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Geochemical Characteristics of B-Li-Cl Type Waters in Geothermal Area: Implications for the Origin of Tawau Hot Springs, Sabah, Malaysia

Fredolin Javino
Department of Minerals and Geoscience,
University of Malaya,
MALAYSIA

Ignatius Adi Prabowo*
Built Environment and Surveying,
Universiti Teknologi Malaysia,
MALAYSIA

Mohd Rashidi Abdull Manap
Department of Chemistry, Faculty of Science,
Universiti Putra Malaysia,
MALAYSIA

Norizah Abdul Rahman
Department of Chemistry, Faculty of Science,
Universiti Putra Malaysia,
MALAYSIA

***Correspondence: E-mail:** prabowo20@graduate.utm.my

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Abstract

Boron (B), Lithium (L), and Chlorine (Cl) are valuable indicators in geothermal detection due to their unique properties and behavior in hydrothermal systems. Volcanic hot springs are generally believed to originate from meteoric circulation or buried seawater and are controlled by equilibrium exchange with magmatic rocks at high temperatures. In this study, we report the B-Li-Cl geochemical characteristics of Tawau hot springs, in the forearc region of Malaysia. The data has been collected from previous studies that analyzed 8 water samples to determine the levels of 10 dissolved elements or components. We performed data correlation analyses to infer the source materials and origins of the hot springs. In addition, we performed numerical modeling of oxygen and hydrogen isotope fractionation to examine the composition of derived fluids as possible candidates of geofluids. The results suggest that Tawau geothermal originated from deep seawater due to subduction before undergoing magmatisation and alteration processes. This interpretation result has a positive correlation with Li and boron. In addition, the geological conditions in the Sabah region, which has subduction zones from two directions, cause a high probability of seawater or marine sediment contribution into the reservoir before finally coming out in the form of a geothermal fluid phase.

Keywords: boron; clorine; geochemical characteristics; geothermal; lithium; tawau hot spring

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INTRODUCTION

Research on the geochemical characteristics of geothermal areas focuses on understanding the chemical composition and processes within geothermal systems. This research is essential for identifying potential geothermal resources and optimising their sustainable use. (Giggenbach, 1992). Analysing the chemical composition of geothermal water usually uses major ions (e.g., Na, K, Ca, Mg, Cl, SO_4), while other minor elements are still little used (e.g., Li, B) (Arrofi et al., 2024; Tang et al., 2007; Umam et al., 2022). Other analyses such as using isotopes (e.g. hydrogen, oxygen) are also often used to trace the origin, movement and interaction of geothermal fluids with surrounding rocks. All these geochemical analyses are used based on the formation mechanism of the geothermal system. For example, the process of studying the alteration of rocks by geothermal fluids, which can provide insight into the temperature and pressure conditions of the system. Then investigate how geothermal fluids interact with different types of rocks, leading to the release or absorption of various elements. In particular, geochemical methods of tracing the origin of geothermal fluids can be combined to obtain more accurate evidence such as Boron and Lithium (Li et al., 2019; Meredith et al., 2013; Millot et al., 2004).

Boron is an excellent tracer for hot fluids in geochemistry due to its unique properties and behaviour in hydrothermal systems. Boron isotopes are very sensitive to changes in fluid temperature and composition, thus providing detailed information on the thermal history and evolution of the fluid (Hirose et al., 2008; Nakajima & Hasegawa, 2007; Xu & Kono, 2002). In the process of water-rock interaction, Boron is released from rocks during interaction with hot fluids, and its concentration and isotopic composition can indicate the extent and nature of this interaction. Boron is incorporated into minerals such as tourmaline, which can be used to trace the path and source of hydrothermal fluids.

In recent years, many researchers worldwide are using Boron as a tracer of hydrothermal fluids originating from subduction melts and they refer to them as slab-dehydrated fluids (Kusuda et al., 2014; Kusuhara et al., 2020; Tsay et al., 2017). In subduction zones, boron helps identify fluid sources, such as seawater, metamorphic fluids and magmatic fluids. In addition, boron can track dehydration reactions in subducting slabs, providing insight into processes occurring at depth. In geothermal systems, Boron is used to study the evolution of geothermal brines and associated hot springs, helping to understand the history and source of the fluid. Monitoring boron levels in geothermal areas can help assess the impact of geothermal exploitation on the environment. In general, based on its behaviour and function, boron is used to identify potential geothermal reservoirs by tracking the movement and origin of hot fluids. It also helps in understanding the impact of mining and other industrial activities on groundwater and surface water quality (Oi et al., 1996; Williams & Hervig, 2004; Wunder et al., 2005).

Lithium is indeed a valuable tracer in geochemistry, especially for studying thermal fluids. Based on its properties and behaviour, naturally occurring lithium has two stable isotopes, ^{6}Li and ^{7}Li, with significant relative mass differences. Lithium is very closely associated with the mantle and primordial (Arrofi et al., 2024; Meredith et al., 2013; Négrel et al., 2010; Umam et al., 2022). The meaning in 'Primordial' is that it refers to something that is ancient, original, or has existed since the beginning of time. The term is often used in scientific and historical contexts to describe the early stages of the universe, Earth, or life. The primordial elements are elements such as hydrogen, helium, Lithium and some other elements that formed in the early stages of the universe, immediately after the Big Bang (Meibom et al., 2003; Sano & Nakajima, 2008).

Based on its solubility properties, Lithium is highly soluble in the fluid phase, which means it can move easily through geological systems. The strong fluid mobility of lithium allows it to move in aqueous, volatile and metallic fluid phases in magma-hydrothermal systems all the way to the earth's surface through porosity or faults (Nukman & Hochstein, 2019; Tabei et al., 2002; Utama et al., 2021). Lithium isotope fractionation (up to 30‰) in natural samples provides a clear signal for tracking fluid origins and interactions. In Water-Rock interaction processes, lithium can track water-rock interactions at low and high temperatures. While in magmatic processes, Lithium helps in understanding magmatic processes, including fluid, rock and magma sources. Lithium is also used to study environmental processes, such as chemical weathering of continental rocks and oceanic crust (Hirose et al., 2008; Iwamori, 2007; Stern, 2002).

Chlorine is a valuable tracer in geochemistry for studying hot fluids due to its unique properties and behaviour in hydrothermal systems. Chlorine has two stable isotopes, $^{\delta 35}Cl$ and $^{\delta 37}Cl$, which undergo fractionation during fluid-rock interactions. This fractionation can provide insight into the sources and processes that influence the thermal fluid. Chlorine concentration is often used as a conservative tracer because it is not significantly affected by chemical reactions, making it a reliable indicator of fluid movement and origin (Acharya et al., 2018; Hendry et al., 2000; Idroes et al., 2019; Singh et al., 2020). In some cases such as magmatic brines, chlorine can trace the assimilation of magmatic brines into hydrothermal systems. Several studies have shown that low $^{\delta 37}Cl$ values in silicate rocks can be attributed to the assimilation of magmatic brines formed and stored in crustal magmas. Chlorine is concentrated in hydrosaline fluids (aqueous fluids enriched with high-density

Cl or brines), which play an important role in the formation of magmatic-hydrothermal ore deposits (Al-ahmadi & El-Fiky, 2009; Arrofi et al., 2024; Asadi et al., 2020).

Based on its role as a thermal fluid source tracer, Chlorine can help trace the source of hydrothermal fluids, distinguishing between magmatic, meteoric and seawater sources. In addition, Chlorine, along with other elements such as iodine-129, can be used to estimate the residence time of hydrothermal fluids in geological formations (Cubadda, 2004; Masuda et al., 1985). Chlorine applications in geothermal systems have been widely used as a reliable tracer. Chlorine can be used to identify and characterise geothermal reservoirs, providing information on fluid sources, pathways, and interactions with surrounding rocks. In addition, the combination of chlorine with other elements such as boron and lithium can help assess the impact of geothermal exploitation on the environment and water quality (Amita et al., 2014; Hendry et al., 2000).

In this study, we conducted data correlation analyses to infer the source material and origin of the Tawau hot springs in Sabah, Malaysia. In addition, we performed numerical modelling of oxygen and hydrogen isotope fractionation to examine the composition of derived fluids as possible candidates of geofluids (geothermal waters).

METHOD

Methodology Research

In this study, we analysed the B-Li-Cl geochemical characteristics of Tawau hot springs, in the forearc region of Malaysia **(Figure 1)**. Data from the study were taken from previous research by Javino et al., (2010) and examined 8 water samples to determine the levels of 10 dissolved elements or components. In his experiment, water temperature, pH, alkalinity and free CO content were measured in situ. The water was put into two polypropylene bottles. One of them was acidified for cation analysis in the laboratory, and the other was kept for anion and stable isotope analysis. The oxygen and hydrogen isotope species of the analysed hot springs and the location of each sample can be seen in **Table 1**.

Table 1. Oxygen and hydrogen isotopes from hot water samples in the Tawau geothermal region, Sabah, Malaysia

No	Sample ID	Longitude	Latitude	Altitude (m)	T(°C)	EC	Deep Temperature (°C)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
1	A2A	117°58'30"	4°21'33"	160	41.1	3910	159	-4.91	-37.0
2	A2C	117°58'30"	4°21'33"	160	54.2	4750	195	-4.83	-39.3
3	A5	117°59'01"	4°22'39"	270	60.0	2600	174	-4.69	-38.7
4	A2B	117°58'30"	4°21'33"	160	60.7	4340	172	-4.97	-39.0
5	A1A	117°58'30"	4°21'33"	163.5	67.8	4300	158	-5.06	-39.8
6	A1B	117°58'30"	4°21'33"	163.5	68.8	4350	152	-5.13	-39.9
7	A4B	117°58'30"	4°21'33"	180	74.8	4380	nm	nm	nm
8	A4A	117°58'30"	4°21'33"	180	77.6	4200	nm	-5.08	-41.2

***Note : nd (not measured); Sources :** Data from the study were taken from previous research by Javino et al., (2010).

Table2. Chemical composition of 10 elements from hot springs in Tawau geothermal area, Sabah, Malaysia

No	Sample ID	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Cl (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)	Li (mg/L)	B (mg/L)
1	A2A	716	68.50	14.60	194	1078	281	567	3.66	46.10
2	A2C	847	75.50	16.10	208	1231	317	627	4.17	51.30
3	A5	858	86.80	13.10	165	1336	297	239	4.73	55.60
4	A2B	792	76.20	16.10	208	1213	315	619	4.07	51.10
5	A1A	815	77.90	16.70	212	1198	312	668	4.12	45.50
6	A1B	810	78.40	16.50	211	1218	313	649	4.15	51.40
7	A4B	838	81.10	16.70	214	1237	323	668	4.18	52.00
8	A4A	837	82.90	16.80	215	1246	323	606	4.28	52.50

Sources : The data of the study was taken from a previous study by Javino et al., (2010).

The dissolved components of the 10 elements can be seen in **Table 2.** Stable hydrogen and oxygen isotopes were analysed with mass spectrometers at the IAEA (Vienna) and the PNOC Laboratories). Correlation analyses of the data were performed to infer the source material and origin of the hot springs. In addition, numerical modelling of oxygen and hydrogen isotope fractionation was also performed to examine the composition of derived fluids as possible candidates of geofluids.

Geology Setting

The geology of Sabah, Malaysia, is complex and interesting due to its diverse tectonic history and rock formations. Sabah lies near the border of three major tectonic plates: the Eurasian, Indo-Australian and Philippine-Pacific plates **(Figure 1)** . This makes it vulnerable to seismic activity. The region experiences a WNW-ESE compressive stress regime due to the movement of these plates. This results in the formation of active strike-slip and strike-slip faults. In geological history, Sabah is characterised by several tectonic events since the early Tertiary period (Anuar et al., 2021).

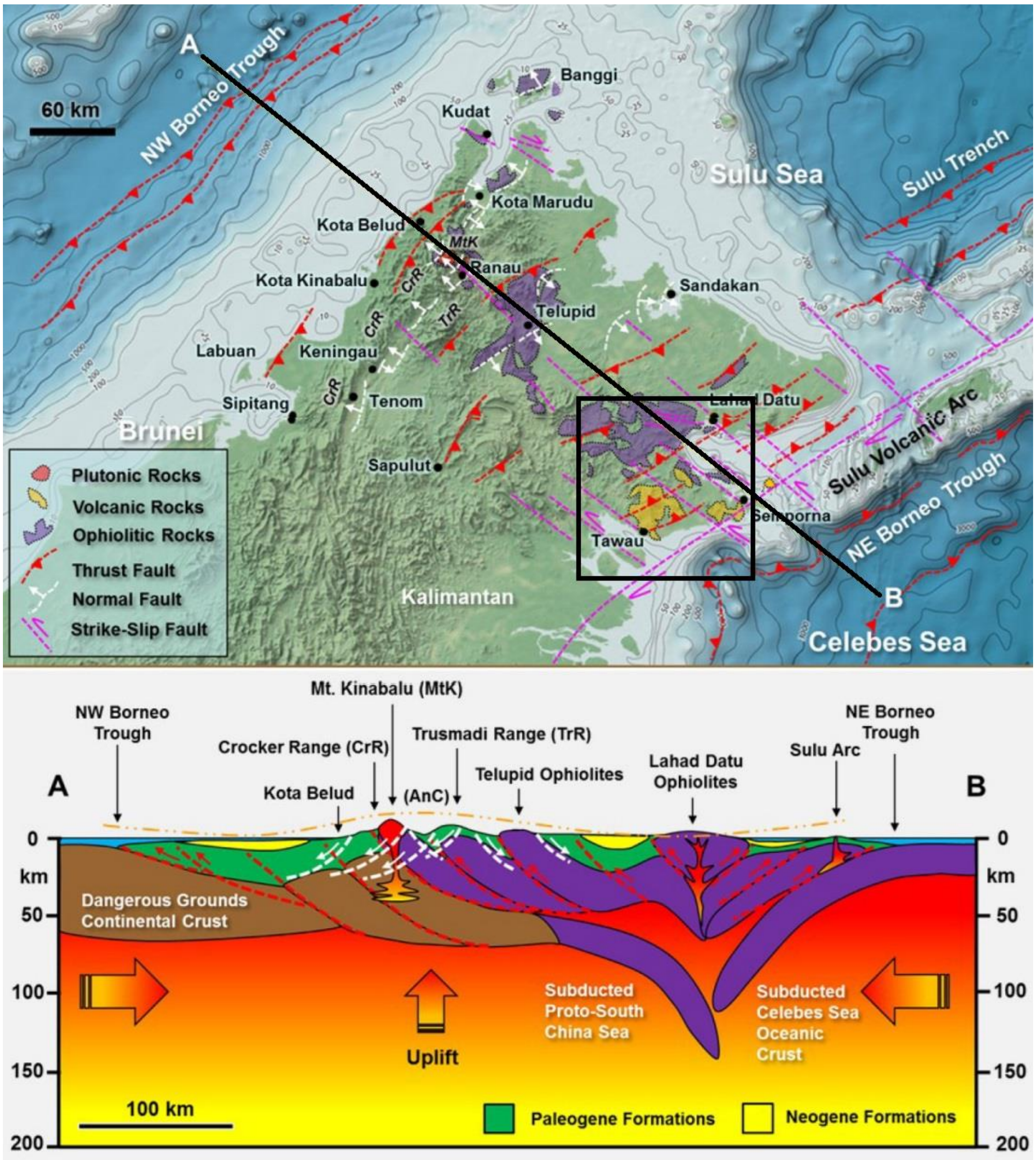

Figure 1. Illustration of active plate movements east of Sabah (the box line is the research area). The South China Sea plate is subducting to the Southeast beneath the Sabah region of Malaysia, while the Sulu-Celebes Sea is generating compression pressure to the Northwest beneath the Sabah region of Malaysia. Image taken from (Tongkul, 2017)

Tectonic activity in the Sabah region of Malaysia includes NW-SE compression, the two subductions approaching each other being a rare event in the rest of the world. Significant tectonic events occurred during the Late Eocene, Early Miocene and Middle Miocene, which caused folding, subduction and uplift. Sabah is largely constructed by thick, folded Upper Cretaceous to Tertiary marine sedimentary rocks. These rocks are interspersed with lavas and plutonites. The basement of Sabah includes ophiolite complexes, which are considered the foundation for sedimentary succession. The Rajang-Crocker accretionary prism consists of deformed deep-sea sediments from the Eocene to Oligocene periods. The region is characterised by NE-SW trending active strike-slip faults and NW-SE trending active shear faults. The Crocker-Trusmadi Mountains are a NE-SW trending uplifted belt, formed due to compressive tectonic forces. Several elongated Quaternary graben-like basins, such as the Tenom, Keningau and Tambunan basins, are present along the crest of the anticlinorium. Tectonic activity in Sabah results in frequent earthquakes, which can have significant environmental impacts. Features such as mud volcanoes and hot springs are evidence of ongoing tectonic processes (Anuar et al., 2021; Tongkul, 2017).

The Tawau geothermal is located approximately 20 km northeast of Tawau City in Sabah, Malaysia **(Figure 2)**. The area is characterised by Quaternary volcanic rocks, including dacitic, andesitic and basaltic lavas and tuffs from Mount Maria and Mount Andrassy. These volcanic rocks overlie Tertiary sedimentary formations. The region shows indications of active geothermal activity, such as steam-heated hot springs and young volcanic craters around Mount Maria. The geothermal system is centred on the southeast slope of Mount Maria, a young andesite to dacite volcano of Miocene to Quaternary age. The system is structurally controlled by NW-trending transclinear faults and transitional tectonics from the late Pliocene to the present. Surface springs in the area show the presence of deep neutral chloride fluids rising and flowing to the Southeast and South, with temperatures around 200°C. Detailed geological, MT geophysical and geochemical surveys have confirmed the presence of an active geothermal system (Anuar et al., 2021; Tongkul, 2017).

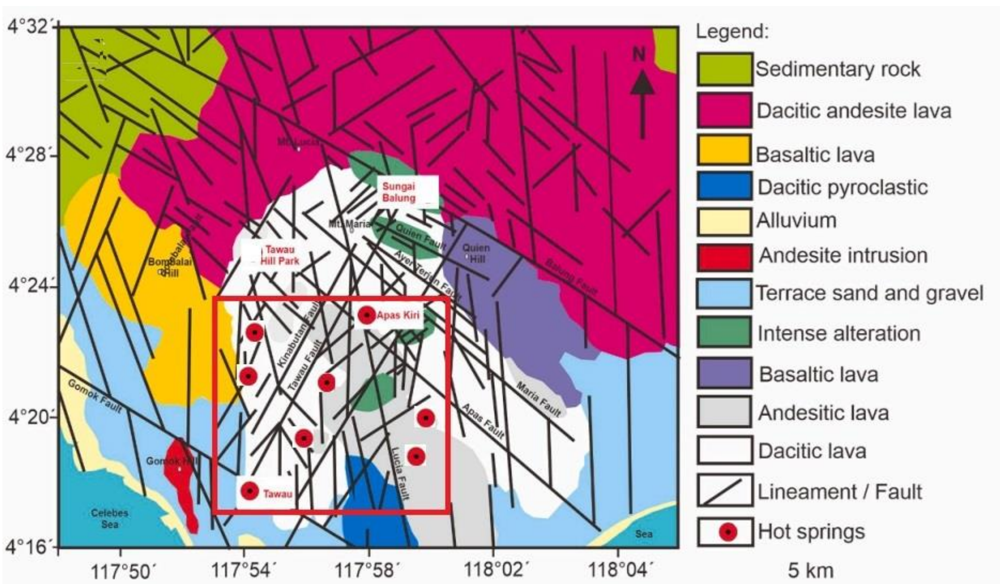

Figure 2. Detailed geological map of hot springs taken from the geothermal region of Tawau, Sabah, Malaysia (red square with 8 location points). Images have been edited and taken from (Anuar et al., 2021)

RESULTS AND DISCUSSION

Piper Plot in Major Elements

Piper plot is a graphical tool used in hydrogeochemistry to visualise the chemical composition of water samples. This tool helps in identifying sources and processes that affect water chemistry (Arevalo, 2013; Jan et al., 2021; Nazri et al., 2016; You et al., 1996). This plot consists of three ternary diagrams representing cations and anions in a way that makes it easier to compare multiple water samples (Acharya et al., 2018; Baba et al., 2020; Deon et al., 2015; Morikawa et al., 2016). From the interpretation results, it can be seen that the hot water samples in the Tawau geothermal area have a dominant sodium and potassium type in the cation triangle and for the anion triangle Tawau geothermal has a dominant chloride type (Javino et al., 2010; Tongkul, 2017). For the overall interpretation of the piper plot, Tawau geothermal has similarities with geothermal in the Taopo Volcanic Zone (TVZ) (Millot et al., 2007, 2012) which has a dominant composition in the sodium-chloride type. These results corroborate the first conjecture that Tawau geothermal has a fluid source derived from magmatisation processes **(Figure 3)**.

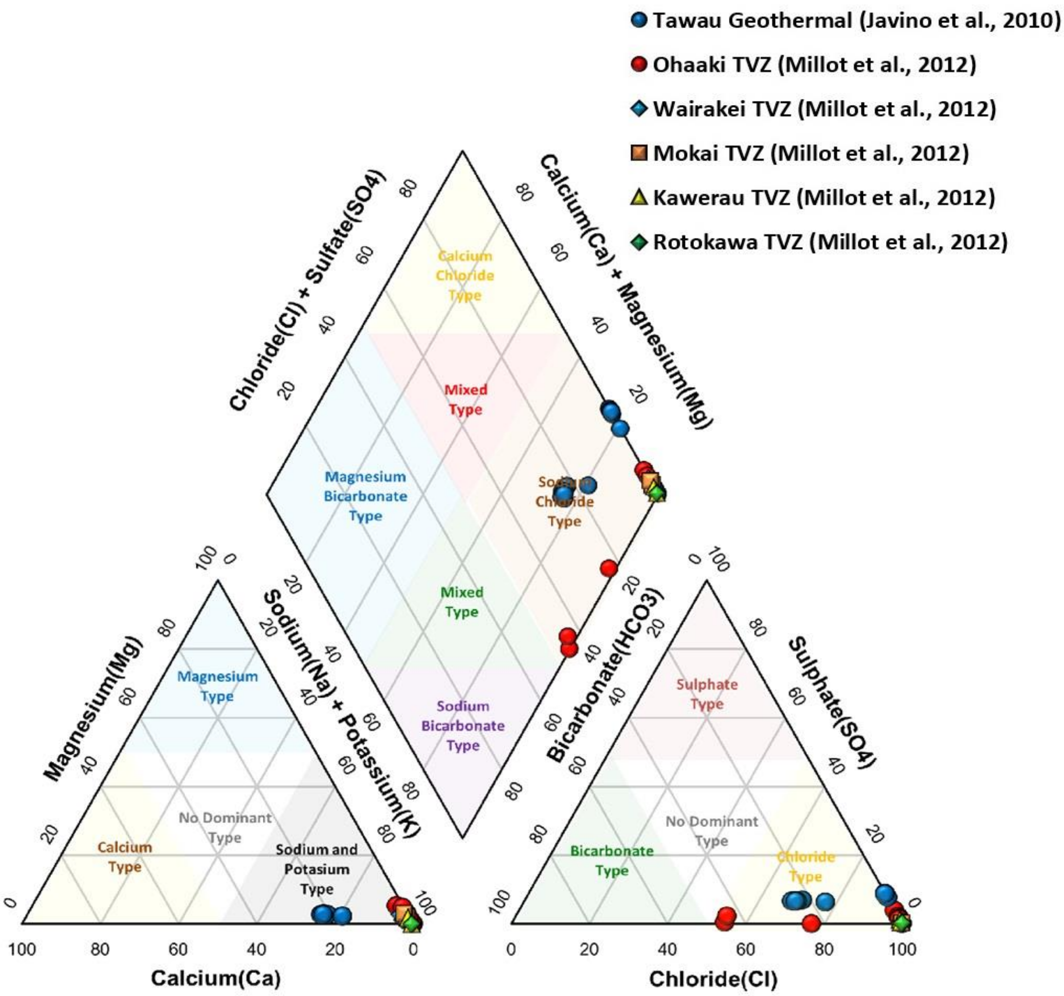

Figure 3. Piper plot interpretation of hot water taken in the Tawau geothermal area, Sabah, Malaysia

Major and Trace Elements

Geothermal waters are usually characterised by examining the behaviour of the main elements (**Table 1** and **Table 2**). In this context, **Figure 4** illustrates the relationship between Cl, which is considered a conservative element, and Na, which is largely controlled by water/rock interactions. While Cl concentrations range between 1078 and 1336 mg/L, Na concentrations range between 716 and 858 mg/L. From a general point of view, we observe a good relationship between Na and Cl **(Figure 4)**, which indicates that the geothermal water shows a large salinity range, with Na and Cl concentrations increasing from A2A, A2C and A5. Other major elements ranged from 68.5 to 86.8 mg/L for K, from 13.10 to 16.80 mg/L for Mg, and from 165 to 215 mg/L for Ca. Anion concentrations ranged from 281 to 323 mg/L for SO_4 and from 239 to 668 mg/L for HCO_3. Regarding trace elements, and of interest for this study: Li concentrations are high, ranging from 3.66 to 4.73 mg/L. B concentrations are also high, ranging between 45.5 and 55.60 mg/L (A5). If we look at all samples by concentration, the B content is homogeneous (Arienzo et al., 2020; Li et al., 2019; Meredith et al., 2013; Millot et al., 2007; Toki et al., 2016).

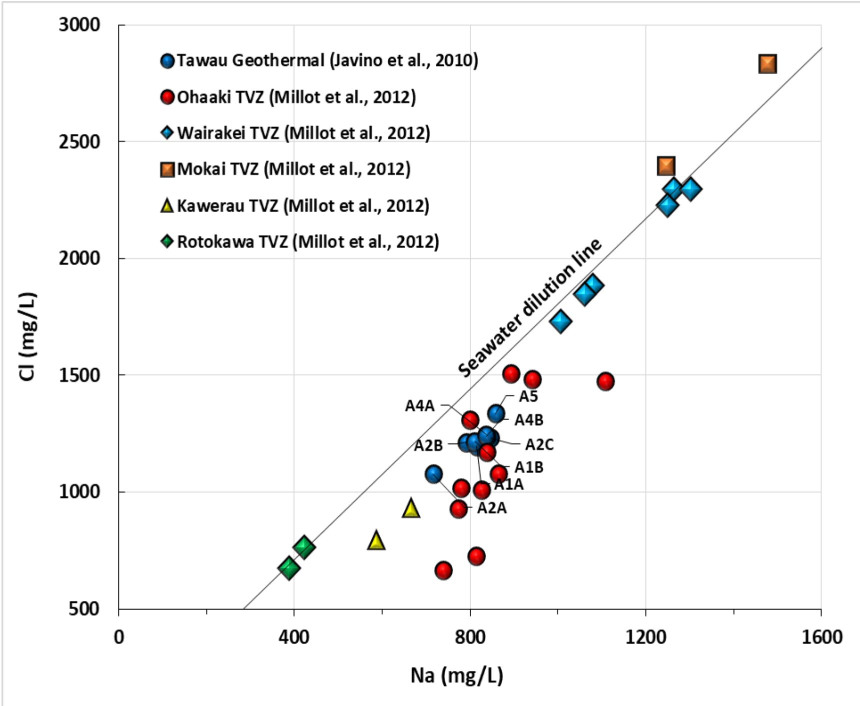

Figure 4. Interpretation of Cl concentration (mg/L) against Na concentration (mg/L). Other literature data were taken from the Taopo Volcanic Zone (TVZ) region by Millot et al., (2012)

Boron, lithium and chlorine concentrations are in line with data reported in the literature for geothermal waters around the world (Arienzo et al., 2020; Arrofi et al., 2024; Meredith et al., 2013; Négrel et al., 2010; Tang et al., 2007; Umam et al., 2022; You et al., 1996). Since Na is mainly controlled by water/rock interactions, it is interesting to investigate the relationship between Na and Li, and B **(Figure 5)**. Firstly, it can be observed that all geothermal waters define a generally positive relationship between Na and Li, indicating that, like Na, Li is mainly controlled by water/rock interactions. Secondly, when B concentration is plotted against Na, a different trend emerges.

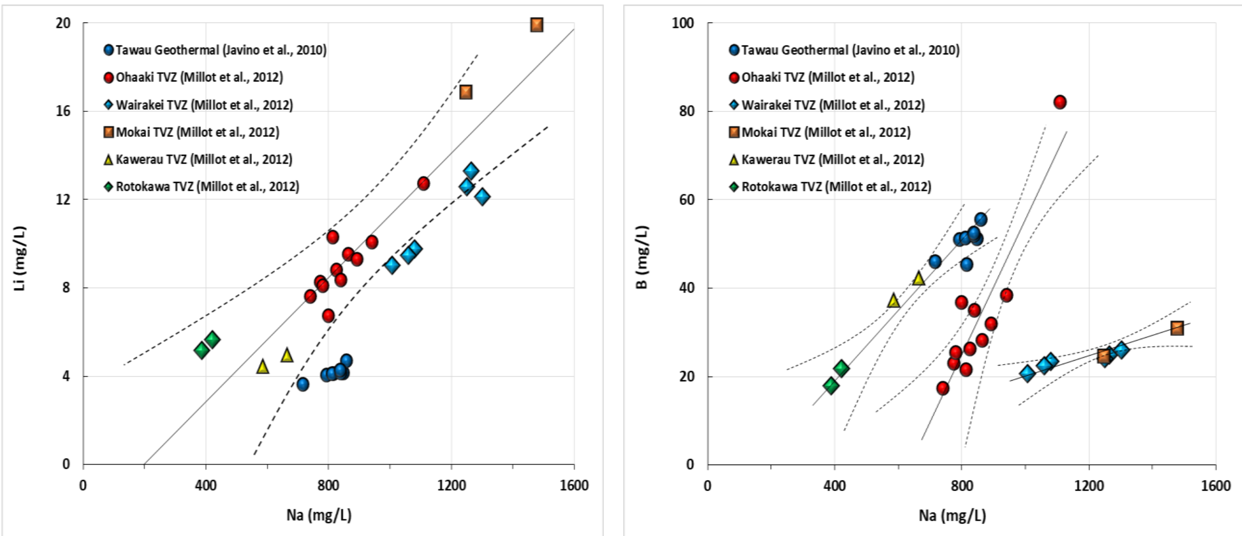

Figure 5. The concentrations of Li, and B are plotted as a function of Na concentration (mg/L). The dashed line represents the uncertainty in the linear correlation of each sample

Indeed, we can observe a distinct positive correlation between B and Na, which means that B is also controlled by water/rock interactions, but there is not one general trend on the scale of the whole geothermal water as observed for Li. From the B vs Na graph, it can be seen that the geothermal samples can be divided into different sample groups: thus, Tawau geothermal water has the same trend as Kawerau and Rotokawa TVZs, while other samples have different trends such as Ohaaki TVZ and Mokai-Wairakei TVZ. Each trend has a correlation with the spatial distribution in the geothermal system. Although the Tawau geothermal system has a different location, the conditions in the Tawau geothermal water are similar to the geothermal conditions in Kawerau and Rotokawa TVZ (Millot et al., 2012).

In addition to the interpretation of Na values, other interpretations such as Temperature plotted against the Li and B concentration function can provide additional information. By calculating the chemical geothermometry **(Figure 6)** we can estimate the reservoir temperature of each sample. The interpretation results show that the Li and B concentrations appear to be relatively constant and independent of fluid temperature. This result suggests that dilution occurs by the mixing of shallower and cooler water (Umam et al., 2022). If the results of the interpretation of hot springs in the Tawau geothermal area are correlated with the geological conditions and geographical location **(Figure 1** and **Figure 2)**, it is possible that the hot springs in the Tawau geothermal area originated from seawater that entered the depths due to subduction before finally undergoing magmatisation and alteration processes (Kazahaya et al., 2014; Morikawa et al., 2016).

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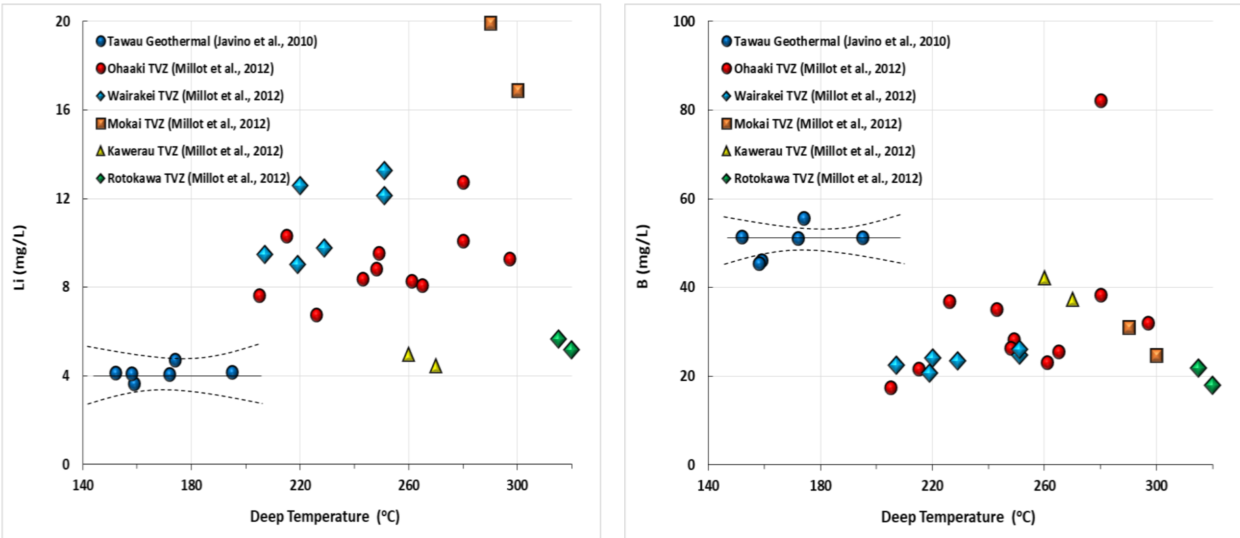

Figure 6. The concentrations of Li, and B are plotted as a function of deep temperature (°C) estimated by geothermometry. The dashed line represents the uncertainty in the linear correlation of each sample

Oxygen and Hydrogen Isotopes

Isotopes of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) are powerful tools for tracking thermal fluids in geochemistry. Oxygen isotopes help identify the source of hot fluids, such as meteoric water (rainwater), seawater, or magmatic water. The $\delta^{18}O$ value can be used to estimate the temperature of the water-rock interaction, as isotope fractionation is temperature-dependent. Oxygen isotopes can reveal mixing processes between different water sources, providing insight into fluid migration and interaction (Coplen, 1982; Mook, 2006). Hydrogen isotopes ($\delta^{2}H$) help determine the origin of hot fluids, distinguishing between meteoric, magmatic and marine sources. The $\delta^{2}H$ value can indicate the evaporation and condensation processes that the hot fluid has undergone. Hydrogen isotopes can track fluid-rock interactions, providing information on the path and depth of fluid movement (Adachi & Yamanaka, 2024; McConnell et al., 2009; Zhao et al., 2009). Combining $\delta^{18}O$ and $\delta^{2}H$ values in a plot (e.g., $\delta^{18}O$ vs $\delta^{2}H$ in **Figure 7**) can provide a comprehensive picture of fluid origin, evolution, and interaction with rocks. These isotopes are used to map geothermal reservoirs, understand fluid recharge areas, and assess the sustainability of geothermal resources (Hosono et al., 2020; Kusuda et al., 2014; Umam et al., 2022).

Based on the results of oxygen and hydrogen isotope interpretation of hot water in the Tawau geothermal area **(Figure 7)**, it can be seen that Tawau geothermal is on a linear plot to seawater (SW). This result is similar to the altered sweater group from data found in central Japan (citation Kazahaya). This interpretation result has a positive correlation with Li and Boron in **Figure 6**. In addition, the geological conditions in the Sabah region, which has subduction zones from two directions, causes a high possibility of seawater or marine sediment contribution into the reservoir before finally exiting in the form of geothermal fluid phase.

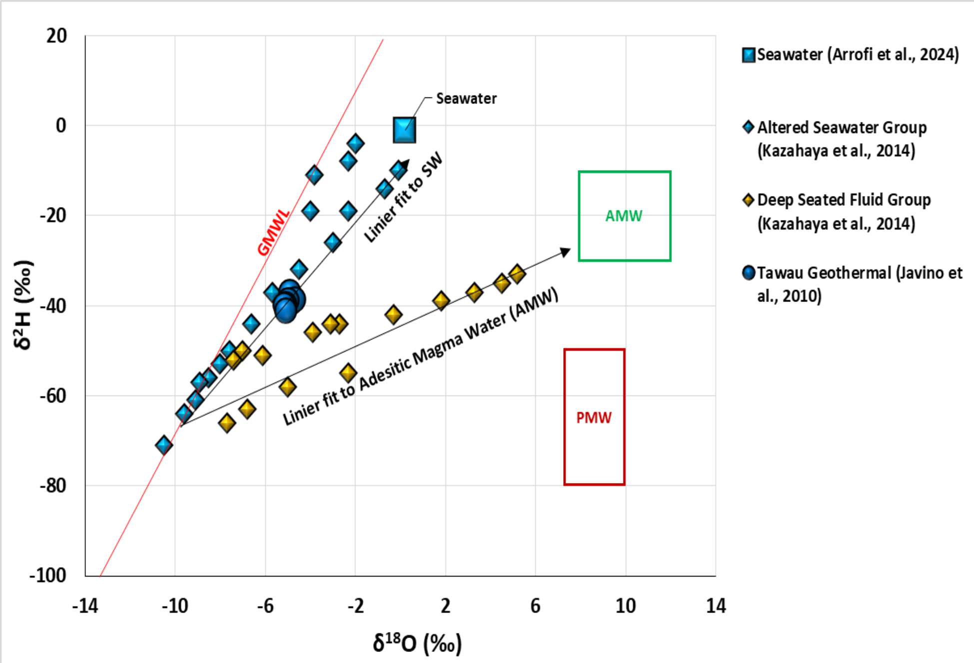

Figure 7. Oxygen and hydrogen isotope interpretations show that the Tawau geothermal plots have consistent results, so they are likely from the same reservoir. The high $\delta^{18}O$ value indicates that the fluid originated from a long process (evolved and altered). This may be due to the opposing subduction zones causing the Sulu-Celebes Sea plate and the South China Sea plate to overlap. These results show that dilution occurs at depth due to plate folding. It is likely that the dilution is caused by the mixing of shallower water (stagnant grounwater) and the high oxygen shift is likely caused by evaporative enrichment (Adachi & Yamanaka, 2024; Yamanaka et al., 2015; Yamanaka & Adachi, 2024)

CONCLUSION

Lithium (Li) concentrations from hot springs in the Tawau geothermal area have high values of 3.66 to 4.28 mg/L. These lithium concentration values indicate that the hot springs originate from deep reservoirs that rise to the surface. Boron concentrations are also quite high (45.5 and 55.6 mg/L) and relatively homogeneous with respect to temperature at depth. Cl values are quite high and have a range similar to seawater, allowing the contribution of seawater into the Tawau geothermal reservoir. Oxygen and hydrogen isotope interpretations of the Tawau geothermal plots are consistent, so they are likely from the same reservoir. However, the high oxygen shift is likely caused by evaporative enrichment. The high $\delta^{18}O$ value indicates that the fluids originated from a long process (evolved and altered). Correlation to geological conditions and geographical location allows the origin of hot springs to be formed due to subduction zones that are in opposite directions that cause the Sulu-Celebes Sea plate and the South China Sea plate to overlap or fold. Stacks or folds of plates that experience magmatisation cause the release of geofluids (reservoir fluids) and come out to the surface in the form of hot spring waters.

AUTHOR CONTRIBUTIONS

Conceptualization, IAP and FJ; methodology, MRAM; software, FJ; validation, NAR, MRAM, and IAP; formal analysis, MRAM; investigation, FJ and IAP; resources, IAP; data curation, NAR; writing—original draft preparation, FJ and MRAM; writing—review and editing, IAP and NAR; visualization, FJ; supervision, IAP; project administration, IAP; funding acquisition, IAP.

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CONFLICTS OF INTEREST
The authors declare no conflict of interest concerning the publication of this article. The authors also confirm that the data and the article are free of plagiarism.

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