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Fluctuation of Depositional Environment in the Bang Mark Coal Deposit, Krabi Mine, Southern Thailand: Stable Isotope Implication

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ABSTRACT: The isotopic composition of organic sulfate-sulfur and pyrite in coal from the Bang Mark coal deposit in the Krabi mine, southern Thailand, was analyzed to determine the depositional environment of the coal. High-sulfur content in coal has $\delta^{34}S$ values that range from +1.6 to +9.8 ‰. Organic sulfur in coal has $\delta^{34}S$ values that vary narrowly from –1.4 to +4.7 ‰. The $\delta^{34}S$ values of pyrite range from –3.0 to +1.4 ‰. The $\delta^{34}S$ values indicate that most of the sulfur in pyrite and coal was derived from a magmatic or hydrothermal source. This sulfur was associated with organic matter during or after deposition. This also suggested that the source of sulfur could have come from hydrothermal mineralization surrounding the area. Twenty-four fossil shell specimens of *Viviparus* sp., *Melanoides* sp., and *Mya arenaria* were analyzed for their content of isotopic $\delta^{13}C$ and $\delta^{18}O$. The $\delta^{13}C$ in these shells have negative values that range from –5.9 to –0.1 ‰ and average –2.9 ± 2.8‰. The $\delta^{18}O$ in these shells has a wider range of negative values, ranging from –11.7 to –2.9‰. It averages –8.1 ± 5.2‰. The $\delta^{13}C$ and $\delta^{18}O$ values indicate freshwater shells in the lower sequence and brackish water shells in the upper sequence. Therefore, the depositional environment of the Bang Mark coal deposit based on stable isotopic study was dominated by freshwater in the beginning and later became brackish water as a result of marine invasion under warmer conditions in a tropical region.

KEYWORDS: Bang Mark coal deposit, Krabi mine, sulfur isotope, carbon isotope, oxygen isotope, $\delta^{34}S$, $\delta^{13}C$, $\delta^{18}O$.

INTRODUCTION

The sulfur compounds found in coal are in the form of inorganic sulfide and sulfate and organic sulfur. Inorganic sulfur occurs as the metallic sulfides pyrite and marcasite and accounts for half of the sulfur abundance. Pyrite occurs in coal in minute crystals, groups of framboidal pyrite, lenses, bands, and nodules. This pyrite is formed by the reaction of hydrogen sulfide gas with iron. The hydrogen sulfide gas results from the reduction of sulfate to hydrogen sulfide gas by anaerobic bacteria.[1] Kaplan[2] suggested two sources of sulfur in coal. These were pyrite formed by biological sulfate reduction and from sulfur incorporated into organic matter during the growth of organisms in marine or brackish water. The organic sulfur in coal forms chemical bonds that can only be decomposed by heating. Therefore, this study had two objectives, to analyze sulfur isotopes in coal and pyrite, and to determine the depositional environment of the Bang Mark coal deposit based on the sulfur isotopes.

Bivalves and other mollusks are most commonly used for carbon and oxygen isotope investigations. Their skeletons contain a wealth of information about the environment in which they grew. The rate and timing of shell growth is controlled by temperature, salinity, age, reproductive cycle, tidal cycle, intertidal position, and nutrient and food availability.[3] The carbon and oxygen isotope composition of calcium carbonate depends on 1) the $d^{13}C$ and $d^{18}O$ values of CO_2 gas in equilibrium with carbonate and bicarbonate ions in solution; 2) fractionation of carbon isotopes between CO_2 gas, the carbonate and bicarbonate ions in the solution, and solid calcium carbonate; 3) temperature; and 4) the hydrogen ion activity (pH) and other chemical properties of the system.[1,4] Marine limestone and calcareous shells of marine organisms generally reflect the carbon isotope ratios of the water in which they formed. The carbon study of shells is used to indicate paleoenvironmental conditions and the oxygen isotope study is used to reflect paleosalinity and paleotemperature changes.[5-7]

The main purpose of this investigation was 1) to study the stable isotope composition and 2) to determine the depositional environment of the Bang Mark coal deposit based on stable isotope composition.

Geology and Sttatigraphy

Geological setting

The Bang Mark coal deposit is situated at the Krabi mine in the Krabi Basin. It is in Khlong Khanan, Muang District, Krabi Province in southern Thailand at latitude 7° 57´ N to 8° 00´ N and longitude 99° 03´ E to 99° 04´ E (Fig 1). The Bang Mark coal deposit has been developed by the Electricity Generating Authority of Thailand. The Krabi Basin is in the eastern part of Krabi Province, between the coast of Phanga Bay and the Khao Chong granite belt. The Tertiary strata of the Krabi Group that fill the basin overlie a Paleozoic and Mesozoic basement. These Tertiary strata include mudstone, claystone, conglomeratic sandstone, fossiliferous calcareous sandstone, fossiliferous limestone, and coal.

In its north and northeast parts, the Krabi Basin is bounded mainly by Carboniferous and Permian rocks, which are white limestone, shale, sandstone, conglomerate, and volcanic tuff. Jurassic and Cretaceous red micaceous shale interbedded with siltstone, micaceous sandstone, and conglomerate (Fig 2) mark the eastern and southern margins of the basin. The coal in the basin was deposited in a forest swamp that was associated with freshwater lacustrine environments.[8] Most of these coal beds are lignite to highly volatile bituminous C coal.[9]

The Bang Mark coal deposit is elongate, trending north northwest to south southeast, and dips 40° to the east. It covers 1.5 square kilometers. The average thickness of coal seams is 17 meters.

Straigraphy of the Krabi group

The Krabi Group can be subdivided into six formations.[10] These formations are the Bang Pu Dum Formation, Pakasai Formation, Khlong Sait Formation, Khuan Muang Formation, Tha Nun Formation, and Huai Khra Formation, in ascending order.

The Bang Pu Dum Formation consists of greenish gray to gray claystone, sandstone, limestone, and carbonaceous claystone with several thin coal seams. It gradually changes to reddish brown and gray claystone, siltstone, and sandstone in its lower part. Its thickness is at least 150 meters. The coal beds in this formation are divided into the Wai Lek and Bang Pu Dum Units. The Wai Lek Unit consists of a coal seam 15 to 20 meters thick that dips 30° to 45° east and is interbedded with thin gray shale. This unit shows in the Wai Lek coal deposit. It was deposited in a small plant in a swampy environment. The Bang Pu Dum Unit consists of yellow to grayish brown shale, shaly sandstone, and a coal seam 10 meters thick that dips 20° east. This unit shows in the Bang Pu Dum coal deposit. It was deposited in a swamp in lake environment.

The Pakasai Formation consists of gray to greenish gray claystone, limestone, and shale that is, in part, calcareous and fossilferous. Sandstone and siltstone occur as interbeds in the western part of the Krabi Basin. The thickness of the formation varies from 50 to 450 meters.

The Khlong Sait Formation consists of gray claystone, fine-grained sandstone, and fossiliferous limestone. Its thickness is about 100 meters.

The Khuan Muang Formation consists of gray to greenish gray, fossiliferous claystone and is slightly silty in part. It has some sandstone interbeds and is about 100 meters thick.

The Tha Nun Formation consists of gray to brownish gray claystone, sandstone, and siltstone. It has thin coal seams in the northern part of the basin and gray to reddish brown claystone with fine- to coarse-grained sandstone in the southern part of the basin. Its thickness is about 100 to 150 meters.

The Huai Khram Formation consists of brownish to gray clays and claystone. It has some sandstone and gravel and its thickness varies from a few meters to 150 meters.

One coal seam in the Bang Mark deposit varies in thickness from 5 to 30 meters in the southern part and has partings in the middle and northern parts. This coal is between the Bang Pu Dum and Wai Lek Units within the Bang Pu Dum Formation.

The Bang Mark coal deposit can be divided into three sequences. The typical characteristics of each sequence, in ascending order, (Fig 3) are:

1. The lower sequence consists of three units: (1) greenish to brownish gray claystone with thin coal interbeds, white sandstone, and coal overlying mudstone and sandstone that has root beds; (2) sandy swelling clay; and (3) the main coal seam. This main coal seam is approximately 7 to 20 meters thick and is composed mainly of large tree trunks. Vertebrate fossil remains are common in its lower part. It has thin, brownish gray claystone with fossil *Nipa* leaves in the upper part of the coal seam. Based on plant fossils, this sequence was deposited in a tidal zone and a brackish swamp environment.[11]

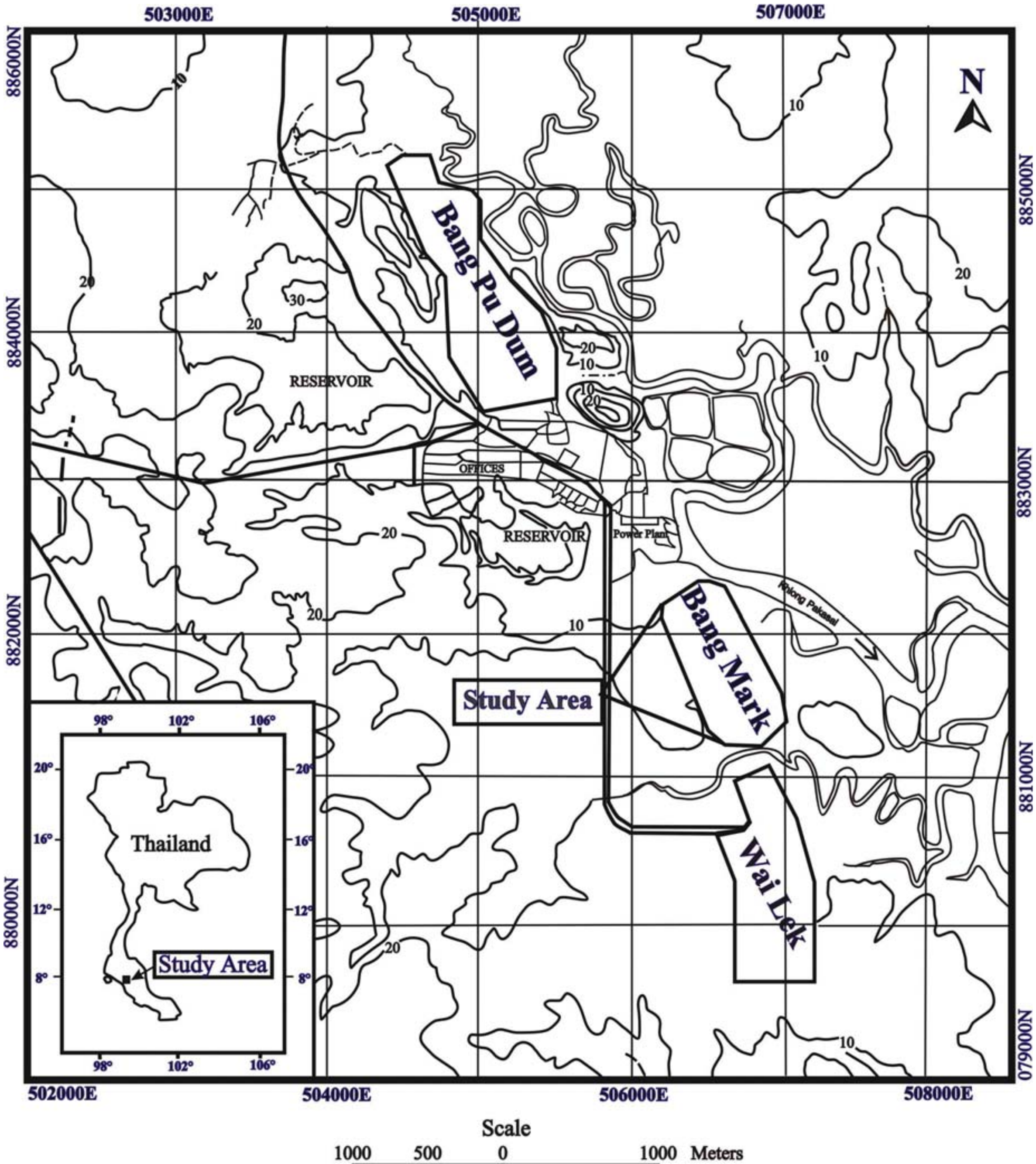

Fig 1. Location of the Bang Mark coal deposit, Krabi mine, southern Thailand (modified from Electricity Generating Authority of Thailand, 1990).

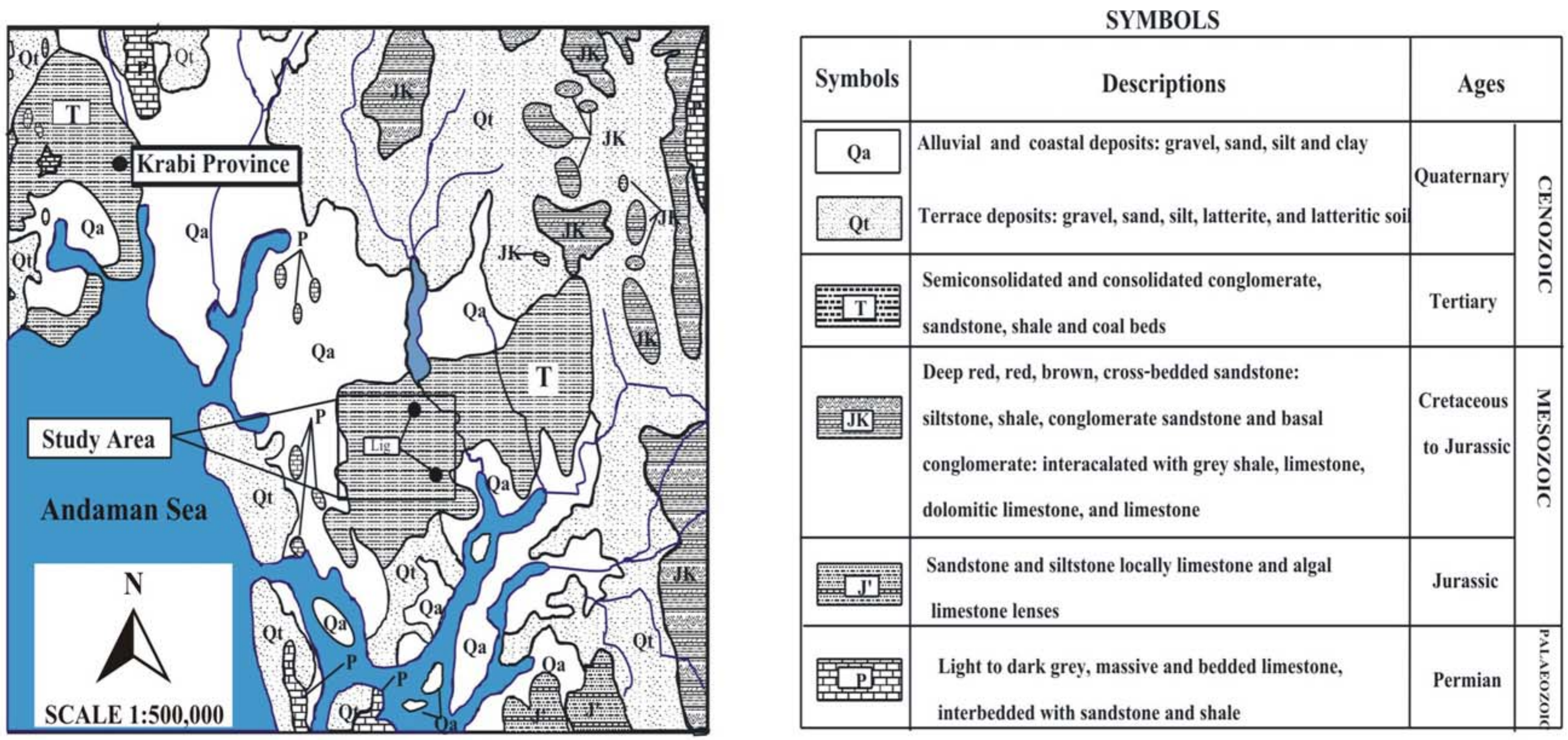

Fig 2. Geological map of the Krabi Basin, southern Thailand (modified from Geological Survey Division of Mineral Resource, 1980).

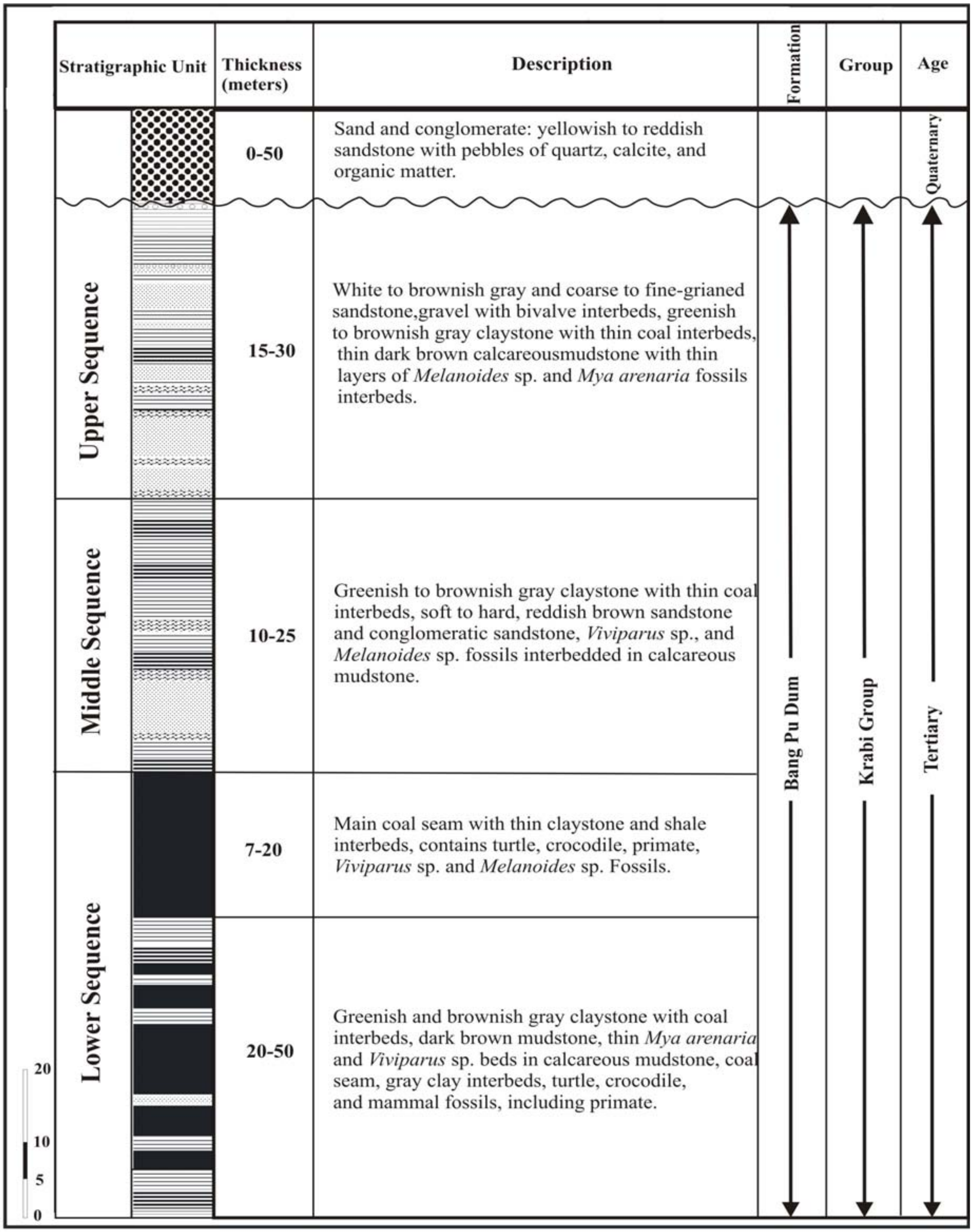

Fig 3. Stratigraphic column on the Bang Mark deposit, Krabi mine, sounthern Thailand (modified from Electricity Generating Authority of Thailand).

2. The middle sequence is hard, greenish to brownish gray claystone with thin interbeds of coal, reddish brown sandstone, conglomeratic sandstone, and calcareous mudstone. The lower part of the sequence is fossiliferous, containing gastropods *Viviparus* sp. and *Melanoides* sp. and pelecypod *Mya arenaria*. The sequence was deposited in a littoral environment of high to moderate energy.

3. The upper sequence is greenish to brownish gray claystone with thin interbeds of coal, white to brown gray sandstone, and calcareous mudstone. It contains gastropod *Melanoides* sp. and pelecypod *Mya arenaria*. The sequence was deposited in a littoral zone with low energy.

The Bang Mark coal and sediment characteristics represent both the Bang Pu Dum and Wai Lek Units. Fossil assemblages occur in both the upper and lower coal beds. The lower part of the Wai Lek Unit contains vertebrate fossils, including the Anthropoid primate *Siamopithecus eocaenus* and an Anthracotheriidae, *Siamotherium krabiense*. These fossils indicate an age of Middle to Late Eocene based on comparison with Late Eocene Anthracotheridae from China and Burma.[12] In the overlying coal beds, the fossils are mainly gastropods and pelecypod, *Viviparus* sp., *Melaniodes* sp., and *Mya arenaria*.

Materials and Methods

Six coal samples and five pyrite samples from the lower sequence of the Bang Mark coal deposit were collected for sulfur isotope determination. The coal samples were dried for 2 to 3 days to remove moisture and were then crushed and homogenized in a rotary mill. The pyrite samples were extracted from the inside of nuggets using a dentist's drill to avoid oxidizing part of the pyrite's surface. Lithologic column and sample positions are shown in Fig 4.

The sulfur in coal samples was extracted by the Eschka method for total sulfur and by combustion of sulfide for organic sulfur. The Eschka method is described in the Japanese Institute of Standards M 8813 (1988). Both types of sulfur were collected and purified in the form of $BaSO_4$. All of the $BaSO_4$ from coal and pyrite was convert to SO_2.[3]

The $^{34}S/^{32}S$ ratios were measured by a stable isotope mass spectrometer (VG-SIRA 10) of the Institute for Study of the Earth's Interior at Okayama University in Japan. The sulfur isotope ratio is expressed in a conventional delta value, d, which is defined as:

$$\delta^{34}S \text{ (per mil)}=((^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{CDT}-1)\times 1000 \quad \text{(vs-CDT)}$$

Where CDT stands for sulfur in Canyon Diablo troilite.

Twenty-four fossil shell specimens of *Viviparus* sp., *Melanoides* sp., and *Mya arenaria* were collected from the Bang Mark coal deposit in the Krabi Basin. The specimens were cleaned in distilled water using an ultrasound washer and were dried at 75 °C for an hour. Each cleaned specimen was milled to powder and homogenized $CaCO_3$ using an agate crusher. After this, 100 percent phosphoric acid expulsion was used to produce CO_2 at 60 °C in a closed reaction. This purified CO_2 was measured in a stable isotope mass spectrometer (Finnigan MAT delta S) of the Research Center for Coastal Lagoon Environments at the Shimane University in Japan. The ratio of organic carbon and oxygen isotopes, $\delta^{13}C$ and $\delta^{18}O$, are presented as ‰ deviation, δ units. The standard Shimane -1.06‰ can be related to the standard PDB of $\delta^{13}C$ and $\delta^{18}O$. The carbon and oxygen isotope compositions are expressed as:

$$\delta^{13}C_{(PDB)} \text{ (per mil)}=((^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)-1)\times 1000 \quad \text{(vs-PDB)},$$

and

$$\delta^{18}O_{(PDB)} \text{ (per mil)}=((^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)-1)\times 1000 \quad \text{(vs-PDB)}$$

Where PDB stands for carbon and oxygen in *Belemnitella americana* from the Pee Dee Formation).

Results and Discussion

Results of $\delta^{34}S$ determinations from coal and pyrite are shown in Table 1. Comparison of the $\delta^{34}S$ values between the total and organic sulfur show a wide range of total sulfur, varying from +1.6 to +9.8‰ (average 5.4 ± 4.4‰). The content varies between 1.9 and 3.9%. The $\delta^{34}S$ values of organic sulfur range from –1.4 to +4.8‰ (average 0.8 ± 4.0‰). The content of organic sulfur varies from 0.9 to 2.0%.The $\delta^{34}S$ values of pyrite have a narrow range, varying from –3.0 to +1.4‰ and averaging –0.7 ± 2.3‰.

The isotopic study shows variation depending on sulfur content. The $\delta^{34}S$ values of organic sulfur in a low sulfur content coal of less than one percent total sulfur vary within a narrow range from +4.6 to +7.3‰.[1] The $\delta^{34}S$ values of organic sulfur in low-sulfur coal suggest a non-marine origin. In addition, the mean of the low sulfur content coal is +4 ± 3‰. The $\delta^{34}S$ values indicate plant growth in freshwater.[13,14] On the other hand, the $\delta^{34}S$ values of organic sulfur in sulfur-rich coal having total sulfur greater than one percent vary more widely, from +2.9 to +24.4‰. This indicates that the high-sulfur coals may have resulted from post-depositional marine or non-marine origin infiltration of sulfur into the coal, along with reduction by bacteria.[1,14] Generally, the sulfur in granitic intrusions and igneous rocks of primary origin have $\delta^{34}S$ values in a narrow range close to zero. It is possible that the oxidation and reduction cycle of biological sulfur

Table 1. Sulfur isotope of the Bang Mark coal and pyrite samples, Krabi mine, southern Thailand.

Samples	Descriptions Position, (Figure 4)	Total Sulfur		Organic Sulfur		Pyrite
		%S	$\delta^{34}S$ (‰CDT)	%S	$\delta^{34}S$ (‰CDT)	(‰CDT)
BMC-1	Lower coal seam C-1	3.2	+4.1	2.0	-1.4	No pyrite
BMC-2	Lower coal seam C-2	3.4	+4.1	1.8	+0.2	-0.2
BMC-3	Middle coal seam C-3	1.9	+6.0	0.9	+0.6	-3.0 and –2.0
BMC-4	Middle coal seam C-4	3.9	+6.7	1.5	+3.0	+0.5
BMC-5	Main coal seam C-5	4.9	+1.6	2.1	-2.4	+1.4
BMC-6	Upper coal seam C-6	3.5	+9.8	1.1	+4.8	No pyrite
		Avg. +5.4 ±4.4(‰)		Avg. +0.8± 4.0 (‰)		Avg. –0.7 ± 2.3 (‰)

Table 2. $\delta^{13}C$ and $\delta^{18}O$ values of shells from the Bang Mark coal deposit, Krabi mine, southern Thailand.

Samples	Species	$\delta^{13}C$(‰ PDB)	Avg. $\delta^{13}C$(‰ PDB)	$\delta^{18}O$(‰ PDB)	Avg. $\delta^{18}O$(‰ PDB)
BMS1-1		-5.7		-5.7	
BMS1-2	*Mya arenaria* sp.	-5.6	-5.7	-5.6	-7.5
BMS1-3		-5.9		-11.2	
BMS2-1		-0.1		-12.8	
BMS2-2	*Viviparas* sp.	-3.8	-1.3	-9.9	-11.7
BMS2-3		-0.1		-12.6	
BMS3-1		-1.6		-7.7	
BMS3-2	*Mya arenaria* sp.	-4.4	-3.1	-8.3	-7.9
BMS3-3		-3.2		-7.9	
BMS4-1		-5.5		-9.2	
BMS4-2	*Mya arenaria* sp.	-2.3	-4.5	-10.0	-9.3
BMS4-3		-5.8		-8.7	
BMS5-1		-4.1		-8.8	
BMS5-2	*Mya arenaria* sp.	-4.2	-4.1	-8.8	-8.8
BMS5-3		-4.1		-8.8	
BMS6-1		-1.8		-8.3	
BMS6-2	*Melanoides* sp.	-1.7	-1.7	-8.2	-8.2
BMS6-3		-1.7		-8.1	
BMS7-1		-1.3		-8.5	
BMS7-2	*Melanoides* sp.	-1.2	-1.2	-8.5	-8.5
BMS7-3		-1.2		-8.5	
BMS8-1		-3.5		-2.2	
BMS8-2	*Mya arenaria* sp.	-1.9	-2.4	-2.2	-2.9
BMS8-3		-1.9		-4.3	
			Avg. –3.0±2.7		**Avg. –8.1±5.2**

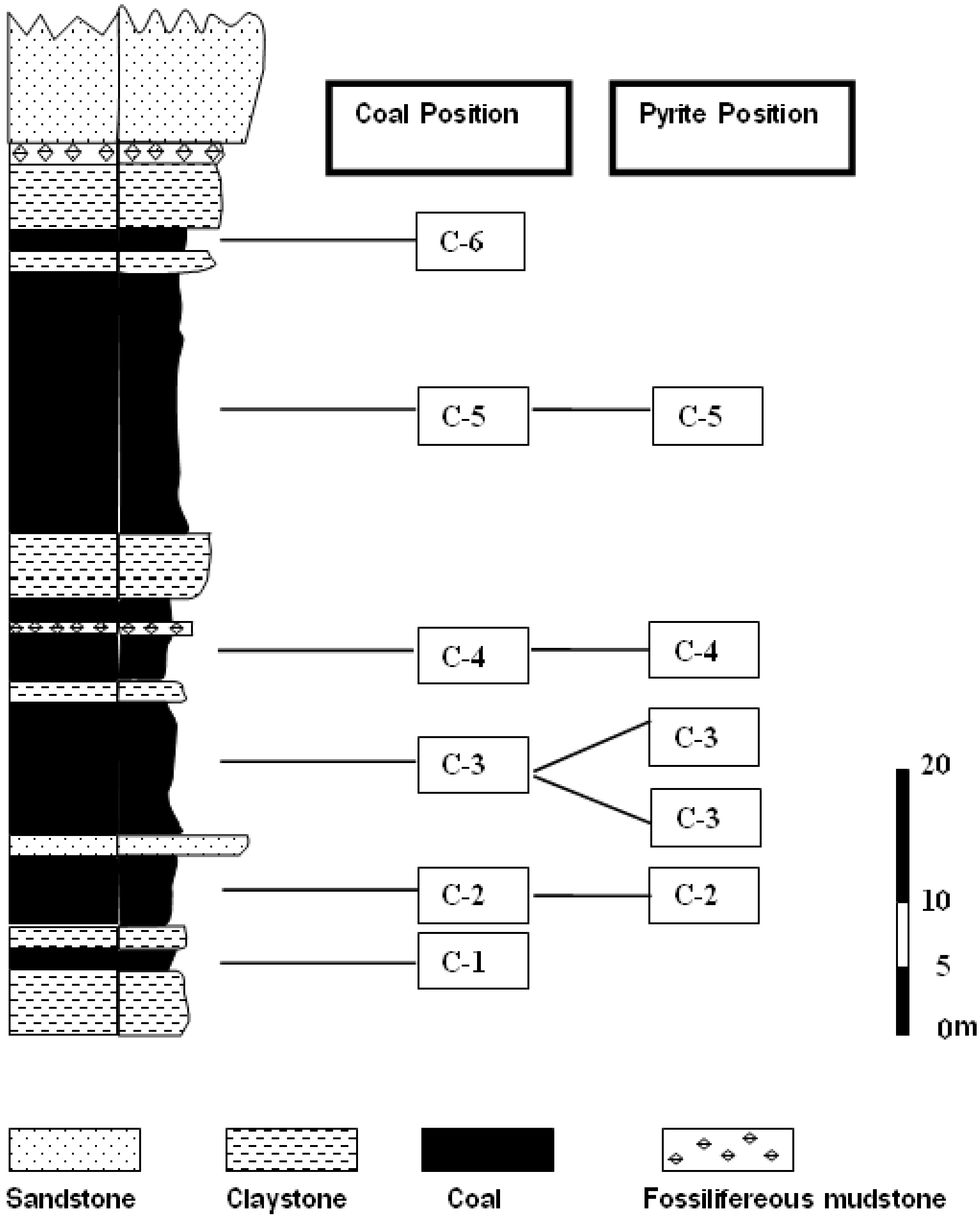

Fig 4. Lithologic column of the lower sequence and its sample positions in the Bang Mark coal deposit, Krabi Mine.

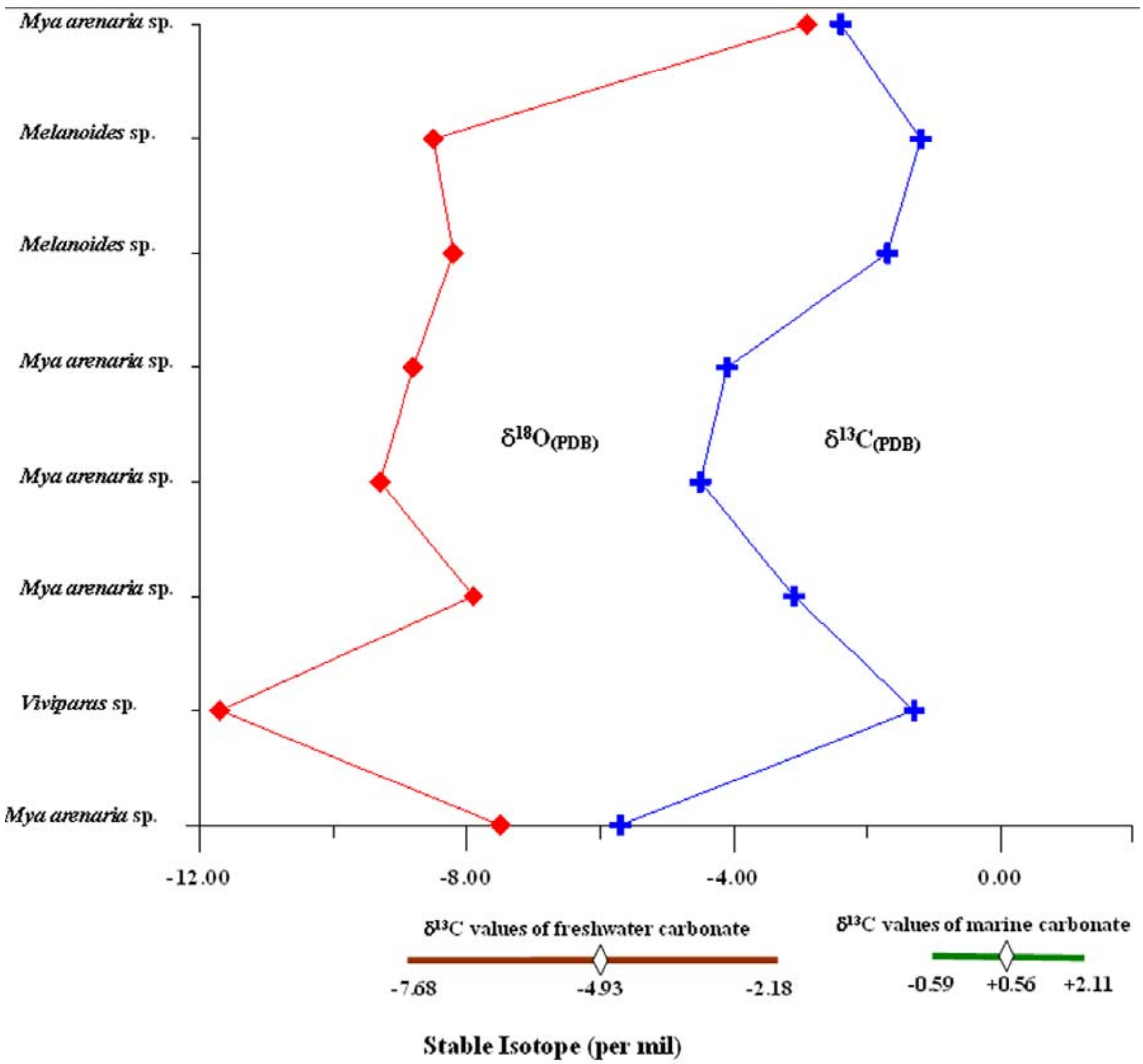

Fig 5. Variation of $\delta^{13}C$ and $\delta^{18}O$ values of shell specimens in the Bang Mark coal deposit, Krabi mine, southern Thailand, which compare to the $\delta^{13}C$ values of the freshwater and marine carbonate.[13]

could have caused some reworking of sediments. The sulfur was derived from igneous and hydrothermal origins in the area.[13]

Table 1 shows the enrichment of $\delta^{34}S$ values in the total, organic sulfur and pyrite. The $\delta^{34}S$ value of coal seams C-1, C-2, C-3, and C-4 are close to zero. These values indicate that the organic sulfur could have originated from either a magmatic or a hydrothermal source.[15,16] In the Krabi mine, diorite in the north and northeastern part could have been a magmatic source and the hot springs in Ban Nua Khlong, Khlong Thom District, could have been the hydrothermal source. This hydrothermal activity could have introduced the sulfur, after deposition of the coal, via fault or fracture zones.

The $\delta^{34}S$ values in main coal seam C-5 are +1.6‰ for total sulfur, –2.4‰ for organic sulfur, and +1.4‰ for pyrite. These values represent biological sulfur oxidization and reduction derived from igneous and hydrothermal origins.

In upper seam C-6, the $\delta^{34}S$ value is +9.8‰ for total sulfur and +4.8‰ for organic sulfur. These are the highest $\delta^{34}S$ values in the C-6 coal seam and indicate that the sulfur was derived from common plants or occurred from reduction by bacteria. Because of the difference in the reactivity of iron and organic matter toward H_2S, this has the effect of increasing the $\delta^{34}S$ values.[1]

The carbon and oxygen isotopic composition of the 24 Bang Mark shell specimens of *Viviparus* sp., *Melanoides* sp., and *Mya arenaria* were negative values (Table 2 and Fig 5). The $\delta^{13}C$ values ranged from –5.7

to –1.2‰ and averaged –3 ± 2.7‰. The $\delta^{18}O$ values ranged from –11.7 to –2.9‰ and averaged –8.1 ± 5.2‰. The $\delta^{13}C$ and $\delta^{18}O$ values of *Viviparus* sp. had a –1.3‰ $\delta^{13}C$ value and –11.7‰ $\delta^{18}O$ value. The $\delta^{13}C$ and $\delta^{18}O$ values of *Mya arenaria* had a narrow range from –5.7 to –2.4‰, and –9.3 to –2.9‰, respectively. The ranges of $\delta^{13}C$ and $\delta^{18}O$ in *Melanoides* sp. were from –1.7 to -1.2‰, and –8.5 to –8.2‰, respectively.

Oxygen isotope abundance is used to determine paleotemperature changes. Positive oxygen isotope values correspond to cold temperature, winter, and negative isotope values are associated with warmer conditions, summer.[3] All of the $\delta^{18}O$ values in the Bang mark specimens are negative values, indicating that the shells were deposited during warm conditions. This result is comparable with palynologic results, such as the presence of *Dipterocarpus*, *Hopea*, *Ilex*, *Quercus*, *Lithocarpus*, *Castanopsis*, *Bursera*, *Caesalpinia*, *Lagerstroemia*, *Alangium*, *Planchonella*, *Paraqium*, *Merremia* sp. These pollen indicated tropical rain forests within a humid environment.[17,18]

Carbon isotope is used to indicate the paleo-environment. In a previous study, shells in marine water had $\delta^{13}C$ values close to 0 ‰ versus the PDB standard,[19] but higher than the $\delta^{13}C$ values in freshwater shells.[1,6,15,20] A comparison of the carbon isotope ratios of marine and freshwater shells showed that the $\delta^{13}C$ variation ranges from –18‰ to 0‰.[1] The mean of $\delta^{13}C$ values in a freshwater carbonate is –4.93±2.75‰. The mean of $\delta^{13}C$ values in the marine carbonate is +0.56±1.55 ‰. The mid- point between the mean of the marine and freshwater carbonate is approximately –2.0‰ of the carbon isotopic composition.[21] The freshwater shells contain significantly lower amounts of $\delta^{13}C$ and $\delta^{18}O$ content than marine shells.[5,22] Also, many freshwater carbonates of biogenic origin have lower $\delta^{13}C$ and $\delta^{18}O$ values than marine carbonates. On the other hand, freshwater shells from tropical environments, where extensive evaporation can lead to ^{18}O enrichment of water in rivers and lakes, often may show oxygen isotope compositions identical to or even enriched in ^{18}O when compared to marine shells.[22]

The negative $\delta^{13}C$ values of *Viviparus* sp. from a calcareous bed interbedded in the coal seam are higher than those of *Mya arenaria* and *Melanoides* sp.[1] This difference indicates that *Viviparus* sp. in the lower part of the middle sequence is associated with more brackish water shells. This could have been caused by a marine incursion into the system.[1, 15] The low of $\delta^{13}C$ values *Mya arenaria* and *Melanoides* sp. indicate that they are a freshwater shells.[1, 15] The $\delta^{13}C$ values in *Mya arenaria* indicate that freshwater shells dominated in the coal seam within the lower and middle sequences since the $\delta^{13}C$ values were less than –2‰.[20] The $\delta^{13}C$ value in *Viviparus* sp., -1.3‰, in the middle sequence indicates they were brackish water shells. The upper sequence also contains brackish water shells, indicated by *Melanoides* sp.

Conclusions

Results of sulfur, carbon, and oxygen isotopic composition were used to determine the paleo depositional environment of the Bang Mark coal deposit. The lower sequence of the coal deposit is a freshwater environment. This is indicated by the low of $\delta^{13}C$ value of *Mya arenaria*. The sulfur isotopic composition indicates that the sulfur could be derived from a magmatic or hydrothermal source and that it was incorporated into organic matter when the organic matter was deposited.

In the middle sequence, the lower part of this sequence is a brackish water environment. This is indicated by the high $\delta^{13}C$ values of *Viviparus* sp., which are associated with brackish water shells.

In the upper sequence, its lower part has low $\delta^{13}C$ values in *Melanoides* sp. This is indicative of brackish water shells. In addition, $\delta^{18}O$ values, of all specimens (*Viviparus* sp., *Melanoides* sp. and *Mya arenaria*) reflect the warm conditions in a tropical region.

In summary, the depositional environment of the Bang Mark coal deposit was non-marine in the beginning and later became brackish water as a result of marine incursion during warmer conditions in a tropical region.

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