

EPR STUDY ON Mn^{2+} HOMOGENEITY IN TRAVERTINE DEPOSITS FROM BORSEC QUARRY

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Abstract. The EPR spectra of 25 samples of travertine collected from the Borsec travertine quarry covering a 400 m span were investigated in order to check for travertine homogeneity. All spectra showed only the presence of Mn^{2+} ions hyperfine sextet, whose last, the sixths line was used to check the travertine homogeneity with respect to manganese content. Both variance and paired correlation coefficients has showed that within experimental errors, the manganese content, as reflected by EPR line shape was uniform, proving the possibility to use Mn^{2+} EPR spectrum as a proxi for provenance study.

Key words: EPR spectroscopy, travertine, marble, Mn^{2+} , provenance.

1. INTRODUCTION

Travertine is a terrestrial sedimentary rock formed in the process of rapid precipitation of carbonate minerals, often in ground and surface geothermally heated hot springs or in a limestone cave. Widely used as decorative material due to its relative softness as building material, its exploitation started early in the ancient history (among other structures, the Colosseum was constructed mostly of travertine) and is continuing nowadays in growing quantities.

Investigations of physical and chemical condition leading to formation of travertine experienced a noticeable quantitative and qualitative development during the last few years [1, 4]. Apart of the interest on basic knowledge of the formation mechanisms of travertine, these investigations have become more popular because of the connections with other typically fields of applied research: archaeometry, provenance determination of artifacts, paleoclimatology, and pollution studies etc.

Even both petrography and compositional analysis had given satisfactory results, sometimes used together as complementary investigation techniques, Electron Paramagnetic Resonance (EPR) spectroscopy proved to be a reliable method in limestone, travertine and marble characterization [1–5]. EPR measurements are cheaper, less time consuming, the powder samples used are not destroyed and can also be analyzed by other techniques [6, 7].

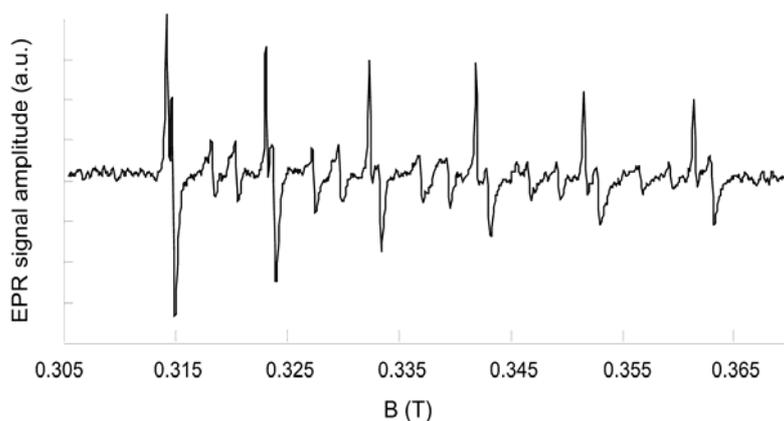


Fig. 1 – A typical X band, room temperature, EPR spectrum of Mn^{2+} ions in marble, displaying the typical hyperfine sextet, each component splitted into two fine structure lines (Dului *et al.* unpublished results).

The use of EPR spectroscopy is based upon the existence of some paramagnetic centers in the sample, the most ubiquitous being Mn^{2+} and Fe^{3+} ions which generally substitute Ca^{2+} ions in calcium carbonate lattice. The presence of both Mn^{2+} and Fe^{3+} ions, due to their distinct paramagnetic behavior, make the mineral suitable to EPR investigation. The characteristic Mn^{2+} fine and hyperfine structure can be used to study the microscopic interaction of the host lattice with the impurity ions. Spectral investigation on carbonate minerals is useful in solving sedimentary petrology problem of Mn^{2+} concentrations and its distribution within the corresponding mineral structure during crystallization. At the same time, the characteristic EPR spectra of Mn^{2+} ions in calcite, consisting of six hyperfine structure line, each of them split into two fine structure doublet (Fig. 1), are characteristic of the physical–chemical conditions at the time of rock formation, and hence, could be considered as a fingerprint of considered deposits.

The potential of EPR spectroscopy in determining the provenance of limestone, travertine, and marble from historic artifacts was successfully used in the past years, provided that some statistical methods of data processing such as correlation analysis or principal component analysis were used in tandem [8–11].

A provenance study gives confident results provided that the possible source of building material proved to be enough uniform of if its variability is well documented. Among the other proxies suitable to estimate rock formation homogeneity, Mn^{2+} EPR spectrum could be of interest, by taking into account the sensitivity of resonance line to manganese content. Although Mn^{2+} EPR spectra could not be used to determine manganese absolute concentration, the variability of line widths or line shape could be very well correlated with manganese content.

At its turn, the variability of line shape could be investigated by using univariate statistics analysis procedure such as one-way ANOVA [12], technique designed to test, at which extent, more samples taken from the same formation, are similar or not. If sample sizes are equal, there is no need for samples to be normally distributed and have similar variances. In our case, samples were represented by the numeric data representing the EPR spectrum of the sixths Mn^{2+} ions line in 20 specimens of travertine collected from Small Borsec Travertine Quarry (Fig. 2).

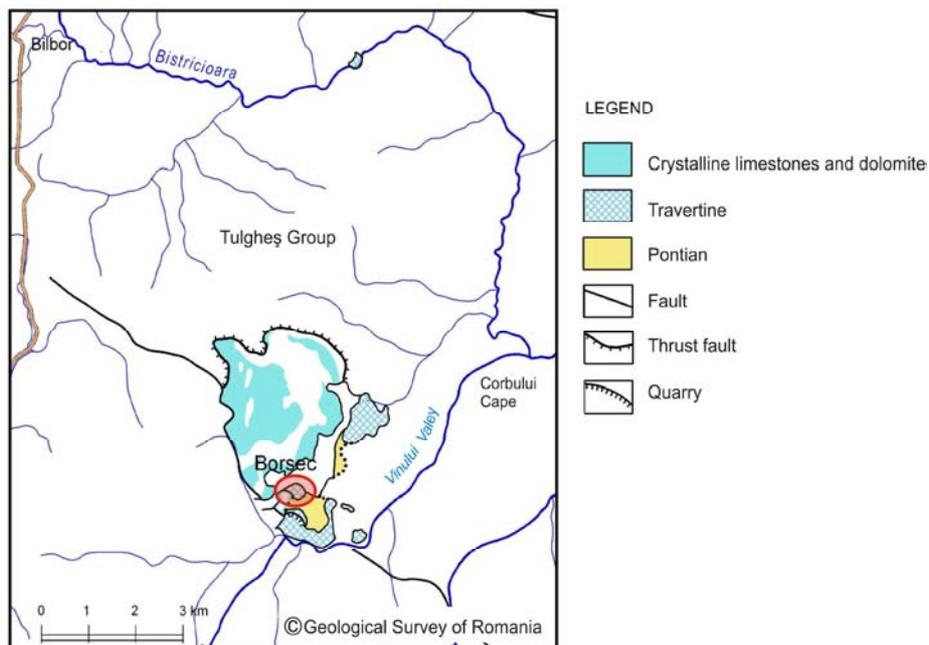


Fig. 2 – Geographical location of Borsec travertine quarry. A circle marks collecting zone.

Hence, the present work has been undertaken with the idea of collecting more information regarding the uniformity of Mn^{2+} EPR spectra of Romanian travertine. This is seen as a first step of establishing a data base for EPR spectrum of travertine and marble from different quarries in Romania.

2. MATERIALS AND METHODS

2.1. TRAVERTINE SAMPLES

The travertine used in this study was sampled from the Romanian travertine quarry in Borsec. Surrounded by four mountain chains, two of orogenetic origin: Bistrita and Ceahlău Mountain and two of volcanic origin: Călimani and Gurghiu Mountains, all neighbor to Borsec areas have a multitude of mineral water springs, some of them containing calcium and magnesium carbonates. The area is rich in deposits of crystalline limestone, dolomite and travertine, the last one being industrially exploited through a quarry. The geological map of the area is presented in Fig. 2.

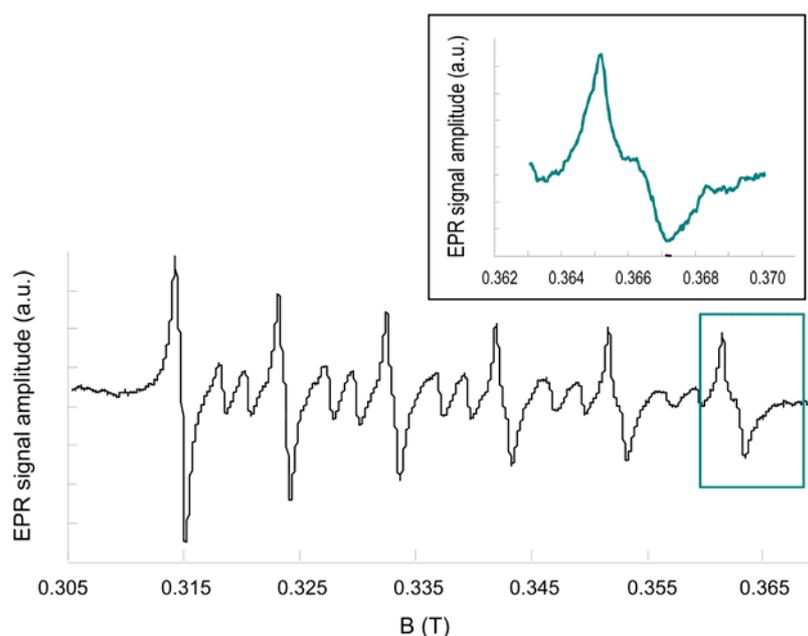


Fig. 3 – The experimental X band, room temperature, EPR spectrum of Mn^{2+} ions in Borsec travertine. The inset illustrate the fine structure of the sixth resonance line further used in this study to verify at which extent the travertine is homogenous with respect to manganese content.

The samples were collected from the entire working front of the travertine quarry, measuring about 400 m, at uniform distances (40 samples \times 10 m distance between samples). After collection, the samples were manually ground by using a bronze hammer on a bronze plate in order to avoid any iron contamination. Then, a second stage grinding in an agate mortar was performed to reach the highest possible homogeneity.

2.2. EPR MEASUREMENTS

All measurements were performed at room temperature by using an X-band JEOL JES-ME spectrometer provided with a PCI-9221 (ADLink Corporation, Taiwan, ROC) multifunctional acquisition board. A proprietary soft written in C# was used to control the magnetic field sweep as well as to acquire the EPR spectra. In order to maximize the signal to noise ratio, we have used the multiple acquisition technique, so that each point of the experimentally recorded spectrum consisted of an average of 200 measurements. Further, recorded spectra were stored as .csv format files, to be easily imported in MS ExcelTM or in other media for advance digital processing and graphic plotting

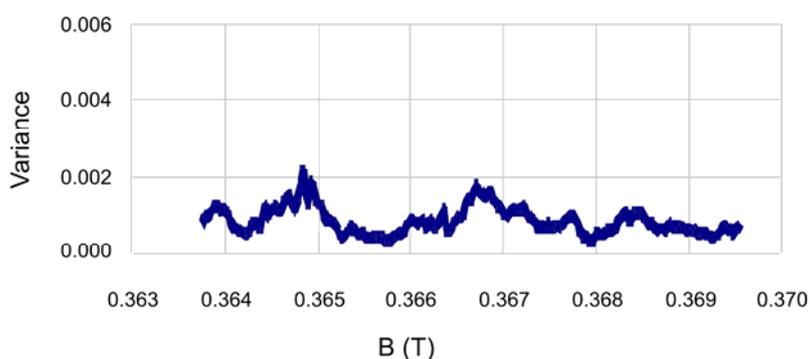


Fig. 4 – The magnetic field dependence of the variance of the sixth EPR resonance line of Mn²⁺ ions in the travertine collected from Borsec travertine quarry.

A typical spectrum of Mn²⁺ ions in travertine as recorded in the above mentioned conditions is reproduced in Fig. 3. Regarding all rerecorded spectra it is worth mentioning the total absence of any broad line specific to Fe³⁺ ions.

3. RESULTS AND DISCUSSION

Literature data [2, 3, 7, 8] had emphasized two methods of determining the specificity of Mn²⁺ like impurity in natural carbonates: calculating the fine structure splitting of the first resonance line or studying the shape of the sixth absorption line as an expression of Mn²⁺ concentration.

In our case, as the Mn²⁺ was enough high so that the fine structure of the first resonance line to be occulted, we have analyzed the sixth line whose fine structure was well represented on the all spectra (Fig. 3, inset).

At a carefully examination, we have remarked that when normalizes do their mass, the EPR spectra of all samples were almost indistinguishable. For this reason, we have restrained our analysis to only 20 samples collected at equal intervals of 20 m.

Further, to evidence any differences between samples, we have computed the variance corresponding to the sixth Mn^{2+} resonance line, as mentioned above, whose graphic dependence on the magnetic field is presented in Fig. 4. As it can be seen from this figure, the variance for the entire set of data presents an almost constant low value, meaning that the chosen segment of spectra is almost identical for all samples.

A one-way ANOVA test performed by means of PAST software [13] has showed that all considered spectra are coincident with a probability of 90% ($p < 0.1$).

To verify at which extent this similarity has a random character, we have calculated the correlation matrix for all pairs of samples, by taking into account the sixth resonance line shape like similitude criterion. The numerical values of the parametric correlation coefficient r as well as of the non-parametric Spearman's ρ correlation rank [12, 13] varied randomly between 0.9722 and 0.9965, without any dependency on the sample position with respect to quarry.

In these conditions we came to the conclusion that, with respect to Mn^{2+} ions content, the Boresec travertine quarry, within the investigated area, appears to be homogenous.

It must be pointed out that the purpose of this study was restrained only to investigate at which extent the data obtained by means of EPR spectroscopy could be used in further provenance study. As the travertine Boresec quarry showed to be enough homogenous, this kind of study would be extended in a next future to other limestone and marbles quarries in order to get a more confident answer regarding the ability of the EPR spectroscopy to be used in provenance study, as well as, to create an extensive database.

4. CONCLUDING REMARKS

By using both one-way Analyse of Variance (ANOVA) and Correlation Analysis of the line shape of the sixth resonance line of Mn^{2+} EPR spectrum in 20 samples of travertine covering a 400 m span of Boresec travertine quarry, we evidenced an almost identity of investigated samples with respect to manganese content. If this peculiarity could be also evidenced for other quarries of limestone or marble, then the EPR spectrum of Mn^{2+} ions in natural carbonates could be considered as an appropriate proxy for provenance studies.

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