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Numerical taxonomy: Mn^{2+} EPR line shape as a criterion in provenance studies

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The Mn^{2+} EPR spectra of 12 marbles and limestones (calcitic, dolomitic and calci-dolomitic) collected from different Greek quarries have been analysed by means of cluster analyses numerical taxonomy. By means of Mn^{2+} EPR line shape this technique allowed classifying all samples in concordance with their mineralogical structure. Accordingly, we have found that while Euclidean and power distances showed to be more adequate in differentiating samples belonging to the same petrologic group, the Perason's correlation coefficient is most suitable to discriminate samples having different mineralogical composition.

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1. Introduction

Numerical taxonomy, a division of multivariate analysis, generates, by analyzing a multitude of numerical features, called taxonomic characteristics, a classification of investigated items, which reflects their degree of similarity. In opposition with evolutionary taxonomy currently used in zoology and botany that weight taxonomic characteristics on the basis of their presumed role in natural selection, numerical taxonomy restricts only to an appropriate analysis of phenetic distances, *i.e.* the extent of resemblance of investigated objects. For this reason the numerical taxonomy is currently used in those branches of science where a strictly evolutionary classification is no absolutely necessary or there is not *a priori* a classification hypothesis, such as paleontology, geochemistry, paleo-climatology, archaeometry or even psychiatry.

Specific to numerical taxonomy is the use of exactly quantified parameters, whose values are expressed only as numbers, experimentally obtained by measuring various characteristics common to all members of a group.

Among different techniques used by numerical taxonomy, the cluster analysis seems to be the most adequate to be used in geology or archaeometry. By means of various algorithms, the cluster analysis allows different objects to be hierarchically grouped in clusters that, at their turn, are arranged in clusters of clusters, etc. At present time there are three types of algorithms to perform a cluster analysis: k-means clustering, two-way joining (block clustering), and joining (tree clustering) [1], the last one being the most used because, its final product, the tree diagram, better illustrates the hierarchy between different clusters [2]. Geochemistry, social sciences, archaeology as well as archaeometry are among the main user of cluster analysis.

In archaeometry, cluster analysis has been used whenever it was necessary to establish taxonomies of stone tools, funeral objects, building materials such as marble or limestone or to establish the provenance of different artifacts [3-5].

Limestone and its metamorphic form, marble belong to the largest category of calcium carbonates. Resistant to weathering, widespread in different varieties and easy to be carved, marbles and limestones were intensively used since antiquity as an excellent material for monumental art [6]. At present time, the question of establishing the real origin of marble and limestone used in antiquity represents an important task of the archaeology as it could gives not only significant information concerning cultural and trade routes but also could be very useful in establishing the authenticity of various object of art made from these materials.

All marbles are made by granular dolomite or limestone of organic nature totally or partially recrystallized by the action of pressure, heat or the presence of aqueous solutions. Depending of the location, marbles could be composed of pure dolomite, pure calcite or a mixture of these minerals. Various minerals such as quartz, mica, graphite, iron oxides, etc. could alter the original white color of marbles, by creating attractive and colorful patterns.

Table 1. The petrologic description of the investigated samples (after ref. [7], modified).

Quarry	Type	Composition	Quarry	Type	Composition
Kerkira	intraclastic limestone	calcite, traces of dolomite	Trizina	sparry calcite	calcite + iron oxides
Nauplio	precipitation limestone	calcite	Dionysos	crystalline limestone	calcite
Drama	dolomitic marble	dolomite, traces of calcite	Aliveri	calcitic marble	calcite, traces of dolomite
Kavalla	calcitic marble	calcite, traces of quartz	Gramatiko	calcitic marble	calcite, traces of dolomite
Thasos	dolomitic marble	dolomite, traces of calcite and magnesite,	Kozani	calcitic marble	calcite
Didimon	dolomitic marble	calcite, small amount of dolomite	Naxos	calcitic marble	calcite

Marbles and limestones represent a category of widespread rocks. Therefore, despite some commune traits such as crystalline structure, there are many other particularities that act as suitable proxies for provenance studies. Various physicochemical parameters such as trace elements or Rare Earth Elements concentrations [3,7,8], δ^{13}C and δ^{18}C isotopic ratio [9], Mn^{2+} paramagnetic ions [4,5,10-17] or other free radicals [13-15], all of them regarding marbles, were investigated by multivariate statistical analysis [4,10,18-20]. It is worth to mention the use of Electron Paramagnetic Resonance (EPR) as a high sensitive and specific spectroscopic method for free radicals and other paramagnetic centers in provenance studies [21-23]. Moreover, Mn^{2+} ions represent ubiquitous radicals in the calcium carbonates of organic origin, making them a favorite object of investigation by EPR and use for such kind of studies [4,5,11-17].

The main aim of any provenance studies is to establish similitude and differences between different objects in order to evidence some common origins. Numerical taxonomy and subsequently cluster analysis shown to be very adequate for provenance studies provided that the investigated samples could be characterized by some numerical parameters, whose values can be experimentally determined. As any EPR line can be converted into a stream numeric data, the above mentioned statistic method could be easily applied to any EPR spectrum.

Structural properties of the systems containing manganese may be revealed by EPR. Being very sensitive to changes in its neighborhood the Mn^{2+} paramagnetic ion may provide valuable information on the materials [24].

Therefore, in this paper we propose a new discrimination criterion based on the analysis of Mn^{2+} EPR spectrum in natural carbonates.

2. Materials and methods

For this study we have used 12 samples of marbles and limestone, collected from quarries located in different geotectonic zones of Greece (Table 1). More details about these samples can be found in ref. [7].

All EPR measurement has been performed at room temperature, by using an X-band JEOL JES ME 3X spectrometer provided with a cylindrical TE_{011} resonant cavity and a 100 kHz modulation with amplitude of 0.032 mT. Microwave power was of 0.6 mW. No more than 100 mg of fine grounded material have measured at once. All EPR spectra have been digitally recorded by means of a 12 bit PCI-1202H acquisition module. DPPH and CaO:Mn^{2+} standard samples have been used for field calibration. Each EPR spectrum has been digitally recorded. StatSoft Statistica 4.5^{TM}, MSExcell^{TM} and Microcal Origin$^{®}$ software have been used for subsequent data analysis.

To avoid any errors introduced by the variation of spectrometer parameters, all measurements have been performed by keeping constant both microwave power level and modulation width. We only adjusted the spectrometer amplification, but this one does not influence the shape of resonance line.

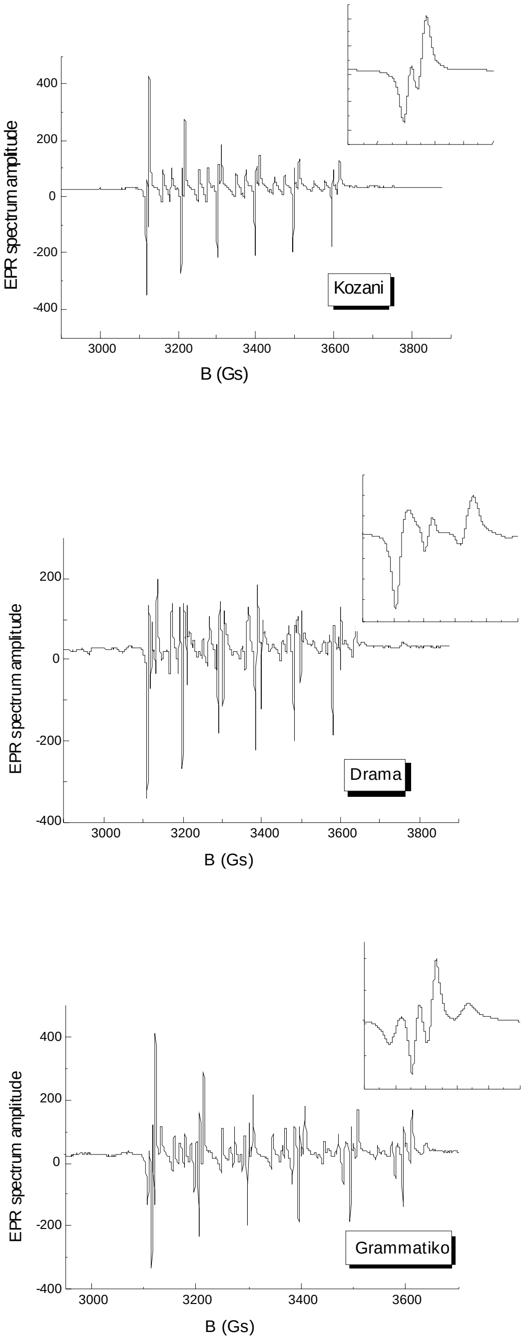

Fig. 1. Mn^{2+} ions EPR spectra in calcitic marble from Kozani, dolomitic marble from Drama, and calcito-dolomitic marble from Gramatiko. Insets illustrate the low field Mn^{2+} EPR lines analyzed in this study.

Before performing any further analysis, each spectrum has been numerically integrated, to obtain the true absorption lines, enabling us not only to determine the number of components of the each EPR spectrum, but also to compare different samples.

This was done by sampling the first Mn^{2+} resonance low-field EPR with a sampling ratio of 0.05 mT into a set of 40 different values centered on the absorption maximum. In this way, the first Mn^{2+} absorption resonance line was converted into a set of n = 40, p_i variables (according to eq. 1-3) that were subsequently analyzed, as described in details in the next section.

It is worth to mention that, due to a relative high concentration of Mn^{2+} in all samples the noise of each experimental spectrum was, for the experimental conditions mentioned above, almost negligible, that has a positive influence on any further statistic analysis

3. Results and discussion

For all investigated samples we have observed three kinds of typical six-lined Mn^{2+} EPR spectra characteristic for a local rhombic symmetry, but different for calcite and dolomite. In the case of mixed samples consisting of a combination of calcite and dolomite, the observed spectrum was a mixture of two above mentioned spectra (Fig. 1).

All spectra consist of six principal lines corresponding to the “allowed Δm_I = 0”, transitions between superfine sub levels within ± ½ Kramers doublet [21,22] and five groups of two lines due to the “forbidden Δm_I = ± 1” transitions. (Fig. 1).

Because of in calcite lattice, manganese ions, substitute for calcium atoms the EPR spectra are relative simple (Fig. 1, Kozani sample).

In dolomite the divalent manganese substitute for both calcium or magnesium atoms, thus generating an intricate EPR spectrum consisting of a superposition, in equal proportion, of two kind of spectra: Mn^{2+} ions in the Ca^{2+} sites and Mn^{2+} ions in the Mg^{2+} sites (Fig. 1, Drama sample).

In the case of calcite rich samples that contain small amounts of dolomite, we have noticed a third kind of spectra was (Fig. 1, Gramatiko sample) consisting of a superposition of the “calcite type” and “dolomite type”, close to Mn^{2+} spectrum in calcite. Extra details concerning the EPR spectra of Mn^{2+} ions in calcite and dolomite can be found in Ref. [25-27].

It must be pointed out that all observed EPR resonance line has an intricate structure that differs by the line-width or in the case of dolomite rich sample by the number of components too. For that reason, two resonance lines having the same position in spectrum, but belonging to two different samples, could be compared by using several criteria, currently applied in numerical taxonomy.

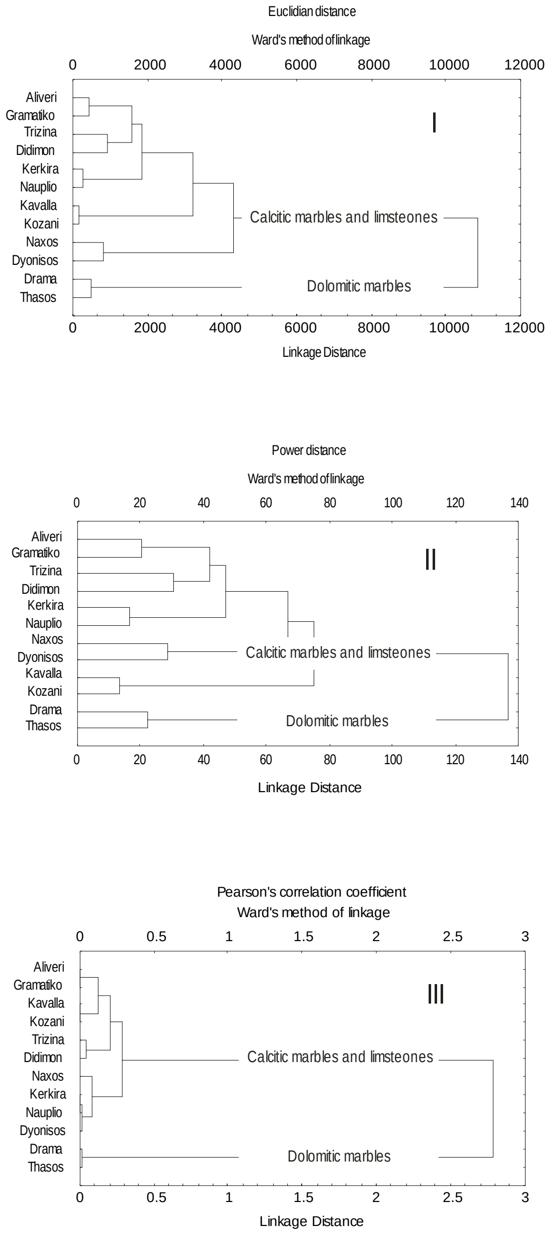

Fig. 2. Three different tree diagrams of the investigated samples based on the Euclidian distances (I), power distances (II) and correlation coefficients (III) between the low field Mn^{2+} EPR lines. In spite of some discrepancies, all diagrams reflect predominantly the mineralogical composition of considered specimens. It must be pointed out that the best discrimination between main clusters is provided by the correlation coefficient.

In our case, we found that Euclidean and power distances one hand as well as the Pearson's correlation coefficient on the other are among the most suitable criteria to classify marbles samples, if they were applied to the first Mn^{2+} resonance absorption lines.

Euclidian distance between two equal sets of n variables p_i and q_i is defined by the equation:

$$d_E = \sqrt{\sum_i (p_i - q_i)^2} \tag{1}$$

In some cases, if it necessary to increase or decrease the progressive weight that is placed on the number of values within a set or on the difference between values, instead of Euclidian distance a power distance can be computed:

$$d_P = \sqrt[m]{\sum_i (p_i - q_i)^k} \tag{2}$$

where m and k are user-defined parameters; k parameter controls the progressive weight that is placed on differences on individual dimensions while the n parameter controls the progressive weight that is placed on larger differences between objects. For k and m equal to 2 the power distance reduces to the Euclidean one.

For the same set of variables, the correlation coefficient $r_{p,\,q}$ is defined as:

$$r_{p,q} = \frac{1}{n}\frac{\sum_i (p_i - \bar{p})(q_i - \bar{q})}{\sigma_p\,\sigma_q} \tag{3}$$

where $\bar{p}$ and $\bar{q}$ are the average values of p_i and respectively q_i set of variables while σ_p and σ_q are the corresponding standard deviations.

In our case, both Euclidian and power distances as well as the correlation coefficients have been used to derive three tree diagrams that allowed quantifying the similarities and differences between all 12 samples (Fig. 2).

By analyzing these diagrams we could make the following observations:

i. Irrespective of the selection criterion, all samples are divided into two main clusters, one containing only dolomitic marbles and other one consisting of calcitic and calcito-dolomitic specimens, reflecting in reality the greatest difference between the EPR spactra of Mn^{2+} in calcite and dolomite. The fact that the calcito-dolomitic samples are classified, in all three diagrams, among calcitic samples can be explained by the low amount of dolomite present in these samples, and consequently to a more resemblance of the EPR spectra to calcitic than to dolomitic type.

ii. Between Euclidean and power distance tree diagrams, the differences consists more in the linkage distance, and less in the distribution of sample within calcitic cluster. At the same time, within this cluster, Kerkira and Nauplio, both limestones, form a subcluster, while in Perason's tree diagram, all limestone samples, *i.e.* Kerkira, Nauplio and Dyonisos are linked together.

iii. Looking at the linkage distance, which quantifies de degree of similarity, it is obvious that the correlation coefficient diagrams are characterized by longer linkage distances than de the other ones signifying that the difference between calcitic type and dolomitic type Mn^{2+} EPR spectra are better evidenced on the first category of diagrams. On the other hand, within each main cluster, Euclidean distances or even better the power distances seems to be more adequate to be used as a discriminating factor between different spectra.

It seems in this way, that the tree diagrams based on the correlation coefficients are more sensitive to the difference marble-limestone than the distances ones. These considerations concerning the use of numerical taxonomy have showed that the cluster analysis represents a useful and, for the time being insufficiently used tools for provenance study.

4. Concluding remarks

By applying the methods of cluster analysis and numerical taxonomy to the analysis of the EPR spectra of Mn^{2+} ions in marble and limestone samples collected from 12 Greek historical quarries, it was possible to classify all samples in concordance with their mineralogical structure. At the same time, it has been shown that the Perason's correlation coefficient is most suitable to distinguish samples having different mineralogical composition while Euclidean and power distances showed to be more adequate in differentiating samples belonging to the same petrologic group.

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