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A STUDY OF IRON IN FIRED CLAY : MÖSSBAUER EFFECT AND MAGNETIC MEASUREMENTS

R. CHEVALIER

DRF/Groupe d'Hyperfines, Centre d'Etudes Nucléaires de Grenoble 85 X, 38041 Grenoble Cedex, France

J. M. D. COEY

Groupe des Transitions de Phases, Centre National de la Recherche Scientifique

R. BOUCHEZ

Laboratoire de Recherche Archéologique, Institut des Sciences Nucléaires
257 X, 38044 Grenoble Cedex, France

Résumé. — Une terre de potier, provenant de la plaine de Gorgan au N-E de l'Iran, a été cuite successivement de 200 à la fusion 1 200 °C, soit dans l'air, soit dans un mélange réducteur (5 % Co dans CO₂ humide). Les spectres Mössbauer mesurés à 296 K et 4,2 K permettent de déterminer la proportion relative du fer soit dans l'hématite ou la magnétite bien cristallisés, soit dans les oxydes ou hydroxydes ferriques à grains fins ou peu cristallisés, soit du fer 2+ ou 3+ dispersés dans les silicates. Dans une cuisson oxydante il n'y plus d'ions Fe²⁺ au-dessus de 500 °C ; et à 1 200 °C tous les ions Fe³⁺ sont dispersés dans les silicates. Un pic d'aimantation (~ 5 uem/g. Fe) apparaît à 1 100 °C associé avec la diminution de la taille des grains fins d'oxyde ferrique avant leur dispersion à 1 200 °C dans les silicates. Dans une cuisson réductrice, des ions Fe³⁺ semblent subsister jusqu'à ~ 1 200 °C, ~ 12 % de fer existe dans la phase magnétite entre 600 et 800 °C puis disparaît rapidement dès 850 °C, ce qui rend compte de la chute rapide de l'aimantation depuis ~ 16 uem/g. Fe à 800 °C à ~ 0 à 1 100 °C.

Abstract. — A potters clay from the Gorgan plain, in N. E. Iran, has been fired successively at temperatures up to the melting point 1 200 °C in an atmosphere of air or 5 % CO in moist CO₂. Mössbauer spectra at 296 K and 4.2 K allow the determination of the relative amounts of iron in well-crystallised haematite or magnetite, of poorly-crystallised and fine-particle ferric oxide or hydroxide, and of iron diluted in the ferrous or ferric form in silicate minerals. In an oxidizing atmosphere there is no ferrous iron in firings above 500 °C and at 1 200 °C, all the ferric iron is diluted in the silicate matrix. A peak in the magnetization which reaches 5 emu/g. Fe near 1 100 °C is associated with a decrease in the size of ferric oxide fine particles before their disappearance at 1 200 °C. In a reducing atmosphere, some ferric iron persists up to about 1 200 °C, 12 % of the iron is in the form of magnetite between 600 and 800 °C, and its progressive disappearance from 850 °C accounts for the drop in magnetization from 16 emu/g. Fe at 800 °C to zero at 1 100 °C.

1. Introduction. — Fired clay is among mankind's most ancient and most useful manufactures. Although an excellent empirical understanding of the firing process has been developed over the ages, a complete fundamental understanding of the complex chemical and mineralogical transformations induced by firing clay has yet to be achieved.

In this paper, we fix our attention on the behaviour of just one element during the firing process — the iron. It is the fourth most abundant element in the Earth's crust, and a major constituent of most clay-grade minerals. The two main measurements reported here, ⁵⁷Fe Mössbauer spectra and bulk magnetic properties, detect only the iron, the latter because iron is by far the most abundant magnetic ion in clay.

Applications of the Mössbauer effect in the study

of the clay minerals have recently been reviewed by one of the authors [1]. The work on heat treatments has almost all involved pure minerals, treated in air. However Simopoulos *et al.* have performed a Mössbauer study on an air-fired Attic clay containing a mixture of minerals whose scope resembles that of the present work [2]. Our clay is perhaps more representative in that most of iron present is diluted in the clay minerals, rather than in the form of iron oxides and hydroxides. We have studied the transformations induced by firing both in oxidizing and reducing atmospheres, and relate the Mössbauer results to the magnetization data which was reported in some detail in reference [3]. Use of the two techniques should allow a complete account of the transformations involving the iron to be developed.

The present work, like that of reference [2], was partly inspired by application of the Mössbauer effect to archaeological problems, and some of the implications in this domain will be discussed.

2. Results. — The clay examined was a reddish-pink used currently for pottery manufacture by the potter of Gorgan a town in north-east Iran. Its elemental composition was as follows: SiO_2 46.7 %, CaO 13.4 %, Al_2O_3 12.1 %, $\text{FeO} + \text{Fe}_2\text{O}_3$ 4.5 %, MgO 3.2 %, K_2O 2.4 %, Na_2O 1.4 %, TiO_2 0.6 %. The weight lost on ignition was 16.6 %. The mineral composition determined by X-ray diffraction, was Quartz 30 %, Calcite 20 %, Feldspar 10 %, Illite 20 %, Chlorite 10 %, Smectite and Kaolinite 10 %. Its Mössbauer parameters at room temperature was previously reported in [4] (C2). Ferrous iron accounts for 29 % of the total absorption and from the isomer shift and quadrupole splitting, it was concluded that this ferrous iron was mainly present in the Chlorite. Out of the remaining 71 % of ferric absorption 12 % was due to well-crystallised Haematite, another 21 % to other concentrated iron oxide or hydroxide phases, possibly coatings on the clay mineral particles, which order or block magnetically in the range 4-300 K, and the remaining 38 % to iron in the clay minerals themselves, mainly the Illite and Smectite. Error are ± 3 %. If equal recoilless fractions can be assumed for all the iron, these figures represent the relative amounts of iron in each phase.

Two sets of firings were studied in detail. Separate samples were fired at each temperature, in one case in air, in the other in an atmosphere of 5 % Co in moist CO_2 . 1 g samples of the dry clay were heated up over five hours, kept at constant temperature T_f for ten hours and then cooled in the furnace over ten hours.

Mössbauer spectra were taken at room temperature and at liquid helium temperature on all the samples, and magnetic hysteresis loops were measured at room temperature. Some typical data are shown in figure 1. The spectra were least-squares fitted with up to two magnetic hyperfine spectra, and two ferrous and one ferric quadrupole doublets. The aim was not so much to fit a subspectrum to every possible iron site, as to reproduce accurately the shape of the spectrum and thus determine the relative absorption of ferrous and ferric iron in both the paramagnetic and magnetically ordered states.

2.1 OXIDIZING FIRINGS. — All trace of ferrous iron had disappeared from the Mössbauer spectra of samples fired in air above 400 °C. The relative intensity of the ferrous quadrupole doublet at 4.2 K was only half of what it was at 296 K. This cannot plausibly be described as a recoilless fraction effect, but is probably due to magnetic ordering of Chlorite at very low temperatures. The Chlorite contains about 10 wt % of iron, and magnetic order at 4.2 K is

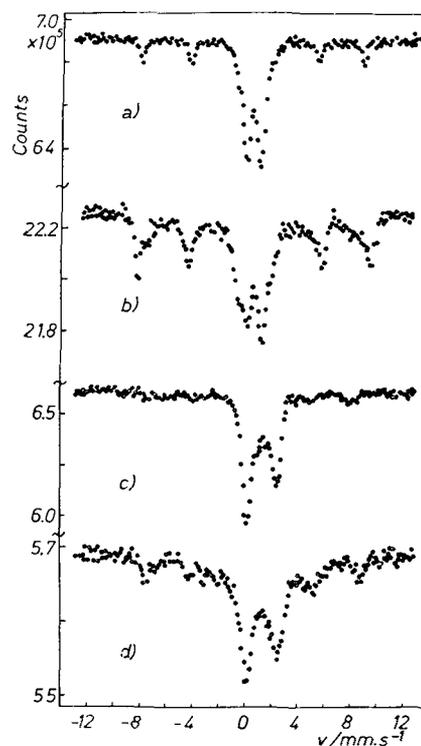


FIG. 1. — Mössbauer spectra of clay fired in an oxidizing atmosphere (air) at 925 °C (*a* and *b*) or in a reducing atmosphere (a mixture of 5 % CO in moist CO_2) at 750 °C (*c* and *d*). *a* and *c* are taken at room temperature whereas *b* and *d* are taken at 4.2 K.

known in other silicates with similar amounts of iron [5, 6].

The well-crystallised ferric oxide which gives a sharp magnetic hyperfine spectrum at 296 K is essentially Haematite. It reaches maximum of 26 % of the total absorption in the 800 °C firing, but disappears completely at 1 200 °C. At 4.2 K its hyperfine field H_{hf} is 530 kOe. It is quite distinct from the second six-line spectrum with broader lines and $H_{hf} \approx 465$ kOe which appears in the spectra at 4.2 K but not at 296 K (Fig. 1*a, b*). This spectrum is attributed to ferric hydroxides or ferric oxide fine particles which block between 4.2 and 300 K. It also disappears in the clay fired at 1 200 °C.

The amount of ferric iron diluted in the silicate matrix, whether in the clay minerals of the unfired clay or their reaction products on heating, is represented by the ferric quadrupole doublet at 4.2 K. This iron is sufficiently dilute, ≤ 5 wt %, that there is little chance that it order magnetically at 4.2 K, and its relative proportion increases fairly steadily with firing temperature from 38 % in the infired clay to 100 % in the clay fired at 1 200 °C. All of these results are summarized on figure 2. If the clay had been heated well above 1 200 °C in air, the reappearance of some ferrous iron would be expected (7).

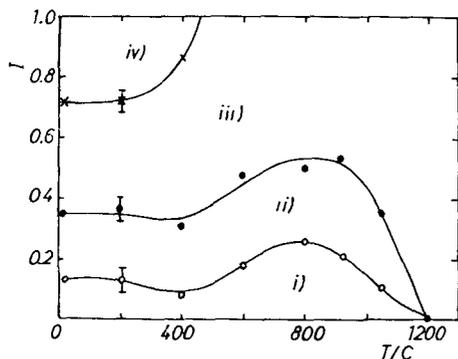


FIG. 2. — Relative Mössbauer absorption of iron in different phases as a function of firing temperature in an oxidizing atmosphere. \circ Magnetically-ordered ferric iron at 296 K, \bullet Magnetically-ordered ferric iron at 4.2 K, \times total ferric ion at 296 K. The numbered regions refer to i) well-crystallised haematite, ii) poorly crystallised or fine-particle ferric oxide and hydroxide, iii) ferric iron dilute in silicate phases, iv) ferrous iron dilute in silicate phases.

2.2 REDUCING FIRINGS. — The behaviour of the iron is completely different when a reducing atmosphere is used for the firings. The relative absorption of the ferrous quadrupole doublets in the room temperature spectra increases steadily with firing temperature, and extrapolates to 100 % near 1 200 °C. At 4.2 K, some of this ferrous absorption has passed into a poorly-defined hyperfine spectrum, suggesting magnetic order in the more iron rich parts of the silicate matrix.

The well-crystallised haematite present in the unfired clay appears to have converted to well-crystallised magnetite by 600 °C. It continues to account for approximately 10 % of the total absorption until fired at 800 °C, but by 950 °C it has essentially disappeared.

The intensity of the ferric quadrupole doublet in the room-temperature spectra decreases steadily with firing temperature, and extrapolates to zero at 1 200 °C. These results are summarised on figure 3.

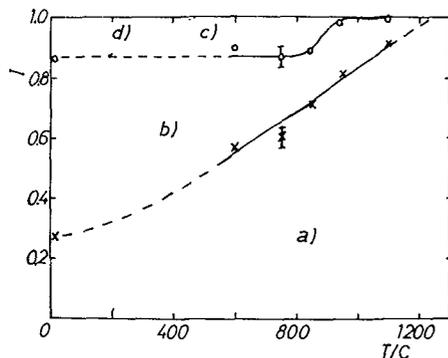


FIG. 3. — Relative Mössbauer absorption of iron in different phases as a function of firing temperature in a reducing atmosphere. \times ferrous iron paramagnetic at 296 K, \circ total iron paramagnetic at 296 K. The lettered regions refer to a) ferrous iron dilute in silicate phases, b) ferric iron dilute in silicate phases, c) magnetite, d) haematite.

We conclude this section with a remark about the colour of the fired clay. The starting material was pink when dry. It turns red then buff when fired in air up to 1 050 °C, but at higher temperatures it becomes pale yellow. When fired in the reducing conditions, it turns grey, but the grey becomes progressively paler as the firing temperature is increased beyond 800 °C.

3. Discussion. — In general terms, three major transformations occur successively when clay is heated in air: dehydroxylation, vitrification and recrystallization. The first is signaled in the Mössbauer spectrum by a large increase in the ferric quadrupole splitting [2, 8, 9] which occurs at ~ 400 °C in our clay. Vitrification is the reaction which is important for pottery production. It usually occurs progressively over an extended temperature range which depends sensitively on the chemical composition especially Ca and Fe^{2+} and is best observed directly in the scanning electron microscope [10, 7]. The decrease in the ferric quadrupole splitting which occurs above about 850 °C in our clay [4] may also be associated with vitrification. Recrystallization of the vitreous silicate matrix normally takes place at a higher temperature provided melting does not occur first.

The results we have obtained for the iron in our clay fired in an oxidizing atmosphere (Fig. 2) indicate that the ferrous iron is all oxidized to the ferric form near the temperature where dehydroxylation occurs. Ferrous iron in pure chlorites is known to be completely oxidised by heating in air at 400-500 °C [11]. Also at about 500 °C, the quantity of well-crystallised ferric oxide begins to increase as the haematite in the original clay is supplemented by haematite produced from the poorly crystallised ferric hydroxide, or else by agglomeration of oxide fine particles. Note that the haematite and magnetite referred to in this paper are not necessarily the pure oxides $\alpha\text{-Fe}_2\text{O}_3$ or Fe_3O_4 , but may have considerable amounts of cation substitution, e. g. Al^{3+} , Ti^{4+} .

The relative absorption due to the fine-particle or poorly crystallised ferric oxide or hydroxide does not vary much with firing temperature up to 1 050 °C. Since this fraction is being depleted by haematite formation above 500 °C, it must be simultaneously replenished with iron which was originally diluted in the clay matrix. A likely reason is the poor solubility of ferric oxide in alkali silicate glasses, so that when vitrification of the dehydroxylated clay sheets occurs, the ferric oxide tends to segregate out into small clusters. Ferric oxide is known to be produced when Biotite is heated in air at 900 °C, and its crystallinity improves at 1 000 °C [12]. The diminution of the amount of iron oxide phases above 950 °C would therefore imply that recrystallization of the silicate matrix has begun, as iron is quite soluble in the crystalline products such as anorthite, spinel or mullite.

The spontaneous magnetization of the fired clay in oxidizing conditions measured at 296 K is shown in figure 4a. Its value throughout, and particularly at the peak at 1 100 °C is far too great to be explained by the amount of haematite present for which

$$M_s \approx 0.5 \text{ emu/g of Fe.}$$

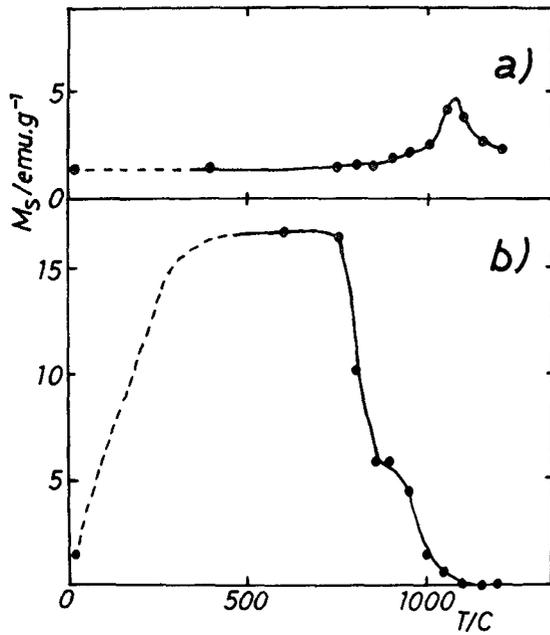


FIG. 4. — Spontaneous magnetization at 296 K of clay fired in a) an oxidizing atmosphere and b) a reducing atmosphere. M_s is given per gram of iron.

The magnetization is likely to come mainly from to fine particles of ferric oxide for which M_s may be typically 1-10 emu/g of Fe, but depends strongly on the particle size, being proportional to $N^{-1/2}$, where N is the number of iron ions in the particle [13]. A reduction in the average particle size near the peak at 1 100 °C is consistent with the increase in the relative amount of fine particles above 900 °C shown

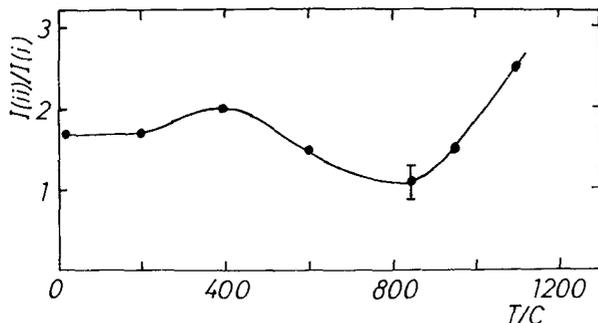


FIG. 5. — The ratio of fine particle to well-crystallised ferric oxides as a function of firing temperature in an oxidizing atmosphere.

in figure 5. One can imagine that the surface atoms of the fine particles of ferric oxide are being dissolved into the recrystallised silicates in this temperature range, thereby reducing the average particle size. Magnetite formation is unlikely for firings in air at these temperatures [7], and it would not produce a peak in M_s .

In the firings in the *reducing* atmosphere the ferric iron is less easy to reduce than the ferrous iron was to oxidize in the firings in air. The most interesting feature is perhaps the existence of magnetite at temperatures up to about 850 °C. The Mössbauer data shows that $\sim 12\%$ of the iron is in that form, at least between 600 and 800 °C, and with a moment $M_s \approx 100$ emu/g, the high value of the magnetization (Fig. 4b) in this range of temperature is nicely accounted for. The fall of the magnetization near 850 °C corresponds to the disappearance of magnetite from the Mössbauer spectrum. It is presumably dissolved in the vitreous silicate matrix, as Fe^{2+} is soluble in silicate glasses, and is even a glass former. All the ions are diluted in the silicate phases by about 1 000 °C in the reducing atmosphere as compared with 1 200 °C in air.

Two other conclusions may be drawn from this work. One concerns the colour of fired clay [14] which can be directly associated with the iron oxides. For the firings in air the product is reddish-pink or buff so long as haematite is present, $T_f \lesssim 1\,000$ in the case of our clay, but at $T_f \approx 1\,200$ °C, where the ferric oxide is absent, the colour is a pale yellow; finally at the melting point $\approx 1\,230$ °C, the colour is dark brown. For the firings in the CO-CO_2 mixture, the product is dark grey so long as magnetite is present, $T_f < 900$ °C, in the case of our clay, but at $T_f \gtrsim 950$ °C the colour becomes a much paler light grey.

The other concerns the use of the proportion of iron in a sherd present in the form of oxide as an indication of firing conditions or age of an ancient ceramic [15]. Our firings in air have demonstrated that this parameter may be a sensitive function of firing temperature, and comparison with the results of a set of firings under slightly different oxidizing conditions (it was kept at the maximum temperature for one hour instead of ten) [1, 3] shows that it depends also on the firing cycle. It would seem to be rather difficult to unravel these effects from those of time, suggested in references [15], unless the original firings are made in a range of temperature or firing conditions to which the proportion of iron in the oxide phase is rather insensitive. This condition appears to be fulfilled around 800 °C in our clay, but not around 1 000 °C.

The results obtained in the present study of laboratory-fired clay will be compared with the Mössbauer and magnetic data on ancient postsherds manufactured from similar *clays* in another paper [16].

Although the transformations of the iron on firing

which we have described may be qualitatively typical of moderately-weathered clays, the same quantitative behaviour cannot be expected regardless of the mineralogical and chemical composition of the starting material.

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