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MÖSSBAUER STUDIES OF ANCIENT POTTERY

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Résumé. — La provenance, la technique de fabrication et le commerce de céramique dans le monde ancien sont un sujet de grand intérêt archéologique en tant qu'indices du niveau artistique et technologique des diverses cultures et leur influence. La spectroscopie Mössbauer peut être appliquée facilement dans l'étude des objets de céramique qui sont des argiles cuites contenant entre 5 et 10 % de fer naturel. Des études sur l'argile crue indiquent la présence du fer en deux états, *a*) comme particules d'oxydes de fer présentant des phénomènes superparamagnétiques, *b*) comme des ions de fer bivalent ou trivalent dans la structure de l'argile. Durant la cuisson à diverses températures jusqu'à 800 °C, on obtient une transformation des oxydes et l'agrégation partielle des particules. Les résultats de ces études ont été appliqués dans l'interprétation des spectres Mössbauer de céramique grecque ancienne. Une étude systématique d'un grand nombre d'échantillons d'origine Mycénéenne et Minoïque a démontré que les paramètres obtenus par l'analyse des spectres peuvent être utilisés pour la caractérisation des deux types de céramique dans un sens statistique. Ces résultats sont intéressants pour des questions archéologiques relatives au commerce de céramique Mycénéenne dans les régions de la Méditerranée orientale. Les potentialités et limitations de la spectroscopie Mössbauer sont discutées vis-à-vis des autres méthodes physiques utilisées en archéologie.

Abstract. — The provenance, manufacturing techniques and trade of pottery in the ancient world are a subject of great archaeological interest as indices of the artistic and technological level of various cultures and their influence. Mössbauer spectroscopy can be readily applied to the study of pottery objects which are fired clays containing between 5 and 10 % natural iron. Studies of unfired clay have shown that iron is present in either of two forms (*a*) as small particles of iron oxides exhibiting typical superparamagnetic behaviour (*b*) as divalent or trivalent iron ions incorporated into the structure of the clay minerals. Upon firing at various temperatures up to 800 °C a transformation of oxides occurs and at least partial aggregation of particles. The results of these studies have been applied to the interpretation of Mössbauer spectra of ancient Greek pottery. A systematic study of a large number of Mycenaean and Minoan samples of well authenticated origin has shown that parameters extracted from Mössbauer spectra can be used for characterization of the two types of pottery on a statistical basis. Such results are relevant for archaeological questions related to the trade of Mycenaean pottery in the eastern Mediterranean. The potential and limitations of Mössbauer spectroscopy as compared with other physical analytical methods currently used in archaeology are discussed.

1. Introduction. — Physical analytical techniques have found widespread application in the elucidation of archaeological problems. In fact, this activity has created a new field with, of course, its own journal, entitled « Archaeometry ». They have undoubtedly contributed at least by providing corroborating evidence in the choice between controversial interpretations of archaeological findings but they have also in some cases given rise to new heated arguments.

Mössbauer spectroscopy is a newcomer in this field and the studies that will be reviewed here have a reconnaissance character as to the problems that can be dealt with meaningfully and fruitfully by this technique. Professor Frauenfelder has formulated a set of rules [1] that govern the application of Mössbauer spectroscopy to fields more or less remote

from the realm of pure physics and our experience so far with the applications in archaeology has completely verified these rules. Of paramount importance in such applications is the establishment of a two way communication between the physicist and the « native » in the field. To get an idea of the difficulty of fulfilling this requirement : The concepts of hyperfine field and recoilless fraction are probably as incomprehensible for the archaeologist as are for the physicist the names of various shapes of ancient vases (skyphos, pelike, kylix) and their corresponding usage. Moreover, in order to secure a native guide one has to arouse his curiosity with some interesting results, and no such results can be obtained without his guidance. It is an incremental process that takes time.

Of the possible applications of Mössbauer spec-

troscopy, the study of pottery is attractive in many respects. Pottery objects are of prime archaeological importance since they are items which were used widely in several functions of everyday life in the ancient world, varying from eating and drinking to burial rites. The quality of the fired clay, the shape and the decoration of the vases, reflect the technological and artistic skill of the potters. Finally, due to its many uses, pottery was the object of extensive trade in ancient times and the establishment of the provenance of pottery wares found in a given archaeological site is important in demonstrating links and mutual influences between different civilizations. Pottery making had reached an unsurpassed degree of technical and artistic perfection in Athens during the 5th century BC and it was a major source of revenue for the city from the trade of its products throughout the Mediterranean.

Clays used for pottery have an iron content of the order of 5 % and Mössbauer spectra can be readily obtained with samples of about 150 mg. As it is well known, at least to the physicist, the usefulness of Mössbauer spectroscopy in the study of iron in clay materials rests on the information that can be obtained on the electronic state and the symmetry at the site of iron ions as well as the magnetic state of the material. This information is expressed quantitatively by the hyperfine coupling parameters obtained from the analysis of Mössbauer spectra. These parameters are expected to vary in different pieces of pottery depending on provenance and/or manufacturing techniques. They could, therefore, in principle, be used for characterization. To what extent this is possible in a way that permits unambiguous assignment of specific spectral features to particular pottery types must be ascertained before approaching archaeological problems. Most of the work that we shall describe is of this «background study» type.

While the study of pottery is the most promising area for application of Mössbauer spectroscopy other systems containing iron as e. g. pigments used in painting, can be studied fruitfully. Results of such studies will be mentioned briefly and some other ideas of possible application will be discussed.

2. Preliminary studies. — The first application of Mössbauer techniques to the study of pottery was reported by Cousins and Dharmawardena [2]. They have examined a group of samples from pottery excavated at Cheam in Surrey, dated at Medieval times. The spectra from a number of samples in this group with light coloured sandy appearance were found to be closely similar, with isomer shift and quadrupole splitting parameters falling within a small range ($i.s. = 0.37-0.32$ mm/s, $QS = 0.89-0.94$ mm/s). A sample of baked pottery from the area gave a similar spectrum, the parameters of which varied regularly with the firing temperature. They noted that superficially similar pottery from another

excavation site about 10 miles from Cheam gave entirely different spectra with parameters again falling within a small range. The spectra were attributed to Fe^{3+} in tetrahedral or octahedral positions in the clay mineral structure. On the other hand a lightly gritted uniform black ware was found to contain both Fe^{2+} and Fe^{3+} . On baking this sample in air at 700° the iron became entirely Fe^{3+} and the color changed to buff. Finally, magnetic hyperfine splitting was observed in a red sandy ware with a black interior indicating the presence of Fe_2O_3 or Fe_3O_4 .

Following this work we have undertaken a study of a group of samples from the excavation of an ancient cemetery near Vitsa in the region of Ioannina in northwestern Greece [3]. The purpose of this study was to find whether a classification of the samples could be made on the basis of Mössbauer results. A preliminary sorting of the samples was possible by visual examination of the spectra. Two typical patterns of samples of two different subgroups are shown in figure 1. The correlation of the classification based on archaeological evidence on the one hand and Mössbauer parameters on the other hand, is summarized in table I. The values of Mössbauer parameters (intensity, isomer shift, quadrupole splitting and effective magnetic field) have small dispersion within each group, but for several of them there are appreciable differences between groups. These results

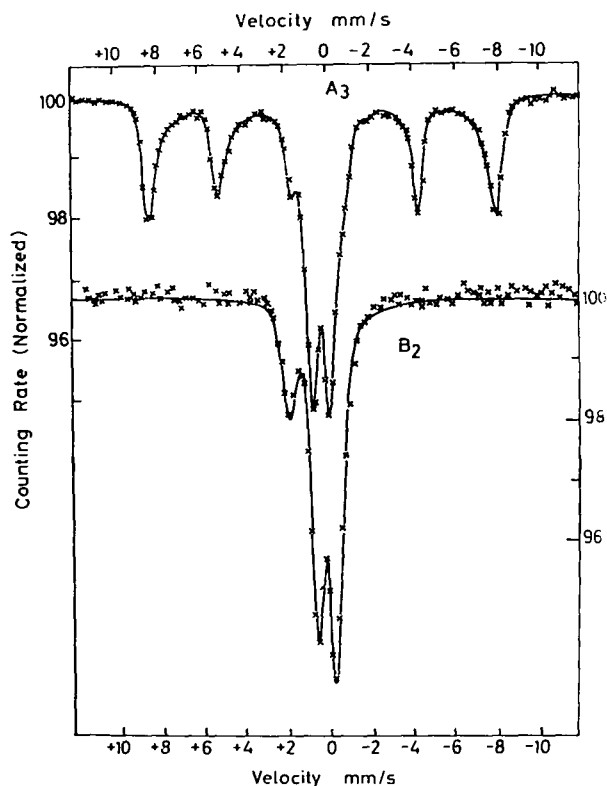


FIG. 1. — Representative Mössbauer spectra from two groups of ancient ware from the Vitsa-Zagorion (northwestern Greece) excavation. A. local made ware about 800 BC; B. Corinthian like ware about 750 BC.

TABLE I

Correlation of Archaeological Evidence and Mössbauer Parameters for Samples of Ancient Greek Pottery

Mössbauer parameters	Grouping by archaeological evidence			
	<i>A</i> (3 samples)	<i>B</i> (4 samples)	<i>C</i> (3 samples)	<i>D</i> (4 samples)
Non-magnetic part				
Fe^{3+} ; ΔQ	0.8	0.7-0.8	0.8	0.7-0.9
<i>i.s.</i>	0.3-0.4	0.3-0.5 (<i>B'</i>) (<i>B''</i>)	0.25-0.35	0.1-0.3
Fe^{2+} ; ΔQ	—	2.1-2.3	—	—
<i>i.s.</i>	—	0.9-1.1	—	—
Magnetic part				
ΔQ	0.4-0.6	—	0.15-0.25	0.2-0.4
<i>i.s.</i>	0.5-0.6	—	0.3-0.5	0.15-0.3
H_{eff}	500-510	—	480-510	475-505
I_{tot}	8-10	6.9-7.5	4.0-6.5	4.5-5.0
$I_{\text{M}}/I_{\text{tot}}$	0.4	0	0.1-0.2	0.2-0.3

ΔQ , Quadrupole splitting in mm/s; *i.s.*, isomer shift in mm/s (relative to iron metal); H_{eff} effective magnetic field in kG; I_{tot} , total absorption in percent per 100 mg of material; $I_{\text{M}}/I_{\text{tot}}$, ratio of absorption of magnetic part to total; *A*, local hand made ware, orange red coarse clay with yellow particles, geometric period about 800 BC; *B*, Korinthian or Korinthian like ware, fine pale clay; *B'*, Korinthian like, geometric period about 750 BC; *B''*, Korinthian oriental like period about 600 BC; *C*, sherds of probable attikizing type, pale brown red fine clay with black glaze on exterior surface, classical period about 500 BC; *D*, local hand made ware, brown red clay, geometric period about 800 BC.

were encouraging in that they demonstrated that the Mössbauer spectra of ancient Greek pottery are sufficiently different to be used at least as supporting evidence for the classification of findings from an archaeological site.

At this point we have decided that in order to understand the origin of the various components and properly interpret the Mössbauer spectra of pottery samples it would be necessary to undertake a study of unfired clays and the transformations that take place upon firing. As it often happens in this type of investigations this side study turned out to be most interesting not only for the results pertaining directly to ancient pottery but also for the physics of iron oxides in clays. We shall open, therefore, a parenthesis in order to give a summary of the results of this investigation.

3. Studies of unfired and fired clays. — The starting material for this investigation was the clay fraction of a soil obtained from a clay pit near Amaroussion, Athens, a location which has been used by Attic potters since ancient times. The separation was effected by sedimentation and centrifugation. Mössbauer spectra of the dried clay fraction at room, liquid nitrogen and liquid helium temperatures are shown in figure 2. The spectra consist generally of a paramagnetic doublet and a six line component indicating the presence of magnetic iron oxides. The major effect of the temperature variation is an enhan-

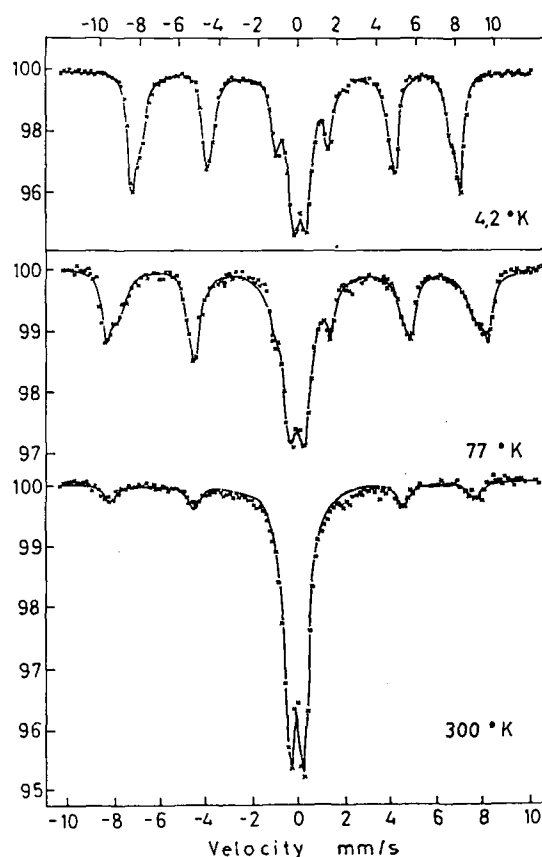


FIG. 2. — Mössbauer spectra of unfired clay at 300, 77, and 4.2 K.

cement of the magnetic component relative to the central paramagnetic doublet at the low temperatures. This is typical behavior of superparamagnetic particles as it has been shown by Mössbauer studies of fine particles of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ [4], [5]. When the size of the particles is of the order of 100 Å they behave as an assembly of paramagnetic particles with magnetic moments of the order of $10^4 \mu_B$ and relaxation times for reorientation of the magnetic moment strongly dependent on temperature and size. For a given size distribution and temperature the Mössbauer spectrum will be separated into a paramagnetic and a magnetic component corresponding respectively to the fraction of particles with relaxation times smaller and greater than the Larmor precession time of the nucleus. Another interesting feature of the spectra at 77 and 4.2 K is the asymmetry in the lines of the magnetic component indicating the presence of two oxide species.

A detailed analysis of the results shown in figure 2 as well as others at intermediate temperatures, in the light of the foregoing considerations leads to the following conclusions: Iron is present in the unfired clay in the form of two oxide species and as a substitutional ion in the clay mineral structure. From the values of the hyperfine parameters the oxide components are identified as $\alpha\text{-Fe}_2\text{O}_3$ [4] and $\beta\text{-FeOOH}$ [6]. The relative magnitude of the structural iron can be determined from the 4.2 K spectrum where superparamagnetic effects should be absent so that the central paramagnetic component arises only from iron ions in the clay mineral structure. Assuming that at this temperature the Debye Waller factors for the oxides and the structural iron are approximately equal the fraction of the latter is estimated at 33 %. This value is in good agreement with the value of 38 % obtained from a determination of structural iron by chemical methods. By subtracting this fraction from the central paramagnetic doublet at higher temperatures, it is possible to estimate the fraction of particles exhibiting superparamagnetic behavior and thereby obtain the particle size distribution. Details of this analysis have been published elsewhere [7]. We mention here only the result that the oxide particles have a size distribution with an average diameter of 130 Å and dispersion of 14 Å.

The effect of firing the clay upon Mössbauer spectra is demonstrated in figure 3 which shows results from samples fired at 400 °C, 600 °C and 800 °C and measured at 77 K. The spectrum of the 400 °C sample shows little, if any asymmetry in the magnetic component, indicating a transformation of the $\beta\text{-FeOOH}$ component. This result is in agreement with the transformation of $\beta\text{-FeOOH}$ into $\alpha\text{-Fe}_2\text{O}_3$ at 673 K found in a Mössbauer study of $\beta\text{-FeOOH}$ by Deszi *et al.* [6]. Superparamagnetic effects are still present as found by a comparison of spectra of this sample taken at room temperature and 4.2 K. An analysis similar to that applied for the unfired

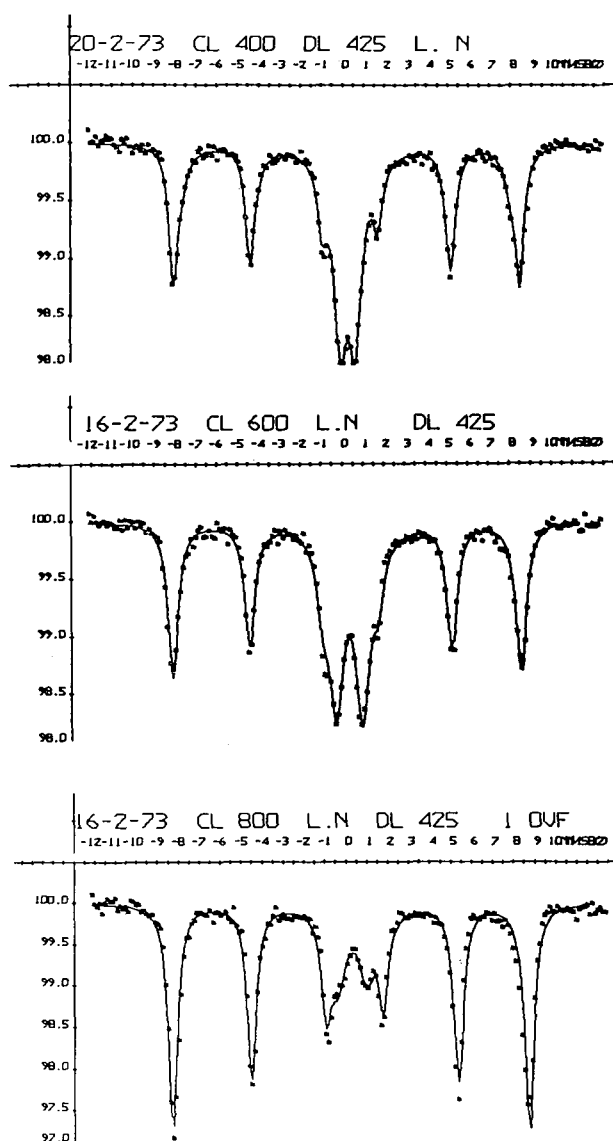


FIG. 3. — Mössbauer spectra at 77 K of three samples of clay fired at 400 °C, 600 °C and 800 °C.

clay yields estimates of 0.34 and 0.15 for the superparamagnetic fraction at room and liquid nitrogen temperature respectively. These values imply an increase in the average diameter of the particles and a broadening of the size distribution.

For the sample fired at 600 °C the major change in the 77 K spectrum is an increase of the quadrupole splitting of the central component. The most probable reason for this change is the change of the environment of the structural iron due to the loss of hydroxyls which is known to occur in clay minerals upon heating between 400 and 600 °C [8], [9]. An accurate analysis of this effect is difficult because the central doublet is a superposition of the components due to structural iron, superparamagnetic fraction and the central lines of the magnetic component. An estimate of the superparamagnetic fraction can be made again by comparison with the room temperature and 4.2 K spectra and it is consistent with the trend toward increased particle size and broadening of the distribution.

Finally the sample fired at 800 °C gives a Mössbauer spectrum at 77 K with dominant magnetic component. In fact a measurement at 4.2 K shows an almost pure $\alpha\text{-Fe}_2\text{O}_3$ spectrum. The central paramagnetic component is estimated at less than 7 % at this temperature, a result that is difficult to understand since this fraction is expected to represent the structural iron which is found to be of the order of 30 % for the samples fired at lower temperatures. A possible explanation is that this result arises from the transformations that start in the clay mineral structural at this temperature [8] which may lead initially to an amorphous system. The result of this transformation may be either a migration of iron ions out of the clay mineral structure and formation of $\alpha\text{-Fe}_2\text{O}_3$ or the inclusion into an amorphous phase with low Debye-Waller factor.

Additional information on the changes in Mössbauer spectra was obtained by measurements on samples of modern Attic pottery. Figure 4 shows the results for two samples obtained from unfired and fired ware. The spectra were recorded at room temperature only, so that it is not possible to estimate the amount of superparamagnetic component for the unfired sample. The most pronounced change upon firing is the increase in the magnetic component. In view of the results discussed previously, it is expected that the magnetic component will be dominant at 77 K and 4.2 K. This point will be discussed further in connection with the samples of ancient pottery.

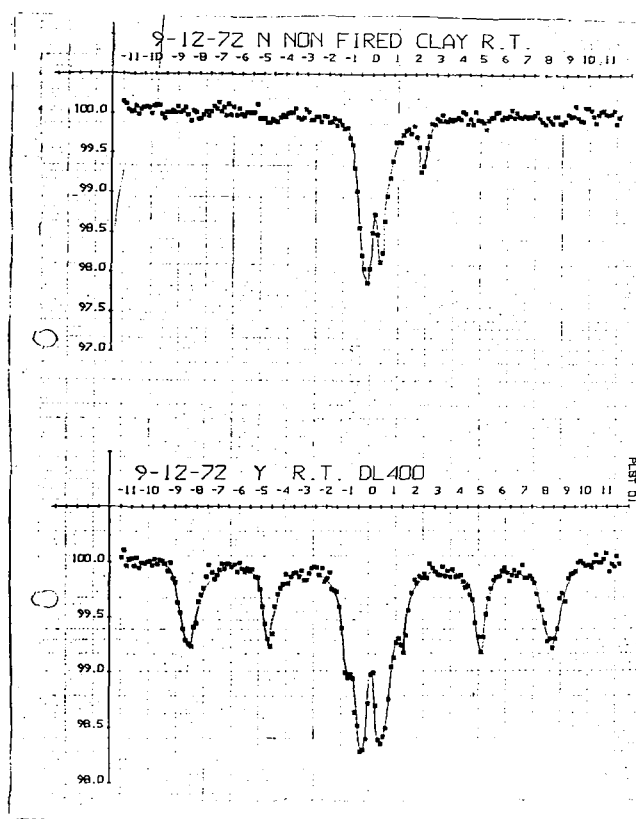


FIG. 4. — Mössbauer spectra at room temperature of a modern Attic clay, before and after firing.

The presence of Fe^{2+} is also clearly seen in the unfired sample. Upon firing in air this component disappears, presumably due to oxidation.

4. Studies of Mycenaean and Minoan pottery. —

The question now can be asked whether important groups of ancient Greek pottery with an homogeneity in style and clay texture and well defined provenance exhibit typical Mössbauer spectra which can be used for differentiation between pieces genuinely belonging to a group and imitations. In order to obtain information on this question we have undertaken a study of 45 samples of Mycenaean and 13 samples of Minoan pottery. Both groups were obtained from excavation sites which determined unambiguously their provenance. The choice of these periods was indicated for several reasons: First, Minoan and to a greater extent Mycenaean pottery were widely distributed in the area of the Eastern and Central Mediterranean during the Greek Late Bronze Age and several questions of provenance are of considerable archaeological importance; second, the shape of vases and the style of decoration of the better quality wares had reached a remarkable degree of homogeneity and sophistication; finally, detailed studies by spectrographic analysis of these groups, on the relationship between composition and provenance have been published by the Oxford group [10]. Neutron activation analysis results have also been reported recently by Harbottle [11].

The Mycenaean samples were further subdivided into three groups as follows:

- (a) 15 samples of non decorated pottery dated at about 13th to 14th century BC.
- (b) 23 samples of decorated pottery of the same period.
- (c) 7 samples of an earlier period (about 16th century BC).

Mössbauer measurements have been completed on the Minoan group and on the first subgroup of the Mycenaean samples. Representative data are shown in figure 5. The Minoan samples give spectra with a moderately strong magnetic component and the main differences are in the presence of divalent iron manifested by the peak near 2 mm/s. Ten out of the 13 samples give spectra similar to those in the figure while the two remaining samples fall in the extremes of this group with correspondingly higher and lower magnetic component. Visual examination of the sherds reveals considerable variations in the color and the texture of the clay. Four samples are of clearly finer clay than the rest. There is no definite correlation, however, that can be made between these variations and the spectral patterns.

Turning now to the Mycenaean sherds we note first that the variation in texture and color are much stronger than in the Minoan group. Seven samples characterized by fine texture and pale color give

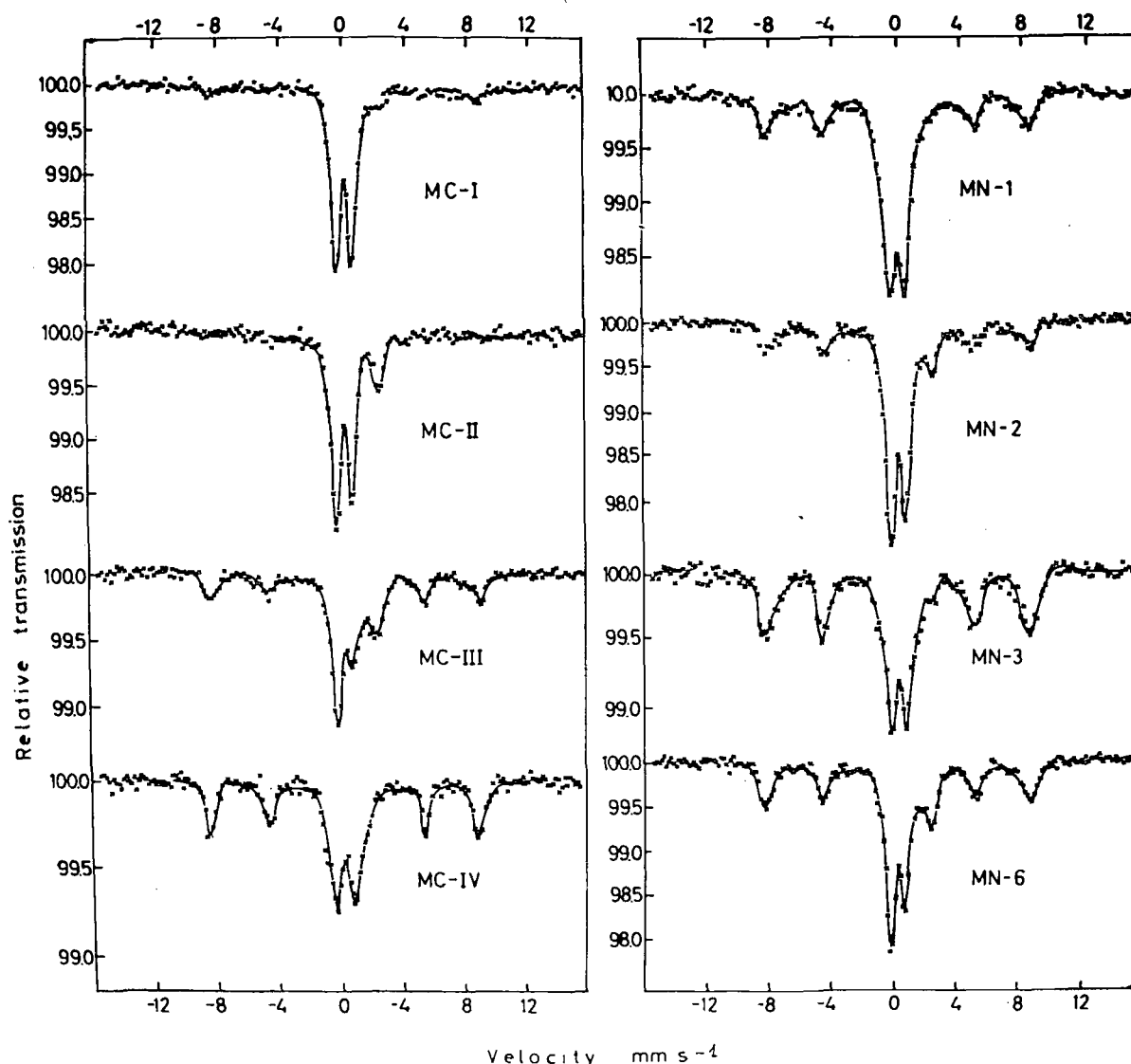


FIG. 5. — Representative Mössbauer spectra at 77 K of two groups of Mycenaean and Minoan pottery.

spectra of the type MC-I or MC-II of figure 5. Again the main difference is in the presence of divalent iron while the almost complete absence of magnetic component is noteworthy. In the remaining samples the variation in the spectral features is more pronounced while a magnetic component of variable magnitude appears. The type MC-III was found in one sample only which was clearly distinguished by a dark brown color, typical of the presence of Fe^{2+} . The remaining samples showed spectra similar to type MC-IV with variations in the magnitude of the magnetic component.

Computer fitting was applied to these results in order to determine whether there are systematic differences in hyperfine parameters obtained from the spectra of the two groups. The analysis is not yet complete but it is worth mentioning some interesting preliminary results, for some of the hyperfine parameters. A histogram for the observed values of the quadrupole splitting of the central paramagnetic component is shown in figure 6. There is a clear

separation between the distributions of values for the Minoan and Mycenaean groups. The concentrations of values of seven samples of the Mycenaean group reflects their textural homogeneity discussed previously, whereas the greater spread of values corresponds to the stronger variation in color and

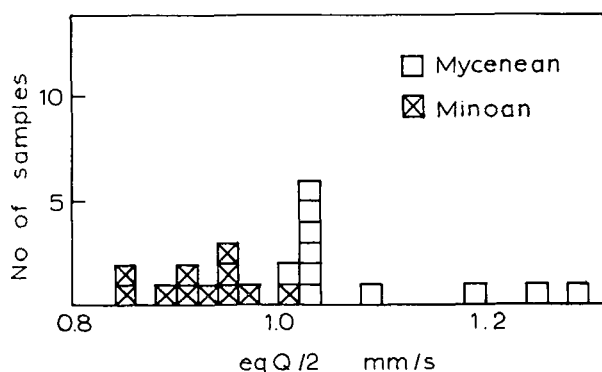


FIG. 6. — Distribution of values of quadrupole splitting for the Minoan and Mycenaean pottery.

texture when all the samples of this group are considered. A similar difference seems to exist in the magnetic hyperfine fields for the two groups. Clearly these results must be extended to a larger number of samples in order to establish their differences on a firm statistical basis.

Another intriguing feature of all the spectra of figure 5, when comparison is made with the results for fired clays discussed previously, is the value of the magnetic component. If firing temperatures above 600 °C were used (there is convincing evidence that Attic potters used firing temperatures near 1 000 °C) the magnetic component should increase considerably as it is shown e. g. by the result on modern pottery. To test the possibility that the pronounced paramagnetic component is due to superparamagnetic effects a measurement was made on one Minoan sample at 4.2 K. The magnetic component was enhanced, but only to a small extent with respect to what would be expected by comparison with the spectra e. g. of the clay sample fired at 600 °C.

It is interesting at this point to make some preliminary

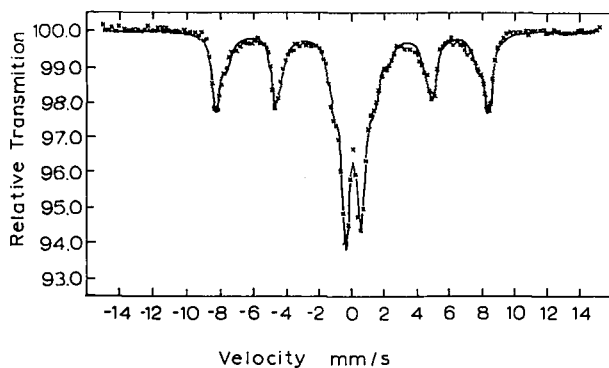


FIG. 7. — Mössbauer spectrum of a typical Minoan sample at 4.2 K.

comparisons with other methods used for pottery characterization and more specifically with spectrographic [10] and neutron activation analysis [11] which have been applied to Mycenaean and Minoan pottery. Both methods give the chemical composition of the samples and the differentiation between the groups is based on systematic differences in elemental composition derived from an examination of the distribution of values for a large number of samples. Most elements are found to have overlapping distributions of values and the distinction is based on one or two that show distinctly different distributions. Typical results from reference [11] are shown in figure 8. Total iron is on the average smaller in the Mycenaean group, a result that is in agreement qualitatively with Mössbauer data, but the two distributions overlap considerably. On the other hand the separation in the chromium distribution is similar to that observed in the values of the quadrupole splitting. These comments should be qualified by the fact that the measurements have not been made on the same samples and it is not known if the sherds which were used for NAA have the same textural variety as in our case.

5. Applications to archeological problems. — In the light of the results obtained so far from Mössbauer studies of ancient pottery, it is pertinent to inquire about the type of problems where Mössbauer spectroscopy can be applied. Typically, the questions that may arise in relation to pieces of pottery found in one archaeological site are the following :

(a) If the style and color of a piece of pottery is found similar to that of pottery made elsewhere, was it made locally as an imitation or was it imported ?

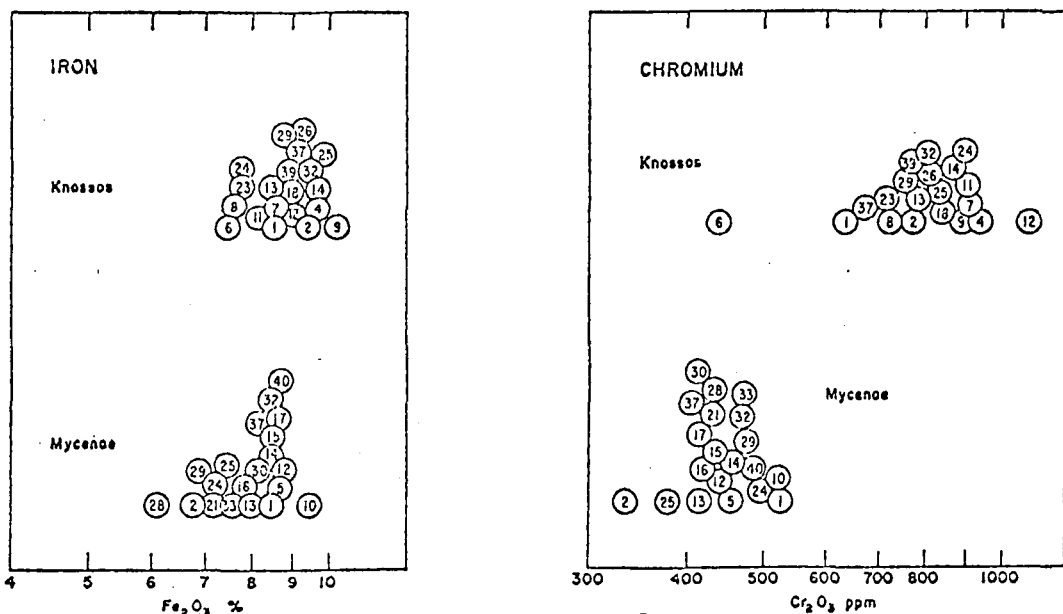


FIG. 8. — Representative distribution of Fe and Cr in Minoan and Mycenaean pottery, determined by neutron activation analysis. (From ref. [11]).

(b) If two pieces of pottery found in the same site have different style and color but the same composition what are the origins of these differences?

We shall illustrate the role which Mössbauer studies can play in such cases by a number of examples.

The first example is a study of pottery found in Tel Ashdod which was a major city of the Philistines, a group of the Sea Peoples that appeared in the eastern Mediterranean and Egypt during the period of the spread and decline of the Mycenaean civilization (ca 1300-1000 BC) [12]. Two distinctly different groups of wares discovered at the excavation (Philistine and Myc III Cl) were found by neutron activation analysis to have the same clay constitution. On the other hand the form, design and fabric of the Myc III Cl pieces were closely similar to other Mycenaean type pottery found elsewhere and especially in Cyprus. The conclusion was that the differences were due to particular manufacturing techniques (kiln conditions) introduced by recently transplanted people. Mössbauer measurements would probably be informative with regard to the differences in pottery making techniques since, as it has been demonstrated, Mössbauer spectra vary considerably according to the firing procedure.

Another example where Mössbauer spectroscopy has been found useful was a study of pottery from two cultural periods found in an excavation at the site of Tureng Tepe (NE of Iran) [13]. Five samples of gray and five of red wares were examined by scintillation spectroscopy and were found to have the same elemental constitution. The Mössbauer spectra, however, were distinctly different, the grey pottery showing a large percentage of Fe^{2+} . This indicated that reducing conditions were used during firing.

A final example is the case of the inscribed stirrup jars from Thebes, which have been the object of a detailed study by Catling and Millet [14] using atomic absorption spectroscopy. These jars bear inscriptions in linear B, a script that was used in the Aegean area during the Late Bronze Age (~1500-1000 BC) to write Greek. Certain words of these inscriptions, attributed to names of the places where the jars have been manufactured, appear also in a linear B tablet found at Knossos. This coincidence was considered a strong indication that the jars originated in Crete. This conclusion is important not only in establishing trade routes and centers during this period but also in providing new arguments in the controversy about the relations of Greece and Crete and in particular the date of decline of the Minoan civilization. The study of the compositional patterns of the clay of the jars has shown that the place of provenance is not unique, for the jars divide into several different sets. Knossos is excluded as the source of any jar but strong evidence was found that east Crete could have provided many of them. No Mössbauer study has been made yet but we mention this case as an exam-

ple of a model study where a physical technique has provided useful results for an important archaeological problem.

In applying Mössbauer spectroscopy (and in fact the other analytical methods also), the question could be properly asked whether pottery from some other areas of the world may give results identical to those of a certain locality. After all clay compositions do not vary considerably and differentiation is based on small differences in the concentration of a few elements. That this is the case also for Mössbauer spectroscopy is illustrated by spectra of three samples of Peruvian pottery shown in figure 9. The samples belong to three different cultural periods, namely the Chancay, Chimu and Nazca period. The basic spectral features are similar between themselves and to those of the Greek pottery. However, more detailed analysis on several samples could reveal differences on a statistical basis as described previously for the Minoan and Mycenaean samples.

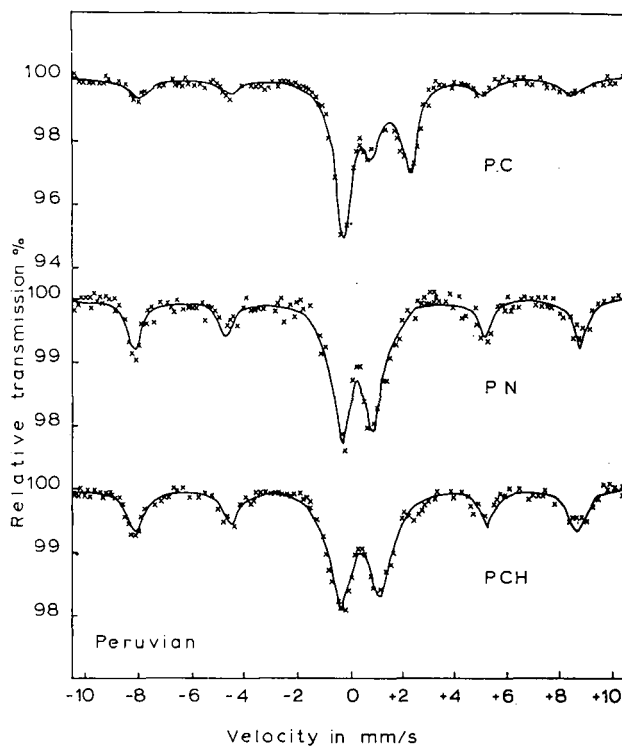


FIG. 9. — Mössbauer spectra at 77 K of three samples of Peruvian pottery of three different cultural periods (PC : Chimu, PN : Nazca, PCH : Chancay).

6. Other studies. — To complete this review we shall mention briefly some other Mössbauer studies in areas other than pottery and possible extensions using other isotopes.

Mössbauer spectroscopy was used in a study of pigments used in painting, which contain a large percentage of iron oxides [15]. Typical pigments of this type are various kinds of natural yellow earth oxides as yellow ochre, raw sienna and raw umber as well as the natural red or reddish brown materials

known as red ochre, burnt sienna and burnt umber. The spectra of these materials exhibit superparamagnetic effects, of a type similar to that found in the clays, with a degree varying according to the origin and the type of the pigment. Such differences could be presumably used for testing the authenticity of paintings. It is interesting to note that scattering geometry was used in this investigation so that the technique is non-destructive and the measurement could, if desired, be made without moving the painting.

With regard to the possibility of using other isotopes, the study of tin alloys is of interest. The development and trade of tin alloys in the ancient world, in particular in the eastern Mediterranean during the Mycenaean period, is of considerable archaeological importance. It is known that the isomer shift of tin alloys depends on the constitution [16] and a systematic study of ancient samples could be interesting. The type of spectra expected in such a study is illustrated in figure 10 which gives results for a bronze piece from the Athens Acropolis. The spectrum may be decomposed in two components of which the major is due to the bronze alloy and the other is identified as SnO.

We are indebted to Prof. Iakovides for the Mycenaean and Minoan samples and to Prof. Danon for the

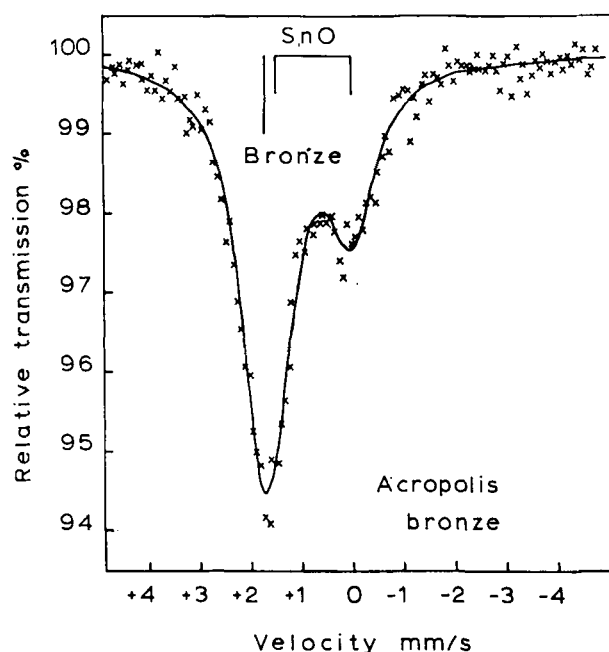


FIG. 10. — Mössbauer spectrum (^{119}Sn) of a bronze fragment from the Athens Acropolis.

Peruvian samples. The assistance of Miss Alikí Moukarika and Mr D. Niarchos in sample preparation and data reduction is acknowledged also.

References

- [1] FRAUENFELDER, H., in *Perspectives in Mössbauer spectroscopy*. Edited by S. G. Cohen and M. Pasternak. (Plenum Press.) p. 239.
- [2] COUSINS, D. R. and DHARMAWARDENA, K. G., *Nature* **223** (1969) 733.
- [3] GANGAS, N. H. J., KOSTIKAS, A., SIMOPOULOS, A. and VOKOTOPOULOU, J., *Nature* **229** (1971) 485-486.
- [4] KÜNDIG, W., BOEMMEL, H., KONSTABARIS, G. and LINDQUIST, R. H., *Phys. Rev.* **142** (1966) 327-333.
- [5] VAN DER KRAAN, A. M. (1972) Doctoral Thesis, Technical University Delft.
- [6] DEZSI, I., KESZTHELYI, L., KULGAWCZUK, D., MOLNAR, B. and EISSA, N. A., *Phys. Stat. Sol.* **22** (1967) 617-629.
- [7] GANGAS, N. H., SIMOPOULOS, A., KOSTIKAS, A., YASSOGLU, N. J. and FILIPPAKIS, S., *Clays and Clay Minerals* **21** (1973) 151-160.
- [8] GRIM, R. E., *Clay Mineralogy* (McGraw-Hill) 1953 p. 235.
- [9] MCKENZIE, K. J. D., *Clay Minerals* **8** (1969) 151-160.
- [10] MILLET, A. and CATLING, H. W., *Archaeometry* **10** (1967) 70-77.
- [11] HARBOTTLE, G., *Archaeometry* **12** (1970) 23-34.
- [12] ASARO, F., PERLMAN, I. and DOTHAN, M., *Archaeometry* **13** (1971) 169-175.
- [13] STEFANI, R., BERTHOD, J., PELLET, J., BOURGUILLLOT, R., CORNU, A., BOUCHEZ, R. and DESHAYES, J. (1973). Paper presented at the International Conference on the Application of Nuclear Methods in the Field of Works of Art, home.
- [14] CATLING, H. W. and MILLET, A., *Archaeometry* **8** (1965) 3-85.
- [15] KEISCH, B., *Archaeometry* **15** (1973) 79-104.
- [16] CORDEY HAYES, M., *Chemical Applications of Mössbauer Spectroscopy*. Edited by V. I. Goldanskii and R. H. Herber (Academic Press) (1968) p. 314.