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MÖSSBAUER STUDY OF ANCIENT FRENCH CERAMICS

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Résumé. — Des échantillons de céramiques anciennes trouvées sur le sol français ont été étudiées par spectrométrie Mössbauer dans le but de caractériser ces matériaux tant du point de vue provenance que du point de vue technique de fabrication.

Les spectres Mössbauer permettent d'obtenir facilement les fractions relatives du Fe^{3+} et du Fe^{2+} contenu dans les poteries et d'en déduire la nature de l'atmosphère pendant la cuisson. Par ailleurs, une comparaison avec les spectres Mössbauer obtenus pour des argiles ayant subi différents traitements thermiques permet d'obtenir des informations intéressantes sur la technique de fabrication des poteries, comme par exemple la température finale de cuisson.

Abstract. — Some samples obtained from ancient French ceramics were studied by Mössbauer spectroscopy in order to test the potential of this method for determining the provenance and the manufacture of pottery. The relative abundance of Fe^{3+} and Fe^{2+} obtained from Mössbauer spectra seems to be an easy way to give information about the atmosphere in the kilns used to fire ancient pottery. On the other hand, the comparison with transformations induced by firing clay characterized by Mössbauer spectroscopy may lead to valuable information regarding the manufacture of ancient pottery as, for instance, the final temperature of firing in it.

1. Introduction. — The provenance, manufacturing techniques and trade of pottery in the ancient world are of great archeological interest to provide information about artistic and technological level of various cultures and their influences. The analytical methods usually used in material science can be readily applied to the study of pottery objects which are only fired clays.

Among these methods, the Mössbauer spectroscopy constitutes at present an interesting way to obtain information on the chemical and physical state of the iron [1]. These information may be used in two ways (i) clays from different areas will contain different minerals in different proportions and the oxidizing or reducing treatment each clay receives during the firing will differ from kiln to kiln; hence, the Mössbauer spectrum of a particular pottery will be of assistance in identifying the provenance of the ware and the nature of the kiln atmosphere during firing [2], [3] (ii). By comparing the spectra given by a sherd with spectra of known minerals and clays after various heating treatment, it may be possible to deduce the conditions in which the pottery was fired especially regarding the higher temperature reached in the kiln and the heating sequence.

2. Mössbauer analysis of iron in clay. — The pottery objects are only typical fired clays containing between 5 and 10 % natural iron, either as Fe^{2+} or Fe^{3+} in octahedral or tetrahedral environments in the clay silicate minerals or as accessory minerals as an admixture or coating of iron oxides [6].

The usefulness of the Mössbauer method as a characterization technic is based on the following results concerning the various states of the iron in clay minerals :

— The oxide $\alpha\text{-Fe}_2\text{O}_3$ normally shows a magnetic hyperfine spectrum (6 peaks) at room temperature, with a magnetic field $H_{\text{eff}} = 515$ kOe, quadrupole splitting $2\varepsilon = 0.17$ mm/s and an isomer shift $\delta = 0.42$ mm/s. Substituted forms as $(\text{Fe}_{1-x}\text{Al}_x)_2\text{O}_3$ can exist with a smaller magnetic field H_{eff} which varies roughly linearly with the substitution rate x , so providing a way to determine x by measuring H_{eff} [4]. The oxide is often present as very small particles exhibiting a typical superparamagnetic behaviour which can lead to the particle size related to the conditions of crystallisation [5].

— The hydroxide such as $\alpha\text{-FeOOH}$ or goethite can exist in clay minerals but disappears after firing and cannot be found in potteries. The Mössbauer pattern is also a magnetic hyperfine spectrum which can show a superparamagnetic behaviour for larger particles than in oxide.

— Iron in the alumina octahedra in place of Al^{3+} ion should behave roughly as if it was in gibbsite environment. So, the Mössbauer spectrum should be a doublet with $2\varepsilon \simeq 0.52$ mm/s and $\delta \simeq 0.38$ mm/s. This doublet is different from the superparamagnetic pattern obtained in the case of small particles of oxides because it is impossible to transform it in a 6 peaks pattern by lowering the temperature.

— Iron in the tetrahedra silica surfaces should exhibit a larger quadrupole splitting.

— Fe^{2+} is characterized by his large isomershift, and a quadrupole splitting ranging from about 1 to 2 mm/s.

These various points are summarized in table I.

The changes occurring on Mössbauer spectra of a clay, after a progressive heating, give usefull information of the behaviour of iron in octahedral or tetrahedral coordination, inside the clay lattice. The figure 1 shows typical changes of the Mössbauer

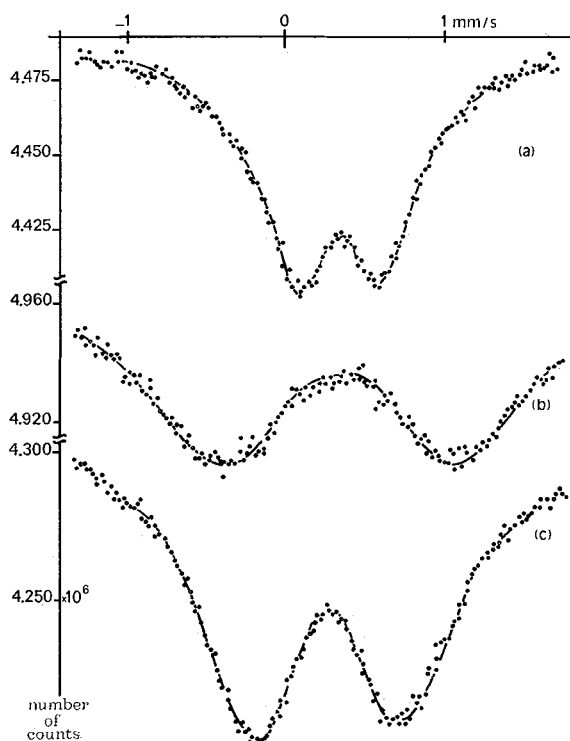


FIG. 1. — Typical Mössbauer spectra of fired clay : a) clay before firing, b) fired at 700 °C, c) fired at 1100 °C.

spectra versus the heating temperature and the curves on figure 2 give the temperature dependence of the quadrupole splitting, the isomer shift and the recoilless

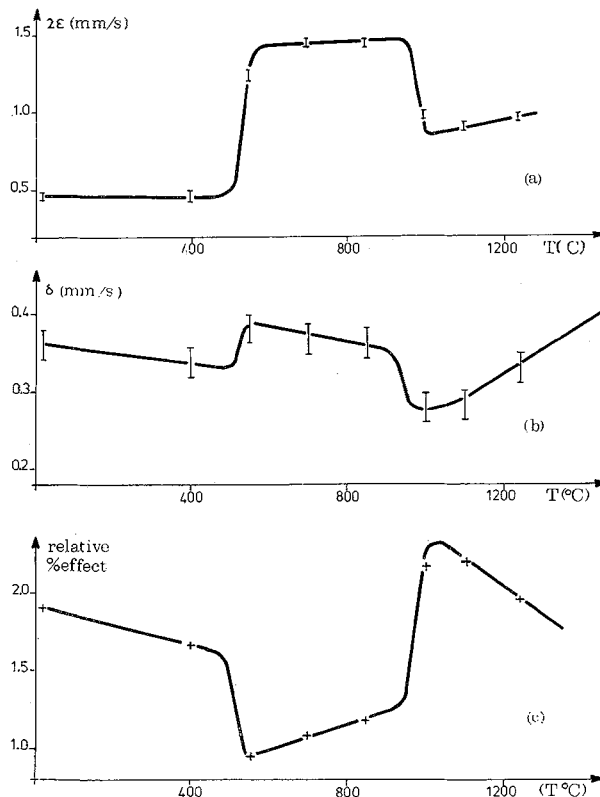
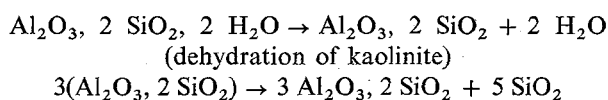


FIG. 2. — Temperature dependence of 2ε (a), δ (b) et relative effect fraction (c).

fraction for iron in the alumina octahedra in place of Al^{3+} ion of a typical clay. Two rather sharp transitions occur near 550 °C and 980 °C corresponding to the following sequence of reaction :



(crystallographic rearrangement of kaolinite to form mullite and cristobalite).

The Mössbauer data are consistent with this reaction sequence. As deshydration proceeds by heating near 550 °C, the spectrum becomes much more diffuse, indicating a loosening of the iron atoms in their

TABLE I

State of the iron	peaks	Room temperature			Temperature of liquid nitrogen			
		H_{eff} (kOe)	δ (mm/s)/Fe	$2\ \varepsilon$ (mm/s)	peaks	H_{eff} (kOe)	δ (mm/s)/Fe	$2\ \varepsilon$ (mm/s)
$\alpha\text{-Fe}_2\text{O}_3$	6	515	0.42	— 0.17	6	533	0.56	+ 0.39
$\alpha\text{-Fe}_2\text{O}_3$ small particles 30 < d < 80 Å	2 (broad) dissymmetrical	0	~ 0.35	~ 0.55	6	533	0.56	+ 0.39
Goethite	6 (broad)	280 à 390	0.40	— 0.30	6	500	0.45	+ 0.33
Goethite small particles 80 < d < 150 Å	2 (broad) dissymmetrical	0	~ 0.40	~ 0.60	6	500	0.45	+ 0.33
Octahedral coordination	2 (broad)	0	0.30 à 0.40	0.45 à 0.60	2	0	~ 0.45	~ 0.45
Tetrahedral coordination	2 (broad)	0	~ 0	0.60 à 0.90	2	—	—	—

substitutional sites; the peaks broadening and the increase of the quadrupole splitting indicate the presence of vacancies in the structure as well as lattice distortions. At further arrangement near 980 °C, the recoilless fraction increases while the quadrupole splitting shows a significant lowering, indicating the progressive annealing of the vacancies, the appearance of a well definite crystallographic environment and giving the evidence that the iron atoms become progressively more firmly bound. Being influenced by the lattice transformations gives the proof that the iron atoms are in substitutional sites.

For the characterization of ancient ceramics, the significant changes in the quadrupole splitting with the heating temperature are very interesting, though the transitions occur at temperatures which slightly vary with iron concentration.

The main points are the following :

(i) a progressive heating from room temperature to near 1 200 °C leads to a final quadrupole splitting of 0.90 mm/s ;

(ii) if the clay is directly fired in a kiln whose temperature has previously reached about 1 000 °C or more, the quadrupole splitting becomes constant after about 5 min and its value is always between 1.06 and 1.30 mm/s. To obtain the former value (0.90 mm/s) it is necessary to reoperate with a progressive sequence of heating since the room temperature.

These very important results may be used, from a technological point of view, to give suggestions about the firing temperature and the firing sequence once applied to ancient pottery.

Let us remark that the temperature dependence of both isomershift and recoilless fraction are strongly dependent on the clay composition and can provide only qualitative information.

3. Samples studied and experimental results. — The pottery shards studied were referenced by their archeological classification :

(i) 68-7-1336 : (red colour) and 68-7-559 : (grey colour) — found in Doué-la-Fontaine (Maine-et-Loire, France) ; manufactured near the 10th century,

(ii) 66-5-394 : (white colour) — found in a kiln at Argentan (France) ; manufactured at the beginning of the 13th century,

(iii) Az : (red colour) — found in the Charente river (France) — manufactured near the 15th century.

The Mössbauer experiments were done with a spectrometer operating in the constant acceleration mode. The 25 mCi source used was prepared by electroplating ^{57}Co onto palladium then reducing and diffusing in H_2 atmosphere at high temperature. The velocity scale and the spectra shift origin have been normalized to a naturel iron absorber whose peak half-width is 0.119 mm/s. All the peak positions are

determined with an accuracy better than 0.01 mm/s and their relative intensities can be evaluated with an error of a few per cent. The magnetic hyperfine field are obtained in the accuracy of a few kOe. The source is at room temperature while the temperature of the studied samples can vary from the boiling point of liquid nitrogen to about 1 100 °C.

The spectra obtained for the pottery shards before any heating treatment can be classified in the three following categories :

(i) those which exhibit only a quadrupole doublet ($2\varepsilon \simeq 0.9$ mm/s and $\delta \simeq 0.3$ mm/s) typical of Fe^{3+} in octahedral coordination. This sort of spectrum is shown on figure 3 and corresponds to the pottery shard 66-5-394,

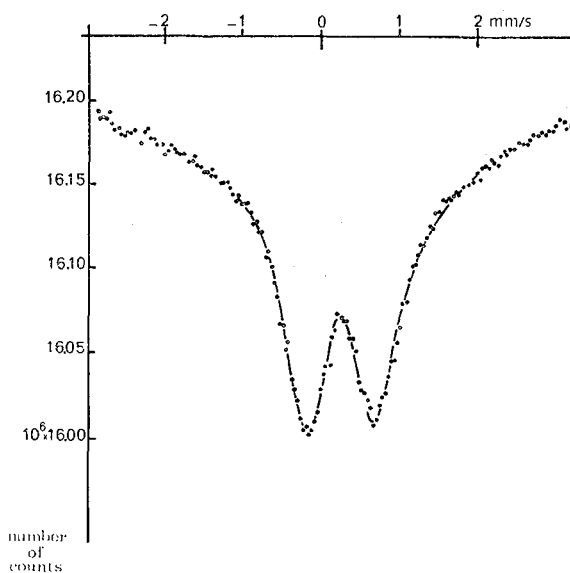


FIG. 3. — Mössbauer spectrum of ceramic with trivalent iron only in octahedral coordination.

(ii) those which exhibit three apparent peaks and which actually can be analysed in two quadrupole doublets corresponding to substitutional Fe^{3+} and Fe^{2+} , as shown on figure 4 for the pottery shard 68-7-559,

(iii) those which are more complicated with both a doublet and a six peaks magnetic pattern corresponding roughly to $\alpha\text{-Fe}_2\text{O}_3$ (Fig. 5) as in the cases of the pottery shards 68-7-1336 and Az.

Table II summarizes these results as well as the data obtained from Mössbauer spectra at liquid nitrogen temperature or after various heating treatments applied to the pottery shards.

4. Characterization of the pottery shards from the Mössbauer data. — As noticed above, the Mössbauer data of table II as well as the remarks regarding the behaviour of minerals clay in Mössbauer spectroscopy after various firing sequences may lead to some conclusions on the chemical and physical state of the iron in pottery shards related to the origin of the clay and

TABLE II

Echantillons	Tempe- rature (K)	H_{eff} (kOe)	6 peaks pattern			Doublet			Relative effect fraction (%)
			δ (mm/s)	2ε (mm/s)	part of the iron (%)	δ (mm/s)	2ε (mm/s)	part of the iron (%)	
66-5-394	300	—	—	—	—	0.265	0.871	100 Fe ³⁺	1.71
The same baked at 1 000 °C	300	—	—	—	—	0.242	0.857	100 Fe ³⁺	1.60
68-7-559	300	—	—	—	—	0.419	1.06	80 Fe ³⁺	3.70
						1.025	2.27	20 Fe ²⁺	
The same baked at 700 °C	300	—	—	—	—	0.363	1.25	100 Fe ³⁺	3.80
The same baked at 1 000 °C	300	—	—	—	—	0.280	0.820	100 Fe ³⁺	6.0
68-7-1336	300	505	0.39	0.21	23	0.30	0.78	77 Fe ³⁺	7.90
	85	528	0.57	0.19	33	0.37	0.83	67 Fe ³⁺	8.30
Az	300	499	0.41	0.17	84	0.31	1.11	16 Fe ³⁺	14.2
	85	526	0.52	0.14	87	0.45	1.30	13 Fe ³⁺	15.4

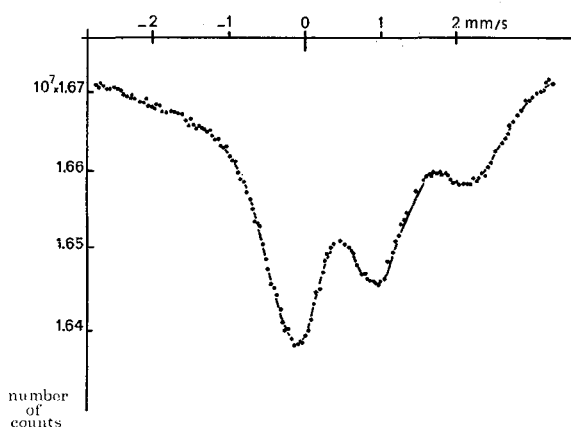


FIG. 4. — Mössbauer spectrum of ceramic containing trivalent and divalent iron in octahedral coordination.

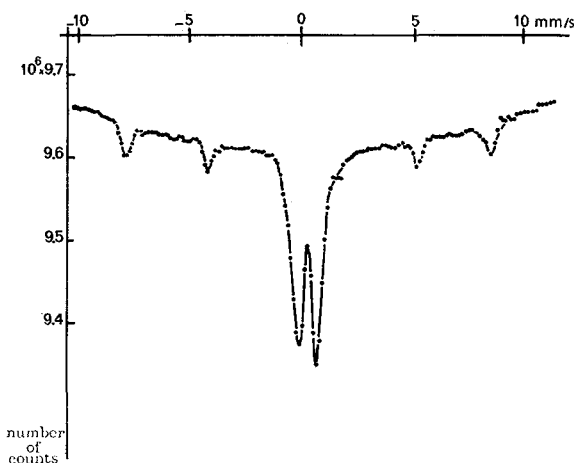


FIG. 5. — Mössbauer spectrum of ceramic containing iron partially as small particles of oxide.

firing techniques. These conclusions are the following for each sample studied in this work :

(i) SAMPLE 66-5-394. — This white ceramic is very poor in iron which is only in form of Fe³⁺ in the place

of Al³⁺ in the lattice (see the typical values of quadrupole splitting and isomer shift).

The kiln atmosphere during firing was rather oxidizing and the temperature reached at least 1 000 °C.

(ii) SAMPLE 68-7-559. — This grey ceramic exhibits two forms of iron : 80 % in the Fe³⁺ state and 20 % in the Fe²⁺ state which can be oxidized by firing in air at 700 °C. All the iron is in substitution of Al³⁺. Hence the Mössbauer data suggest that the clay was, once, partially reduced during firing at over 1 000 °C.

(iii) SAMPLE 68-7-1336. — The iron is present in either of two forms : as iron oxide α -Fe₂O₃ (33 %) partially in small particles exhibiting typical superparamagnetic behaviour, and as trivalent iron ions incorporated into the structure of the clay mineral (67 %). The hyperfine magnetic field is smaller (505 kOe) than for a pure α -Fe₂O₃ (515 kOe) and could suggest that the iron would be partially substituted by various impurities, probably aluminium through some exchange process with the clay. The substituting rate would be near 10 %. The clay was not reduced during firing and the Mössbauer data suggest a progressive heating sequence from room temperature to over 1 000 °C.

(iv) SAMPLE Az. — The results are very similar in appearance to that obtained for sample 68-7-1336. However, the largest part of the iron is in form of oxide α -Fe₂O₃ (87 %) where iron would be substituted by about 16 % of impurities. Let us remark that in samples (iii) and (iv), the reduced magnetic field may be due to other substitutional impurities than Al and even other factors like vacancies, small particles sizes, can produce the same effects.

Regarding the experimental values of the quadrupole splitting, it could be thought that ceramics 68-7-559 and Az were directly fired in a previously heated kiln, but such a treatment seems to be very unlikely and this point certainly requires further studies to be made clear.

5. **Conclusion.** — The Mössbauer spectroscopy as a characterization technique applied to the study of pottery objects can provide useful information regarding technological level of various cultures and leads to quantitative conclusions such as the determination of the firing temperature, or the knowledge of the kiln atmosphere during firing.

An interesting possibility is to operate with a backscattering technic which is really a non-destructive method and so, to examine large pottery shards and even unbroken potteries without necessity of sampling (here, backscattering technic has been applied in the case of sample 66-5-394).

It seems difficult to obtain the firing temperature with a good accuracy because of the rather weak

changes of the quadrupole splitting in clay after the rearrangement in mullite and cristobalite. The method may be improved by a comparison of the recoilless fraction among a large number of samples having similar compositions.

On the other hand, the problem of the provenance of the ceramics related to the mineral composition of the heated clay or the firing characteristics might be rather hard ; for instance, it can be noticed that the pottery shards 68-7-1336 and 68-7-559, both found in Doué-la-Fontaine, exhibit different mineral compositions, different oxidized and reduced state and perhaps different heating sequence. Certainly, more definitive conclusions need the observation of the ceramics through several analytical methods.

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