CALCIUM CARBONATE AS A POSSIBLE DOSIMETER FOR HIGH IRRADIATION DOSES

Alicia Negron-Mendoza[a], Roberto M. Uribe[b], Sergio Ramos-Bernal[a]
Claudia Camargo-Raya[a], Virginia Gomez-Vidales[c] and Kensei Kobayashi[d]

[a] Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México (UNAM), México D.F. 04510, México
E-mail: negron@nucleares.unam.mx

[b] Kent State University College of Technology, Kent OH, USA

[c] Instituto de Química, Universidad Nacional Autónoma de México UNAM, México D.F., México
[c] Yokohama National University, Japan

Abstract

The aim of this work is to analyze the interactions of 5 MeV electron beam radiation and a 290 MeV/u Carbon beam with calcium carbonate (powder) at 298 K and at different irradiation doses, for the potential use of calcium carbonate as a high-dose dosimeter. The irradiation doses with the electron beam were from 0.015 to 9 MGy, and with Carbon beam from 1.5 kGy to 8 kGy. High-energy radiation induces the formation of free radicals in solid calcium carbonate that can be detected and measured by electron paramagnetic resonance (EPR). An increase of the EPR response for some of the free radicals produced in the sample was observed as a function of the irradiation dose. The response of one of the radicals decreased with the dose. These measurements are reproducible; the preparation of the sample is simple and inexpensive; and the signal is stable for several months. The response curves show that the dosimeter tends to saturate at 10 MGy. Based on these properties, we propose this chemical compound as a high-dose dosimeter, mainly for electron irradiation.

Keywords: calcium carbonate, EPR, dose effect, high-energy ionizing radiation

1. INTRODUCTION

Research on the interaction between solids and radiation has helped to complement the knowledge of solid structures and reactions, making it possible to expand the uses and applications of radiation. As result of such interactions, free radicals can be produced.
The large variety of compounds that retain free radicals for long periods after they were produced by irradiation includes carbonates, which are among the most abundant minerals in the Earth's crust. Due to their ubiquity—they occur from limestone and marble to invertebrate exoskeletons—these compounds play a significant role in the natural sciences,

and important information about paleoclimatology, paleogeography and archeological chronology can be obtained from their analysis (Bahain *et al.* 1994; Nokhrin, 2006). The analysis of such samples can be performed by EPR of the free radicals produced in the carbonate fraction. The use of carbonates for dating, retrospective dosimetry and other applications has been intensively studied (Murali et al 2001; Herrera *et al.* 2005; Nokhrin *et al.* 2006; Ureña *et al.* 2009; Romanyukha and Trompier, 2011; Verona *et al.* 2013). These studies were performed with gamma radiation in the low doses range of 1 to 1500 Gy. To our knowledge, no prior reports are at high doses of irradiation with electron and heavy ions, as in this report.

Several industrial or commercial applications require the use of high-radiation doses. Some of the most common applications for radiation are the sterilization of single-use medical products, food irradiation to reduce pathogens, and modifications of materials to improve their properties. For all of these applications, researchers need to know the doses these items have received.

Dosimeters used for different applications should be calibrated using irradiation conditions as close as possible to the conditions used when the irradiation dose is to be measured (Miller *et al.* 2000). Most dosimeters are calibrated at room temperature using well-characterized gamma ray sources.

A variety of dosimetry devices have been used for high-dose measurements in various environments—dye and chemical systems, both liquid and solid—but for some of these devices, modest alterations in the environment could change the chemical transformation rate, and corrections might be required. The choice of the particular dosimeters best suited for a given application depends on the specific conditions under which the measurements must be made.

The aim of this work is to test the applicability of commercial calcium carbonate for potential use as an inorganic dosimeter for high-irradiation doses, based on the formation of free radicals by high-energy radiation (5 MeV electron beam and 290 MeV/u Carbon beam) and using EPR (electron paramagnetic resonance) for its detection.

2. EXPERIMENTAL PROCEDURES

2.1 Samples

Sample: calcium carbonate (Sigma-Aldrich, Co. USA), of the highest purity available. Some samples were from J. T. Baker®, USA.

Sample preparation. Solid carbonate, as a powder, was put in glass tubes. One set of samples was kept in air, and the other set in evacuated glass tubes.

2.2 Irradiation

The irradiation was conducted using two sources. The first was an accelerator producing a 5 MeV electron beam at the NEO Beam facility in Northeast Ohio, USA. The doses were from 0.015 to 9 MGy. The second was a 290 MeV/u Carbon ion beam at the heavy ion irradiation source "HIMAC" (Heavy Ion Medical Accelerator) at NIRS (National Institute of Radiological Sciences) in Chiba, Japan. The irradiation doses were 1.5, 4 and 8 kGy. The

experiments were performed using the biology beam line. Some samples were irradiated with gamma rays at ICN-UNAM in the Gammabeam 651 PT unit at 0.800 kGy, 1.5 kGy, 1.5 MGy, and 5.25 MGy at room temperature.

2.3 Electron paramagnetic resonance (EPR) measurements

The EPR analysis was conducted at the Instituto de Química-UNAM on 30±0.1 mg of sample in a quartz tube at room temperature with a JEOL JES-TE300 spectrometer operating X-Band fashions at a 100 kHz modulation frequency and a cylindrical cavity in the mode TE_{011}. The external calibration of the magnetic field was made with a precision gauss meter, JEOL ES-FC5. The spectrometer settings for all spectra were as follows: center field, 335.5 ± 4 mT; microwave power, 8 mW; microwave frequency, 9.43 GHz; modulation width, 0.032 mT; time constant, 0.1 s; amplitude, 32; sweep time, 120 s; 1 scans. The readings were taken at the vertical peak height. The sample irradiated at 6.5 MGy with the electron beam, a sample irradiated at 5.25 MGy with gamma radiation and the sample irradiated with the 290 MeV/u Carbon beam (1.5 kGy) were measured, changing the microwave power to observe the behavior of the peaks at g=2.00034 and 2.0031.

3. RESULTS AND DISCUSSION

The EPR spectra of the irradiated calcium carbonate consisted primarily of a group of six lines, in the center field attributable to coupling with an I=5/2 assigned to Mn^{2+}, obtained as an impurity in the sample. Additional free radical peaks identified as radiation-induced defects were observed at the center of this group (332.670-340 mT). The EPR spectra consisted of narrow lines. The signals present in our samples were as follows: (1) g=2.019, (2) g=2.007, (3) g=2.0058, (4) g=2.0031 (5) g=2.0034, (6) g=2.0005, and (7) g=1.9939. For dosimetric purposes, we followed the evolution of peaks 3 and 5. The signal with g=2.0034 (5) was better resolved and easier to assign.

Other authors report these signals for low-dose gamma irradiation, in the so-called asymmetric EPR signal near g=2 (Callens *et al.* 1998). Although there have been many efforts to study these signals, little is known about their origin of them, and controversies remain in their assignment. (Barabas *et al.* 1989, Callens *et al.* 1998; Seletchi, 2007; Rudko *et al.* 2010).

It is beyond the scope of this paper to assign the nature of the radicals derived from irradiation of our experiments; also, our samples were irradiated at high doses, and the same species do not necessarily dominate at high and low doses. However, some data in the literature for the analysis of carbonate samples of different origins show various radicals and their assignment.

Several paramagnetic species such as CO_2^- (surface and bulk), CO_3^{3-}, CO_3^-, CO^- and some unknown radicals in the range of 2.00010 to 2.01 have been proposed, and for some of these molecular ions, more than one different type may occur. Romanyukha *et al.* 2010, reported that population of different radical species dominate the spectra depending on the radiation source used (X-ray, UV and gamma radiation). Most of these reports are

performed with gamma radiation, only two with heavy ions (^{238}U and ^{197} Au) to study crystal lattice damage (Nagabhushana *et al.* 2008, Pabst *et al.* 2010).

The radical with g=2.0006 is the most important signal for EPR-dating natural carbonates, such as shells or stalactites (Barabas *et al.* 1989; Barabas *et al.* 1992; Debuyst *et al.* 1993 and Callens *et al.* 1998; Nokhrin *et al.* 2006). It has been unambiguously associated with the isotropic CO_2^- radical and identified in various carbonate samples (Barabas *et al.* 1992; Debuyst *et al.* 1993). The signal at g=1.997 is indicative of the presence of this radical. In general, CO_2^- centers are very stable at room temperature and can be detected for years.

It was speculated that the signal at g=2.0058 was due to organic radicals. However, this signal appeared in very pure synthetic crystals, and it is most likely due to CO^- (Barabas, et al 1989). It has also been assigned as CO_3^- (McMillan and Marshall, 1968; Serway and Marshall, 1967).

The peak at g=2.0034 has been assigned to the molecular ion CO_3^{3-} (Barabas et al 1989; Jacobs *et al.* 1989), although there is also a large discrepancy in this assignment (Barabas *et al.* 1989); more recent reports for other authors have assigned this signal to CO_3^- (Murali *et al.*, 2001; Herrera *et al.*, 2005; Gilinskaya, 2005).

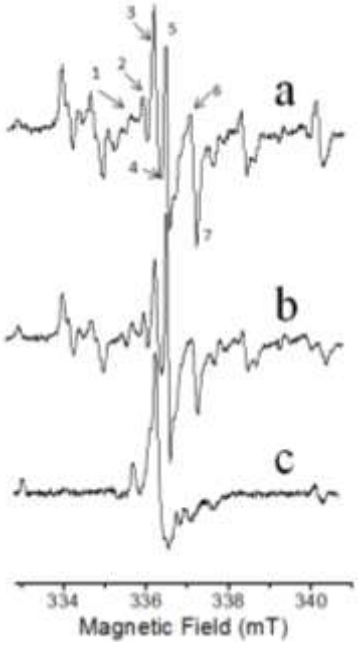

Fig.1 EPR spectra for samples irradiated with a) 5 MeV electron beam; b) gamma radiation and c) 290 MeV/u Carbon beam.

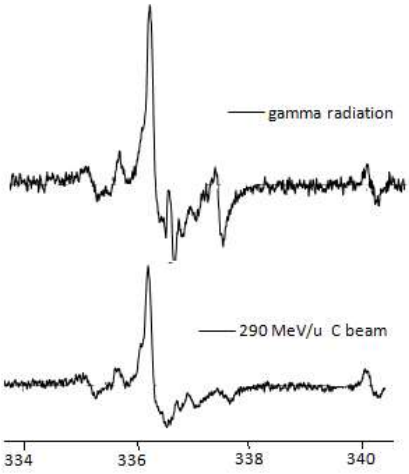

Fig.2 EPR spectra for samples irradiated with a) gamma radiation and b) 290 MeV/u Carbon beam with a dose of 1.5 kGy.

The signal at g=2.0031was assigned to CO_3^{3-} (McMillan and Marshall 1968).

Figure 1 shows the EPR spectra of the samples irradiated with the 5 MeV electron beam, ^{60}Co gamma rays and 290 MeV/u Carbon beam. Figure 2 shows the EPR spectra for samples irradiated at 1.5 kGy with gamma radiation and 290 MeV/u Carbon beam. As these figures

show, the EPR spectra of the electron- and gamma-irradiated samples present the same pattern, but the populations of the radicals develop slightly differently. The sample irradiated with the Carbon beam shows differences in the intensity of the signals and the general aspect of the spectra. In this sample the signal g=2.0058 (peak 3) is the highest signal, and the signal at

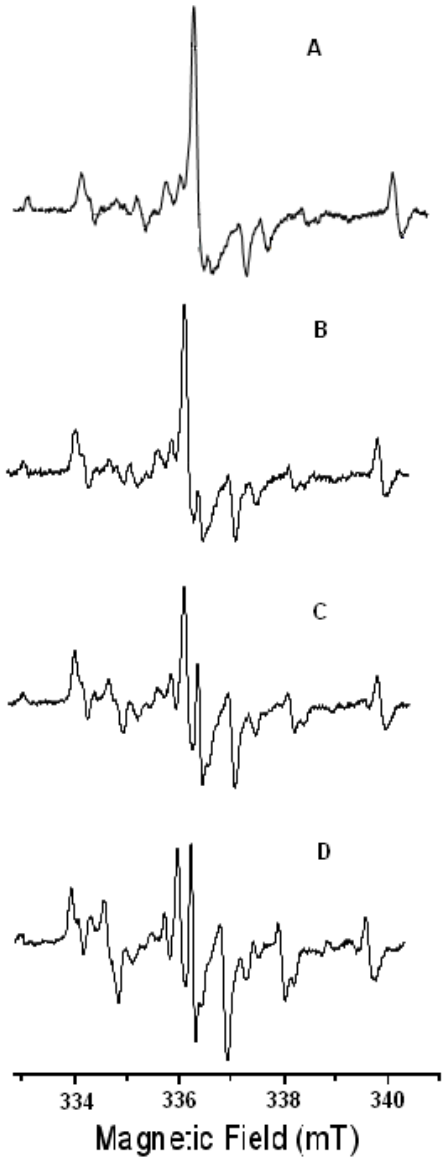

Fig. 3 Effect of the irradiation dose in the EPR spectra of calcium Carbonate irradiated with 5 MeV electron beam. Legend A= 0.74 MGy, B=1.5 MGy, C=6.5 MGy and D=9 MGy.

g=2.0034 (peak 5) is practically absent in relation to the electron- or gamma-irradiated samples at the same doses (1.5 kGy).

The samples irradiated by gamma rays at low doses (800 Gy) and high doses (1.5 MGy and 5 MGy) present the same signals (not shown) and another small signal, g=2.0031. These signals increase with the dose

Figure 3 shows the EPR spectra for samples irradiated with the 5 MeV electron beam at different absorbed doses. A small signal with g=2.0058 appears when the material is not exposed to ionizing radiation. As the irradiation dose increased, peak 3 decreased and peak 5 increased regularly.

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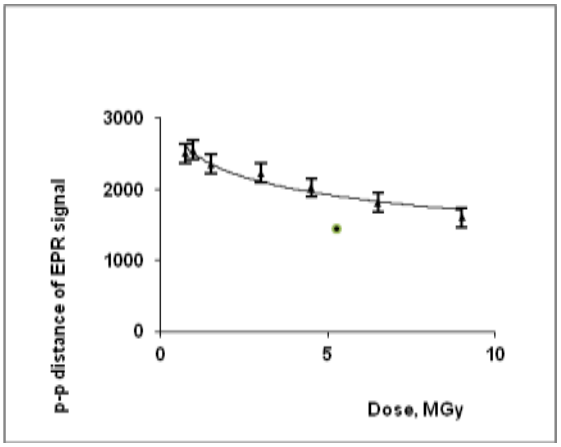

Fig 4 EPR signal intensity in arbitraries units for the peak 3 in a sample irradiated with electron beam

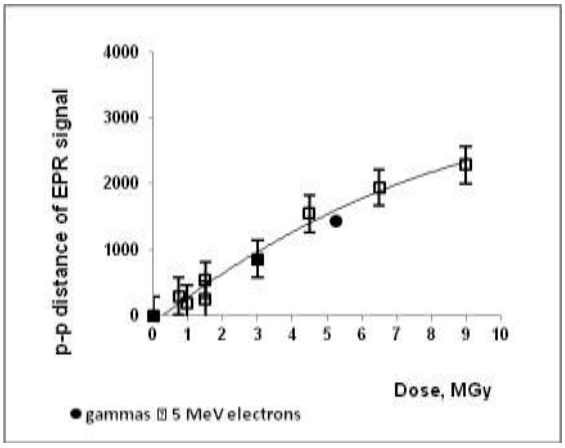

Fig 5 EPR signal intensity in arbitraries units for the peak 5 in a sample irradiated with electron beam

The response of calcium carbonate to high-energy radiation (electrons and some points for gamma radiation) is presented in Figures 4 and 5 as EPR signal intensity in arbitrary units versus absorbed doses in the range 0.7-9 MGy for the peaks (3) at g=2.0058 and peak (5) at g=2.0034. All signals (except g=2.0058) grow with the adsorbed dose. The signal at g=2.0006 (peak 6) is present in the samples, but it is not the principal signal. The signal at g=2.0034 (peak 5) is the most important line in the spectrum at high doses, and can be followed for more than one year. An experiment changing the microwave power from 0.25 mW to 32 mW for samples irradiated with electrons (6 MGy), gamma radiation (5.25 MGy) and 290 MeV/u Carbon beam, allowed us to distinguish whether there were two

signals centered at g=2.0034 and 2.0031 or if they were on the same line (Figures 6 and 7). Microwave saturation begins at around 10 mW. In these experiments, the sample irradiated with gamma radiation presented a greater signal strength for the peak at g=2.0034 (peak 5), as well as a lower strength of the signals at g=2.0058 (peak 3) and at g=1.998 (peak 7). For the sample irradiated at 6.5 MGy with electrons, this signal showed lower intensity. These results led us to conclude that electrons and gamma radiation produced different population of the same type of radicals.
The solid dosimeter does not present a good response to heavy ion irradiation, perhaps due to the low irradiation dose used or to a different penetration and/or interaction into the sample.

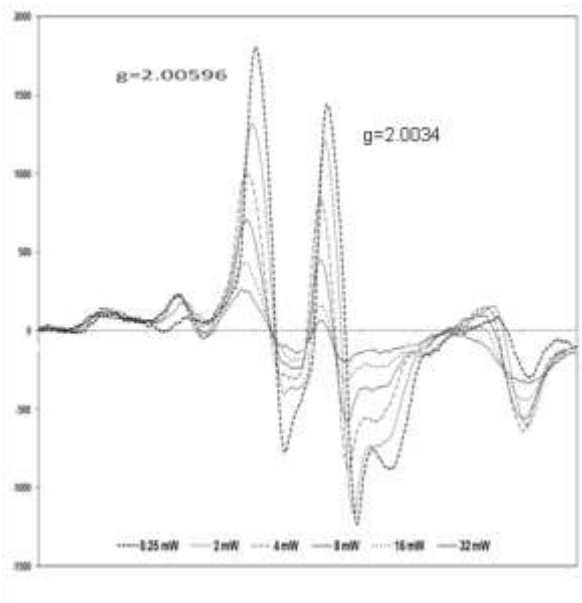

Fig 6 EPR spectra of a sample irradiated with 5 MeV electrons with a dose of 6.5 MGy at different microwave power

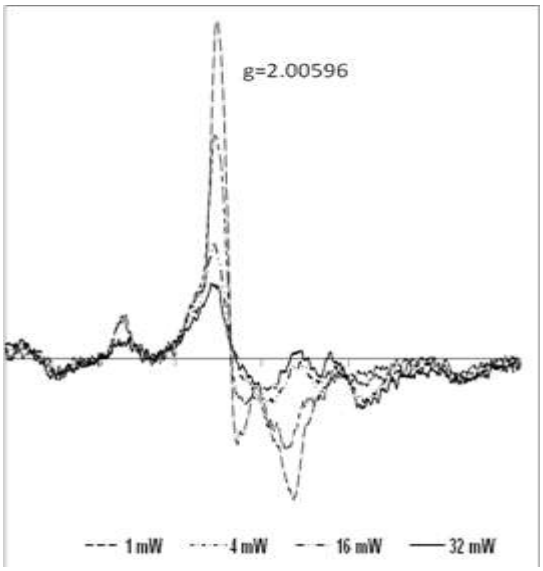

Fig 7 EPR spectra of a sample irradiated with 290 MeV/u Carbon beam with a dose of 1.5 kGy at different microwave power.

Heavy ion irradiation may have formed different species, thought the crystal lattice damage. However, little is known about this damage produced on minerals like carbonates (Nagabhushana *et al.* 2008, Pabst *et al.* 2010) and the interaction with C ions may yield different species. Further studies are needed to know the nature and changes in the structure of the carbonates induced by heavy ions, and the possible formation of CaO and CO_2.
The fading of the samples was followed by analysis at different periods after irradiation to measure the signal evolution over time. The signals changed approximately 2% globally over 40 days. It was possible to follow the signal for more than one year after irradiation with the different types of energy used.

There are potential complications to the use of calcium carbonate as a high-dose dosimeter. Its use is limited to commercial synthetic samples with high quality, because with natural samples, the EPR spectra can change considerably from one sample to the next and can become complicated by paramagnetic impurities. Additionally, the stability of the EPR centers may change with the nature and mineralogy of carbonates (Bahain *et al.* 1994). Some samples were irradiated with a different commercial trademark and there was no difference, but changing the counter-ion from Ca^{2+} to Mg^{2+} produced changes in the spectra.
The spectra are composite and may behave differently as a function of the type of irradiation used. On the other hand, it is known that the irradiation of solid carbonates can induce the formation of organic compounds (Albarrán and Collins, 1994), which will contribute to the signals at approximately at g=2.005 (peak 3) and at g=1.998 (peak 7).

4. REMARKS

We studied the behavior of calcium carbonate as a powder under high-radiation doses. We used EPR spectroscopy to follow the variation in signals with increasing absorbed dose. The response of two of the free radicals detected is not linear, but is represented by a second-order polynomial function. Two types of radiation (gamma and electrons) produced the same radicals observed. Further studies are needed for the behavior with heavy ions. The analysis is reproducible, the samples are easily prepared for irradiation, measurements and they are stable for a long period of time (more than a year). The preliminary results show that systems using $CaCO_3$ may serve to measure high irradiation doses, especially for electron irradiation.

Acknowledgments

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