

## **CHAPTER 3**

### **SAMPLE COLLECTION AND ANALYTICAL METHODS**

#### **3.1 Sample collection and preparation**

##### **3.1.1 Sample collection**

###### **Fang basin**

The drill-cutting samples from petroleum exploration well from western part of the Fang basin were provided by the Northern Petroleum Development Centre, Defence Energy Department. A total of 36 cutting samples were collected from a depth between 544.1 and 1146.05 m of Mae Sot Formation in the Fang-MS well (Figures 3.1). The interval of the samples is 10 m. The samples consist principally of carbonaceous mudstone, silty mudstone, siltstone and mudstone. The description of each sample is shown in Appendix I.

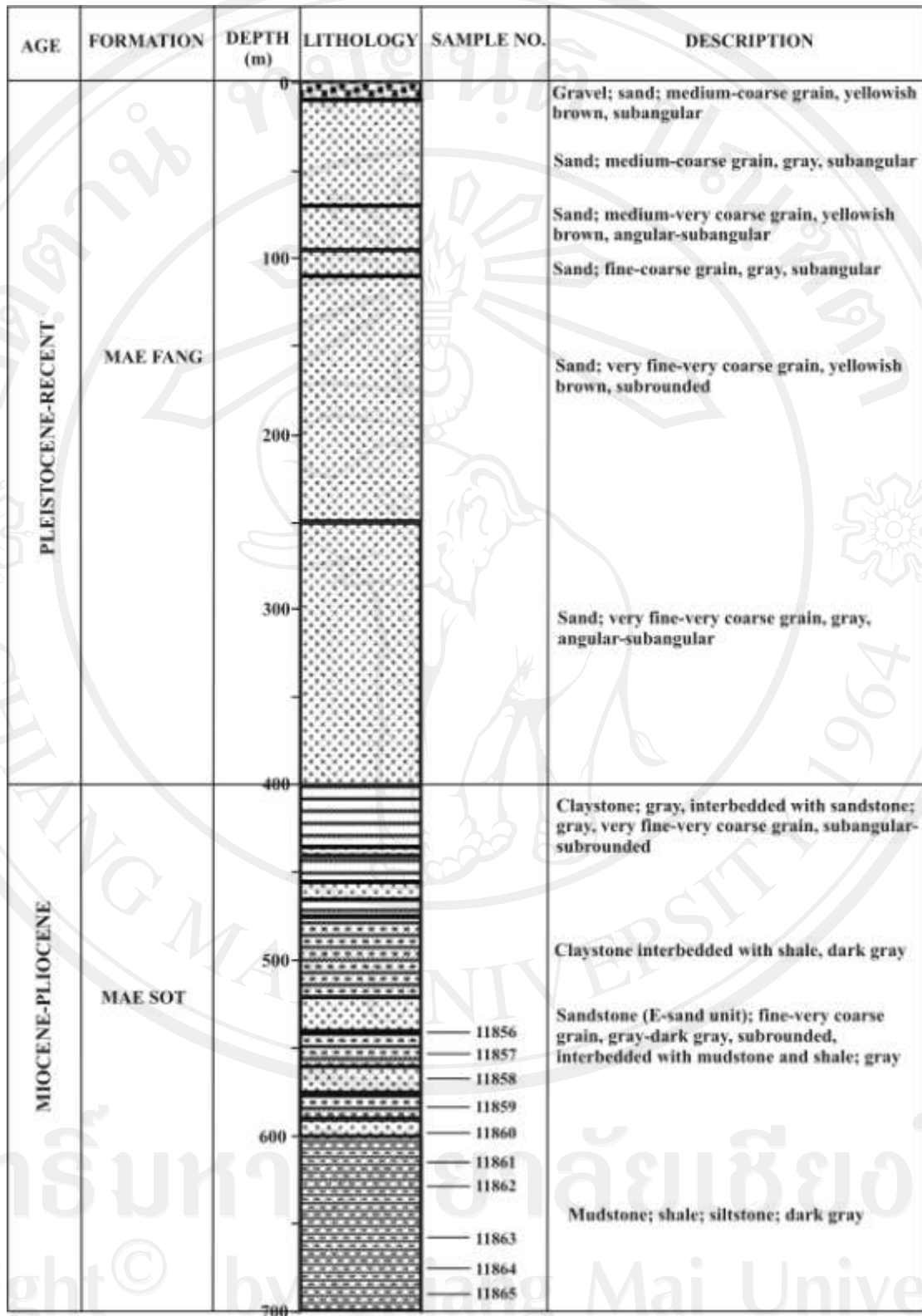
###### **Na Hong, Li and Mae Sot basins**

A total of 16 outcrop samples from Na Hong were collected from the small Pakla creek near abundant coal mine. The samples consist principally of coaly mudstone, mudstone and oil shale. The 10 Li outcrop samples are collected from outcrops of interburden coal in Lanna Lignite Resources Coal Mine (Pa Kha sub-basin). The outcrop samples consist principally of coaly mudstone, mudstone and oil shale. The 6 Mae Sot samples are collected at Ban Huai Kalok close to the Thai-Myanmar border. The description of each sample is shown in Appendix I.

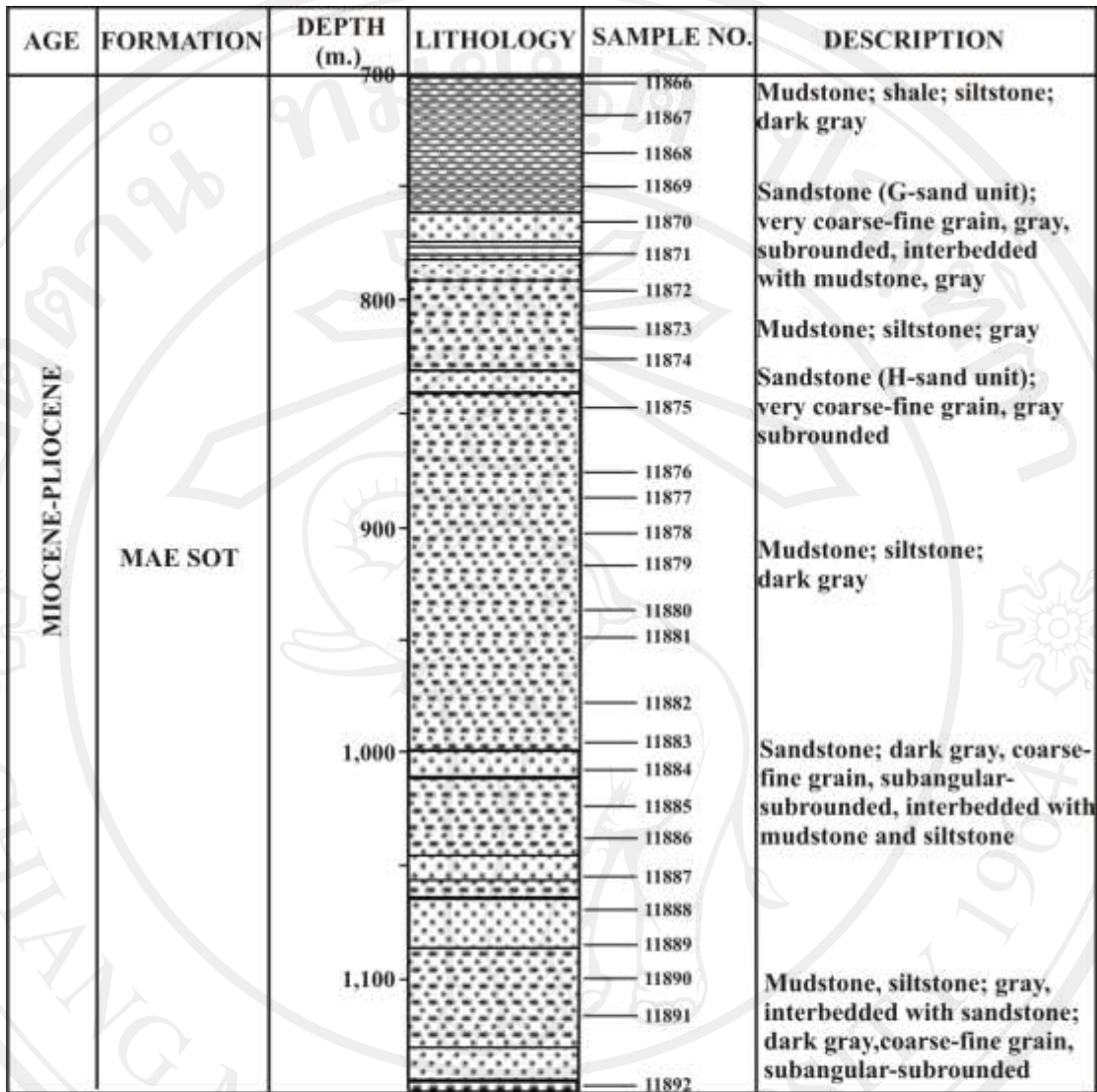
Sample collection in these three basins was made in an excavation. The excavation was cut to expose fresh surfaces and the outer surface was removed before collecting samples. The separate samples were sealed by aluminum foil, packed in a plastic bag, and then labeled with the necessary information.

###### **Phitsanulok basin**

The drill-cutting samples from P-SK well in Phitsanulok basin were selected



**Figure 3.1** Generalised stratigraphic column for well Fang-MS, showing stratigraphic levels and sample numbers of samples collected.



Legends



Gravel



Mudstone, shale



Sandstone and sand



Siltstone



Claystone

Figure 3.1 (Cont.).

based on mud log studies. All samples were collected from shale intervals identified on the mud log. The total of 43 cutting samples from the Yom, Pratu Tao, Chum Saeng and Lan Krabu Formations were collected from the depth of 900–3,070 m. The sample interval is 50 m (Figures 3.2). The description of each sample is shown in Appendix I.

### **Suphanburi basin**

The drill-cutting samples from SP1 and SP2 wells in Suphanburi basin were selected based on lithologic log studies. Ninety cutting samples from the SP1 well were collected from depth between of 1,000 – 2,840 m of A to D units and the interval of the samples is 5 to 15 m (Figures 3.3). The 60 cutting samples from SP2 well were collected from a depth between of 1,000 - 2,100 m of A to D units and the interval of the samples is 10 m (Figures 3.4). The description of each sample is shown in Appendix I.

#### **3.1.2 Preparation of samples**

Outcrop samples (oil shale, coaly mudstone and mudstone) were air dried for 1-2 days to remove moisture. The samples were crushed to size range of 1 - 4 mm. After that only 1 g of samples were crushed to size less than 250  $\mu\text{m}$ . for Rock-Eval pyrolysis, total organic carbon (TOC) analysis, total carbon (TC) analysis, total sulfur (TS) analysis and extraction.

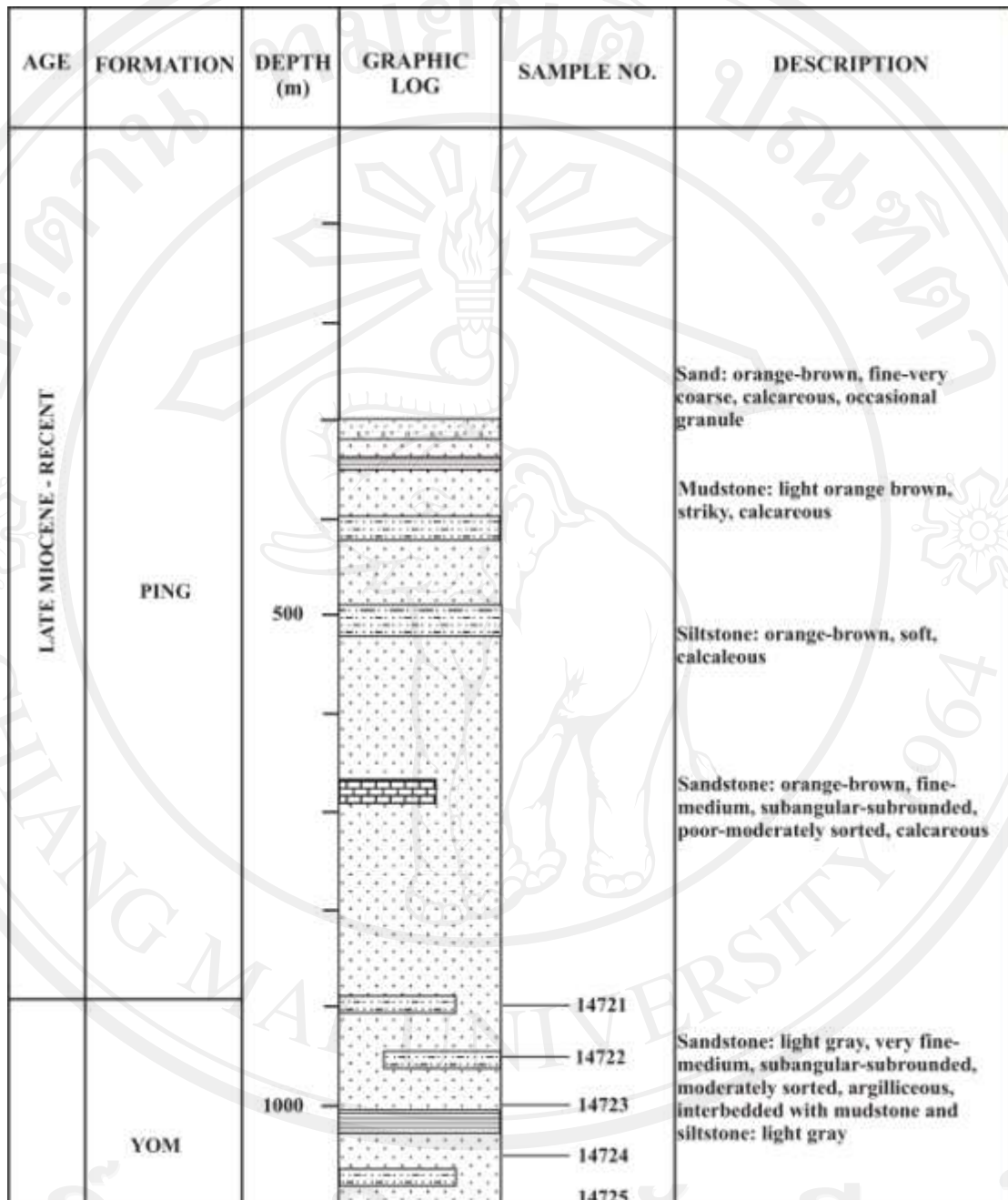
Cutting samples were prepared as below;

(1) The unwashed cutting samples were washed by water over a sieve to remove mud from drilling process and all pollutants soluble in water and dried at room temperature.

(2) After water washing and drying, cutting samples were selected to size range of 1-4 mm. by sieve before removing solid pollutants and iron chip by magnetic pen.

(3) After that 1 g. of cutting samples were taken crushed to size less than 250  $\mu\text{m}$ . for Rock-Eval pyrolysis, total organic carbon (TOC) analysis, total carbon (TC) analysis, total sulfur (TS) analysis and extraction.

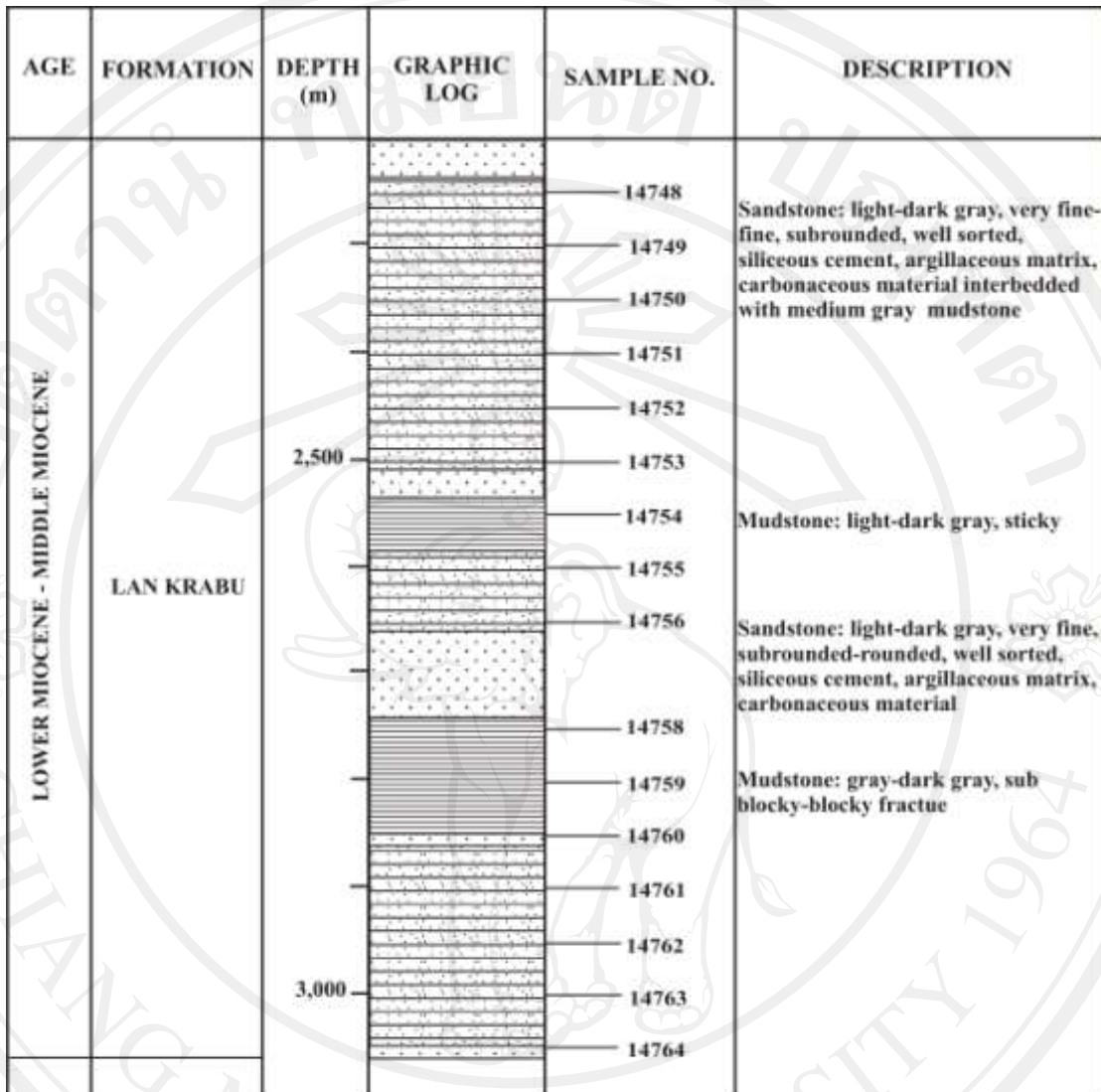




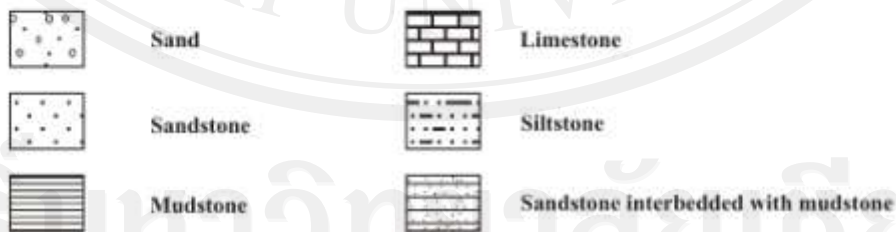
**Figure 3.2** Generalised stratigraphic column for well P-SK, showing stratigraphic levels and sample numbers of samples collected (modified from PTTEP, 2001).

AGE	FORMATION	DEPTH (m)	GRAPHIC LOG	SAMPLE NO.	DESCRIPTION
LOWER MIOCENE - MIDDLE MIOCENE	YOM			14726	Sandstone: light gray, very fine-medium, subangular-subrounded, moderately sorted, argillaceous matrix, loose, interbedded with mudstone: light gray, light brown
				14727	
				14728	
				14729	
				14730	
				14731	
	PRATU TAO	1,500		14732	Sandstone: light gray, very fine-fine, subangular-subrounded, well sorted, siliceous cement, argillaceous matrix, carbonaceous material
				14733	
				14734	
				14735	
				14736	
				14737	
	CHUM SAENG	2,000		14738	Mudstone: light-dark gray, orange brown, sticky
				14739	
				14740	
				14741	
				14742	
				14743	
			14744	Mudstone: dark gray, greenish gray, sub blocky-blocky fracture	
			14745		
			14746		
				14747	

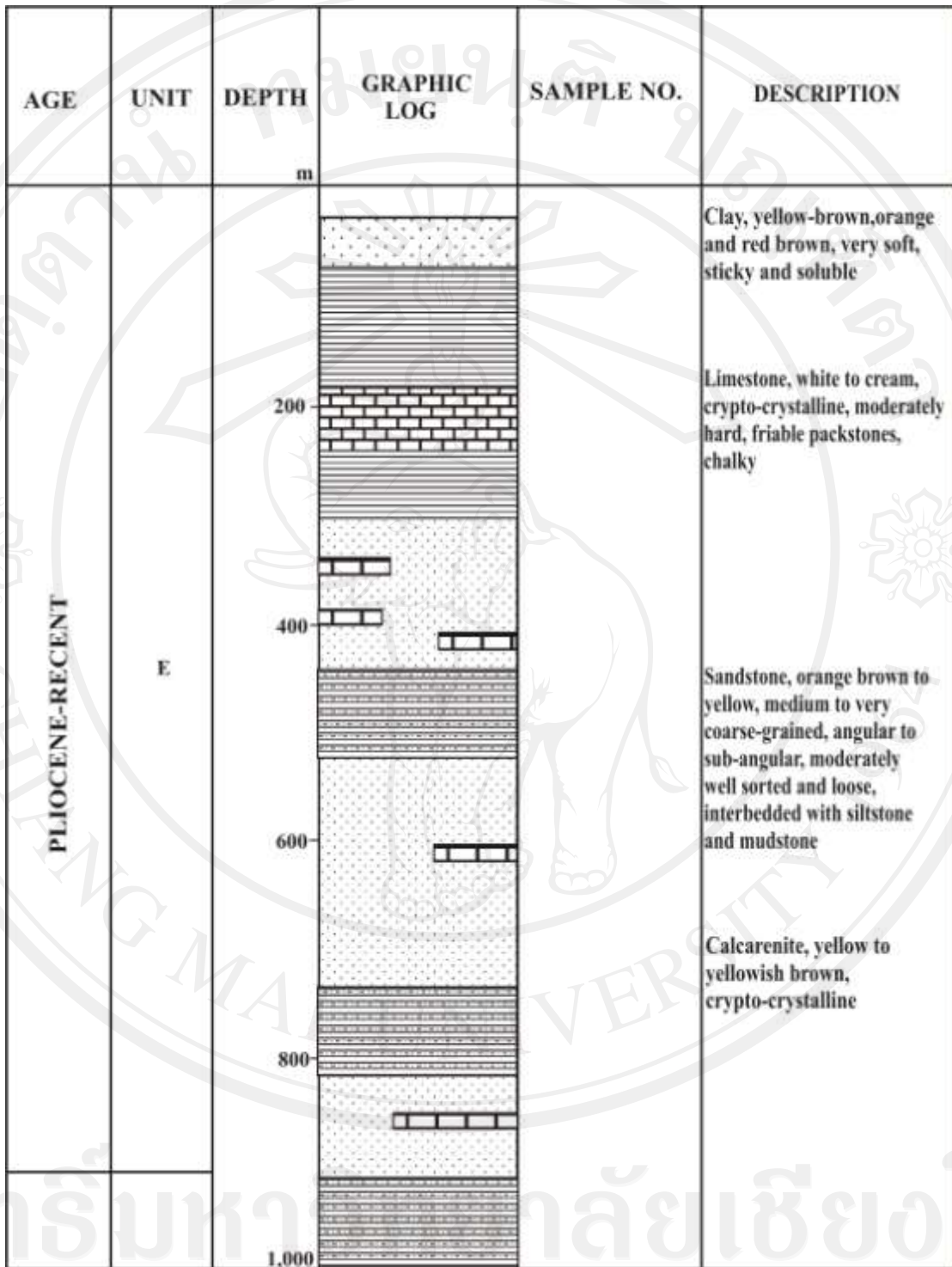
Figure 3.2 (Cont.)



**Legends**



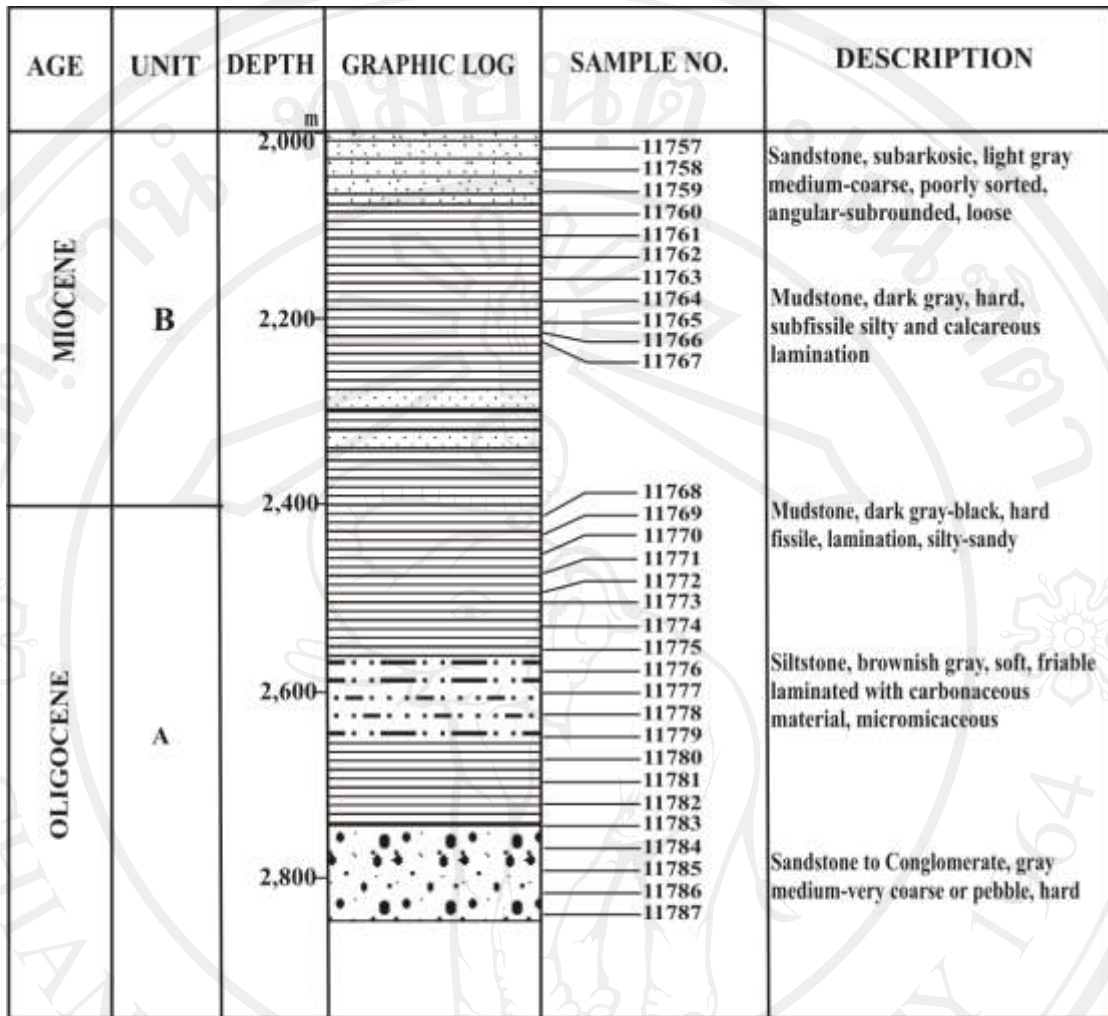
**Figure 3.2 (Cont.)**




**Figure 3.3** Generalised stratigraphic column for well SP1, showing stratigraphic levels and sample numbers of samples collected (modified from PTTEP, 1986).











**Legends**


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
Sand, Gravel,  
Sandstone, Conglomerate
- 

Siltstone
- 

Sandstone
- 

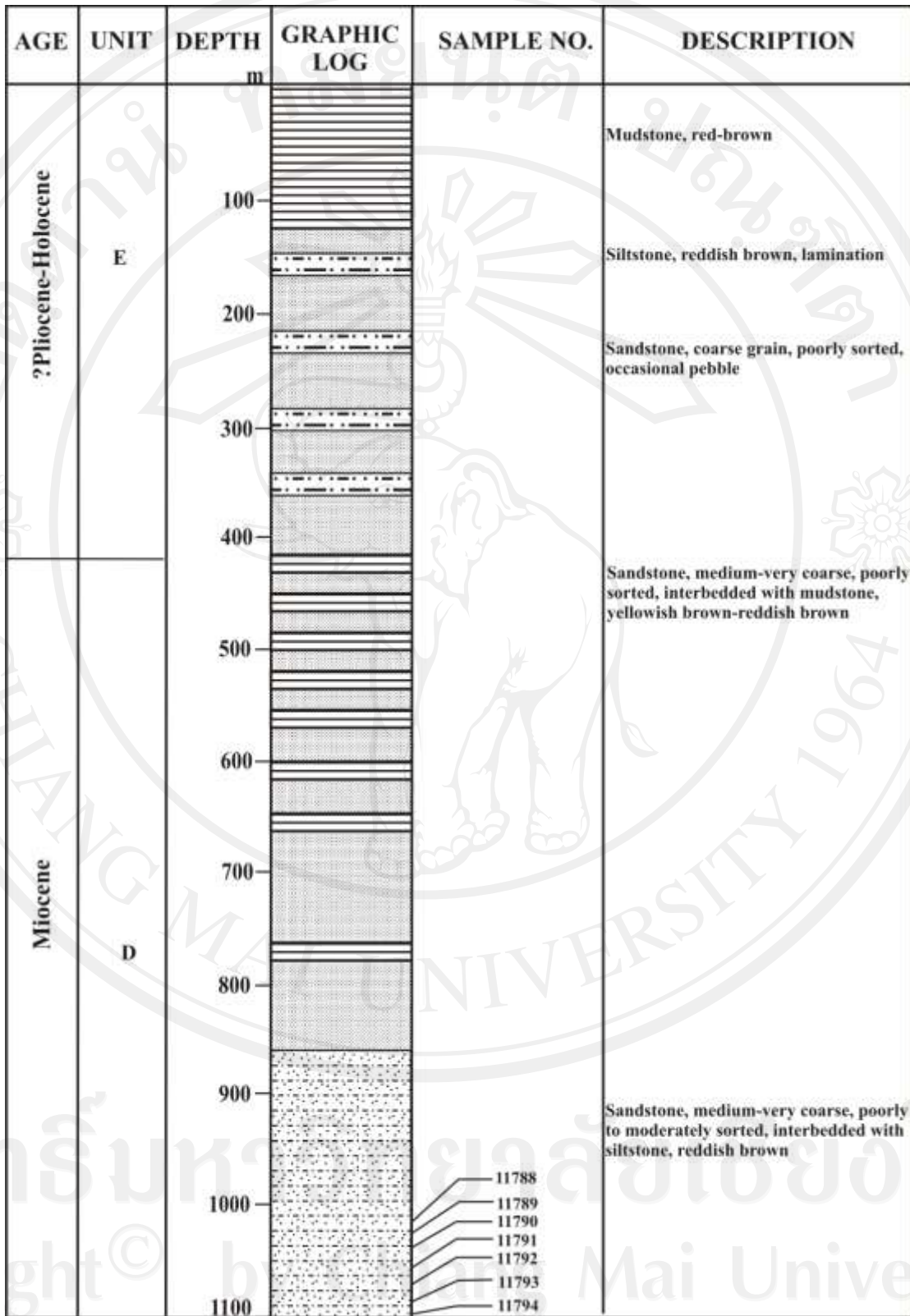
Limestone
- 

Claystone
- 

Siltstone interbedded with mudstone
- 

Mudstone interbedded with sandstone

**Figure 3.3 (Cont.)**



**Figure 3.4** Generalised stratigraphic column for well SP2, showing stratigraphic levels and sample numbers of samples collected (modified from PTTEP, 1986).

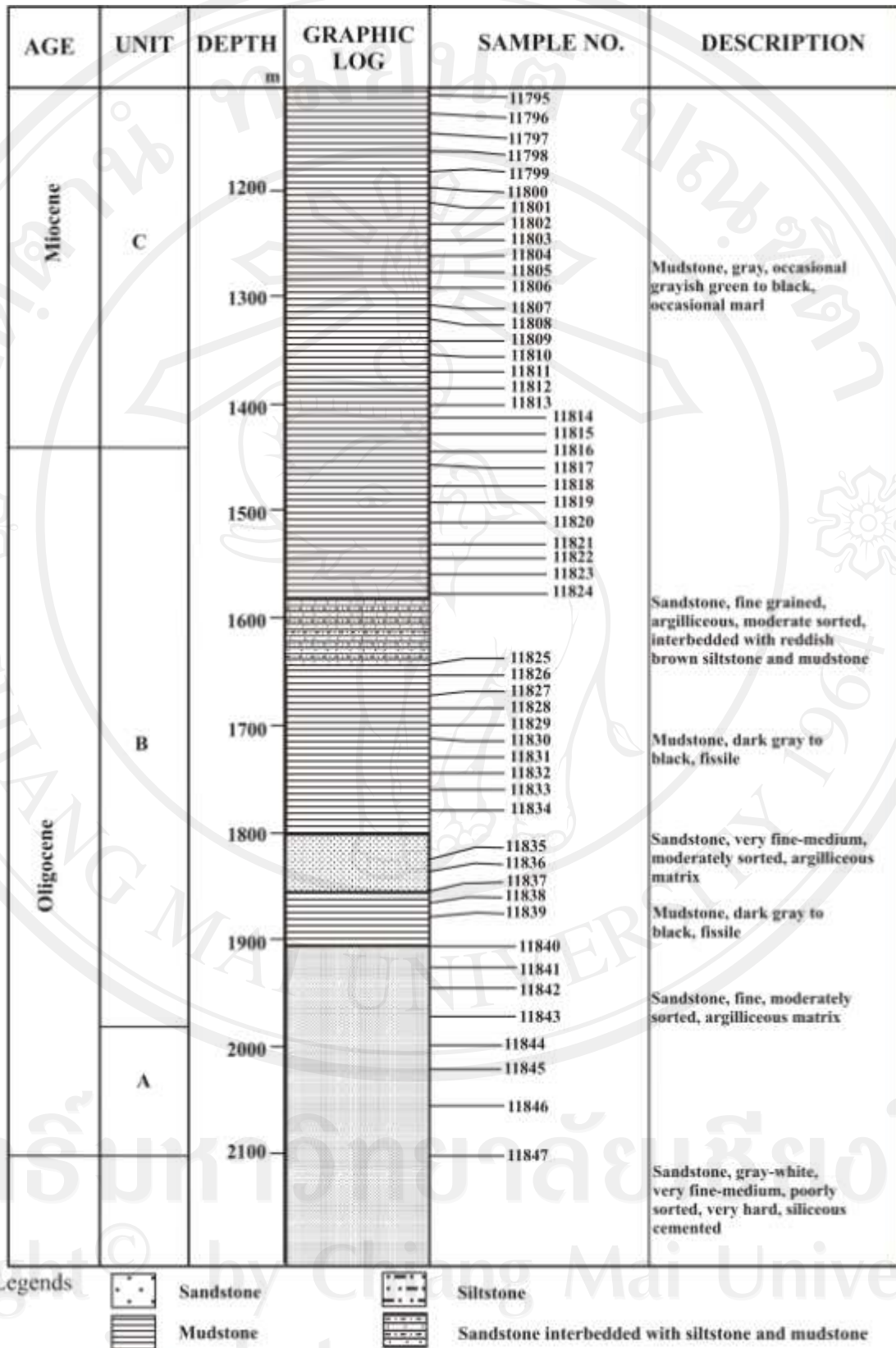


Figure 3.4 (Cont.)



## 3.2 Methodology

### 3.2.1 Total organic carbon (TOC) analysis, total carbon (TC) analysis and total sulfur (TS) analysis

The TOC of rock sample is measured by combustion of the organic matter under air or oxygen atmosphere, at a temperature of 1500°C (LECO CS-200 induction furnace). Carbonates should be removed by HCl acid treatment before combustion due to carbonate decomposition at high temperature. The TC and TS is measured by CS-200 Carbon/Sulfur infrared absorption.

#### 3.2.1.1. LECO™ CS200 for TC, TOC and TS analysis

The analysis begins by weighing a sample into a ceramic crucible on a balance. Accelerated material (iron chip) is added, the crucible is placed on the loading pedestal. Furnace closure is performed automatically, and then the combustion chamber is purged with oxygen to drive off residual atmospheric gases. After purging, oxygen flow through the system is restored and the induction furnace is turned on. The pure oxygen environment and the heat generated by this coupling cause the sample to combust. During combustion all elements of the sample are oxidized. Carbon bearing elements are reduced, releasing the carbon, which immediately binds with the oxygen to form CO and CO<sub>2</sub>, the majority being CO<sub>2</sub>. Also, sulfur bearing elements are reduced, releasing sulfur, which binds with oxygen to form SO<sub>2</sub> (LECO Corporation, 2007). System configuration is shown in Figure 3.5

Sample gases are swept into the carrier stream. Sulfur is measured as sulfur dioxide in the first IR cell. A small amount of the carbon monoxide is converted to carbon dioxide in the catalytic heater assembly while sulfur dioxide is removed from the system in a cellulose filter. Carbon is measured as carbon dioxide in the IR cell, as gases flow through the IR cells.

#### 3.2.1.2 Infrared Radiation, Absorption and Detection

The infrared radiation (IR) source consists of nichrome wire which is resistance-heated to 850°C. The IR source radiates visible energy as well as all wavelengths in the infrared spectrum. The description below uses carbon dioxide although; the same principle applies to sulfur detection. Carbon dioxide absorbs IR

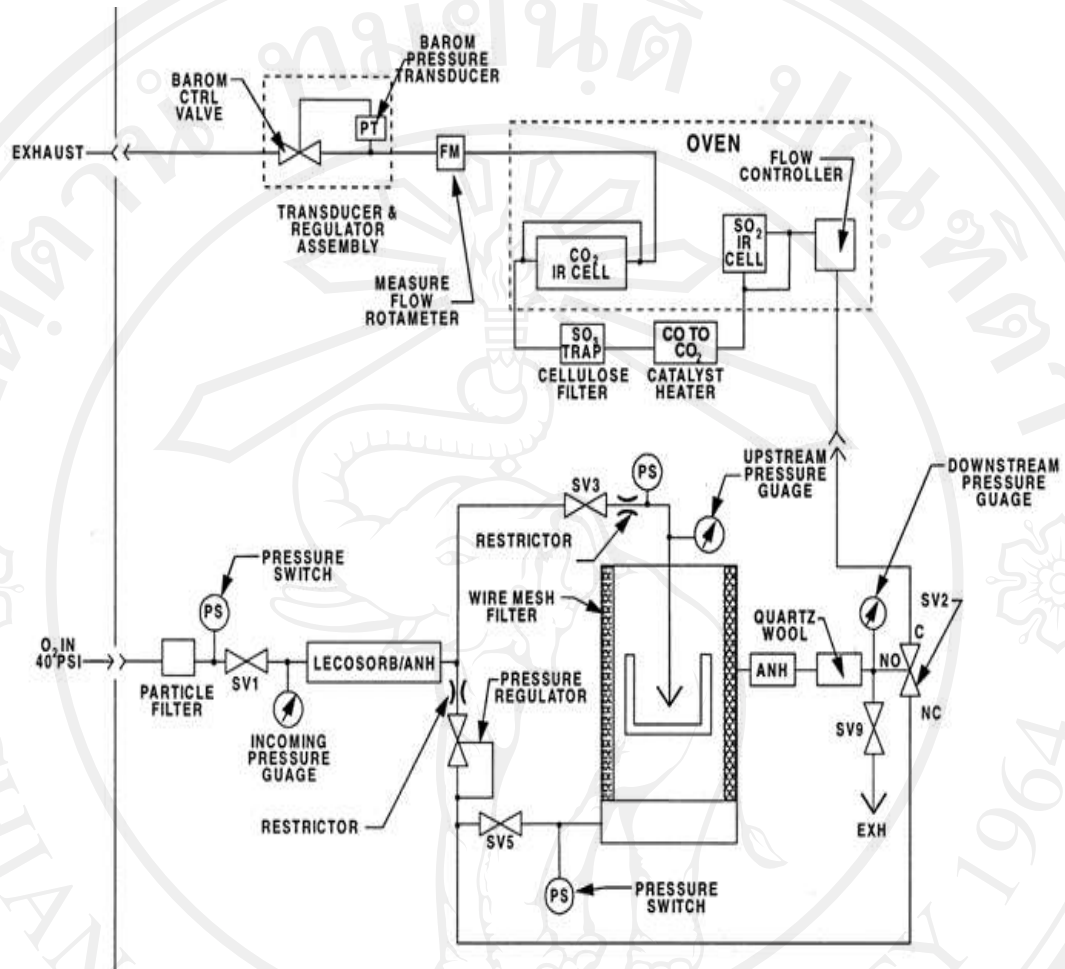


Figure 3.5 LECO CS-200 gas flow diagram (LECO Corporation, 2007).

energy at a precise wavelength within the IR spectrum. Energy from the IR source is absorbed as the gas passes through the cell, preventing it from reaching the IR detector. All other IR energy is prevented from reaching the IR detector by a narrow bandpass filter. Because of the filter, the absorption of IR energy can be attributed only to carbon dioxide (CO<sub>2</sub>). The concentration of CO<sub>2</sub> is detected as a reduction in the level of energy at the detector. The total carbon, as carbon dioxide, is detected on a continuous and simultaneous basis. The cell consists of an IR source, a narrow bandpass filter, a condensing cone, an IR energy detector and the cell body. Radiated energy is chopped at a rate of 87.5 Hz before it enters the cell body. The chopped energy enters the cell body through a window, travels through the cell body, then exits through a second window and a precise bandpass filter. The selective filter passes only the CO<sub>2</sub> absorption wavelength into a condensing cone which concentrates the energy on the detector. The solid state detector is AC coupled to a preamplifier. As the gas concentration increases, the voltage to the preamplifier decreases (LECO Corporation, 2007).

### **3.2.1.3 Sampling preparation for TOC analysis**

- (1) The test tubes for analysis were washed by acetone and dried, and then weighted.
- (2) The 300 mg grinded samples were added into test tubes and the test tubes were weighted again.
- (3) The 0.2 M HCl acid was added to the grinded samples shivered to remove carbonate and heated up at 65°C for 1 hour in an oven.
- (4) More 0.2 M HCl acid was added and then shivered. After that kept at 65°C for more than 1 hour then centrifuged at 1900 round/min. for 15 minutes.
- (5) Discarded the acid, and washed samples several times by the ionize water to wash away the HCl and remove after centrifuged at 1900 round/min. for 15, 20 and 25 minutes.
- (6) The samples were placed in an oven and left to dry at 90°C for 24 hours.
- (7) The heated samples were taken into desiccator to cool down for 20 minutes and weighted.

#### 3.2.1.4 TOC, TC and TS analytical procedure

(1) The 4 blank ceramic crucibles were analyzed to set the blank value by adding 1 spoon iron chip accelerator and 1 spoon lecocel (-20 to +40 mesh), analyse by using program for sediment TOC for TOC analysis and program for sediment TC and TS for TC and TS analysis

(2) The 3 standards were analyzed for calibration by adding 50 mg Reference Lake Sediment (LKSD-1), added 1 spoon iron chip accelerator and 1 spoon lecocel. Ranges of standard are C% 11.80 – 12.80 and S% 1.47 – 1.70.

(3) The samples were analyzed by using 50 mg sample, adding 1 spoon iron chip accelerator and 1 spoon lecocel.

#### 3.2.2 Rock-Eval pyrolysis

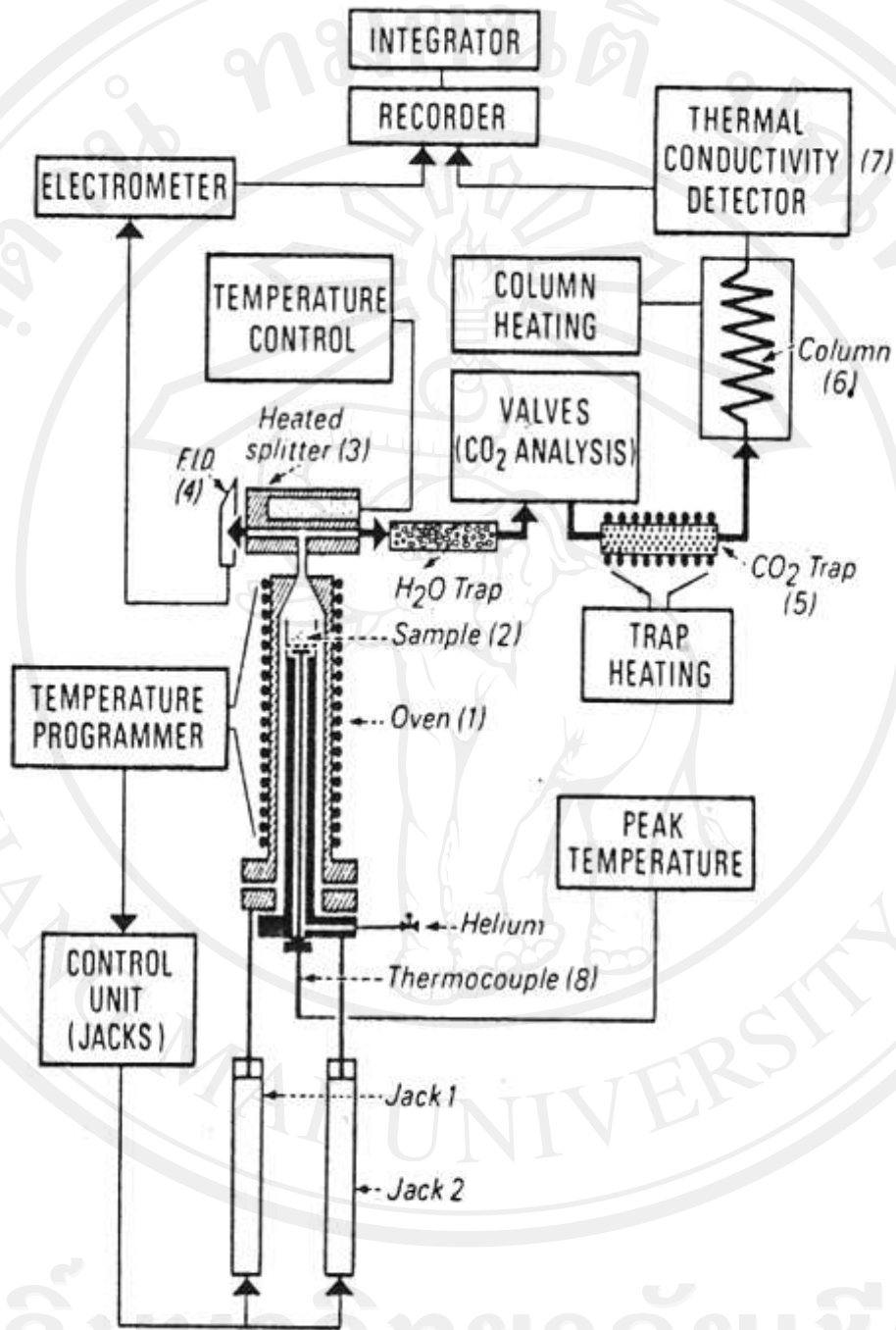
The Rock-Eval pyrolysis (Figure 3.6) method is widely used by the petroleum Industry. The analysis is automated. Results are computed by using a microprocessor and given as listings. This method allows one to characterize the type of organic matter, to calculate the residual potential of the sample and its total organic carbon and to evaluate the thermal evolution it has undergone.

The Rock-Eval pyrolysis method consists of a programmed temperature heating (in a pyrolysis oven) in an inert atmosphere (helium) of a small sample to quantitatively and selectively determine (1) the free hydrocarbons contained in the sample and (2) the hydrocarbon- and oxygen-containing compounds (CO<sub>2</sub>) that are volatilized during the cracking of the unextractable organic matter in the sample (kerogen).

A small amount of rock is heated under a helium atmosphere at 300°C for three minutes, and then temperature is increased by 25°C/min up to 600°C. As soon as generated, pyrolysis products are swept along to the detectors by the helium flow, therefore only primary cracking reactions do happen (open system). During heating, the following events are observed (Figure 3.7);

(a) Free hydrocarbons, oil and gas, contained in the organic matter are vaporized at around 300°C. This thermo-vaporization for a period of three minutes give a peak, called the **S<sub>1</sub> peak**, expressed in mg HC/g of rock.





**Figure 3.6** Principal of the Rock-Eval pyrolysis device (Tissot and Welte, 1978).

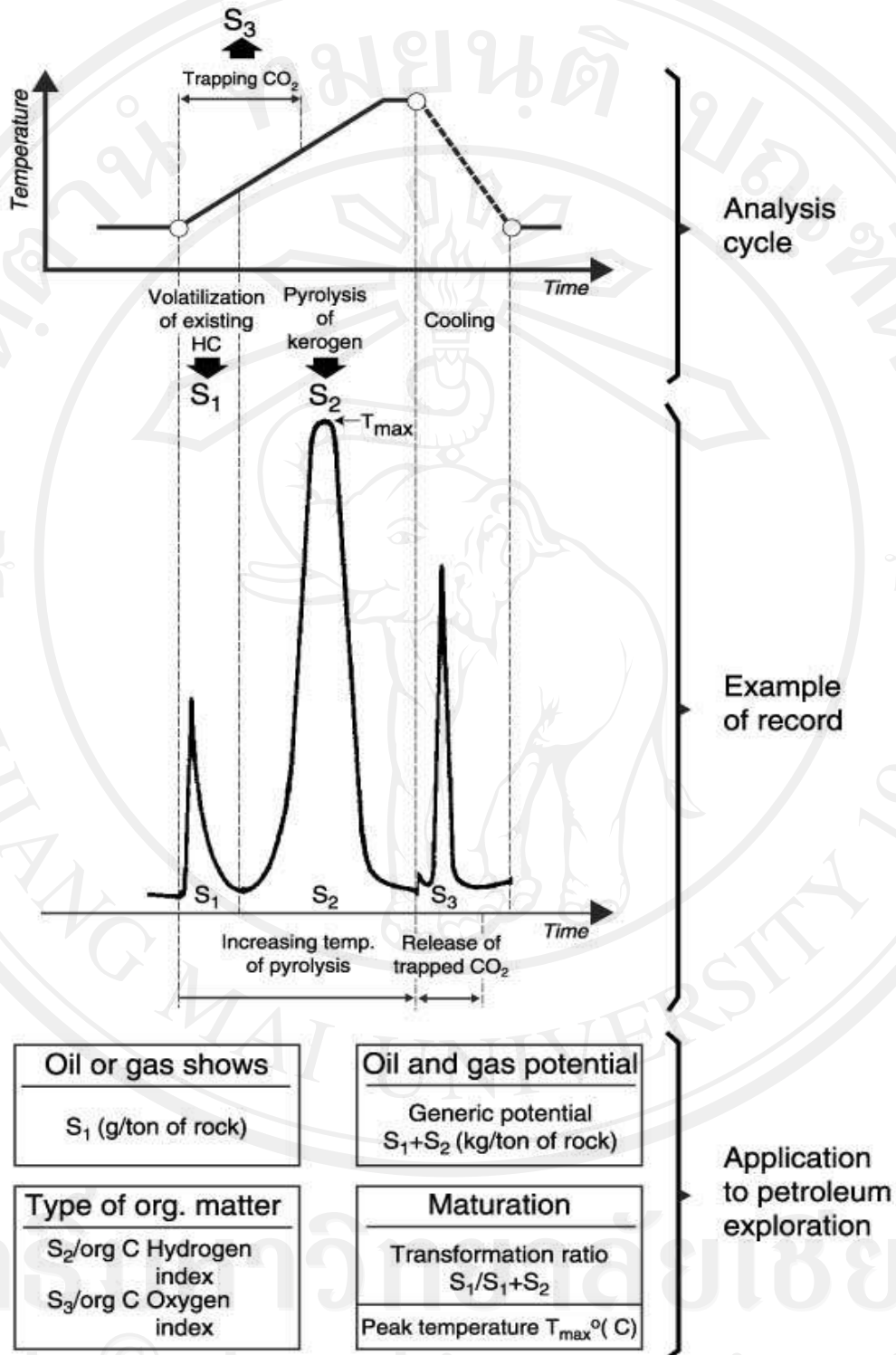


Figure 3.7 Cycle of analysis and example of record (Tissot and Welte, 1978).

(b) Between 300 and 600°C, hydrocarbon and oxygen containing compounds are expelled from the rock during the cracking of both kerogen and heavy extractable compounds such as resins and asphaltenes. Hydrocarbons form the **S<sub>2</sub> peak** which corresponds to present potential of the rock sample. S<sub>2</sub> is expressed in mg HC/g of rock. **Hydrogen Index (HI)** is  $(S_2/TOC)*100$ . Oxygen compounds decomposed between 300 and 390°C, and the resulting CO<sub>2</sub> is measured as the **S<sub>3</sub> peak** which is expressed in mg CO<sub>2</sub>/g of rock. **Oxygen Index (OI)** is  $(S_3/TOC)*100$  and is expressed in mg HC/g of rock. **Production Index (PI)** is  $S_1/(S_1+S_2)$ .

(c) The temperature for which the S<sub>2</sub> peak is maximum (**T<sub>max</sub>** expressed in °C) was found to vary with the thermal evolution formerly undergone by the rock sample under analysis.

(d) The organic carbon remaining after the recording of the S<sub>2</sub> peak (**C<sub>R</sub>**) is measured by oxidation under air (or oxygen) atmosphere at 600°C. The CO<sub>2</sub> obtained is the **S<sub>4</sub> peak**, expressed in mg CO<sub>2</sub>/g of rocks. The total organic carbon (TOC expressed in weight %) is automatically computed from peaks S<sub>1</sub>, S<sub>2</sub> and S<sub>4</sub>.

### 3.2.2.1 Rock-Eval Pyrolysis procedure

(1) The 50 mg standard (calibration samples IEP 55000) was added into crucible for calibration. (note: T<sub>max</sub> 412 – 422 °C, S<sub>1</sub> 0.23 - 0.34 mg HC/ g Rock, S<sub>2</sub> 12.82 – 14.66 mg HC/ g rock and S<sub>3</sub> 0.81 – 1.07 mg HC/ g rock)

(2) The empty crucible was analyzed for set blank value.

(3) The 50 mg standard was added into crucible to check standard value.

(4) The empty crucible was analyzed to check blank value.

(5) And then the 50 mg ground samples were added into crucible.

## 3.2.3 Gas Chromatography and Gas Chromatography- Mass Spectrometer

### 3.2.3.1 Sample selection

The TOC, S<sub>1</sub> and S<sub>2</sub> value were used as the screening parameter to select the sample for gas chromatography and gas chromatography-mass spectrometer. 27 samples were chosen from Fang, Na Hong, Li, Mae Sot, Phitsanulok and Suphanburi basins by the following criteria;

- 4 samples of Fang-MS well from Fang basin: TOC  $\geq$  1.9 wt%,  $S_1 \geq$  0.07 mg HC/g rock and  $S_2 \geq$  7.5 mg HC/g rock.
- 4 samples from Na Hong basin: TOC  $\geq$  10.0 wt%,  $S_1 \geq$  1.0 mg HC/g rock and  $S_2 \geq$  45.0 mg HC/g rock.
- 2 samples from Li basin: TOC  $\geq$  25.0 wt%,  $S_1 \geq$  2.0 mg HC/g rock and  $S_2 \geq$  150.0 mg HC/g rock.
- 2 samples from Mae Sot basin: TOC  $\geq$  20.0 wt%,  $S_1 \geq$  3.0 mg HC/g rock and  $S_2 \geq$  150.0 mg HC/g rock.
- 5 samples from P-SK well of Phitsanulok basin: TOC  $\geq$  1.0 wt%,  $S_1 \geq$  0.5 mg HC/g rock and  $S_2 \geq$  4.0 mg HC/g rock.
- 5 samples from SP1 well and 5 samples from SP2 well of Suphanburi basin: TOC  $\geq$  3.0 wt%,  $S_1 \geq$  0.1 mg HC/g rock and  $S_2 \geq$  10.0 mg HC/g rock.

### 3.2.3.2 Extraction and separation

Approximately 2 g. of powdered samples were Soxhlet extracted for 72 hours using an azeotropic mixture of chloroform and methanol. Asphaltenes were precipitated out from the extracts using n-pentane. The remaining extract was separated by column chromatography into three fractions: aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds.

After removal of the asphaltene, the sample was further analyzed by a large column chromatography containing silica gel. A fraction containing the saturated and monoaromatic hydrocarbons was eluted with hexane and a fraction containing mainly triaromatic hydrocarbons with hexane/dichloromethane (75:25, v/v). The polar compounds were not recovered. A fraction enriched in branched chain and cyclic saturated hydrocarbons was prepared from the saturated/monoaromatic hydrocarbon fractions using medium performance liquid chromatography (MPLC).

### 3.2.3.3 Gas chromatography

The saturated fractions were analysed on a Hewlett Packard 5890 gas chromatograph fitted with a 25 m HP-1 column (30 m long, 0.25 mm wide and film thickness 0.10  $\mu$ m). The temperature program was 5.0°C/min from 80-300°C, followed by 15 min at 300°C.



### 3.2.3.4 Gas chromatography-mass spectrometer

Gas chromatography-mass spectrometry (GC-MS) of saturated hydrocarbons was carried out on a Hewlett Packard 5890 gas chromatograph connected to a HP5971A mass selective detector. The GC was fitted with a Phenomenex ZB-5 (30 m long, 0.25 mm wide and film thickness 0.10  $\mu\text{m}$ ). The temperature program was 30°C/min from 70-100°C and 4°C/min from 100-308°C followed by 8 min at 308°C. Saturated hydrocarbon fractions of samples were dissolved in iso-octane, and the concentration was 1 mg/100  $\mu\text{m}$ . The mass spectrometer was operated in the electron impact (EI) mode with electron energy of 70 eV and analysis was done in the selected ion monitoring (SIM) mode. The fractions obtained by reverse phase HPLC were analysed in full scan mode by scanning from 50 to 500 u at 1.1 cycles/s (concentration: 0.01-0.1 mg/100  $\mu\text{l}$  iso-octane).

### 3.2.4. Petrography

#### 3.2.4.1. Organic petrography

Each sample was analysed in reflected white light and fluorescence-inducing blue light in oil immersion using a Zeiss incident light microscope and a swift point counter. A total of 300 points (macerals and minerals) were counted in each sample. The kerogen analyses were likewise carried out by means of point-counting. The coal maceral group terminology was used to type organic material (Hutton *et al.*, 1994), and the following entitle were recorded: liptinitic terrestrial organic matter (OM) and terrestrial OM, the latter divided if possible into vitrinitic OM and inertinitic OM. Intimately associated organic and mineral matter were counted as organo-mineral matrix. Pyrite and mineral matrix were also recorded.

Kerogen classification was based on the scheme developed by Mukhopadhyay *et al.* (1985), where each kerogen type among other things is characterized by a specific maceral composition and hydrogen index range (Table 3.1). A total of 12 kerogens (alginite, algodetrinite, sapropelinite I, sapropelinite II, liptodetrinite, resinite A, resinite B, particulate liptinite (mainly B), liptodetrinite, vitrinite (collotelinite, humosapropelinite) and inertinite) analyses were carried out.

**Table 3.1** Kerogen classification (From Mukhopadhyay *et al.*, 1985).

Kerogen type	Maceral composition		Fluorescence properties	Range of Hydrogen Index (mg HC/g TOC)	H/C Atomic ratio	Peak generation (% R <sub>o</sub> )	Generated Hydrocarbon
	Major	Minor					
I	Alginite Algodetrinite Sapropelinite I	Bacterial remnants Sapropelinite II	Greenish yellow for alginite	> 700	> 1.5	0.6-0.9	Mainly oil
IIa	Sapropelinite II Liptodetrinite Resinite (A+B)	Particulate Liptinite (A+B) Alginite Corpogelinite	Orange to orange brown for sapropelinite II Yellow for resinite (A+B)	400-700	1.1-1.5	0.6-0.9 0.3-0.7 (for resinite)	Mainly oil; Major gas in higher maturation (> 1.3 %R <sub>o</sub> )
IIb	Particulate liptinite (mainly B) Liptodetrinite	Alginite Sapropelinite II Collodetrinite Humosapropelinite	Yellow for sporinite, cutinite etc.	150-400	0.8-1.3	0.7-1.1	Oil and gas
III	Vitrinite (Collotelinite, Humosapropelinite)	Resinite Inertinite Sporinite	Dark brown for resinite	25-150	0.5-0.8	0.8-1.0 (oil) 1.0-1.5 (gas)	Mainly gas
IV	Inertinite	Vitrinite		<25	0.5	No source of hydrocarbon	Minor gas (no source for liquid hydrocarbon)

### 3.2.4.2 Vitrinite reflectance measurements

Vitrinite Reflectance (VR) is the most commonly used organic maturation indicator in the petroleum industry. This is mainly because it is quick and non-destructive. Vitrinite is common as a residue in source rocks.

As coal rank increase, and the chemical composition of the vitrinite correspondingly changes, the vitrinite macerals become increasingly reflective. Therefore, the percentage reflection of a beam of normal incident white light from the surface of polished vitrinite is a function of the rank (maturity) of the maceral.

The reflectivity (VR) may either be recorded as  $R_v$  max% or  $R_o$ %. Both are measurements of the percentage of light reflected from the sample, calibrated against a material which shows ~100% reflectance (i.e. a mirror). Because vitrinite is 'anisotropic'; reflectance will be greatest on the bedding parallel surfaces and least on surfaces cut orthogonal to the bedding. Surfaces cut at angles between these two extremes will have intermediate reflectance. Consequently, under (cross) polarised light, the reflectance of the vitrinite maceral observed will depend upon its position relative to the plane of polarisation of the light. In cross polars, the vitrinite will, in a  $360^\circ$  rotation of the stage, have two reflectance maxima and two reflectance minima. It is the average % reflection of the two reflectance maxima which provides analysts with the value  $R_v$  max%. This methodology is that of choice in Australia. In the USA and Europe,  $R_o$ % is measured. This is simply the reflection off macerals from a normal incident beam of non-polarised light.

Rocks and cutting samples are separated and washed, and then mounted in resin. These resin blocks are then ground and polished to a high standard. Poor polishing will lead to spurious reflection measurements. Sample preparation will take ~ 1 day. The blocks will obviously contain particles of vitrinite plus other macerals (i.e. liptinites and inertinites) which will need to be recognised and discarded. The number of individual reflection measurement will be dependent on the abundance of vitrinite in the sample, but should be in the order of 70 vitrinite measurements.

The equipment used was a Leitz MPV-SP system, which was calibrated against a standard of 0.515 % $R_o$ . A total of 70 measurements per sample conducted in monochromatic light and oil immersion was the optimum; however, commonly this

was not possible. The reflectance measurement procedure is in accordance with the standards outlined by Stach *et al.* (1982).

### 3.2.4.3 Sample selection

The TOC and HI values were used as a parameter to select the sample for maceral analysis and vitrinite reflectance measurement. Samples from Fang, Na Hong, Li, Mae Sot, Phitsanulok and Suphanburi basins were chosen by the following criteria:

- 19 samples from Fang-MS well: TOC  $\geq$  1.0 wt% and HI  $\geq$  220 mg HC/g TOC
- 4 samples from Na Hong: TOC  $\geq$  10.0 wt% and HI  $\geq$  250 mg HC/g TOC
- 3 samples from Li: TOC  $\geq$  7.0 wt% and HI  $\geq$  300 mg HC/g TOC
- 2 samples from Mae Sot: TOC  $\geq$  20.0 wt% and HI  $\geq$  650 mg HC/g TOC
- 14 samples from P-SK well of Phitsanulok basin: TOC  $\geq$  0.8 wt% and HI  $\geq$  220 mg HC/g TOC
- 14 samples from SP1 well and 14 samples from SP2 well of Suphanburi basin: TOC  $\geq$  1.0 wt% and HI  $\geq$  100 mg HC/g TOC

### 3.2.4.4 Sample preparation

Particulate pellets suitable for optical analyses were prepared by crushing the samples to a grain size between 63  $\mu$ m and 1 mm. Approximately 15 ml of a dried (24 hrs at 60°C) homogenized sample split was embedded in epoxy. Following hardening the sample was cut vertically into two pieces and the 'new' face was ground and polished using  $\frac{1}{4}$   $\mu$ m diamond powders for the final polish to obtain a smooth surface. The preparation procedure thus takes into account the grain size and density induced separation during embedding in epoxy resin.