

EPR AND X-RAY DIFFRACTION INVESTIGATION OF SOME GREEK MARBLES AND LIMESTONES

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Abstract. 12 different marble and limestone samples collected from well-known Greek quarries have been investigated by X-ray diffraction and electron paramagnetic resonance (EPR). X-ray diffraction spectra permitted to determine both major (calcite and dolomite) and minor (quartz or magnesite) mineralogical components. EPR has been used to investigate the same samples unirradiated and after 10 kGy gamma-ray irradiation. The unirradiated samples display typical EPR spectra of Mn²⁺ in calcite and dolomite as well as a superposition of these while some samples displayed EPR free radicals signals of centers (low field signal) and centers (high field signal). From X-ray diffraction and EPR spectra it was possible to extract numerical values of several numerical parameters such as dolomite to calcite ratio, EPR intensity parameter, and low field to high field EPR signals intensity ratio. These values as well as the correlation coefficients between the digital functions that described the low field Mn²⁺ ions EPR line have been used as entry data for cluster analysis to quantify the resemblance and differences between analyzed samples.

Key words: marble, EPR, X-ray diffraction, provenance.

1. INTRODUCTION

Marble represented from ancient times (5th millennium BC) one of the most used material for architecture and sculpture [1]. From that time until present, marble has been extracted from more than 50 quarries [2] while an intense trade has spread it over the entire Mediterranean basin, and even beyond it. This fact raises the question of determining the origin of the marble used in ancient architecture and sculpture. A correct assignment of the provenance of an ancient work of art carved in marble can furnish valuable information concerning the trading circuits as well as the cultural interconnections.

Petrographically, marbles represents granular natural limestone or dolomite of organic nature that have been recrystallized under the influence of external agents such as heat, pressure or the presence of aqueous solutions. Marbles consist of a mosaic of various proportion of calcite and dolomite grains often interbedded with other minerals such as quartz, mica, graphite, iron oxides, pyrite, etc., minerals representing impurities in the original organic limestone, which reacted during metamorphism to form new compounds. It is obvious that, in spite of some commune characteristics originating in the petrologic composition and structure of marble and limestones, there is a great number of particularities that make the actual marble extremely diverse. Provided that within a quarry or at least within some part of it the marble is homogenous enough, there is a large variety physical characteristics that can be used as markers in provenance studies. Several physicochemical parameters such as trace elements or REE concentrations [3-5], $\delta^{13}\text{C}$ and $\delta^{18}\text{C}$ isotopic ratio [6] intensity of specific thermoluminescence glow curve peaks [7], Mn^{2+} ions [8-15] or other free radicals [7, 13,14, 16] EPR spectra parameters have been used to solve this problem. As all mentioned techniques can finally furnish numerical value of these parameters, various classification rules based on a multivariate statistical analysis [5, 8, 17–19] have been used for a correct assignment of investigated specimens.

EPR represents the most adequate technique for investigating a great variety of paramagnetic centers such as transition elements ions or free radicals [20–22]. Among the first category of paramagnetic centers, Mn^{2+} have been extensively investigated in marble and limestone, as manganese is a ubiquitous element in the calcium carbonates of organic origin [8–16, 20].

Free radicals can be generated in solid sample by irradiating them with ionizing radiation such as X or gamma rays, alpha or even beta rays. Such ionizing rays can be generated by natural occurring radioactive elements within samples or by irradiating them with X or gamma-ray generated by external sources. In this way, the EPR lines of the free radicals spectrum of irradiated sample are enhanced with respect to non-irradiated ones. Despite the fact that the number of free radicals is up to 10-15 KGy proportional to the absorbed dose, their concentration depends in a complex manner on the presence of trace elements. In this way, by irradiating a set of different samples with the same kind of radiation and at the same absorbed dose, the EPR resonance lines thus generated or enhanced could be used as a supplementary discriminating factor for the provenance studies [13].

Another method currently used in mineralogy and petrology but insufficiently applied in provenance study of natural carbonates is X-ray diffraction that makes possible identification of the minerals that compose the investigated sample [13]. As natural marbles contains, often together with major constituents, such as calcite or dolomite, other minor components, a quantitative determination of mineralogical composition could be very useful in provenance studies.

In a previous paper [5], we have reported our results concerning the concentrations of 22 major, as well as trace, elements in marble specimens collected from 12 Greek quarries. In this study we present the experimental results

concerning the EPR spectra of Mn^{2+} and other free radicals in the same specimens of marbles in connection with the crystallographic data as obtained from X-ray diffraction investigation.

Table 1

Petrologic description of the investigated samples (after ref. [5] modified).
Sample composition is in accordance with X-ray diffraction data

Place	Geo-tectonic zone	Type	Color	Texture	Composition
Kerkira	Ionian	intraclastic limestone	white-yellowish	compact, brecciated	calcite, traces of dolomite
Nauplio	Pindos	precipitation limestone	white-yellowish	fine banded	Calcite, dolomite
Drama	Rhodope	dolomitic marble	white-yellowish	fine grained	dolomite, traces of calcite
Kavalla	Rhodope	calcitic marble	white - grayish	massive, medium granular	calcite, traces of quartz
Thasos	Rhodope	dolomitic marble	white	massive, micro - granular	dolomite, traces of calcite and magnesite,
Didimon	Parnasian	dolomitic marble	cream-grayish	mezzo to mono-crystalline	dolomite, small amount of calcite
Trizina	Parnasian	sparry calcite	red-brownish	micro-crystalline to mezzo-crystalline	calcite + iron oxides
Dionysos	Subpelagonian	crystalline limestone	white	massive, micro - granular	calcite
Aliveri	Pelagonian	calcitic marble	bicolor white - grayish ; white - brownish	massive, banded	calcite, traces of dolomite
Gramatiko	Pelagonian	calcitic marble	white	massive, micro - granular	calcite, traces of dolomite
Kozani	Pelagonian	calcitic marble	white	massive, medium granular	calcite
Naxos	Pelagonian	calcitic marble	white	massive, micro - granular	calcite

2. MATERIALS AND METHODS

2.1. SAMPLES

12 samples of marbles and limestone have been collected from well-known Greek quarries located over insular and continental Greece, and belonging to different geotectonic zones [5, 24]. The respective quarries have been intensively exploited since antiquity. From the investigated samples, only 9 specimens could be considered as pure marble, other 3 were unmetamorphosed limestone (see Table 1).

From each sample, three aliquots have been taken for subsequent analysis. Two of them weighing about 150 mg have been used for EPR and X-ray diffraction measurements, while the third one, of about 0.5 g, has been used for INAA [5]. Before examination, each sample has been crushed, finely ground in an agate mortar and homogenized.

2.2. IRRADIATION

The irradiation has been performed at room temperature by using the ^{60}Co irradiation facilities of the Institute of Physics and Nuclear Engineering in Bucharest. The absorbed dose was determined by means of a Super Fricke chemical dosimeter. All samples have been irradiated at an absorbed dose of 10 kGy.

2.3. X-RAY DIFFRACTION MEASUREMENTS

The mineral phases in marble and limestone samples have been investigated by using a DRON-3 diffractometer with $\text{Cu K}\alpha$ radiation provided with a graphite monochromator and a scintillation counter. Samples were analyzed from 5° to 65° ($0.01^\circ 2\theta$ step).

2.4. EPR MEASUREMENTS

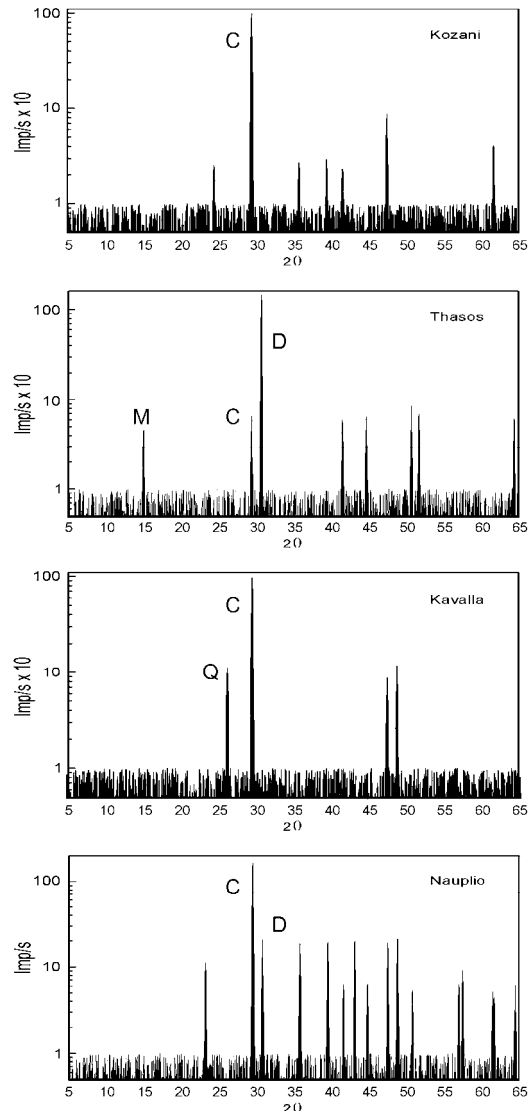
All EPR measurements have been performed at room temperature, by using an X-band JEOL JES ME 3X spectrometer provided with a cylindrical TE011 resonant cavity and a 100 kHz modulation. The finely ground material (maximum 0.1 mm) has been introduced in quartz tubes (~ 2 cm sample length 0.3 mm inner diameter). In order to ease any intercomparison of the experimental spectra, all of them have been recorded by using the same modulation, i.e. 0.032 mT for a microwave power of 0.6 mW. All spectra have been digitally registered by using a 16-bit acquisition card at a sampling rate of the magnetic field varying between 0.025 and 0.49 mT. The microwave frequency has been measured by using a digital Takeda Riken TR 5502D frequency meter while the induction of the magnetic field has been continuously monitored by a digital T.W. BELL Model 20 teslameter. DPPH standard sample has been used for field calibration.

3. RESULTS AND DISCUSSION

3.1. X-RAY DIFFRACTION SPECTRA

Some typical X-ray diffraction spectra are reproduced in Fig. 1. As the investigated samples were composed primarily either of calcite, either of dolomite,

Fig. 1 – Four X-ray diffraction spectra showing both major (calcite and dolomite) and minor (quartz or magnesite) mineralogical components: C – calcite; D – Dolomite; M – Magnesite; Q – Quartz.



the predominate lines belonged to one of this minerals. From this point of view, all the analyzed spectra could be divided into three categories: calcite dominant (Dionysos, Kavalla, Kozani, Nauplio, Naxos and Trizinia), calcite with small amount of dolomite (Gramatiko, Kerkira and Aliveri) and dolomite dominant (Drama, Thasos, and Didimon). Some samples (Fig. 1) also contained small amounts of other minerals such as quartz (Kavalla) or magnesite (Thasos). To describe the mineralogical composition of each sample, we have used the ratio of dominant diffraction lines area of dolomite ($2\theta = 3.096$ nm) and calcite ($2\theta = 2.940$ nm) [25] as proportional to dolomitic to calcitic phases ratio.

Together with the EPR Intensity Parameter (IP) [12] these values were used to characterize each sample (Table 2 and the next subsection).

3.2. Mn²⁺ ERP SPECTRA

All samples displayed very clear Mn²⁺ ions EPR spectra for a local rhombic symmetry. We have observed, in concordance with the mineralogical composition, mainly three types of Mn²⁺ EPR spectra: Mn²⁺ ions in calcite, Mn²⁺ ions in dolomite and Mn²⁺ in mixed samples consisting of a combination of calcite and dolomite (Fig. 2 a-c).

The spectra of the first kind (Dionysos, Kavalla, Kozani, Nauplio, Naxos and Trizinia) consist of six principal lines corresponding to the “allowed $\Delta m_l = 0$ ”, where m_l represents the magnetic quantum number (Fig. 2a) of the manganese nuclear spin I, transitions between superfine sublevels within $\pm \frac{1}{2}$ Kramers doublet [22,23]. In between the allowed transitions there are five groups of lines, each group consisting of two lines due to the “forbidden $\Delta m_l = \pm 1$ ” transitions between the same levels. In calcite, CaCO₃, manganese ions, as a rule, substitute for calcium atoms in the calcium carbonate lattice generating the characteristic spectrum described above.

The second kind of spectra was identified by us in the dolomite rich samples (Drama and Thasos) (Fig. 2b). In dolomite CaMg(CO₃)₂, the divalent manganese substitute for both calcium or magnesium atoms, thus generating an intricate EPR spectrum consisting of a superposition of two kind of spectra: Mn²⁺ ions in the Ca²⁺ sites and Mn²⁺ ions in the Mg²⁺ sites.

The third kind of spectra was observed in calcite rich samples that contain small amounts of dolomite (Gramatiko, Kerkira and Aliveri) (Fig. 2c). It represents a superposition of the “calcite type” and “dolomite type” spectra that give a specific shape close to Mn²⁺ spectrum in dolomite.

The Mn²⁺ spectrum of the Didimon sample represents somehow an exception as Mn²⁺ spectrum, by taking into account the high intensity of free radicals component, resembles neither the typical “calcite” nor the “dolomite” spectra (Fig. 2d).

More details concerning Mn²⁺ EPR spectra in calcite and dolomite can be found in [26-28]. To characterize in a quantitative manner the concentration of manganese ions from each sample, we have used the IP [12] that allow correcting the integral area A of a resonance line for sample mass m , spectrometer gain S_g and modulation amplitude δB :

$$IP = K \frac{A}{\delta B S_g m}. \quad (1)$$

It must be underlined that the eq. (1) can be used only in the absence of saturation; otherwise the amplitude of the resonance line is no more proportional to the square root of microwave field power. In our case, we have kept constant both

modulation width and microwave power so IP could be considered, for each kind of sample (calcitic or dolomitic) proportional to manganese concentration.

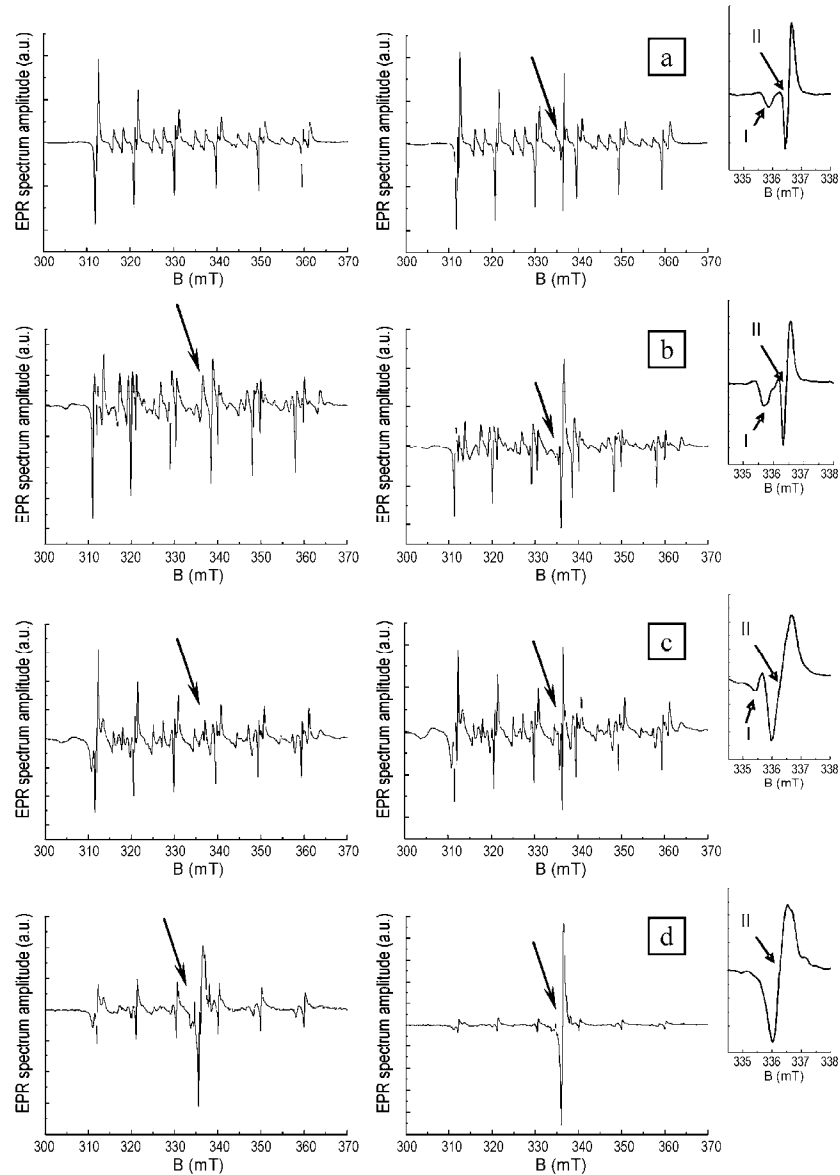


Fig. 2 – Typical EPR spectra of unirradiated (left) and 10 kGy gamma-ray irradiated (middle) calcitic marble from Kozani (a), dolomitic marble Drama (b) and calcito-dolomitic marble from Aliveri (c) and Didimon (d). Arrows points towards the free radical EPR lines whose spectra as resulted by subtracting unirradiated spectra from irradiated ones are reproduced in the right column. The observed resonance lines are characterized by $g = 2.0048 \pm 0.008s$ (I) and respectively $g = 2.0002 \pm 0.0008$ (II) g-factors.

Table 2

Numerical values of IP, “I” to “II” center amplitude ratios and dolomite to calcite for each sample

Sample	IP		"I"/"II"		D/C	
Kerkira	172272	± 415	0.093	± 0.008	0.013	± 0.002
Nauplio	563	± 24	0		29.0	± 2.5
Drama	12551	± 112	0.137	± 0.0130	87.0	± 5.0
Kavalla	44550	± 211	0.060	± 0.007	0	
Thasos	3714	± 61	0		78.0	± 4.8
Didimon	9583	± 98	0		6.8	± 0.8
Trizina	1088042	± 1043	0.101	± 0.011	0	
Dionysos	622587	± 789	0.563	± 0.059	0	
Aliveri	13987	± 118	0.213	± 0.019	0.029	± 0.003
Gramatiko	8799	± 94	0.175	± 0.002	0.013	± 0.002
Kozani	26538	± 163	0.085	± 0.008	0	
Naxos	21883	± 148	0.080	± 0.008	0	

It is obvious that, in these conditions, it is impossible to determine the absolute concentration of manganese, but IP numerical value can be used as an extra variable to characterize each sample. As a result, we have calculated the numerical values of the IP parameter (Table 2) for the low magnetic field ($m_1 = 5/2$) resonance lines [9].

The absorption EPR lines, as resulted from a numerical integration of the first derivative of experimental lines, can be very helpful not only in identifying the number of components of the EPR spectrum, but also in establishing similarities between different samples. For this purpose, we have calculated the correlation coefficient between the numerical data that describe the resonance line of each sample. As all spectra have been recorded in the same experimental conditions (excepting the spectrometer gain, but this one does not influence the shape of resonance line) we have restrained this analysis only to the low magnetic field ($m_1 = 5/2$) Mn^{2+} resonance lines. The numerical values of the correlation coefficient r have been further used to derive a tree diagram that allowed establishing, in a quantitative manner, similarities and differences between all 12 samples (Fig. 3a). As it results from this tree diagram, all samples can be divided into two main clusters, which exactly reflect the presence of the main minerals (calcite and dolomite). At the same time, the calcite cluster can be divided into two sub-clusters, one of them corresponding to pure calcite samples (Kozani, Kavalla, Dionysos and Naxos), the other one consisting of the calcite samples with small amount of dolomite (Aliveri, Gramatiko, Kerkira, Nauplio and Didimon) or the calcite sample with high Mn^{2+} IP (Trizina).

In this way, the analysis alone of the shape of the EPR resonance lines can be used to quantify the similarities between various marble samples in provenance studies [19].

3.3. FREE RADICALS EPR SPECTRA

Another characteristic, commonly to all EPR spectra of irradiated samples, consists of the presence of narrow resonance lines characterized by gyromagnetic factors very close to 2, typical for different free radicals. As expected, the amplitudes of their resonance line inversely correlates with the amplitude of Mn^{2+} lines, this fact pleading for a low concentration of corresponding paramagnetic free radicals. We have noticed the presence of free radicals lines, only in some unirradiated sample, *i.e.* Nauplio, Drama, Thasos, Didimon, Aliveri and Gramatiko, while, as mentioned above, in all irradiated specimens we observed their presence. After gamma-ray irradiation, in the first case, the amplitude of these lines considerably increased (Table 3). To get more information about the free radicals EPR spectra, we have subtracted from the EPR spectra of each irradiated sample the corresponding EPR spectra of unirradiated specimens.

In this way, we have been able to isolate the EPR signals generated by gamma-ray irradiation. The most common signals, observed for nine EPR spectra *i.e.*, Aliveri, Dionysos, Drama, Gramatiko, Kavalla, Kerkira, Kozani, Naxos, and Trizina consist of two lines, one with g-factor $g = 2.0048 \pm 0.0008$ (low field, spectrum *I* on Fig. 2) and other slightly asymmetric characterized by $g = 2.0002 \pm 0.0008$ (high field, spectrum *II* on Fig. 2). The last one has also been observed in the EPR spectrum of both unirradiated and irradiated Didimon samples.

Table 3

Presence and behavior of “*I*” and “*II*” centers EPR signal before and after irradiation with 10kGy of ^{60}Co gamma rays

Place	Type	Unirradiated	Irradiated	Irradiated to unirradiated intensity ratio	Remarks
Kerkira	intraclastic limestone	-	+		Typical type “ <i>I</i> ” and type “ <i>II</i> ” signals
Nauplio	precipitation limestone	++	+++	3.5 ± 0.6	Complex signal
Drama	dolomitic marble	+	++	8.5 ± 0.8	Typical type “ <i>I</i> ” and type “ <i>II</i> ” signals
Kavalla	calcitic marble	-	++		Typical type “ <i>II</i> ” signal
Thasos	dolomitic marble	++	+++	3.5 ± 0.5	Complex signal, a superposition of different species including type “ <i>II</i> ”
Didimon	dolomitic marble	+++	++++	5.2 ± 1.0	Only type “ <i>II</i> ” signal
Trizina	sparry calcite	-	++		Type “ <i>II</i> ” signal masked by very large Mn^{2+} lines

Table 3 (continued)

Dionysos	crystalline limestone	-	+		Typical type "P" and type "II" signals
Aliveri	calcitic marble	+	++	30.8 ± 3.0	idem
Gramatiko	calcitic marble	+	++	27.4 ± 3.0	idem
Kozani	calcitic marble	-	+++		idem
Naxos	calcitic marble	-	++		idem

- absent; + weak; ++ intense; +++; ++++ very intense

Tree Diagram for 12 Greek Marbles and Limestones

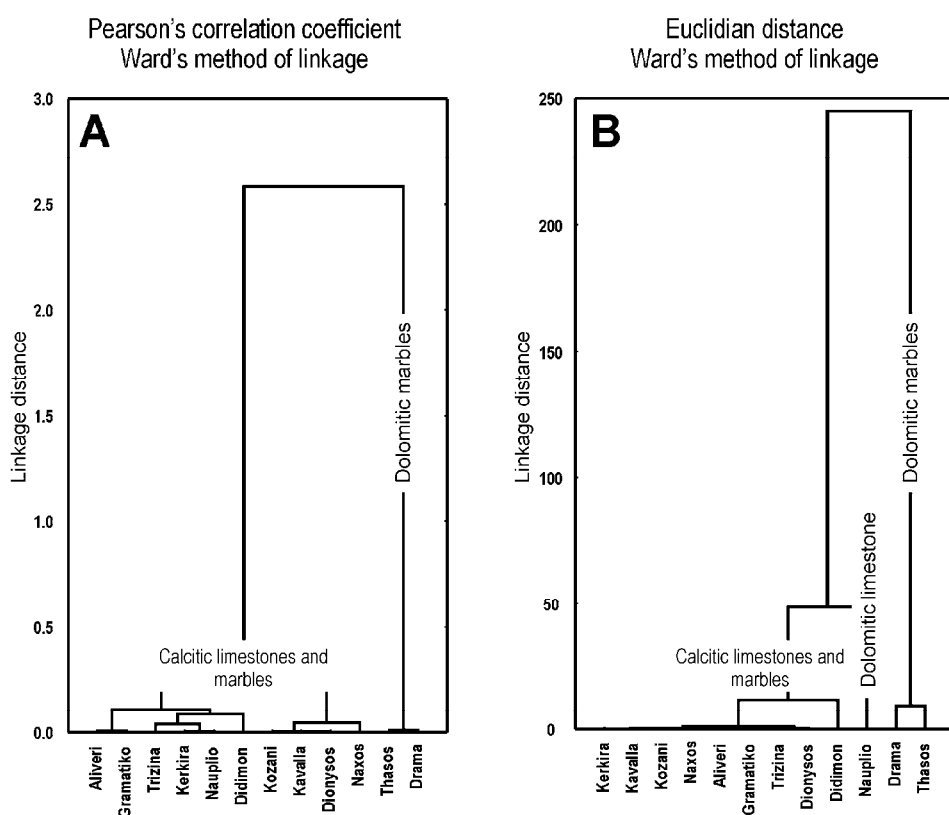


Fig. 3 – Tree diagrams of the investigated samples based on the correlation between the low field Mn²⁺ EPR lines (a) as well as the difference between some X-ray and EPR free radicals parameters (b). Despite some discrepancies, both diagrams reflect predominantly the mineralogical composition of considered specimens.

The remaining two samples, Nauplio and Thsaos have shown more complex free-radicals EPR spectra, consisting of an unresolved superposition of several resonance lines whose amplitude sensibly increase after gamma-ray irradiation too.

By taking into account the good time stability, the fact that the intensity of corresponding resonance line increases with absorbed dose as well the numerical values of g-factors, we could attribute these lines to sulfide radical (low field line *I*; “*A*” centers in ref. [10, 13, 20], “*B*” centers in ref. [22] and to higher field line *II*; “*B*” centers in ref. [7, 10, 20] as well as “*C*” centers in ref. [13]. This conclusion is sustained by the method of preparation utilized by us that excluded the use of any drilling operation and consequently the generation of so called “drilling centers” as described in [11, 16, 20]. The absence of the fine structure of these centers, previously reported, is most probably due to both modulation width and magnetic field finite sampling rate.

It must be pointed out that the Nauplio sample represents a specimen of precipitation limestone characterized by a low value of dolomite to calcite ratio while Thasos sample is a true dolomitic marble. These peculiarities could explain the fact that the free radicals EPR spectrum for Nauplio and Thasos specimens is quite different from the other investigated sample.

Also, we have calculated the amplitude ratio of unirradiated type “*I*” to type “*II*” resonance lines in the case of the nine samples that presented both kinds of EPR lines. We consider that this ratio, together with IP and dolomite to calcite ratio could be useful for the provenance studies. (Table 2).

The behavior of the type “*I*” and type “*II*” resonance lines before and after irradiation with 10kGy of ^{60}Co gamma rays are illustrated in Table 3. When present in unirradiated samples, both these signals increased after irradiation with the same ratio, but the fact that only some samples presented these signals before irradiation, makes the irradiated to unirradiated sample ratio unsuitable for provenance studies.

All the data reproduced in Table 2 have been used to draw an additional tree diagram characterizing the same samples (Fig. 3b). As we have used different parameter, the resulting tree diagram slightly changed, but the main division into two clusters, one dolomitic and one containing the other samples, was preserved.

In this way, the quantitative information obtained from both X-ray diffraction and EPR spectra could be successfully used in assessing similarities and differences between samples, which in their turn could be very profitable in provenance studies or geochronology.

4. CONCLUDING REMARKS

X-ray diffraction, as well as EPR data concerning 12 specimens of marble and limestone collected from well-known Greek quarries, allowed us to obtain numerical values of some numerical parameters, such as dolomite to calcite ratio, EPR intensity parameter, EPR free radicals signal type “*I*” to signal type “*II*” ratio. All these parameters are intrinsically related to the mineralogical composition of the sample, to the content of Mn^{2+} ions as well as to the presence of paramagnetic

free radicals. To them we have added digital functions that describe the Mn^{2+} resonance lines. In this way a numerical data base resulted to be used in provenance studies or geochronology.

Based on these parameters, we have generated two tree diagrams, one of them based on the similarities between the shapes of the Mn^{2+} low field EPR resonance lines, the other one obtained by using the numerical values of the above mentioned parameters. Despite some minor differences, both diagrams reflect the mineralogical composition of samples that most likely represents one of the main criteria in discriminating this kind of samples.

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