COMPARATIVE STUDY ON ESR SPECTRA OF CARBONATES*

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This paper is a comparative study on Electron Spin Resonance (ESR) spectra of carbonates such as mollusk shells collected from the Black Sea Coast (Romania), Mediterranean Coast (Cyprus), Tyrrhenian Sea Coast (Italy) and Atlantic Coast (Mauritania). Additionally we have been analyzed the ESR spectra of limestone, marbles, stalactites and corals. Some of the carbonate samples revealed the same characteristic Mn²⁺ spectrum with an additional free radical peak in the centre of sextet, at a g value in the range of 2.0006–2.0062. The differences into the ESR spectra of carbonates have been observed depending on their species, geographical origin, harvesting year, geologically age and dose. The gamma-irradiated samples exhibited a complex spectrum consisting of $\text{CO}_3^2-$, $\text{CO}_3^{3-}$, $\text{CO}_3^{4-}$, $\text{SO}_4^{2-}$ and $\text{SO}_5^{2-}$ species.

1. INTRODUCTION

Electron Spin Resonance (ESR) represent a specialized spectroscopic method of investigation restricted only to atomic and molecular paramagnetic centers (PC) that contains at least one unpaired electron. Beside different kind of PC, transition elements ions or radiation induced free radicals are relatively frequently found in environmental samples. Concerning the last ones, it is worth to mention that their concentration monotonously increases with absorbed dose, and, if they are trapped in insulators, their lifetime could reach thousands of years.

Among an astonishing variety of compounds able to retain for a long time radiation free radicals, natural carbonates play a significant role mainly due to their occurrence in multitude varieties, beginning with natural limestone and marble and finishing with invertebrate exo-skeleton. For this reason and for a relative simplicity of their crystalline lattices, natural carbonates were intensively investigated by means of ESR.

Some ESR spectra of unirradiated carbonates consists of six, double lines plus ten single ones between the doublets, the other samples show the same


characteristic Mn$^{2+}$ spectrum with an additional free radical peak in the centre of sextet, whereas a lot of specimens exhibit a single line. Some differences into the ESR spectra obtained before and after irradiation processing of CaCO$_3$ containing hard tissues have been observed depending on their species, geographical origin, harvesting year, geologically age, dose, etc. [4, 23, 24].

Elementary defects induced by ionizing radiation: an “electron center” CO$_3^{3-}$ with 25 electrons and a “hole center”, CO$_3^-$, with 23 electrons are stable only at low temperatures. Another “electron center” more stable than CO$_3^{3-}$ and also formed by radiation is the CO$_2^-$ molecular ion. For natural calcites, the “electron center”, SO$_2^-$ ($g = 2.0057$) and the “hole center”, SO$_3^-$( $g = 2.0036$) from impurities result in additional signals [8].

Many studies show that the ESR amplitude of free radicals enhances exponentially with the additive dose:

$$ I(D) = I_0 + I_S \left[ 1 - \exp\left( -\frac{D}{D_0} \right) \right] $$  \hspace{1cm} (1)

where $I_0$ and $I_S$ are the intensities corresponding to the unirradiated spectrum and to the saturation level, $D$ is the artificial radiation dose and $D_0$ is the dose corresponding to the $I_S(1 - e^{-1})$ value (0.63 of the maximum intensity), however some experimental indicates a linearly increase of ESR signal intensity with the added dose [5, 9, 14].

A wide range of carbonates including bivalve and gastropod shells collected from the Black Sea Coast (Romania), Tyrrhenian Sea Coast (Italy), Mediterranean Coast (Cyprus) and Atlantic Coast (Mauritania), corals, limestone, stalactites and marbles were subjected to an ESR study in order to analyze their spectral feature.

### 2. EXPERIMENTAL

The ESR spectra of carbonate samples were performed at ambient conditions by using an X-band JEOL JES MX 3X spectrometer provided with a TE$_{011}$ cylindrical resonant cavity and 100 kHz modulation frequency. The samples in powder form were placed separately into quartz tubes with a 3 mm inner tube diameter. The position of tube in the cavity was not changed during the whole experiment in order to ensure the uniform and reproducible measurements of the sample. The optimal conditions of ESR measurement were: microwave frequency 9.50 GHz, modulation amplitude 1–2 G, microwave power 4 mW, sweep time 5 min and response time 0.3 s. The $g$ factors of the observed
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Signals have been determined by using a 2.2-diphenyl-1-picryl-hydrazil (DPPH) as well as CaO:Mn2+.

3. ESR STUDY OF MOLLUSK SHELLS

Mollusk shells are composed mainly of 95–99% crystalline form of calcium carbonate (CaCO3), mostly aragonite (orthorhombic, metastable) and/or calcite (trigonal/ rhombohedral, stable) and an organic part of the protein called “conchiolin”. The bivalve and gastropod shells are usually formed of three distinct layers: the outermost thin layer (periostracum), the middle layer (ostracum or prismatic layer) is the thickest and the innermost layer (hypostacum, nacreous layer or mother-of-pearl) consisting of stacks of aragonite and/or amorphous CaCO3 tablets, approximately 0.5–1 μm thick, separated from their neighbors by their organic membranes [21]. The presence of ESR signals in periostracum and nacreous layers at g ≈ 2.0 and g ≈ 4.1 was attributed to Fe3+ ions [16]. Recent researches show the osteogenic properties of nacre, as a biomaterial for bone implants.

Since the levels of carbon dioxide in the sea have increased, making the water more acidic, the sea snails and the other marine organisms have found it harder to secrete CaCO3 in order to build their shells. As the pH of sea water decreases, it is not clear how it chemistry will change or how ecosystems will adapt. The effect of the petroleum pollution on the lipid composition of some organisms is well studied. In gastropods the Diesel fuel treatment caused insignificant effects in the fatty acid composition of lipids since these changes appear to be stronger in the evolutionary less advanced organisms [18]. It is generally assumed that the external coloration, pigmentation pattern and composition of fossil shells are determined by genetic mechanism and by the physical/chemical environment in which the mollusk lived [28]. The pigmentation pattern is directly correlated to the mechanisms that control the growth of the shell in order to achieve the optimal shape [1]. The analysis of nacre texture provides some information about the nature of shell growth. Fiber textures appear only in gastropods and cephalopods although the crystallographic features of their nacre tablets are different [3]. The growth of shell crystals is initiated from a mineralizing solution by the extra-cellular matrix (ECM). One of these theory reveals that the organic matrix (OM) may control crystal nucleation, polymorph selection and crystal orientation [12] and an alternative assumption shows that a class of granulocytic hemocytes would be directly involved in shell crystal production [15, 20].

Acidic proteins control mineral formation and crystal growth [7]. The major role of phosphoproteins in the regulation of calcium carbonate biomineralization has been also studied [2]. The ferritin, the principal protein for iron
storage is also involved in shell formation [29]. The most acidic of all the mollusk shell matrix proteins, Aspein is responsible for directed formation of calcite in the shell [27]. Another molecule involved in the calcification process, mucoperlin, is a protein of the nacreous layer, with some mucin-like characteristics, able to interact with Ca\(^{2+}\) and/or to interfere with CaCO\(_3\) precipitation [13]. Its primary role may be to finish the crystal growth and to combine crystals. Lustrin isolated from the nacreous layer with a highly modular structures with Gly-, Ser-, Cys- and Pro-rich domains protects the OM against degradations and ensures elasticity to the shell [22].

The analysis of chemical constituents of the shell (SiO\(_2\), Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), MgO, CaO, SO\(_3\), Cl, Na, K, Sr, etc.) indicates that the content of CaO for the shells is the same as for the limestone. However, the sea shells contain a large amount of alkali metals and chlorine. The desulphurization characteristics of the sea shells have been studied by using a bubbling fluidized bed coal combustor [17]. In the CaCO\(_3\) crystal structure, the divalent trace elements (alkaline earth and transition elements) occupy regularly a lattice site and the monovalent trace elements (alkali metals) are non-selectively distributed into the shell as inclusions of carbonates and/or amorphous compounds [19].

Unirradiated shells from a large variety of bivalve and gastropod species were subjected to ESR measurements in order to emphasize the great differences between their spectra (Fig. 1).

The ESR spectra of *Mytilus galloprovincialis*, *Moerella tenuis* and *Chamelea gallina* bivalve shells consist mainly of a group of six lines of Mn\(^{2+}\) (Fig. 1a, b, d). An additional free radical peak identified as the radiation-induced defects (CO\(_2^−\), CO\(_3^{−}\), CO\(_3^{2−}\) and SO\(_2^−\)) stabilized by impurities at a \(g = 2.0059\) was observed at the center of this group for *Mytilus galloprovincialis* specie. For the other samples, no characteristic manganese signals or weak intensity of Mn\(^{2+}\) hf lines were observed while the central signal presents a lot of possible forms: no line (*Strombus* sp. – Fig. 1e), a single one at a \(g = 2.0062\) (*Cardium* sp. – Fig. 1c), doublets at \(g_1 = 2.0026\) and \(g_2 = 2.0053\) (*Conus* sp. – Fig. 1f) depending of the shell varieties, but also may be from their compositions. A very intense signal characterized by gyromagnetic factors: \(g_1 = 2.0006\) and \(g_2 = 2.0053\) was noticed in the case of *Murex* sp.

The \(g\) spectroscopic splitting factor of unknown signal was determined using the standard signal with a known \(g_0\) factor:

\[
g = g_0 \left(1 - \frac{\Delta H}{H_0}\right) \tag{2}\]

The magnetic field separation \(\Delta H\) between the third and fourth line and the resonance field \(H_0\) were considered 8.69 mT and 339 mT respectively at the X-band frequency.
Fig. 2 – ESR spectra of unirradiated samples: a) Mytilus galloprovincialis, b) Moerella tenuis, c) Cardium sp. d) Chamelea gallina, e) Strombus sp., f) Conus sp., g) Murex sp.

4. ESR STUDY OF CORALS

Coral reefs have the potential to provide information about coral growth and climate over the past several centuries. According to the von Bertalanffy function we can write:

\[ L_t = L_{\infty} \left(1 - e^{-Kt}\right) \]  

\( L_t \) is individual length at age \( t \), \( L_{\infty} \) is asymptotic length (maximum expected length, \( K \) is a growth constant, and \( t \) is individual age [6].
Annual skeletal density bands and the growth rate of corals (in the range 4–20 mm/year) are correlated with the light level and water temperature.

The high precision of the $^{230}$Th/$^{234}$U method for dating a closed system (there are no other changes to isotopic ratios other than that caused by radioactive decay) such as young corals is well established. The activity ratio $^{234}$U/$^{238}$U and the concentration of uranium (2–4 ppm) in corals are very close to the value typical of seawater in contrast to shells which contain a much reduced level of uranium in the range 0.001–0.6 ppm [26].

The determination of Sr/Ca, U/Ca and Mg/Ca ratios in fossils corals can also provide information on past sea surface temperatures [10]. Stable oxygen isotope ratios $^{18}$O provide a record of sea surface temperature and surface salinity [11].

The variation in $^{18}$O of coral skeletal reflects variation in the growth rate while carbon isotope ratios $^{13}$C showed significantly inverse correlation with linear growth rates. In shallow faster-growing corals, oxygen and carbon isotopic ratios reveal out-of-phase annual fluctuations, whereas in deep slower growing corals oxygen and carbon isotope fluctuations are in phase [25].

The impurities-associated signals such as $\text{SO}_2^-$ and $\text{SO}_3^-$ are useful for assessing the historical environmental change and the ESR signal of $g = 2.0007$ is the most suitable one for dating corals.

Since the live coral skeletons are homogeneous in uranium distribution while dead skeletons indicate heterogeneities, we performed ESR spectra on different samples of the same *Millepora* coral specie and an ESR spectrum of *Poecillopora verrucosa* coral skeleton (Fig. 3). The ESR intensity of Mn$^{2+}$ hf lines observed in the core of *Millepora* coral is more intense when compared to that in external skeleton (Fig. 4a, b).

Only a very weak singlet line is observed in ESR spectrum of *Poecillopora verrucosa* coral skeleton, while no characteristic manganese signals were identified (Fig. 4c).

![Fig. 4 – ESR spectra of: a) external skeleton of *Millepora* coral, b) a core of *Millepora* coral skeleton, c) *Poecillopora verrucosa* coral skeleton.](image)

5. ESR STUDY OF LIMESTONE, MARBLES AND STALACTITES

Limestone is the prothlith for marble. It is a sedimentary deposit of either calcite or aragonite – $\text{CaCO}_3$ (44% CO$_2$, and 56% CaO) or dolomite –
CaMg(CO₃)₂ (47.9% CO₂, 30.4% CaO and 21.7% MgO) or a mixture of both. The pure white marbles have none or only trace amounts of accessory minerals such as: iron oxides and sulphides, graphite, chlorite, etc.

The Mn²⁺ sextet is clearly visible in ESR spectra of limestone and marble. An additional line between the third and fourth Mn²⁺ lines at a $g = 2.0060$ is observed, in the case of a limestone sample from Kouriou Temple – Cyprus (Fig. 5a, and Fig. 6a, b).

The ESR spectrum of marble from Ruschița – Romania exhibits the well known Mn²⁺ peaks. It consists of six double lines plus 10 single ones between the doublets. The absence of free radicals in the center of Mn²⁺ sextet indicates the purity of marble (Fig. 7).

Stalactite is a type of speleothems form from the deposition of calcium carbonate and other minerals, which is precipitated from mineralized water solutions:

$$\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \Leftrightarrow \text{Ca(HCO}_3\text{)}_2$$

(4)

The stalactites contain brown rings due to clay minerals. The red and orange coloration of speleothems is due to the iron oxide, the blue hue derives from manganese and the dark brown is related to the limonite that is dissolved from the overlying rocks. The relatively transparent pure stalactite illustrated in Fig. 5.b. reveals a high growth rate inside the cave. The amplitude of Mn²⁺ lines
is much stronger in a limestone than in a stalactite maybe due to repulsion of manganese ions in the recrystallization of CaCO₃ during the stalactite growth (Fig. 8).

Fig. 8 – ESR spectrum of a stalactite sample (Borsec – Romania).

6. CONCLUSIONS

This comparative study on ESR spectra of limestone, marble, stalactites, coral skeletons and mollusk shells with different geographical origins carried-out the typical spectrum of carbonates. Some spectra of unirradiated limestone, bivalve and gastropod shells revealed additional free radical peaks between the third and fourth hf lines of Mn²⁺. No significant variation in linewidth of carbonates spectra was observed, but a remarkable variation in ESR amplitudes has been observed. The most important paramagnetic species existent in the ESR spectra of carbonates are: CO₂⁻, CO₃⁻, CO₃⁻, SO₂⁻ and SO₃⁻ radicals in the range 2.0010–2.0062.

Strong similarities in ESR spectra of limestone and marbles were observed, while the ESR spectra of mollusk shells and coral skeletons showed great differences due their complex structures. The distinctive features of stalactites ESR spectra require a more detailed study.

REFERENCES


Fig. 1 – Bivalve and gastropod shells collected from:
Tyrrenian Sea Coast, Italy: d) *Chamelea gallina*,
Mediterranean Sea Coast, Cyprus: e) *Strombus* sp.
Atlantic Coast, Mauritania: f) *Conus* sp., e) *Murex* sp.
Fig. 3 – Coral skeletons – Philippines:
a) Millepora sp., b) Poecilopora verrucosa.
Fig. 5 – a) Limestone and marbles found at Kouriou Temple (Cyprus), b) A white stalactite collected from Borsec (Romania).