ANNALI

DELLA FACOLTA' DI AGRARIA DELL'UNIVERSITA'

SASSARI

studi sassaresi

ANNALI

DELLA FACOLTA' DI AGRARIA DELL'UNIVERSITA'

SASSARI

studi sassaresi

Istituto di Chimica Agraria dell'Università di Sassari

(Direttore: Prof. *C. Gessa*)

A. PREMOLI[1] · P. MELIS[1] · C. GESSA[1] · S. DEIANA[2] · M. PETRERA[3]

EFFECTS OF Al SUBSTITUTION ON GOETHITE FORMATION

RIASSUNTO

Alcune goethiti alluminose, sintetizzate in laboratorio, sono state caratterizzate mediante tecniche diffrattometriche, termometriche, spettrometriche e chimiche. La quantità massima di alluminio incorporata nella struttura del minerale era pari a 32.7 moli %. I risultati hanno dimostrato che la presenza dello ione Al^{+} gioca un ruolo fondamentale sulla cristallizzazione della goethite. Per bassi valori di sostituzione il processo risulta favorito, mentre è ostacolato per valori superiori a 10 moli %.
L'aumento della stabilità termica delle goethiti indotto dalla presenza dell'alluminio è contrastato dalla minore cristallinità delle particelle. Infatti, la temperatura del picco endotermico di deidrossilazione del campione contenente 32.7 moli di Al % risulta inferiore a quella del campione contenente 20 moli di Al %. Questo comportamento è confermato dal trattamento con ossalato che, per valori simili di cristallinità, estrae quantità minori di ferro dai campioni a maggior contenuto in alluminio.

ABSTRACT

Goethites containing up to 32.7 mole % Al were synthesized and characterized through diffractometry, spectrometry, DSC and chemical techniques. Results indicate that crystal growth was favoured or hindered depending on the percentage of aluminum incorporated into the structure. Goethites to which 5-10 mole % Al were initially added crystallized best, as shown by the highest crystallite dimensions calculated from X-ray and Mössbauer analyses, and by the lowest surface areas values. Over such substitution degree goethite crystallization was hindered and for sample synthesized in presence of 40 mole % Al the separation of a discrete amount of gibbsite and bayerite occurred.
Both crystallinity and Al-substitution degree influenced the goethite dehydroxylation endothermic peak temperature playing a competitive action in the peak shift. In fact, the increase in the thermal stability induced by the presence of Al^{+} ions into the structure was counteracted by the decrease due to the particle size reduction.
The stabilizing effect of aluminum was confirmed by the oxalate treatment which removed from the Al-free sample a Fe amount higher than that from the sample containing about 20 mole % Al, although both had similar crystallinity.

[1] Istituto di Chimica Agraria, Università di Sassari.

[2] Istituto per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, C.N.R., Sassari.

[3] Istituto di Ricerche Montedison «Donegani», Novara.

INTRODUCTION

During the weathering of primary minerals, iron-predominantly bound in silicates in the reduced state-is released and successively precipitated as oxide or hydroxide. Its formation in soils takes place in presence of a great number of extraneous ions which can be adsorbed or incorporated in the crystal structure, affecting its chemical and physical properties.

The influence of extraneous ions on Fe-hydroxide crystallization has been studied by several researchers (Norrish & Taylor, 1961; Thiel, 1963; Lewis & Schwertmann, 1979; Nalovic et al., 1975). Among these ions, Al^{3+} has particular importance being widely diffused in soils. Taylor & Schwertmann (1978) found that at pH 5.5-7.0 under N_2 the goethite formation is favoured by the presence of Al at $Al/(Al + Fe)$ levels between 0.09 and 0.30. Highly Al-substituted goethites were synthesized by Fey & Dixon (1981) through rapid oxidation of mixed $FeCl_2$-$AlCl_3$ solutions at pH 6.8 in presence of CO_2. This procedure is particularly interesting allowing a substitution degree up to 33 mole % Al, value similar to that found in some natural goethites (Fitzpatrick & Schwertmann, 1982).

In this paper the influence of Al substitution on goethite properties was investigated through diffractometry, spectrometry, DSC and chemical techniques.

MATERIALS AND METHODS

Goethites were synthesized by the method of Schwertmann (1959). $FeCl_2$ and $AlCl_3$ solutions were mixed to give different $Al/(Al + Fe)$ molar ratios and kept at pH-stat 6.8 under an O_2:CO_2 gas mixture. When complete oxidation was reached, the suspensions were adjusted to pH 6.0, dialysed for an appropriate period and finally lyophylized.

X-ray powder diffraction analysis was carried out on samples heated to 110°C under vacuum for 24 hours, using a Philips X-ray diffraction unit PW 1730 with CoK_α radiation at rates of 0.25° 2θ/min. The goniometer was carefully aligned according to the manufacturer's instructions. The 2θ scale was calibrated using a standard silicon powder specimen, which was also employed as internal standard.

DSC and TG measures were obtained with a Mettler TA 3000 instrument, equipped with a TG 10 TA processor unit for evaluating and analyzing the thermal data. An empty aluminum sample pan was used as reference material. A heating rate of 10°/min was employed. The melting constants of indium were used as standards in the DSC experiments. Samples to be subjected to thermal analyses were equilibrated in a $Mg(NO_3)_2$ atmosphere.

Surface area was determined by the B.E.T. method; the programmed measurements were elaborated by a Commodore CBM mod. 8032 computer controlling a C. Erba sorptomatic apparatus.

A few mgs of material, dispersed by sonification in 1-2 ml of distilled water were dried on Formvar coated grids for examination with a Zeiss electron microscope mod. 109.

Mössbauer spectra were recorded at 298 and 77°K using an Elscint AME-40C spectrometer with constant acceleration and 57 Co(Rh) source. Velocity calibration was made using a high-grade metallic iron foil. The experimental data were fitted with Lorentzian components by a least squares fit computer program.

IR spectra were recorded on KBr pellets with a Beckman 4250 spectrophotometer. For selective dissolution analyses 0.1 gs of sample were treated with acidified ammonium oxalate (5mg/2ml) according to the method reported by Schwertmann (1964): dissolved Fe (Fe_o) and Al were determined using a plasma spectrophotometer mod. SMI IV. The same apparatus was employed to measure total Fe and Al content.

RESULTS AND DISCUSSION

The chemical composition of the synthesized products is reported in table 1.

From X-ray diffractograms it appears that Fe^{3+} has been precipitated as goethite (Fig. 1). Reflections at 21.20 and 21.90 2θ in sample n. 5 indicate the crystallization of pure Al phases, respectively gibbsite and bayerite.

The numbers of reflections and their intensity vary with the molar composition of the samples and are indicative of the different rate of crystallization induced by Al^{3+} ions. In fact, samples to which 5 and 10 mole % Al were added crystallized best, as indicated by the sharpness of all the peaks. On the contrary, goethites

Table 1 Chemical composition and Al/(Al + Fe) molar ratios of synthetic Al-goethites
Composizione chimica e rapporti molari Al/(Al + Fe) delle Al-goethiti sintetiche

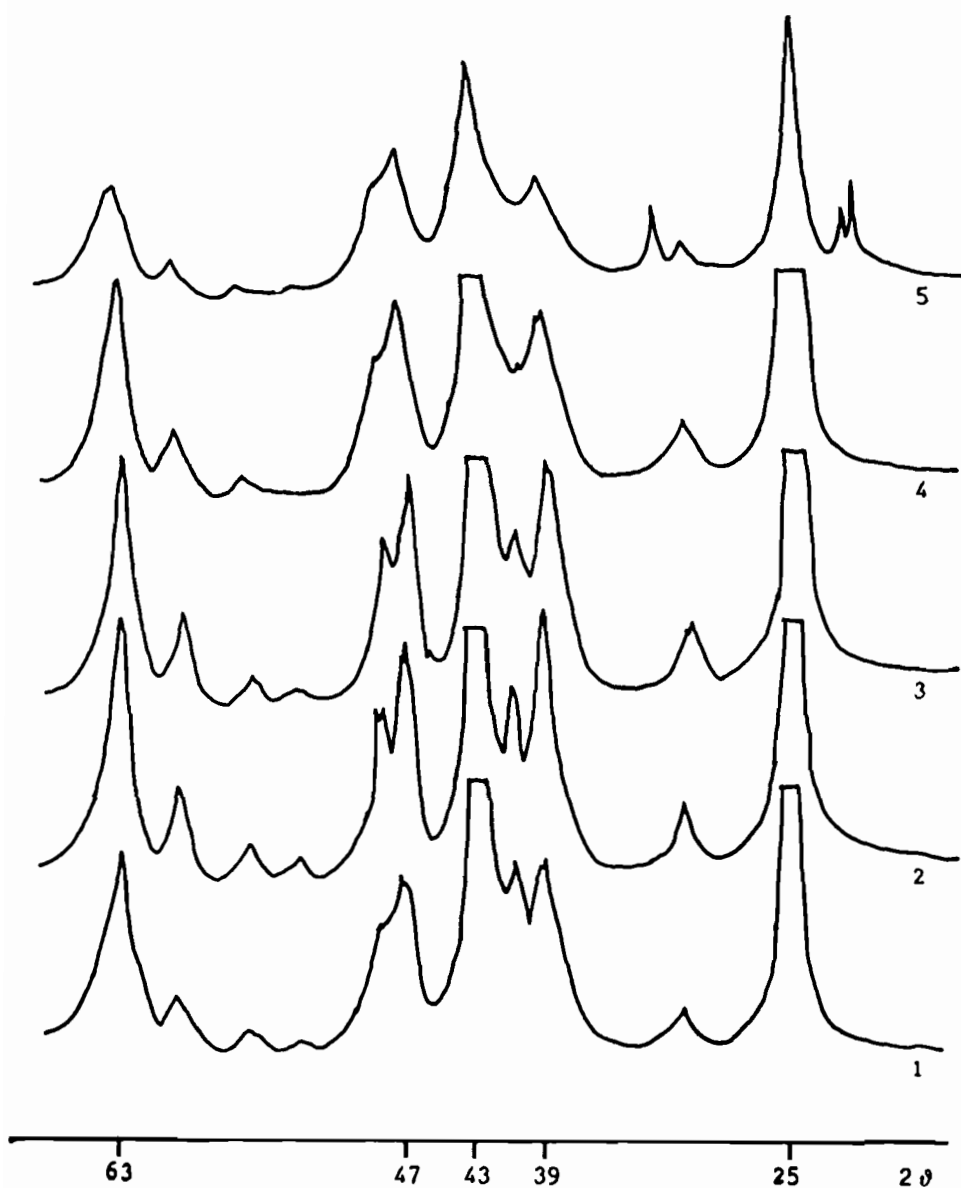| Sample	Chemical composition				X-ray analysis		IR spectroscopy		
	Fe_2O_3 %	Al_2O_3 %	H_2O %	Al/(Al + Fe) mole %	d... Å	Al/(Al + Fe) mole %	δOH cm⁻¹	νOH cm⁻¹	O_2 cm⁻¹
1	76.3	—	23.2	0.0	2.454	0.0	893	795	465
2	75.8	2.6	21.0	5.1	2.447	5.1	—	—	—
3	72.8	5.7	22.7	11.0	2.438	11.6	910	804	475
4	64.2	10.4	26.4	20.3	2.427	19.6	918	810	485
5	48.3	21.1	30.4	40.6	2.409	32.7	922	812	490

Fig. 1 - X-ray powder diffractograms of synthetic Al-goethites at 110°C. Numbers identify the samples.
Diffrattogrammi ai raggi X di polveri di Al-goethiti sintetiche a 110°C. I numeri identificano i campioni.

which formed in presence of higher amounts of Al show a progressive lowering of intensity and a broadening of the diffraction peaks with increasing Al content. Further, the rate of substitution, estimated by the shift of the 111 line, as stated by Vegard's law (Klug & Alexander, 1974, page 562) (Tab. 1), shows that nearly all the Al added has been incorporated into the goethite structure in samples n. 2, n. 3 and n. 4, whereas in sample n. 5 it is equal to 32.7 mole % Al; value comparable with that reported by Schwertmann and Taylor (1977) as the probable upper limit of Al tolerable in the goethite structure.

The mean crystallite dimension (MCD) of the synthetic products was calculated from the width at half height (WHH) of the 111 reflection, using the Sherrer equation (Klug & Alexander, 1974, page 687). The values, reported in Fig. 2, indicate the highest MCD of samples and n. 3, demonstrating that the crystallization is favoured by a low Al percentage.

DSC curves are reported in Fig. 3. Sample n. 1 shows a shoulder at about 93°C followed by a strong peak at 100°C attributable to two types of adsorbed water having different affinities for the surface.

The other samples reveal only a dehydration endotherm effect which does not shift, but appears broader and broader with increasing Al content. A second endothermic effect due to the dehydroxylation of the mineral appears in all samples shifting from 217 to 280°C as the Al-substitution increases up to 20 mole % Al. It is broader and more asymmetrical in samples n. 4 and n. 5 probably due to the higher size range of the particles. A decrease in the peak temperature is observed for sample n. 5, where an additional endothermal effect is observed. The latter is attributed to the presence of separated Al phases as confirmed by its reduction following treatment with NaOH (curve 5a) and in agreement with XRD analysis.

By integrating the dehydroxylation peak area measured dynamically, it was possible to estimate a crystallinity index (CI) as follows:

$$CI = \frac{\Delta H}{\Delta H_s} \times 100$$

where ΔH refers to the entalpy of transformation of the synthetic product and ΔH_s to that of a natural goethite used as a standard.

As shown in Fig. 2 the trend of the CI values is similar to that of MCD ones.

The DSC data clearly indicate that the dehydroxylation temperature is strongly affected both by the Al-substitution degree and by the crystallinity indexes, increasing as these two factors increase. The effect of the first factor is particularly clear comparing samples n. 1 and n. 4, which have the same CI and MCD, but a very different temperature of the endothermic peak (217 and 280°C, respectively).

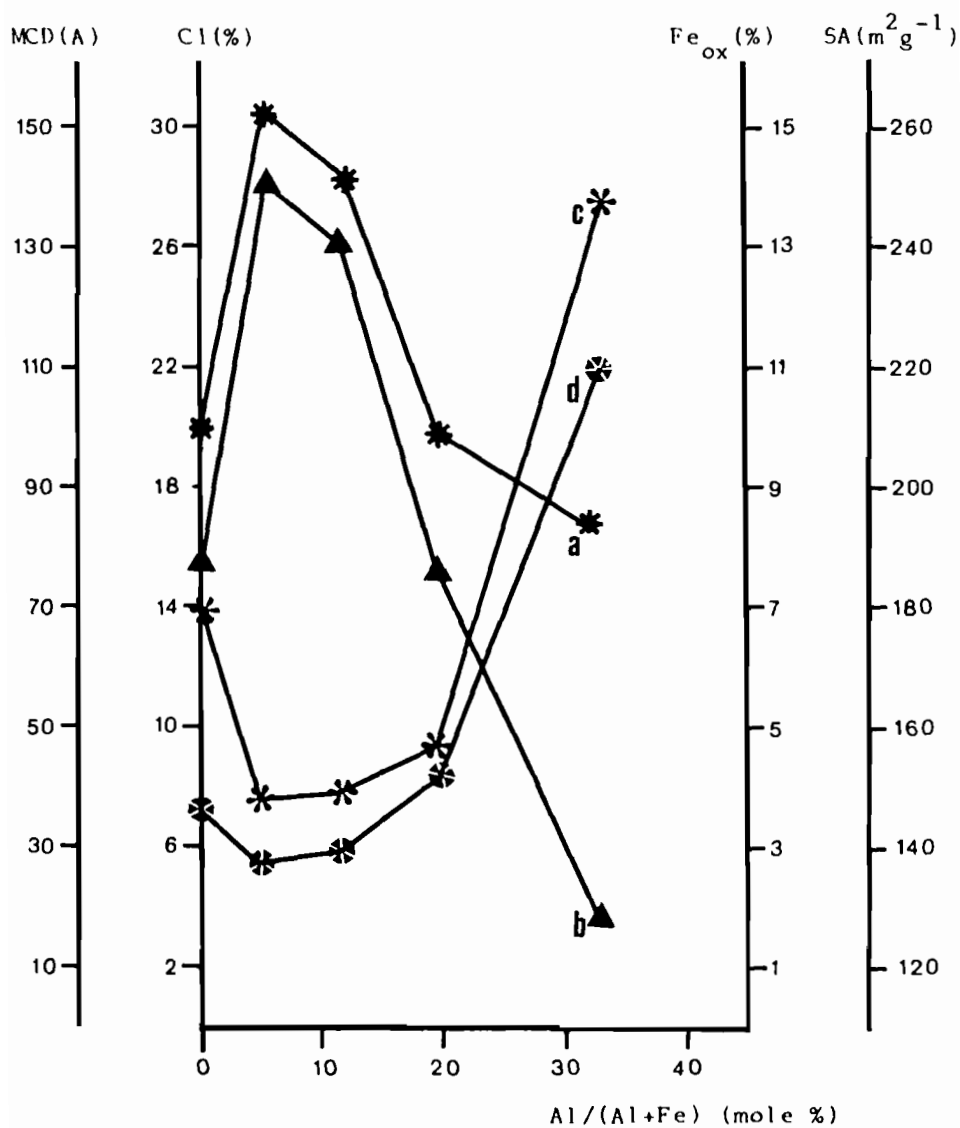Since Al, over a certain substitution degree, hinders crystallization, a competitive

60

Fig. 2 - Relationship of (a) mean crystallite dimension, (b) crystallinity indices (CI), (c) Fe extracted by oxalate treatment (Fe$_{ox}$), and (d) surface area (SA) to composition of sybthetic Al-goethites.

Relazione tra (a) dimensione media dei cristalliti, (b) indice di cristallinità (CI), (c) Fe estratto con il trattamento con ossalato (Fe$_{ox}$), e (d) area superficiale (SA), e composizione delle Al-goethiti sintetiche.
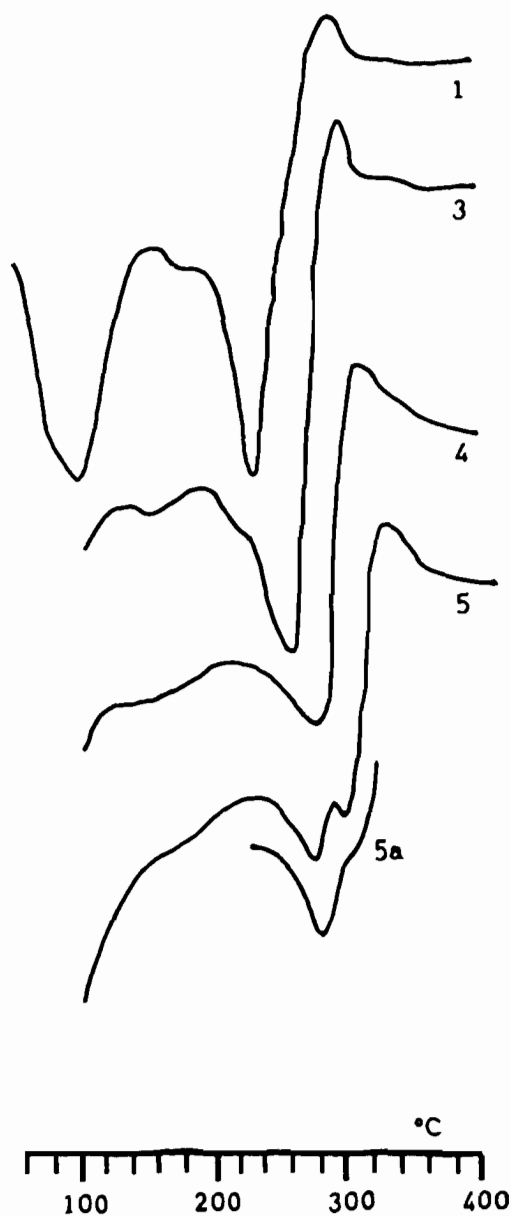
Fig. 3 - DSC curves of synthetic Al-goethites. Numbers identify the sample (a: after NaOH treatment).
Curve DSC delle Al-goethiti sintetiche. I numeri identificano I campioni (a: dopo trattamento con NaOH).

action of the two factors occurs which can cause a decrease of the dehydroxyla-
tion temperature. This is well evident comparing samples n. 4 and n. 5: in fact, the
latter, although having higher Al content (Tab. 1), shows a lower endothermic ef-
fect which has to be connected to its considerably lower CI.

In all samples there is evidence of an exothermic peak immediately following that
of dehydroxylation which has been attributed to the transformation of goethite to
disordered hematite (Rooksby, 1961).

As expected, the Fe_{ox} amount shows a similar trend to that of SA, which is opposi-
te to that of CI. The data suggest that the presence of Al in the goethite structure
increases its stability: the oxalate treatment removed a Fe percentage from sam-
ple n. 4 lower than that from sample n. 1, although both samples had the same
crystallinity. The lowest Fe_{ox} values of samples n. 2 and n. 3 are connected not on-
ly to the substitution effect but also to the decrease in SA.

The stabilizing effect of Al could be only partly due to the shortening of the
H-bonds between OH-groups in the Al-goethite (Schwartzmann & Sparr, 1969;
Schwertmann, 1984), as shown by increased frequency of the major goethite IR
absorption bands (Tab. 1).

The spectrum of sample n. 5 reveals two additional OH-bending bands at 1025 and
975 cm^{-1} and OH-stretching bands at 3620, 3520 and 3430 cm^{-1} (not reported),
which once again confirm that a distinct Al-phase is present.

Of the three parameters which characterize the Mössbauer spectrum, isomer shift
(IS), quadrupole splitting (QS) and magnetic hyperfine field (H_{eff}), only the latter is
diagnostic for Fe(III) oxides and hydroxides because of the relatively large diffe-
rences between the effective internal magnetic fields of such compounds.

At room temperature only a superparagnetic doublet of Fe^{3+} (IS = 0.40 mm s^{-1}; QS
= 0.62 mm s^{-1}) appears in all spectra, whereas at 77°K a magnetically split sextet
attributable to α-FeOOH is registered. For the Al-free sample the H_{eff} value is 472
KOe. A representative Mössbauer spectrum refering to sample n. 5 is reported in
Fig. 4a.

In coprecipitated samples a broadening of the adsorption lines is observed indica-
ting Al for Fe substitution in the goethite structure. The effect of Al-substitution is
well evidenced by the distribution of the H_{eff} values (Fig. 5) calculated from the outer-
most peaks of the experimental spectra which indicate a widening and a shift to lo-
wer field values per increasing Al/(Al + Fe) ratios. In similar cases, Goodman & Le-
wis (1981) showed that it was incorrect to fit the spectra to a single component and
also that the use of two 6-line components was not satisfactory, since in such sam-
ples the magnetic field probably does not have a uniform value throughout. The si-
tuation is further complicated by the superparamagnetic relaxation effects revealed
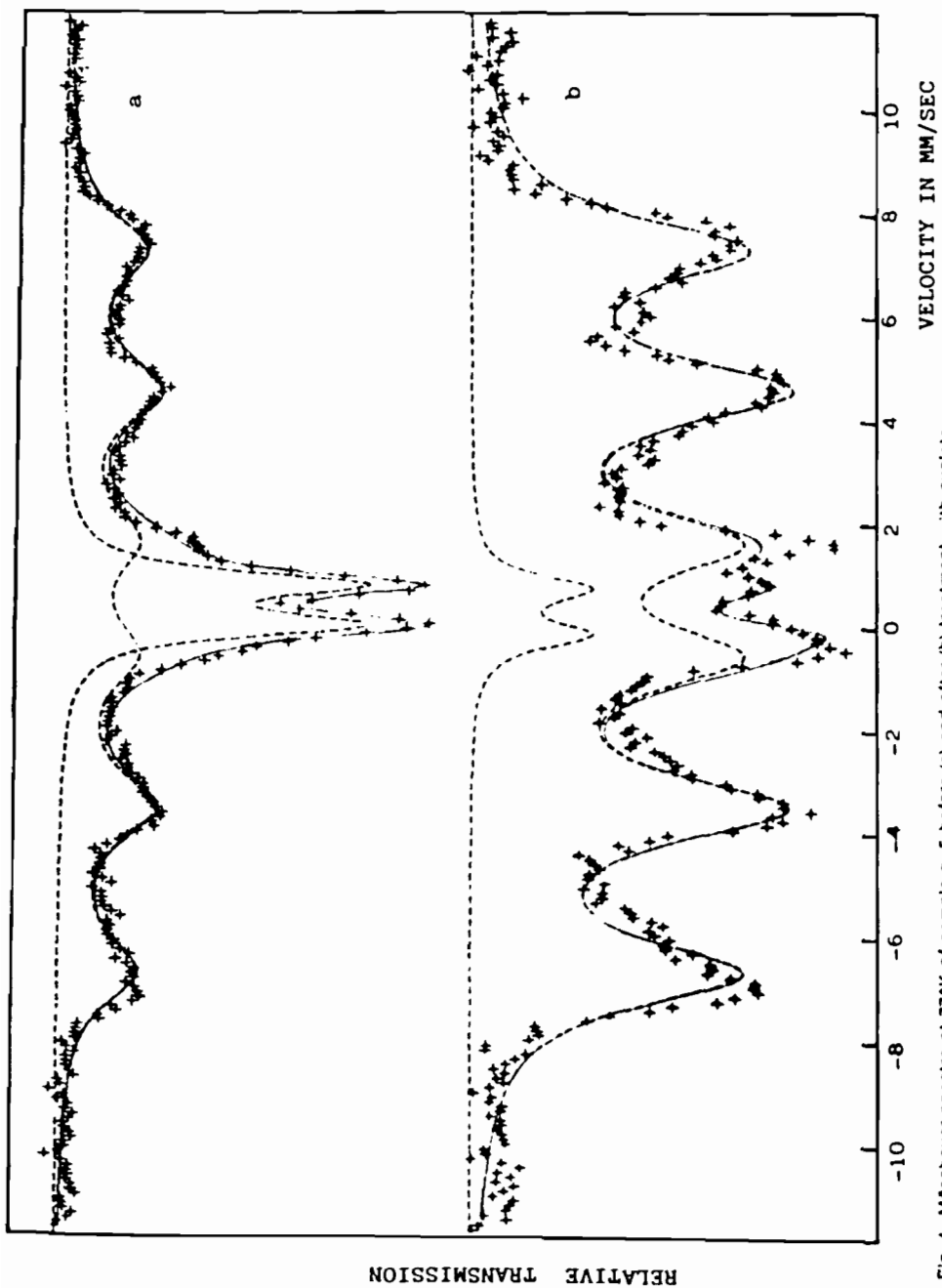by the assence of any magnetic splitting of the spectra at room temperature, contra-

Fig. 4 - Mössbauer spectra at 77°K of sample n. 5 before (a) and after (b) treatment with oxalate.
Spettri Mössbauer a 77°K del campione n. 5 prima (a) e dopo il trattamento con ossalato.
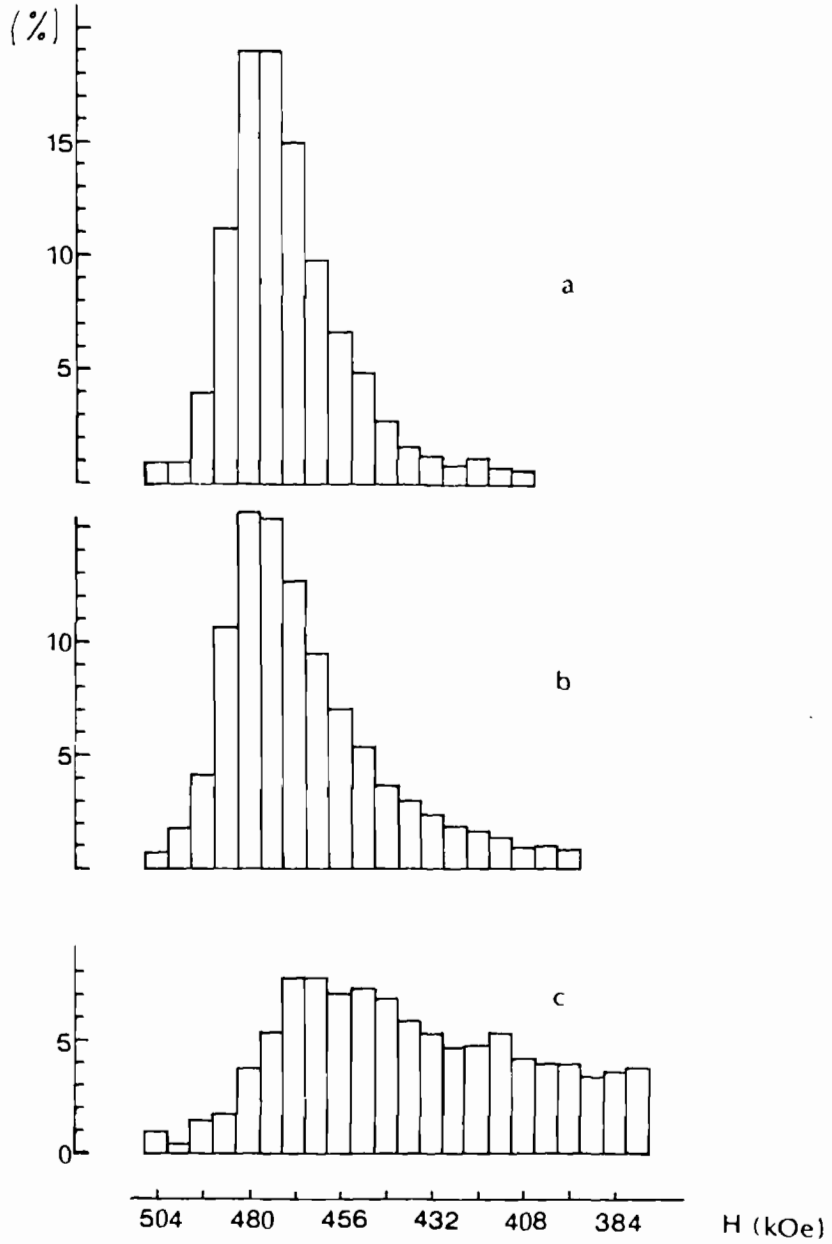
Fig. 5 · H$_{eff}$ value distribution in sample n. 1 (a), n. 3 (b) and n. 5 (c).
Distribuzione del valore H$_{eff}$ nei campioni n. 1 (a), n. 3 (b) e n. 5 (c).

Table 2 Hyperfine field values of Al-substitued goethites at 77°K

Valori del campo iperfine delle goethiti Al-sostituite a 77°K

Sample	H_{app} [a] KOe	H_{calc} [b] KOe	SA m²g	H_{pred} [c] KOe
1	480	472.1(5)	145	482
2	481	473.9(5)	138	476
3	481	473.8(4)	140	467
4	472	561.2(7)	152	455
5	458	434.0(1)	220	429

[a] Obtained from a visual estimate of the position of maximum absorption for the outermost peaks.

[b] Obtained from a computer fit to one magnetically ordered component with the exception of the 40% sample, where also a quadrupole doublet was included. Unacceptable values of χ^2 are found in each case.

[c] Values predicted from the relation H(KOe) = 498-1.36 (%Al) - 0.11 (A) of Golden et al. (1979, where A is the surface area in m² g⁻¹.

ry to that expected for large α-FeOOH particles. The hyperfine field values at 77°K of Al-substituted goethites, estimated in different ways, are summarized in Table 2. The values calculated from computer fits to one 6-line component (H_{calc}) are affected by unaccetable values of χ^2, though they conform reasonably well to those predicted (H_{pred}) by the relation of Golden et al. (1979). This relation, therefore, can not be considered as descriptive of the physical situation because the predicted value represents neither the hyperfine field value of all the particles, nor that of the majority of them, as indicated by a comparison with H_{app}. For these reasons it is concluded that the best description of the physical situation in Al-substituted goethites should be that given in Fig. 5 representing the normalized population of the different H_{eff} values. The distribution is derived from the slope of the outermost peaks of the Mössbauer spectra by assigning to each H_{eff} value a population proportional to the corresponding resonant absorption intensity.

The shift towards relatively lower values of H_{eff} for increasing Al/(Al + Fe) ratio may be due to an increased Al for Fe substitution and/or to a decrease in particle size. It is not easy to distinguish between the two effects also because the particle size is known to decrease for increasing substitution.

In the case of Al-substitution up to 10% the XRD analysis shows that the mean particle size increases in respect to pure α-FeOOH. This is confirmed by the Mössbauer analysis since the distribution of H_{eff} in sample n. 3 is very similar to that of pure α-FeOOH. A similar result can only be explained by the fact that an H_{eff} decrease due to Al-substitution is compensated by an H_{eff} increase caused by the large particle size.

Oxalate treatment does not modify to a significant degree the Mössbauer spectra for samples with Al/(Al + Fe) ≤ 0.2. Only slight variations in the distribution of the hyperfine field values were observed, indicating that oxalate may remove some of
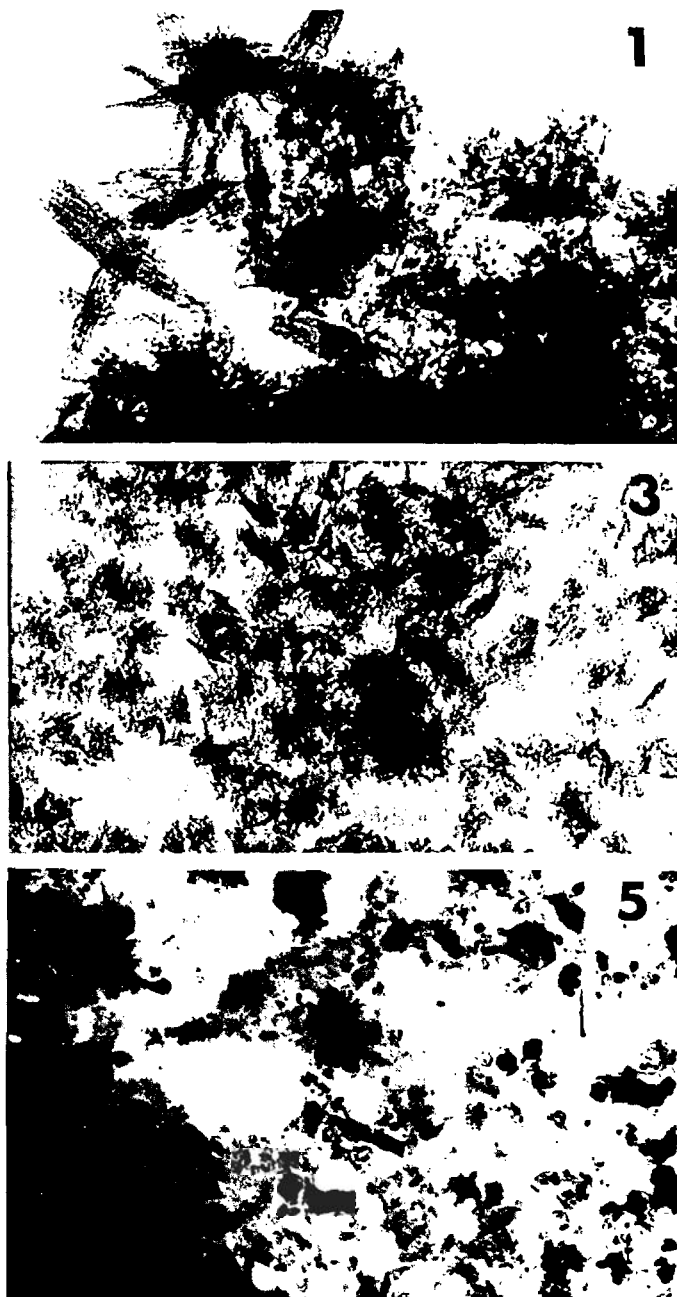
Fig. 6 - Transmission electron micrographs of synthetic Al-goethites. Numbers identify the sample.
Fotografie al microscopio elettronico delle Al-goethiti. I numeri identificano il campione.

the smallest crystals. The effect of oxalate extraction on sample n. 5 is shown in Fig. 4b: the central Fe^{3+} doublet, usually attributed to amorphous phases or to very small Al-substituted particles — still superparamagnetic at 77°K — is strongly reduced. In samples with $Al/(Al + Fe) \leq 0.2$ the iron extracted by oxalate may therefore come either from small amounts of amorphous phases, not detected by Mössbauer and XRD, or from the magnetically ordered particles of Al-goethites, in agreement with the findings of Goodman and Lewis (1981).

Some electron micrographs of the synthesized products are reported in Fig. 6. The morphology of Al-free sample is typical of goethite, showing the material to be composed of needle-like crystals oriented parallel to the z axis. They appear to be striped in the same direction indicating a distinct substructure as suggested by Galbraith et al. (1979) but which has not yet been satisfactorily explained.

Sample n. 5 shows some evidence of the separation of a discrete Al phase crystallized as gibbsite and bayerite. No incipient lath or needle formation was observed relative to the iron phase which was characterized by irregular clusters of near spherical particles. However, the electron diffraction (not reported) identified a goethite structure although the reflections were weaker and more diffuse than those of the other patterns.

In samples n. 3 and n. 4 the acicular morphology is still evident, even if it appears partially disrupted as a result of the Al-substitution. These observations are not to be considered in contrast with those reported above because they seem to concern how crystallites organize into aggregates. Micrographs suggest that Al-substitution, either favouring or hindering the growth of crystallites, lowers the affinity between the surfaces limiting, therefore, the aggregate formation.

REFERENCES

FEY M.V. and DIXON J.B., 1981 · Synthesis and properties of poorly crystalline hydrated aluminous goethites. Clays and Clay Min. 29, 91-100.

FITZPATRICK R.W. and SCHWERTMANN U., 1982 · Al-substituted goethite · an indicator of pedogenic and other weathering environments in South Africa. Geoderma 27, 335-347.

GALBRAITH S.T., BAIRD T. and FRYER J.R., 1979 · Structural changes in β-FeOOH caused by radiation damage. Acta Crystallogr. A35, 197-200.

GOLDEN D.C., BOWEN L.H., WEED S.B. and BIGHAM J.M., 1979 · Mössbauer studies of synthetic and soil-occurring aluminium-substituted goethite. Soil Sci. Soc. Am. J. 43, 802-808.

GOODMAN B.A. and LEWIS D.G., 1981 · Mössbauer spectra of aluminous goethites (α-FeOOH). J. Soil Sci. 32, 351-363.

KLUG H.P. and ALEXANDER L.E., 1974 · X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 2nd ed., Wiley, New York.

LEWIS D.G. and SCHWERTMANN U., 1979 · The influence of aluminium on the formation of iron oxides. IV. The influence of [Al], [OH] and temperature. Clays and Clay Min. 27, 195-200.

NALOVIC L., PEDRO G. and JANOT C., 1975 - Demonstration by Mössbauer spectroscopy of the role played by transitional trance elements in the crystallo-genesis of iron hydroxides. 3° Proc. Int. Clay Conf. Mexico City, 601-610.

NORRISH K. and TAYLOR R.M., 1961 - The I isomorphous replacement of iron by aluminum in soil goethites. J. Soil Sci. 12, 294-306.

ROOKSBY H.P., 1961 - Oxides and hydroxides of aluminum and iron. Pp. 354-392 in: The X-ray Identification and Crystal Structures of Clay Minerals (G. Brown editor). Mineralogical Society, London.

SCHWARTZMANN E. and SPARR H., 1969 - Die Wasserstoff-brückenbindung in Hydroxiden mit Diaspor-structur: Z. Naturforsch. 24b, 8-11.

SCHWERTMANN U., 1964 - Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalate-Lösung. Z. Pflanzenernaehr. Duend. Bodenkd. 105, 194-202.

SCHWERTMANN U. and TAYLOR R.M., 1977 - Iron oxides. Pp. 145-180 in: Minerals in Soil Environments (J.B. Dixon and S.B. Weed editors). Soil Sci. Soc. Am., Medison, Wisconsin.

TAYLOR R.M. and SCHWERTMANN U., 1978 - The influence of Aluminum on iron oxides. Part I. The influence of Al on Fe oxide formation from the Fe(II) system. Clays and Clay Min. 26, 373-383.

THIEL R., 1963 - Zum system α-FeOOH· α-AlOOH. Z.Anorg. Allg. Chem. 326, 70-78.