical contents are listed in Table 2. The concentration procedure used before

TABLE 2.

Sample	Location	Ref. No.	Part. Size μ	Free Fe_2O_3%	Iron mineral determination
Red Soil	Barbados	19503	<2	7.5	6% Goethite
Kraznozem	Ballarat Vic.	2042	<5	9.5	3% Goethite 6% Haematite
Kraznozem	Victoria	2087	<5	6.5	3% Haematite
Terra rossa	Adelaide	16061	<2	6.5	3% Goethite
Meadow Podzdic	Frodsley Tasmania	H 53/4	<0.5	4	3.5% Goethite

estimating the mineral contents of soils low in total free iron oxide consisted of an attack with 20% HF for two minutes. This technique, suggested by Norrish, unfortunately attacks some of the crystalline free iron oxides. This could account for the discrepancy between the free iron content and the estimated mineral content in some of the soils. A better method using NaOH has since been developed and is reported in Chapter V.

The above results present conclusive evidence that, in the soils examined, the 330°C. exothermic D.T.A. peak is due to organic matter. The almost complete elimination of the exotherm by the dithionite free iron removal treatment, Fig. 1 curve 3, would appear to contradict this conclusion, although in actual fact it provides supporting evidence. Mitchell and Mackenzie (1954) reported that a dithionite extraction was capable of removing small amounts of organic matter, and this is borne out by the reduction in carbon content after this treatment, Table 1.

The variation in total Fe_2O_3 after the molar citrate and dithionite treatments suggests that there is 0.9% Fe_2O_3 present in a compound which is responsible for the enhanced exotherm in curve 4 Fig. 1. Furthermore, there is a variation of 0.2% carbon between the same two treatments. Since it has been established that the compound responsible for the exothermic reaction is organic, (Curves 5, 6 and 7, Fig. 1.), and that in the case of the Barbados soil, it contains iron it seems reasonable to assume that it is in the form of an iron-organic complex.

Organic matter is also responsible for the exothermic reactions exhibited by the other soils examined but no work was done to establish the presence of iron in this material. However, because of their similarity both in nature and their response to peroxidation, it is likely that these exotherms are also due to an iron-organic complex.

Schwertmann in a private communication after the publication of these results stated that his concurrent work has led him to a similar conclusion about the nature of this exotherm. As stated in Chapter 2, no evidence really exists for the presence in normal soils of an amorphous iron oxide gel which gives this exothermic reaction (Schwertmann 1959b),(Tamura and Jackson 1953).

Schwertmann (1959a) also finds that in soils which definitely do contain amorphous iron oxide, the thermograms show, instead of the exotherm at $330^\circ C$, a low temperature endotherm indicative of adsorbed water. As crystallisation proceeds the temperature of this endotherm increases as the water becomes lattice bound. This behaviour is consistant with the formation of the soil iron oxides from the slow oxidation-hydrolysis gel advocated in Chapter II.

Mitchell (1958) also in a private communication, discloses that Mackenzie's recent D.T.A. work, in which he uses an inert atmosphere, casts some doubts on his previous interpretation of this exothermic reaction.

The above discussion indicates that this exothermic reaction is not conclusive evidence for the presence of amorphous iron oxides. Previous identifications based on the presence of this exotherm have probably been biased by the inability to account for the total measured free iron oxides. The difficulty associated with the quantitative determination of these crystalline oxides, especially when the total Fe_2O_3 content is low, has most probably led to a large number of soils being classified as containing amorphous iron.

It is suggested that previous interpretations of amorphous iron oxide based on this exothermic peak be regarded as doubtful and that the compound responsible for the reaction is probably an iron-organic complex.

The actual composition of the compound or compounds responsible for this exothermic reaction may be investigated at a future date in co-operation with an organic chemist.

CHAPTER V.

THE CHEMISTRY OF SOIL GOETHITES.

1. Introduction.

During routine X-ray diffraction examination of some soil colloids from Dandaragan, W.A., Norrish (1947) observed lines which could not be identified from the standard diffraction patterns. After heat treatment, however, most of these lines disappeared, and one diffraction line at 2.69 Å was observed to increase in intensity. This line was identified in the heated sample as belonging to haematite. Although the unidentified lines resembled those of goethite, which would crystallise to haematite on heating, the measured spacings did not agree with those published for goethite. The increase in intensity of the 2.69 Å line is also consistent with the initial presence of goethite, as this also has a line at 2.68 Å which is weaker than the coincident haematite line.

Prior to this, and unknown to Norrish, Correns and Engelhardt (1941) reported the occurrence of oolitic goethites which contained aluminium in their lattices, and which, as a consequence, gave a diffraction pattern different from normal mineral goethite. The shift in the diffraction spacings was in the direction of smaller

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d/n values; that is, smaller distances between the atomic planes in the crystallites. Since Al^{+++} has a smaller ionic radius than Fe^{+++}, the progressive substitution of Al for Fe would cause the observed reduction in unit cell size.

Subsequent knowledge of Correns' and Engelhardt's observations led Norrish (unpublished) to postulate that aluminium may also be present in soil goethites. If this were the case, the unidentified lines in the diffraction patterns of the Dandaragan soils could well be attributed to aluminiferous goethite. Moreover the shift in the diffraction spacings was in the direction consistent with this substitution of Al for Fe.

The extraction of relatively large amounts of aluminium during free iron removal treatments (Williams et al. 1958, Williams 1950, Mackenzie 1954) also lends support to this theory of aluminiferous goethites in soils, as these treatments were specifically designed to remove only the iron oxides.

Furthermore, soil goethites differ in the ease with which they are extracted by these free iron removal treatments. This is true even when the goethites are of the same approximate particle size and are present at the same level of concentration.

The object ot this investigation was to determine whether aluminium could be detected and estimated in soil goethites, and to find whether any correlation exists between its presence and the three anomalies described, viz., the change in the diffraction pattern, the aluminium dissolved by free iron removal treatments, and the variations in the efficacy of these treatments

The substitution of Al^{+++} for Fe^{+++} ions is common in many minerals, because they are of their same approximate size. This substitution also appears to be quite common amongst the iron oxide group of minerals; Scheffer et al (1957) gave a reference to the stabilising effect of aluminium in maghemite, and Beneslavsky (1957) noted the occurrence of aluminous goethites and haematites in bauxite deposits. However, there appears to have been no prior investigation of substituted goethites in soils.

2. <u>Choice of Sample</u>.

Although the anomalous goethites are encountered in many different soil types and in association with many different minerals, it was necessary to restrict this investigation to those soils which met certain requirements. Selection was governed by the following criteria.

(a) Goethite had to be the only detectable free iron oxide,

(b) No free aluminium oxides were to be present,

(c) The d_{111} goethite spacing had to be less than 2.44 Å.

(d) Kaolin was to be the only or dominant clay mineral.

If iron oxide minerals other than goethite were present, then there could be an inaccuracy in allocating the total estimated Fe_2O_3 to the individual forms. Similarly, if a free aluminium oxide, or a ready source of soluble aluminium were present, it would be impossible to say how much of the total Al_2O_3 could be attributed to the goethite if substitution had occurred. The presence of kaolin rather than other layer lattice silicates was desired because it could be readily removed without any appreciable attack on the iron oxides present.

Therefore soils which met the above requirements could be treated to suitably concentrate the goethite for a detailed chemical and diffraction study.

The concentration procedure (which will be described in the following section) was capable of removing small quantities of free aluminium oxides, so that condition (b) was not really critical.

The soils used in this investigation are listed in Table 1, and the mineralogy of their $<2\mu$ fraction is given in Table 2.

TABLE 1.

Location and Soil Types from which Goethite was Extracted.

Sample No.*	Depth in Inches	Great Soil Group	Location
BS29	21-32	Laterite	Western Aust.
H165	54-60	Krasnozem	Tasmania
19264	6-15	Red Earth	Queensland
A708	22-25	Yellow Podzolic	Victoria
P1027	6-12	R. Brown Podzolic	Western Aust.
A543	16-22	Yellow Podzolic	Sth. Australia

* C.S.I.R.O. Division of Soils Number.

3. Methods.

(a) Sample Preparation.

The soils were dispersed by mechanical agitation in 200 ml. water to which 2 ml. N NaOH had been added. Particle size[x] separations were made at 2, 5, and 20μ by repeated decantation during sedimentation under gravity. (Baver 1948). Separations at 0.5μ were also found to be necessary and were made using a Sharples super-centrifuge. The fractionated suspensions were flocculated with NaCl and then washed free of chloride with water and ethanol and dried from the latter at 100°C. At this stage the samples were examined by X-ray diffraction to see if any interfering mineral which had previously been undetected in examination of the whole soil, was present.

(b) Concentration Techniques.

The separates were then boiled in 5N NaOH for a period between 30 and 60 minutes. (It was found necessary to carry out this procedure in a large conical flask fitted with a refluxing system to maintain the concentration). This treatment completely removes kaolin whereas the triphormic clay minerals vary in their susceptability. The residues were washed to pH7 with water and then with cold 0.5N HCl and were dried from

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[x] Footnote: The particle sizes quoted here correspond to equivalent spherical diameters of clay particles with a density of 2.65. For goethite with a density of 4.3 the e.s.d. will be reduced by a factor of 1.4, i.e. the sizes will be 1.4, 3.6, 14 and 0.36μ.

alcohol. If all the chloride is not removed prior to the alkali attack, sodalite, $(3\left\{Na_2Al_2Si_2O_8\right\} 2NaCl)$ is precipitated. However, this is removed by the HCl wash, which must be repeated if sodalite is detected.

Further X-ray diffraction photographs were taken to ensure the final suitability of the samples and the results of these analyses appear in Table 2.

(c) Free Iron Removal.

Free Iron oxides were removed by the sodium dithionite reduction technique as revised by Mackenzie (1954). Water suspensions of 100-200 mg. of the caustic soda treated clays were heated to 60°C. and one gram of sodium dithionite was then slowly added with constant stirring. The suspension was maintained at this temperature on a sand bath for a further 30 minutes. After centrifugation, the super-natant liquor was decanted into a 400 ml. brewer's beaker. The residue was washed with 0.1N HCl, centrifuged, and the washings added to the beaker. This whole treatment was repeated at least twice more. The solution extracts from any one sample were either combined or kept separate, depending on the aim of the experiment, as in some cases, the relative amounts of mineral extracted by successive treatments were required rather than a total analysis. No sodium citrate buffer was used in these extractions because even by itself, this reagent is capable of removing aluminium from clays. Therefore, by using dithionite under these conditions, the iron oxides were probably the only minerals attacked. The effectiveness of the dithionite extraction is shown by the mineralogy of the residues after treatment (Table 2.) Iron and aluminium determinations were then carried out on the individual or combined extracts of each sample or particle size.

(d) Estimation of Iron and Aluminium.

Ten ml. of AR grade 30% H_2O_2 were added to each of the extracts which were then boiled for 5 minutes. This destroyed any remaining dithionite reagent and oxidised any colloidal sulphur that may have been precipitated. Excess boiling caused hydrolysis and the precipitation of a very fine grained hydrated iron oxide.* (Commercial grade hydrogen peroxide was at first used resulting in the precipitation of phosphates, as this reagent usually contains a large amount of phosphoric acid added as a stabiliser.) The solutions were allowed to cool, and one gm. of AR NH_4 Cl was added to each solution. Using methyl red as an indicator, the group 3 hydroxides were precipitated with 1:1 NH_4OH added dropwise with stirring. A few extra drops were added after the indicator end point had been reached, and the excess was then boiled off. The precipitates then separated out as heavy floccules and were allowed to stand until the solution had cooled. The flocculated suspensions were filtered through sintered glass mercury

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* Presumed to be an hydrated iron oxide by analogy with ppte. formed on boiling $Fe_2(SO_4)_3$. See Chapter II.

filters (No. 2.)., and the filtrates were checked for the absence of iron with potassium thiocyanate.

The precipitates were washed with water and then allowed to drain well without drying. They were then dissolved in hot 0.5N H_2SO_4 into 50 ml. volumetric flasks and made to volume with this acid. Iron was determined on the solutions by fluorescent X-ray spectroscopy. A calibration curve was prepared using standard solutions of iron in 0.5 N H_2SO_4 and the analysis blank consisted of this acid. A linear relationship was found between the fluorescent intensity and the concentration of iron up to 5 mg. per ml. Amounts of aluminium were subsequently introduced into the standard solutions, and provided that the aluminium concentration was less than one third of the iron in solution, the calibration curve was not affected. The concentration of iron in the unknown samples was kept below 5 mg. per ml.

Aluminium was estimated colorimetrically using Alizarin Red S as an Indicator. (Bond 1957). Unfortunately in this technique the presence of large amounts of iron markedly influences the determination. To remove the iron, 25 ml. aliquots of the 50 ml. solutions prepared above were electrolysed using a Pt. wire anode and a mercury pool cathode passing 2 amperes for 2 hours. The migrating Fe^{+++} ions on reaching the cathode were amalgamated, but the Al^{+++} ions remained free. The super-natant liquor after electrolysis was pippetted off and added to a 100 ml. volumetric flask. The electrodes were washed five times with water and the washings, were also added to the flask before they were made to volume with water. These solutions were then used for the aluminium estimations by the method referred to above.

(e) X-ray Techniques.

Mineralogical examination of the clays and residues were carried out using 5.73 and 19 cm. diameter X-ray powder diffraction cameras. The variation in cell size was demonstrated by the accurate measurement of the d_{111} goethite spacing (2.44 Å) on a Norelco high angle goniometer. For this measurement AR grade $Pb(NO_3)_2$ was added as an internal standard - the goethite line being referred to the (311) $Pb(NO_3)_2$ line at 2.370 Å (Swanson et al. 1955). The diffractometer was oscillated backwards and forwards over both these peaks which were reproduced on a chart recorder calibrated in angular values of 2θ. The time constant of the electronic measuring equipment and the scanning speed of the goniometer were adjusted so as not to produce any significant broadening or displacement of the diffraction peaks. A scanning speed of $\frac{1}{8}^{\circ}$ (2θ) per minute (using 1° slits) and a time constant of 10 seconds were found to be the most satisfactory conditions. After correction by reference to the standard, the mean of four values of the goethite (111) spacing was obtained. The standard deviation in measuring each peak was 0.0004 Å. (In the angular region concerned this error arose from a 0.32 mm variation in fixing the peak position.) Absolute errors could be greater than this because of the difficulty in locating the centres of broad diffraction peaks.

TABLE 2.

Mineralogy of the Soil Samples Before and After Chemical Treatment.

Sample	Before Treatment		After NaOH Attack		After NaOH + Dithionite Ext.*	
BS29	Kaolin	m	Goethite	m	Goethite	l
	Goethite	m	Quartz	tr	Quartz	m
	Quartz	tr	Anatase	tr	Anatase	tr
	Gibbsite	l	Rutile	tr	Rutile	tr
			Unidentd. Clay	tr	Mica	tr
H165	Kaolin	m	Goethite	m	--	
	Goethite	mo	Quartz	tr		
19264	Kaolin	m	Goethite	m	Quartz	l
	Goethite	mo	Quartz	tr	Anatase	m
A 708	Kaolin	m	Goethite	m	Goethite	tr
	Goethite	mo	Quartz	tr	Quartz	mo
	Quartz	tr	Anatase	tr	Anatase	l
			Mica	tr	Rutile	l
					Mica	tr
P1027	Kaolin	m	Goethite	m	Quartz	tr
	Goethite	vl	Quartz	tr	Anatase	vl
	Quarts	vl	Haematite	m	Mica	m
	Mica	vl	Mica	l	Talc	tr?
	Vermic.	vl			Vermic.	tr?
	Haematite	vl				
A 543	Kaolin	m	Goethite	mo	Goethite	tr
	Goethite	l	Muscovite	m	Muscovite	m
	Mica	m				

m much; mo moderate; l little; vl very little; tr trace.

* Residue after three dithionite extractions, each for thirty minutes.

4. Results.

The efficiency of the alkali attack in concentrating the goethite is clearly seen from Table 2. Even after elimination of the free iron from these treated clays, no kaolin was detected in the residues. (Table 3.) Mica, however was present in sufficient quantities to allow identification in a few samples after the dithionite treatment, and hence it can be seen that the precaution of not using the citrate buffer was justified. (The mica was not detected in the original sample because its concentration was below the limit of detection.) The iron oxides themselves were slightly attacked during the NaOH digestion - 2% of the total iron was removed from H165. Since chemical and diffraction measurements were carried out on the residues this slight attack can be ignored.

It is apparent from Table 3, which gives the analyses of the dithionite extracts from alkali treated clays, that considerable quantities of aluminium were removed along with the iron. It seems probable that the aluminium is in some way combined with the goethite because the preliminary alkali digestion would have removed any aluminium which would normally be susceptable to the less severe dithionite extraction. (A fine grained diaspore suffered less than 1% loss when subjected to the standard dithionite treatment.) As no aluminium bearing minerals were present after the NaOH attack in quantities permitting detection, the assumption that the aluminium is contained within the goethite seems quite reasonable.

In Table 3 are also given the d_{111} spacings of the goethites and their corresponding molar compositions, assuming that all the iron and aluminium in the dithionite extracts originated from the goethites. The (111) spacing was chosen as an index of cell size variation because of its sensitivity to change in all unit cell dimensions. It can be seen from the last column of Table 3 that, for soil goethites, these spacings are significantly lower than for a pure mineral variety.

A linear relationship between the d_{111} goethite spacings and composition was found, and is shown in Fig. 1. Because there exists a large variation between various soil goethites, both in their molar composition and their d_{111} spacings, it is possible that a similar variation through a range of values could exist in any one sample. This would not be evident from the data in Table 3, as the results presented there are the averages for the whole samples. It was necessary therefore to carry out diffraction and chemical measurements on various particle size ranges and also, to measure (111) spacings on the residue of successive dithionite extractions of particular sizes.

Table 4 shows the experimental data from the analyses of successive dithionite extractions of different particle size fractions of BS 29 (NaOH treated). Also

TABLE 3.

Chemical Compositions[•] and (111) Spacings of Goethites and Diaspore.

Sample <2μ	Dithionite Extract % Composition		Goethite Composition Mole Fraction [*]		d_{111} A.U.
	Fe_2O_3	Al_2O_3	FeOOH	AlOOH	
BS29 (NaOH)	58.3	6.36	.855	.145	2.436
H165 "	59.8	13.8	.735	.265	2.426
H165 "	58.2[+]	13.2[+]	.738[+]	.262[+]	2.426
H165	13.4	3.48	.712	.288	2.426
19264 "	41.8	6.23	.811	.189	2.431
A708 "	45.4	7.46	.795	.205	2.431
P1027 "	61.0	6.53	.856	.144	2.433
A543 "	25.9	3.66	.818	.182	2.427
Ferrite Yellow Pigment	81.4	0.45	.992	.008	2.451
Mineral Goethite <5μ	-	-	1.0[x]	0	2.449
Mineral Diaspore	-	-	0	1.0[x]	2.318

[•] Iron and aluminium extracted by 3 dithionite treatments unless otherwise stated. Mn was less than 0.05% in all samples except H165 which contained 0.18%.

[+] Digestion in 6N HCl.

[x] Assumed to be pure.

[*] FeOOH + AlOOH = 1.

TABLE 4.

Iron and Aluminium Removed by Successive Dithionite Treatments of BS29.

Particle Size.	Dithionite Extraction	Fe_2O_3 %	Al_2O_3 %	Ignition, Loss 400° C.	Insoluble Residue %	Total %	$\frac{FeOOH}{AlOOH}$
<0.5μ	1	45.1	3.0				9.6
	2	13.5	3.0				2.9
	3	5.8	1.3				2.85
	Total	64.4	7.3	--*	12	--	
0.5-2μ	1	43.5	3.4				8.2
	2	11.5	2.3				3.2
	3	3.5	0.61				3.6
	Total	58.5	6.3	13.1	23	100.9	
2-5μ	1	38.7	2.6				9.5
	2	11.4	1.7				4.3
	3	4.3	0.61				4.5
	Total	54.4	4.9	11.5	28.6	99.4	
5-20μ	1	35.4	2.5				9.1
	2	5.8	0.67				5.5
	3	0.07	0.13				0.3
	Total	41.3	3.3	9.9	45.3	99.8	

100 to 150 mg. of sample were used for each analysis.

* Insufficient material to estimate an ignition loss.

shown here is the variation in the FeOOH: AlOOH ratio with successive treatments. The proportions of iron to aluminium extracted during the first treatment are approximately the same for each particle size, whereas the ratios in the second and third extractions appear reasonably constant within a particular particle size range. Ratios of Fe/Al extracted during the second and third treatments of each sample are all less than the ratios obtained in the corresponding first extractions. The ratio for the third extraction of the 5 - 20μ fraction is very low due to the fact that a neglible amount of iron was removed, so that even a trace of aluminium from other sources or an error in its estimation would alter the ratio considerably.

From the total Al_2O_3 and Fe_2O_3 contents of the various fractions of BS 29 (given in Table 4), molar compositions have been calculated. These values together with the d_{111} spacing measured before dithionite extraction, are listed in Table 5.

The data in this table shows that the aluminium content of the goethite decreases with increasing particle size, and the d_{111} spacing shows an accompanying change.

TABLE 5.

Composition of Soil Goethite BS 29, as a Function of Particle Size.

Particle Size* in Microns	Molar Compos. FeOOH	Molar Compos. AlOOH	Molar Ratio FeOOH/AlOOH	d_{111} A.U.
<0.5	.849	.151	5.6	2.433
0.5 - 2	.855	.145	5.9	2.436
2 - 5	.863	.137	7.1	2.436
5 - 20	.888	.112	8.0	2.444

* The coarser fractions are mixtures which contain much fine material in addition to the coarse material - see text.

Powder diffraction examination of the dithionite residues of the various particle sizes of BS29 showed that goethite was still present in the smallest fraction (<0.5μ) even after three treatments. This would account for the goethite detected in the residue in the <2μ sample in Table 2.*

For reasons mentioned in an earlier section, unbuffered dithionite was used for free iron extraction. Since 3 treatments did not completely remove goethite in a nominal <.5μ fraction it is realised that the method used is not particularly effective, at least

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* Footnote. G. Turton (priv. comm. to Dr. Norrish) of the C.S.I.R.O. DIV. OF SOILS found that only about half the goethite in the <2μ fraction of BS29 was removed by a modification (Haldane 1956) of the acid oxalate method of Jeffries (1941, 1946).

with these aluminiferous goethites. A recent method of Mehra and Jackson, (1960), in which both citrate and bicarbonate buffers were used completely removed the goethite from the 2 - .5μ fraction of BS29 in one treatment. (Table 6.) The molar composition obtained by this method agreed reasonably well with that obtained from three successive unbuffered dithionite treatments (Table 4). The effectiveness of this method is possibly due, as suggested by Mehra and Jackson, to the increased reducing power of the dithionite at pH7.5. Moreover the citrate may play an important part in the removal of aluminiferous goethite because of the ease with which it can itself remove aluminium from soil. (Saunders, 1959).

TABLE 6.

Iron and Aluminium Removed From BS 29 (0.5 - 2μ NaOH) by Dithionite - Citrate System Buffered with Sodium Bicarbonate (Mehra and Jackson, 1960.)

Extraction	Fe_2O_3	Al_2O_3	Molar Composition.	
			FeOOH	AlOOH
1	61.2	6.5		
2	0.3	not detected		
Total	61.5	6.5	.864	.136

The variation in d_{111} spacing of two samples before and after one dithionite extraction is shown in Table 7. In each case the treatment results in a change in the spacing of more than 10 times the error in fixing the position of a peak, and is therefore significant.

TABLE 7.

Variation in d_{111} Spacing Produced by One Dithionite Extraction.

Sample	d_{111} Spacing	
	Before Dithionite extraction	After 1 Dithionite extraction
BS29 2 - .5μ	2.436 A.U.	2.431 A.U.
H165/10 $<2\mu$	2.426 A.U.	2.420 A.U.

5. Discussion.

The above X-ray and chemical data present conclusive evidence that aluminium isomorphously replaces iron in soil goethites, producing changes in lattice dimensions proportional to the degree of substitution. The maximum replacement actually measured was 25 mole %, which is of the order found by Correns and Engelhardt (1941). This 25% replacement was an average value for all the less than 2 micron material of sample H165. Since one dithionite extraction considerably reduced the d_{111} spacing of the residue, it must be assumed that this $<2\mu$ fraction contained some material with a higher degree of substitution. From Fig. 1, the d_{111} spacing of the above residue suggests a 33 mole % replacement of AlOOH for FeOOH. It is not known how far substitution can proceed, it may even form a complete series between the two end members goethite and diaspore.

Many other goethitic soils besides those listed in this paper have been examined by X-ray diffraction, and have exhibited lower than normal d_{111} spacings. (Their mineralogy, however, did not permit satisfactory concentration of the goethite for more detailed chemical and diffraction analyses.) In fact, in the experience of this laboratory, it is unusual to find a $<2\mu$ goethite with a normal cell size. (in soils)

This partially explains the large amounts of aluminium extracted during free iron removal techniques, the relative amounts of iron and aluminium often being comparable to those shown in Table 3. (Williams et al. 1958, Williams 1950, Mackenzie 1954.). This extraction of aluminium has led to some of these iron removal treatments being referred to as methods for removal of "sesquioxides." However a dithionite extraction probably removes more aluminium from clay minerals (Williams et al. 1958, Mitchell and Mackenzie 1954, Mackenzie 1954.) than from the free aluminium oxides

(1% diaspore was removed by 2 dithionite extractions.)

This could render previous interpretations of the extract analyses liable to serious error, as hitherto goethite has not been considered as a source of aluminium. Furthermore, in a total analysis of a soil clay by acid digestion, it would be necessary to allocate some aluminium to the goethite present before compiling a mineralogical balance sheet.

Examination of Table 4 shows that in sample BS29 the highest aluminium replacement occurs in the smallest particle sizes. Sample H165, which showed the greatest degree of substitution, (Table 3), had the smallest average particle size, (Table 8), demonstrated by surface area determinations and electron micrographs. The surface area determinations were done using Nitrogen absorption techniques, and the results are given in Table 8. The variations in surface area for different particle size ranges is not as marked as it should be. This is because the particle size separations were carried out prior to NaOH digestion which would have increased the dispersion. This is shown in the electron micrographs of these samples reproduced in Chapter III. It is seen from these micrographs that there are many particles smaller than their nominal size range.

TABLE 8.

Surface Areas of Various Goethites.

Sample	Particle Size in microns (nominal)	Surface Area in M^2 per gm.
H165	<2	88.8
BS 29	<0.5 2-0.5 2-5	50.9 21.7 20.2
19264	<2	88.8
Synthetic Ferrite-Yellow	<2	10.8

Furthermore, Table 4 also shows that the first extract of the various particle sizes of BS29 has the highest iron:aluminium ratio, while in extracts 2 and 3, where the goethite was less readily removed, the ratio decreased markedly. This leads to the observation that <u>the higher the degree of isomorphous replacement, the more difficult is the removal of the goethite by sodium dithionite</u>. As a consequence, the 5-20μ fraction of this sample was more easily removed (complete after 2 treatments) than the $<0.5\mu$ (incomplete after 3 treatments). Mehra and Jackson (1960) state that in general, haematite is more easily removed from soils than is goethite, and this has been the general experience in this laboratory. Schwertmann (1959b) finds the opposite to be true, but, as he does not mention particle sizes, it could be that the goethites which he was using were coarse and had a consequent lower aluminium content. Alternatively, the goethites may have been unsubstituted and of a small particle size due to the early stages of ageing of an amorphous gel (oxidation-hydrolysis type, see Chapter II).

The ultimate particle size of a substituted soil goethite may be determined during its formation stages. If the iron and aluminium were co-precipitated and aged, then the resultant lattice deformity could limit the size to which a crystal may grow.

On plotting the chemical composition against the d_{111} spacing of the goethites, a linear relationship is found, Fig. 1. (The measurements of Correns and Engelhardt do not fit this graph, nor do they bear any obvious relationship to each other.) The broken line in Fig. 1 joins the d_{111} spacings of mineral goethite and diaspore (Not shown on the graph). In each of these minerals it is *assumed* that there is no isomorphous substitution. It can be seen that this line departs from the experimental line obtained with soil goethites. It is considered that this is due to the unequal contraction of the three axes as aluminium replaces iron. The d_{111} spacing is most sensitive to changes in the *c* axis, which is the smallest

as $\frac{1}{d_{hkl}} = \sqrt{\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}}$ i.e. $\frac{1}{d_{111}} = \sqrt{\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}}$

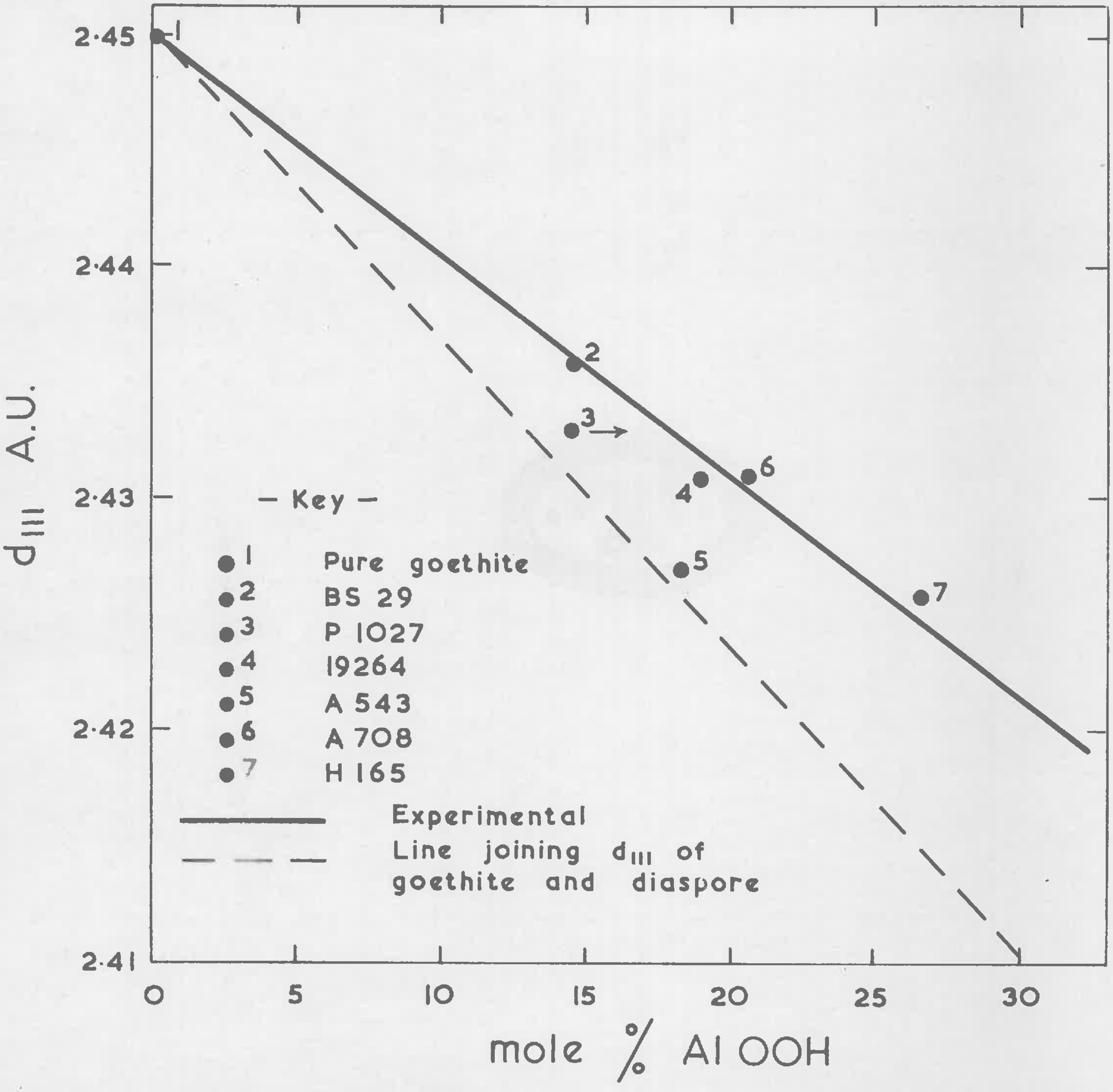

Fig. 1 Relationship between d_{111} and Al content of soil goethite.

Assuming that there is an associated volume decrease on the incorporation of aluminium, this decrease must be accomplished primarily by contraction of the <u>a</u> and <u>b</u> axes.

There is also a reduction in the diffracted intensity of the d_{111} line of goethite with the degree of substitution. Since the intensity of a diffracted line is proportional to the square of the structure factor, $|F|$, these latter values were calculated for goethite, diaspore and for compounds of intermediate composition. A linear relationship was found to exist between $|F|$ and degree of substitution, and the calculated values are given in Table 10. Use of this linear relationship was made in the estimation of goethites by X-ray diffraction and is described in Chapter III.

TABLE 10.

Variation in Structure Factors with Isomorphous Replacement.

Sample Composition	$\lvert F\rvert_{111}$
FeOOH	118
$(Fe_{.75}Al_{.25})OOH$	103
$(Fe_{.50}Al_{.50})OOH$	88
$(Fe_{.25}Al_{.75})OOH$	74
AlOOH	59

In Fig. 1 it is seen that two soil goethites give values which depart from the postulated linear relationship. Sample 3, P1027, unfortunately was found to contain almost as much haematite as goethite, and therefore, the total iron extracted during the dithionite treatment does not represent the iron component of the substituted goethite. The sample would better fit the proposed relationship if the aluminium: iron ratio were increased by allocating some Fe_2O_3 to the haematitic form. No reason was apparent for the marked departure of sample 5, A543.

From the results of Table 7, showing the variation in d_{111} spacing of the residues after dithionite treatment, and Table 4 showing the variation in spacing and replacement with particle size, it is not surprising that soil goethites exhibit in general, broad diffraction lines. The super-position of the patterns of the poly-phase system is probably a major contributor to this line broadening.

In Chapter II it was mentioned that goethite syntheses carried out were commenced primarily in connection with this aspect of isomorphous substitution. Various techniques were tried, and, on a few occasions, aluminiferous goethites with a decreased d_{111} spacing were formed. Results, however, were not always reproducible. (In the most successful method a solution of ferric sulphate was hydrolysed at 90°C. for four hours. The precipitate was washed and added to freshly precipitated aluminium hydroxide which had been washed to neutrality. The two precipitates were intimately shaken in water and then added to a gold lined pressure "bomb" to a specific volume of 0.9. The capsule was then sealed and left at 105°C. for about 20 hours. The precipitate was washed with 1 N NaOH to remove the excess $Al(OH)_3$ and was then dried from alcohol and examined by X-ray diffraction.)

From the results presented, it must be concluded that aluminiferous goethites do exist in soils. It is also conceivable that the extent of the aluminium substitution is related to weathering conditions and hence soil type. The results also demonstrate that the presence of aluminium is responsible for:--

(a) The variation in diffraction spacings;
(b) The difficulty of removal by sodium dithionite;
(c) The presence of some aluminium in the free iron removal extracts; and
(d) The apparent broad nature of soil goethite diffraction patterns.

The presence of aluminium in soil goethites may also influence either directly or indirectly the absorption or fixation of phosphates. Lattice strains introduced by the substitution of the smaller ions may cause a polarising effect, as a result of which, phosphate may be absorbed by anion exchange. Again, the limitation imposed by the lattice strains would allow a greater surface area to be available for adsorption. Furthermore, since aluminium and iron have different pH ranges of solubility, an aluminiferous goethite, with both these elements exposed, could affect a chemical precipitation of phosphate over a wider range of soil conditions than a normal goethite.

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