

## MÖSSBAUER STUDY OF GLOZEL TABLET 198 b1

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### INTRODUCTION

Recently a great deal of discussion began again about the authenticity and age of pottery and other ceramics found at Glozel (in central France near Vichy) from 1924 onwards. Although most, but not all, archaeologists have considered these fakes for quite some time, recent thermoluminescence measurements by KcKerrell *et al.* (1974) gave evidence tentatively suggesting that they were about twenty centuries old. Comment on these results has been made by various authors including Aitken and Huxtable (1975), Renfrew (1975), Hall (1975), and Warren (1975). Subsequent thermoluminescence measurements (François *et al.* 1977) confirmed the tentative dating, though the data obtained for the last firing of a small proportion of the objects examined were within the last thousand years; tablet 198 b1 is in that category, being dated in the range A.D. 1100–1350, as was first done by Aitken and Huxtable (1975). Although the possibility that the thermoluminescence itself has been faked by clandestine operators using artificial irradiation has been examined and rejected (McKerrell *et al.* 1975, Aitken and Huxtable 1975) information provided on Glozel samples by independent experimental techniques is obviously of value, especially in providing data on the physical and chemical state of these samples and thus complementing and strengthening the results of dating methods. Barbetti (1976) has made archaeomagnetic measurements on several Glozelian ceramic artifacts and he suggests that on the basis of the ancient magnetic field intensities evaluated from some of the samples, these artifacts could not have been fired in the interval between 1500 B.C. and A.D. 1500. This conclusion is based on the assumption that no rapid changes of the geomagnetic field intensity occurred in this interval. However, more recent archaeomagnetic measurements, by Shaw (1979), on Gallo Roman pottery from central France give evidence that a sharp fluctuation did occur during the period of interest.

From his archaeomagnetic measurements Barbetti also obtained information in respect of firing temperature; the estimated firing temperature was below 300°C for one of the objects he examined but above 600°C for three of the objects, above 550°C for one object, and above 500°C for tablet 198 b1. Estimates for the firing temperature for ten Glozel objects – not including tablet 198 b1 – have been reported by Ahmed and Mejdahl (1976) on the basis of room temperature Mössbauer spectroscopy on these samples and on laboratory-fired present day Glozel clay. These estimates give firing temperatures below 400°C for most of the objects with a value of 465°C for one of them. As was pointed out by Ahmed and Mejdahl there is some ambiguity in the interpretation of the parameter used and Differential Thermal Analysis (DTA) for seven of these objects showed that only two were poorly fired, the other five having a firing temperature in excess of 600°C (Mejdahl 1980).

The importance of the consequences of the low firing for the archaeomagnetic and thermoluminescence ages of these objects points to the need for more confident estimates of the firing temperatures and for a better understanding of the physical and chemical structure of these objects. Glozel tablet 198 bl has been thoroughly examined for its thermoluminescence (Aitken and Huxtable 1975) and archaeomagnetic properties (Barbetti 1976). Therefore, this sample was considered as appropriate for further investigation by Mössbauer spectroscopy in order to (i) provide a description of the chemical and physical form of iron present in the sample and (ii) to estimate the tablet's firing temperature.

#### EXPERIMENTAL

Portions of the tablet sample were refired up to 1000°C in steps of 200°C for two hours in air. One sample was refired at 500°C also, because this firing was important for the estimation of the firing temperature (see below). Ahmed and Mejdahl (1976) found that the Mössbauer spectral parameters of Glozel clay saturate at each firing temperature after one hour firing time.

Mössbauer spectra of the original and the samples refired at 400°C, 500°C, 600°C and 1000°C were obtained with a constant acceleration spectrometer in transmission geometry, at room temperature, 80 K, 16 K and 4.2 K. The samples refired at 200°C and 800°C as well as the material extracted from the original sample after magnetic separation *via* a bare magnet were measured at 300 K, 80 K and 16 K. A 50 mCi <sup>57</sup>Co source in Rh matrix was used. The absorber used for these measurements contained 75 mg cm<sup>-2</sup> of sample in powder form.

The experimental spectra were computer fitted with a least squares constrained programme. Areas were calculated from peak intensities and linewidths resulting from the fit of the spectral lines *via* lorentzians.

#### EXPERIMENTAL RESULTS AND DISCUSSION

We present first the results from the analysis of the spectra of the original sample at various measuring temperatures in order to obtain an understanding of the structures of the material as seen by Mössbauer spectroscopy. Subsequently the results referring to the refired samples are given.

##### a) *Data on the original sample*

Figure 1 shows the Mössbauer spectra of the original sample at various measuring temperatures. The gross features of these spectra indicate the presence of two sextets and of at least one doublet situated at the centre of the spectrum. A sextet is characteristic of iron in a magnetically ordered state while a doublet corresponds to iron ions in a paramagnetic state.

In view of these features computer fits of the spectra were performed with two sextets and two doublets. One should note that the need for two paramagnetic sites at 4.2 K and the strong superparamagnetic trend shown by the spectra of figure 1 make plausible the addition of a third doublet in the analysis of the 16 K, 80 K and 300 K spectra in order to account for the contribution of the superparamagnetic particles. However, the analysis at these temperatures was also made with two doublets only, because the fitting of the spectra did not significantly improve on the introduction of more doublets while at the same time the uncertainty in the parameters thus deduced evidently increased. Table 1 summarizes the results from this analysis.

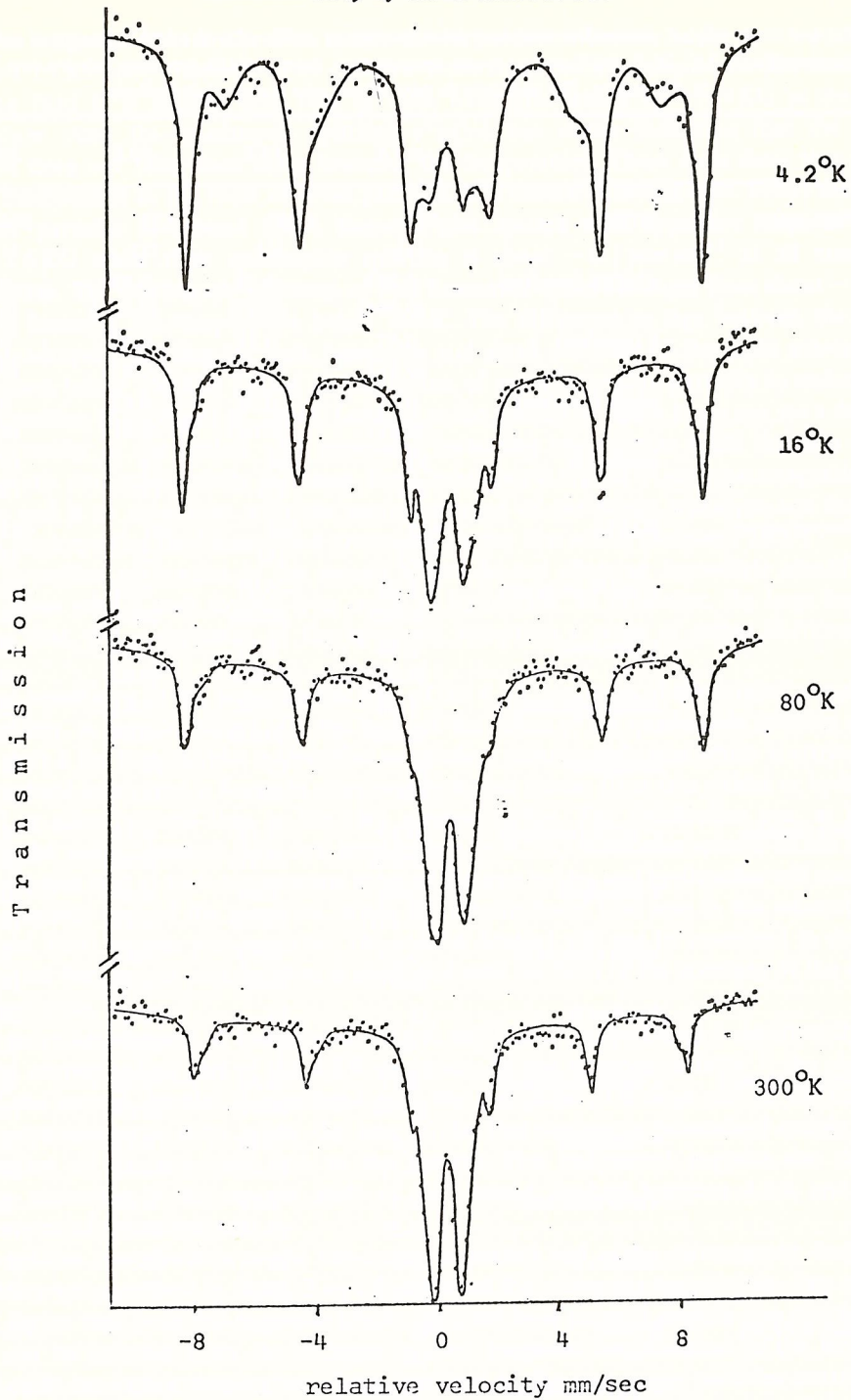


Figure 1 Mössbauer spectra of the original sample at various measuring temperatures. The solid lines represent least square fits to the data points.



Table 1 *Hyperfine parameters deduced from spectra of a Glozel tablet 198 bl unrefired sample, measured at 4.2 K, 16 K, 80 K and at room temperature. Isomer shifts are given relative to a  $^{57}\text{Co}$  in Rh source. The numbers in parenthesis give standard deviations.*

		4.2 K	16 K	80 K	300 K
<i>First sextet</i>	<i>H</i> (KG)	528 (1)	531 (1)	528 (1)	506 (1)
	$e^2qQ/4$ (mm/sec)	-0.083 (0.004)	-0.09 (0.03)	-0.091 (0.005)	-0.10 (0.01)
	$\delta$ (mm/sec)	0.52 (0.01)	0.38 (0.01)	0.39 (0.01)	0.35 (0.01)
	width (mm/sec)	0.55 (0.01)	0.33 (0.01)	0.43 (0.01)	0.35 (0.02)
	fraction %	52 (2)	34 (2)	29 (2)	19 (2)
	<i>Second sextet</i>	<i>H</i> (KG)	445 (2)	504 (1)	501 (2)
$e^2qQ/4$ (mm/sec)		-0.04 (0.03)	-0.07 (0.02)	0.01 (0.02)	-0.11 (0.02)
$\delta$ (mm/sec)		0.48 (0.03)	0.37 (0.02)	0.41 (0.02)	0.34 (0.02)
width (mm/sec)		1.04 (0.04)	0.53 (0.03)	0.42 (0.04)	0.53 (0.04)
fraction %		34 (2)	17 (2)	10 (2)	16 (2)
<i>First doublet</i>		$e^2qQ/4$ (mm/sec)	0.53 (0.02)	0.59 (0.01)	0.55 (0.01)
	$\delta$ (mm/sec)	0.46 (0.03)	0.64 (0.03)	0.59 (0.01)	0.50 (0.01)
	width (mm/sec)	0.73 (0.07)	0.53 (0.05)	0.41 (0.03)	0.35 (0.01)
	fraction %	11 (1)	16 (3)	15 (2)	18 (1)
<i>Second doublet</i>	$e^2qQ/4$ (mm/sec)	0.47 (0.08)	0.55 (0.01)	0.50 (0.03)	0.47 (0.01)
	$\delta$ (mm/sec)	0.8 (0.1)	0.28 (0.02)	0.27 (0.01)	0.24 (0.01)
	width (mm/sec)	0.7 (0.2)	0.59 (0.02)	0.60 (0.02)	0.51 (0.01)
	fraction %	3 (1)	33 (3)	46 (2)	47 (1)
<i>Bulk <math>\alpha\text{-Fe}_2\text{O}_3</math></i>	<i>H</i> (KG)	542 (1)	—	—	516
	$e^2qQ/4$ (mm/sec)	0.200 (0.003)	—	—	-0.103
	$\delta$ (mm/sec)	0.378 (0.008)	—	—	0.257



Of the magnetic sextets, the first makes the largest contribution to the spectrum and is attributed to  $\alpha\text{-Fe}_2\text{O}_3$  (haematite) as deduced from its hyperfine parameters. The saturation hyperfine field  $H$  is smaller than that of bulk haematite which is  $\sim 544$  KG at the same temperature. Also the quadrupole splitting  $e^2qQ/4$  has values indicating that the Morin transition does not take place upon lowering the temperature. These facts show that in our sample haematite is in the form of small particles. It is known (Künding *et al.* 1966) that small haematite particles of around 180 Å diameter give spectra with hyperfine magnetic fields of  $531 \pm 6$  KG while their quadrupole splitting is about  $-0.1$  mm sec<sup>-1</sup> at all measuring temperatures. The quadrupole splittings of bulk haematite spectra changes from about  $-0.1$  to  $0.2$  upon lowering the temperature below 260 K. The difference in sign between the values of the quadrupole splitting for bulk haematite and small particles of the same substance at temperatures below 260 K is caused by the failure of small haematite particles to undergo the Morin transition (Künding *et al.* 1966). Looking at the spectra of figure 1 one can see a decrease in the intensity of the sextets with increasing measuring temperature while the area of the paramagnetic part substantially increases. Such behaviour is typical of superparamagnetic small particles and is in agreement with the non-occurrence of the Morin transition and the small value of the hyperfine field mentioned previously for the first sextet (Schroerer 1969).

The hyperfine parameters of the second sextet do not allow an immediate identification of this phase with a well formed iron oxide or hydroxide. In particular, the large linewidth indicates that this component of the spectrum comprises a range of rather ill-formed iron phases.

It was possible to fit the paramagnetic part of the 4.2 K spectrum of the original sample with two doublets, as seen in table 1. On the basis of the values of the quadrupole splitting and the isomer shift  $\delta$  the first doublet is identified as trivalent paramagnetic iron which is attributed to the 'structural iron'. Iron is found in clays mainly in two forms: (i) as free oxides or hydroxides and (ii) as substitutional ions in the clay mineral lattice. The distribution can, at least in principle, be easily obtained from low temperature ( $\sim 4.2$  K) Mössbauer spectra on the basis of the assumption that at such temperature most of the iron oxides and hydroxides will contribute to the magnetic part of the spectrum, while the substitutional iron ions in the mineral lattice (structural iron) remain paramagnetic. The second doublet will not be examined in detail for the moment because its area fraction is small and near the limit of the accuracy of the analysis of the spectrum.

The paramagnetic part of the spectra at 16 K and higher temperatures is significantly larger than the corresponding part of the 4.2 K spectrum. As one observes in table 1, the change in area of the second doublet is associated with the transition of a large part of the oxides to the superparamagnetic state, while the area of the first doublet is determined mainly by the contribution of the structural iron to the spectra. This assignment explains also the large decrease occurring in the isomer shift of the second doublet between 4.2 K and higher temperatures of measurements.

The relative contributions of the two magnetic sextets and of the paramagnetic doublets of the spectra are presented in figure 2 as a function of the measuring temperature. One observes in this figure that both the magnetic phases detected have unusual particle size distributions. These can be inferred from the decrease of their magnetic contributions in the Mössbauer spectra with increasing temperature: large fractions of the iron oxide particles contribute at 4.2 K to both magnetic sextets but become superparamagnetic at a temperature as low as 16 K. Furthermore, the findings that upon a small increase of the temperature from 4.2 to 16 K about

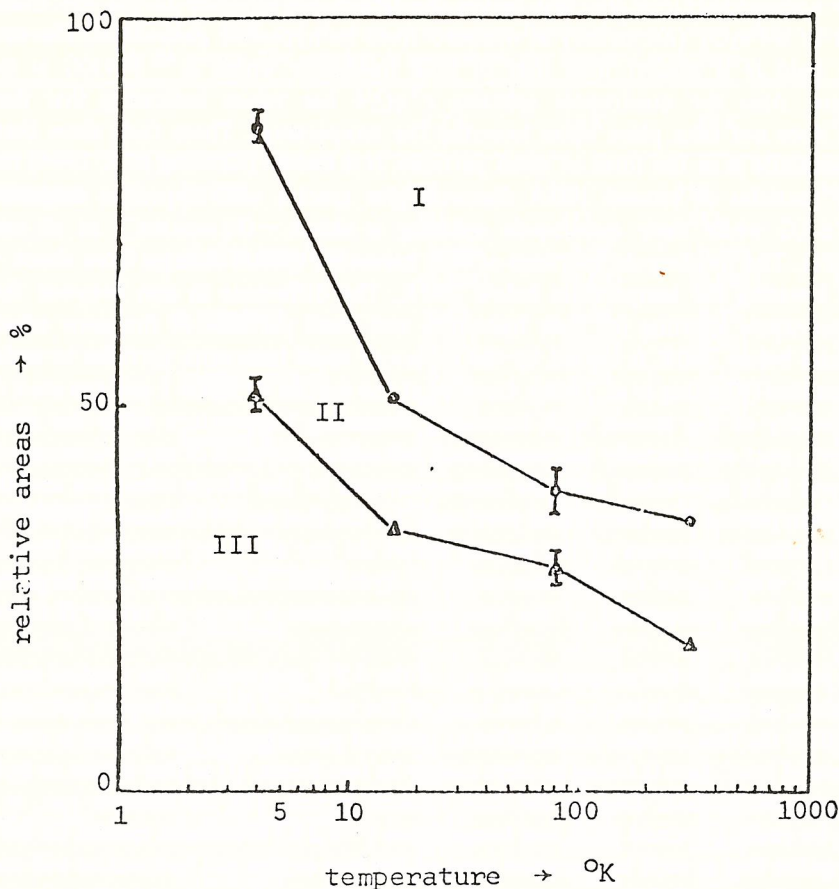


Figure 2 Relative areas of spectral components of the unrefired Glazel tablet 198 bl sample, plotted versus measuring temperature. Regions: I Paramagnetic doublets, II 2nd magnetic sextet and III magnetic  $\alpha\text{-Fe}_2\text{O}_3$ . Solid lines have been drawn as boundaries of the regions and therefore they do not infer any functional dependence.

half of the second sextet becomes paramagnetic, while at the same time its linewidth decreases by a factor of 2 and its hyperfine field increases, indicate that the major part of this sextet represents very fine particles. The hyperfine parameters of this sextet as well as those of the second doublet at temperatures higher than 4.2 K resemble those observed for haematite particles smaller than 50 Å in diameter (Schroerer 1969) or for amorphous  $\text{Fe}_2\text{O}_3$  (Van Diepen and Popma 1976).

Moreover, the spectra of the material extracted magnetically from the original tablet showed distinctively, beside the major haematite phase, a second iron phase also and thus enabled the confirmation of its identification with very fine  $\text{Fe}_2\text{O}_3$  particles. This latter fact suggests that the second iron oxide phase consists of the products of strong weathering of the well formed haematite, originally present in the sample as the only major iron oxide.

On the basis of the results mentioned above the iron phases detected in the sample studied



can be described as follows. About 85% of the iron is in the form of small  $\text{Fe}_2\text{O}_3$  particles, more than half of which are in the form of well formed haematite of about 100 Å size. The rest of them have very small size (< 50 Å) and are most probably weathering products. The remaining 15% of the iron in the sample is substitutional iron in the clay mineral lattice, as will be further elucidated *via* the analysis of the 4.2 K spectra of the refired samples. Furthermore, the fact that only trivalent iron compounds have been detected in the sample indicates that if this tablet was fired (see below), the firing conditions must have been oxidizing.

#### b) Data on the refired samples

In view of the complexity of the iron phases present in the original sample, the study of their transformations upon refiring has been made mainly on the basis of spectra measured at 4.2 K due to the relative simplicity of the spectra at this temperature. Before presenting the results from these data, we briefly summarize the main findings from Mössbauer studies of the transformations of iron present in clays upon firing (Coey 1978, Simopoulos *et al.* 1975).

When clay is fired in air at increasingly higher temperatures first, below about 400°C, the hydroxides usually present in the clay transform to haematite. Following this the clay mineral lattice begins to lose its hydroxyls at around 500°C. This change gives rise to a highly asymmetric environment for the structural iron ions and Mössbauer spectra reflect this change in the crystallographic environment as a rise in the quadrupole splitting of the corresponding component. The dehydroxylation process takes place over a range of temperatures and is completed at around 800°C. Upon completion of the dehydroxylation process and sometimes even before, the iron ions start migrating to the mineral grain's surface where they are oxidized and thus contribute to a certain extent to an increase of the haematite particle size. This process is completed at around 900°C. This change can be detected as a decrease in the structural iron component of the spectra and an increase in the haematite contribution to the magnetic sextets. Finally, at around 1000°C the clay mineral lattice is transformed to new crystalline silicate phases (e.g. mullite) in which  $\alpha\text{-Fe}_2\text{O}_3$  begins to dissolve.

The changes undergone by the clay upon firing allow us to deduce in some favorable cases the firing temperature of a pottery artifact by refiring it. As long as the refiring temperature is below that of the original firing, no change in the Mössbauer spectra is expected. However, as soon as the original firing temperature is exceeded, the ceramic will carry on with its transformations from where it stopped in the original firing and this may be detected as a change in the characteristics of the Mössbauer spectrum. This method has been followed in the present study, because it is at least in principle far more reliable than the method used up to now (Ahmed and Mejdahl 1976, Janot and Delcroix 1974). According to this previous method the firing temperature of an ancient pottery sherd has been determined by comparing the Mössbauer spectra of the sherd with those of laboratory fired modern clay collected from the same location as the ancient object. Evidently, one cannot be certain about the identity of the clay thus collected and the clay used by the ancient potter for the manufacture of the pottery sherd under study. This uncertainty is hardly changed in the cases – such as the present one (McKerrell *et al.* 1974) – for which neutron activation analysis or other elemental analysis gives the same elemental constitution for the ancient sherd and the modern clay sample; this is because the elemental constitution leaves out the effects of the manufacturing techniques, such as clay treatments and firing cycle.

Figure 3 shows the spectra of the refired samples measured at 4.2 K. It was possible to fit these spectra with two sextets and two doublets as in the case of the original sample at the same



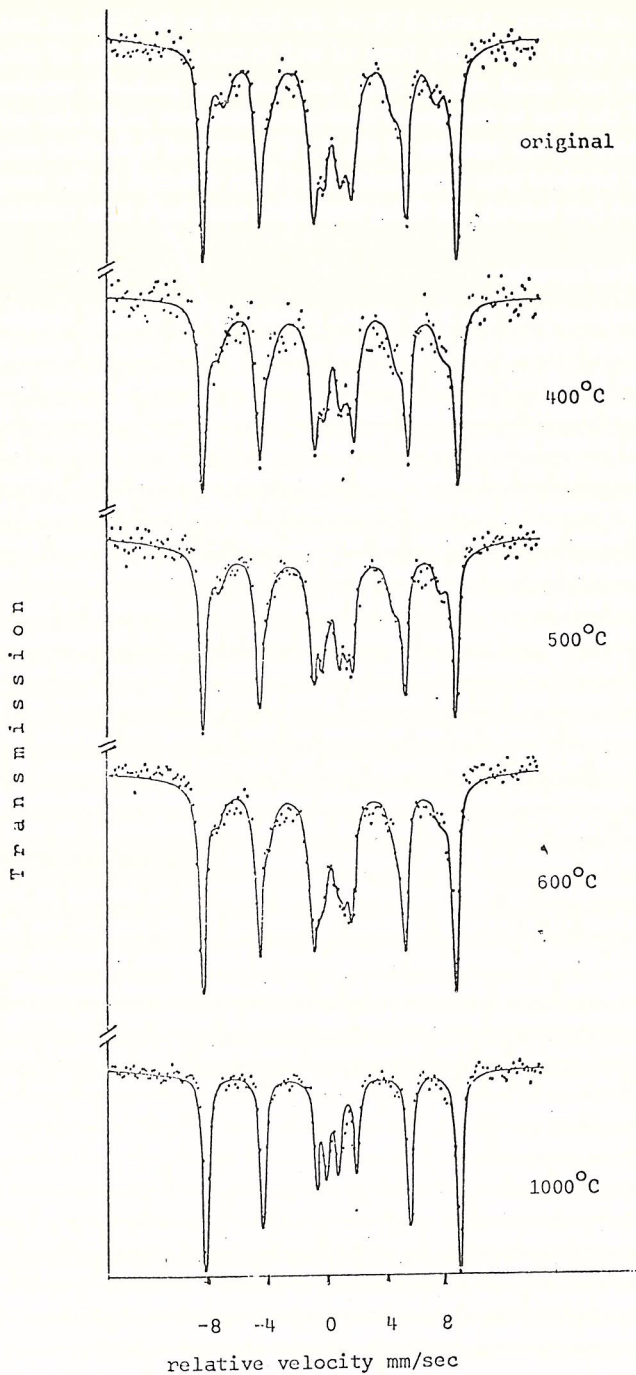


Figure 3 Mössbauer spectra at  $4.2^{\circ}\text{K}$  of a sample from Glozel tablet 198 b1 before and after refiring at various temperatures. Refiring temperatures are shown next to each spectrum. The solid lines represent least square fits to the data points.

Table 2 *Hyperfine parameters derived from Mössbauer spectra of Glozel tablet 198 bl samples unrefired and refired at 400°C, 500°C, 600°C and 1000°C. Absorber temperature at 4.2 K. Source at room temperature. Isomer shifts are relative to a  $^{57}\text{Co}$  in Rh. The numbers in parenthesis give standard deviations.*

	Firing temp	Original	400°C	500°C	600°C	1000°C
<i>First sextet</i>	<i>H</i> (KG)	528 (1)	532 (6)	529 (3)	529 (1)	528 (1)
	$e^2qQ/4$ (mm/sec)	-0.083 (0.004)	-0.089 (0.007)	-0.071 (0.004)	-0.072 (0.004)	-0.089 (0.002)
	$\delta$ (mm/sec)	0.52 (0.01)	0.37 (0.01)	0.36 (0.01)	0.36 (0.01)	0.43 (0.01)
	width (mm/sec)	0.55 (0.01)	0.50 (0.02)	0.47 (0.01)	0.47 (0.01)	0.40 (0.01)
	fraction %	52 (2)	42 (4)	51 (2)	52 (2)	78 (2)
<i>Second sextet</i>	<i>H</i> (KG)	445 (2)	470 (4)	464 (3)	467 (2)	-
	$e^2qQ/4$ (mm/sec)	-0.04 (0.03)	-0.03 (0.04)	0.01 (0.03)	-0.05 (0.01)	-
	$\delta$ (mm/sec)	0.48 (0.03)	0.33 (0.04)	0.33 (0.03)	0.37 (0.03)	-
	width (mm/sec)	1.04 (0.04)	1.33 (0.07)	0.92 (0.04)	1.10 (0.05)	-
	fraction %	34 (2)	47 (6)	32 (3)	29 (4)	-
<i>First doublet</i>	$e^2qQ/4$ (mm/sec)	0.53 (0.02)	0.53 (0.06)	0.57 (0.02)	0.61 (0.01)	0.45 (0.01)
	$\delta$ (mm/sec)	0.46 (0.03)	0.27 (0.08)	0.26 (0.02)	0.15 (0.01)	0.29 (0.01)
	width (mm/sec)	0.73 (0.07)	0.6 (0.1)	0.56 (0.06)	0.72 (0.03)	0.59 (0.02)
	fraction %	11 (1)	7 (2)	12 (2)	12 (1)	22 (1)
<i>Second doublet</i>	$e^2qQ/4$ (mm/sec)	0.47 (0.08)	0.57 (0.05)	0.59 (0.04)	0.63 (0.02)	-
	$\delta$ (mm/sec)	0.8 (0.1)	0.6 (0.2)	0.7 (0.1)	0.58 (0.02)	-
	width (mm/sec)	0.7 (0.2)	0.6 (0.4)	0.5 (0.2)	0.54 (0.03)	-
	fraction %	3 (1)	4 (2)	5 (2)	7 (1)	-

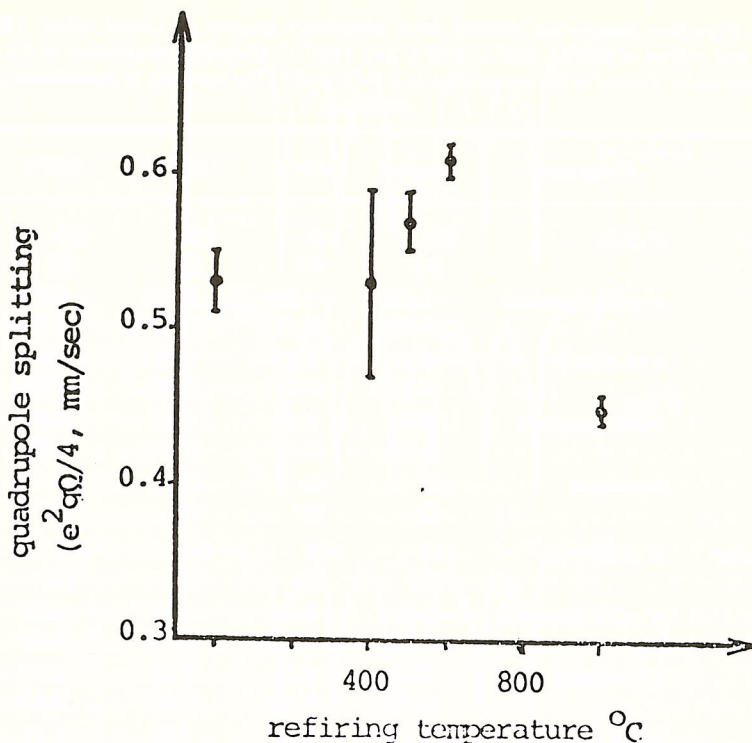


Figure 4 Quadrupole splitting ( $e^2qQ/4$ ) of the structural iron component (first doublet in table 2) versus refriring temperature. The point at  $0^\circ\text{C}$  refriring temperature corresponds to the unrefired sample.

temperature. From this figure and the parameters obtained from these fits (table 2) we observe that: (i) the features of the spectra remain practically unchanged up to refriring temperatures of  $400^\circ\text{C}$ ; (ii) from  $400^\circ\text{C}$  and up to  $600^\circ\text{C}$  refriring temperatures, a gradual increase in the quadrupole splitting of the first doublet takes place. Figure 4 shows this variation; (iii) at  $1000^\circ\text{C}$  the spectrum consists of one sextet corresponding to well formed small haematite particles and one doublet with hyperfine parameters corresponding to trivalent iron oxide dissolved in the mineral phases formed at this high temperature (Simopoulos *et al.* 1975).

These facts are in agreement with the transformations known to occur to iron present in clays upon firing in air. In particular, the changes occurring in the first doublet upon refriring support the assignment of this doublet to the structural iron. Furthermore, the increase of the quadrupole splitting of the first doublet between  $400^\circ\text{C}$  and  $600^\circ\text{C}$  indicates the continuation or the onset of the dehydroxylation of the mineral lattice and thus puts the upper limit of the possible original firing temperature of the tablet at  $600^\circ\text{C}$  as a maximum and  $500^\circ\text{C}$  as a minimum.

This estimate is compatible with the archaeomagnetic measurements (Barbetti 1976) on this tablet, which show that the 90% of the sample magnetization lies below about  $500^\circ\text{C}$ .

Turning now to the estimation of a lower limit for the firing temperature, one can point out that: (i) fitting the paramagnetic part of the room temperature spectrum of the original sample with one doublet gives a quadrupole splitting of about  $0.51\text{ mm sec}^{-1}$ . Comparing



this value with the values of quadrupole splitting deduced *via* a similar analysis of the room temperature Mössbauer spectra of fired present day Glozel clay (Ahmed and Mejdahl 1976) one obtains a firing temperature of about 400°C; and (ii) unfired soils contain fine iron hydroxides as e.g. goethite, which transform to haematite at firing temperatures up to 400°C, with the result that the Mössbauer spectra of the unfired soil and the soil fired in air at 400°C show marked differences. Such differences have not been observed between the original sample and the sample refired at 400°C.

From these observations the lower limit of the firing temperature is estimated as 400°C, although an even lower firing temperature cannot be definitely rejected on grounds of the present data. However, the archaeomagnetic data on this tablet (Barbetti 1976) are not compatible with such a lower value.

A final remark should be added about the second doublet of the spectra at 4.2 K. One observes in table 2 that the quadrupole splitting of this spectral component varies with refiring temperature in the same way as the splitting for the structural iron, while its isomer shift is markedly larger than that of the first doublet. These facts make plausible the identification of this doublet as another structural iron component, possibly rehydroxylized structural iron, a phase expected (Grim and Bradley 1948, Kingery 1974) to have been generated from absorbed water; for such low fired clay as that of the present tablet sufficient water absorption would take place in not too long a time. If the above identification is correct, then the presence of this phase sets the lower limit for the original firing temperature above 400°C.

#### CONCLUSIONS

The present Mössbauer study of Glozel tablet 198 bl allowed: (a) the identification of the chemical and physical form of iron present in the tablet and (b) the inference of its firing conditions. In particular, the results reveal that: (i) most, 85%, of the iron is in the form of Fe<sub>2</sub>O<sub>3</sub>, while the rest is as trivalent structural iron bound into the clay mineral grains, (ii) about 60% of the oxide particles are well formed haematite of about 100 Å in diameter, while the rest of them are particles of less than 50 Å in size, probably the products of weathering, and (iii) the firing atmosphere was oxidizing and the firing temperature definitely smaller than 600°C and probably greater than 400°C.

The low firing temperature and the strong weathering – as manifested by the presence of large amounts of very fine oxide particles – are compatible with each other, since very little or no sintering occurs among clay mineral grains at firing temperatures less than 600°C. The strong weathering is of course consistent with prolonged burial but taken together the findings point to a possible source for systematic error in the thermoluminescence date obtained for this tablet and for the dates obtained for other low fired objects, though it must be emphasized at once that this effect could hardly cause fake ceramics to give thermoluminescence dates that were ancient. The interference to the thermoluminescence reliability is associated with the changes in the radiation dose received by any poorly fired ceramic during burial because of the large cation exchange capacity retained by low fired clay (Hedges and McLellan 1976) – interchange of uranium, thorium or potassium could mean that the radioactive content as measured today does not give a reliable evaluation of the average level during the centuries of burial. According to Mejdahl (1980) such interference is unlikely in respect of Glozel objects because the soil radioactivity is close to that of the objects, and also, the radioactivity of poorly fired objects does not differ significantly from that of well fired ones.

The interest in the finds at Glazel makes a strong case for further work in order to clarify the chemical and physical structure of these objects, and relationship to firing conditions, before one can complete their archaeometric description.

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