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Multifrequency EPR study on radiation induced centers in calcium carbonates labeled with ^{13}C

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Abstract. In calcite and aragonite, γ-irradiated at 77 K, several paramagnetic centers were generated and detected by EPR spectroscopy; in calcite, CO_3^- (orthorhombic symmetry, bulk and bonded to surface), CO_3^{3-}, NO_3^{2-}, O_3^-, and in aragonite CO_2^- (isotropic and orthorhombic symmetry) depending on the type of calcium carbonate used. For calcium carbonates enriched with ^{13}C more detailed information about the formed radicals was possible to be obtained. In both natural (white coral) and synthetic aragonite the same radicals were identified with main differences in the properties of CO_2^- radicals. An application of Q-band EPR allowed to avoid the signals overlap giving the characteristics of radical anisotropy.

Key words: aragonite • calcite • dosimetry • EPR spectroscopy • γ-irradiation • radicals

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Introduction

Calcium carbonates are commonly found in nature, especially in rocks in all parts of the world. The basic constituent unit in all carbonate minerals is the CO_3^{2-} ion [1]. This inorganic material occurs in three crystallographic forms: aragonite, calcite, and vaterite but the calcite with hexagonal symmetry is the only thermodynamically stable form. Naturally occurring calcite contains a variety of metal impurities in the carbonate lattice, which are usually substituted for Ca^{2+}. Several papers related to calcium carbonates mainly concern the study of the paramagnetic Mn^{2+} ions present in these structures as the most popular impurity [1, 2].

Impurity-related paramagnetic defects, usually associated with anions, are formed by ionizing radiation (UV, α, β, γ, n) and observed in synthetic and natural carbonates. The EPR studies of the irradiated carbonates showed the different spectra for the natural and synthetic samples and for the synthetic samples of different origin [3–5].

The studies of the nature and properties of the radiation defects in calcium carbonates are very important because of their numerous applications, e.g. in medicine, retrospective dosimetry or dating of archeological remnants [6–8].

Radical species like CO_3^-, CO_3^{3-}, and CO_3^- can be generated in calcium carbonates by γ- or UV-radiation. In calcite and aragonite exposed to ionizing radiation, different paramagnetic centers are formed.

Some of them are very stable at room temperature and can be used for the measurement of absorbed radiation dose as well as for dating due to a very long lifetime (about 10^6 years) [1]. Additionally, the nature and behavior of EPR spectra recorded in calcite or aragonite are different. Several papers about EPR measurements of calcium carbonates have recently been published, some dealing with carbonate radicals generated after γ-irradiation [9].

The EPR spectra of irradiated calcium carbonates recorded in X-band are complex and are not easy to interpret because of the overlap of spectra. However, the spectra recorded in Q-band are usually much better resolved, and the assignment of individual paramagnetic species in the complex spectra is easier [10]. Other techniques have been used for the study of radical dynamics in calcite, e.g. electron spin echo spectroscopy [11]. Up to now, all published works concern only the interpretation of EPR spectra recorded after irradiation at room temperature.

The purpose of the present work is to reconsider the problem by analyzing the EPR spectra in a more detailed way and to compare the behavior of carbonate radicals recorded in the temperature range 77–293 K using X- and Q-band EPR technique. Samples enriched with ^{13}C are used to obtain additional information about the assignment of carbon-centered radicals. Several types of carbonate and nitrate radicals, occurring in calcium carbonates samples, will be discussed based on present work and literature data.

Experimental

The aragonite and calcite samples (with ^{12}C and ^{13}C) were synthesized at the Institute of Ceramics and Building Materials, Warsaw (ICiMB) [12]. The aragonite with natural carbon isotope abundance was precipitated from solutions Na_2CO_3 and $CaCl_2$ in the presence of crystallization centers. The dried powder was grounded in a rotary-vibratory mill to a grain size of $D_{(50)}$ 3.2 μm. The calcite with natural carbon abundance was obtained through the calcinations of aragonite in the temperature of 510°C. The aragonite and calcite with ^{13}C isotope were obtained in the same way, with the application of Na_2CO_3-C^{13} reagent from Cambridge Isotope Laboratories, Inc. Commercially available calcite powders from POCH (Gliwice, Poland) and Johnson Matthey Chemicals (JMC) and naturally occurring aragonite, white coral (*Anthozea*), were used in the study as reference samples and compared with the ICiMB calcite and aragonite powders.

The samples were placed into Suprasil quartz tubes and then irradiated at 77 K with a dose of 5 kGy in Gamma Chamber 5000 (dose rate 5 kGy/h) and/or Issledovatel ^{60}Co (0.5 kGy/h) sources.

Electron paramagnetic resonance experiments were performed using EPR spectrometer ESP-300 Bruker (X-band) equipped with a nitrogen cryostat with variable temperature unit and ELEXSYS 500E (Q-band). EPR spectra in X-band were carried out with the temperature range 100 to 300 K. The magnetic field and the microwave frequency were measured using a Bruker ER 035M NMR Gaussmeter and a HP 5342A microwave frequency counter, respectively. Q-band spectra were recorded at room temperature. The magnetic field and the microwave frequency were measured using a Bruker ER 036 NMR Teslameter and a HP 5345A microwave frequency counter, respectively. All samples were measured with a wide range of microwave power (10 μW/10 mW). The assignment of the spectra to the corresponding radicals was supported by computer simulations of the experimental spectra with the 'SimFonia' program (Bruker).

Results and discussion

Calcite

The EPR spectra of the two types of calcite, POCH and JMC, both irradiated at 77 K are similar and complex (Fig. 1). At low temperature (Fig. 1a,c) the most intense is anisotropic orthorhombic spectrum with g factor values: $g_x = 2.0136$, $g_y = 2.0184$, $g_z = 2.0058$ (POCH), according to simulation (Fig. 1e). Based on literature data [1], the signal is assigned to CO_3^- radical anion located in calcite crystalline lattice. In the POCH sample, other less intense signals were recorded. One of them is characterized by g tensor values $g_x = 2.0029$, $g_y = 2.0176$ and $g_z = 2.0105$, close to the parameters of O_3^- radical anion (unstable above 160 K) observed in hydroxyapatite [3]. The next spectrum for POCH sample with $g_x = 2.0086$, $g_y = 2.017$, $g_z = 2.006$ was previously identified as CO_3^- located on the surface of crystallites [3].

The spectra of JMC sample, recorded at low temperature, are complex too. In comparison to POCH sample, there are no signals derived from O_3^- and CO_3^- localized on surface. Instead, there are a few overlapped signals not easy to interpret. Their most probable origins are the sulfur-containing impurities. These types of species belong to the radicals with orthorhombic symmetry, SO_2^- with $g_x = 2.0089$, $g_y = 2.0058$, $g_z = 2.0022$, and SO_3^- with $g_x = 2.0030$, $g_y = 2.0035$, $g_z = 2.0025$ in agreement with analogous g tensor components reported for similar systems [13].

The signal assigned to CO_3^- radicals anion was unstable and disappeared almost completely above 160 K. At 200 K two other signals dominate in both calcites spectra (Fig. 1b,d). One of them is a narrow axial line corresponding to g tensor components $g_{||} = 2.0013$; $g_\perp = 2.0028$. Analogous signal was reported previously in γ-irradiated calcite and hydroxyapatite and was assigned to CO_3^{3-} [1, 3]. This radical was EPR detected by us starting from 100 K, but the spectrum intensity is lower in comparison with CO_3^- (orthorhombic). At 200 K, when CO_3^- disappears, CO_3^{3-} reaches its importance. The radical is stable even at room temperature for days. The second signal, present in spectra of both types of calcite, is a multiplet of narrow lines. For better resolution Q-band EPR spectroscopy was used
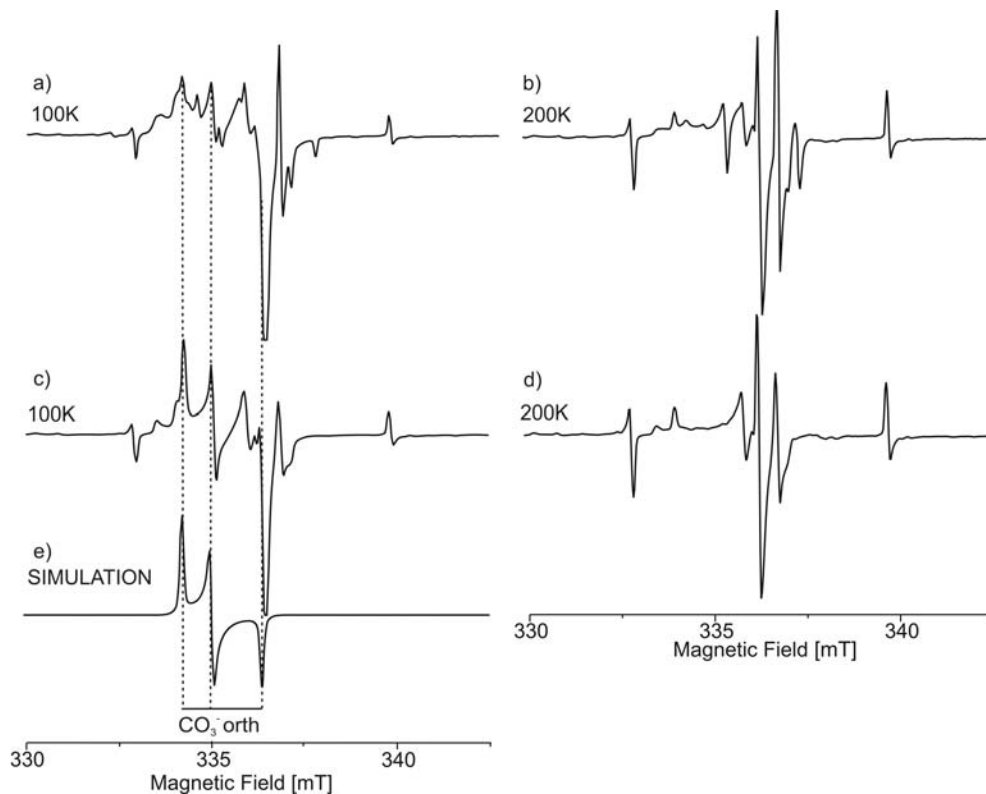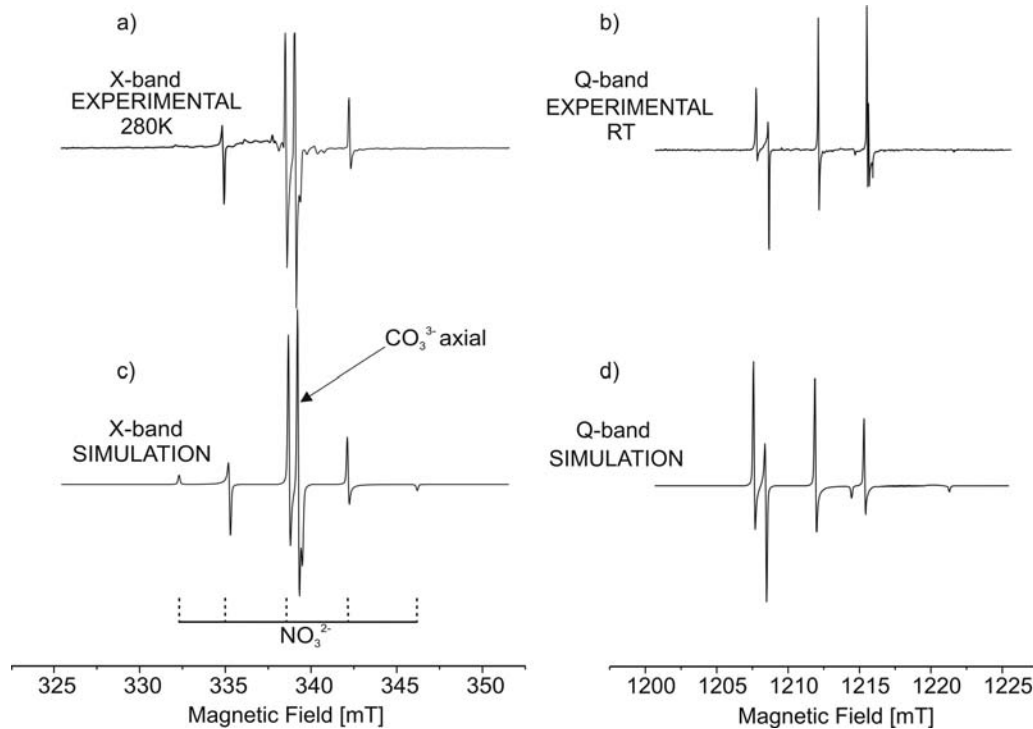
Fig. 1. X-band EPR spectra of γ-irradiated at 77 K calcite from POCH (a,b) and JMC (c,d) (both recorded at 100 K and 200 K, microwave power 1 mW), (e) the simulation of EPR spectrum assigned to CO_3^- radical.

(Fig. 2). The comparison of *g* values and hyperfine splittings measured at two different frequencies shows that the spectrum is consistent with axial *g* and *A* tensors and the unpaired electron interacts with one nucleus with spin $I = 1$. The best fit of the spectra at both frequencies was obtained for $g_{\text{II}} = 2.0023$, $g_\perp = 2.0059$, $A_\perp = 3.44$ mT, $A_{\text{II}} = 6.85$ mT.

Almost the same parameters were reported earlier and assigned to NO_3^{2-} center [1]. This radical is relatively stable at room temperature and is recordable by weeks and was observed by us even at 100 K.

Figure 3 shows the spectra of calcites synthesized in ICiMB. One of the sample was enriched with ${}^{13}C$ isotope. The spectra are complex and differ signifi-

Fig. 2. EPR spectra of γ-irradiated at 77 K calcite from POCH recorded at room temperature at X-band (a) and Q-band (b) together with theoretical spectra (c) and (d), respectively, simulated with the parameters given in the text.
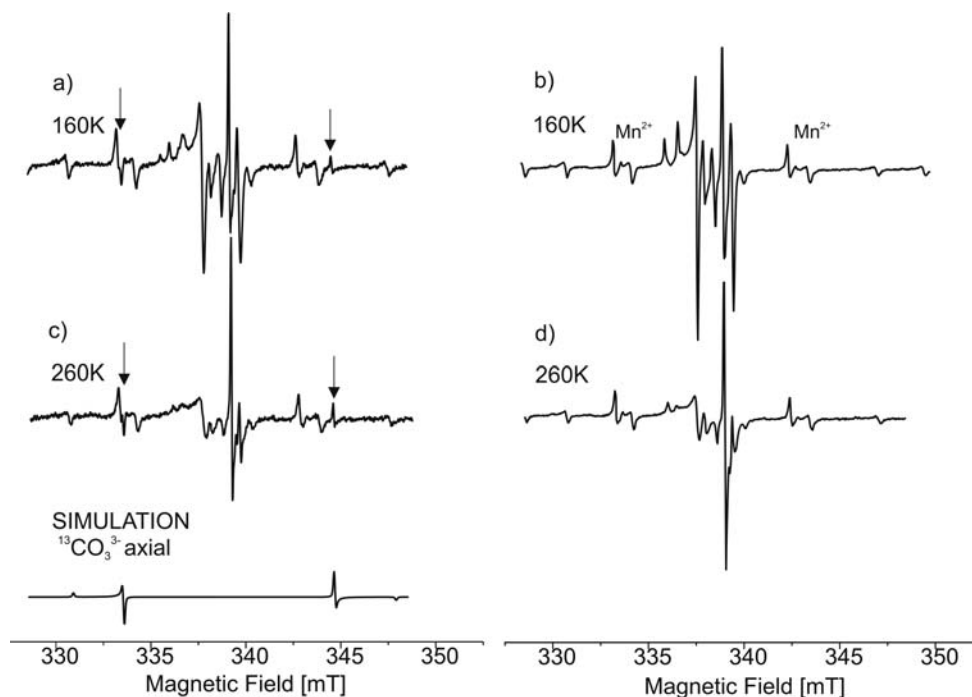
Fig. 3. EPR spectra of γ-irradiated synthetic calcite recorded at 160 K and 260 K, with natural content of carbon isotopes (b,d); and enriched with ^{13}C (a,c) together with the simulated spectrum for $^{13}CO_3^{3-}$ radical anion. The arrows indicate the lines of ^{13}C doublet.

cantly in comparison to those for commercial samples from POCH and JMC. In both samples with natural carbon isotopes and enriched with ^{13}C, the signals in the region close to *g* about 2 are similar and consist of several lines. The spectra of calcite sample with ^{13}C do not show any doublets that could come from CO_3^- radical anion with hyperfine interaction *A* tensor components $A_x = 1.08$ mT, $A_y = 1.03$ mT, and $A_z = 1.37$ mT and *g* tensor $g_x = 2.0136$; $g_y = 2.0184$; $g_z = 2.0058$ [1]. Some of them represent third and fourth lines of multiplet due to Mn^{2+} nuclei present in the samples as impurity (Fig. 3b). The simulation allowed to assign the remaining lines to $A_\perp = 11.13$ mT, $A_{||} = 17.12$ mT, and $g_\perp = 2.0031$ and $g_{||} = 2.0013$, which are consistent with CO_3^{3-} radical of axial symmetry reported earlier [1]. The spectrum due to CO_3^{3-} was visible from 100 K until room temperature.

It is worthy to notice, that the signals of CO_3^-, NO_3^{2-} and O_3^- were not seen in both synthetic samples, with natural and enriched ^{13}C content, indicating that nitrate impurities are absent. The carbonate impurities are represented by CO_3^{3-} but it is possible that CO_3^- radicals, detected in POCH and JMC samples, could be connected with structural defects in their crystalline lattice. This hypothesis is confirmed by the fact that carbonate CO_3^{3-} radicals are observed starting from low temperature when the mobility of species is low and lattice rearrangement is not possible.

Aragonite

Figure 4 shows the EPR spectra of synthetic aragonite samples (ICiMB) irradiated at 77 K with natural abundance of carbon (a,c) and enriched with ^{13}C

isotope (b,d). In both cases the spectra are complex. In the spectrum of both aragonite samples weak signals due to Mn^{2+} ions and/or defects in crystalline lattice are visible. At low temperature the six-line multiplet is dominant in both samples. The multiplet can derive from metal ion impurities and/or defects in crystalline lattice. A similar signal was recorded in the EPR spectrum of white coral sample irradiated at 77 K. Thus, the carbon-centered radicals are not generated at low temperature. After thermal annealing, the spectra change significantly. Starting from 230 K in sample containing natural carbon isotope content the six-line multiplet disappeared and new signals with *g* factor of about 2 appears (Fig. 4c). In order to analyze this fragment of the spectrum, the Q-band EPR spectroscopy was used (Fig. 4e). It is clearly seen that two signals, overlapping at X-band, are present. One of them is isotropic with $g = 2.0006$ which was earlier observed by Debuyst *et al.* [14] in white coral γ-irradiated at room temperature and assigned to tumbling CO_2^- radical located in the occluded water. The second radical exhibits an orthorhombic symmetry in agreement with *g* tensor components, $g_1 = 2.0030$, $g_2 = 2.0020$, $g_3 = 1.9974$, identical to those observed for biological hydroxyapatites and assigned to CO_2^- radical but connected with crystallite surface [3]. Both signals are stable until room temperature.

The thermal changes of spectra in the aragonite labeled with ^{13}C proceed in the same way (Fig. 4d). At 230 K, the six-line multiplet decreases and new signals gained their importance. The thermal changes of spectra in the sample with ^{13}C proceed in the same way (Fig. 4d). At 230 K, the multiplet signal decreases and new signals gained their importance. One of them is a doublet of isotropic lines due to $I(^{13}C) = ½$ with $A_{iso} = 14.8$ mT and $g = 2.0006$, derived
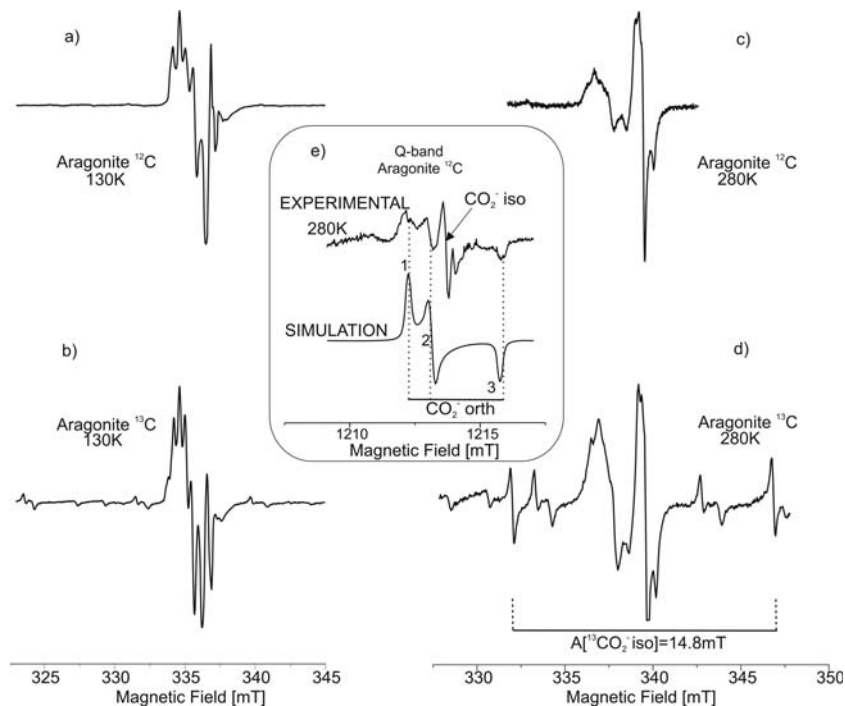
Fig. 4. X-band EPR spectra of synthetic aragonite with ^{12}C (a,c) and ^{13}C (b,d). Q-band EPR spectrum and simulated spectrum of orthorhombic $^{12}CO_2^-$ radical (e).
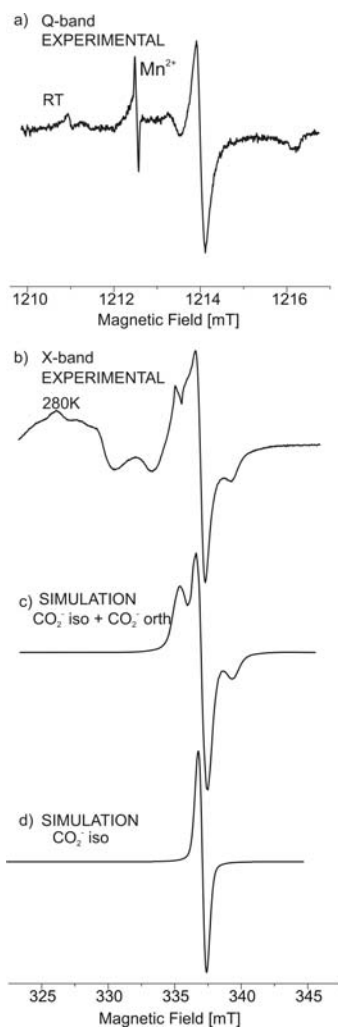
Fig. 5. EPR spectra recorded in Q-band (a) and X-band (b) of natural white coral and the spectrum simulated for the stable CO_2^- radical.

from $^{13}CO_2^-$ radicals located in the occluded water and allowing for the estimation of temperature of CO_2^- radical formation. The same thermal induced changed were observed for the sample synthesized with the natural content of carbon isotopes but the overlap of the lines precluded their analysis.

In order to compare the results obtained for synthetic and natural aragonites (ICiMB) and white coral, the measurements were performed in the temperature range 100–300 K after irradiation at 77 K. Figures 5a and 5b show the spectra recorded at Q- and X-band, respectively, which appeared to be identical. Accordingly, it can be deduced that in both aragonites, the synthetic and the natural the same two CO_2^- radicals are generated as a result of similar composition of the crystalline lattice.

All radicals described above are summarized in Table 1 containing our and other authors EPR data.

Conclusions

The spectra of calcium carbonate samples, γ-irradiated at 77 K and measured during thermal annealing by EPR spectroscopy, were complex and changed with temperature. In calcite samples, depending on sample origin, different radicals were generated because of different impurities included in crystalline lattice. In the samples from POCH and JMC at room temperature an anisotropic EPR line due to NO_3^{2-} radical dominated whereas in those synthesized in ICiMB it was not found. Only in spectra of commercial samples the signal due to CO_3^- is EPR detected whereas that assigned to CO_3^{3-} radical was observed in all studied samples. Both radicals were observed starting from the lowest temperature, but CO_3^- radical disappeared, whereas CO_3^{3-} center were visible until room temperature. We postulate that

Table 1. EPR parameters of selected radicals in irradiated carbonate materials

Materials	Radical	g Factors			A tensor [mT]			Ref.
		g_x	g_y	g_z	A_x	A_y	A_z	
Calcite	**POCH**							
	CO_3^- orth.	2.0136	2.0184	2.0058	–			This work
		2.0132	2.0194	2.0055	–			[1]
	CO_3^- surf.	2.0086	2.0170	2.0060	–			This work, [3]
	CO_3^{3-} axial.	$g_{II} = 2.0013, g_\perp = 2.0028$			–			This work
		$g_{II} = 2.0016, g_\perp = 2.0032$			–			[1]
	NO_3^{2-} axial.	$g_{II} = 2.0023, g_\perp = 2.0059$			3.44	3.44	6.85	This work
		$g_{II} = 2.0017, g_\perp = 2.0060$					6.80	[1, 15]
	O_3^-	2.0029	2.0176	2.0105	–			This work, [3]
	JMC							
	CO_3^- orth.	2.0136	2.0185	2.0055	–			This work
	CO_3^{3-} axial.	$g_{II} = 2.0013, g_\perp = 2.0028$			–			This work
	NO_3^{2-} axial.	$g_{II} = 2.0023, g_\perp = 2.0059$			–			This work
	ICiMB ^{12}C CO_3^{3-} axial.	$g_{II} = 2.0013, g_\perp = 2.0031$			–			This work
	ICiMB ^{13}C $^{13}CO_3^{3-}$ axial.	$g_{II} = 2.0013, g_\perp = 2.0031$				11.13	17.12	This work, [1]
Aragonite	**ICiMB ^{12}C**							
	CO_2^- iso.	$g_{iso} = 2.0006$			–			This work, [1]
	CO_2^- orth.	2.0030	1.9974	2.0020	–			This work
		2.0032	1.9974	2.0015	–			[1]
	ICiMB ^{13}C							
	$^{13}CO_2^-$ iso.	$g_{iso} = 2.0006$				14.8		This work, [1]
	CO_2^- orth.	2.0030	1.9974	2.0020	–			This work
		2.0032	1.9974	2.0015	15.8	15.6	18.9	[1]
	White coral CO_2^- iso.	$g_{iso} = 2.0006$			–			This work, [1]

differences between carbonate radicals are due to effect of location of the centers in crystalline lattice.

Both aragonite samples, synthetic and natural white coral after γ-irradiation at 77 K showed similar EPR behavior. At low temperature a six-line multiplet, due to paramagnetic impurities and/or lattice defects, appeared in EPR spectra. Above 200 K, the multiplet lost its importance, but the carbonate CO_2^- radicals were formed. At room temperature two different CO_2^- radicals, one located in the occluded water with the isotropic spectrum and second, dominating, with orthorhombic spectrum were observed.

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