

## CHARACTERIZATION OF GOETHITE AND HEMATITE IN A TUNISIAN SOIL PROFILE BY MÖSSBAUER SPECTROSCOPY

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**Abstract**—As part of the characterization of a Tunisian red soil profile, six samples, taken at different depths, were investigated by Mössbauer spectroscopy at room temperature and at 80 K to obtain information about the various types of Fe oxides present. By considering magnetic hyperfine field distributions, the spectra of goethite and hematite were well resolved. Chemical analyses of the samples revealed a partial substitution of Fe by Al and Mn. The spectral behavior of the goethite was predominantly influenced by crystallinity and amount of Al substitution which resulted in a reduction of the magnetic hyperfine field. The effect of Mn substitution was much more pronounced in the hematite spectrum as a consequence of a stronger suppression of the Morin transition by Mn than by Al.

**Key Words**—Aluminum, Goethite, Hematite, Iron, Manganese, Mössbauer spectroscopy, Soil.

### INTRODUCTION

Mössbauer spectroscopy is a useful tool for the characterization of iron minerals in soils and clays, and, when used in conjunction with chemical and X-ray powder diffraction analyses, can provide a quantitative estimate of the iron content of various species present in an unknown sample (see, e.g., Bancroft, 1973). One source of error in such analyses is that the Mössbauer recoilless fraction of goethite ( $\alpha$ -FeOOH) may differ from specimen to specimen and seems to be indirectly related to the water content of the mineral (Chambaere *et al.*, 1984). An even larger error may result from an incorrect interpretation of the spectrum. For example, many iron species in soils, goethite in particular, are poorly crystalline, and effects due to small crystallite size lead to an asymmetric distribution of the magnetic hyperfine field and reduce its average value (Mørup *et al.*, 1983). Al-substitution also introduces line broadening and a reduction of the average magnetic hyperfine field (Golden *et al.*, 1979; Goodman and Lewis, 1981; Fysh and Clark, 1982; Murad and Schwertmann, 1983).

Although goethite and hematite have different average hyperfine fields, the area under the sextets of both phases cannot be accurately determined from an analysis of only a few sextets having Lorentzian shape. The outer steep flanks of the asymmetric goethite peaks are usually not satisfactorily described, resulting in an underestimation of the hematite content of the sample. Only for samples containing poorly crystalline goethite or goethite with substantial Al substitution, resulting in a goethite doublet at room temperature, is the hematite sextet well resolved. For all other samples, mea-

surements must be made of low-temperature spectra (4 K) in which asymmetric line broadening due to small-crystallite effects are largely reduced. Unfortunately, most applied Mössbauer spectroscopy is performed at room temperature or at about 80 K using liquid nitrogen. At 80 K the asymmetry of the goethite peaks is perceptible and increases with increasing temperature. At room temperature the broadening may be so pronounced that a conventional fit with a limited number of Lorentzians is not practicable. To obtain valid results from such spectra the distributions of the hyperfine parameters must be considered. Murad (1982) showed that the spectra of goethite can be satisfactorily described by a distribution of magnetic hyperfine fields, assuming that the isomer shift and quadrupole splitting are not affected by the crystalline imperfections.

In the present paper, a Mössbauer study of Tunisian soil samples is presented wherein it is shown that even from room-temperature spectra containing broad and asymmetric peaks, reasonable qualitative and quantitative results can be obtained if the spectra are analyzed in terms of hyperfine field distributions. The merit of such an approach has also been demonstrated for synthetic Al-substituted goethite-hematite mixtures by Amarasiriwardena *et al.* (1986).

### MATERIALS AND METHODS

The samples were collected at different depths in a red soil in northwestern Tunisia (near Tamera, about 100 km west of Tunis). The area is presently covered with a degraded cork oak forest. The parent material (sample 198) is a red hematitic iron core, covered with a yellow crust that consists mainly of goethite and clay. The macroscopic characteristics of the samples are:

Table 1. Dithionite-citrate-bicarbonate (DCB) extractable Fe, Al, and Mn and oxalate-extractable Fe and Mn in Tunisian soil samples.<sup>1</sup>

Sample	DCB			Oxalate		Fe(ox)/Fe(DCB)
	Fe	Al	Mn	Fe	Mn	
201S	16.81 (0.888)	0.96 (0.105)	0.12 (0.007)	0.31	0.13	0.02
201H	53.60 (0.936)	1.41 (0.051)	0.73 (0.013)	0.31	0.37	0.01
200	29.84 (0.906)	1.41 (0.089)	0.17 (0.005)	0.21	0.12	0.01
199	49.57 (0.955)	0.98 (0.039)	0.29 (0.006)	0.17	1.17	0.01
198Y	35.20 (0.887)	1.31 (0.068)	1.76 (0.045)	0.36	7.66	0.01
198R	59.76 (0.963)	0.32 (0.011)	1.63 (0.026)	0.22	0.28	0.01

<sup>1</sup> All values are wt. %; values between brackets are atomic fractions relative to total amount of Fe + Al + Mn.

*Sample 201.* Between 30 and 80 cm depth; 2.5 YR 4/6 red; aggregate of very coarse, hard fragments (sub-sample 201H) and softer, millimeter-sized aggregates (sub-sample 201S).

*Sample 200.* Between 80 and 120 cm depth; 2.5 YR 3/6 dark red, weakly developed, subangular blocky structure; hard when dry.

*Sample 199.* Between 120 and 180 cm depth; 10 YR 6/8 brownish yellow, with 5 YR 4/8 yellowish red mot-tles; massive; hard when dry.

*Sample 198.* At about 190 cm depth; 10 R 3/2–3/6 dusky red hard material (sub-sample 198R) covered with a 7.5 YR 6/8 reddish yellow, clayey crust (sub-sample 198Y) containing purplish black manganese oxides.

The samples were dried at room temperature and ground in a ball mill. Total iron oxides were determined by the dithionite-citrate-bicarbonate (DCB) extraction method (Mehra and Jackson, 1960); oxalate-soluble iron and manganese was determined after Schwertmann (1964). The extracts were analyzed colorimetrically for iron using sulfosalicylic acid. Al and Mn concentrations were measured by atomic absorption spectroscopy. The results are given in Table 1. The negligible oxalate-iron extractability suggests the lack of ferrihydrite in all the samples.

X-ray powder diffraction revealed the presence of goethite in all samples. Only in samples 198R and 201S could the hematite reflections be unambiguously determined. Reflections of quartz were observed in the

untreated samples 201H, 201S, and 200, and sample 198Y shows intense reflections of the zinc-manganese oxide, chalcophanite (JCPDS Powder Diffraction File 15-807). After DCB treatment reflections of kaolin-group minerals, mica and quartz were noted in the XRD pattern of all the samples.

Mössbauer spectra were collected on a conventional constant-acceleration spectrometer. A <sup>57</sup>Co source in Rh matrix with an activity of about 20 mCi was used. Velocity calibration was obtained with iron foil as a reference absorber. Absorbers of the six samples were made with a thickness of about 10–20 mg Fe/cm<sup>2</sup>. Spectra were run until the number of off-resonance counts per channel reached about 10<sup>6</sup> (unfolded). Low-temperature measurements were carried out in a continuous-flow cryostat with a stability of 0.1 K.

The Mössbauer spectra were analyzed using a computer program which took the distributions of the hyperfine parameters into account. The fitting procedure was based on the method of Wivel and Mørup (1981), which was extended so that it could be applied to each sextet or doublet component. In this method the experimental spectrum of each component was fitted by a sum of Lorentzian sextets or doublets for which the intensities were derived from a constrained linear least-squares algorithm. Other parameters, such as isomer shift ( $\delta$ ), line-area ratios, and quadrupole splitting ( $2\epsilon_Q$ ) for a magnetically ordered component, were obtained from a combination of the least-squares method by means of an iteration procedure. The least-squares method implied the inversion of a  $N \times N$  matrix in which  $N$  is the total number of basic Lorentzian sextets or doublets. For multiple components,  $N$  was in the range 50–100; thus, the fitting was very time consuming when the iteration was carried through. To save computing time, the iteration procedure was omitted. Indeed, reliable values of the isomer shift and the quadrupole splitting were obtained from fitting a few sextets to the spectra using a conventional procedure (e.g., Chrisman and Tumolillo, 1971). Further, the line area ratio was assumed to be 3:2:1, which seemed to be a good approximation for both goethite and hematite fractions.

## RESULTS AND DISCUSSION

The Mössbauer spectra at 80 K (Figure 1) are mainly composed of two sextets which can be attributed to goethite and hematite. They exhibit rather sharp lines which at first glance have symmetrical shape; however, fitting the spectra with magnetic hyperfine field distributions reveals the asymmetric character of the lines. The results of the fitting, together with the relative

Figure 1. Mössbauer spectra of Tunisian soil samples at 80 K and the corresponding magnetic hyperfine field distribution of goethite (left) and hematite (right).

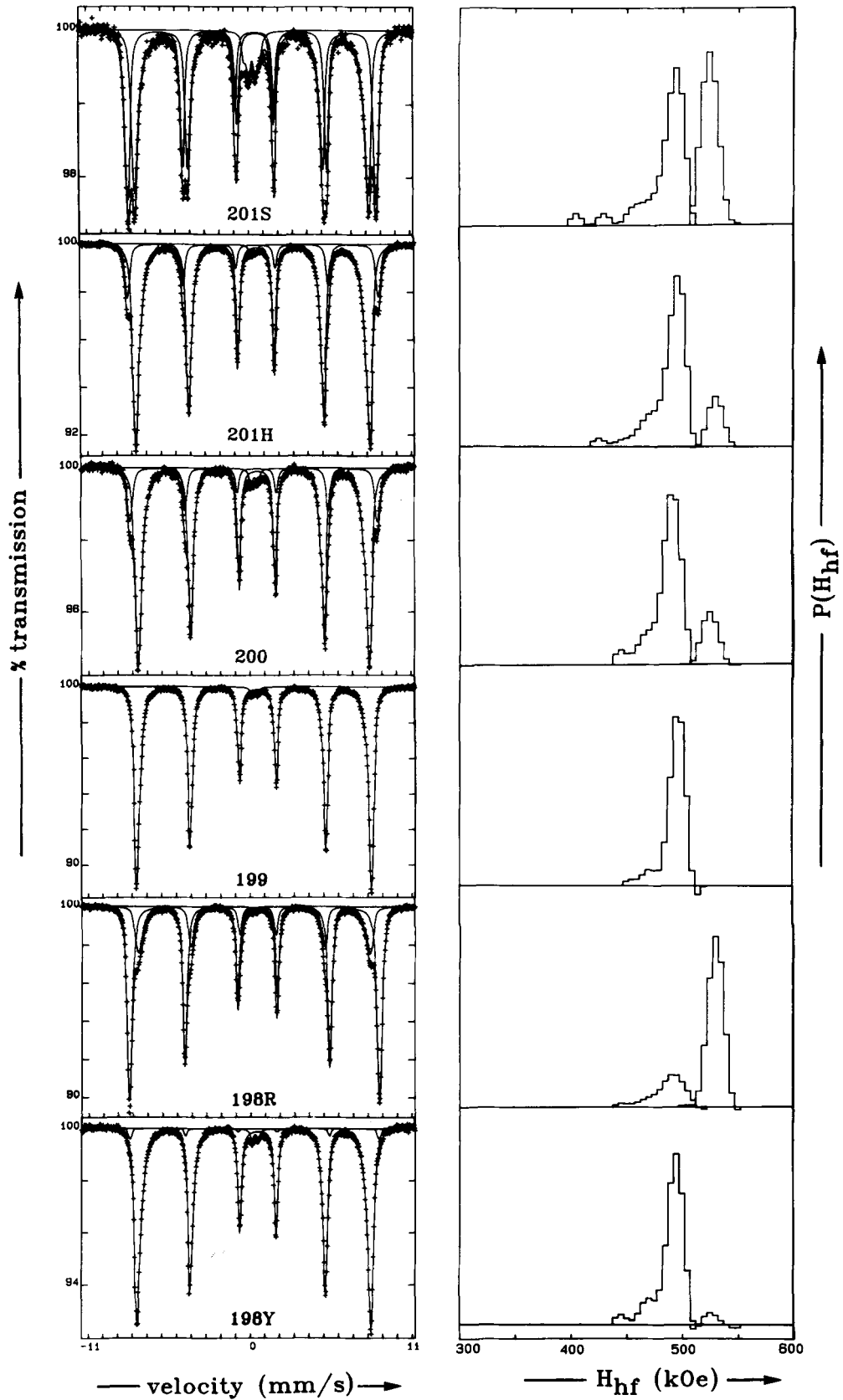


Table 2. Average magnetic hyperfine field ( $H_{\text{hf}}$ ), quadrupole splitting ( $2\epsilon_Q$  and  $\overline{\Delta Q}$ ), isomer shift ( $\delta$ ) (versus metallic iron), and relative areas ( $S_{\text{rel}}$ ) at 80 K and room temperature in Mössbauer spectra of Tunisian soil samples.

Sample <sup>1</sup>		80 K					RT					
		$H_{\text{hf}}$ (kOe)	$2\epsilon_Q$ (mm/s) fixed	$\delta$ (mm/s) fixed	$\overline{\Delta Q}$ (mm/s)	$S_{\text{rel}}$ (%)	$S_{\text{rel}}^*$ <sup>2</sup> (%)	$H_{\text{hf}}$ (kOe)	$2\epsilon_Q$ (mm/s) fixed	$\delta$ (mm/s) fixed	$\overline{\Delta Q}$ (mm/s)	$S_{\text{rel}}$ (%)
201S	H	525	-0.19	0.48	—	42	30	487	-0.20	0.38	—	37
	G	483	-0.25	0.48	—	52	65	241	-0.27	0.37	—	54
	D	—	—	0.41	0.45	6	5	—	—	0.38	0.60	9
201H	H	531	-0.19	0.48	—	17	6	497	-0.20	0.39	—	17
	G	487	-0.25	0.48	—	82	94	261	-0.27	0.37	—	82
	D	—	—	0.41	0.44	1	—	—	—	0.38	0.69	1
200	H	525	-0.19	0.48	—	18	6	489	-0.20	0.38	—	15
	G	483	-0.25	0.48	—	80	92	243	-0.27	0.37	—	82
	D	—	—	0.41	0.45	2	2	—	—	0.38	0.57	3
199	G	493	-0.25	0.48	—	99	99	322	-0.27	0.37	—	98
	D	—	—	0.41	0.45	1	1	—	—	0.38	0.54	2
198Y	H	524	-0.19	0.48	—	3	—	500	-0.20	0.39	—	2
	G	489	-0.25	0.48	—	96	99	289	-0.27	0.37	—	93
	D	—	—	0.41	0.45	1	1	—	—	0.38	0.58	5
198R	H	530	-0.19	0.48	—	75	69	504	-0.20	0.39	—	77
	G	485	-0.25	0.48	—	25	31	212	-0.27	0.37	—	22
	D	—	—	0.41	0.44	<1	—	—	—	0.38	0.70	1

<sup>1</sup> H = hematite, G = goethite, D = doublet.

<sup>2</sup>  $S_{\text{rel}}^*$  = relative area from conventional fitting procedure.

areas,  $S_{\text{rel}}$ , obtained from a conventional procedure, are summarized in Table 2. The underestimation of the hematite fraction for a simple two-sextet fitting is clearly illustrated in the values of the relative areas derived from both fitting procedures. This effect is well pronounced, even for sample 199R which contains mainly hematite. Moreover, a small hematite fraction was determined in sample 198Y, although the corresponding sextet was not directly visible in the spectrum and could not be resolved by the conventional fitting.

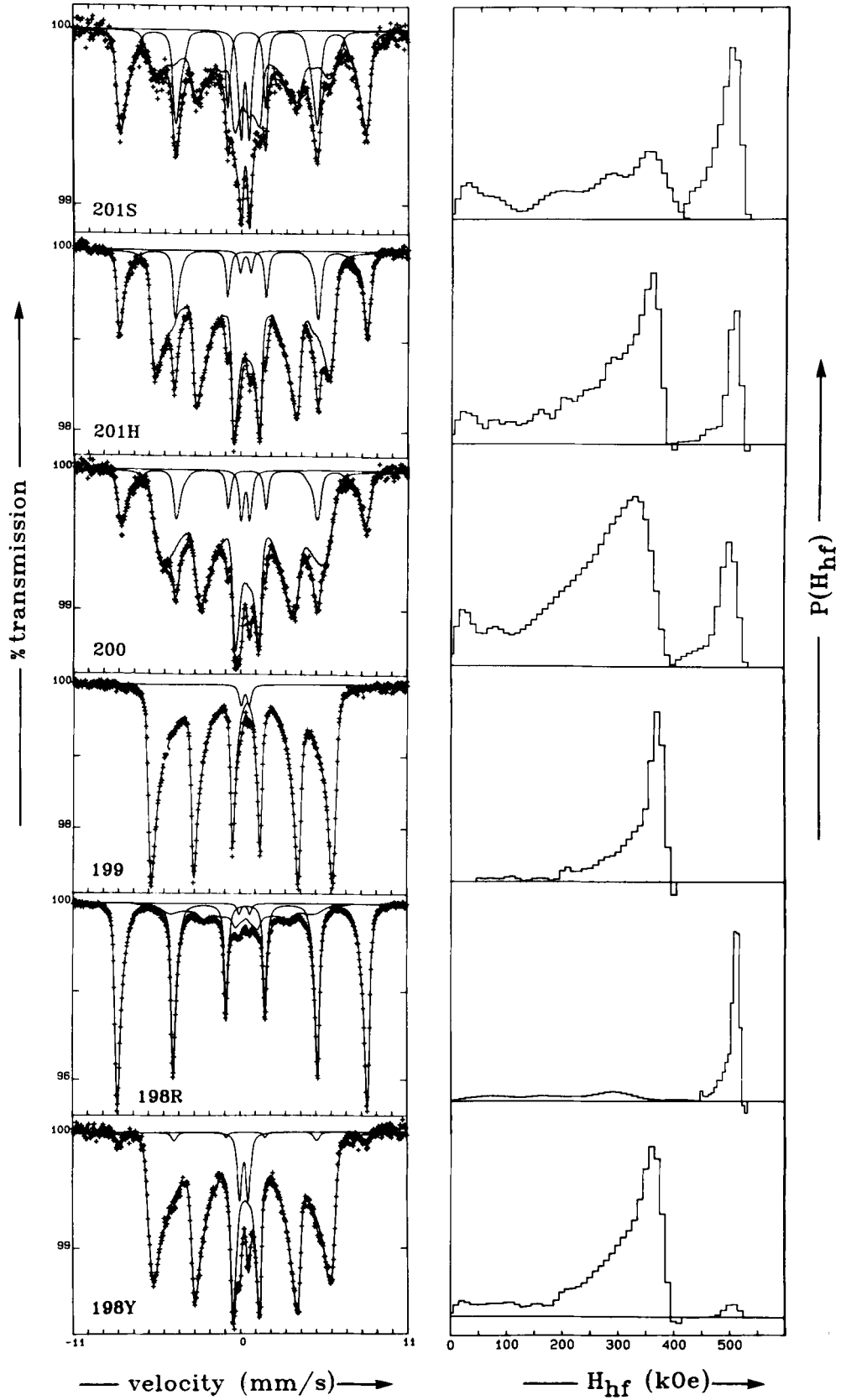
In contrast to the 80 K spectra, the room-temperature (RT) spectra exhibit very broad and asymmetric lines for the goethite fraction (Figure 2) that can be attributed mainly to small-crystallite effects. Estimates of the average isomer shift and quadrupole splitting for the goethite and hematite at room temperature were also obtained from the conventional fitting of the spectra of samples 199 and 198R, respectively. The results of the distribution fittings are summarized in Table 2. The relative areas obtained from the RT spectra agree within a few percent with the values derived from the 80 K spectra. In some samples, however, part of the goethite fraction still appears as a doublet at room temperature due to the presence of some very small goethite microcrystals. This doublet is pronounced in the RT spectrum of sample 198Y. Because the average magnetic hyperfine field is rather high (489 kOe), the sample probably contains a rather broad distribution of particle sizes.

The quadrupole interaction for the hematite phase is negative at 80 K for all samples, typical of hematite not showing the Morin transition, and is thus in a weakly ferromagnetic state at 80 K. Van der Kraan (1972) observed that hematite with particle sizes <300 Å show no Morin transition above 77 K. In the present study, however, the XRD 110 and 104 hematite reflections were relatively narrow, and particle dimensions larger than 2000 Å were estimated. This size range may eliminate small-particle effects as the cause of the absence of the Morin transition. For Al substitution, no antiferromagnetic state was observed in the Mössbauer spectra at 77 K for substitutions larger than about 8% (De Grave *et al.*, 1981). This substitution limit was only surpassed in samples 201S and 200; hence Al alone cannot be responsible for this effect. The relatively large amount of Mn in the DCB extracts after oxalate treatment, however, indicates the presence of Mn-substituted iron oxides. According to the magnetization measurements of Flanders and Remeika (1965), the Morin transition temperature of hematite is more drastically decreased by substitution of Mn than by Al. Therefore, the absence of the Morin transition in the hematite of our samples may be due to Mn substitution in addition to Al substitution.

The average magnetic hyperfine field of hematite at 80 K is 530 kOe for samples 198R and 201H and ~525 kOe for samples 198Y, 200, and 201S. These values are lower than those of pure hematite, i.e.,  $540 \pm 2$

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Figure 2. Room-temperature Mössbauer spectra of Tunisian soil samples and the corresponding magnetic hyperfine field distribution of goethite (left) and hematite (right).



kOe. As argued above, all hematite is in the weakly-ferromagnetic state at 80 K for which the magnetic hyperfine field is about 8 kOe lower than in the normal antiferromagnetic state (De Grave *et al.*, 1981). Moreover, substitution of Fe by non-magnetic ions such as Al<sup>3+</sup> also decrease the hyperfine field. The rather low hyperfine field in samples 198Y, 200, and 201S is explainable by their relatively large Al content. The effect of Al on the hyperfine field is even much more pronounced in the RT spectra. The average value gradually decreases from 504 to 487 kOe within the sample series 198R, 201H, 200, and 201S, in accord with their increasing Al content. As expected, the substitution of magnetic Mn ions did not strongly influence the hyperfine field in a direct way.

The average magnetic hyperfine field of goethite at 80 K and room temperature shows only a crude correlation with the Al content, which is obvious because the average field of goethite, particularly at room temperature, is also strongly affected by the crystallite size. A clearer correlation was observed between the hyperfine field and the goethite content of the sample, a possible indication that the crystallinity of the goethite increases with the amount of goethite relative to the total iron oxides in the sample.

The remaining doublet was fitted with a quadrupole splitting distribution. Except for sample 201S, the relative areas only amount to a few percent, and therefore no significant assignments could be inferred. The average quadrupole splitting,  $\Delta Q$ , is  $\sim 0.6$  mm/s and 0.44 mm/s at room temperature and 80 K, respectively (Table 2), which may be attributed to trivalent iron in many oxides, silicates, and clay minerals.

### CONCLUSIONS

The present study of six samples of red Tunisian soil has shown that reliable data can be obtained from Mössbauer spectra containing goethite and hematite if the distributions of the magnetic hyperfine fields are taken into account. In this way hematite in the presence of goethite can easily be resolved down to 3% of relative area in the spectra. Moreover, comparative data can be derived from spectra having broad and asymmetric lines, where conventional fitting usually fails. The Mössbauer spectrum of goethite appears to be a function of crystallinity and Al substitution. On the other hand Mn substitution plays an additional role in the hyperfine data of hematite, due to the suppression of the Morin transition.

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