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Research article

Geothermometry in High-Temperature Reservoirs of the Geothermal Springs in Southern Thailand: Insights from Cations and Silica Geothermometers

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Abstract: Geothermal springs have provided a unique opportunity to study the geothermal system of geological processes. A reservoir temperature estimation based on the chemical geothermometers is vitally essential for assessing the exploration and development of geothermal resources. The paper represents the various techniques of geothermometers with comparisons between the silica (quartz and chalcedony) and the cation geothermometers (Na–K–Ca and K–Mg) for the high exit temperature (temp. ≥55°C) of geothermal springs in southern Thailand. The Na–K–Ca geothermometer presented more elevated reservoir temperatures than the K–Mg, silica and chalcedony geothermometers, about 20–30°C. The preliminary assumed difference between the geothermometers may indicate that the shallow subsurface conditions are mixed with groundwater.

Keywords: Geothermometer; reservoir temperature; geochemistry; geothermal spring; southern Thailand

1. Introduction

Variations in chemical constituents of geothermal spring waters indicate the changes experienced by sampled fluid in its past flow [1, 2, 3]. Most essential parameters like reservoir temperatures, flow patterns, sources of recharge, and type of reservoir rocks can be estimated through chemical analysis of fluids reaching the surface of natural hot springs or wells [4, 5]. A geochemical concentration has estimated reservoir temperatures and the ratio of certain elements; these are called "geothermometers" comprising silica (quartz and chalcedony) and cation (e.g., Na-K-Ca and K-Mg) geothermometers [6, 7]. Significantly, the geothermometers rely on the temperature-dependent equilibrium with time constants, used to estimate specific temperatures at depth [8, 9]—resulting in geothermal reservoir temperatures reflected by solute concentrations of solute ratios. Significantly, the silica geothermometer is reservoir temperature controlled by SiO_2 solubility [8, 9].

An efficiency factor of the silica geothermometer of geothermal reservoirs consists of (1) mixing and boiling processes as the most significant interference, (2) a defective crystalline structure of chalcedony, and (3) a pH value of geothermal waters (not exceed 9) [7, 8, 9]. Cation geothermometers (e.g., Na-K, Na-K-Ca, and K-Mg) with slow re-equilibration are theoretically more effective in accurately assessing a deep-reservoir temperature. Still, they are often affected by shallow processes. In this study, we focus on non-volcanic geothermal areas (e.g., Malaysia and Thailand) where low to medium temperature reservoirs are ranged from 100 to 180°C (10, 11). For this condition, some geothermal springs in Southern Thailand are of distinctive importance in estimating subsurface temperature as a key parameter for evaluating the economic potential for a geothermal electricity plant. Overview the geothermal springs in Southern Thailand are characterized by medium to high exit temperatures of approximately 40 to 80°C with a wide range of dissolved chemical compositions [4, 5]. Most of the hot spring waters are hot-types with bicarbonate-rich waters. Observations of surface and groundwater and geothermal fluids discharged from geothermal springs and drilling show that the chemical compositions vary within wider limits [3, 5]. For all geothermal springs in southern Thailand, the accurate heat sources are unknown. It can be either an igneous body where radioactive decay produces heat or a higher heat flow onshore basin development [2, 4].

2. Methodology

2.1 Field Overview

At least 30 geothermal spring sites are located in eight geothermal provinces in the southern region of Thailand, which consist of Chumphon (CP), Ranong (RN), Surat Thani (SR), Phang Nga (PG), Krabi (KB), Trang (TR), Phatthalung (PL), and Yala (YL) provinces, as shown in Figure 1. Exit temperatures are between 40 and 80°C. A summary of information for the study sites can be briefly described.

2.1.1. Ranong geothermal province (RN1-RN6)

As one of the larger geothermal systems in the southern region, the RN geothermal field is located in Ranong Province. It is famed for natural hot springs, thus drawing the attention of local and foreign visitors (Figure 1). Altogether, seven natural hot spring sites are located in the RN geothermal field, with exit temperatures between 40 and 75 °C; RN1 and RN6 areas have the highest temperature in this system. The RN1 site is praised as the famous landmark of Ranong City, also providing spa and hot massage therapy nearby. While the RN6 site was discovered in the deep forest in Kapoe District, located approximately 60 km south of Ranong city, the site is protected by the Ranong Forest Preservation and Protection Division. All hot spring sites located close to the Ranong Fault Zone are on major strike-slip faults [2, 5].

2.1.2. Surat Thani geothermal province (SR1-SR9)

The SR geothermal field is located in the western part of the southern region, with nine natural hot springs recorded. The exit temperatures range from 40 to 70 °C, while the SR3, SR7, and SR9 sites show the highest exit temperature in this system (Figure 1). SR3 is in Tha- Chang District, located on public land close to the main railway line (Bangkok - Hat Yai) and relatively close to Thailand's Gulf. SR7 is already developed for tourism; its larger pond is visible from the main road. In contrast, SR9 is located in a national park area. The general geology surrounding the SR geothermal field is characterized by isolated steep-sided hills of Permian limestones, tower karsts and granitic mountains on the western margins [1, 3].

2.1.3. Phang Nga geothermal province (PG1-PG3)

The PG geothermal field on the western side of the southern region, approximately 100 km north of Phuket city, is shown in Figure 1. At least three natural hot spring sites can be found in this geothermal system, with exit temperatures recorded from 45 to 78 °C; only one place, PG1, has an exit temperature of up to 78 °C. The PG1 site can be found close to and on the banks of the Pai Phu River. Rocks in and around the PG1 site are predominantly granites distributed in the southeastern and sedimentary/metamorphic rock units, which cover other regions [2, 5].

2.1.4. Phatthalung geothermal province (PL1-PL4)

The PL geothermal field is located in Phatthalung Province, as shown in Figure 1. This system has four hot spring sites with exit temperatures between 41 and 57 °C. A general geological setting is exposed, containing Cambrian to Quaternary rocks. Cambrian rocks comprise white to light grey-coloured fine-grained sandstone and quartzite, and Ordovician rocks are mainly grey-coloured, finely crystalline to coarse-grained limestones [1, 3].

2.1.5. Yala geothermal province (YL1)

The Yala geothermal field is located in southernmost Thailand near the border with Malaysia, as shown in Figure 1. Detailed investigations have been affected by continuous armed conflicts in this area since 2004; therefore, geological and geophysical survey data are limited. However, the YL site is a famous tourist attraction, mainly for Malaysian guests, and has an exit temperature above 80 °C [1, 3].

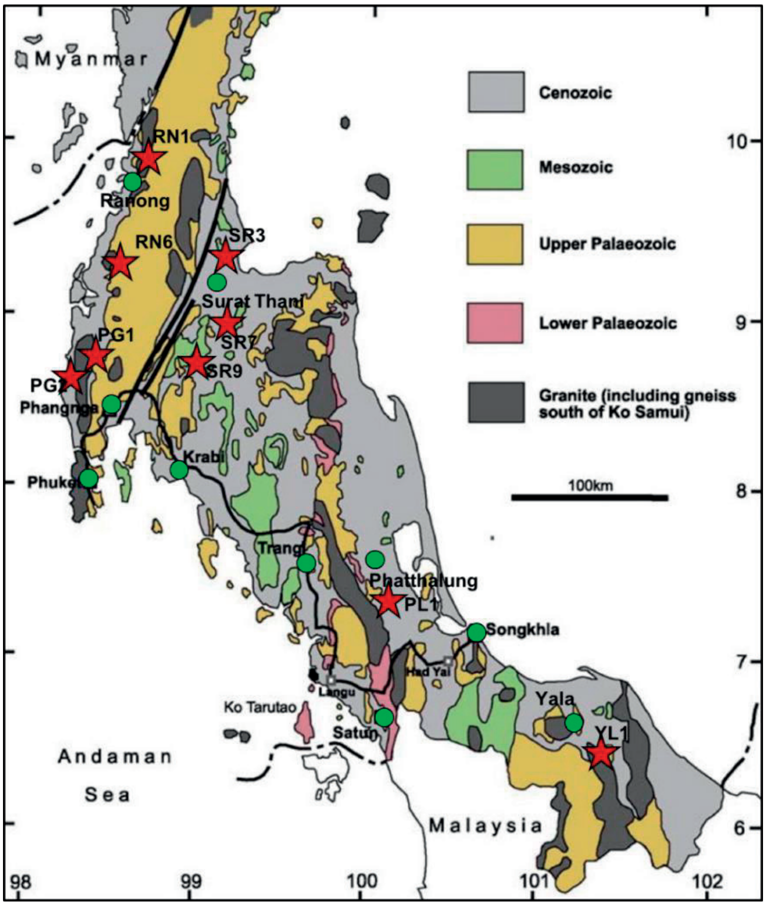

Figure 1. Simplified geological map and location of geothermal hot spring systems part of Southern Thailand (based on Department of Mineral Resources, 1999)

2.2. Samples and Analytical Methods

Based on the property of the geothermal groundwater is usually mixed with freshwater/saltwater and has undergone various chemical reactions during its flow through different geological formations. Therefore, investigating the appropriate reservoir temperatures of geothermal groundwater in southern Thailand was expressed with specific geochemical signatures to the other components of the various operations in water sampling and analysis. Nine water samples with high exit temperatures greater than or equal to 55°C were collected in five geothermal provinces, comprising Ranong (RN1 and RN6), Surat Thani (SR3, SR7 and SR9), Phang Nga (PG1 and PG2), Phatthalung (PL1), and Yala (YL1) sites. All the water samplings were carried out in April 2021. The multi-parameter water quality analyser measured exit temperature and pH values at the sampling sites. One litre of each sample collected for the major and trace element analysis was filtered on-site and stored in polyethene bottles cleaned by rinsing several times with the waters sampled solution. Whereas a nitrogen oxoacid (HNO3) was utilized to acidify (pH < 2) a portion of the water samples for cations analysis. In contrast, significant anions were kept unacidified for chemical analysis. The geochemical analysis was performed at the Laboratory of Water Analysis Co., Ltd. (ISO/IEC 17025:2017), Phra Nakhon Si Ayutthaya, Thailand. The methods of chemical analysis and detection limits of these parameters are exhibited in Table 1. The ionic balance error of cations and anions of all water samples is ranged from 0.15 to 6.23%.

Table 1. Methods used and Detection limits of geochemical analysis

Parameters	Method used	Detection limits (mg/L)
pH	In-house method: TM 001	-
Total dissolved solids, TDS	In-house method: TM 017	25
Chloride, Cl^-	In-house method: TM 008	6
Calcium, Ca^{2+}	EDTA Tritrimetric	0.01
Magnesium, Mg^{2+}	EDTA Tritrimetric	0.01
Potassium, K^+	Direct Air-Acetylene Flame	0.01
Sodium, Na^+	Direct Air-Acetylene Flame	0.005
Sulfate, SO_4^{2-}	Turbidimetric	1
Bicarbonate, HCO_3^-	Titration	1
Silica, SiO_2	In-house method: TM 030	1.1

2.3. Chemical Geothermometers

The site-specific selection of the geothermal springs in Southern Thailand among the high exit temperatures greater than or equal to 55°C consisted of nine hot springs located in five geothermal provinces that included Ranong (RN1 and RN6), Surat Thani (SR3, SR7 and SR9), Phang Nga (PG1 and PG2), Phatthalung (PL1) and Yala (YL1). Various silica and cation geothermometers were used to estimate reservoir temperatures (tR, in °C) of the geothermal springs in southern Thailand. Silica geothermometers, which are the most common types to estimate subsurface temperatures of geothermal reservoirs, are based on the solubility of quartz and chalcedony (SiO_2 content, unit; mg/L) [7, 9], whereas cation geothermometers (Na-K-Ca and K-Mg geothermometers) are based on the ion exchange reaction of Na^+, K^+, Ca^{2+} and Mg^{2+} concentrations (unit; mg/L) with a temperature-dependent equilibrium constant [6, 7, 8, 9], as shown in Eq. (1) to (4):

Quartz $$t_R(°C) = \left[\frac{1309}{5.19-\log(SiO_2)}\right] - 273.15 \quad (1)$$

Chalcedony $$t_R(°C) = \left[\frac{1032}{4.69-\log(SiO_2)}\right] - 273.15 \quad (2)$$

Na-K-Ca $$t_R(°C) = \left[\frac{1647}{\log\left(\frac{Na}{K}\right)+\beta\left[log\left(\frac{\sqrt{Ca}}{Na}\right)+2.06\right]+2.47}\right] - 273.15 \quad (3)$$

when $\beta = 4/3$ for t<100 °C; $\beta = 1/3$ for t>100 °C

K-Mg $$t_R(°C) = \left[\frac{4410}{14-\log(K^2/Mg)}\right] - 273.15 \quad (4)$$

3. Results and Discussion

3.1. Groundwater properties

Geochemical characteristics analyzed from the local groundwater samples of geothermal springs in Southern Thailand are listed in Table 2. The relative errors of ion balance (cation and anion) were below 5% in each sample. High TDS (total dissolved solids) value of 12,610 mg/L was found at the SR3 geothermal spring. All the geothermal groundwater samples were near-neutral to weakly alkaline; pH value was 6.8 at the SR9 geothermal spring and greater than 7.0 at the other hot springs, and was up to 8.0 at the RN1, RN6 and YL1 geothermal springs. A concentration of Na^+ is ranged from 12.1 to 64.5 mg/L in most geothermal spring sites, except the SR3 (Na^+=3,655 mg/L) represented a saltwater intrusion into the geothermal aquifer (Table 2). Cl^- the content was the dominant anion in the SR3 (6,630 mg/L), while HCO_3^- the content was the dominant one in the PG2 and PL1 geothermal spring waters. Moreover, Mg^{2+} concentrations were very low to the medium of approximately 0.02 to 42.5 mg/L in most geothermal waters except the SR3 and SR7 hot springs.

Table 2. Exit temperatures (Exit temp., °C), pH values, and concentrations of major geochemical constituents in geothermal spring waters (mg/L) from southern Thailand

Hot spring	Exit temp. (°C)	TDS (mg/L)	pH	Content (mg/L)							
				SiO_2	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	SO_4^{2-}
RN1	65	330	8.3	79.3	48.4	2.8	44.1	0.02	4.8	182	19.3
RN6	75	580	8.1	111.0	51.3	3.5	28.1	0.90	13.3	177	10.0
SR3	60	12,610	7.9	58.5	3,655.0	115.0	840.0	148.00	6,630.0	117	746.0
SR7	70	1,980	7.9	60.7	64.5	13.6	381.0	75.20	21.0	117	1,180.0
SR9	62	1,300	6.8	62.0	12.1	4.6	265.0	42.50	8.9	131	830.0
PG1	78	280	7.8	77.7	84.0	3.3	6.9	0.18	5.8	145	11.9
PG2	55	390	7.7	25.5	39.1	3.7	45.5	10.80	8.1	250	4.3
PL1	57	255	7.8	97.6	76.6	6.4	16.7	0.45	5.8	200	3.1
YL1	80	335	7.9	98.2	75.8	7.2	17.2	0.52	6.1	195	2.9

3.2. Geothermometers

The reservoir temperatures estimated from the cation geothermometers (Eq., 3-4) are usually higher than those obtained from silica geothermometers (Eq., 1-2) [8, 9,10], as shown in Table 3 and Figure 2. The Na–K-Ca geothermometer (Eq., 3) gives anomalously high temperatures ranging from 128 to 182°C, whereas the K–Mg geothermometer (Eq., 4) yields the maximum temperature of around 114°C;. In contrast, the silica geothermometer (Eq., 1) and chalcedony geothermometer (Eq., 2) estimated temperatures vary between 80 and 135 °C. Therefore, the K–Mg geothermometer results are considered more consistent with reservoir temperature estimates from the silica (particularly chalcedony) geothermometer [11, 12, 13]. Reservoir temperatures estimated by the quartz geothermometer are about 20–30 °C higher than those by the chalcedony geothermometer [12, 13, 14] shown in Figure 2.

Table 3. Calculating results of the silica and cation geothermometers (°C) for the geothermal springs in Southern Thailand

Hot spring	Reservoir temperature (°C) computed by different chemical geothermometers			
	quartz (Eq.1)	**chalcedony (Eq.2)**	**Na-K-Ca (Eq.3)**	**K-Mg (Eq.4)**
RN1	124.6	96.7	127.9	113.5
RN6	113.9	84.9	154.3	46.1
SR3	109.3	79.9	142.9	92.9
SR7	111.1	81.9	176.9	50.9
SR9	112.1	83.0	182.0	35.2
PG1	123.6	95.5	132.4	87.8
PG2	112.5	83.4	128.9	96.5
PL1	127.9	100.2	142.0	111.8
YL1	135.8	109.0	158.9	93.0

Whereas the comparisons for quartz, chalcedony, Na-K-Ca, and K-Mg geothermometers used to calculate reservoir temperatures corresponding to all hot spring sample sites are shown in Figure 2.

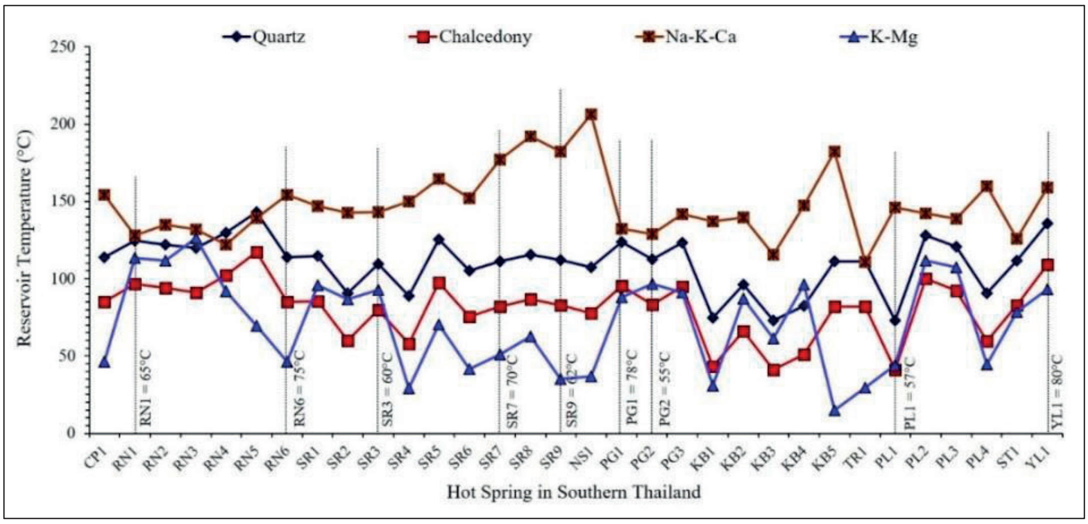

Figure 2. Reservoir temperatures calculated using different geothermometers.

On the other hand, the relationships between silica contents, exit temperatures, and reservoir temperatures calculated with the quartz-silica geothermometer using the hot spring water composition are plotted in Figure 3a. These parameters are strongly correlated except for some geothermal spring samples from low exit temperature hot springs. For the Na–K geothermometer, the relationship between log (K/Na) composition, the exit temperature, and reservoir temperature is shown in Figure 3b. Na/K ratios of geothermal spring water samples are more sensitive to temperature changes than the silica contents, as shown in Figure 3. Also, except for some geothermal spring samples from low exit temperature hot springs, these parameters are negatively correlated but not strong. Therefore, the subsurface temperatures estimated by the silica-quartz geothermometer could represent a suitable reservoir temperature for the geothermal springs (exit temperature, ≥55°C) ranging from 110 to 135°C.

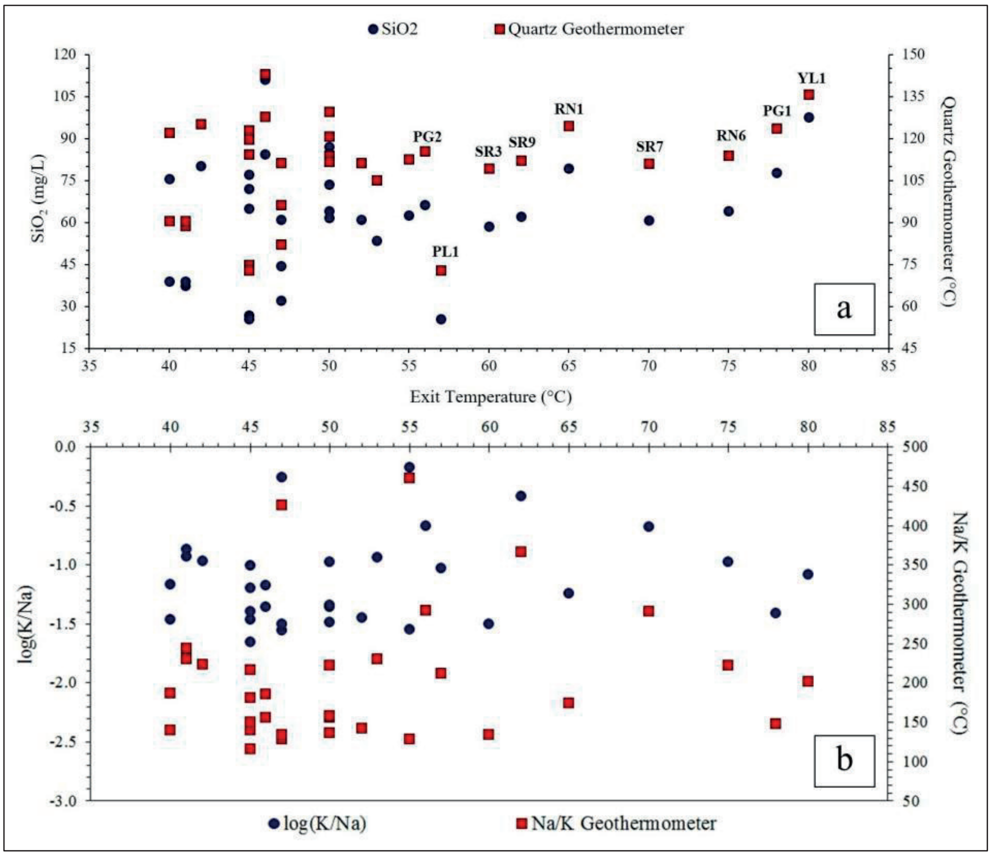

Figure 3. (a) Quartz and (b) Na–K geothermometer temperatures, as well as SiO_2 and log (K/Na) contents in relation to exit temperatures for hot springs from Southern Thailand.

4. Conclusions

The application of chemical geothermometers in geothermal springs of southern Thailand is an essential technique for understanding the chemical composition and for the estimation of geothermal reservoir temperatures. However, conducting detailed studies at the geothermal spring sites is also necessary to better understand the geological setting where these natural hot springs are found. As silica is chemically more inert, the silica geothermometer temperatures can be assumed to provide more reliable reservoir temperatures. The quartz geothermometer has better values than the chalcedony one, as the chalcedony relates to the quartz content. Variations in the cation geothermometers, Na-K-Ca and K-Mg, derived from the mixing of the hot water can explain temperatures with shallow groundwater; at some locations near the shoreline, also with seawater. Silica geothermometers, and especially the quartz ones, provide more realistic reservoir temperatures, but the absolute values are relatively low in comparison.

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