Applied Radiation and Isotopes 111 (2016) 26–30

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Effects of temperature during the irradiation of calcium carbonate

Alicia Negrón-Mendoza [a,*], Claudia Camargo-Raya [a], Virginia Gómez-Vidales [b], Roberto M. Uribe [c], Sergio Ramos-Bernal [a]

[a] Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México (UNAM), México D.F. 04510, México
[b] Instituto de Química, Universidad Nacional Autónoma de México UNAM, México D.F., México
[c] Kent State University College of Applied Engineering, Sustainability and Technology, Kent, OH, USA

HIGHLIGHTS

- Gamma irradiation of $CaCO_3$ at different doses and temperatures was studied.
- High radiation induces the formation of free radicals in solid calcium carbonate.
- Gamma irradiation of $CaCO_3$ produced a composite spectra measured by EPR.
- There is a strong effect on the radicals formed as a function of temperature.

ARTICLE INFO

Article history:
Received 1 November 2015
Received in revised form
1 February 2016
Accepted 9 February 2016
Available online 13 February 2016

Keywords:
Calcium carbonate
Gamma radiation
Low temperature
Free radicals

ABSTRACT

Calcium carbonate received gamma irradiation at different doses (0–309 kGy) and temperature regimes (77–298 K) to study the effects of irradiation temperature. The changes were followed by EPR spectroscopy. We observed the formation of a composite EPR spectrum, even at low radiation doses and temperature. There was a strong effect on the evaluation of the radicals formed as a function of irradiation temperature, probably due to the diffusion in the frozen powder and the recombination of some radicals at room temperature.

1. Introduction

High radiation induces the formation of free radicals in solid calcium carbonate that are detectable and measured by electron paramagnetic resonance (EPR). Natural samples from minerals like limestone, invertebrate exoskeletons, and mineralized tissues (teeth, bones) reveal several paramagnetic centers that are present from gamma-irradiated calcium carbonate, as part of their constituents. Therefore, they are attractive minerals for dating, retrospective dosimetry, and other applications in the natural sciences. Those paramagnetic centers remain for thousand years, if trapped, and their concentration increases with the dose (Seletchi and Duliu, 2007). However, the EPR spectra differ between natural and synthetic samples and according to the samples' origin.

On the other hand, the use of high-energy electrons or gamma radiation to modify and improve the properties of materials is a well-established technique at ambient temperature (Woolston et al., 2009). However, other applications involve irradiation at low temperatures to increase the reaction efficiency, which decreases the number of free radicals in the bulk material. Polyethylene fibers can be co-polymerized with several chemical compounds at low temperature (dry ice temperature, 195 K) to produce free radicals in the bulk polymer. Later on, the irradiated polymer is put in contact with the grafting material, and these active chemical species promote chemical grafting (Rohani et al., 2007; Hajare et al., 2010). In addition, more experiments are simulating the low-temperature conditions of extraterrestrial environments, and a reliable dosimeter at the conditions used is necessary to control the process and measure the dose.

This research was focused on studying whether an irradiation temperature dependency exists in calcium carbonate when it is exposed to gamma rays at low temperatures (77 K, 195 K, and 298 K), and evaluates its possible uses as a dosimeter for low-temperature irradiation.

* Corresponding author.
E-mail address: negron@nucleares.unam.mx (A. Negrón-Mendoza).

http://dx.doi.org/10.1016/j.apradiso.2016.02.004
0969-8043/

2. Materials and methods

2.1. Samples

Commercially obtained samples of calcium carbonate from Sigma-Aldrich Co., USA, with 99.95% purity were used without any purification as powder. Other carbonate samples from different trademarks were analyzed to compare with the Sigma-Aldrich sample. Additionally, a calcium sulfate sample was also measured. Samples were placed in the Dewar cylinder irradiation assembly and thermally equilibrated for at least one hour before placement at the gamma source. After irradiation, the samples were kept in an entirely dark place with controlled humidity before analysis. Using X-rays, we confirmed that there is no damage to the crystal structure even at high radiation doses, and that it corresponds to a calcite crystal structure.

2.2. Dosimetry

To prepare the solutions, we used triple-distilled water according to the standard procedures used in radiation chemistry (O′ Donnell and Sangster, 1970). A Fricke-copper dosimeter was used for the source calibration. The optical density value was measured by UV spectrophotometry at 304 nm using a “Cary 100” instrument. The doses were corrected by the reading temperature.

2.3. Irradiation

Irradiations were carried out at the 60-cobalt Gammabeam 651 PT irradiation facility at Instituto de Ciencias Nucleares, UNAM. The samples were irradiated at selected irradiation times in a closed glass tube, inside a Dewar flask filled with different refrigerant solutions to produce different irradiation temperatures. The dose rate at room temperature was 197 Gy/min.

2.4. Electron paramagnetic resonance (EPR) measurements

The EPR measurements were made in a Jeol JES-TE300 spectrometer at Instituto de Química, UNAM, operating at X-Band with a 100 KHz modulation frequency and a cylindrical cavity in the mode TE_{011}. The magnetic field received external calibration with a precision gaussmeter, Jeol ES-FC5. For the geometry in the cavity to be reproducible, the samples were placed in a flat-type quartz cell. Then, they were measured at room temperature.

The spectrometer settings for all of the spectra were as follows: center field, 335.4; microwave power 1 mW, microwave frequency 9.43 GHz, modulation width 0.079 mT; time constant 0.1 s; amplitude 1×100; sweep time 120 s; 2 scans. The readings were made at the vertical peak-to-peak height of the line, which is marked with an asterisk in the figures shown below. Spectral acquisition and manipulations were performed using the program ES-IPRITS/TE. The EPR spectra were recorded as a first derivative, and the main parameters, such as the g-factor values, were calculated according to Weil et al. (1993). There was no significant difference regarding whether the irradiations were performed in fractions rather than in a single continuous irradiation (less than ~1%). The EPR readings of the duplicate samples had a difference of less than 1%. The response of the dosimeter was measured as the peak-to-peak distance of the first derivative of the EPR signal.

Additionally, we measured a sample that was irradiated at 85 kGy; and at 77 K, we changed the temperature in the spectrometer from 113 to 295 K, left it at room temperature for 21 h, and measured its EPR spectrum again.

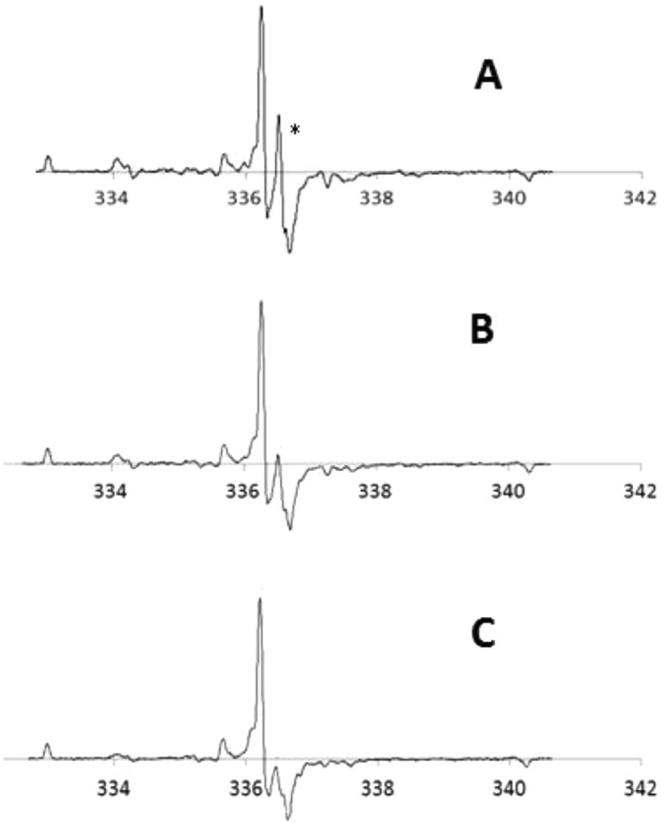

Fig. 1. Effect of the irradiation dose in the EPR spectra of calcium Carbonate irradiated with gamma radiation at 298 K. Legend: (A) 309.7 kG; (B) 144 kGy; (C) 70.9 kGy.

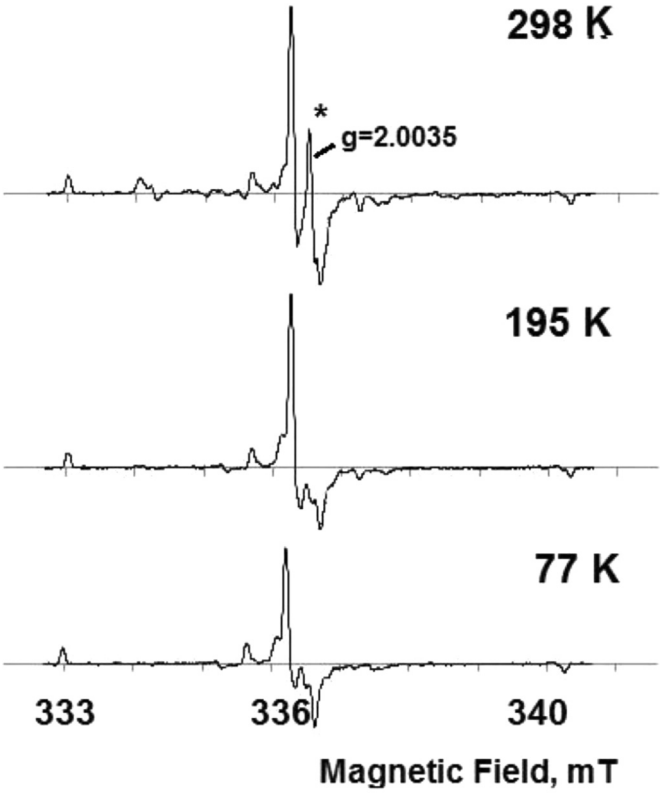

Fig. 2. Effect of the irradiation temperature in the EPR spectra for samples irradiated with gamma radiation at the same time and at (A) 298 K, (B) 195 K and (C) 77 K.