MÖSSBAUER STUDY OF MYCENEAN AND MINOAN POTTERY

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Résumé. — On a examiné par spectroscopie Mössbauer deux séries d'échantillons de poteries mycéniennes et minéennes d'origine bien authentifiée. L'analyse des spectres mesurés à 77 K a révélé que des paramètres tels que l'éclatement quadrupolaire ou l'aire totale d'absorption peuvent être utilisés pour distinguer les échantillons des deux séries. Les spectres montrent que le rapport oxydes magnétiques sur l'ensemble des oxydes augmente énormément lorsqu'on diminue la température de 4,2 K à 1,4 K ce qui suggère une désintégration des particules d'oxyde. En comparant avec les résultats obtenus pour des poteries modernes et d'époques intermédiaires on voit que le degré de désintégration est fonction du temps. La possibilité d'utiliser la spectroscopie Mössbauer pour le datage de céramiques anciennes est discutée.

Abstract. — Two series of samples of Mycenean and Minoan Pottery of well authenticated origin have been examined by Mössbauer Spectroscopy. The analysis of spectra taken at 77 K showed that parameters such as the quadrupole splitting and the total absorption area can be used for differentiating between the samples of the two series. The spectra show a dramatic increase of the ratio of the magnetic to total oxides, when the temperature is lowered from 4.2 to 1.4 K, suggesting a disintegration of the oxide particles. Comparison with results from modern pottery and pottery of intermediate ages shows that the degree of disintegration is a function of time. The possibility of using Mössbauer spectroscopy for dating ancient ceramics is discussed.

The study reported in this paper is part of a program aimed at exploring the applicability of Mössbauer spectroscopy to archaeological problems related to ancient pottery. Mycenean and Minoan pottery are two representative groups of ceramic wares of the Greek Late Bronze age, with well developed style and manufacturing technique, and the establishment of characterization parameters from Mössbauer spectroscopy would be an important new tool for the elucidation of archaeological problems related to the manufacture and trade of these items.

Preliminary results of Mössbauer measurements on two groups of 15 Mycenean and 13 Minoan samples have been reported earlier [1]. Typically the spectra at 77 K consist of a central quadrupole doublet and a six line magnetic component of varying relative intensities but in all cases with the central doublet dominant. In a first attempt to discover parameters that could be used for characterization of the two groups, the distribution of values for the quadrupole coupling constants of the central component was examined and it was found that a small systematic difference exists between the two groups (Fig. 1*a*). Similar comparisons can be made for other parameters extracted from Mössbauer spectra. Figure 1*b* shows the distribution of the values of the total area of the spectrum as determined from computer fits with one six line component and a quadrupole doublet.

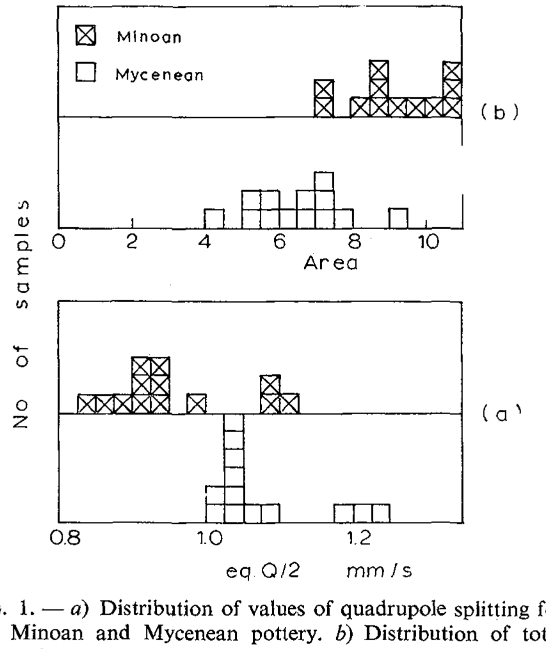

FIG. 1. — *a*) Distribution of values of quadrupole splitting for the Minoan and Mycenean pottery. *b*) Distribution of total areas of Mössbauer spectra at 77 K of Minoan and Mycenean samples.

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The foregoing results demonstrate that the information obtained from Mössbauer spectra of the Mycenean and Minoan samples studied exhibits sufficient specificity to be used for characterization, at least on a phenomenological basis. In order to clarify the physical origin of these differences a detailed study was undertaken of two representative samples of the two groups.

Mössbauer spectra of the Mycenean sample at 77 K, 4.2 K and 1.5 K are shown in figure 2. The most

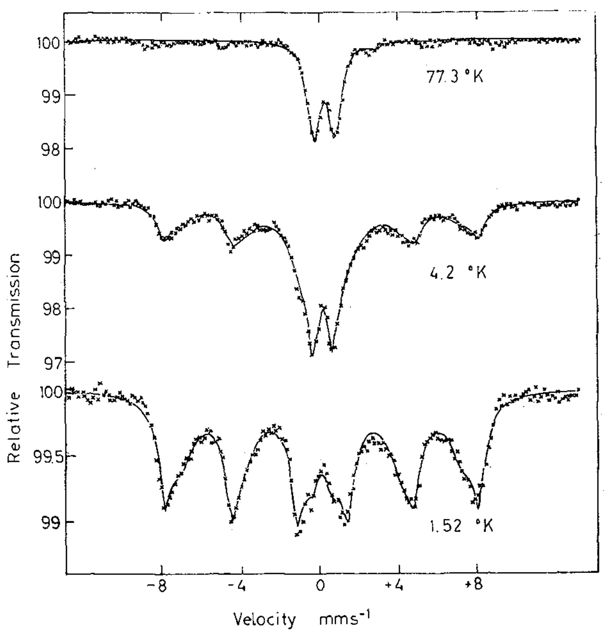

FIG. 2. — Mössbauer spectra of a representative Mycenean sample at 77, 4.2 and 1.5 K. The solid lines represent computer least square fits. Two magnetic components have been used for the spectra at 4.2 and 1.5 K in order to approximate the effective field distribution.

prominent change observed as the temperature decreases is a pronounced increase of the magnitude of the magnetic component. Its relative value changes from nearly 0 at 77 K to 0.5 at 4.2 K and 0.9 at 1.5 K. Similar behavior is observed for the Minoan sample for which spectra are shown in figure 3. In this case the central doublet almost vanishes at 1.4 K. Such results strongly suggest an iron oxide system with small average particle size exhibiting superparamagnetic behavior with blocking temperatures of the order of a few degrees Kelvin. In fact the similarity with recently reported Mössbauer studies of iron oxides gels [3] is striking. It was suggested in this investigation that a new type of disordered magnetic structure is established. This may also be the case for the Mycenean and Minoan samples and in fact a transverse field of 8 kG applied at 1.4 K on the Minoan samples does not lead to significant change in the Mössbauer spectrum.

These results are in direct contrast to observations on modern fired clays. In a detailed study of the

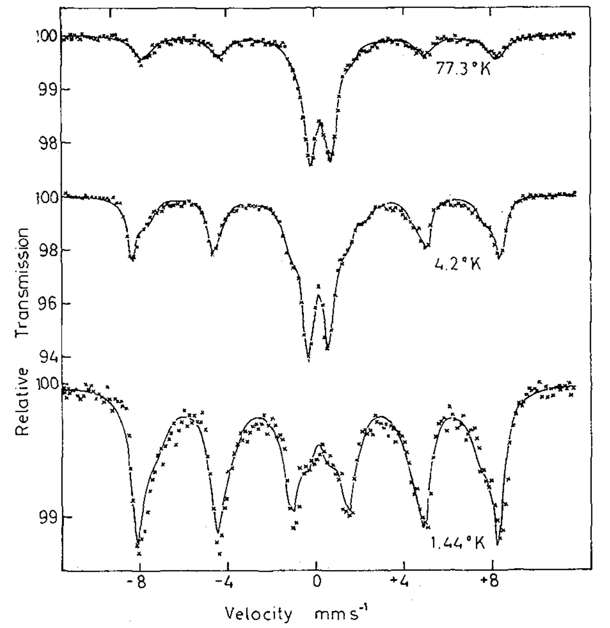

FIG. 3. — Mössbauer spectra of a representative Minoan sample at 77, 4.2 and 1.4 K. The sdlid lines represent computer least square fits.

effects of firing on a typical Attic clay [4] it was found that the magnetic oxides ratio (i. e. the ratio of the area of the six line component to the spectrum of the total area) is close to 1 at 4.2 K and retains a high value even at room temperature. Furthermore, it is found that firing at progressively higher temperatures to 900 °C produces a significant increase in the particle size of oxides, and a broadening of the distribution. Thus, the results of the ancient pottery samples indicate that a reverse process takes place in which time is at least one of the relevant factors.

In order to provide further support for this conclusions, measurements were also made on two samples of pottery of intermediate ages between that of the Mycenean-Minoan samples (~ 1 500 B. C.) and the present. These samples were obtained from an Attic sherd (~ 500 B. C.) and a piece of Byzantine pottery dated at ~ 600 A. D. The data from all samples are summarized in figure 4 which gives the magnetic oxide ratios as a function of temperature. The blocking temperature for a given sample can be estimated from the temperature at which the ratio attains the value of 0.5. For comparison the same ratio for an unfired clay sample is shown by dashed lines in the same figure [5]. A difference of nearly two orders of magnitude for the blocking temperature between the Mycenean-Minoan and modern clay samples is inferred while the data for the Byzantine sample fall in an intermediate range. The values for the Attic sample are lower than expected on the basis of the date of the pottery and the origin of this discrepancy is not understood at present. The gross features of figure 4, however, indicate unambiguously that a time

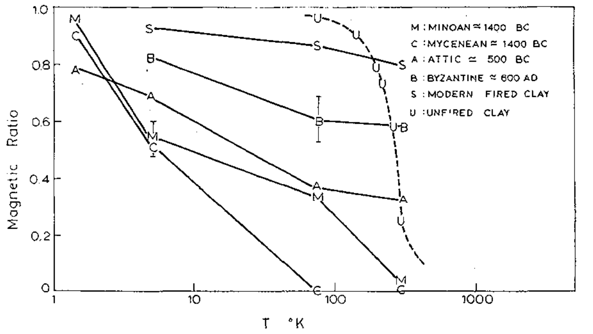

FIG. 4. — The ratio of the area ot the magnetic component to total area as a function of temperatures from Mössbauer spectra of pottery of various ages. The dashed curve represents the ratio of unfired clay sample.

dependent process is operative in establishing the particle size distribution and this result is substantiated by the measurements on the Mycenean and Minoan samples discussed earlier.

A tentative interpretation of the above results can now be formulated as follows : the unfired clay from which pottery is manufactured contains iron in the form of small oxide particles of average diameter about 150 Å and as a constituent of the clay minerals [5]. Firing at 800-900° results in an increase in particle size and a transformation of the structural iron into oxide form [4]. The resulting oxide particles in the ceramic object are then subject to disintegration processes in which time is at least one important parameter. Other factors that may be operative in determining the final distribution observed at present in ancient pottery samples are the environmental conditions (as e. g. humidity and pH of the soil in which they were buried) and the initial distribution in the unfired clay.

Clearly, further investigation will be required in order to establish this interpretation, but the evidence for the presence of a time dependent disintegration process for iron oxide particles in fired clays is sufficiently strong to envisage interesting applications of Mössbauer spectroscopy in the study of ancient ceramics. Even if the establishment of a time scale of sufficient accuracy to be of practical interest will prove difficult due to the complicating factors mentioned above, applications for authentication purposes is a distinct possibility.

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