

MAGHEMITE IN SOILS AND ITS ORIGIN

I. PROPERTIES AND OBSERVATIONS ON SOIL MAGHEMITES

R. M. TAYLOR* AND U. SCHWERTMANN

*Institut für Bodenkunde, Technische Universität München,
Freising-Weihenstephan, West Germany*

(Received 20 March 1974)

ABSTRACT: A magnetic iron oxide is a common constituent of ferruginous concretions in highly weathered Australian soils and is generally associated with varying proportions of hematite and occasionally with goethite. The X-ray diffraction pattern and the low Fe (II) contents (4–15% of total Fe) of this magnetic phase identify it as maghemite which was further confirmed by IR and DTA. This maghemite is only slightly soluble in dithionite but readily in 1:1 HCl or oxalic acid. From the Fe (II) contents and mineralogical associations in soil concretions, conditions for maghemite formation under near pedogenic conditions are suggested.

INTRODUCTION

Although not as common as goethite and hematite, maghemite, the ferromagnetic form of Fe_2O_3 , occurs in many soils especially in highly weathered oxidic soils of tropical and subtropical climates e.g. Hawaii (Matsusaka & Sherman, 1961), Australia (Adetoye, 1970), India and Africa (Frankel & Bayliss, 1960), as well as in soils of the more temperate regions, e.g. Holland (Van der Marel, 1951), Germany (Schwertmann & Heinemann, 1959), Japan (Kojima, 1964), Russia (Avdoninia, 1965) and Canada (Pawluk, 1971).

Detailed properties of these natural occurrences have not been given nor has its formation been satisfactorily explained. Frequently, its formation is attributed to the dehydration of lepidocrocite or goethite in the presence of organic matter, or to the oxidation of magnetite. Although easily prepared from lepidocrocite by heating to 300°C (dehydration), this mode of formation can only have occurred under conditions of heating which, in the presence of organic matter, also convert other Fe minerals, e.g. goethite, to maghemite (Van der Marel, 1951; Schwertmann & Heinemann, 1959). Oades & Townsend (1963) also reasoned that the firing of soils could not be responsible for many of the occurrences cited in the literature, and suggested rather that it formed by a pedogenic process from the Fe oxides

* Present address: CSIRO, Division of Soils, Private Bag, Glen Osmond, South Australia, 5064. The research was carried out at the Institut für Bodenkunde, Techn. Univers. München.

present through the action of organic matter at normal temperatures. They further state that the presence of Fe(II) is a necessary initial requirement, which is in accord with the structural studies of Mackay (1960) and Bernal, Dasgupta & Mackay (1959).

The abundance of maghemite in soils is often greater than could be expected from the amount of magnetite supplied by the parent rock and thus the oxidation of magnetite to maghemite may not be important in soils except those formed on basic igneous rocks initially rich in magnetite. Bonifas & Legoux (1957) for example, have shown that massive maghemite in lateritic weathering products arose from the oxidation of the high concentrations of magnetite in the basic dunite rock. Moreover, the sharp discontinuity between the concentration of magnetic material in the magnetic concretions and either the non-magnetic ones or the associated matrix further suggest that the magnetism is not due to residual magnetite or to a product of its oxidation. Although fine grained magnetites are known to oxidize at low temperatures (Farrell, 1972), coarse grained samples, as could be expected from residual primary minerals, alter on thermal oxidation to hematite rather than maghemite (Farrell, 1972; Feitknecht, 1965).

It is the purpose of this paper to report some observations made on the pedogenic maghemites from different localities. From these observations an indication is given as to what may be important parameters during maghemite formation in soils.

MATERIALS AND METHODS

Ferruginous soil concretions* were chosen for this investigation. They were collected from lateritic, podsollic, krasnozemic and solodic soils from various parts of Australia (see Table 1). The magnetic variety was separated by a hand magnet and its proportion of the total weight of concretionary material (> 1 mm) was determined. A maghemite rich sample from a mineral deposit in Conakry, Ghana, was included for comparison.

Representative samples of the magnetic and non-magnetic concretions from the same horizon were ground, and X-ray powder diffraction photographs taken using Co $K\alpha$ radiation and a 5.73 cm diameter camera. Diffractograms were also run on these samples to record the (220) and (311) \dagger diffraction peaks at *c.* 2.95 and 2.52 Å respectively.

Fe(II) was determined by solution of samples in 6 N H_2SO_4 at 100°C and subsequent colorimetric determination using $\alpha\alpha'$ dipyridyl and correcting for total Fe which was determined colorimetrically using sulfosalicylic acid. In a few samples the total Fe was checked by atomic absorption and fluorescent X-ray spectroscopy (Norrish & Hutton, 1969). Fe removed by dithionite and HCl extractions was determined by atomic absorption techniques.

* The term 'concretion' is used here without implying concentric layering although this was present in some samples.

\dagger Indices refer to a cubic system. For the tetragonal modification indices are (313).

TABLE 1. Ferruginous soil concretions; soil type, depth of sampling and associated minerals

Sample identi- fication no.	Soil type, parent material	Profile depth (cm)	Sample type	Minerals identified by X-ray diffraction*				
				G	H	M	Ka	Q
18858	Yellow solodic	35-40	matrix	++	++		+++	+++
18763	on basalt		non-mag.	++	++++			+
18764			magnetic	+	++++	+		++
18692	Red solodic	10-15	non-mag.		++++		++	++
18691	on basalt†		magnetic		++++	+++		
18657		35-40	magnetic		++++	+++		+
18694		60-65	magnetic	+	++++	+++		+
19003	Lateritic	60	matrix				+++	++
19024	podzolic on		non-mag.	+	+		++	++
18964	granite‡		magnetic		+	+++	+	+
19256	Krasnozem on	10-15	matrix	++	++		++++	++
18766	basalt		non-mag.	++++	+		++++	
18761'			magnetic		+++	+++		
20849		15-20	non-mag.	+++			++++	+
20850			magnetic		++	+++		+
18575		35-40	non-mag.	++	++		++++	+
18574			magnetic		+++	++++		+
19002	Brown podzolic	10-15	matrix	++	+		++++	+
19036	on basalt		non-mag.	+++	+++		++	++
19037			magnetic	+	++++	+++		+
—		30-35						
20847			non-mag.	++++	++		+++	+
20848			magnetic	++	+++	++++		+
18953	Krasnozem	60-65	matrix	++			+++	+
19205	on trachyte		non-mag.		++++			++
18988			magnetic	++	+	++++		+
20852		70-75	non-mag.		+++		+++	+
20851			magnetic		++++	++++		+
20845	Red earth	50-65	non-mag.		+++		++	++
20846	on dolerite		magnetic		+++	++++	+	+
18912	Podzolic soil	30-45	matrix				++	++++
18987	on alluvium		non-mag.	++	++		+++	++
18965			magnetic		+++	++	++	+

* Mineral estimations are relative only and were done visually on X-ray powder diffraction photographs; +++ greater than 40%; ++ 20-40%; + 10-20% and + less than 10%. G, Goethite; H, hematite; M, maghemite; Ka, kaolin; Q, quartz.

† The non-magnetic sample contained about 20% mica.

‡ All samples contained between 20-40% gibbsite and the concretions in addition contained up to 20% boehmite.

RESULTS AND DISCUSSION

Mode of Occurrence and Mineralogy

Generally the magnetic concretions from the Australian soils were associated in the same horizon with morphologically similar non-magnetic concretions. The average diameter was between 2 and 10 mm. Concentric layering of the Fe oxides was observed in thin sections. Many concretions were composed of smaller discrete concretions which had been cemented. The magnetic and non-magnetic concretions (> 1 mm) together constituted up to about 60% of the total soil in some horizons and the proportion of the total concretions which were magnetic was in some cases as high as 98%. This magnetic proportion varied down the profile usually showing a maximum at a depth between 20 and 30 cm. In some profiles the proportion of concretionary material in the whole soil exhibited a double peak whereas the magnetic component only showed one which did not always correspond to the position of maximum total concretions. No relationship between the proportions of magnetic material and clay content was observed in the few samples examined. Whereas the magnetic concretions were predominantly maghemite in association with varying proportions of hematite, the iron oxide phases in the non-magnetic concretions were goethite and/or hematite. Besides the differences in the Fe mineralogy the association with other minerals was also different (Table 1). The non-magnetic concretions generally contained greater amounts of the soil matrix minerals. The average Fe content of non-magnetic concretions was about 66% of that in the associated magnetic samples. This higher density of Fe minerals in the magnetic concretions is in agreement with the recent observations of Pawluk & Dumanski (1973). One interpretation of these observations is that maghemite formed in regions with higher total amounts of Fe(II) in solution possibly resulting in a lower rate of oxidation of the Fe present.

X-ray diffraction and crystal chemistry of the maghemite samples

Super structure X-ray diffraction lines which aid in a positive identification of maghemite rather than magnetite are generally only present in the fully ordered tetragonal modification (Oosterhout & Rooyman, 1958) and were not detected in any of the pedogenic maghemites examined.

The Fe(II) and total Fe contents of the samples are given in Table 2. From X-ray diffractograms the integrated intensity of the (104) hematite peak was used to obtain a semi-quantitative estimation of the hematitic Fe, the remainder, including all the Fe(II), being attributed to the associated maghemite, although it is realized from published analyses (Deer, Howie & Zussman, 1962) that some very crystalline and massive hematites can have up to 1.7% of their total Fe in the Fe(II) state. The consequent deduced compositions of the maghemitic component of the concretions are given in Table 2 where the Fe(II) expressed as a percentage of the total Fe of the maghemite varies in the range 4–15%. Although Fe(II) in the maghemite-magnetite series ranges from 0 to 33.3% of the total Fe, Fasiska (1967) in a review

of their composition states that in magnetite the Fe:O ratio can vary only between 0.75 and 0.744 ($n = 1.00-0.91$, Table 2) whereas in maghemite the ratio can lie between 0.67 and 0.72 ($n = 0-0.57$). In which case the low Fe(11) contents of our samples ($n = 0.14-0.43$) would identify them as maghemites.

TABLE 2. Total Fe and Fe(11) contents and deduced composition of the maghemite component

Sample identification no.	Total Fe (%)	Fe due to hematite (%)	Fe due to maghemite (%)	Fe(11) in sample (%)	Maghemite* composition n in $\text{Fe}_{2+n}\text{O}_{3+n}$	Width at half height maghemite peak (2θ)
18691	59.1	33.0	26.1	3.12	0.36	0.38
18657	57.7	36.1	21.6	2.27	0.32	0.43
18694	56.7	29.8	26.9	1.26	0.14	0.35
18761	52.4	24.9	27.5	2.10	0.23	0.40
18574	51.1	20.6	30.5	2.97	0.29	0.43
18764	42.6	34.2	8.4	1.08	0.39	0.55
18988	32.0	3.6	28.4	2.29	0.24	0.50
18964	24.1	4.3	19.8	2.52	0.38	0.55
18965	32.5	23.7	8.8	1.26	0.43	0.55
19037	46.4	32.7	13.7	1.27	0.28	0.35
Conakry	64.0	13.2	50.8	0.93	0.05	0.16
Magnetite (theoretical)	72.4	—	—	24.10	1.00	—

$$* n = \frac{\text{Fe}^{2+}/\text{Total Fe in maghemite}}{0.333}$$

No confirmation of identification can be expected from X-ray diffraction data. Although appearing contradictory to Fasiska (1967) Basta (1959) suggests that one could expect a continual linear change in cell size with composition in pure members of the maghemite-magnetite series. However the high degree of isomorphous substitution that can occur in soil iron oxides (Norrish & Taylor, 1961), and especially in spinels (Lewis, 1970; Basta, 1959) and maghemites (Beneslavskii, 1957) would make the reliable estimation of composition from diffraction spacings impossible, and identification as maghemite can only be made on the Fe(11) content. Even allowing for errors in the distribution of the total Fe between the two phases, the Fe:O values would still place them in the maghemite range.

The possibility of isomorphous substitution of Al for Fe in these samples is suggested by the low range of the d_{220} * X-ray diffraction spacings. These values varied between 2.938 and 2.954 Å whereas this spacing for pure maghemite is quoted as 2.950 Å and for magnetite as 2.967 Å†. Van der Marel (1951) quotes Michel & Pouillard (1949) as suggesting that Al diminishes the cell size of $\gamma \text{Fe}_2\text{O}_3$.

* The d_{220} line was chosen in preference to the most intense line because it was generally free from interferences.

† The spacings quoted for maghemite and magnetite are from the 1972 index to the Powder Diffraction File compiled and published by the Joint Committee on Powder Diffraction Standards, Pennsylvania, U.S.A.

The widths at half height of the X-ray diffraction peaks* were chosen as an indication of the degree of crystallinity and particle size of the maghemites. The values given for most samples are between 0.35 and $0.55^\circ 2\theta$ (Co $K\alpha$ radiation) which is in the lower part of the range obtained for a series of synthetic maghemites (0.42 – 1.13) produced at pH 6–7 and 20 – 30°C (Taylor & Schwertmann, 1974). The sample from Conakry is somewhat more crystalline, ($0.16^\circ 2\theta$).

The IR spectrograms of the reference sample from Conakry and one soil concretion were taken after treatment with dithionite which concentrated the maghemite by preferential removal of associated hematite (see below). Absorption bands between 1000 and 1100 cm^{-1} arose from silicate impurities and there were further bands at c. 690 , 630 , 580 , 560 and between 440 and 470 cm^{-1} . Although not well resolved these bands can be taken as characteristic of maghemite as demonstrated recently by Farrell (1972) and are due to various Fe-O stretching vibrations and O-Fe-O deformations. They also occur in the spectrograms of synthetic maghemites (Taylor & Schwertmann, 1974).

Pairs of samples, consisting of a magnetic and non magnetic concretion from each of four different soils were examined by DTA. The magnetic ones all showed a weak endothermic peak between 745 and 780°C which did not occur with the non-magnetic samples. This endotherm can therefore be attributed to the maghemite \rightarrow hematite transformation. Endothermic reactions between 500 and 600°C indicate dehydroxylation of layer lattice silicates and were more frequent in the non-magnetic samples in accordance with the observed mineralogical differences between the two varieties (Table 1). Additional endotherms at 300 – 350°C were seen where goethite was present and exotherms at 350°C which were not restricted to magnetic samples were interpreted as indicating organic matter, thus supporting Oades & Townsend (1963).

Chemical Fe removal treatments

The iron minerals of the magnetic concretions were less readily removed by the dithionite-citrate method of Mehra & Jackson (1960) than were those of the non-magnetic samples. However in neither group of samples was all the Fe removed by two successive 30 min extractions at 75°C on 100 mg samples. A subsequent treatment in boiling 5 N HCl still failed to remove from 2 to 6% of the original total Fe. Table 3 shows the relative amounts of Fe removed by these two treatments from the magnetic and non-magnetic concretionary material of different soil profiles. The major part of the Fe in the non-magnetic concretions was dithionite soluble whereas in the magnetic samples a much larger proportion was removed in the subsequent acid treatment. The ratio of HCl extractable/dithionite extractable Fe is constantly higher for the magnetic samples than for the associated non-magnetic material.

The relative proportions of maghemite and hematite in some of these samples (Table 2) indicates that the difficulty soluble Fe cannot be attributed solely to the

* Width at half height of a well crystalline material was $0.14^\circ 2\theta$.

maghemitic phase, nor is there any apparent relationship between the amounts of iron removed by the standard treatments used to the total quantities of Fe present. The sum of dithionite and HCl extractable Fe is often a few percent, 6% at most, less than the measured total Fe. In a few cases this difference could be partly attributed to the presence of ilmenite which was detected in X-ray powder photographs of the residue after the dithionite and HCl treatment. If this difference between the total and the extracted Fe were all attributed to 'non free iron oxides', rather than to more difficultly soluble maghemite, the value of n in Table 2 would be increased, generally by less than 0.1.

TABLE 3. Chemical treatment for removing Fe

Sample identification no.	Concretion type	Dithionite sol. Fe % of sample	HCl sol. Fe after dithionite % of sample	Total Fe % of sample	HCl sol. dith. sol.
(a) Using $2 \times \frac{1}{2}$ h dithionite extractions (pH 9)					
18763	non mag.	20.0	18.9	43.2	0.95
18764	mag.	20.4	26.5	51.0	1.30
18692	non mag.	22.2	15.5	43.4	0.70
18691	mag.	11.0	43.0	60.8	3.9
20845	non mag.	10.8	1.8	14.5	0.16
20846	mag.	17.8	13.5	35.9	0.76
20847	non mag.	21.2	11.8	37.1	0.55
20848	mag.	18.9	27.1	51.9	1.4
20849	non mag.	15.0	5.3	22.4	0.35
20850	mag.	13.3	35.3	53.2	2.6
20852	non mag.	21.1	9.2	32.9	0.43
20851	mag.	12.8	15.9	31.4	1.24
18657	mag.	11.4	ND	58.2	—
(b) Using 2×1 h dithionite extractions					
18763	non mag.	27.3	12.2	43.2	0.45
18764	mag.	25.0	21.0	51.0	0.84
18692	non mag.	27.2	9.9	43.4	0.36
18691	mag.	14.3	39.5	60.8	2.8
(c) Using $2 \times \frac{1}{2}$ h dithionite extractions using 20 ml 0.3 M acid ammonium oxalate (pH 5.5) instead of citrate-bicarbonate solution.					
18764	mag.	41.5	5.9	51.0	0.14
18691	mag.	36.2	19.4	60.8	0.53
18657	mag.	25.9	ND	58.2	—
(d) Using $2 \times \frac{1}{2}$ h extractions at 75°C in 20 ml 0.3 M acid ammonium oxalate (no dithionite) (pH 3)					
18657	mag.	37.0	ND	58.2	—

With an increase in the duration of the dithionite extraction (see Table 3) the proportion of total Fe removed by this treatment is increased, thereby reducing the HCl soluble/dithionite soluble ratio. However the total amount extracted is reason-

ably constant and the variation in this ratio between the two types of concretion is still quite marked. Whereas the increased extraction with increased treatment times suggests the removal of more difficultly soluble material possibly due to differences of particle size or crystallinity, there is some effect due to mineralogical differences.

One could conclude from these experiments that maghemite does not appear to be as susceptible as hematite to the dithionite extraction treatment. X-ray powder diffraction photographs taken before and after extraction showed that maghemite had been concentrated with respect to hematite. Oades & Townsend (1963) on the other hand were able to reduce the magnetic susceptibility of soil clays, presumably by maghemite removal by a much milder dithionite extraction technique.

Whereas dithionite extract on the magnetic concrectionary material preferentially removes hematite thus concentrating maghemite, X-ray powder diffraction photographs showed that heating in oxalic acid preferentially dissolves the maghemite leaving the residues more hematitic. Table 3 shows the effects of combining dithionite and oxalate extractions on some powdered magnetic concrectionary material. The citrate-bicarbonate complexing-buffer reagent of the Mehra & Jackson (1960) technique was replaced by 20 ml 0.3 M acid ammonium oxalate solution and the proportion of the total Fe removed in sample 18764 increased from 40 to 81% whereas doubling the extraction times only increased the extraction from 40 to 49%. Similarly, in sample 18691, the Fe extracted using the composite reagents increased from 18 to 59% whereas doubling the time only increased the extraction to 23%.

On a further magnetic sample 18657 the two half hour conventional dithionite extractions removed only 20% of the total Fe which increased to 44% when the citrate-bicarbonate solution was replaced by acid ammonium oxalate (pH 5.5). However, when acid ammonium oxalate was used alone (pH 3) the extraction increased to 64% of the total Fe. This behaviour is in line with the observations of Gamble & Daniels (1972) who found that magnetite was relatively unreactive in dithionite but was partly dissolved in 0.2 M acid (\sim pH 3) ammonium oxalate.

This higher solubility of maghemite in oxalic acid may be explained by its Fe(II) content. It is well known that the dissolution rate of ferric oxides and hydroxides in oxalate is markedly increased by the presence of Fe(II), explaining why goethite is more soluble in oxalate under ultra violet light due to photochemical reduction, (de Endredy, 1963), or after addition of Fe(II) ions (Fischer, 1973). Also it has been shown that goethitic bog iron ores were completely soluble in acid ammonium oxalate when siderite as a source of Fe(II) was present (Schwertmann, 1959). This reaction with oxalate would necessarily modify the estimation of amorphous iron oxides (Schwertmann, 1959) when maghemite is present.

Factors affecting the genesis of maghemites

Harrison & Peterson (1965) in discussing the formation of a magnetic mineral on the floor of the Indian Ocean speculated that in a soil with a source of Fe(II), and which is isolated somewhat from ready sources of oxygen, authigenic magnetite might form and be subsequently further oxidized to maghemite. This hypothesis

concerning the effect of oxidation rate is in agreement with the interpretation given earlier to the mineralogical differences between the associated magnetic and non-magnetic concretions, and in line with the suggestion of Oades & Townsend (1963).

If then magnetic and associated non-magnetic ferruginous concretions from the same horizon of a soil can be considered to have formed during the same weathering cycle then it is possible that the differences in the iron mineralogy of the two concretionary types might have resulted from small differences in the micro-aeration of the environment. Due to the polycyclic nature of the soils this theory cannot be tested. However, from our interpretations of the above observations it seemed reasonable to postulate that maghemite formation may be induced under pH and temperature conditions that normally give rise to hematite and/or goethite, merely by altering the rate of oxidation of a Fe(111)-Fe(11) system. A series of successful syntheses of maghemite were subsequently carried out and are reported in part II of this paper.

ACKNOWLEDGMENTS

The authors acknowledge gratefully the technical assistance given by Mrs A. Campbell, Miss R. Baker and Mr H. Konczala of the CSIRO Division of Soils, Adelaide and Mrs U. Maul and Mr H. Schneiderbauer of the Institut für Bodenkunde, TU München, Freising-Weihenstephan. One of us (RMT) gratefully acknowledges the grant made by the Deutsche Forschungsgemeinschaft towards this cooperative research project.

REFERENCES

- ADETOYE F. (1970) *Am. Miner.* **55**, 925.
 AYDONINIA M.P. (1965) *Trans. Inst. Geol. Akad. S.S.S.R.* **70**, 283.
 BASTA E.Z. (1959) *Econ. Geol.* **54**, 698.
 BENESLAVSKII S.I. (1957) *Dokl. Akad. Nauk. S.S.S.R.* **113**, 1130.
 BERNAL J.D., DASGUPTA D.R. & MACKAY A.L. (1959) *Clay Min. Bull.* **4**, 15.
 BONIFAS M. & LEGOUX P. (1957) *Bull. Serv. Carte géol. Als.-Lorr.* **10**, (2).
 DE ENDREDEY A.S. (1963) *Clay Min. Bull.* **5**, 209.
 DEER W.A., HOWIE R.A. & ZUSSMAN J. (1962) *Rock Forming Minerals*. Vol. 5. Non-Silicates, p. 23, Longmans, London.
 FARRELL D.M. (1972) *Mines Brch. Invest. Rep. IR. 72-118*. Dept. of Energy Mines and Resources, Canada.
 FASISKA E.J. (1967) *Corros. Sci.* **7**, 833.
 FEITKNECHT W. (1965) *Colloques int. Cent. natn. Rech. scient.* **122**.
 FISCHER W.R. (1973) *Trans. Int. Soil Sci. Soc. Comm. V and VI*, Stuttgart, 37.
 FRANKEL J.J. & BAYLISS P. (1960) *J. sedim. Petrol.* **36**, 193.
 GAMBLE E.E. & DANIELS R.B. (1972) *Proc. Soil Sci. Soc. Amer.* **36**, 939.
 HARRISON C.G.A. & PETERSON M.N.A. (1965) *Am. Miner.* **50**, 704.
 KOJIMA M. (1964) *Nippon Dojo-Hinogaku Zasshi*, **35**, 171.
 LEWIS J.F. (1970) *Am. Miner.* **55**, 793.
 MACKAY A.L. (1960) *Reactivity of Solids*. Proc. 4th Int. Symp. Amsterdam, 1960, 571.
 MATSUSAKA Y. & SHERMAN G.D. (1961) *Soil Sci.* **91**, 239.
 MEHRA O.P. & JACKSON M.L. (1960) *Clays Clay Miner.* In: Proc. 7th Conf. 317.
 MICHEL A. & POUILLARD E. (1949) *Compt. Rend. Acad. Sci. Paris*, **228**, 680.
 NORRISH K. & TAYLOR R.M. (1961) *J. Soil Sci.* **12**, 294.
 NORRISH K. & HUTTON J.T. (1969) *Geochim. cosmochim. Acta*, **33**, 431.
 OADES J.M. & TOWNSEND W.N. (1963) *J. Soil Sci.* **14**, 179.

- OOSTERHOUT G.W. VAN & ROOYMANNS C.J.W. (1958) *Nature*, **181**, 44.
- PAWLUK S. (1971) *Can. J. Soil Sci.* **51**, 113.
- PAWLUK S. & DUMANSKI J. (1973) *Proc. Soil Sci. Soc. Am.* **37**, 124.
- SCHWERTMANN U. (1959) *Z. Pflanzenern., Düng., Bodenkunde*, **84**, 194.
- SCHWERTMANN U. & HEINEMANN B. (1959) *Neues Jb. Miner.* **3**, 174.
- TAYLOR R.M. & SCHWERTMANN U. (1974) The synthesis of maghemite under near pedogenic conditions.
- VAN DER MAREL H.W. (1951) *J. sedim. Petrol*, **21**, 12.