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Sulfur Isotopic Implication of Middle Miocene Marine Incursion in Northern Thailand

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ABSTRACT: A sulfur isotopic study was undertaken to identify environmental changes of the middle Miocene Mae Moh and Chiang Muan coal fields in northern Thailand. Samples of coal, gypsum, and pyrite were collected from the mine fronts and processed for sulfur isotopic analysis. In the Mae Moh coal field, the $\delta^{34}S$ values of pyrite from the Q and K coal zones are between +4.2 and +10.9 per mil and indicate that the source of sulfur came from organic sulfur. The $\delta^{34}S$ values of +11.2 to +12.1 per mil of gypsum from the K zone coal indicate non-marine sulfate. The $\delta^{34}S$ values of J zone coal are highly variable from -18.8 to +17.2 per mil. The $\delta^{34}S$ value of +17.2 per mil in the lower part of the J zone indicates a freshwater source. In the middle part of the J zone, the $\delta^{34}S$ values of -5.8 to +8.8 per mil may indicate a volcanic source, and are confirmed by volcanic debris. In the upper part of the J zone, the very low $\delta^{34}S$ values of –18.8 to –15.5 per mil may indicate a marine incursion during coal deposition in middle Miocene. This is confirmed by the $\delta^{34}S$ values of gypsum, which are +16.1 to +18.6 per mil, from red beds lying above the J zone. In a minor I coal zone, where the pyrite is replaced in gastropods, the $\delta^{34}S$ values of pyrite are between +30.6 to +34.2 per mil, suggesting that the sulfur was reworked from red beds by bacterial reduction. In the Chiang Muan coal field, the high positive δ^{34}sulfur values of total sulfur from LS and LM zones (+12.1 and +10.3 per mil, respectively) indicate that the LS and LM were deposited in fresh water environment. The δ^{34}sulfur values of pyrite from U2 coal zone are between –15.6 and –11.2 per mil, which show the associated with marine sulfate. The similar $\delta^{34}S$ values of black gypsum from the U1 coal zone show that the source of sulfur could have come from the oxidation of sulfide in coal. The different $\delta^{34}S$ values between the organic sulfur, total sulfur, and pyritic sulfur in the U2 zone suggest that marine incursion occurred during the deposition of the U2 coal. This is indicated by the similar $\delta^{34}S$ values of pyritic and organic sulfur.

Keywords: sulfur isotope, Mae Moh coal field, Chiang Muan coal field, marine incursion, Middle Miocene, Northern Thailand.

INTRODUCTION

Most of Cenozoic basins in Thailand originated during the Early Tertiary as a result of extensional rifting related to the collision between the Indian plate and the Asian plate.[1] These basins are characterized by north-south trending half-grabens and grabens that are filled with sedimentary rocks. The strata in these basins can be divided into syn-rift and post-rift sequences. Rifting of the onshore basins continued until Pliocene, whereas rifting of the offshore basins continued only to the Early Miocene. This rifting promoted extensive lacustrine deposition.[2,3] In northern Thailand, the basins are rich in coal and oil shale deposits. Large deposits of oil shale occur in the Mae Sod basin, whereas large lignite and coal deposits occur in the Mae Moh and Li basins.

Most of coal in northern Thailand is mined to be used in power plants and in the cement industry. Combustion of coal usually produces large quantities of polluting gases and waste, inducing environmental problems that often lead to health hazards. The environmental problems come mainly from the quality of coal used, especially from a high sulfur content coal.[4] A large amount of sulfur in the form of pyrite and gypsum is usually found in coal and its associated rocks.

The study of depositional environments and sources of sulfur in coal in northern Thailand is necessary to understand the high sulfur formation. A sulfur isotope study is useful to identify the sources of sulfur in coal and sediments.

The middle Miocene Mae Moh coal field and the Chiang Muan coal field are being mined and are the focus of this study due to their significantly high sulfur content in some coal sequences that are being mined. The Mae Moh basin, Thailand's largest proven coal deposit, is located in Lampang Province, in northern Thailand. The mine is operated by the Electricity Generating Authority of Thailand. The total coal reserves of the mine are approximately 1,047 million tons. Current annual production from the mine is approximately 13 million tons, which supports 20 percent of Thailand's electrical power requirements. Chiang Muan is a small mine with approximately 10 million tons of coal reserves. It is located in Payao Province, also in northern Thailand. The mined coal is mainly sent to Mae Moh power plants for electricity generation.

STUDY AREA

Mae Moh Coal Field

The Mae Moh coal field is located at 18° 18' 21" north latitude and 99° 44' 02" east longitude, 26 kilometers east of the city of Lampang and approximately 630 kilometers north of Bangkok. The oval shaped basin covers an area of 104 square kilometers. Coal occurs in six zones, the S, R, Q, K, J, and I zones. Present-day mining is restricted to the upper part, comprises of Q, K, and J zones.

The Mae Moh basin developed as a Tertiary north-south faulted graben that was flanked by marine Triassic rocks to the north, east, and west. These marine Triassic rocks, which constitute the Lampang Group (Fig 1), are mainly limestone, shale, and sandstone. The Tertiary rocks of the Mae Moh basin constitute the Mae Moh Group.[5] This sequence has been divided into three formations on the basis of seismic data[6] and deep borehole data. The paleomagnetic study of Mae Moh stratigraphy shows that the Mae Moh group was deposited in Middle Miocene.[7] It was supported by mammalian fossil, proboscidean, *Stegolophodon* sp., rhinocerotid, *Gaindatherium* sp., and mustelid carnivore, *Siamogale thailandica* sp.[8,9] Watanasak[10,11] concluded on the basis of pollen and spore content of core samples from a drill hole that the Mae Moh referred to Middle Miocene. Pleistocene basalt occurs at the southern part of the Mae Moh basin.[12] A thin veneer of Quaternary fluvial sediments, ranging up to 15 meters in thickness, covers the basin.

Mae Moh Group Straigraphic Succession

The three formations of the Mae Moh Group are, in ascending order, the Huai King Formation, Na Khaem Formation, and Huai Luang Formation (Fig 2). Each formation consists of clastic rocks that differ strongly in lithology, sedimentary structure, degree of consolidation, and fossil types. Stratigraphic descriptions from the bottom to the top are as follows:

Huai King Formation

The Huai King Formation was the initial deposition during rifting of the basin. It consists of semi-consolidated, fine-grained and coarse-grained clastic rocks that have small scale fining upward sequences. It underlies the coal of the S zone of the Na Khaem Formation. The thickness of the Huai King Formation varies from less than 15 meters on the edge of the basin to 150 meters in the central part of the basin. The formation has two distinct parts. The lower part consists mainly of coarse-grained strata that grade upward from conglomeratic sandstone to clayey siltstone. Breccias of local origin occur at the base of this unit. The sandstone is green, gray, and purple and is mottled red and yellow. The siltstone is gray to red and is also mottled. Some thin carbonate layers that contain fossil shell debris occur within the siltstone sequence. The upper part of the formation is a silty claystone sequence. This fining upward sequence grades from sandstone or conglomeratic sandstone to interbedded red and gray claystone and silty claystone. Calcareous and mottled horizons also occur. The rocks in this part of the formation represent rifting and rapid filling with strong to moderate fluvial energy. The lower part of the formation was deposited in a fluvial environment of braided rivers. The upper part of the formation is fluvial meandering river and overbank deposits.[13]

Na Khaem Formation

The Na Khaem Formation varies in thickness from 250 to 400 meters and consists of mudstone that has five zones of coal. The mudstone is gray to greenish gray, very calcareous, and contains abundant fossils of gastropods, fish, ostracods, and plants. It also has burrows and borings. Near the coal zones, the mudstone is either conglomeratic, calcareous, fossiliferous, or siliceous. The formation has three major economic coal seams and divides into three members such as Member III, II. And I, in ascending order.[14]

Member III (underburden)

Member III is the lowest member, which varies in thickness from 150 to 230 meters, consists of claystone interbedded with the coal of the R and S zones. These beds are variously colored, very calcareous, and conglomeratic. The gastropods *Viviparus* sp. and *Physa* sp. occur in the upper part. Other fossils include fish, ostracods, and plant roots.

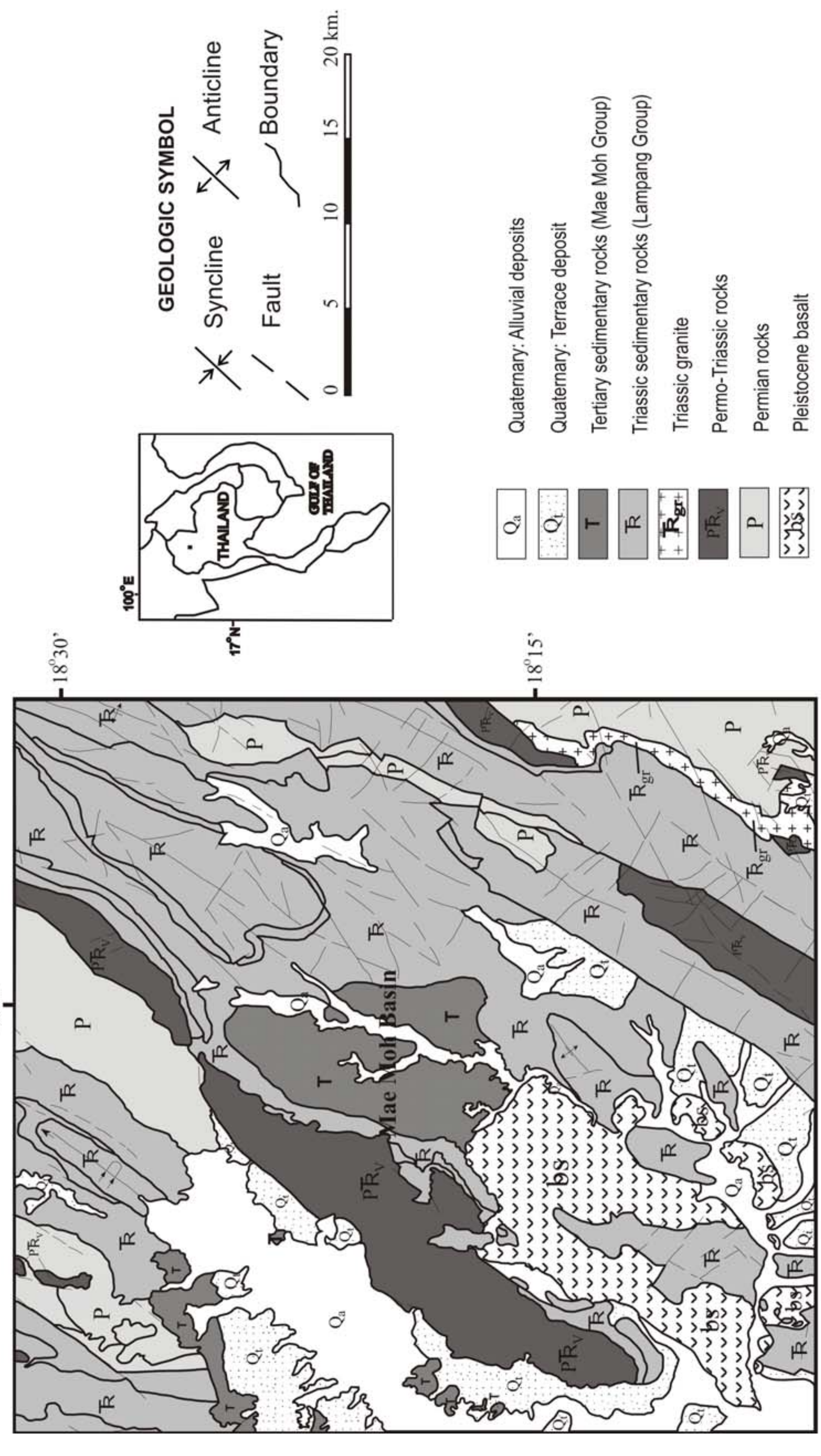

Fig 1. Geological map of the Mae Moh basin and surrounding rock units (modified from Charoenprawat *et al*, 1994).

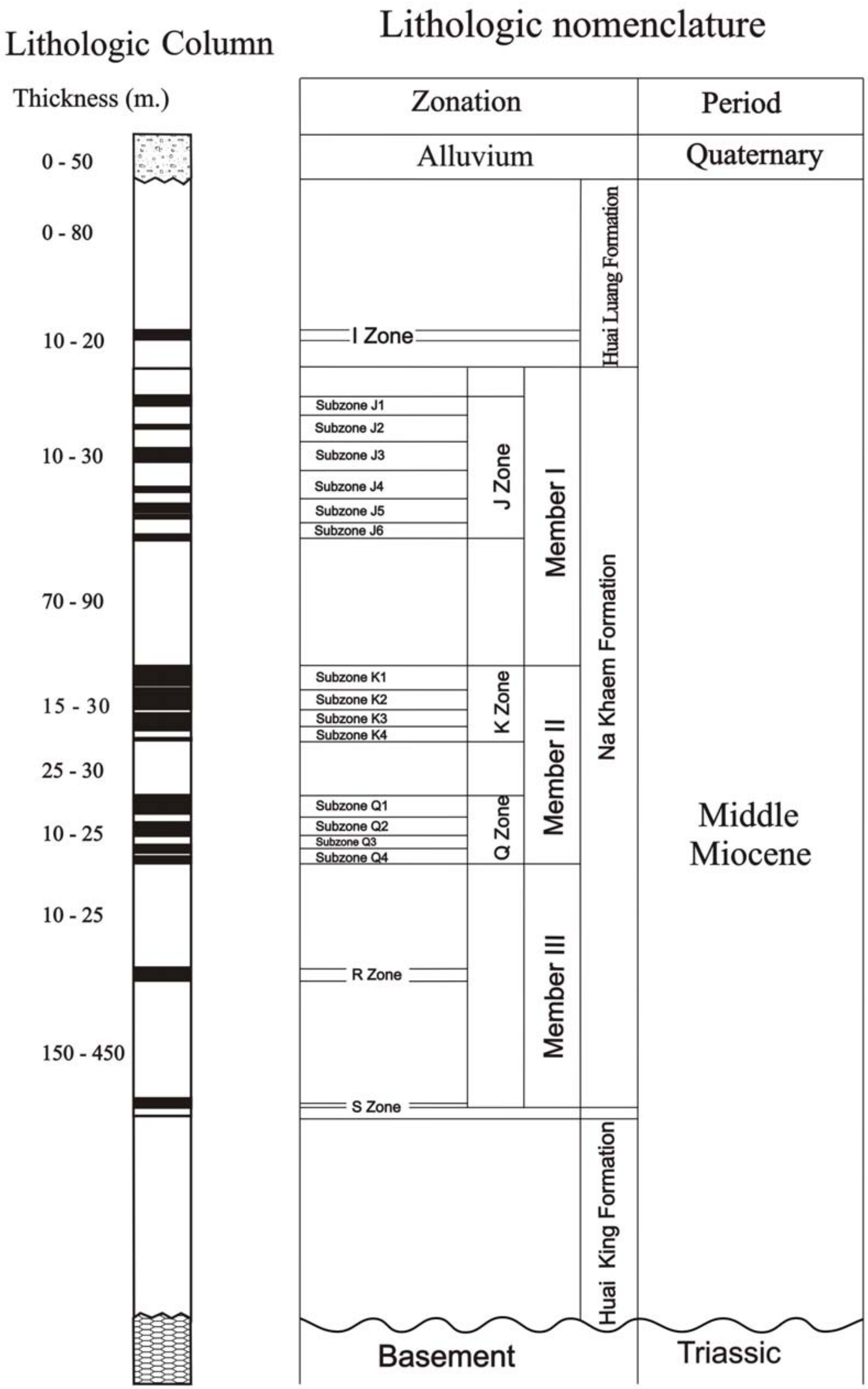

Fig 2. Stratigraphic sequence of the Mae Moh mine (not in scale, modified from Jitapankul *et al* 1985).

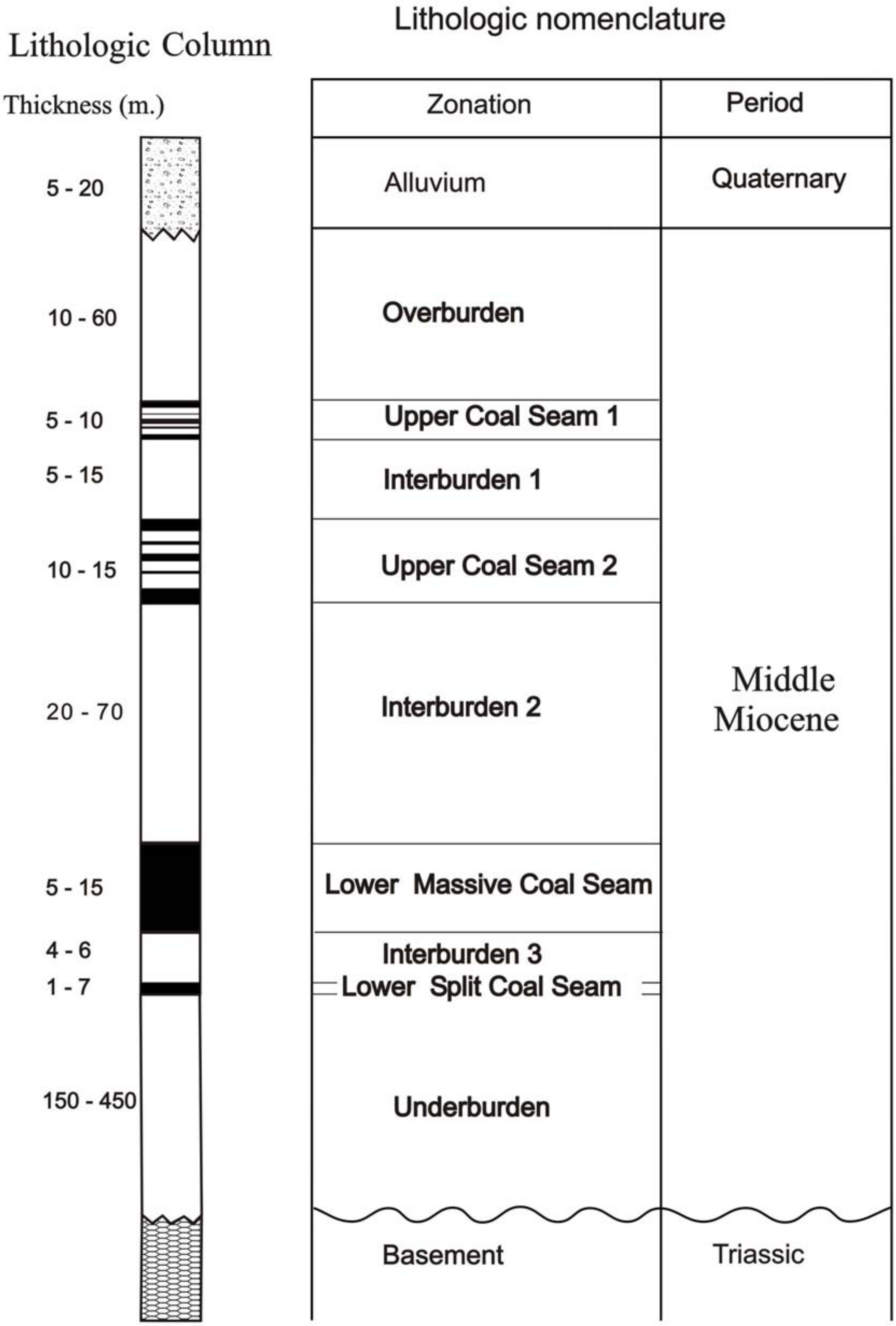

Fig 3. Stratigraphic column of Chiang Muan coal field (not in scale, modified from Nagaoka *et al*, 2003; Kunimatsu *et al*, 2003 and Nakaya *et al*, 2003).

Member II

This middle sequence member is the most economically attractive coal sequence. It consists of the Q and K coal zones and is separated into three parts by gray claystone.

Q zone: This zone contains the stratigraphically lowest coal currently mined in the Mae Moh mine. The zone consists of interbedded soft, brown coal that has abundant partings of light brown claystone. This claystone has abundant siliceous and calcareous white spots of diatoms, pyritized *Viviparus* sp., and plant remains. Total thickness varies from 25 to 30 meters. The coal in the zone is a massive seam in the central part of the mine, but is split in the north and south parts of the mine.

Interburden: A sequence of mostly claystone separates the Q and K zones. This sequence is 10 to 30 meters thick. The claystone varies in color from brown, brownish gray, gray, green, to greenish gray. Fossils of fish, gastropods such as *Viviparus* sp., and plant roots are common but ostacods are rare.

K zone: Coal in the K zone marks the upper portion of member II. It consists of 10 to 30 meters of black to brownish black, brittle coal interbedded with soft lignite and partings of light yellowish gray to gray, silty claystone. Fossils occur in the upper part of the zone. These include such gastropods as *Planobis* sp., *Viviparus* sp., and *Melanoides* sp., fish, plant, and vertebrate fossils. The coal in the zone is a massive seam in the central part of the mine, but is split in the northern and southern parts of the mine. Vertebrate fossils include proboscidean, *Stegolophodon* sp., rhinocerotid, *Gaindatherium* sp., and mustelid carnivore, *Siamogale thailandica* sp.[8,9]

Member I

Member I, the uppermost member, varies in thickness from 80 to 180 meters and consists of semi-consolidated claystone and mudstone and, occasionally, very calcareous and pyritic siltstone and volcanic debris. The upper 36 meters of this member contain 6 thin coal seams that constitute the J zone (J1 to J6). The gastropod fossils, *Melanoides* sp., *Physa* sp., and *Viviparus* sp., are common in partings of the J zone.

The uppermost 15 to 20 meters of member I is a transition zone. This zone is a distinctive suite of claystone, siltstone, and silty claystone. It marks the transition from the reducing environment of lacustrine deposition typical of the Na Khaem Formation to the oxidizing conditions characteristic of the alluvial deposits of the Huai Luang Formation.

Huai Luang Formation

The Huai Luang Formation is the uppermost unit of the Mae Moh Group. It consists mainly of semi-consolidated and unconsolidated strata that are red to brownish red and have interbedded gray layers. It was named Red Bed by Longworth-CMPS Engineers.[6] The formation is predominately claystone, siltstone, and mudstone and has some lenses of sandstone and conglomerate in the central part of the basin. The only macrofossils found in the formation are gastropods, bivalves, and plant remains in the I zone, though there is abundant gypsum and pyrite, along with rare root structures and frame structures. The thickness of the formation varies from less than 5 meters to 350 meters. Its middle part consists of gray and greenish gray claystone separated by I zone coal. The color of the formation changes upward, becoming red at the top. Its lithology indicates fluvial deposition in the lower part, swamp deposition in a lacustrine environment in the middle part, and braided river deposition in a fluvial environment in the upper part.[15]

Chiang Muan Coal Field

The Chiang Muan coal field is in the western part of the Chiang Muan basin, which is in Tambon Ban Sra, Chiang Muan District, Payao Province, in northern Thailand. The Chiang Muan basin has an elongated shape, trends north-south, and parallels flanking mountains. The coal field is approximately 775 kilometers north of Bangkok and 90 kilometers east of Payao township. It covers an area of 7 square kilometers at 18° 56' 00" north latitude, 100° 15' 00" east longitude. The Chiang Muan Mine Company mines good quality sub-bituminous coal from two of four coal-bearing intervals. These four coal intervals are the lower split coal seam, lower massive coal seam, upper coal seam 2, and upper coal seam 1 (Fig 3). The rocks that flank the Chiang Muan basin are marine Triassic and Jurassic red beds. These marine Triassic rocks form the Lampang Group (Fig 4) and are mainly conglomerate, sandstone, and shale. They occur along the north, east, and west flanks of the mine and are overlain by Jurassic sandstone. The southern part of the mine is flanked by Jurassic andesitic tuff. The Tertiary rocks of the Chiang Muan Formation consist of conglomerate, sandstone, mudstone, claystone, and coal. The paleomagnetic study of Chiang Muan Formation concluded that Chiang Muan Formation was deposited in Middle Miocene.[16] Moreover, the mammalian fossils in both of lower and upper coal seam indicate Middle Miocene age.[17,18] Quaternary fluvial deposits form a thin veneer cover throughout the basin. These fluvial deposits are up to 21 meters thick and consist of dark gray and light to medium brown unconsolidated topsoil, clay, silt, and gravel. The gravel occurs at the base of these deposits and the alluvium deposits are on the top.

Chiang Muan Stratigraphic Succession

The Tertiary clastic sequence in the Chiang Muan coal field has nine zones. These zones are, from bottom to top, underburden or UB, lower split coal seam or LS,

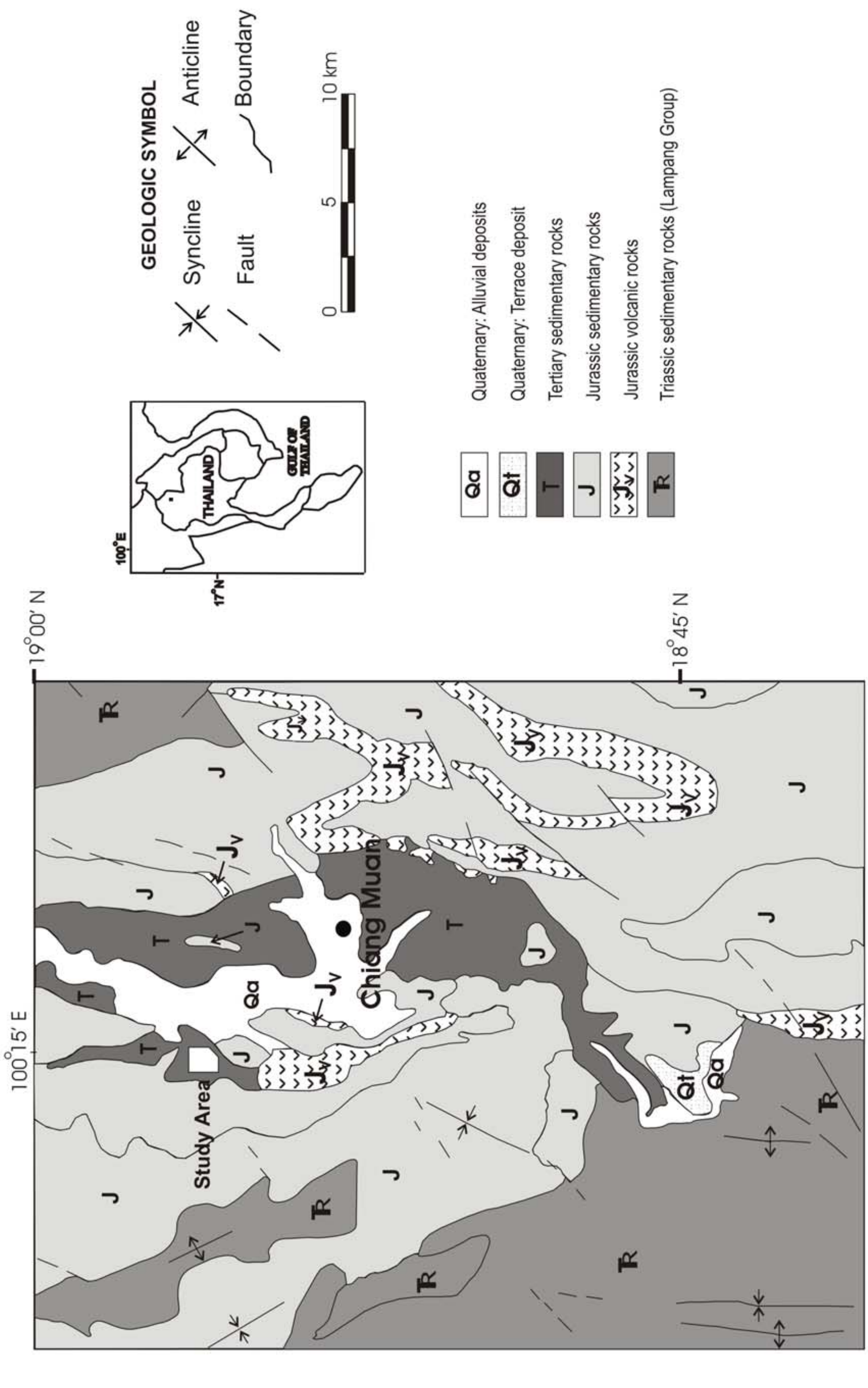

Fig 4. Geological map of the Chiang Muan basin and surrounding rock unit (modified from Charoenprawat et al, 1994).

interburden 3 or IB3, lower massive coal seam or LM, interburden 2 or IB2, upper coal seam 2 or U2, interburden 1 or IB1, upper coal seam 1 or U1, and overburden or OB. Fig 3 shows the stratigraphy of the coal field.

Underburden, UB

This zone is the lowest part of the sequence. It consists of reddish brown and gray conglomerate, pebbly sandstone, sandstone, clayey sandstone, sandy claystone, silty claystone, and claystone. Thickness of the zone exceeds 20 meters.

Lower split coal seam, LS

This zone consists of gray to black clastic beds. Its thickness varies from 1 to 7 meters. The zone's lower portion is dark gray carbonaceous claystone. Fossils in this lower part are the skeletons, teeth, and tusks of Gomphotheriidae of *Tetralophodon* cf. *Xiaolongtanensis*, pig bones and teeth, crocodile bones and teeth, bird bones, fish bones and teeth, and turtle plates. The upper part of the zone is poor quality brownish black coal 0.5 to 1.5 meters thick.

Interburden 3, IB3

The interburden 3 zone is light gray and pink silty claystone. It is medium hard and is 4 to 6 meters thick. No fossils were found in the zone.

Lower massive coal seam, LM

This zone is the main economically attractive coal zone. It consists of gray to black clastic beds made up mainly of tree trunks and its thickness varies from 10 to 15 meters. The lower portion of the zone is dark gray carbonaceous claystone. Fossils found in this claystone are the skeletons, teeth, and tusks of Gomphotheriidae of *Tetralophodon* cf. *Xiaolongtanensis*, hominoid teeth, rhinocerotid teeth, deer skeletons, turtle temora and plates, a Suidae pig molar, and pig bones. The upper part of the zone is good quality black, hard coal that is 7 to 10 meters thick.

Interburden 2, IB2

This zone consists of reddish brown, yellow, yellowish gray, and gray clastic beds. Poorly consolidated granule and pebble conglomerate occur in small lenses and thin layers in the lower, middle, and upper parts of the zone. Boulders and cobbles of sandstone occur in the upper part. The zone's thickness varies from 35 to 70 meters. No macrofossils were found in the zone.

Upper coal seam 2, U2

This zone is mainly gray claystone and coal. Its thickness varies from 15 to 30 meters. The coal occurs in the middle part and is separated into five cycles by light gray claystone. The zone contains hominoid teeth, rhinocerotid teeth, deer skeletons, turtle temora and plates, a Suidae pig molar, and crocodile fossils. The thickness of coal beds in this zone varies from 0.5 to 5 meters.

Interburden 1, IB1

This zone consists of light gray, medium hard, silty claystone and gray, non-silty claystone. Its thickness varies from 4 to 10 meters. Crocodile bones and turtle fossils occur in this zone.

Upper coal seam 1, U1

This zone consists of gray, fine-grained clastic beds and its thickness varies from 10 to 15 meters. There are five cycles of interbedded claystone and coal in the zone's lower part. The thickness of these coal beds varies from 0.5 to 1 meter. The middle part of the zone is greenish gray claystone that has gastropod fossils of *Brotia costula costula*, *Brotia costula varicosa, Melanoides* sp., *Bellamya* sp., and *Paludomus* sp., bivalve fossils of *Chamberlainia* sp. and *Indonaia* sp., mastodon bones, crocodile teeth, and plant seeds and leaves. The zone's upper part is greenish gray to reddish claystone and carbonaceous claystone. Gypsum and pyrite occur throughout the zone.

Overburden, OB

This zone is the uppermost unit of the sequence and is divided into two parts. The lower portion is gray sandy claystone, claystone, and mudstone. There are two hard calcareous bands. The upper part is yellowish brown and brown sandy claystone, clayey sandstone, and clayey siltstone. No fossils were found in this zone. The zone's thickness varies from 5 to 60 meters.

Materials and Methods

Samples of gypsum, pyrite, and coal were collected from the mine fronts. The sampling points are shown in Fig 5. Twenty-two of these samples were from the Mae Moh mine. These were one coal sample from the I zone, ten coal samples from the J zone, two gypsum samples from the red beds in the northwest pit, two gypsum samples from the red beds in the northeast pit, two gypsum samples from the K zone, three pyrite samples from the I zone, one pyrite sample in a mud ball from the K3A zone, and one pyrite sample in a mud ball from the Q4A zone. Sixteen samples were from the Chiang Muan mine. These were three coal samples from the U1 zone, four coal samples from the U2 zone, one coal sample from the LM zone, one coal sample from the LS zone, four gypsum samples from the U1 zone, and three pyrite samples from the U2 zone.

Sulfur isotopic analyses were performed at the Institute for the Study of Earth's Interior of the Okayama University in Japan. The total sulfur in coal samples was dissolved, purified, and converted to barium sulfate by using the Eschka method.[19] One gram of coal was placed in a quartz boat inside a quartz tube in a combustion train similar to that described by Nakai and Jensen[20] and Ohizumi *et al*.[21] The coal was ignited with an electric furnace at 900° Celsius under purified oxygen to extract

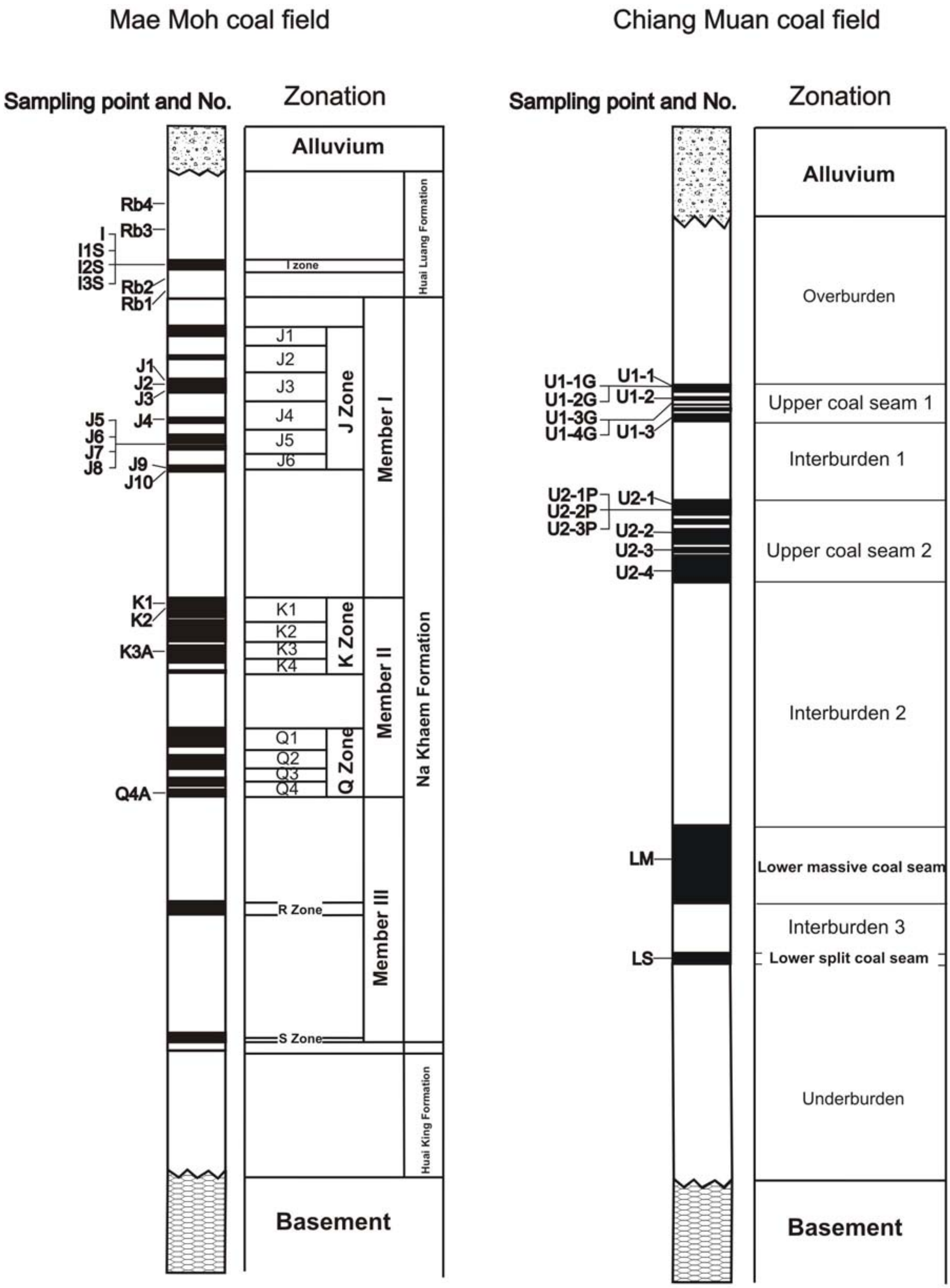

Fig 5. Sample location in lithological positions of Mae Moh and Chiang Muan coal field (not in scale).

organic sulfur. The sulfur gas was transformed and purified to barium sulfate. Pyrite samples were oxidized to barium sulfate with a bromine-nitric acid mixture using the method described by Sakai and Matsubaya.[22] Gypsum samples were converted to barium sulfate using the method of Kusakabe and Chiba.[23]

All of the barium sulfate from coal, pyrite, and gypsum was converted to sulfur dioxide for sulfur isotopic analysis using the method described by Yanagisawa and Sakai.[24] The sulfur dioxide gas was run on a stable isotope mass spectrometer, model VG-SIRA10. The sulfur isotopic ratio was expressed in a conventional delta notation:

$$\delta^{34}S = ((^{34}S/^{32}S)_x/(^{34}S/^{32}S)_{CDT} - 1) \times 1000$$

where X and CDT stand for a sample and sulfur in Canyon Diablo troilite, respectively. The overall accuracy of sulfur isotopic analysis was < 0.2 per mil.

Results and Discussion

The sulfur isotopic analyses of the Mae Moh mine samples are listed in Table 1 and Table 3. The $\delta^{34}S$ value of pyrite from the Q zone is +4.2 per mil. The $\delta^{34}S$ value of pyrite from the K zone is +10.9 per mil. The $\delta^{34}S$ values of gypsum from the K zone are between +11.2 and +12.1 per mil. The $\delta^{34}S$ values of gypsum from the red beds in the Huai Luang Formation are between +16.1 and +18.6 per mil. The $\delta^{34}S$ values of pyrite from the I zone are very high and show a narrow range, from +30.6 to +34.2 per mil. The $\delta^{34}S$ values of J zone coal range widely from -18.8 to +17.2 per mil and from –23.2 to +9.4 per mil for total sulfur and organic sulfur, respectively, whereas $\delta^{34}S$ values of total sulfur and organic sulfur of I zone coal are +11.3 and +0.2 per mil, respectively.

Table 1. $\delta^{34}S$ values of coal from the Mae Moh coal field.

Sample No.	Description	Total sulfur[a] S content,%	Total sulfur[a] $\delta^{34}S$,‰	Evolved SO_2[b] S content,%	Evolved SO_2[b] $\delta^{34}S$,‰
I	Coal in I zone	2.9	+11.3	0.3	+0.2
J1	Coal in J3A bed	6.5	-18.8	3.4	-23.2
J2	Coal in J3B1 bed	6.6	-15.5	-	-
J3	Coal in J3B2 bed	6.6	-4.5	3.5	-8.7
J4	Coal in J4 bed	5.9	-0.5	-	-
J5	Coal in J5A bed	6.7	+1.5	3.5	-1.1
J6	Coal in upper J5B bed	6.7	-3.3	-	-
J7	Coal in lower J5B bed	6.4	+4.4	1.7	+1.7
J8	Coal in J5C bed	6.3	+8.8	-	-
J9	Coal in J6A bed	5.8	-0.6	-	-
J10	Coal in J6B bed	4.3	+17.2	0.3	+9.4

Remark *: Insufficient sample for analysis
[a]: Measured by Eschka method
[b]: Measured by combustion method

Table 2. $\delta^{34}S$ values of gypsum and pyrite from the Mae Moh coal field.

Sample No.	Description	$\delta^{34}S$,‰
Rb1	Gypsum from red beds in northwest pit	+16.1
Rb2	Gypsum from red beds in northwest pit	+16.3
Rb3	Gypsum from red beds in northeast pit	+18.6
Rb4	Gypsum from red beds in northeast pit	+18.4
K1	Gypsum from K zone	+12.1
K2	Gypsum from K zone	+11.2
I1S	Pyrite in *Margarya* sp. from I zone	+32.3
I2S	Pyrite in *Margarya* sp. from I zone	+34.2
I3S	Pyrite in *Margarya* sp. from I zone	+30.6
K3A	Pyrite in mud ball from K3A zone	+10.9
Q4A	Pyrite in mud ball from Q4A zone	+4.2

The results of sulfur isotopic analyses of Chiang Muan mine samples are listed in Table 2 and Table 4. The $\delta^{34}S$ values of pyrite from the U2 zone are between –15.6 and –11.2 per mil. The $\delta^{34}S$ values of black gypsum from the U1 zone are –10.1 and –10.7 per mil, whereas the $\delta^{34}S$ values of colorless gypsum from the U1 zone have a narrow range from +4.7 to +5.4 per mil. The $\delta^{34}S$ value of LS zone coal for total sulfur is +12.1 per mil. The $\delta^{34}S$ value of LM zone coal for total sulfur is +10.3 per mil. The $\delta^{34}S$ values of U2 zone coal are between +4.3 and +8.1 per mil and from +2.8 to +3.7 per mil for total sulfur and organic sulfur, respectively. The $\delta^{34}S$ values of U1 coal are between from –18.1 and –9.7 per mil for total sulfur. In sample no. U1-1, the organic sulfur $\delta^{34}S$ value is –12.4 per mil.

For the sulfur isotope study of gypsum and pyrite, the +4.2 per mil $\delta^{34}S$ value of pyrite from the Q zone in the Mae Moh coal field is a low value. This value indicates that the source of sulfur should come from organic sulfur. The medium high $\delta^{34}S$ values of gypsum from the K zone are +12.1 and +11.2 per mil. These values are similar to values of non-marine sulfate.[25] The medium high $\delta^{34}S$ value of pyrite from the K zone is +10.9 per mil. This value indicates that the source of sulfur came from organic sulfur. The pyrite could be from an organic-rich swamp that is caused by use of organic oxysulfur compounds in dissimilatory respiration by sulfur-reducing bateria. This process would take place in a closed system.[26] However, the fossils, such as those from Q and K zones, support deposition of gypsum and pyrite in a closed system of freshwater.

The high $\delta^{34}S$ values of gypsum from the red bed zone in northwest pit of Mae Moh coal field are +16.1 and +16.3 per mil. The high $\delta^{34}S$ values of gypsum from the red bed zone in northeast pit of Mae Moh coal field are +18.6 and +18.4 per mil (Fig 6). These values are consistent with a gypsum source from marine sulfate.[27] The $\delta^{34}S$ values of Tertiary increase to +21.8 per mil at the Miocene epoch.[28] The sediments in red beds were

Table 3. δ ^{34}S values of coal from the Chiang Muan coal field.

Sample No.	Description	Total sulfur[a]		Evolved SO_2[b]	
		S content,%	δ ^{34}S,‰	S content,%	δ ^{34}S,‰
I	Coal in I zone	2.9	+11.3	0.3	+0.2
U1-1	Coal in U1 zone	6.9	-9.7	3.5	-12.4
U1-2	Coal in U1 zone	1.4	-14.8	-	-
U1-3	Coal in U1 zone	3.9	-18.1	-	-
U2-1	Coal in U2 zone	3.3	+7.7	1.4	+3.7
U2-2	Coal in U2 zone	2.6	+4.3	-	-
U2-3	Coal in U2 zone	5.7	+7.1	-	-
U2-4	Coal in U2 zone	3.5	+8.1	0.8	+2.8
LM	Coal in LM zone	1.2	+10.3	0.01	*
LS	Coal in LS zone	2.3	+12.1	0.01	*

Remark *: Insufficient sample for analysis
[a]: Measured by Eschka method
[b]: Measured by combustion method

Table 4. δ ^{34}S values of gypsum and pyrite from the Chiang Muan coal field.

Sample No.	Description	δ ^{34}S,‰
Rb1	Gypsum from red beds in northwest pit	+16.1
U1-1G	Black gypsum in U1 zone	-10.1
U1-2G	Black gypsum in U1 zone	-10.7
U1-3G	Colorless gypsum in U1 zone	+4.7
U1-4G	Colorless gypsum in U1 zone	+5.4
U2-1P	Pyrite in U2 zone	-15.6
U2-2P	Pyrite in U2 zone	-15.4
U2-3P	Pyrite in mud ball from U2 zone	-11.2

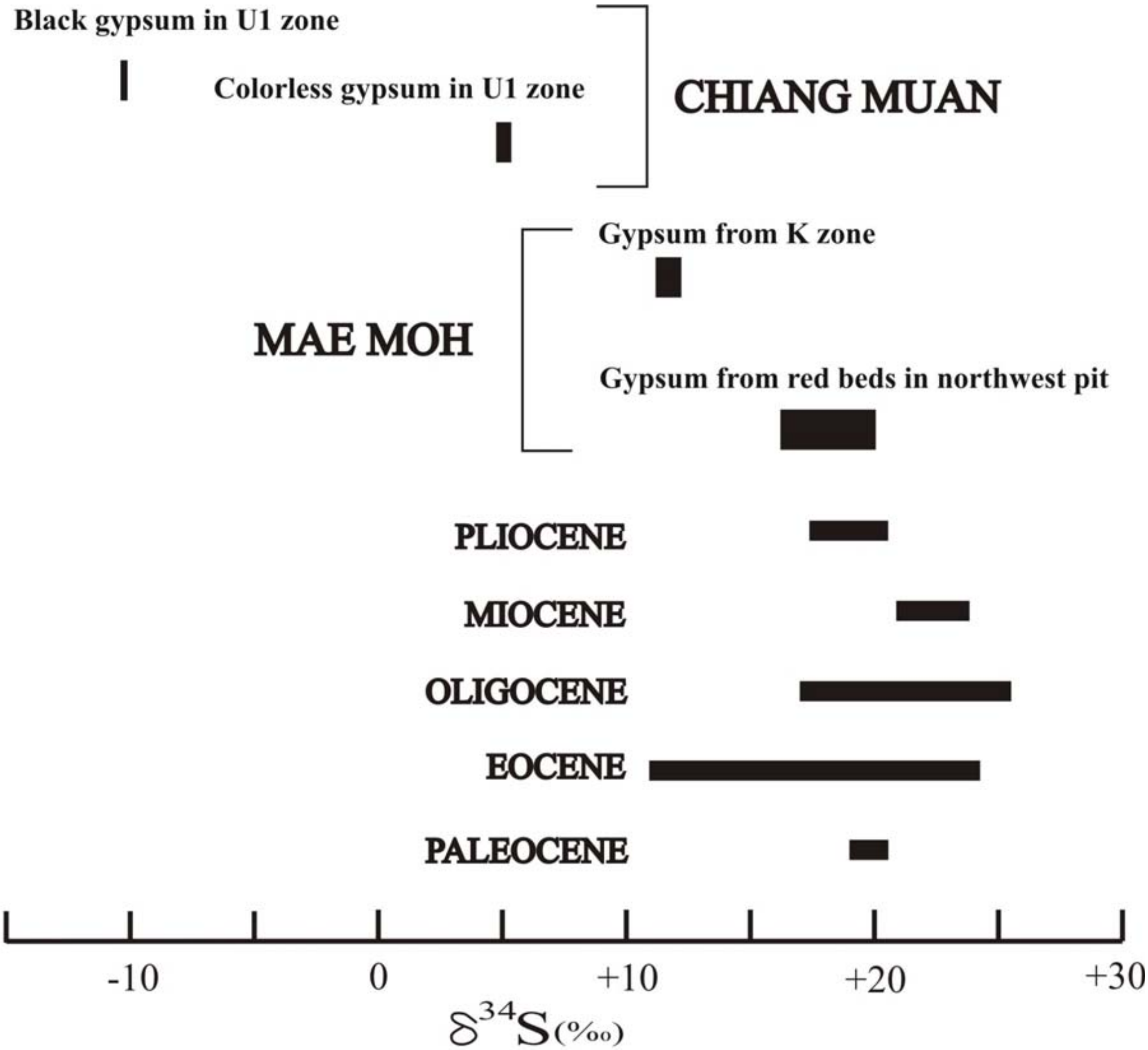

Fig 6. The sulfer isotope values of marine evaporates in Tertiary (modified from Claypool *et al*, 1980; Nielsen *et al*, 1991 and Takaya, 2001).

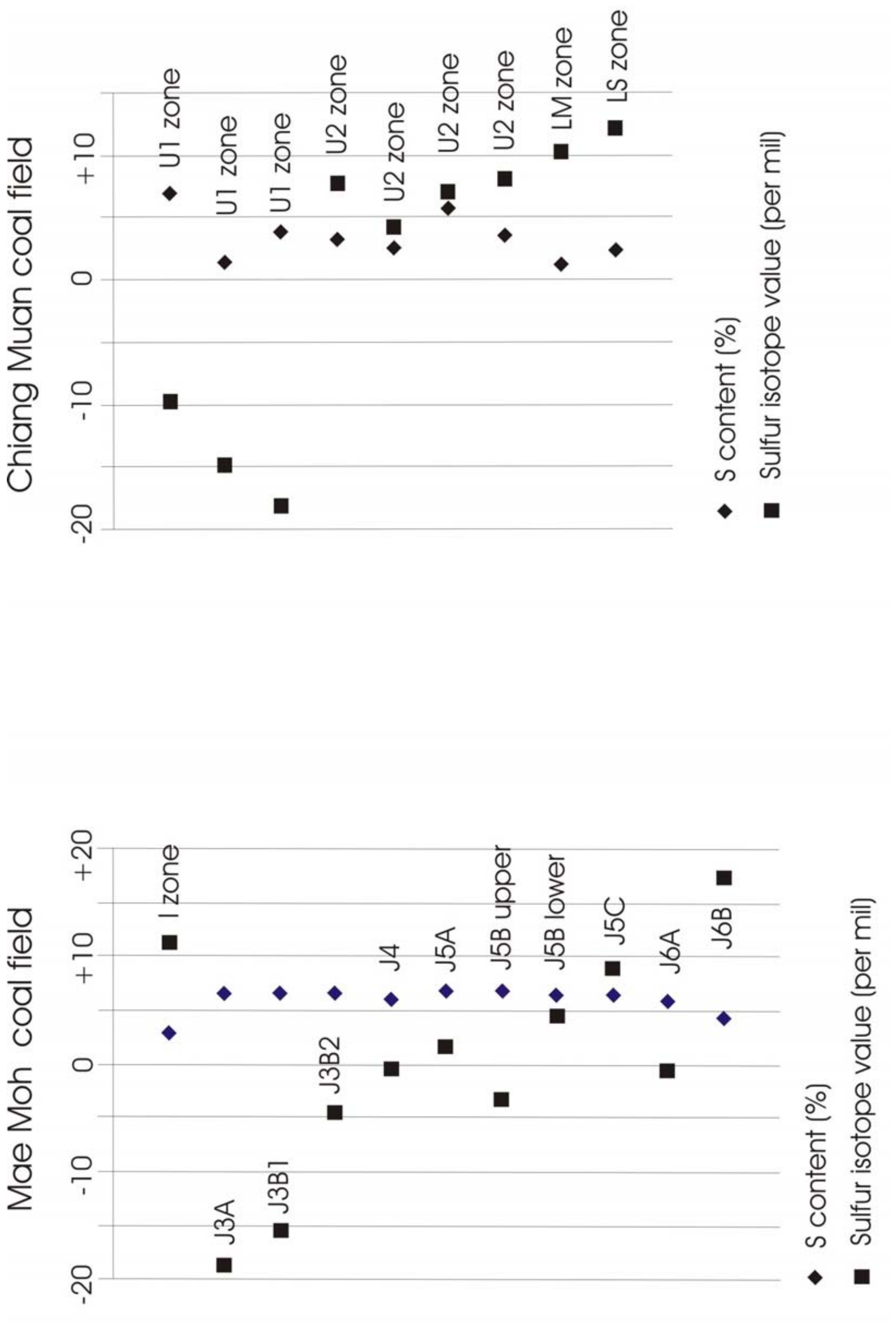

Fig 7. Graph of sulfur isotope values and sulfer content of total sulfer in coal from Mae Moh and Chiang Muan coal field.

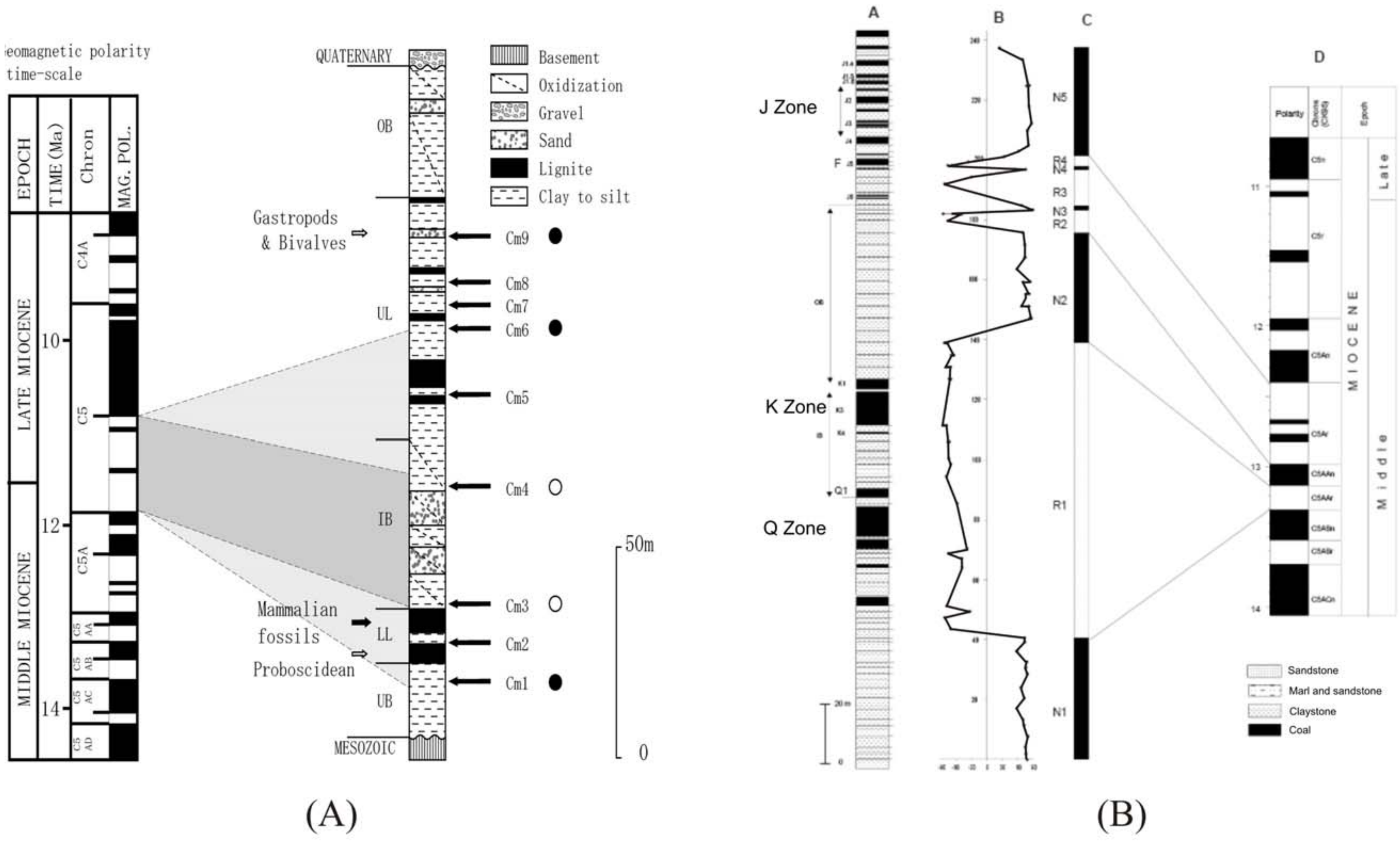

Fig 8. Paleomagnetic study in the Miocene sedimentary rock from Chiang Muan (a) and Mae Moh (b) coal field (modified from Nagaoka *et al*, 2003 and Benammi *et al*, 2002).

deposited in a fluvial environment.[13,15] However, the $\delta^{34}S$ values of gypsum indicate that there was marine incursion during sediment deposition. The marine incursion can be confirmed by the sulfur isotopic study from Tankaya.[29] The high $\delta^{34}S$ values of gypsum from red beds are between +16.4 to +20.0 per mil. The similarity of the $\delta^{34}S$ in this study and Tankaya[29] show marine source.

The very high $\delta^{34}S$ values of pyrite in the gastropod samples, *Margarya* sp., from I zone coal of Mae Moh coal field are +30.6 +32.3, and +34.2 per mil. These values could indicate a sulfur source from reduction of sulfate by bacteria to sulfide during coal deposition.[30] The very high $\delta^{34}S$ values of pyrite samples strongly indicate a closed system of freshwater environment.[31] The source of pyrite in the gastropod, *Margarya* sp., samples from I zone coal could be from reduction of freshwater sulfate by bacteria. Tankaya[29] studied the source of sulfur in pyrite from I zone coal and, based on intermediate negative $\delta^{34}S$ values of -13.6 and –7.8 per mil, which correspond to gypsum from red beds, concluded that the source of sulfur was derived from a marine incursion. Moreover, the sulfur of the gypsum from red beds indicates marine sulfate. The I zone is the zone between red beds, so its sulfur could be derived from a sulfate marine source, which was found as gypsum in the red beds below this I zone. This is the other reason that pyrite can be formed after coal was deposited. Nonetheless, the sulfur in this zone needs to be further analyzed and compared with these data.

The very low $\delta^{34}S$ values of pyrite, –15.6, -15.4, and –11.2 per mil, from the U2 zone in the Chiang Muan coal field indicate an open system relative to seawater sulfate.[32] The very low $\delta^{34}S$ values of black gypsum from U1 zone are -10.7 and –10.1 per mil. These values are close to the $\delta^{34}S$ values in coal from the U1 zone. The source of sulfur could come from the oxidation of sulfide in coal to sulfate.[33] On the other hand, the $\delta^{34}S$ values of colorless gypsum from the U1 zone are low positive values, being +4.7 and +5.4 per mil. These values indicate non-marine sulfate.[34]

For the sulfur isotope study of coal, Smith and Batts[35] suggested that the $\delta^{34}S$ values of organic sulfur in low-sulfur coal are representative of the isotopic composition of sulfate in a freshwater environment in which the coal was deposited. These values are in the LM, LS, and U2 zones in the Chiang Muan mine and also occur in the lower portion of the J and I zones in the Mae Moh basin.

The very low $\delta^{34}S$ values of total sulfur in high-sulfur coal, in samples U1-1, U1-2, and U1-3 from the Chiang Muan mine and J5, J7, and J10 from the Mae Moh mine (Fig 7), indicate a marine incursion during plant growth and early deposition.[28] These very low sulfur values indicate that the sea level changed during the depositional period. There was a marine incursion in northern Thailand in the middle Miocene. The cause of sea level change could be from the changing of the polarity of paleomagnetic. The paleomagnetic study of middle Miocene Mae Moh and Chiang Muan coal field showed the reverse paleomagnetic in the middle Miocene (Fig 8).[7,16] Additionally, volcanic debris in strata in the middle part of the J zone in the Mae Moh mine could have been another source of sulfur.[36] The basins between the Mae Moh basin and the Chiang Muan basin have to be investigated to confirm this high sea level change. Moreover, there is the evidence of marine incursion during Miocene at Phrae Basin in northern Thailand. The Palynological study of PH1 and PH2 well samples from Phrae basin showed the specimens of *Florschuetzia semilobata*, *Florschuetzia trilobata* and *Zonocostites ramonae* indicating marine influences on deposition.[37]

Conclusions

In the Mae Moh coal field, the $\delta^{34}S$ values of pyrite from the Q and K zone (+4.2 and +10.9 per mil respectively) indicate that the source of sulfur was from organic sulfur. The $\delta^{34}S$ values of gypsum from the K zone (+11.2 to +12.1 per mil) have sulfur values similar to non-marine sulfate. The K zone and Q zones were deposited in a freshwater environment. The $\delta^{34}S$ value of +17.2 per mil in the lower part of the J zone indicates a freshwater source. In the middle part of the J zone, the $\delta^{34}S$ values of -5.8 to +8.8 per mil may indicate a volcanic source, and are confirmed by volcanic debris. In the upper part of the J zone, the very low $\delta^{34}S$ values of –18.8 to –15.5 per mil may indicate a marine incursion during coal deposition. On the other hand, the $\delta^{34}S$ values of gypsum from the red bed zone (+16.1 to +18.6 per mil) indicate a sulfur source from marine sulfate. This indicates a marine incursion during red bed deposition. The $\delta^{34}S$ values of pyrite in the gastropod samples from I zone coal (+30.6 to +34.2 per mil) indicate a sulfur source from bacterial reduction of sulfate to sulfide.

In the Chiang Muan coal field, the high δ^{34}sulfur values of total sulfur from LS and LM zones (+12.1 and +10.3 per mil respectively) indicate that the LS and LM were deposited in fresh water environment. During the U2 coal deposited, there was a marine incursion, as indicated by the source of sulfur isotope in pyrite from this zone (–15.6 to –11.2 per mil). Moreover, the low δ^{34}sulfur values of total sulfur from U1 coal zone (-18.1 to –9.7 per mil) indicate a normal marine environment during plant growth and early deposition and a later change to a freshwater environment.

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