

## IRON OXIDE MINERALOGY OF SOME SOILS OF TWO RIVER TERRACE SEQUENCES IN SPAIN

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### ABSTRACT

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The iron oxides of soils of two river terrace sequences in Spain which show an increasing degree of redness with age were studied. Clay fractions contained only small amounts of oxalate-extractable Fe. Goethite and hematite, the only crystalline Fe-oxides identified, were determined quantitatively by X-ray diffraction (XRD) after concentrating the Fe-oxides by boiling in 5N NaOH and subtracting the step-counted diffractogram of the deferrated clay from that of the non-deferrated clay, obtaining thus a "pure" Fe-oxide diffractogram. EDTA extracted hematite preferentially to goethite as is seen by loss of red colour and by XRD. A good correlation was found between the content of hematite in the fine earth and a redness rating based on Munsell notations.

In the Guadalquivir River sequence,  $Fe_d$  and  $Fe_d/Fe_t$  increased with age. The amount of both goethite and hematite formed from silicate-Fe increased with soil age but hematite increased more than goethite, possibly due to the xeric soil environment. Also, goethite increased in crystallinity as indicated by a decrease in XRD line broadening and  $Fe_o/Fe_d$  ratios. No such trends were found in the Esla River sequence, possibly because the initial alluvium was already highly weathered as shown by high  $Fe_d/Fe_t$  values (0.8) irrespective of terrace level.

Al substitution in goethite calculated from XRD increased with soil age, reflecting the increasing acidity of the soils. Al substitution in hematite was markedly lower.

### INTRODUCTION

Red soils are very common in Mediterranean areas but knowledge of the nature and properties of the Fe-oxides responsible for their colour is still limited. Until recently, it was believed that the red colour was due to the presence of X-ray amorphous oxides with or without a certain amount of hematite (Lamouroux and Segalen, 1969; Lamouroux, 1972; Lamouroux and Quantin, 1973). This hypothesis was partly based on the dissolution curves obtained by Segalen's method which consists of repeated treatments

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with 8N HCl (Segalen, 1968). The Fe-oxide fraction which initially and rapidly dissolved was taken as the amorphous fraction. This fraction also appeared to be responsible for the red colour. However, Quantin and Lamouroux (1974), using 4N HCl, found that the rate of dissolution of the Fe-oxides of some other red soils was constant, a finding that seemed to indicate a crystalline rather than an amorphous nature. Lamouroux (1972) has suggested that the Fe-oxide responsible for the red colour is cryptocrystalline "pre-hematite", the crystallization of which is hindered by the presence of clay silicates. Very low amounts of Fe extractable with acid ammonium oxalate, which gives a rough estimate of the "amorphous" Fe-oxides (Schwertmann, 1959, 1964, 1973), support the hypothesis that the Fe-oxides responsible for the red colours are predominantly crystalline. Singer (1977) found low  $Fe_o/Fe_d$  (oxalate/dithionite extractable Fe) ratios for red soils of Israel developed on basalt and scoria, and Torrent has found that the  $Fe_o/Fe_d$  ratio for red soils of Spain, irrespective of parent material and environment, rarely exceeds 0.15 and is usually lower than 0.07.

Corroborating the former ideas, Gangas et al. (1973) found by Mössbauer spectroscopy that most of the  $Fe_d$  in a Rhodoxeralf of Greece was in the form of hematite of ultra-fine particle size (131 Å in mean diameter). Lamouroux et al. (1977) showed that hematite was responsible for the red colour of several soils from Lebanon. Part of the hematite appeared in very small, < 100 Å particles (by Mössbauer) which were less soluble by Segalen's method and less red than the larger particles. Bresson (1974) observed, by electron microscopy, aggregates made up of small particles, 30–50 Å in diameter, both in red Mediterranean soils and in red soils of the Jura region of France.

If, as suggested by the former data, hematite is responsible for the colour of red Mediterranean soils, failure to detect it in the clay fraction by X-ray diffraction (XRD) must be attributed to its low content and/or poor crystallinity.

Soils of river terrace sequences in Spain show, in general, increasing red colouration with increasing elevation above the present river level, i.e. with soil age. Therefore, they can be considered soil chronosequences with respect to the reddening process, provided that the parent material of all the terraces is similar and was not red to start with. This condition is seldom fulfilled due to the natural variability of the alluvium. However, even when the parent material is not the same, trends can be expected in the nature and contents of Fe-oxides in the soils of increasingly older terraces. With this in mind, the purpose of the present study was to establish the nature and origin of the Fe-oxides in some soils of two river terrace sequences in Spain.

## THE STUDY AREAS

The first study area is located in the Esla River valley in the Province of Léon (Fig.1). Mean annual temperature is 11.5°C and mean annual precipita-

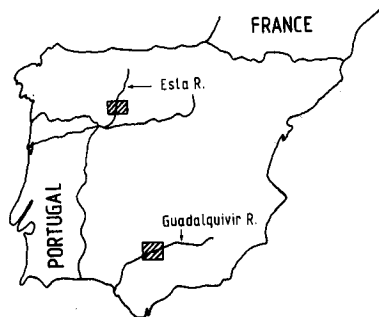


Fig.1. Location of the two study areas.

tion is about 450 mm with a marked summer drought. Terrace heights above the present river level range from 3–4 m to 160 m. The soils are Haploxeralfs and Palexeralfs, have very few weatherable minerals in the sand and silt fraction, and have illitic–kaolinitic clays. The soils have an acid pH (5.8–6.0) except for T3-3 and T10-2 (both pH 7.8) which are presently under irrigation (Torrent, 1976).

The second study area is located in the Guadalquivir River valley in the Province of Córdoba (Fig.1). Mean annual temperature is 18°C and mean annual precipitation is about 650 mm with a summer drought. Terrace heights range from 5–6 m to 210 m. The soils are Inceptisols on the very low terraces and Alfisols (Haploxeralfs, Rhodoxeralfs and Palexeralfs) on the higher ones. Sand and silt fractions have weatherable minerals. Clays from soils of the low terraces contain illite and kaolinite, and, commonly, vermiculite, smectite and/or different interstratified minerals. Clays from soils of the high terraces are usually illitic–kaolinitic or kaolinitic. All samples have an alkaline pH (7.3–8.4) which decreases slightly with terrace height. Most likely, however, the present pH does not reflect weathering conditions in the past because most of the soils are Alfisols. All samples had organic matter contents < 0.5%.

## METHODS

### *Field sampling*

Only horizons which showed a uniform colour were sampled in an effort to preclude study of mottled, slightly hydromorphic soils which are common on the high terraces of both sequences. However, some soils, as noted later, did show some evidence of hydromorphic conditions. As a rule, sampling of Alfisols was done in the upper part of the B2t horizon because it usually was the horizon of most pronounced red colour (Table I).

TABLE I

## General soil data

| Sample                         | Terrace height<br>above present<br>river level<br>(m) | Classification* <sup>1</sup> | Horizon* <sup>2</sup> | Depth<br>(cm) | Colour        |               | Textural* <sup>2</sup><br>class | Mineralogy* <sup>3</sup> |
|--------------------------------|---|------------------------------|-----------------------|---------------|---------------|---------------|---------------------------------|--------------------------|
|                                |   |                              |                       |               | moist         | dry           |                                 |                          |
| <i>Esta sequence</i>           |   |                              |                       |               |               |               |                                 |                          |
| T3-3                           | +3  | Palixeralf                   | B2t                   | 64-90         | 7.5YR 4.5/3.5 | 8.5YR 5/4     | sc                              | I,K                      |
| T8-2                           | +8  | Haploxeralf                  | B2t                   | 20-53         | 5YR 3.5/6     | 6.5YR 5.5/5.5 | scl                             | I,K                      |
| T10-2                          | +10   | Haploxeralf                  | B2t                   | 22-50         | 4YR 4/5       | 6.5YR 5.5/5   | sl                              | I,K                      |
| T20-2                          | +20   | Palixeralf                   | B2t                   | 21-60         | 3.5YR 3.5/6   | 5YR 5/7       | sc                              | I,K                      |
| SP-2                           | +40   | Haploxeralf                  | B2t                   | 27-68         | 2.5YR 3.8/7   | 5YR 5/7       | scl                             | I,K                      |
| P-2                            | +60   | Palixeralf                   | B2t                   | 20-60         | 2.5YR 4/5.7   | 4.5YR 5/7     | c                               | I,K                      |
| <i>Guadaluquivir sequence:</i> |   |                              |                       |               |               |               |                                 |                          |
| EL-2                           | floodplain  | Xerofluent                   | C                     | 30-50         | 7.5YR 4/2.5   | 8YR 5/3       | ls                              | I,K,S                    |
| GU-6                           | +10   | Xerochrept                   | B2                    | 130-150       | 6.5YR 4.5/5   | 8.5YR 5/4     | l                               | I,K,V,T                  |
| EA-1                           | +18   | Rhodoxeralf                  | B2t                   | 30-45         | 4YR 4/4       | 5YR 4.5/6     | sc                              | I,K,T                    |
| BO-1                           | +100  | Palixeralf                   | B2t                   | 25-35         | 2YR 3.5/7     | 2YR 3.5/6     | c                               | I,K,T                    |
| QT-1                           | +210  | Palixeralf                   | B2t                   | 20-30         | 0.5YR 3.5/7   | 3YR 4.5/6     | c                               | K,I                      |

\*<sup>1</sup> Soil Taxonomy (Soil Survey Staff, 1975).\*<sup>2</sup> Soil Survey Manual (Soil Survey Staff, 1951).\*<sup>3</sup> I = illite, K = kaolinite, S = smectite, V = vermiculite, T = interstratified (unspecified).

## Laboratory methods

### Sample preparation

Soil samples were saturated with Na using NaCl, washed with water and dispersed with Na<sub>2</sub>CO<sub>3</sub> at pH 9. Separation at 2 μm was made by gravity sedimentation. The clays were flocculated with NaCl, washed free of chloride and resuspended in water.

### Fe-oxide fractionation and dissolution

Dithionite soluble Fe (Fe<sub>d</sub>) was determined by the DCB method of Mehra and Jackson (1960) and oxalate extractable Fe (Fe<sub>o</sub>) by the method of Schwertmann (1964). Total Fe (Fe<sub>t</sub>) was determined after hydrofluoric acid attack (Pratt, 1965). EDTA-extractable Fe was determined by mixing one part of clay suspension (25 mg clay/ml) with five parts of an EDTA extractant (0.1 M in EDTA and 0.2M in ammonium acetate at pH 4.75 (after Borggaard, 1976)), the extraction being carried out in a water bath at 90°C for periods up to 18 h. Fe in all extracts was determined by atomic absorption spectroscopy (AAS) with a Perkin-Elmer 420 instrument.

### Fe-oxide determination by XRD

Iron oxide minerals were concentrated prior to XRD by treatment with boiling 5N NaOH (Norrish and Taylor, 1961)\*. The EDTA-treated samples were also concentrated with NaOH after washing three times with 0.1N HCl, once with water and once with 1N NaOH.

XRD patterns were obtained using CoK $\alpha$  radiation and a Philips PW 1050 vertical goniometer equipped with a 1° divergence slit, a 0.2 mm receiving slit, a 1° scatter slit and a diffracted beam graphite monochromator. A scanning speed of 1°/min and a time constant of 2 sec were used. Self-supporting powder mounts were prepared by back-filling the samples into aluminium frames and then gently pressing the material against filter paper to minimize preferred orientation. To facilitate more detailed XRD analysis of the iron oxides, an XRD subtraction technique was used. Powder mounts of both NaOH treated and NaOH treated + DCB treated (deferrated) preparations of each sample were step-scanned at intervals of 0.05° 2 $\theta$  from 35° to 45° 2 $\theta$  and counted for 200 sec per increment. Instrumental conditions were otherwise the same as above. By trial and error subtraction of the deferrated patterns from the corresponding Fe-oxide containing patterns, diffractograms of the Fe-oxides were obtained which were essentially free of peaks due to other minerals (Schulze, 1979).

\* There was some concern that the 5N NaOH treatment might alter the Fe-oxides. Golden (1978) observed no differences in the Mössbauer spectra of a soil clay before and after the NaOH treatment and Bigham et al. (1978a) and Janot et al. (1971) noted no changes in natural Fe-oxides after treatment with boiling 5N NaOH or similar alkali. The NaOH treatment was felt to be acceptable because present evidence does not show that soil Fe-oxides are significantly altered by the treatment.

Baselines and peak profiles were manually sketched in to "best fit" the points of the spectra. The area of the (111) peak of goethite,  $I_G(111)$  the (110) peak of hematite,  $I_H(110)$ , and the combined peak consisting of the (130) peak of goethite and the (104) peak of hematite,  $I_G(130) + I_H(104)$ , were measured by planimetering the areas. The ratios  $I_G(111)/I_H(110)$  and  $(I_G(130)+I_H(104))/I_G(111)$  were calculated. Peak positions and width at half height (WHH) were also measured. The measured WHH's were corrected for instrumental line broadening by reference to an instrumental line broadening function derived from 5–20  $\mu\text{m}$  quartz powder.

Mixtures of pure synthetic goethite and hematite with goethite:hematite ratios of 90:10, 70:30, 50:50 and 30:70 wt.% were also step-scanned. The (111) peak of the standard goethite had a corrected WHH of  $0.35^\circ 2\theta$  and the (110) peak of the standard hematite had a corrected WHH of  $0.11^\circ 2\theta$ .

The relative and absolute amounts of goethite and hematite were calculated by two different methods.

*Method I.* The goethite:hematite ratio in the sample was determined by comparing the XRD peak intensity ratios to a graph prepared from the standard goethite-hematite mixtures. Absolute percentages of goethite and hematite in the clay fraction were then calculated by allocating the difference between  $\text{Fe}_d$  and  $\text{Fe}_o$  to these two minerals because no other crystalline Fe-oxide phases were present.

*Method II.* The weight fraction of goethite in the NaOH-treated clay was determined using the formula:

$$\text{Weight fraction goethite} = \frac{\mu_x^* I_x S}{\mu_s^* I_s}$$

where  $I_x$  and  $I_s$  are the integrated intensities of the (111) line of goethite in the sample and in the standard, respectively,  $\mu_x^*$  and  $\mu_s^*$  are the mass absorption coefficients of the sample and the standard and  $S$  is the weight fraction of goethite in the standard (e.g., Brindley, 1961). A 90:10 goethite:hematite mixture was used as the standard. Hematite was determined in the same way using the (110) line of hematite and a mixture of 30:70 goethite:hematite as the standard. To calculate  $\mu_s^*$ , mass absorption coefficients of 39.6 and 42.2 were used for goethite and hematite, respectively. To calculate  $\mu_x^*$ , illite with an average  $\mu^*$  of 57.6 was assumed to be the major silicate component present and  $\text{Fe}_d$  was partitioned between hematite and goethite as determined by Method I\*<sup>1</sup>.

#### *Al substitution*

Average Al substitution in the Fe-oxide fraction of the NaOH-treated clay

\*<sup>1</sup> Partitioning of  $\text{Fe}_d$  into goethite and hematite based on Method I is of no great influence on  $\mu_x^*$  because  $\mu^*$  for both hematite and goethite is very similar. Al substitution in both goethite and hematite has a negligible influence on  $\mu^*$  for  $\text{CoK}\alpha$  radiation.

was determined by analyzing DCB extracts for Fe and Al by AAS. The citrate-bicarbonate buffer alone can dissolve appreciable amounts of Al while dissolving only small amounts of Fe (Weaver et al., 1968). In an effort to remove this easily soluble Al which is not in Fe-oxides, the samples were treated with the citrate-bicarbonate buffer at 75°–80°C, i.e. the same as the DCB procedure but without dithionite, and then washed once with the citrate–bicarbonate buffer prior to the DCB treatment. Al substitution in the goethite was estimated from d(111) using a relationship calculated from the data given by Thiel (1963). For hematite, Al substitution was estimated using d(110) and a relationship derived from synthetic Al-hematites synthesized under near-pedogenic conditions (Schwertmann et al., 1979).

### *Redness rating*

Dry and moist soil colours were determined in daylight but direct sunlight was avoided. Colours of clay suspensions after EDTA treatment (4.2 mg/ml) were measured in artificial light (fluorescent lamps) in glass tubes of 15 mm diameter, interpolating visually between colour chips when necessary. Colours measured in this manner at time 0 of EDTA treatment were consistently yellower than those of the soil samples. However, differences in redness rating between samples were similar for both methods.

The soils and EDTA extracted clays were given a redness rating for their red colour somewhat similar to that used by Hurst (1977) according to the following expression:

$$\text{Redness rating: } \frac{H \times C}{V}$$

The numerical values of  $C$  and  $V$  are those of chroma and value, respectively, of the Munsell notation. The numerical values of  $H$  are: 12.5 for Munsell hue of 7.5R; 10 for 10R; 7.5 for 2.5YR; 5 for 5YR; 2.5 for 7.5YR and 0 for 10YR. These values were chosen because: (a) they provide a good discrimination for goethite- and hematite-determined colours (pure, fine goethite is close to 10YR and pure, fine hematite is close to 7.5R), and (b) they are easy to remember.

### *Electron microscopy*

Samples were ultrasonically dispersed in ethanol and a drop of the suspension was dried on a carbon-coated copper grid. The samples were examined with a Zeiss EM 10 transmission electron microscope operated at 80 kV.

## RESULTS AND DISCUSSION

### *Fe-oxide fractionation and dissolution*

All soils of the Esla sequence show similar  $\text{Fe}_d$  values and  $\text{Fe}_d/\text{Fe}_t$  ratios

(Table II). These ratios are high (around 0.80) which suggests a high degree of weathering even in the younger terraces. Because the soils of the Esla sequence have widely different ages, the youngest terrace being about 3,300 years and the oldest probably pre-Rissian, it was expected that weathering in situ alone would have led to an increase in the  $Fe_d/Fe_t$  ratio with age. Inasmuch as such a trend is not apparent, one must conclude that the initial parent alluvium of all the soils had a similar, and already high,  $Fe_d/Fe_t$  ratio probably caused by intensive weathering in the source areas of the alluvium and not so much by weathering after alluvium deposition.

The soils of the Guadalquivir sequence show an increase in  $Fe_d$  and the  $Fe_d/Fe_t$  ratio with age (Table II). This suggests that weathering of the Fe-bearing minerals of the alluvium has been adding increasing amounts of oxide-Fe to the clay fractions with time. As expected (see Introduction), the  $Fe_o/Fe_d$  ratios of all samples were low ( $< 0.1$ ), indicating the Fe-oxides to be mainly crystalline in nature.

After 0.5 h extraction at  $90^\circ C$ , EDTA extracts amounts of Fe similar to those extracted by oxalate. Thus, after several hours of treatment a substantial part of the crystalline Fe-oxides is dissolved. No sharp breaks are observed in the EDTA extraction curves, and most of them have linear parts between 2 and 10 h of extraction (Figs. 2, 3). No unequivocal conclusion can be drawn from this type of kinetic curve.

For the Esla sequence, no trends, either in the speed of dissolution or in the shape of the curves, are observed (Fig. 2), suggesting that the solubility of the Fe-oxides, like their concentration, is independent of pedogenic time. In contrast, in the Guadalquivir sequence, lower percentages of Fe are dis-

TABLE II

Percentages of  $Fe_t$ ,  $Fe_d$  and  $Fe_o$  and  $Fe_d/Fe_t$  and  $Fe_o/Fe_d$  ratios for the clay fraction and percent  $Fe_d$  in the NaOH-treated clay

| Sample                        | $Fe_t$ | $Fe_d$ | $Fe_o$ | $Fe_d/Fe_t$ | $Fe_o/Fe_d$ | $Fe_d$ in NaOH treated clay |
|-------------------------------|--------|--------|--------|-------------|-------------|-----------------------------|
| <i>Esla sequence:</i>         |        |        |        |             |             |                             |
| T3-3                          | 7.9    | 6.3    | 0.61   | 0.80        | 0.10        | 10.4                        |
| T8-2                          | 7.1    | 5.7    | 0.48   | 0.81        | 0.08        | 10.7                        |
| T10-2                         | 7.7    | 6.0    | 0.59   | 0.78        | 0.10        | 10.9                        |
| T20-2                         | 7.5    | 6.0    | 0.20   | 0.80        | 0.03        | 13.7                        |
| SP-2                          | 8.1    | 6.8    | 0.38   | 0.84        | 0.06        | 18.1                        |
| P-2                           | 7.6    | 6.3    | 0.34   | 0.83        | 0.06        | 19.2                        |
| <i>Guadalquivir sequence:</i> |        |        |        |             |             |                             |
| EL-2                          | 5.8    | 2.2    | 0.32   | 0.37        | 0.15        | 4.0                         |
| GU-6                          | 7.0    | 3.4    | 0.28   | 0.48        | 0.08        | 7.5                         |
| EA-1                          | 6.6    | 3.4    | 0.18   | 0.51        | 0.05        | 9.3                         |
| BO-1                          | 6.8    | 4.2    | 0.18   | 0.62        | 0.07        | 22.0                        |
| QT-1                          | 6.9    | 5.2    | 0.22   | 0.75        | 0.04        | 26.9                        |



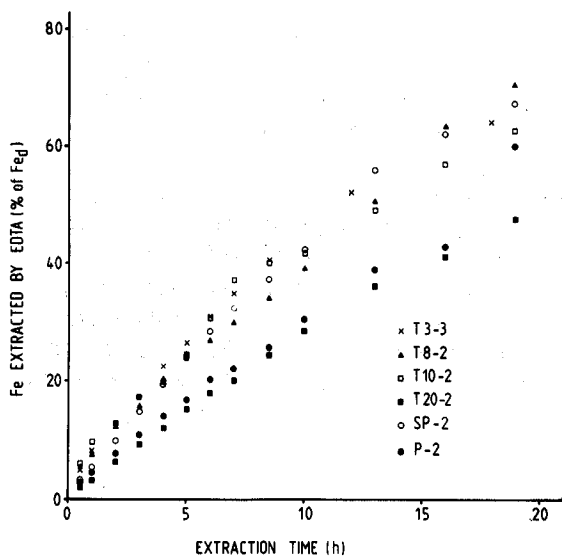


Fig.2. Percentage of  $Fe_d$  extracted by EDTA, plotted against extraction time for soil clays of the Esla sequence.

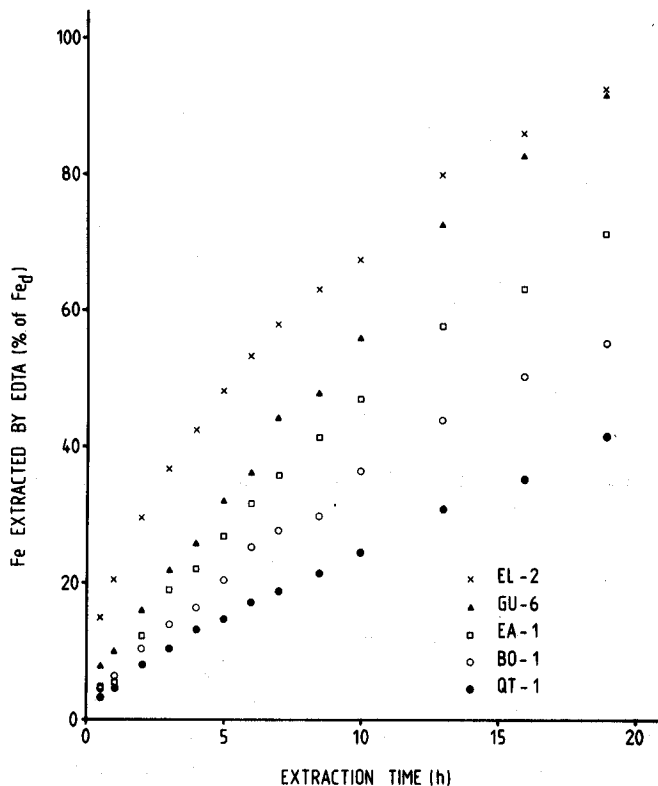


Fig.3. Percentage of  $Fe_d$  extracted by EDTA, plotted against extraction time for soil clays of the Guadalquivir sequence.

solved as the age increases (Fig.3), suggesting improvement of overall crystallinity with increasing  $Fe_d$  and pedogenic age. This concept is supported by a decrease in the WHH of the (111) goethite line (Table IV) and by a weak trend of decreasing  $Fe_o/Fe_d$  (Table II) with age, neither of which is observed for the Esla sequence.

Extracted clays from both the Guadalquivir (Fig.4) and the Esla sequences show a decrease in the redness rating with increasing extraction time. Most of the colour change occurs in the first 6 h of treatment. Preferential extraction of the Fe-oxides responsible for the red colour (presumably hematite) seems therefore to be a common feature in red Mediterranean soils irrespective of the extraction method used. Extractions with both EDTA and HCl (Lamouroux and Segalen, 1969; Lamouroux and Quantin, 1973) lead to the same conclusion.

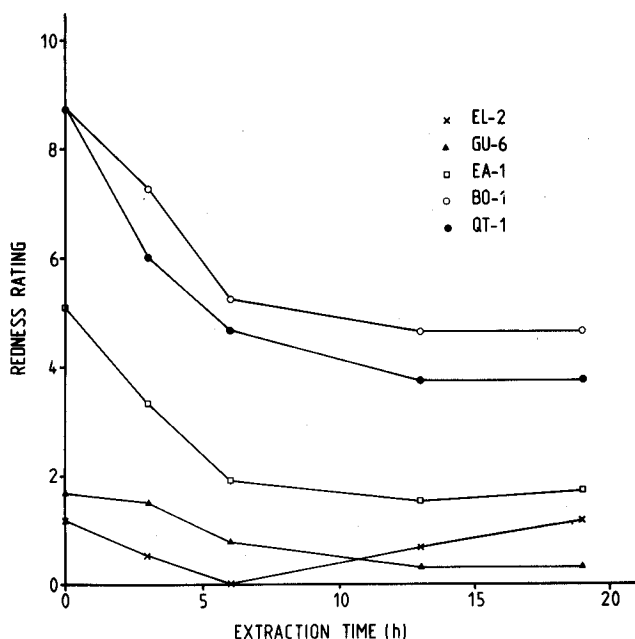
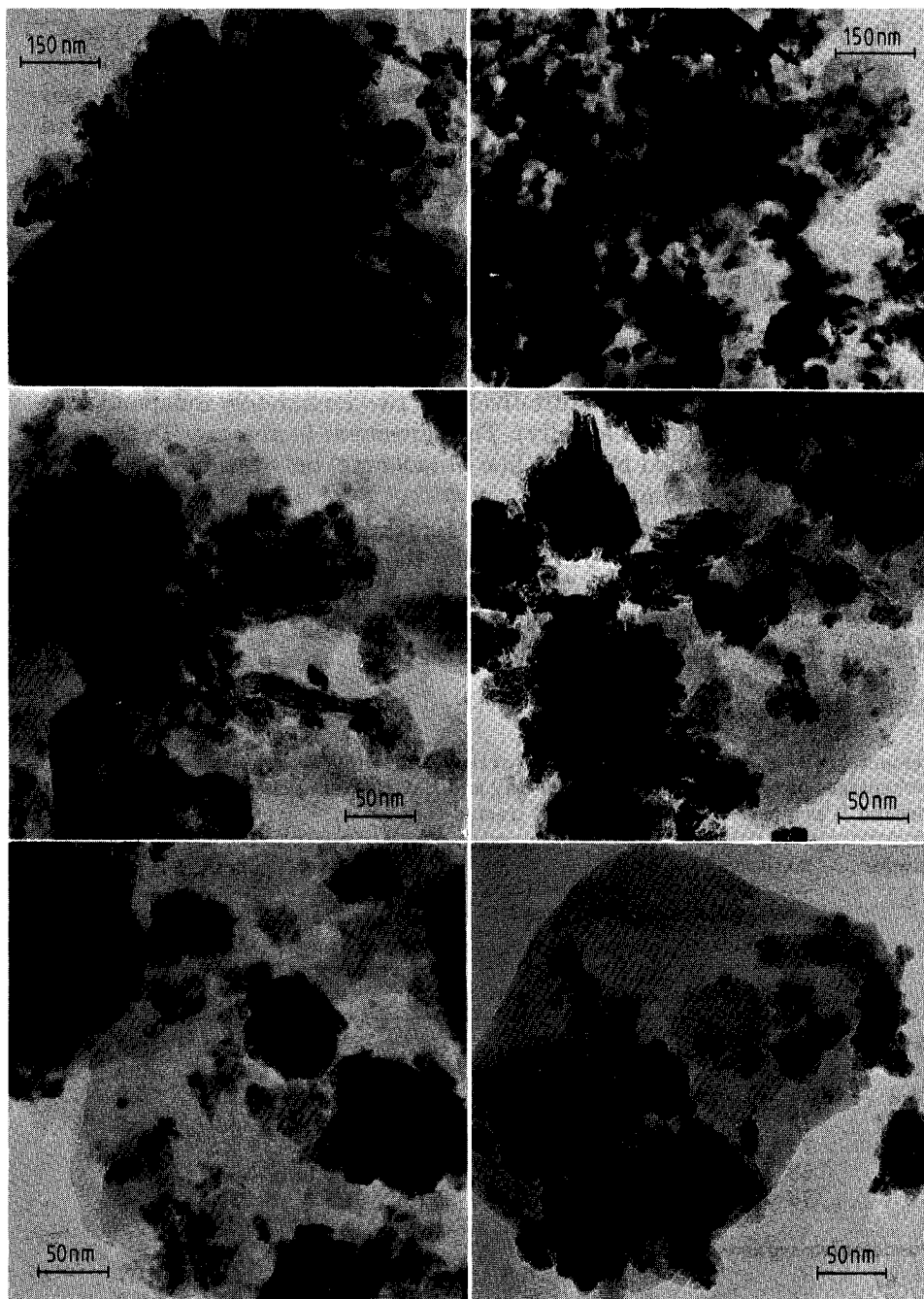


Fig.4. Redness ratings for the clay fractions from the Guadalquivir sequence as a function of EDTA extraction time. See text for explanation of redness rating.

### *Fe-oxide mineralogy*

Electron micrographs of the NaOH-treated clay clearly show the darker Fe-oxide particles as distinct from less-dense silicate clay particles (Fig.5). No definite distinction between goethite and hematite can be made from crystal morphology although particles with an acicular shape are believed to be goethite, whereas, isometrical particules are more likely to be hematite (Schwertmann and Taylor, 1977).



**Fig. 5.** Transmission electron micrographs of NaOH-treated clays from sample T8-2 (left half of plate) and QT-1 (right half).

The goethite:hematite ratios estimated from the  $I_G(111)/I_H(110)$  and from  $(I_G(130)+I_H(104))/I_G(111)$  differ unsystematically by less than 25%. Values in Table III are therefore averages. The percentages of goethite and hematite determined by Method II are very similar to the ones determined by Method I (for goethite  $r = 0.933$  and for hematite  $r = 0.986$ ). Furthermore, the relationship between the content of Fe estimated from the amount of goethite + hematite (with Method II) and  $Fe_d$  of the NaOH treated clay is highly significant (Fig. 6). Ideally, the regression coefficient of this relationship should be unity but is in fact lower ( $b = 0.83$ ). A correlation with  $r = 0.88$  and  $b = 0.94$  was found for an analogous case with goethite and lepidocrocite (Schwertmann and Fitzpatrick, 1977). The results underline the fortunate possibility that, in contrast to clay silicates, crystalline Fe-oxides can be determined quantitatively by two completely independent methods (by XRD and chemically). The agreement increases with the similarity, as determined by XRD line broadening, between Fe-oxides in the standards and in the samples.

Percentages of goethite and hematite remaining after EDTA treatment could not be determined by XRD because the iron oxide contents of the treated samples were too low. However, disappearance of the hematite peaks preceded disappearance of the goethite peaks, a result consistent with the observed decrease in the redness rating (Fig.4).

TABLE III

Percentages of goethite (Gt) and hematite (Hm) calculated by Method I expressed as percentages of crystalline oxides, total clay and NaOH-treated clay, and calculated by Method II as a percentage of the NaOH-treated clay

| Sample                        | Method I              |    |            |     | Method II         |      |                   |      |
|-------------------------------|-----------------------|----|------------|-----|-------------------|------|-------------------|------|
|                               | crystalline Fe-oxides |    | Total clay |     | NaOH-treated clay |      | NaOH-treated clay |      |
|                               | Gt                    | Hm | Gt         | Hm  | Gt                | Hm   | Gt                | Hm   |
| <i>Esla sequence:</i>         |                       |    |            |     |                   |      |                   |      |
| T3-3                          | 93                    | 7  | 8.4        | 0.6 | 13.8              | 1.0  | 16.6              | 2.5  |
| T8-2                          | 71                    | 29 | 5.8        | 2.4 | 10.8              | 4.4  | 11.7              | 6.0  |
| T10-2                         | 78                    | 22 | 6.5        | 1.9 | 11.8              | 3.4  | 14.5              | 4.6  |
| T20-2                         | 74                    | 26 | 6.5        | 2.4 | 15.1              | 5.5  | 17.5              | 7.6  |
| SP-2                          | 58                    | 42 | 5.6        | 4.1 | 15.0              | 10.9 | 13.9              | 11.9 |
| P-2                           | 75                    | 25 | 6.9        | 2.3 | 21.0              | 7.0  | 22.4              | 9.6  |
| <i>Guadalquivir sequence:</i> |                       |    |            |     |                   |      |                   |      |
| EL-2                          | 81                    | 19 | 2.3        | 0.5 | 4.3               | 1.0  | 5.5               | 1.7  |
| GU-6                          | 88                    | 12 | 4.2        | 0.6 | 9.5               | 1.3  | 9.5               | 2.2  |
| EA-1                          | 59                    | 41 | 2.9        | 2.0 | 8.0               | 5.5  | 7.3               | 6.3  |
| BO-1                          | 41                    | 59 | 2.5        | 3.6 | 12.8              | 18.4 | 10.2              | 16.4 |
| QT-1                          | 56                    | 44 | 4.2        | 3.3 | 22.0              | 17.2 | 19.7              | 17.0 |

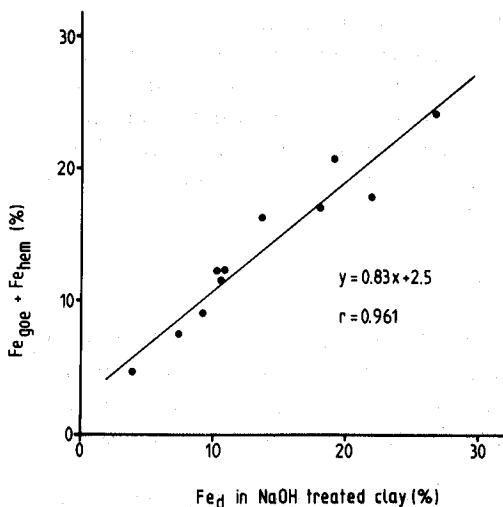


Fig.6. Correlation between the sum of goethite-Fe ( $Fe_{goe}$ ) and hematite-Fe ( $Fe_{hem}$ ) as determined by XRD using Method II and percent  $Fe_d$  in the NaOH-treated clay.

For the Esla sequence no clear trend in the amounts of goethite and hematite with increasing age of terrace is evident (Table III). If, as postulated earlier, weathering was already advanced at the time of deposition, the goethite:hematite ratio might have been partly determined by the pedoclimate in the source area. Therefore, further changes in situ cannot be clearly detected.

In the Guadalquivir sequence the amounts of both goethite and hematite increased with increasing age of terrace (Table III) but the relative increase of hematite is greater than that of goethite. This suggests that from the Fe released, relatively more hematite than goethite was formed with time, indicating a pedoclimate favourable to hematite. Only in the highest terrace soil, QT-1, does the hematite content not increase further probably due to the somewhat moister, hydromorphic conditions observed in this profile.

The reasons for hematite formation being favored over goethite formation could be as follows. Hematite appears to have ferrihydrite as a necessary precursor which, through internal rearrangement and dehydration converts to hematite (Fischer and Schwertmann, 1975). In the dry and warm soils of the xeric moisture regime in the Mediterranean region, the formation of hematite is favored because: (1) organic matter is rapidly decomposed and therefore Fe released from silicates is not organically complexed but is precipitated as ferrihydrite; and (2) a higher temperature accelerates the dehydration of ferrihydrite to hematite. Inversely, in moister and cooler soils, hematite is suppressed in favour of goethite because: (1) more organic matter is present, which complexes the Fe and suppresses ferrihydrite formation; and (2) if ferrihydrite is formed, lower temperatures retard its dehydration. This then favours transformation via solution to goethite.

TABLE IV

Position and corrected width at half height (WHH) of the goethite (111) and hematite (110) peaks: Al substitution in the Fe-oxides calculated from XRD peak positions and determined from DCB extracts of NaOH-treated clays with no previous EDTA treatment and with EDTA treatments of 12 and 18 h

| Sample                        | Goethite (111) |         |                  | Hematite (110) |           |                  | Aver. Al substitution in Fe-oxides (mole %) |             |          |          |
|-------------------------------|----------------|---------|------------------|----------------|-----------|------------------|---|-------------|----------|----------|
|                               | d (Å)          | WHH °2θ | Al sub. (mole %) | d (Å)          | WHH (°2θ) | Al sub. (mole %) | Calc. # <sup>1</sup>                        | before EDTA | 12h EDTA | 18h EDTA |
| <i>Esla sequence:</i>         |                |         |                  |                |           |                  |   |             |          |          |
| T3-3                          | 2.445          | 0.52    | 6                | 2.521          | 0.28      | 0                | 5.6   | 10.8        | 10.3     | 11.0     |
| T8-2                          | 2.442          | 0.60    | 9                | 2.517          | 0.54      | 3                | 7.3   | 12.0        | 10.0     | 9.6      |
| T10-2                         | 2.442          | 0.38    | 9                | 2.518          | 0.28      | 3                | 7.7   | 10.1        | 9.6      | 9.0      |
| T20-2                         | 2.439          | 0.50    | 11               | 2.520          | 0.50      | 0                | 8.1   | 11.7        | 12.4     | 12.7     |
| SP-2                          | 2.440          | 0.50    | 10               | 2.517          | 0.50      | 3                | 7.1   | 8.0         | 11.3     | 11.8     |
| P-2                           | 2.434          | 0.48    | 15               | 2.517          | 0.56      | 3                | 12.0  | 12.7        | 15.0     | 14.5     |
| <i>Guadalquivir sequence:</i> |                |         |                  |                |           |                  |   |             |          |          |
| E1-2                          | 2.446          | 0.83    | 6                | 2.521          | 0.16      | 0                | 4.9   | 11.1        | 13.1     | 13.5     |
| GU-6                          | 2.445          | 0.61    | 6                | 2.520          | 0.30      | 0                | 5.3   | 10.4        | 10.9     | 11.9     |
| EA-1                          | 2.439          | 0.70    | 11               | 2.517          | 0.42      | 3                | 7.7   | 7.9         | 15.6     | 15.8     |
| BO-1                          | 2.437          | 0.52    | 12               | 2.515          | 0.38      | 5                | 7.9   | 7.4         | 11.3     | 13.2     |
| QT-1                          | 2.435          | 0.38    | 14               | 2.517          | 0.37      | 3                | 9.2   | 7.4         | 13.0     | 14.0     |

\*<sup>1</sup> Calculated average substitution using Al substitution values from XRD peak positions and percent goethite and hematite as determined by Method I (Table III).

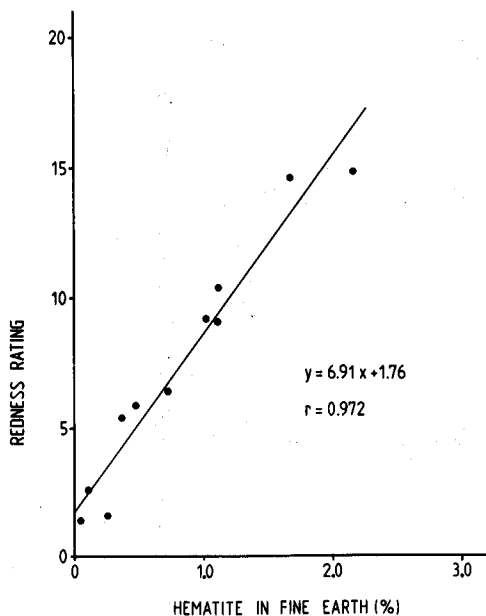


Fig. 7. Correlation between redness rating and percent hematite in the fine earth.

redness and hematite content was recently established for New Zealand soils (Childs et al., 1978).

## CONCLUSIONS

In the Esla sequence, the uniformly high  $Fe_d/Fe_t$  ratios and the absence of clear trends in Fe-oxide properties with time indicate that the original terrace sediments were highly weathered before deposition. Subsequent pedogenic weathering has therefore had little effect on the overall Fe-oxide properties.

In the Guadalquivir sequence, the release of Fe from primary minerals by weathering of relatively unweathered parent materials and its subsequent oxidation has resulted in a net increase in the amount of Fe-oxides and an increase in the  $Fe_d/Fe_t$  ratio with time. A relative increase in hematite over goethite indicates that the environment favors the formation of hematite. The iron oxides, particularly goethite, become more crystalline with increasing pedogenic age. Increasing Al substitution in both goethite and hematite, as determined by XRD line shift, most likely reflects a decrease in the soil pH with time.

The results show that detailed analysis of soil Fe-oxides (mineral species, amount, crystallinity, Al substitution) can be useful for soil genesis studies.

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