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MÖSSBAUER STUDY OF TRANSFORMATIONS INDUCED IN CLAY BY FIRING

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Abstract—The clay fraction of an Attic soil has been fired at temperatures up to 1100°C and the transformations induced by firing were studied by Mössbauer spectroscopy. The unfired clay contained iron in the form of small particles of α-Fe_2O_3 and β-FeOOH and as a substitutional ion in the clay mineral structure. A transformation of β-FeOOH to α-Fe_2O_3 is observed in the region of 200–400°C followed by dehydroxylation of the clay mineral between 500 and 800°C. A disintegration of the clay mineral structure is inferred above 800°C, followed by recrystallization in an iron-rich phase, most probably in the form of very fine particles. The room temperature spectra of the fired samples indicate that an increase in particle size of the oxides occurs upon firing.

INTRODUCTION

In a recent study by Gangas *et al.* (1973a), referred to hereafter as (I), it has been demonstrated that Mössbauer spectroscopy is an effective technique in elucidating the chemical form and structure of iron compounds in clay materials. The main result was that, in the typical Attic Clay studied in (I), iron is primarily present in the form of fine particles of iron oxides identified as α-Fe_2O_3 and β-FeOOH and, to a lesser extent, as a substitutional ion in the structure of the clay mineral. From an analysis of the temperature dependence of Mössbauer spectra which exhibited clearly superparamagnetic behavior of oxide particles, it has been found that the average size is in the range of 100 Å. This result is of particular interest in demonstrating the effectiveness of Mössbauer spectroscopy in the study of a problem which is accessible to few other techniques.

The extension of this work to an investigation of the effects of firing in clays is of interest for several reasons. First, it would establish an alternative technique for following the transformations of iron oxides and clay minerals which occur upon progressive heating up to about 1000°C and have been studied previously by other physical methods, notably X-ray powder diffraction and DTA. Second, it would provide information for interpreting Mössbauer spectra of samples of pottery, particularly in applications of this method to archaeological questions related to the provenance and manufacture of ancient pottery wares, In fact the motivation for this work originated in previous Mössbauer studies of ancient Greek pottery at our laboratories (Kostikas *et al.*, 1974).

In this paper we report the results of Mössbauer studies on clay samples extracted from an Attic soil and fired at temperatures up to 1100°C in an oxidizing atmosphere. Preliminary results of this work have been reported earlier (Gangas *et al.*, 1973b). We present now a detailed analysis of Mössbauer spectra obtained at three different temperatures and the conclusions that can be drawn regarding the clay components in which iron is found, their transformations with firing and the effects of heat treatment on the particle size of iron oxides.

EXPERIMENTAL PROCEDURE

The clay used in this investigation was extracted from a typical soil used by contemporary potters in the vicinity of Athens. The separation of the clay fraction from the soil was effected by dispersion of the sample with sodium hexametaphosphate and water flotation. Mineralogical analyses performed in connection with previous work on this soil (I) have shown that the clay consists mainly of illite, some kaolinite and vermiculite and interstratified systems of illite–chlorite and possibly vermiculite. Ten samples were prepared from the dried clay and fired at different temperatures, starting from 200°C and progressing by 100°C steps up to 1100°C. The firing procedure consisted of placing all the samples in a furnace and increasing the temperature by 100°C steps. At each step the temperature was kept constant for 1 hr. At the end of the hour the corresponding sample was removed from the furnace and allowed to cool down to room temperature. The time required for equilibration of temperature between steps was less than 10 min. Mössbauer spectra of 150 mg samples

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of the fired as well as of the unfired clay were obtained at room, liquid nitrogen and liquid helium temperatures with a conventional constant acceleration spectrometer using a ^{57}Co source. The experimental spectra were computer fitted with a least square program which allowed for the variation of parameters of two six line (magnetic) components and two doublet (paramagnetic) components. Areas were calculated from peak intensities and linewidths resulting from the fitting with correction for background.

EXPERIMENTAL RESULTS

The structure of the observed spectra consists generally of two parts: a six line pattern arising from magnetic hyperfine splitting in magnetically ordered compounds and a central doublet pattern due to quadrupole splitting. The structure and relative intensity of the components of each pattern depends on the temperature T_m at which the measurement is made as well as on the temperature T_f at which the sample was fired.

The major effect of the variation in measuring temperature is an enhancement of the magnetic part relative to the central paramagnetic doublet pattern as the temperature decreases. As already discussed in detail in (I) with regard to the unfired clay, this effect can be attributed to superparamagnetic behavior of iron oxide particles of small size. At 4·2°K it is expected that the magnetic moment of practically all the oxide particles will be blocked, so that the remaining paramagnetic doublet may be attributed entirely to iron in the structure of the clay mineral.

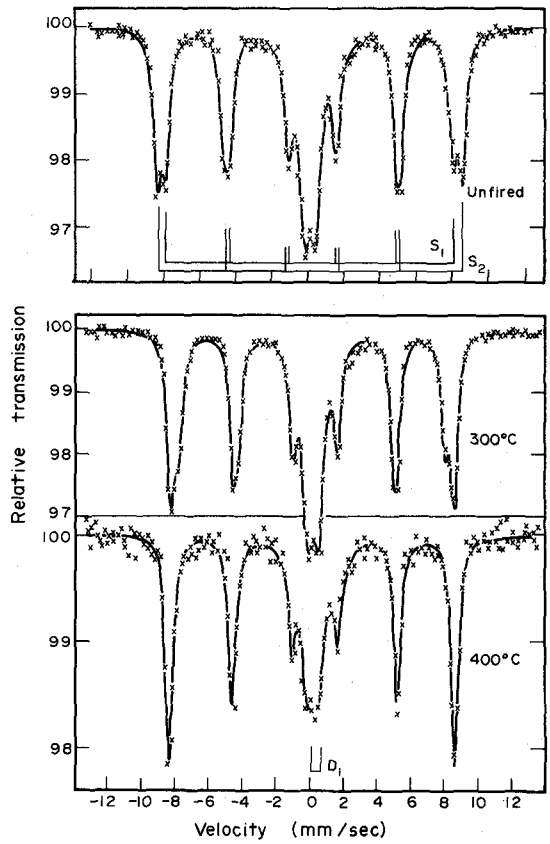


Fig. 1. Mössbauer spectra of clay unfired and fired at 300 and 400°C, obtained at 4·2°K. S_1, S_2: Fe_2O_3 and β-FeOOH magnetic sextets respectively. D_1: Paramagnetic doublet.

Table 1. Hyperfine parameters derived from Mössbauer spectra of clay unfired and fired at 200, 300 and 400°C. Absorber and source temperature is 4·2°K. The values for small particles of α-Fe_2O_3 and β-FeOOH are included for comparison. Isomer shifts are given relative to a ^{57}Co in Cu source. Numbers in parentheses give estimated errors in last significant digit

Component	Firing temperature °C	H KG	$e^2qQ/4$ mm/sec	δ mm/sec	Half width mm/sec	Fraction %
S_1 (α-Fe_2O_3)	Unfired	528(2)	−0·081(4)	0·202(4)	0·257(6)	33
	200	528(2)	−0·088(2)	0·199(2)	0·239(4)	33
	300	528(1)	−0·081(2)	0·205(2)	0·257	42
	400	529(3)	−0·093(3)	0·202(3)	0·252(6)	68
S_2 (β-FeOOH)	Unfired	498(2)	−0·124(3)	0·207(3)	0·267(6)	37
	200	497(2)	−0·124(2)	0·202(2)	0·265(4)	36
	300	496(2)	−0·108(3)	0·204(3)	0·270(3)	27
D_1 (structural)	Unfired		0·297(4)	0·181(5)	0·361(9)	30
	200		0·309(2)	0·179(3)	0·366(5)	31
	300		0·308(2)	0·173(3)	0·386(6)	31
	400		0·32(1)	0·209(1)	0·46(3)	32
α-Fe_2O_3[a] (77°K)		527	−0·0925	0·38[c]		
β-FeOOH[b] (77°K)		482	−0·1	0·6[d]		
β-FeOOH[e] (77°K)		485(5)	—	—		

[a] Kündig *et al.*, 1966.
[b] Dezsi *et al.*, 1967.
[c] Relative to Fe metal at room temp.
[d] With respect to a Cr source.
[e] Voznyuk *et al.*, 1973.

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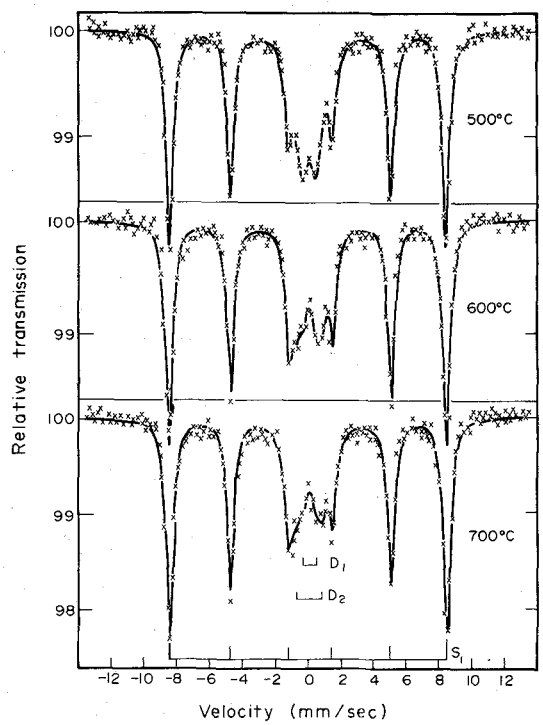


Fig. 2. Mössbauer spectra of clay fired at 500, 600 and 700°C, obtained at 4·2°K.

The changes in the spectra as the firing temperature is progressively increased can be conveniently presented with reference to three temperature regions as follows.

The first region includes the unfired clay and firing temperatures up to 400°C. Corresponding spectra measured at 4·2°K are shown in Fig. 1. A marked feature of the spectra of the unfired clay and for T_f = 300°C is the clear splitting of the magnetic part in two components, indicating the presence of two oxide species in the clay. These results have been fitted with two sextets and one doublet and the hyperfine parameters obtained by these fits are listed in Table 1. It is noted that the magnetic component with the lower magnetic field diminishes with increasing firing temperature and is no longer present at 400°C. From the values of the hyperfine parameters the oxide components may be identified as α-Fe_2O_3 and most probably β-FeOOH. To substantiate this assignment, values of hyperfine parameters for small particles of these oxides calculated from data by Kündig *et al.* (1966), Voznyuk and Dubinin (1973) and Dezsi *et al.* (1967) are included in Table 1. This will be discussed in detail later.

The spectra of the samples fired at temperatures higher than 400°C and up to 800°C feature mainly a broadening of the paramagnetic doublet. This effect is most clearly demonstrated in the measurements at 4·2°K which are shown in Fig. 2. The paramagnetic part of these spectra was fitted with two quadrupole doublets D_1 and D_2 with splittings 0·34 mm/sec and 0·8 mm/sec respectively while the magnetic part was fitted with one six line pattern. The spectral parameters derived from this analysis are listed in Table 2. In view of the remark made previously that the central doublet is due to structural iron, the changes observed in this temperature region may be attributed to transformations in the clay mineral structure. In fact it is known by studies of clays with other techniques that a dehydroxylation process takes place in the clay mineral in this temperature region. This point will be discussed in detail in the next section. We note only here that the component with the larger quadrupole splitting grows at the expense of the narrow one.

Additional changes in the structure of the central paramagnetic part of the spectrum are observed in the region of firing temperatures from 900°C to 1100°C. The results of measurements at 4·2°K are shown in Fig. 3. For the firing temperature of 900°C

Table 2. Hyperfine parameters of Mössbauer spectra obtained at 4·2°K with clays fired at 500, 600, 700, 800 and 900°C. Numbers in parentheses give estimated errors in last significant digit

Component	Firing temperature °C	H KG	$e^2qQ/4$ mm/sec	δ[a]	Half width mm/sec	Fraction
S_1 (α-Fe_2O_3)	500	527(1)	−0·089(2)	0·147(2)	0·251(3)	69
	600	527(1)	−0·091(2)	0·138(2)	0·269(4)	75
	700	527(2)	−0·092(2)	0·145(3)	0·264(4)	73
	800	530(1)	−0·095(2)	0·141(2)	0·213(3)	78
	900	524(1)	−0·098(2)	0·133(2)	0·326(4)	92
D_1 (structural)	500	—	0·38	0·150(9)	0·42(2)	25
	600	—	0·336	0·15(1)	0·30(3)	9
	700	—	0·336	0·13(1)	0·29(6)	5
D_2 (structural)	500	—	0·8	0·15(1)	0·4(1)	6
	600	—	0·8	0·10(1)	0·37(3)	16
	700	—	0·8	0·12(2)	0·50(4)	22
	800	—	0·8	0·12(3)	0·61(4)	21
	900	—	0·49	0·08(4)	0·51	8

[a] Relative to ^{57}Co in Cu source at 4·2°K.

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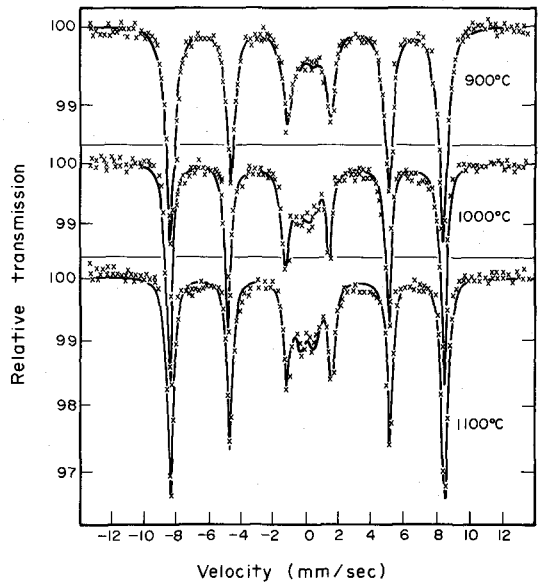


Fig. 3. Mössbauer spectra of clay fired at 900, 1000 and 1100°C, obtained at 4·2°K.

the paramagnetic part is almost completely absent. A paramagnetic part appears again at $T_f = 1000$°C and more clearly at 1100°C. The nature of this component, however, is different from that observed at lower firing temperatures since the quadrupole splitting is different. This is further demonstrated by measurements on the 1100°C sample at 1·4°K first in the absence of a magnetic field and then with a magnetic field of 8 kG applied in a direction normal to the γ-rays. The paramagnetic component persists in the first case, although with an intensity lower than that observed at 4·2°K, while with an applied field it is reduced to practically zero. This indicates that this component is due to a magnetically ordered species in the form of fine particles.

Significant variations, as a function of firing temperature, are also observed in the room temperature spectra shown in Fig. 4. On the other hand, comparison of this data with that of Figs. 1 and 2 at the same firing temperature reveals a strong enhancement of the paramagnetic component. The magnetic components are correspondingly smaller in the spectra of Fig. 4. This is clear evidence for superparamagnetic behavior of oxide particles which is also corroborated by the measurements at 77°K. The results of Fig. 4 show that as the firing temperature increases the relative intensity of the magnetic component increases and, correspondingly, the linewidth decreases. The variation of linewidth as a function of temperature is shown in Fig. 5. The two prominent changes observed are an abrupt step at $T_f = 400$°C and a more gradual decrease above $T_f = 600$°C. The large linewidth below $T_f = 400$°C for the room temp spectra may be attributed to size distribution and/or relaxation broadening for the fraction of α-Fe_2O_3 that is magnetic at this temperature (Van der Kraan, 1973). The abrupt decrease at $T_f = 400$°C

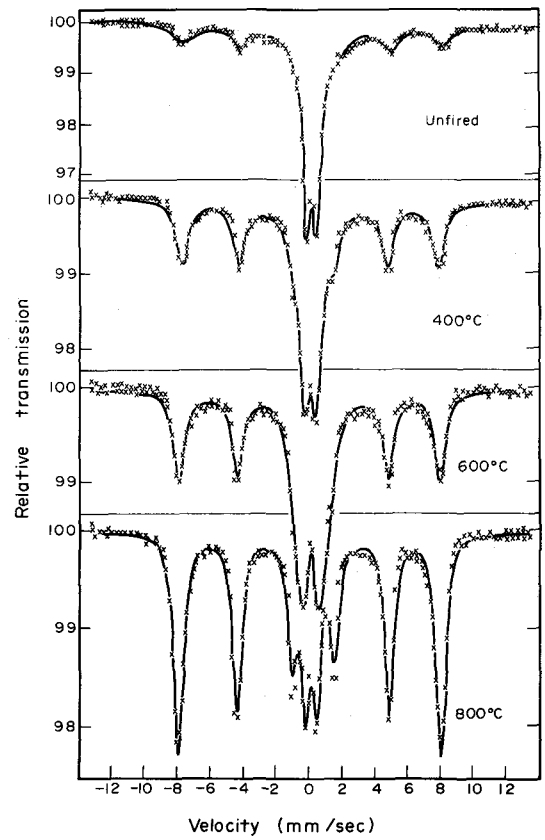


Fig. 4. Mössbauer spectra of clay unfired and fired at 400, 600, and 800°C, obtained at room temp.

may be associated with the appearance of large α-Fe_2O_3 particles arising from the transformation of β-FeOOH observed at this temperature. The further

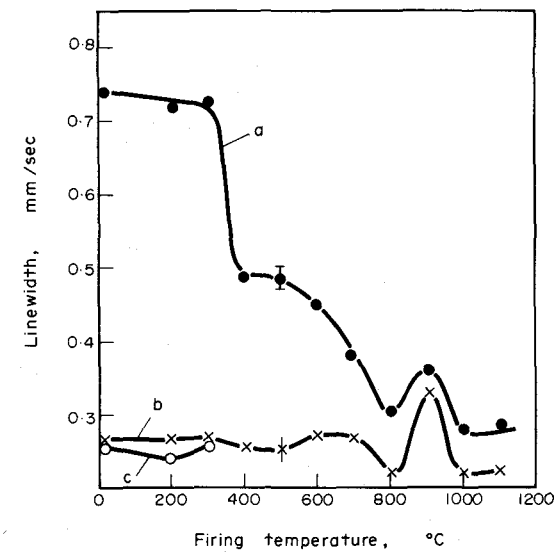


Fig. 5. Variation of the linewidth of the magnetic components of the room temperature and 4·2°K spectra as a function of firing temperature; (a) Magnetic sextet at room temperature (b) α-Fe_2O_3 magnetic sextet at 4·2° and (c) β-FeOOH magnetic sextet at 4·2°K.

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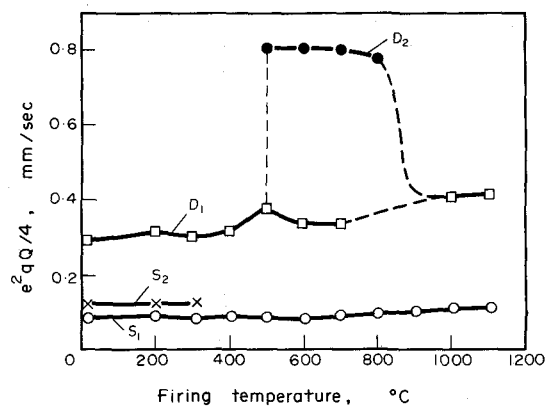


Fig. 6. Variation of the quadrupole splitting of the various components of the 4·2°K spectra with firing temperature. D_1 and D_2 correspond to the two paramagnetic doublets.

decrease above $T_f = 600$°C, in conjunction with the observed increase in relative intensity, suggests an increase in particle size of the oxides.

The distinct stages occurring in the transformations of the clay upon firing, can be further illustrated by a plot of the quadrupole splitting of the various components of the spectra as a function of temperature. This is shown in Fig. 6 as determined from the data at 4·2°K. The most prominent feature in this plot is the appearance of a second paramagnetic doublet with high quadrupole splitting at about 500°C and the disappearance above 800°C. It is also noted that the quadrupole splitting takes a higher value for $T_f = 1000$°C and 1100°C than in the first region, i.e. up to $T_f = 400$°C. The quadrupole splitting of the magnetic part remains practically constant throughout the firing temperature interval studied.

DISCUSSION

The experimental results described in the previous section demonstrate that the Mössbauer spectra of the studied clay samples undergo distinctive changes as the firing temperature varies. We shall discuss the implications of these results for the transformations that occur in the clay material during firing.

From the data of the unfired sample it is concluded that the iron is present in three components which are best resolved in the spectrum at 4·2°K shown in Fig. 1. The two magnetic components are identified as small particles of α-Fe_2O_3 and β-FeOOH through their hyperfine parameters listed in Table 1 by comparison with previously reported values for these oxides. The value of the effective magnetic field for β-FeOOH reported by Dezsi *et al.* (1967) was measured at 77°K. These authors report also a value of 300°K for the Neel temperature of this oxide which is the temperature at which antiferromagnetic order occurs. Using this value, the effective magnetic field at 4·2°K may be estimated at 490 kG in good agreement with the effective magnetic field of the second magnetic component S_2. The small size of the oxide particles is primarily demonstrated by the typical superparamagnetic behavior in the 77°K and room temp spectra and also by the value of the quadrupole splitting of the α-Fe_2O_3 component.

The assignment of the second component to β-FeOOH may be questioned on the ground of the existing uncertainty that β-FeOOH occurs naturally in soils (Mackenzie, 1957; Rooksby, 1961). Two other possible oxide species giving rise to this component may be α-FeOOH and γ-FeOOH. The latter can be definitely ruled out since its Neel temperature has been reported as 77°K and the hyperfine field at 4·2°K is 460 kG (Johnson, 1969) which is much smaller than the value observed for the component S_2. Mössbauer studies of α-FeOOH (Johnson, 1969) have determined a value for the hyperfine field of 504 kG and a Neel temperature of 400°K. The value of the hyperfine field is, therefore, somewhat higher than the observed value for the component S_2. A comparison of Neel temperatures would require a detailed study of the temperature dependence of S_2 which is not available at present. Additional support, however, for attributing the component S_2 to β-FeOOH is provided by the transformation to α-Fe_2O_3 by firing near 400°C in agreement with the results of Deszi *et al.* (1967).

The paramagnetic part of the 4·2°K spectrum of the unfired clay is attributed to iron in the clay mineral structure. The specific types of clay minerals present have not been determined for this sample but since it has been extracted from the same soil used in (I), a similar constitution is expected. The sample should consist mainly of illite, some kaolinite and vermiculite and interstratified systems of illite–chlorite and possibly vermiculite. The relative amount of iron substitution in the clay minerals can be determined from the ratio of the area of the paramagnetic component to the total area of the spectrum. As shown in Table 1 the structural iron amounts to about 30 per cent of total iron.

The transformations occurring by firing can be conveniently discussed by following the variation in the relative areas of the various components of the spectrum at 4·2°K as a function of firing temperature. If we assume that recoil free fractions are the same for the three components, the variation of areas gives quantitative information about the disappearance and growth of various iron containing phases. A plot of the normalized areas *vs* firing temperature is given in Fig. 7. In the region up to 400°C the outstanding feature is the decrease in the area of the magnetic component S_2 attributed to β-FeOOH and the corresponding increase of S_1 identified as α-Fe_2O_3. The transformation of β-FeOOH to α-Fe_2O_3 by heating has been investigated by Deszi *et al.* (1967), with Mössbauer spectroscopy on synthetically prepared samples. According to their results the transformation is complete in a few hours at 400°C, essentially in agreement with Fig. 7. It is noted that the area of the paramagnetic part, attributed to structural iron

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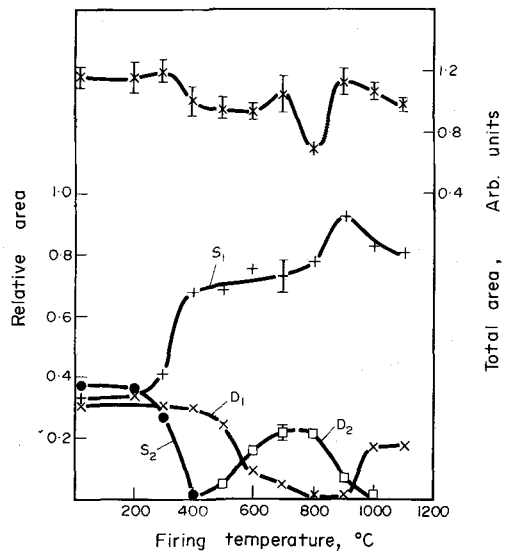


Fig. 7. Variation with firing temperature of the normalized areas of the various components of the spectra obtained at 4·2°K. The variation of the total area of the spectrum with firing temperature is also given in arbitrary units.

remains constant within experimental error, indicating that no significant changes occur in this temperature range.

The second region of firing temperature in which distinctive changes occur, extends from 400 to 800°C. This region is marked by the growth of a paramagnetic component D_2 with high quadrupole splitting and broad lines at the expense of the doublet D_1 observed below 400°C. It is apparent that this change is associated with dehydroxylation of the clay minerals because this process would leave the lattice in a highly disorganized state. Thus the asymmetry in the coordination of iron is expected to increase, leading to an increase in quadrupole splitting, while the increased disorder would give rise to inhomogeneous broadening due to variations of the quadrupole splitting from site to site. Similar results have been found by Mackenzie (1969) in a study of iron impurities in kaolinite and by Janot and Delcroix (1974) who have studied the effects of firing on a typical clay in order to draw conclusions about the firing temperatures of ancient French ceramics. On the other hand the dehydroxylation process in this range of temperatures has been studied extensively by DTA techniques. According to Grim (1968) an endothermic peak corresponding to the loss of lattice water is observed between 500 and 700°C in illite samples. The size and temperature interval of the peak vary from sample to sample, apparently due to differences in structural and compositional attributes.

At the firing temperature of 800°C the paramagnetic component D_1, with the lower quadrupole splitting, is almost totally absent. At this temperature the total area of the spectrum undergoes a significant drop as shown in the plot of the total area included in Fig. 7. Closer examination of the data shows that this drop occurs almost entirely in the paramagnetic component, indicating a decrease in the recoil free fraction. This would imply a general loosening of the iron in the clay mineral structure. Previous work on illites by other techniques (Grim, 1968) has shown that the destruction of the illite structure starts at about 850°C. It appears therefore that the observed decrease in the recoil free fraction marks the initiation of disintegration of the clay mineral structure.

The very small paramagnetic component at 900°C and the corresponding increase in the relative area of the magnetic component suggest that with progressive heating the iron diffuses out of the lattice and appears in the form of some magnetic oxide phase. Further transformation of this phase occurs upon heating to 1100°C, as manifested by the appearance of a paramagnetic component with quadrupole splitting $e^2qQ/2 = 0.82$ mm/sec. The disappearance of this component at 1·4°K upon the application of a magnetic field can be explained by a very small particle size for this phase. This interpretation is consistent with the value of the quadrupole splitting since at very small sizes the surface atoms have a significant contribution and tend to increase the quadrupole splitting as it was shown by the results of Van der Kraan (1973). It may be conjectured that the appearance of this component with very small particle size is related to the initiation of vitrification processes in which small iron oxide particles are precipitated.

Another important aspect of the effects of firing is the apparent increase in particle size of the oxide component of the clay as the firing temperature increases. This is implied by the data of Fig. 4 which show clearly a significant enhancement of the magnetic part between the spectrum of the unfired clay and the spectrum of the clay fired at 800°C. Quantitative details of the particle size distribution cannot be obtained with accuracy since the dependence on measuring temperature has not been studied in detail. An additional complication arises from the fact that the Neel temperature of β-FeOOH is close to room temperature, so that part of the paramagnetic doublet in the spectra measured at this temperature may be due to paramagnetic β-FeOOH. Furthermore the presence of a structural iron component results in additional uncertainty in the calculation of the true superparamagnetic ratio. A rough estimate can be made for the unfired clay and the clay fired at 900°C giving average particle sizes of 130 and 160 Å respectively. This means that firing the clay up to 900°C resulted in doubling the average volume of the oxide particles.

CONCLUSIONS

The results presented in this paper demonstrate that Mössbauer spectroscopy can provide a detailed description of the iron containing phases in a clay and of the transformations that occur upon firing.

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For the specific sample studied, a typical clay extracted from an Attic soil, the main findings can be summarized as follows:

(a) The initial clay contains iron in the form of small oxide particles identified as α-Fe_2O_3 and β-FeOOH as well as a substituted iron in the clay mineral structure.

(b) A transformation of β-FeOOH into α-Fe_2O_3 is observed upon heating the clay progressively to 400°C.

(c) Further heating to temperatures up to 800°C affects the part of the spectrum attributed to structural iron and is associated with dehydroxylation of the clay mineral.

(d) At 900°C the structural component is practically absent, indicating that the iron has formed some magnetic phase during the disintegration of the clay mineral structure. Further heating to 1000 and 1100°C leads to the growth of a new paramagnetic component which probably is due to very small oxide particles.

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