

MÖSSBAUER STUDIES OF SMALL PARTICLES OF IRON OXIDES IN SOIL

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(Received 8 June 1972)

Abstract—A soil of Attica (Greece) has been studied by Mössbauer spectroscopy and magnetization measurements in order to ascertain the nature and form of iron oxides present in it. The room temperature spectra consist of a paramagnetic doublet and a small magnetic sextet. At liquid nitrogen temperature the magnetic component increases considerably at the cost of the paramagnetic component. This behavior is typical of superparamagnetism exhibited by ultrafine magnetic particles. From the values of hyperfine parameters extracted by computer fits of the spectra, the particles can be identified mainly as α -Fe₂O₃. The theory of superparamagnetism, in conjunction with Mössbauer and magnetization data, is discussed in detail. Application of this theory to the data for the clay fraction of the soil leads to the conclusion that the oxide particles have a size distribution with a mean particle diameter of 131 Å and a width of 14 Å.

INTRODUCTION

IRON compounds have been investigated extensively in conjunction with their role in soil chemistry and soil physics. Iron oxides are found in the soil as aggregates in various mixtures with manganese, aluminum and silicon oxides or as coatings attached to the surface of clay minerals mainly and to the sand and silt minerals to a smaller extent.

Mössbauer spectroscopy has proved to be a valuable technique in providing information about the structural and chemical aspects of the presence of iron and its compounds. Applications to mineralogy have been reviewed by Maddock (1972) and by Hertzberg (1970). An important factor in the interpretation of Mössbauer spectra of iron compounds in soil is the particle size of these compounds. It has been shown by Kündig *et al.* (1966) and by McNab *et al.* (1968) that for magnetic iron compounds with a particle diameter in the range of 100–500 Å Mössbauer spectra at room temperature exhibit typical nonmagnetic features. In a recent survey study of specimens of clay separates from various parts of the world, Yassoglou *et al.* (unpublished data) found only a few cases of magnetic iron oxides which displayed prominent magnetic Mössbauer spectra at room temperature, while at liquid nitrogen temperature most of the samples showed magnetic spectra.

Recent Mössbauer studies of ancient Greek pottery by Gangas *et al.* (1971) showed the possi-

bility of classification of wares by information obtained from such spectra. One criterion for this classification was the ratio of the magnetic to the nonmagnetic component of the spectra of the fired clay. In order to exploit further this technique and understand better the connection between the particle size of iron oxides in soil and the corresponding Mössbauer spectra, it became clear that an extensive study of such systems was necessary.

This paper gives the results of a study of iron compounds present in soil materials collected from a site near Athens. The same area has been used as a source of clay by Attic potters since ancient times. It has been found that the ratio of the magnetic to the nonmagnetic component of the Mössbauer spectrum varies with temperature and particle size in a manner consistent with superparamagnetic behavior. This result explains the absence of prominent magnetic hyperfine splitting from most of the room temperature spectra of minerals containing iron oxides. Furthermore, from an analysis of the variation of this ratio with temperature, the particle size distribution has been obtained.

THEORY

The usefulness of Mössbauer spectroscopy in the study of iron in clay materials rests on the information obtained on the electronic state and the symmetry at the site of iron ions as well as the magnetic state of the material under investigation. This information is obtained from parameters,

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extracted from the Mössbauer spectrum, which depend on hyperfine interactions; i.e. the interactions between the electrons and the nucleus of the iron ion. The theory describing these interactions in general and their connection with Mössbauer spectroscopy in particular is well known and has been reviewed by several authors. (e.g. Wertheim, 1964).

We shall summarize in this section the salient features and discuss the relevant theoretical background.

The Mössbauer pattern which arises from an iron ion in a given lattice site may have one of the following three forms: (a) A single line in the case of an iron ion in a paramagnetic material at a site of cubic symmetry; (b) a doublet under the same conditions as above but with a site symmetry lower than cubic; and (c) a six-line pattern when the nuclear levels are split by a hyperfine magnetic field.

We shall elaborate further on the conditions required for case (c) since they are of direct interest for the present investigation. For the observation of a magnetic hyperfine pattern, a net magnetic field must be present at the nucleus over a time interval of the order of the nuclear Larmor precession time. This condition is satisfied in the case of magnetic materials where a spontaneous magnetization leads to an average magnetic field different from zero during the nuclear precession time. This field is closely proportional to the average magnetization in a magnetic domain.

Hyperfine magnetic patterns are also observable in paramagnetic materials when the relaxation time for flipping of the magnetic moment between different spin-states is long compared to a nuclear lifetime and the Larmor precession time (Blume and Tjön, 1968).

A third case of immediate interest is that of an assembly of single domain fine particles of a magnetic material. The magnetic properties of such an assembly have been reviewed by Jacobs and Bean (1963). These systems exhibit paramagnetic behavior, i.e. absence of hysteresis and remanence magnetization, but with a magnetic moment which may be as large as that of 10^5 atoms coupled ferromagnetically. Such a behavior, known as superparamagnetism, is mainly due to a process of magnetization reversal and has been

examined theoretically by Néel (1962) and Brown (1959). The basic result of this theory is that the probability for magnetization reversal for a particle of volume v at temperature T is proportional to:

$$\frac{1}{\tau} = \alpha f \exp(-Cv/kT) \quad (1)$$

where τ is the relaxation time and C is the anisotropy constant. The geometrical factor α gives the number of different easy directions between which the magnetization vector can flip. The factor f is the Larmor frequency of the magnetization vector in a coercive field H_c defined by:

$$H_c = C/M_o \quad (2)$$

where M_o is the magnetization of the material.

The properties of antiferromagnetic fine particles have been examined by Néel (1962). He concludes that such a fine particle may possess a permanent magnetic moment due to incomplete cancellation of the magnetic sublattices. The susceptibility of such particles consists of two parts, one due to superparamagnetism and the second due to the ordinary antiferromagnetic part. At low temperatures and for very fine particles the first contribution may completely mask the second. The relaxation time for magnetization reversal is expected to follow a relation similar to equation (1) although it is argued by Néel that surface rather than volume anisotropy may play a significant role.

On the basis of this theory the observation of magnetic hyperfine splitting in Mössbauer spectra of an assembly of fine particles depends on the value of the relaxation time which is determined by the particle size. For τ much longer than the Larmor precession time, the usual six-line pattern of the ferromagnetic material is expected to appear. The application of Mössbauer spectroscopy to superparamagnetism has been reviewed by Collins *et al.* (1967). Typical results in finely divided particles of α -Fe₂O₃, prepared under conditions in which the size could be controlled, have been obtained by Kündig *et al.* (1966). A similar study on fine particles of Fe₃O₄ has been reported by McNab *et al.* (1968). In both cases the results have been interpreted by the theory of superparamagnetism. When a distribution of particle size is present, the spectrum will contain both a paramagnetic part and a hyperfine magnetic splitting component. As the temperature is lowered, the magnetic component will increase at the expense of the paramagnetic* component, as more particles have relaxation times long enough

*In what follows, the term "superparamagnetic" will be used for the description of the paramagnetic component, which is due to the fast flipping of the magnetization vector.

to observe magnetic hyperfine splitting. The ratio of the superparamagnetic part to the total area of the spectrum can be related to the particle size distribution by the following considerations:

We observe first that the factor Cv in the exponent of equation (1) is the energy barrier for flipping of the magnetization between two easy directions. As shown below, Mössbauer measurements can lead only to a distribution of the values of the product Cv , so that an independent estimate of at least one parameter of the size distribution, e.g. the median value v_m , must be available in order to calculate the anisotropy constant, and vice versa. Moreover the origin of anisotropy may be other than volume anisotropy, e.g. surface or shape anisotropy. For these reasons the anisotropy energy $E = Cv$ is considered as a more appropriate variable for the description of the particle distribution. In the following we give a brief account of the theory of superparamagnetism based on the concept of the anisotropy energy.

Let $P(E)$ be the probability density for the particles with anisotropy energy E . Then the fraction of particles with energies lower than E is:

$$F(\epsilon < E) = \int_0^E P(\epsilon) d\epsilon \quad (3)$$

with the condition

$$\int_0^\infty P(\epsilon) d\epsilon = 1. \quad (4)$$

The function $F(\epsilon < E)$ can be related to the ratio of the superparamagnetic to total area of the Mössbauer spectrum at a given temperature by determining the value of E which defines the transition from superparamagnetic to ferromagnetic behavior. If we assume that this occurs when:

$$\tau = \tau_0 \quad (5)$$

where τ_0 is the Larmor precession period of the nucleus, we obtain from equation (1):

$$E = kT \ln(\tau_0 \alpha f). \quad (6)$$

With this relation we obtain from equation (3)

$$F(\epsilon < E) = \int_0^E P(\epsilon) d\epsilon = \int_0^T g(t) dt = R(T) \quad (7)$$

where $R(T)$ is the observed ratio and $g(t)$ is related to $P(\epsilon)$ by the transformation:

$$g(t) = k \ln(\tau_0 \alpha f) P\{kt \ln(\tau_0 \alpha f)\}. \quad (8)$$

Equation (7) also gives:

$$g(T) = \frac{dR}{dT}. \quad (9)$$

Thus from the observed ratio $R(T)$ it is possible to derive the distribution function g and with equation (8) to determine the function P . If a specific functional form is assumed, e.g. a Lorentzian distribution, the parameters defining it can be determined by fitting the experimental ratio $R(T)$.

The above derivation was based on the assumption that there is a sharp transition from superparamagnetic to ferromagnetic behavior so that the particles with $\epsilon < E$ will show a quadrupole doublet while those with $\epsilon > E$ will show a six line Mössbauer spectrum. It is known, however, from several studies of Mössbauer relaxation effects that when $\tau \sim \tau_0$, complex intermediate spectra are observed starting with an asymmetric broadening of the lines of the quadrupole doublet (Blume and Tjön, 1968). Due to the volume distribution, however, only a small number of particles have $\tau \sim \tau_0$ and at each temperature T the relaxation component of the spectrum is not discernible.

Superparamagnetic behavior can also be detected with bulk magnetization measurements. In this case, as indicated earlier, the system behaves like a paramagnet and for an assembly of particles with volume distribution $P(v)$, the magnetic moment per g σ produced by an external field is:

$$\sigma = \sigma_s \int_0^\infty v L\left(\frac{vM_0H}{kT}\right) P(v) dv / \int_0^\infty v P(v) dv \quad (10)$$

where σ_s is the saturation magnetic moment per gram of the specimen, $L(x)$ is the Langevin function and M_0 the magnetization of the pure compound; i.e. the magnetic moment of a particle of volume v is $\mu = vM_0$. In this expression it has been assumed that the interaction between the particles is small. Thus, bulk magnetization data can also be used to obtain the particle size distribution. In this case the remanent magnetic moment as a function of temperature gives the fraction of particles for which the relaxation time is longer than the observation time. Here, however, the observation time is of the order of seconds so that the corresponding ratio $R(T)$ will be shifted to lower temperatures.

METHODOLOGY

The studied soil sample was collected from the C horizon of red Mediterranean (rhodoxeralf) soil

profile located in Amarousion, a suburb of Athens, Greece, and developed on Quaternary alluvial deposits.

The sample was dispersed with sodium hexametaphosphate and the clay and silt fractions were separated from the sand by wet sieving and centrifugation according to Jackson (1968).

Free iron oxides were removed from the sample by dithionite dissolution. Oxide and structural ferric and ferrous iron were determined according to Roth *et al.* (1968) using a Perkin-Elmer 303 Atomic Absorption Spectrophotometer. X-ray diffraction diagrams were obtained from oriented clay films with $\text{CuK}\alpha$ and $\text{FeK}\alpha$ radiations using a Philips Norelco unit. Diffraction patterns were also taken by a Debye-Scherrer camera at room and at liquid nitrogen temperatures.

Mössbauer spectra of 150 mg samples ($\cong 0.1 \text{ mg/cm}^2 \text{ Fe}^{57}$) were obtained with a conventional constant acceleration spectrometer at temperatures between 77°K and room temperature (295°K).

Since the Mössbauer spectra of the bulk soil, the silt and the clay fractions contained contributions from both the free iron oxides and the iron located in the structure of the minerals, spectra were also obtained from the deferrated clay samples. Thus, the contribution to the resonance absorption by the iron -57 nuclei in the free oxide phase in the clay was determined by subtracting the absorption of the deferrated sample from that of the non-deferrated sample.

Analysis of all Mössbauer spectra was performed with a least squares fitting program, which allowed for the superposition of two magnetic hyperfine splitting and two quadrupole splitting patterns.

Finally, measurements of the magnetic moment of the deferrated and non-deferrated clay samples were made by a vibrating sample magnetometer PAR 155.

RESULTS AND DISCUSSION

The chemical data in Table 1 show that iron is present in the sample in significant amounts both as "free" iron oxides and as a constituent of the structure of other minerals. The largest part of the element is in the ferric state, while a smaller portion as ferrous iron is found in the structure of the clay and silt minerals. The predominance of the ferric state is anticipated due to the oxidative environment of the sampled soil horizon. The Mg^{2+} saturated and glycerol-solvated clay samples showed X-ray diffraction maxima at 7.1, 10.07, 11.1 Å and a weakly resolved maximum at 14.5 Å.

Table 1. Structural and "free" iron content of the studied soil fractions

Sample	Chemical analysis			
	Structural		"Free"	Total
	Fe ²⁺ %	Fe ³⁺ %	Fe ³⁺ %	Fe %
Bulk	0.9	2.3	4.7	7.9
Silt	0.8	1.0	3.2	5.0
Clay	1.8	2.7	8.6	13.1

On K saturation and heating to 110°C–200°C the 14.5 Å peak disappeared and the 10 Å peak was enhanced. At 550°C the 7.1 Å peak disappeared and only the 10 and 11 Å peaks remained in the diagram.

The above data indicate that the clay fraction consists mainly of illite, some kaolinite and vermiculite, and interstratified systems of illite-chlorite and possibly vermiculite. There is no evidence of X-ray detectable crystalline iron oxides in the diagrams and in the films which were obtained at room and at liquid nitrogen temperatures. Mössbauer spectra of the bulk soil, silt and the clay fractions are shown in Fig. 1 for room and liquid nitrogen temperatures. Their structure consists generally of a six line magnetic hyperfine splitting component arising from the superposition of the line patterns labeled as S_1 and S_2 and one quadrupole doublet labeled as D . In the case of the silt fraction, a second quadrupole doublet with higher splitting than the first is apparent, indicating the presence of ferrous iron in the asymmetrical octahedral site of mica minerals (Yassoglou *et al.*, 1972).

The most interesting features shown by the spectra of Fig. 1 are: (a) For a given fraction, an increase in the relative magnitude of the magnetic to the nonmagnetic component when the temperature is lowered from 295 to 77°K. This increase is especially pronounced in the clay fraction. (b) At a fixed temperature an increase in absorption from the silt to the clay fraction of the soil. This increase indicates a corresponding increase in iron content.

The enrichment in iron is confirmed by the chemical data of Table 1. All these data show an approximately threefold increase in iron between the silt and clay fractions. Moreover, the content of "free" iron in the samples (which is removable by the dithionite treatment) is presumably present in the form of free oxides and increases by a factor greater than two from the silt to the clay fractions.

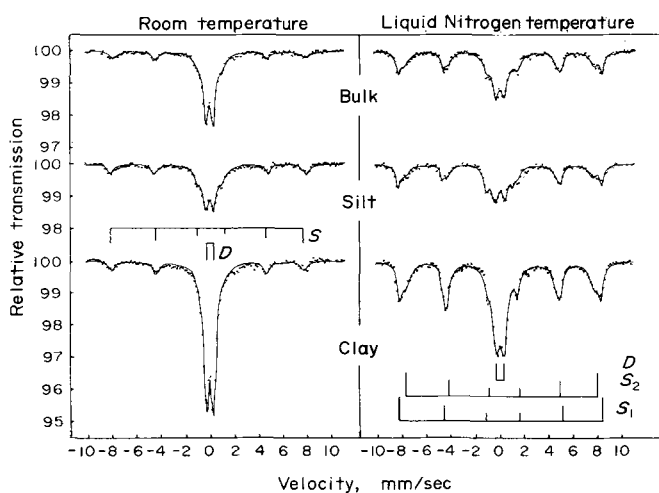


Fig. 1. Mössbauer spectra of the bulk soil, the silt and clay fractions at room and liquid nitrogen temperature. The solid lines have been calculated with the parameters of Table 2.

The existence of free oxides is already shown by the six-line components (S_1 and S_2). The structural iron is expected to contribute only to the quadrupole doublet D since the relaxation time should be large due to strong spin-spin interactions. In fact paramagnetic hyperfine splitting has not been observed so far in clay minerals.

These results, in conjunction with the absence of X-ray lines characteristic of iron oxides in the clay fraction, lead to the conclusion that iron oxides are present in the form of fine particles and are therefore expected to show superparamagnetic behavior. If this is the case, the increase of the magnetic component at the expense of the quadrupole doublet, as the temperature is lowered, can be attributed to an increase in the relaxation time as outlined in Section 2. Computer fits of the spectra are shown by the solid line in Fig. 1. The room temperature spectra were fitted with a superposition of one quadrupole doublet D and one magnetic sextet S . The magnetic part of the low temperature spectra shows clear asymmetry which could be explained as a result of the decrease of the hyperfine field with particle size. This decrease would lead to a distribution of hyperfine fields corresponding to the particle volume distribution. In the analysis of the spectra this has been taken roughly into account by assuming two values of the hyperfine field and correspondingly two magnetic components S_1 and S_2 . An alternative explanation of the asymmetry would be that it is due to the presence of two oxide species with different hyperfine fields.

The results of this analysis are summarized in

Table 2 which lists the parameters for each component of the spectrum at room and liquid nitrogen temperatures. For comparison, the parameters for bulk and fine particles of α - Fe_2O_3 taken from Kündig *et al.* (1966) are also included. It is noted that the values of the effective magnetic field for component S_1 in the silt sample lies between the values for bulk and 180 Å particles of α - Fe_2O_3 . The corresponding value for the clay sample is lower than the value for 180 Å particles. This variation is consistent with the interpretation that the hyperfine field decreases as the particle size decreases and implies that the clay sample contains particles of size smaller than 180 Å. Further evidence for this conclusion will be discussed later. On the other hand the quadrupole splitting for S_1 agrees in magnitude and sign with the value for 180 Å of α - Fe_2O_3 particles. Moreover, the quadrupole splitting of the central component in the clay sample agrees with the results of Kündig *et al.* (1966). It may be concluded that the iron is present predominantly in the form of fine particles of α - Fe_2O_3 .

The second magnetic component S_2 has considerably lower effective field and larger line width than those of sextet S_1 . This component may be attributed to the presence of a second oxide species. The parameters of Table 2 agree with those found by Deszi *et al.* (1967) for β - FeOOH . This identification is supported also by the variation of the magnetic field with temperature for the component S_2 of the clay fraction which was studied in greater detail as discussed below. An alternative interpretation for S_2 is that it arises from a distribu-

Table 2. Mössbauer parameters of the studied soil fractions

Sample	Characterization of lines*	Magnetic field (kg)		Quadrupole splitting (mm/sec)		Isomer shift (mm/sec)	
		295°K	77°K	295°K	77°K	295°K	77°K
Bulk	<i>D</i>			0.62 ± 0.01	0.70 ± 0.02	0.17 ± 0.02	0.26 ± 0.01
Soil	<i>S</i> ₁	495 ± 2	527 ± 1	-0.16 ± 0.01	-0.16 ± 0.03	0.23 ± 0.02	0.27 ± 0.02
	<i>S</i> ₂		490 ± 2		-0.34 ± 0.07		0.28 ± 0.02
Silt	<i>D</i>			0.68 ± 0.03	0.84 ± 0.06	0.15 ± 0.02	0.265 ± 0.02
	<i>S</i> ₁	508 ± 2	530 ± 2	-0.20 ± 0.03	-0.16 ± 0.03	0.18 ± 0.02	0.27 ± 0.02
	<i>S</i> ₂		490 ± 2		0.34 ± 0.04		0.25 ± 0.02
Clay	<i>D</i>			0.62 ± 0.03	0.64 ± 0.06	0.16 ± 0.02	0.25 ± 0.02
	<i>S</i> ₁	492.4 ± 2	523 ± 2	-0.16 ± 0.03	-0.17 ± 0.03	0.18 ± 0.02	0.28 ± 0.04
	<i>S</i> ₂		488 ± 2		-0.23 ± 0.04		0.29 ± 0.02
α -Fe ₂ O ₃	<i>S</i> ₁	518 ± 6	542 ± 6	-0.21 ± 0.03	0.35 ± 0.03	0.205 ± 0.02	
Bulk (c)							
α -Fe ₂ O ₃ 180 Å(c)	<i>S</i> ₁	503 ± 6	527 ± 6	-0.22 ± 0.23	-0.195 ± 0.03	0.195 ± 0.03	

**D*—paramagnetic ferric doublet, *S*₁—first magnetic sextet, with the larger H_{eff} *S*₂—second magnetic sextet with the lower H_{eff} .

(b) With respect to Pd (Co⁵⁷) source.

(c) Data were taken from Kündig *et al.* (1966).

tion of magnetic fields in α -Fe₂O₃ particles due to the observed decrease of the magnetic field with particle size. This alternate is less likely, however, since the two components become quite distinct at temperatures between 77°K and room temperature.

The clay fraction was further studied in detail in order to obtain the particle size distribution. For this purpose it is necessary to determine the contribution to the Mössbauer spectrum of iron ions that are included in the structure of the minerals, predominantly in octahedral positions. The spectrum at room temperature of the deferrated clay sample* from which oxides have been removed is shown in Fig. 2. The ferric doublet has the same hyperfine parameters as those of the doublet of the non-deferrated clay sample, but displays a smaller absorption. The small peak at positive velocities corresponds to a ferrous doublet which probably resulted from the reduction of the structural ferric iron during the deferration treatment. The parameters of this doublet correspond to iron in the symmetrical octahedral site which is the most accessible to oxidation-reduction (Yassoglou *et al.*, 1972).

The quadrupole doublet in the clay sample can be considered as a superposition of the component due to superparamagnetic fine particles and that due to the paramagnetic structural iron. Thus, by measuring the deferrated (NFO) and non-deferrated clay samples at various temperatures

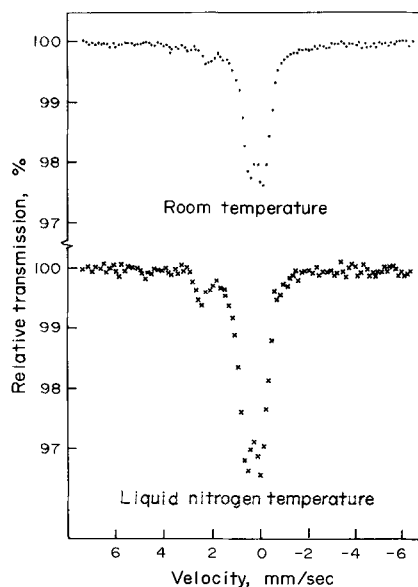


Fig. 2. The Mössbauer spectra of a sample obtained from the clay fraction after chemical treatment which removes the free oxides (sample NFO).

it is possible to determine the superparamagnetic component. The results from measurements at five different temperatures are given in Table 3. Columns 2 and 3 give the absorption areas of the magnetic (*S*₁ and *S*₂) and nonmagnetic *D* components of the clay sample and column 4 gives the absorption area of sample NFO. These values resulted from computer fits of Mössbauer spectra and are corrected for background. The super-

*This sample will be designated in what follows by the symbol NFO.

Table 3. Mössbauer absorption area of clay fraction

1 Temperature (°K)	2 Magnetic oxides	3 Paramagnetic oxides Total	4 Structural	5 Free	6 Total oxides	7 Superparamagnetic ratio (%)
295	1.8 ± 0.1	8.8 ± 0.4	3.6 ± 0.2	5.2	7.0	75 ± 7
263	6.4 ± 1.2	7.4 ± 0.4	3.6 ± 0.2	3.8	9.2	42 ± 10
236	7.1 ± 0.3	7.4 ± 0.4	4.8 ± 0.2	2.6	9.6	27 ± 3
200	7.1 ± 0.4	7.0 ± 0.4	5.1 ± 0.3	1.9	9.1	21 ± 2
144	8.3 ± 0.4	6.8 ± 0.3	5.9 ± 0.3	0.9	9.2	10 ± 1
77	3.3 ± 0.4	6.0 ± 0.3	5.7 ± 0.3	0.4	8.6	4 ± 0.4

paramagnetic component, calculated as the difference of columns 3 and 4, is listed in column 5 and the total area is listed in column 6. Finally the values of the ratio $R(T)$, of superparamagnetic to total area, are presented in column 7 and are plotted by crosses (x) in Fig. 3. The two magnetic components S_1 and S_2 are considered as having the same value of the anisotropy constant C .

Equations (7 and 8) show that the derivative of $R(T)$ determines the function g which is directly related to the size distribution function P . In order to make the analysis more specific we shall assume a Lorentzian form for g , as this form is suggested by the experimental values of $R(T)$:

$$g(t) = \frac{(\Delta T)/\pi}{(T - T_m)^2 + (\Delta T)^2} \quad (11)$$

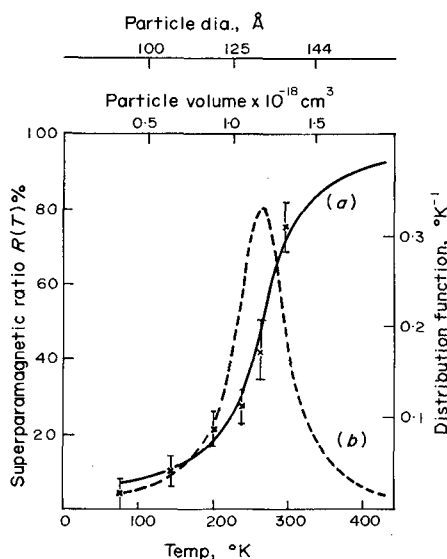


Fig. 3. (a) The ratio $R(T)$ of superparamagnetic to total area of the part of Mössbauer spectrum due to free oxides. (b) The distribution function of particle size. Both curves are calculated from equations (12 and 15) (see text).

or

$$g(x) = \frac{1}{\pi(\Delta T)} \frac{1}{x^2 + 1} \quad (11)$$

where $x = (T - T_m)/\Delta T$ and $1/\pi$ is the normalization factor. Then:

$$R(T) = \frac{1}{\pi} \tan^{-1} \left(\frac{T - T_m}{\Delta T} \right) + \frac{1}{2} = \frac{1}{\pi} \tan^{-1} x + \frac{1}{2}. \quad (12)$$

The fit of the expression of equation (12) to the experimental values of the ratio $R(T)$ gives for T_m and ΔT the values 265 and 41°K respectively. The functions $R(T)$ and $g(T)$ calculated with these parameters are plotted also in Fig. 3, which shows that $R(T)$ is in good agreement with the experimental values. This agreement justifies the choice of the distribution shape.

The probability distribution of the anisotropy energy may now be determined from equation (8). The Larmor precession period for the excited state of Fe^{57} is $\tau_0 = 2.5 \times 10^{-8}$ sec. In $\alpha\text{-Fe}_2\text{O}_3$, with the magnetization lying on a plane perpendicular to the trigonal axis, there are three equivalent easy directions of magnetization, therefore $\alpha = 2$. Also the anisotropy energy density may be written $K \cos 3\varphi$ where φ is the angle measured from an easy direction. Then the energy barrier between two directions is $2K$, so that $C = 2K$ in equation (1). The value of K has been determined by Kündig *et al.* (1966). The average of two independently calculated values is $K = (4.4 \pm 1.1) \times 10^4 \text{ erg cm}^{-3}$. The value of f may be estimated from equation (2):

$$f = \frac{2K}{M_0} (n_{\text{eff}} \mu_B / h) \quad (13)$$

With $M_0 = 2n_{\text{eff}} \mu_B \rho N_A / A$, where n_{eff} is the number of Bohr magnetons μ_B per Fe ion, h Planck's constant, ρ the density, A the molecular weight and N_A Avogadro's number, we obtain

$$f = KA / \rho N_A h. \quad (14)$$

With the appropriate values for Fe_2O_3 , $f = 7.7 \times 10^3$ K and from equation (6) we obtain:

$$\frac{E}{T} = k \ln(\tau_0 \alpha f) = 3.9 \times 10^{-16} \text{ erg } ^\circ\text{K}^{-1}$$

and using equation (11) the anisotropy energy distribution is:

$$P(E) = \frac{1}{\pi} \frac{(\Delta E)}{(E - E_m)^2 + (\Delta E)^2} \quad (15)$$

with

$$E_m = 1.04 \times 10^{-13} \text{ erg and } \Delta E = 0.16 \times 10^{-13} \text{ erg.}$$

The corresponding volume distribution is obtained using the relation $E = 2Kv$ in the case of volume anisotropy. This gives $v_m = 1.17 \times 10^{-18} \text{ cm}^3$ and $\Delta v = 0.18 \times 10^{-18} \text{ cm}^3$. Assuming spherical particles, the equivalent average diameter is $d_m = 131 \text{ \AA}$. This result agrees with the fact that the Mössbauer spectra of the studied fraction are very similar to the spectrum of the sample with particles of size 135 \AA in the work of Kündig *et al.* (1966) (Fig. 3 of that paper).

Thus, we may conclude that the particle size distribution determined in this way is consistent with the required value of the anisotropy energy and the value of the anisotropy constant.

A question which merits some discussion is the decrease of the hyperfine field with decreasing particle size. The hyperfine field is expected to be proportional to the spontaneous magnetization of the sublattice to which the ion belongs. The variation of the spontaneous magnetization with particle size has been studied by Abeledo and Selwood (1961) in nickel-silica gel preparations with particle sizes between 30 and 85 \AA . They found a reduction of the Curie point to about 92 per cent of the bulk value. This reduction would lead to a corresponding decrease in the spontaneous magnetization with respect to the bulk material which would be most pronounced near the Curie point. This effect explains, at least qualitatively, the decrease in hyperfine field with particle size.

The measurements of the magnetic moment of the clay and NFO samples are presented in Fig. 4. The variation of magnetic moment versus magnetic field for NFO, which contains only structural iron, is given by curve (b) and is typical of a paramagnetic material. The magnetic moment versus H of the clay sample, given by curve (a), contains the contribution of both the structural iron and the free oxides. The much faster saturation behavior is characteristic of superparamagnetic particles

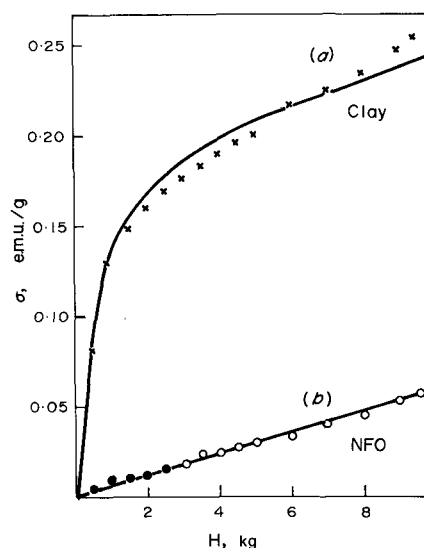


Fig. 4. Magnetic moment versus magnetic field for the clay fraction and sample NFO: (a) Clay sample. (b) Sample NFO. The solid line in (a) has been calculated assuming superparamagnetic behavior for the free oxides and paramagnetic behavior for the iron in the lattice (see text).

(Collins *et al.*, 1967). Superparamagnetic behavior is expected in the magnetization measurements at room temperature since for the average anisotropy energy $E_m = 1.04 \times 10^{-13} \text{ erg}$ determined previously, equation (1) gives a relaxation time $\tau = 2 \times 10^{-8} \text{ sec}$, much shorter than the observation time which is of the order of seconds.

A fit of the results for the magnetic moment of the clay fraction (curve (a) in Fig. 4) can be obtained by using equation (10) and the distribution of particle sizes obtained above for the superparamagnetic iron oxides, plus the paramagnetic contribution of the iron in the lattice (curve (b) in Fig. 4). We introduce as parameters the magnetization M_0 of the $\alpha\text{-Fe}_2\text{O}_3$ and the saturation magnetic moment per g σ_s of the specimen. The best fit to the experimental results is obtained with the values:

$$M_0 = 81.5 \text{ e.m.u. cm}^{-3}$$

$$\sigma_s = 9.6 \times 10^{-3} \text{ e.m.u. g}^{-1}.$$

The value of the magnetization may be compared with the values obtained previously for fine particles of $\alpha\text{-Fe}_2\text{O}_3$ by Bando *et al.* (1955).

CONCLUSIONS

The principal results of this investigation are the following:

(a) Iron oxides are present in the clay fraction of a

soil sample obtained from the location of Amarousion (Athens) in the form of small particles of $\alpha\text{-Fe}_2\text{O}_3$, predominantly exhibiting superparamagnetic behavior.

(b) An analysis of the temperature dependence of the ratio of the superparamagnetic to the total area of Mössbauer spectra gives the distribution of anisotropy energy and particle size. Assuming a Lorentzian form for the distribution, the median volume and dispersion were determined as $v_m = 1.17 \times 10^{-18} \text{ cm}^3$ (dia. $d_m = 131 \text{ \AA}$) and $\Delta v = 0.18 \times 10^{-18} \text{ cm}^3$ ($\Delta d = 14 \text{ \AA}$) respectively.

(c) Magnetization measurements agree with and confirm the Mössbauer results. The average magnetic moment per particle is found to be $1.0 \times 10^4 \mu_B$ and the magnetization $81.5 \text{ e.m.u. cm}^{-3}$.

On the basis of these results we may conclude that:

(i) Superparamagnetism is responsible for the fact that magnetic hyperfine splitting does not appear in most cases of Mössbauer spectra obtained at room temperature with clay fractions of various soils (Yassoglou *et al.*, unpublished results).

(ii) Most of the free iron oxides in the C horizon of the rhodoxeralf soil of Attica, Greece, is in the form of ultra fine particles of hematite ($\alpha\text{-Fe}_2\text{O}_3$).

(iii) The derived particle size distribution is rather narrow in comparison with the distributions found for small particles prepared in the laboratory (Kündig *et al.*, 1966; McNab *et al.*, 1968). This narrow distribution may be attributed to natural processes during the development of the soil.

(iv) The particle size distribution can possibly lead to characterization of soil and pottery wares.

Finally, the results of this investigation point out the need of further study of the nature and dynamics of the evolution of these small size iron oxide particles in the soil. Some new facts may be found which will contribute to the understanding of the conflicting data on the role of iron oxides in the development of soil structure.

Acknowledgements—The authors would like to thank Dr. Anagnostopoulos for illuminating discussions and assistance with the magnetization data and Miss K. Kalogeropoulou for her assistance in the computer calculations.

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Résumé—Un sol d'Attique (Grèce) a été étudié par spectroscopie Mössbauer et par des mesures de magnétisation afin de préciser la nature et la forme des oxydes de fer qu'il contient. Les spectres à température ambiante consistent en un doublet paramagnétique et un petit sextuplet magnétique. A la température de l'azote liquide, le composant magnétique augmente considérablement au dépend du composant paramagnétique. Ce comportement est typique du superparamagnétisme que montrent les particules magnétiques ultra-fines. Grâce aux valeurs des paramètres hyperfins calculés à partir

des spectres par des ajustements à l'ordinateur les particules peuvent être identifiées comme étant principalement du α -Fe₂O₃. La théorie du superparamagnétisme est discutée en détail conjointement aux données Mössbauer et de la magnétisation. L'application de cette théorie aux données obtenues pour la fraction argileuse du sol conduit à la conclusion que les particules d'oxyde ont une distribution de taille caractérisée par un diamètre particulaire moyen de 131 Å et une largeur de 14 Å.

Kurzreferat—Ein Boden aus Attika (Griechenland) wurde mit Hilfe von Mössbauer-Spektroskopie und Magnetisierungsmessung untersucht, um Natur und Ausbildung der darin enthaltenen Eisenoxide zu bestimmen. Die bei Raumtemperatur ermittelten Spektren bestehen aus einer paramagnetischen Dublette und einem kleinen magnetischen Sextett. Bei der Temperatur flüssigen Stickstoffs nimmt die magnetische Komponente auf Kosten der paramagnetischen beträchtlich zu. Dieses Verhalten ist typisch für Superparamagnetismus, wie ihn ultrafeine magnetische Teilchen zeigen. Aus den Hyperfeinstrukturparametern, die durch Computerauswertung der Spektren erhalten wurden, ergibt sich, daß die Teilchen als α -Fe₂O₃ anzusprechen sind. Die Theorie des Superparamagnetismus wird in Verbindung mit den Mössbauer- und Magnetisierungsdaten in ihren Einzelheiten diskutiert. Die Anwendung dieser Theorie auf die an der Tonfraktion des Bodens erhaltenen Ergebnisse führt zu der Schlußfolgerung, daß die Oxidteilchen eine Größenverteilung besitzen, die durch einen mittleren Teilchendurchmesser von 131 Å und eine Dicke von 14 Å gekennzeichnet ist.

Резюме—Посредством спектроскопии Мессбауера и измерения намагниченности изучается землистая масса из Атики (Греция) для определения характера и форм присутствующих в ней окисей железа. Спектр Мессбауера при комнатной температуре состоит из парамагнитного дублета и небольшого магнитного секстета. При температуре жидкого азота магнитный компонент значительно повышается за счет парамагнитного компонента. Это поведение является типовым для суперпарамагнетизма, проявляемого сверх малыми магнитными частицами. По данным, извлеченным ЭВМ частицы можно идентифицировать главным образом как α -Fe₂O₃. Подробно изучается теория супермагнетизма в связи с Мессбауером и данными намагничивания. Применение этой теории по отношению к данным по фракциям глины в земле ведет к заключению, что частицы окиси распределены по размеру со средним диаметром частицы 131 Å, шириной 14 Å.