Electron Paramagnetic Resonance Study of Defects in γ-irradiated Marine Mussel *(Mytilus galloprovincialis)* and Scallop *(Pecten jacobaeus)* Shells

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EPR studies have been performed on some gamma-irradiated marine mussels *(Mytilus galloprovincialis)* and scallops *(Pecten jacobaeus)* from the families of *Mytilidae* and *Pectinidae*, respectively. Before γ-irradiation, the EPR lines of *Mytilus galloprovincialis* indicated the existence of Mn^{2+} ions, which were not observed in the powders of scallop shells. γ-irradiation induced defects in powders of *Mytilus galloprovincialis* shells, were attributed to orthorhombic CO_3^-, axial CO_3^{3-}, orthorhombic CO_2^-, freely rotating CO_2^-, freely rotating SO_2^-, axial SO_3^-, isotropic PO_4^{2-} and organic free radicals. γ-irradiation induced defects in powders of *Pecten jacobaeus* shells were attributed to orthorhombic CO_3^-, axial CO_3^{3-}, orthorhombic CO_2^-, freely rotating CO_2^-, freely rotating SO_2^-, and axial SO_3^- free radicals. The EPR parameters of the free radicals were compared with literature data on similar defects.

Key words: EPR; Free Radicals; γ-irradiation; Mussel; Scallop.

1. Introduction

Carbonates are common minerals in nature. They grow in an aqueous environment, with various impurities. Calcium carbonate is widespread on the earth's surface as a main constituent of mollusk shells, coral, limestone, speleothem [1].

Naturally occurring marine cabonates consist mainly of two minerals (calcite and aragonite or vaterite). Aragonite shells and aragonitic mineral deposits undergo slow metamorphism into calcite [2, 3]. Aragonite is a *polymorph* of $CaCO_3$, different from calcite and vaterite. It is less stable than calcite and is readily converted into calcite at normal pressure and temperature. Many organisms, such as mollusks and corals, build their skeletons of aragonite. The structure of aragonite is orthorhombic, having a higher density and hardness than calcite. Marine $CaCO_3$ shells are mostly composed of microcrystalline calcite or aragonite, and in lesser amounts of $Ca_3(PO_4)_2$, $MgCO_3$, $CaSO_4$, SiO_2, $(Al, Fe)_2O_3$, and organic parts, such as mucopolysaccharides and a protein, much of which is called conchiolin. In addition to these major and minor constituents, trace amounts of Mn, Cu, Ti, Pb, Co, Bi, Cd, Mo, Sn, Ag, Au, Sr, As and Rb have also been found [4].

The crystal structure of calcite and aragonite has extensively been studied [5 – 7], and radiation-induced paramagnetic defects such as CO_2^-, CO_3^-, CO_3^{3-}, SO_2^-, SO_3^-, O_3^-, O^- were identified in these minerals [8 – 14]. Some of these radicals, such as CO_2^-, CO_3^{3-}, SO_3^-, have long lifetimes, which permit their use in dosimetry and archaeological dating [12, 15 – 19].

The aim of this study is to determine radiation-induced paramagnetic defects and their *g* and *A* values in some naturally occurring marine materials (*Mytilus galloprovincialis* and *Pecten jacobaeus*) by investigating their unirradiated and gamma irradiated states.

2. Experimental

In this work we examined two different naturally occurring marine shells. The samples of black marine mussels (*Mytilus galloprovincialis)* and scallop (*Pecten jacobaeus*), from the families of *Mytilidae* and *Pectinidae,* respectively, were collected from the Black Sea coasts near Samsun, a province of Turkey. These shells were washed, dried and finely powdered, using

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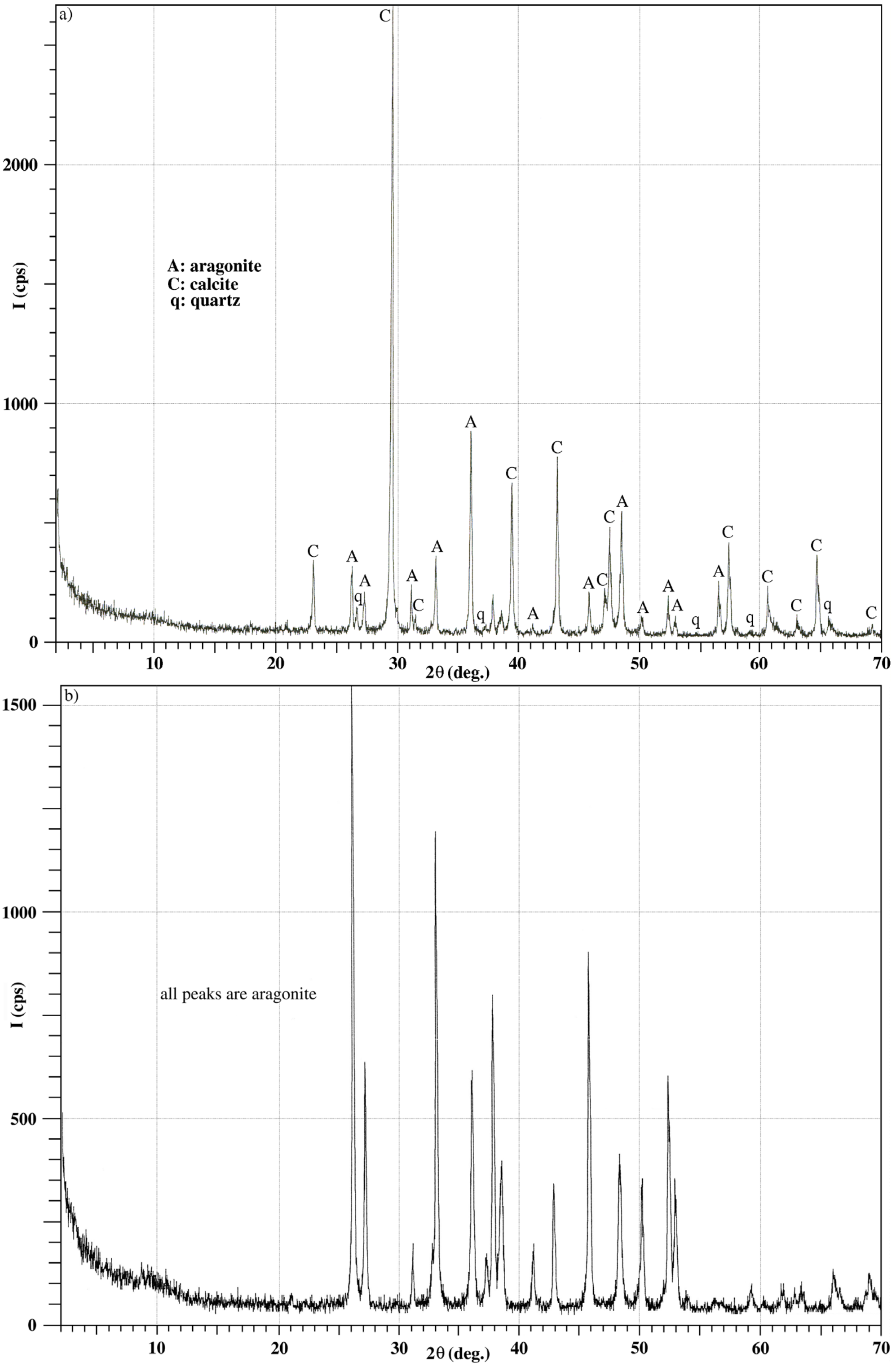

Fig. 1. XRD spectrograms of a) mussel *(Mytilus galloprovincialis)* and b) scallop *(Pecten jacobaeus)* shells.

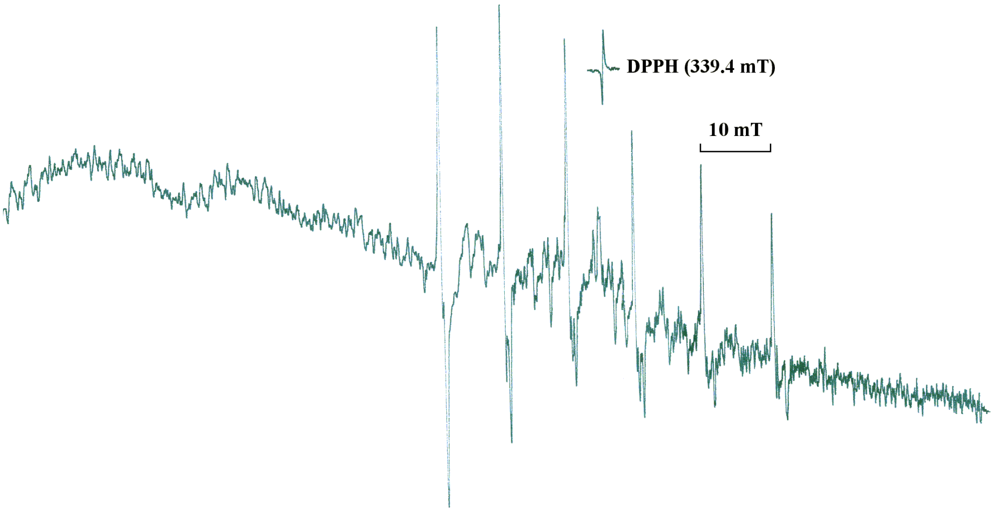

Fig. 2. EPR spectrum of none-irradiated powders of marine mussel shell *(Mytilus galloprovincialis)* at ambient temperature.

an agate mortar. The powders were irradiated with a ^{60}Co γ-ray source at ambient temperature to a dosage of about 20 kGy. The EPR spectra were recorded with a Varian E-line 109C model X-band EPR spectrometer, using about 2 mW microwave power, and 100 kHz magnetic field modulation. The g factors were found by comparison with the g value 2.0036 of a diphenylpicrylhydrazyl sample. For the identifications of the contents of minerals their X-ray powder diffraction spectrograms were obtained in Tubitak Research Institute at Gebze-Istanbul with a Schimadzu XRD-6000 instrument with a Cu^{2+} X-ray tube operating at $\lambda = 1.5405$ Å. All measurements were carried out at ambient temperature.

3. Results and Discussion

The X-ray powder diffraction results of marine mussel (*Mytilus galloprovincialis)* and scallop (*Pecten jacobaeus*) shells, shown in Fig. 1, indicate that mussel and scallop shells consist mainly of $CaCO_3$ (calcite and aragonite) and less SiO_2.

Before γ-irradiation, powders of *Mytilus galloprovincialis* shells indicated the existence of the EPR lines of Mn^{2+} ($I = 5/2$, 100% natural abundance), as shown in Figure 2. The EPR parameters of Mn^{2+} are $g_{\text{iso}} = 2.0055$, $A_{\text{av}} = 9.5$ mT. The spectrum consists of two sets of $\Delta M_I = 0$ allowed hyperfine lines ($M_S = -\frac{1}{2} \leftrightarrow +\frac{1}{2}$), corresponding to the different symmetries around the Mn^{2+} ions. Between the allowed transations, forbidden doublets ($\Delta M_I \neq 0$) [20] are also seen in Figure 2. Similar observations have been reported for most of $CaCO_3$ materials [21, 22]. The EPR signal of Mn^{2+} has not been observed from unirradiated *Pecten jacobaeus* shells. The reason for the non-observation of the EPR spectrum of *Pecten jacobaeus*

Table 1. The EPR parameters of defects induced by γ-irradiation of marine mussel *(Mytilus galloprovincialis)* and scallop *(Pecten jacobaeus)* shells in this study.

Samples	Species	Assignment	Symmetry	g Values	$A(^{31}P)$ (mT)
Mussel *(Mytillus galoprovincialis)*	C1	CO_3^-	orthorhombic	$g_x = 2.0115$	
				$g_y = 2.0173$	
				$g_z = 2.0052$	
				$g_{\text{av}} = 2.0113$	
	C2	CO_3^{3-}	axial	$g_\perp = 2.0035$	
				$g_\parallel = 2.0014$	
	C3	CO_2^-	orthorhombic	$g_x = 2.0032$	
				$g_y = 1.9973$	
				$g_z = 2.0018$	
				$g_{\text{av}} = 2.0007$	
	C4	CO_2^-	freely rotating	$g = 2.0007$	
	S1	SO_2^-	freely rotating	$g = 2.0057$	
	S2	SO_3^-	axial	$g_\perp = 2.0038$	
				$g_\parallel = 2.0024$	
	P	PO_4^{2-}	isotropic	$g_{\text{av}} = 2.0069$	3.75
	X	Organic?		$g = 2.0045$	
Scallop *(Pecten jacobaeus)*	C5	CO_3^-	orthorhombic	$g_x = 2.0107$	
				$g_y = 2.0177$	
				$g_z = 2.0057$	
				$g_{\text{av}} = 2.0113$	
	C6	CO_3^{3-}	axial	$g_\perp = 2.0035$	
				$g_\parallel = 2.0014$	
	C7	CO_2^-	orthorhombic	$g_x = 2.0032$	
				$g_y = 1.9973$	
				$g_z = 2.0018$	
				$g_{\text{av}} = 2.0007$	
	C8	CO_2^-	freely rotating	$g = 2.0007$	
	S3	SO_2^-	freely rotating	$g = 2.0061$	
	S4	SO_3^-	axial	$g_\perp = 2.0038$	
				$g_\parallel = 2.0024$	

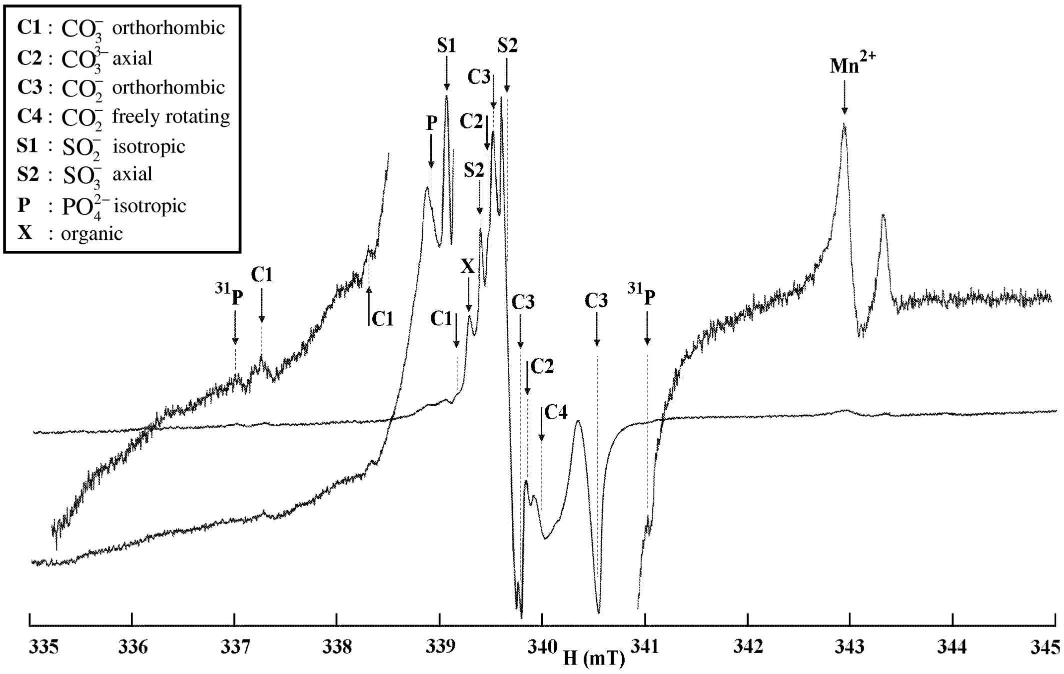

Fig. 3. EPR spectrum of γ-irradiated powders of marine mussel shell *(Mytilus galloprovincialis)* at ambient temperature.

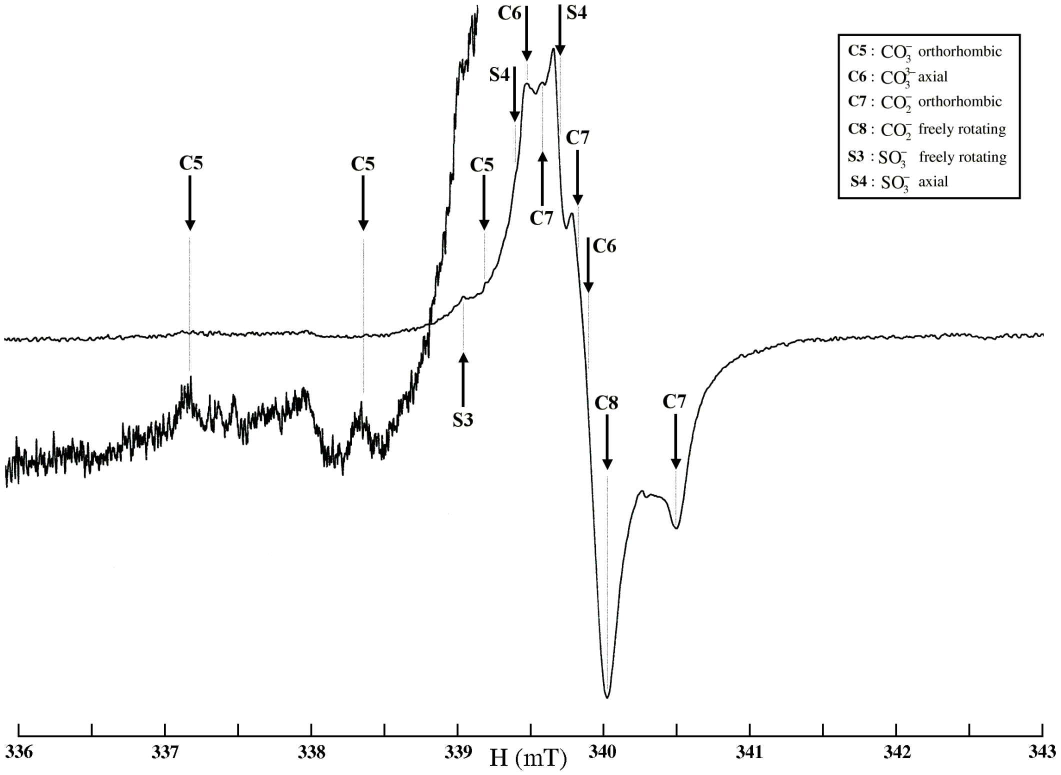

Fig. 4. EPR spectrum of powders of γ-irradiated marine scallop shell *(Pecten jacobaeus)* at ambient temperature.

shells at ambient temperature may be due to the presence of manganese in trivalent state. The Mn^{3+} ion with its low spin ($S = 0$) is diamagnetic and hence becomes an EPR silent.

The EPR spectrum of powders of γ-irradiated *Mytilus galloprovincialis* shell is given in Figure 3. This spectrum can be explained by the existence of the radicals CO_3^-, CO_3^{3-}, CO_2^-, SO_2^-, SO_3^-, PO_4^{2-} and organic (it may be humic acid or others) radicals. The g values of all observed radicals and the hyperfine coupling constant of the ^{31}P nucleus with a free electron in PO_4^{2-} are given in Table 1.

The EPR signals at $g_x = 2.0115$, $g_y = 2.0173$, $g_z = 2.0052$ may be due to orthorhombic CO_3^- free radical. The EPR signals at $g_\perp = 2.0035$, $g_\parallel = 2.0014$ were attributed to axial CO_3^{3-} free radical [8, 23, 24]. The EPR signals at $g_x = 2.0032$, $g_y = 1.9973$, $g_z = 2.0018$ may be due to an orthorhombic CO_2^- free radical, which is often found in natural carbonates, especially of marine origin. The well-resolved isotropic signal at $g_{\text{iso}} = 2.0007$ may be due to freely rotating CO_2^- radicals [24, 25]. These radiation defects are usually observed in irradiated calcite and aragonite and are used as dose markers for these mineral structures. The CO_2^- free radicals are already known to be able to rotate around either the x-axis [26, 27] or the y-axis [28]. The EPR spectrum of the present study contains signals of several CO_2^- species with different g factors. This indicates possibly that the CO_2^- radicals are located in several slightly different environments in the crystal lattice. The aforementioned carbonate derived radicals are characterized by only slightly different principal g values in the vicinity of $g = 2$ and hence can give rise to strongly composite and overlapping spectra.

The EPR signal at $g_{\text{iso}} = 2.0057$ may be due to freely rotating SO_2^- [7, 16, 29, 30]. SO_2^- is an electron-type center. It is a bent radical with 19 electrons. We attributed the EPR signals at $g_\perp = 2.0038$, $g_\parallel = 2.0024$ to axial SO_3^- free radical [1, 23]. These signals with axial symmetry are only dependent on the SO_3^- concentration in calcite [1]. Intensity of these signals varies, depending on the age and location of the specimens. The SO_3^- radical formed from SO_3^{2-} in $CaCO_3$ is a hole-type center and has 25 valence electrons. We could not observe any hyperfine lines of the ^{13}C and ^{33}S nuclei in these free radicals. The sulfite radical signals in natural carbonate specimens are usable for assessing the historical and regional variation of the sulfite concentration in the environment, which may reveal the history of acid rain [16, 31].

Table 2. The EPR parameters of species in the literature.

Species	g Values	A (^{13}C) (mT)	A(^{33}S) (mT)	A(^{31}P) (mT)	Refs.
CO_3^-	$g_x = 2.010$	$A_x = 1.08$			[35]
	$g_y = 2.018$	$A_y = 1.03$			
	$g_z = 2.0056$	$A_z = 1.37$			
	$g_{\text{av}} = 2.0112$	$A_{\text{av}} = 1.16$			
CO_3^-	$g_x = 2.018$	$A_x = 1.03$			[8]
	$g_y = 2.010$	$A_y = 1.37$			
	$g_z = 2.0056$	$A_z = 1.03$			
	$g_{\text{av}} = 2.0112$	$A_{\text{av}} = 1.16$			
CO_3^{3-}	$g_\perp = 2.0029$	$a_{\text{iso}} = 11.10 \pm 0.05$			[24]
	$g_\parallel = 2.0014$				
CO_3^{3-}	$g_\perp = 2.0031$	$a_\perp = 11.13$			[9]
	$g_\parallel = 2.0013$	$a_\parallel = 17.12$			
CO_3^{3-}	$g_\perp = 2.0034$				[23]
	$g_\parallel = 2.0017$				
CO_2^-	$g_x = 2.0032$	$a_{\text{iso}} = 14.85 \pm 0.05$			[24]
	$g_y = 2.0017$				
	$g_z = 1.9976$				
	$g_{\text{av}} = 2.0006$				
CO_2^-	$g_x = 2.0032$	$A_x = 15.8$			[35]
	$g_z = 2.0015$	$A_z = 18.9$			
	$g_y = 1.9974$	$A_y = 15.6$			
	$g_{\text{av}} = 2.0007$	$A_{\text{av}} = 16.77$			
CO_2^-	$g_x = 2.0032$				[36]
	$g_z = 2.0016$				
	$g_y = 1.9973$				
	$g_{\text{av}} = 2.0007$				
CO_2^-	$g = 2.0006$				[24]
CO_2^-	$g = 2.0006$				[25]
CO_2^-	$g = 2.0007$				[37]
SO_2^-	$g_{\text{iso}} = 2.0057$				[29]
SO_3^-	$g_\perp = 2.0036$				[29]
	$g_\parallel = 2.0021$				
	$g_{\text{av}} = 2.0031$				
SO_3^-	$g_\perp = 2.0038$		$A = 13.2$		[1]
	$g_\parallel = 2.0024$				
PO_4^{2-}	$g_x = 2.0122$			$A_x = 1.87$	[38]
	$g_z = 2.0072$			$A_z = 1.85$	
	$g_y = 2.0033$			$A_y = 2.00$	
	$g_{\text{av}} = 2.0076$				
PO_4^{2-}	$g_{\text{av}} = 2.0057$			$A = 3.42$	[32]
Organic radicals	$g = 2.0040$ to 2.0045				[39]

The isotropic signal at $g_{\text{iso}} = 2.0069$ is probably related to a phosphate radical, which may be due to the PO_4^{2-} free radical. The hyperfine coupling constant of the ^{31}P ($I = 1/2$, 100% natural abundance) nucleus was found as $A_{\text{iso}} = 3.75$ mT. The hyperfine coupling constant for the PO_4^{2-} radical is reported in the literature as 3.42 mT [32] and is very close to the $A_{\text{iso}} = 3.75$ mT value obtained in this work. The hyperfine coupling constant for some of phosphate radicals is reported in the literature as 3.8 – 8.8 mT [33]. The EPR signals of the PO_4^{2-} radical can not observed above 20 mW microwave power. In carbonates, sulphates and other oxygen salts, the ions CO_3^{2-}, PO_4^{2-}, SO_4^{2-}, etc. can trap holes or gain electrons. The formation of the PO_4^{2-} free radical may probably be due to a trapped hole of PO_4^{3-} ($PO_4^{3-} + e^+$), or to the substitution $SiO_4^{3-} \rightarrow PO_4^{2-} \cdot P_2O_8$ minerals are known to be sometimes present as substitutional impurity in calcite structures, resulting in PO_4^{4-}, PO_4^{2-}, PO_3^{2-}, PO_2^{2-} and PO_4^0 radicals [33].

The isotropic signal marked with X at $g_{\text{iso}} = 2.0045$ in Fig. 3 could not be identified. It might not be linked to the carbonate, sulfate or phosphate radical families. It can be attributed to humic acid and other types of organic radicals which are reported in the literature as having g values between 2.0040 and 2.0045 [34].

At the ambient temperature EPR spectrum of powders of γ-irradiated *Pecten jacobaeus* shell is shown in Figure 4. In this sample the observed signals are due to CO_3^-, CO_3^{3-}, CO_2^-, SO_2^- and SO_3^- radicals, as *Mytilus galloprovincialis* with similar EPR parameters. γ-irradiation induced defects in powders of *Pecten jacobaeus* shell were attributed to orthorhombic CO_3^- ($g_x = 2.0177$, $g_y = 2.0107$, $g_z = 2.0057$), axial CO_3^{3-} ($g_\perp = 2.0035$, $g_\parallel = 2.0014$), orthorhombic CO_2^- ($g_x = 2.0032$, $g_y = 1.9973$, $g_z = 2.0018$, $g_{\text{av}} = 2.0007$), freely rotating CO_2^- ($g_{\text{iso}} = 2.0007$), freely rotating SO_2^- ($g = 2.0061$), and axial SO_3^- ($g_\perp = 2.0038$, $g_\parallel = 2.0024$) free radicals, as given in Table 1 . These signals appear clearly when the microwave power is around 10 mW.

The EPR parameters of the radicals discussed above seem to be in agreement with the literature results and are listed in Table 2.

4. Conclusion

This investigation shows that unirradiated *Mytilus galloprovincialis* powders include paramagnetic Mn^{2+} ions, but no EPR signal of Mn^{2+} was observed from the unirradiated *Pecten jacobaeus* shells. The EPR spectrum of γ-irradiated *Mytilus galloprovincialis* powders are attributed to various carboxyls (orthorhombic and isotropic CO_3^-, axial CO_3^{3-}, orthorhombic CO_2^-, freely rotating CO_2^-), sulphuryls (freely rotating SO_2^- and SO_3^-), phosphoryl (PO_4^{2-}) and organic free radicals.

The EPR spectrum of γ-irradiated *Pecten jacobaeus* powders are attributed to various carboxyl free radicals. These paramagnetic defects induced by ionizing radiation are usually observed in structures of irradiated calcite and aragonite.

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