

IRON OXIDE AND CLAY MINERALS AND THEIR RELATION TO COLOURS OF RED AND YELLOW PODZOLIC SOILS NEAR SYDNEY, AUSTRALIA

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ABSTRACT

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The iron oxide and clay minerals in some typical red and yellow podzolic soils from New South Wales have been investigated by X-ray diffraction and infra-red spectroscopy. The dominant iron oxide mineral is goethite containing about 13–14 mol % AlOOH, this being the mineral which gives the yellow soils their characteristic colour. The red soils also contain finely divided hematite which masks the colour of the goethite. Lepidocrocite was not detected in any of the soils examined. The dominant clay minerals are kaolinite and dioctahedral interstratified illite–smectite, the latter being more concentrated in the finer clay fractions, especially in soils developed on calcareous greywacke. In the red podzolic soil developed on Ashfield shale, illite–smectite is strongly interlayered with well-ordered aluminous material. Dickite occurs in this soil.

INTRODUCTION

The investigation by Walker (1960) of the soils of the County of Cumberland, N.S.W., showed that the podzolic soils developed on shales and sandstones of the Wianamatta series and their erosion products are coloured red on the hills and yellow in the valleys and along some of the stream terraces. The cause of this colour difference has never been established. The traditional viewpoint, that red soils owed their colour to hematite, orange soils to lepidocrocite and yellow soils to goethite, was dispelled by Schwertmann and Lentze (1966), who concluded that soil colour is not a reliable guide in this respect. A similar conclusion was reached by Ségalen (1969) for some tropical red and yellow soils, and again for some American red and yellow podzolic soils by Soileau and McCracken (1967). The present study attempts to characterize the iron oxide and clay minerals in the red and yellow podzolic soils in the County of Cumberland and to seek a relationship between mineralogy and colour.

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MATERIALS

The red and yellow podzolic soils were placed in separate groups by Walker (1960) because of their characteristic colours. The yellow soils are richer in organic matter and have distinctly bleached A horizons.

Samples were collected from five profiles representing intense red (893) and yellowish-brown (993) soils, and a catena of red, brownish yellow and yellow soils (20, 23 and 1) on a 200 m long slope. The parent material of 893 is Ashfield shale, and of the other soils is Minchinbury sandstone, a calcareous greywacke (Lovering, 1956). Some properties of these soils are given in Table I, and fuller descriptions of Profiles 89 and 99 in Tables II and III.

The profiles are all duplex (Northcote, 1971) exhibiting a sharp textural change between A and B horizons. The subsoils are usually medium to heavy clay in texture and contain 30–60% of $< 2 \mu\text{m}$ clay. The particle size analyses and chemical properties of these soils are given by Walker (1960).

The samples used were collected from the horizon of maximum chroma, a B horizon (Northcote, 1971), thus minimizing the effect of organic matter which masks the mineral colours.

METHODS

Sample preparation: The soils were dispersed ultrasonically (Edwards and Bremner, 1967) and the clay fractions were separated using appropriate centrifuge speeds and settling times. The 2.0–0.02 μm fraction of all the soils was used for mineralogical identification. The 0.2–0.02 and the $< 0.02 \mu\text{m}$ fractions of soils 893 and 993 were also studied. For X-ray examination, the clays were saturated with Mg to enable identification of vermiculite by the method of Walker (1958) and those for investigation by infra-red spectroscopy were Na saturated because this cation is more readily dehydrated than Mg (Farmer and Russell, 1967).

Concentrates of the iron oxide minerals were obtained from the 2.0–0.02 μm fractions of all soils using two one-hour extractions with boiling 5M NaOH (Norrish and Taylor, 1961). The second extraction was found necessary to remove kaolin completely. This procedure resulted in a three to five times concentration of the iron minerals.

The X-ray investigation was made using a Philips 2 kW X-ray diffractometer with iron-filtered $\text{CoK}\alpha$ radiation. Sedimented aggregates of the clay fractions were examined in the untreated air-dry state, after heating to 300°C, and after glycerol sorption. Random powder specimens of the clay fractions from 893, 993 and 23 were also studied. The 2.0–0.02 μm fraction of these clays was extracted with boiling 5% Na_2CO_3 for 5 min, with *M* KCl, with boiling 0.1M HCl for 90 min or with *M* NH_4F to investigate the interlayered materials.

The iron oxide concentrates were examined in randomly oriented form after the addition of lead nitrate to act as internal standard for the measure-

TABLE I

Some features of the soils used in the investigation

Sample No.	Depth of sample (cm)	Horizon	Munsell colour	Colour	Soil group (Walker, 1960)	Soil type (Walker, 1960)	Parent material in Wianamatta series
893	28-38	B ₁	2.5YR4/6	red	Red	Cumberland Clay loam	Ashfield shale
993	30-35	B ₁	10 YR5/6	yellowish-brown	Yellow	Austral Clay loam	Minchinbury sandstone
1	55-60	B ₂	2.5 Y6/4	light yellowish-brown	Podzolic	Austral Clay loam	Minchinbury sandstone
20	50-55	B ₂	5 YR6/6	reddish-yellow	Podzolic	Cumberland Clay loam	Minchinbury sandstone
23	35-40	B ₂	10 YR6/6	brownish yellow	Red	Cumberland Clay loam	Minchinbury sandstone

TABLE II

Profile 99

Northcote Principal Profile Form: Dy 2.41.

Great Soil Group: Yellow Podzolic

Location: Camden, N.S.W.

Lat. 34°06' S

Long. 150°36' E

Topography: undulating to hilly

Climate: average annual rainfall 73 mm

average annual evaporation 114 mm

Parent material: Minchinbury sandstone

Sample No.	Depth (cm)	Description
991	0—7	A ₁ horizon; 10 YR 5/3 (dry) brown (V/C2)*, 10 YR 3/1 (moist), very dark grey (V/C1), whole coloured; loam; between 1/3 and 4/5 of soil consists of polyhedral peds 1.5 cm diameter breaking down with a weak force to polyhedral peds 0.5 cm, peds are rough faced; fabric earthy; the peds are brittle at moderately moist stage using a small force; pH 6.5, trace of Cl abundant roots; diffuse boundary to
992	—20	A ₂ horizon; 10 YR 7/3 (dry) very pale brown (V/C3), 10 YR 5/3 (moist) brown (V/C2), whole coloured and conspicuously bleached; sandy loam; apedal massive; coherent and seasonally hard setting; the soil is brittle with a moderate force at moderately moist stage; pH 6.5; trace Cl; abundant roots; clear boundary to
993	—60	B ₁ horizon; 10 YR 5/6 (dry) yellowish brown (V/C4), 10 YR 5/4 moist yellowish brown (V/C2), whole coloured, description of smooth ped face, horizon of maximum chroma; medium clay; over 4/5 of material consists of angular prismatic peds (40 × 10 × 10 cm) breaking with a small force to angular blocky peds (5 cm), peds mostly shiny and smooth faced; the peds are crumbly when subjected to strong force when dry; pH 4.0; nil Cl.

*V/C: Value/Chroma rating as defined by Northcote (1971).

ment of the 111 spacing of goethite (Norrish and Taylor, 1961).

Infra-red spectra of randomly oriented clay specimens dispersed in 12 mm diameter potassium bromide pressed discs were recorded over the range 4000 to 400 cm⁻¹ on a Grubb Parsons Spectromaster. Discs contained 170 mg KBr and either 2 mg or 0.3 mg sample.

RESULTS AND INTERPRETATION

(1) *The iron minerals*

The iron oxide concentrates yielded X-ray diffraction patterns characteristic of goethite. Quartz, anatase and a clay mineral were also detected.

TABLE III

Profile 89

Northcote Principal Profile Form: Dr 2.41
 Great Soil Group: Red Podzolic
 Location: within 10 km of Profile 99
 Topography: gently undulating
 Climate: see Profile 99
 Parent material: Ashfield shale

Sample No.	Depth (cm)	Description
891	0-11	A ₁ horizon; 10 YR 5/3 brown (dry) (V/C2), 10 YR 3/3 dark brown (moist) (V/C5), whole coloured; sandy clay loam; less than 1/3 of soil comprised of sub-angular prismatic rough faced peds (13 × 7 × 7 cm) breaking with a small force to polyhedral peds (0.5 cm), coherent seasonally hard setting; when dry, using a strong force, the soil is brittle; pH 6.0; Cl absent; earthy fabric; 1% of small manganiferous concretions (2 mm); roots abundant, irregular textural boundary, clear colour boundary to
892	-24	A ₂ horizon; 10 YR 7/3 very pale brown (dry) (V/C3), 7.5 YR 4/4 brown (moist) (V/C5), whole coloured, conspicuously bleached; clay loam; less than 1/3 of soil comprised of weakly developed angular prismatic, rough faced peds (12 × 6 × 6 cm), breaking with a small force to fragments; coherent, seasonally hard setting. When dry the soil breaks with a strong force and is brittle; pH 6.0; trace Cl; about 5% of manganiferous concretions; clear textural boundary, gradual colour boundary to
893	-51	B ₁ horizon; 2.5 YR 4/6 red (dry) (V/C5b), 2.5 YR 3/6 dark red (moist) (V/C5b), whole coloured, description of shiny ped face, horizon of maximum chroma; heavy clay; most of the soil comprised of coherent, angular, smooth-faced prismatic peds (27 × 4 × 4 cm) breaking with a weak force, to angular blocky peds (4 cm); when moderately moist a strong force is required to crumble the soil; pH 5.0; trace Cl; roots present, no textural or colour boundary to
894	-78	B ₂ horizon; essentially similar to 893 but about 40% mottling with 10 YR 6/6 brownish yellow (moist) (V/C4)
895	-100	B ₂ horizon; a further mottle colour present 10 YR 6/2 light brownish grey (moist) (V/C2); texture decreases from heavy clay at -78 cm to sandy clay -100 cm; otherwise properties similar to 893.

The 22-45° 2θ region (Fig.1) exhibits goethite reflections at 4.17, 2.68, 2.56 and 2.43 Å. Thiel (1963) has demonstrated that increasing aluminium content causes a decrease in the 130, 021, 111 and 140 spacings of goethite, which, for the pure mineral, occur at 2.69, 2.58, 2.45 and 2.19 Å, respectively. The small variation in these spacings from soil to soil suggests that Al substitution in the goethites does not vary appreciably. This is borne out by

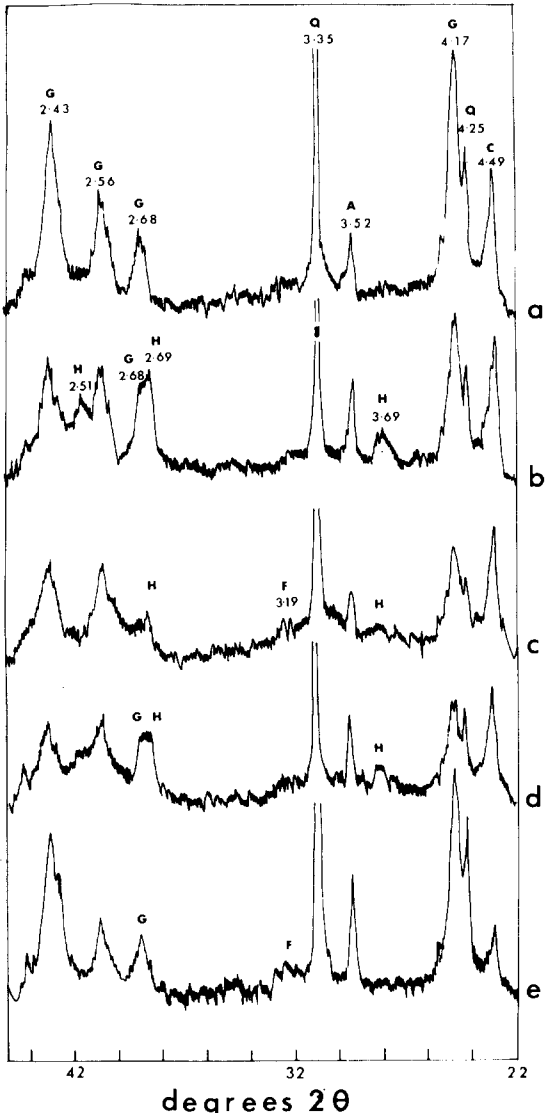


Fig.1. X-ray diffraction diagrams of the iron oxide concentrates of podzolic soil clays (2.0–0.02 μm): a, 993, yellow; b, 893, red; c, 20, red; d, 23, brownish yellow; e, 1, yellow.
 A = anatase; C = clay; F = felspar; G = goethite; H = hematite. Spacings in Å.

estimates of AlOOH content of the goethites from the 111 spacings (Table IV) using the data of Thiel (1963).

Hematite reflections at 2.69 and 3.69 Å were found only in the concentrates of the red podzolic soils 893 and 20 and the brownish yellow soil 23 (Fig.1b, c, d). They were not detectable in concentrates from the two yellow

TABLE IV

Composition of goethite in red and yellow podzolic soils

Sample No.	Soil group	d (111) goethite* (Å)	Al in goethite** (mol %)
893	Red Podzolic	2.433	14
993	Yellow Podzolic	2.436	14
1	Yellow Podzolic	2.436	14
23	Red Podzolic	2.436	14
20	Red Podzolic	2.434	14

*Each value mean of four determinations of spacing using PbNO_3 as internal standard.

**Determined using data of table 2, Thiel, 1963.

podzolic soils (Fig.1a, e). No evidence for lepidocrocite could be found either in the original clays or the concentrates.

As particle size of clay fractions from soil 893 decreases, the content of goethite increases as shown by increasing intensity of the goethite infra-red absorption band at 3160 cm^{-1} (Fig.2a, b, c). Enhancement of goethite absorption in this region by the concentration procedure is shown in Fig. 2d, e and f for soils 893, 993 and 23. These spectra show that kaolinite has been entirely removed by the concentration procedure as has most of an illite-smectite phase. The residual absorption occurring at $3620\text{--}3630\text{ cm}^{-1}$ (Fig. 2d, e, f) appears to be due to illite. This was indicated when the residue obtained by dissolving the iron oxide phases in warm dilute HCl gave an infra-red absorption pattern identical with that of well-characterized Fithian illite. Iron oxide concentrates of both the smectite-rich soil (23) and the kaolinite-rich soil (893) appear to contain about the same amount of residual illite which gives rise to the 4.49 Å reflection in all soil concentrates in Fig.1.

The spectra of the concentrates in the $1250\text{--}750\text{ cm}^{-1}$ region (Fig.3a, b, c) show that illite and quartz are present, and that their absorption bands are superimposed on those of goethite near 910 and 800 cm^{-1} . The precise frequency of the former goethite band is therefore uncertain, but it must lie between 910 and 920 cm^{-1} . According to the relationship of Jonas and Solymar (1970), these frequencies correspond to a substitution of Al for Fe^{3+} in goethite of 10–16% which agrees well with the 14% estimated from the 111 goethite reflection of concentrates from all of the soils investigated (Table IV).

Electron diffraction patterns of the iron oxide concentrates confirm goethite in 993 and 893, and hematite in 893. Electron optical examination shows that the iron mineral particles are small ($< 100\text{ Å}$), and suggests that they are quite well crystallised as Fig.4 shows.

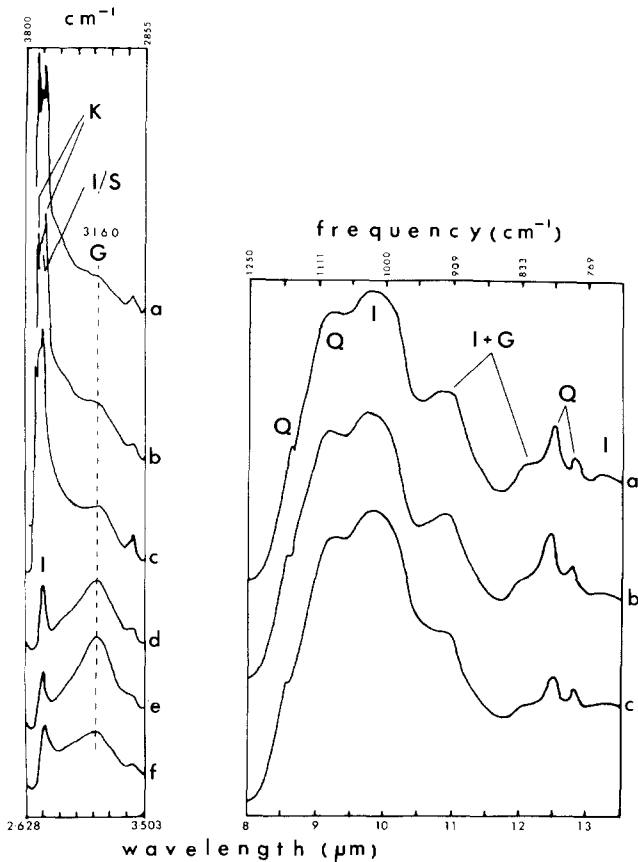


Fig.2. Infra-red absorption spectra of KBr pressed disks. Clay fractions of the red podzol 893: a, 2.0–0.02 μm ; b, 0.2–0.02 μm ; c, < 0.02 μm . Iron oxide concentrates of: d, soil 893; e, soil 993; f, soil 23. Disks contain 2 mg sample and 170 mg KBr. G = goethite; I = illite; K = kaolinite; S = smectite.

Fig.3. Infra-red absorption spectra of KBr pressed disks of iron oxide concentrates obtained from red and yellow podzolic soils: a, soil 893, red; b, soil 993, yellow; c, soil 23, brownish yellow. Disks contain 2 mg iron oxide concentrate and 170 mg KBr. G = goethite; I = illite; Q = quartz.

The clay minerals

The yellow podzolic soil (sample 993). Kaolinite is indicated by a strong X-ray reflection at 7.2 \AA which is unchanged by either glycerol sorption or heating at 300°C (Fig.5a). The mineral is confirmed by its infra-red absorption pattern (Figs.6f, 7f; compare Farmer and Russell, 1964), particularly by the presence of bands near 3700, 3620 and 915 cm^{-1} . It is undoubtedly the dominant mineral in the 2.0–0.02 μm fraction and is still present in the 0.2–0.02 μm fraction. In the < 0.02 μm fraction, however, kaolinite could be

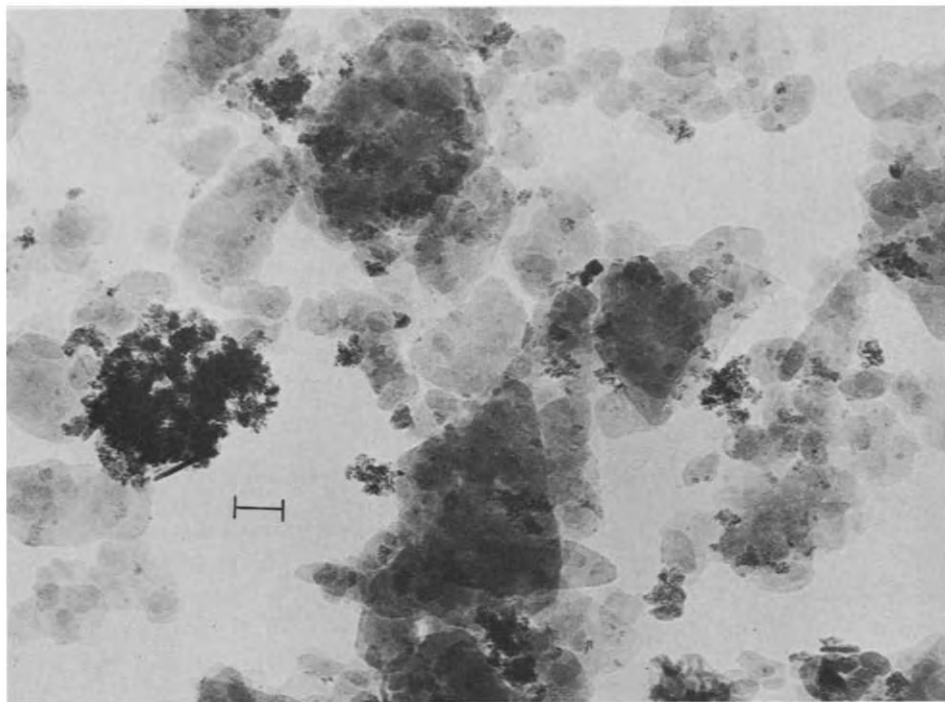


Fig. 4. Electronmicrograph of the 2.0–0.02 μm fraction from red podzolic soil 893. Marker represents 1000 Å. Clusters of electron-dense particles consist of goethite and hematite.

detected only by infra-red spectroscopy (Fig. 6h, 7h).

The clays also contain an interstratified expandible mineral. In the 2.0–0.02 μm fraction this is manifested by a broad X-ray reflection near 14 Å (Fig. 5a), which moves towards 18 Å after glycerol sorption, the diffuseness and asymmetry of the reflection indicating interstratification (Fig. 5b); heating at 300°C causes collapse to 10 Å, which indicates the absence of interlayer contaminants. A sharp reflection at 1.50 Å given by the randomly oriented sample indicates that the mineral is dioctahedral. The X-ray data are consistent with interstratified illite–smectite, which, by comparison with the calculated profiles of Reynolds and Hower (1970), contains about 60% illite and 40% smectite. This interstratified material probably gives rise to the broad diffuse infra-red absorption band near 3630 cm^{-1} (Fig. 6f), and the weak illite absorption band at 832 cm^{-1} (Fig. 7f') (Oinuma and Hayashi, 1968). The weak shoulder at 870 cm^{-1} suggests that the illite–smectite phase contains a proportion of octahedral ferric iron. X-ray diffraction indicates that this phase becomes more abundant with decreasing particle size, and this is supported by the infra-red results (Fig. 6g, h).

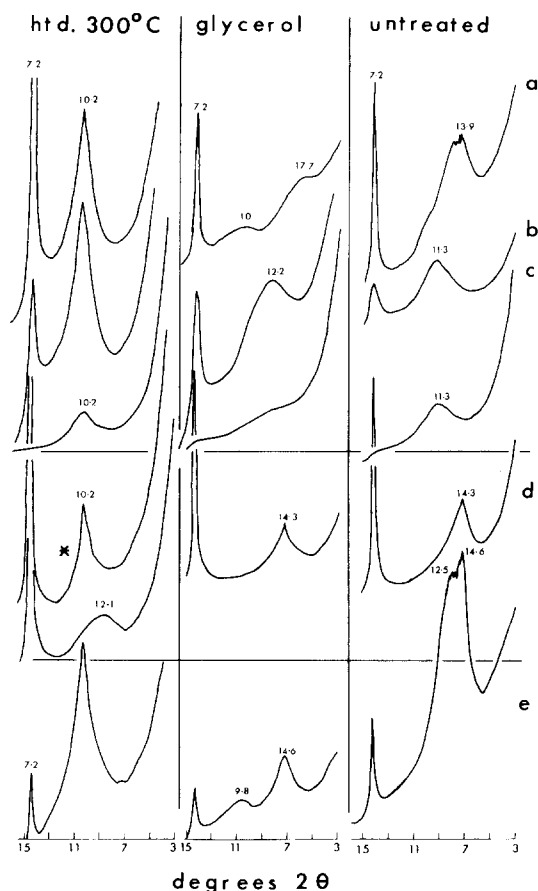


Fig. 5. X-ray diffraction diagrams of sedimented aggregates of podzolic soils: a, 993, 2.0–0.02 μm ; b, 993, 0.2–0.02 μm ; c, 993, < 0.02 μm ; d, 893, 2.0–0.02 μm (the curve marked * corresponds to treatment with NH_4F before heating); e, 23, 2.0–0.02 μm . Spacings in Å.

The red podzolic soil (sample 893). The 2.0–0.02 μm fraction of this soil (Fig. 5d, 6d) is even more kaolinitic than sample 993. The strong absorption band at 3652 cm^{-1} suggests either a *b*-axis disordered kaolinite of Pugu type or a mixture of kaolinite and either dickite or nacrite (Farmer and Russell, 1964). X-ray diffraction examination of a randomly oriented sample shows well-defined non-basal reflections at 4.46, 4.36 and 4.18 Å, which are characteristic of highly crystalline kaolinite but not of the *b*-axis disordered form. The presence of dickite is suggested by sharp reflections at 4.27 and 3.79 Å but no evidence was obtained for the occurrence of nacrite. The X-ray evidence is, therefore, consistent with a mixture of kaolinite and dickite.

X-ray diffraction again indicates the presence of an interstratified mineral

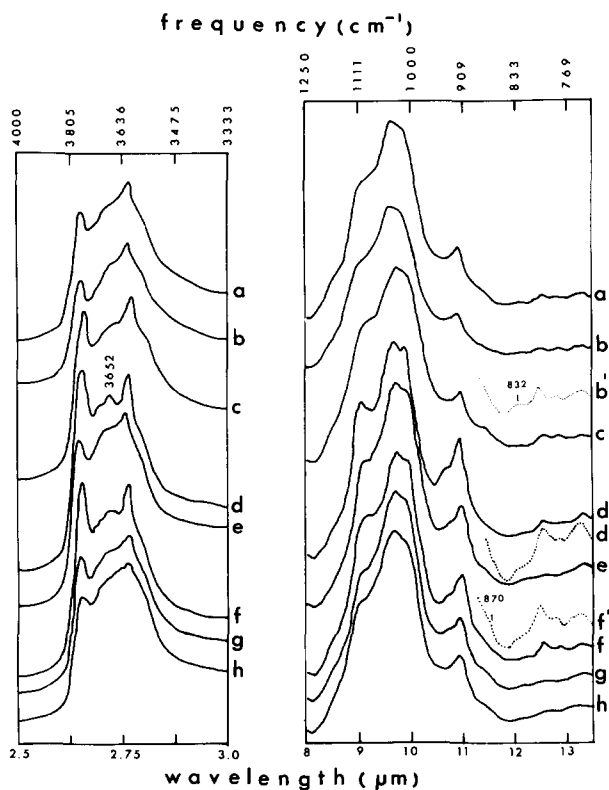


Fig.6. Infra-red absorption spectra of KBr pressed disks of podzolic soil clay fractions: a, soil 20, 2.0–0.02 μm ; b, soil 23, 2.0–0.02 μm ; c, soil 1, 2.0–0.02 μm ; d, soil 893, 2.0–0.02 μm ; e, soil 893, < 0.02 μm ; f, soil 993, 2.0–0.02 μm ; g, soil 993, 0.2–0.02 μm ; h, soil 993 < 0.02 μm . Disks contain 2 mg clay and 170 mg KBr.

Fig.7. Infra-red absorption spectra of KBr pressed disks of podzolic soil clay fractions: a, soil 20, 2.0–0.02 μm ; b, soil 23, 2.0–0.02 μm ; c, soil 1, 2.0–0.02 μm ; d, soil 893, 2.0–0.02 μm ; e, soil 893, < 0.02 μm ; f, soil 993, 2.0–0.02 μm ; g, soil 993, 0.2–0.02 μm ; h, soil 993 < 0.02 μm . Disks contain 170 mg KBr and either 0.3 mg clay (solid lines), or 2.0 mg clay (broken lines).

containing some smectitic interlayers but it is not identical with the one previously described. In the untreated state the basal reflection occurs at about 14.3 Å and is asymmetrical towards the high-angle side (Fig.5d). Glycerol treatment leaves the position of the reflection unchanged but it becomes more symmetrical. Some of the expansible material is strongly interlayered as indicated by the broad 12.1 Å reflection after heating to 300°C. Treatment with *M* KCl, boiling 5% Na₂CO₃ or 0.1*M* HCl all failed to induce collapse to 10 Å after heating to 300°C, indicating the presence of a resistant non-exchangeable material in the interlayer position. Only the comparatively severe treatment with *M* NH₄F removed this material and produced a sharp, almost

symmetrical, 10 Å reflection after heating (Fig.5d*). The interlayer is, therefore, probably well organised and highly aluminous.

The infra-red spectrum (Fig.7d), shows no discrete absorption near 870 cm^{-1} suggesting that the smectite in the red podzolic soil contains very little octahedrally coordinated Fe^{3+} . The finest clay ($< 0.02\ \mu\text{m}$) gives an almost featureless X-ray diffraction pattern, but a well-defined infra-red spectrum (Figs. 6e, 7e) which indicated that this fraction contains kaolinite and rather more illite—smectite than the $2.0\text{--}0.02\ \mu\text{m}$ fraction. The X-ray and infra-red results for the $0.2\text{--}0.02\ \mu\text{m}$ fraction are not presented but they demonstrate that this size fraction has a composition intermediate between that of the $2.0\text{--}0.02$ and $< 0.02\ \mu\text{m}$ material.

The yellow podzolic soil (sample 1), the "brownish-yellow" podzolic soil (sample 23) and the red podzolic soil (sample 20). All three soils belong to a catena developed on Minchinbury sandstone. Because the infra-red spectra are very similar (Fig.6a, b, c, 7a, b, b', c) only the midslope soil (23) was examined by X-ray diffraction (Fig.5e). The diffraction pattern of the $2.0\text{--}0.02\ \mu\text{m}$ fraction shows that this soil contains much more of the interstratified phase than soils 893 and 993. Kaolinite is present but dickite could not be unambiguously identified. Examination after heat treatment showed that the clay is not interlayered.

DISCUSSION

The results strongly suggest that the iron oxide minerals impart red and yellow colours to the podzolic soils. All soils contain a well-crystallized aluminous goethite containing 13–14% AlOOH and this mineral appears to be responsible for the colour of the yellow podzolic group. The aluminium content might possibly enhance the yellowness as suggested by Norrish and Taylor (1961). The colour of the goethite in the red and brownish podzolic soils is masked by hematite. No evidence was found for the presence of lepidocrocite. The fineness of these soil minerals ($< 100\ \text{Å}$) will contribute to their effectiveness as colouring agents. For goethite, this fineness may well be a consequence of its aluminous nature (Thiel, 1963; Jonas and Solymar, 1970).

Several observations appear relevant concerning the distribution of goethite and hematite. Berner (1969) has shown that goethite is unstable in favour of hematite in most situations near the earth's surface, so that the transformation goethite \rightarrow hematite should be the rule. This process appears to be accelerated by higher temperatures, as inferred by Walker (1967) in his study of the calcareous soils of the Sonoran desert which formed at various periods since the Pliocene. This adds weight to Schwertmann's (1971) proposal that hematite formation was favoured in the hotter climates of the past. Geomorphological evidence in the County of Cumberland (Walker and Hawkins, 1957) suggests that the red and yellow podzolic soils may well be residual soils which date from more arid soil-forming eras. Both Van Houten (1973)

and Walker (1974) have provided evidence that red beds can form in moist as well as arid climates provided the environment is alkaline (pH 7.5) and sufficient time elapses for the conversion of goethite to hematite. This process, however, does not seem likely in the Sydney region where the maximum pH in present-day podzolic soils is 6.5 and usually decreases with depth. The current process may, therefore, be the reconversion of hematite to goethite due to the effects of organic compounds as proposed by Schwertmann (1971). This is supported by Walkers' (1960) finding that the yellow podzolic soils contain more organic matter.

Further evidence for this hypothesis is provided by the field observation that modern soil formation on a truncated Tertiary laterite near Sydney, has given rise to a yellow podzolic soil. In this profile the red and white colours characteristic of the mottled zone of the laterite become yellow and white over a vertical distance of about 10 cm. The mottle pattern in the red and yellow zone is identical suggesting that red colour has been converted to yellow *in situ* without translocation of the iron.

The finding of dickite in the clay fraction of one of the red podzolic soils (893), especially at 28–38 cm depth, is particularly noteworthy as this mineral occurs rarely in soils and infrequently in sedimentary deposits. It seems likely that the dickite in the red podzolic soil is inherited. Dickite appears to be a characteristic mineral in the Triassic rocks of the Sydney Basin, which comprises the Narrabeen group, the Hawkesbury sandstone and the Wianamatta group. Thus, Loughnan et al. (1964) found dickite in the Narrabeen sandstone and the same mineral was recorded by Bayliss et al. (1965) in the Hawkesbury sandstone. The Wianamatta group, from which the red podzolic soils are derived, directly overlies the Hawkesbury sandstone. Because of this stratigraphic association, it might be inferred that the dickite is inherited from the Wianamatta group.

CONCLUSION

The dominant iron oxide mineral in some typical red and yellow podzolic soils from New South Wales is goethite containing 13–14 mol % AlOOH . This mineral appears to give the yellow soils their characteristic colour. The red soils also contain finely divided hematite which masks the colour of the goethite. The principal clay minerals are kaolinite and dioctahedral interstratified illite–smectite, the latter being more abundant in the finer clay fractions. Dickite was found in the red podzolic soil and is apparently of inherited origin.

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