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ESR Spectroscopy as a Tool for Identifying Joining Fragments of Antique Marbles: The Example of a Pulpit by Donatello and Michelozzo

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ESR spectroscopy is one of the physicochemical techniques used to characterize archaeological white marbles and obtain information about their quarries of provenance. This is done by measuring selected spectral features of the Mn^{2+} impurity ubiquitously present in marbles and developing a statistical classification rule from the variable vectors measured for a significant number of samples of known provenance (the quarry database). Now we show that the overall variability exhibited by the same spectroscopic features decreases rapidly with the linear dimensions of the sampled block and can be used to distinguish fragments belonging to the same piece of stone from those simply originating from the same quarry. Application of the method to the seven marble panels of the Donatello pulpit in Prato (Tuscany) shows that they have all been cut from the same single block and their different degradation must be ascribed to differential weathering and to the different conservation treatments undergone in the past. The limits and possible drawbacks of the method are also discussed.

Key Words: **ESR; marbles; provenance; fragments assembly; variance.**

INTRODUCTION

Within the Mediterranean world the tradition of marble carving dates back to the Vth millennium BC (*1*). Much later the use of white and colored marbles for sculpture and architecture became extremely important in the Greco–Roman civilization. During the Roman imperial period marble was a visible sign of social and political prestige and a complex organization was developed for its commercialization. Marbles were brought to Rome from throughout the Mediterranean basin, where more than 50 quarrying sites were actively exploited (*2, 3*). Therefore investigation of this material is a relevant archaeological problem which, dealt with also on a scientific basis, not only may widen the knowledge of the artworks we inherited from the past, but also may shed light on the technical skills indispensable for extraction and working and may contribute to a detailed picture of the economical relationships and trading routes between different countries.

There are two main problems facing the study of archaeological marbles. The first, which has been the object of active work during the past decades (*4–6*), is the determination of the quarries of provenance. Several physicochemical techniques, from neutron activation analysis of trace elements (*7*) to the determination of the carbon and oxygen isotope ratios (*8*), may give partial answers to this problem. However, it is now generally recognized (*9, 10*) that reliable results need the combined use of several methods as well as of petrographic and art-historical information. Furthermore the multivariate nature of the problem must be exploited by defining proper classification rules based on statistical analysis of the variable vectors measured for the quarry samples. In the field of marble provenance ESR spectroscopy, primarily based on the measurement of selected spectral features of the Mn^{2+} impurity commonly present in marbles, may give an important contribution, which has been recently reexamined (*11–13*).

A second question frequently posed by archaeologists and art historians and often overlooked in the scientific literature deals with the possibility of identifying joining fragments, namely marble fragments originating from the same piece of stone as opposed to fragments simply belonging to the same quarry. Such information, when available, may allow us to recognize forgeries and later restorations, detect different stages of the manufacturing process, and monitor the reassembly of large artifacts.

Intuitively we may expect a physicochemical parameter to exhibit a smaller variability within a single block of specified dimensions than within the whole quarry. In fact, using the values of the ^{13}C and ^{18}O isotope shifts, it has been possible to reassemble Greek stelae and identify incorrectly associated fragments (*14*). However, later work has shown that the variability of the isotope shifts within a marble block is usually a substantial fraction of the all-quarry variability, making fragments association extremely uncertain (*15, 16*). Such difficulty might be overcome by exploiting the multivariate nature of the problem. In the following a solution has been attempted by using the simultaneous overall variability of a set of spectroscopic variables. It may be added that, although results from ESR spectroscopy have been employed, the underlying idea appears to be more generally valid and might be extended to other measuring techniques or different materials for which similar problems exist.

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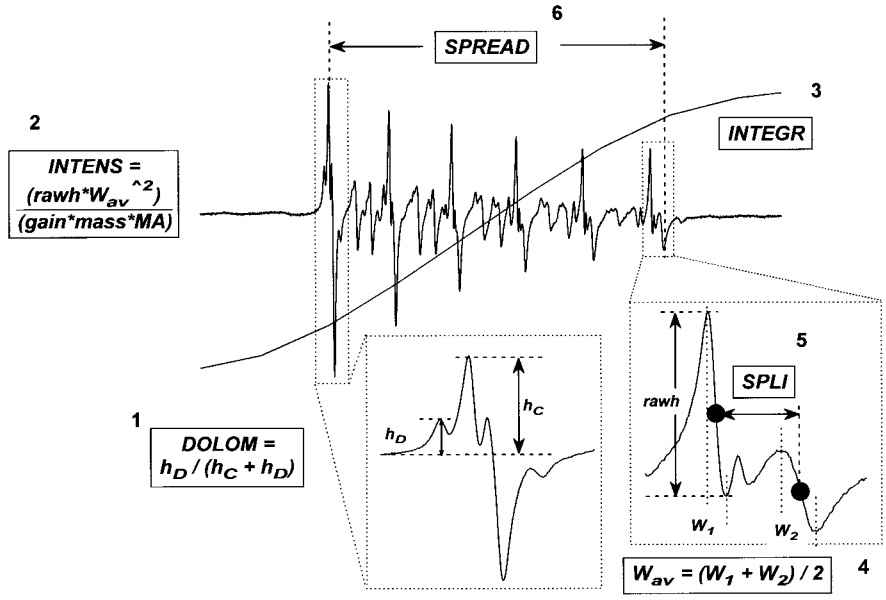

FIG. 1. Room temperature, X-band, powder ESR sample spectrum of marble. Satellites due to dolomite are clearly visible. The definition and derivation of the six ESR variables is schematically given. (Reproduced with permission from Ref. *13*).

THE MARBLE SPECTRUM AND THE CHOICE OF ESR VARIABLES

The ESR spectrum of marble is primarily due to traces of the high-spin Mn^{2+} ion substitutionally diluted into the lattices of calcite or dolomite (the rombohedral double carbonate $CaMg(CO_3)_2$), which are the main constituents of marble. Therefore, three different spectra may be observed corresponding to the paramagnetic ion entering the Ca^{2+} site of calcite (CC spectrum) and the Ca^{2+} and Mg^{2+} sites of dolomite (CD and MD spectra). The three spectra are well known and have been described several times in the literature (*17, 18*). Their g and metal hyperfine values are rather similar, but they can be easily distinguished on the basis of largely different values of the axial zero-field parameter ($|D|$ = 8.1 mT for the CC spectrum and 0.32 and 15.2 mT for the CD and MD spectra, respectively). Figure 1 illustrates the frequent and important example of a calcitic marble containing a small amount of dolomite, clearly detectable as satellite lines flanking the main doublets. The satellites are due to the MD spectrum, whereas the CC lines are buried under the main spectrum and are hardly detectable.

Of the many variables which can be extracted from the ESR marble spectrum six were chosen and are schematically defined in Fig. 1. They are the dolomitic manganese (DOLOM), the manganese intensity (INTENS), the total intensity (INTEGR), the linewidth (W_{av}), the splitting of the high-field doublet (SPLI), and the total extension of the spectrum (SPREAD). The choice of the six ESR variables followed criteria which try to balance the ease of measurement with the potential discriminating ability have been discussed in detail elsewhere (*13, 19*). However, a few comments are due here.

Some of the variables do not correspond to conventionally defined spectroscopic quantities. However, they make the data collection step easier and faster and have been used conveniently in this context. The DOLOM variable was estimated from the relative heights of the MD and CC spectra. Since, in the dolomite lattice, Mn^{2+} substitutes Ca^{2+} as well and the substitution ratio is variable, this means that the variable DOLOM, although related to the amount of dolomite in the sample, does not coincide with it. In addition the variable value was obtained by measuring peak heights and not areas or integrals. Similar problems arise with the variable INTENS. The choice of the low-field line of the M_I = 5/2 doublet was made simply on the basis of better line resolution and larger linewidth. Both DOLOM and INTENS do not measure absolute concentrations, but simply represent easily measurable and comparable concentration-dependent parameters.

The total intensity obtained by double integration of the entire spectrum is strongly correlated with the variable INTENS, but contains useful additional information in that it is related to the total paramagnetic intensity of the sample and not only to the Mn^{2+} concentration. The last two variables, SPLI and SPREAD, are concentration-independent parameters and introduce a different type of information. They are related, respectively, to the zero-field splitting term and to the electron-nuclear hyperfine parameter. As such they probe the symmetry and total strength of the crystal field around the cationic site and, hence, the effect of the formation processes and origin of the particular sample. From this point of view use of the g value as an additional variable would certainly be helpful. However, in the case of the Mn^{2+} ion, its variability is so small that reliable measurements would probably require an excessive experimental effort.

A final point concerns the possible effect of pressure shocks, caused by grinding, on the spin-Hamiltonian parameters and intensity of the Mn^{2+} signal. Careful studies have shown that pressures of the order of 1 Gpa or the shock caused by drilling, besides introducing several paramagnetic lattice defects, may considerably lower the intensity of the Mn^{2+} spectrum (*20*). Manual grinding of small amounts of marble (50–100 mg) is probably the mildest procedure for obtaining the powdery material necessary for the measurements. In spite of this, grinding is expected to contribute to the overall experimental error, increasing the variability of the measurements. Additional work is in progress in our laboratory to quantify this effect.

THE METHOD FOR IDENTIFYING JOINING FRAGMENTS

Since the variability behavior of the six spectroscopic variables defined above may depend on the particular quarry investigated, seven different quarries were sampled with the aim of screening a reasonably large number of cases in geographically distinct locations. The sampled quarries are Tacca Bianca (Seravezza), Polvaccio (Torano, Carrara), Canalgrande and Fantiscritti (Miseglia, Carrara), Fossacava (Colonnata, Carrara) in the large Italian quarrying district of the Apuan Alps, Logiotatis (Kinidaros) in the Greek island of Naxos, and finally a modern quarry within the historical quarrying district near the Roman town of Aphrodisias in Western Anatolia.

About 20 samples were collected from each quarry so as to be representative of the entire working front of the quarry, which usually extended from 30 to 100 m in width and 10 to 20 m in height. In addition, and for each quarry, 10 to 17 samples were collected from three artificial single blocks or fragments of approximate linear dimensions of 1 m, 50 cm, and 20 cm (hereafter referred to as large, medium, and small blocks). The entire external surface of the blocks was sampled, with the maximum distance between samples being almost twice the linear dimension of the sampled block ($\sqrt{3}$ of the edge length in the case of cubic shape). In the case of Canalgrande and Logiotatis no medium block was sampled and for Aphrodisias only the small block is available. In addition a single sample from Polvaccio (hereafter referred to as Snglpt), repeatedly reprepared and measured, has been used as a reference to check the reproducibility of the technique.

Therefore the experimental values of the six variables mentioned above were measured for a total of 369 samples, grouped into 25 quarry or block data sets. Subsequently it was verified that the dolomitic content often did not change at all within a single set and was not a suitable variable choice for this study. Table 1 lists the mean values and the corresponding standard deviations obtained for the remaining five variables for each set, whereas the variable DOLOM will not be mentioned any further.

The general variability behavior exhibited by the ESR variables is shown by the sample plot in Fig. 2, where the standard deviations (σ) measured within the Fossacava quarry and expressed as percentages of the whole quarry value are reported as a function of the block dimensions. Qualitatively similar plots are given by the other six quarries. Inspection of Fig. 2 indicates that , although the variability of a single ESR variable may decrease regularly with the block dimensions (see for instance the behaviour of the INTENS variable), much more often the single-variable variability within a block, even a small one, is a substantial fraction of the entire quarry value. In addition many inconsistencies are present and the σ values found for small blocks may be roughly equal to or even higher than those found for larger ones or for the whole quarry. Similar results confirm previous literature findings (*16*) and make extremely uncertain the possibility of associating marble fragments on the basis of the values of single-variable variabilities.

Despite this it may be reasonable to assume that the information sought is, in fact, present although masked by noise due to experimental errors, inadequate sampling, and similar reasons. Use of a parameter accounting simultaneously for the overall variability of the experimental variables may dampen such noise, bringing to light the required information. A way of doing this is simply to use the all-variable product of the standard deviations. More rigorously, and taking into account variable correlation, the variable's covariance matrix may be used, i.e., the square root of its determinant (*21*). Such a parameter, hereafter called total-σ, reduces to the simple product of standard deviations introduced above (product-σ) for uncorrelated variables. In our case the linear correlation coefficient for the ESR variables, taken two by two, is usually below 0.30. The only exception are the INTENS and INTEGR variables which, measuring related physical quantities, are strongly correlated ($\approx$0.90).

Indeed Figure 3 shows that all the sampled quarries, with the exception of Canalgrande, exhibit a decrease in variability, as expressed by the total-σ parameter, which is not only substantial and regular, but also remarkably similar. In Fig. 4 the average of the total-σ values for the six quarries is plotted against the square-rooted inverse of the approximate linear dimensions of the quarries or blocks. Nonlinear fitting of the experimental data points indicates that they follow rather closely a simple exponential decay law.

On going from the quarry to the blocks the decrease in variability is about one order of magnitude and seems large enough for the purpose of fragment association, although between the blocks discrimination appears unfeasible. The Snglpt total-σ value is at least two orders of magnitude smaller with respect to the quarry and shows that the method is satisfactorily reproducible. The results of the Canalgrande quarry are difficult to explain. They may be due to the fact that a general model for decrease in variability cannot be put forward. A second, and perhaps more likely, possibility is that sampling was not carried out properly and the available data are not representative of the effective quarry variability. Unfortunately new sampling of Canalgrande has not been possible and, at present, we must conclude that fragment association is

TABLE 1
Mean Values and Standard Deviations (in Parentheses) of the Five ESR Variables for the 25 Quarry and Block Data Sets and for the Pulpit Data Set Used in This Work[a]

Provenance	Block	NoS[b]	SPLI	INTENS	INTEGR	W_{av}	SPREAD
Tacca B.	Quarry	19	15.19 (.15)	0.405 (.14)	2.065 (.48)	3.69 (.34)	488.0 (2.2)
	Big	13	15.47 (.08)	0.466 (.10)	2.237 (.40)	4.13 (.21)	489.2 (.93)
	Medium	10	15.52 (.09)	0.845 (.03)	3.181 (.39)	3.89 (.20)	487.7 (1.11)
	Small	10	15.44 (.11)	0.834 (.16)	2.952 (.41)	3.96 (.09)	491.6 (.93)
Polvaccio	Quarry	20	15.05 (.12)	1.012 (.34)	3.766 (1.32)	3.96 (.14)	482.5 (2.8)
	Big	16	15.23 (.10)	0.884 (.22)	3.381 (.72)	3.87 (.25)	489.2 (.86)
	Medium	12	15.19 (.09)	0.912 (.24)	3.680 (.89)	4.05 (.14)	487.3 (.75)
	Small	12	15.02 (.09)	0.668 (.14)	2.278 (.40)	4.03 (.12)	482.6 (1.2)
Canalgr.	Quarry	13	15.16 (.17)	0.718 (.31)	2.818 (1.16)	4.10 (.14)	485.2 (1.17)
	Big	14	15.45 (.11)	0.906 (.20)	3.140 (.93)	4.15 (.23)	487.5 (1.33)
	Small	17	15.19 (.10)	1.136 (.20)	3.835 (.64)	4.12 (.15)	489.2 (2.15)
Fantiscritti	Quarry	20	15.14 (.14)	0.863 (.34)	3.314 (1.60)	4.04 (.15)	487.3 (.74)
	Big	9	15.33 (.07)	1.118 (.28)	4.371 (1.26)	4.11 (.11)	490.4 (.76)
	Medium	10	15.14 (.07)	0.535 (.08)	2.704 (.75)	4.05 (.13)	486.5 (1.23)
	Small	11	15.29 (.07)	0.578 (.15)	2.069 (.46)	3.97 (.11)	489.5 (1.42)
Fossacava	Quarry	23	15.23 (.15)	0.620 (.25)	2.566 (.98)	4.21 (.18)	489.4 (1.95)
	Big	11	15.12 (.16)	0.612 (.14)	2.781 (.66)	4.26 (.13)	487.1 (1.59)
	Medium	12	15.27 (.08)	0.438 (.09)	1.774 (.30)	4.15 (.14)	488.7 (.56)
	Small	10	15.17 (.10)	0.333 (.06)	1.626 (.22)	4.09 (.21)	486.0 (.93)
Logiotatis	Quarry	19	15.45 (.14)	0.675 (.37)	2.839 (1.1)	2.92 (.25)	487.1 (.95)
	Big	14	15.34 (.08)	0.643 (.24)	2.215 (.83)	3.19 (.08)	486.0 (1.2)
	Small	12	15.48 (.07)	0.311 (.04)	0.825 (.13)	3.17 (.11)	488.3 (1.1)
Aphrodisias	Quarry	18	15.52 (.21)	0.105 (.08)	1.041 (.71)	3.17 (.52)	489.4 (1.55)
	Small	11	15.60 (.17)	0.107 (.04)	0.926 (.20)	3.33 (.16)	490.2 (.95)
Singlept.	Snglpt	9	15.13 (.04)	0.610 (.04)	1.894 (.13)	3.93 (.12)	485.1 (2.11)
Pulpit	Pulpit	13	15.07 (.06)	0.402 (.16)	2.500 (1.12)	3.69 (.13)	486.5 (.87)

[a] The variables SPLI, W_{av}, and SPREAD are given in Gauss, whereas INTENS and INTEGR, divided by the corresponding values of the standard, are pure numbers.
[b] NoS is the number of samples for each set.

more properly carried out using the results obtained for the specific quarry of provenance, instead of the general (average) model.

THE PULPIT MARBLES

The method developed so far has been tested by investigating the marbles of the pulpit originally located outside the *Duomo di Prato* (Tuscany) at the right corner of the façade and realized by Donatello and Michelozzo between 1434 and 1438. The pulpit, shown in Figs. 5 and 6 before its recent restoration, is made of seven, separate marble panels all of which were seriously, although differently, degraded. A tentative explanation of this fact has been put forward suggesting that the panels could be made of different marbles or at least of marbles from the same quarry, but from different stocks.

The study, carried out on 13 samples, 2 for each panel except one, started by determining their provenance with the aid of a recently established ESR and petrographic database (*13*). Speaking of an artifact manufactured in Tuscany, use of local marble from the Carrara quarries may seem obvious and the preliminary provenancing work not strictly necessary. However, there are at least three different reasons why provenancing has been undertaken. In the first place no precise historical information is available on the origin of the pulpit marbles and, although Donatello was asked to employ white Carrara marbles, he was also allowed to use any material which could be already available at the *Opera del Duomo.* As a matter of fact, reuse or reworking of ancient marbles, a material imported from throughout the Mediterranean basin during the Roman period, had been common in Italy until the beginning of the XIXth century and several examples of this practice are known. Second, more precise information concerning the quarry and not only the provenance site was needed for the subsequent joining fragments work. Finally, the pulpit marbles were used also to test the ESR performance in distinguishing marbles, which can hardly be discriminated in some other way. The results, discussed elsewhere (*22*), indicate that the pulpit marbles come, indeed, from the Carrara region and can be unequivocally distinguished from apparently similar Greek or Turkish varieties. More precisely they come from the Miseglia district, which, together with Torano and Colonnata, is one of the three Carrara quarrying areas. The specific quarry of provenance could not be identified with certainty. However, two historical quarrying locations, Fantiscritti and Canalgrande, are known for Miseglia and the pulpit marble must come from one of the two.

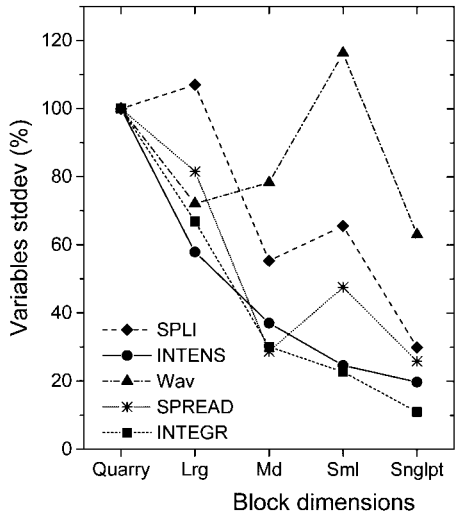

FIG. 2. Sample plots of the standard deviation (σ) of the five ESR variables vs decreasing block dimensions within the Fossacava quarry. Related plots of the other quarries are qualitatively similar. The σ value is given as a percentage of the quarry value.

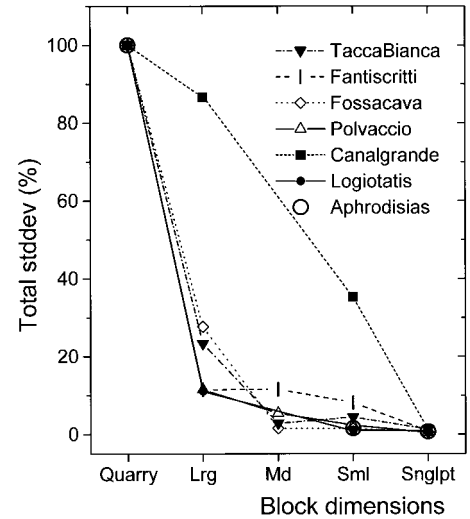

FIG. 3. Total-σ value vs block dimensions for the five ESR variables and seven sampled quarries. The total-σ is given as a percentage of the respective quarry. With the exception of Canalgrande, all of the other six quarries show a similar decrease of variability with the decreasing block dimensions. The medium block has not been sampled for the Canalgrande and Logiotatis quarries. For the Aphrodisias quarry only three data points are available (Quarry, Sml, and Snglpt) and no line plot has been drawn. The peculiar behavior of Canalgrande is discussed in the text.

To verify whether the seven panels all come from the same single block, the total variability of the 13 data points has been first compared with the variability graph obtained for Fantiscritti. Figure 7 shows that, within this quarry, but also within the average variability plot, the pulpit total standard deviation is located very close to the dimensions of the large block and is definitely smaller (14.7%) than the quarry total-σ. Since the decrease in variability exhibited by Canalgrande is considerably smaller, this finding remains perfectly valid if provenance from this quarry is supposed. As anticipated the method sensitivity is not enough to distinguish between blocks of different dimensions, but seems capable of discriminating clearly between marbles simply coming from the same quarry and those belonging to the same single block. The response of the method, in case of incorrect fragment assembly, is exemplified by reporting in Fig. 7 the total-σ value of the three Fantiscritti blocks combined together. It turns out that the variability of the "mixed block" sharply increases, reaching a value comparable with the entire quarry (98.1%).

A final comment, suggested by the above results, is that discrimination between a quarry and its single blocks, based on the analysis of the total-σ values, may be easier than discriminating between two specific quarries. This is especially true when the quarries belong to the same basin and are geographically close, as exemplified by Fantiscritti and Canalgrande. In this case, and in the absence of the scale factor represented by the amplitude of the sampled area, both the ESR variables and their variability may be remarkably similar, hampering reliable discrimination.

ADVANTAGES AND DRAWBACKS

Several well-established uni- or multivariate statistical techniques are available for testing the existence of significant differences between means and establishing whether different data sets have been sampled from the same population (*23*). Usually, however, these approaches cannot be applied to the problems discussed in the present work simply because only a

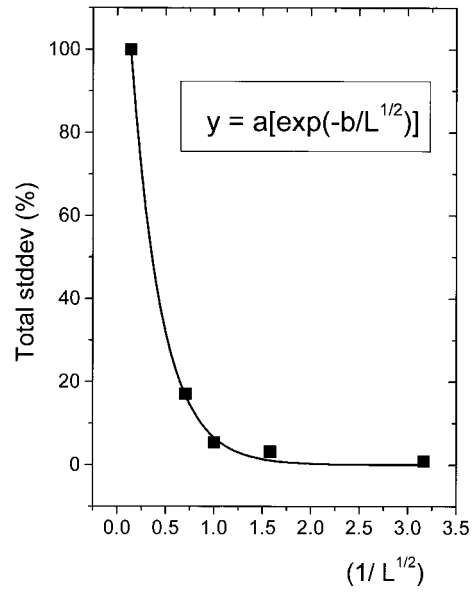

FIG. 4. Plot of the average total-σ values (symbols) for six of the seven sampled quarries vs the square-rooted, inverse linear dimensions of the quarries and blocks. L is the approximate maximum distance between samples in meters (quarry, 50 m; large block, 2 m; medium block, 1 m; small block, 0.4 m; Snglpt, 0.1 m). The parameters for the exponential best fit (line plot) are $a = 156.6$ and $b = 0.3155$.

FIG. 5. General view of the marble pulpit by Donatello and Michelozzo in its original location, outside the Duomo di Prato. The picture (Alinari 10006) was taken before 1893, when it was first published by Bode (*24*).

very few samples can be normally drawn from each fragment of an archaeologically important artifact and this hampers the use of standard statistical procedures.

For this reason we have tried to complement the small data set taken from the artifact with additional information related to the variability shown by the whole quarry and by marble blocks of predefined dimensions. In this way, comparing the variability within and between the fragments with the quarry and blocks references it has been possible to set up a qualitative criterion to decide whether the fragments originate from a single block. The example of the pulpit marbles is instructive in that the properties of the seven panels would have been difficult to analyze in a different way, having only 13 samples available.

This type of approach, of course, also shows important limitations. Generally speaking the method is less powerful than the standard techniques for the analysis of variance and its outcomes remain qualitative. In addition the sensitivity of the method may not be enough to identify one spurious fragment among several joining ones. Finally comparing fragments two by two may give uncertain results for two different reasons. First of all, the total number of available samples can be too small even for this kind of less demanding approach. Second, finding that the two fragments are joining may be simply due to accidental similarity of their mean vectors of variables. Obviously this possibility becomes less likely if simultaneous comparison of three or more fragments is performed.

CONCLUSIONS

This study represents an initial attempt to solve the problem of reassembling fragments of archaeological marbles on the

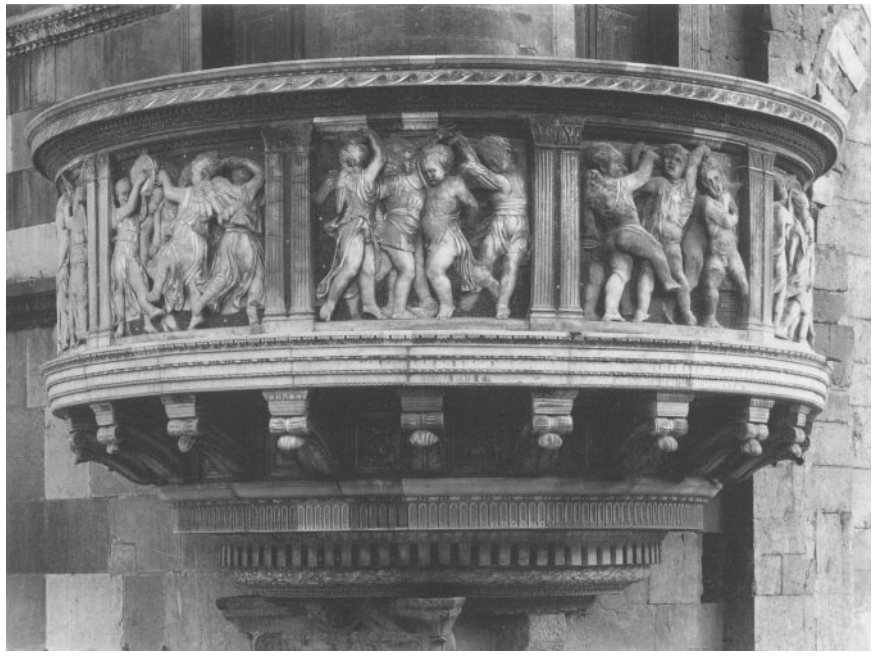

FIG. 6. Another view of the pulpit showing the seven marble panels in more detail (Alinari 10006).

basis of physicochemical information and confirms the important role that purely conventional ESR spectroscopy may have in the challenging archaeometric problem of marble characterization and provenancing.

Given the scarcity of the experimental data points usually available, standard statistical techniques are difficult to apply and alternative, even if less powerful, approaches must be devised.

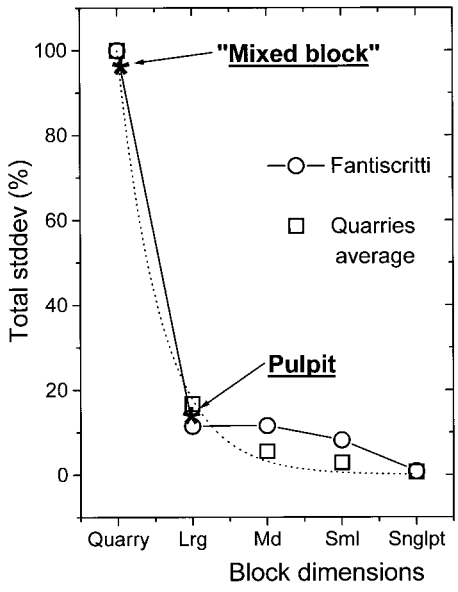

FIG. 7. Plots of the Fantiscritti and average variability data vs block dimensions. The total pulpit variability is about 15% of the total quarry value and locates this data set close to the dimensions of the large and medium blocks. As opposed to this a "mixed block," obtained combining together all of the data points of the three Fantiscritti blocks, shows a substantial increase in variability with a total-σ value comparable to the whole quarry (98%).

The method proposed is based on the measurement of some ESR properties of the Mn^{2+} marble spectrum and the subsequent comparison of the multivariate variabilities shown by sampled volumes of various dimensions. It seems to give reliable, although qualitative, information when several fragments are compared, whereas less certain results are obtained from the comparison of only two fragments. The sensitivity of the method for detecting single, nonjoining fragments in a group of homogeneous ones must still be explored in detail.

EXPERIMENTAL SECTION

ESR Spectroscopy

Conventional, room temperature X-band ESR spectra have been recorded on weighted amounts of finely ground samples (ca. 30 mg) packed in standard, constant-diameter ESR quartz tubes, using a computer-controlled Varian E-9 spectrometer. Under these conditions the sample height is lower than 5 mm and the powder is fully contained within the cavity region corresponding to maximum and constant sensitivity. Proper location of the sample was initially found by checking the intensity of the signal and then kept constant with the aid of a simple Teflon spacer. Also the instrumental settings were kept constant as follows: frequency 9.10 GHz, microwave power 12 db (12.5 mW), modulation amplitude 1 G, time constant 0.1 or 0.3 s, with corresponding recording times of 4 or 8 min. Only the spectrometer gain, which was found to be approximately linear, was varied according to the sample signal intensity.

All measurements were normalized using intensity and field

linearity standards. The former was a freshly prepared, 100-ppm toluene solution of dpph (Aldrich, 95% purity); the latter was a standard dolomitic limestone with a known Mn^{2+} content (N368 BCS, Bureau of Analysed Samples, Newham Hall, Newby, Middlesbrough, Cleveland, UK). A detailed description of the measuring and standardizing procedures has been reported elsewhere (*13*) and is given also in a specifically designed web site (*19*).

Materials

The 369 quarry samples used for this work have been collected during sampling campaigns carried out in the past 2 years. They have been used as such, taking care of grinding freshly fractured, unweathered fragments.

Thirteen samples were available for analyzing the seven marble panels composing the Donatello pulpit. In fact, only one sample could be taken from the first panel, instead of the two samples drawn from each of the other six. Only the original parts of the panels were sampled, excluding the marble frames which have undergone later restoration. The samples were taken from the upper left and right sides, in proximity to the fastening holes, and were in the form of irregular chips or cylindrical cores (diameter 6 mm) weighing from 150 to 400 mg. Before measuring, traces of degradation, dark crusts, and patinas were carefully removed, mechanically, from the samples. All measurements were performed twice and the average results were used subsequently.

Statistical Data Analysis

The calculations reported in this work have been performed with the commercial statistical package SYSTAT 8.0 (SPSS Inc.)

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