

วิธีการสกัดตามลำดับชั้นเพื่อศึกษารูปแบบของซิลิเกตในตะกอนบริเวณแอสทอรี่



นางสาวดรุณวรรณ สกฤณา

สถาบันวิทยบริการ

จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

SEQUENTIAL EXTRACTION METHOD FOR THE STUDY OF SILICATE SPECIATION  
IN ESTUARINE SEDIMENT

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สถาบันวิทยบริการ

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การศึกษานี้ได้พัฒนาวิธีการสกัดซิลิเกตในตะกอนด้วยวิธีการสกัดตามลำดับชั้น โดยรูปแบบของซิลิเกตที่ศึกษามีอยู่ 5 รูปแบบได้แก่ แมงกานีสที่อยู่ร่วมกับซิลิเกต (Mn-Si) อลูมิเนียมที่อยู่ร่วมกับซิลิเกต (Al-Si) เหล็กที่อยู่ร่วมกับซิลิเกต (Fe-Si) ซิลิเกตที่เกิดจากซากของสิ่งมีชีวิต (B-Si) และซิลิเกตที่อยู่ในโครงสร้างผลึกแร่ (Res-Si) โดยทำการศึกษาในตะกอนขนาด < 114  $\mu\text{m}$ , >114  $\mu\text{m}$  และ non-sieve จากปากแม่น้ำแม่กลอง บางปะกง และเจ้าพระยา ผลการศึกษาพบว่าซิลิเกตที่อยู่ในโครงสร้างผลึกแร่เป็นรูปแบบที่พบมากที่สุดในตะกอนทั้ง 3 ตัวอย่าง ตามด้วยซิลิเกตที่เกิดจากซากของสิ่งมีชีวิต เหล็กที่อยู่ร่วมกับซิลิเกต อลูมิเนียมที่อยู่ร่วมกับซิลิเกต และแมงกานีสที่อยู่ร่วมกับซิลิเกต ยกเว้นในตะกอนขนาด < 114  $\mu\text{m}$  จากแม่กลองและเจ้าพระยา ที่พบ อลูมิเนียมที่อยู่ร่วมกับซิลิเกตในปริมาณที่มากกว่า เหล็กที่อยู่ร่วมกับซิลิเกต

นอกจากนี้ยังทำการวิเคราะห์ปริมาณรวมของซิลิเกตในตะกอนด้วยวิธี X-ray fluorescence spectrometry (XRF) และการสกัดด้วยกรด ( $\text{HF-HClO}_4\text{-HNO}_3$ ) เพื่อนำมาประเมินความถูกต้องของวิธีสกัดที่พัฒนาขึ้นและยังวิเคราะห์ชนิดแร่ในตะกอนด้วยวิธี X-ray diffractometry พบแร่ในกลุ่ม neoformation หรือ neocrystalline ซึ่งช่วยยืนยันการมีอยู่จริงของรูปแบบซิลิเกตในตะกอน

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ภาควิชา.....วิทยาศาสตร์ทางทะเล..... ลายมือชื่อนิสิต.....  
สาขาวิชา.....วิทยาศาสตร์ทางทะเล..... ลายมืออาจารย์ที่ปรึกษา.....  
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KEY WORD: SILICATE SPECIATION / SEDIMENT / SEQUENTIAL EXTRACTION

DAROONWAN SAKUNA : SEQUENTIAL EXTRACTION METHOD FOR THE STUDY OF SILICATE SPECIATION IN ESTUARINE SEDIMENT. THESIS ADVISOR : ASST. PROF. SIRICHAH DHARMVANIJ, Ph.D., THESIS COADVISOR : ASSOC. PROF. PUNYA CHARUSIRI, 106 pp. ISBN 974-17-2980-4.

The silicate extraction method was developed by using the principal of sequential extraction method. Five of silicate species, namely manganese bound silicates (Mn-Si), aluminum bound silicates (Al-Si), iron bound silicates (Fe-Si), biogenic silicates (B-Si) and residual silicates (Res-Si) were examined in sediments from Mae Klong, Bang Pakong and Chao Phraya estuaries. These sediments were divided into < 114  $\mu\text{m}$ , >114  $\mu\text{m}$  and non-sieved. The results indicated that residual silicates are the highest species in all three sediment samples, following by biogenic silicates, iron bound silicates, aluminum bound silicates and manganese bound silicates. Except in sediment size < 114  $\mu\text{m}$  from Mae Klong and Chao Phraya, the aluminum bound silicates are higher than iron bound silicates.

Total silicates hve been analyzed by X-ray fluorescence spectrometry (XRF) and acid digestion ( $\text{HF-HClO}_4\text{-HNO}_3$ ) in order to assess the accuracy of the sequential extraction method. Moreover, mineralogical analysis by X-ray diffractometry reveals minerals occurring in neoformation or neocrystalline group, which verify the existence of the silicate species in the sediments.

Department.....Marine Science..... Student's signature.....  
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## CHAPTER I

### INTRODUCTION

Most of silicates in the aquatic ecosystem, derived from the weathering of continental rocks, are transported to the sea via stream or river (Chamley, 1990; Pye, 1994; Treguer et al., 1995). During its transportation, both dissolved and particulate silicate can be dramatically modified by processes occurring in the aquatic ecosystem, such as adsorbed or coated on the surface of the suspension, precipitation or coagulation, uptake by organisms in primary productivity; these organisms may die and release silicates back into solution. Some silicates are stored in hard skeleton or shells that cannot be digested and later accumulate as the bottom sediments (Carlson and Schwertmann, 1981; Demaster, 1981; Aston, 1983; Laodong et al., 1986; Raiswell and Canfield, 1996; Heiskanen and Keek, 1996; Konhauser and Urrutia, 1999). Processes mentioned above, can result in the removal of silicates from solution into particulate form and later sink to the bottom as sediment, which take place in estuarine region where freshwater mixed with seawater (Burton and Liss, 1976 and Laodong et al., 1986). Low concentration of silicates that finally exported to the sea, support this statement too (Aston, 1983; Conley, 1997; Rocha et al., 1998). Therefore, the study of silicates in sediments especially its speciation, is the key to better understanding of the processes and biogeochemical cycles in the aquatic ecosystem.

However, a numerous studies of silicates in the sediments were emphasized on biogenic silicates owing to its valuable paleoceanographic record of changes in the strengths and spatial variation of surface ocean productivity (Ritetti-Shati et al., 1998; Rocha et al., 1998; Pike and Kemp, 1999). But, from geochemical balance calculation of silicates, it was found that total amount of biogenic silicates; which accumulate in the sediments, is not enough to counter-balance overall silicates. So it is likely that other forms of silicate in the sediments has to be taken into account. The aim of this study is to support the existence of silicate speciation in estuarine sediments such as manganese bound silicate (Mn-Si), aluminum bound silicate (Al-Si), iron bound

silicate (Fe-Si), biogenic silicate (BSi) and residual silicate (Res-Si). And finally to present an extraction method for the study silicate speciation in estuarine sediment.

### Objectives

1. To determine silicates in estuarine sediments by using sequential extraction technique.
2. To study silicate speciation in the estuarine sediments.

### Scope of the work

1. Extract silicate speciation: Mn-Si, Al-Si, Fe-Si, BSi and Res-Si by sequential extraction method.
2. Determine total silicates by XRF technique and acid digestion to confirm the results.
3. Grain size of the sediments to be analyzed are divided into groups namely < 114  $\mu\text{m}$ , >114  $\mu\text{m}$  and non-sieved.
4. Synthesize reference materials for testing the effectiveness of the extraction method.
5. Analyze the other estuarine sediments with the extraction method.

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## CHAPTER II

### SILICATE SPECIATION IN SEDIMENTS

#### 2.1 Forms of silicate in sediments.

Estuaries are transition zones in which seawater is mixed with, and diluted by fresh water. The mixing of the two different waters makes estuaries very complex environments. Accordingly, estuaries can also be thought of as filters, capable of reducing the river load of dissolved and particulate matter to the oceans (Burton and Liss, 1976 and Dyer, 1979). The modification of the river-transported materials takes place in estuaries via a number of physical, chemical and biological processes that involve dissolved-particulate speciation changes such as complexation and chelation reactions with organic and inorganic ligands, hydrolysis, dissociation, polymerization and association, physical and chemical sorption onto mineral surfaces, ion exchange, precipitations and co-precipitation and surface precipitation of trace components, and processes involving biological material like biosorption, biologically catalyzed redox reactions etc.

Considering silicate concentration in fresh and seawater, it was found that silicate is a major component in freshwater while in seawater; silicate tends to be a micronutrient (Martin and Maybeck, 1979 and Chester, 1990). And most silicates tend to be removed from the water in estuaries. This chapter will review only principle mechanisms or processes, which involved in the removal of silicate from water.

#### 2.1.1 Coagulation

Coagulation is the process in which coagulants and mixing destabilize and agglomerate colloidal and suspended material into flocs, so the coagulum settles as a relatively dense precipitate. Hence noting the increase in turbidity or decrease in transmitted light can follow coagulation. Moreover, coagulation has been considered to be the result of van der Waals attraction which at the moment of collision draws two particles together, unless opposed by a hydration barrier layer or by the electrostatic

repulsion forces between the similarly charged particles, or both (Griffen, 1992 and Bohuslav, 1993).

### **2.1.2 Flocculation**

According to Bohuslav (1993), flocculation means a process to enhance agglomeration or collection of smaller floc particles into larger, more easily settleable particles through gentle stirring by hydraulic or mechanical mechanisms.

### **2.1.3 Adsorption and precipitate by hydrous oxides**

Adsorption is the enrichment (positive adsorption, or briefly, adsorption) or depletion (negative adsorption) of one or more components in an interfacial layer. In certain case a decision as to whether the actual distribution of a component between the interfacial layer and the bulk phases should be looked upon as enrichment or depletion may depend on the choice of the reference system. Moreover, when two phases are put into contact, the composition of one or both bulk phases may be changed by the partition of one or more components between these phases. In adsorption structure of the absorbent and/or the chemical nature of the adsorptive may be modified. Silicates, both soluble and colloidal, can be removed in neutral or slightly alkaline solution by co-precipitation with or by adsorption upon freshly formed insoluble metal hydroxides such as manganese hydrous oxide (Harder, 1974 and Chester, 1990) iron hydroxide (Kostka and Luther, 1993 and Raiswell and Canfield, 1996), and aluminum hydroxide (Healy et. al.,1973 and Macklin and Aller, 1984).

### **2.1.4 Deposition of colloidal silicate**

Deposition of colloidal particles on a surface from a dilute solution may occur when conditions of pH and salt concentration are close to those causing coagulation or precipitation. Deposition occurs when the colloidal particles collide and combine with the solid silicate surface. The concentration of colloid must be suitably low. Because a concentrated solution would otherwise be rapidly coagulated and no coating obtained.

Deposition of colloid is greatly accelerated and the deposits are much more dense and hard when soluble silicate is deposited along with the colloidal particles. In natural environment, almost any imaginable set of condition can occur at one time or another. Further deposition of silicate can occur until the silicate deposit becomes completely impervious. This effect is seen in some opal. In addition, deposition of colloidal particles requires the presence of a potential coagulating agent, usually small concentrations of polyvalent metal ions. Silicates are in turn adsorbed on coagulating agent forming colloidal particles and deposit.

### **2.1.5 Removal by Biogenic Materials**

Due to its role as a nutrient for various plankton species especially diatom, plants and animals, the silicate concentration in aquatic habitats varies considerably. Silicates are utilized for their growth, building their skeleton and shell etc (Paasche, 1973; Werner, 1977).

### **2.2 Sequential extraction technique for the study of silicate speciation in sediment.**

Many geochemical variables, different processes and various structures of compound affect the speciation of silicate in sediment. Sequential extraction approach has been widely used in an attempt to extract selectively discrete geochemical component of sediments. In each extraction method the sequence is designed to attack a single phase by using an appropriate reagent or reagents. With this approach we can separate the different sources of substance in the sediments: the biogenous portion composed by biological remains; the lithogenous portion of continental origin which does not change during its transfer through the water column; the authigenic or hydrogenous portion due to neof ormation in the water column (Martin et. al., 1987).

The possible silicate speciation includes manganese bound silicate (Mn-Si), aluminum bound silicate (Al-Si), iron bound silicate (Fe-Si), biogenic silicate (B-Si) and residual silicate (Res-Si). All selected species used in this study are likely to exist in natural estuarine sediment by inferring from principle processes mentioned in section 2.1. There has been no previous study on silicate speciation. However, the formation of

silicate speciation in the estuarine sediment has the same mechanism as phosphate or trace metal partitioning. Therefore, we select the extraction methods from previous studies done by other workers as list in table 2.1, which to be applied to silicate extraction in this study. Selected method are arranged in a sequence conformed to strength of the chemical extractants, bonding strength of the speciation and subsequent analysis for dissolved silicate in each extractant by forming silicomolybdate complex. Details of the proposed sequence are as follows:

Step I Manganese bound Silicate (Mn-Si), This easy reducible fraction is firstly extracted with hydroxylamine and nitric acid solution. However, if it is left to react with the extractant for too long, iron oxides would dissolved in the extractant. To minimize crossing phase by iron oxides, the extraction in this step would follow Sompongchaiyakul method (1989) because of the resemblance in characteristics of the sediment sample.

Step II Aluminum bound silicate (Al-Si) is extracted with ammonium fluoride solution. This method was firstly employed to extract aluminum bound phosphate (Al-P) extraction method. Therefore, it should be equally effective in Al-Si extraction since Al-Si and Al-P are both adsorbed on suspended aluminum oxides surface (Lijklema, 1980; Laodong, 1986; Lebo, 1991; Konhauser and Urrutia, 1999). The advantage of using ammonium fluoride is no iron oxide contamination in the supernatant (Chang and Jackson, 1957).

Step III In order to extract iron oxides, we used a mixture of Na-citrate and Na-acetate solution and follow by Na-dithionite powder, to reduce ferric oxide which subsequently form a chelate with citrate. Kostha and Luther (1994) concluded that iron oxides were extracted by dithionite extractant, possibility in amorphous form.

Table 2.1 Some of the extraction schemes

Target Fractions	Reagents and Conditions	Sources
Mn – oxides	- 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCL}$ + 0.01 M $\text{HNO}_3$ , pH 2, 15 min	Sompongchaiyakul, 1989.
Al – oxides	- 0.5 M $\text{NH}_4\text{F}$ , pH 7, 1 hr.	Chang and Jackson, 1957.
Fe – oxides	- 0.5 g Na dithionite in 0.2 M Na-citrate/ 0.35 M Na-acetate, pH 4.8, 60°C, 4 hr.	Kostha and Luther, 1994.
Biogenic silicate	- 2 M ( $\text{Na}_2\text{CO}_3$ ), 85°C, 5 hr.	Mortlock and Froleich, 1989
Residue	-conc. HF and aqua regia ( $\text{HClO}_4$ and $\text{HNO}_3$ ), 200 °C, 9 hr.	This study

Step IV Hot Sodium bicarbonate ( $\text{Na}_2\text{CO}_3$ ) is used to react with biogenic silicate or opal. Before starting the procedure, hydrochloric acid and peroxide are added to remove diluting phases such as carbonate and organics, and to assist in disaggregating the sediment and make the attack of the target phase by this solution easier (Mortlock and Froleich, 1988).

Step V The latest fraction to be extracted is silicates arranged in crystalline or mineral forms by using concentrated acid such as HF,  $\text{HClO}_4$  and  $\text{HNO}_3$ , heated at 200 °C in a teflon bomb. All residues are digested until only clear solution remains in the teflon bomb.

### 2.3 Factors affecting extraction efficiency

Factors, which affect the extraction efficiency, are reaction time, extractant concentration, pH of the solution, extraction time and time of color development. Changes in these factors would likely result in identifiable changes in the extraction of targeted fractions or partial fractions to be extracted. Hence, these factors are individually tested as follows:



### 2.3.1 pH

pH involves in extraction in 2 aspects :

- pH of the extraction solutions : Shift in this factor promotes dissolution of non-targeted phases and also re-adsorption of the extracted silicates in the aliquot (Lijklema, 1980; Schlüter and Rickert, 1998).
- pH during color formation : In color development step or silicomolybdate complex formation, the suitable pH range of the reagent solution to form this complex is 0.8-2.5. Out of this range it would be interfered by other substances such as phosphate , arsenate and fluoride (Grasshoft, 1999).

### 2.3.2 Color development time

Enough time must be allowed for the sample to completely reacts with molybdate, to form silicomolybdate. After a certain line, the extinction value will get lower than what is during measured the optimized period and will cause an error on calculation of silicate concentration (indirect effect to sequential extraction efficiency).

### 2.3.3 Concentration of extracting reagents

The concentrations of extracting reagents are one of the most important factors on the efficacy of sequential extraction method. The optimized extractant concentration will not only give the maximum extracted target phase in the supernatant but also help reducing contamination from non-targeted phase whereas diluted reagents might not be able to attack all of the targeted phase.

### 2.3.4 Extraction time

After optimizing the concentration, the extraction time is the next factor to be considered. It has the same effect as described above.

Lastly, in order to the extraction efficiency, reference materials are very helpful. In reference material is a material or substance in which one or more of whose property values are sufficiently homogenous, stable, and well established to be used for

calibration of an apparatus, the assessment of measurement, method, or for assigning values to materials. There are three broad types of reference materials

- Standard reference material (SRM) : a certified reference material (CRM) issued by the National institute of Standard and technology (NIST).
- Certified Reference Material (CRM) : a reference issued and certified by an organization generally accepted to be technically component.
- In-house Reference Material : a material developed by a laboratory for its own internal use.

For this study, there is neither SRM nor CRM. Synthesis of in -house reference material was carried out and which will be described in Chapter III.



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## CHAPTER III

### METHODOLOGY

#### 3.1 Study area

The sediment samples were collected from Mae Klong (MK), Bang Pakong (BP) and Chao Phraya (CP), estuaries by Petersen grab as shown in Fig. 3.1 The Chao Phraya estuarine sediment was exclusively used in testing effectiveness of the proposed sequential extraction method. After the extraction method had been optimized, the method was then used in analyzing the other sediment samples.

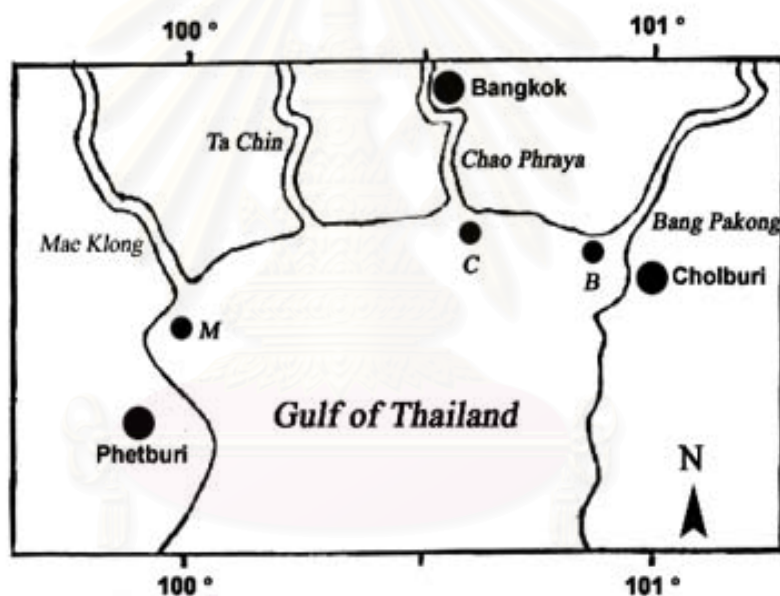


Figure 3.1 The index map showing sampling location at estuaries of Mae Klong, Bang Pakong and Chao Phraya.

#### 3.2 Sample collection and subsampling

Sediments that were not in direct contact with the grab surface was put into a clean plastic bag and frozen immediately. The samples were later freeze-dried. Lumps of freeze-dried sediment were crushed in an agate mortar, the samples were then homogenized by the Coning and Quartering method (Walton, 1978).

The homogenized sample was then divided into 2 portions. The first portion is used in size distribution analysis. The second portion is dry-sieved through a 114  $\mu\text{m}$  nylon sieve and later divided into 3 subportions namely; <114  $\mu\text{m}$ , >114  $\mu\text{m}$  and non-sieved sediment samples. (see more details in Appendix A and B).

### 3.3 Preparation of labwares and reagents for silicate analysis

Labwares used in this study should be plastic in order to reduce contamination of silicate from glass. Before use, all of them were soaked in 15 % (V/V)  $\text{HNO}_3$  at least overnight then rinsed with double distilled-deionized water (DDW), which was used throughout this study.

### 3.4 The experimental procedures

The experiments were started with testing factors, which affect efficiency of the extraction method. In each sample, the results of total digestion are compared with the summation of all silicate species that were extracted by sequential method. Synthesis of reference materials to help verify the effectiveness of the optimized extraction method. Finally, the other sediment samples were determined with the optimized method (Figure 3.2). Determination of major oxides and total silicate by X-ray fluorescence spectrometry and mineral characteristic by X-ray diffractometry were also carried out (Methods are shown in Appendix C and D).

### 3.5 Factors affecting extraction efficiency

Factors which influence efficiency of the sequential extraction method such as pH, extractant concentration, extraction time and time of color development, were tested to find the suitable condition for the extraction.

#### 3.5.1 Optimum time for color development

According to method proposed by Mortlock and Froelich (1989), it was suggested that at least 12 h to overnight, is needed for the completion of

silicomolybdate complex formation. Therefore, this experiment was designed to find the optimal time for the silicomolybdate complex formation.

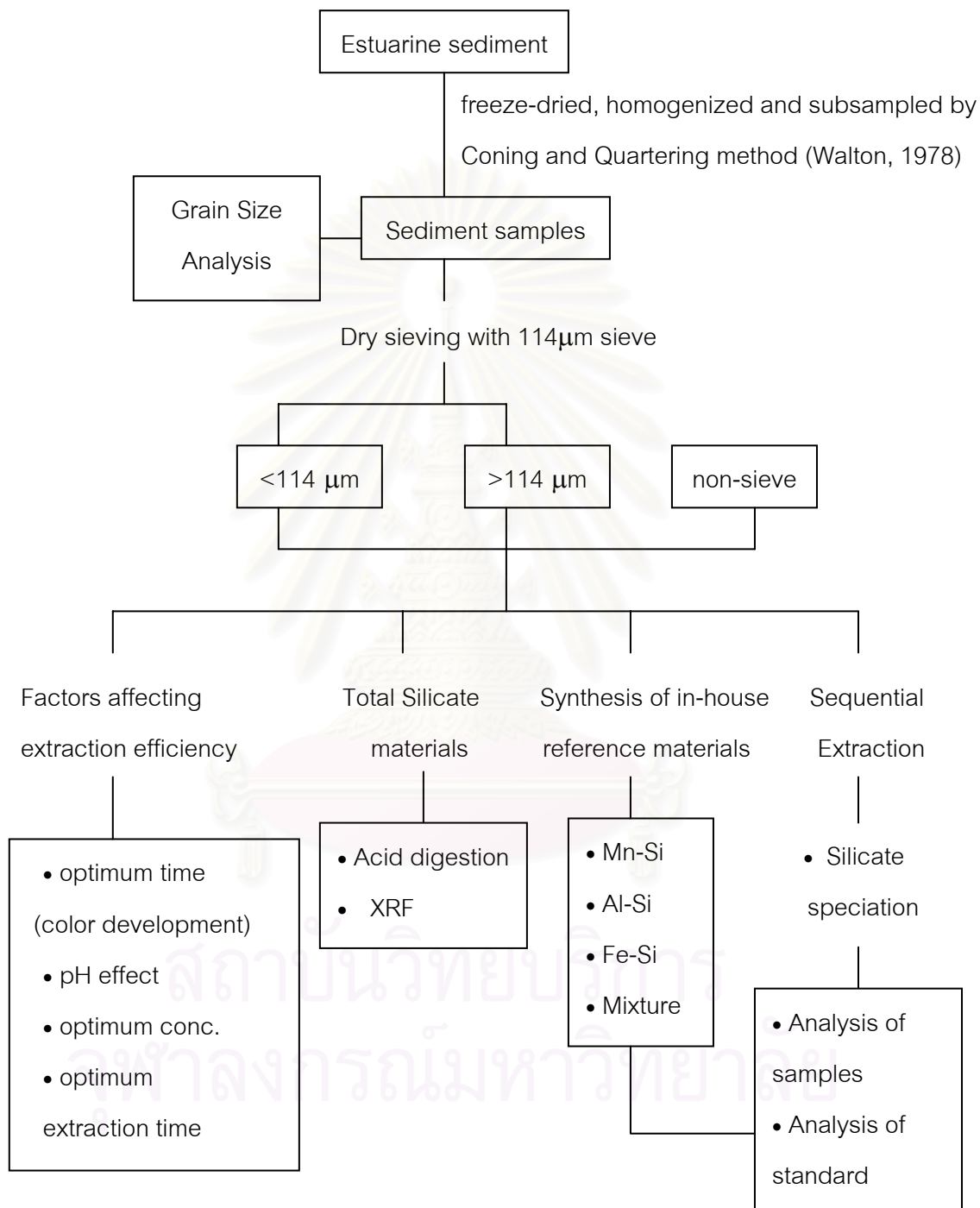


Figure 3.2 A flow chart of analytical procedure.

### Apparatus

- A Spectrophotometer (MiltonRoy ® Spectronic 401)
- A Micropipette (100-1000 µl Eppendorf ®)
- 25 ml. pipettes
- 30 ml polyethylene bottles with lids
- 1 cm quartz cuvettes.

### Reagents

- Molybdate reagent : Dissolve 16.0 g of analytical reagent ammonium paramolybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot\text{H}_2\text{O}$  in 1000 ml DDW. Store the solution in a tightly capped polyethylene bottle out of direct sunlight. The solution is stable indefinitely, but should be discarded if it forms a white precipitate or turns faintly blue and gives a high reagent blank.
- Metol-sulfite reagent : Dissolve 12 g of anhydrous sodium sulfite  $(\text{Na}_2\text{SO}_3)$  in 1000 ml of DDW, then add 20 g of metol and stir until dissolve. Filter the solution through a no. 1 Whatman filter paper, and store refrigerated in an amber ground-glass stoppered bottle. This solution is stable for 1-2 months provided that the bottle is tightly capped. Discard if the solution develops a faint brown color.
- Oxalic acid reagent : Dissolve 60 g of analytical reagent quality oxalic acid dihydrate  $(\text{COOH})_2\cdot 2\text{H}_2\text{O}$  in 1000 ml of DDW and store in a polyethylene bottle. This solution is stable indefinitely.
- Sulfuric acid reagent : Slowly add 300 ml of concentrated, analytical-reagent-quality sulfuric acid into 770 ml of DDW. Cool to room temperature and store in a polyethylene bottle.

- Hydrochloric acid reagent : Add 48 ml of concentrated HCl to 952 ml of DDW and store in a polyethylene bottle.
- Molybdate working solution : Mix molybdate reagent, HCl reagent and DDW in volume proportion of 1:1:5 . Prepare this mixture for immediate use. It is stable for at least 6-12 h. Store in a polyethylene bottle out of direct sunlight.
- Reducing working solution : Mix equal volume of metol-sulfite, oxalic acid reagent and sulfuric acid reagent. Adding the sulfuric acid last. It is stable for 4-6 h, but should be prepared immediately before use.
- Standard silicate stock solution : Weigh out 0.960 g of dried sodium silicofluoride ( $\text{Na}_2\text{SiF}_6$ ) and dissolve the salt by DDW. Then quantitatively transfer the solution to a 1000-ml volumetric flask. Mix and transfer the solution to a polyethylene bottle for storage. The solution is stable indefinitely.

### Procedure

Pipette 17.5 ml of the molybdate working solution into a dry, clean polyethylene bottle. Pipette 125  $\mu\text{l}$  of diluted standard silicate into the bottle and immediately mix by swirling. Cap the bottle and allow them to react for exactly 20 min. Pipette 7.5 ml of reducing working solution into the bottle, cap tightly and mix thoroughly by swirling. In order to see effect of time on color development. The experiments were repeated by carrying the whole process and measuring the absorption at 10, 10.5, 11, 11.5, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 24, 26 h.

### **3.5.2 pH effect**

The pH of molybdate working solution, before and after adding diluted, extracted solution as well as the reducing working solution, was checked to ensure that they are in the range of 0.8-2.5.

### Apparatus

- pH meter (Accumet ® BASIC AB 15)
- The other apparatus are the same as described in section 3.5.1.

### Reagents

- The same reagents are required as in section 3.5.1, except for the standard silicate solution, which is not used.

### Procedure

Pipette 17.5 ml of the molybdate working solution into a dry, clean polyethylene bottle. Pipette 125 µl of the diluted, extracted solution into the bottle and immediately mix by swirling. Immerse the electrode probe into the solution and read the pH. Leave the solution for exactly 20 min to allow formation of silicomolybdate complex, then pipette 7.5 ml of reducing working solution into the bottle, cap tightly and mix thoroughly by swirling. Immerse electrode probe into the solution and re-read the pH.

#### 3.5.3 Optimum extractant concentration

The objective of this experiment is to find the extractant concentrations which give the most extractable fraction without cross phase from other fraction. We have to find the optimum concentration of each extractant at every step before proceeding to the next step of sequential procedure.

### Apparatus

- 50 ml polyethylene centrifuge tubes with lids
- Pasteur pipettes
- A Micropipette (100-1000 µl Eppendorf ®)
- 50 ml Volumetric flasks



- A Shaker
- A Spectrophotometer (MiltonRoy ® Spectronic 401)
- A Centrifuge (Centurion Scientific ® 1040 series)

### Reagents

- Hydroxylamine hydrochloride solution : Dissolve hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) in DDW. Add from a pipette 6.92 ml of concentrated, analytical- reagent-quality  $\text{HNO}_3$  and make up the volume to 1000 ml in a volumetric flask. Store the solution in a polyethylene bottle. The weigh of hydroxylamine hydrochloride to be used depends on its concentration which can be calculated from equation A.
- Ammonium fluoride solution : Dissolve ammonium fluoride ( $\text{NH}_4\text{F}$ ) in DDW. Make the volume to 1000 ml in a measuring flask. Store the solution in a polyethylene bottle. The weight of ammonium fluoride to be used depends on its concentration which can be calculated from equation A.
- Na-citrate/ Na-acetate solution : Dissolve sodium citrate and sodium acetate in DDW. When the volume is closed to 1000 ml, adjust pH to 4.8 with 0.1 M HCl and then make up the volume to 1000 ml in a volumetric flask. Keep the solution in a polyethylene bottle. The weight of sodium citrate and sodium acetate to be used depends on their concentrations, which can be calculated from equation A. The concentration proportion of sodium citrate and sodium acetate is 0.1 M:0.175 M
- Na dithionite : Used in a powder form.

The chemical reagent weight are calculated from :

$$g = M/MW.$$

Whereas:  $g$  = weight of the chemical reagent (gram)

$M$  = concentration of the solution (Molar)

$MW$  = molecular weight of the chemical reagent

### Sequential Extraction Procedure

#### Step I Manganese bound Silicate

1. Transfer six replicates of 0.5 g of sediment sample into centrifuge tubes. Each tube was added from a pipette 10 ml of 0.2, 0.3, 0.4, 0.6, 1 and 1.5 M Hydroxylamine hydrochloride solution respectively.
2. Shake the tubes for 15 min and then centrifuge at 3000 rpm for 20 min. Separate the supernatant by a pasteur pipette.
3. Dilute the supernatant 50 times, analyzed silicate concentration by forming silicomolybdate complex according to Mortlock and Froelich method as described in section 3.6.

#### Step II Aluminum bound Silicate

1. Extracted manganese bound silicate with the optimal concentration described in step I
2. After removed the supernatant, shake the residue in each tube for 1 h respectively with 25 ml 0.4, 0.5, 0.6, 0.8, 1 and 1.5 M ammonium fluoride solution.
3. Centrifuge for 20 min at 3000 rpm and removed the supernatant.

4. Dilute the supernatant 50 times, analyze aluminum bound silicate by forming silicomolybdate complex according to Mortlock and Froelich method as described in section 3.6

#### Step III Iron bound Silicate

1. Extract manganese bound silicate and aluminum bound silicate sequentially with the optimal concentrations of the extractants in each step.
2. Add 0.5 g of Na dithionite and then 10 ml of Na-citrate/NaOAc solution to get concentration ratios of 0.1:0.175, 0.2:0.35, 0.3:0.525, 0.4:0.7 and 0.6:1.05 M in each tube respectively.
3. The tubes were shaken with a vortex mixer and placed in a covered, constant-temperature bath at 60 °C for 4 hours.
4. Every hour the tubes were removed and shaken vigorously to resuspend the solids and quickly returned to the water bath.
5. After 4 h, the tubes were immediately centrifuge for 20 min at 3000 rpm and remove the supernatant.
6. Dilute the supernatant 50 times, analyzed iron bound silicate by forming silicomolybdate complex according to Mortlock and Froelich method as described in section 3.6

#### 3.5.4 Optimum extraction time

After finding optimum concentrations of the extractants, one should also find an optimum time for the extraction. The experimental procedures are the same as in the tests for optimal concentration except the extraction time were varied instead.

### Apparatus

- 50 ml polyethylene centrifuge tubes with lids
- Pasteur pipette
- A digital clock
- A Micropipette (100-1000  $\mu$ l Eppendorf ®)
- 50 ml Volumetric flasks
- A Shaker
- A Spectrophotometer (MiltonRoy ® Spectronic 401)
- A Centrifuge (Centurion Scientific ® 1040 series)

### Reagents

- 0.3 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ +0.1M  $\text{HNO}_3$  solution : Dissolve 20.847 g of analytical-reagent-quality hydroxylamine hydrochloride  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 6.92 ml of 65%  $\text{HNO}_3$ . Make final volume 1000 ml with double distilled de-ionized water (DDW). Store the solution in a tightly capped polyethylene bottle.
- 0.6 M  $\text{NH}_4\text{F}$  solution : Dissolve 22.2 g of analytical-reagent-quality ammonium fluoride  $\text{NH}_4\text{F}$  in 1000 ml of double distilled de-ionized water (DDW). Store the solution in a polyethylene bottle.
- 0.2 M Na-citrate/0.35 M NaOAC solution (pH4.8) : Dissolve 58.82 g of Na-citrate and 28.7105 g of Na -acetate (NaOAC) in warm water. Adjust pH to 4.8 with 0.1 M hydrochloric acid. Dilute the solution to final volume 1000 ml. Store the solution in a polyethylene bottle.
- Na-dithionite : Used in a powder form.

## Procedure

### Step I Manganese bound Silicate

1. Transfer eleven replicates of 0.5 g of sediment sample into centrifuge tubes. Each tube was added from a pipette 10 ml of 0.3 M  $\text{NH}_2\text{OH}\cdot\text{HCl}+0.1\text{M HNO}_3$  solution respectively
2. Shake each tube for 10, 15, 20, 25, 30, 45, 60, 75, 90, 105 and 120 min respectively and then centrifuge at 3000 rpm for 20 min. Separate the supernatant by pasteur pipettes.
3. Dilute the supernatant 50 times, analyze manganese bound silicate by forming silicomolybdate complex according to Mortlock and Froelich method as described in section 3.6

### Step II Aluminum bound Silicate

1. Extract manganese bound silicate with the optimum extraction time found in the previous step.
2. After removing the supernatant, shake the residue in each tube with 25 ml of 0.6 M  $\text{NH}_4\text{F}$  solution for 45 min, 1, 1.25, 1.5, 1.75, 2.25, 2.5, 3 and 3.5 hours respectively.
3. Centrifuge for 20 min at 3000 rpm and remove the supernatant.
4. Dilute the supernatant 50 times, analyze aluminum silicate by forming silicomolybdate complex according to Mortlock and Froelich method as described in section 3.6

### Step III Iron bound Silicate

1. Extract manganese bound silicate and aluminum bound silicate sequentially with the optimal concentrations of the extractants in each step.
2. Add 0.5 g of Na dithionite and then 10 ml of 0.2 M Na-citrate/0.35 M NaOAC solution, control pH at 4.8 in each tube.
3. The tubes were shaken well with a vortex mixer and placed in a covered constant-temperature bath to 60 °C for 3.75, 4, 4.25, 4.5, 4.75, 5, 5.25, 5.5, 5.75 and 6 hours.
4. Every hour the tubes were removed and shaken vigorously to resuspend the solids and quickly returned to the water bath.
5. Once the time limits were reached, the tubes were immediately centrifuge for 20 min at 3000 rpm and remove the supernatant.
6. Dilute the supernatant 50 times, analyze iron bound silicate by forming silicomolybdate complex according to Mortlock and Froelich method as described in section 3.6

### 3.6 Determination of dissolved silicate

Dissolved silicate is determined by molybdate-blue spectrophotometry (Mortlock and Froelich, 1989). The molybdate working solution reacts with silicate ions to form silicomolybdate complex, only the reactive silicate will form this complex. Then measured dissolve silicate by spectrophotometer within optimum time after adding reducing working solution in order to eliminate the interference of color development

#### Apparatus

- A Spectrophotometer (MiltonRoy ® Spectronic 401)

- A Micropipette (100-1000  $\mu$ l Eppendorf ®)
- 25 ml. pipettes
- 30 ml polyethylene bottles with lids
- 2 quartz cuvettes

### Reagents

- Molybdate reagent : Dissolve 16.0 g of analytical-reagent ammonium paramolybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot \text{H}_2\text{O}$  in 1000 ml DDW. Store the solution in a tightly capped polyethylene bottle out of direct sunlight. The solution is stable indefinitely, but should be discarded if it forms a white precipitate or turns faintly blue and gives a high reagent blank.
- Metol-sulfite reagent : Dissolve 12 g of anhydrous sodium sulfite  $(\text{Na}_2\text{SO}_3)$  in 1000 ml of DDW, then add 20 g of metol and stir until dissolve. Filter the solution through a no. 1 Whatman filter paper, and store refrigerated in an amber ground-glass stoppered bottle. This solution is stable for 1-2 months provided that the bottle is tightly capped. Discard if the solution develops a faint brown color.
- Oxalic acid reagent : Dissolve 60 g of analytical-reagent-quality oxalic acid dihydrate  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$  in 1000 ml of DDW and store in a polyethylene bottle. This solution is stable indefinitely.
- Sulfuric acid reagent : Slowly add 300 ml of concentrated analytical-reagent-quality sulfuric acid into 770 ml of DDW. Cool to room temperature and store in a polyethylene bottle.
- Hydrochloric acid reagent : Add 48 ml of concentrated HCl to 952 ml of DDW and store in a polyethylene bottle.

- Molybdate solution : Mix molybdate reagent, HCl reagent and DDW in volume proportion of 1:1:5 . Prepare this mixture for immediate use. It is stable for at least 6-12 hours. Store in a polyethylene bottle out of direct sunlight.
- Reducing solution : Mix equal volume of metol-sulfite, oxalic acid reagent and sulfuric acid reagent. Adding the sulfuric acid last. It is stable for 4-6 h, but should be prepared immediately before use.
- Standard silicate stock solution : Weigh out 0.960 g of dried sodium silicofluoride ( $\text{Na}_2\text{SiF}_6$ ) and dissolve the salt by DDW. Then quantitatively transfer the solution to a 1000-ml volumetric flask. Mix and transfer the solution to a polyethylene bottle for storage. The solution is stable indefinitely.
- Standard silicate working solution : Dilute standard silicate stock solution 10, 20, 50, 100 and 200 times with DDW. These working standard solutions are stable indefinitely.

### Procedure

Pipette 17.5 ml of the molybdate working solution to a dry, clean polyethylene bottle. Pipette 125  $\mu\text{l}$  of the diluted, extracted sample into the bottle and immediately mix by swirling. Cap the bottles and allow them to react for exactly 20 min. Pipette 7.5 ml of the reducing solution into the bottle, cap tightly and mix thoroughly by swirling. Stand the solution 12 hours to complete the reduction of the silicomolybdate complex. Read the corrected absorbance of the solution in a 1 cm cell in a spectrophotometer peaked at 812 nm against reagent and turbidity blanks.

Corrected absorbance of solution is calculated as following :

$$A_{\text{corrected}} = A_{\text{sample}} - A_{\text{RB}} - A_{\text{TB}}$$

Whereas :  $A_{\text{corrected}}$  = corrected absorbance of sample



$A_{\text{sample}}$  = absorbance of sample

$A_{\text{RB}}$  = absorbance of reagent blank

$A_{\text{TB}}$  = absorbance of turbidity blank

Note :  $A_{\text{sample}}$ ,  $A_{\text{RB}}$ ,  $A_{\text{TB}}$  are subtracted by the absorbance of cell to cell blank before calculation.

### Calibration

A series of working standards prepared and reagent blank of extractant were measured their absorbance at wavelength of 812 nm. After correcting absorbance values by using the equation above, this absorbance were used to prepare a standard calibration curve for silicate in the same matrix as those of extractants. Linear regression analysis was applied to the calibration curve the relative coefficient ( $r^2$ ) of the relationship between concentration and absorbance of silicate standard were calculated. Acceptable relative coefficient of standard calibration curve showed not be less than 0.9995.

### Calculation of silicate concentration

Concentrations of silicate in extracted solutions were calculated from the linear equation of standard calibration curve by using corrected absorbance ( $A_{\text{corrected}}$ ) of the extracted solutions. After that, the calculated concentrations were multiplied by the degrees of dilution.

### 3.7 Sequential Extraction

Silicate species are extracted into five fractions by four selective extraction steps and a total residual digestion. The procedure allows silicate species associated with manganese bound oxides (Mn-Si), aluminum bound oxides (Al-Si), iron bound oxides (Fe-Si), Biogenic (B-Si) and residual digestion (Res-Si) to be estimated (see Figure 3.3).

All extracted solutions were analyzed for their silicate content by Mortlock and Froelich method in section 3.6

#### Apparatus

- A Spectrophotometer (MiltonRoy® Spectronic 401)
- A Micropipette (100-1000 µl Eppendorf®)
- 50 ml polyethylene centrifuge tubes with lids
- 30 ml polyethylene bottles with lids
- 2 quartz cuvettes
- A Shaker
- A Centrifuge (Centurion Scientific® 1040 series)
- Pasteur pipettes
- A Water bath

#### Reagents

- 0.3 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  +0.1M  $\text{HNO}_3$  : Dissolve 20.847 g of analytical-reagent-quality hydroxylamine hydrochloride  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 6.92 ml of 65%  $\text{HNO}_3$ . Make final volume 1000 ml with double distilled de-ionized water (DDW). Store the solution in a tightly capped polyethylene bottle.
- 0.6 M  $\text{NH}_4\text{F}$  : Dissolve 22.2 g of analytical reagent quality ammonium fluoride  $\text{NH}_4\text{F}$  in 1000 ml of double distilled de-ionized water (DDW). Store the solution in a polyethylene bottle.
- 0.2 M Na-citrate/0.35 M NaOAC (pH4.8) : Dissolve 58.82 g of Na-citrate and 28.7105 g of Na-acetate (NaOAC) in warm water. Adjust

pH to 4.8 with 0.1 M hydrochloric acid. Dilute the solution to final volume of 1000 ml. Store the solution in a polyethylene bottle.

- Na-dithionite : Used in a powder form.
- 2 M  $\text{Na}_2\text{CO}_3$  : Dissolve 211.98 g of Sodium carbonate in 1000 ml of double distilled de-ionized water (DDW). Store the solution in a polyethylene bottle.
- HF 47%
- Aqua Regia : Mix conc. $\text{HClO}_4$  65% and conc. $\text{HNO}_3$  65% in volume proportions of 4:1

#### Procedure

Weigh 0.5 g sediment sample into a 50 ml centrifuge tube with a cap and then sequentially extract at the room temperature as follows :

##### Step I Manganese bound Silicate

1. Exactly 10 ml of 0.3 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ +0.1M  $\text{HNO}_3$  solution was added to the tube, shake on a shaker for 15 min.
2. Then centrifuge at 3000 rpm for 20 min. Separate the supernatant by a pasteur pipette.
3. Dilute the supernatant 50 times, analyze manganese bound silicate by forming silicomolybdate complex according to Mortlock and Froelich method as described in section 3.6

##### Step II Aluminum bound Silicate

1. After removing the supernatant in step I, shake the residue with 25 ml of 0.6 M  $\text{NH}_4\text{F}$  solution for 1.25 h.

2. Centrifuge for 20 min at 3000 rpm and remove the supernatant.
3. Dilute the supernatant 50 times, analyze aluminum bound silicate by forming silicomolybdate complex according to Mortlock and Froelich method as described in section 3.6

#### Step III Iron bound Silicate

1. Add 0.5 g of Na dithionite to the residue from previous step and then 10 ml of 0.2 M Na-citrate/0.35 M NaOAC solution, pH of the solution in the tube after extracted in step II should be controlled at 4.8.
2. The tube was shaken with a vortex mixer and placed in a covered constant-temperature bath to 60 °C for 4 h.
3. Every hour the tube was removed and shaken vigorously to resuspend the solids and quickly returned to the water bath.
4. After a total of 4 h, the tube was immediately centrifuge for 20 min at 3000 rpm and removes the supernatant.
5. Dilute the supernatant 50 times, analyze iron bound silicate by forming silicomolybdate complex according to Mortlock and Froelich method as described in section 3.6.

#### Step IV Biogenic Silicate

1. Add 5 ml of 10% H<sub>2</sub>O<sub>2</sub> solution to the residue, and after about 30 min, add 5 ml of a 1 M HCl
2. Then 40 ml of 2 M Na<sub>2</sub>CO<sub>3</sub> solution was added. The tube was then capped, shaken with a vortex mixer.
3. Place the tube in a covered constant-temperature bath pre-heated to 85°C

4. After about 2 h and again at 4 h, the tube is removed and shaken vigorously to resuspend the solids and quickly returned to the water bath.
5. After a total of 5 h, the tube is removed and immediately centrifuged at 3000 rpm for 20 min.
6. Transfer the supernatant to a polyethylene bottle and analyze biogenic silicate by forming silicomolybdate complex according to Mortlock and Froelich method as described in section 3.6.

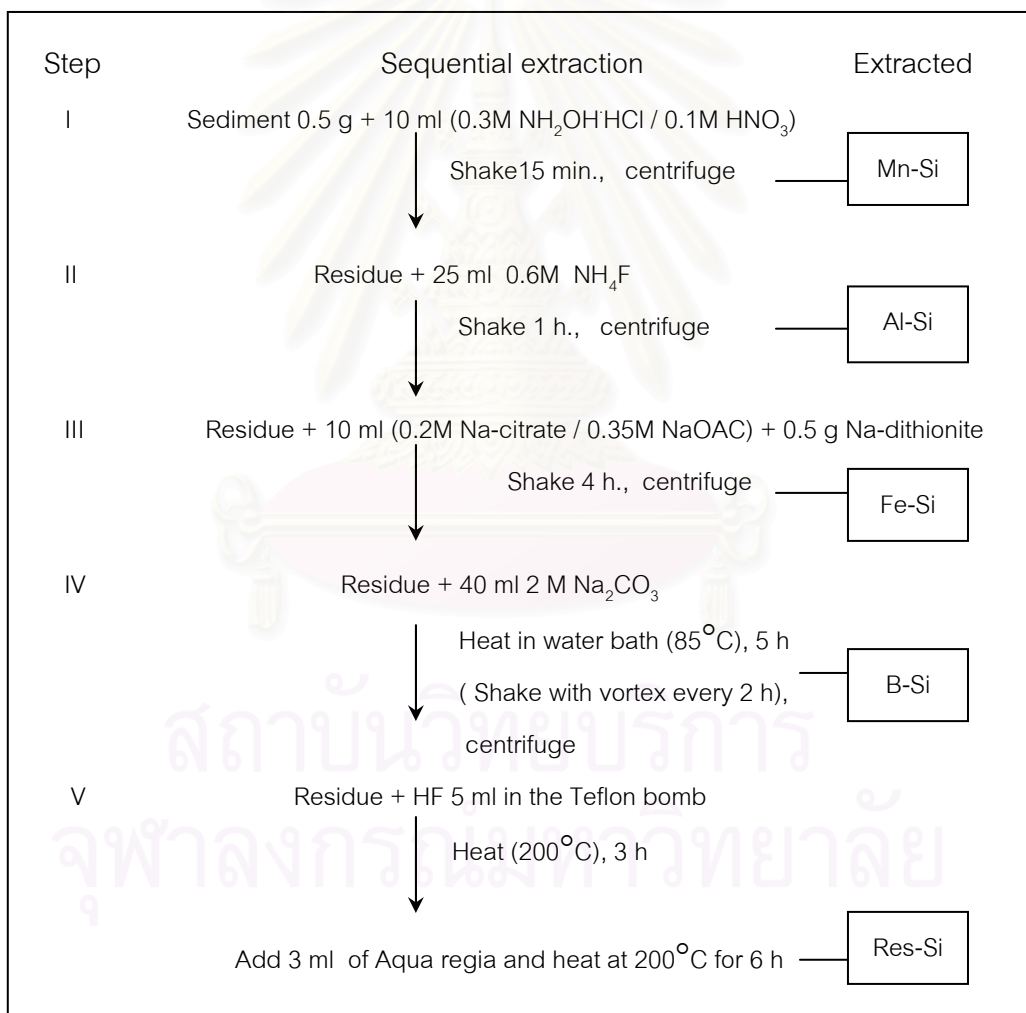


Figure 3.3 A Schematic diagram of the targeted, sequential extraction method for silicate partitioning in sediment.

### Step V Residual Silicate

1. Transfer the residue from step IV to a teflon bomb, rinse the tube well. Dry the residue in the teflon bomb before digestion by placing the bomb in an oven at 60°C
2. Add 5 ml of conc. HF. Heat at 200°C for 3 hr. Allow the solution to cool and then add 3 ml of aqua regia, continue heating at 200°C for 6 hr.
3. Transfer the clear supernatant to a 100 ml polyethylene volumetric flask and made up volume to the mark. Then dilute 100 times.
4. The supernatant from this step is analyzed for the residue silicate by forming silicomolybdate complex according to Mortlock and Froelich method as described in section 3.6

### 3.8 Total Silicate

Finding total silicate of the sediment sample can help confirming the results of the sequential extraction method. Sum of all silicate species that were extracted by sequent method are compared to total silicate from the acid digestion method and XRF method (see their details in Appendix C).

#### 3.8.1 Total Acid Digestion

Concentrated acids were used in digesting the sediment in a teflon bomb. Heat the bomb to accelerate the reaction. After digestion, only clear acid solution remained in the bomb. Measure the silicomolybdate complex by Mortlock and Froelich method (1989) as described in section 3.6

#### Apparatus

- A Teflon bomb

- A Fume hood
- A Balance
- An Oven

#### Reagents

- HF 47%
- Aqua Regia : Mix 65% conc.HClO<sub>4</sub> and 65% conc.HNO<sub>3</sub> in volume proportions of 4:1

#### Procedure

Transfer 0.5 g of sediment into a Teflon bomb. Under fume hood, add 5 ml of HF and place into an oven at 200°C for 3 h. Add 3 ml aqua regia and heat at 200°C for 6 h. Allow it to cool, and then make up volume to 100 ml with a polyethylene measuring flask. The digested solution was diluted before analyzing silicomolybdate complex according to Mortlock and Froelich method as outlined in section 3.6

#### **3.9 In-house reference materials**

In order to verify the efficiency of the extraction sequence, synthesizing of authigenic silicate to represent the different extraction pools was tried by applied from Loadong's method (1986; figure3.4). These synthesized silicates were extracted by using single phase batch extractions.

#### Apparatus

- A Shaker
- An Oven
- A Thermometer
- 1000 ml bottles with lids.

### Reagents

- Artificial seawater : Dissolve of 30 g sea salt (scientific grade) in deionized water and make volume to 1 L. Filter the solution through a no. 1 Whatman filter paper, and store in a glass bottle.
- 4 M NaOH solution : Dissolve 160 g of NaOH in deionized water and make volume to 1 L. Keep solution in a glass bottle.
- 0.1 M FeCl<sub>3</sub> solution : Dissolve 16.221 g of FeCl<sub>3</sub> in deionized water and make volume to 1 L. Keep solution in a glass bottle.
- 0.1 M MnCl<sub>3</sub> solution : Dissolve 19.791 g of MnCl<sub>3</sub> in deionized water and make volume to 1 L. Keep solution in a glass bottle.
- 0.1 M AlCl<sub>3</sub> solution : Dissolve 24.143 g of AlCl<sub>3</sub> in deionized water and make volume to 1 L. Keep solution in a glass bottle.
- 0.05 M Na<sub>2</sub> SiO<sub>3</sub> · 5H<sub>2</sub>O solution : Dissolve 10.607 g of Na<sub>2</sub> SiO<sub>3</sub> · 5H<sub>2</sub>O in deionized water and make volume to 1 L. Keep solution in a glass bottle..

### Procedure

Transfer 500 ml of the artificial seawater into a series of 1000 ml bottles, divided into four groups. Each bottle in each group was added with 100 ml of 0.1 M FeCl<sub>3</sub>, 0.1 M MnCl<sub>3</sub>, 0.1 M AlCl<sub>3</sub> and Mix respectively. Then adjust pH to about 8 – 9 by adding 10 ml of 4.0 M NaOH solution while stirring. The bottle was then diluted to 900 ml with DDW. Leave solutions containing colloidal precipitates, overnight. After that, add 100 ml of Na<sub>2</sub>SiO<sub>3</sub> in to each bottle. So final volumes were 1000 ml with a chlorinity of 11–12 ‰. Shake the solution for 0.5 hour and then leave in an incubator at 25°C overnight. The precipitates were aged at room temperature for 15 days with interval shaking and then aged under 60-70 °C for another 3-4 days, in order to accelerate the crystallization. The products were filtered with a suction pumps and washed with DDW



to remove colloidal particles and  $\text{CaCO}_3$  formed. Dry the products and /or reference materials in an oven at temperature not over than  $60^\circ\text{C}$ .

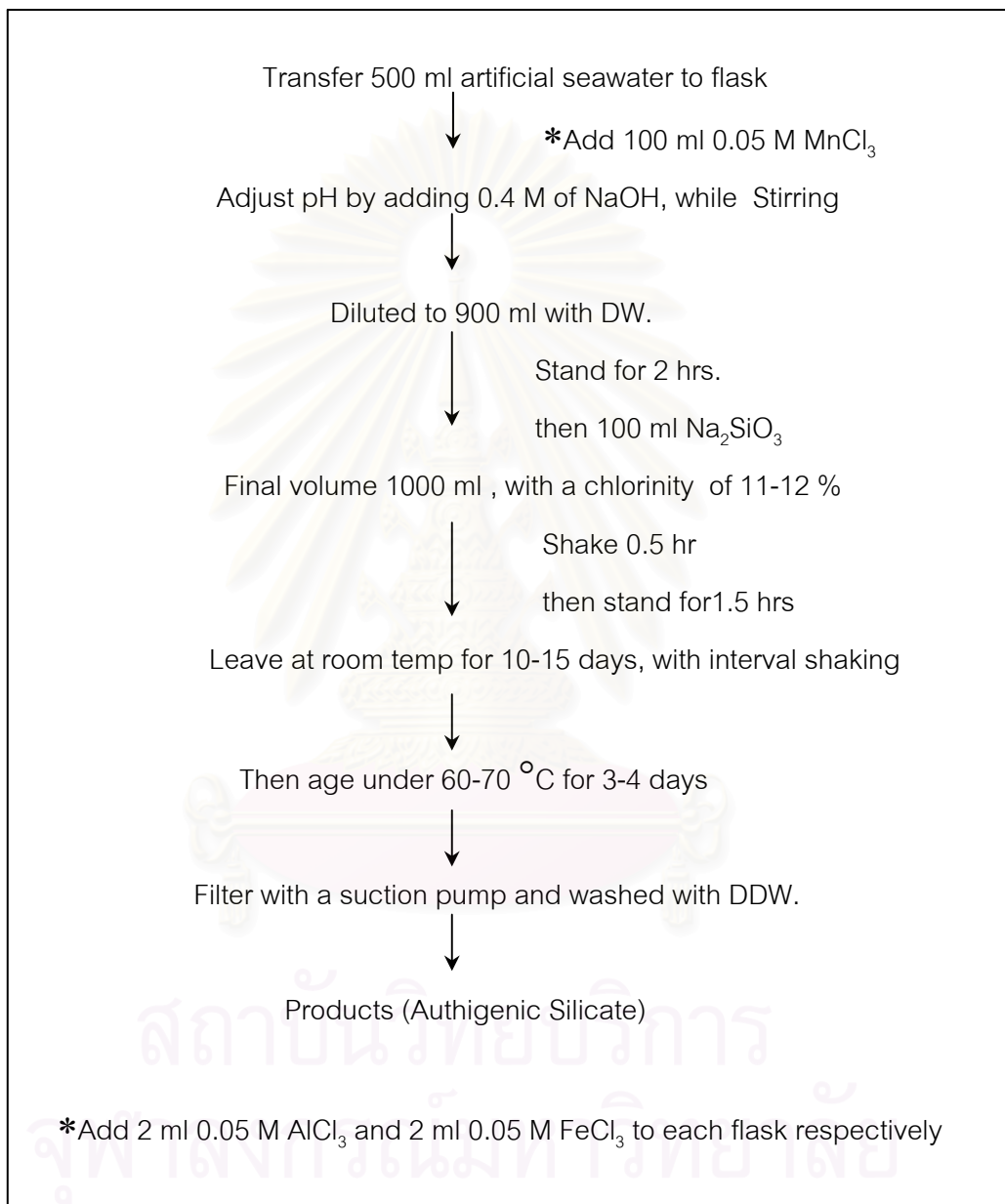


Figure 3.4 A Flow diagram for synthesis of in-house reference silicate materials.

## CHAPTER IV

### RESULTS

#### 4.1 Characteristics of the sediment samples

All sediment samples are dry-sieved through a 114  $\mu\text{m}$  nylon sieve to avoid iron and aluminum contamination from the sieve itself. Actually, a 125  $\mu\text{m}$  sieve is supposed to be used but nylon one was not available. Sediment size  $<125 \mu\text{m}$  comprises of very fine sand, silt and clay, which are very active to sorption process (Stone and English, 1993). Every values are adjusted with size correction before reporting. Size correction is the normalization of sediment values in each size by eliminate organic, iron oxide and carbonate that cement or coat the sediment (see in Appendix B). These may cause an error on size determination. The results of the particle size distribution of estuarine sediment samples and size correction are present in table 4.1

Table 4.1 Characteristics of the estuarine sediment

Sediment	Particle size distribution			Texture	Size correction	
	Sand	Silt	Clay		< 114	> 114
	(%)	(%)	(%)		$\mu\text{m}(\%)$	$\mu\text{m}(\%)$
Mae Klong (MK)	44.2	36.0	19.8	Silty Clayey Sand	65.5	34.5
Bang Pakong (BP)	0.2	44.6	55.2	Silty Clay	87.5	12.5
Chao Phraya (CP)	30.5	45.4	24.1	Silty Clayey Sand	74.5	25.5

#### 4.2 pH effect

- pH of the reagents for forming silicomolybdate complex were measured before and after the addition of diluted extracted solution in order to confirm that they are in the range of 0.8-2.5 (Table 4.2)

Table 4.2 pH of molybdate before and after adding the extracted solution and reducing reagents for color development.

Extracted Solution	Molybdate Solution		Reducing Solution
	Before	After	
Mn-Si	1.1	1.1	0.9
Al-Si	1.1	1.1	0.9
Fe-Si	1.1	1.1	0.9
B-Si	1.1	1.1	0.9
Res-Si	1.1	1.1	0.9

- pH of the extractants were checked before and after mixing with the sediments as shown in table 4.3, to ensure that the extractant is most effective in the extracting the targeted and optimized during extraction.

Table 4.3 pH of the extractants before and after mixing with the sediments

Extractant type	pH	
	initial	after shaking with sediment
For Mn-Si	2.5	2.5
For Al-Si	7.0	7.0
For Fe-Si	4.0	4.0
For B-Si	12.5	12.5
For Res-Si	0.8	0.8

#### 4.3 Time for color development

Figure 4.1 shows out that silicomolybdate complex formation reaches the optimum time when the absorbance does not increase with time. The absorbance drops again when the time is over the optimum range. So measurement of the absorbance beyond the optimum time can cause error in silicate analysis.

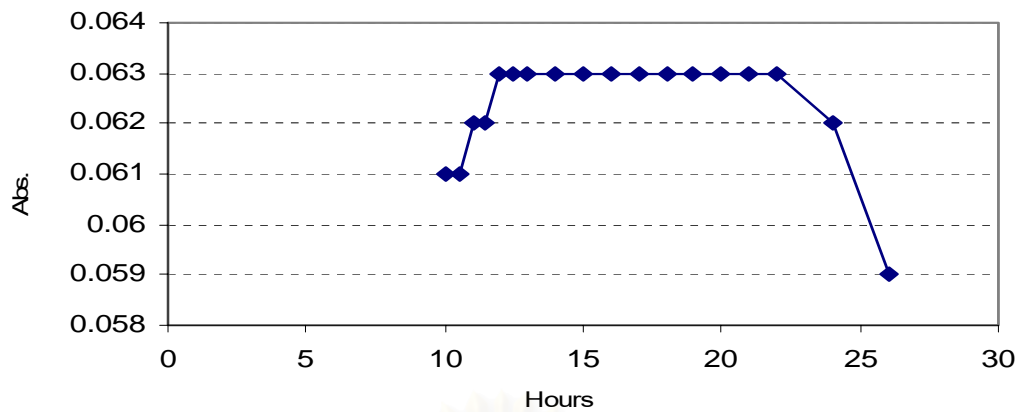


Figure 4.1 The optimum time for color development.

#### 4.4 Optimum extraction concentration

- For manganese bound silicates (Figure 4.2 A), it is observed from that the absorbance of silicate increase until the concentration of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) is at 0.3 M. After that the absorbance is stable even though the concentration is higher. Therefore, 0.3 M of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  should be able to reduce all of manganese bound silicates in sediment and chosen to be the optimum concentration for extraction of manganese bound silicates.

- The result for aluminum bound silicates is quite different as presented in figure 4.2 B. The absorbance increases stepwise, first at 0.6 M and then at 1.5 M. The second increase of absorbance seems to result from dissolution of other fraction because the whole aluminum bound silicates are extracted at 0.6 M and the absorbance is stable in higher concentration (0.8, 1 and 1.2 M). Hence at 1.5 M the increase in absorbance should not involve aluminum bound silicates and the optimum concentration is at 0.6 M of  $\text{NH}_4\text{F}$ .

- The result of iron bound silicates is in contrast to both mentioned above. The absorbance is stable at the beginning. After that it decreases and then stable. These might be interference from acetate ( $\text{COOH}^-$ ) in chelating formation with citrate (Kostha and Luther, 1994). Although lots of Na-dithionite reduce ferric oxide to form chelation. Thus 0.2 M Na-citrate/ 0.35 M Na-acetate is like to be the best concentration for iron bound silicates

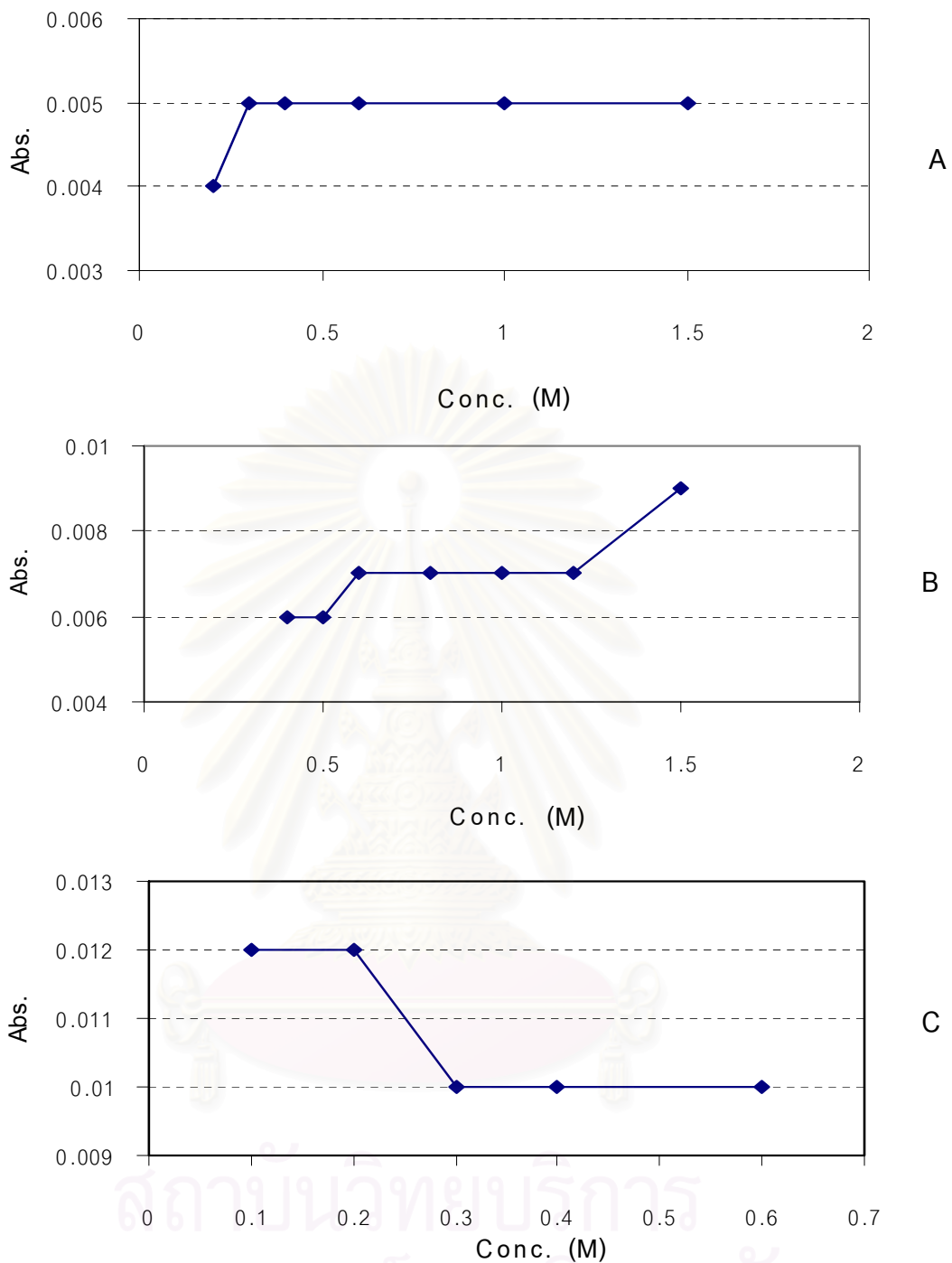


Figure 4.2 The optimum extractant concentration

A : Mn-Si.

B : Al-Si.

C : Fe-Si.

#### 4.5 Optimum extraction time

The optimum extraction time is the shortest time possible to extract all interested species 10 min, 1 hour and 15 min, and 3 hours and 45 min are the optimum time for Mn-Si, Al-Si and Fe-Si respectively. It should be noted that this experiments have to be carried out after the previous experiments in 4.4

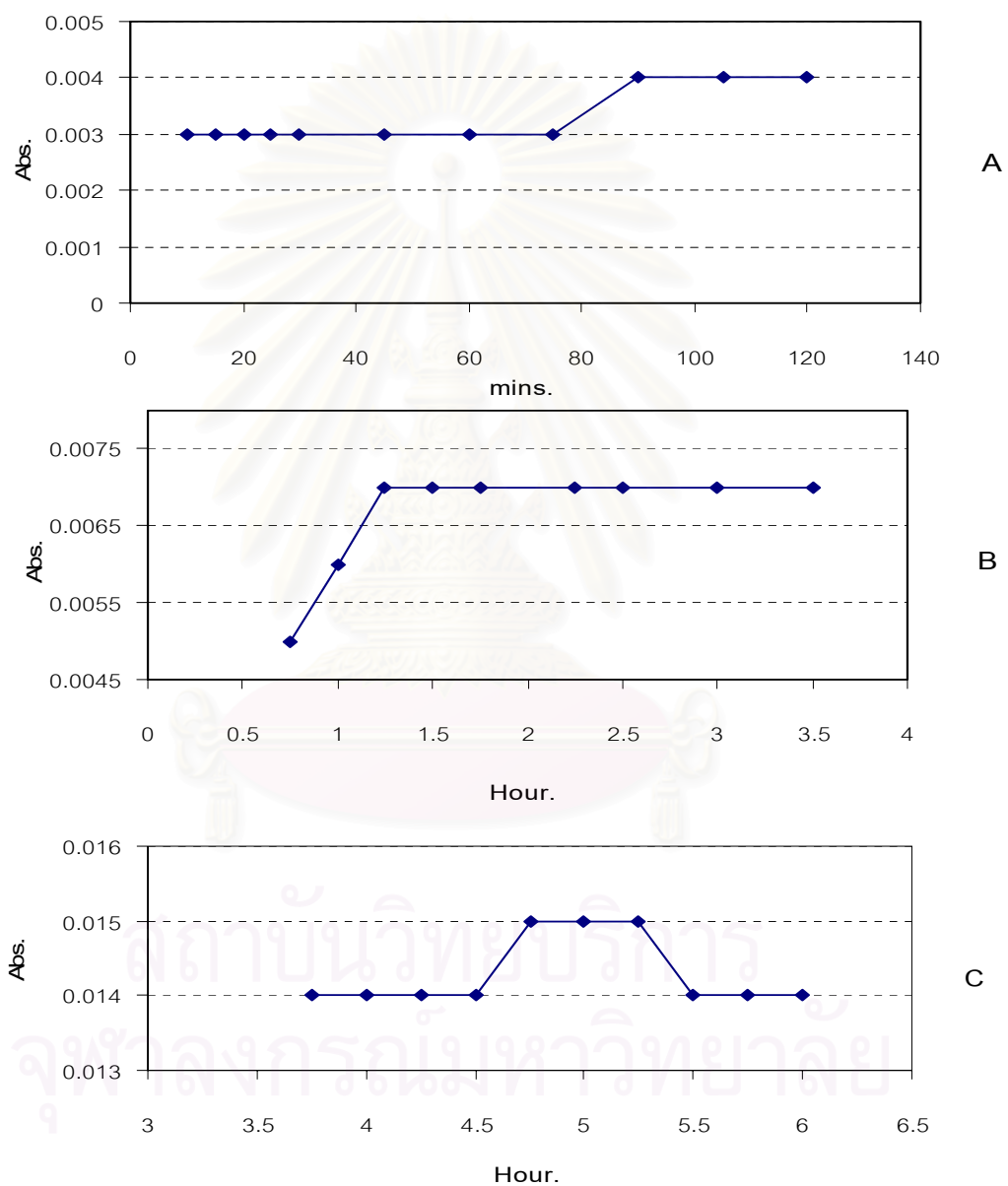


Figure 4.3 The optimum time for extraction

A : Mn-Si

B : Al-Si

C : Fe-Si

## 4.6 Sequential Extraction

The analytical results of sequential extraction method are presented separately for each sample.

### 4.6.1 Mae Klong sediments

Res-Si is relatively higher than B-Si, Fe-Si, Al-Si and Mn-Si, respectively in all subsamples except in sample size  $< 114 \mu\text{m}$  where the values of Al-Si is higher than Fe-Si.

Table 4.4 Silicate speciation in Mae Klong sediments. (n=10)

Speciation	$< 114 \mu\text{m}$	$> 114 \mu\text{m}$	Non-sieve
	mg Si/g (dried sediment)	mg Si/ g (dried sediment)	mg Si/ g (dried sediment)
Mn-Si	$0.332 \pm 0.000$	$0.141 \pm 0.000$	$0.469 \pm 0.000$
Al-Si	$2.289 \pm 0.001$	$1.077 \pm 0.0005$	$3.371 \pm 0.001$
Fe-Si	$2.278 \pm 0.001$	$1.148 \pm 0.000$	$3.428 \pm 0.0005$
B-Si	$3.662 \pm 0.000$	$1.587 \pm 0.0005$	$5.244 \pm 0.0005$
Res-Si	$215.800 \pm 0.000$	$89.667 \pm 0.000$	$305.454 \pm 0.001$

### 4.6.2 Bang Pakong sediments

The silicate speciation in three subsamples of Bang Pakong sediment (Table 4.5) shows that Res-Si is relatively higher than B-Si, Al-Si, Fe-Si and Mn-Si, respectively.

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Table 4.5 Silicate speciation in Bang Pakong sediments.

Speciation	< 114 $\mu\text{m}$ mg Si/ g (dried sediment)	> 114 $\mu\text{m}$ mg Si/ g (dried sediment)	Non-sieve mg Si/ g (dried sediment)
Mn-Si	0.617 $\pm$ 0.000	0.076 $\pm$ 0.0005	0.692 $\pm$ 0.001
Al-Si	4.520 $\pm$ 0.000	0.522 $\pm$ 0.0005	5.041 $\pm$ 0.000
Fe-Si	3.064 $\pm$ 0.000	0.428 $\pm$ 0.000	3.489 $\pm$ 0.000
B-Si	5.499 $\pm$ 0.001	0.686 $\pm$ 0.000	6.185 $\pm$ 0.000
Res-Si	283.950 $\pm$ 0.000	35.613 $\pm$ 0.000	319.564 $\pm$ 0.000

#### 4.6.3 Chao Phraya sediments

Res-Si is relatively higher than B-Si, Fe-Si, Al-Si and Mn-Si, respectively in all subsamples except in sample size < 114  $\mu\text{m}$  where the values of Al-Si is higher than Fe-Si.

Table 4.6 Silicate speciation in Chao Phraya sediments.

Speciation	< 114 $\mu\text{m}$ mg Si/ g (dried sediment)	> 114 $\mu\text{m}$ mg Si/ g (dried sediment)	Non-sieve mg Si/ g (dried sediment)
Mn-Si	0.562 $\pm$ 0.0005	0.167 $\pm$ 0.000	0.729 $\pm$ 0.0005
Al-Si	2.995 $\pm$ 0.000	0.899 $\pm$ 0.001	3.897 $\pm$ 0.000
Fe-Si	2.969 $\pm$ 0.0015	0.931 $\pm$ 0.001	3.898 $\pm$ 0.000
B-Si	4.018 $\pm$ 0.000	0.984 $\pm$ 0.000	4.997 $\pm$ 0.0015
Res-Si	245.452 $\pm$ 0.000	78.080 $\pm$ 0.000	323.524 $\pm$ 0.001

#### 4.7 Total Silicate in sediments

To confirm the silicate speciations, which were extracted by sequential extraction method, total silicates were investigated. Two total silicate procedures XRF and acid digestion were tried in order to specify the best method. The results are shown in tables 4.7, 4.8 and 4.9



Table 4.7 Total silicate in Mae Klong sediment.

Method	< 114 $\mu\text{m}$	> 114 $\mu\text{m}$	Non-sieve
	mg Si/ g (dried sediment)	mg Si/ g (dried sediment)	mg Si/ g (dried sediment)
XRF	222.290	111.120	335.640
Acid digestion (n=10)	$224.706 \pm 0.001$	$93.590 \pm 0.001$	$318.308 \pm 0.001$

Table 4.8 Total silicate in Bang Pakong sediment.

Method	< 114 $\mu\text{m}$	> 114 $\mu\text{m}$	Non-sieve
	mg Si/ g (dried sediment)	mg Si/ g (dried sediment)	mg Si/ g (dried sediment)
XRF	254.830	35.530	297.780
Acid digestion	$297.780 \pm 0.002$	$37.313 \pm 0.002$	$334.646 \pm 0.002$

Table 4.9 Total silicate in Chao Phraya sediment.

Method	< 114 $\mu\text{m}$	> 114 $\mu\text{m}$	Non-sieve
	mg Si/ g (dried sediment)	mg Si/ g (dried sediment)	mg Si/ g (dried sediment)
XRF	216.970	71.400	281.880
Acid digestion	$255.950 \pm 0.002$	$81.042 \pm 0.002$	$337.121 \pm 0.002$

#### 4.8 Mineralogical analysis

This experiment was set up to confirm the existence of silicate species in sediment and in in-house reference materials. Montmorillonite, Chamosite, Kaolinite, Vermiculite and Phillipsite are found in the samples as shown in Figs 4.4, 4.5, 4.6 and 4.7. More details about XRD's results are presented in Appendix E.

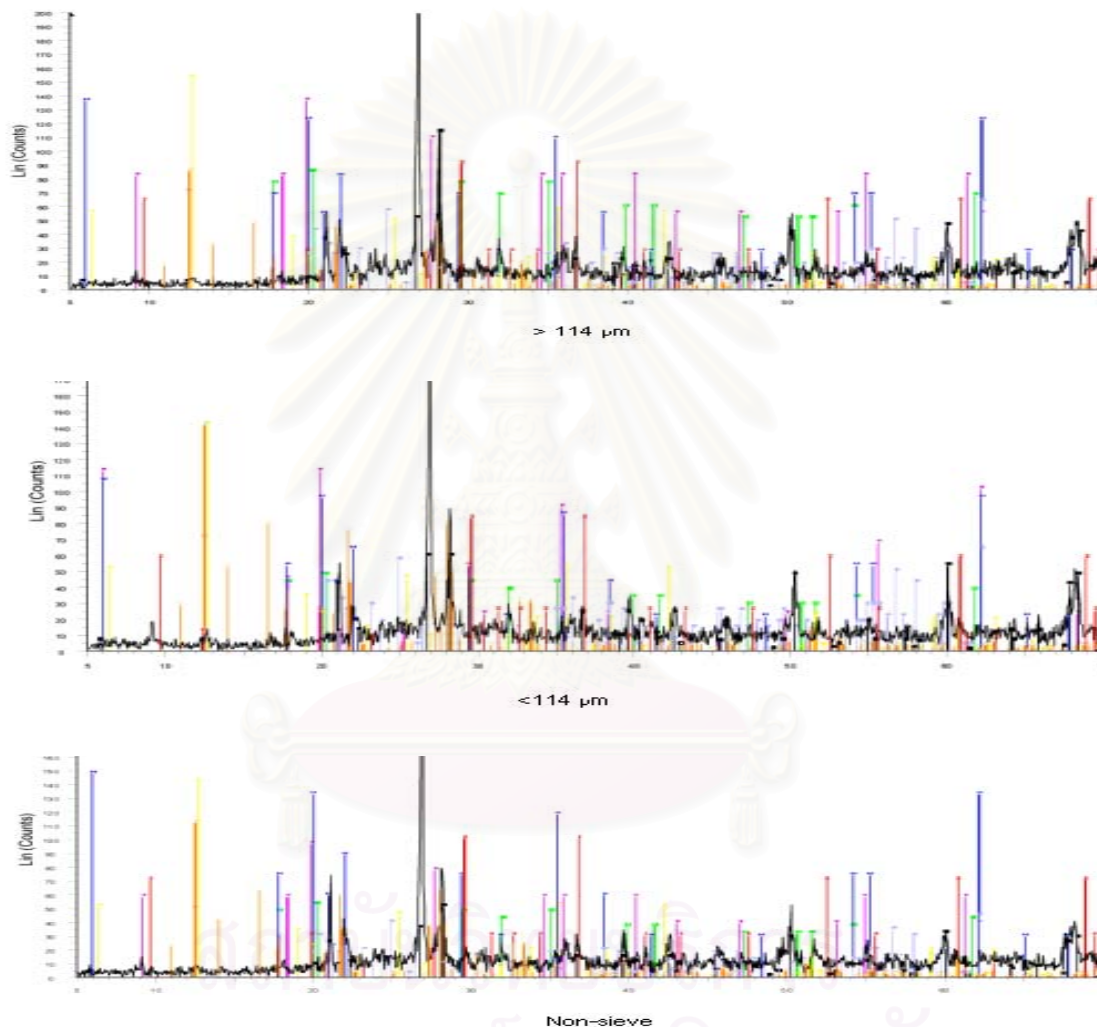


Figure 4.4 X-ray diffractogram in Mae Klong sediments

- 07-0304 Montmorillonite, heated  $-\text{Na-Mg-Al-Si}_{40}\text{11}$
- 02-0239 Montmorillonite (clay)  $-\text{CaMg}_2\text{AlSi}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$
- 02-0014 Montmorillonite (clay)  $-\text{NaMgAlSi}_2(\text{OH})\text{H}_2\text{O}$
- 85-1356 Chamosite  $-(\text{Mg}_{1.5}\text{Fe}_{7.9}\text{Al}_{2.6})(\text{Si}_{6.2}\text{Al}_{1.8}\text{O}_{20})(\text{OH}_{16})$
- 14-0164 Kaolinite  $-\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
- 02-0628 Vermiculite  $(\text{Mg}, \text{Fe}^{2+}, \text{Al})_3(\text{Si}, \text{Al})_4(\text{OH})_2 \cdot 4\text{H}_2\text{O} / 22\text{MgO} \cdot 5\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \cdot 22\text{SiO}_2 \cdot 40$
- 73-1419 Phillipsite  $-\text{Na}_4\text{KAl}_5\text{Si}_{11}\text{O}_{32}(\text{H}_2\text{O})_{10}$
- 83-0542 Quartz  $-\text{SiO}_2$
- 83-0444 Quartz  $-\text{SiO}_2$

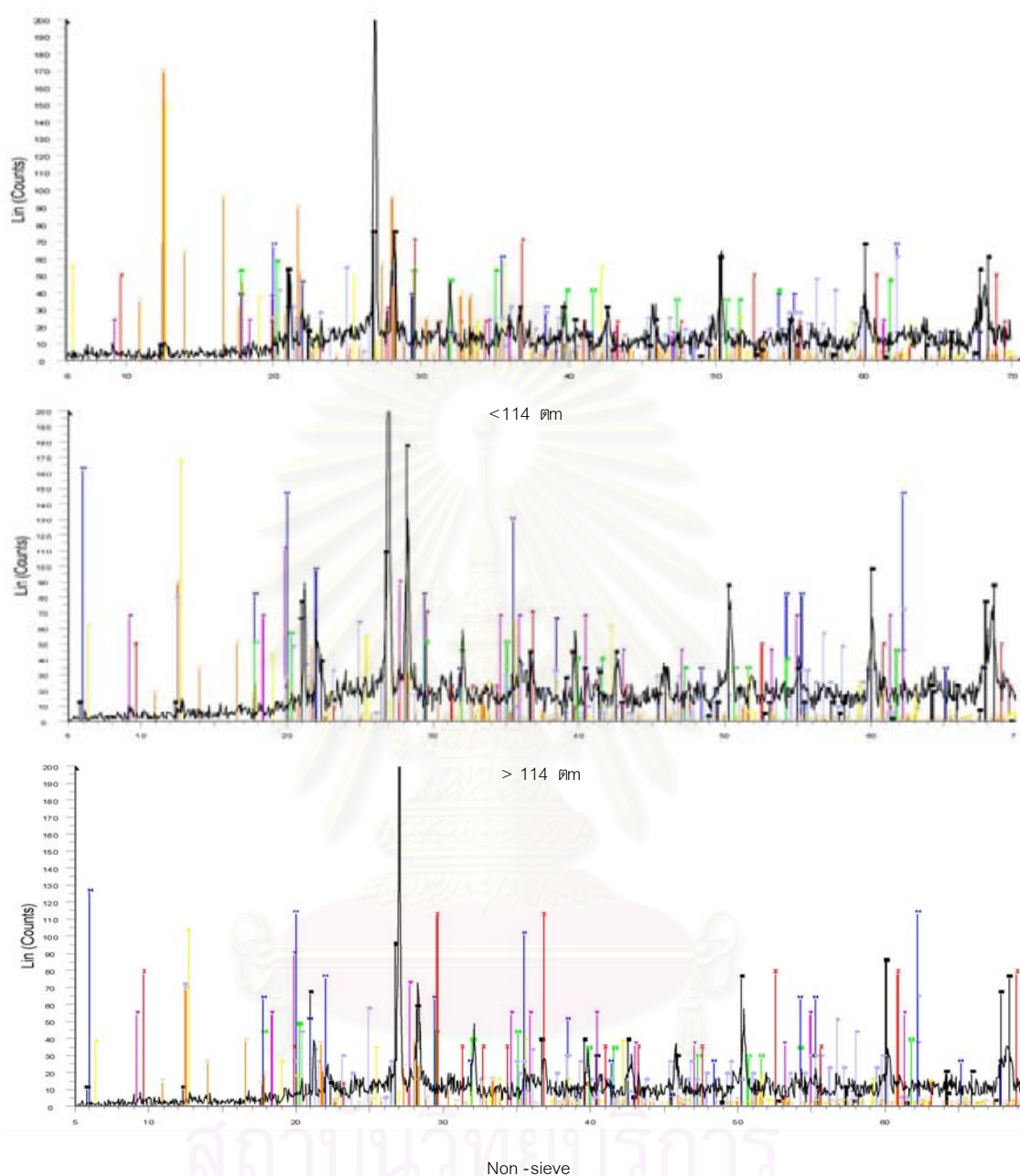


Figure 4.5 X-ray diffractogram in Bang Pakong sediments.

- ▼ 07-0304 Montmorillonite, heated  $-\text{Na-Mg-Al-Si}_{40}_{11}$
- 02-0239 Montmorillonite (clay)  $-\text{CaMg}_2\text{AlSi}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$
- 02-0014 Montmorillonite (clay)  $-\text{NaMgAlSi}_2(\text{OH})\text{H}_2\text{O}$
- 85-1356 Chamosite  $-(\text{Mg}_{1.5}\text{Fe}_{7.9}\text{Al}_{2.6})(\text{Si}_{6.2}\text{Al}_{1.8}\text{O}_{20})(\text{OH}_{16})$
- 14-0164 Kaolinite  $-\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
- 02-0628 Vermiculite  $(\text{Mg}, \text{Fe}+2, \text{Al})_3(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O} / 22\text{MgO} \cdot 5\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \cdot 22\text{SiO}_2 \cdot 4\text{H}_2\text{O}$
- 73-1419 Phillipsite  $-\text{Na}_4\text{KAl}_5\text{Si}_{11}\text{O}_{32}(\text{H}_2\text{O})_{10}$
- 83-0542 Quartz  $-\text{SiO}_2$
- 83-0444 Quartz  $-\text{SiO}_2$

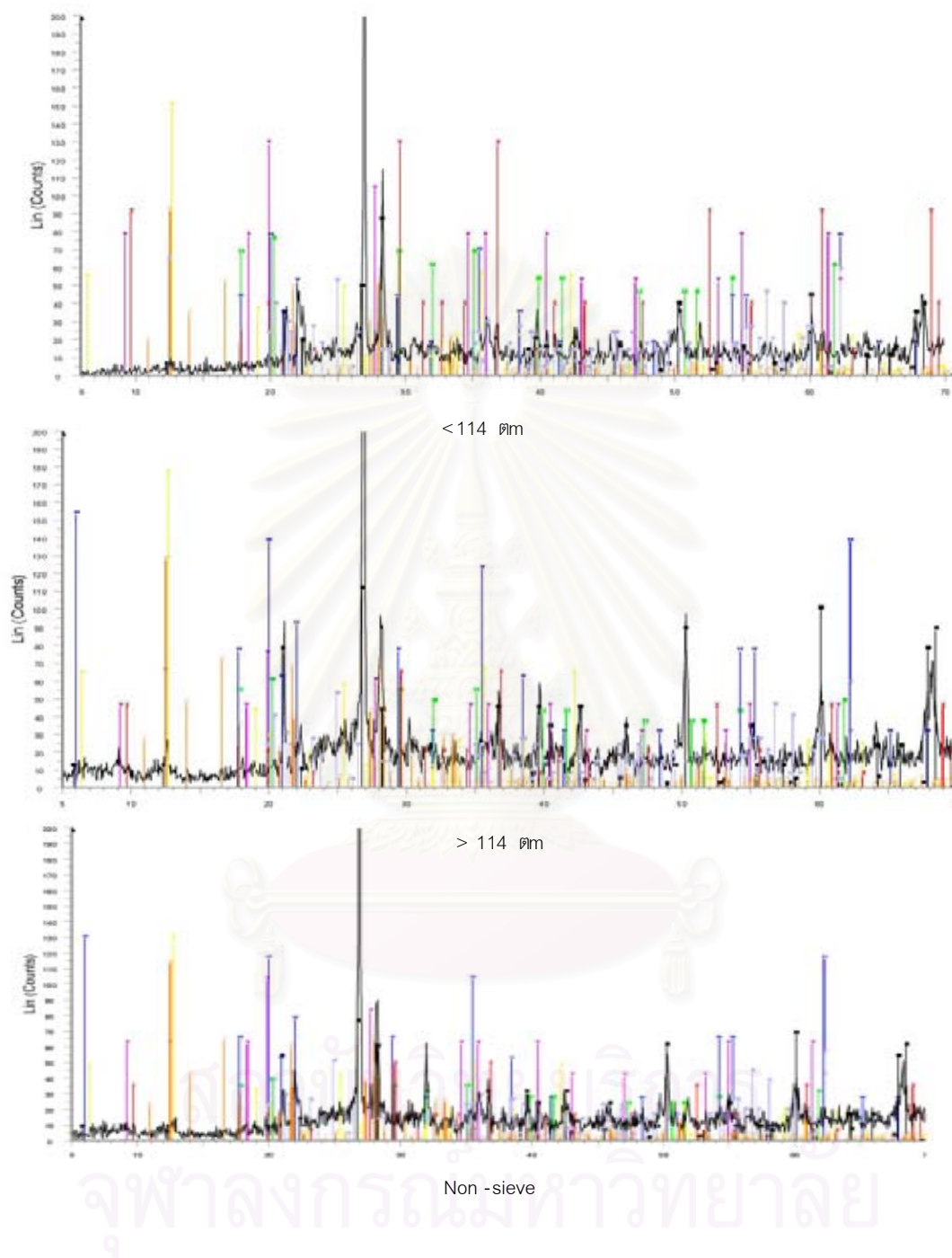


Figure 4.6 X-ray diffractogram in Chao Phraya sediments

- |  |   |
|--|---|
|  | 07-0304 Montmorillonite, heated $\text{-Na-Mg-Al-Si}_4\text{O}_{11}$  |
|  | 02-0239 Montmorillonite (clay) $\text{-CaMg}_2\text{AlSi}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$  |
|  | 02-0014 Montmorillonite (clay) $\text{-NaMgAlSi}_2(\text{OH})\text{H}_2\text{O}$  |
|  | 85-1356 Chamosite $\text{-(Mg}_{1.5}\text{Fe}_{7.9}\text{Al}_{2.6})(\text{Si}_{6.2}\text{Al}_{1.8}\text{O}_{20})(\text{OH}_{16})$   |
|  | 14-0164 Kaolinite $\text{-Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  |
|  | 02-0628 Vermiculite $(\text{Mg, Fe}+2, \text{Al})_3(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}/22\text{MgO} \cdot 5\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \cdot 22\text{SiO}_2 \cdot 40$ |
|  | 73-1419 Phillipsite $\text{-Na}_4\text{KAl}_5\text{Si}_{11}\text{O}_{32}(\text{H}_2\text{O})_{10}$  |
|  | 83-0542 Quartz $\text{-SiO}_2$  |
|  | 83-0444 Quartz $\text{-SiO}_2$  |

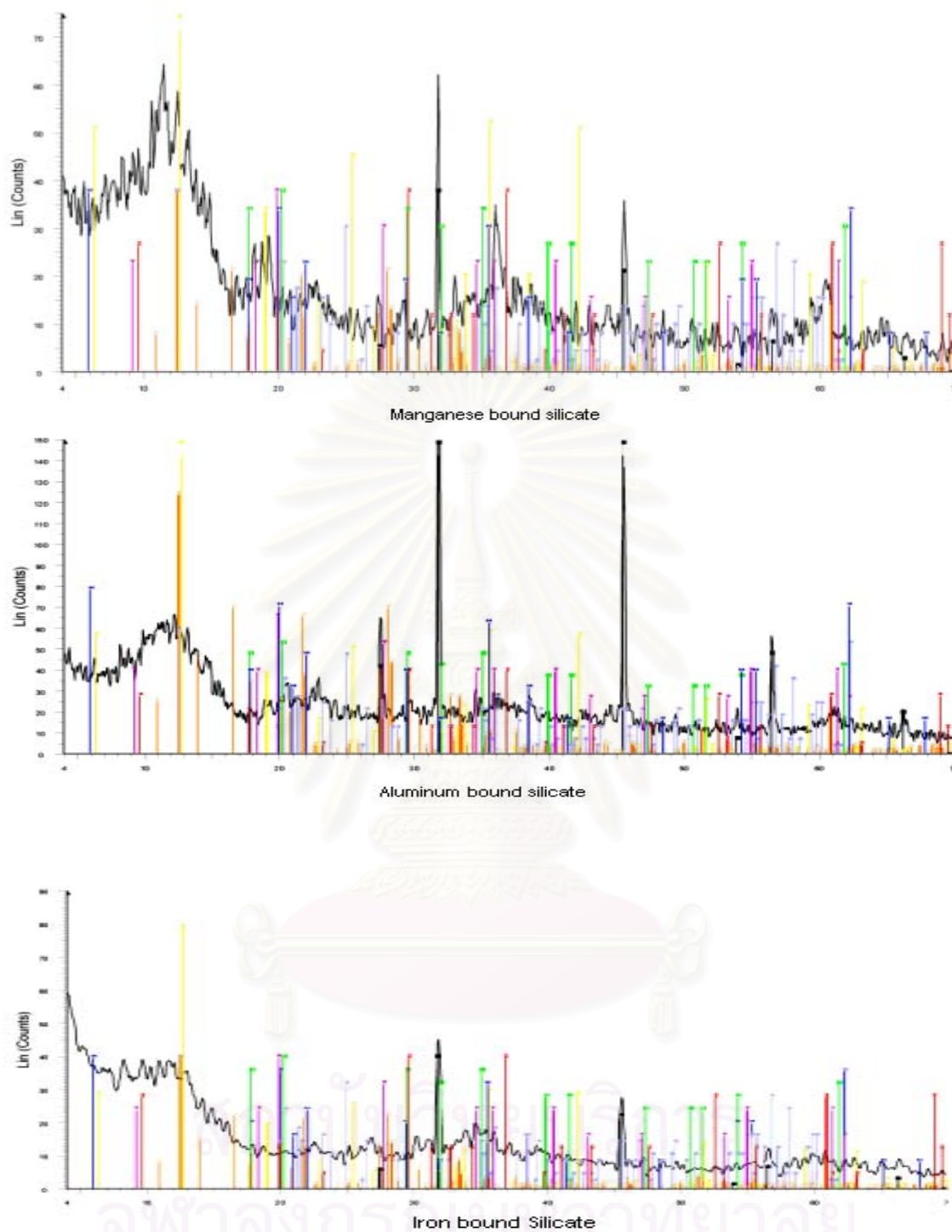


Figure 4.7 X-ray diffractogram in in-house reference materials

- 07-0304 Montmorillonite, heated  $-\text{Na-Mg-Al-Si}40_{11}$
- 02-0239 Montmorillonite (clay)  $-\text{CaMg}_2\text{AlSi}(\text{OH})_2 \cdot \text{H}_2\text{O}$
- 02-0014 Montmorillonite (clay)  $-\text{NaMgAlSi}_2(\text{OH})\text{H}_2\text{O}$
- 85-1356 Chamorite  $-(\text{Mg}_{4.3}\text{Fe}_{7.3}\text{Al}_{2.0})(\text{Si}_{6.2}\text{Al}_{4.8}\text{O}_{28})(\text{OH}_{16})$
- 14-0164 Kaolinite  $-\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
- 02-0628 Vermiculite  $(\text{Mg}, \text{Fe}+2, \text{Al})3(\text{Si}, \text{Al})4010(\text{OH})2 \cdot 4\text{H}_2\text{O}/22\text{MgO} \cdot 5\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \cdot 22\text{SiO}_2 \cdot 40$
- 73-1419 Philliprite  $-\text{Na}_3\text{KAl}_3\text{Si}_{11}\text{O}_{52}(\text{H}_2\text{O})_{18}$
- 05-0628 Halite, *syn*  $-\text{NaCl}$

## CHAPTER V

### DISCUSSION AND RECOMMENDATIONS

#### 5.1 Accuracy of the sequential extraction method

The accuracy of the sequential method (SQE) can possibly be determined by comparing sum of all silicate speciations with total silicate from XRF and acid digestion. The two total silicate methods were originally chosen because XRF, generally applies series of certified reference materials to calibrate its accuracy. While acid digestion, owing to its nature can solubilize all sediment into a solution. Final measurement of silicate are done by forming silicomolybdate complex. This process is similar to SQE.

Table 5.1 Comparison between sum of all silicate species with total silicate from XRF and acid digestion. (mg Si/g dried sediment.)

Samples	SQE (n=10)	Acid digestion (n=10)	XRF
Mae Klong (< 114 $\mu\text{m}$ )	224.36 $\pm$ 0.002	224.71 $\pm$ 0.001	222.29
Mae Klong (> 114 $\mu\text{m}$ )	93.62 $\pm$ 0.001	93.59 $\pm$ 0.001	111.12
Mae Klong (non-sieve)	317.97 $\pm$ 0.003	318.31 $\pm$ 0.001	335.64
Bang Pakong (< 114 $\mu\text{m}$ )	297.65 $\pm$ 0.001	297.58 $\pm$ 0.002	254.83
Bang Pakong (> 114 $\mu\text{m}$ )	37.33 $\pm$ 0.001	37.313 $\pm$ 0.002	35.53
Bang Pakong (non-sieve)	334.97 $\pm$ 0.001	334.65 $\pm$ 0.002	297.78
Chao Phraya (< 114 $\mu\text{m}$ )	256.00 $\pm$ 0.002	255.95 $\pm$ 0.002	216.97
Chao Phraya (> 114 $\mu\text{m}$ )	81.06 $\pm$ 0.002	81.04 $\pm$ 0.002	71.40
Chao Phraya (non-sieve)	337.05 $\pm$ 0.003	337.12 $\pm$ 0.002	281.88

The sums of silicate species by SQE are relatively closer to total silicate from acid digestion than those from XRF. This may cause by the uncertainty of the analytical XRF results which depend on the combination of errors introduced mainly by the sample preparation, the different measurement of silicate, the measurement of both peak and background intensities, the slope “m” of the calibration line and the corrections of matrix effects (Rousseau, 2001). On the other hand, total silicates results from acid digestion were repeated 10 times whereas total silicates determined by XRF have no repeatability value. Accordingly, total silicate calculated from acid digestion was chosen as reference in comparing with the sums of silicate species by SQE in order to find the accuracy of SQE. This way SQE does provide accurate silicate extraction results (Table 5.2).

Table 5.2 Accuracy of SQE reported in % difference from total silicate from acid digestion.

Sample	Sum of silicate speciation by SQE (mg Si/g sed.)	% Difference from Acid digestion
MK (< 114 $\mu\text{m}$ )	224.36	0.15
MK (> 114 $\mu\text{m}$ )	93.62	0.03
MK (non-sieve)	317.97	0.11
BP (< 114 $\mu\text{m}$ )	297.65	0.02
BP (> 114 $\mu\text{m}$ )	37.33	0.03
BP (non-sieve)	334.97	0.10
CP (< 114 $\mu\text{m}$ )	256.00	0.02
CP (> 114 $\mu\text{m}$ )	81.06	0.02
CP (non-sieve)	337.05	0.02

## 5.2 Verification of silicate speciation in sediment

The efficiency of the extraction sequence was verified by using in-house reference materials. The in-house reference materials must be first tested by XRD. The results show that these materials cannot be examined by XRD because of broadband peaks. Which might arise from amorphous form or crypto / microcrystalline forms of these synthesized materials. Therefore, an efficiency assessment of the sequential extraction method by in-house reference materials was not possible. However, after extracted in-house reference materials with conc. acid they can determine the amount of silicate and metals (AAS method) in sample (see in table 5.3). This means that we can synthesize the authigenic silicate with proposed conditions (in chapter III); in other words, it shows high potential to form authigenic silicate in natural estuarine environment.

Table 5.3 The amount of silicate and metals in reference materials sample (Metal = Mn, Al, Fe respectively)

In-house reference	Acid digestion (mg Si/g sed.)	AAS (mg Metal/g sed.)
Mn-Si	252.65	543.85
Al-Si	255.35	286.01
Fe-Si	253.46	530.38

## 5.3 Silicate Speciation

Res-Si is the dominant form of silicate speciation in the estuarine sediment. Since silicate is the major component of the continental rocks, which is the important source of silicate in aquatic ecosystem. Due to less dissolution of biogenic silicate when compared with three other speciations. It was found biogenic silicate is the next dominant form. For iron bound silicate, aluminum bound silicate and manganese bound silicate are found in the same magnitude. This might be result from the formation of



these forms, which are mostly adsorbed to the particles. However, manganese bound silicate is an easy reducible form thus it is the lowest amount in the estuarine sediment.

## 5.4 Conclusions and recommendations

### 5.4.1 Conclusions

- The silicate speciation in Mae Klong sediment indicates that residual silicate is relatively higher than biogenic silicate, iron bound silicate, aluminum bound silicate and manganese bound silicate respectively. In sediment size  $< 114 \mu\text{m}$ ; however, aluminum bound silicate is higher than iron bound silicate.

- In Bang Pakong, it is found that, residual silicate is relatively higher than biogenic silicate, follows by iron bound silicate, aluminum bound silicate and manganese bound silicate respectively.

- In Chao Phraya, it is found that, residual silicate is relatively higher than biogenic silicate, follows by iron bound silicate, aluminum bound silicate and manganese bound silicate respectively. In sediment size  $< 114 \mu\text{m}$ ; however, aluminum bound silicate is higher than iron bound silicate.

- From XRD study, it found Montmorillonite, Chamosite, Kaolinite, Vermiculite and Phillipsite. These minerals can be categorized into neoformation minerals or neocrystallize minerals group that prove the existence of silicate speciation in sediment.

- The accuracy of sequential extraction is done by compared sum of all silicate speciation with total silicate from acid digestion and XRF. The results show that the sum of all silicate speciation is very close to acid digestion whereas significantly different from XRF. Anyhow the difference is less than 20%.

### 5.5 Recommendations

Improvement of the synthesis procedure can be achieved by checking all factors that affect crystal formation such as pH, temperature and synthesis time etc. The improved materials can be used to assess the efficiency of sequential extraction in each speciation.

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APPENDICES

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## APPENDIX A

### Particle size distribution analysis

Particle size distribution (PSD) of sediment samples in this study was carried out by the hydrometer technique (Ingram, 1971). This classical method is based on the density of settling particles from suspension. The greater the density of suspension, the greater the buoyant force on the hydrometer and the higher the reading. As particles settle out of the suspension, the density decreases and a lower reading is observed. Since temperature influences the settling rate, the temperature must be checked and kept constant throughout the determination. Hydrometer reading should also be corrected for the use of dispersing agent.

#### Apparatus

- A Hydrometer
- A Sedimentation cylinder
- A Plunger
- A Electric blender
- 500 ml beakers

#### Reagents

- 5% Calgon solution: dissolved 35.7 g of Sodium hexametaphosphate and 7.94 g of anhydrous sodium carbonate in distilled water, then dilute to 1L.
- Amyl alcohol

#### Procedure

1. Weigh 50 g freeze-dried sediment in a 500 ml beaker.

2. Add 50ml of 5% Calgon and then add 150 ml of distilled water, mix well and let it stand overnight.
3. Transfer the suspension into an electric blender and mix the suspension for 1-2 min.
4. Carefully pour the suspension into a sedimentation cylinder. Be sure to wash all of the sample into cylinder.
5. Add distilled water to the cylinder until the level reaches 1000 ml.
6. Using a plunger, stir the suspension in the cylinder up and down 20 times.
7. Add 2-3 drops to 1 ml of Amyl alcohol to eliminate bubble after vertical mixing.
8. Remove the plunger and start counting the time.
9. Carefully lower the hydrometer into the cylinder and read when 40 seconds have elapsed.
10. Remove the hydrometer after reading. Rinse and wipe dry. This reading gives the amount of silt and clay in the sample.
11. Measure and record temperature of suspension.
12. After the first reading, allow the cylinder to stand undisturbed for 2 hours.
13. Place the hydrometer in the cylinder and make the 2-hour reading. This reading indicates the amount of clay in the sample. Also measure the suspension's temperature. (Ideally, the temperature should be kept constant throughout the determination).
14. Blank is also determined by the same method described above.



15. Calculate the percentage of sand, silt and clay and then determine the sediment texture by using the texture triangle (see figure A1).

Calculation

$$\%(\text{Silt} + \text{Clay}) = \frac{[(R_s - R_b) + 0.36(T_s - T_b)] \times 1000}{\text{wt of sample}} \dots\dots\dots \text{First 40 seconds}$$

$R_s$  = density of sample at the first 40 seconds

$R_b$  = density of blank at the first 40 seconds

$T_s$  = temperature of sample at the first 40 seconds

$T_b$  = temperature of blank at the first 40 seconds

$$\% \text{ Clay} = \frac{(R_s - R_b) + 0.036(T_s - T_b) \times 100}{\text{wt of sample}} \dots\dots\dots \text{Next 2 hours.}$$

$R_s$  = density of sample at 2 hours

$R_b$  = density of blank at 2 hours

$T_s$  = temperature of sample at 2 hours

$T_b$  = temperature of blank at 2 hours

$$\% \text{ Silt} = \%(\text{Silt} + \text{Clay}) - \% \text{ Clay}$$

$$\% \text{ Sand} = 100 - \%(\text{Silt} + \text{Clay})$$

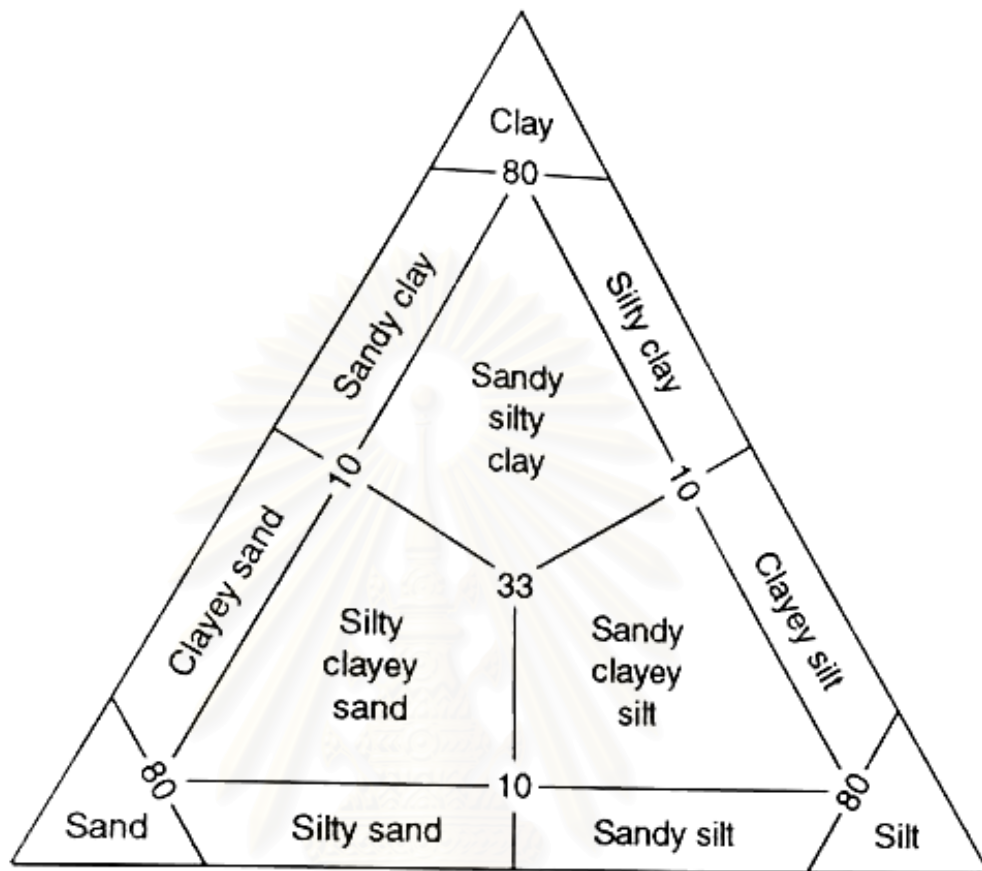


Figure A.1 Triangular classification diagram for particle size distribution (PSD) according to Gorsline (1960).

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## APPENDIX B

### Removal of substances that interfere with dispersal

The decision as to whether or not to remove carbonates, organic matter, iron oxides, or soluble salts depends on the purpose of the analysis and the composition of the sediment sample.

#### Removal of Carbonates (Ingram, 1971)

This procedure is not recommended if mineralogical studies are to be made on the sample.

1. Place the sample in a 250 to 600 ml. Beaker. Add 25 ml DDW and Stir.
2. Add 10% HCl slowly until effervescence stops. If carbonate material is abundant, the addition of 10% HCl will eventually result in a very large volume of liquid. When the beaker is nearly full, concentrated acid may be added very slowly or the excess liquid may be decanted or siphoned off.
3. Heat to 80 to 90 °C. Add HCl until effervescence stops. A more exact procedure is to add HCl until a pH of 3.5 to 4 is reached and maintained.
4. If much carbonate material is present, the dissolved calcium ions will interfere with the dispersal of sample, will hinder the removal of organic matter with the H<sub>2</sub>O<sub>2</sub> treatment, and will precipitate as calcium oxalate in the iron removal treatment. Wash sample with very dilute HCl. Repeat washing two or three times.

#### Removal of Organic Matter (Jackson, Whitting and Pennington, 1949)

This procedure will seldom remove all the organic matter but is still very helpful in dispersing the sediment. This procedure may be stopped after any step, when most of the organic matter has been removed.

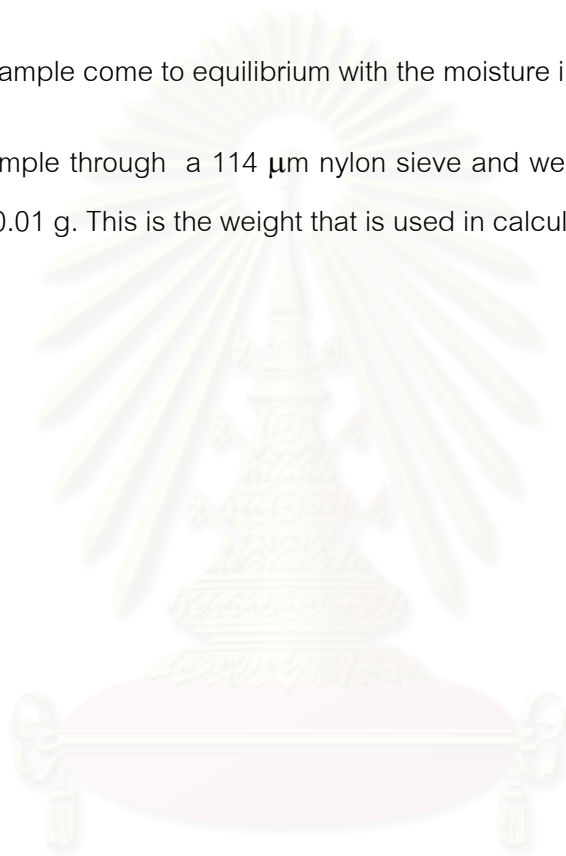
1. If little organic matter is present, place the sample in a 400 ml, beaker and add 100 ml of 6 %  $\text{H}_2\text{O}_2$  slowly and with constant stirring. Cover and heat to 40 °C for 1 hour. Bring to a brief boil at the end of the heating period to remove excess  $\text{H}_2\text{O}_2$ .
2. If much organic material is present, do the following :
  - (a) Remove excess clear liquid by decantation after gravity settling or centrifuging.
  - (b) Add 30%  $\text{H}_2\text{O}_2$  very slowly while stirring until frothing stops. Do not let sample froth over. Avoid contact of skin with 30%  $\text{H}_2\text{O}_2$ , for this reagent will cause burns.
  - (c) Heat to 40 °C on a hot plate for 10 min. It may be necessary to remove sample from heat and to cool with a jet of cold water to prevent frothing over. Use a larger beaker if samples consistently froth over.
  - (d) Evaporate to a thin plate but not to dryness. Add 10 to 30%  $\text{H}_2\text{O}_2$ , cover with watch glass and digest at 40 to 60 °C for 1 to 12 hours. Repeat until organic matter is removed.
  - (e) Bring to a brief boil to remove excess  $\text{H}_2\text{O}_2$ .

#### Removal of Iron oxides (Leith, 1950)

1. Place sample in a 400 ml beaker and add water to make a volume of about 300 ml.
2. Place aluminum (a cylinder of sheet aluminum is preferable but any form of recoverable aluminum will do) in beaker.
3. Add 15 g Oxalic acid (powder or concentrated solution containing 15 g) and boil gently for 10 to 20 min. Add more oxalic as needed to remove all the iron.

### Drying and Sieving

1. After removal of interferences in the sediment sample. Dry sample in air or in an oven at 40°C. If no clay is present, the drying may be done in an oven at 100°C. The drying process will be speeded up if the sample is spread out in a thin layer on a large watch glass, aluminum plate and so on.
2. Let the sample come to equilibrium with the moisture in the room air.
3. Seive sample through a 114 µm nylon sieve and weigh sample in each size to nearest 0.01 g. This is the weight that is used in calculating percentages .



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## APPENDIX C

### Elemental composition analysis

Elemental composition of sediment samples in this study was qualitatively and quantitatively analyzed by X-ray Fluorescence technique. This non-destructive method is based on the fact that primary X-ray irradiates emission of fluorescent X-ray occurs after the atom. Since fluorescent X-ray of each element has specific wavelength, this can be utilized to specify element in sample according to Bragg's law (qualitative analysis). Furthermore, the intensity of fluorescent X-ray is also measured for quantitative analysis.

A Siemens SRS3000 sequential X-ray fluorescence spectrometer (XRF) compatible with SPECTRA3000 software was utilized in this study. This spectrometer was installed at the laboratory of the WBB Clay and Minerals Company. Diagram of this X-ray unit is shown in Figure B1. Sediment samples were prepared by fused cast bead method (according to ISO/DIS12677) before analyzing elemental composition by XRF. Thirty-two certified reference materials were prepared by the same way as samples and used in determining calibration graphs or equations and for correction of matrix effect. Three Japanese standards of sedimentary rocks (JLK-1, JSd-1 and JSd-3) from Geological survey of Japan (1999) were analyzed as samples to check the accuracy and precision of the instrument and methodology. Loss on ignition (LOI) testing was also conducted to measure the accuracy of the analysis.

#### Principal of X-ray fluorescence spectrometer

According to figure C.1, samples are irradiated with primary X-ray to emit Fluorescent X-ray. The Fluorescent X-ray is then controlled to become parallel beam (by a slit of goniometer) straightforward onto the surface of a plane crystal. Then the fluorescent X-ray diffract from the plane crystal according to Bragg's law ( $2d\sin\theta = n\lambda$ ). A detector that rotates at the same velocity of a goniometer measures the energy of the X-ray quanta (intensity of X-ray) whereas goniometer measure the reflection angle ( $\theta$  and  $2\theta$ ) of X-ray. The energy is then converted into electrical impulses or counts and

used in calculation of concentration of element from the equations of X-ray intensities and concentration of elements by computer software (SPECTRA3000)

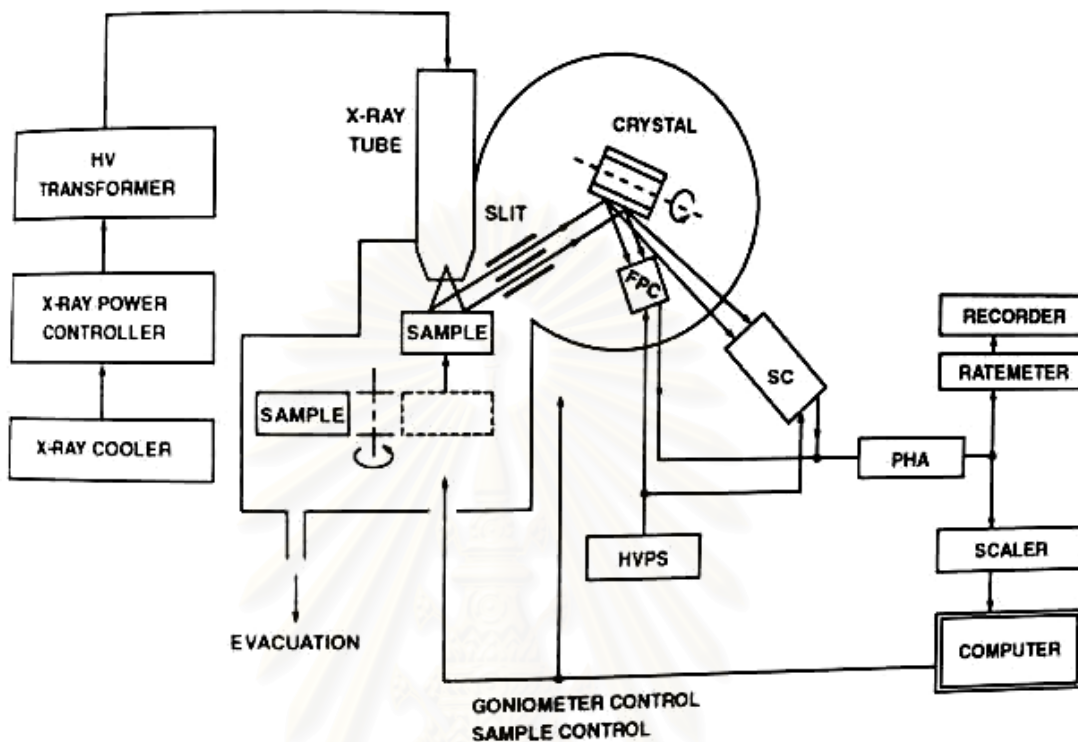


Figure C.1 Diagram of X-ray fluorescence spectrometer.

#### Preparation of sample

Sediment sample of this study were prepared by fused cast bead method according to ISO/DIS12677 (1998). The sediment powder is fused with a suitable flux to destroy its mineralogy and particulate composition.

#### Apparatus

- A Platinum-gold crucible and lid
- Claisse Flux machine, three burner fusion system
- A Vacuum dessicator
- A Balance

- An Oven
- A Hood

#### Reagents

- Lithium metaborate,  $\text{Li}_2\text{B}_4\text{O}_7$  (A.R. grade)
- Lithium Iodide,  $\text{LiI}$  (A.R. grade)

#### Procedure

Dry sediment sample overnight in an oven at  $110^\circ\text{C}$ , cool in a vacuum desiccators. 1 g of the sediment sample was weighed into a platinum-gold crucible with 5 g of pure lithium metaborate and then mixes well. One drop of lithium iodide solution was added into the platinum crucible to prevent crack of glass bead after cooling down. Fuse at  $1,000^\circ\text{C}$  with the fluxer machine. After used flux is poured on to a platinum lid, let it cool for 5 min. Label the bead with a piece of label paper and store in a polyethylene seal-bag and then the bag should be stored in the vacuum desiccator until XRF analysis.

#### LOI testing

Loss on ignition (LOI) is used in estimating sediment moisture, organic matter, organic carbon and carbonate content. LOI is considered to be an essential parameter for the XRF analysis. By ignoring LOI the total cannot be used as a measure of the accuracy of the analysis. LOI has been traditionally done by gravimetric method.

#### Apparatus

- Platinum crucibles
- A Muffle furnace
- A Balance



- A Vacuum desiccator

### Procedure

Weigh 2 g of a dried sample into a platinum crucible. Then place the platinum crucible into a furnace. Heat at 1,000 °C for 4-10 hr and cool it in a vacuum desiccator. Finally, weigh and calculate % of loss on ignition.



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## APPENDIX D

### X-ray diffractometry

Mineral composition of sediment samples in this study was qualitatively analyzed by X-ray Diffraction technique. A diffracted beam is composed of many waves that have been scattered by atoms in a crystal that were in the path of the incident beam. Reflection is the bouncing back of visual light as a surface phenomenon in a layer that is about  $\frac{1}{2}$  thick. The diffraction of waves only occurs at certain angles, called Bragg angles, where Bragg's law is satisfied. In contrast, reflection takes place at any angle of incidence. With a diffracted beam the intensity coming out of the crystal is significantly smaller than the initial intensity. Reflective beams have almost the same intensity coming out as going in.

All samples were examined for their relative mineralogical constituents on random aggregates by X-ray powder diffractometer (XRD) with the Ni filtered Cu K $\alpha$  radiation at scanning speed 0.05 $^{\circ}$ /sec. The XRD allows one to determine the phases present rapidly and with precision. Unoriented samples are necessary to determine diffraction maxima other than the (001) basal spacing series. Since the clays are inferred to have a natural tendency to be oriented, they invariably give poor (hkl), or non-basal, reflections. The sample must be ground finely and lightly packed into a shallow cavity in a metal plate (Fig. D.1). Care must be taken to avoid any physical pressure on the particles.

In the XRD spectra of clay, there are several diagnostic zones which give characteristic diffraction maxima. The powder spectra are usually obtained using an X-ray tube with a copper anticathode. Most XRD diffractogram begin at about 4 $^{\circ}$ /2 $\theta$  and run to about 70 $^{\circ}$ /2 $\theta$  using copper radiation.

The major problem in XRD is that, since clay particles are very small, a coherent domain in a single crystal will also be very small and will not give strong diffraction maxima, so that most of these maxima will be invisible to give a decent intensity of diffracted X-ray. This is aggravated by the fact that the clays are found

essentially in two dimensional forms, due to their sheet structure. If the greatest diameter of a clay particle is 2 micrometers, the smallest is smaller by a factor of 10-20 or more. This reduces the diffraction power of the atomic planes even more in most of the crystallographic directions.

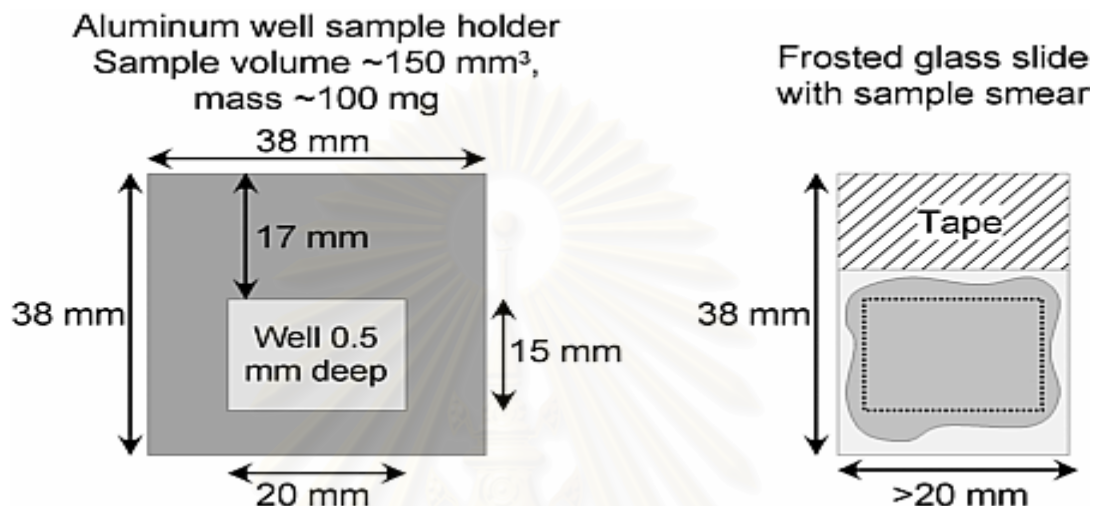


Figure D.1 Sample preparation for X-ray diffraction method.

The uniaxial powder diffractometer and the use of oriented clay samples are the method for solving these problems. The machine uses a parallel X-ray beam of large cross-section which impinge on a thinly dispersed powdered sample (several tens or hundreds of milligrams are necessary) lying essentially in a single plane. The cones of X-ray powder diffraction are intersected by a detector which discriminates the profile of each diffraction cone on a single circular arc, thus giving a series of diffracted X-ray intensity bands on a continuous trajectory.

However, the X-ray diffractometer is not enough in itself. The mechanism of creating a more intense diffraction pattern than would be normal for small crystallites had to be more than a new machine. The trick is to utilize the inherent sheet structure of clays. In orienting the clays, making them lie one on top of the other in the same plane, the diffraction effect is enhanced for the small crystallites. The orientation procedures a pseudo-macrocrystal which diffracts approximately as if thousands of the crystallites became a single large crystal. The resulting diffraction characteristics are thus enhanced in the crystallographic direction parallel to the sheet structure. However, the

drawback is that other diffracting planes in the crystals which are not parallel to the sheet structure are almost totally lost to the diffraction spectrum. The X-ray beam sees only the planes parallel to the diffraction of orientation.

As a result, the identification of clay mineral is done almost entirely on the spacing of the crystallographic planes parallel to the sheet structure. This is called the basal spacing of the clays and is of fundamental importance to any discussion of clay mineralogy. Out of these, this is the characteristic of some clay types to change their cell dimension in the direction of the sheet structure by swelling. The incorporation of different polar molecules changes the basal spacing of expanding clays, that allows a more precise definition of these clay types. X-ray identification then often implicates a manipulation of the crystal composition, by inserting or removing different molecules from between the loosely held-sheet layers. Therefore, a thorough identification of a clay aggregate necessitates several XRD identifications. These operations determine the swelling properties of the clays.

The two standard polar molecules currently used to affect swelling are water and ethylene glycol, which give a  $5^{\circ}$  A and  $7^{\circ}$  A increase in sheet thickness, respectively. In this study, ethylene glycol was used to test montmorillonite. The 3 states that are characteristic of clay are thoroughly dried sample (heat at  $550^{\circ}$  C), glycollated and water-vapour-saturated. The preparation of an oriented clay sample can be performed several ways. Figure C.2 shows details of the sample preparation. The first step is to separate clay fraction out of the ground sample by dispersing material in water using Calgon (Sodium polymetaphosphate) as dispersing agent. The slurry was allowed to settle in 10 cm test tube for 6 hours. The suspension appearing as muddy water was decanted and centrifuge. The centrifuge clay fraction was resuspended in a smallest volume of water, poured on to a glass slide and allow to dry to produce an air-dried oriented sample. This sample is called oriented sample which is used for analyzing clay minerals by X-ray diffractometry.

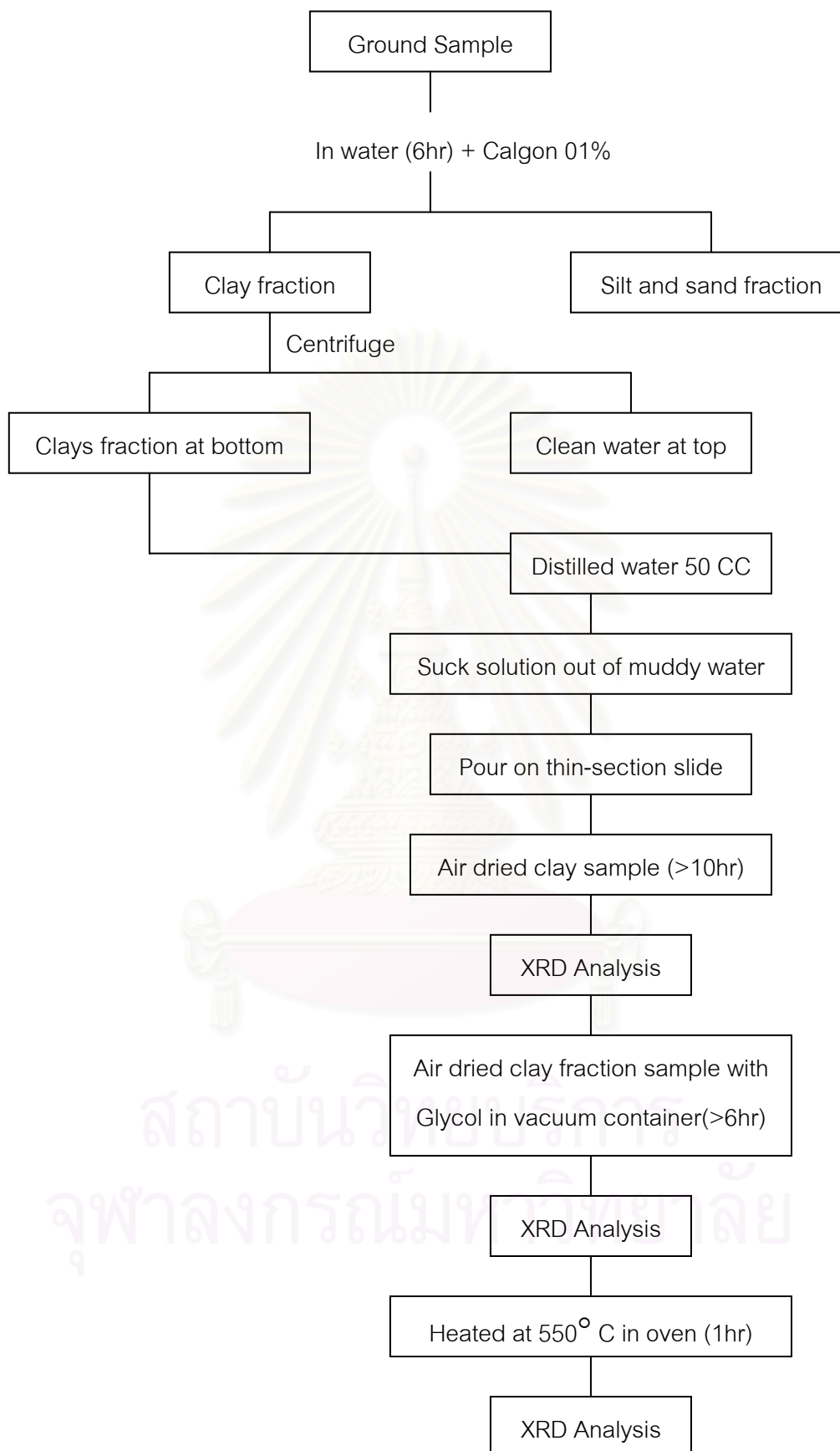


Figure D.2 Details of the oriented sample preparation.

The montmorillonite. The standard polar molecules currently used to effect swelling is ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ ), which gives a  $7^\circ \text{A}$  increase in sheet thickness, respectively. Differential retention rates of glycol molecules by the various clay species gives one an additional means of identification of the clay species present. If the sample comprises smectite group mineral, peak intensity of smectite from glycollated sample will shift about  $0.4^\circ - 0.6^\circ / 2\theta$  because montmorillonite absorbs ethylene glycol. Moreover, when the glycollated sample is heated at  $550^\circ \text{C}$  in oven for 1 hour, the peak at  $7^\circ \text{A}$  will disappear, suggesting that the sample is composed of smectite group mineral.



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## APPENDIX E

## Minerals composition analysis

Details of each minerals which are found in each sediment and each size, are shown as following :

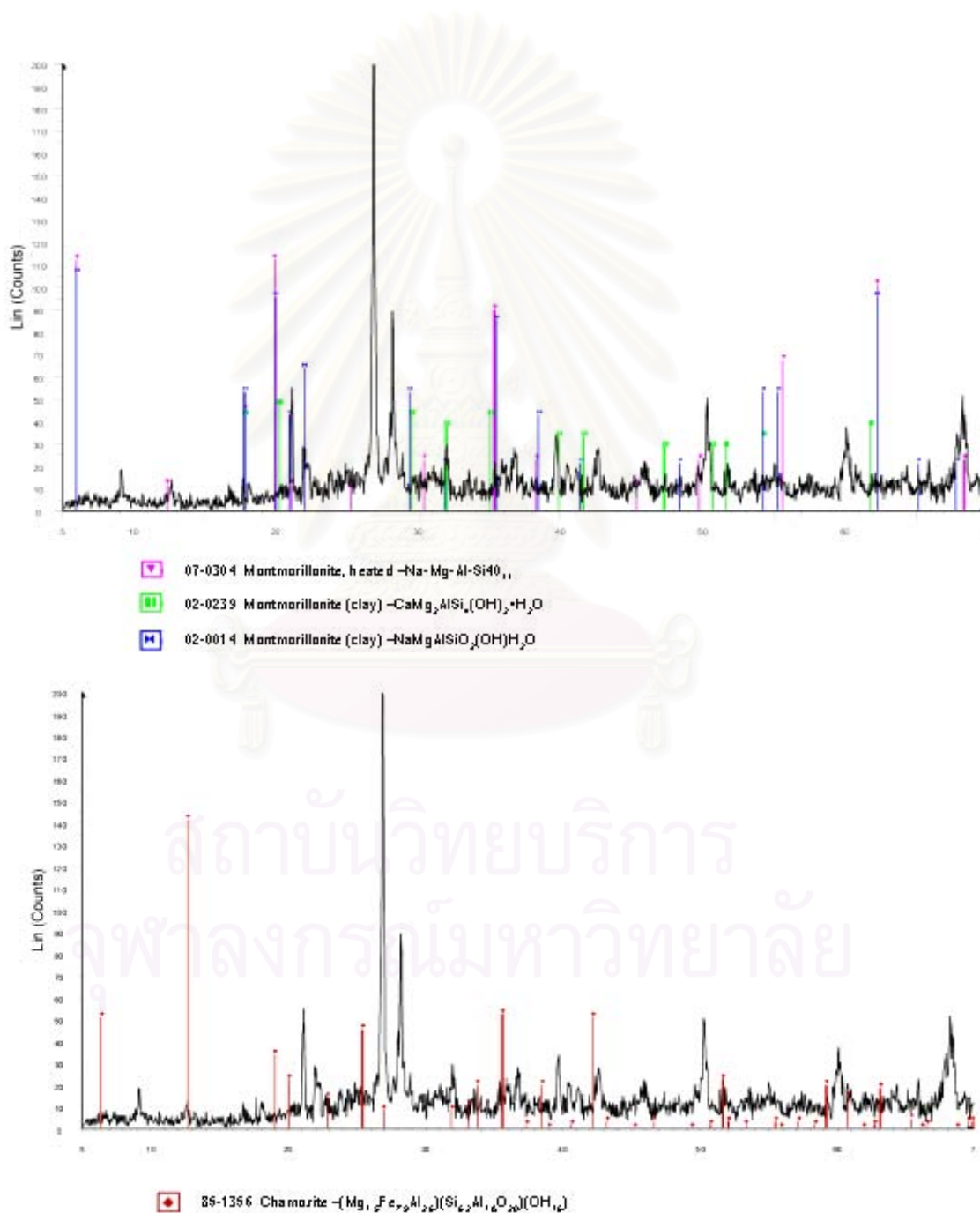


Figure E.1 X-ray diffractogram in <math> <114\mu\text{m}</math> Mae Klong sediment.

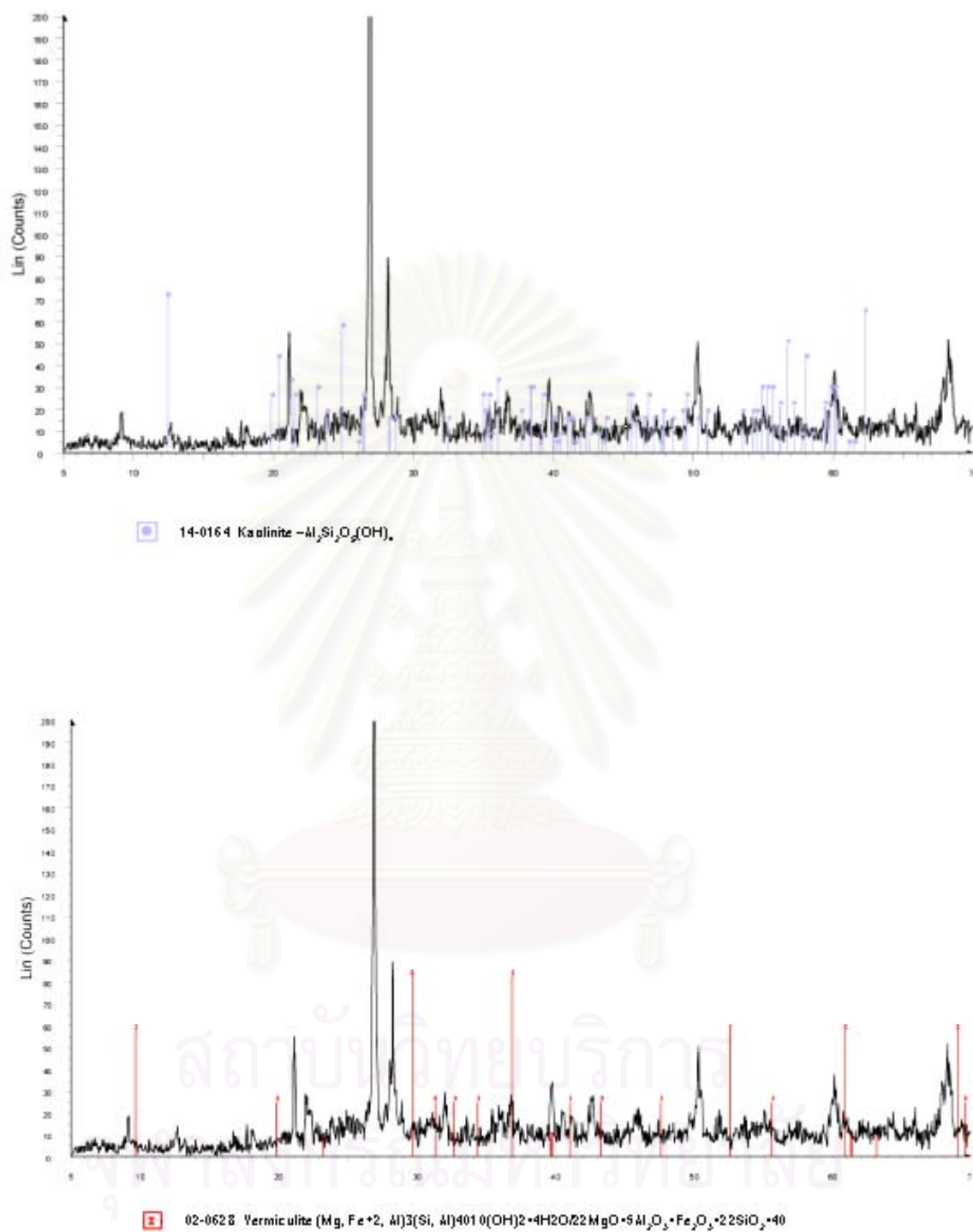


Figure E.1 X-ray diffractogram in &lt;math&gt;&lt;114\mu\text{m}&lt;/math&gt; Mae Klong sediment.(cont.)



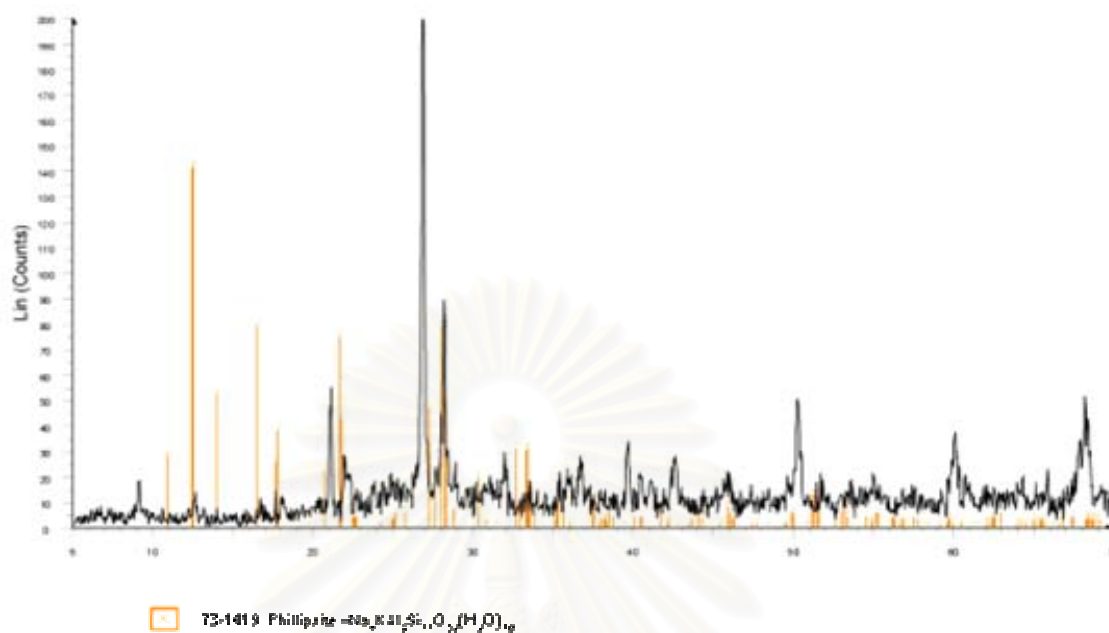


Figure E.1 X-ray diffractogram in <math><114\mu\text{m}</math> Mae Klong sediment.(cont.)

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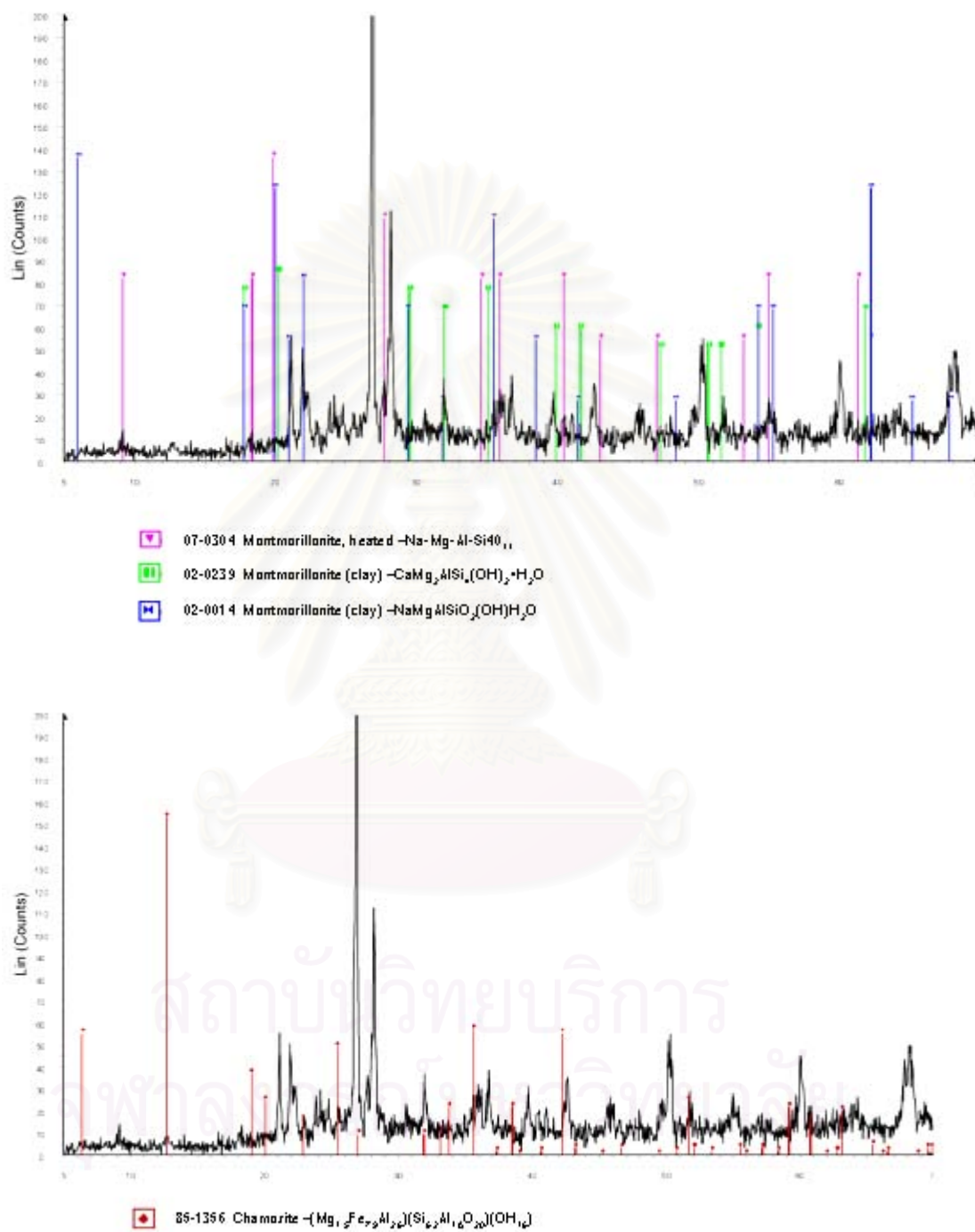


Figure E.2 X-ray diffractogram in  $>114\mu\text{m}$  Mae Klong sediment.

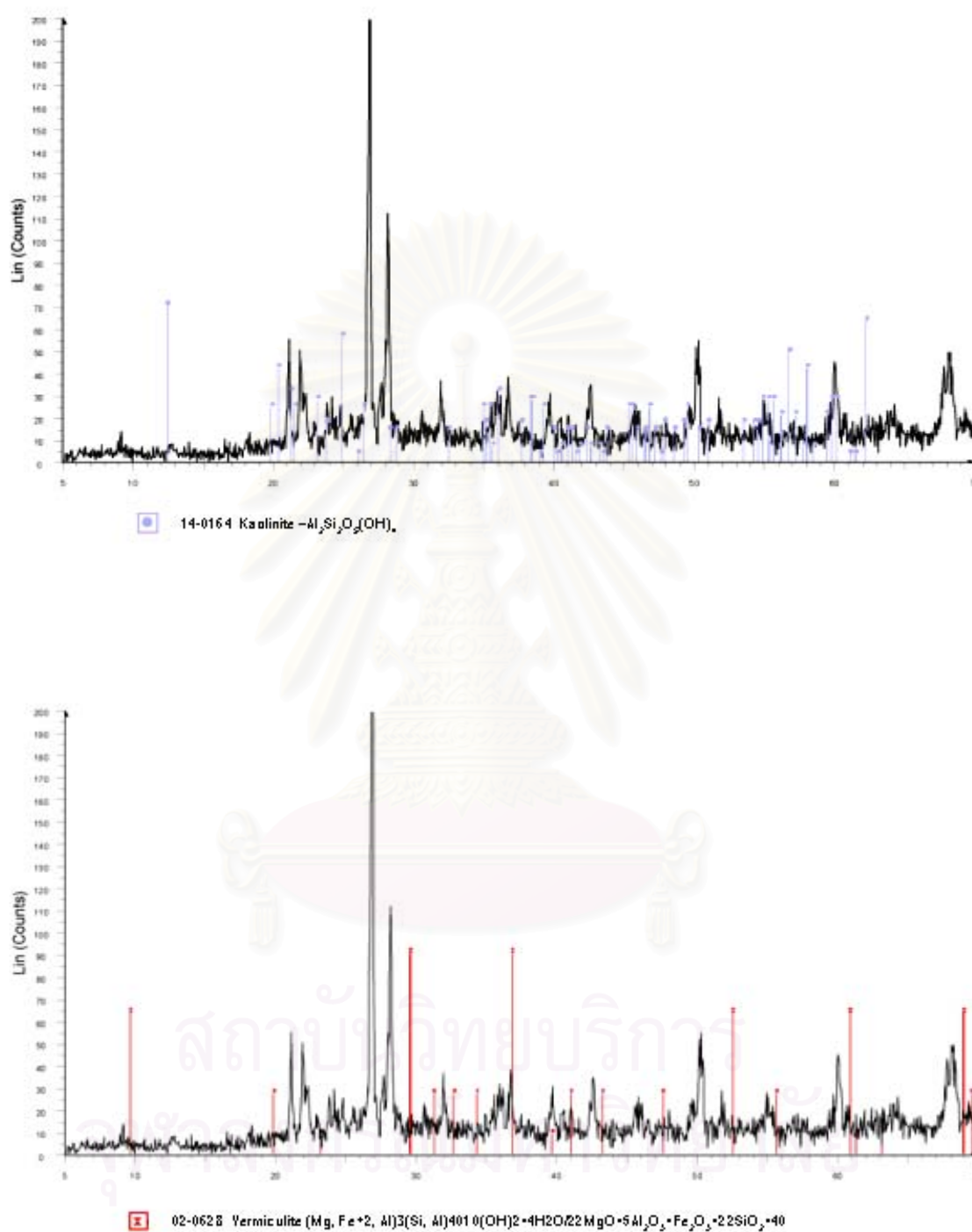


Figure E.2 X-ray diffractogram in  $>114\mu\text{m}$  Mae Klong sediment. (cont.)

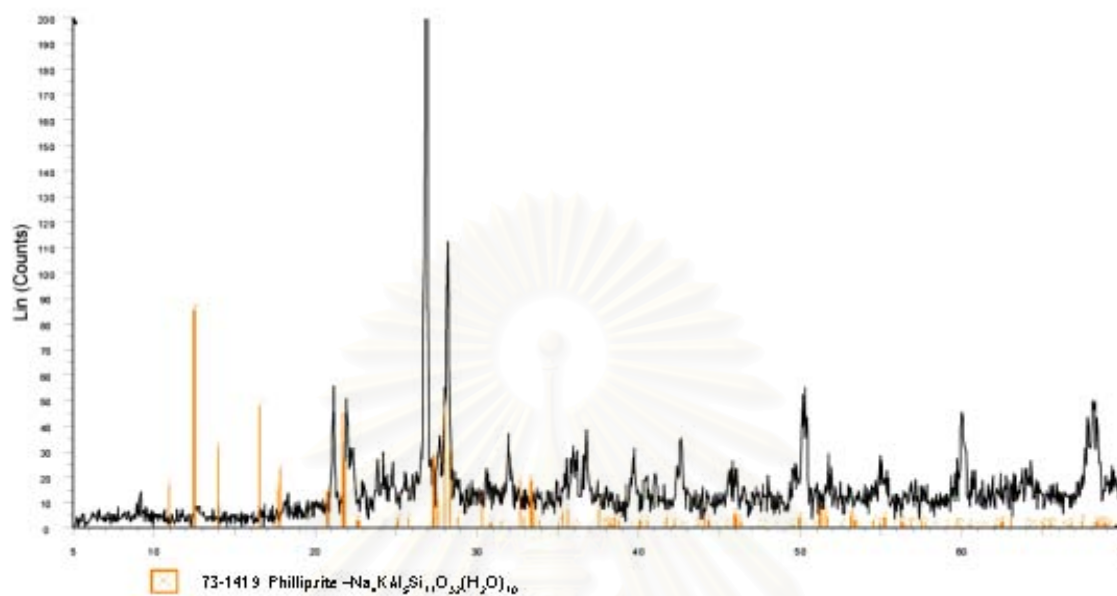


Figure E.2 X-ray diffractogram in  $>114\mu\text{m}$  Mae Klong sediment. (cont.)

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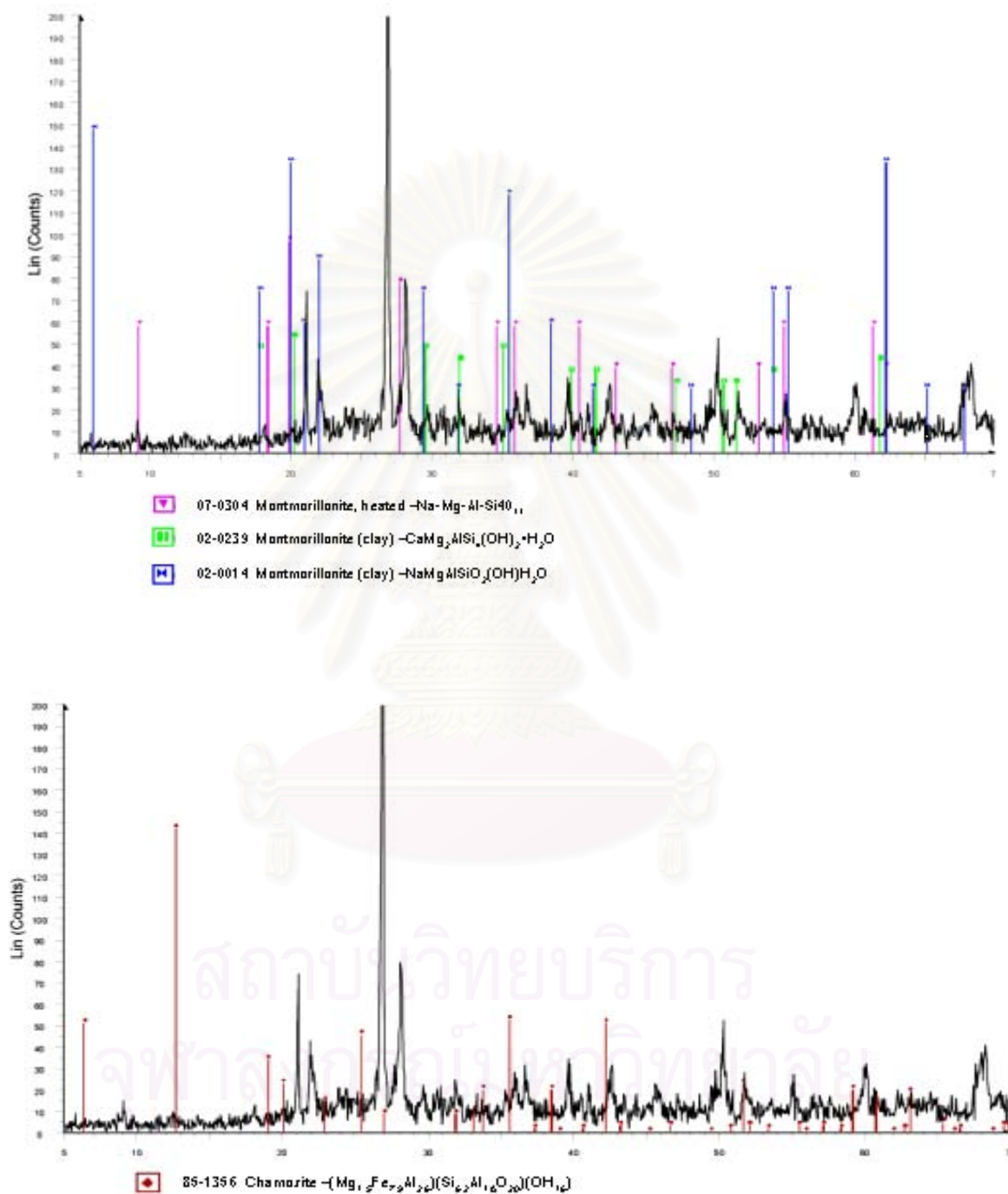


Figure E.3 X-ray diffractogram in non-sieve Mae Klong sediment.

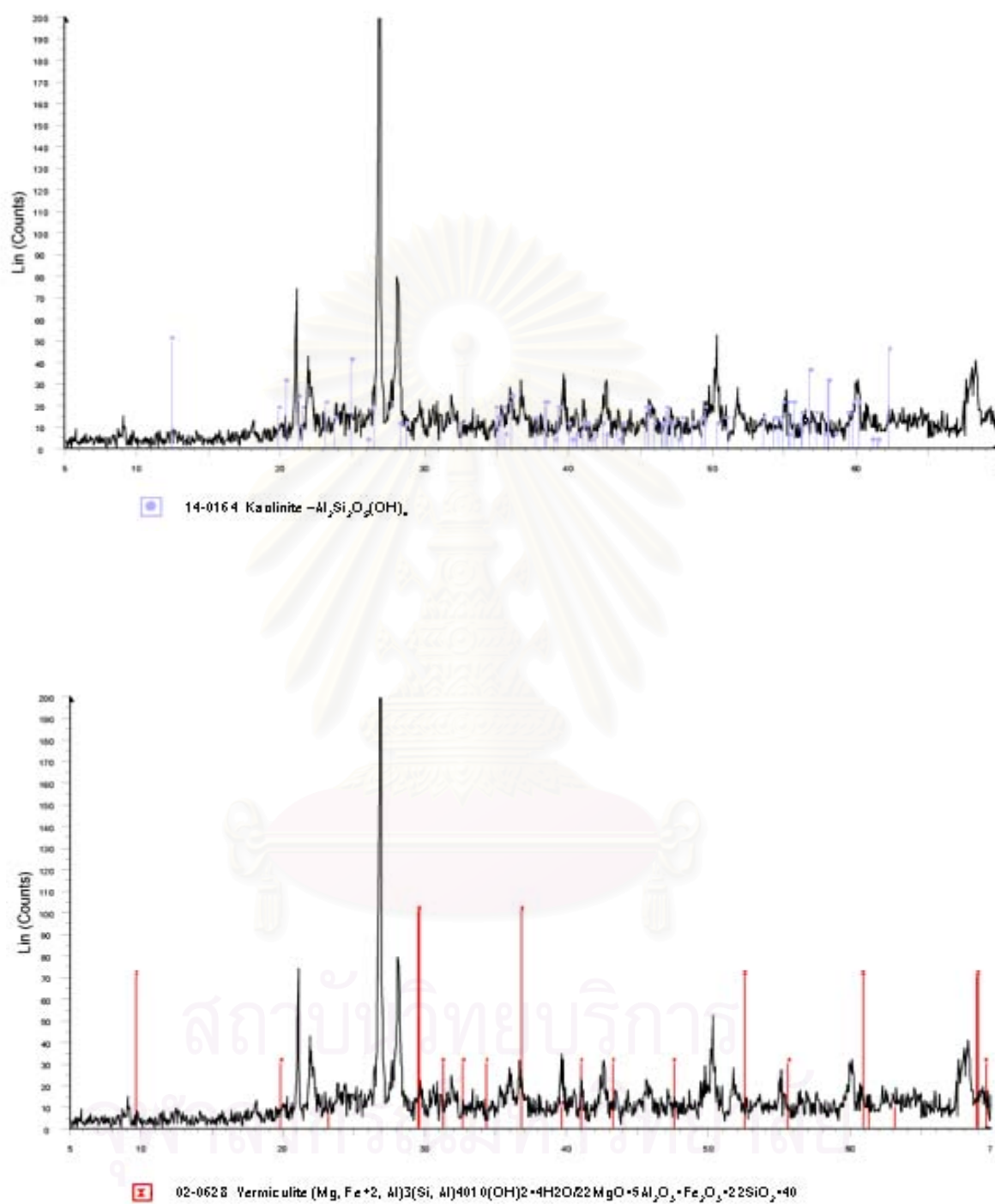


Figure E.3 X-ray diffractogram in non-sieve Mae Klong sediment (cont.)

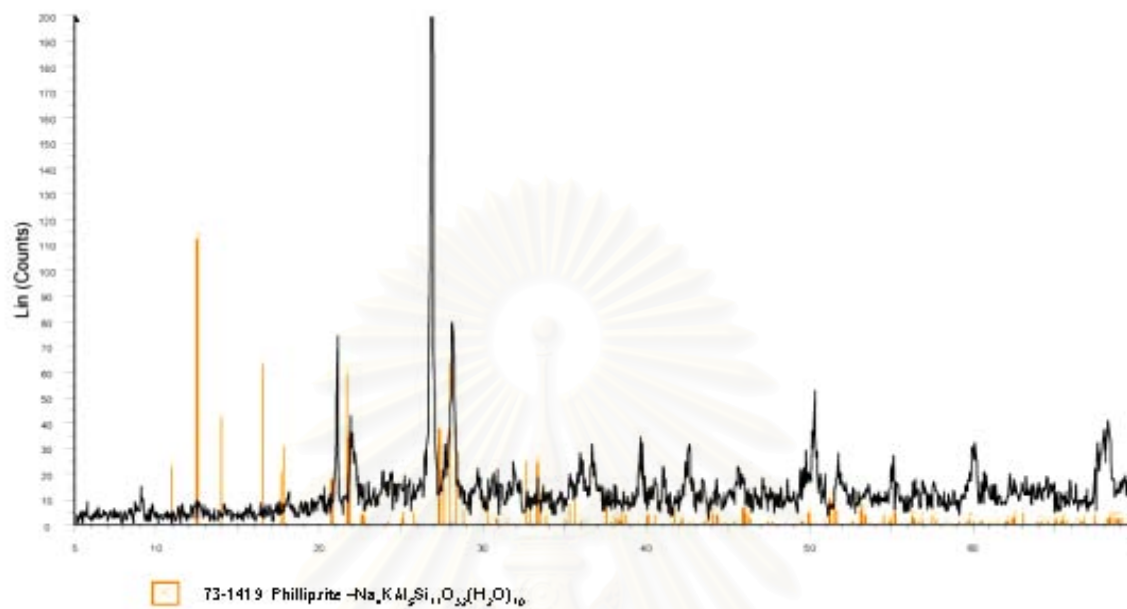


Figure E.3 X-ray diffractogram in non-sieve Mae Klong sediment (cont.)

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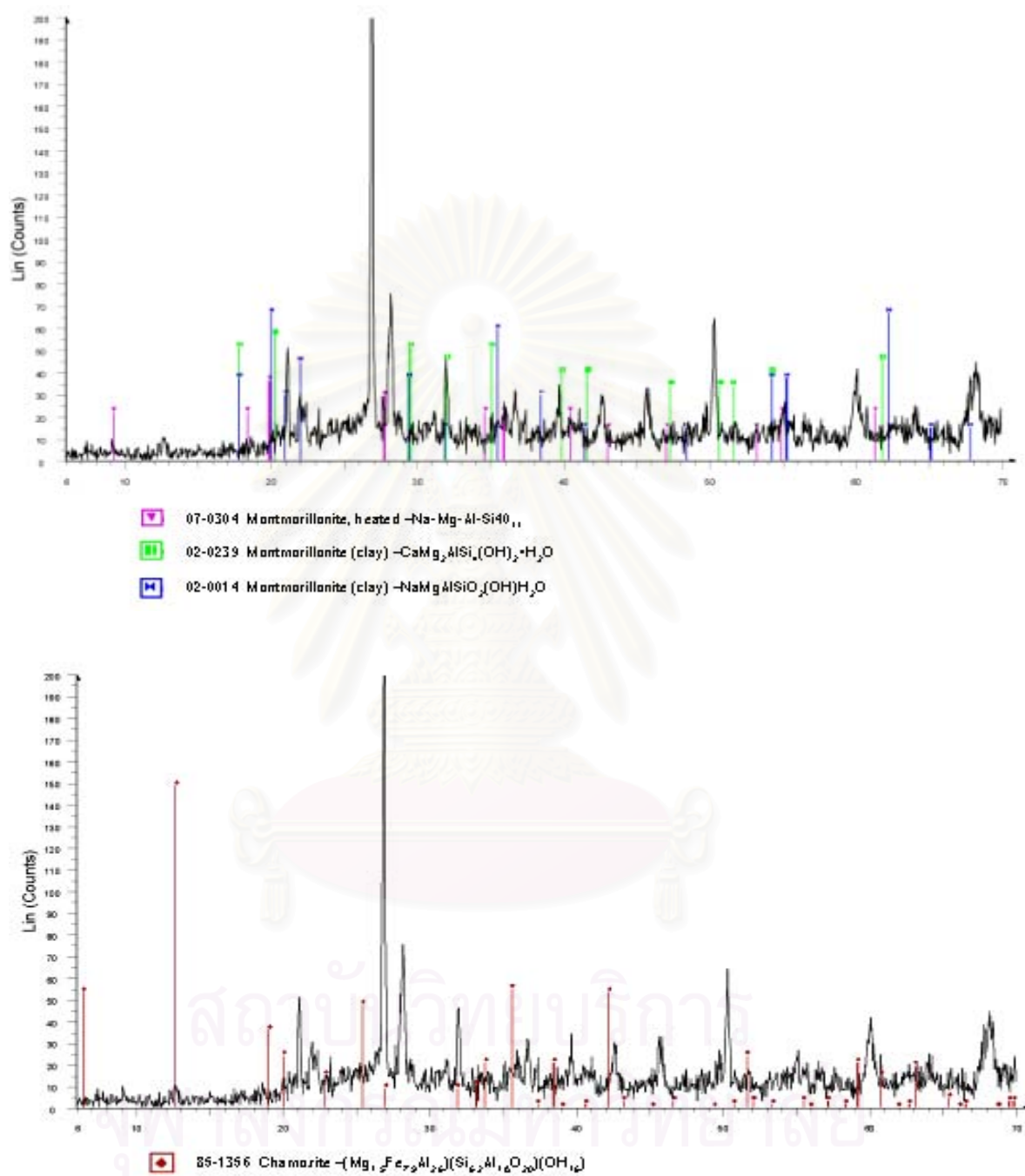


Figure E.4 X-ray diffractogram in <math><114\mu\text{m}</math> Bang Pakong sediment.



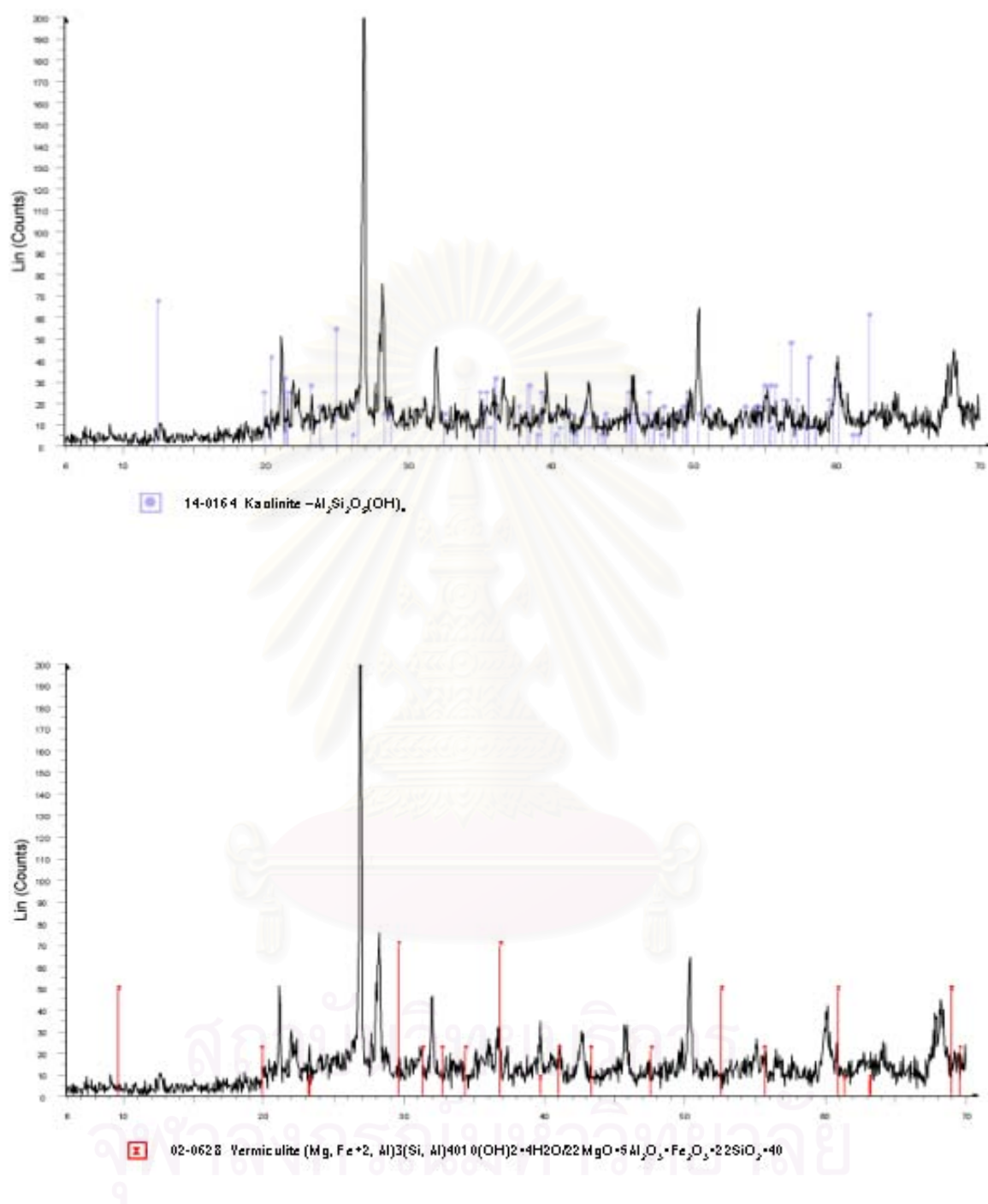


Figure E.4 X-ray diffractogram in <114μm Bang Pakong sediment (cont.)

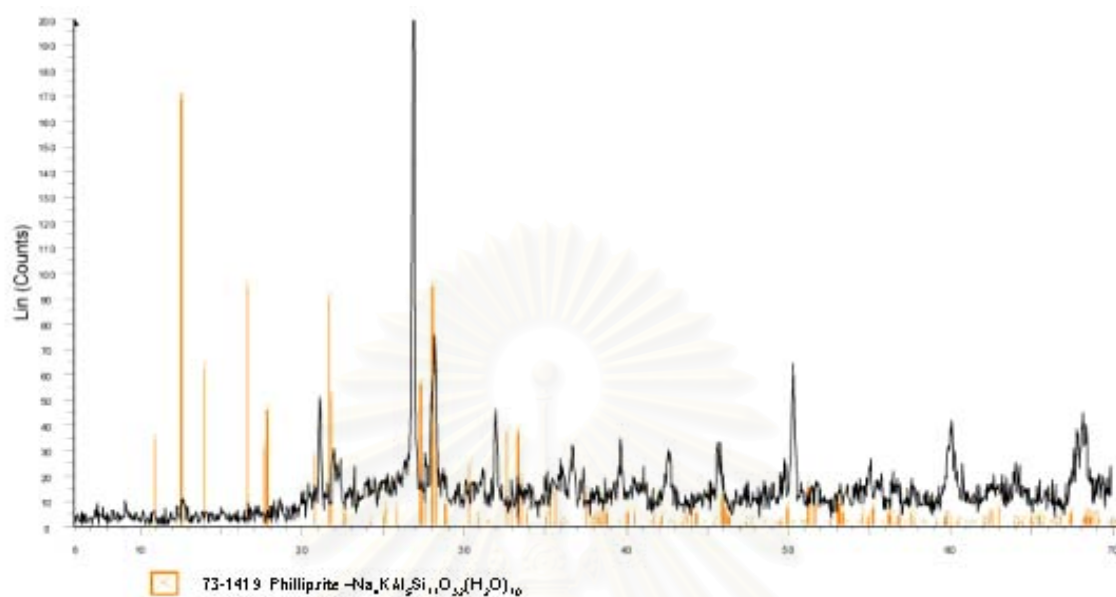


Figure E.4 X-ray diffractogram in <math><114\mu\text{m}</math> Bang Pakong sediment (cont.)

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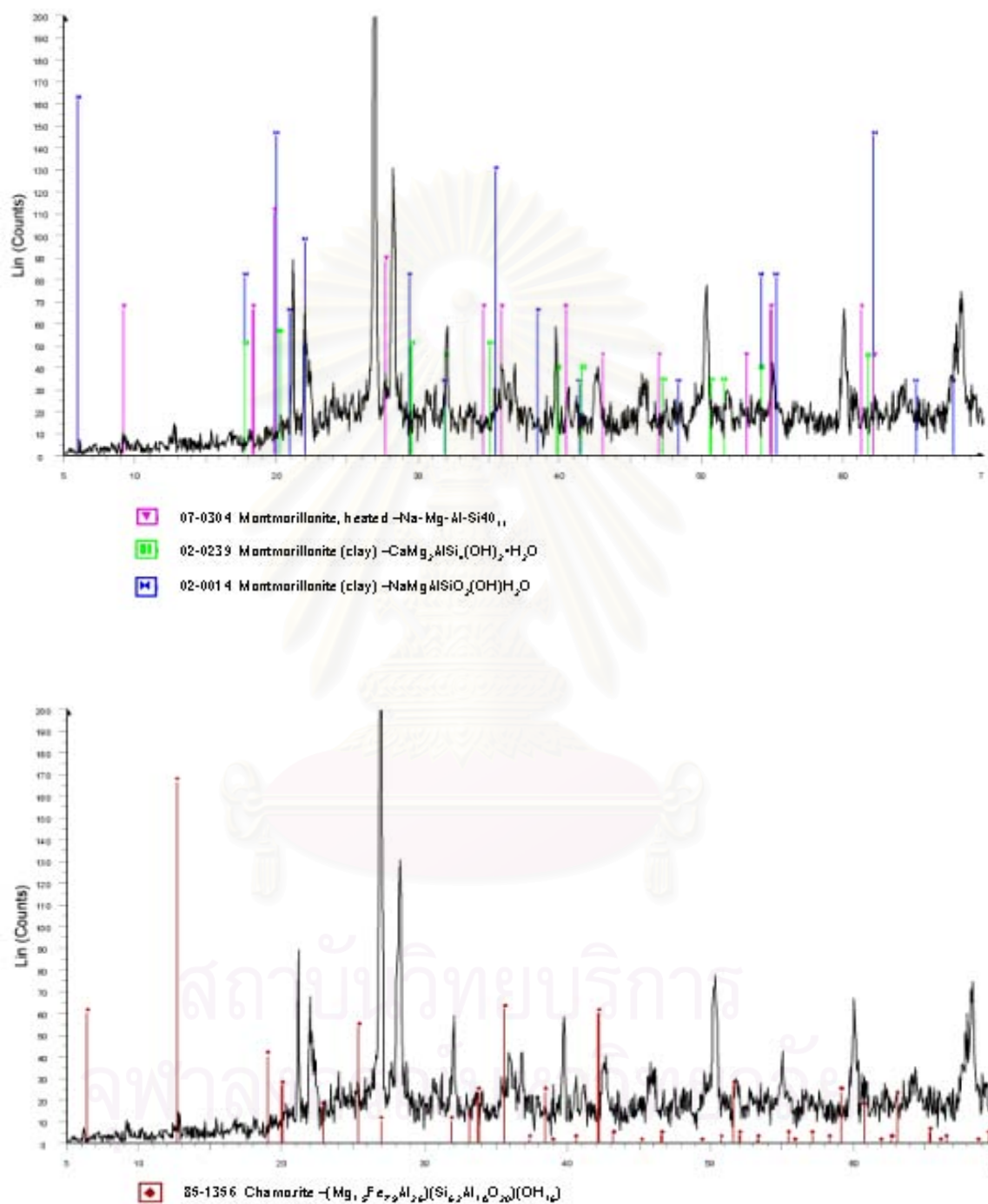


Figure E.5 X-ray diffractogram in >114 $\mu$ m Bang Pakong sediment

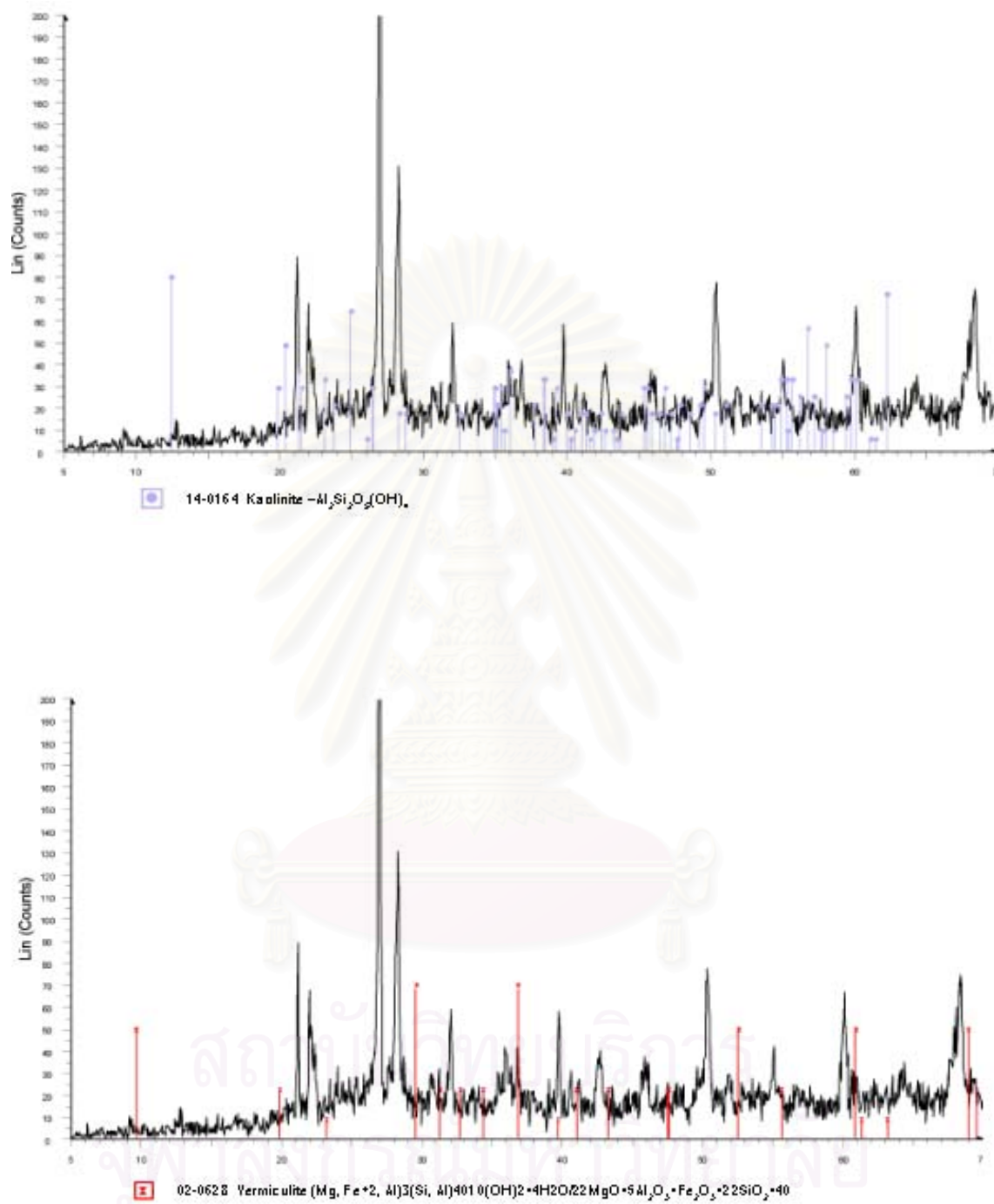


Figure E.5 X-ray diffractogram in  $>114\mu m$  Bang Pakong sediment (cont.)

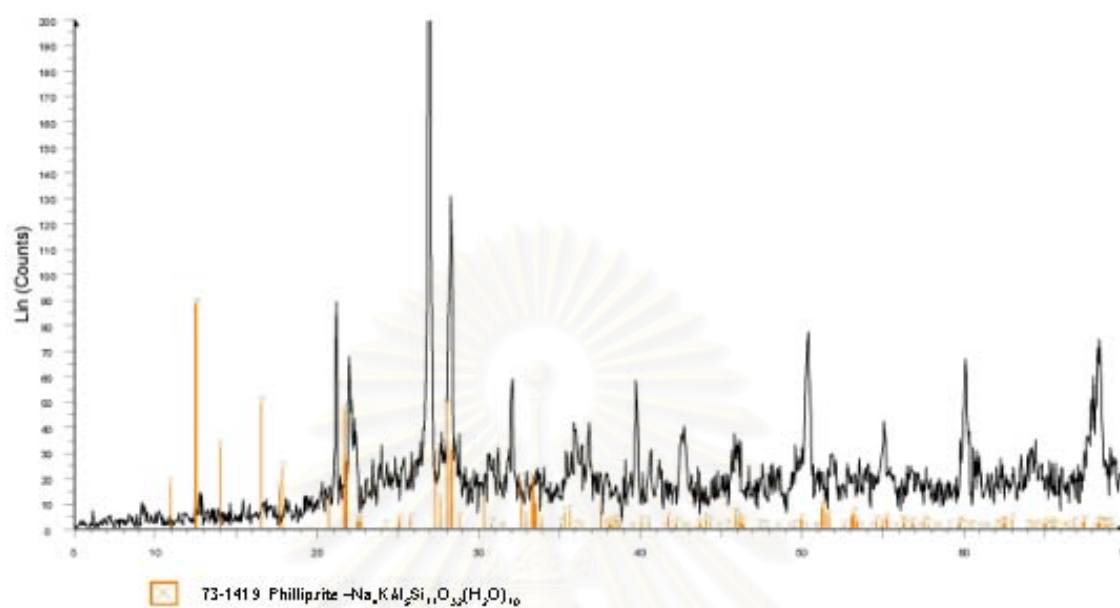


Figure E.5 X-ray diffractogram in  $>114\mu\text{m}$  Bang Pakong sediment (cont.)

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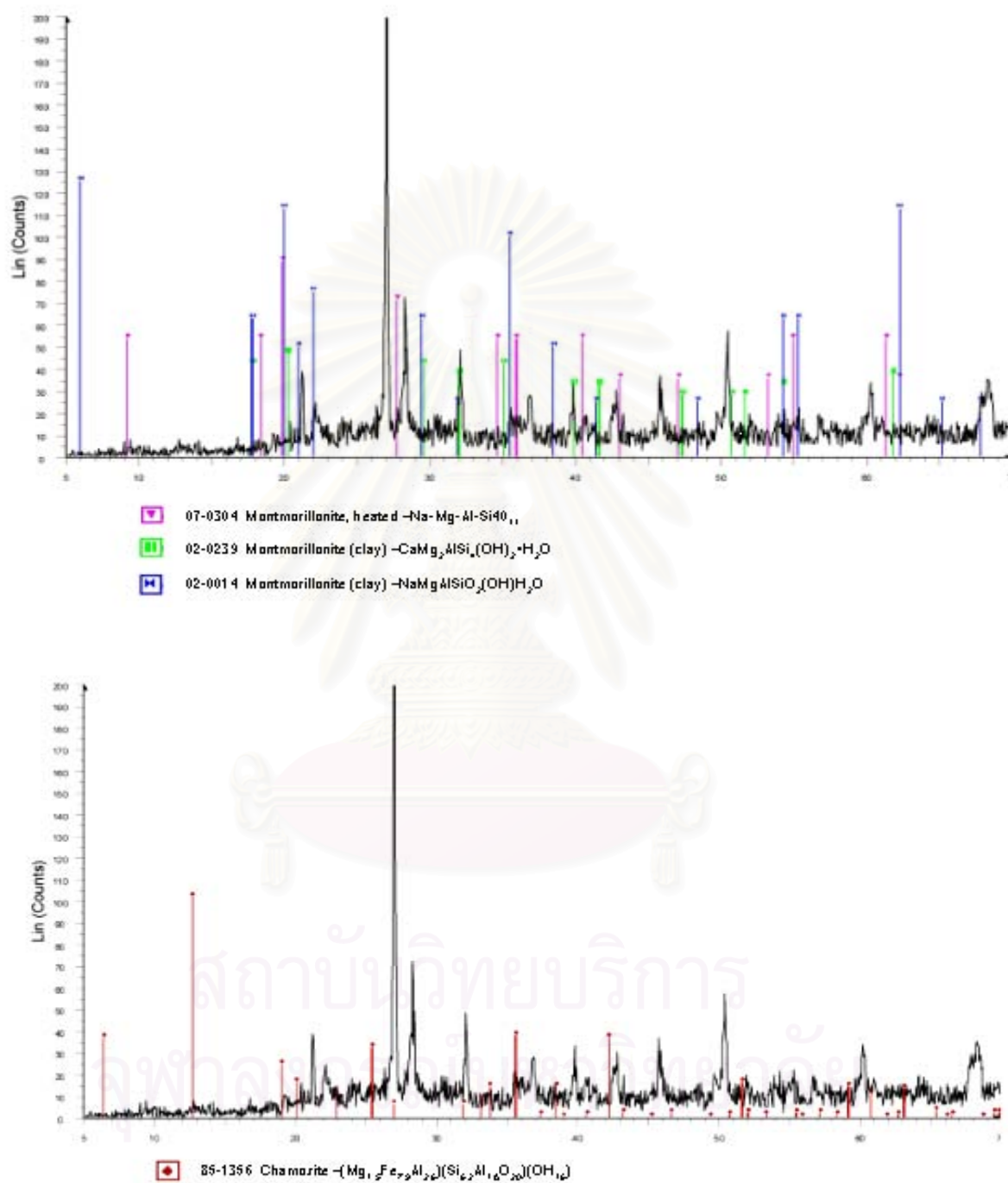


Figure E.6 X-ray diffractogram in non-sieve Bang Pakong sediment

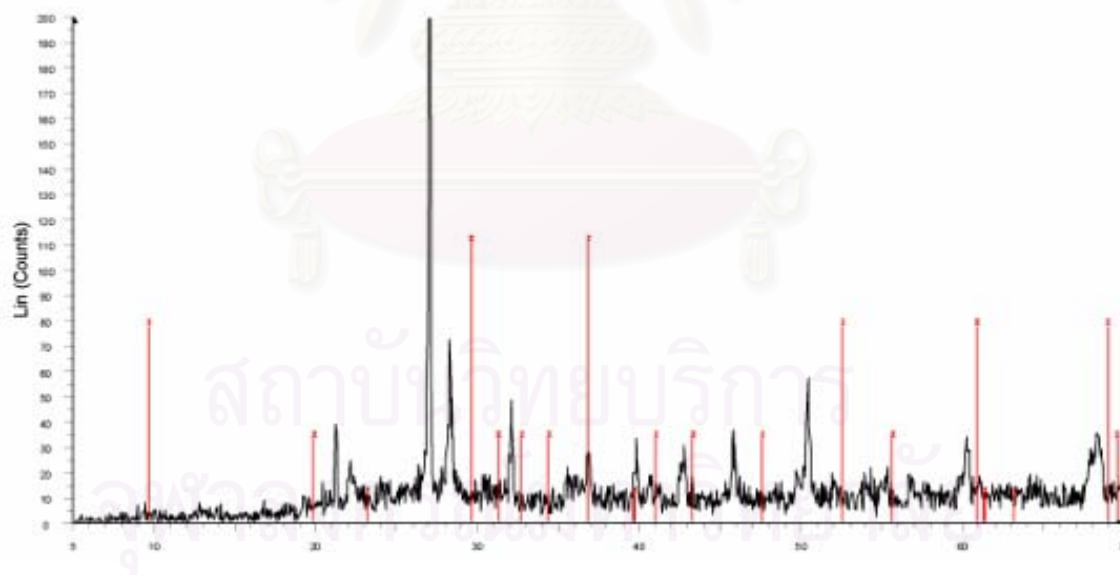
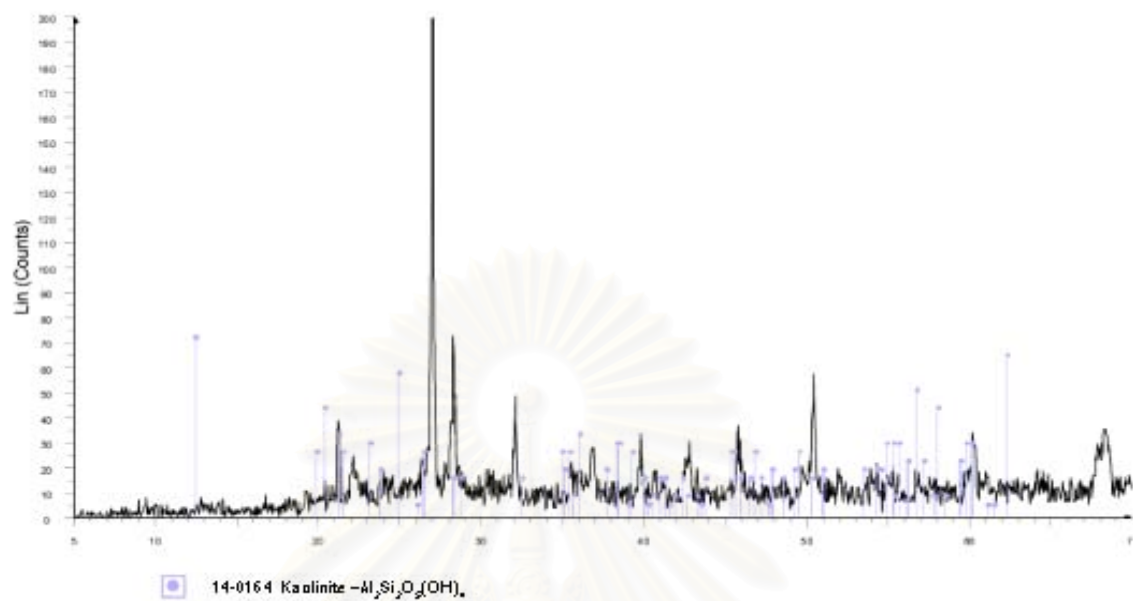


Figure E.6 X-ray diffractogram in non-sieve Bang Pakong sediment (cont.)

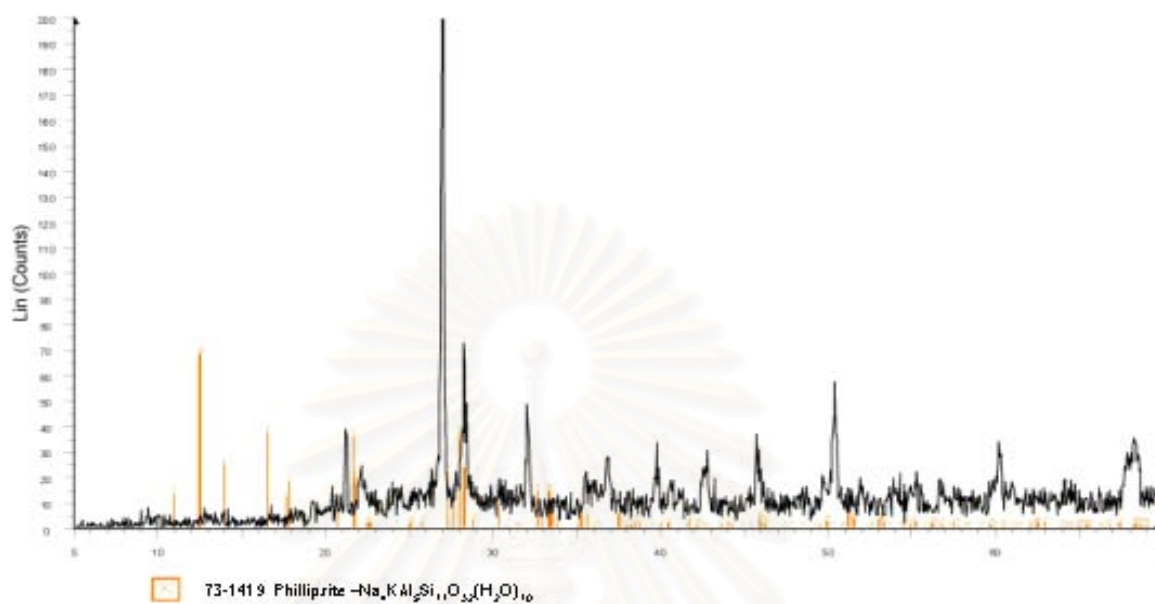


Figure E.6 X-ray diffractogram in non-sieve Bang Pakong sediment (cont.)

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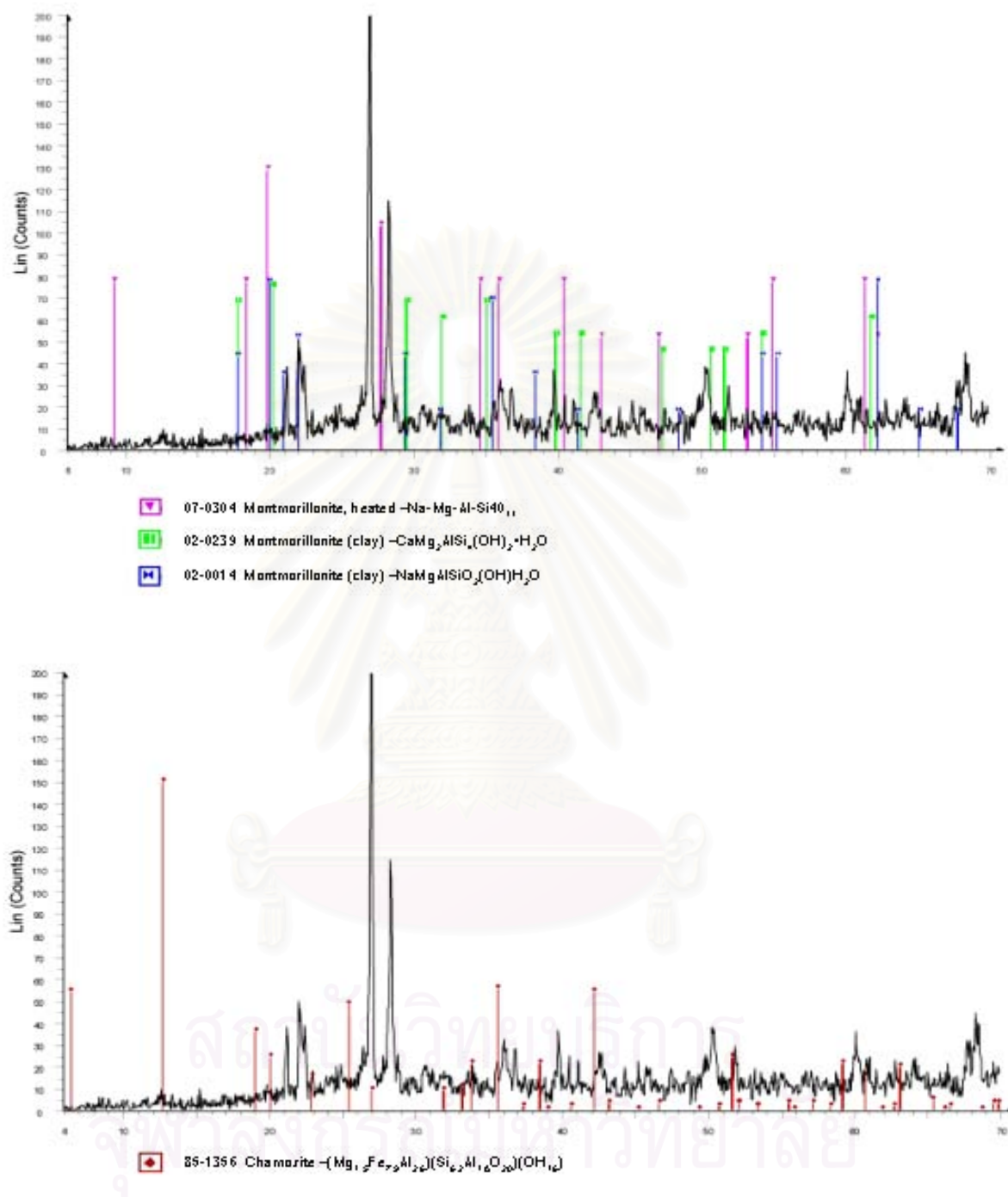


Figure E.7 X-ray diffractogram in <math><114\mu\text{m}</math> Chao Phraya sediment.

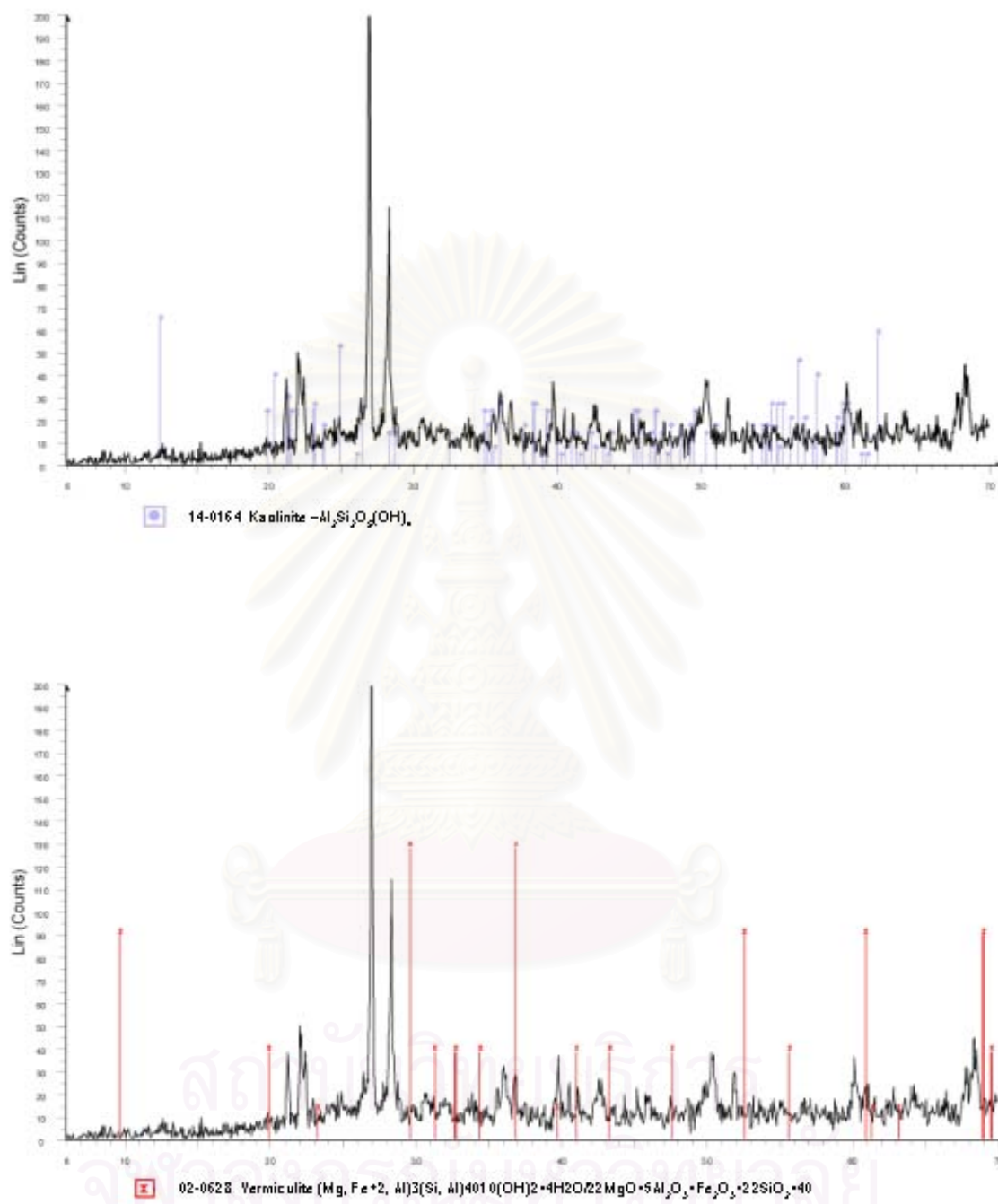


Figure E.7 X-ray diffractogram in <math> <114\mu\text{m}</math> Chao Phraya sediment (cont.)

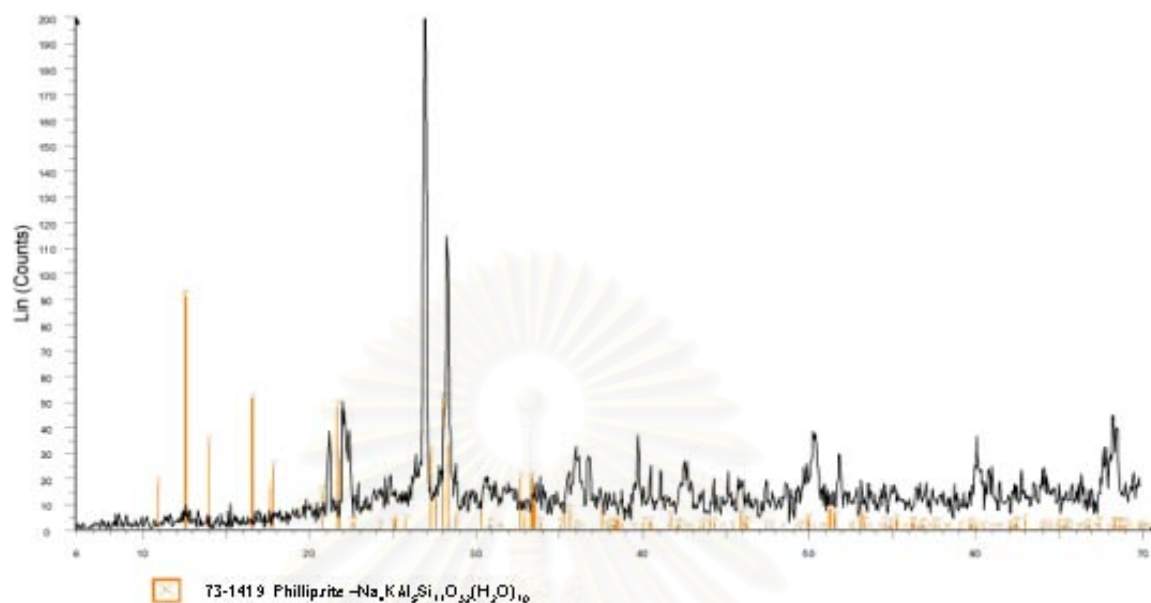


Figure E.7 X-ray diffractogram in <math><114\mu\text{m}</math> Chao Phraya sediment (cont.)

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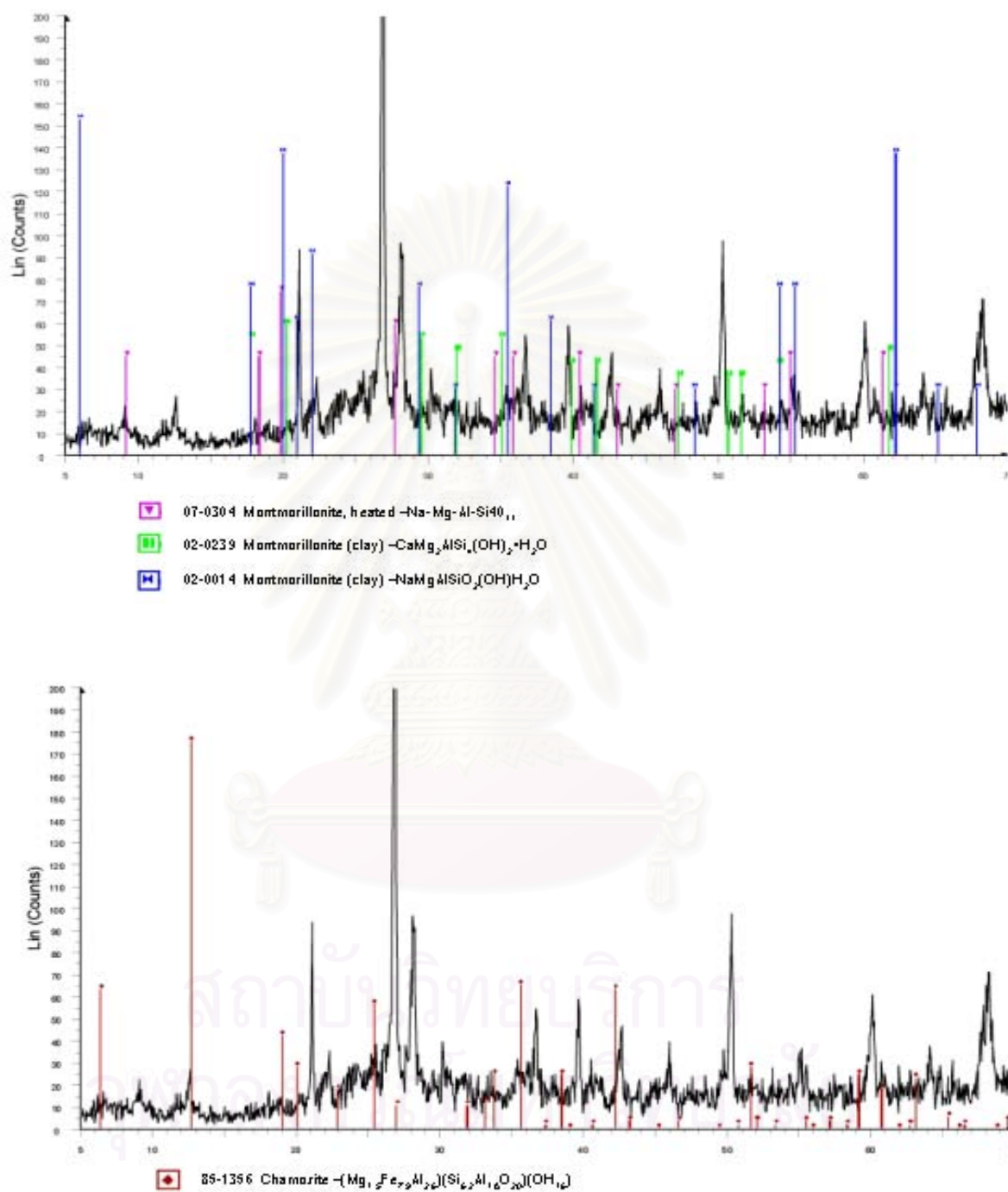


Figure E.8 X-ray diffractogram in  $>114\mu\text{m}$  Chao Phraya sediment.

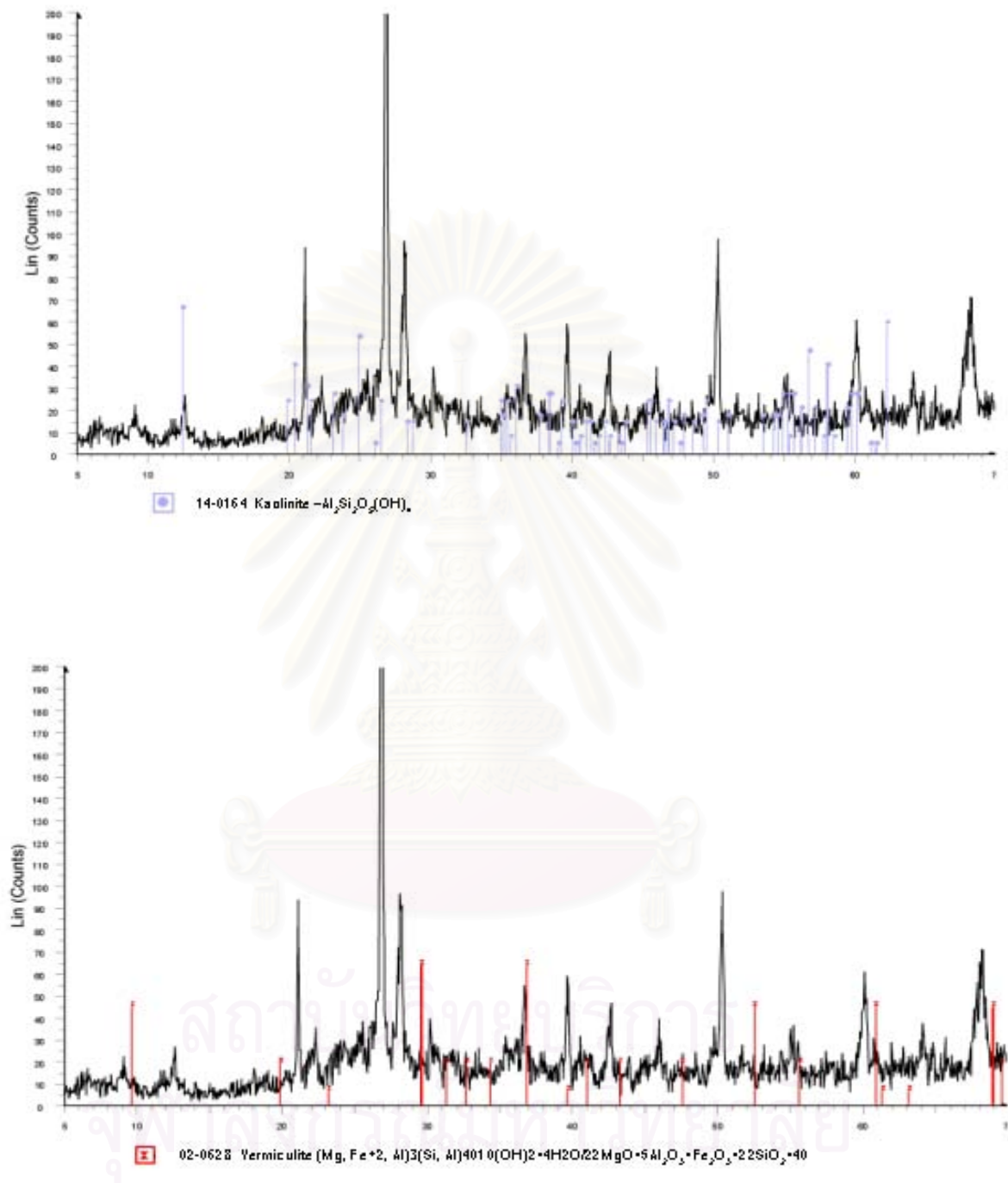


Figure E.8 X-ray diffractogram in  $>114\mu\text{m}$  Chao Phraya sediment (cont.)

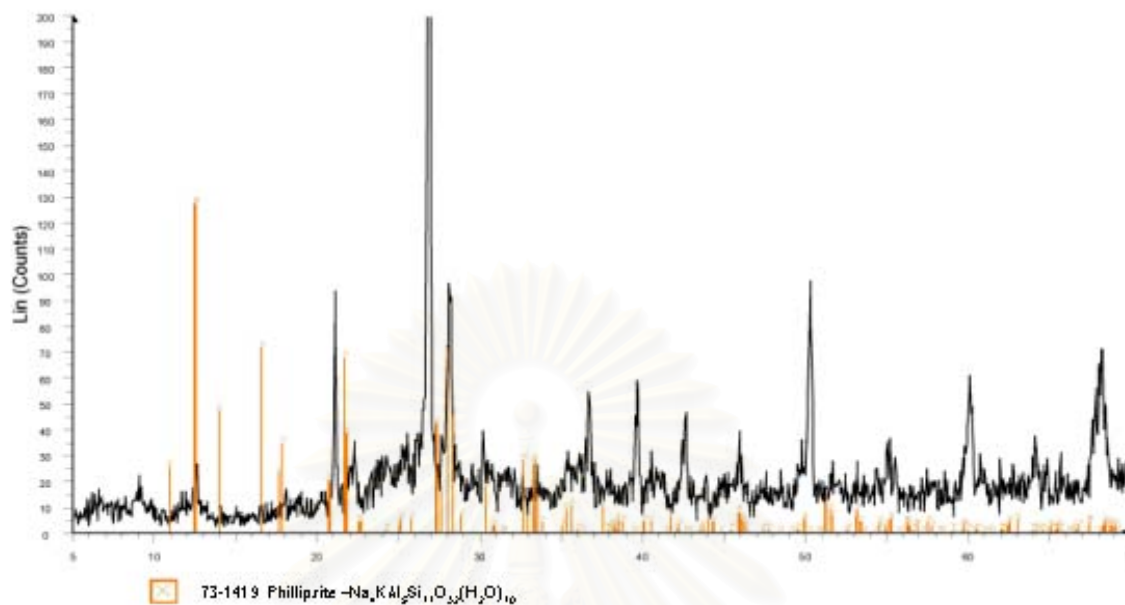


Figure E.8 X-ray diffractogram in  $>114\mu\text{m}$  Chao Phraya sediment (cont.)

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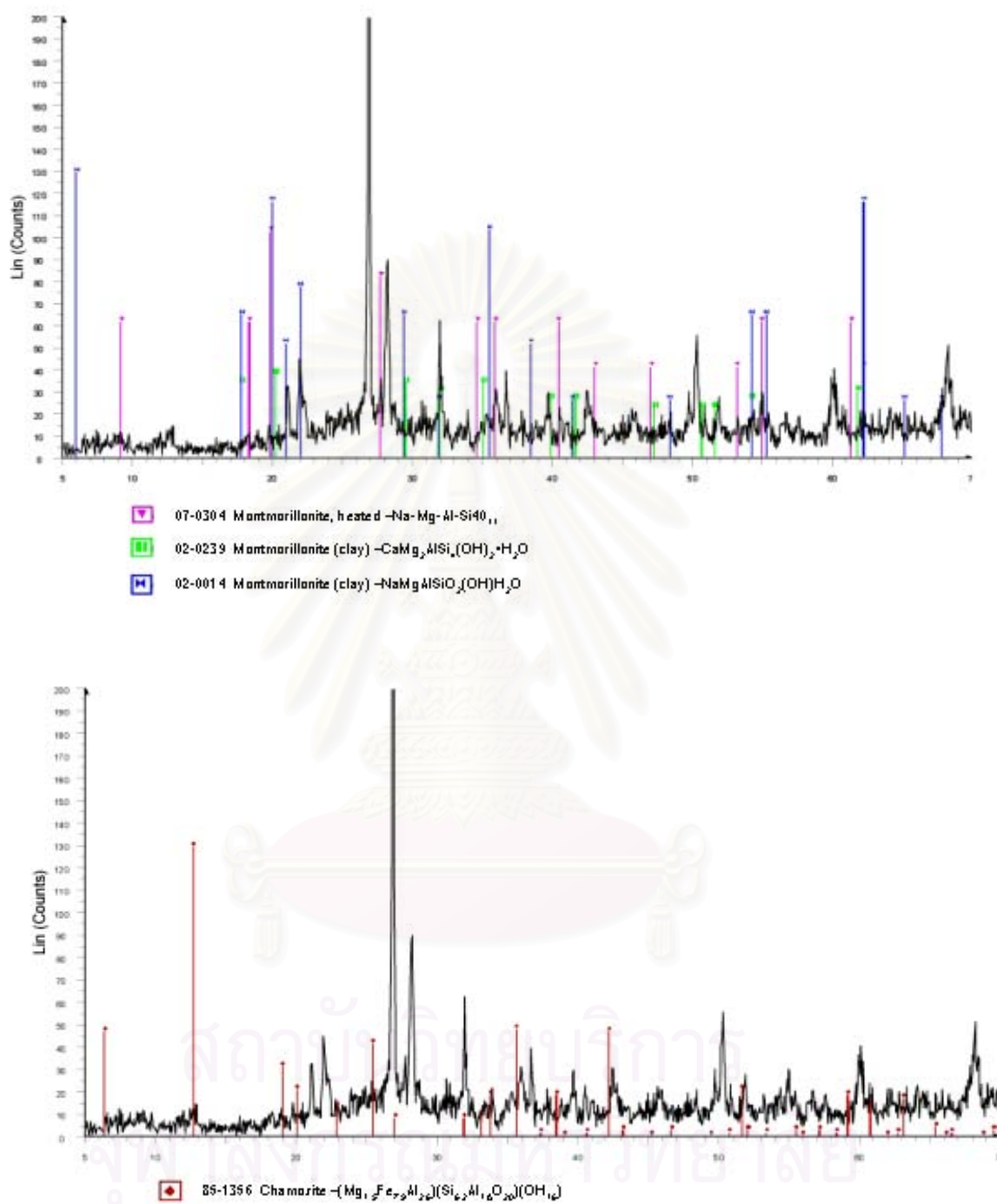


Figure E.9 X-ray diffractogram in non-sieve Chao Phraya sediment.

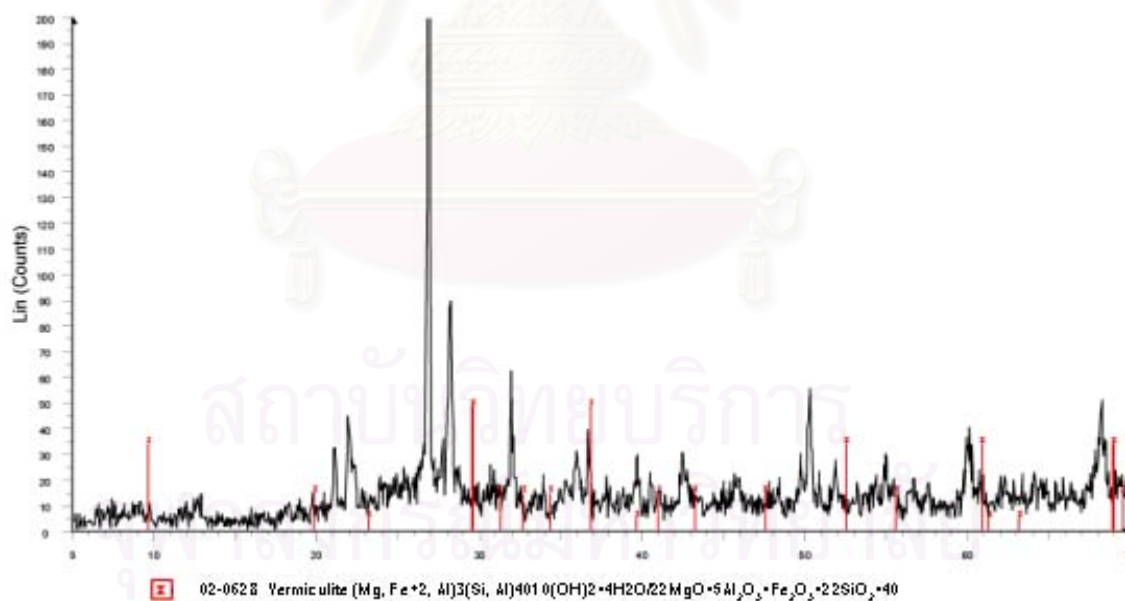
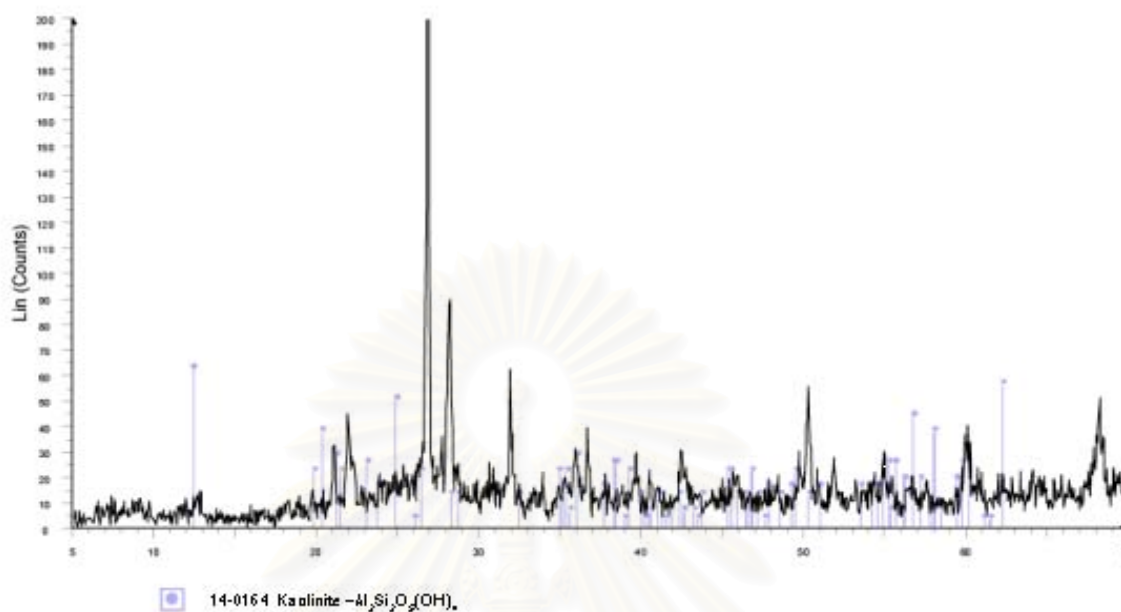


Figure E.9 X-ray diffractogram in non-sieve Chao Phraya sediment (cont.)



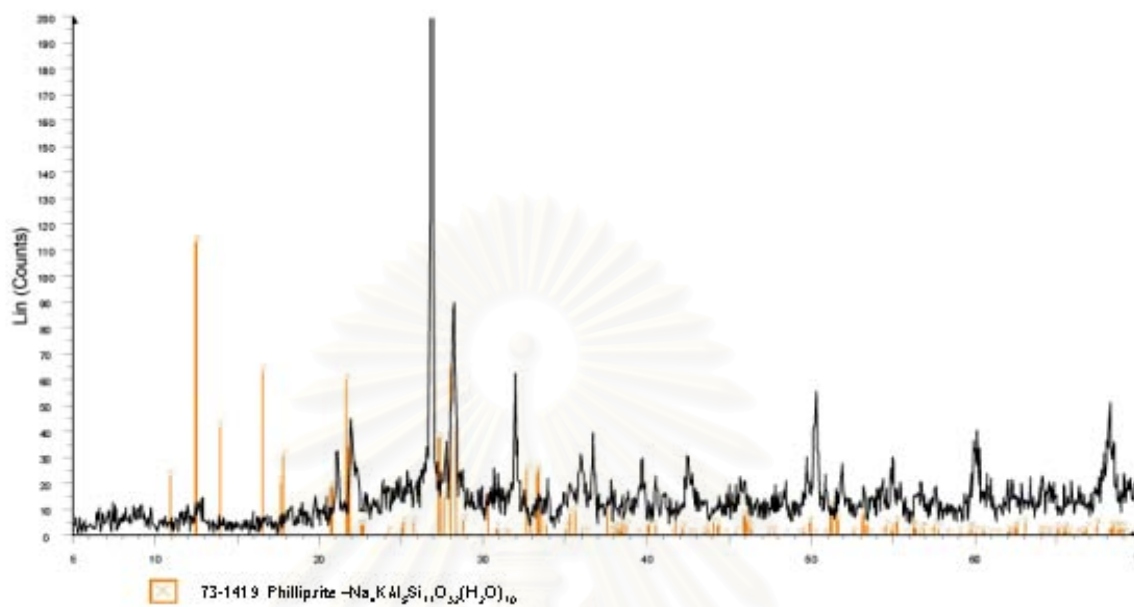


Figure E.9 X-ray diffractogram in non-sieve Chao Phraya sediment (cont.)

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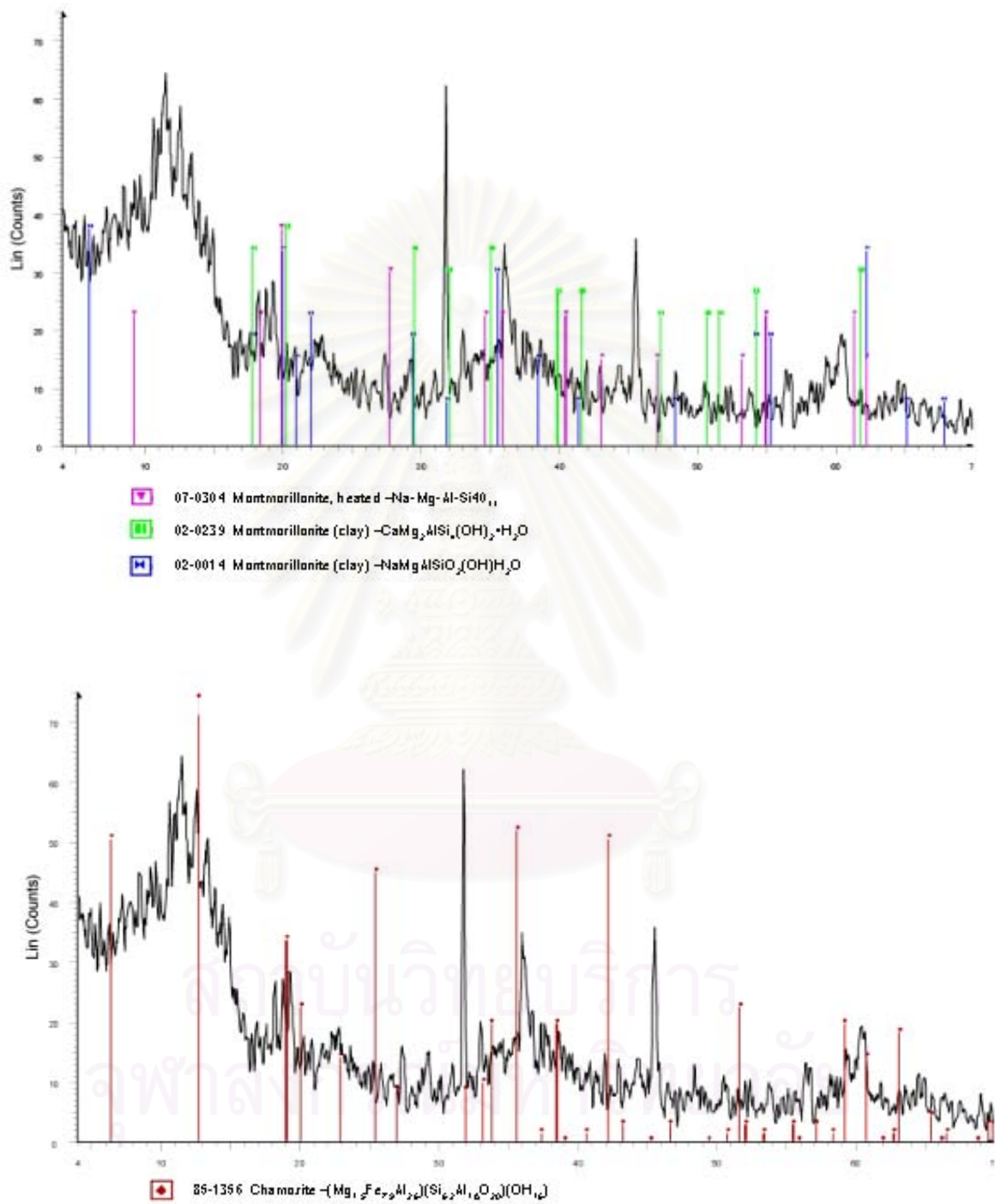


Figure E.10 X-ray diffractogram in Manganese bound silicate sediment.

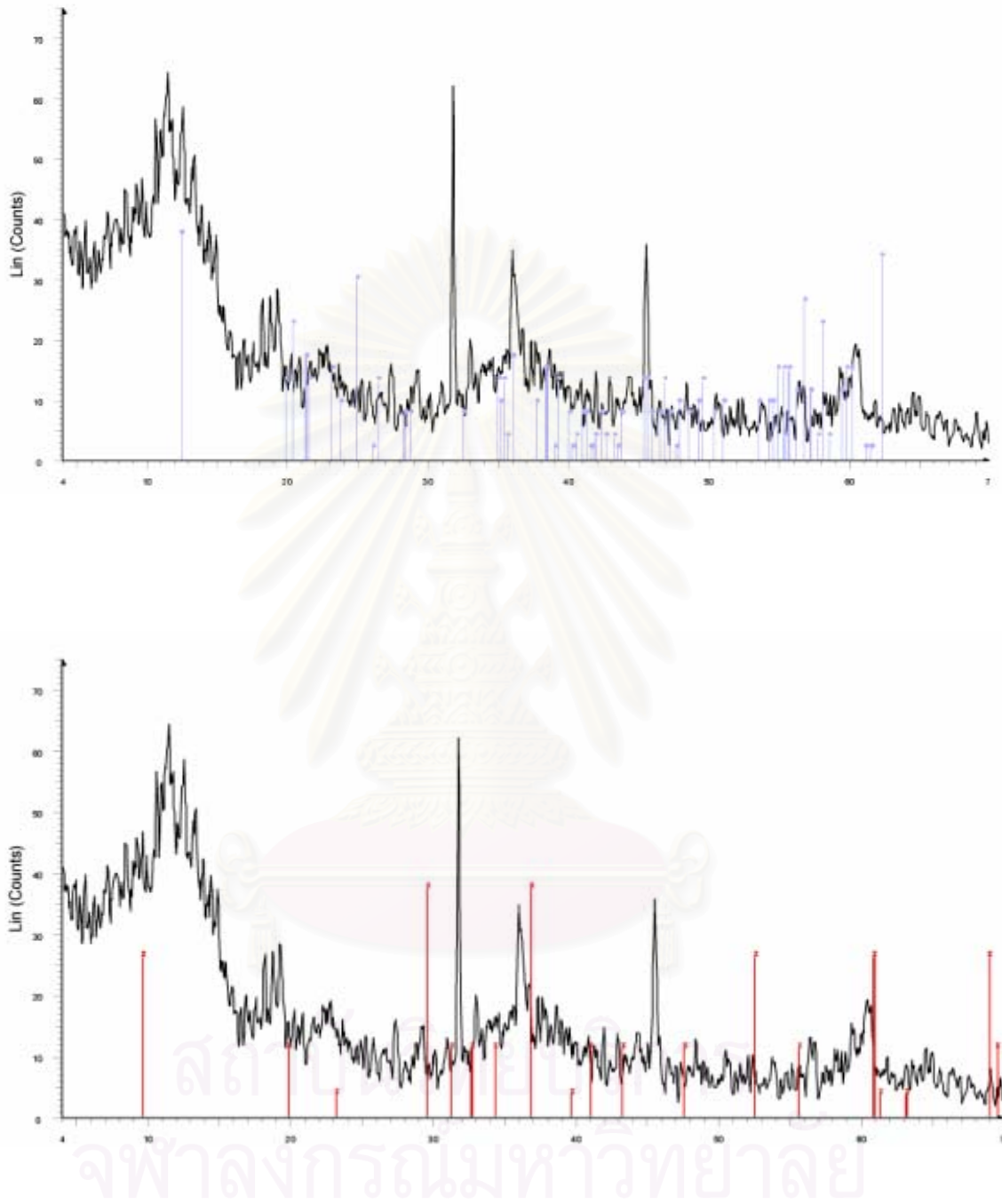


Figure E.10 X-ray diffractogram in Manganese bound silicate sediment.(cont.)

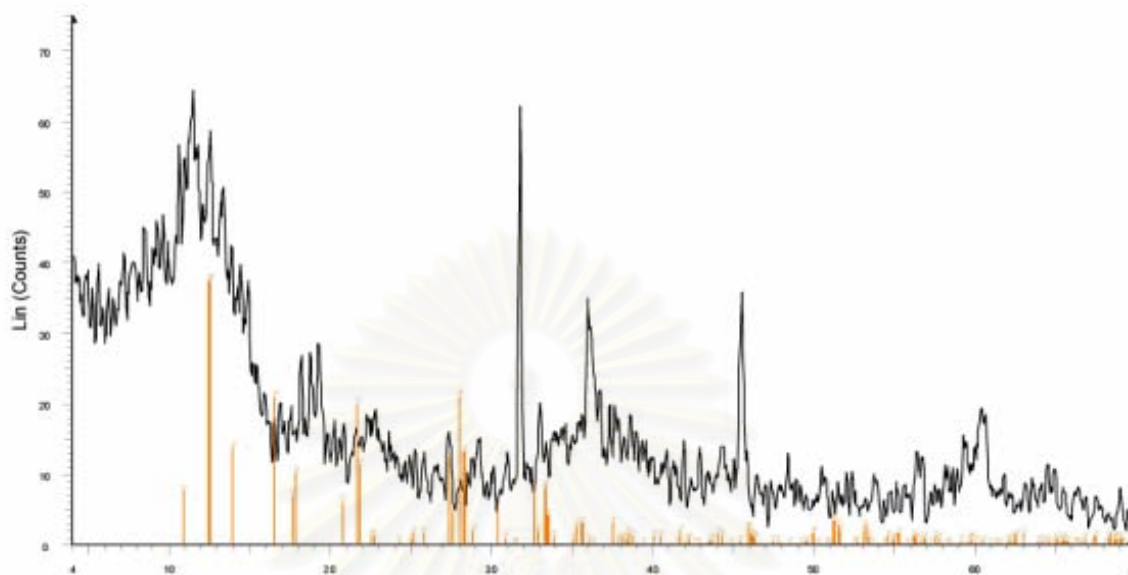


Figure E.10 X-ray diffractogram in Manganese bound silicate sediment.(cont.)

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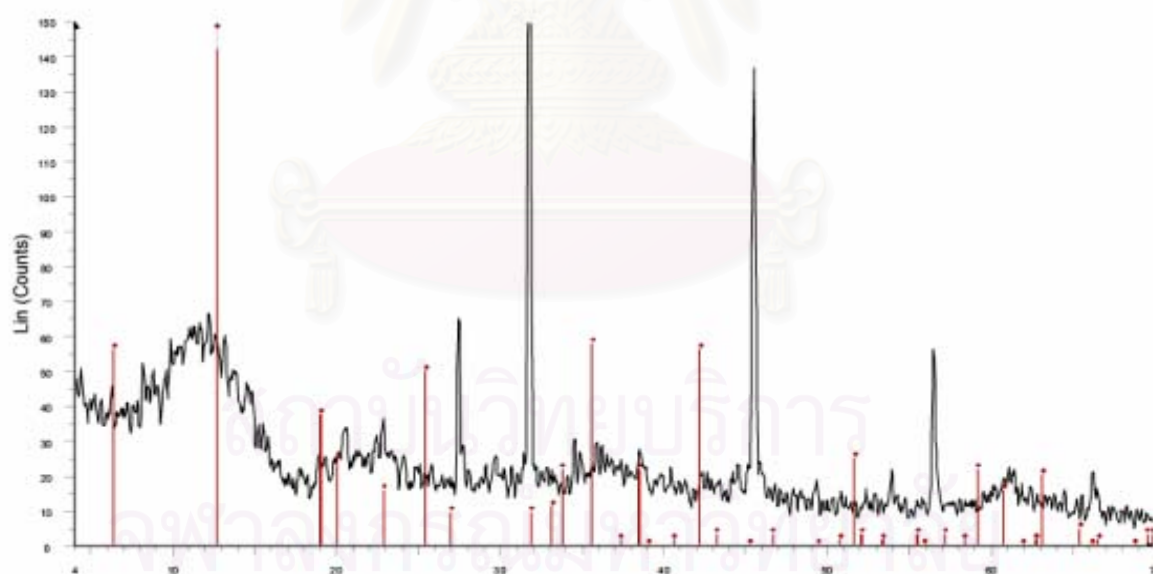
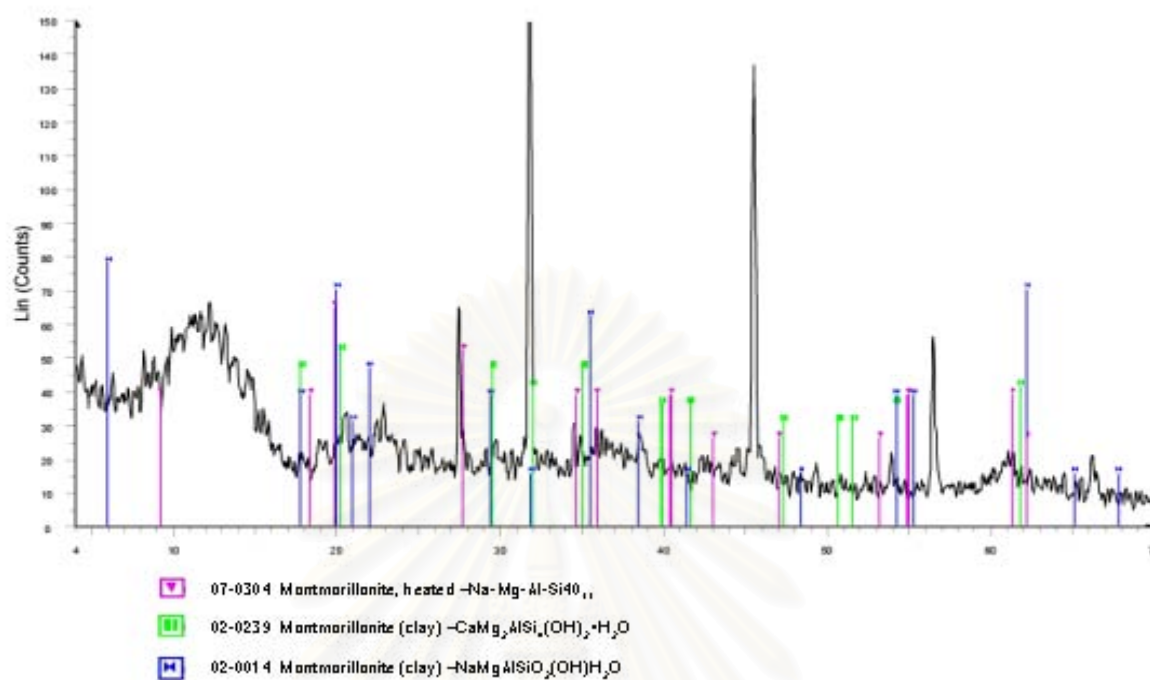


Figure E.11 X-ray diffractogram in Aluminum bound silicate sediment.

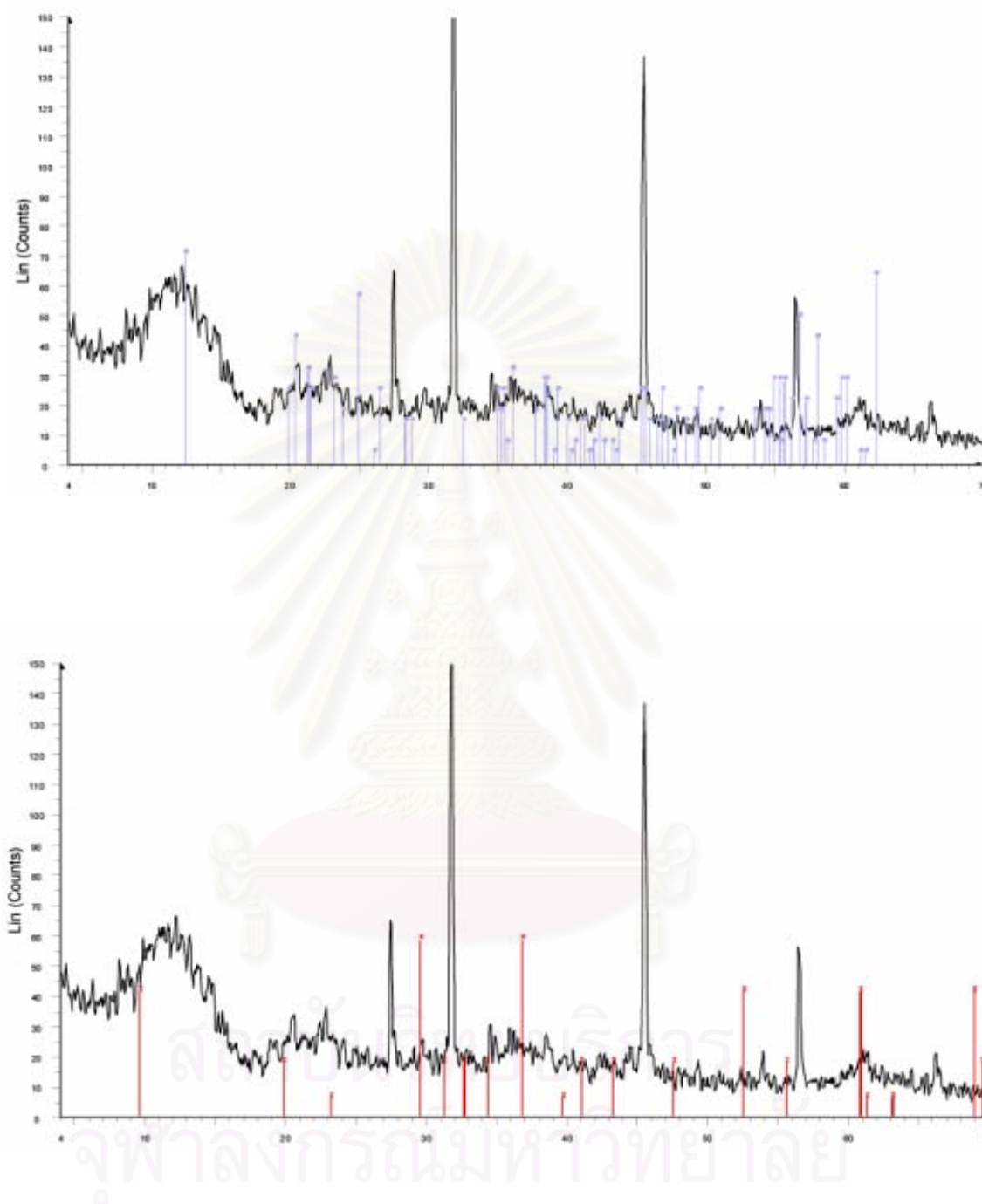


Figure E.11 X-ray diffractogram in Aluminum bound silicate sediment.(cont.)

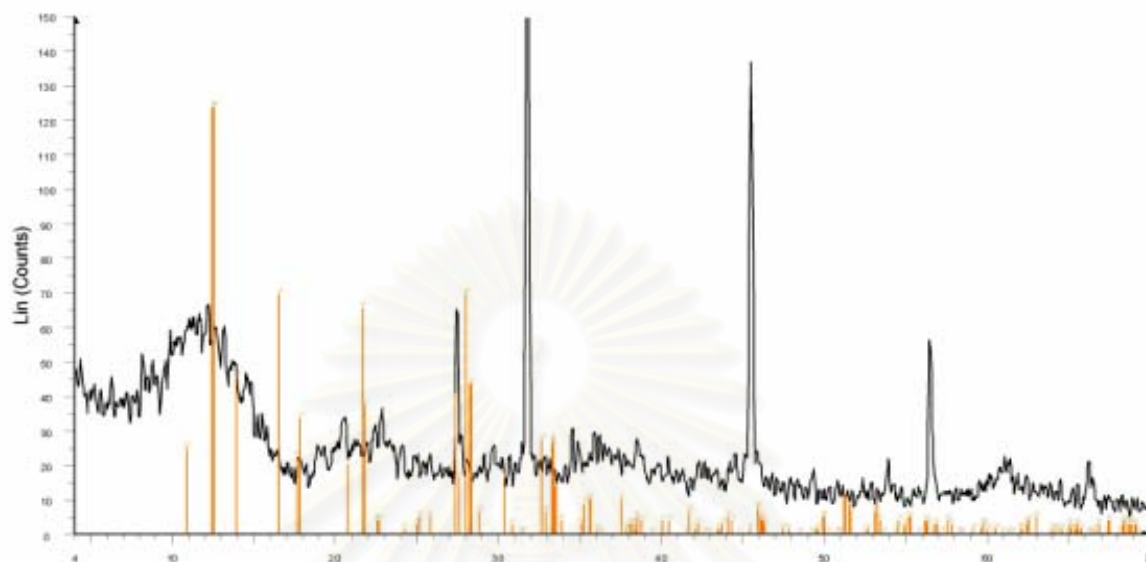


Figure E.11 X-ray diffractogram in Aluminum bound silicate sediment.(cont.)

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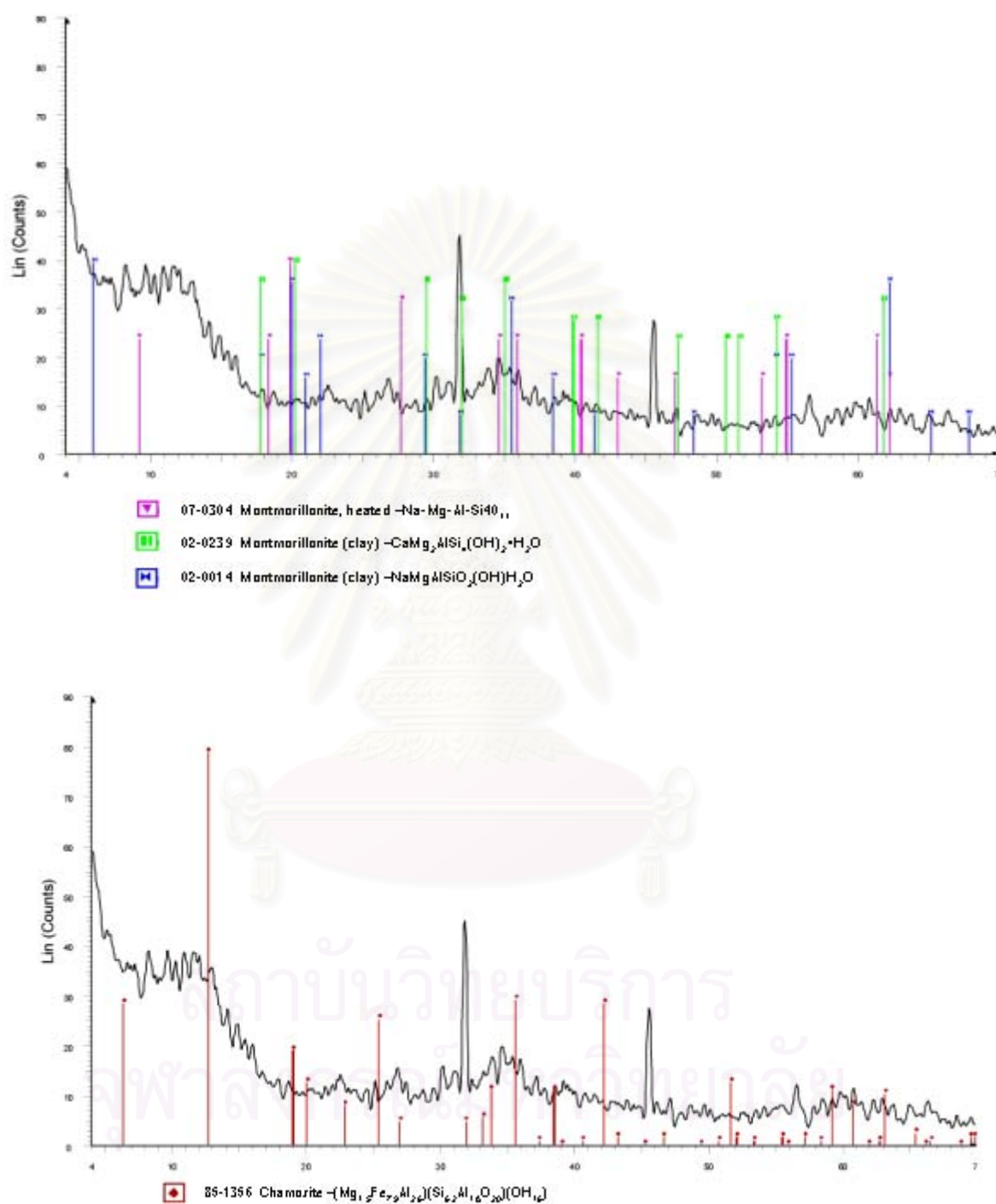


Figure E.12 X-ray diffractogram in Iron bound silicate sediment.



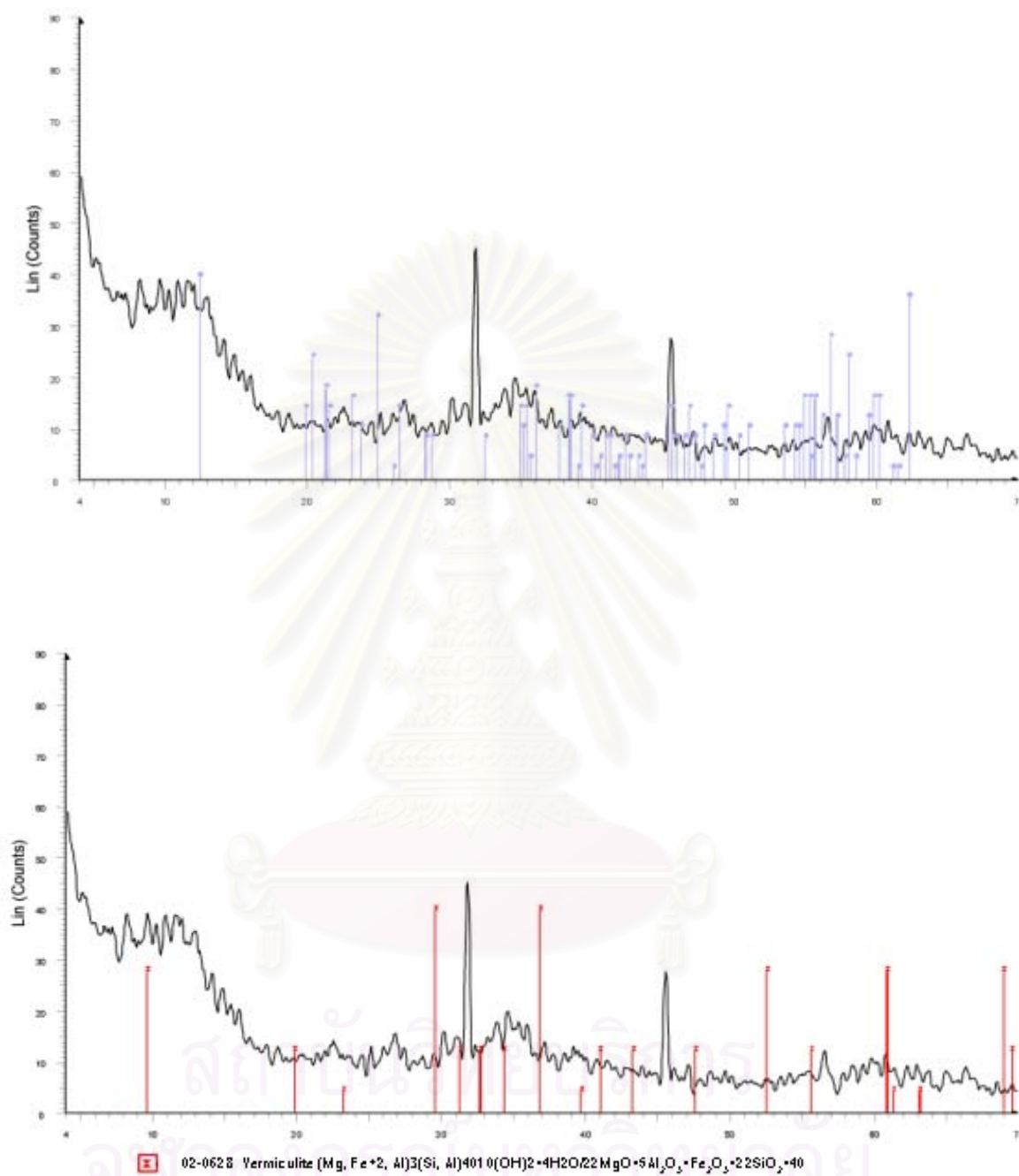


Figure E.12 X-ray diffractogram in Iron bound silicate sediment.(cont.)

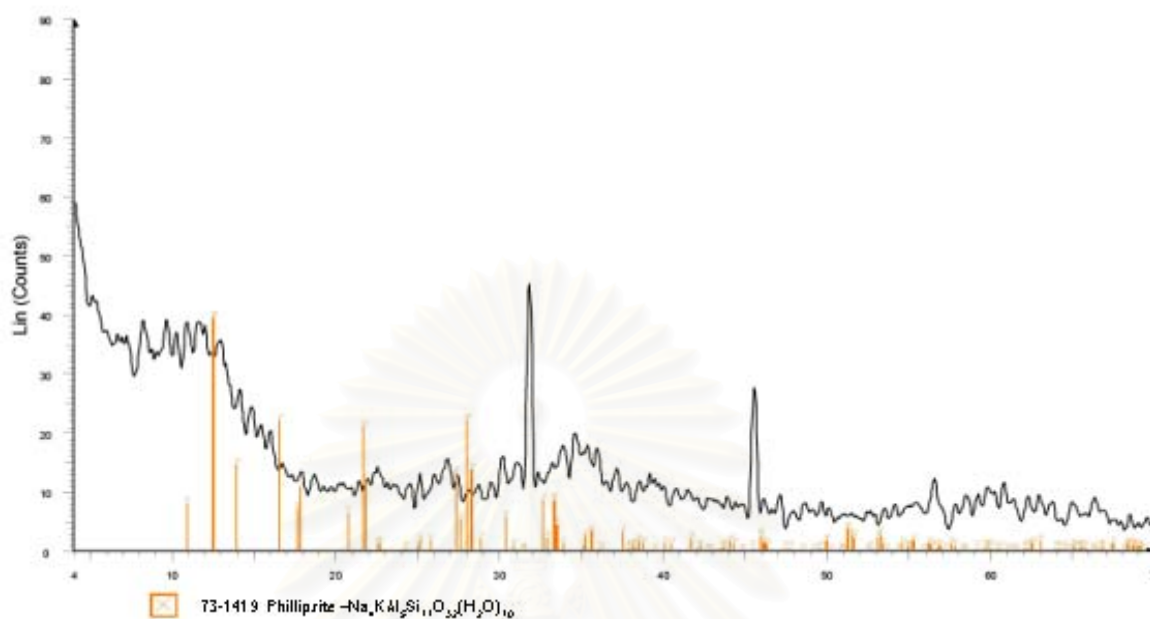


Figure E.12 X-ray diffractogram in Iron bound silicate sediment.(cont.)

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## BIOGRAPHY

Daroonwan Sakuna was born on April 7, 1979 in Phitsanuloke. She graduated with a Bachelor Degree of Science in 1999 from Department of Marine Science, Faculty of Science, Chulalongkorn University. The she continued her master study for a Master Degree in Chemical Oceanography at the same department.



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