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Geochemical Characterization of Hot Spring Waters from Southern Thailand as the Base for Geothermal Energy Utilization

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Abstract

Hot springs, which are the surface expressions of active geothermal systems at depth, are widely found in countries around Asia, especially in Southeast and East Asia, and can be tapped as a renewable energy source without CO_2 emissions. However, much information about such geothermal systems and their potential for heat and energy production is hidden in the geochemical compositions of hot spring waters. Here, a geochemical survey was conducted on hot springs from nine geothermal provinces in southern Thailand. Thirty samples were analyzed to investigate geochemical relationships, understand geochemical characteristics, identify the origin and mixing of hot waters and calculate the reservoir temperature using different chemical geothermometers. The surface temperatures of the hot springs range from 40 to 80°C. Among cations of sodium, calcium, and potassium show higher concentrations than anions for bicarbonate, sulfate, and chlorine. Most of the hot spring waters show a K-Na-bicarbonate-rich water signature, reflecting homogeneity in the hydrochemical processes of the various hot spring systems. Calculated silica and cation geothermometer temperatures show no clear correlation, indicating possible mixing between the original hot waters and groundwater at near-surface depths, which is supported by the Na-K-Mg ternary diagram distribution. All hot springs in southern Thailand can be characterized as low-enthalpy systems, thus having the potential for electricity production through binary power plant systems.

Keywords: Hot spring; Southern Thailand; Geochemistry; Geothermometer

1. Introduction

Economic growth in developing countries, especially on the Asian continent, is expected to lead to a strong increase in energy demand in the coming decades (Zaman *et al.,* 2019). In this context, geothermal resources, widely available in many parts of Asia, represent an alternative source of energy for many of these countries and as a domestic energy source, it simultaneously provides advantages when compared to increasing imports of fossil fuels (Zaman *et al.,* 2019; Lund *et al.,* 2021).

Thailand is among the countries in Asia that are facing such a situation and future scenario; however, geothermal resources are available, as indicated by numerous hot spring sites with surface temperatures ranging from 35 to 100 °C from north to south. For southern Thailand alone, nine geothermal provinces with thirty hot springs were reported with surface temperatures ranging from 40 to 80 °C, including Chumphon, Ranong, Surat Thani, Phang Nga, Krabi, Trang, Phatthalung, Satun, and Yala (Lund *et al.,*2021; Ngansom *et al.,* 2019).

Generally, the hot springs in southern Thailand can be broadly classified into two groups: one in a general granitic setting with surface temperatures equal to or higher than 60 °C, and another group in a sedimentary or metamorphic rock setting with surface temperatures lower than 60 °C (Raksaskulwong, 2004). Ranong and Phang Nga geothermal provinces, however, are related to major fault zones, the Khlong Marui Fault (KMF) and Ranong Fault (RF) zones, which cross the southern peninsula from SW to NE (Watkinson *et al.,* 2008). Surat Thani geothermal province with nine hot springs (SR1-SR9) and Ranong geothermal province with six hot springs (RN1-RN6) represent the two areas with the highest number of hot spring manifestations in southern Thailand (Ngansom *et al.,* 2019). The natural saline hot spring (KB4) in Krabi, called "Saline Hot Spring Khlong Thom", is part of a unique geothermal province located in the western part of southern Thailand, close to the shoreline of the Andaman Sea (Ngansom *et al.,* 2016).

Preliminary geological mapping, geochemical analysis, and drilling were carried out by the Department of Mineral Resources of Thailand (DMR) and Department of Groundwater Resources from 1983 to 2016 (Chuaviroj, 1988; Raksaskulwong, 2008). Reservoir temperatures, which represent computed reservoir temperatures, of hot springs in southern Thailand based on quartz geothermometer ranged from 100 to 120 °C, whereas the chalcedony geothermometer gave a range from 80 to 100 °C (Ngansom *et al.,* 2020). Shallow boreholes in the depth range of 50 m to 150 m were drilled in the Ranong, Phang Nga, and Krabi geothermal provinces to estimate the thermal gradient. The thermal logging of shallow boreholes indicated a thermal gradient of 0.044–0.58 °C/m (Ngansom *et al.,* 2019, 2020). Electrical resistivity sounding surveys, which were carried out at several hot spring sites (e.g., SR3, PG1) revealed conductive layers at shallower depths containing hot fluids with higher contents of dissolved solids, followed by a highly resistive zone, which can be fractured, thus allowing the hot water to flow upwards (Ngansom *et al.,* 2016, 2020). To estimate the geothermal potential, detailed geochemical characterization of hot spring waters has already been carried out (Ngansom *et al.,* 2016, 2020). However, in earlier studies, a complete geochemical analysis of both major and trace elements was not reported, which is important for a better understanding of the hydrogeological aspects of such geothermal systems.

In this study, the cation-anion compositions of hot springs were analyzed to identify the chemical properties of hot waters and to understand the relationships between geochemical reactions due to water-rock interactions and the subsequent mixing of original hot water and groundwater. Integrated multicomponent solute geothermometry applying the silica (quartz and chalcedony) and cation (Na-K, Na-K-Ca, and K-Mg) methods were used to estimate reservoir temperatures. Here, two key aspects were addressed: (1) the relationship between hot waters and their reservoir rocks as a fundamental control on the chemical characteristics of hot spring waters and (2) suitable geothermometers to determine reservoir temperatures and (3) to identify the effects of groundwater mixing processes during the ascent of hot spring waters. Obtained results allow a comprehensive understanding of the characteristics of hot spring systems in southern Thailand, which are essential for planning future steps of geothermal resource development as part of the 100% renewable energy initiative.

2. Materials and Methods

2.1 Site Description

Geological settings of hot springs in southern Thailand

The Department of Mineral Resources of Thailand (DMR) reported at least thirty hot springs in southern Thailand distributed in nine geothermal provinces (Figure 1, Table 1). Locations and geological settings indicate the occurrence of a number of these springs along major active strike-slip fault zones, the Ranong Fault Zone (RFZ) and south of it the Khlong Marui Fault Zone (KMFZ) (Watkinson *et al.,* 2008) (Figure 1).

Farther south, a NW–SE trend extends from the TR1 hot springs of the Trang geothermal province down to the YL1 hot spring of the Yala geothermal province in the southernmost area and perhaps farther south to the northern regions of neighboring Malaysia. Field observations indicate that the majority of hot springs occur in lower elevation areas in various geographic environments, including salt marshes, marshy areas, riverbeds, and bedrock surfaces.

The majority of hot springs with temperatures equal to or higher than 60 °C in southern Thailand are found along the RF and KMF zones (Figure 2a-2b, 2d). A large number of these hot springs are prominent at localities of the major fault zones. On the other hand, three-quarters of the hot springs in southern Thailand with temperatures lower than 60 °C are situated within areas of sedimentary rocks or close to granitic bodies (Watkinson *et al.,* 2008) (Figure 2c-2f). A geographic distribution of the hot springs, as illustrated by the map, appears to follow a west to east alignment, which represents the major strike-slip fault zones crossing the peninsula (Watkinson *et al.,* 2008). Moreover, previous geological studies reported that two geothermal provinces, Ranong and Phang Nga (Figure 2a and 2d), are associated with granite rocks as possible heat sources of these geothermal systems, with radiogenic heat generated from these granitic rocks (Ngansom *et al.,* 2020; Watkinson *et al.,* 2008).

2.2 Sample collection, preparation and analyses

Thirty hot spring water samples were collected from nine selected geothermal provinces in southern Thailand that represent the geographical trends of the hot springs described above. A summary of hot springs in southern Thailand and their locations is given in Table 1. The surface temperature of the water samples was measured at sampling points by using a standard thermometer. Hot spring water samples were stored in 1,000 mL polyethylene bottles, which had been rinsed with deionized water twice prior to sampling (Eaton, 2005). Sampled hot spring waters were analyzed for SiO_2, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Fe^{2+}, SO_4^{2-}, HCO_3^{-}, Cl^{-}, and Mn at the Central Equipment Division, Faculty of Science, Prince of Songkla University, Thailand. The methods of analysis and detection limits of these elements are summarized in Table 2.

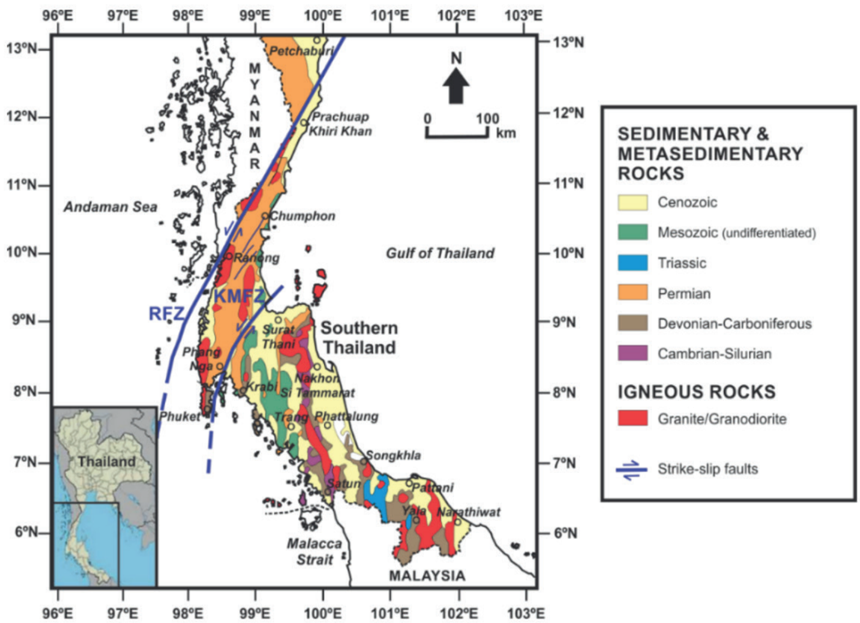

Figure 1. Geological map of southern Thailand showing the distribution of geothermal provinces as well as the trends of the Ranong Fault zone (RF) and the Khlong Marui Fault zone (KMF)

Figure 2. Hot springs in nine geothermal provinces; (a) Ranong (RN1) (b) - (c) Surat Thani (SR7 and SR3), (d) Phang Nga (PG1) (e) Krabi (KB4) and (f) Trang (TR1)

Table 1. Summary of hot springs in southern Thailand with locations

Geothermal province	Hot spring (Code)	Surface temperature (degree, °C)	Location, UTM (WGS-84)	
			East (m)	North (m)
Chumphon (CP)	CP1	50	512222	1075014
Ranong (RN)	RN1	65	462169	1100516
	RN2	40	460000	1094700
	RN3	45	461030	1093400
	RN4	50	462290	1094275
	RN5	46	456192	1080300
	RN6	75	470810	1060430
Surat Thani (SR)	SR1	45	521107	1034893
	SR2	40	520518	1033905
	SR3	60	522412	1031459
	SR4	41	555129	1009502
	SR5	42	545897	972938
	SR6	53	503522	979890
	SR7	70	529417	991895
	SR8	56	530806	991094
	SR9	62	524947	977116
Phang Nga (PG)	PG1	78	441455	960807
	PG2	55	437870	975306
	PG3	45	420496	918037
Krabi (KB)	KB1	45	499622	900439
	KB2	47	500183	891731
	KB3	45	510462	888220
	KB4	47	512329	873475
	KB5	47	523171	876867
Trang (TR)	TR1	52	551391	818787
Satun (ST)	ST1	50	628046	756311
Phatthalung (PL)	PL1	57	625096	823266
	PL2	46	608944	810077
	PL3	50	604490	816432
	PL4	41	615661	850513
Yala (YL)	YL1	80	729730	646758

Table 2. Methods used and detection limits of analyzed cations and anions at the Central Equipment Division, Faculty of Science, Prince of Songkla University, Thailand

Parameters	Method used	Detection limits (mg/L)
Fluoride, F^-	Photometric	0.1
Chloride, Cl^-	Argentometric	0.1
Iron, Fe^{2+}	Inductively Couple Plasma (ICP)-OES	0.005
Calcium, Ca^{2+}	Inductively Couple Plasma (ICP)-OES	0.01
Magnesium, Mg^{2+}	Inductively Couple Plasma (ICP)-OES	0.01
Potassium, K^+	Inductively Couple Plasma (ICP)-OES	0.01
Sodium, Na^+	Inductively Couple Plasma (ICP)-OES	0.005
Sulfate, SO_4^{2-}	Photometric	1
Bicarbonate, HCO_3^-	Titration	1
Silica, SiO_2	Inductively Couple Plasma (ICP)-OES	1

3. Results and Discussion

3.1 Chemistry of hot spring waters

The geochemical compositions of thirty hot spring water samples are given in Table 3. Two hot springs with the highest surface temperatures in southern Thailand were recorded at 80 °C at YL1 in the southernmost part of Thailand, followed by PG1 with a temperature of approximately 78 °C (Table 1). The lowest temperature was recorded at RN2 and SR2, with values of approximately 40 °C. The pH values of the hot spring waters varied between 6.8 and 8.4 (Table 3), while the pH values recorded at SR9 and PG2 were approximately 6.8, and those at RN3 and SR5 were approximately 8.4. The latter value was relatively high when compared with the other hot springs, which provided relatively homogeneous values ranging between 7 and 8 (Table 3).

The concentrations of cations obtained from analyzed hot spring water samples indicate that SiO_2 contents range from the lowest value of 25.5 mg/L at KB3 and ST1 to the highest value of 111 mg/L at RN5 with an average of 62.1 mg/L (Table 3). Nevertheless, KB4 has exceptionally high concentrations of Ca^{2+} (1,005 mg/L), Mg^{2+} (250 mg/L), K^+ (169 mg/L), Na^+ (5375 mg/L), and Fe^{2+} (0.02 mg/L) compared with other hot springs analyzed (average values recorded are 187.51, 36.95, 20.54, 577.64, and 0.25 mg/L for Ca^{2+}, Mg^{2+}, K^+, Na^+ and Fe^+, respectively; Table 3).

On the other hand, relatively high Ca^{2+} contents of approximately 840-933 mg/L were recorded at SR1, SR3 and KB2 compared to the rest of the hot spring except for KB4. Calcium contents recorded at other hot springs of these geothermal provinces range between values of 2.6 mg/L and 515 mg/L. Relatively high concentrations of Na^+ with values from 2.3 mg/L to 4,450 mg/L were recorded in the other hot springs, excluding KB4 (Table 3). Meanwhile, relatively low concentrations of K^+ and Mg^{2+} (e.g., KB5, RN3, and PG2) were recorded in most of the hot springs analyzed, with values that varied between 1.3 mg/L and 132 mg/L for K^+ and from 0.01 mg/L and 156 mg/L for Mg^{2+}. For the bulk of the hot spring water samples analyzed, the Fe^{2+} and Mn concentrations recorded were extremely low and often undetectable.

For the anion concentrations, KB4 is also characterized by exceptionally high contents of HCO_3^- (229 mg/L), SO_4^{2-} (929 mg/L) and Cl^- (9,579 mg/L) compared to other hot springs, with average values of 169.93, 205.42, and 1,058.28 mg/L, respectively.

3.2 Classification of hot spring waters

All hot spring samples from nine geothermal provinces in southern Thailand were classified using Piper plots (Piper *et al.,* 1944) (Figure 3). The plot indicates that Na^+, K^+, and SO_4^{2-} are the dominant ions in the hot spring waters. In contrast, some hot spring waters are saline (avg. TDS, 2,610 mg/L) and characterized by a dominant Na^+-K^+-SO_4^{2-} composition, which may indicate mixing with seawater (Piper *et al.,* 1944; Subtavewung *et al.,* 2005) (Figure 3). Most hot springs in southern Thailand are typically Ca^{2+}-HCO_3^- type due to meteoric water origin (Figure 3).

Table 3. Cation and anion concentrations, pH value, and total dissolved solid (TDS) of hot spring waters from Southern Thailand

Hot springs	pH	TDS (mg/L)	cation (mg/L)						anion (mg/L)			
			Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	Mn	SiO_2	Cl^-	SO_4^{2-}	HCO_3^-
CP1	7.8	580	63.5	6.8	89.5	29.80	0.03	0.04	64.2	112.0	8.0	354
RN1	8.3	330	48.4	2.8	44.1	0.02	0.00	0.10	79.3	4.8	19.3	182
RN2	8.3	330	46.4	3.2	44.1	0.03	3.00	0.02	75.5	11.0	44.9	189
RN3	8.4	330	46.9	3.0	44.3	0.01	0.00	0.01	72.0	10.0	44.9	190
RN4	8.2	240	46.1	2.0	17.8	0.05	0.05	0.02	87.0	5.9	7.0	151
RN5	8.3	310	51.3	3.5	28.1	0.90	0.22	0.20	111.0	13.3	10.0	177
RN6	8.1	580	63.5	6.8	89.5	29.80	0.03	0.04	64.2	112.0	8.0	354
SR1	7.7	13690	3850.0	132.0	933.0	156.00	0.47	0.08	65.0	7020.0	839.0	103
SR2	7.8	7180	1855.0	64.2	400.0	74.80	0.35	0.08	39.0	3403.0	427.0	112
SR3	7.9	12610	3655.0	115.0	840.0	148.00	0.35	0.16	58.5	6630.0	746.0	117
SR4	8.3	270	20.5	2.4	27.8	22.40	0.22	0.16	37.4	21.0	26.0	181
SR5	8.4	320	55.9	6.0	20.9	2.47	0.35	0.16	80.2	14.0	7.0	210
SR6	8.1	740	44.8	5.2	97.1	28.00	0.47	0.08	53.6	14.0	306.0	132
SR7	7.9	1980	64.5	13.6	381.0	75.20	0.22	0.08	60.7	21.0	1180.0	117
SR8	7.2	62	59.7	12.8	69.6	21.90	0.01	0.01	66.3	12.2	295.5	120
SR9	6.8	1300	12.1	4.6	265.0	42.50	0.23	0.02	62.0	8.9	830.0	131
PG1	7.8	280	84.0	3.3	6.9	0.18	0.03	0.03	77.7	5.8	11.9	145
PG2	6.8	390	108.6	3.1	2.6	0.08	0.01	0.01	62.5	7.3	77.5	135
PG3	6.9	5100	1250.0	50.3	515.0	32.80	0.15	0.58	77.0	3097.0	22.0	62
KB1	7.2	350	24.9	2.5	86.3	20.00	0.32	0.03	26.8	29.6	4.9	329
KB2	7.3	16120	4450.0	125.0	975.0	270.00	0.19	0.03	44.4	9290.0	891.0	105
KB3	7.2	3300	986.0	22.1	382.0	74.00	0.30	0.03	25.5	1656.0	63.8	229
KB4	7.2	11690	5375.0	169.0	1005.0	250.00	0.02	0.05	32.1	9579.0	929.0	229
KB5	7.0	480	2.3	1.3	86.3	32.20	0.11	0.01	61.0	8.9	205.0	156
TR1	7.1	590	79.1	2.8	82.1	29.20	N/A	0.02	61.0	189.0	60.0	162
ST1	7.7	265	39.1	3.7	45.5	10.80	0.14	0.01	25.5	8.1	4.3	250
PL1	8.0	255	72.9	3.2	3.0	0.03	0.06	0.01	84.3	7.2	5.6	115
PL2	8.0	240	69.7	3.2	5.1	0.04	0.01	0.01	73.6	6.3	4.9	125
PL3	6.9	418	21.7	2.9	21.9	6.48	0.01	0.01	38.9	7.3	6.4	128
PL4	7.7	250	80.7	2.6	5.0	0.24	0.03	0.01	61.6	17.0	3.5	137
YL1	7.8	330	76.6	6.4	16.7	0.45	0.04	0.08	97.6	5.8	3.1	200

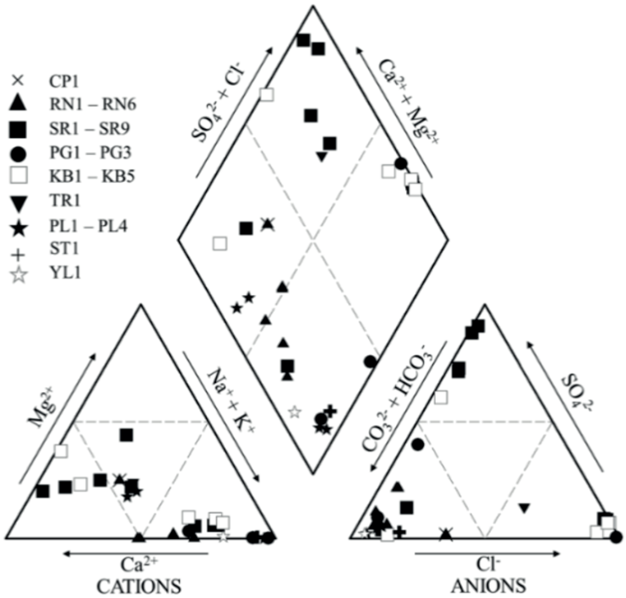

Figure 3. Classification of hot spring waters of all geothermal provinces using Piper diagram

Triangular plots of the major cations and anions (Figure 4a) are used to map hot spring water types in southern Thailand. The analysis illustrates that hot springs are K^+-Na^+-bicarbonate-rich waters (Figure 4a), and all hot spring water samples plot in the bicarbonate water field with the exceptions of SR3, KB2 and KB4, which plot in the neutral chloride water field due to relatively high Cl^- contents. In Figure 4b, all samples plot close to the $Na^+ + K^+$ a field excluding SR1 and SR3, which is characterized by higher Ca^{2+} content. Figure 4c displays the Na^+ type of the studied hot springs, where most hot water samples plot close to the Na+ field, except for some hot springs in the Surat Thani geothermal province, which plot close to the SO_4^{2-} field (Figure 4c).

All hot spring water samples plot in the immature area (Figure 5a) of the Na^+-K^+-Mg^2 ternary diagram, which means they are chemically not in equilibrium. The data in the $10Mg^{2+}/(10Mg^{2+}+Ca^{2+})$ versus $10K^+/(10K^++Na^+)$ binary plot do not indicate any equilibration between reservoir rocks and waters (Figure 5b). Consequently, there are no linear relationships in the Ca^{2+} vs. Cl^- (Figure 6a), Mg^{2+} vs. Cl^- (Figure 6b), and SO_4^{2-} vs. Cl^- plots (Figure 6c).

With the exception of Surat Thani (SR1, SR3, SR7, and SR9) and Krabi (KB2 and KB4), most of the hot spring sites have low SO_4^{2-} contents, suggesting a non-volcanic origin (Baioumy *et al.,* 2015). These hot spring waters are classified as Na-bicarbonate, Na^+-SO_4^{2-}, Na^+-SO_4^{2-}-Cl^- bicarbonate and Ca^{2+}- SO_4^{2-} types, which are possibly caused by mixing with seawater (Ngansom *et al.,* 2016; Subtavewung *et al.,* 2005). This interpretation is supported by the location and geological setting of the hot spring sites, which show that the studied hot springs have been reported either in or close to the Gulf of Thailand for the Surat Thani geothermal province and the Andaman Sea for the Krabi geothermal province (Ngansom *et al.,* 2016; Fournier, 1913). However, the chemical analyses of hot spring water samples in southern Thailand indicate mixing of hot waters with groundwater/freshwater near the surface in a shallow reservoir, which is often determined through geophysical surveys as mentioned above (Ngansom *et al.,* 2016; Baioumy *et al.,* 2015).

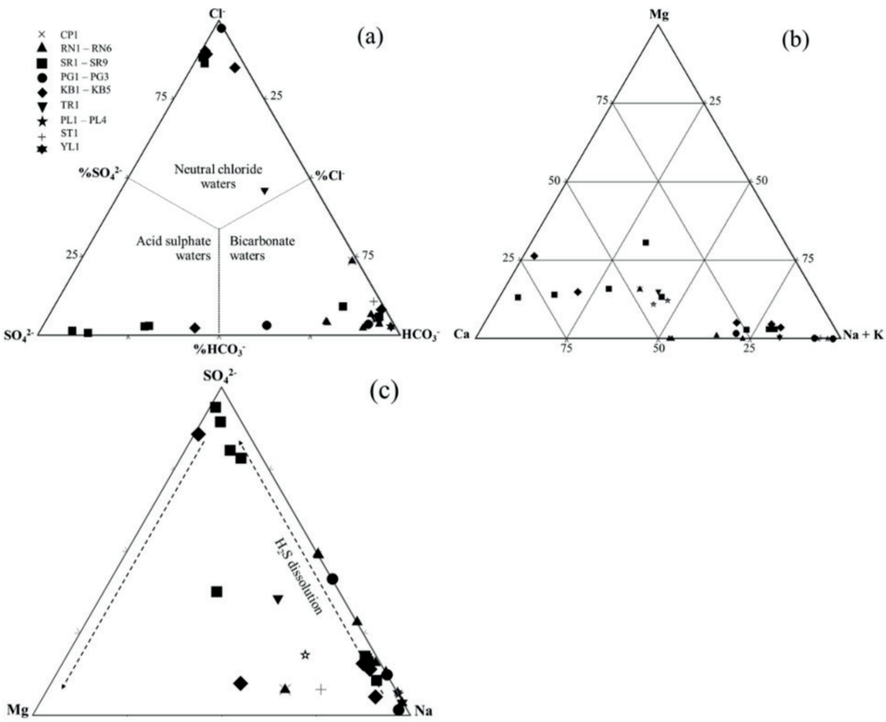

Figure 4. Classification of water using triangular plots for major cations and anions (a) Cl^{-}-SO_4^{2-}-HCO_3^{-} plot, (b) Mg^{2+}-Ca^{2+}-(Na^{+}+K^{+}) plot, and (c) SO_4^{2-}-Mg^{2+}-Na^{+} plot

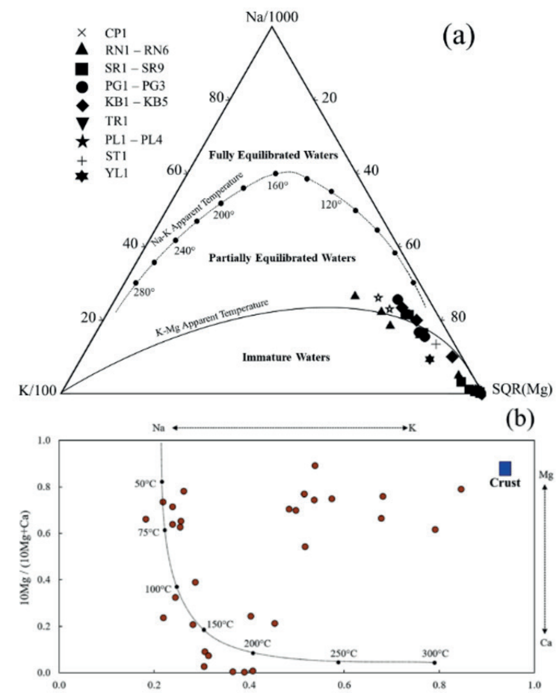

Figure 5. Assessment of subsurface temperature and water-rock equilibrium using (a) Na^{+}-K^{+}-Mg^{2+} of Giggenbach (1988) and (b) binary $10Mg^{2+}/(10Mg^{2+}+Ca^{2+})$ vs. $10K^{+}/(10K^{+}+Na^{+})$ diagram

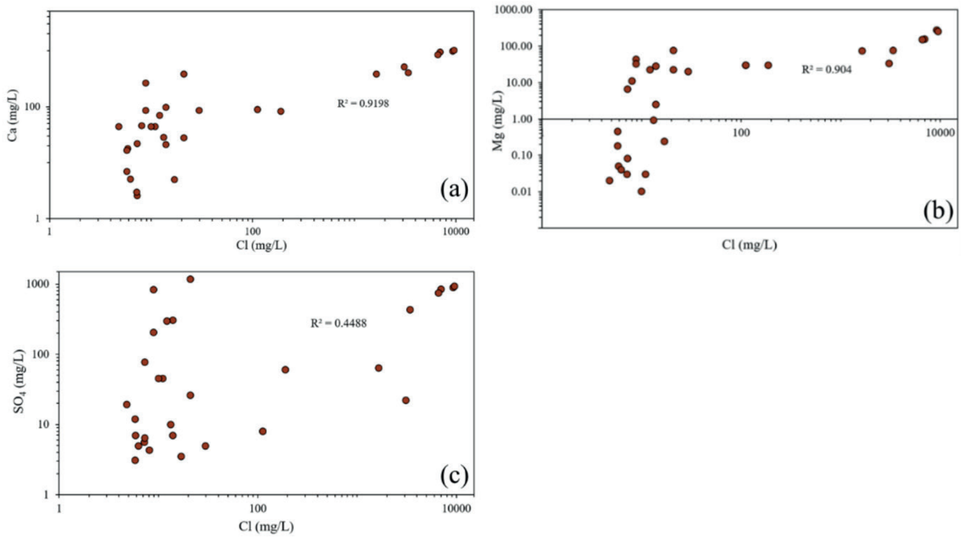

Figure 6. Binary plots of Cl^- versus (a) Ca^{2+}, (b) Mg^{2+}, and (c) SO_4^{2-} with all showing no clear correlation

3.3 Chemical geothermometers

A comparison of different geothermometers has been proposed, using both silica and cation applications. Cation geothermometers are based on slow re-equilibrating reactions (Dávalos-Elizondo *et al.,* 2021; Kanjanapayont, 2014), while those using silica concentrations in solutions are based on fast re-equilibrating reactions (Fournier, 1913; Fournier, 1977). Geothermometers with slow re-equilibration are theoretically more effective in terms of real assessments of deep temperatures, but they are often affected by shallow processes (Fournier, 1977). For example, the K-Na geothermometer is often unreliable when applied to hot springs that emerge after mixing with groundwater circulating in aquifers hosted in pyroclastic K-rich alkaline formations (Fournier, 1977; Fournier, 1983). On the other hand, geothermometers with fast re-equilibration often give estimated deep temperatures much lower than real temperatures (Fournier, 1983; Henley *et al.,* 1984). To estimate reservoir temperatures (tR, in °C) of the hot springs in southern Thailand, various silica and cation geothermometers were used (Fournier, 1913; Fournier, 1983), as shown below:

$$\text{Quartz; } t_R\,(°C) = \left[\frac{1309}{5.19-\log S}\right] - 27315 \quad (1)$$

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

$$\text{Na-K; } t_R\,(°C) = \left[\frac{1390}{1.750+\log(Na/K)}\right] - 273.15 \quad (3)$$

$$\text{Na-K-Ca; } t_R\,(°C) = \left[\frac{1647}{\log(Na/K)+\beta[\log(\sqrt{Ca}/Na)+2.06]+2.47}\right] - 273.15 \quad (4)$$

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

$$\text{K-Mg; } t_R\,(°C) = \left[\frac{4410}{14-\log(K^2/Mg)}\right] - 273.15 \quad (5)$$

A summary of reservoir temperatures from these computations is shown in Table 4 and Figure 7a with a comparison between various geothermometers. Generally, reservoir temperatures of quartz geothermometers as shown in Equation (1) are generally lower than those of cation geothermometers in Equation (3) - (5). Numbers from the quartz geothermometer range from 73 °C in KB3 to 143 °C in RN5, while temperatures calculated from the Na-K geothermometer in Equation (3) vary between 115 °C and 426 °C in KB3 and KB5. On the other hand, reservoir temperatures calculated from the chalcedony, Na-K-Ca and K-Mg geothermometers are much lower than those of the quartz and Na–K geothermometers. The chalcedony geothermometer in Equation (2) has estimated reservoir temperatures ranging from 41 °C for KB3 to 117 °C in RN5. Values of the K-Mg geothermometer range from 15 °C for KB5 to 126 °C in RN3.

The difference between the reservoir temperatures from the silica contents and those from the K-Mg geothermometer can be explained by hot water mixing with seawater (Kanjanapayont, 2014; Fournier, 1977), while the effects of K^+ and Mg^{2+} contents are more significant than the silica contents of the original hot spring waters. Although there is no correlation between the two low-temperature geothermometers using K-Mg and silica (Figure 7b), they show comparable estimated reservoir temperature values. Figure 7c represents the equilibration reservoir temperatures of quartz and chalcedony. In this study, no correlations were observed between reservoir temperatures calculated from different chemical geothermometers (Figure 7d). Although hot spring waters from all geothermal provinces in southern Thailand do not attain a full equilibrium line of the $10Mg^{2+}/(10Mg^{2+}+Ca^{2+})$ versus $10K^+/(10K^++Na^+)$ binary plot (Figure 5b), most of them intersect this line in a temperature range from 90 to 120°C, which is consistent with the estimated reservoir temperature ranges from silica geothermometers (Table 4).

Table 4. Temperatures calculated from silica and cation geothermometers as well as enthalpy of hot springs in Southern Thailand

Hot springs	Reservoir Temperature (°C)					Enthalpy (kJ/kg) calculated from quartz geothermometer
	quartz (Eq.1)	chalcedony (Eq.2)	Na-K (Eq.3)	Na-K-Ca (Eq.4)	K-Mg (Eq.5)	
CP1	113.9	84.9	222.5	154.3	46.1	476
RN1	124.6	96.7	174.2	127.9	113.5	521
RN2	122.1	93.8	187.1	134.9	111.4	510
RN3	119.6	91.2	181.5	131.7	126.1	500
RN4	129.6	102.1	155.5	122.1	91.8	542
RN5	143.1	117.1	185.8	139.0	69.5	598
RN6	113.9	84.9	222.5	154.3	46.1	476
SR1	114.5	85.6	139.7	146.9	95.8	478
SR2	90.6	59.9	140.3	142.6	86.6	379
SR3	109.3	79.9	134.5	142.9	92.9	457
SR4	88.7	57.9	230.9	150.1	29.1	371
SR5	125.2	97.3	223.1	164.5	70.4	523
SR6	105.1	75.4	230.1	152.1	41.5	439
SR7	111.1	81.9	290.5	176.9	50.9	464
SR8	115.5	86.6	292.4	192.0	62.8	483
SR9	112.1	83.0	366.7	182.0	35.2	469
PG1	123.6	95.5	148.1	132.4	87.8	517
PG2	112.5	83.4	128.2	128.9	96.5	470
PG3	123.1	95.0	149.7	141.5	90.9	515
KB1	74.8	43.2	216.6	137.0	30.7	313
KB2	96.4	66.0	127.9	139.6	87.2	403
KB3	72.8	41.2	115.4	115.4	61.4	304
KB4	82.2	51.0	134.5	147.4	96.1	344
KB5	111.3	82.1	425.9	182.2	15.1	465
TR1	111.3	82.1	142.1	110.7	29.6	465
ST1	72.8	41.2	211.6	146.0	44.0	304
PL1	127.9	100.2	156.1	142.0	111.8	534
PL2	120.8	92.4	158.2	138.7	107.3	505
PL3	90.5	59.8	244.2	159.8	44.6	378
PL4	111.8	82.7	136.4	126.0	78.4	467
YL1	135.8	109.0	201.8	158.9	93.0	568

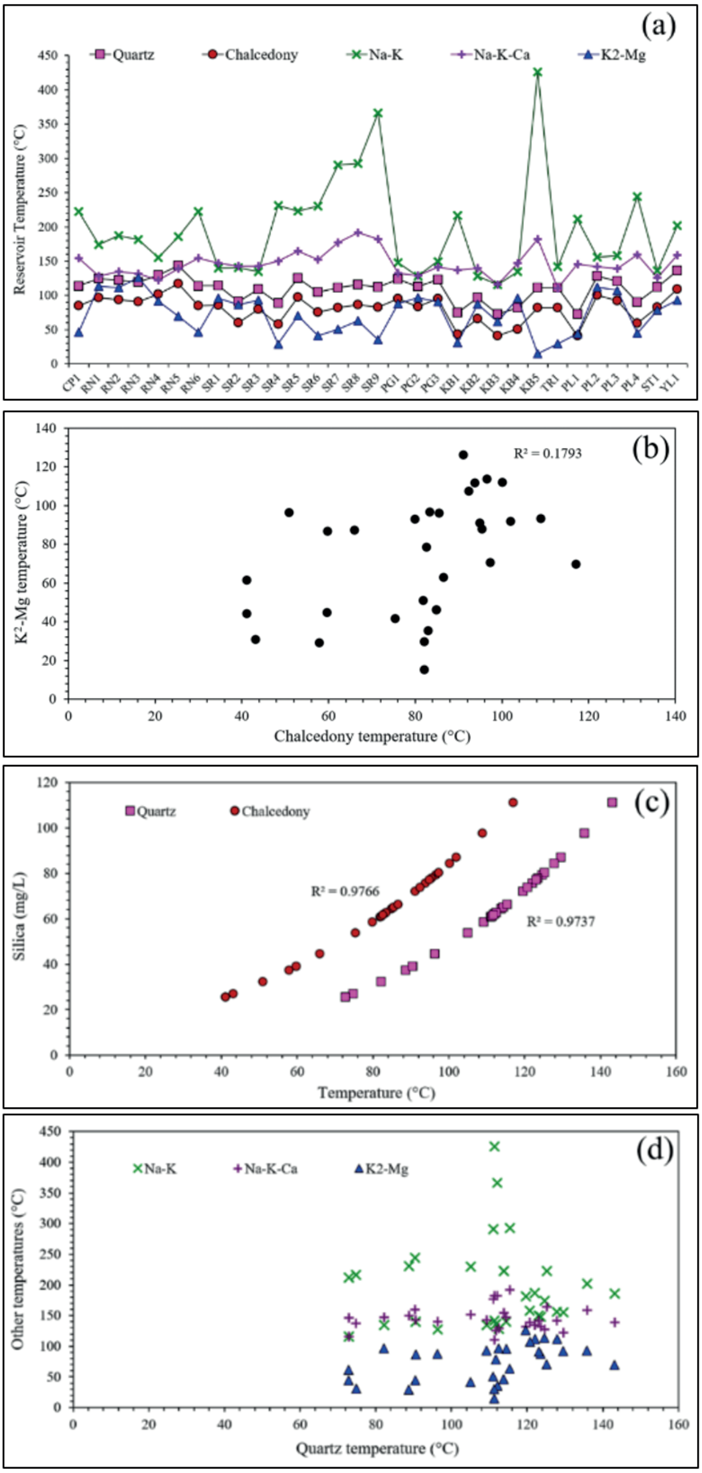

Figure 7. (a) Comparison between the various geothermometers; (b) no correlation is observed between the two low-temperature geothermometers (K–Mg and chalcedony); (c) Equilibration temperatures of quartz and chalcedony geothermometers show an exponential increase of such geothermometers; (d) Lack of correlations between the temperatures calculated from the different solute geothermometers

Very often, freshwater/groundwater from near the surface is mixed with the original hot waters. This mixing makes direct application of chemical geothermometers impossible (Baioumy *et al.,* 2015). Under favorable conditions, the original temperature of the hot water and the fraction of groundwater in the mixture can be estimated by measuring the silica content of the hot spring water, as well as the temperature and silica content of groundwater at the site. Hence, the enthalpy was used to determine the temperature of the hot water and the proportions of hot spring water and groundwater (Baioumy *et al.,* 2015; (Dávalos-Elizondo *et al.,* 2021). Here, in the hot spring waters in southern Thailand, the enthalpy was estimated from the quartz geothermometer with values ranging from 304 kJ/kg to 598 kJ/kg (Table 4). The highest enthalpy values correspond to RN5, followed by YL1 with 598 kJ/kg and 568 kJ/kg, respectively. On the other hand, KB3 and ST1 exhibited the lowest enthalpy values of approximately 304 kJ/kg (Table 4). Geothermal systems with reservoir fluid enthalpies less than 800 kJ/kg and corresponding reservoir temperatures of less than approximately 190 °C are characterized as having low enthalpy. Electrical energy from such systems can be generated through binary power plants (Stober *et al.,* 2012). Moreover, the chemical properties of the hot spring waters reflect the local geology of the specific sites. The exceptionally high contents of Na^+, Mg^{2+}, Cl^-, and SO_4^{2-} in the hot spring water at KB2, KB4 SR1 and SR3 are likely related to contamination of these aquifers by seawater/brackish water from the ocean via intrusion through rivers that connect the hot springs with the ocean. For southern Thailand, only PG1 and RN6 were found in locations that both were in contact with igneous rocks (Watkinson *et al.,* 2008) and had high concentrations of radiogenic elements (Ngansom *et al.,* 2020).

4. Conclusions

Geochemical data from more than 30 hot springs in nine geothermal provinces in southern Thailand indicate that most of the hot springs contain K^+-Na^+ bicarbonate-rich waters. A shallow geothermal reservoir related to near-surface structures is likely the zone of mixing of original hot waters with existing groundwater or seawater intruded in near-coastal aquifers. The geochemical data, as displayed in the Na^+-K^+-Mg^{2+} ternary diagram, clearly show that the sampled hot waters are not in equilibrium with their associated reservoir rocks. This inference is also supported by the fact that there is no clear correlation between the silica and cation geothermometers. From the different geothermometers applied to indicate reservoir temperatures, namely, quartz, chalcedony, Na-K, Na-K-Ca, and K-Mg, the quartz geothermometer provides the best representation of reservoir temperatures of hot springs in southern Thailand, which range from 73 °C to 143 °C. While the hot springs in southern Thailand represent different geological provenances, no clear evidence was found with respect to the effect of geological formations on the composition of these hot waters, indicated by the homogeneity in the cation and anion compositions of these hot spring waters from all geothermal provinces. Furthermore, hot spring waters in southern Thailand are suggested to have an intermediate enthalpy range of 304 to 598 kJ/kg; these values indicate that they have the potential to generate heat and represent possible sources for geothermal power plants generating electricity without CO_2 emissions.

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