SCANNING ELECTRON MICROSCOPY OF SECONDARY MINERALS IN FE-MN GLAEBULES

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Introduction .-

One form of accumulation of Fe and Mn in soils results in micromorphologically distinct entities which are collectively termed as glaebules by Brewer (1.964). The glaebules are subdivided into concretions, nodules and septaria based on their fabric characteristics and recently Gallaher et al (1.973a; 1.973 b, 1.974a; 1.974 b) have examined these types in great detail. In the field, glaebules are described as mottles, nodules or concretions. The very spherifical concretions with shiny surfaces are referred to as buckshots or shots (Wheeting, 1.936). Features, currently called as plinthite (USDA, 1.976) or petroplinthite (Sys, 1.968; Eswaran et al, 1.972) are also considered as glaebules.

Glaebules have been studied from different points of view. Comparison of the glaebular material from the rest of the s-matrix (Gallaher et al, loc. cit.; Sherman et al, 1.954; Pendleton et al, 1.942) have indicated that mineralogically they may be different or similar depending on the age of the soils studied. Many workers (Drosdoff et al, 1.940; Sherman et al, 1.954; Sokolova et al 1.968) have observed that the amount of iron increases as the size of the concretions decrease whilst manganese showed a reverse trend. Formation of glaebules is frequently related to a fluctuating water table (Drosdoff et al, 1.940; Beater, 1.940; Sherman et al, 1.954; Blume 1.967; Sokolova et al, 1.968). The first stage requires

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a nucleus of deposition in the s-matrix and microorganisms have been attributed to initiate this (Drosdoff et al, 1.940; Sokolova et al, 1.968). Eswaran (1.968) however observed that mottles were confined to plasma-rich parts of the s-matrix and as suggested by Smith (1.936), the receding water front tends to converge towards the plasma-rich zones with a concomitant accumulation of iron in these zones. Growth of concretions or nodules is attributed to an accretionary process resulting from successive precipitations of iron on these centres.

The accretion of iron or manganese results in a compact matrix with low porosity (Cescas et al, 1.970). Employing the scanning electron microscope (SEM) they postulated that infilling of former voids in the s-matrix by iron resulted in the low porosity. They also noted little difference in porosity in the banded and non-banded zones. Another initial study of concretions with the SEM was by Pawluk et al, (1.973). They studied magnetic and non-magnetic concretions and observed slight difference in fabric but as their observations were at relatively low magnifications, they did not pick out any minerals. XRD analyses however indicated the presence of goethite and some haematite and maghemite. Elemental mapping with the electron microprobe showed a definite zoning pattern for Fe in the magnetic concretions.

More recently, McHardy et al, (1.975) observed some mottles with the SEM. They coupled their studies with the electron microprobe and showed the accumulation of birnessite on plasma surfaces. Identification of secondary minerals with the SEM has been very successful in petroplinthite. Eswaran et al, (1.972) showed micrographs of goethite and some manganese minerals in some laterites. More recently, Eswaran et al, (1.977) have shown the formation of gibbsite.

There are a range of secondary minerals that may

accumulate in glaebules. Many of these cannot be identified by optical techniques and in some cases XRD is of little assistance due to masking by amorphous materials. This specially applies to manganese minerals which do not produce sharp peaks on XRD even with the use of Fe Kα radiation. In many cases, the manganese is present as a thin film on void walls or coating grains or plasma aggregates, making it difficult to identify the minerals present. SEM is a useful instrument for such cases as has been shown by McHardy et al, (1.975).

The objective of this study is to characterise with the SEM, a small range of secondary minerals encountered during our studies of glaebules. The intention is to document the morphologies of these minerals in soils but we should emphasise that the same mineral may take other forms or habits or even pseudomorph other minerals, depending on the conditions of formation. Consequently, such documentation will in time establish the range of forms that could be encountered in soils.

Material and methods .-

Soils from Malaysia, Australia, India and Zaire were employed in this study and Table I, gives their classification and location. Sample No. 6 is equivalent to sample No. 15 of Taylor et al, (1.964), who report about 78 % of Mn_3O_4 in similar nodules and birnessite as the main manganese mineral. Samples No. 7 and 8 are laterite or petroplinthite nodules employed in this study to confirm earlier observations. Sample No. 9 is a manganese rich vein from Hawaii which Patterson, (1.971) reports as being composed of lithiophorite.

Table I

Materials employed in the study

Soil Name	Locality	Parent material	Classification
1. Kabu	Malaysia	Alluvial	Aeric Tropaquept
2. Kubang	Malaysia	Alluvial	Fluvaquentic - Eutropept.
3. Pauh	Malaysia	Alluvial	Plinthaquic Tropu - dult.
4. Hutan	Malaysia	Alluvial	Aeric Tropaquept.
5. Batu Anam	Malaysia	Shale	Aeric Tropaquept.
6. Taylor (15)	Australia	-	-
7. -	India	-	Petroplinthic Ha - plustalf.
8. -	Zaire	-	Petroplinthic Ha - plustox.
9. -	Hawaii	Basalt	(Saprolite).

Glaebules from the Malaysian soils were handpic - ked, washed with dilute acid to remove surface coating and this material was used for the mineralo-chemical and scanning electron microscopic (SEM) work. Thin sections of the soil material containing the glaebules were made for the micromorphological study.

The glaebules were crushed to a fine powder and XRD, DTA, TGA and partial elemental analysis were performed on this. Iron was also extracted with citrate - dithionite bicarbonate (CDB) procedure of Mehra et al (1.960) and ammonium oxalate-oxalic acid procedure of Schwertmann (1.964). Initially XRD was performed em - ploying copper radiation. Later cobalt radiation was used to identify iron minerals and iron radiation for mangane-

se minerals. Manganese mineral are most difficult to identify even with and Fe tube and complimentary analysis with DTA is necessary.

Results and discussion .-

Mineralo-chemical properties :

Partial elemental analysis and the extractable iron contents of the glaebules are given in Table 2. Analysis of the non-glaebular material is also given for comparison. There is a very high concentration of iron in the glaebules and manganese appears insignificant. As will be shown later in the micromorphological study, manganese is confined to small parts of the s-matrix and in these zones, it is almost pure manganese concentrations. The very high iron content in the soil material of Kabu Series is due to a high amount of very fine concretion which are present in the less than 2 mm fine earth fraction and which cannot be easily picked out.

The CDB iron forms about 80-90 % of the total iron in both glaebules and the soil material. Oxalate extractable iron is insignificant in all cases.

A range of minerals are present in these glaebules and these are summarised in Table 3. Table 3 was arrived at by running XRD on several concretions from the soil. As in the case of the Kabu Series, the manganese mineral in one concretion may be birnessite and in another feitknechtite. During the SEM studies, it was also observed that the mineral in the crust of a concretion may be totally different from that in the core. The best example is the manganese concretion from Australia -Sample 6- where there is nsutite in the thin crust whilst the bulk of the sample is birnessite. As a result of these problems, every small fragment of the concretion that was studied with SEM, was later analysed with XRD.

Table 2

Chemical Composition of Glaebules in some Malaysian Soils

Soil Series	Horizon	Glaebules Total Analysis (%)				
		Si_2O	Al_2O_3	Fe_2O_3	MnO	TiO_2
Kabu	$(B)_{2g}$	17.62	12.33	58.75	0.45	0.79
	IIB_{31cn}	14.35	13.68	59.57	0.44	0.61
	IIB_{32cn}	20.20	12.94	57.36	0.87	0.70
	C	19.65	13.55	55.65	0.37	0.84
Kubang Pauh	C_{1g}	22.08	8.14	57.16	0.11	0.46
	IIC_{cn}	27.76	12.94	53.86	0.04	0.66
	$IIIC_{cn}$	37.89	16.81	41.49	0.04	0.82
Batu Anam	$(B)_2$	30.38	15.12	40.99	0.03	0.62

nd : not determined

Soil						
Fe_2O_3 (%)		Total Analysis (%)			Fe_2O_3	
Oxal. Fe_o	Free Fe_d	Fe_2O_3	MnO	TiO_2	Oxal. Fe_o	Free Fe_d
0.40	47.23	3.65	0.02	1.33	0.30	2.65
0.36	54.50	9.42	nd	nd	0.20	7.31
0.33	51.03	21.97	0.52	1.09	0.28	18.10
0.25	55.50	25.98	nd	nd	0.14	10.98
0.32	52.24	2.10	0.01	1.05	0.03	0.36
0.26	48.78	5.54	0.01	0.93	0.20	3.36
0.46	40.55	7.65	0.01	1.26	0.17	6.28
1.48	32.16	-	-	-	-	-

Table 3

Mineralogy of the glaebules

Soil Name	Fe Minerals				Mn Minerals				
	Go.	Ha.	Le.	AFe.	Bi.	Ns.	Ft.	Li.	AMn.
Kabu			(X)	X	X		X		X
Kubang	X	X							
Pauh	X	X							X
Hutan	X		(X)						
Batu Anam	X	X							
Taylor (15)					X	X			
India	X								
Zaire		X							
Hawaii								X	

Mineral names respectively from left to right: Goethite; Haematite; Lepidocrocite; Amorphous iron; Birnessite; Nsutite; Feitknechite; Lithiophorite; Amorphous manganese.

Micromorphological study .-
Iron Minerals

Petroplinthite

SEM micrographs of the iron forms in petroplinthite have been presented earlier (Eswaran et al, 1.973) but a few micrographs are included here for comparison with the other iron forms to be illustrated later. Plate I shows thin section micrographs of some petroplinthite nodules taken with transmitted polarised and incident light. In plate Ia, the characteristic droplets (Hamilton, 1.964) of iron are present. In Plate Ib, which is of the laterised shale (Batu Anam) the droplets are so numerous that they appear coalesced and as a reddish mass. The individual droplets are discernable under high magnifications. Plate Ic is the same thin section viewed under incident light. The yellow band in Plate Ib, running subcutanic to the voids, is also goethite. Under incident light (Plate Ic), there is no difference between the lustre of the goethite as droplets and that present as a band. In Plate Id, which is of the laterite from Zaire, an aggregate of iron minerals is present on the left of the micrographs. XRD of similar laterites indicate the presence of high amounts of hematite. In transmitted light, the aggregate of haematite is reddish to opaque in colour.

SEM micrographs of the haematitic laterite are presented in Plate II a,b,c. An iron sheath is seen in Plate IIa and this is composed of haematite. Higher magnifications of the sheath (Plate IIb, c) show that it is composed of closely packed discoids of haematite. Although the sheath appears smooth at low magnifications, the discoids do not show any specific packing pattern. Some crystal intergrowths are also present.

Goethite has a different morphology under the SEM. In Plate IId,e,f, the goethite crystals have a lenticular

shape and are also slightly larger. Crystal intergrowth- is also common in this mineral. As shown by Eswaran et al, (1.973) the droplets observed in thin sections correspond to aggregates of such lenticular goethite crystallites. The yellow banded goethite (Plate Ib,c) has a totally different morphology under the SEM. Plate III shows some SEM micrographs of the banded goethite in Batu Anam Series. The bands are composed of a very dense packing of acicular goethite; the goethite needles are arranged parralled to the void wall (Plate IIIa,b,c). In Plate III d,e, f the tips of the needles are shown. In some cases, the acicular goethite is coated by a layer of amorphous iron and the tips are not visible. The goethite neddles may also grow from a point outwards and as a result, a section has a rosette appearance (Plate IIId).

These are only two of the many habits of goethite , other habits are possible and it is necessary to study different samples to establish the variations.

Petroplinthite differs from plinthite in having an outer crust which may range in thickness from 0.2 to 2 mm, in the former. Studies of several petroplinthite nodules indicate that the crust is frequently composed of acicular goethite whilst the softer material within has lenticular goethite and haematite. The crust is also composed- of pure goethite with little or no diluents such as kaolinite or quartz; the core on the other hand is soil material enriched with iron.

Concretions .-

Concretions (Brewer, 1.964) have a concentric fabric and the concretions in Kubang Series are shown in Plate IVb. Comparing the fabric of the concretion with that of the enclosing soil material and relating these to overlying and and underlying horizons, it is concluded that these are authigenic formations. There is generally

a void in the center of each concretion and in many cases some organic remains may be detected. It is supposed that a living root formed the nucleus for the formation of the concretion . The concentric banding indicates perio - dic or interrupted supply of iron; a former iron rich co re forms a template for further concentration of iron and so the concretion grows by accretion. The amount of iron arriving at the surface of a former concretion is not the same in each period and as a result there are bands of almost pure iron, followed by zones where there was just enough iron to cement the s-matrix. When growth by accretion results in two or more adjoining concretions touching each other, the subsequent supply of iron starts to coat both the concretions, resulting in a compound pedological feature.

Depending on the type of the plant, the rhizosphere of the root may be oxidising or reducing. Plate IVc, d, shows an extreme case of the involvement of roots in the precipitation of iron. Goethite has crystallised within the root in this sample from Hutan Series. The goethite is of the acicular type.

The SEM was employed to attempt to provide more-details in the above observations. Plate Va is a SEM micrograph showing the concretion in Kubang Series. The concretion in Kubang Series is partially fractured to remove one of the outer bands. The concretion or buckshot has a smooth and shiny surface; the surface exposed af - ter removal of the outer band is also smooth and shiny . The smooth surface is frequently attributed to transport but as shown previously, it is a specific property of such concretions. In Plate Vb, the concretion is fractured diagonally and the zonation is evident. The compact zones are the iron rich bands; the rougher areas show the presence of quartz and other diluents. The iron minerals in the concretions is goethite (XRD) and high magnification of the

surface indicates that the bands are composed of acicular crystals of goethite.

The core of the concretion is usually soft and composed of non-cemented soil material. XRD analysis of the core generally does not pick cut any crystaline iron minerals. Plate Vc, d, show the core of the Kabu concretion (Plate IVb). The matrix is slightly compact and porous and a large iron coated void is present (Plate Vc). Plate Vd id a higher magnification of the void wall showing the cutanic accumulation of amorphous iron. Ferrans composed of amorphous iron frequently have a globular form (Eswaran et al, 1.971) and a similar form is seen here.

The goethite infilled root cells in Hutan Series (Plate IVc,d) are shown in Plate Ve,f. The goethite crystals are acicular as in the case of Batu Anam Series. The infilling of the iron was probably after the death of the root. Living roots are known to cause the precipitation of the iron from the soil solution in the rhizosphere; the resulting feature may take the form of pedo-tubules as shown by Bidwell et al, (1.968) .

Manganese minerals .-

Due to the number of oxidation states that manganese can attain and exist, a range of oxides and oxyhydrates are possible. McKenzie (1.971) has recently reviewed the subject of manganese oxides in soils and shown that the number of manganese minerals frequent in soil does not exceed more than six. In studies of thin sections, manganese is observed to accumulate as mangans or to stain parts of the s-matrix or form nodules and concretions with or without iron. The manganese mineral is seldom identified in micromorphological studies perhaps due to the inherent difficulties in making such an identification. Scanning electron microscopic characterisation of manganese in soils is scarce. In the present study, a few manga

nese minerals are observed with the SEM ; for more details of the mineralogy and chemistry of these and other manganese minerals, the following are useful contribu - tions: McKenzie (1.971); Taylor et al (1.964) and Ross et al (1.976).

Lithiophorite .-

Lithiophorite - $(Al,Li)MnO_2(OH)_2$ - with a monoclinic crystal system is present in acid soil environments. Taylor et al (1.964) have observed that they form black coatings on void walls and sometimes they cement soil materials to form nodules. A sample of lithiophorite (Patterson, 1.971) containing only traces of lithium - Patterson considers that this may be an aluminum member of the mineral -was scanned to observe the morphology. Plate VIa, b, show aggregates of the mineral on a void wall in a sample of saprolite on basalt. The large crystals are formed due to the space available for crystal growth. Sample No. 6 employed by Taylor et al (1.964) in their studies on lithiophorite was also scanned. The manganese in this nodule is present as a very thin film on the surface of the soil material and no crystalline forms could be discerned with the SEM even at a magnification of 20,000. XRD confirmed the presence of lithophorite in this sample and so it is concluded that the crystals are too fine. A similar problem exists with the concretion of Kabu Series where XRD indicates the presence of the mineral but with negative results with SEM.

Nsutite .-

The mineral was first identified in the Nsuta deposits in Ghana (McKenzie, 1.971) and does not appear to be frequent in soils. It is named as γMnO_2 and McKenzie et al (1.971) have included a TEM micrograph of naturally occuring nsutite. The morphology of the mineral is as short acicular crystals.

Neither Taylor et al (1.964) or Ross et al (1.976) who employed some of Taylor's samples report the presence of nsutite. A routine XRD examination of a crushed concretion of Taylor et al (1.964) Sample No. 15 only indicated the presence of birnessite as reported by the original authors and Ross et al (1.976). The concretion was fragmented to separate the thin outer crust and the softer core for SEM studies. The presence of birnessite was confirmed in the core material, but the crust is composed largely of nsutite. Plate VIc, d show the short acicular crystals completely covering a quartz grain. XRD of this particular crust confirmed the presence of nsutite. However, when the crust of another concretion from Sample 15 of Taylor et al (1.964) was examined, it was found to be almost pure birnessite.

Birnessite .-

Birnessite or MnO_2 or manganese manganite is considered to be the most widely spread manganese mineral (Taylor et al, 1.964; McKenzie, 1.971; Ross et al, 1.976), though Taylor (1.968) reports them to be more frequent in alkaline horizons. One of the first SEM micrographs of birnessite in soils was published by McHardy et al (1.975) and they indicate that the sponge like morphology of the mineral is very characteristic.

In Plate IIb, some manganese concentration is seen as a black accumulation between the concretions. A similar piece of soil material was scanned and in Plate VIe, f shows the accumulation of birnessite in the fracture surface. The morphology is similar to the published micrographs of McHardy et al (1.975). The Kabu Series is formed as alluvium but the ground water is supplied with the dissolution products of the adjoining limestone hills. From the few observations on occurence of birnessite in the soils of Peninsular Malaysia, it is always present in

these subsurface horizons which have a high base saturation. The only exception was the occurence of birnessite in some manganese concretions in oxisols developed on limestones, but in this case it could be assumed that the base saturation was high at the time of manganese segregation.

Amorphous manganese oxides or oxihydrates .-

This, as amployed by the authors, is a nebulous term which refers to all those forms which do not give reflections on XRD. Eswaran et al (1.973) showed some SEM micrographs of such forms present in some laterites. Manganese minerals as a rule give poorly differentiated peaks in XRD even with an Fe tube and as a result what is referred to as amorphous may be very finely crystalline.

Some of the voids in the concretions from Pauh Series had black manganese staining. SEM studies (Plate VII a,b,c) gave the typical globular or amydaloidal aspect observed previously (Eswaran et al, 1.973). At high magnifications (Plate VIIc) some very fine crystallites are discernable. Due to the negative results from XRD of the same sample, the material is considered amorphous.

Feitknechtite .-

Feitknechtite or β - MnOOH appears to be rare in soils. Some transmission electron micrographs of the mineral published by earlier workers are included in the review of McKenzie (1.971). The mineral consists of hexagonal plates of about 0.5 m diameter.

In addition to the iron concretions in Kabu Series (Plate IIIb), there were a few manganese concretions. Birnessite is present in the core of these concretions but in the crust, hexagonal plates of feitkechtite (Plate VII d,e,f) are present. XRD of the crust confirmed the mineral.

Thin section morphology of manganese minerals .-

Although a number of minerals have been identified with the SEM and confirmed with XRD, these cannot be differentiated in thin sections. In most cases these manganese concentrations are opaque and so in thin section descriptions, only general terms such as manganese nodules or mangans can be employed. When the manganese is present as a thin film, even SEM observations yield little information and a microprobe is necessary to confirm the presence of manganese in the clay platelets.

Plate I.

a . Thin-section micrograph of laterite from India. X 80.
b. Thin-section micrograph of laterised shale in Batu Anam Series. X 80.
c. Thin-section micrograph in incident light of the laterised shale. X 120.
d. Thin-section micrograph (incident light) of laterite from Zaire. X. 120.

Plate II.

a,b,c. Band of haematite in laterite from Zaire. (a) X 200; (b) X 10,000; (c) X20,000.
d,e,f. Lenticular crystals of goethite in laterite sample from India. (d) X 500; (e) X 5,000; (f) X 25,000.

Plate III.

Bands of acicular goethite present as goethans in the laterised shale of Batu Anam Series. (a) X 500; (b) X 5,000; (c) X 10,000 (d) X 1000 ; (e) X 5,000 ; (f) X 10,000

Plate I

Plate II

Plate III

Plate IV

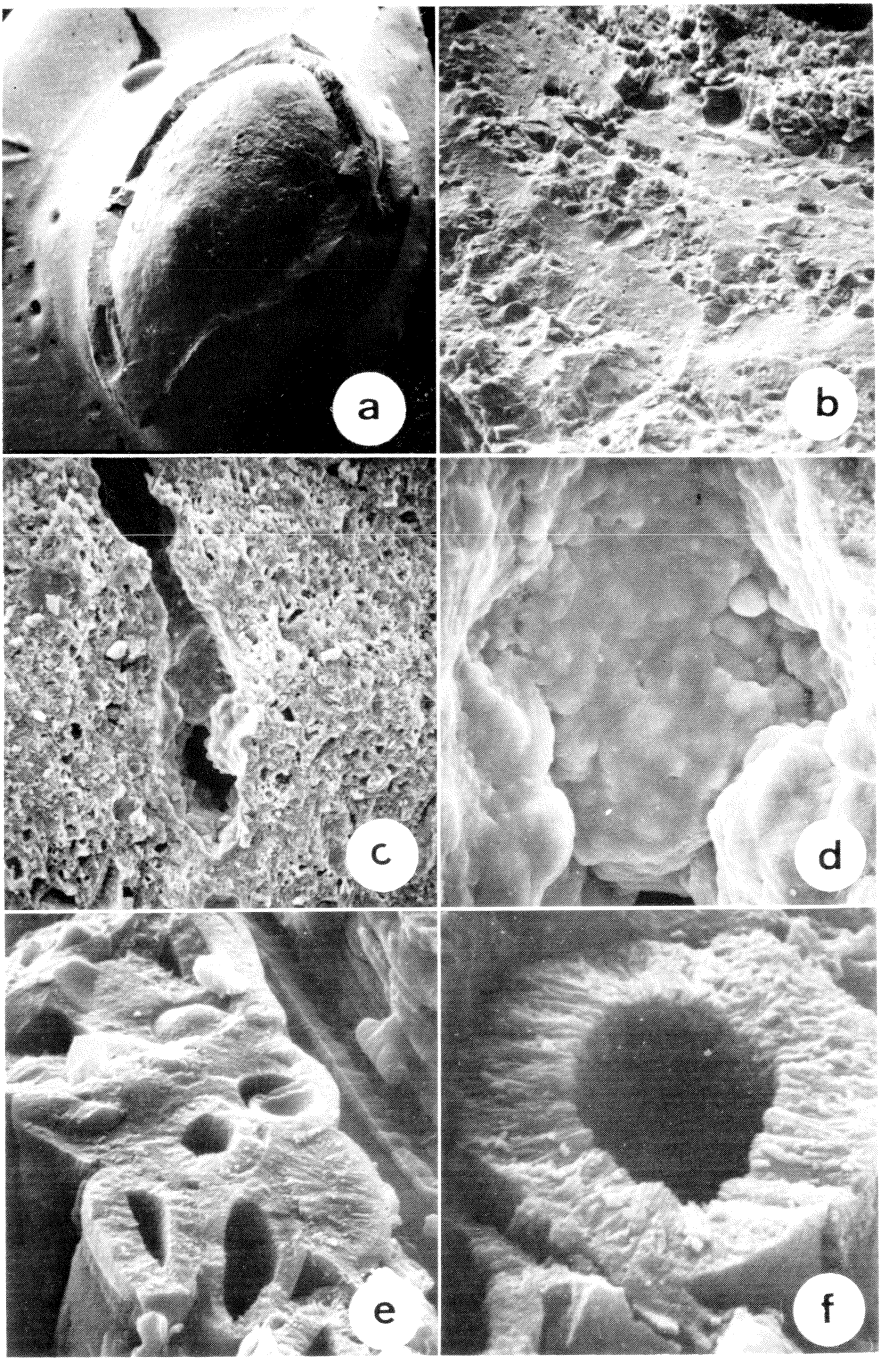

Plate V

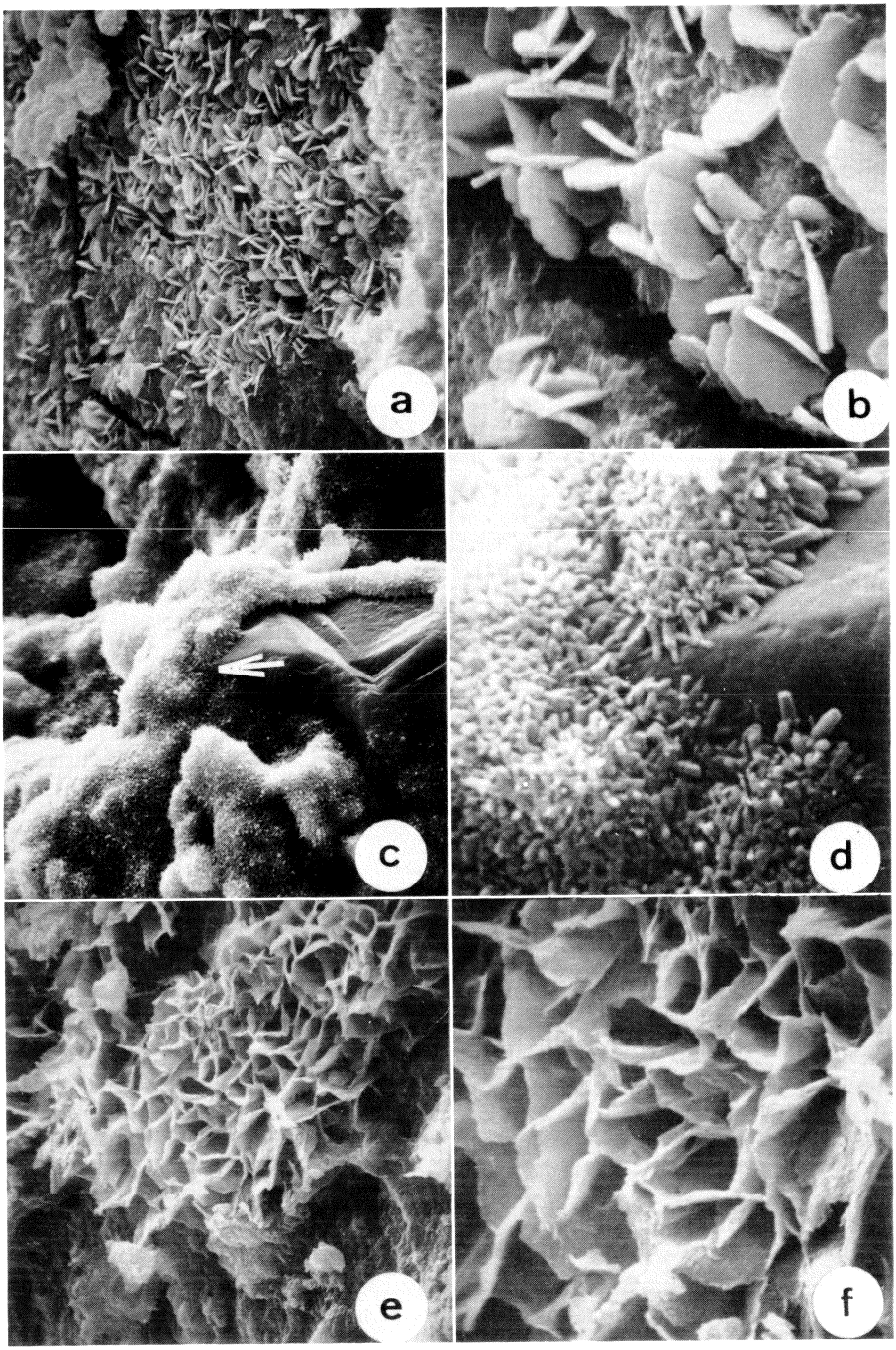

Plate VI

Plate VII

Plate IV.

a. Spherical concretions in Kubang Series. X 80
b. Sesquioxidic concretions with associated manganese enriched matrix in Kabu Series. X 80.
c,d, Goethite enriched root cells in Hutan Series. (c). X 40; (d) X 120.

Plate V.

a. Partially fractured concretion of Kubang Series. X 200.
b. Transverse section of concretion of Kubang Series showing the concentric fabric. X 2,000.
c. Core of sesquioxidic concretion in Kabu Series with a void coated with amorphous iron. X 500.
d. Morphology of ferran in above (c). X 5,000.
e,f. Goethite in root cells in Hutan Series. – c.f. Plate IV c,d. – (e) X 2,000; (f) X 5,000.

Plate VI.

a,b. SEM micrograph of lithiophorite on ped face. (a) X 2,000; (b) X 10,000.
c,d. SEM micrograph of nsutite in manganese concretions from Australia. (c) X 5,000; (d) 20,000.
e,f. SEM micrograph of birnessite in Kabu Series. (d) X 5,000 (f) 10,000.

Plate VII.

(a,b,c) SEM micrographs showing globular aggregates of manganese lining a void wall in a concretion in Pauh Series. (a) X 500; (b) X 5,000; (c) X 20,000.
(d,e,f) SEM micrographs showing feitknechtite crystals in concretion of Kabu Series. (d) X 500; (e) X 5,000; (f) X 20,000.

SUMMARY

Iron, iron-manganese and manganese glaebules were studied to evaluate the type of iron or manganese minerals present. SEM micrographs of the following are included:

haematite, goethite, amorphous iron oxyhydrate.

Lithiophorite, nsutite, birnessite, feitknechtite.

and amorphous manganese oxide.

With respect to goethite, two crystal habits are shown and it is indicated that many minerals may show more than one habit.

Many of these minerals may not be identified in thin sections and so ancillary techniques such as SEM and XRD are needed to indicate their presence.

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