

Electron Spin Resonance Study of Tertiary Sediments in Mae Moh Basin, Lampang Province

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Abstract: Electron Spin Resonance (ESR) studies have been carried out on Tertiary sediment collected from Mae Moh basin, well known for its lignite mining in Lampang province of the northern Thailand, a stratigraphic bedding plane in the sediment that formed in geological time of about 13 million years ago. Each individual sedimentary bed has its own unique assemblage and occurs in a stratigraphic succession which allows for close stratigraphic correlations to be made within the Tertiary of Mae Moh Group. The ESR spectra of sediments confined within the basin at the stratigraphic depth between 100 m and 800 m were carried out. The ESR spectra corresponding to Fe^{3+} , Mn^{2+} , SO_3^- , SO_2^- , CO_2^- , CO_3^- and E'_1 were observed. This result indicated that the sediment consisted of iron oxide (Fe_2O_3), quartz and calcite (CaCO_3).

Key words: Mae moh mine, Electron Spin Resonance (ESR), tertiary sediments

INTRODUCTION

Mae Moh basin is a basin in northern Thailand originated during the early Tertiary that was to become the age of Mammals (Griscom and Beltran-Lopez, 2002). Recently Songtham *et al.* (2005) report that Mae Moh basin has the largest lignite deposit and is the biggest coalmine in Thailand

Electron Spin Resonance (ESR) is a physical method of observing resonance absorption of microwave power by a solid possesses unpaired electron. The unpaired electrons can be generated by irradiation of a solid with energetic radiations such as X-ray and nuclear radiation. In fact, nearly all substances, if irradiated long enough will show a resonance spectrum. The first successful experiment to observe ESR was performed by Zavoisky (1945). Since then, ESR technique has found wide variety of applications in chemistry, physics, biology and even in the process control and clinical analysis. Zeller *et al.* (1967) and McDougall (1968) suggested that ESR could also be used in geology and archaeology (Engin *et al.*, 2006).

This study presents ESR spectra of Fe^{3+} , Mn^{2+} and E'_1 center in iron oxide and quartz and Mn^{2+} , SO_3^- ,

SO_2^- , CO_2^- and CO_3^- in carbonate from claystone deposits at Mae Moh basin. Each individual sedimentary bed has its own unique assemblage and occurs in a stratigraphic succession, which allows close stratigraphic correlations to be made within the Middle Miocene, Mae Moh Group. This study is of great importance since it is the first ESR study of sediment to be carried out in Neogene's basin of Thailand and will be used as a reference data and be placed in evidence for the first time.

Geology (Songtham *et al.*, 2005): The Mae Moh basin is situated in the Mae Moh District of Lampang Province, which is about 26 km east of Lampang City. It is distributed in the area of about 135 square km, 7 km in east-west and 16 km in north-south as shown in Fig. 1. The basin floor is about 320-340 m above mean sea level.

Recently, Vichaidid *et al.* (2007), employed ESR spectroscopy technique to date the freshwater fossil shells in sediments collected from Mae Moh basin. The ESR age of the fossil shells was found to be about 13 million years.

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Fig. 1: Location of the Mae Moh basin, situated in Lampang Province

The Tertiary sediments called the Mae Moh Group consist of three formations, namely the Huai King, Na Khaem and Huai Luang formations, in ascending order. The total thickness of three formations is nearly 1,000 meters as shown in Fig. 2.

The Huai King formation unconformably overlies the basement rock, Lampang Group. It consists of a sequence of upward grading conglomerate, sandstone and pebbly sandstone, siltstone and finally fining upwards into interbedded red and gray claystone. The uppermost part of the formation is marked by a thin layer of coal named the S coal zone.

The Na Khaem formation is a coal measure comprising three main coal zones, Q, K and J assigned to Middle Miocene age. This formation has been divided into three members as Member III, Member II and Member I, in ascending order. The Member III, or the so-called Underburden (UB), is a greenish gray to gray claystone with a thin layer of coal, named the R-coal zone. The Member II is composed of two main coal zones, which are the Q coal zone in the lowermost part and the K coal zone in the uppermost part and are intercalated by an Interburden (IB) of claystone. The member I is a thick Overburden (OB) consisting of claystone with a series of coal layers named the J coal zone. The J coal zone is an intercalation between claystone and six main coal layers.

The Huai Luang formation is composed of claystone and siltstone with some sandstone and conglomerate

lenses. A red to brownish red colour is the general characteristic of this formation with some gray layers interbedded in some horizons. A form of gypsum, selenite, is abundant in this formation. There is a coal zone, named I coal zone, in the middle of the formation.

Songtham *et al.* (2005) also reported that during the Middle Miocene, the Mae Moh basin was a large swamp where living organisms such as fish and various species of aquatic molluscs lived. The molluscs might have appeared and disappeared throughout the time depending on environmental changes that altered the composition of the molluscan assemblages changed from horizon to horizon, resulting in the formation of five molluscan zones (*Paludina* Molluscan Zone, Planorbidae Molluscan Zone, *Bellamya* Planorbidae *Paludina* Molluscan Zone, *Melanoides* sp. cf. *M. tuberculata* Molluscan Zone and *Margarya* Molluscan Zone) as shown in Fig. 2.

The purpose of this study is to study the ESR spectra of sediments confined within Red Bed layer (RB) from Huai Luang formation and within three gray claystone layers (overburden, OB; interburden, IB; underburden, UB) from Na Khaem formation.

MATERIALS AND METHODS

The sediments collected from Huai Luang and Na Khaem formations were washed and cleaned in ultrasonic bath using distilled water. Then, the samples

were gently ground with a mortar and the grains were sieved in order to separate the size fraction of 75-250 μm . The separated grains were etched by 5% HCl acid for a few minutes in order to remove the surface defect signal at $g = 2.0002$ caused by the pressure in grinding (Griscom and Beltran-Lopez, 2002). The size fraction was, then washed repeatedly in distilled water and allowed to dry at a temperature of 40°C. All sample preparation procedures were performed in dim red light to avoid the samples being exposed to light. Each sample was divided into three aliquots, approximately 300-500 mg each. These were loaded into fused quartz sample tubes with a nominal inside diameter of 3 mm to

fill a height of 2.5 cm. The sample was placed at the center of microwave cavity for ESR measurement. All ESR measurements were carried out at room temperature. The ESR spectra were recorded using a Bruker spectrometer (E500) operating in the X band of microwave range. The operating conditions adopted during the experiment were as follows: 349 mT central magnetic field; 350, 100 and 10 mT scan ranges; 0.1 mT field modulation amplitude; 100 kHz modulation frequency; 0.63 mW microwave power; 5.12 ms conversion time; 163.84 ms time constant. DPPH with a g-value of 2.0036 was used as an internal standard for g-factor calculations.

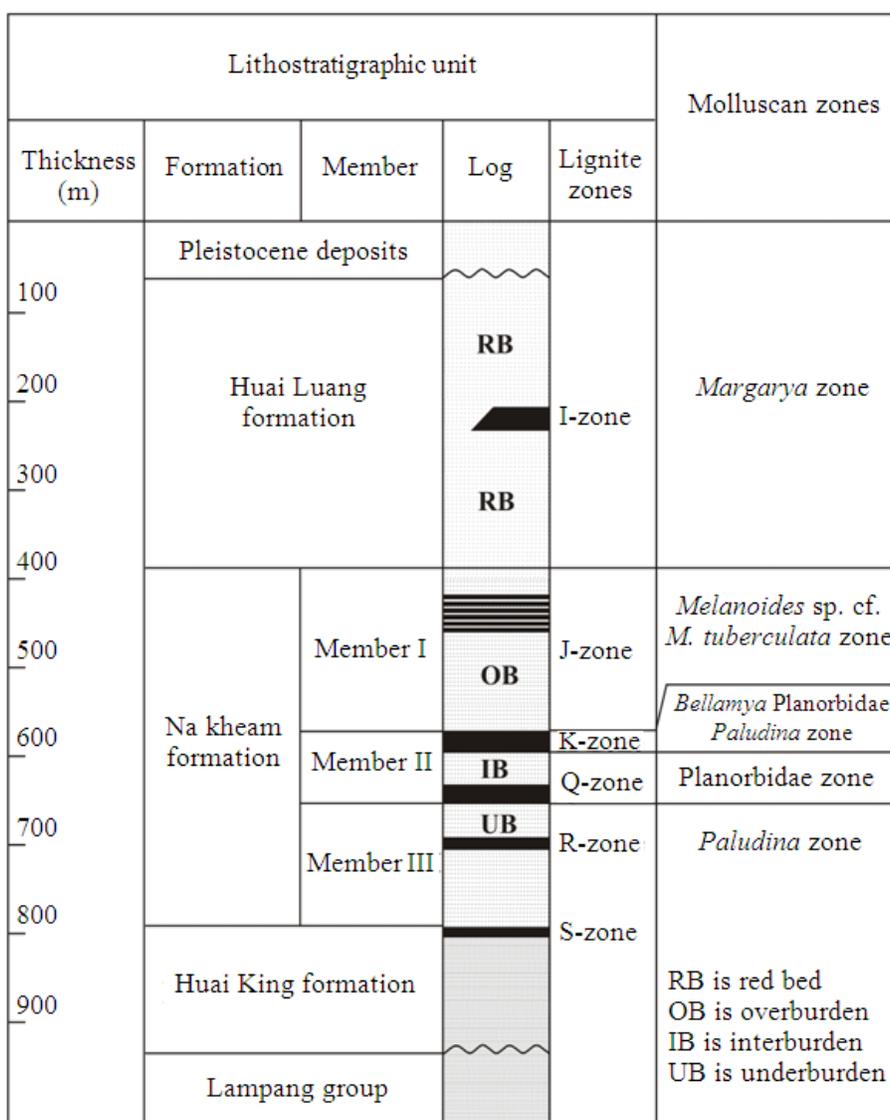


Fig. 2: Schematic lithostratigraphic units and molluscan zone of the Mae Moh Group

RESULTS

The structure of sediments and claystones was investigated by XRD measurements. Figure 3 shows XRD patterns of sediments confined within Red Bed (RB) layer from Huai Luang formation and OB, IB and UB layers from Na Khaem formation.

ESR spectra, in a scan magnetic field range of 350 mT, of sediments from RB layer and gray claystones from OB, IB and UB layers are shown in Fig. 4.

The ESR signal of sediments from RB layer was further investigated by scanning the magnetic field in narrower ranges of 100 mT and 10 mT and the obtained ESR signals are shown in Fig. 5 and 6, respectively.

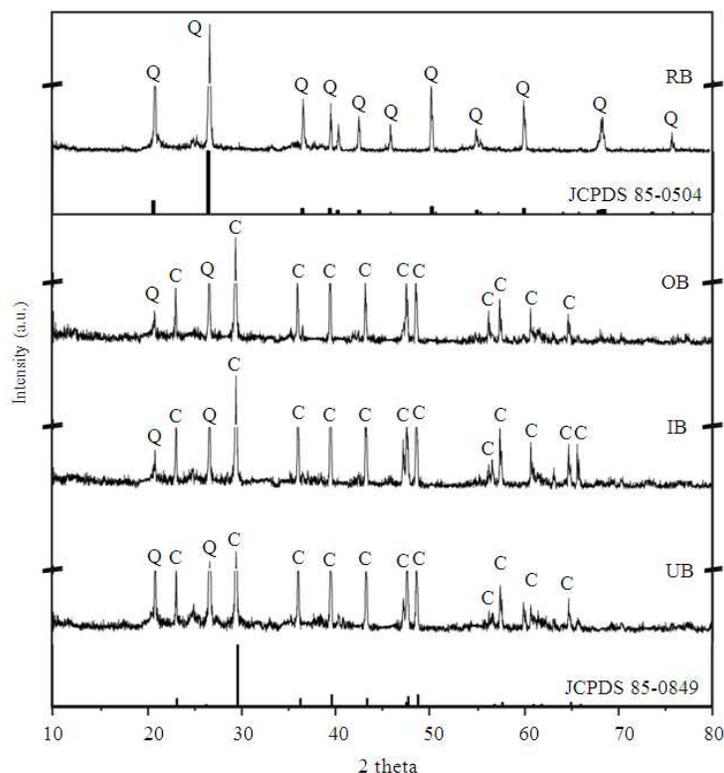


Fig. 3: X-ray powder diffraction patterns of sediments collected from Red Bed (RB) layer and gray claystone from Overburden (OB), Interburden (IB) and Underburden (UB) layers. C = Calcite, Q = Quartz

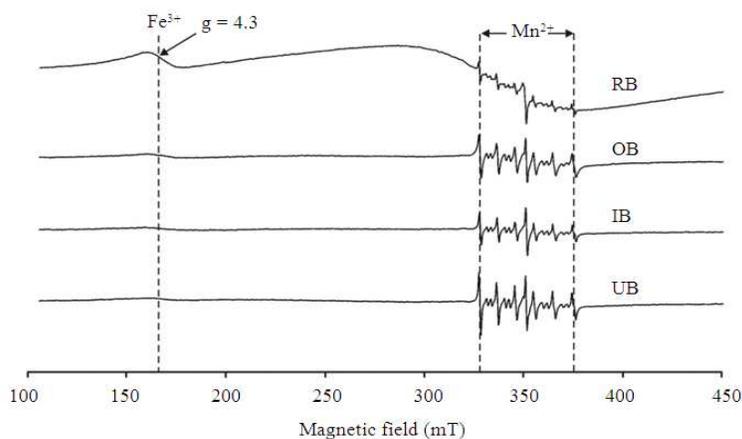


Fig. 4: ESR spectra of sediments from Red Bed (RB) layer and gray claystone from OB, IB and UB layers. Scan range is 350 mT

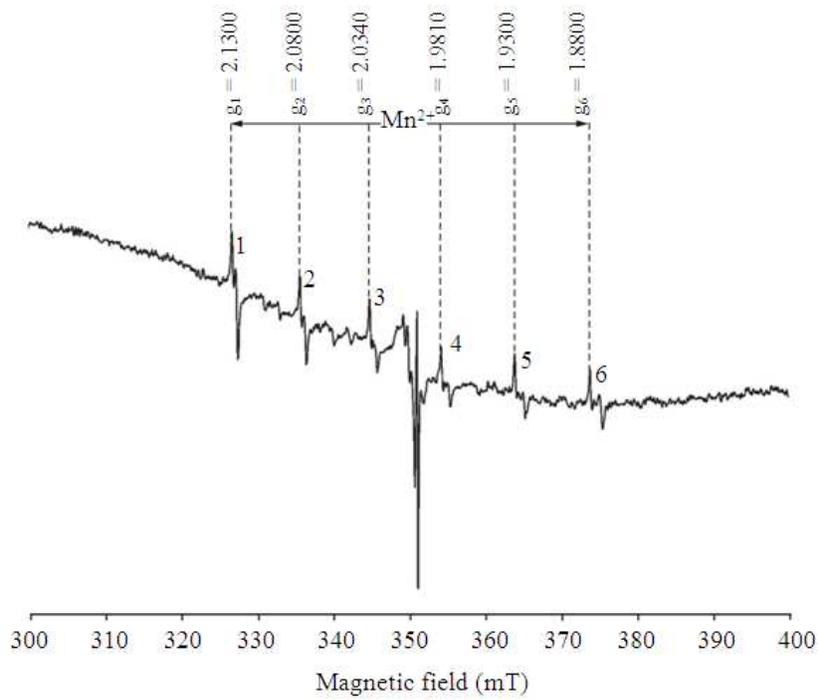


Fig. 5: The sextet hyperfine signals of Mn^{2+} organic radicals around $g = 2.00$ of sediments from RB layer. Scan range is 100 mT

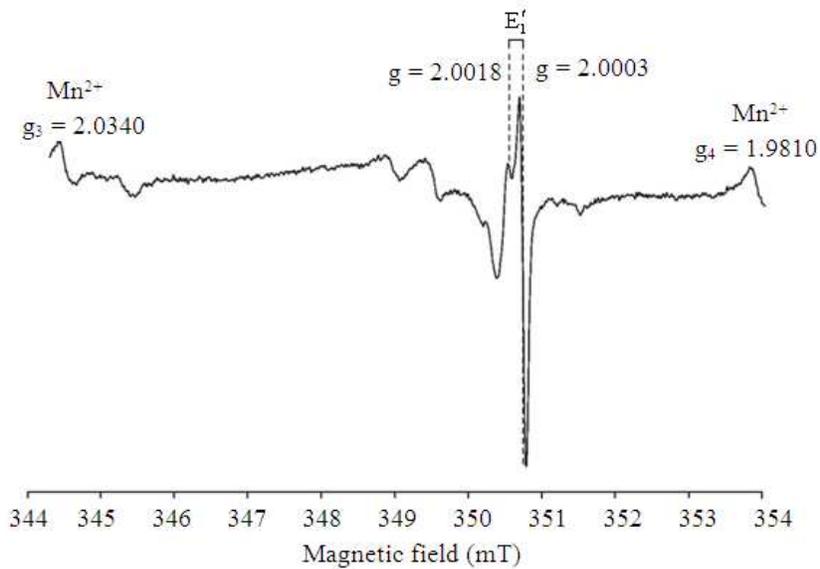


Fig. 6: ESR spectra of the E_1' center at $g = 2.0018$ and $g = 2.0003$ of sediments from RB layer. Scan range is 10 mT

ESR spectra of sediments from three gray claystone layers (OB, IB and UB) are shown in Fig. 7. The central ESR peaks were further investigated by scanning the magnetic field in a narrower range of 10 mT and the obtained ESR signals are shown in Fig. 8.

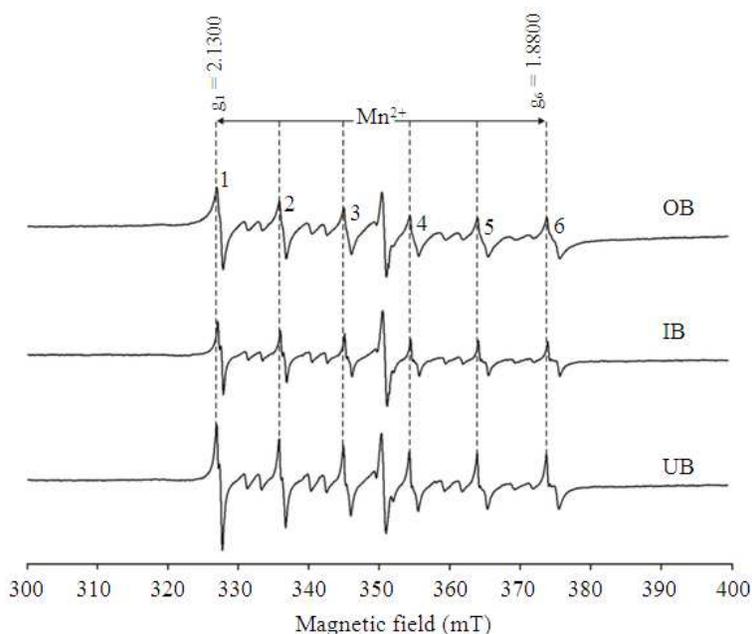


Fig. 7: The sextet hyperfine signals of Mn^{2+} organic radicals around $g = 2.00$ of gray claystone from OB, IB and UB layers. Scan range is 100 mT

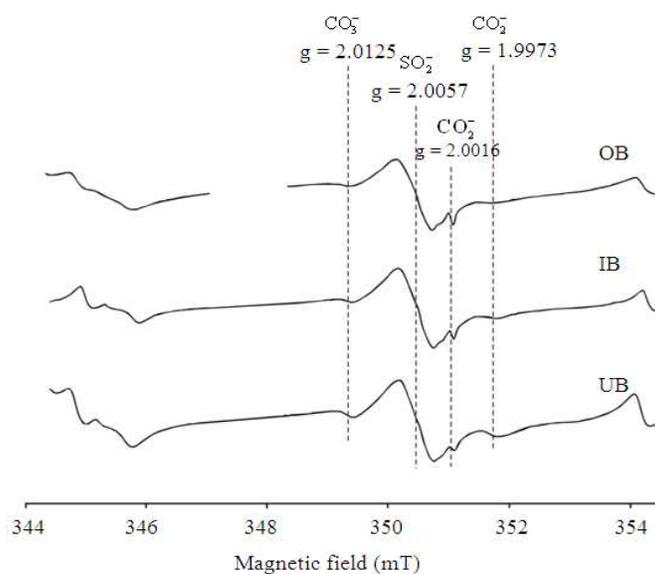


Fig. 8: ESR spectra of gray claystone from OB, IB and UB layers associated with CO_3^- at $g = 2.0125$, SO_3^- at $g = 2.0057$ and CO_3^- at $g = 2.0016$ and $g = 1.9973$. Scan range is 10 mT

DISCUSSION

The diffraction peaks shown in Fig. 3, according to JCPDS file numbers 85-0504 and 85-0849, show that the sediments in RB layer consist mostly of quartz

while those in OB, IB and UB consist mainly of calcite and some fraction of quartz.

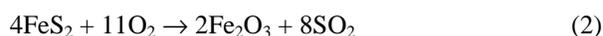
The ESR signal associated with Fe^{3+} at $g = 4.3$ (Ikeya, 1993) was observed only in RB layer. However, the hyperfine sextet of Mn^{2+} ions of organic

radicals around $g = 2.0$ were observed in samples from all layers as clearly.

As can be seen in Fig. 5, a sharp ESR signal was observed at a magnetic field of about 350 mT. Moreover, the magnified ESR signal in Fig. 6 shows two sharp peaks at $g = 2.0018$ and $g = 2.0003$ which are attributed to E'_1 center or SiO_3^{3-} in quartz (Ikeya, 1993; Ulusoy, 2002; Jani *et al.*, 1983). The ESR results indicate that the sediments in RB layer consist of iron oxide and quartz which agree with XRD results. It should be pointed out that the XRD pattern shown in Fig. 3, no peaks of iron oxide were observed due to its less amount contained in the sediment.

Quartz or silica (SiO_2) is a special type of silicate where each oxygen atom is bonded with two Si atoms to form a three-dimensional network in a crystalline form. Quartz is the most common rock-forming mineral next to feldspars and exists in most rocks of sedimentary, igneous and metamorphic origins. A vacancy and interstitial type defects in SiO_2 are together called a "Frenkel pair". The following three pairs occurred in SiO_2 ; (i) a paired oxygen vacancy and interstitial O^{2-} which is not stable at room temperature, (ii) a paired Si vacancy and Si interstitial is energetically not stable and (iii) a paired E'_1 center (an electron at an oxygen vacancy) which is associated with ESR signals of sediment sample in Red Bed (RB) layer from Huai Luang formation, is stable and is observed in natural quartz and irradiated amorphous SiO_2 . The model for E'_1 center in quartz is an unpaired electron in a dangling sp^3 hybrid orbital of pyramidal SiO_3^{3-} where an oxygen ion, O^- , is extracted from a SiO_4 tetrahedron (Ikeya, 1993; Jani *et al.*, 1983; Silsbee, 1961).

The selenite-bearing red bed sandy claystone is considered as secondary deposit formed sometimes after the formation of Huai Luang. It is believed that the environment during this secondary formation was in arid condition. The hydrous calcium sulfate crystals, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, are said to be resulting from solution cavities through precipitation of calcium sulfate-bearing groundwater that was saturated under an arid condition. The presence of selenite is in contrast to the massive gypsum, frequently associated with evaporite deposits in playa in the arid environment which formed beds parallel to nearby sedimentary strata. However, the selenite crystals from the Huai Luang formation are randomly scattered like nodules in red bed of sandy claystone without forming beds. The gypsum crystals, selenite and red bed were secondarily formed by some proposed chemical reactions such as ones present below:



The source of calcium came from limestone (CaCO_3) of the Lampang Group that decayed to become lime (CaO). The lime reacted with sulfur trioxide (SO_3) (derived from SO_2) and water forming selenite crystals ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in saturated groundwater under an arid environment according to Eq. 1-3. For the sediments in RB layer, the iron oxide (Fe_2O_3) produced from the oxidizing of pyrite (FeS_2) according to Eq. 2 partially changed the color of original flood plain sediments into the red bed formation containing the selenite crystals. This is why the red bed formation retains some original color of greenish gray sandy claystone occurring in some places (Songtham *et al.*, 2005).

It is seen in Fig. 7 that the sextet hyperfine and the forbidden transitions associated with Mn^{2+} ions of organic radicals are similar in all three layers.

The ESR signals, as shown in Fig. 8, at $g = 2.0125$, 2.0057 and 2.0016 and 1.9973 correspond to CO_3^- , SO_2^- and CO_2^- molecular ions, respectively (Ikeya, 1993; Serway *et al.*, 1969; Kai and Miki, 1992; Katzenberger *et al.*, 1989; Barabas, 1992).

The results indicated that the sedimentary consisted largely of carbonates. Carbonates are common minerals in nature. The basic constituent unit in all carbonate minerals is the CO_3^{2-} molecular ion. Calcium carbonate (CaCO_3) has two main crystal structures of calcite and aragonite. Calcite with trigonal (rhombohedral) symmetry is the only thermodynamically stable form of pure CaCO_3 at room temperature and under atmospheric pressure (Ikeya, 1993). Elementary defects induced by ionizing radiation are electron centers (CO_3^{3-}) and hole centers (CO_3^-). An oxygen vacancy with an electron, actually the CO_2^- molecular ion, is also formed by radiation (Zavoisky, 1945).

CONCLUSION

The Tertiary sediments confined within the Mae Moh basin, well known as the lignite mining in the Lampang province of Northern Thailand were studied using ESR spectroscopy technique. The sediments were collected from Red Bed layer (RB) of Huai Luang formation and three gray claystone layers (OB, IB and UB) of Na Khaem formation which deposited at the stratigraphic depth between 100 m and 800 m. The ESR results showed that the sediments in RB layer consist of iron oxide and quartz whereas those in OB, IB and UB

layers consist largely of carbonates. In this study, the E'_1 center was also observed in quartz for the sediment collected from RB layer. Recently, E'_1 centers have been used for ESR dating (Ulusoy, 2002; Lee and Yang, 2003; Bartoll *et al.*, 2001). Therefore, the E'_1 centers found in the present study can be used for ESR dating of the formation in the future.

ACKNOWLEDGMENT

The researchers would like to thank EGAT (Electricity Generating Authority of Thailand) and DMR (Department of Mineral Resources) for providing scientific assistance, access to the mine and company data when staying at the mine. We would like to thank NSRL OAP (National Standard Radioactivity Laboratory, Office of Atoms for Peace) for supporting gamma irradiation exposures and NAA techniques and the Department of Chemistry, Mahidol University for providing ESR facilities. This study was funded by the King Mongkut's University of Technology Thonburi under The National Research University Project.

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