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A study based on ESR, XRD and SEM of signal induced by gamma irradiation in eggshell

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Abstract

ESR (electron spin resonance), XRD (X-ray diffraction) patterns and SEM (scanning electron microscopy) of irradiated calcium carbonate ($CaCO_3$) in eggshell was investigated. The ionizing radiation produces an electron centre CO_3^{3-}, a hole centre CO_3^-, and the CO_2^- molecular ion also formed. The ESR centre with $g_{//} = 1.9977$ and $g_{\perp} = 2.0021$ was identified as the same found in hydroxyapatite. The work aims to standardize the samples preparation method and the conditions of measured for practical application by the specialist in emergency dosimetry. In this regard, practical consideration of sample preparation conditions and properties such as grain size, ESR spectra, and the temperature dependence of the signal were studied in detail. Dose response appears to be linear between 3 Gy and 1 kGy. No dose rate dependence was observed. The morphology of the calcined eggshell presented extensive morphological change on the calcinations process. Careful analyses of the ESR spectra are presently in progress in order to undertake and identify the radicals involved.

Keywords: Dosimetry; Radiation accident; ESR; Eggshell; Calcium carbonate

1. Introduction

More types of retrospective dosimeters are needed to handle all accident contingencies. Reflecting on this event the IPEN (Instituto de Pesquisas Energéticas e Nucleares) and the IFUSP (Instituto de Física da Universidade de São Paulo) have sponsored studies directed on the possible occurrence of accidental overexposure.

By using signals from long-lived free radicals induced by ionizing radiation in crystals, ESR spectrometry can reconstruct accidental exposures. ESR is a non-destructive technique that applies physical principles based on the number of unpaired spins created on irradiation.

The $CaCO_3$ crystalline phases found in eggshells show a strong ESR signal that grows linearly with added dose over a large range of dosage, and its stability suggests that this material can be used in dosimetry (Kai et al., 1988).

Elementary defects induced by ionizing radiation are comprised of electron and hole centres, CO_3^{3-} and CO_3^-. An oxygen vacancy with an electron, actually the CO_2^- molecular ion, is also formed by radiation (Serway and Marshall, 1967; Baffa and Mascarenhas, 1985; Calens et al., 1987; Skinner, 1989, 2000; Debuyst et al., 1991; Barabas, 1992; Ikeya, 1993; Oduwole et al., 1993; Onori and Pantaloni, 1995; Kai, 1996; Stoesser et al., 1996; Schramm et al., 1998).

2. Materials and methods

The chicken eggshells were washed in distilled water and the inner membrane was removed. After drying, the eggshells were crushed manually to obtain powder with grain size between 80–200 μm.

Each 200 mg of sample was irradiated with dose ranging from 3 Gy to 1 kGy by γ-rays from a ^{60}Co source, at room temperature, under electronic equilibrium conditions. Such condition exists when the number and energy of secondary electrons (generated by the primary photons) entering the volume of

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interest are equal to the number and energy of the secondary electrons leaving this place. In our case the electronic equilibrium was established by surrounding the samples with 3 mm of Lucite™. After irradiation, the dosimeters were stored for approximately 24 h to eliminate ESR transient signal.

The ESR measurements were performed using a conventional X-band spectrometer Bruker–EMX (Bruker Instruments, Billerica, MA) with a standard rectangular cavity (model ER 4102 ST). The spectra were obtained using the field modulation of 100 kHz, the microwave power was 0.2 mW, frequency of 9.727 GHz and 348.0 mT central magnetic field.

The XRD (X-ray diffraction) patterns of eggshell samples were obtained using Rigaku DMAX 2000 XRD, which was operated at 40 kV and 20 mA with a scanning speed of $2° min^{-1}$.

A study of shell samples using SEM (scanning electron microscope) was initiated to observe the microscopic structures and morphological characteristics of the eggshell powder.

3. Results and discussion

Fig. 1 shows the first derivative of the ESR absorption spectrum at room temperature for an irradiated eggshell powder in which three molecular ions, CO_3^{3-}, CO_3^- and CO_2^- are observed. The g values are indicated.

Under ionizing irradiation, the $CaCO_3$ contained in the eggshell loses one electron leaving a hole in the CO_3^- molecular structural unit of the microcrystalline calcite structure. The released electron can be trapped by another CO_3^{2-} unit, forming thus an electron centre, CO_3^{3-}.

The orthorhombic and axial CO_2^- molecular ions shows the anisotropic lines centred at $g=1.9977\pm0.0002$. They have been reported due to the radiation-induced inorganic free radicals (Marshal et al., 1964; Murata et al., 1993; Oduwole et al., 1993; Regulla et al., 1994; Wieser et al., 1994; Onori and Pantaloni, 1995; Engin and Demirtas, 2004).

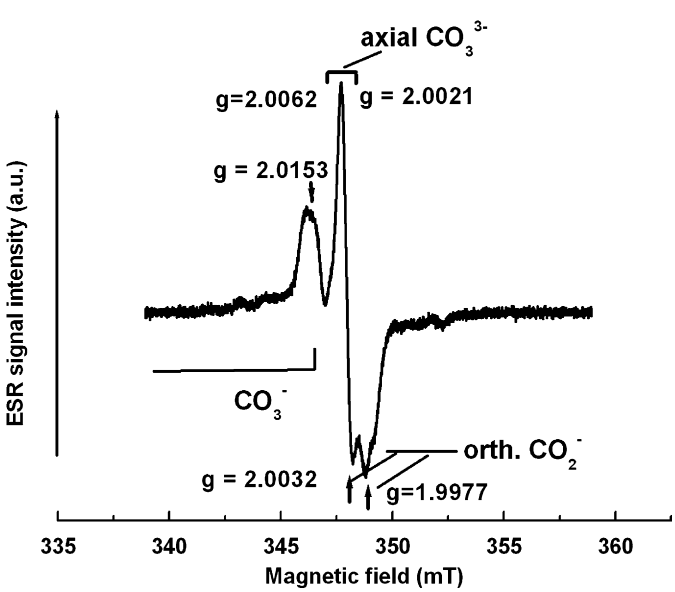

Fig. 1. First derivative of the absorption curve (arbitrary units) of powder eggshell irradiated with ^{60}Co gamma-rays (500 Gy) at room temperature with respect to the applied magnetic field (mT).

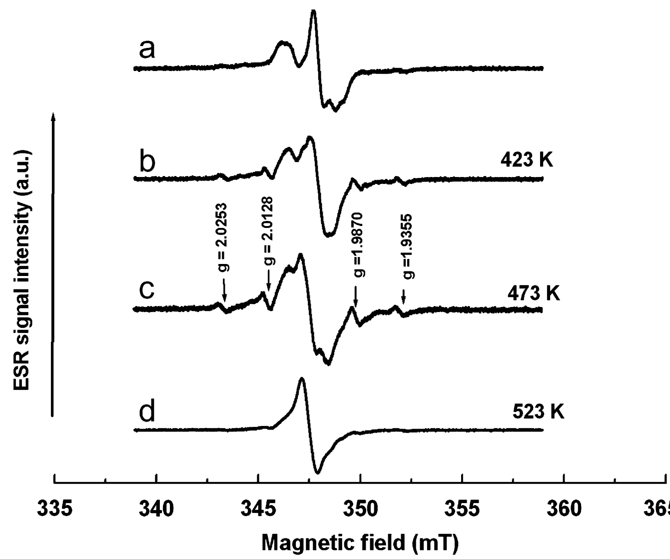

Fig. 2. First derivative of the ESR curve (a.u.) of powder eggshell irradiated (500 Gy) with respect to the applied magnetic field (mT): (a) without thermal treatment; (b) 423 K; (c) 473 K; (d) 523 K. The annealing time was 1 h for all temperatures.

The spectrum is the same for other doses, the intensity increases linearly with the absorbed dose and their spectral features are comparable to those previously observed in irradiated calcite (Regulla et al., 1994).

The thermal stability (see Fig. 2) of the $g = 2.0021$ centre was studied in order to establish whether a change in spectral form occurs. The annealing time was 1 h for all temperatures after the irradiation.

At the temperatures between the 423 and 473 K superposition of a hyperfine structure was observed. This signal quartet seems to grow by the heating process which may be due to combusted organic compounds. The radiation was found to have no effect on organic signal. In these organic radicals, unpaired electrons interact with nearby protons, and then the ESR signal is split into two lines by coupling with the nuclear spin of a proton. Each line is split into two further lines because the presence of the additional protons. These effects were similarly observed with the eggshells exposed to u.v. light at room temperature (Regulla et al., 1994).

After heating at 473 K the previously observed spectrum has disappeared and a strong new single line centred at $g \sim 2.0006$ appeared (523 K).

Fig. 3 shows powder XRD pattern for an eggshell. It is in excellent agreement with the pattern for calcite (JCPD card number 5-0586). The intensity correspondence is very good, despite larger line broadening. The changes in the pattern are observed only when the temperature is increased to 1073 K. In this case the calcium carbonate ($CaCO_3$) transforms into calcium oxide (CaO) producing also carbon dioxide (CO_2) (Muñoz et al., 2003).

The treatments at the higher temperatures eliminate the CO_3^{2-} units by releasing CO_2, leaving CaO in the place of the

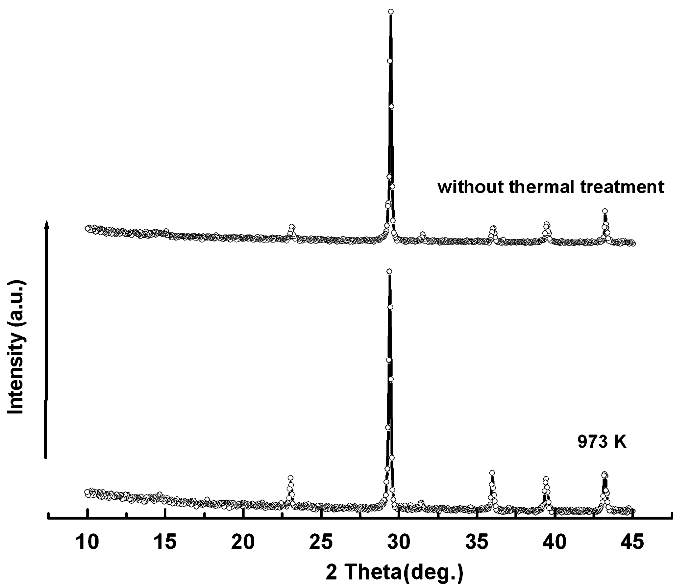

Fig. 3. X-ray diffraction pattern for eggshell: (a) without thermal treatment; (b) with thermal treatment 973 K.

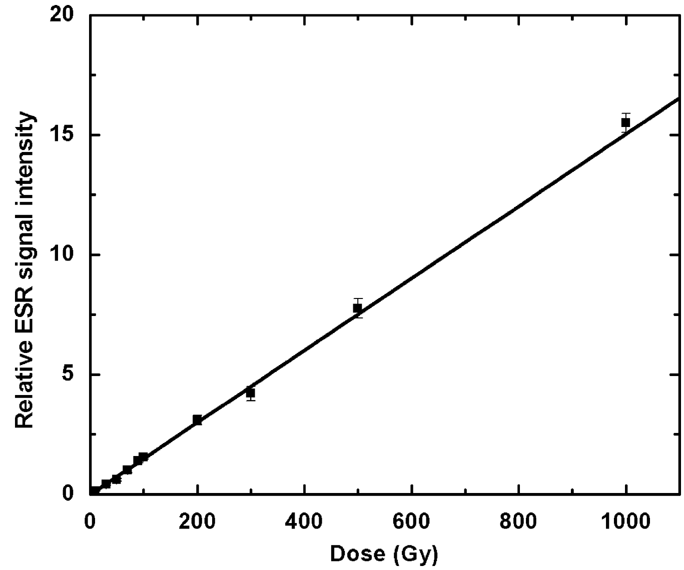

Fig. 5. Dose response curve of powder eggshell irradiated with gamma rays of ^{60}Co at room temperature.

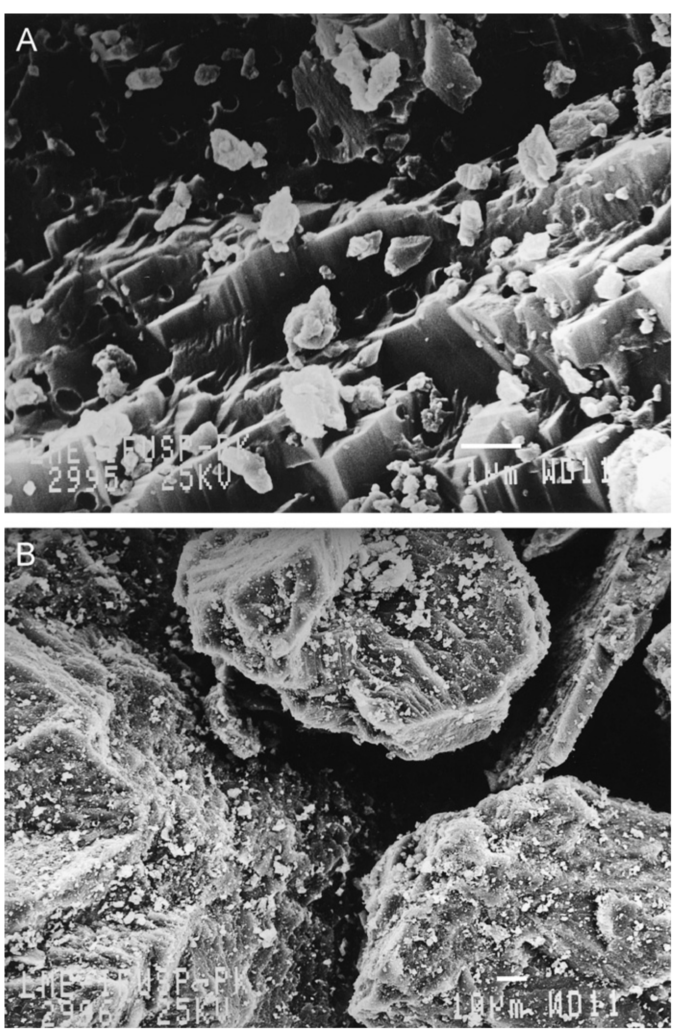

Fig. 4. Photomicrograph of powder eggshell (grain size $< 80\,\mu m$): (A) raw sample; (B) heated (673 K during 1 h).

carbonate. Thus the strong ESR line at $g \sim 2.0006$ is the hole centre left by the ionization of the O^{2-} ion of CaO.

Fig. 4 shows a photomicrograph of eggshell powder, presenting the morphology of its constituent material. The samples were divided into two groups: one part was not heated (Fig. 4A) and the other heated to 673 K for 1 h (Fig. 4B). With the magnification showed in Fig. 4A it is possible to observe the interface between the smooth and granular regions, where the samples are seen to be aggregates of smaller fractions tied together by their organic component.

The outer region appeared to be effectively completely mineralized with a micro-texture. In the inner part a block-like structure of 2–3 μm × 3–4 μm a less compact area exist with an organic structure of fibrous sheets.

The morphology of the heated eggshell is shown in Fig. 4B, where it is apparent that these samples present an extensive morphological change on the calcinations process. At higher temperature, the surface of the crystals was roughened, and polycrystalline aggregates were observed. Some authors have shown that $CaCO_3$ phase was detected in raw eggshell while the CaO was detected in the calcined eggshell. The $CaCO_3$ was completely decomposed and changed to CaO at about 1073 K (Lee and Oh, 2003; Muñoz et al., 2003).

The dose dependence of the signal amplitude was found to be linear with the dose (Fig. 5). The non-irradiated sample has produced an ESR background signal that was subtracted from all the measurements. The post-irradiation fading resulted in no-significant decay.

4. Conclusion

Studies of nature and properties of radiation defects in calcium carbonates are promising for ESR dosimetry. The radiation-induced $g = 2.0021$ ESR centre in eggshells was found to be appropriate for dosimetry in range from 3 Gy to 1 kGy, with a precision of 95%. Because of its thermal stability, the eggshells appeared promising for dosimetric applications. Eggshells represent a reliable alternative dosimeter for high-level area and accident dosimetry, because they are common in most households.

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