A NEW METHODOLOGY FOR THE PROVENANCE OF MARBLE BASED ON EPR SPECTROSCOPY*

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Fifteen years of research in investigating the characteristics of the EPR spectra of different types of white marble from several quarries in the Eastern Mediterranean has produced an accumulation of a large number of data, and much experience. Statistical treatment of these EPR data (statistical distributions and parameter correlations), has led to the selection of 10 parameters that are useful for quarry discrimination. Apart from the EPR parameters, the maximum grain size, measured with a stereomicroscope, has been found very useful. Boxplots have been found to be very useful as a first easy visual tool for evaluating the discrimination capacity of each parameter.

On the basis of these results, a new methodology for determining the provenance of an archaeological sample was developed in stages, using a different pair or combination of parameters each time. In the first stage, the Penteli, Naxos, Hymettus and Proconnessus quarries are completely separated from each other. However, overlapping occurs between the parameter fields of Paros and Proconnessus, Paros and Hymettus and between the two archaic quarries of Melanes and Apollon on Naxos. If the sample is located in a non-overlapping area, its provenance is obvious and easily determined. If the sample lies in one of the above three overlapping areas, an additional stage is necessary, in which other parameters are used to eliminate or decrease the overlap. Despite the partial overlapping of Paros with other quarries, the famous Lychnites marble of Paros, which was quarried underground, is clearly distinguished.

KEYWORDS: EPR SPECTROSCOPY, MARBLE, QUARRIES, PROVENANCE, GRAIN SIZE, STATISTICAL ANALYSIS

1. INTRODUCTION

Since 1988, at the first meeting of specialists in Italy (Herz and Waelkens 1988) on marble analysis, marble provenance researchers have realized that the provenance of white marble is not a trivial task. Several techniques have been applied, each one having its advantages and limitations. No technique applied alone can resolve all of the provenance questions, especially if there is no archaeological or art-historical information available to restrict the number of quarries and confine the problem. Neutron activation analysis, which was promising at first, proved to have limited capability in quarry discrimination and is used nowadays only in conjunction with petrographic data (Moens et al. 1992; Matthews et al. 1995). Petrographic analysis again is not so informative by itself (Herz 1955) and, most importantly, needs a large sample, which is not very frequently obtainable from ancient works of art. Carbon and oxygen
stable isotope analysis, which is the most commonly used technique, has numerous overlapping areas (Herz 1988; Moens et al. 1992), and fails to identify the provenance in many cases unless it is combined with other techniques such as cathodoluminescence, which is used as a complementary technique (Barbin et al. 1992). The need was therefore obvious to develop new techniques that would produce good quarry discrimination and provide alternative solutions for the overlapping parameter fields of the older techniques.

Electron paramagnetic resonance (EPR) spectroscopy was proposed at first by Cordischi et al. (1983) but was soon abandoned. The intensity of the sixth doublet in the central spectrum of Mn$^{2+}$ was used as a discrimination parameter, as well as the width of the external Mn$^{2+}$ sextet peaks. The authors also proposed the use of the fraction of dolomite in the marble, calculated by the ratio of the high-Mn$^{2+}$ peak intensities in the EPR spectrum. Great overlaps occurred between different quarries. Lloyd et al. (1985, 1988) used the first Mn$^{2+}$ doublet intensity and also detected several radiation damage peaks. More recently, Armiento et al. (1997) used the technique again, insisting on its potential for overcoming the limitations of neutron activation and stable isotope analysis in investigation of the provenance of marble.

More detailed and systematic work on the EPR spectrum of marble was carried out by Maniatis et al. (1988), Mandi et al. (1992) and Mandi (1993). Different peaks in the region of the spectrum around $g = 2.0000$ were identified along with two peaks created by mechanical treatment (Maniatis and Mandi 1992). Hierarchical aggregative cluster analysis was applied to the results, and a bank of 170 samples founded an initial EPR database. The database has now expanded greatly (Polikreti 1999) and a large number of archaeological samples of various origins have been analysed, with very promising success (Butz et al. 1999; Goette et al. 1999; Maniatis et al. 2000).

This paper continues the previous studies and presents 15 years of research on EPR spectroscopy for investigation of the provenance of marble at the Laboratory of Archaeometry, NCSR ‘Demokritos’. All of the EPR parameters were studied systematically for the first time, and treated statistically, including tests for natural distributions, correlations between parameters and comparative boxplots. On the basis of these results, and in combination with measurements of the maximum grain size of the marble crystals, a new methodology was developed, and is proposed, for quarry discrimination.

2. SAMPLES AND EXPERIMENTAL TECHNIQUES

The present work includes EPR data of 422 samples in total: 278 samples from Penteli, 28 samples from Hymettus, 49 samples from Proconnessus, 61 samples from Naxos and 21 samples from Paros. Dolomitic samples from Thassos were not included in this work, since the EPR spectrum of dolomitic marble is distinctly different from that of calcitic marble and can be easily identified (Cordischi et al. 1983; Lloyd 1988; Mandi 1993). Except for Thassos (Vathy, Saliari, Mouriana), no other ancient quarry of pure dolomitic marble has been reported to have been used in the Aegean in Antiquity. Therefore, dolomitic samples with a maximum grain size around 2 mm are usually ascribed to Thassos.

Geological samples were subjected to the following standard treatment: 10 min etching in hydrochloric acid (0.5 N), washing with deionized water, drying and then gentle grinding in an agate mortar (grain sizes around 63–180 µm). Severe mechanical treatment was avoided, since it has proved to induce essential alterations in the marble spectrum (Maniatis and Mandi 1992).
2.1 Grain size measurements

The maximum grain size (MGS) was measured for all the samples using a stereoscopic microscope on a freshly broken surface. It is not possible to prepare thin sections from the very small samples that are usually available from archaeological monuments. The MGS measurements made with the stereoscope have proved to be very close to those for thin sections (Mandi 1993) and, as such, they give a fast and reliable quantitative parameter for marble texture.

2.2 EPR measurements

The EPR instrument used was a BRUKER ER-200D-SRC with an ER-035M NMR Gaussmeter and an Anritsu MF76A microwave frequency counter. The microwave frequency was 9.5 GHz (X-Band). EPR spectroscopy involves the resonant absorption of microwave power by a few milligrams of sample in powder form placed in a cavity inside a quartz tube, across which a magnetic field (0–6000 Gauss) is scanned. In solids, it detects paramagnetic atoms and ions, unpaired electrons and free radicals, which in marble originate from the replacement of Ca atoms, crystal defects or the presence of accessory minerals. The main advantages of the technique for determining the provenance of marble are (i) its simplicity, the measurement lasting for 10 minutes, (ii) that the sample is rather small, about 200 mg of marble powder being needed, and (iii) most importantly, the EPR spectrum contains a lot of information that can be quantified into at least 10 parameters. Details of the experimental procedure may be found in Mandi et al. (1992) and Mandi (1993).

The quantity of the sample needed for a reliable measurement is determined by the position of the quartz tube in the cavity. Figure 1 shows the first low-field Mn$^{2+}$ peak intensity versus sample weight for two different positions of the tube in the cavity: position A, with maximum sensitivity at the end of the tube and position B where the end of the tube is situated 2 mm lower. Position A seems to be advantageous due to the higher sensitivity at low sample weights, which is the situation with the archaeological samples. However, the maximum intensity reached

![Figure 1 Mn$^{2+}$ peak intensity versus sample weight for position A (maximum sensitivity with a small amount of sample) and position B (end of the tube 2 mm lower).](image-url)
at position A is very low, which becomes critical when the weak, low-field peaks are measured. For this reason, we chose position B as the standard position for the EPR measurements (Mandi 1993).

Three spectra are taken for each sample at different instrumental conditions, as follows:

(i) **Spectrum 1**: Mn$^{2+}$ sextet (Fig. 2), central field = 3360 Gauss, sweep width = 600 Gauss, modulation amplitude = 0.4 Gpp, microwave power = 8 mW, time constant = 100 s, scan time = 100 s.

(ii) **Spectrum 2**: the region around $g = 2.0000$ (Fig. 3), central field = 3360 Gauss, sweep width = 50 Gauss, modulation amplitude = 0.4 Gpp, microwave power = 0.8 mW, time constant = 200 s, scan time = 500 s.

(iii) **Spectrum 3**: the low-field region (Fig. 4), central field = 1450 Gauss, sweep width = 2500 Gauss, modulation amplitude = 10 Gpp, microwave power = 31 mW, time constant = 100 s, scan time = 100 s.

All spectra were taken with a frequency modulation of 100 kHz.

Figure 2  A typical EPR spectrum of calcitic marble showing Mn$^{2+}$ peaks corresponding to the transitions with $m_z$ = −1/2 to +1/2, $\Delta m_j = 0$. It consists of six double lines plus 10 single ones ('forbidden absorptions') between the doublets.

Figure 3  Typical EPR spectrum of calcitic marble expanded in the Central Region around $g = 2.0000$. 
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The total error of the peak height measurements was calculated at 10%. This includes both the reproducibility of the measurement and the stability variations of the EPR spectrometer.

3. NORMALIZATION AND UNIFICATION OF EPR MEASUREMENTS

The intensities of all the peaks measured here are expressed in relative units. This was done by taking the height of the first derivative of each peak and normalizing it to a gain of $1 \times 10^6$. In our case, relative units actually mean centimetres measured on the plotted spectrum with a standard rule. The tuning of the EPR instrument and the stability check were done with an internal laboratory standard, which was a sample of calcitic marble from the Penteli quarries. Inevitably, this gave the measurements carried out in this laboratory an individual character, which means that it is not easy for other workers, who wish to measure marble using EPR in their own laboratories, to make use of our plots. This is understandable, as the technique is not very widely used yet and the methodology is under development. Each laboratory has its own data and sample bank, which are the result of many years of field and laboratory work and a lot of resources.

A further problem in normalizing the measurements was the lack of a suitable international standard. This standard should be a clean calcite or a marble sample. However, such a sample does not exist internationally. The closest standard material available is the limestone KH1 (Kalkstein) of the German company JENA. We have measured this material, but as it is heavily ground and homogenized the peak heights do not represent the true concentrations of Mn$^{2+}$ or other ions. It has been shown (Maniatis and Mandi 1992) that intense grinding leads to a drastic decrease in the Mn$^{2+}$ peaks and, in addition, new grinding peaks are induced. However, in an attempt to normalize our data to an international standard we have obtained a correction factor that would normalize our relative units measured for Mn$^{2+}$ to this international standard. This factor is 0.032; that is, multiplying our intensity relative units by this factor normalizes our measurements to the KH1 that is measured at exactly the same instrumental conditions as our samples (see section 2.2). We could not obtain correction factors for the rest of the peaks, as these peaks are not present in the JENA limestone.

For a true unified normalization of the measurements we propose using two different types of white marble, one calcitic and one dolomitic. This, however, has to be agreed and prepared accordingly for distribution among laboratories in the future.
4. EVALUATION OF EPR DATA

4.1 The EPR parameters

The following parameters were measured for each of the samples analysed using EPR spectroscopy. Parameters representing intensity are expressed in relative units; that is, the height of the first derivative of the relative peak at an amplification of $1 \times 10^6$. The widths of peaks are measured in Gauss.

$\text{Mn}^{2+}$. The intensity of the first low-field doublet of the Mn$^{2+}$ sextet (transitions with $m_S: -1/2 \rightarrow +1/2$, $\Delta m_I = 0$) ($h_1$ in Fig. 2).

Overlap. The ratio $h_1/h_2$ of the intensities in Figure 2, which gives a measure of the overlap between the two peaks of the first low-field Mn$^{2+}$ doublet (Polikreti 1999).

Width. The half width at half maximum (HWHM) of the fifth low-field Mn$^{2+}$ forbidden ($m_S: -1/2 \rightarrow +1/2$, $\Delta m_I = \pm 1$) peak (Fig. 3). It increases with increasing Mn$^{2+}$ concentration but also with the presence of other paramagnetic centres in the vicinity of Mn$^{2+}$ (Pilbrow 1990).

Dolomite ($g = 1.9765$). The intensity of a small peak, in the vicinity of the sixth low-field forbidden ($m_S: -1/2 \rightarrow +1/2$, $\Delta m_I = \pm 1$) Mn$^{2+}$ peak, which represents the dolomite concentration (Fig. 3).

Peaks $g = 2.0044$, $g = 2.0037$ and $g = 1.9998$. The intensities of these peaks, which are due to orthorhombic CO$_2^-$ radical, anisotropic CO$_2^-$ and axial CO$_2^-$ radicals, respectively (Fig. 3; Mandi 1993).

Peaks $g = 14.25$, $g = 5.9$ and $g = 2.9$. The intensities of these peaks, which are due to Fe$^{3+}$ in the calcium carbonate lattice (Fig. 4; Marshal and Reinberg 1963; Polikreti 1999).

Peak $g = 4.3$. The intensity of the corresponding peak, with a strong component due to Fe$^{3+}$ in orthorhombic symmetry (silicates and oxides; Komunsiski et al. 1981) and a weak one due to Fe$^{3+}$ in the carbonate lattice (Fig. 4).

Peak $g = 2.7$. The intensity of the corresponding peak due to an unidentified paramagnetic centre in muscovite (Fig. 4; Polikreti 1999).

The common procedure in provenance studies is to use all measured parameters for cluster or principal component analysis. These types of statistical treatments have been used extensively for elemental concentrations of minor and trace elements. However, no experience has been acquired on the bulk statistical treatment of EPR spectroscopic parameters, and so the field is open. The EPR spectrum contains information related not only to the concentration of certain ions but also to their physical and chemical environment, which perturbs the intensities and other measurable quantities. In order to gain some insight into the nature and variation of the EPR parameters, we performed some statistical distribution tests and investigated the correlation between them.

4.2 The statistical distribution of the EPR parameters and the MGS

The Kolmogorov–Smirnov normality test was performed in order to find out whether a set of samples from the same quarry could come from a normally distributed population. We chose the Kolmogorov–Smirnov test rather than the $\chi^2$ test because the former is more sensitive at the distribution tails, where the frequencies are small (Davis 1986). The Kolmogorov–Smirnov test is used when the mean and standard deviation of the distribution are known a priori, but the test that we used here is a version after Lilliefors (1967), which computes these parameters from the actual data.
Normality was tested at the 5% level of significance on our Penteli data. Penteli was chosen because its sample size is near 300, which ensures reliable statistical results. However, the peaks at $g = 2.0037$, $g = 1.9998$ and $g = 2.0044$ are absent from the Penteli EPR spectrum, so we also used the Proconnessus data (sample size ~50).

The parameters Mn$^{2+}$ (Fig. 5), $g = 14.25$, $g = 5.9$, $g = 2.9$ and $g = 4.3$, follow a lognormal distribution, which was expected, as it is known that trace element concentrations follow a lognormal distribution in the same quarry (Moens et al. 1989). The parameter Width follows a normal distribution. The parameters Overlap, Dolomite, $g = 2.7$, $g = 2.0044$, $g = 2.0037$ and $g = 1.9998$ do not follow either of the two tested distributions.

The parameter MGS would be expected to follow a lognormal distribution since, according to Marsal (1987), this is the distribution followed by grain sizes. However, from the normality tests for the MGS, both normal and lognormal distributions were accepted for Penteli (Fig. 6). For this reason, we tested the data sets from two other quarrying regions, Proconnessus and Naxos-Apollon. Unfortunately, none of the extra data helped us to reject one of the two distributions. Finally, we adopted the lognormal distribution because it gave slightly lower Kolmogorov–Smirnov $d$ values for all of the tested data sets. Apart from that, it is obvious from Figure 6 that the lognormal curve fits slightly better than the normal to the histogram shape, at least for the Proconnessus and Naxos-Apollon data sets.

The results for the distribution, followed by each parameter studied, are summarized in Table 1.

4.3 Correlations between parameters

The correlation coefficient used here is Pearson’s $r$ (Bevington 1969; STATISTICA for Windows 5.0 A) and all of the values shown on the graphs are highly significant ($\alpha = 0.05$).

Correlation of Mn$^{2+}$ with Overlap  Correlation is expected theoretically, since a high concentration of Mn$^{2+}$ causes broadening of the EPR peaks. Figure 7 (a) shows Mn$^{2+}$ versus Overlap (correlation coefficient = 0.65). It appears that, for Mn$^{2+}$ values larger than 2500 r.u., some samples show extremely high values of Overlap. The presence of these outliers, which obviously change the slope of the regression line, can be explained by the presence of accessory minerals.
Figure 6  Kolmogorov–Smirnov tests for MGS ($\alpha = 0.05$): (a), (b) Penteli quarries ($d_a = 0.0531$ for $N = 278$); (c), (d) Proconnesus quarries ($d_a = 0.1266$ for $N = 49$); (e), (f) Naxos-Apollon quarry ($d_a = 0.1384$ for $N = 41$).

Mn$^{2+}$ in clay minerals—muscovite, for example—gives a sextet of peaks with almost the same $g$ values with those of Mn$^{2+}$ in calcite (Polikreti 1999). The atypical broadening observed thus expresses the combined effect of two different factors, one characterizing the marble itself and the other the presence of secondary minerals. For these reasons, the parameter Overlap was not used in quarry discrimination.

Correlation of Width with Overlap  Correlation is expected theoretically, since these parameters are different expressions of the width of Mn$^{2+}$ peaks. Figure 7 (b) shows Width versus Overlap (correlation coefficient = 0.48). It appears that for Width values larger than 7 Gauss,
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Table 1  Statistical distributions for the EPR parameters and the MGS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Distribution*</th>
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<tbody>
<tr>
<td>MGS</td>
<td>Lognormal</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>Lognormal</td>
</tr>
<tr>
<td>Overlap</td>
<td>Normal</td>
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<tr>
<td>Width</td>
<td>–</td>
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<tr>
<td>Dolomite</td>
<td>–</td>
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<tr>
<td>g = 2.0044</td>
<td>–</td>
</tr>
<tr>
<td>g = 2.0037</td>
<td>–</td>
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<tr>
<td>g = 1.9998</td>
<td>–</td>
</tr>
<tr>
<td>g = 14.25</td>
<td>Lognormal</td>
</tr>
<tr>
<td>g = 5.9</td>
<td>Lognormal</td>
</tr>
<tr>
<td>g = 4.3</td>
<td>Lognormal</td>
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<tr>
<td>g = 2.9</td>
<td>Lognormal</td>
</tr>
<tr>
<td>g = 2.7</td>
<td>–</td>
</tr>
</tbody>
</table>

*A dash (–) denotes a distribution that is neither normal nor lognormal.*

Figure 7  Correlations between a) Mn²⁺ and Overlap, b) Width and Overlap, c) g = 14.25 (Fe³⁺ in the CaCO₃ lattice) and g = 4.3 (Fe³⁺ in accessory minerals and the CaCO₃ lattice), d) g = 14.25 and g = 2.9 (Fe³⁺ in the CaCO₃ lattice).
some samples show extremely high values of Overlap. Those samples are expected to show a large value of Width, since large concentrations of paramagnetic ions (Mn$^{2+}$ for this case) are theoretically known to cause a broadening of the EPR peaks.

Correlation of peak $g = 4.3$ with $g = 14.25$ and $g = 2.9$. As mentioned earlier, the peak $g = 4.3$ originates from Fe$^{3+}$ in two sites, one in the calcium carbonate matrix and the other in the silicate minerals and iron oxides. Therefore, its correlation with peaks $g = 14.25$ (see Fig. 7, $r = 0.48$) and $g = 2.9$ ($r = 0.44$), which originate from Fe$^{3+}$ in the calcium carbonate matrix, can be expected in cases where the concentration of secondary silicate minerals is negligible.

However, in cases where the secondary minerals are present in significant amounts, the intensity of peak $g = 4.3$ increases independently and its correlation with $g = 14.25$ is eliminated. In this way we can explain the outliers in Figure 7 (c), which shows clearly the dual nature of the peak with $g = 4.3$. Therefore, such a peak would not be considered suitable for quarry discrimination.

Correlation of peak $g = 14.25$ with $g = 2.9$ and $g = 5.9$. These peaks are highly correlated (for $g = 14.25$ and $2.9$, $r = 0.936$ (Fig. 7 (d)); for $g = 14.25$ and 5.9, $r = 0.864$; and for $g = 2.9$ and 5.9,

![Boxplots for (a) MGS, (b) Mn$^{2+}$ and (c) Width (r.u. = relative units).](image-url)

Figure 8  Boxplots for (a) MGS, (b) Mn$^{2+}$ and (c) Width (r.u. = relative units).
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This result was expected considering the fact that these peaks are due to Fe$^{3+}$ substituting for Ca$^{2+}$ in the CaCO$_3$ lattice. Since they are correlated with the same paramagnetic centre, only the first one, which is the more intense (Fig. 4), was chosen for use in quarry discrimination.

According to the previous discussion, all of the parameters of Table 1 except for Overlap, $g = 5.9$, $g = 4.3$ and $g = 2.9$ are accepted for use in the quarry discrimination procedure.

4.4 Comparative boxplots

Boxplots are a very convenient representation for evaluating visually the discrimination effectiveness of parameters and selecting the most suitable one for discriminating between two particular quarries. Figures 8 and 9 show comparative diagrams, with the medians and ranges of all the parameters mentioned above, for all of the quarrying areas included in the data bank.

![Boxplots](image)

Figure 9  Boxplots for (a) $g = 14.25$, (b) $g = 2.0044$, (c) Dolomite, (d) $g = 2.0037$, (e) $g = 1.9998$ and (f) $g = 2.7$ (r.u. = relative units).
Figure 8 (a) shows that, using grain sizes (MGS) alone, the Penteli and Hymettus quarries are discriminated from Naxos and Proconnessus. In Figure 8 (b), Mn$^{2+}$ obviously discriminates Penteli from all the other quarries. The parameter Width (Fig. 8 (c)) shows large differences between different quarries, although it does not seem to discriminate any one of them. In general, Naxos-Melanes, Paros and Hymettus show lower values of Width than Naxos-Apollon, Penteli and Proconnessus. The parameter $g = 14.25$ does not seem to be effective in discrimination, since almost all quarries overlap (Fig. 9 (a)). The parameter Dolomite appears mainly in Penteli, Hymettus and Proconnessus (Fig. 9 (c)). It also appears in Naxos-Apollon, but only in two samples. Naxos-Apollon and Penteli do not show the peak at $g = 2.0044$ (Fig. 9 (b)), Naxos-Melanes and Penteli do not show the peak at $g = 2.0037$ (Fig. 9 (d)) and Naxos-Melanes, Naxos-Apollon and Penteli do not show the peak at $g = 1.9998$ (Fig. 9 (e)). Finally, the peak at $g = 2.7$ appears only in Penteli and Paros (Fig. 9 (f)).

Obviously, one parameter alone cannot provide a good discrimination between different quarries. A closer study of the boxplots shows that, for the majority of the cases, only one parameter can be decisive for discriminating between two quarries. This led us to apply a stage-based approach, where at each stage we treated the discrimination of no more than two or three quarries. This ‘gradual’ discrimination turned out to be not only successful but also more flexible, since the addition of new quarries involved treating overlapping areas only with the most suitable combination of parameters.

5. A STEPWISE APPROACH FOR QUARRY DISCRIMINATION

5.1 First quarry discrimination stage: the MGS–Mn$^{2+}$ diagram

Grain size is the most commonly used characteristic in discriminating between marble quarries. Estimation of the grain size, by the naked eye, was used for the first time by Lepsius (1890), and is still used today to classify marble into three types: fine-grained, medium-grained and coarse-grained. However, very few researchers have made systematic measurements and given ranges of values for different ancient quarries (Moens et al. 1988).

Mn$^{2+}$ seems to be the key ion in provenance determination, since most of the techniques used (except isotopic analysis), measure Mn$^{2+}$ concentrations either directly, as in neutron activation analysis and EPR spectroscopy, or indirectly, as in cathodoluminescence.

The importance of these two parameters led us to use MGS and the Mn$^{2+}$ EPR peak intensity, for the first time together, in a first approach to quarry discrimination. Figure 10 shows an MGS–Mn$^{2+}$ diagram for seven of the most important ancient quarries. Logarithms of the parameters are used, since MGS and Mn$^{2+}$ follow a lognormal distribution and a logarithmic scale gives a more confined distribution, especially in cases of extremely large values. The standard probability ellipses shown are drawn with 95% confidence limits.

The Penteli quarrying area is obviously the only one that is clearly and fully separated from all of the other quarries. All Penteli samples show a remarkably small variation of MGS and Mn$^{2+}$.

From the Naxos quarries, only the Apollon (NAXOS A) and Melanes (NAXOS M) quarries are included, as the most important known ancient quarries on the island. On South Naxos the exploitation seems to have been mainly surficial and not systematic, although there are very many archaeological artefacts made using the marble from this area. The Naxos quarries seem to have essential differences from the other quarries, in MGS values as well as in Mn$^{2+}$ values.

The Proconnessus quarries are separated into two fields, called Proconnessus 1 (PROCON 1 in Fig. 10) and Proconnessus 2 (PROCON 2). Those fields correspond to two different
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geographical regions, the first in the western part of the quarrying area (Yalanci Palatya, Koyustu, Camlik, Mandira and Aksoy) and the second in the eastern part (Silinte, Dogu Camlik: Asgari and Matthews 1995). Obviously, the differentiation (mainly in Mn$^{2+}$) reflects differing geological histories of diagenesis and metamorphosis of the marble formations. This can also be detected by isotopic analysis (Asgari and Matthews 1995), where the high Mn$^{2+}$ intensities correspond to high $\delta^{18}O_{\text{Pee}}$ values. However, EPR discrimination is better defined and more clear.

The Proconnesian quarries overlap with the Parian ones.

The Lychnites (PAROS L in Fig. 10) and Lakkoi (PAROS LK) ellipses correspond to the two best known Parian marble types (Maniatis and Polikreti 2000): the famous Lychnites, with their characteristic transparency and MGS values from 0.7 to 1.3 mm, and Lakkoi marble (formerly referred to as Chorodaki or Heridaki), which does not show any remarkable transparency and has MGS values that vary from 1.5 to 3.5 mm. These two types of Parian marble obviously cannot be separated in this diagram. However, we continue to plot them separately due to the fame of the quality and beauty of the Lychnites. There are only six Lakkoi samples, and consequently we cannot give reliable statistical results. That is why they are plotted as individual points.

Finally, on the MGS–Mn$^{2+}$ diagram we can spot the following major overlapping areas:

(i) overlap 1, Naxos M – Naxos A;
(ii) overlap 2, Paros L – Hymettus;
(iii) overlap 3, Paros L – Paros LK – Proconnessus 1.

5.2 Second discrimination stage: overlapping quarry diagrams

One of the most useful and promising advantages of EPR is the large number and variety of the marble spectrum parameters. We are going to use this potentiality in what follows, in order to eliminate, if possible, the overlaps between the different quarry ellipses.
Overlap 1: Naxos-Melanes – Naxos-Apollon  The most critical differences between these quarries are as follows:

(i) Melanes shows larger values of MGS than Apollon;
(ii) Melanes shows lower values of Width;
(iii) Melanes show larger values of the peak at \( g = 14.25 \);
(iv) Melanes does not show the peak at \( g = 2.0037 \), which occurs in Apollon;
(v) Melanes shows the peak at \( g = 2.0044 \), which does not occur in Apollon.

From all the previous differences, (iv) and (v) are decisive. If the sample of unknown origin falls into overlapping area 1 and shows a peak at \( g = 2.0037 \), then its provenance is ascribed to Apollon. If it shows a peak at \( g = 2.0044 \), it is ascribed to Melanes.

If the sample shows neither a peak at \( g = 2.0037 \) nor one at \( g = 2.0044 \), then we have to use the rest of the parameters to investigate its provenance. Consequently, we decided to use MGS and \( g = 14.25 \), since these two give a more satisfactory separation (Fig. 11). An overlapping area still exists, but the result is superb, since we are able to make such a fine discrimination between two quarrying regions on the same island with such similar types of marble. Additionally, no other technique can discriminate between Naxos-Melanes and Naxos-Apollon.

Overlap 2: Paros–Proconnessus  Discrimination between Paros and Proconnessus is problematic not only for EPR spectroscopy but also for isotopic analysis and other techniques (Moens et al. 1992; Barbin et al. 1995; Walker and Matthews 1995; Armiento et al. 1997). The problem is particularly serious for discriminating with stable isotopes between the Lakkoi marble (called Paros-2 or Chorodaki in the isotopic literature) and the whole of Proconnessus island.

In our initial diagram (Fig. 10), the fine Lychnites samples (grain sizes < 1.3 mm) do not risk being confused with Proconnessus. The problem is therefore confined to distinguishing between the Paros-Lakkoi and Proconnessus-1 marbles.

A first distinguishing characteristic is that, at Paros, no dolomite has been detected by EPR spectroscopy, in all of the samples analysed. Of course, this is only an indication and is not so

![Figure 11](image-url)
The provenance of marble based on EPR spectroscopy

A comparison between the Paros and Proconnessus EPR parameters leads to the following observations: (i) In general, Paros shows lower values of Width than Proconnessus; (ii) the peak with $g = 1.9998$ is very rare in the Paros samples, but occurs very frequently in the Proconnessus samples.

Apart from the above parameters, we have also used Mn$^{2+}$ and MGS, which proved to be helpful in the first stage of discrimination. After many trials with different combinations of these four variables, we concluded with the following optimum choices:

$$\text{MGS/Width versus } \text{Mn}^{2+} - 100 \times \text{peak height of } g = 1.9998.$$  

MGS gives the weak separation observed at the first stage, but division by Width enhances the degree of separation. For the second combined variable, we used Mn$^{2+}$ and enhanced its discrimination potential by subtracting from it the intensity of $g = 1.9998$. The multiplication factor of 100 was used to normalize the peak intensity of $g = 1.9998$ to a level comparable with Mn$^{2+}$, which is of the order of 300. Subtraction was preferred rather than addition, simply because it makes the new data begin with a zero value instead of another random value.

In Figure 12, these parameters are used to produce a Paros–Proconnessus separation plot. The samples LK5 and LK6 are the only ones that confuse the otherwise clear picture. This attempt, although not perfect, is very important, since it certainly separates a certain percentage of the analysed samples.

The contribution of this approach is expected to be useful in clarifying marbles of the Hellenistic and Roman periods, which is when the Proconnessus quarries began to be used.

Overlap 3: Paros–Hymettus

We have to note here that the transparency and texture of Parian marble is very different from that of Hymettus, given the high grade of metamorphosis of the former. Consequently, we would not expect confusion between Paros and Hymettus samples. However, in certain circumstances, art-historical dilemmas of this nature can occur. The

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Figure 12  A combined parameters diagram for separating PAROS (L and LK) from PROCON (1 and 2).
provenance of the ‘Hecatombedon Inscription’, for example, is such a case, where Paros and Hymettus are both possible and uncertain quarrying areas of origin (Orlandos 1958; Butz et al. 1999).

The most important differences between the Paros and Hymettus parameters are that the Paros MGS values are larger than those of Hymettus, and the peaks with \( g = 2.0037, g = 2.004 \) and \( g = 1.9998 \) are rare in Paros samples but usual in Hymettus samples.

Simple combinations of these parameters lead us to two new variables:

\[
\text{Mn}^{2+} - 10 \times (g = 2.0044) \quad \text{versus} \quad \text{Width} - 5 \times \log (g = 1.9998).
\]

The peak with \( g = 2.0037 \) was not used, since after many different trials it proved to be unsatisfactory for discrimination of the two quarries. \( \text{Mn}^{2+} \) gives a weak discrimination of the first stage, which is enhanced by subtracting \( g = 2.0044 \) from it. We constructed the second parameter in the same way. The multiplication factors and subtraction were used for the same reasons as explained in the Paros–Proconnessus case.

Figure 13 shows a separation plot for Paros and Hymettus, using the previous combined parameters for the \( x \)- and \( y \)-axes. Samples LK5 and LK6, which fall near the Hymettus samples, have—luckily enough—large maximum grain sizes, an observation that eliminates the possibility of assigning their provenance to Hymettus by mistake.

6. APPLICATIONS AND POTENTIAL OF THE METHODOLOGY

The above methodology was applied to a large number of archaeological samples, approximately 120 pieces, from different periods and places in the Mediterranean and across Europe. The results were very meaningful from the archaeological and art-historical point of view. Most of these results are published (Maniatis et al. 1988; Kokkorou-Alewras et al. 1995; Kanda-Kitso 1996; Kaninia 1997; Kokkorou-Alewras 1997; Pollini et al. 1998; Butz et al. 1999; Goette et al. 1999; Kane et al. 1999; Maniatis and Polikreti 2000; Maniatis et al. 2000) and several more papers are in preparation.
In most cases, when an archaeological or art-historical problem on marble provenance arises, it is focused on two or three quarrying areas. Questions on the origin of a marble in general, where all the quarries worldwide are open, rarely occur and are thus meaningless. The majority of the researchers use archaeological or art-historical information to focus the question to a limited number of locations. In addition, no technique can be considered as a panacea in resolving all provenance problems by itself, and in several cases the provenance investigation ends up by confining the problem to an uncertainty between two or three specific quarries. The stepwise approach that we propose here is thus very convenient due to its flexibility to treat quarries in pairs or triples. It can be really valuable in cases where there is sound archaeological or art-historical information, or in cases where EPR is used together with another technique.

Some possibilities for new applications that are opened up with the proposed methodology include the discrimination, to a great extent, between the two archaic quarries (Melanes and Apollon) on the island of Naxos, an inherent difficulty faced with a lot of other techniques, including that of stable isotope analysis. Another unique outcome of the methodology is that it can discriminate between the quarries on the island of Proconnessus, placing them into two specific geographical regions on the island. No other technique can make such a fine distinction. Another advantage is the decrease in the Paros–Proconnessus overlap, a discrimination that is a real headache for marble provenance investigators.

One of the main advantages of the proposed methodology is the simplicity of the statistical procedure. This makes the graphs readable by anyone, and the location of a sample on a graph is easily found.

Expansion of the data bank in the future, with the addition of new quarries, is expected to cause more overlapping problems, which would be fully or partially resolved by treating the quarries in pairs and selecting the parameters between which there is the best discrimination.

### 7. CONCLUSIONS

This work has provided, for the first time, a thorough investigation of EPR spectroscopy as a technique for the determination of the provenance of marble. A number of parameters were measured in different parts of the spectrum for each sample. In addition, the measurement of maximum grain size with an optical microscope provided an extra independent parameter. All of the parameters were studied; their natural distribution and the correlations between them were investigated. Some of the parameters were found to correspond to the same paramagnetic centres and others to express more than one physical property. Neither of these parameters was used in quarry discrimination.

Furthermore, the parameters were tried in pairs and in combinations, in order to check their usefulness for quarry discrimination. The overlapping areas between different quarries were systematically investigated, and by the use of different combinations they were diminished or strongly decreased. In this way, a new methodology was developed and proposed, based on a stepwise approach, which progressively increases the resolution of the technique.

The ultimate conclusion of this work is that the use of carefully selected parameters from EPR spectroscopy and the maximum grain size of marble provide a tool of great potential for the characterization of the provenance of marble used in ancient monuments.

The new methodology was applied to a large number of archaeological and art-historical cases, with a promising high rate of success. Inevitably, some special cases of quarries whose parameters overlap do remain unresolved, even after many attempts to increase the resolution. The most characteristic example is the coarse-grain Parian marble, compared with that of
Proconnessus. However, this particular problem is encountered with several other techniques, and it is under investigation at the present time.

Some further advantages of the EPR technique itself are the simplicity of measurement and the fact that the sample is not destroyed. It is therefore advisable in any archaeological or art-historical problem involving the provenance of a marble monument to first use the EPR—maximum grain size technique with the methodology proposed and then, if the problem has not been solved, to proceed with other techniques that dissolve or destroy the sample, such as carbon and oxygen stable isotope analysis.

Our database is expanding rapidly to include samples from the area of the Macedonian Kingdom in northern Greece and Anatolia, on which we will be reporting in the near future.

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APPENDIX

The stepwise approach that we have adopted is the result of many different trials with different methodologies. We also performed Principal Component Analysis (PCA) with all the parameters used in the stepwise approach, but the result was a total diffusion between the quarries. Further detailed trials were attempted by selecting only parameters that exhibited the greatest differentiation between different quarries, but the results were no better, failing to produce any useful differentiation between the quarries. It is only when one performs transformations of selected parameters that one can produce a meaningful result. The set of transformed parameters obtained by trial and error in order to enhance differentiation with PCA are as follows: log(MGS), log(Mn²⁺), log²(g = 1.9998) and MGS/Width. By using these parameters with PCA, a satisfactory result is obtained (Fig. 14), since it discriminates Penteli clearly from all other quarries—and both of the Naxian quarries to a good degree. As for the rest of the quarries, the discrimination is similar to that produced with the stepwise approach.

After a great number of different data treatments, we believe that the stepwise approach that we have presented in this work is preferable to the PCA alternatives for several reasons. First, the stepwise approach discriminates readily and fully the different quarrying areas on the island of Proconnessus, a benefit that we lose completely with the PCA treatments. Second, each overlapping area can be treated separately, a fact that may prolong the whole methodology but that offers a better chance of discrimination. This is very useful when we have to solve problems that are focused on two specific quarries as a result of art-historical information, or on an overlapping region between two quarry fields of another technique (e.g., stable isotopic
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Figure 14  A principal component analysis for all the quarries mentioned in this work. The parameters used are log(MGS), log(Mn$^{2+}$), log($g_1 = 1.9998$) and MGS/Width.

Both of these situations are very frequent in the analysis of marble from ancient artefacts. Finally, the use of simple combinations of the initial parameters makes the graphs suitable for use by other researchers.

REFERENCES


K. Polikreti and Y. Maniatis


Lepsius, R. G., 1890, Griechische Marmorstudien, Königliche Akademie für Wissenschaften, Berlin.


Mandi, V., 1993, Provenance determination of the marble of ancient monuments with the techniques of electron paramagnetic resonance spectroscopy and neutron activation analysis (in Greek), Ph.D. thesis, Department of Chemistry, University of Athens.


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