CHAPTER 3

SAMPLE COLLECTION AND ANALYTICAL METHODS

This chapter describes how the samples were collected. The descriptions include where the samples came from. After that, chemical treatments from the samples collected as well as chemical procedure are explained step by step. The analytical conditions consist of proximate analysis, ultimate analysis, X-ray diffraction analyses, X-ray fluorescence spectrometry analyses, Induced couple plasma optical emission spectrometry analyses, Coal petrography, Sulfur isotope, and Carbon-Oxygen isotope.

3.1 Sample collection

The samples of this study are listed in Table 3.1, which collected from the outcrop in the mine quarries from the 3 basins (Mae Moh, Chiang Muan, and Mae Teep coal fields) and coal pit from 2 basins (Ngao and Wang Nua coal fields). The samples consist of dark gray to light gray claystone, red claystone, brownish gray claystone, brownish gray oil shale, and coal. Each bed within the stratigraphic succession was described and the stratigraphic levels of the samples collected were determined by using measuring tape. Each sample was collected in such a manner to avoid as much as possible contamination from other samples. Trenching to expose a fresh surface was always done before collecting a sample. The outer outcrop surface was always removed in order to obtain fresh inner material. Packing in a plastic bag, sealing, and labeling with the necessary information was always done in the same manner for the each sample including sample number, and location.

Table 3.1 The number of samples for geochemical analysis.

Geochemical analysis	Mae Moh coal field	Chiang Muan coal field	Mae Teep coal field	Ngao coal field	Wang Nua coal field
Proximate analysis	29	9	12	1	2
Ultimate analysis	29	9	12	1	2
X-ray diffractometry technique (XRD)	111	34	44	3	7
X-ray fluorescence technique (XRF)	101	34	42	2	6
Induced couple plasma technique (ICP)	38	34	-	-	-
Coal petrography study	27	18	25	10	6
Carbon and oxygen isotope study	30	14	-	12	-
Sulfur isotope study	38	16	1	1	1
CHNS analysis	101	34	42	1	2
Total	504	202	178	31	26

3.1.1 Mae Moh basin

The exposure Tertiary sediments in the Mae Moh coal mine include only part of the whole sequence. Only the Na Khaem Formation and Huai Luang Formation were observed (Figure 3.1). The samples collected were briefly described in Appendix A. The Huai King Formation and almost all of Member III of the Na Khaem Formation were unexposed. Only 3 sample from Member III of the Na Khaem Formation was collected (UB1 to UB3). Four coal samples (Q1 to Q4) and 10 parting claystone samples (QS1 to QS10) were collected from the Q coal zone (Figure 3.2). Six coal samples and 5 parting claystone samples were collected from the K coal (Figure 3.2). The Interburden Unit (IB), sandwiched between Q and K zones, is a claystone unit and only 5 claystone samples were collected (IB1 to IB5) (Figure 3.1).

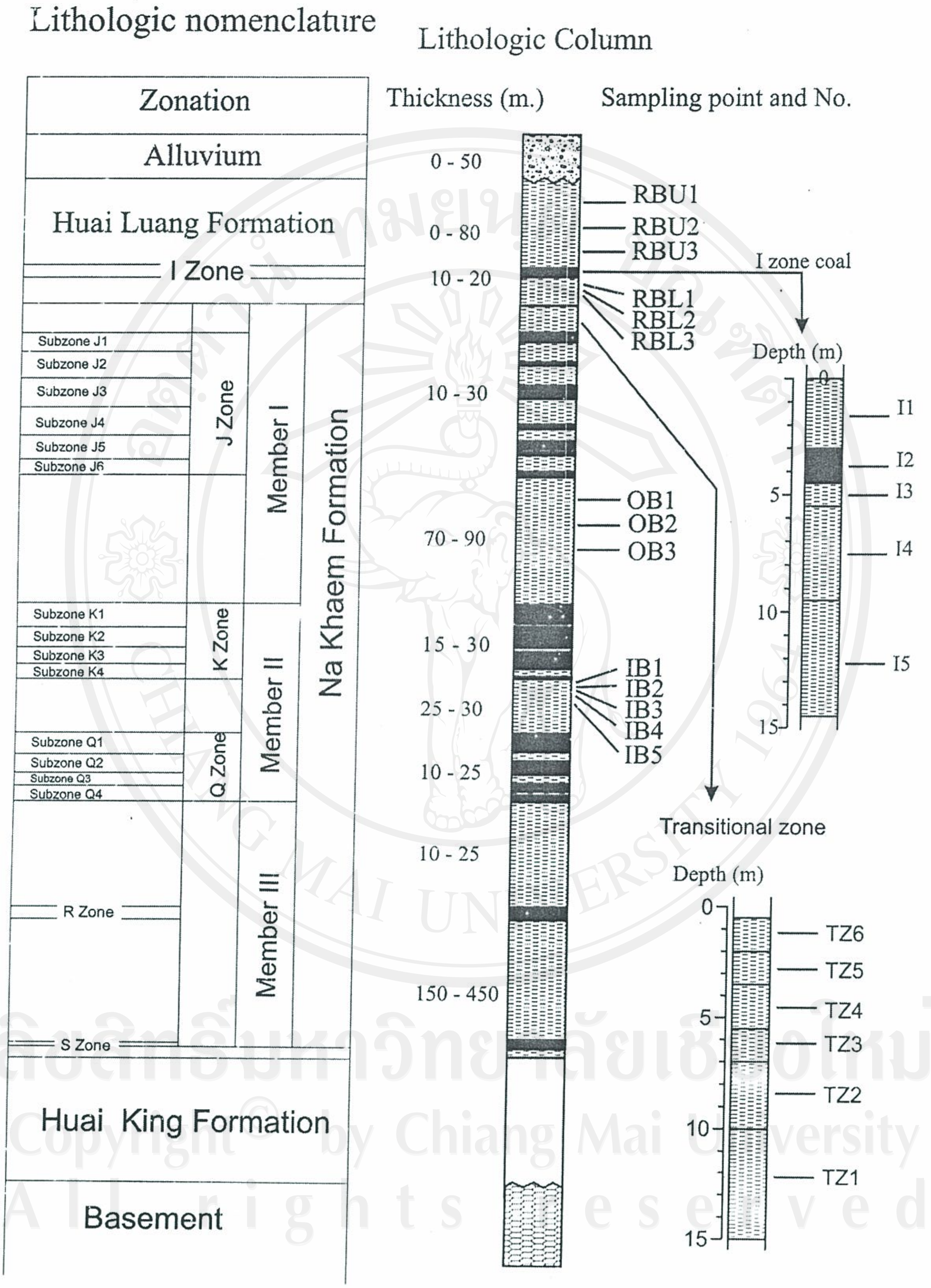

Figure 3.1 A partial schematic stratigraphic succession of Mae Moh coal field, showing stratigraphic levels of the samples collected.

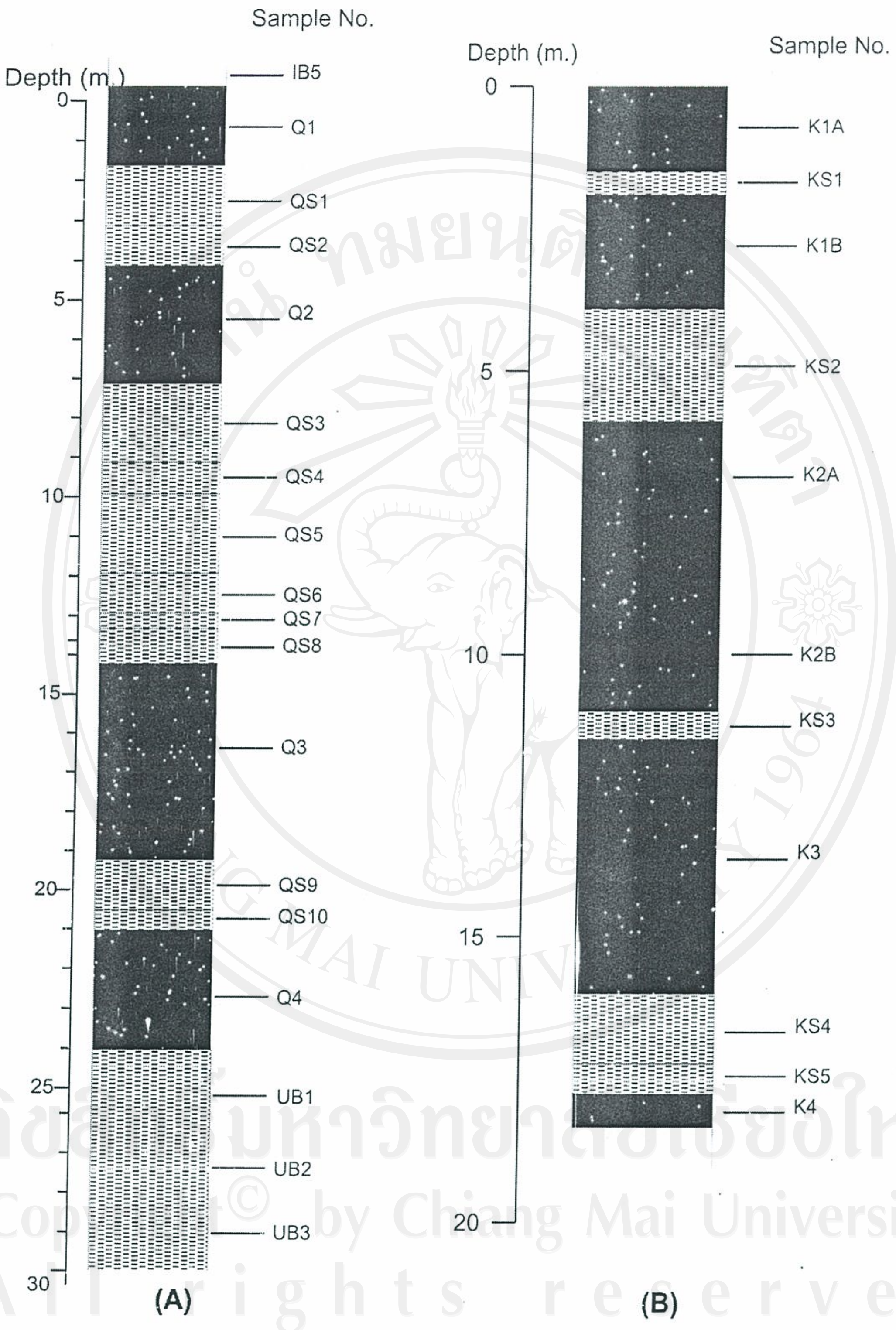

Figure 3.2 A partial schematic stratigraphic succession of Q zone coal (A) and K zone coal (B) of Mae Moh coal field, showing stratigraphic levels of the samples collected.

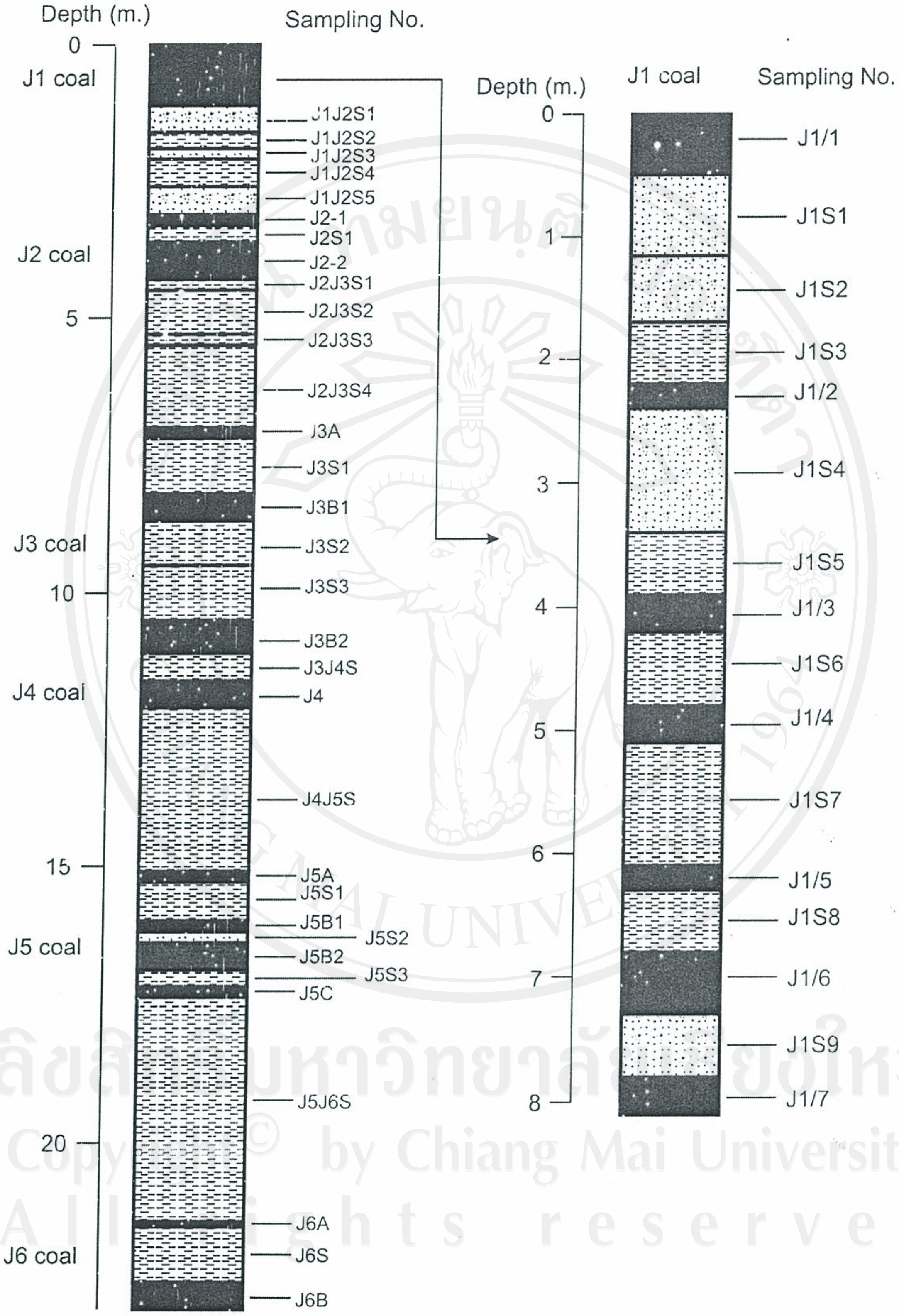

Figure 3.3 A partial schematic stratigraphic succession of J zone coal of Mae Moh coal field, showing stratigraphic levels of the samples collected.

At J coal zone, there were 19 coal samples and 29 parting claystone samples (Figure 3.3). The Overburden Unit (OB), sandwiched between K and J zones, is a claystone unit and only 3 claystone samples were collected (OB1 to OB3). The transitional zone (TZ), the uppermost of Na Khaem Formation, is claystone unit and 6 claystone samples were collected (TZ1 to TZ6). Huai Luang Formation is the upper formation of Mae Moh Group. This formation is mostly red color, so was called “Red Bed”. The red bed consists of conglomerate, sandstone, claystone, and a minor coal seam (I zone coal). Only 1 coal sample and 4 claystone samples were collected from the I coal zone. There are 3 samples from Red Bed above I zone coal (RBU1 to RBU3) and 3 samples from Red Bed under I zone coal (RBL1 to RBL3).

For the carbon and oxygen isotopic study, there were 3 *Bellamya* sp. samples from the underburden unit. Three *Bellamya* sp. samples were collected from the claystone parting between K3 and K4 coal. Three *Bellamya* sp. samples were collected from the claystone in K2 coal. Three Planorbidae samples were collected from K1 coal. Three *Bellamya* sp. samples were collected from J5 coal. Three *Melanoides* sp. samples were collected from J4 coal. Three *Bellamya* sp. samples were collected from J4 coal. Six *Margarya* sp. samples were collected from I zone coal. The samples collected were briefly described in Appendix A.

For the sulfur isotopic study, there were 38 samples. One coal sample and 1 pyrite sample were collected from Q zone coal. Two coal samples, 1 pyrite sample, and 2 gypsum samples were collected from K zone coal. There were 19 coal samples from J zone coal. One coal sample and 5 pyrite samples were collected from I zone coal. And 6 gypsum samples were collected from red bed unit (Appendix A).

3.1.2 Chiang Muan basin

Twenty-five sediment samples and 9 coal samples were collected from the Chiang Muan coal field from every unit (Figure 3.4). Samples were shortly described as in Appendix A. Two samples were collected from Underburden unit (UB). One coal sample and one carbonaceous claystone sample were collected from Lower split coal seam (LS) unit. Two claystone samples were collected from Interburden 3 (IB3) unit. One coal sample and one carbonaceous claystone sample were collected from Lower massive coal seam (LM) unit. Four samples were collected from Interburden2 (IB2)unit. Four coal samples, 3 claystone samples, and 1 sandstone samples were collected from Upper coal seam 2 (U2) unit. One claystone sample was collected from Interburden1 (IB1) unit. Three coal samples and 3 claystone samples were collected from Upper coal seam 1 (U1) unit. Five claystone samples were collected from Overburden (OB) unit. Two samples of red unconsolidated sand were collected from the Quaternary sediment overlain the Overburden (OB) unit.

For the carbon and oxygen isotopic study, there were 5 *Hyriopsis* sp., 3 *Melanoides* sp., *Bellamya* sp., and 3 *Brotia costula varicosa* sp. from claystone at Upper coal seam 1 (U1) unit. The samples collected were briefly described in Appendix A.

For the sulfur isotopic study, there were 16 samples. There were 1 coal sample from Lower split coal seam (LS) unit, 1 coal sample from Lower massive coal seam (LM) unit. Four coal samples and 3 pyrite samples were collected from Upper coal seam 2 (U2) unit. Three coal samples and 4 gypsum samples were collected from Upper coal seam 1 (U1) unit (Appendix A).

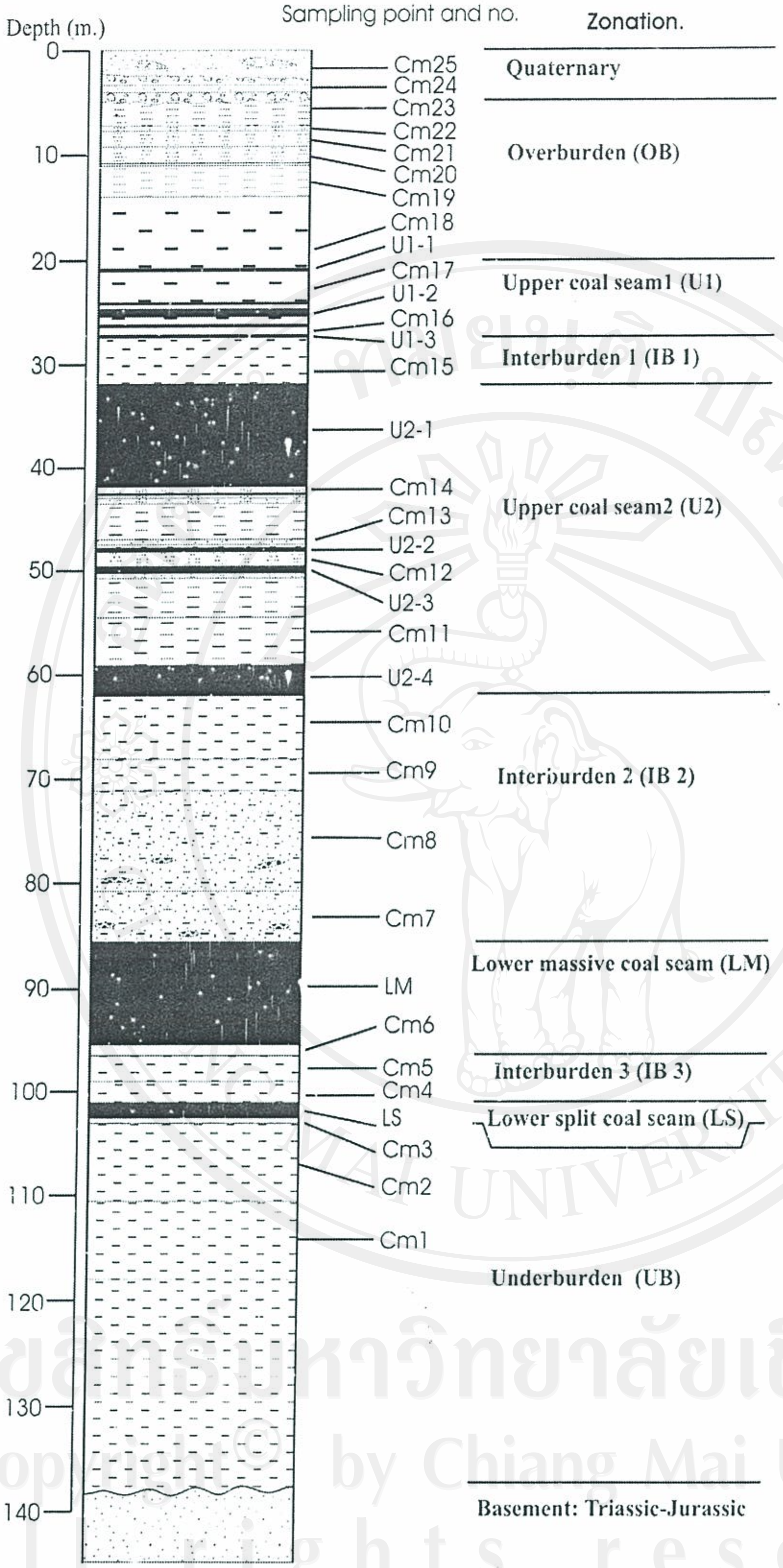

Figure 3.4 A partial schematic stratigraphic succession of Chiang Muan coal field, showing stratigraphic levels of samples collected.

3.1.3 Mae Teep basin

Thirty sediment samples and 12 coal samples were collected from the Mae Teep coal field from almost every unit (Figure 3.5). Samples were shortly described as in Appendix A. Six claystone samples were collected from Underburden unit (UB1 to UB6). Twelve coal sample (MTC1 to MTC12), 5 claystone sample (MTP1 to MTP5), and 2 oil shale samples (MTP6 and MTP7) were collected from Main coal seam unit. Seventeen samples were collected from Overburden unit (OB1 to OB17).

3.1.4 Wang Nua basin

Four sediment samples (Q1, Q2, OB1, and OB2) and 2 coal samples (C1 and C2) were collected from the pit. There was 1 pit located at Ban Mun, Wang Nua District, Lampang Province (Figures 3.6 and 3.7).

For the carbon and oxygen isotopic study were made from shell, there were 1 *Hyriopsis* sp., 6 *Margarya* sp., and 3 *Brotia* sp. from claystone at Unit B. The samples collected were briefly described in Appendix A.

3.1.5 Ngao basin

Only two coal samples (C1 and C2) were collected from the pit. The coal is underlain by gravel beside Huai Ton Phung (Figures 3.8 and 3.9).

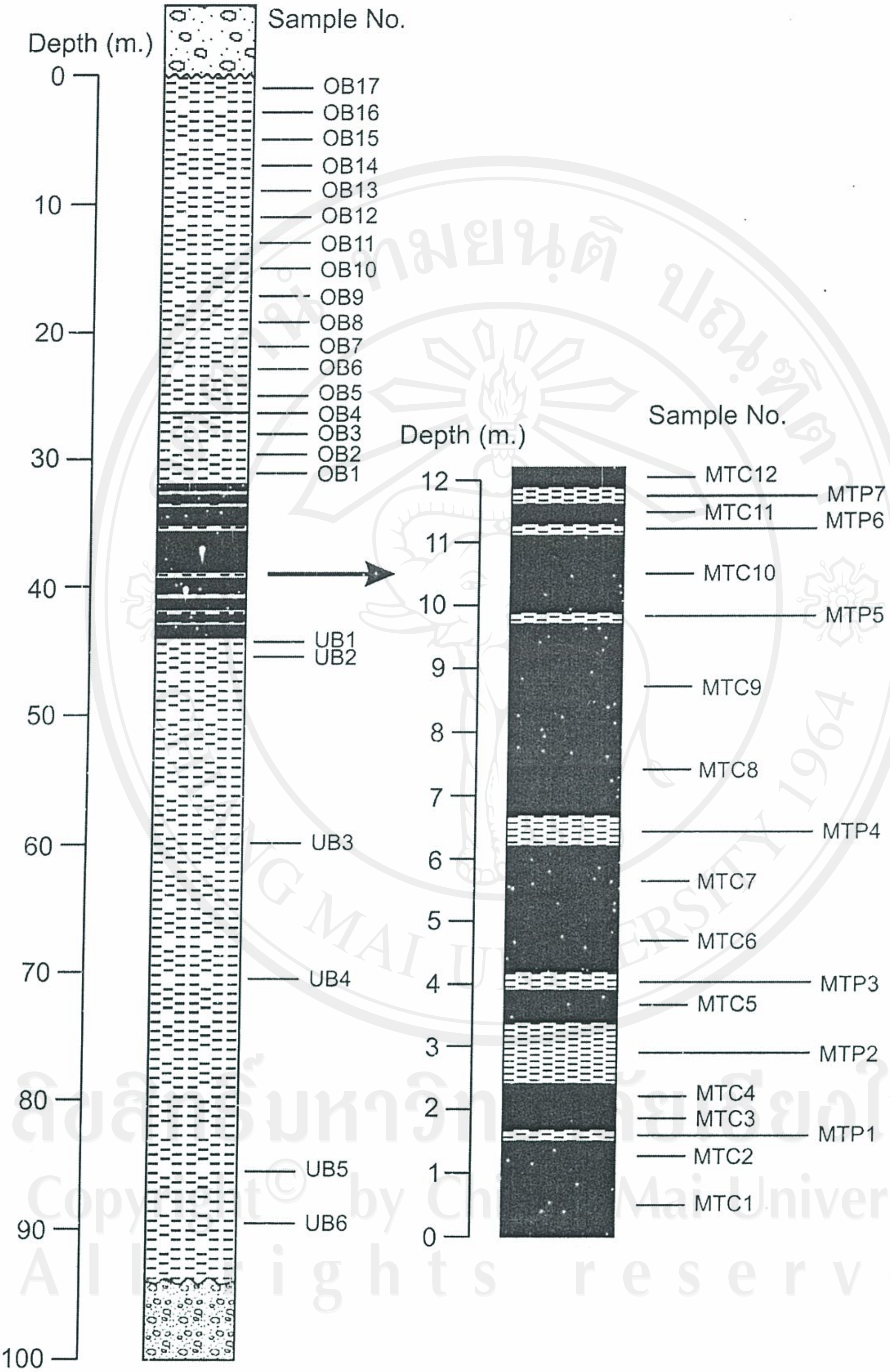

Figure 3.5 A partial schematic stratigraphic succession of Mae Teep coal field, showing stratigraphic levels of samples collected.

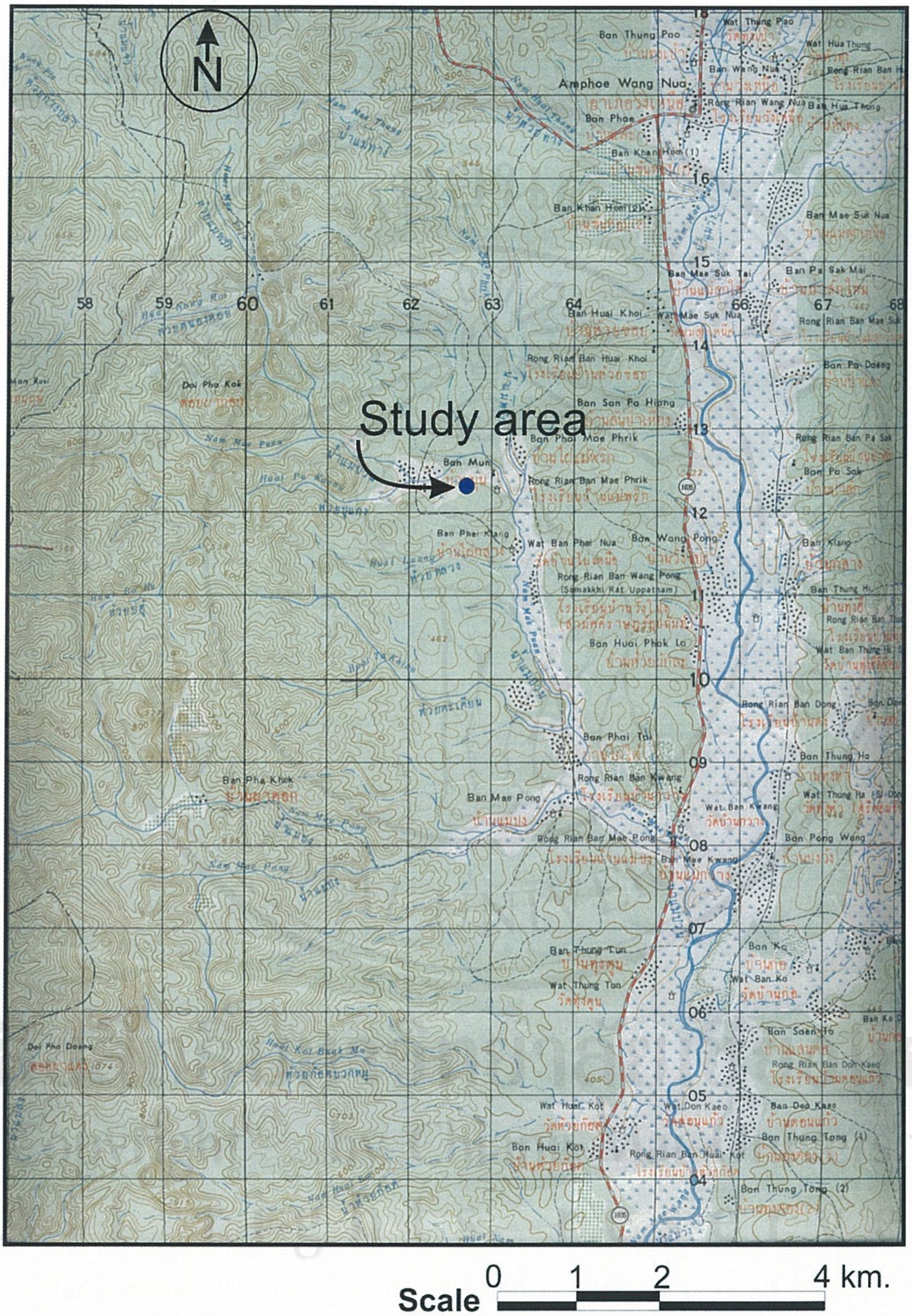

Figure 3.6 The study area of Wang Nua pit at grid reference 627123, Sheet Wang Nua.

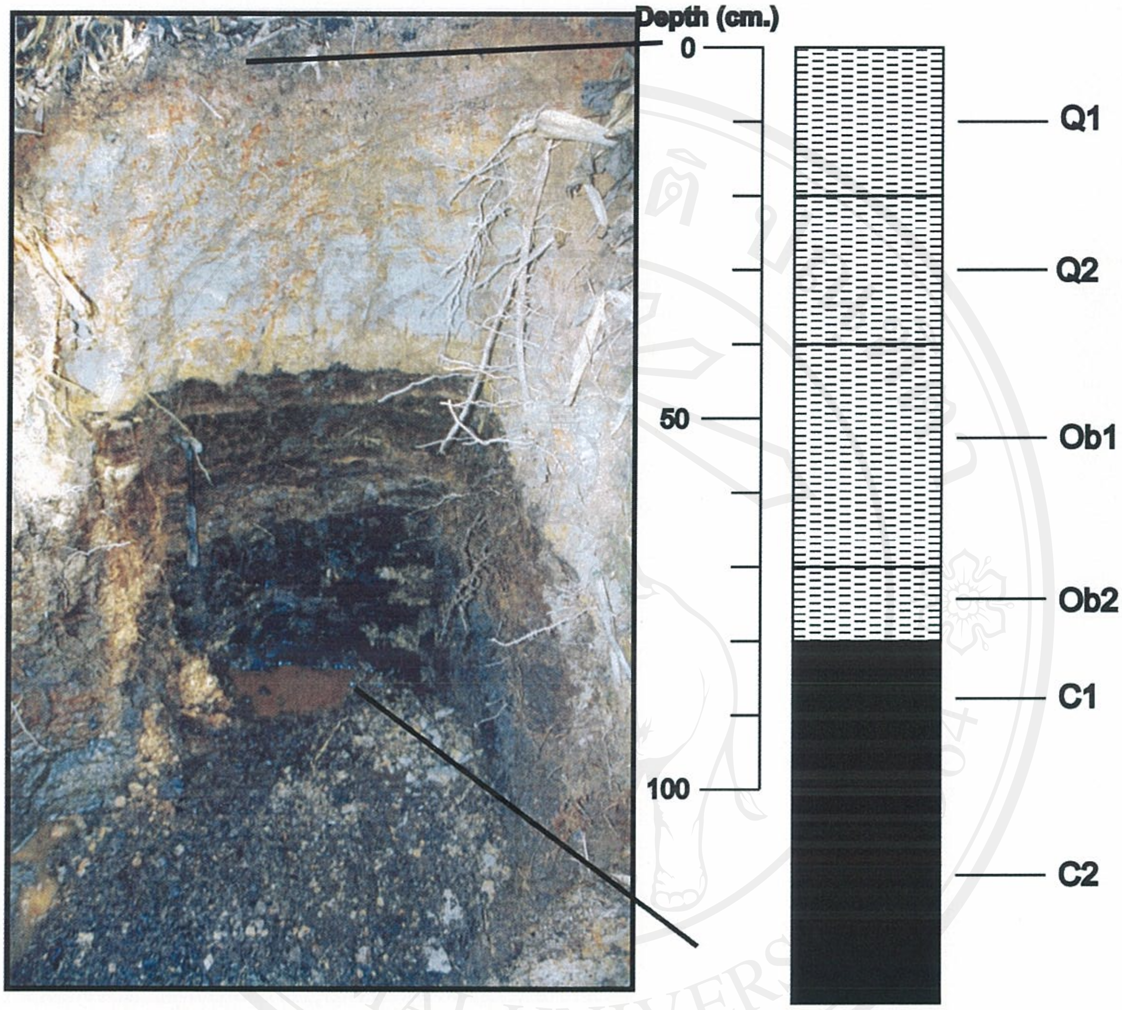

Figure 3.7 A partial schematic stratigraphic succession of Wang Nua pit, showing stratigraphic levels of the samples collected and photograph.

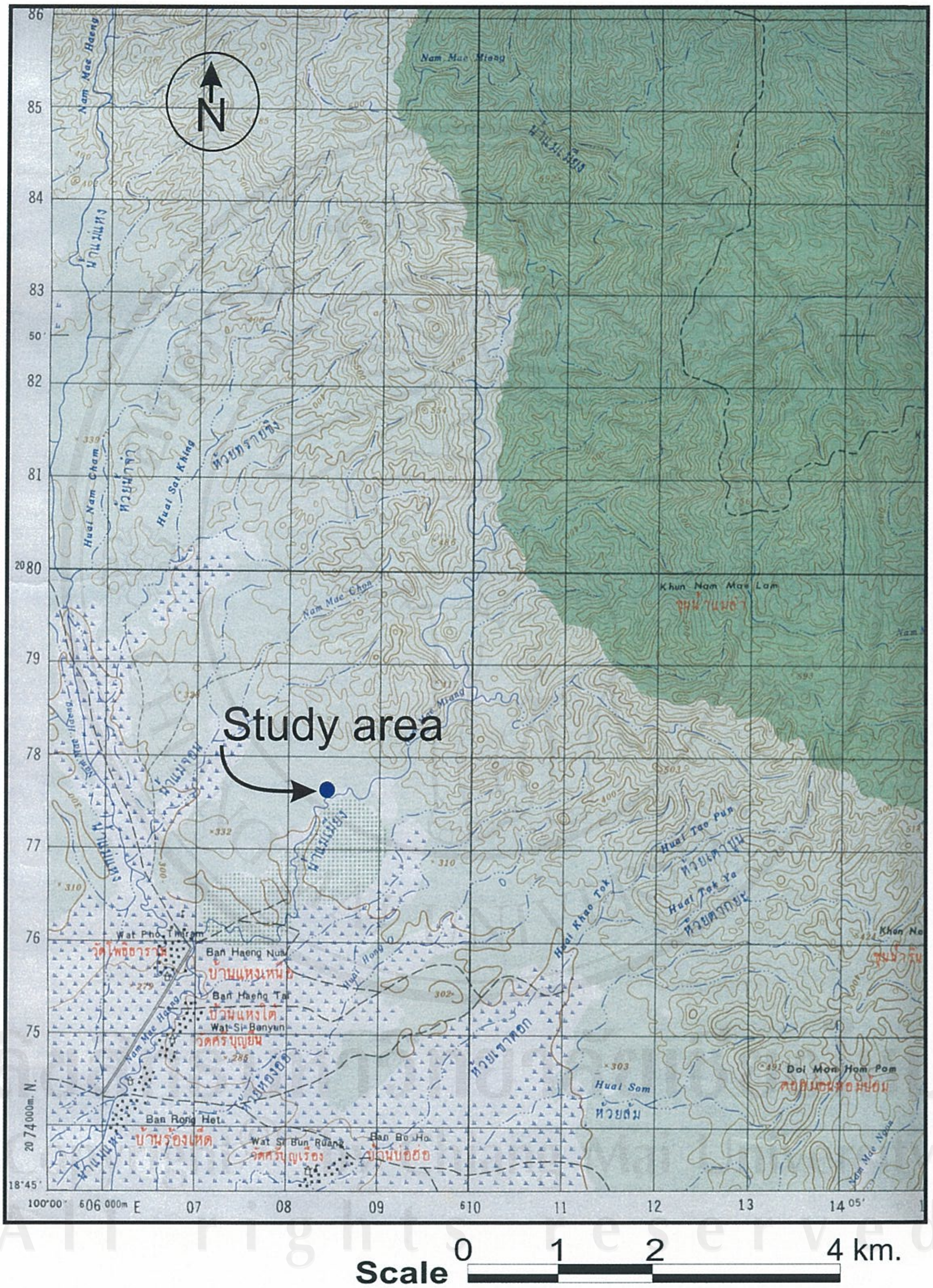

Figure 3.8 The study area of Ngao pit at grid reference 084776, Sheet Ngao.

Figure 3.9 The Photograph of Ngao pit, showing coal under gravel at Ban Heang Nua, Ngao District, Lampang Province.

3.2 Analytical conditions

3.2.1 Sample preparation

All samples were air dried for 3 to 5 days to remove adventitious moisture. After this, samples were crushed by hand in a ceramic mill to an average size less than 2 millimeters. Approximately 0.5 kilogram of each rock sample was milled and homoginized to –200 mesh. These samples were used for X-ray and chemical analyses. Coal samples were milled to –200 mesh and were used for proximate and ultimate analyses and for geochemical characterization. Sample preparation used for the coal petrography and sulfur isotope determination will be discussed later.

3.2.2 Proximate and ultimate analyses

3.2.2.1 Proximate analysis

This analysis determines the amount of moisture and volatile matter and calculates the amount of fixed carbon in coal samples. Procedures follow those described in British Standard, BS 1016 (1973), for proximate analysis

Moisture content

Approximately 1 gram of sample was weigh in a translucent silica dish for moisture determination. This dish was covered and placed in an oven chamber at a temperature of 110^0 C for 1 hour. Following this, the sample was placed in a desiccator and weighed as soon as it was cold to determine the moisture content.

Ash content

After determining moisture content, the dish with the sample was placed uncovered in a furnace chamber and heated to 900^0 C for 90 minutes. After this, the sample was cooled in a desiccator and then weighed for ash content

Volatile matter content

Approximately 1 gram of sample was used to determine volatile matter content. The weighed sample in a closed translucent silica crucible was placed on supports and inserted into a furnace chamber. The sample was then heated to 900^0 C for exactly 7 minutes. Following this, the crucible was removed from the furnace and, without disturbing the cover, cooled in a desiccator. After this, the cold sample was weighed. The percentage loss of weight minus the percentage moisture equals the volatile matter content.

Fixed Carbon

Fixed carbon is a calculated value. It equals the sum of moisture, ash, and volatile matter percentages subtracted from 100. All percentages should be on the same moisture reference base.

Fixed carbon percent = 100-(moisture percent + ash percent + volatile matter percent)

3.2.2.2 Ultimate analysis

Ultimate analysis was applied to the analysis of coal and rock samples. The

Ultimate analysis had studied at the Research Center for Coastal Lagoon Environments, Shimane University, Matsue, Japan.

The carbon, hydrogen, nitrogen, and sulfur concentration were measured by combustion method at about 1800° C in a Carlo Erba elemental analyzer EA1108 after removal of carbonates with HCl. For preteatment, 15 milligrams of sample was placed in a thin Ag film cup, and 1M-HCl added several times and dried at 110° C for 30 minutes. The dried sample was then wrapped in the thin Sn film for combustion. Data accuracy, especially of Sulfur, was checked by comparison with the same procedure using only a thin Sn film cup without HCl. BBOT (2,5-Bis-(5-tert-butyl-benzoxazol-2-yl)-thiophen: FISONS Instruments) was used for the standard, and standard regression line method was employed for quantitative analysis.

3.2.3 X-ray diffraction

The mineralogy was determined in 2 different sample types:

1. Untreated samples of bulk mudstone, shale, and claystone.
2. Treated samples of bulk coal by H_2O_2.

The XRD instrument in this study can be divided into 2 types. The Rigaku Rotaflex (model RTP 300 RC) was used for study the sample from Chiang Muan coal field. The Bruker D8 Advance was uased for the samples from Mae Moh coal field, Mae Teep coal field, Ngao basin, and Wang Nua basin.

3.2.3.1 Rigaku Rotaflex (model RTP 300 RC) instrument parameters

Minus 200 mesh bulk samples were pressed onto aluminum slide holders and analyzed on a rotating anode Rigaku Rotaflex (model RTP 300 RC) X-Ray diffractometer. The diffractometer operated under the following conditions:

- Co K α radiation, 1.790210A^0
- 45 kV and 160 mA
- scans from 2 to 82^0 2θ for untreated samples
- step scan with a counting time of 2 seconds for a step of 0.05^0 2θ

3.2.3.2 Bruker D8 Advance instrument parameters

Minus 200 mesh bulk samples were pressed onto slide holders and analyzed on a rotating anode Bruker D8 Advance X-Ray diffractometer. The diffractometer operated under the following conditions:

- Cu K α radiation, 1.5406 A^0
- 40 kV and 30 mA
- scans from 2 to 60^0 2θ for untreated samples
- step scan with a counting time of 1 seconds for a step of 0.04^0 2θ

The longer wavelength of cobalt gave better resolution at low angles 2θ than the wavelength of copper and, therefore, gave better definition of the first order clay mineral reflections. The primary beam intensity, which was an order of magnitude higher than conventional X-ray machines, permitted better peak resolution and mineral detection down to approximately 1 percent. Minerals were identified from d-spacings and relative peak intensities using the JCPDS PDF-2 data base retrieval/display system.

3.2.4 X-ray fluorescence spectrometry analyses

X-ray fluorescence spectrometry is a fast and efficient means of determining the concentration of major oxides (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, K_2O, Na_2O, P_2O_5, Cr_2O_3 and SO_3) and trace elements (As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, V, Zn and Zr)

The XRF instrument in this study can be divided into 2 types. A Phillips PW 1450 wavelength dispersive spectrometer was used for study the major oxide of sample from Chiang Muan coal field. The Philips MagixPro PW 2400 Sequential X-ray Spectrometer (wavelength dispersive system) was uased for the both of major oxide and trace elements of samples from Mae Moh coal field, Mae Teep coal field, Ngao basin, and Wang Nua basin.

3.2.4.1 The Phillips PW 1450 wavelength dispersive spectrometer

3.2.4.1.1 Sample preparation

Prior to fusion, the Loss on Ignition (LOI) was determined from the weight loss after roasting about 1.0 gram powdered specimen at 1000 °C for 2 hours. A mixture of 0.5 gram of the roasted sample and 6.5 grams flux, composed of 50% lithium tetraborate and 50% lithium metaborate, was accurately weighed out. The fusion was performed by a Claisse Fluxer at the temperature about 950-1000° C.

3.2.4.1.2 Instrument parameters

All samples were analyzed on the Phillips PW 1450 wavelength dispersive spectrometer using the following instrumental parameters:

-W tube with a lithium fluoride 200 crystal using both scintillation and flow proportional detectors

-X-ray tube operated at 40 kV and 50 mA

The net (background corrected) intensities were measured; and the concentrations were calculated against the calibrations derived from 18 international standard reference materials. The inter-element matrix corrections were done by the CiLT program (Les logiciels R. Rousseau Inc.). The reporting detection limit is about 0.01 wt% and the accuracy for most of the elements (oxides) is better than 5%.

3.2.4.2 the Philips MagixPro PW 2400 Sequential X-ray Spectrometer (wavelength dispersive system)

3.2.4.2.1 Sample preparation

The Loss on Ignition (LOI) was determined from the weight loss after roasting about 1.0 gram powdered specimen at 1000 °C for 2 hours. The samples were measured from pressed power prepared by mixing 5 grams of sample powder with 1 gram wax of $C_6H_8O_3N_2P$. The powder was compacted by pressure 200 KN.

3.2.4.2.2 Instrument parameters

All samples were analyzed on Philips MagixPro PW 2400 Sequential X-ray Spectrometer (wavelength dispersive spectrometer) using the following instrumental parameters:

-Rhodium (Rh) tube with a lithium fluoride 200 using both scintillation and flow proportional detectors

-X-ray tube may be operated at 60 kV and current of up to 125 mA; at a maximum power level of 4 kW.

The net (background corrected) intensities were measured; and the concentrations were calculated against the calibrations derived from 8 international standard reference materials. The inter-element matrix corrections were done by the SuperQ version 3.0 program. The reporting detection limit is about 0.01 wt% and the accuracy for most of the elements (oxides) is better than 5%.

3.2.5 Induced couple plasma optical emission spectrometry analyses

Trace elements (As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, V, Zn and Zr) were analyzed using the ICP-OES, Perkin Elmer, the Optima 3000 system for the sample from Chiang Muan coal field.

Sample preparation

One-tenth gram of each sample was placed in a LDPE bottle and treated with a 4 ml Aqua regia ($3HNO_3$: 1HCl) at 200° C for 2 hours, diluted to 50 milliliters with water and leave it for a night.

3.2.6 Coal petrography

3.2.6.1 Sample preparation

Coal briquets were prepared using a binder that held all coal particles securely during grinding, polishing, and observation. After polishing, at least 60 percent of the cross sectional area of each briquet had to be coal.

Briquets were made by adding an activator, or hardener, and epoxy resin in a ratio of 1 to 5.5 to each sample. This mixture was stirred thoroughly and, initially, a few drops were added to a coal sample that had been placed in a small container. The coal and resin were then stirred thoroughly and more resin was added, a few drops at a time, until all the coal was wet with resin and the coal particles cohered into one mass.

The internal surfaces of a mold, including plungers, were coated with a release agent. The lower plunger was then inserted and the mold was filled with the coal-resin mixture.

Briquets were allowed to harden adequately for polishing. Four to eight hours at 35 to 40° C was sufficient for hardening.

Coal briquets were ejected from the molds using the special attachment on the press. After being ejected, the briquets were labelled.

3.2.6.2 Preparation of briquet surface

One of the base surfaces of the briquets was ground and polished on a lap to obtain a surface suitable for microscopical examination. Grinding and polishing done by hand manipulation and with an automatic attachment. Both grinding and polishing required several stages to complete. The first stage of polishing was done on a high-speed polishing machine using silicon carbine grit 400 micrometers followed with alumina grit 600 and 1000 micrometers. The second polishing stage was also done on a high speed polishing machine and used chromium oxide and magnesium oxide grit. The third and the fourth stages were done by hand. The polishing media for these two stages was spread out on the cloth of the polishing wheel as slurry in distilled water.

The macerals will be identified by using reflected light microscope. Fluorescence light is applied if necessary, especially for the liptinite group.

3.2.7 Sulfur isotope

Determination of total sulfur with the Eschka method

Coal samples were analyzed using the Eschka method (Japanese Industrial Standards Committee, 1988). The Eschka ignition mixture was prepared by mixing two parts of magnesium oxide with one part of sodium carbonate. One-half gram of coal was mixed with 1.25 gram of the Eschka mixture. The resulting mixture was transferred to a cruicible, which had 0.5 gram of Eschka mixture in the bottom, and the Eschka-coal mixture was covered with another 0.5 gram of Eschka mixture.

The Eschka-coal mixture in the crucible was heated, with the furnace door slightly open, to 800 °C in one hour. The mixture was kept at 800°C for one and a half hours. After ignition, the material was placed in a 500 milliliters beaker that contained 20 to 30 milliliters of water. The material was then heated and 15 milliliters of hydrochloric acid was added to dissolve the material. The beaker was covered by a watch glass and the solution was boiled for 5 minutes to expel carbon dioxide. After this, the solution was filtered and washed with hot water in another 500 milliliters beaker. Ammonium hydroxide was added to neutralize the solution. Then one milliliter of hydrochloric acid and sufficient water were added to make a solution volume to 250 milliliters. This solution was then heated to boiling and 10 milliliters of barium chloride solution was added while constantly stirring. The resulting barium sulfate precipitate was digested for one hour at 90°C. The barium sulfate was then determined by gravimetry.

Determination of combustible sulfur in coal

Coal samples were combusted using the apparatus shown in Figure 3.10 (Nakai and Jensen, 1967 and Ohizumi and others, 1997). One to 1.5 grams of coal was accurately weighed and used for combustion at 900°C. The resulting gases were oxidized in a 3% H_2O_2 solution to form sulfate ions. After oxidation, the solution was passed through a membrane filter and one milliliter of hydrochloric acid and 10 milliliters of barium chloride solution were added, while stirring constantly. The barium sulfate precipitate was digested for one hour at 90°C, recovered, and determined again by gravimetry.

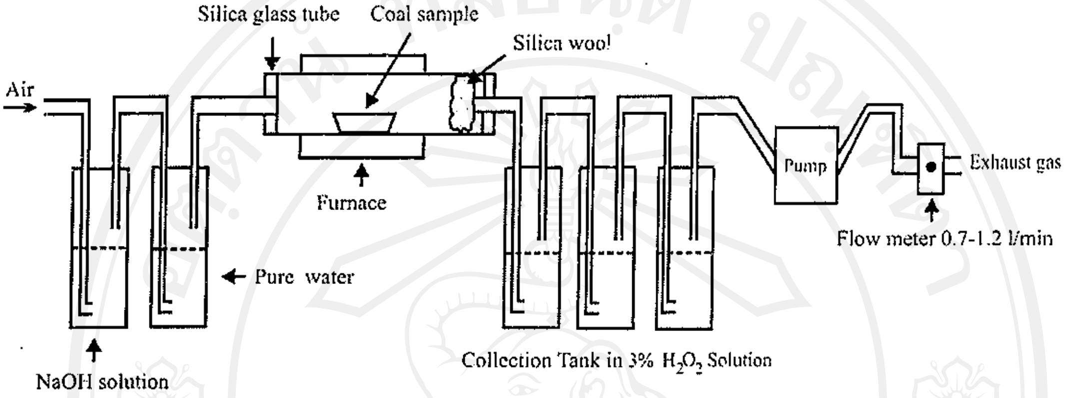

Figure 3.10 Apparatus for coal combustion (modified from Nakai and Jensen, 1967; Ohizumi and others, 1997)

Conversion of pyrite to barium sulfate

Pyrite samples were oxidized to barium sulfate with a Br_2-HNO_3 mixture using the method described by Sakai and Matsubaya (1976). The resulting solution was evaporated almost to dryness and 10 milliliters of 0.1 molar sodium carbonate solution was added to the mixture. Heating continued until the solution dried, leaving only a salt. Then 0.5 milliliter of concentrated hydrochloric acid and 100 milliliters of water were added to dissolve the salt. The solution was then filtered through a membrane filter of 0.45 micrometers, and passed through a cation exchange column to remove all cations. The sulfate ion in the eluent was revovered as barium sulfate.

Conversion of gypsum to barium sulfate

Gypsum samples were converted to barium sulfate using the method of Kusakabe and Chiba (1983). A 100 milligrams gypsum sample was dissolved in 150 milliliters of 0.1 molar hydrochloric acid in a beaker. This solution was heated to 80° C on a hotplate to dissolve the gypsum. The resulting solution was filtered through a membrane filter and the filtrant was collected. This filtrant was then passed through a cation exchange column. The eluent, including washing water, was collected in a 300 milliliters beaker. This solution was boiled and barium chloride solution was slowly added while stirring to form barium sulfate precipitate.

Sulfur isotope analysis

Sulfur in samples was purified and precipitated as barium sulfate. Ten milligrams of barium sulfate, 100 milligrams of vanadium pentaoxide, and 100 milligrams of silica dioxide were mixed into a nine-millimeter diameter silica glass tube and covered by silica glass wool. Another wad of glass wool was pushed into the tube about two cm above the reaction mixture. The tube was heated at 450° C for about 30 minutes in open air to remove any organic contamination. Two grams of copper wire were placed on the upper glass wool wad. The tube was then connected to the preparation line. The copper wire was brought to a red glow by heating the glass tube with a torch until no appreciable outgassing was observed by a Pirani vacuum gauge. This procedure removed oxide coating as well as any volatile contamination in the copper. The silica glass tube was then heated to 950° C to cause decomposition. After decomposition, the resulting sulfur dioxide gas was passed through a multi-trap and then through a n-pentane trap for purification. After this, the gas was collected in a sample tube. The sulfur dioxide gas in the sample tube was then ready for sulfur isotopic analysis (Yanagisawa and Sakai, 1983; Figure 3.11). 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:

$$\delta\,^{34}S = ((^{34}S/^{32}S)\text{sample}/(^{34}S/^{32}S)_{CDT} - 1) * 1000$$

where CDT is the standard of Canyon Diablo Troilite. The overall accuracy of sulfur isotopic analysis was < 0.2 ‰.

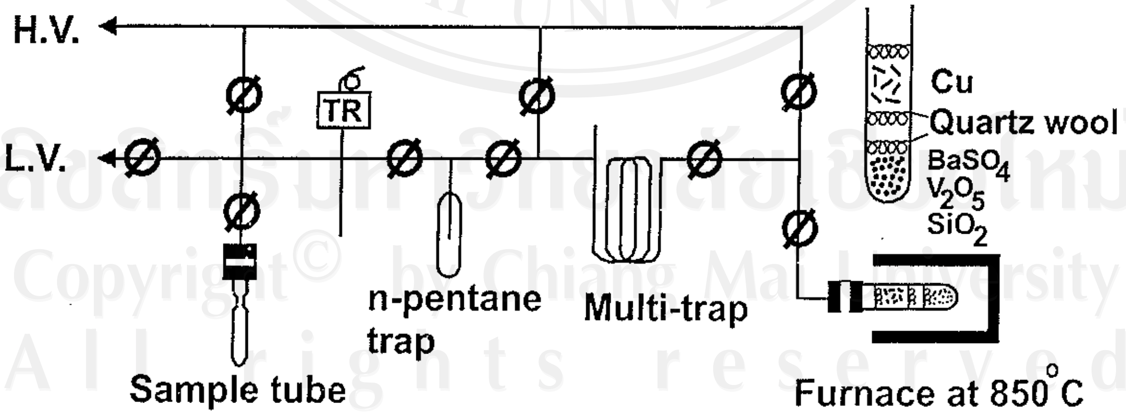

Figure 3.11 The vacuum line for the preparation of sulfur dioxide (modified from Yanagisawa and Sakai, 1983).

3.2.8 Carbon and oxygen isotopes

Samples were cleaned in distilled water using an ultrasound washer and then were dried at 75°C for an hour. Then each sample was powdered using agate crusher. Oxygen and carbon isotopic compositions of samples were determined at Research Center for Coastal Lagoon Environments, Shimane University, Japan. The sample powders were reacted with 100% H_3PO_4 at 60°C in a closed reaction vessel and analyzed with a Finnigam Mat delta S mass spectrometer. The Shimane standard, -1.06 ‰ relative to the Belemnitella american from the Cretaceous PeeDee Formation standard (PDB) for $\delta\ ^{13}C$ and +26.59 ‰ relative to standard Mean Ocean Water (SMOW) for $\delta\ ^{18}O$, was used as a reference. The oxygen and carbon isotopic compositions are expressed by using the equation of Craig (1957):

$$\delta\ ^{13}C\ (‰) = ((^{13}C/^{12}C)\text{sample}/(^{13}C/^{12}C)\text{standard} - 1) * 1000\ (\text{vs. PDB})\text{ and}$$

$$\delta\ ^{18}O\ (‰) = ((^{18}O/^{16}O)\text{sample}/(^{18}O/^{16}O)\text{standard} - 1) * 1000\ (\text{vs. SMOW})$$