ES09: การเปรียบเทียบสัญญาณอิเล็กตรอนสปินเรโซแนนซ์ ของแคลไซต์ธรรมชาติก่อนและหลังฉายรังสี

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บทคัดย่อ

จากการศึกษาสัญญาณอิเล็กตรอนสปินเรโซแนนซ์ (ESR) ของแคลไซต์ธรรมชาติ ซึ่งรวบรวมจากจังหวัดสระบุรี ทางภาคกลางของประเทศไทย พบสัญญาณ ESR ที่เด่นชัดหกตำแหน่ง ใกล้เคียงบริเวณ g = 2.0000 ซึ่งสอดคล้องกับสัญญาณของ Mn^{2+} ที่มีนิวเคลียร์สปิน I = 5/2 หลังจากนำตัวอย่างฉายรังสีแกมมาที่ 1,000 Gy แล้ว พบสัญญาณ ESR ปรากฏเด่นชัดเพิ่มขึ้นที่ g = 2.0016 โดยสอดคล้องกับสัญญาณของ CO_2^- จากการวิเคราะห์สัญญาณ ESR นี้ แสดงให้เห็นว่า ปริมาณอิเล็กตรอนอิสระจะเพิ่มขึ้น เมื่อตัวอย่างผ่านการฉายรังสี ข้อมูลในงานวิจัยนี้สามารถใช้เป็นข้อมูลพื้นฐานที่สำคัญ สำหรับงานวิจัยทางด้านธรณีวิทยาและการหาอายุแคลไซต์ ด้วยวิธีการเพิ่มปริมาณรังสีได้

คำสำคัญ: ESR แคลไซต์ธรรมชาติ อิเล็กตรอนอิสระ การฉายรังสีแกมมา

Comparison of ESR Spectra of Natural Calcite before and after Gamma Irradiation

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Abstract

Electron Spin Resonance (ESR) of natural calcite samples collected from Saraburi province, in central Thailand, was investigated. The ESR spectra showed strong sextet hyperfine signals around g = 2.0000, corresponding to the nuclear spin of Mn^{2+} (I = 5/2) and resembled organic radicals. The radicals produced by gamma-irradiated natural calcite, whose *g* factors were near *g* = 2.0016, were attributed to CO_2^- center. The analysis of ESR spectra showed that the ESR signal intensity of these free radicals increased gradually with increasing absorbed dose. This analytical research has proven the reliability and dependability of ESR studies and could be of importance in providing reference data for ESR dating analysis additive irradiation method.

Keywords: ESR, natural calcite, free radicals, gamma-irradiation

1. Introduction

Electron Spin Resonance (ESR) occurs whenever a system such as an atom, a molecule, an ion, or a defect and impurities in a solid possesses unpaired electrons. In many cases, this condition is brought about by irradiation of a solid with energetic radiations such as ultraviolet, X-ray, or nuclear radiation. In fact, nearly all substances will show a resonance spectrum if they are irradiated with an adequate time. The first successful experiment to observe ESR was performed by Zavoisky[1]. Since then the ESR technique has been studied and made available in a wide variety of applications in chemistry, physics and biology. It is also used in process control and clinical analysis. Zeller et al.[2], Zeller[3] and Levy[4] suggested that ESR could also be used in geology and archaeology[5].

Calcite is a carbonate mineral and the most stable polymorph of calcium carbonate ($CaCO_3$). The basic constituent unit in all carbonate minerals is the CO_3^{2-} molecular ion. Calcium carbonate has two main crystal structures of calcite and aragonite. Calcite with rhombohedral symmetry is the only thermodynamically stable form of pure $CaCO_3$ at room temperature and atmospheric pressure[1]. The ESR spectra of unirradiated carbonate consist of six peaks of Mn^{2+} organic radicals with 5 sets of double lines, each of which is in each Mn^{2+} interval. All samples show the same characteristic Mn^{2+} spectrum with an additional free radical peak in the centre of the sextet, whereas a lot of specimens exhibit a single line. Some differences of the ESR spectra obtained before and after irradiation process of $CaCO_3$ mineral have been observed that depend on mineral characteristics such as species, geographical origin, harvesting year, geological age, dose, etc[6].

In this paper, we present the results of an ESR analysis before and after irradiation of natural calcite samples collected from Saraburi province, in central Thailand. Our research and analysis have proven the reliability and dependability of ESR studies. This research could be of importance in providing reference data for the additive irradiation method of ESR dating analysis.

2. Method

2.1 Sample material and sample preparation

Natural calcite samples (shown in Fig 1) were collected from Saraburi province, in central Thailand. The samples were washed and cleaned in an ultrasonic bath, followed by etching with 5% hydrochloric acid for 1 h then cleaned with distilled water. After that, the samples were gently ground with a mortar, and the grains were sieved in order to separate a fraction of the size 75–250 μm from the others. The separated grains were again etched by 0.5% acetic acid for a few minutes to remove the surface defect which produced the signal at g = 2.0002 and was caused by the pressure in grinding[5]. The grains were, then, washed repeatedly in distilled water and allowed to dry at 40^{o}C. All sample preparation procedures were performed in a dim red light.

Fig 1 The natural calcite samples were collected from Saraburi province, in central Thailand.

2.2 Gamma irradiations

Artificial γ-irradiations were carried out with a cobalt-60 source (GammaCell-220E), which delivered 3.404 Gy/s irradiation field, certified by the High-Dose Dosimetry Calibration Laboratory (HDCL), Ionizing Radiation Metrology Group, Bureau of Technical Support for Safety Regulation, Office of Atoms for Peace, Thailand (OAP), and the artificial dosages were given at 1,000 Gy in a few minutes.

2.3 ESR measurements

All ESR measurements were carried out at room temperature. The ESR spectra were obtained using an EPR Bruker spectrometer, Model A300 operating in the X band. The spectrometer operating conditions adopted during the experiment were as follows: 350 mT central magnetic field; 10 and 100 mT scan ranges; 0.1 mT field modulation amplitude; 100 kHz modulation frequency; 0.632 mW microwave power; 5.12 ms conversion time; 40.96 ms time constant. The stable free radical diphenylpicrylhydrazyl (DPPH) with a g-value of 2.0036 was used as an internal standard for g-factor calculations.

3. Results and Discussions

Fig 2 shows ESR spectra of natural calcite samples before irradiation process in 350 mT central magnetic field with a scan magnetic field range of 100 mT. All ESR spectra clearly confirmed the Mn^{2+} ion substitution at the calcium sites of the carbonate structure. Each spectrum consists mainly of a group of six peaks of Mn^{2+} organic radicals around g= 2, which are attributed to $\left|-1/2\right\rangle \rightarrow \left|1/2\right\rangle$ sextet fine structure transition (electron spin S = 5/2 and nuclear spin I = 5/2) of Mn^{2+} ions. The weaker pairs of peaks between the main peaks are the so-called 'forbidden transitions' in which both electron and nuclear spin states have changed, i.e. $\Delta m_s = 1$, $\Delta m_I = 1$.

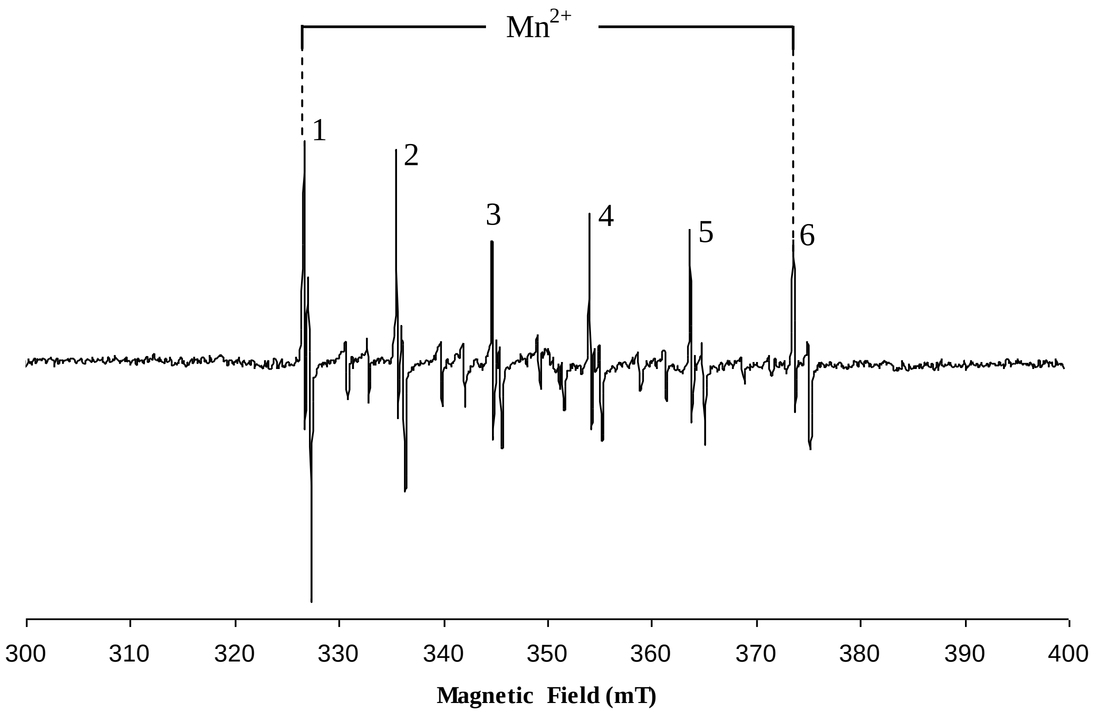

Fig 2 ESR spectra of natural calcite samples before irradiation.

Fig 3 shows the comparison of ESR spectra before and after irradiation of natural calcite samples in 350 mT central magnetic field with a scan magnetic field range of 100 mT. The ESR signals after irradiation of natural calcite samples as shown in the ellipse had increased and appeared strong enough for ESR dating.

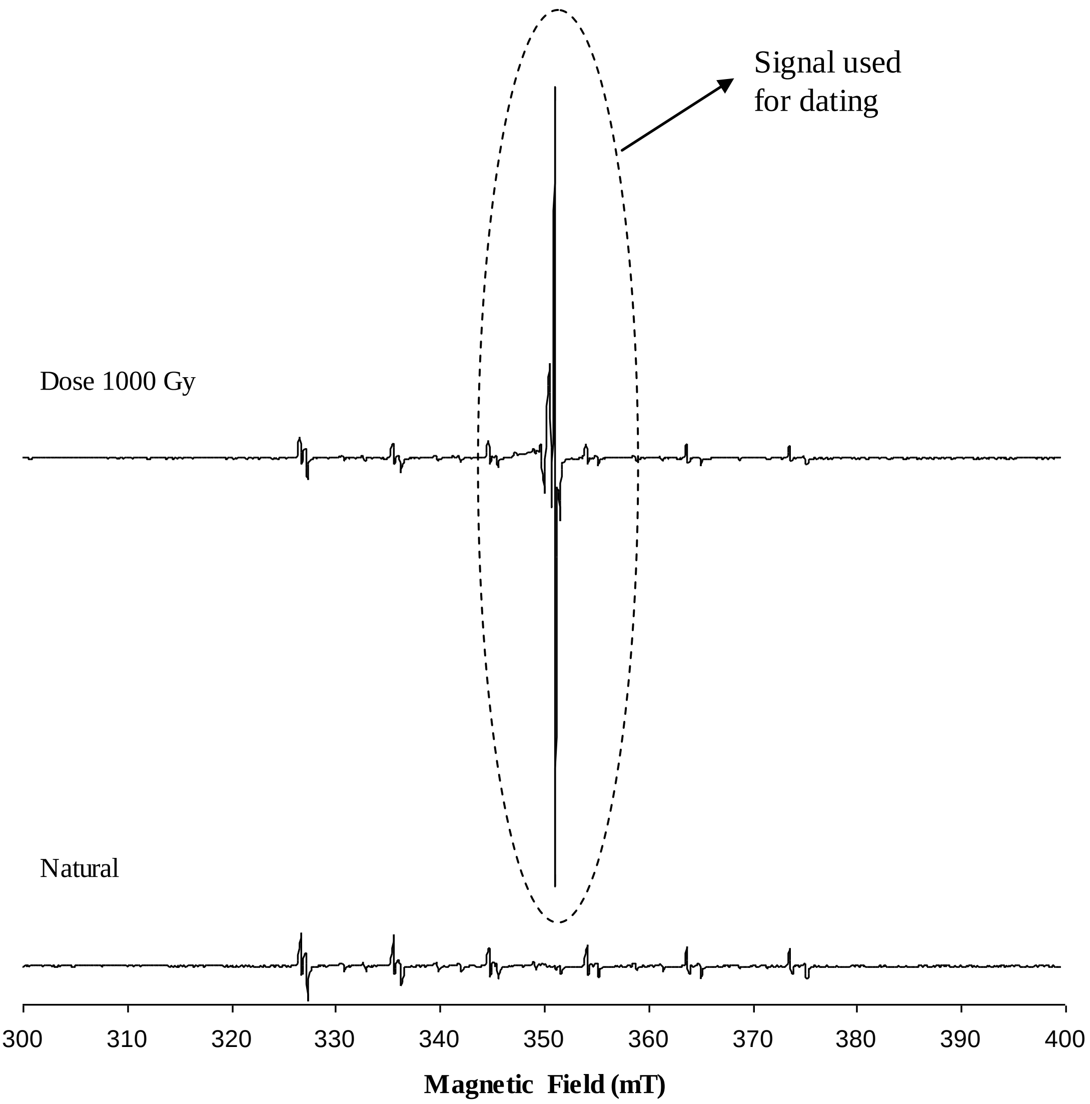

Fig 3 ESR spectra of natural calcite samples before irradiation (bottom) and after irradiation (top).

Fig 4 shows ESR signals of natural calcite samples after 1,000 Gy of Cobalt-60 irradiation with a scan magnetic field range of 10 mT. The radicals produced by gamma-irradiated natural calcite, whose *g* factors were near g = 2.0016 and negative peak g = 1.9973, were attributed to CO_2^- center.

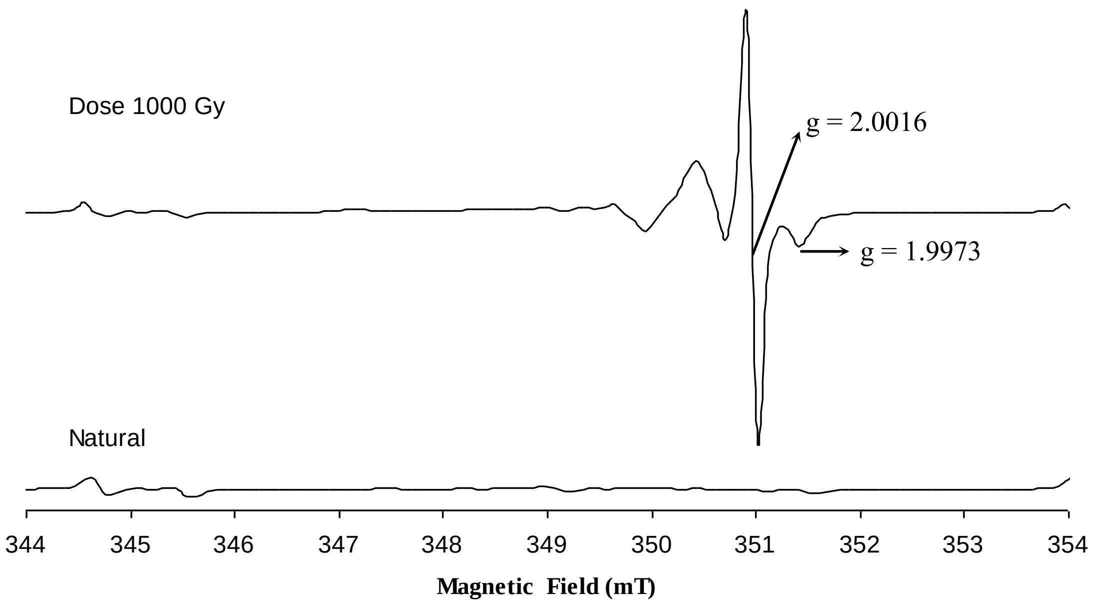

Fig 4 ESR spectra of natural calcite samples after irradiation showing the g factors

4. Summary

The of ESR signals of before and after irradiation of natural calcite samples show that the radicals produced by gamma-irradiated natural calcite, whose *g* factors were near *g* = 2.0016, were attributed to CO_2^- center. This signal has practically been used as a dating signal because the absolute intensity per unit weight of the sample is proportional to the known age and gamma irradiation has enhanced the intensity[1,5,8]. The analysis of ESR spectra showed that the ESR signal intensity of these free radicals increased gradually with the increase of absorbed dose[1,6]. Our research and analysis have proven the reliability and dependability of ESR studies. This research could be of importance in providing reference data for ESR dating analysis additive irradiation method.

5. Acknowledgments

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