

# ELECTRON SPIN RESONANCE (ESR) OF GAMMA-IRRADIATED OYSTER SHELLS

Delson U. Schramm\*\*, Marta M. Cattani\*, Nélida L. Del Mastro\* and Alexandre M. Rossi\*\*

\*IPEN-CNEN/SP  
Travessa R, 400 Cidade Universitária  
05508-900 São Paulo, SP  
e-mail: mmcattani@if.usp.br

\*\*CBPF-CNPq/RJ  
Rua Xavier Sigaud 150, 22290-180  
FAX: 021-541-2047, Rio de Janeiro- Brazil.  
e-mail: delson@cbpfsu1.cat.cbpf.br

## ABSTRACT

Nonirradiated and gamma-irradiated mollusc shells were studied by EPR. Four paramagnetic species ascribed to  $\text{CO}_2^-$  and  $\text{SO}_3^-$  radicals were identified in the EPR spectra. Three paramagnetic centers are attributed to  $\text{CO}_2^-$  ions of isotropic ( $g = 2.0007$ ) and orthorhombic symmetries and the fourth species are associated with axially symmetric  $\text{SO}_3^-$  radicals ( $g_{\parallel} = 2.0036$ ,  $g_{\perp} = 2.0021$ ). These radicals are present in the EPR spectra of nonirradiated samples suggesting that they can also be created by sample mechanical treatment. As a consequence,  $\text{SO}_3^-$  and  $\text{CO}_2^-$  centers can be used in high dose EPR dosimetry with precautions.

## INTRODUCTION

Mollusc shells are composed of organic matrices with small crystal domains of calcium carbonate deposited in them. These carbonate materials can be calcitic or aragonitic and are able to host stable EPR active paramagnetic species induced by ionizing radiation. Most of these radiogenic species are attributed to  $\text{CO}_2^-$ ,  $\text{SO}_2^-$  and  $\text{SO}_3^-$  radicals [1]. EPR technique has proved to be a useful tool for dating and radiation dosimetry and many works have been published about the use of paramagnetic centers in assessing accumulated radiation doses, specially in carbonate shells [2 - 8].

The study of the dose response of different paramagnetic defects produced by radiation is essential to EPR dosimetry. From this knowledge, it is possible to define EPR species which can be used as dose markers and determine their sensitivity to radiation, as well as the minimum radiation dose for which they have a reasonable intensity to be clearly detected. A fairly small minimum dose of 0.2 Gy was already found for sea water mollusc shells [2].

In this work, we evaluate the radiation dose production of different signals present in the EPR spectra of irradiated marine oyster shells, and compare the signal

to gamma-dose sensitivity of these signals with the ones reported in the literature [2].

## EXPERIMENTAL

Marine oyster shells (*Crassostrea brasiliiana*) from Cananéia, São Paulo, were selected for the EPR experiments. Some of them were gamma-irradiated by a  $^{60}\text{Co}$  source at IPEN/SP with absorbed doses of 0.18, 0.5, 1.0, 2.0, 5.0, 10 Gy, 0.75, 1.5 and 3.0 kGy (dose rate about 400Gy/h for the higher doses and 40Gy/h for the lower doses) and some specimen were left unirradiated. After the irradiation, the samples were ground to powder (90 - 125  $\mu\text{m}$ ) and separated into ten aliquots of 71.4 mg each. The 9.5 GHz EPR measurements were carried out at room temperature in a Bruker ESP300E spectrometer with 100kHz modulation amplitude of 0.5 Gauss.

## RESULTS AND DISCUSSION

EPR spectra of a gamma-irradiated oyster shell, recorded at high and low microwave powers, are shown in Fig. 1. At least four paramagnetic species associated with

$\text{CO}_2^-$  and  $\text{SO}_3^-$  radicals can be identified. The  $\text{CO}_2^-$  ions give rise to EPR signals with isotropic ( $g = 2.0007$ ) [9 - 11] and orthorhombic symmetries [9, 11]. Two orthorhombic  $\text{CO}_2^-$  species can be identified, one with narrow lines (0.7 Gauss wide,  $g_{xx} = 2.0022$ ,  $g_{yy} = 1.9971$ ,  $g_{zz} = 2.0026$ ) and another with broad lines (3 Gauss wide,  $g_{xx} = 2.0017$ ,  $g_{yy} = 1.9973$ ,  $g_{zz} = 2.0032$ ) lines. The  $\text{SO}_3^-$  radicals are responsible for the axially symmetric 0.4 Gauss linewidth spectrum at  $g_{\perp} = 2.0036$  and  $g_{\parallel} = 2.0021$  [12]. This latter species is better observed at low microwave power (1 mW, Fig. 1). All nonirradiated samples present a well defined  $\text{SO}_3^-$  EPR spectrum and weak signals at the same  $g_{\perp}$  positions of  $\text{CO}_2^-$  centers. At low doses ( $D < 700$  Gy), radiation induced signals are greatly masked by strong  $\text{Mn}^{2+}$  signals, which would cause some inaccuracy in the line intensity measurements. In order to overcome this problem, a baseline correction was performed (Bruker WIN-EPR software) to eliminate, at

least partially, the influence of the  $\text{Mn}^{2+}$  lines on the radiation damage spectra. Spectra of  $\text{CO}_2^-$  radicals cannot be well defined in samples irradiated with doses lower than 10 Gy.

Line intensity of  $\text{SO}_3^-$  spectrum is not proportional to dose in the 0.18 - 10 Gy interval suggesting that pre-dose signal contribution can vary from a sample to another (figure 2a). From figure 2b, it can be observed that at doses higher than 10 Gy, the signal to dose response of both species follows a growth exponential curve given by the Barabas et al. (1988) [13] analytical model with saturation level of about 3 kGy for the  $\text{SO}_3^-$  species and about 1 kGy for the  $\text{CO}_2^-$  centers. This result indicates that (i) pre-dose signal contribution has a small influence on the overall spectrum and (ii) the signal to dose sensitivity of the species does not present a large variation among the studied samples.

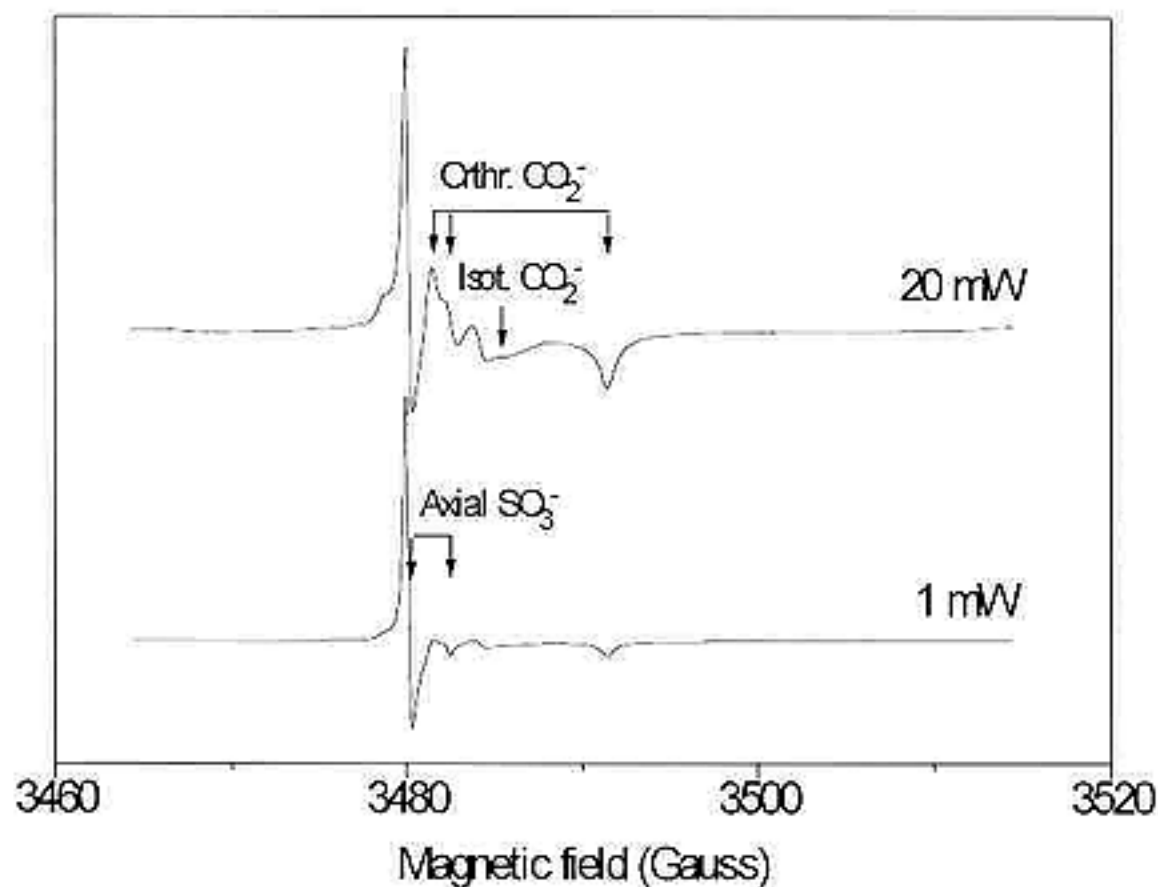


Figure 1. EPR Spectra of Mollusc Shells irradiated with 3.0 kGy Gamma Dose, recorded at low (1 mW) and high (20 mW) Microwave Powers. The Identification of the Radiation Produced Paramagnetic Species is also shown.

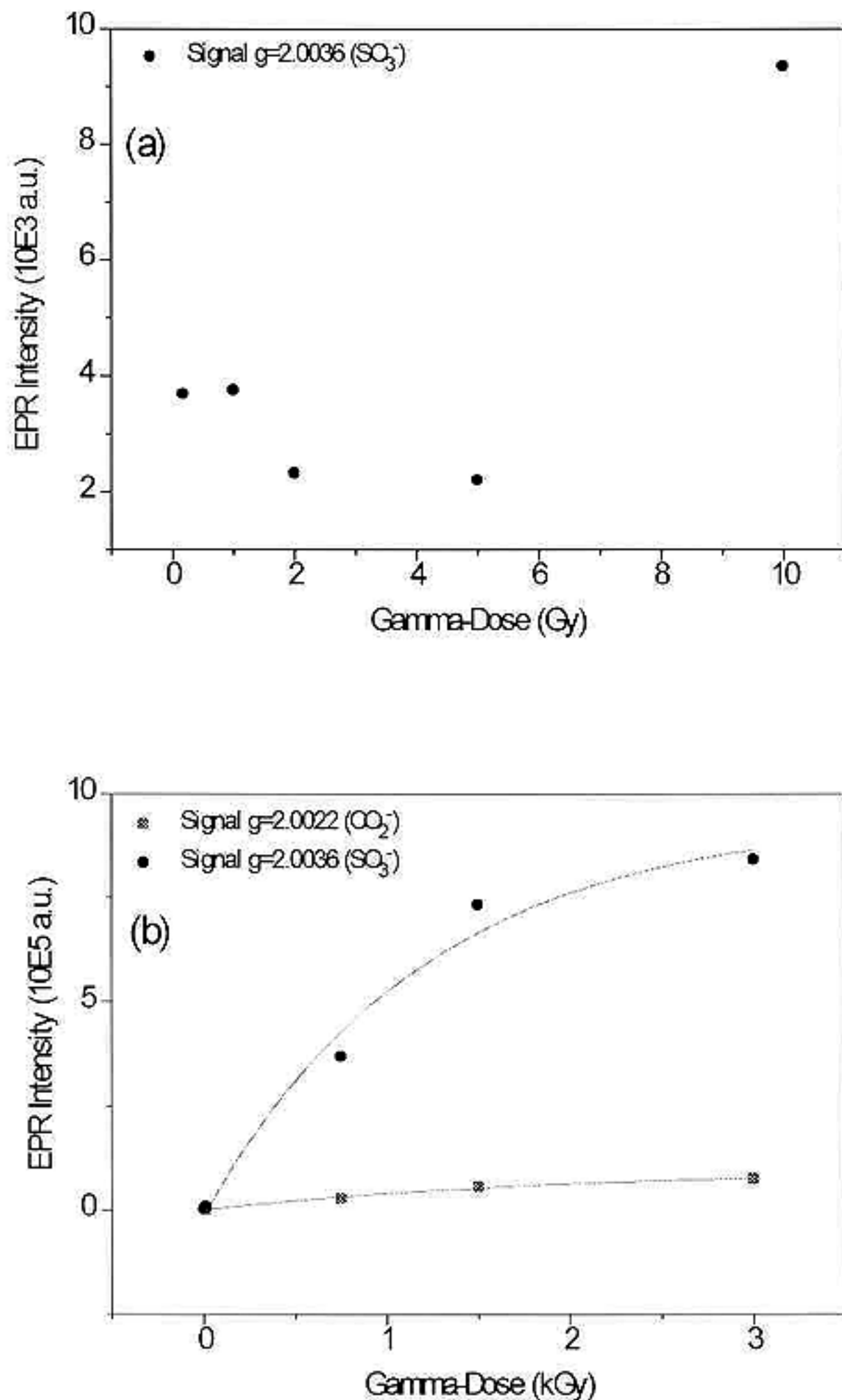


Figure 2. Gamma-Dose Response Curves of the EPR Signals at  $g = 2.0022$  and  $g = 2.0036$ , recorded at 20 mW and 1 mW Microwave Powers, respectively, in the ranges (a) 0.18 - 10.0 Gy and (b) 10.0 Gy - 3.0 kGy.

## CONCLUSIONS

The EPR spectra of irradiated oyster shell samples are composed by lines attributed to  $\text{Mn}^{2+}$  ions,

$\text{CO}_2^-$  and  $\text{SO}_3^-$  radicals. The  $\text{Mn}^{2+}$  spectrum, present in all the studied samples, can difficult the dosimetry of the irradiated carbonates, principally at low doses. The signal to dose sensitivity is smaller than the one verified by

Stachowicz et al. (1995) [2] for sea water mollusc shells. In this work, it was not possible to resolve the  $\text{CO}_2^-$  spectrum for doses lower than 10 Gy, whereas in the samples studied by the latter authors, the radiation induced spectra is well defined for doses of 0.2 - 4.0 Gy. The weak signal to dose sensitivity observed in the studied samples could be due to the presence of  $\text{Mn}^{2+}$  ions in the vicinity of the paramagnetic radicals. Spectra of  $\text{SO}_3^-$  and probably of  $\text{CO}_2^-$  radicals are detected in nonirradiated samples, suggesting that they can also be created by sample mechanical treatment (tribodefects). These pre-dose signals may impose limitations on the carbonate dosimetry for doses lower than 10 Gy. For doses higher than 10 Gy, when pre-dose contribution is no longer important, the dose response of  $\text{CO}_2^-$  and  $\text{SO}_3^-$  species follows a well defined growth saturation curve of the type described by Barabas et al. (1988) [13].

### ACKNOWLEDGEMENTS

The authors gratefully acknowledge CNPq and CAPES, for financial support. The authors wish to thank Fazenda Lacostra, for the oyster supply.

### REFERENCES

- [1] Ikeya, M. New Applications of Electron Spin Resonance: Dating, Dosimetry and Microscopy., World Scientific, Singapore, New Jersey, London, Hong Kong, chapter 6, 1993.
- [2] Stachowicz, W., Michalik, J., Burlinska, G., Sadlo, J., Dziedzic-Goclawska, A. and Ostrowski, K. Detection Limits of Absorbed Dose of Ionizing Radiation in Molluscan Shells as Determined by EPR Spectroscopy. *Appl. Radiat. Isot.*, vol. 46, num. 10, p. 1047-1052, 1995.
- [3] Ikeya, M. and Ohmura, K. Dating of Fossil Shells with ESR. *J. Geol.*, vol. 89, p. 247-251, 1981.
- [4] Ikeya, M. and Ohmura, K. ESR Age of Pleistocene Shells measured by Radiation Assessment. *Geochem. J.*, vol. 18, p. 11, 1984.
- [5] Radtke, U., Mangini, A. and Grün, R. ESR Dating of Marine Fossil Shells. *Nucl. Tracks Radiat. Meas.*, vol. 10, num. 4-6, p. 879-884, 1985.
- [6] Skinner, A. F. ESR Dosimetry and Dating in Aragonitic Mollusks. *Appl. Radiat. Isot.*, vol. 40, num. 10-12, p. 1081, 1989.
- [7] Molodkov, A. The Problem of Long-Term Fading of Absorbed Palaeodose on ESR Dating of Quaternary Mollusc Shells. *Appl. Radiat. Isot.*, vol. 40, num. 10 - 12, p. 1087, 1989.

[8] Molodkov, A. ESR Dating of Non-Marine Mollusc Shells. *Appl. Radiat. Isot.*, vol. 44, num. 1-2, p. 145, 1993.

[9] Debuyst, R., Bidiambabu, M. and Dejehet, F. Diverse  $\text{CO}_2^-$  Radicals in  $\gamma$ - and  $\alpha$ -Irradiated Synthetic Calcite. *Bull. Soc. Chim. Belg.*, vol. 99, num. 8, p. 535, 1990.

[10] Debuyst, R., Bidiambabu, M. and Dejehet, F. An EPR Study of  $\gamma$ - and  $\alpha$ -Irradiated Synthetic Powdered Calcite Labelled with Carbon-13. *Nucl. Tracks Radiat. Meas.*, vol. 18, num. 1 - 2, p. 193, 1991.

[11] Rossi, A. M. and Poupeau, G. Radiation-Induced Paramagnetic Species in Natural Calcite Speleothems. *Appl. Radiat. Isot.*, vol. 40, num. 10 - 12, p. 1133, 1989.

[12] Kai, A. and Miki, T. Electron Spin Resonance of Sulfite Radicals in Irradiated Calcite and Aragonite. *Radiat. Phys. Chem.*, vol. 40, p. 469-476, 1992.

[13] Barabas, M., Bach, A. and Mangini, A. An Analytical Model for the Growth of ESR Signals. *Nucl. Tracks Radiat. Meas.*, vol. 14, num. 1 - 2, p. 231, 1988.