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ลักษณะเฉพาะทางธรณีเคมีของน้ำพุร้อนบ่อคลิ้ง  
จังหวัดราชบุรีและน้ำพุร้อนหินดาด จังหวัดกาญจนบุรี

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GEOCHEMICAL CHARACTERISTICS OF BOR KLUENG HOT SPRING, RATCHABURI  
PROVINCE AND HIN DAD HOT SPRING, KANCHANABURI PROVINCE

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**Abstract**

Hot spring is one of the important natural resources for consuming, tourism or even generating electricity. Our purposes are to study the geochemical properties of hot spring from Hin Dad hot spring, Thong Pha Phum district, Kanchanaburi Province and Bor Klueng hot spring, Suan Phueng district, Ratchaburi Province. Water samples from each hot spring were collected for measure cations, anions, silica contents and stable isotope ( $\delta D$  and  $\delta^{18}O$ ) and imply their geochemical characteristic. The physical properties of both hot springs have been measured, Hin Dad hot spring has a surface temperature of 42.2°C, pH of 7.56, and conductivity of 835 uS/cm, and Bor Klueng has a surface temperature of 52°C, pH of 7.82, and conductivity of 242 uS/cm. The results on piper diagram shows that Hin Dad is dominated by  $Ca^{2+}$ ,  $HCO^-$  and  $CO_3^{2-}$ , it is temporary hardness water or shallow fresh groundwater, which ions come from dissolving of calcite, Bor Klueng is dominated by  $Na^+$ ,  $K^+$ ,  $HCO^-$  and  $CO_3^{2-}$ , it is alkali carbonate water or deep groundwater influenced by ion exchange, the ions come from contacting between hot water and surrounding rocks. Both hot springs are immature waters according to Na-K-Mg ternary diagram. The reservoir temperature calculated from Na-K-Ca geothermometry of Hin Dad ranges 300-380°C and Bor Klueng ranges 310-390°C, from silica geothermometry of Hin Dad ranges 50-65°C and Bor Klueng ranges 64-78°C, but the temperature from Na-K-Ca geothermometer is not appropriate because the water-rock interaction didn't reach the equilibrium. The water source of both hot springs is from rainwater in Kanchanaburi, determined by stable isotope data. The contents of ions which exceed the drinking water limit from Hin Dad hot spring is Pb, and for Bor Klueng hot spring is As, F and Pb, both of them aren't suitable for consumption. Due to medium reservoir temperature (50-70 °C) of both hot springs, their proper use is for tourism, bathing and drying agriculture products. This study can be implied for other hot springs in Thailand which have similar properties.

**Keywords:** Hot spring, Geochemistry

ลักษณะเฉพาะทางธรณีเคมีของน้ำพุร้อนบ่อคลิ้ง จังหวัดราชบุรี และน้ำพุร้อนหินดาด จังหวัด  
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**บทคัดย่อ :**

น้ำพุร้อนเป็นทรัพยากรธรรมชาติที่มีความสำคัญอย่างหนึ่งทั้งในแง่ของการเป็นแหล่งน้ำสำหรับอุปโภค แหล่งท่องเที่ยว หรือผลิตกระแสไฟฟ้าจากพลังงานความร้อนใต้พิภพ โดยงานวิจัยนี้มีจุดมุ่งหมายเพื่อศึกษาคุณสมบัติทางธรณีเคมีของน้ำพุร้อนหินดาด อำเภอทองผาภูมิ จังหวัดกาญจนบุรี และน้ำพุร้อนบ่อคลิ้ง อำเภอสวนผึ้ง จังหวัดราชบุรี โดยเก็บตัวอย่างน้ำจากน้ำพุร้อนทั้งสองแห่งเพื่อทำการวัดปริมาณไอออนบวก ไอออนลบ ซิลิกา และไอโซโทปเสถียรของออกซิเจน-18 และดิวเทอเรียม และทำการตรวจวัดคุณสมบัติทางกายภาพของน้ำพุร้อนทั้งสองแห่ง โดยน้ำพุร้อนหินดาดมีอุณหภูมิพื้นผิว 42.2 องศาเซลเซียส ค่า pH เท่ากับ 7.56 และค่าการนำไฟฟ้าเท่ากับ 835 uS/cm และน้ำพุร้อนบ่อคลิ้งมีอุณหภูมิพื้นผิวเท่ากับ 52 องศาเซลเซียส ค่า pH เท่ากับ 7.82 และค่าการนำไฟฟ้าเท่ากับ 242 uS/cm จากแผนภาพไพเพอร์พบว่าในน้ำพุร้อนหินดาดจะพบไอออนหลักคือ  $Ca^{2+}$   $HCO^-$  และ  $CO_3^{2-}$  จัดเป็นน้ำกระด้างชั่วคราวหรือน้ำบาดาลจืดที่ได้รับผลจากการละลายของแร่แคลไซต์ ส่วนน้ำพุร้อนบ่อคลิ้งจะพบไอออนหลักคือ  $Na^+$   $K^+$   $HCO^-$  และ  $CO_3^{2-}$  จัดเป็นน้ำประเภท  $Na-HCO_3^-$  หรือน้ำบาดาลในระดับลึกที่ได้รับผลจากการแลกเปลี่ยนไอออน โดยไอออนเกิดจากการทำปฏิกิริยาระหว่างน้ำร้อนและหินรอบข้าง ผลจากแผนภาพสามเหลี่ยม Na-K-Mg พบว่าการทำปฏิกิริยาระหว่างน้ำพุร้อนทั้งสองกับหินรอบข้างแห่งยังไม่เข้าสู่ภาวะสมดุล จากการคำนวณอุณหภูมิของแหล่งกักเก็บโดยใช้สมการ Na-K-Ca พบว่าน้ำพุร้อนหินดาดมีอุณหภูมิแหล่งกักเก็บอยู่ในช่วง 300-380 องศาเซลเซียส น้ำพุร้อนบ่อคลิ้งมีอุณหภูมิแหล่งกักเก็บอยู่ในช่วง 310-390 องศาเซลเซียส และจากการคำนวณโดยใช้สมการของซิลิกา พบว่าน้ำพุร้อนหินดาดมีอุณหภูมิแหล่งกักเก็บอยู่ในช่วง 50-65 องศาเซลเซียส น้ำพุร้อนบ่อคลิ้งมีอุณหภูมิแหล่งกักเก็บอยู่ในช่วง 64-78 องศาเซลเซียส แต่เนื่องจากน้ำพุร้อนทั้งสองแห่งยังไม่เข้าสู่สมดุล อุณหภูมิของแหล่งกักเก็บจากสมการ Na-K-Ca จึงไม่เหมาะสม จากข้อมูลไอโซโทปเสถียรสามารถบอกแหล่งที่มาของน้ำได้ว่ามาจากน้ำฝนที่ตกในบริเวณจังหวัดกาญจนบุรี เมื่อเทียบปริมาณไอออนที่พบกับค่ามาตรฐานน้ำดื่มพบว่าน้ำพุร้อนหินดาดมีปริมาณของ Pb เกินค่ามาตรฐาน และน้ำพุร้อนบ่อคลิ้งมีปริมาณของ As, F และ Pb เกินค่ามาตรฐาน น้ำพุร้อนทั้งสองจึงไม่เหมาะสมสำหรับการบริโภค จากค่าอุณหภูมิของแหล่งกักเก็บของน้ำพุร้อนทั้งสองแหล่งมีอุณหภูมิอยู่ในช่วงปานกลาง (50-70 องศาเซลเซียส) การใช้ประโยชน์ที่เหมาะสมจึงเป็นด้านการท่องเที่ยว การแช่น้ำร้อน และตากแห้งผลิตภัณฑ์ทางการเกษตร การศึกษาน้ำพุร้อนนี้สามารถประยุกต์กับแหล่งน้ำพุร้อนอื่นๆ ในไทยได้อีกด้วย

**คำสำคัญ:** น้ำพุร้อน ธรณีเคมี

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# CHAPTER 1

## INTRODUCTION

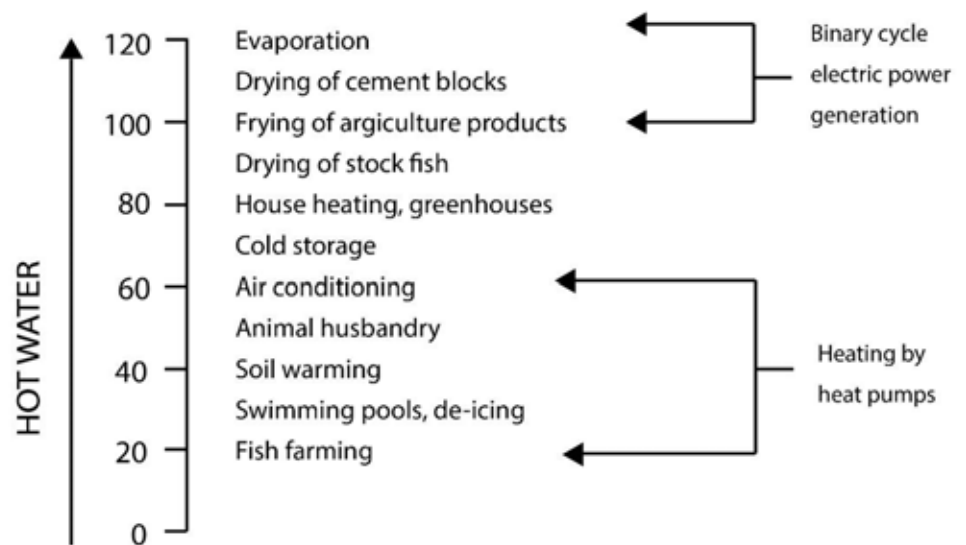
### 1.1 Rationale

Hot spring or thermal spring is a spring with water temperature higher than the air temperature of surrounding region. The first definition of hot spring is the water issues considerably higher than that of the ground (OED, 1989) but this has limitation to explain the marine hot spring. The second definition, the spring with water temperature above 36.7 °C or above the human body temperature, is widely accepted. For the thermal spring, some definitions are also existed; spring with water temperature above 36.7 °C (Meinzer, 1923) the spring where the water temperature is higher than local mean air temperature (Bates and Jackson, 1987). However, the variation of temperature due to seasonal change is not considered; and the spring water mean temperature is higher than the mean air temperature (Waring, 1965; Edmunds et al., 1968; Pentecost et al., 2003)

Hot springs are an important natural resource, which can be developed for tourism and/or a source of geothermal energy. Their potential depends on temperature and volume of reservoir and amount of flowing water through the reservoir (D. E. White, 1965). Hot springs can be found around the world and high enthalpy hot springs have been used to produce electricity from geothermal energy in several countries since 1913. Over 80 countries have identified the geothermal resources and 58 countries have quantified records of geothermal utilization (Fridleifsson, 2001), e.g. hot spring is used to produce energy about 1.7 MW in the UK (Gluyas, 2018).

In Thailand, 118 hot springs have been found, especially in the northern, western and southern part of the country (Raksakulwong, 2015). The surface temperature of hot springs in Thailand ranges between 40 – 100 °C. Generally, hot springs in northern Thailand have the highest surface temperature of 80-100 °C or higher, medium-temperature in southern Thailand (60-80°C). For the springs in

western and eastern have the lowest surface temperature (40-60 °C). High-temperature hot springs in the northern part of the country are usually used for generating geothermal energy and drying process (Raksakulwong, 2015). The medium-temperature hot springs are used for tourism and agriculture like boiling bamboo shoots or eggs and the low-temperature hot springs (40-60 °C) are used for public water, recreational ground tourism and health therapy (Raksakulwong, 2015). The usage of hot springs in Thailand depends on its surface temperature following the Lindal diagram (Figure 1.1).



**Figure 1.1** Temperature range and using of hot spring (modified from Lindal, 1973)

The Department of Mineral Resources (DMR) has divided hot springs in Thailand into 2 types: (1) hot spring related or originating from an igneous rock fracture (2) hot spring founded in a sedimentary rock layer overlying granitic basement (DMR, 2004). The DMR has surveyed and measured temperature, pH and fluoride content from hot springs around Thailand (DMR, 2001). Also, the Department of Groundwater (DWG) has examined 16 hot springs, which have the highest temperature, measured their chemical properties e.g. pH, Total Dissolved solids (TDS), anions ( $\text{CO}_3^{2-}$ ,  $\text{HCO}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ ), cations ( $\text{SiO}_2$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{As}^{2+}$ ). In DWG study, the concentration of Na-K-Ca and  $\text{SiO}_2$  are used for calculating reservoir temperature (White et al., 1952; Fournier, 1972; Arnórsson et al.,

1983). Accordingly, the result shows that only 5 hot springs may have a potential for being a geothermal energy source (Department of Groundwater Resource, 2016). The hot springs in Chiang Mai and Chiang Rai have a surface temperature of 80°C or above, so they are expected to have the most potential for geothermal energy production (Singharajwarapan et al., 2012). Hot springs in Chaing Mai are systematic study and developed to produce electricity from geothermal energy since 1979, current production of 150-250 KW and still ongoing evolving new system (Ramingwong, 2000; Korjedee, 2002; Singharajwarapan, 2012).

In the recent years, there are some studies on hot spring in Thailand. In northern Thailand, there is a study about a naturally-occurring health hazard in drinking-water resources due to the effect of fluoride from the occurrence of the hot springs (Chuah et al., 2015). In southern Thailand, hot springs in Ranong were examined based on a geological and geophysical method for the detailed study (Chaturongkawanich, 1997), hot springs in Surat Thani were studied using magnetotelluric and gravity survey for utilizing geothermal energy (Chaturongkawanich, 2001). Modeling for water reservoir and heat sources of hot springs in Phang Nga province was studied based on a geological survey, resistivity and magnetotelluric data (Ngansom et al., 2017). In eastern Thailand, a hot spring in Chantaburi has been reported to be a Na-HCO<sub>3</sub><sup>-</sup> water, high pH (9.0) which exceed the consuming recommendation and low reservoir temperature about 77-98 °C. This hot spring is considered as properly used for heating, drying or tourism (Charusiri, 2003). In western Thailand, Bor Klueng hot spring in Ratchaburi province has been investigated for the diversity of bacteria and notify high sulfur contents (Kanokratana, 2004). Hin Dad hot spring in Kanchanaburi has been studied for tourism management and resistivity for subsurface exploration together with electrical images (Giao, 2008). Nevertheless, there is still no data on chemical compositions for both Hin dad and Bor Klueng hot springs.

Both Hin Dad and Bor Klueng hot springs are famous for tourism in Western Thailand and are a source of water for people in the local area. Based on previous

research, elemental contents in hot spring (e.g. Si, Na, K and Ca) can be used to calculate reservoir temperature (Fournior and Truesdell, 1972; Arnórsson et al., 1983; Yock, 2009), stable isotope of oxygen ( $\delta^{18}\text{O}$ ) and deuterium ( $\delta\text{D}$ ) to determine the source of water by comparing with Local Meteoric Water Line (Rafic, 2008; Zachary, 2017). Also, the chemistry of water can be used to predict corrosion, slag, and effect in an environment (Wright, 2008). Therefore, the geochemistry data from Hin Dad and Bor Klueng can give insight into the reservoir temperature, the source of water and properly used and management of this hot spring.

## 1.2 Objectives

1. To study elemental compositions and stable isotope ratio ( $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) of Hin Dad and Bor Klueng hot spring.
2. To compare geochemical characteristics of Bor Klueng and Hin Dad hot springs.

## 1.3 Study Area

The study area is located in western Thailand (Figure 1.2). Hin dad hot spring is in Thong Pha Phum district, Kanchanaburi province (14°39' N, 98°43' E). Bor Klueng hot spring is in Suan Phueng district, Ratchaburi province (13°31' N and 99°14' E). The climate of the study area is influenced by the southwest monsoon in summer (May-October) which brings warm and moist air from the Indian Ocean toward Thailand causing abundant rainfall in the region, and the northeast monsoon brings cold and dry air mass during winter (November-February). Between March to May, the precipitation might come from the tropical cyclones. The nearest weather station in for both hot spring is Kanchanaburi station, the stable isotope data of D and  $^{18}\text{O}$  is measured from the precipitation stored in this station from 2013 to 2015 (Figure 1.3). Hot springs in this region can have seasonal variation in temperature affected by the southwest monsoon. When the precipitation rate increases, hot spring can discharge more water, the temperature of hot spring might drop due to evaluated flow rate.



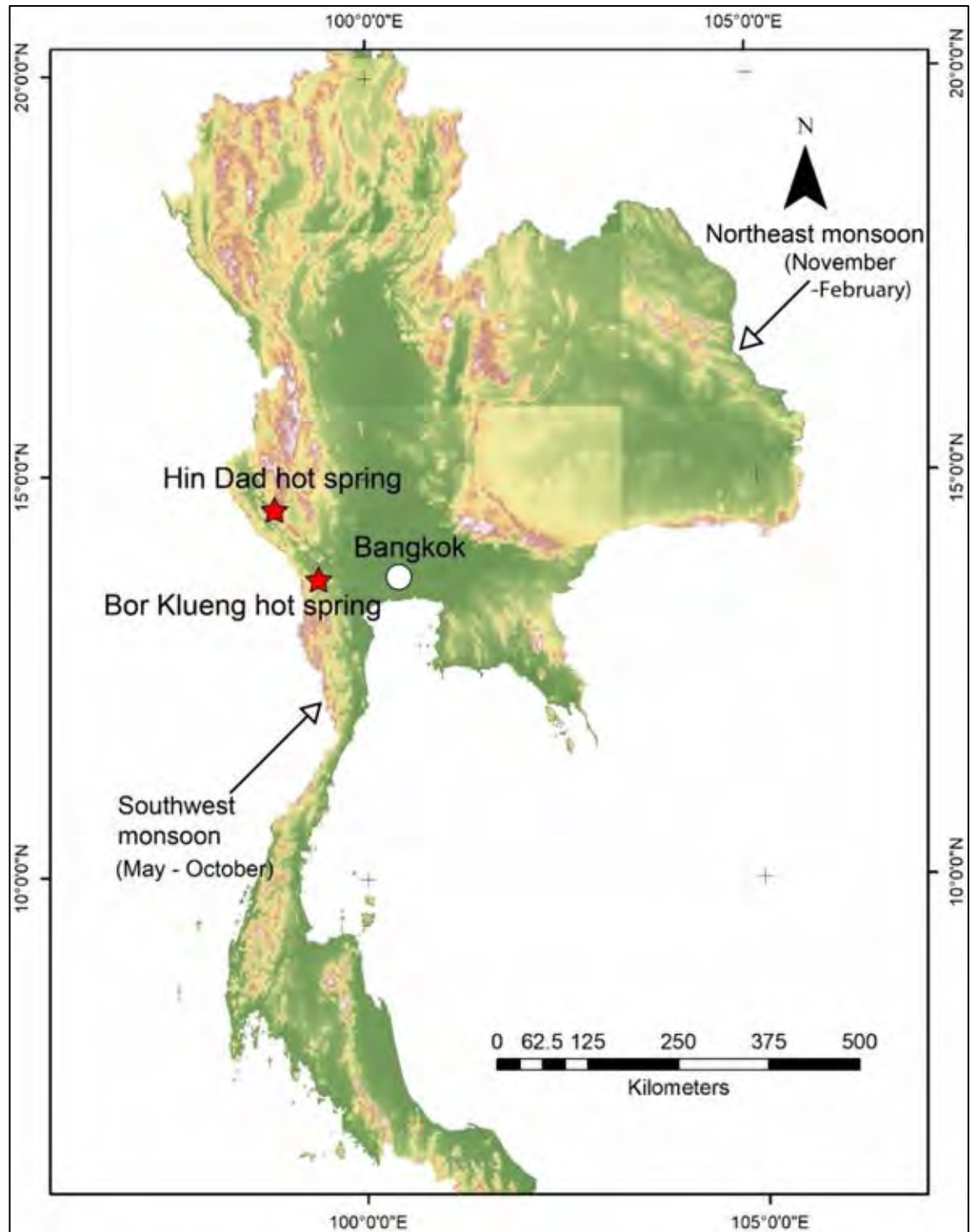
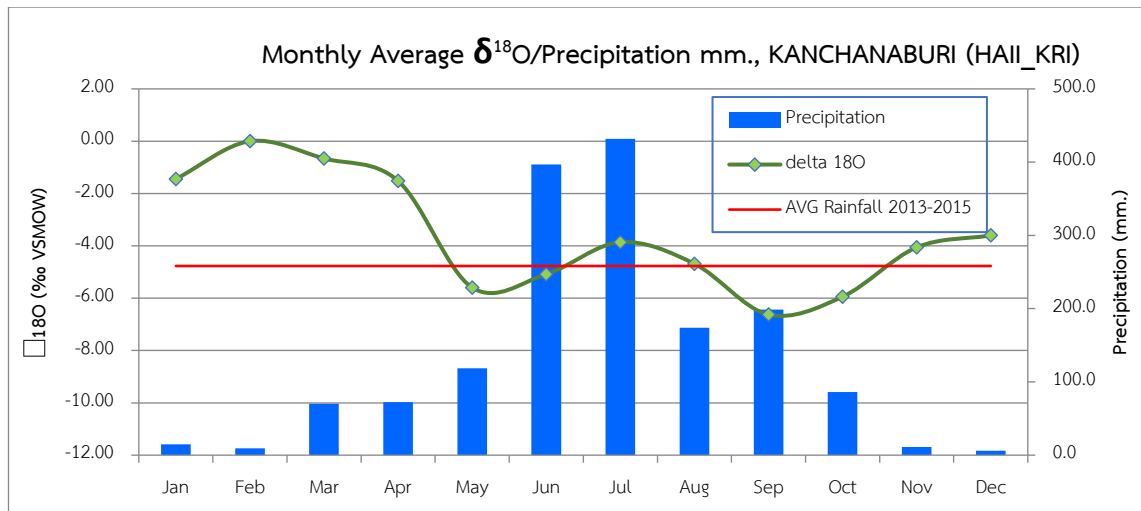


Figure 1.2 Location of study area



**Figure 1.3** monthly average of precipitation and oxygen isotopes ( $\delta^{18}\text{O}$ ) of Kanchanaburi from 2013-2015. The red line is annual average rainfall and the green line is mean  $\delta^{18}\text{O}$  values of each month (data from TINT, 2015)

#### 1.4 General Geology

Hin Dad hot spring is situated in unit Qa (Figure 1.4), consisting of an alluvium quaternary sediment. The nearest rock units are unit Ju and Pr; Ju consists of mudstone, siltstone, sandstone, and limestone, while Pr consists of limestone and dolomitic limestone interbedded with chert (DMR, 2007). It is surrounded by the minor fault of Three pagoda fault group (DMR, 2000), 5 km in Northeast direction. The heat source of this hot spring might come from the movement of fault or the decay of U-Th from nearby Kgr unit.

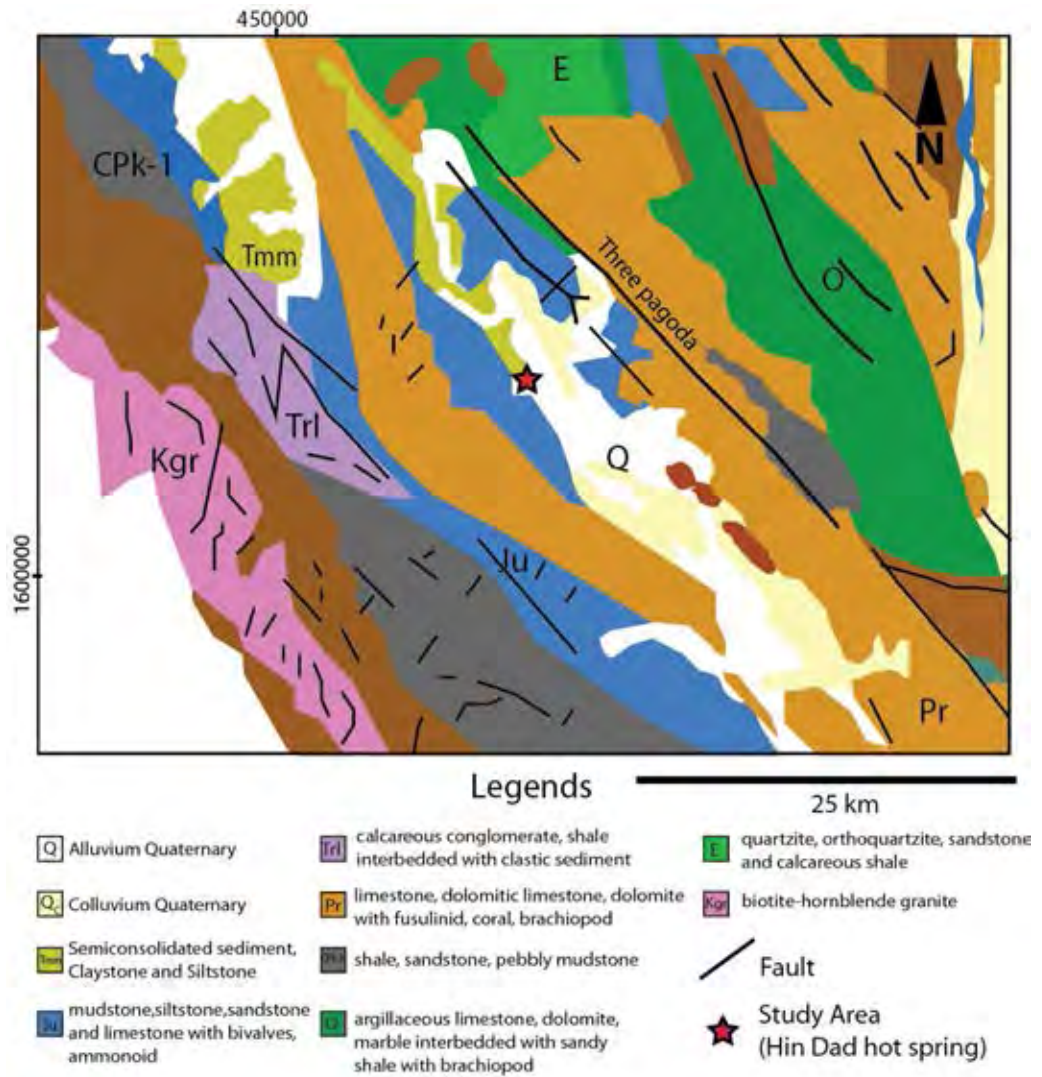


Figure 1.4 Geological map of Kanchanaburi province (modified from DMR, 2007) with the location of Hin Dad hot spring (red star).

Bor Klueng hot spring is in unit Kgr (Figure 1.5), which is biotite-hornblende granite, muscovite granite, and porphyritic granodiorite. It is also located in the area of the minor fault of Three pagoda fault group, 22 km east from major fault and 10 km east from the minor fault (DMR, 2000).

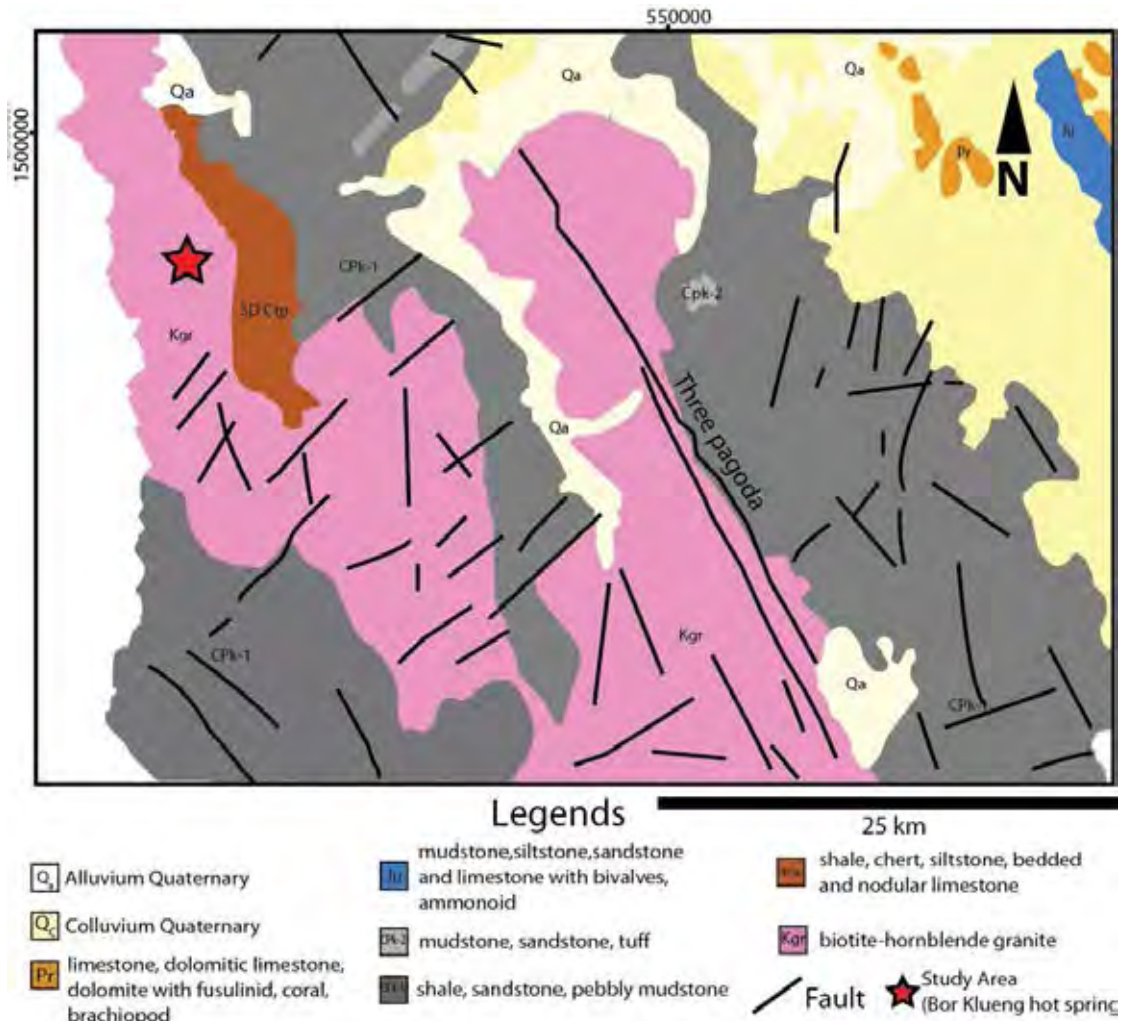


Figure 1.5 Geological map of Ratchaburi province (modified from DMR, 2007) with the location of Bor Klueng hot spring (star).

## 1.5 Literature Reviews

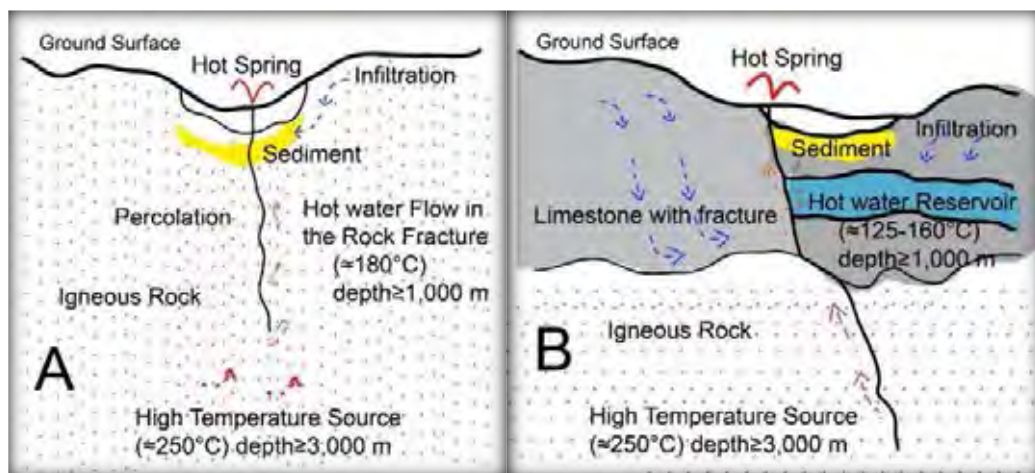
### 1.5.1 Research on Hot springs in Thailand

Hot springs in Thailand can be classified by their origin into 2 types (Figure 1.6);

(A) Hot springs which are directly related to igneous rock fracture.

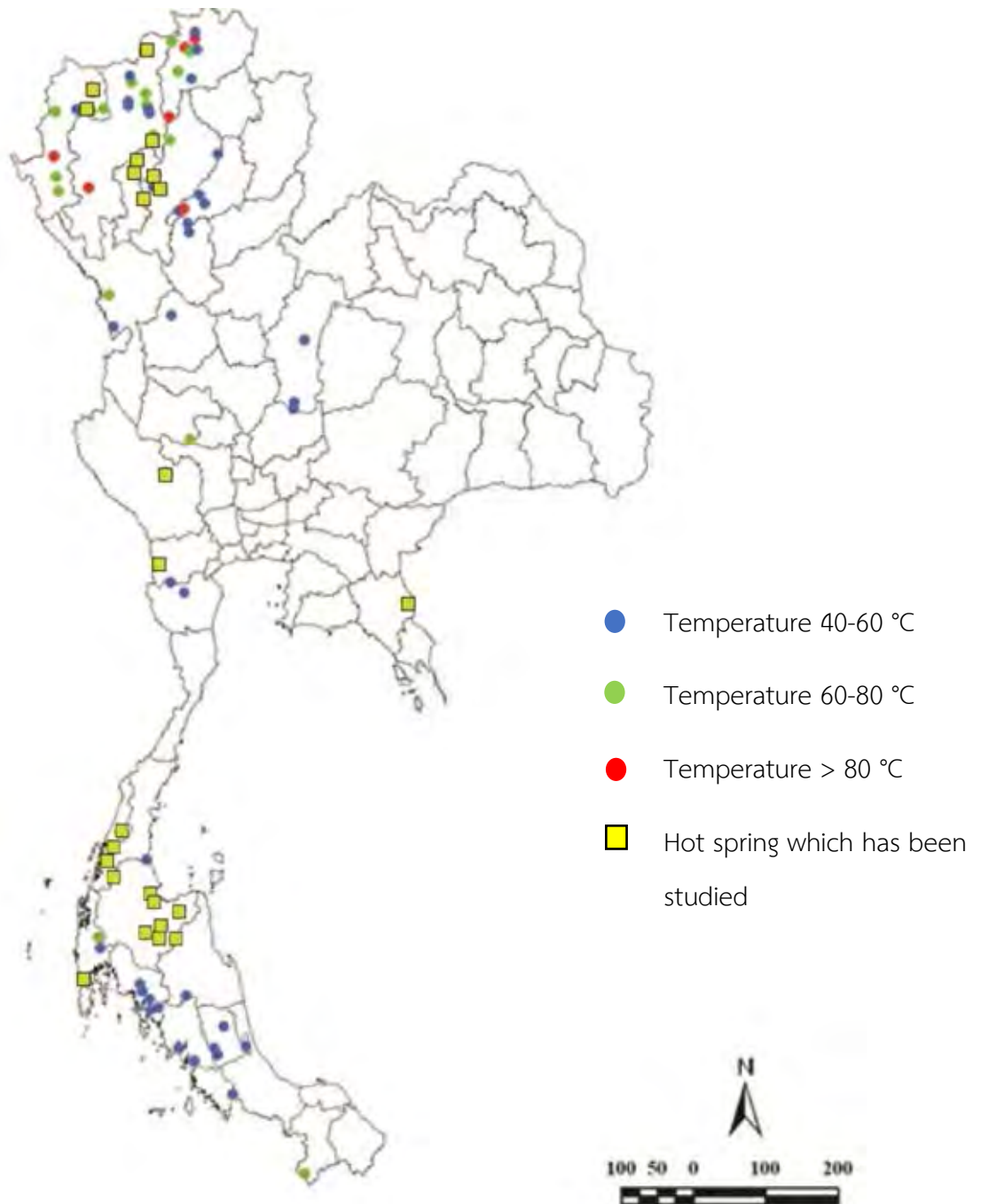
(B) Hot springs founded between sedimentary rock layers over a granitic basement.

Commonly the hot spring type (A) exhibits higher temperatures and mineral contents than type (B) (Giao, 2007)



**Figure 1.6** Two models of hot springs in Thailand; (A) hot spring which water directly heated from igneous rock and (B) hot spring which lies over sedimentary terrain, infiltration through rock fracture and heated by granitic basement (Figure from Giao, 2007)

118 hot springs have been found and examined the surface water temperature in Thailand (Figure 1.6) (GTSC, 2016). Only 5 hot springs have been studied in detail based on Department of Groundwater Resources data.



**Figure 1.7** Distribution of hot springs in Thailand and their surface water temperature. The blue color circles show the sites that have a surface water temperature of 40-60 °C, green color circles 60-80 °C, red color circles >80 °C and yellow color square show the sites that have been studied in detail and published the data.

### 1.5.2 Silica Geothermometry

When silicate minerals react with water, they will form  $\text{HSiO}_4^{3-}$  solution and reach equilibrium, the solubility of silica depends on temperature and pressure. Therefore, the silica content in hot spring water can be used for calculating underground reservoir temperature (White et al., 1956; Fournier, 1977; Fournier and Potter, 1982; Arnórsson et al., 1998). Silica has many polymorphs those are quartz, chalcedony, cristobalite, coesite or even amorphous silica, which have dissimilar solubility. Therefore, there are several equations to calculate reservoir temperature from each type of silica (Fournier, 1977). During the last four decades, several equations have been reviewed and updated by researchers for accurate results based on the type of silica and the purpose of their study.

In this study, the equations No.1-9 in Table 1.1 are used for calculating reservoir temperature, which was proposed by Arnórsson et al (1998), Arnórsson (2000), Fournier (1977) and Fournier and Potter (1982). These equations cover every polymorph of silica that may occur in hot spring, the results from calculation will be a range of possible reservoir temperature (Fournier, 1977).

No.	Polymorph	Equation	Range (°C)	Reference
1	Quartz-no steam loss	$t (^{\circ}\text{C}) = \frac{1309}{5.19 - \log S} - 273.15$	25-250	Fournier (1977)
2	Quartz <sup>a</sup>	$t (^{\circ}\text{C}) = \frac{1522}{5.19 - \log S} - 273.15$	25-250	Fournier (1977)
3	Quartz	$t (^{\circ}\text{C}) = 42.198 + 0.28831S - 3.6686 \times 10^{-4}S^2 + 3.1665 \times 10^{-7}S^3 + 77.034 \log S$	25-900	Fournier and Potter (1982)
4	Quartz <sup>a</sup>	$t (^{\circ}\text{C}) = -53.5 + 0.11236S - 0.5559 \times 10^{-4}S^2 + 0.1772 \times 10^{-7}S^3 + 88.390 \log S$	-	Fournier and Potter (1982)
5	Quartz	$t (^{\circ}\text{C}) = -55.3 + 0.3659S - 5.3954 \times 10^{-4}S^2 + 5.5132 \times 10^{-7}S^3 + 74.360 \log S$	0-350	Arnórsson et al. (1998)

6	Quartz <sup>a</sup>	$t (^{\circ}\text{C}) = \frac{-66.9 + 0.1378S - 4.9727 \times 10^{-5}S^2 + 1.0468 \times 10^{-8}S^3 + 87.841 \log S}{1}$	0-350	Arnórsson (2000)
7	Chalcedony	$t (^{\circ}\text{C}) = \frac{1032}{4.69 - \log S} - 273.15$	0-250	Fournier (1977)
8	Chalcedony	$t (^{\circ}\text{C}) = \frac{1112}{4.91 - \log S} - 273.15$	-	Arnórsson (2000)
9	Amorphous Silica	$t (^{\circ}\text{C}) = \frac{731}{4.52 - \log S} - 273.15$	0-250	Fournier (1977)

S represents silica concentration as SiO<sub>2</sub> in mg/kg.

<sup>a</sup> Silica concentration in water initially in equilibrium with quartz after adiabatic boiling to 100°C

**Table 1.1** Equations for silica geothermometer (modified from Hassan, 2016)

### 1.5.3 Na-K-Ca Geothermometry

Besides Silica, Sodium, Potassium, and Calcium have been used for calculating reservoir temperature (Fournier and Truesdell, 1972). These elements are incorporated into the water during the water-rock interaction. Rocks have various minerals (e.g. feldspar, clay mineral, biotite), at the proper temperature and pressure they can dissolve in water and reach equilibrium between a plagioclase and K-feldspar. We can also calculate the reservoir temperature from the concentration of Na, K and Ca (Fournier and Truesdell, 1972; Santoyo, 2012) Many equations have been published for different ratio of Na-K-Ca, different temperature, and pressure.

No.	Ions	Equation	Range (°C)	Reference
10	Na-K	$t (^{\circ}\text{C}) = \frac{856}{\log (\text{Na/K})+0.857} - 273.15$	25-250	Truesdell (1976)
11	Na-K	$t (^{\circ}\text{C}) = \frac{1217}{1.483 - \log (\text{Na/K})} - 273.15$	-	Fournier (1979)
12	Na-K	$t (^{\circ}\text{C}) = \frac{833}{0.857 - \log (\text{Na/K})} - 273.15$	-	Tonani (1980)
13	Na-K	$t (^{\circ}\text{C}) = \frac{933}{0.857 - \log (\text{Na/K})} - 273.15$	25-250	Arnórsson et al. (1983)



14	Na-K	$t (^{\circ}\text{C}) = \frac{1178}{1.470 - \log (\text{Na}/\text{K})} - 273.15$	-	Nieva and Nieva (1987)
15	Na-K	$t (^{\circ}\text{C}) = \frac{1390}{1.750 - \log (\text{Na}/\text{K})} - 273.15$	-	Giggenbach et al. (1988)
16	Na-K	$t (^{\circ}\text{C}) = \frac{876.3(\pm 26.26)}{\log \left( \frac{\text{Na}}{\text{K}} \right) + 0.8775(\pm 0.0508)} - 273.15$	-	Santoyo and Díaz-González (2010)
17	Na-K-Ca	$t (^{\circ}\text{C}) = \frac{1670}{2.24 + \log (\text{Na}/\text{K}) + \beta * \log (\text{Ca}^{1/2}/\text{Na})} - 273.15$	-	Fournier and Truesdell (1973)

Na K and Ca concentrations are given in mg/kg

**Table 1.2** Equations for Na K and Ca geothermometry (modified from Hassan, 2016)

For a high concentration of calcium, Fournier and Truesdell (1973) have developed the Na-K-Ca geothermometer (equation No.17), it is an equilibrium between Na-K feldspars plus conversion of calcium aluminosilicate minerals to calcite. This equation has the main advantage in comparison with quartz geothermometer and Na-K geothermometer.

For the equation No. 17, using  $\beta = 4/3$ , cations concentration in mg/kg and calculate temperature, if calculated temperature  $< 100^{\circ}\text{C}$  or  $[\log (\text{Ca}^{1/2}/\text{Na}) + 2.06]$  is negative, then change  $\beta$  to  $1/3$  and calculate again (Arnórsson, 2000). *Note: these geothermometers work best with high reservoir temperature ( $> 160^{\circ}\text{C}$ ) (Boden, 2016)*

### 1.5.4 Water chemistry diagram

#### 1.5.4.1 Piper Diagram

The Piper diagram is a visualized way to represent chemical composition of water sample in the hydro-geological study, it consists of 2 ternary diagrams and 1 diamond diagram (Figure 1.8). Ternary diagram of the bottom left is for plotting cations, on the right is for plotting anions, then project those plotted spots into the central diamond diagram. The cations are calcium, magnesium, and sodium plus potassium cations. The anions are sulfate, chloride, and carbonate plus hydrogen carbonate anions. The results on piper diagram can be grouped by hydrochemical facies, but there are various of classifications, up to the criterions and also can determine the hydrochemical processes and geological formations of the hot spring.

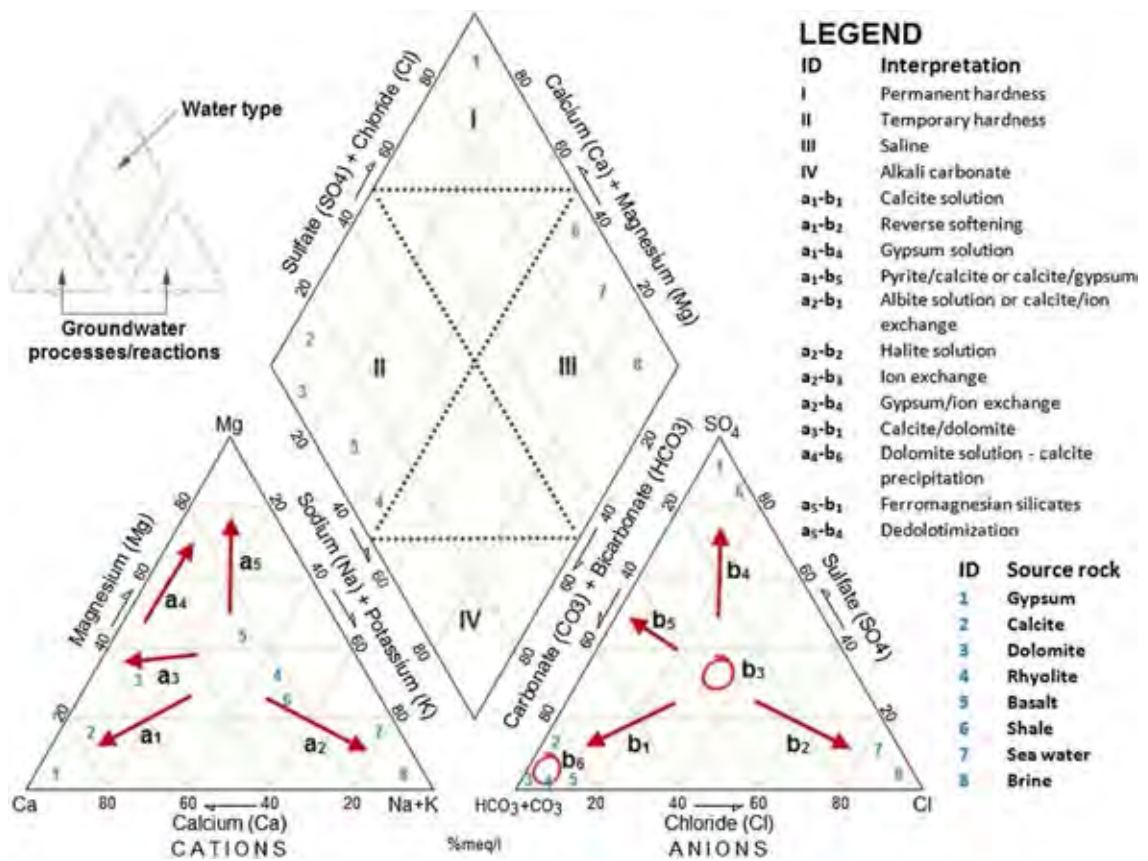


Figure 1.8 Piper plot and descriptions (Hounslow, 1995)

Type I water on a diamond diagram is calcium sulfate waters (gypsum groundwater and mine drainage), type II is calcium bicarbonate waters (shallow fresh groundwater), type III is sodium chloride waters (marine and deep ancient groundwater) and type IV is sodium bicarbonate waters (deep groundwater influenced by ion exchange). Piper diagram can also be used for determining the water-rock interaction. The plot ID No.1-8 in the diagram is used to identify the source rock.

#### 1.5.4.2 Ternary diagram Cl-SO<sub>4</sub>-HCO<sub>3</sub>

Different types of geothermal water can be classified using the chloride-sulfate-bicarbonate ternary diagram which proposed by Giggenbach (1999), the dissolved ions in hot spring water may originate from the original water but mostly they're coming from water-rock interaction or possibly dissolves of magmatic gas. The proportion of Cl-SO<sub>4</sub>-HCO<sub>3</sub> is varied through the different source, the results from this diagram are shown below.

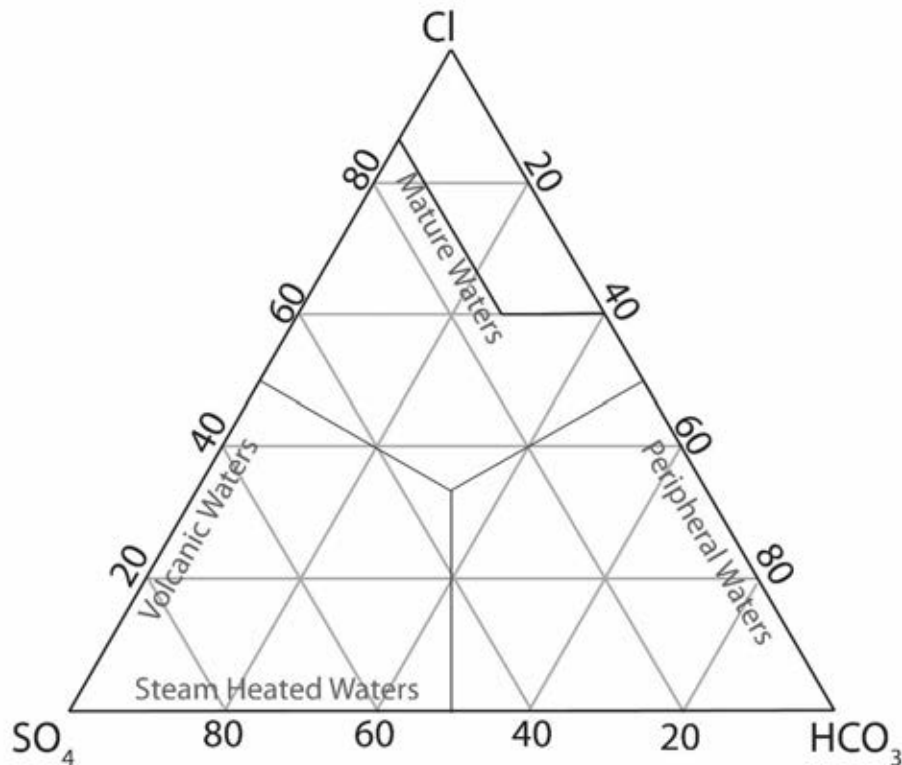


Figure 1.9 Cl-SO<sub>4</sub>-HCO<sub>3</sub> Ternary diagram (Giggenbach, 1999)

### 1.5.4.3 Ternary diagram Na-K-Mg

The concentration of ions dissolved in the hot spring is temperature dependent, but their reactions are not fast at low temperature, so Giggenbach has provided the ternary diagram which uses concentration of Na,  $K \cdot 10$  and  $1000 \cdot \sqrt{Mg}$  to determine the stage of equilibrium, that is immature waters, partially equilibrated waters and fully equilibrated waters, which shown below (Giggenbach, 1999).

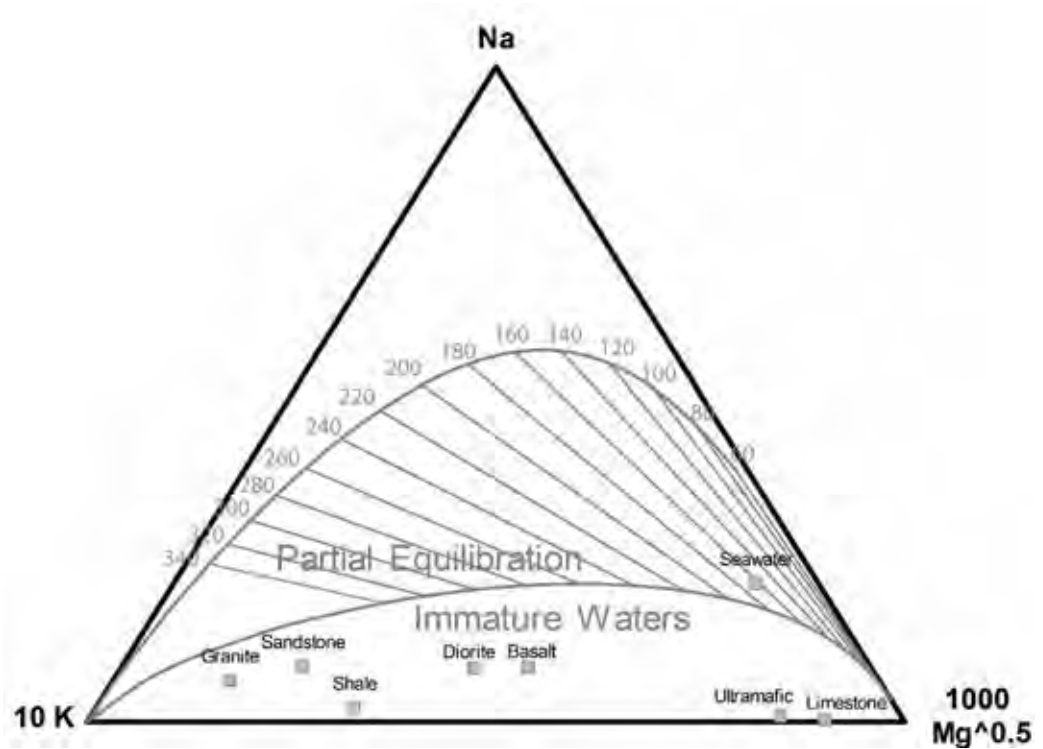


Figure 1.10 Na-K-Mg Ternary diagram (Giggenbach, 1999)

### 1.5.5 Stable isotopes of $\delta D$ and $\delta^{18}O$

The water molecule ( $H_2O$ ) consists of Hydrogen atom (H) and Oxygen atom (O). Normally Hydrogen has 2 stable isotopes  $^1H$  and  $^2H$  (or Deuterium, D), Deuterium has a natural abundance of about 0.0156% of all the naturally occurring hydrogen in the ocean. Oxygen has 3 stable isotopes  $^{16}O$ ,  $^{17}O$  and  $^{18}O$ . The most abundant isotope on earth is  $^{16}O$ , the ratio of  $^{18}O$  and  $^{16}O$  is often measured for interpreting changes in paleohydrology, paleoenvironment and paleoclimate (Sharp, 2017)

The ratio of D/H and  $^{18}\text{O}/^{16}\text{O}$  can be written by  $\delta\text{D}$  and  $\delta^{18}\text{O}$ , which come from

$$\delta\text{D} = \frac{[\text{D/H sample} - \text{D/H standard(SMOW)}] \times 1000}{\text{D/H standard(SMOW)}}$$

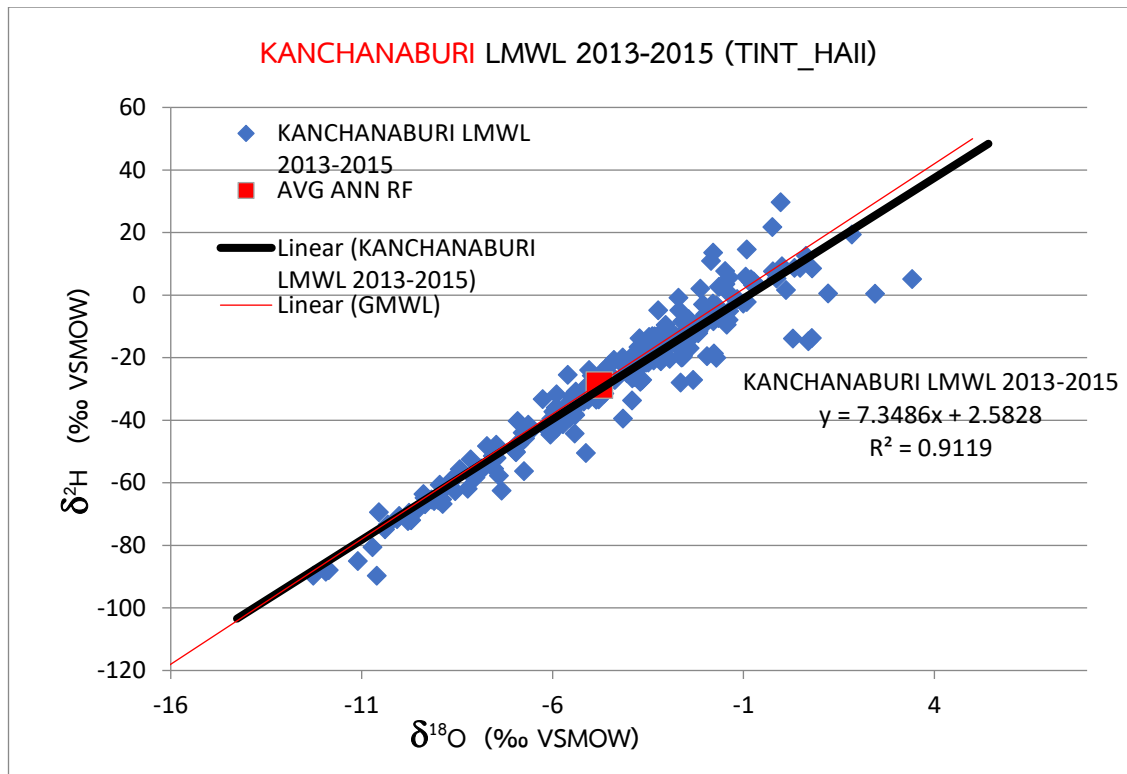
and

$$\delta^{18}\text{O} = \frac{[^{18}\text{O}/^{16}\text{O sample} - ^{18}\text{O}/^{16}\text{O standard(SMOW)}] \times 1000}{^{18}\text{O}/^{16}\text{O standard(SMOW)}}$$

reported in Per-mille (‰) (Drever, 2002).

Variation in  $\delta\text{D}$  and  $\delta^{18}\text{O}$  is caused by isotope fractionation process that partition stable isotope between 2 substances (Hoefs, 1997). We can use  $\delta\text{D}$  and  $\delta^{18}\text{O}$  data to determine the source of hot spring water by comparing with local meteoric water line (LMWL) in the study area. The local meteoric water line is a line created by plotting local rain  $\delta\text{D}$  on an X-axis and  $\delta^{18}\text{O}$  on a Y-axis then generating an equation on linear regression. If  $\delta\text{D}$  and  $\delta^{18}\text{O}$  of samples have the same relationship with LMWL, this suggests that the source of spring water comes from rainwater. If not, the isotopic lines from groundwater and magmatic water in the local area have to be generated to find the relationship of their  $\delta\text{D}$  and  $\delta^{18}\text{O}$ .

For this study, we use  $\delta\text{D}$  and  $\delta^{18}\text{O}$  data from the nearest rain or weather station, Kanchanaburi, for creating LMWL (Figure 1.11).



**Figure 1.11** Local Meteoric Water Line from Kanchanaburi (2013- 2015) is used for plotting  $\delta D$  and  $\delta^{18}O$  for comparing with global meteoric water line (red line) (TINT, 2015)

## CHAPTER 2

### METHODOLOGY

#### 2.1 The study sites

Hin dad hot spring is located in Thong Pha Phum district, Kanchanaburi Province and Bor Klueng hot spring are in Suan Phueng district, Ratchaburi Province, 140 km southeast from Hin Dad (Figure. 2.1).

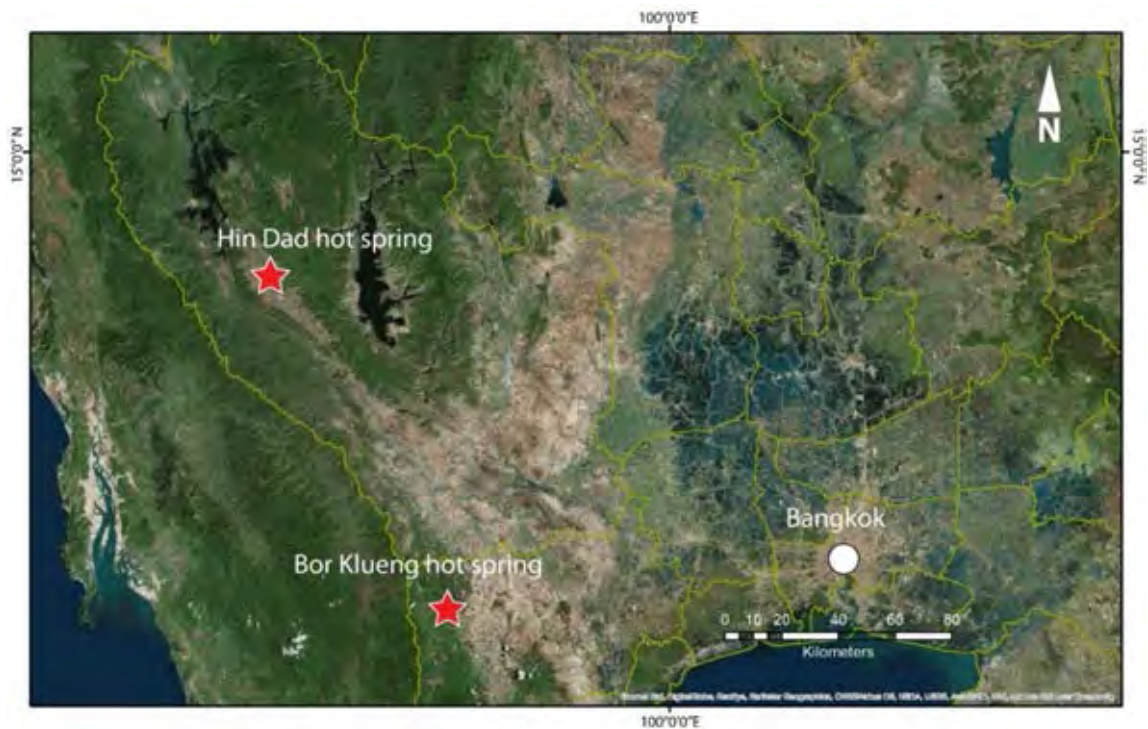


Figure 2.1 Location of study area

Hin Dad hot spring is well developed for tourism, which comprises of 3 bathing concrete pools and one artificial brick well. The brick well has a water plume which fills the rest pools. Along the hot spring pool, there is the small canal which water flows from the mountain (Figure. 2.2).



**Figure 2.2** Hin Dad hot spring, In red circles; (A) the small artificial brick well, (B) bathing concrete pools and (C) the small canal which flow by the hot spring.

Bor Klueng hot spring is a natural hot stream. It occurs as flowing of hot water from the rock fragment with c. 10-meters-width hot stream. This water is mixed with the fresh cold stream water flowing from the mountain. The water has a plenty of green algae and pale sulfur odor (Figure 2.3). Bor Klueng hot spring is widely used for tourism and health therapy like bathing, soaking feet. The local people also boil their agriculture products like bamboo shoot or eggs with the hot spring.



**Figure 2.3** Appearance of Bor Klueng hot spring, in the red circle, is the sampling point.



## 2.2 Water Analysis

### 2.2.1 Water analysis in the field

In the field survey, the surface temperature and conductivity were measured by the AquaPro Water Quality Tester (EC) and pH by portable pH meter. The water samples were collected using a syringe to drain water about 10 cm under the water surface. Each site was collected 4 samples, for measuring cations, anions,  $\delta D$ ,  $\delta^{18}O$  and silica content, each measurement has different procedures. Hin Dad hot spring samples were collected from the small artificial brick well (red circle A) and Bor Klueng hot spring was collected samples at the red circle.

#### Measuring temperature, conductivity, and pH of each site.

For temperature and conductivity, put the thermos and conductivity meter 10 cm under the water surface, wait until the value is steady and collect data. For pH, put the pH probe of pH meter under the water surface, wait until the value is steady and collect data.



Figure 2.4 Measuring temperature and conductivity

### Collecting water samples

For measuring cations, the water was collected in a 150 ml HDPE bottle, to prevent bacteria growing by adding 2-3 drops of concentrated Nitric acid. For measuring anions, 0.2-micron filter was used for filtering water sample and store in a 150 ml HDPE bottle. For measuring silica, adding Deionized water (DI) 9 ml per 1 ml of a water sample for diluting and store in a plastic tube.



**Figure 2.5** Collect samples for measuring silica, dilute with DI water 9:1

For measuring  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , the water samples were collected 10 cm under the water surface to prevent isotope fractionation with air, filter with 0.2-micron filter and store in a 20 ml PE bottle (caution: do not leave any bubble inside the bottle to prevent evaporation).



**Figure 2.6** Collect samples for measuring  $\delta^{18}\text{O}$  and  $\delta\text{D}$  using 0.2-micron filter

## 2.2.2 Water analysis in the laboratory

The cations, anions and stable isotope of water samples were analyzed in the laboratory at Thailand Institution of Nuclear Technology (TINT), Nakhon Nayok province and at Department of Geosciences, National Taiwan University, Taipei, Taiwan.

### Cations

For ions group 1 (Li, Na, NH<sub>4</sub>, K, Mg and Ca), the samples are measured by Ion Chromatography because these group of ions tends to have larger value (in ppm). For ions group 2 (Fe, Al, Mn, Zn, Cu, Cd, Pb and As), the samples are measured by Inductively coupled plasma mass spectrometry (ICP-MS) because these group of ions tends to have smaller value (ppb).

There are several steps for measuring elements in the samples as follows;

1. For elements group 1, prepare mix standard solution with the concentration of 0 (DI water), 1, 2.5, 5, 10, 20, 50 and 100 ppm from mixing of single standard metal (SIGMA-ALDRICH, 1,000 ppm). For elements group 2, prepare the standard solution with the concentration of 0 (DI water), 0.5, 1, 2, 5, 10, 20, 50 and 100 ppb from mix standard metal (Agilent technologies).
2. Each standard and sample was transferred in a 1.5-ml vial with a hole plug. The vials were then loaded on a rack for measurement.
3. Analyses commenced with a blank (DI water), and the standard solutions were measured from lowest to highest concentrations, and then followed by water samples.



**Figure 2.7** Single standard solution SIGMA-ALDRICH  
from left to right K, Na, Mg, Ca, Li and NH<sub>4</sub>



Figure 2.8 1.5 mL vial

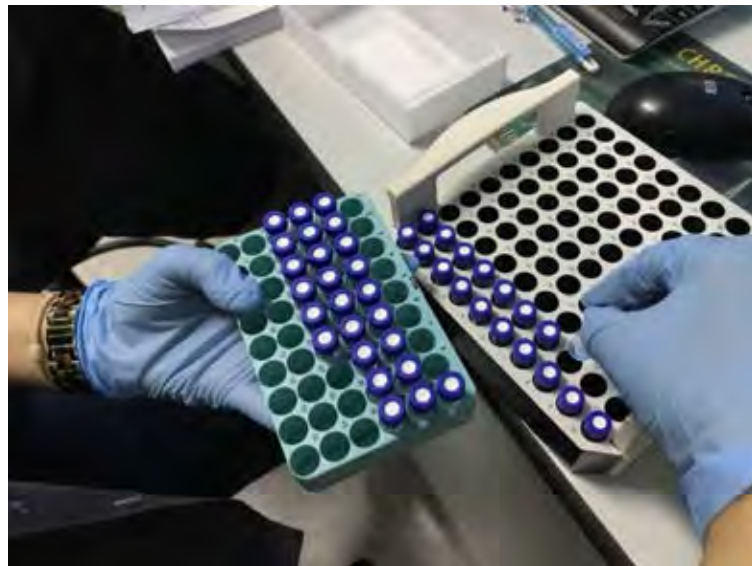


Figure 2.9 transfer all vials into a rack



Figure 2.10 Mix standard solution for ICPMS



Figure 2.11 Ion Chromatography

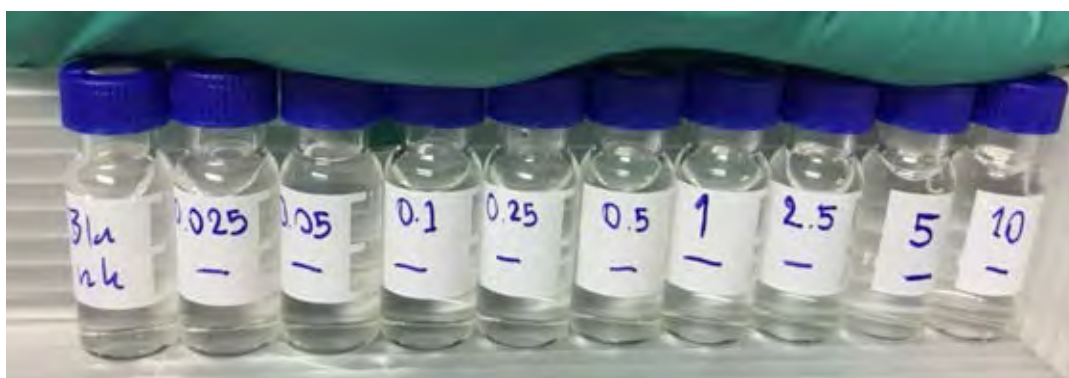


Figure 2.12 Inductively coupled plasma mass spectrometry (ICP-MS)

## Anions

$F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$  and  $PO_4^{3-}$  are measured by Ion Chromatography (IC)

1. Prepare mix standard solution with the concentration of 0 (DI water), 0.025, 0.05, 0.1, 0.25, 0.5, 1, 2.5, 5 and 10 ppm from mixing of single standard solution (SIGMA-ALDRICH, 1,000 ppm).
2. Each standard and sample was transferred in a 1.5-ml vial with a hole plug. The vials were then loaded on a rack for measurement.
3. Analyses commenced with a blank (DI water), and the standard solutions were measured from lowest to highest concentrations, and then followed by water samples.



**Figure 2.13** Single standard solution SIGMA-ALDRICH  
from left to right  $NO_3^-$ ,  $Br^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $F^-$ ,  $Cl^-$  and  $I^-$



**Figure 2.14** Mix standard solution for anion with varied concentration

For measuring  $\text{HCO}_3^-$ , a titration method has been applied.

1. A water sample was introduced in a vial in the titration kit, filling 1/3 of the vial.
2. Then 2–3 drops of R-2 indicator solution was added to the vial. The sample would turn blue if pH value ranged 4–7.
3. A dropper syringe was fully filled with R-3 acid solution.
4. The R-3 acid solution was slowly dropped from the dropper syringe into the testing vial that contained water sample. We waited until the color of the sample turned to red then stopped dropping and recorded the volume of R-3 that had been using the syringe.
5. We rinsed the testing vial with DI water and repeated procedures No.1–4 twice.
6. The concentration of  $\text{HCO}_3^-$  (in ppm) was calculated by multiplying the volume of used acid with 60.



**Figure 2.15** a titration kit, consists of a dropper syringe, R-1 and R-2 indicator, R-3 acid solution and sample syringe.



Figure 2.16 a testing vial contain water sample after adding 2-3 drops of R2

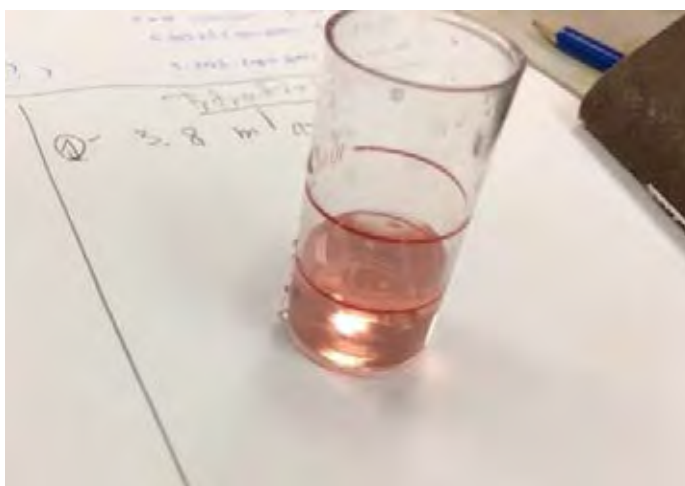


Figure 2.17 after dropping R-3 acid solution until the solution reach end point, turn to red.

### Stable Isotopes ( $\delta D$ , $\delta^{18}O$ )

1. The VSMOW standard solutions with  $\delta^{18}O$  values of -11.82, -5.6, and 1.64 ‰ were prepared.
2. Each standard and sample was transferred in a 1.5-ml vial with a plug. The vials were then loaded on a rack for measurement.
3. Analyses commenced with a blank (DI water), and the standard solutions were measured from lowest to highest concentrations, and then followed by water samples.



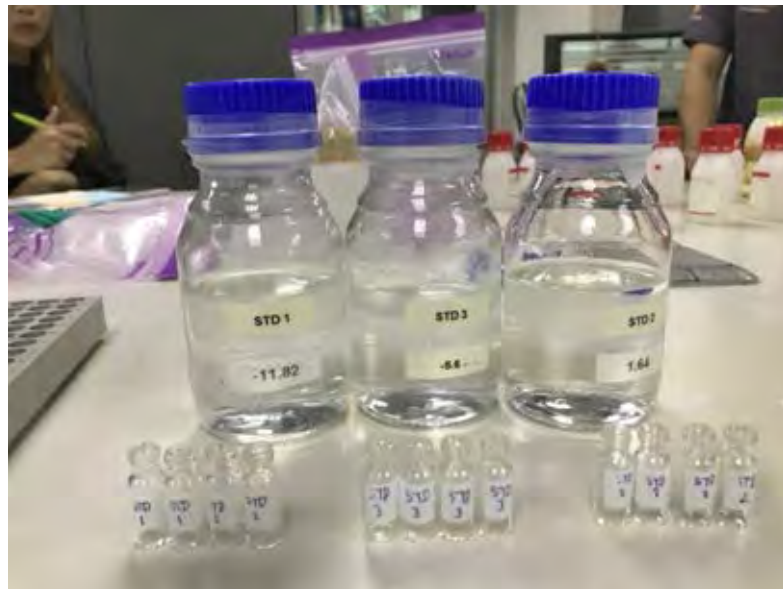


Figure 2.18 VSMOW standard solution



Figure 2.19 Hin Dad and Bor Klueng water sample for measuring stable isotope in PE bottles.

## CHAPTER 3

### RESULTS

#### 3.1 Field Data

Hin Dad hot spring was surveyed and collected samples on 7 October 2017, the air temperature was 32 °C. The hot spring has a temperature of 42.2 °C, the conductivity of 835 uS, pH of 7.56, TDS of 760 ppm. Bor Klueng hot spring data was measured on 8 October 2017, the air temperature was 30 °C and there's slightly rainfall. The temperature of Bor Klueng hot spring is 52°C, the conductivity of 242 uS, TDS of 760 ppm and pH of 7.82.

Physical Properties	Hin Dad		Bor Klueng	
	Measured (2017)	DMR (1999)	Measured (2017)	DMR (1999)
Surface Temperature	42.2 °C	40°C	52 °C	56°C
Conductivity	835 uS	-	242 uS	-
TDS	760 ppm	-	181 ppm	-
pH	7.56	7.36	7.82	8.02

**Table 3.1** Summary of physical properties of study areas.

## 3.2 Laboratory Data

### 3.2.1 Elemental Composition

The cations can be grouped into 2 groups, major elements that are Si, Al, Ca, Mg, Na, K, Fe, and Mn, which are elements that 95% of the earth's crust and the rest are minor elements, Li, Zn, Cu, Cd, Pb, and As. The most of concentration of major cations for Bor Klueng hot spring is higher than Hin Dad hot spring (Li, Na, K, and Si) except Ca and Mg which are significantly high for Hin Dad hot spring, while Fe and Mn are slightly equal.

The anions of Hin Dad and Bor Klueng can be divided into 3 groups,  $F^-$  and  $Cl^-$  of Bor Klueng hot spring is higher than Hin Dad hot spring, the next group is  $Br^-$ ,  $NO_3^-$  and  $PO_4^{3-}$  for both hot springs are slightly equal, and the last group is  $SO_4^{2-}$  and  $HCO_3^-$ , Hin Dad hot spring has higher amount of which than Bor Klueng hot spring.

The summary of cations and anions are shown in Table 3.1 and 3.2. Hin Dad hot spring has a significantly high concentration of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$  and  $HCO_3^-$ , while Bor Klueng hot spring has a notably high concentration of  $Na^+$ ,  $K^+$ ,  $Al^{+3}$ , and  $F^-$  compare to each other.

Ion	Concentration (ppm)	
	Hin Dad	Bor Klueng
Li <sup>+</sup>	0.04	0.09
Na <sup>+</sup>	12.49	29.37
K <sup>+</sup>	3.48	8.41
Ca <sup>2+</sup>	151.97	10.85
Mg <sup>2+</sup>	24.44	0.97
Fe <sup>2+</sup>	0.07	0.06
Al <sup>3+</sup>	0.03	0.12
Mn <sup>2+</sup>	0.02	0.01
Zn <sup>2+</sup>	0.61	0.27
Cu <sup>2+</sup>	0.001	0.003
Cd <sup>2+</sup>	<0.01	0.00
Pb <sup>2+</sup>	0.07	0.02
As <sup>2+</sup>	0.01	0.01
Si <sup>4+</sup>	20.80	29.20

**Table 3.2** Concentration of cations

Ion	Concentration (ppm)	
	Hin Dad	Bor Klueng
F <sup>-</sup>	0.76	4.35
Cl <sup>-</sup>	2.81	4.16
Br <sup>-</sup>	2.26	2.21
NO <sub>3</sub> <sup>-</sup>	0.51	1.02
PO <sub>4</sub> <sup>3-</sup>	0.18	0.18
SO <sub>4</sub> <sup>2-</sup>	125.43	3.58
HCO <sub>3</sub> <sup>-</sup>	463.75	112.89

**Table 3.3** Concentration of anions

According to results of elemental composition, we use the piper diagram to interpret groundwater processes and water type. Hin Dad hot spring water can be plotted on the Ca-rich zone in cations diagram and on the  $\text{HCO}_3^- + \text{CO}_3^{2-}$  zone in the anions diagram, which indicates the calcite source rock and the groundwater process dissolving of calcite, according to the diamond diagram, the water type is temporary hardness water or shallow fresh groundwater. Bor Klueng hot spring water can be plotted on the Na + K zone in the cations diagram and on the  $\text{HCO}_3^- + \text{CO}_3^{2-}$  zone in anions diagram, according to the diamond diagram, the water type is alkali carbonate water or deep groundwater influenced by ion exchange.

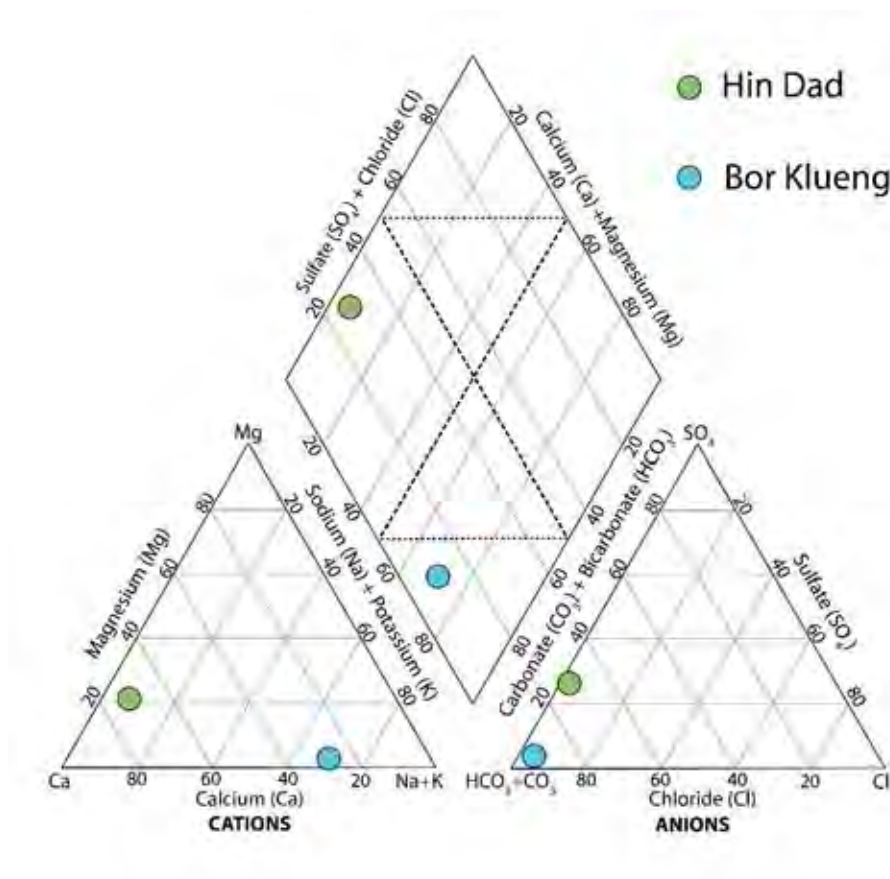


Figure 3.1 Results on the piper diagram

The Cl-SO<sub>4</sub>-HCO<sub>3</sub> diagram shows that both hot springs water is peripheral waters, which can mean 1) they originate from rainwater or 2) they're mixing with surface water.

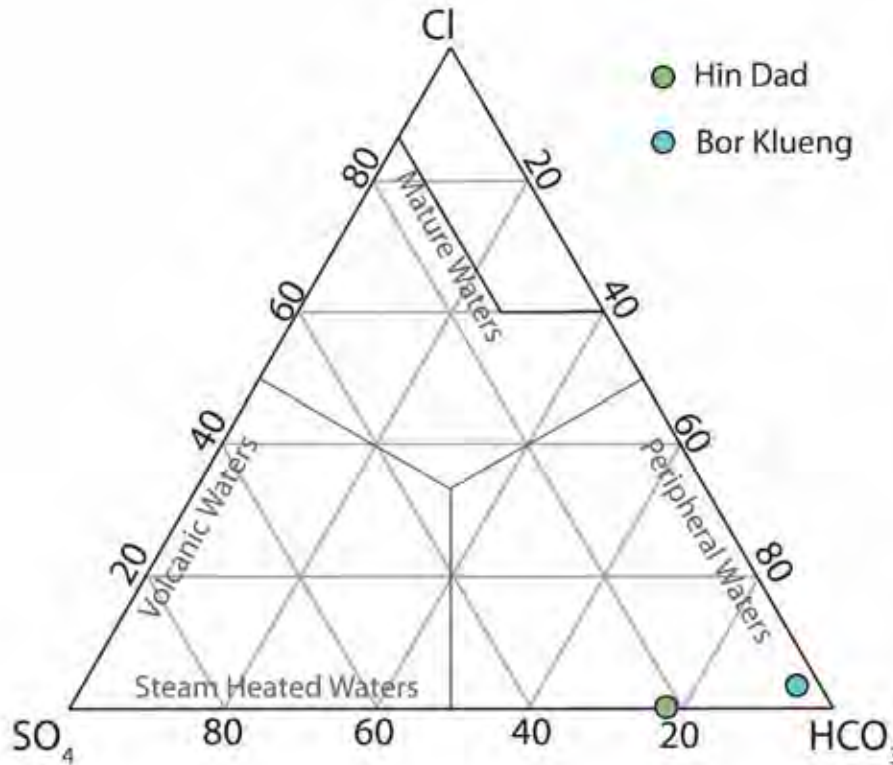


Figure 3.2 Results on the SO<sub>4</sub>-HCO<sub>3</sub>-Cl ternary diagram

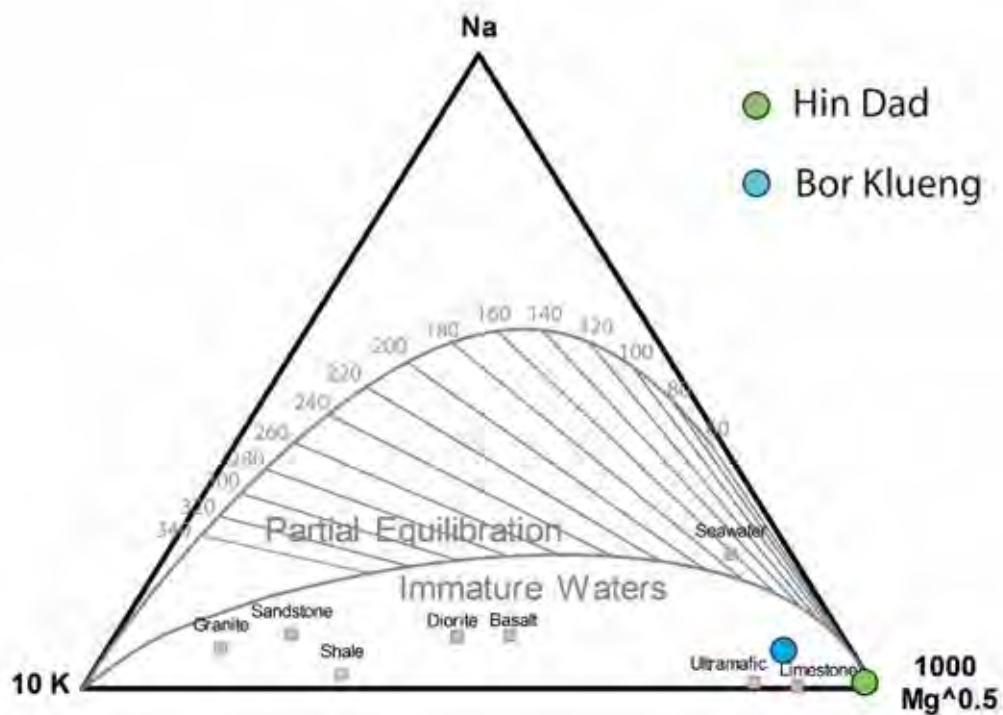
The concentration of Na, K and Ca is used to calculate the reservoir temperature by using Na-K, Na-K-Ca geothermometer. The results are shown in the following table 3.5. Most calculation shows the temperature of Hid Dad reservoir is range between 300-380 °C, Bor Klueng ranges between 304-385 °C.

No.	Ions	Proposed by	Hin Dad (°C)	Bor Klueng (°C)
10	Na-K	Truesdell, 1976	333.2887	338.1767
11	Na-K	Fournier, 1979	324.1449	327.4719

12	Na-K	Tonani, 1980	388	394		
13	Na-K	Arnórsson et al., 1983	330	334		
14	Na-K	Nieva and Nieva, 1987	309	312		
15	Na-K	Giggenbach et al., 1988	330	333		
16	Na-K	Santoyo and Díaz-González, 2010	Min 300	Max 380	Min 304	Max 385
17	Na-K-Ca	Arnórsson, 2000	318	813		

**Table 3.4** Reservoir temperature calculating from Na-K-Ca geothermometer

According to the Na-K-Mg ternary diagram, both Hin Dad and Bor Klueng are fallen in the zone of immature waters, which mean they haven't reached the equilibrium with rocks, or they might be interfered by fresh groundwater.



**Figure 3.3** Results on the Na, K, Mg ternary diagram

### Silica Concentration

The concentration of silica ( $\text{SiO}_2$ ) of equal to the concentration of  $\text{Si}^{4+}$ . Hin Dad hot spring has  $\text{Si}^{4+}$  of 20.8 ppm and Bor Klueng hot spring has  $\text{Si}^{4+}$  of 29.2 ppm, which can calculate reservoir temperature by using silica geothermometer equation (Table 3.6)

No.	Equation	Proposed by	Hin Dad (°C)	Bor Klueng (°C)
1	Quartz-no steam loss	Fournier (1977)	65	78
2	Quartz <sup>a</sup>	Fournier (1977)	120	135
3	Quartz	Fournier and Potter (1982)	150	163
4	Quartz <sup>a</sup>	Fournier and Potter (1982)	65	79
5	Quartz	Arnorsson et al. (1998)	50	64
6	Quartz <sup>a</sup>	Arnorsson (2000)	52	66
7	Chalcedony	Fournier (1977)	33	47
8	Chalcedony	Arnorsson (2000)	36	50
9	Amorphous Silica	Fournier (1977)	-45	-34

**Table 3.5** Reservoir temperature calculating from silica geothermometer

As the results, the reservoir temperature of both Hin Dad hot spring and Bor Klueng hot spring from the calculating are slightly low. The temperature from equation 1, 4, 5 and 6 are the proper temperature selected by comparing with surface temperature, the reservoir temperature should higher than the surface temperature.



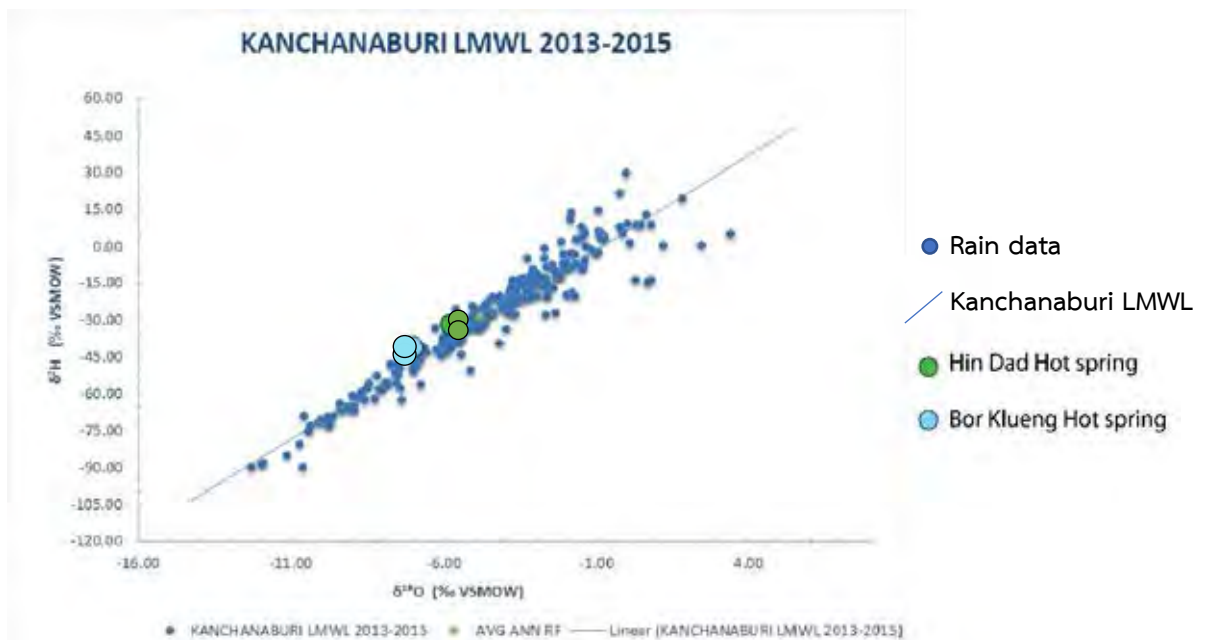
## Stable Isotope

The values of  $\delta D$  and  $\delta^{18}O$  are measured by the CRDS machine, the results are reported (per-mille ‰) in the following table.

	Hin Dad (‰)		Bor Klueng (‰)	
	$\delta^{18}O$	$\delta D$	$\delta^{18}O$	$\delta D$
	-5.58	-34.08	-7.07	-43.17
	-5.56	-33.77	-7.08	-43.52
	-5.55	-33.68	-7.08	-43.64
Average	-5.56	-33.85	-7.08	-43.44

**Table 3.6** Results of stable isotope

The value of  $\delta^{18}O$  for Kanchanaburi range from 3 to -15 ‰ and the value of  $\delta D$  range from 34 to -110 ‰, the local meteoric water line of Kanchanaburi has  $R^2$  of 0.9119. When plotted  $\delta D$  and  $\delta^{18}O$  of both Hin Dad hot spring and Bor Klueng hot spring on this graph, they're fit in the local meteoric water line of Kanchanaburi (Figure 3.4)



**Figure 3.4** Local Meteoric Water Line in 2013-2015 of Kanchanaburi with plotted stable isotope data (TINT, 2015)

## CHAPTER 4

### DISCUSSIONS

#### 4.1 Chemical compositions

Hin Dad hot spring has pH of 7.56 and Bor Klueng hot spring has pH of 7.86. In comparison with reported values from DMR in 1999, Hin Dad has pH of 7.36 and Bor Klueng of 8.02, small variation can be observed. This can be explained by the time of collecting data, spot and seasonal variation of measuring.

According to the results of elemental composition, the blue-highlighted ions are  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{CO}_3^{2-}$ , these group of ions commonly dissolve from carbonate minerals e.g. calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) or rhodochrosite ( $\text{MnCO}_3$ ). This suggests that Hin Dad hot spring water has reacted with surrounding calcareous rock. This support from piper diagram Hin Dad hot spring water can be plotted on the Ca-rich zone in cations diagram and on the  $\text{HCO}_3^- + \text{CO}_3^{2-}$  zone in the anions diagram, which indicate the calcite source rock and the groundwater process dissolving of calcite, according to the diamond diagram the water type is temporary hardness water or shallow fresh groundwater, which is the same as Khaochaison hot spring in Phthalung and Pong Dued hot spring in Chiang Mai.

In the other way, the yellow-highlighted ions are the group of ions which commonly related with the minerals in granitic rock e.g. orthoclase ( $\text{KAlSi}_3\text{O}_8$ ), muscovite ( $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F}, \text{OH})_2$ ) and Na-rich plagioclase ( $\text{NaAlSi}_3\text{O}_8$ ), it can be indicated that Bor Klueng hot spring water has reacted with surrounding granitic rock. Bor Klueng hot spring water plotted on the Na + K zone in the cations diagram and on the  $\text{HCO}_3^- + \text{CO}_3^{2-}$  zone in anions diagram of Piper diagram, according to the diamond diagram the water type is alkali carbonate water or deep groundwater influenced by ion exchange. But the ions from the granitic rock in Bor Klueng hot spring are quite low compared to which are reported from Fang

hot spring in northern Thailand which has the surface water temperature range from 90 – 130 °C (Wood et al., 2018). At Fang hot spring, the concentration of Na, Al, F, and SiO<sub>2</sub> is much higher than Bor Klueng. This indicates that at the higher temperature hot water reacts more easily with the surrounding rock. This idea is the concept of mineral solubility, the increase in temperature means the more endothermic mineral can dissolve, which is proved by the equilibrium modeling of Na-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O system to high temperature (Moller, 1988) and the result on the piper diagram of Bor Klueng is the same as Pong Nam Ron in Chantaburi (Charusiri, 2003).

Ion	Concentration (ppm)	
	Hin Dad	Bor Klueng
Na <sup>+</sup>	12.49889	29.36831
K <sup>+</sup>	3.486198	8.40709
Ca <sup>2+</sup>	151.9798	10.8521
Mg <sup>2+</sup>	24.44409	0.973211
Mn <sup>2+</sup>	0.02	0.006
Al <sup>3+</sup>	0.03	0.122
F <sup>-</sup>	0.758	4.351
SO <sub>4</sub> <sup>2-</sup>	125.427	3.583
HCO <sub>3</sub> <sup>-</sup>	463.75	112.887

**Table 4.1** Show the ions which have high difference, the blue highlight are the ions which mostly founded in carbonate rock and the yellow highlight are the ions which mostly founded in granitic rock.

Therefore, Hin Dad spring water is safe for drinking and consuming, but the high concentration of bicarbonate can cause slag problem to the boiling system. In contrast, Bor Klueng hot spring water has the concentration of arsenic, fluoride and lead exceed the drinking water limit. Using this water for drinking is not recommended. However, it is possible for recreation.

Elemental/ substance	Symbol/ formula	Normally found in freshwater/surface water/groundwater	Health-based guideline by the WHO	Hin Dad (ppm)	Bor Klueng (ppm)
Aluminum	Al		0.2 mg/l	0.03	0.122
Arsenic	As		0.01 mg/l	0.008	0.011
Cadmium	Cd	< 1 ug/l	0.003 mg/l	<0.001	0.0002
Chloride	Cl		250 mg/l	2.809	4.16
Copper	Cu		2 mg/l	0.001	0.003
Fluoride	F	< 1.5 mg/l (up to 10)	1.5 mg/l	0.758	4.351
Iron	Fe	0.5 - 50 mg/l	No guideline	0.074	0.062
Lead	Pb		0.01 mg/l	0.074	0.019
Manganese	Mn		0.5 mg/l	0.02	0.006
Sodium	Na	< 20 mg/l	200 mg/l	12.49	29.36
Sulfate	SO <sub>4</sub>		500 mg/l	125.427	3.583
Zinc	Zn		3 mg/l	0.612	0.269

**Table 4.2** WHO guideline for natural and drinking water with a concentration of ions in Hin Dad and Bor Klueng, the yellow label shows the excess value over WHO guideline (modified from WHO, 1993)

## 4.2 Surface temperature and Reservoir temperature

The surface temperature of Hin Dad hot spring is lower than Bor Klueng hot spring about 10°C. According to the geological map of the study area, Hin Dad is located in the calcareous sedimentary terrain and Bor Klueng the is located in the granitic terrain. From the models of hot springs in Thailand, the hot springs which lie on the granitic terrain tend to have higher temperature and mineral contents than the hot springs which lie on the sedimentary terrain (Giao, 2007). Since they are directly heated by granitic rock, which can explain the higher temperature at Bor Klueng hot spring.

The conductivity of Hin Dad hot spring of 864 uS which is higher than 242 uS of Bor Klueng hot spring. These results agree with total dissolved solids (TDS), Hin Dad hot spring has TDS of 760 ppm and Bor Klueng of 181.25 ppm. The conductivity and TDS values suggest that Hin Dad hot spring has more dissolved ions than Bor Klueng hot spring. Based on the geological map of the study area, the higher value of conductivity and TDS of Hin Dad can result from the dissolution of calcite from the surrounding rock. While Bor Klueng hot spring has low conductivity and TDS even it is located in the granitic terrain. This can be explained by mixing process of hot water with the stream water or the rainwater. Bor Klueng hot spring's occurrence is the natural hot stream which has the cold stream from the mountain flowing side by side.

The results of reservoir temperature from silica geothermometer of Hin Dad hot spring range from 50 – 65 °C and Bor Klueng hot spring should be range from 64 – 78 °C from the equation No.1 of Quartz-no steam loss (Fournier ,1977), No.4 of Quartz<sup>a</sup> (Fournier and Potter, 1982), No.5 of Quartz (Arnorsson et al., 1998) and No.6 of Quartz<sup>a</sup> ( Arnorsson, 2000) . The other equations of silica geothermometer (Table 3.6) including Na-K and Na-K-Ca geothermometer (Table 3.5) show the improper value because the surface temperature of both hot springs is in the medium range (about 40-60°C). However, the values from the rest equation (No.2,3) is about 2 or 3 times greater than the surface temperature, or

even minus value from chalcedony. The other equations of Na-K-Ca geothermometer are not suitable for calculation medium temperature hot spring, because the reaction isn't at the equilibrium (Figure 3.3). The reasonable equation also shows that Bor Klueng hot spring has higher reservoir temperature than Hin Dad hot spring. This can also be observed in the surface temperature.

The heats source from both hot springs may come from convection current and heat transfer from the shallow crust, from the model of hot springs in Thailand (DMR, 1999) but for a more precise heat source, we need to continue further study. The potential of being geothermal energy might be not possible due to the low-temperature reservoir, but still can be used for other benefits such as agriculture or health therapy.

### 4.3 Stable Isotope

The value of  $\delta D$  and  $\delta^{18}O$  in Hin Dad hot spring are higher than Bor Klueng hot spring. We assume that the rainwater of both Hin Dad and Bor Klueng coming from the same meteoric water source as plotted in Figure 1.3. The southwest summer monsoon is the main contribution of rainfall in both areas. However, Bor Klueng is located further inland (about 10 km. Figure 1.2). The traveling distance of southwest monsoon when it gets into the continent until reaching the destination recharge area, the further distance means the monsoon rain losing its  $\delta D$  and  $\delta^{18}O$  due to isotope fractionation. In addition, Bor Klueng hot spring is shielded by the higher mountain and has higher elevation (elevation of Bor Klueng hot spring = 180 m) than Hin Dad hot spring (elevation of Hin Dad hot spring = 100 m), when the southwest monsoon travels across the higher mountain, likely to precipitate more and the remaining monsoon lose  $\delta D$  and  $\delta^{18}O$  in higher amount.

Month	Nakhon Sawan		Kanchanaburi	
	$\delta^{18}\text{O}$	$\delta\text{D}$	$\delta^{18}\text{O}$	$\delta\text{D}$
Jan	-	-	-1.44	-4.96
Feb	-	-	0	0
Mar	-1.11	-4.34	-0.65	0.04
Apr	-2.04	-15.74	-1.51	-0.11
May	-3.60	-17.69	-5.59	-35.52
Jun	-5.20	-34.96	-5.08	-28.35
Jul	-5.28	-39.40	-3.85	-22.17
Aug	-6.60	-45.24	-4.68	-29.07
Sep	-9.58	-67.50	-6.62	-45.40
Oct	-9.56	-65.89	-5.94	-41.76
Nov	-6.05	-39.72	-4.05	-28.80
Dec	-1.68	-10.35	-3.59	-21.23

**Table 4.3** shows the stable isotope data of rainwater in Kanchanaburi and Nakhon Sawan from 2012-2015, the red highlight is the interesting period (TINT, 2015)

According to table 4.3, in the effect of southwest monsoon (May-October), the value of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in Kanchanaburi is higher than in Nakhon Sawan, this supports the effect of traveling distance (Figure4.1) of the monsoon for the decreasing of  $\delta\text{D}$  and  $\delta^{18}\text{O}$ . In addition, the recharge area of Bor Klueng is more impervious due to surrounding granitic rock, the rainwater needs more time to infiltrate and percolate, so it loses  $\delta\text{D}$  and  $\delta^{18}\text{O}$  from more evaporation time.

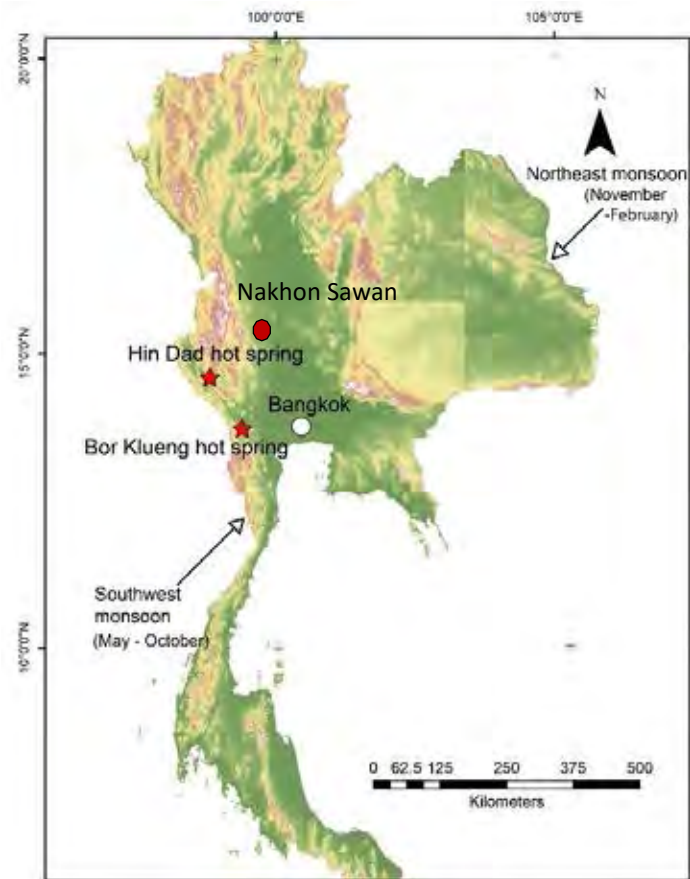


Figure 4.1 Show location of both hot springs and location of Nakhon Sawan



## CHAPTER 5

### CONCLUSION

Hin Dad hot spring is the natural hot spring which has been developed for tourism located in the calcareous sedimentary terrain, while Bor Klueng hot spring is natural hot stream located in granitic terrain. Hin Dad hot spring has a surface temperature of 42.2°C, pH of 7.56, and conductivity of 835 uS, and Bor Klueng has a surface temperature of 52°C, pH of 7.82, and conductivity of 242 uS. Hin Dad cation is dominated by  $\text{Ca}^{2+}$ , anion is dominated by  $\text{HCO}^-$  and  $\text{CO}_3^{2-}$ , it is temporary hardness water or shallow fresh groundwater, which ions come from dissolving of calcite, also  $\text{SO}_4^{2-}$  ion in Hin Dad hot spring is significantly high, this group of ions is the major ions in calcareous rock, ions and water type of Hin Dad hot spring is same as Khaochaison in Phattalung province and Pong Dued hot spring in Chiang Mai, Bor Klueng cation is dominated by  $\text{Na}^+$  and  $\text{K}^+$  ion, anion is dominated by  $\text{HCO}^-$  and  $\text{CO}_3^{2-}$ , it is alkali carbonate water or deep groundwater influenced by ion exchange, the ions and water type of Bor Klueng hot spring is same as Pong Nam Ron hot spring in Chantaburi, also  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Al}^{3+}$ , and  $\text{F}^-$  in Bor Klueng hot spring is higher than which in Hin Dad, this group of ion is mostly found in felsic rock, ions in both hot springs come from interaction between hot water and surrounding rocks but the temperature isn't high enough so the reaction doesn't reach the equilibrium. According to Na-K-Mg ternary diagram, both hot springs are immature waters which might mix with cold groundwater. The reservoir temperature calculated from Na-K-Ca geothermometry of Hin Dad ranges 300-380°C and Bor Klueng ranges 310-390 °C, the reservoir temperature calculated from silica geothermometry of Hin Dad ranges 50-65°C and Bor Klueng ranges 64-78°C, but the temperature from Na-K-Ca geothermometer aren't suitable because the water-rock interaction didn't reach the equilibrium. The stable isotope data of Bor Klueng hot spring is more depleted than Hin Dad hot spring, but both of them have the same relationship between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  as same as local meteoric water line in Kanchanaburi which can be implied that the hot spring

water source is recharged by rainwater or have mixed with rainwater. The contents of heavy ions which exceed the water drinking limit provided by WHO for Hin Dad hot spring is Pb, and for Bor Klueng hot spring is As, F and Pb, which mean both of them aren't suitable for consumption but the sampling point is represented the source of water not the water in the bath pool. The heat source of both hot springs is from convection current in the earth's crust refer from the models of hot spring which Department of Mineral Resource have published, Hin Dad hot spring lies on sedimentary terrain over the granitic basement, and Bor Klueng hot spring lies on the granitic terrain. The proper use for both hot springs is a tourist attraction, bathing and drying agriculture products, due to medium reservoir temperature (50-70 °C) of them.

#### **Recommendation for future work**

- 1) Geochemical data of hot spring can give insight into tectonic in this area together with the other stable isotope in hot spring like helium or sulfur. There are about one hundred of hot springs which are still lack of geochemical data, and this data should be compiled with the geophysical data for better understanding of and management of the hot spring in Thailand. We hope this study will attract people to realize the importance of hot spring and continue study on this topic.
- 2) The sampling point is represented the water source, but the water in bath pool need to be examine later.
- 3) In this study, only the representative of the rainy season in Thailand (southwest monsoon, May-October), more detailed data in different in the season should be considered.

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