

A study into the mobility of iron in podzolized Sarawak upland soils by means of selective iron extractions

J. P. Andriesse

Department of Agricultural Research, Royal Tropical Institute, Amsterdam, the Netherlands

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Summary

An evaluation is given of existing iron extraction methods which were tested on major upland soils from Sarawak. The results indicate the presence of relatively large amounts of crystalline free iron oxides gradually increasing with depth, a virtual absence of new iron accumulations in the amorphous form and a great activity of organic acids in complexing iron in surface horizons. Additional field information provides evidence of large accumulations of iron oxides at great depth in cracks and joints of sedimentary rocks. These characteristics may be explained by the following reasoning.

In all soils investigated, there has been relative accumulation of crystalline iron oxides through desilication during an early stage in soil formation. This was followed by a loss of iron in varying degree from the upper horizons, which can most likely be attributed to fossil argilluviation and weathering of iron-rich clay, or possibly to fossil reduction with transport in ferrous form. The latter would presuppose poorly drained conditions prior to the strong dissection resulting in the present landscape.

The strong and extensive accumulation of iron oxides at great depth in cracks and joints may be attributed to the oxidation and precipitation of ferrous and ferric iron mobilized upon initial oxidation of pyrites in the weathering front of the sedimentary rocks. Lateral movements of soil water may play a role in this.

The fact that pyrophosphate-extractable iron appears to exceed oxalate-extractable iron in most soils, in contrast to the situation in temperate regions, may point to a difference in the nature of the iron-organic complexes, which is worth further investigation. (See note on page 12.)

Review of iron extraction methods

During the previous decade much attention has been given to the study of the nature and amounts of secondary iron and aluminium forms in soils, with the aim to

relate these to soil forming processes and classification.

Schwertmann (1959) revived the well-known Tamm's method of extracting amorphous iron with ammonium oxalate and, after modification, the method has been successfully used by Schwertmann (1964), McKeague & Day (1966) and by Blume & Schwertmann (1969) to differentiate amorphous secondary iron (including that bound to organic matter) from total secondary or free iron, the latter being extracted by dithionite-citrate-bicarbonate (Mehra & Jackson, 1960). The difference between the two obtained values comprises the crystalline oxides.

The ratio between oxalate-extractable iron (Fe_o) and dithionite-extractable iron (Fe_d) has been used by Blume & Schwertmann (1969) as a relative measure of the degree of aging or crystallinity of free iron oxides and is therefore called the 'activity ratio' or Fe_o/Fe_d ratio. This ratio was applied with success to differentiate between main soil horizons in soils of Germany.

It should be noted that Baril & Bitton (1967) discovered that the oxalate extraction also removes appreciable amounts of iron from magnetite and the usefulness of this extraction for soils rich in this mineral is therefore somewhat diminished.

McKeague (1966) & Bascomb (1968) contributed to this new development by suggesting a method which made it possible to distinguish between inorganic amorphous iron compounds and those of organic complexed nature. The latter are present particularly in podzolic soils. The authors successfully tested the use of pyrophosphate extraction for the organic complexed iron forms on a number of Canadian soils and suggest that the difference between Fe_o and Fe_p (pyrophosphate-extractable iron) would be a good measure for amorphous inorganic iron.

However, Bascomb (1968) found that potassium pyrophosphate extracted both organic iron and fresh (not aged) amorphous iron oxides.

Apparently, as a result of these findings Ball & Beaumont (1972) regards the Fe_p , analysed according to their method, as the mobile fraction while they infer that the Fe_o comprises the mobile *plus* stable amorphous fractions, the latter representing the aged amorphous hydrous oxides accumulated in situ.

The difference between aged gels and the crystalline forms is, according to Van de Giessen (1966), merely a matter of crystallinity grade or crystal size, the aged gels or 'amorphous' iron oxides having a micro-crystallinity as could be shown by electron microscopy.

In more recent investigations McKeague et al. (1971) presented evidence that the oxalate-extractable iron is not so specifically inorganic as previously thought; it contains also part of the organic complexed iron, namely the Fe-fulvic acid complexes.

The latter are regarded as the most mobile of the organic complexed forms since they are easily soluble in water. The relationship between iron forms in soils and the existing differential solubility tests is shown in Table 1.

Although existing selective iron extractions have so far been mainly conducted with temperate soils the proposed chemical methods appear sufficiently realistic to investigate their usefulness for genetic studies of tropical soils, particularly those of a podzolic nature in which mobilization and transport of iron are important processes. A comparative study was therefore carried out on a selection of Sarawak upland soils of which the results are presented in this paper.

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Table 1. Iron forms in soils as extracted by specific methods.

	Fe _t	Fe _d	Fe _o	Fe _p
a. Silicate-bound iron and compound metal oxides such as ilmenite	x ¹	—	—	—
b. Crystalline free iron oxides (mainly goethite and hematite)	x	x	—	—
c. Amorphous hydrous iron oxides (aged gels)	x	x	x	—
d. Fulvic acid complexed iron ('mobile fraction')	x	x	x	x
e. Iron in other organic forms	x	x	—	x
f. Magnetite	x	(small amounts)	(in part)	—

¹ x = extractable.

Materials and methods

Some particulars of the chosen soil series are given in Table 2. Full details are described by Andriess (1972, 1975).

Samples of all horizons of the selected profiles were dried at 40 °C and thereafter the fine earth fraction (< 2 mm) was obtained by gentle breaking of the structural elements and sieving. The fine earth was thereafter crushed to a particle size of less than 150 µm.

Dithionite extraction was carried out according to Mehra & Jackson (1960), ammonium oxalate/oxalic acid extraction by the method proposed by McKeague & Day (1966) and sodium pyrophosphate extraction according to McKeague (1967).

The iron in the extracts was measured by atomic absorption spectrophotometry (ASS) for which a Techtron, type AA4, was employed. Addition of lanthanum to the solutions is necessary to mask interferences. To avoid precipitation of lanthanum with ammonium oxalate and sodium pyrophosphate, the lanthanum solution should

Table 2. Main characteristics of selected upland soils from Sarawak.

No	Profile name	Derivation	Local soil group	USDA Soil Taxonomy (1976)	FAO/UNESCO World Soil Legend (1974)
1	Tarat	Basalt	Lateritic	Typic Haplorthox	Orthic Ferralsol
2	Gumbang	Quartz andesite	Red-Yellow Podzolic	Oxic Dystropept	Xanthic Ferralsol
3	Serin	Arkose	Red-Yellow Podzolic	Tropeptic Haplorthox	Xanthic Ferralsol
4	Semongok	Shale/mudstone	Red-Yellow Podzolic	Typic Dystropept	Dystric Cambisol
5	Gading *	Adamellite	Red-Yellow Podzolic	'Psammentic' Haplorthox	Xanthic Ferralsol
6	Nyalau *	Quartz sandstone	Red-Yellow Podzolic	'Psammentic' Haplorthox	Xanthic Ferralsol

* These series represent border-cases between Ultisols and Oxisols.

be prepared in 1.2 *N* HCl.

Measurements in the ammonium oxalate extracts were done two hours after addition of the lanthanum solution, whereas those in the pyrophosphate extracts had to be carried out before organic matter started to flocculate as a result of addition of lanthanum.

Interferences of foreign ions and components in the soil extract upon addition of lanthanum were not observed. Also, organic matter present in the pyrophosphate extract did not affect the measurements of iron.

Total iron was measured by X-ray fluorescence with a Philips PW 1540/15 unit with a 1.6 kW generator and 2 kW Cr tube.

Results

The results for the various extractable forms of iron are given in Table 3, but before discussing their implications some comments must be given on the obtained values.

Differences between Fe_t and Fe_d are a fair measure for presence of silicate bound iron and Blume and Schwertmann (1969) use this as a parameter to weathering stage. The values obtained are generally in agreement with the mineralogical composition of the soils as was investigated by the author (1975), but Fe_d appears to be rather low since the mineralogy indicates the virtual absence of silicate-bound iron, and therefore Fe_t and Fe_d values should be almost the same. Tests in this laboratory indicate that the method advocated by Mehra & Jackson (1960) suffers from the fact that the crucial extraction temperature of 80 °C is difficult to maintain and that small deviations beneath this temperature result in extraction of considerably less iron. Probably, the method proposed by Holmgren (1967) which is based on a cold dithionite extraction but with prolonged shaking should give better results. The latter method, with some modifications, was tested out in this laboratory and gave consistently higher values for Fe_d , which could be reproduced with more accuracy than those obtained by the hot extraction method (Quak & Mulder, 1975). The unexpected large differences between Fe_t and Fe_d , particularly in soils with high amounts of Fe_d are therefore explained by the limitations of the method used. (The negative value for $Fe_t - Fe_d$ in the A_{12} horizon of the Gading series is probably due to an analytical error.)

The Fe_d , but particularly the Fe_o values of the Gumbang series are probably influenced by the high magnetite content in samples of this profile, as shown by mineralogical studies. As indicated, both extracts remove iron from magnetite (Baril & Bitton, 1966; Gamble & Daniels, 1972).

The surface horizon of the Nyalau series is probably contaminated with eroded material from upslope areas because the Fe_t content of that sample is anomalously high.

The Fe_p values of surface horizons appear in general to be higher than Fe_o values, exceptions being the Gumbang and the Tarat series. For the Gumbang this exception may be explained by the fact that magnetite tends to give too high obtained Fe_o values and in reality Fe_p may be higher than Fe_o . In the Tarat series the difference may be of genetic significance.

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Table 3. Extractable and total iron in major Sarawak Upland soils.

Soil series	Depth (cm)	Horizon	Total Fe ₂ O ₃ (%)	Extractable (%) by		
				sodium dithionite	ammonium oxalate	sodium pyrophosphate
Tarat	0-8	A ₁	25.4	14.64	1.06	0.82
	8-28	B ₁	26.1	16.65	0.66	0.54
	28-54	B/C	27.0	15.44	0.54	0.09
	54-100	C	25.2	16.02	0.34	0.02
Gumbang	0-9	A ₁	2.7	1.37	0.61	0.47
	9-28	B ₁	3.8	1.60	0.54	0.44
	28-44	B ₂	3.4	2.00	0.37	0.33
	44-67	B/C	3.5	2.06	0.22	0.21
	67-100	C	3.9	2.35	0.20	0.19
Serin	0-10	A ₁	4.4	3.60	0.37	0.59
	10-25	A ₂ (E)	5.5	4.18	0.39	0.53
	25-75	B ₁	5.5	4.00	0.20	0.13
	75-115	B ₂	6.9	4.86	0.11	0.04
	115-135	B/C	6.4	4.86	0.09	0.00
Semongok	0-9	A ₁	5.5	2.92	0.83	0.89
	9-29	B ₁	5.3	3.37	0.61	0.83
	29-68	B ₂	4.4	3.66	0.60	0.96
	75-88	IIB ₂	8.7	4.46	0.50	0.56
	88-115	IIB/C	8.0	3.55	0.50	0.37
Gading	0-7	A ₁	2.7	2.17	0.26	0.51
	17-20	A _{1 2}	2.4	2.52	0.23	0.57
	30-50	B ₁	2.9	2.80	0.21	0.46
	70-100	B _{2 1}	5.2	4.35	0.11	0.06
	100-120	B _{2 2}	5.3	4.98	0.10	0.03
	> 120	C*	6.6	2.57	0.23	0.04
Nyalau	0-9	A ₁	5.7	1.09	0.26	0.33
	9-30	A ₂ (E)	2.8	1.94	0.31	0.40
	30-63	B ₁	2.1	1.83	0.20	0.23
	63-110	B ₂	4.3	2.63	0.09	0.09
	110-150	B/C	3.8	2.86	0.07	0.09

* Weathered rock discontinuity.

Noteworthy is, however, that in soils so far studied by Bascomb (1968), McKeague & et al. (1971) and Ball & Beaumont (1972) the pyrophosphate-extractable iron was always lower than the oxalate-extractable iron. All these authors worked with soils from temperate regions, in which much of the organic iron fraction consists of fulvic acid complexes. The fact that Fe_p exceeds Fe_o in most of the humid tropical soils reported here, shows that the interpretation of the difference (Fe_o minus Fe_p) as aged 'amorphous' oxides breaks down, and that there must be a fraction of the iron extracted by pyrophosphate and not by oxalate. This fraction may well be organic, but of a different nature from the main organic-bound iron fractions in the soils of temperate regions studied by the quoted authors. (See note on page 12.)

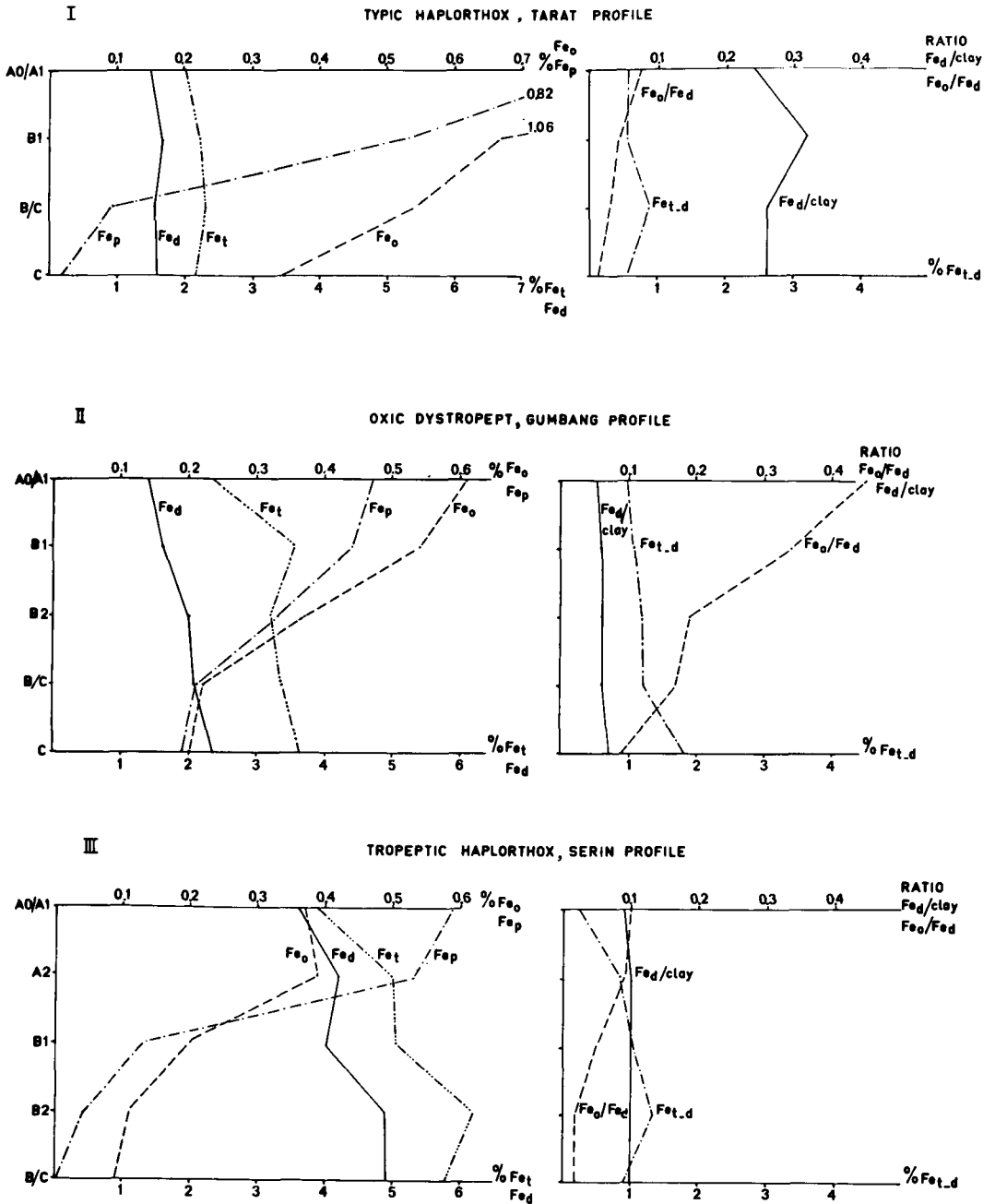


Fig. 1. Depth functions of various iron extraction forms (Fe_o = ammonium oxalate; Fe_p = sodium pyrophosphate; Fe_d = sodium dithionite/citrate; Fe_t = total) and derived relationships of main upland soils in West Sarawak.

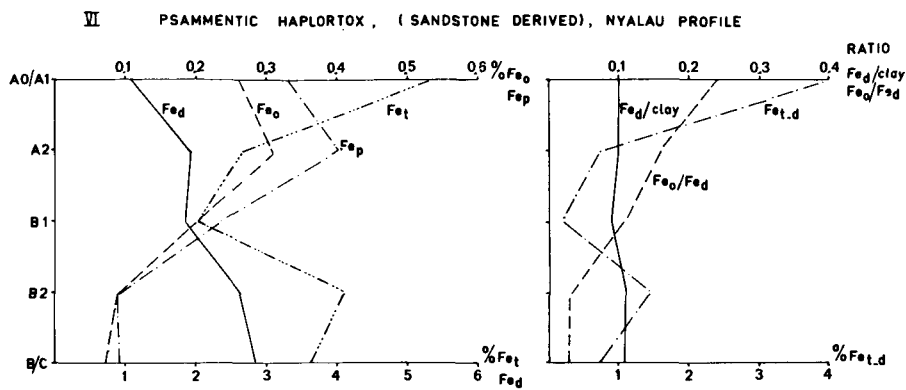
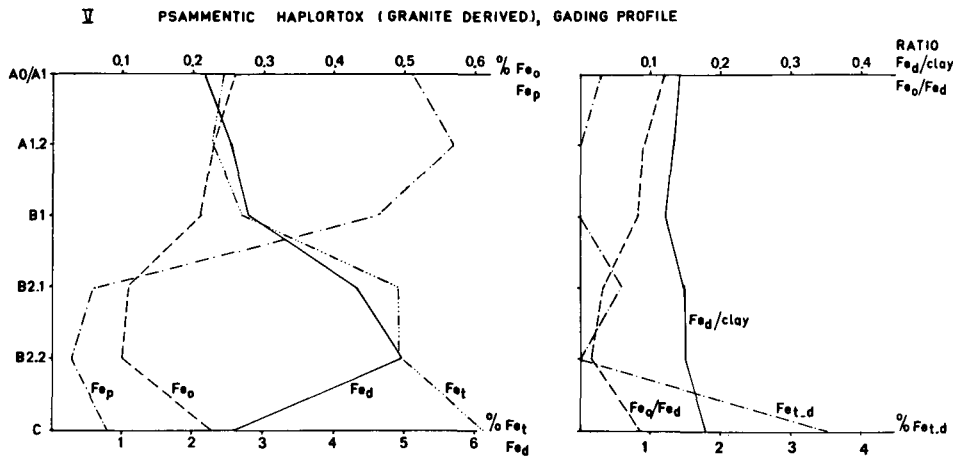
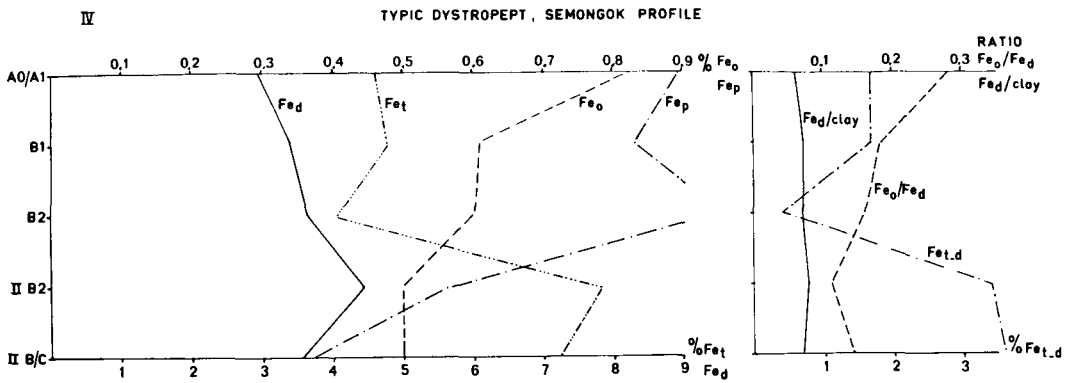


Fig. 1. (continued).

Genetic implications

Depth functions of the various iron forms and derived ratios were prepared from the values given in Table 3. The depth functions are shown in Fig. 1.

The following observations can be made. $Fe_t - Fe_d$ is a parameter for judging weathering stage of the soil unless high amounts of magnetite and ilmenite are present. In the selected soils Fe_d amounts to 75 % or more of the total iron, which indicates that all soils are highly weathered.

The Fe_d values increase and the amounts of Fe_o and Fe_p decrease with depth in all profiles, which suggests that the degree of crystallinity of iron oxides increases with depth. This is also apparent from the decreasing 'iron activity' ratios (Fe_o/Fe_d) which, according to Blume & Schwertmann (1969), would indicate a high degree of aging in subsoils and high iron activity in topsoils. If the observed increase in pedo-genetic or free iron in the subsoils would be the result of recent or continuing removal of free iron from the topsoils with subsequent accumulation in the subsoil, one would expect the amount of 'aged gels' to increase with depth since these represent transitional stages from the mobile fraction removed from the surface horizons to the crystalline fraction accumulating in the subsoil.

Such 'aged gels' are extracted by oxalate but since this agent also extracts fulvic acid complexed iron regarded as the mobile fraction, the amount of 'aged gels' is difficult to judge from Fe_o values alone.

This can, however, be approximated from the relationship existing between Fe_o and Fe_p . Since Fe_o represents 'aged gels' plus fulvic acid complexed iron, and Fe_p all organic complexed iron, a relation between Fe_o and Fe_p can only point to a high relative importance of fulvic complexed iron in both extractions.

Fig. 1 shows such a close relationship suggesting that the proportion of 'aged gels' in Fe_o is indeed low. Although the diminishing content of Fe_o with depth may be largely a function of decreasing content of fulvic acid complexed iron it could obscure a possible increase of very low absolute amount of the 'aged gels' occurring at depth. This would then be so insignificant, however, that it cannot explain the comparatively large difference between the crystalline iron compounds (approximated by $Fe_d - Fe_o$) and the amorphous compounds indicated as Fe_o . This absence or near absence of a transitory iron form (aged gels) in the subsoils is of genetic importance since it implies a very low rate of accumulation or absence of a new accumulation process. Only in the Tarat series there may be significant new accumulation, because in this profile the amounts of 'aged gels' are proportionally more important, as suggested by the substantial difference between Fe_o and Fe_p figures.

The significant amounts of organic complexed iron forms particularly in the surface horizons suggest a high activity of the organic matter in mobilizing iron. Since it is mainly the fulvic acid part of the mineralized organic material which plays an active role in the mobilization of iron (Oades, 1963; Segalen, 1964), the relative contents of fulvic acids in the soils would be an important pointer to the magnitude of iron removal.

Table 4, derived from Andriess (1975), shows that indeed in all samples fulvic acids are dominant over humic acids, surface soils of some profiles forming the only

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Table 4. C/N ratios, humic and fulvic acid contents of mineral horizons of main Upland soils in West Sarawak.

Soil series	Horizon	C in dry fine earth (%)	N in dry fine earth (%)	C/N ratio	Contribution (mg) per g C in dry fine earth			Humic acid/fulvic acid ratio
					humic acid	fulvic acid	total	
Tarat	A ₁	4.61	0.48	9.6	6.9	8.2	15.1	0.84
	B ₁	1.40	0.18	7.8	2.0	11.2	13.2	0.18
	B/C	0.93	0.10	9.3	2.7	7.8	10.5	0.35
	C	0.44	0.05	8.8	2.0	5.2	7.2	0.39
Gumbang	A ₁	5.51	0.45	12.2	10.4	8.0	18.4	1.30
	B ₁	1.02	0.11	9.3	2.0	5.3	7.3	0.37
	B ₂	0.62	0.06	10.3	2.0	3.6	5.6	0.56
	B/C	0.43	0.05	8.6	1.2	3.3	4.5	0.36
	C	0.39	0.04	9.8	1.7	2.5	4.2	0.68
Serin	A ₁	2.52	0.25	10.1	5.4	9.7	15.1	0.56
	A ₂ (E)	0.76	0.09	8.9	1.4	5.3	6.8	0.26
	B ₁	0.51	0.08	10.2	1.8	2.6	4.4	0.47
	B ₂	0.37	0.03	12.3	1.6	1.5	3.1	1.06
	B/C	0.15	0.02	7.5	2.9	-	2.9	-
Semongok	A ₁	3.18	0.27	11.7	12.1	7.2	19.3	1.70
	B ₁	0.86	0.11	7.8	2.4	4.8	7.2	0.50
	B ₂	0.57	0.08	7.1	2.1	3.3	5.4	0.64
	IIB ₂	0.36	0.06	6.0	2.7	1.8	4.5	1.50
	IIB/C	0.26	0.09	2.9	1.4	2.8	4.2	0.50
Gading	A ₁	1.69	0.13	13.2	3.8	5.5	9.3	0.69
	A _{1 2}	0.63	0.09	7.2	1.0	4.6	5.6	0.22
	B ₁	0.27	0.03	8.0	0.5	3.1	3.6	0.14
	B _{2 1}	0.22	0.02	10.0	0.7	4.0	4.7	0.18
	B _{2 2}	0.21	0.03	7.6	0.3	1.8	2.1	0.17
Nyalau	A ₁	4.23	0.25	16.9	9.5	7.1	16.6	1.34
	A ₂ (E)	0.54	0.08	6.8	1.2	2.9	4.1	0.41
	B ₁	0.19	0.03	6.3	0.7	1.5	2.2	0.47
	B ₂	0.19	0.02	9.5	0.5	1.6	2.1	0.31
	B/C	0.09	0.03	3.0	0.7	1.6	2.3	0.43

exceptions. The mobilization of iron in the surface horizons through complexing with fulvic acids would be most effective for iron present in the colloidal fraction and the relation between pedogenetic iron and clay was therefore expressed in a diagrammatic form in Figs 1 and 2 by the Fe_d/clay ratios. A strong relationship between clay content and free iron can be seen in the Serin, Semongok and Nyalau profiles. It may be coincidental that these profiles also represent the only soils developed on sedimentary rocks but it could suggest a possible relationship with the mode in which iron is found in the parent materials derived from them. In the present cases, this is mainly as finely divided goethite. This would tend to accumulate in the colloidal fraction upon weathering.

Discussion

These analytical results lead to the conclusion that there has been iron removal in varying degree from the surface horizons in all soils. However, there is no evidence for any appreciable recent accumulation in the lower horizons. The Fe_d values within the soil profiles do indicate that some sort of accumulation process must have taken place but the highly crystalline nature of this fraction points to great age. Although the presence of 'aged gels' in lower horizons of some profiles cannot be discounted, they seem to play a very secondary role in any accumulation process.

In addition to this evidence of a probable 'fossil' accumulation process of iron within the normal profile depth, there is substantial field information that hard limonite sheets have formed in cracks and joints of argillaceous rocks such as those underlying the Semongok series. In Sarawak this is generally the case in carbonaceous shales and sandstones of littoral origin (Andriess, 1972). An explanation for both types of iron accumulation, that occurring at great depth and that present within the profile depth is therefore required.

Andriess (1970), when studying the development of the Podzol morphology in an age sequence of coastal sands in Sarawak, found that an intermediate 'red weathering' stage occurs, largely as a result of weathering of ilmenite to leucoxene and free iron oxides, before removal of iron oxides from surface horizons and development of the full Podzol morphology. The results of the present study suggest that in the upland soils, likewise, two stages of iron accumulation and mobilization can be recognized: an early stage of relative iron accumulation (rubefaction) caused by weathering of the primary minerals and desilication, followed by a stage of iron mobilization and removal from the surface horizons.

The nature of this latter process is not yet clear. Several possibilities come to mind.

- Argilluviation and subsequent weathering of iron-rich clay. The present percentage aluminium saturation is too high for argilluviation. Some non-continuous, partly weathered ferriargillans observed in thin sections indicate that the process may have been active in the past (Andriess, 1972, 1975).

- Cheluviation by fulvic acids. Iron transport by fulvic acids may be assumed to stop as soon as the metal/fulvic ration becomes high enough (cf. experiments by Schnitzer & Skinner, 1964, who demonstrated the insoluble nature of such complexes). The appreciable amounts of free iron oxides in the upper horizons, much in excess of the contents in Podzols, would contribute iron to, and hence precipitate, possible ferric-fulvic complexes after only a short distance of transport. Moreover, no horizon of organic matter accumulation has been observed in the profiles, so that this possibility must be ruled out.

- Reduction and transport in ferrous form. Most of the soils are well drained but could possibly have been imperfectly or poorly drained before the dissection of the landscape to the present local base level. Reduction and transport of ferrous iron in these soils would be at most fossil, if it has taken place at all.

Transport of ferric and ferrous iron mobilized by the oxidation of pyrite in extremely acid conditions may explain the formation of the limonite sheets at great

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depth (but not the iron oxide accumulations in all the soil profiles). Soils in some localities (e.g. Semongok series) are imperfectly drained and in addition, the sedimentary parent rocks of most of these contain pyrite. Strong acidification due to oxidation in the initial stage of soil development could have mobilized iron in ferric form. Under these conditions large amounts of ferrous iron may also have been transported downward. This process may even continue until the present, but at considerable depth, in the present weathering front of the rocks.

Conclusions

The iron oxides accumulated in subsoils within the profile depth are most probably related to a fossil argilluviation process, followed by weathering of iron-rich clay. Other possible mechanisms for this accumulation appear unlikely, although, transport under supposed poorly drained conditions prior to the dissection of the present landscape remains theoretically possible. The present high chelating activity in the surface horizons as evidenced by the relatively high amounts of fulvic acids cannot be considered responsible for the iron translocation. The fact that Fe_p exceeds Fe_o in most soils, in contrast to the situation in soils of the temperate zone may point to a difference in the kinds of Fe-organic complexes occurring in these two environments. (See note on p. 12.)

The limonite sheets in joints and cracks of sedimentary rocks at great depth below the soil profile are most probably formed by an oxidation and precipitation of ferrous iron and precipitation of ferric iron mobilized through the initial oxidation of pyrites in the weathering front of these rocks. This is a continuing process but not related to the iron distribution patterns within the normal profile depth. An aspect worth investigating is the degree to which lateral rather than vertical movement of soil water has played a role in this iron accumulation process.

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Note

Subsequent to the finalization of this manuscript I was made aware of the work done by Wada & Higashi (1976) with humus complexes of Andosols. Their studies indicate that pyrophosphate does little dissolve young humus forms but extracts large amounts from the older forms, presumably because of the higher amounts of mobile aluminium. It is suggested that humus forms of temperate and tropical regions may differ likewise. Also, recent work of Taylor & Schwertmann (1978) indicates that soils with a high Al-level iron in the Fe(II) system had a preference to form goethite upon oxidation with a high possibility for Al to partly substitute Fe in the goethite. Herbillon (pers. comm.) suggests that this aluminiferous goethite might also be preferentially dissolved by pyrophosphate causing the Fe_p to become higher than Fe_o .

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