Journal of the Korean Magnetic Resonance Society **2004**, *8*, 37 - 46

ESR Study on the Thermal Annealing Effects of Irradiated Human Tooth Enamel by X and γ-rays

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Received April 1, 2004

Abstract : When human tooth enamel is exposed to the X-ray or γ-rays, free radicals and defects are created in a small quantity of carbonate enclosed in the tooth enamel. The intensity of the ESR signal of the free radicals is almost proportional to the absorbed radiation dose. However this dosimetric character is affected to some extent with the measurement temperature and thermal treatment of the samples. We found that the shape of the ESR signals of the samples is dependent upon the measurement temperature, the thermal annealing prior to the irradiation and that after the irradiation.

INTRODUCTION

The electron spin resonance(ESR) spectrometry for the samples of tooth enamel has been extensively used for radiation dosimetry [1-4], geological, archaeological dating [1-2,5], and medical purpose.[6-7] The ESR signal by irradiated tooth enamel results from the carbonate included 3 ~ 4 % in hydroxyapatite.[8]

In general, when tooth enamel is exposed to a radiation X-ray or γ-ray, free radicals are created as carbonate-induced radicals of CO_2^-, CO_3^-,CO_3^{3-} etc. The ESR signal of the radicals is observed because of the paramagnetic property of the free radicals.[9-10] The shape of ESR signal is variously asymmetric near $g = 2$ and the measurement of ESR dosimetry is

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based on the peak-to-peak amplitude of the signals.[11-12]

The intensity of ESR signal of these free radicals is almost proportional to the absorbed radiation dose, but the shape of ESR signal is peculiarly changed slowly with respect to time, since only the free radical CO_2^- is stable and other free radicals are unstable and changeable. Especially, the saturation characteristics of ESR signals are not only changed due to defects as well as free radicals included in hydroxyapatities, but also due to the thermal annealing of them.[8,13]

The aim of our research is to identify the dominant free radical species and to investigate the thermal effects of ESR dosimetric signals of the samples. Also, we compare the properties of preannealed samples with those of postannealed ones.

EXPERIMENTAL PROCEDURE

Human tooth extracted through dental treatment was obtained from practicing dentists The tooth enamel samples were cut and removed mechanically from human teeth by dentine cutter microsaw. We prepared the enamel for the sample to be crushed and sieved to diameter about 0.3 ~ 0.5 mm grains to remove anisotropic ESR signal.[8,14] The human tooth enamel was irradiated with a continuous spectrum of X-rays with average photon energy of about 6 MeV and γ-rays from ^{60}Co photons. The doses are controlled by different exposing times. Preannealed tooth enamel was prepared by thermal treatment prior to irradiation and postannealed one was made through opposite process. We prepared both preannealed tooth enamel and postannealed one through heating from 293 ~ 523 K for 30 min at each step.

A quartz tube containing a 50 *mg* sample was put into the cavity of the ESR equipment. We used a JEOL, JES PX2300 system as the ESR spectrometer. The ESR spectrometer was operated with X-band, which means a 9.48 GHz microwave frequency for the resonance, with a 100 kHz modulation, and its amplitude 0.2 mT. Isothermal heat treatments were carried out for those samples in muffle furnace in which they were placed at temperature in the range of 293 ~ 523 K in air for 30 min at each step.

RESULT AND DISCUSSION

Fig. 1 shows the ESR absorption signal intensity (I_1 + I_2 shown in Fig. 2) due to dosimtric free radical(CO_2^-) of both tooth enamels heated prior to irradiation, and ones heated after irradiation for 30 min in the annealing temperature range of 293 ~ 523 K at each step.

In the range of 293 ~ 373 K, there is almost the same ESR signal intensity for those samples but it varies above 373 K. The ESR absorption signal intensity of the preannealed tooth enamel and the postannealed one at 443 K are increased to about 18 and 25% respectively, in comparing with unheated irradiated tooth enamel with 50 Gy. We propose that this is due to different amount of water molecules included in tooth enamel according to the process of heat treatment. That is, after irradiation of samples, the defects, CO_2, CO_2^{2-} ,CO_3^{3-} etc., are created in tooth enamel. As suggested by Murata et al.[15], these defects can be considered as follows:

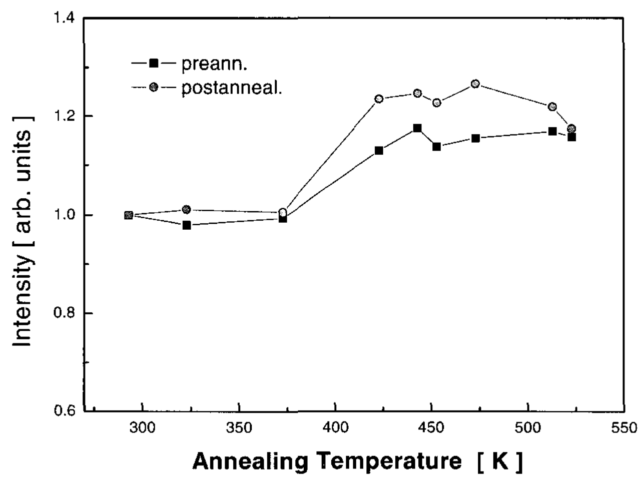


Fig. 1. Intensities of the ESR signal of both preannealed tooth enamels and postannealed ones irradiated with 50 Gy are measured at room temperature as a function of the annealing temperature.

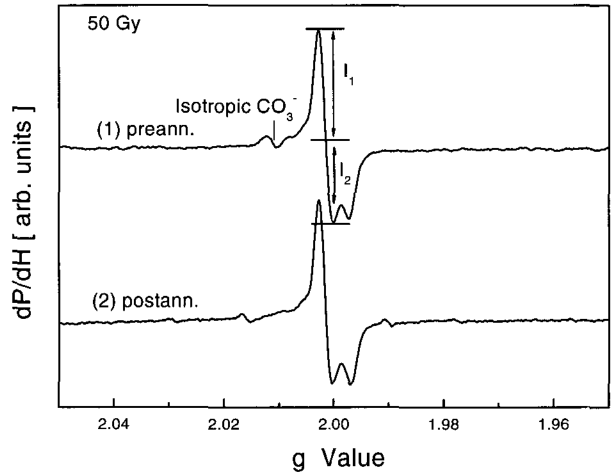
$$CO_2 + \text{water} + e^- \rightarrow CO_2^- + \text{water}.$$
$$CO_2^{2-} + \text{water} + \text{hole} \rightarrow CO_2^- + \text{water}.$$
$$CO_3^{3-} + \text{water} \rightarrow CO_2^- + O_2^- + \text{water}.$$

Therefore, in case of preannealed sample, the intensity of ESR signal is relatively smaller than postannealed spectrum. Because the defects created from irradiated tooth enamel is less influenced by water molecules in case of preannealed sample as compared with postannealed one. In the region of $T \geq 293$ K, the intensity of the ESR signal increases until it reaches about 27% in case of postannealed tooth enamel at 473 K; however, in the region of $T > 473$ K, the intensity of the ESR signal decreases with increasing annealing temperature.

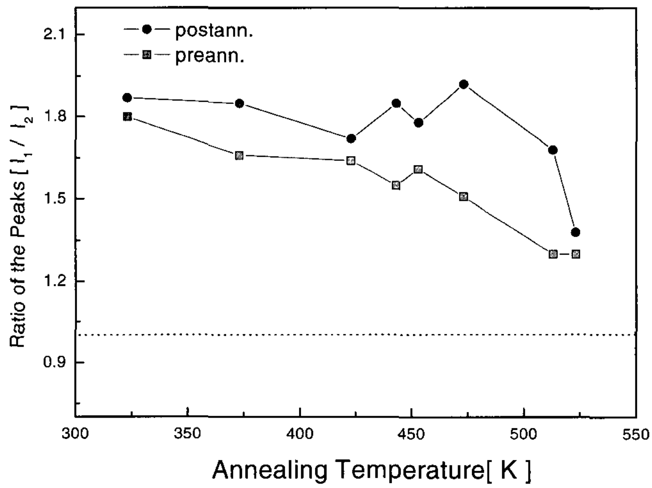
The ESR absorption signal intensity of preannealed tooth enamels, in the range of 453 K $\leq$ T $\leq$ 523 K, is shown to increase be almost same. They have been measured almost same to both irradiated tooth enamels pre- and postannealed for 30 min at 523 K. Fig. 2 shows the ESR spectra (Fig. 2 (a)) and signal intensity ratios (I_1/I_2) of both pre- and postannealed tooth enamel samples for 30 min irradiated with 50 Gy (Fig. 2(b)).

Top spectrum at typical g-value about $g = 2.0114$ of Fig. 2 (a) shows the signal of isotropic CO_3^- radical with preannealed sample at 453 K, but with postannealed one (bottom spectrum of Fig. 2 (a)) it is not detectable. We suggest that this is attributed to the increased lattice vacancy due to removal of organic materials and water molecules included in tooth enamel by heat treatment prior to irradiation. Whereas, in case of postannealed samples, the ESR spectrum shows additive signal of organic radicals instead of CO_3^- radical above the annealing temperature 423 K for 30 min.[16]

Fig. 2 (b) shows the ESR signal intensity ratios (I_1/I_2) of both pre- and postannealed samples shown in Fig. 2 (a). The peak ratios (I_1/I_2) were slowly decreased in preannealed tooth enamel samples with increasing annealing temperature. The peak ratio of the ESR signal intensity was measured about 1.3 at 523 K. However, the peak ratio of ESR signal intensity in postannealed samples was estimated almost averaged value of about 1.8 in the temperature range of 293 ~ 473 K and T 〉 473 K, and this ratio decreased with increasing annealing temperature. Therefore, the ESR spectra of postannealed samples result from the dominant orthorhombic CO_2^- radicals ($g_x = 2.0030$, $g_y = 2.0016$, $g_z = 1.9973$) in the range of 293 K $\leq$ T $\leq$ 473 K.



(a)



(b)

Fig. 2. ESR spectra at 453 K; (a) and intensity ratios(I_1/I_2) from the ESR spectra of both preannealed samples and postannealed ones for 30 min in the annealing temperature range 320 ~ 523 K irradiated with 50 Gy; (b).

Whereas, preannealed samples can be shown by a relatively increasing the number of tumbling CO_2^- radicals of g = 2.0006 with annealing temperature. The increased tumbling CO_2^- radicals of preannealed sample can be explained by the increased lattice vacancies near CO_2^- radicals with temperature. This effect is measured by the fact that the intensity ratios (I_1/I_2)of ESR signal in the preannealed samples decrease as the intensity I_2 increases until it reaches at 523 K.

In the postannealed samples, the peak-to-peak linewidth of CO_2^- radicals remains unchanged until the 453 K and the intensity ratios (I_1/I_2)of ESR signal decrease as the intensity I_2 increase from 473 K to 523 K. This is due to the increase of isotropic CO_2^- since the organic radicals are evaporated above 473 K. In the region of T ≥ 493 K, we measured the ESR spectrum of isotropic SO_2^- (at g = 2.0055, as shown in Fig. 3) radical of both irradiated teeth enamels with 50 Gy pre- and postannealed.

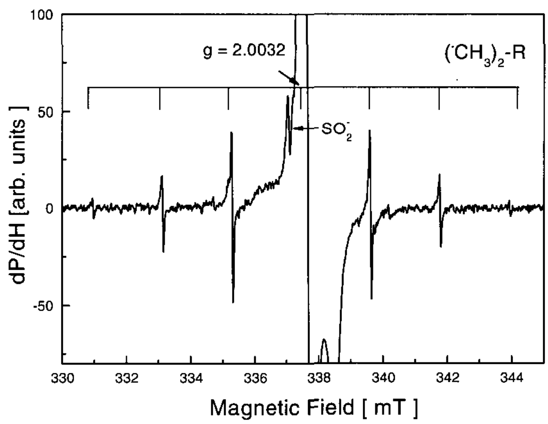
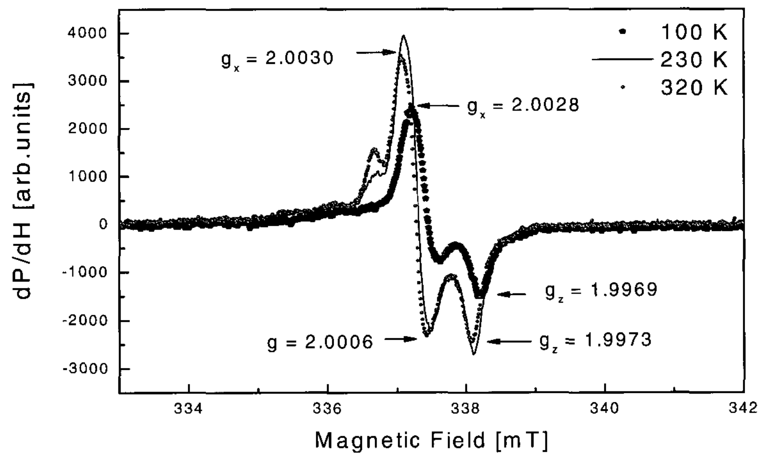
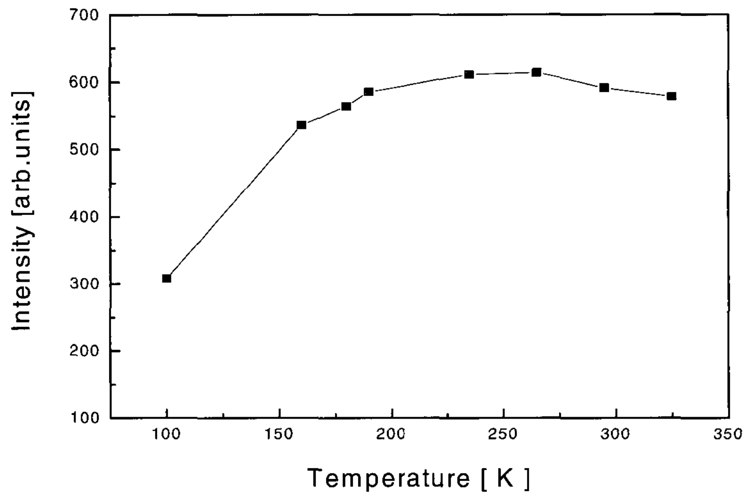


Fig. 3 ESR spectrum of postannealed tooth enamel (radiated with 3 kGy) at 453 K is measured at room temperature. This shows septet components of the signal.



(a)



(b)

Fig. 4. ESR signals at various temperatures (a) and intensities of the ESR signal compared with the signals at 320 K (b) of unheated tooth enamel (radiated with 0.5 kGy) as a function of temperature.

Fig. 3 shows the ESR absorption spectra of postannealed tooth enamel irradiated with 3 kGy, for 30 min of isothermal annealing temperature 453 K. As shown in Fig. 3, the ESR septet signal which is centered on the top of the CO_2^- signal at $g = 2.0032$ whose sample was postannealed above 423 K is measured in room temperature. However, this kind of septet signal isn't observed in preannealed samples. This free radical component was reported as a dimethyl $[(\bullet CH_3)_2 - R]$ radical by Vanhaelewyn et al.[9,17] too, although they are observed only a set of quintet components in a fossil hippopotamus tooth enamel.

As our experimental result, ESR signal centered at $g = 2.0032$, as shown in Fig. 3 is observed to consist of septet resonance lines with intensity ratios close to approximately 1 : 6 : 15 : 20 : 15 : 6 : 1 separated by about 2.2 mT. Thereby, we confirmed that it is the hyperfine structure of the dimethyl radical.

Fig. 4 shows the ESR signals at various temperatures ; (a) and the signal intensities compared with the signal at 320 K ; (b) of unheated tooth enamel as a function of temperature in the range of 100 ~ 320 K. Above 230 K, the ESR spectrum is dominated by an orthorhombic signal($g_x = 2.0030$, $g_z = 1.9973$) which is attributed to radicals CO_2^- etc. and below 230 K, axial component signals ($g_x = 2.0028$, $g_z = 1.9969$) of radicals CO_2^-. In the Fig. 4(b), the intensity of ESR signal decreases about 6% from 230 to 320 K. In the region of $T \leq 230$ K, the intensity of ESR signal decreases as the temperature is decreased.

CONCLUSIONS

When tooth enamel is under the heat treatment prior to and after irradiation, we have shown the differences of the ESR spectra attributed to a few different free radical species each other. In case of preannealing above 453 K, the ESR spectrum is dominated by CO_2^-, CO_3^- radicals etc. and in case of postannealing, it is dominated by CO_2^-, and dimethyl radical. Besides the ESR spectrum is dominated by an orthorhombic signals which are attributed to CO_2^- for the postannealed samples, whereas, it is dominated by an axial component signal for the preannealed samples. However, when the tooth enamels are under the heat treatment above 493 K, the ESR spectrum is detected with isotropic SO_2^- radical regardless of pre or postannealed samples.

According to the heat treatment at 453 K of irradiated tooth enamels with 50 Gy, the intensity of ESR signal of postannealed samples increased about 7% as compared with preannealed samples.

Therefore, these effects should be considered to understand and improve dose evaluation in using ESR dosimetry and archaeological dating etc..

Acknowledgements

We used a JEOL, JES PX2300 system as the ESR spectrometer in Cooperative Laboratory Center, Pukyong National University.

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