INDONESIAN JOURNAL ON GEOSCIENCE
Geological Agency
Ministry of Energy and Mineral Resources

Journal homepage: https://ijog.geologi.esdm.go.id
ISSN 2355-9314, e-ISSN 2355-9306

Combining Lithium Isotope Systematics, Stable Isotopes, and Major Elements as a Powerful Tool for Detection of the Slab-Dehydrated Fluids in Southwestern Japan

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Manuscript received: October 15, 2024; revised: May 18, 2025;
approved: May, 19, 2026; available online: August, 4, 2026

Abstract – This study aims to evaluate whether an integrated geochemical approach using lithium isotope systematics (δ^7Li), Li and Cl concentrations, Cl/Li ratios, stable isotopes (δD and δ^{18}O), and major-element compositions can provide useful constraints on the contribution of thermal water to the hydrothermal system. The study is based entirely on previously published geochemical data. Lithium isotope (δ^7Li) data for four Arima samples reported by Umam *et al*. (2022) were re-evaluated together with Li and Cl concentration data reported by Umam *et al*. (2022) and Kusuda *et al*. (2014). Major-element concentrations and stable isotope (δD and δ^{18}O) data for Arima hot spring waters reported by Kusuda *et al*. (2014) were also integrated into the analysis. The four Arima samples with available δ^7Li data have δ^7Li values < 5‰ and Cl/Li ratios < 1000 and are interpreted as representing thermal water. Although δ^7Li data are not available for the Arima samples reported by Kusuda et al. (2014), 13 of these samples are interpreted as thermal water based on Li concentrations > 0.1 mg/L, Cl concentrations > 1000 mg/L, and Cl/Li ratios < 1000. One sample is interpreted as representing mixing water and has a Cl concentration of 435 mg/L. These results suggest that integrating lithium isotope systematics with Li and Cl concentrations, Cl/Li ratios, stable isotopes, and major-element compositions may provide a useful geochemical framework for evaluating the characteristics and possible contribution of slab-dehydrated fluids to the hydrothermal system.

Keywords: Arima hot spring waters, slab-dehydrated fluids, lithium isotope systematics, stable isotopes, major elements, powerful geochemical analysis

How to cite this article:
Umam, R., 2026. Combining Lithium Isotope Systematics, Isotope Stable, and Major Elements as a Powerful Tool for Detection of The Slab-Dehydrated Fluids in Southwestern Japan. *Indonesian Journal on Geoscience*, 13 (3), p.393-407. DOI: 10.17014/ijog.13.3.393-407

Introduction

Background

For more than a decade, the emergence of fluids originating from the Earth's mantle, especially in subduction zone areas (slab-dehydrated fluids/thermal waters), has been considered to play an important role in geodynamic processes (Nakajima and Hasegawa, 2007; Shiomi and Park, 2008). Its role in the process of island origin has been known for a long time. In addition, the activity of the emergence of slab-dehydrated fluids has a dramatic effect on various rock properties and indicates the control of other geophysical processes in the area around the slab (Morikawa *et al*., 2008). Specifically, slab-dehydrated fluids are fluids that are formed from the process of slabs entering the Earth, are dehydrated, and undergo

a long process of water-rock interaction before finally being released through faults or fractures around subduction zones (Morikawa *et al*., 2008; Stern, 2018; Umam *et al*., 2022).

In the process, hydrated areas differ from dehydrated areas, such that the low-velocity zone beneath the lithosphere, which was originally interpreted as a partial melting zone, can be viewed as a hydrated zone (Wyllie, 1974). Meanwhile, zones with higher temperatures, pressure, and trapping can be considered dehydration zones (Harlaux *et al.,* 2017; Tanimizu *et al*., 2021; Zhang *et al*., 2020). Recently, it has been suggested that the high depletion of upper mantle elements is caused by melt dehydration above the 410 km discontinuity (Morikawa *et al*., 2008; Stern, 2018; Umam *et al*., 2022).

Geological Settings

Based on previous research studies, hot spring water in the Kinki region, southwestern Japan, is thought to have a close relationship with the subduction process (Umam *et al*., 2026; Figure 1). One of the most well-known, the Arima hot spring water, has been confirmed to come from deep groundwater as a result of the subduction process (Kusuda *et al*., 2014; Nakamura *et al*., 2016). However, along with the development of geochemical analysis, many researchers continue to conduct research to find analytical methods that are more sensitive and effective in analyzing geofluids. The development of geofluid analysis methods has become a special topic in the field of geoscience.

Over the past two decades, many researchers have analyzed several hot spring waters in the southwest of Japan and have speculated that some of the hot spring waters that appear are closely related to the subduction process by the Philippine Sea Slab (PHS). Various methods have been carried out, such as He gas analysis (Meibom *et al*., 2003; Sano and Nakajima, 2008; Tedesco, 1997), tremor activity (Obara, 2002; Sano and Nakajima, 2008), geochemical analysis using REE (Nakamura *et al*., 2014), and others to strengthen this suspicion.

Southwestern (SW) Japan is a nonvolcanic region that has many representative hot spring waters for research in recent years (Morikawa *et al*., 2016). Some hot spring waters that appear around

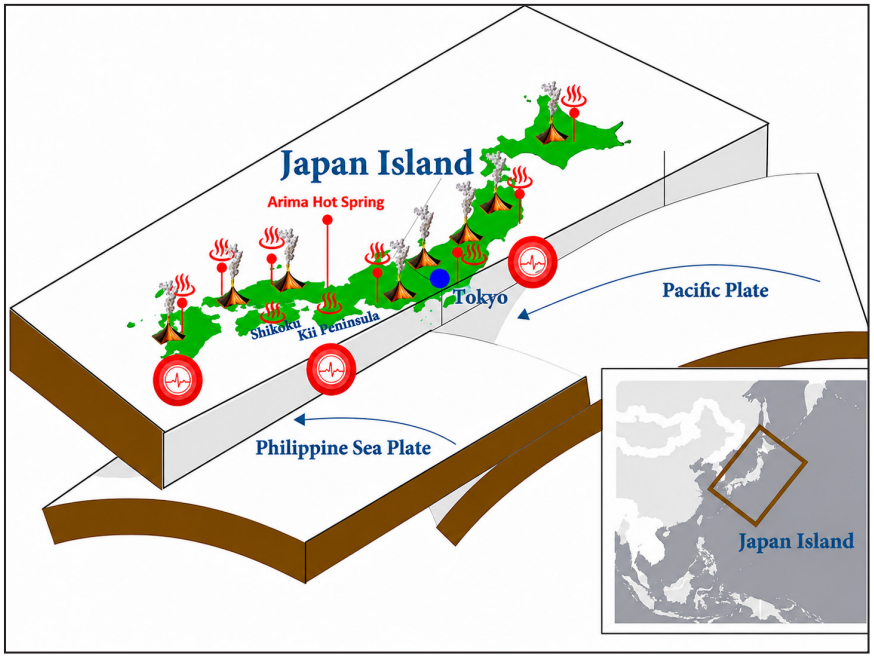

Figure 1. Schematic illustration of the tectonic setting of the Japanese Archipelago, showing the subduction of the Philippine Sea Plate beneath southwest Japan and its relationship to the occurrence of deep-seated fluids. The Arima hot spring area is highlighted, indicating the upward migration of slab-derived fluids generated during slab dehydration processes.

the Median Tectonic Line (MTL) are in SW Japan (Morikawa *et al*., 2016). MTL is a large fault that is still actively moving in the SW region of Japan, starting from the Shikoku region and extending to the Kinki region. Some researchers suspect that MTL movement activities have a contribution with hot spring water that occurs in the SW region of Japan (Taira, 2001; Tabei *et al*., 2002; Iwamori, 2007). However, these approaches remain limited in resolving both fluid origin and geochemical processes simultaneously, particularly in nonvolcanic subduction settings. Therefore, an integrated geochemical framework is required.

This study aims to test whether a combined geochemical approach using lithium isotope systematics (δ^7Li), stable isotopes (δD and δ^{18}O), major and trace elements (*e.g*. Cl, Li, and Cl/Li ratios) can effectively detect and characterize the contribution of slab-dehydrated fluids to surface and shallow groundwater systems in the Arima region. To achieve this objective, previously published lithium isotope (δ^7Li) data for four Arima samples reported by Umam *et al*. (2022) were re-evaluated together with Li and Cl concentration data reported by Umam *et al*. (2022) and Kusuda *et al*. (2014). These data were integrated with previously published stable water isotope (δD and δ^{18}O) and major-element data, primarily from Kusuda *et al*. (2014). These data were integrated with previously published datasets of stable isotopes and major elements. The interpretation is based on comparing geochemical signatures, including δ^7Li values, Cl concentrations, and Cl/Li ratios, to distinguish between thermal water, meteoric water, and mixing processes.

The novelty of this study lies in the integrated use of lithium isotope systematics together with stable isotopes and major elements as a unified geochemical framework.While previous studies have primarily relied on single tracers (e.g. He isotopes or REE), this study proposes a multiparameter approach that improves the sensitivity and reliability of detecting slab-derived fluids. Furthermore, this study explores the relationship between δ^7Li and Cl/Li ratios as indicators of fluid-rock interaction processes, including lithium adsorption and desorption mechanisms. This perspective provides new insights into the behaviour of lithium in hydrothermal systems and offers an alternative interpretation beyond conventional dilution-based models. Overall, this integrated approach contributes to a more comprehensive understanding of slab-derived fluid signatures in nonvolcanic subduction settings, particularly in the Arima hydrothermal system.

Methods and Materials

Data Sources and Reanalysis

No new sampling, sample preparation, or geochemical measurements were conducted as part of the present study. Instead, this study integrated and re-evaluated previously published geochemical datasets for the Arima hydrothermal system. Lithium isotope (δ^7Li) data for four Arima samples were obtained from Umam *et al*. (2022). Previously published Li and Cl concentration data were obtained from both Umam *et al*. (2022) and Kusuda *et al*. (2014) and were used to evaluate Li concentrations and calculate Cl/Li ratios. Stable isotope (δD and δ^{18}O) and major-element data were also compiled from previously published studies, including Kusuda *et al*. (2014). Readers are referred to the respective original publications for information on the original samples and datasets.

The datasets from these previous studies were used according to the geochemical parameters available in each publication. Because the availability of individual parameters differs among the published datasets, the present study does not assume that all geochemical variables were measured for all Arima samples. Instead, each parameter was evaluated within the limits of the available published data and subsequently compared with the other geochemical indicators where appropriate. This approach allows the different published datasets to be considered within a common interpretative framework without implying that the original samples were collected or analyzed specifically for the present study.

Accordingly, δ^7Li was evaluated only for the samples for which lithium isotope data had previously been reported. For the broader Arima dataset,

Li and Cl concentrations and the corresponding Cl/Li relationships provide additional parameters that can be compared with the available stable-isotope and major-element information. The distinction between datasets with and without δ^7Li measurements is maintained throughout the present study so that the interpretation does not imply the existence of lithium isotope measurements where such data are unavailable.

Lithium isotope compositions are expressed in conventional delta notation as:

$$\delta^7\text{Li}\ (‰) = [(^7\text{Li}/^6\text{Li})\text{sample} / (^7\text{Li}/^6\text{Li})\ \text{standard} - 1] \times 1000 \quad \text{.....(1)}$$

The δ^7Li values used in the present study are those previously reported by Umam *et al*. (2022); no new lithium isotope measurements or recalculation of the original isotope ratios were performed as part of the present study. Lithium isotope data were available only for the four Arima samples reported by Umam *et al*. (2022), whereas δ^7Li data were not available for the Arima samples reported by Kusuda *et al*. (2014).

In the present study, these previously published datasets were integrated and re-evaluated by comparing δ^7Li values, Li and Cl concentrations, calculated Cl/Li ratios, stable isotope compositions, and major-element chemistry. This integrated reanalysis was used to examine whether these geochemical parameters, individually and in combination, provide additional constraints on the characteristics and possible contribution of slab-dehydrated fluids to the Arima hydrothermal system.

This reanalysis therefore focuses on relationships among the published geochemical parameters rather than on reproducing the original analytical procedures. The previously reported values constitute the observational basis of the present study, whereas their integration and comparison within a common geochemical framework constitute the analytical approach applied here. In this way, the present study seeks to evaluate the extent to which multiple geochemical indicators can be used together to improve interpretation of fluid characteristics within the Arima hydrothermal system in Southwestern, Japan.

Result And Analysis

The previously published data for the four Arima samples reported by Umam *et al*. (2022) (Table 1) show high Chlorine (Cl) concentrations ranging from 15200 mg/L to 36500 mg/L. Despite the lower Cl concentration from these thermal waters compared to modern seawater (± 19,000 lmg/L) (Kazahaya *et al*., 2014; Oi *et al*., 1996), it still exceeds that of the shallow ground and surface water (Ii *et al*., 2019).

Based on the data from Arima hot spring waters reported by Kusuda et al. (2014), sodium (Na) concentrations are high, ranging from 18 mg/L to 20,077 mg/L, and potassium (K) concentrations range from 3 mg/L to 2,593 mg/L. The concentration of calcium (Ca), magnesium (Mg), and sulphate (SO_4) range from 8 lmg/L to 3,006 lmg/L, 0 mg/L to 511 mg/L, and 0.7 mg/L to 59.02 mg/L.

Based on the Piper diagram (Figure 2), the Arima hot spring water samples reported by Kusuda et al. (2014) generally plot within the sodium chloride (Na-Cl) water type field. The sodium chloride type are mostly found in coastal area (Chandrasekar *et al*., 2014; Satriani *et al*., 2012), geothermal waters area (Deon *et al*., 2015; Giggenbach, 1991; Millot *et al*., 2012; Nukman and Hochstein, 2019; Siregar and Kurniawan, 2018; Giggenbach, 1992; Winters and Cawvey, 2015), or from the mantle (deep fluids) (Ii *et al*., 2019; Kusuda *et al*., 2014) in the groundwater category. Meanwhile, Piper diagrams are excellent for tracking the origins of early groundwater based on species dominance (Kumar *et al*., 2009; Nazri *et al*., 2016; Ravikumar and Somashekar, 2017; Singh *et al*., 2020; Umar Kura *et al*., 2013). However, further confirmation is still needed regarding the origin of the Arima hot water samples, whether they are derived from sea water intrusion, or underwater volcanoes, or from the mantle (deep fluids) due to the subduction process.

The interpretation results of the stable isotope (Figure 3) showed that Arima hot spring waters (Kusuda *et al*., 2014) have a range of δD from -51.05 ‰ to -34.12 ‰ with a shift value δ^{18}O

Table 1. Previously published Li and Cl concentrations and lithium isotope (δ^7Li) data for Arima hot spring waters and seawater, together with calculated Cl/Li ratios

Fluid Type (Source)	Location	Sample Name	Li (ppm)	Cl/Li (wt./wt.)	Cl (ppm)	δ^7Li (‰)
Seawater (Oi *et al*., 1996)	Sezaki, Japan	Seawater	0.17	111764.709	19000	30
Geofluids (Deep Groundwater Water) (Kusuda *et al*., 2014)	Arima Type Fluids (Non Volcanic Area), Southwestern Japan	L1	38.16	436.740	16666	nm
		L2	40.75	526.110	21439	nm
		L3	6.5	521.846	3392	nm
		L4	0.03	466.666	14	nm
		L5	35.78	701.173	25088	nm
		L6	30.76	675.747	20786	nm
		L7	14.42	606.241	8742	nm
		L8	36.69	703.952	25828	nm
		L9	22.97	637.222	14637	nm
		L10	20.86	735.043	15333	nm
		L11	0.05	8700	435	nm
		L12	2.08	622.115	1294	nm
		L13	51.9	771.348	40033	nm
		L14	33.81	1082.579	36602	nm
Groundwater samples (Umam *et al*., 2022)	Arima hot spring waters	A1	25.8	694	17900	1.5
		A2	46.4	733	34000	1.4
		A3	45.9	795	36500	1.5
		A4	27.2	559	15200	1.6

*nm: not measured

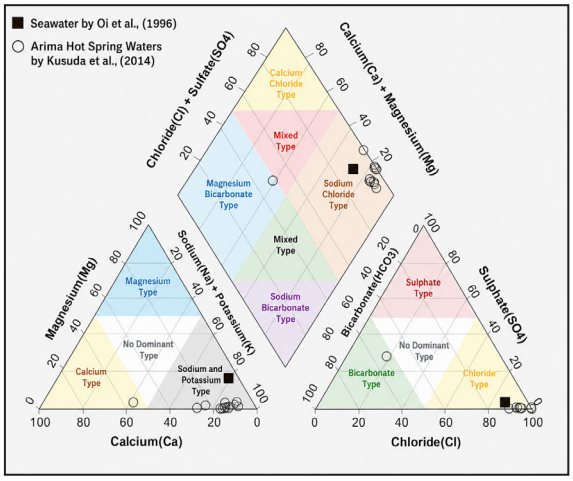

Figure 2. Piper diagram showing the hydrochemical facies of Arima hot spring waters (Kusuda *et al*., 2014) compared with seawater (Oi *et al*., 1996). Most samples plot within the Na-Cl type field, indicating a strong influence of deep-seated saline fluids. The clustering of samples near the sodium-chloride end member suggests a dominant contribution from high-salinity geothermal fluids rather than shallow meteoric sources. Minor deviations toward mixed-type fields indicate local mixing processes and secondary water-rock interaction.

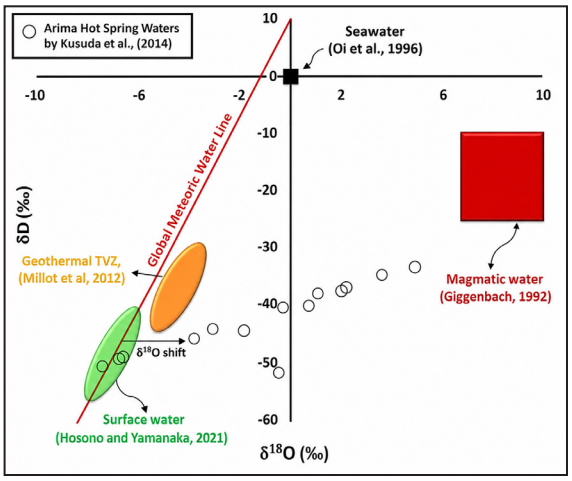

Figure 3. Stable isotope composition (δD vs. δ^{18}O) of Arima hot spring waters (Kusuda *et al*., 2014) compared with seawater (Oi *et al*., 1996), surface water (Hosono and Yamanaka, 2021), geothermal fluids from TVZ (Millot *et al*., 2012), and magmatic water (Giggenbach, 1992). Most samples show a positive δ^{18}O shift. from the Global Meteoric Water Line (GMWL), indicating significant water–rock interaction at elevated temperatures. The distribution of samples suggests mixing between deep geothermal fluids and meteoric water.

ranging from -7.88 to 4.98 (from the Global Meteoric Water Line). According to Matsubaya *et al*. (1973), a high shift value occurs due to the long water-rock interaction process compared to surface or meteoric water. Furthermore, thermal water samples exhibit a higher shift than surface water and are similar to the geothermal waters from TVZ, New Zealand (Millot *et al*., 2012). Based on the results of interpretation using stable isotopes, several Arima hot spring waters have plots that are close to other types of water, such as surface water and geothermal waters (Deon *et al*., 2015; Giggenbach, 1991; Millot *et al*., 2012; Nukman and Hochstein, 2019; Siregar and Kurniawan, 2018; Giggenbach, 1992; Winters and Cawvey, 2015). Thus, stable isotopes still require other evidence to more accurately detect the origin of Arima hot spring waters.

Using the Cl/Li ratio of thermal water in Japan, Kazahaya *et al*. (2014) conducted a previous study that yielded highly helpful information, the Cl/Li ratio > 1,000 is a distinctive feature of hydrothermal waters. While Millot *et al.* (2012) and Tanimizu *et al*. (2021) confirmed that lithium (Li) is very sensitive to high temperatures. Furthermore, groundwater with a high Li concentration is commonly found in the inner layer, namely the mantle (Meredith *et al*., 2013; Nishio *et al*., 2010; Tang *et al*., 2007; Tomascak, 2004). Information on the high Li concentration in groundwater supports the results of You *et al*. (1996) comparing the behaviour of Lithium (Li) and Boron (B) when experiencing temperature changes (Figure 4).

Based on the interpretation of Figure 5, the

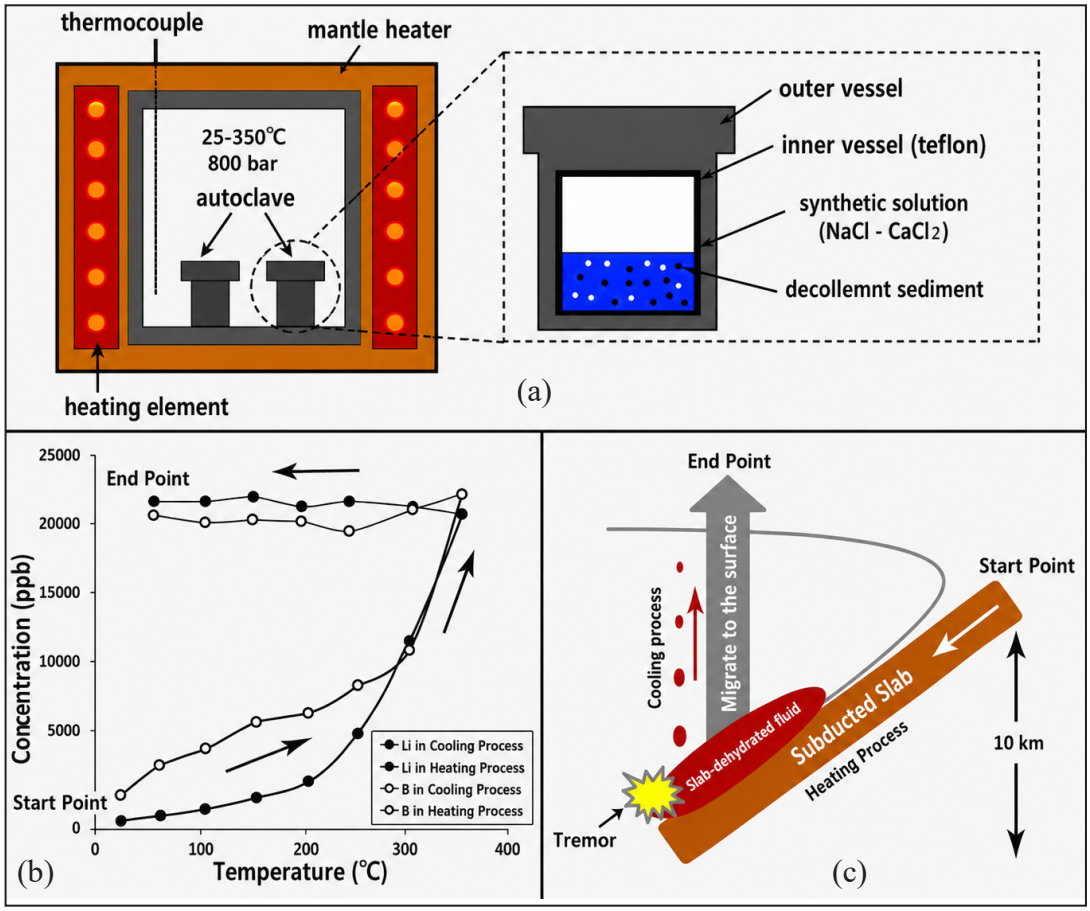

Figure 4. a). Experimental setup for simulating fluid-rock interaction under hydrothermal conditions (25-350°C, 800 bar) using an autoclave system with synthetic saline solution and sediment (You *et al*., 1996); b). Temperature-dependent behaviour of Li and B during heating and cooling processes, highlighting the sensitivity of Li to thermal conditions and fluid evolution; c). A conceptual model linking slab dehydration processes to fluid migration, illustrating the generation of slab-derived fluids and their ascent toward the surface.

four Arima samples previously reported by Umam *et al*. (2022) have Li concentrations > 25 mg/L and Cl concentrations ranging from 15200 mg/L to 36500 mg/L. Meanwhile, the Arima hot spring water samples (Kusuda *et al*., 2014) had Li concentrations ranging from 0.03 mg/L to 51.9 mg/L (Table 1), and several samples had Cl concentrations < 1,000 (Table 2).

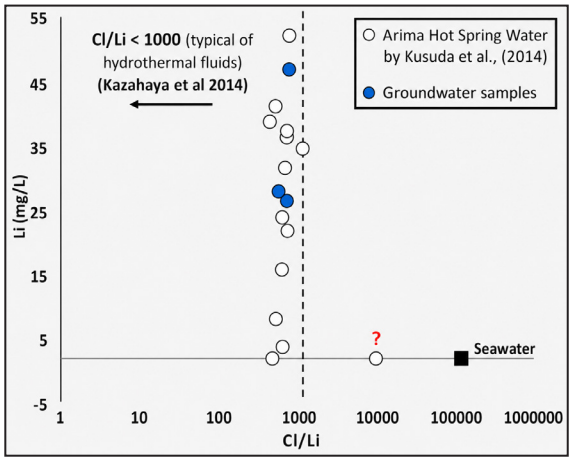

Figure 5. Relationship between Li concentration and Cl/Li ratios for groundwater samples (Umam *et al*., 2022) and Arima hot spring waters (Kusuda *et al*., 2014) compared with seawater (Oi *et al*., 1996). The dashed line (Cl/Li = 1,000) represents the commonly used threshold for hydrothermal fluids (Kazahaya *et al*., 2014). The four Arima samples previously reported by Umam *et al*. (2022) plot in the low Cl/Li (<1000) and high Li concentration field while several literature samples show higher Cl/Li values, indicating variability in fluid processes and possible mixing or geochemical modification.

The interpretation of Li concentrations and Cl/Li ratios (Figure 5) for the four Arima samples previously reported by Umam *et al*. (2022) shows Cl/Li values < 1000. Meanwhile, several samples of Arima hot spring waters (Kusuda *et al*., 2014) has a Cl/Li value > 1,000. The results of research by Kazahaya *et al*. (2014) using forty-nine hot springs spread throughout Japan show that magmatic water has a Cl/Li > 1,000 (in weight ratio) with Cl > 1000 mg/L.

The results of the interpretation of lithium isotopes (δ^7Li) and Cl/Li ratios (Figure 6) show that the four Arima samples previously reported by Umam *et al*. (2022) have δ^7Li < 5‰ and Cl/Li values < 1000. Meanwhile, seawater (Oi *et al*., 1996), which also has a Cl value > 1,000 mg/L, has δ^7Li >> 5‰. Based on the interpretation results, δ^7Li and Cl/Li ratios might be able to be divided into three regions: firsty δ^7Li < 5 ‰ and Cl/Li < 1,000 is the thermal water category; second δ^7Li < 5 ‰ and Cl/Li < 1,000 are categories of

Table 2. Previously published stable isotope and major-element data for Arima hot spring waters and seawater

Fluid Type (Source)	Location	Temp (°C)	Isotope stable		Major element (mg/L)						
			δ^{18}O (‰)	δD (‰)	Mg^{2+}	Na^{+}	K^{+}	Ca^{2+}	Cl^{-}	SO_4	HCO_3^{-}
Seawater (Oi *et al*., 1996)	Sezaki, Japan	12.6	0	0	1400	10600	431	934	19000	2470	nm
Geofluids (Deep Groundwater Water) (Kusuda *et al*., 2014)	Arima Type Fluids (Non Volcanic Area), Southwestern Japan	22.3	-0.35	-40.44	284	9623	959	629	16666	6.54	3803
		25.9	1.09	-38.51	114	12618	1372	985	21439	0.7	3154
		32.1	-0.7	-51.05	35	1743	208	491	3392	1.12	781
		19.1	-7.88	-50.27	1	18	3	23	14	59.02	30
		95.3	2.07	-38.15	15	11945	2525	2192	25088	2.41	26
		88.3	0.77	-40.5	12	10127	2153	1845	20786	2.41	203
		80.3	-4.09	-45.92	15	4700	1000	627	8742	24.92	473
		88.3	2.22	-37.71	17	12189	2593	2356	25828	2.77	137
		61.5	-1.85	-44.69	29	7805	1388	1283	14637	10.3	435
		33.3	-3.26	-44.31	144	9014	332	860	15333	1.69	1623
		19.4	-7.27	-48.92	0	23	4	8	435	15.27	93
		19.5	-7.08	-48.56	4	704	131	108	1294	23.06	150
		29.2	4.98	-34.12	136	20077	1930	3006	40033	10.25	1293
		32.2	3.61	-35.11	511	18379	112	2598	36602	2.43	214

*nm: not measured

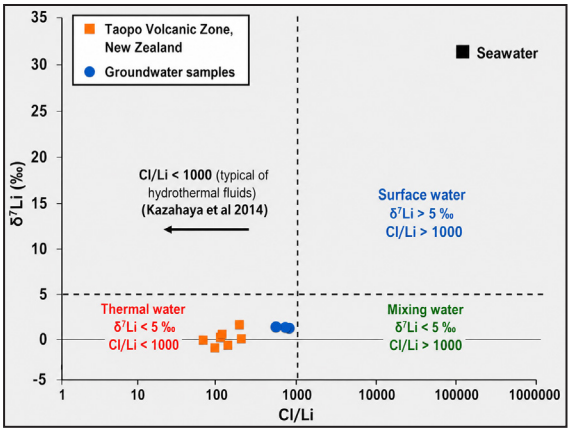

Figure 6. Relationship between lithium isotope composition (δ^7Li) and Cl/Li ratios for groundwater samples (Umam *et al*., 2022), compared with geothermal fluids from the Taupo Volcanic Zone (TVZ) (Millot *et al*., 2012), and seawater (Oi *et al*., 1996). Dashed lines (δ^7Li = 5 ‰ and Cl/Li= 1,000) define three geochemical fields: thermal water, mixing water, and surface water. Groundwater samples cluster in the low δ^7Li (<5‰). and low Cl/Li (<1,000) field, consistent with deep hydrothermal fluids, while seawater plots in the high δ^7Li and high Cl/Li fields.

mixing between thermal water and surface water (including shallow groundwater); the third δ^7Li > 5 ‰ and Cl/Li > 1,000 are the surface water category (including shallow groundwater).

Even though the Arima data on hot spring waters (Kusuda *et al*., 2014) does not have lithium isotope (δ^7Li) data, based on interpretation of Li, Cl concentrations (Table 1) and Cl/Li ratios (Figure 5), as well as categories of fluid (Figure 6), almost all Arima hot spring water (Kusuda *et al*., 2014) can be estimated to have Li > 0.1 mg/L, Cl > 1,000 mg/L, and Cl/Li < 1000, which are thermal water categories. On the other hand, one of the Arima hot spring waters (Kusuda *et al*., 2014), which has a Li < 5 mg/L, Cl < 1,000 mg/L, and Cl/Li > 1,000, is not in the thermal water category, but it is likely to be in the mixing water category because it has a fairly high Cl value, namely, 435 mg/L (Table 1), and the sample collection location is in the Arima hot spring water area (far from the coastal area).

Discussion

The combined interpretation of major elements (Figure 2), stable isotopes (Figure 3), and lithium systematics (Figure 5 and Figure 6) provides a progressively refined understanding of the origin and evolution of Arima hydrothermal fluids. The Piper diagram (Figure 2) shows that most samples belong to the Na-Cl type, indicating a strong influence of saline, deep-seated fluids (Kusuda *et al*., 2014). However, this hydrochemical signature is not unique and may also result from seawater intrusion or prolonged water-rock interaction. Similarly, stable isotope data (Figure 3) exhibit a clear δ^{18}O shift indicative of high-temperature water-rock interaction, but overlapping fields between meteoric, geothermal, and mixed waters limit their ability to uniquely constrain fluid origin.

Additional ambiguity is observed in the Cl/Li relationships (Figure 5), where inconsistent patterns occur within the same hydrothermal system. Some samples display Cl/Li ratios traditionally associated with deep fluids, whereas others show contrasting behaviour that can not be explained solely by mixing or dilution. This inconsistency highlights a key limitation of using Cl/Li as a direct tracer of fluid sources. The integration of lithium isotope systematics (Figure 6) resolves this ambiguity. The groundwater samples consistently plot in the low δ^7Li (<5‰) and low Cl/Li (<1,000) fields, clearly distinguishing them from seawater and indicating a strong contribution from deep hydrothermal or slab-derived fluids. Unlike major elements and stable isotopes, δ^7Li provides a more direct and process-sensitive constraint on fluid origin due to its response to water-rock interaction (Umam *et al*., 2024).

Importantly, the combined δ^7Li-Cl/Li framework demonstrates that Cl/Li ratios primarily reflect lithium mobility controlled by adsorption–desorption processes rather than fluid sources. This reinterpretation explains the observed inconsistencies and indicates that variations in Cl/Li are governed by different stages of fluid-rock interaction. The integration of lithium isotope classification into the stable isotope framework (Figure 7) further refines fluid interpretation. Although δD-δ^{18}O data

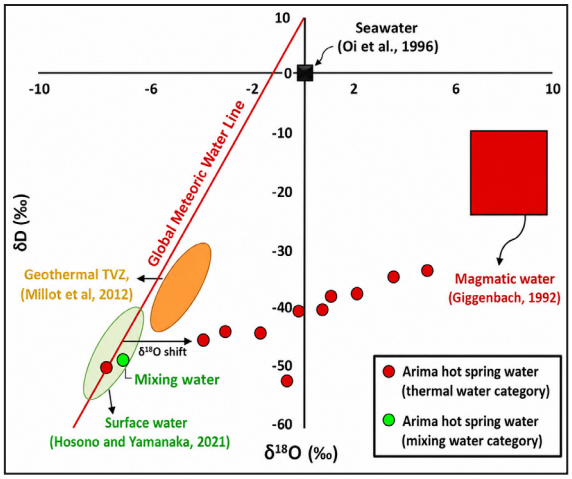

Figure 7. Stable isotope composition (δD - $\delta^{18}O$) of Arima hot spring waters combined with lithium-based hydrochemical classification. The diagram shows δD versus $\delta^{18}O$ values of Arima hot spring waters, together with reference fields for seawater, magmatic water, geothermal waters, surface water, and mixing water. Based on the hydrochemical criteria of Kusuda *et al*. (2014) , most Arima hot spring waters are classified as thermal waters, characterized by relatively high Li concentrations (>0.1 mg/L), high Cl concentrations (>1,000 mg/L), and low Cl/Li ratios (<1,000) (Table 1). In contrast, one sample with lower Cl concentration, lower Li concentration, and higher Cl/Li ratio is interpreted as mixing water (see Figure 5). Although lithium isotope data are not plotted in this figure, Li concentration and Cl/Li ratios are used to support the hydrochemical classification of the plotted samples.

alone show overlapping fields, the addition of lithium systematics clearly separates thermal water from mixing water. Thermal waters exhibit larger $\delta^{18}O$ shifts, reflecting stronger water-rock interaction, whereas mixing waters plot closer to the meteoric field due to dilution effects (Umam *et al*., 2026).

Samples with similar stable isotope signatures can belong to different fluid categories when lithium systematics are considered. This demonstrates that stable isotopes alone may mask differences in fluid origin and evolution. Overall, this study shows that conventional tracers (major elements and stable isotopes) are insufficient to resolve fluid origin in complex hydrothermal systems (Siregar *et al*., 2026a; Siregar *et al*., 2026b). The integration of lithium isotope systematics provides a robust and process-sensitive tracer that significantly improves the identification of slab-dehydrated fluids. This combined approach establishes a new geochemical framework in which:

- $\delta^{7}Li$ serves as a tracer of fluid origin and water-rock interaction.
- Cl/Li reflects lithium mobility controlled by adsorption-desorption processes.

Such a framework offers a more reliable method for detecting slab-derived fluids in non-volcanic subduction settings, including the Arima Hydrothermal System.

By integrating lithium isotope systematics with stable isotope data and major element compositions (Piper diagram analysis), a clearer distinction of fluid types and characteristics can be achieved (Figure 7 and Figure 8). This combined approach enhances the resolution of fluid classification beyond what can be obtained from individual tracers. Figure 7 shows that several Arima hot spring waters (Kusuda *et al*., 2014) exhibit relatively small $\delta^{18}O$ shifts and plot near the surface water field. However, when lithium isotope systematics are incorporated, these samples can be more accurately distinguished according to their fluid origin. Samples represented by red

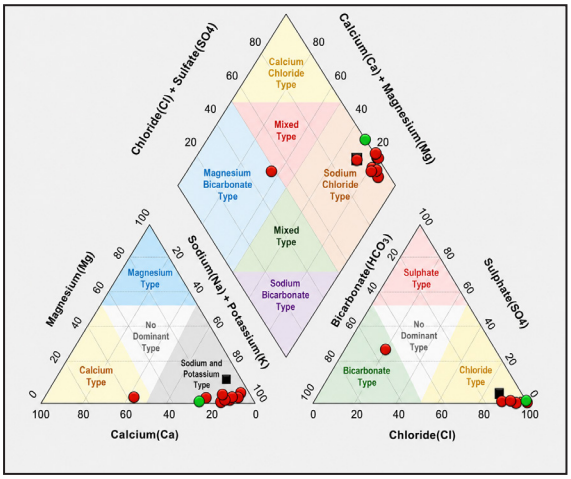

Figure 8. Piper diagram integrated with lithium isotope-based fluid classification for Arima hot spring waters. Red circles represent thermal water, while green circles indicate mixing water, based on $\delta^{7}Li$ and Cl/Li classification. Most samples cluster within the Na-Cl type field, while mixing water samples show slight deviations, reflecting dilution and interaction with shallow groundwater. This integrated approach highlights that similar hydrochemical facies can represent different fluid origins. When lithium isotope systematics are considered.

circles correspond to thermal waters dominated by slab-derived fluids, while green circles indicate mixing between thermal water and surface or shallow groundwater.

This classification is consistent with the major element interpretation (Figure 8), where the mixing water samples (green circles) still exhibit relatively high Cl concentrations (*e.g.* ~435 mg/L; Table 1) and fall within the Na-Cl type field. This suggests that even mixed waters retain a significant contribution from deep hydrothermal fluids. Although many samples from Kusuda *et al*. (2014) plot within the same Na-Cl field, the integration of lithium isotope systematics allows further discrimination of fluid origin and evolutionary processes. This demonstrates that similar hydrochemical facies can mask fundamentally different fluid histories.

Most samples classified as thermal water (red circles) cluster within the Na-Cl type field, confirming the dominant influence of deep, saline hydrothermal fluids. This is consistent with previous interpretations based on major element chemistry. However, the incorporation of lithium isotope systematics reveals that not all samples within the same Na-Cl facies share the same origin or evolutionary history. Mixing water samples (green circles) also plot near the Na-Cl field but show slight deviations toward other hydrochemical facies, reflecting dilution by surface or shallow groundwater. Despite these deviations, their relatively high Cl concentrations indicate that they still retain a significant contribution from deep hydrothermal fluids (Umam *et al*., 2025).

Importantly, Figure 8 demonstrates that hydrochemical classification alone is insufficient to distinguish fluid origin, as both thermal and mixing waters can occupy similar positions in the Piper diagram. The addition of lithium isotope systematics enables discrimination between these fluid types, even when their major element compositions appear similar. This result reinforces the interpretation that major element chemistry primarily reflects bulk composition, while lithium isotopes provide insight into fluid origin and geochemical processes. The combined approach therefore offers a more comprehensive framework for interpreting hydrothermal systems.

Conclusions

This study demonstrates that the integration of lithium isotope systematics, stable isotopes, and major element geochemistry provides a robust framework for identifying the origin and evolution of hydrothermal fluids in the Arima System, southwestern Japan. The previously published Li concentration and lithium isotope (δ^7Li) data for the four Arima samples reported by Umam *et al*. (2022) show low δ^7Li values (<5‰) and low Cl/Li ratios (<1000), clearly distinguishing them from seawater, which exhibits significantly higher δ^7Li values and Cl/Li ration. Cl/Li, three fluid categories can be defined: (1) thermal water (δ^7Li <5 ‰ and Cl/Li <1,000), (2) mixing water between thermal and surface water, and (3) surface or shallow groundwater (δ^7Li >5 ‰ and Cl/Li >1,000). The interpretation of these previously published Arima data in the present study places the four samples within the thermal water category, indicating a strong contribution from slab-dehydrated fluids.

Although lithium isotope data are not available for the Arima hot spring waters reported in previous studies (Kusuda *et al*., 2014), their Li concentrations (>0.1 mg/L), Cl concentrations (>1,000 mg/L), and Cl/Li ratios (<1,000) suggest that most samples also belong to the thermal water category. In contrast, one sample with relatively low Li (<5 mg/L), low Cl (<1000 mg/L), and high Cl/Li (>1000), despite having moderate Cl (~435 mg/L), is interpreted as mixing water, reflecting interaction between thermal fluids and surface or shallow groundwater.

Major element compositions (Piper diagram) indicate that most samples belong to the Na-Cl type, suggesting a strong influence of saline deep fluids. However, this signature alone is not diagnostic of fluid origin. Similarly, stable isotopes (δD-δ^{18}O) indicate significant water-rock interaction but cannot uniquely distinguish between fluid sources due to overlapping fields. Furthermore,

this study demonstrates that Cl/Li ratios are primarily controlled by lithium mobility through adsorption–desorption processes rather than fluid source, which explains the inconsistencies observed when using Cl/Li as a standalone tracer.

In contrast, lithium isotope systematics (δ^7Li) provide a more sensitive and process-based tracer, enabling clearer discrimination between thermal, mixed, and surface waters. The integration of lithium isotopes into stable isotope and major element interpretations significantly improves the resolution of fluid classification and resolves ambiguities in conventional geochemical approaches.

Overall, this study establishes a new geochemical framework in which δ^7Li serves as a tracer of fluid origin and water-rock interaction, while Cl/Li reflects lithium mobility controlled by adsorption-desorption processes. This combined approach provides a reliable and powerful method for detecting slab-dehydrated fluids in nonvolcanic subduction settings, and can be applied to other hydrothermal systems worldwide.

Acknowledgements

The authors would like to express sincere gratitude to Professor Masaharu Tanimizu, Dr Yasunori Mori, Mr Ryo Nakai, and Mr Naoto Sugimoto for their valuable support and assistance during the hot spring water sampling in The Kii Peninsula, Japan. Their expertise, guidance, and generous collaboration greatly contributed to the success of the data collection process. The author would like to thank anonymous reviewers for their constructive reviews. This research was funded by The Nishimura Foundation from Mandom Company, Japan, and The Centre for Research in Radiation, Isotopes, and Earth System Sciences (CRiES), University of Tsukuba, Japan.

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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