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Origin and Evolution of Saline Spring Water in North and Central Laos Based on Hydrochemistry and Stable Isotopes (δD , $\delta^{18}O$, $\delta^{11}B$, and $\delta^{37}Cl$)

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Abstract: This paper discusses the origin and evolution of saline springs in north and central Laos, based on chemical and stable isotopes (δD , $\delta^{18}O$, $\delta^{11}B$, and $\delta^{37}Cl$). All the saline springs in this study are of the Na–Cl geochemical type. The geochemical and water isotope values suggest that the saline springs in this study are mainly derived from meteoric water and/or ice and snow melt from the surrounding mountains and that they also experienced strong evaporation and intense rock–water interactions. The ionic ratios, characteristic coefficients, ternary Ca–SO₄–HCO₃ phase diagrams, and saturation indices of minerals show that the dissolution of halite, sulfate, and carbonate rocks may be the solute sources for saline springs in this study, whereas the underground brines in the Thakhek potash mining area are geochemically influenced by the dissolution of carnallite and sylvite. The global geothermal $\delta^{11}B$ –Cl/B relationship and $\delta^{11}B$ values (5.50 to 36.01‰) of saline springs suggest a continental origin of B. This B is most likely derived from marine carbonate rocks and marine evaporates (gypsum and halite) of the late Cretaceous, which is similar to the saline springs of the Nangqen–Qamdo–Simao Salt Basin. The $\delta^{37}Cl$ value (−0.12 to +0.79) and the Cl/Br ratio (4076 to 9853) show that dissolution of late cretaceous marine halite layers, atmospheric precipitation, and water–rock interactions between volcanic rocks, mudstones, and sandstone can restrict the $\delta^{37}Cl$ values in saline springs. Results from silica geothermometry and multi–mineral equilibrium diagrams indicate that the reservoir temperatures for the saline springs range from 87–137 °C and experience deep circulation. Hydrochemical characteristic coefficients suggest that saline springs in the Muang Say basin may have leached sylvite and carnallite and that the potash exploration prospect in this area is relatively good.

Keywords: saline springs; stable isotopes; recharge and solute sources; reservoir temperatures; marine evaporites; potash exploration prospect

1. Introduction

The Khorat Plateau (see Figure 1B) is one of the world's most valuable targets for the exploitation of potassium salts, which contains Sakon Nakhon Basin and Khorat Basin.

The Muang Say, Vientiane, and Khammouane salt basins, located 100–600 km north of the Khorat Plateau, include extensive and thick late Cretaceous continental red beds, evaporite deposits, and saline springs [1–5]. The composition of dissolved salts in salty groundwater and brines of saline springs can be used as an important indicator for hydrochemical prospecting and determination of the genesis of evaporites. Many geological studies, based on the geochemical properties of drill cores [6–8], have been conducted on the giant potash deposits in the Khorat Plateau and the Khammouane basin. Similar research has not yet been undertaken in the Muang Say and Vientiane basins that occur in north and central Laos, due to legal restrictions and environmental concerns. No detailed chemical and isotopic characteristics that can assist in determining the origin and evolution of the saline springs or for assessing the prospecting potential of these salt basins therefore exist. It is therefore of great theoretical and practical significance to systematically analyze the cyclic evolutionary process, recharge mechanisms, and solute sources of the saline springs, which will assist in understanding its metallogenic potential and the genesis of the evaporites. This paper discusses the origin and evolution of saline springs in north and central Laos, based on chemical and stable isotopes, including solute and recharge sources, reservoir temperatures, a spring circulation model, as well as new potash exploration prospects.

Spring hydrochemistry assists in understanding solute sources and reservoir temperatures. δD and $\delta^{18}O$ are excellent tracers for determining water recharge sources, the route of water circulation, and water–rock interactions [9–13], which are the most important parameters to distinguish between atmospheric and oceanic origins of spring water. Seawater and brines have high concentrations of Cl and B, and these two elements experience important isotopic fractionation during the formation and evolution of brines. B is soluble in water and chemically active, which makes it an effective tracer for determining groundwater salinity sources. Because of the relatively large mass difference between ^{10}B and ^{11}B [14–16], boron isotopes are widely used for tracing the origins of salt lakes and brines [17–20], tracing the loop of ocean sediments [21], tracing the domestic wastewater [22–24], and analyzing the evolution of hydrothermal fluids [25–29]. Chlorine is a conservative hydrophilic element that has two stable isotopes, ^{35}Cl and ^{37}Cl . These isotopes can be used to determine magmatic fluid in volcanic regions [30], the origin of salinity in fluid inclusions [31], water–rock interactions with rock alterations [32–36], to describe hydrothermal processes [37,38], and to assess crustal recycling in the mantle or ocean [39,40]. The fractionation of Cl isotopes during the migration of chlorine in water and salt mineral deposits has been researched extensively [41,42]. These studies indicate that the lighter isotope (^{35}Cl) is preferentially fractionated into the resin phase, whereas the heavier isotope (^{37}Cl) partitions into the aqueous phase during crystallization. B and Cl isotopes have been used to characterize hot springs and brines and as tracers to determine the solute source and formation environment of springs and evaporite deposits. These springs and evaporite deposits occur not only in China, for example, in the western Tarim Basin [43], the Yangbajing geothermal field, Tibet [44], and Southern Tibet [45], but also abroad, for example, in the Eastern Desert of Egypt [46], the Khammouane potash deposits in Laos [7], the Gulf Coast Basin of United States [47], Eastern Canada [48], and the Ibusuki coastal geothermal region in Japan [49]. Hydrochemistry and stable isotopes can therefore be used to analyze the origin and evolution of saline springs in this study.

The main goal of this study was to use the hydrogeochemical and isotopic characteristics (δD , $\delta^{18}O$, $\delta^{11}B$, and $\delta^{37}Cl$) of the saline springs to identify its recharge mechanisms, solute sources, circulation depth, and reservoir temperatures. The above data was used to develop a conceptual model of spring circulation and potash exploration prospects. The hydrochemical characteristics of the springs and evaporite deposits in this study area are also compared to results from saline springs and underground brines in the surrounding area (the Lanping–Simao basin, Krabi province, the Thailand and potash mining area, and central Laos), and $\delta^{11}B$ values in saline springs are compared to international geothermal systems.

2. Geological and Hydrogeological Setting

The Southeast Asian continent contains the South China Block (SCB), the Indochina Block, the Sibumasu Block, the Sukhothai Block, and the Qamdo–Simao Block. These blocks are bounded by fault zones and sutures, including the Ailaoshan Suture, the Red River Fault, the Dien Bien Phu Fault, the Nan Suture, the Jinghong Suture, and the Song Ma Suture (Figure 1B). The heterogeneous collisions of these Gondwana-derived microcontinents that occurred during the Indosinian orogeny are closely linked with the closing of the Tethyan Ocean during the late Permian to early Triassic [50–52]. The Indosinian Block, one of the largest tectonic units in Southeast Asia, is the result of the collision between India and Asia during the Cenozoic [53]. It is bounded to the west by the Lincang, Sukhothai Terrane, and the Inthanon Suture Zone and to the east by the Ailaoshan and Song Ma Sutures [54,55], which has also been transected by the Dien Bien Phu Fault and the Ailaoshan–Red River Fault [1]. The Qamdo–Simao Block extends west from the Jinghong and Nan Sutures to the Jinshajiang, Ailaoshan, and Song Ma Sutures in the east [54,55]. The Simao Basin that is located to the south of the Qamdo–Simao Block is a typical continental rift basin that formed during the Jurassic–Cretaceous period [56], during the collision with the SCB during the late Triassic [57] or late Permian–early Triassic [58].

Figure 1. (A). Geological sketch map and sampling sites in north and central Laos (modified from Geological map of Lao People's Democratic Republic, 1991) (B). Tectonic framework of central SE Asia showing the location of study area [54].

Laos is located in the northernmost part of the Indochina Peninsula. It is bordered by China's Yunnan to the north, Cambodia to the south, Vietnam to the east, Myanmar to the northwest, and Thailand to the southwest. The research area is in the north-central

part of Laos, which includes the Muong Say Basin, Vientiane Basin, and Khammouane Basin. The magmatic and sedimentary rocks in northern Laos are mainly controlled by the Nan–Dien Bien Phu Suture Zone and the Truong Son Belt [1]. The Muong Say Basin is an important salt-bearing basin that connects the Simao and Vientiane basin, which is located between the Jinghong suture and the Dien Bien Phu fault [59]. The Mesozoic lithological association has typical lacustrine sedimentary characteristics [51,60] and is similar to the late Cretaceous Mengyejing formation in the Simao Basin [60] (Figure 2). The Mengyejing Formation consists of three salt members from bottom to top and the lower part of the upper salt member contains an important sylvite layer. The Mesozoic outcrops in the Muong Say Basin [61] are characterized by purple and red continental mudstones that are interbedded with red siltstone sandstone and that are accompanied by mud conglomerates and gypsum. The Late Cretaceous continental red beds containing evaporites from the Muong Say Basin are also present in the Simao, Vientiane, and Khammouane Basins. These red beds are unconformably overlain by the late Cretaceous evaporites and clastic deposits [2–4]. The Vientiane and Khammouane Basins belong to the middle part of the Indochina block, and these two basins are located in the northern boundary of the Sakon Nakhon Basin. The Sakon Nakhon Basin is a subbasin of the Khorat Plateau (Figure 1B). The Khorat Plateau (14°00′–19°00′ N, 101°00′–106°00′ E) is an area of ~170,000 km² in northeastern Thailand and central Laos and is bounded to the north by the Trung Son Tectonic Belt, to the northeast by the Song Da–Song Ma Suture and the South China Plate, to the south by the Wang Chao left–lateral strike–slip fault, and to the west by the Inthanon Suture and the Sibumasu Block [50,52,55,59] (Figure 1B). The Khorat Plateau has experienced a complex tectonic evolution, which included (1) the formation of semi–graben basins [55], which was caused by a series of tectonic events (including collision, thermal subsidence, stratigraphic inversion, stitching, and stretching between the Sibumasu block and the Indo–China block after late Cambrian); (2) the deposition of the nonmarine Khorat Group (T₁–K₁) during the Mesozoic era [62,63]; (3) the deposition of marine salt-bearing strata (the Maha Sarakham Formation) in the late Cretaceous, which forms an unconformable contact with the underlying Khok Kruat Formation [64]; and (4) the uplift of the Phu Phan anticlinorium. The collision between the Indo–China Block, the Sibumasu Block, and the South China Block during the early Paleocene led to the uplift of the Phu Phan anticlinorium along the NW–SE direction, which divided the plateau into the Khorat Subbasin in the south and the Sakon Nakhon Subbasin in the north [5,59,63,64] (Figure 1B). The Maha Sarakham Formation in northern–eastern Thailand, also named the Nong Box Formation in the Khammouane Basin and the Tabong Formation in the Vientiane Basin, central Laos [65], is an important salt-bearing stratum in the study area. The Maha Sarakham formation contains three distinctive salt-bearing members (upper, middle, and lower). Each salt-bearing member is composed of an evaporite unit and a clastic unit. The clastic unit is dominated by reddish to brown mudstone and muddy siltstone, while the evaporite unit in upper and middle salt-bearing members is typified by halite that is interbedded with laminated black–grey anhydrite or gypsum. The lower salt-bearing evaporite unit comprises five layers from top to bottom and is characterized by a potash layer (sylvite, carnallite, and minor boracite), which are colorless to smoky halite beds that are interbedded with off–white anhydrite stringers and form a sharp contact with the underlying early Cretaceous grey quartz sandstone [5] (Figure 2). The study area has a typical tropical monsoon climate. The Neogene–Quaternary strata in the study area form a porous aquifer, which is characterized by conglomerate, sandstone, and siltstone. The Cretaceous salt-bearing strata form a weak fractured aquifer and are composed of clastics and evaporates. Based on gravity prospecting, the NW–NE trending faults may act as potential water migration channels that cause surface and halite dissolution. Stratigraphy and depositional patterns indicate the existence of extensive and thick late Cretaceous continental red beds and evaporites, and the thickness of late Cretaceous saline stratigraphic units is about 3 km. Underground saline springs within the study area can be used to study the genesis and metallogenic potential of these evaporites.

Figure 2. (A). Lithostratigraphy of the saliferous strata in the Laos and northeast Thailand [65]; (B). Phanerozoic stratigraphic correlation of Northeast Thailand–Vientiane Basin–Gammon Basin of Laos; (C). Lithostratigraphic column of the Mengyejing Formation in the Simao basin, southwestern China (modified from Wang et al., 2014); (D). Lithostratigraphic column of the Late Cretaceous section in the Muong Say Basin [65].

3. Sampling and Methods

Eight saline spring water samples were collected during the winter (January) of 2015. One sample each was collected at the Muang Ou Tai, West Moding, Mankuang Saltworks, South Pak–Lay, and Thakhek sampling sites, and three samples were collected in the Muang Say Basin (see Figure 1A, Table 1). To compare the results of this study with neighboring regions, we consider the data of saline spring water and underground brines from the Khammouane Province in central Laos [66], the Simao Basin in the Yunnan Province, China [67,68], and the Krabi Province in Thailand [69].

The pH and temperature of the spring water were measured on-site using a Hach HQ40d portable meter. All the water samples were filtered through a 0.45- μm membrane and preserved in clean HDPE bottles, except for the samples that were collected for Cl isotopic analysis. After filtration, the samples for cation analysis were acidified to $\text{pH} < 2$ using ultrapure concentrated nitric acid. All the chemical analyses were conducted in the Qinghai Institute of Salt Lakes, at the Chinese Academy of Sciences. The samples were analysed for major cations (K, Na, Ca, and Mg) and trace elements (Br, Sr, Li, B, Si) using inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). These methods have an analytical precision better than 0.1%. Unfiltered water samples were analyzed for major anions (F, Cl, and SO_4) using ion chromatography (IC; Dionex 120, Dionex, Sunnyvale, CA, USA) with an uncertainty of $\pm 5\%$. Major anions (HCO_3 and CO_3) were determined via hydrochloric acid titration using phenolphthalein and a mixed solution of methylene blue and methyl red as indicators (with an uncertainty $< \pm 1\%$). The hydrogen and oxygen isotopic compositions were measured using a MAT 253 stable isotope ratio mass spectrometer (Thermo Fisher Scientific, USA) at the National Research Center for Geoanalysis (NRCGA, PRC) located at the Chinese Academy of Geological Sciences. The δD and $\delta^{18}\text{O}$ values are reported relative to the Vienna Standard Mean Ocean Water (VSMOW) isotopic standard. The respective precision for δD and $\delta^{18}\text{O}$ were $\pm 3.0\text{‰}$ and $\pm 0.2\text{‰}$. The $\delta^{11}\text{B}$ and $\delta^{37}\text{Cl}$ were measured at the Qinghai Institute of Salt Lakes at the Chinese Academy of Sciences using the P-TIMS method in a Triton thermal ionization mass spectrometer, which are based on an improved method for the high-precision isotopic measurement of boron and chlorine, with a precision of $\pm 0.3\text{‰}$ for $\delta^{11}\text{B}$ and $\pm 0.2\text{‰}$ for $\delta^{37}\text{Cl}$ [70]. The sample preparation for the measurement of $\delta^{11}\text{B}$ included a two-column ion-exchange procedure [16,18,71]. Firstly, these saline spring water samples, containing about 10 μg B and using 2 M NH_4OH to remove cations, were passed through a coupled peristaltic pump coupled with a 0.8 mL Amberlite IRA 743 B-specific resin column. The amberlite IRA 743 B-specific resin was regenerated by 10 mL of 2 M HCl, 20 mL of pure water, and 10 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and was washed to neutral pH before use. The B was then eluted from the resin with 10 mL 75 °C and 0.1 M HCl, and the eluent was evaporated at 60 °C to 0.5 mL. Thereafter, the residue was diluted with pure water (low B water) and passed through a 0.15-mL anion-cation mixed resin to further purify the sample and remove HCl. Finally, 10 μg mannitol was added to the eluent and vaporized to 0.3 mL at 60 °C for mass spectrometry analysis. The measured $^{11}\text{B}/^{10}\text{B}$ value of NIST SRM 951 was $4.00514 \pm 0.1\text{‰}$ (2σ , $n = 6$). The analysis of Cl isotopic compositions and chemical separation of Cl followed the procedure as follows. All spring water samples were first passed through the H-cation exchange resin column (~ 300 mesh, resin type: Dowex 50 WX8) to transform the Cl into a HCl solution and were then eluted through the Cs column to collect newly formed CsCl solutions [33,70]. About 10 μg of Cl (as CsCl) was loaded and dried onto a tantalum (Ta) filament. The Ta filament was heated under a vacuum system (using a current of 2.5 A for 1 h) and was covered with 2.5 μL of graphite slurry (80% of ethanol plus 80 μg of graphite). The samples were placed into the mass spectrometer until the pressure of the ion source was lower than 2.5×10^{-7} mbars. The $\delta^{37}\text{Cl}$ values of the water samples from springs were calculated as follows. The reported $\delta^{37}\text{Cl}$ values are plotted relative to the Standard Mean Ocean Chloride (SMOC). The average $(^{37}\text{Cl}/^{35}\text{Cl})_{\text{smoc}}$ was 0.318990 ± 0.000041 (2σ , $n = 6$), which is in agreement with the certified value of Xiao. The expressions for $\delta^{11}\text{B}$ and $\delta^{37}\text{Cl}$ are shown below [72,73].

$$\delta^{11}\text{B}(\text{‰}) = \left[\left(\left(^{11}\text{B}/^{10}\text{B} \right)_{\text{sample}} / \left(^{11}\text{B}/^{10}\text{B} \right)_{\text{standard}} - 1 \right) \times 10^3 \right]$$

$$\delta^{37}\text{Cl}(\text{‰}) = \left[\left(\left(^{37}\text{Cl}/^{35}\text{Cl} \right)_{\text{sample}} / \left(^{37}\text{Cl}/^{35}\text{Cl} \right)_{\text{standard}} - 1 \right) \times 10^3 \right]$$

4. Results

Tables 1 and 2 show the results of the chemical and isotopic analyses of the saline spring water samples from north and central Laos. The saline springs in this study have total dissolved solids (TDS) of 11.65–311.27 g/L and a pH of 6.85 to 7.60. The outlet temperatures of the saline springs range from 8.5 °C to 14 °C. The values of the stable isotopes of the water (δD and $\delta^{18}O$) range from -101.0 to -42.5 ‰ and from -12.3 to -6.1 ‰ V-SMOW, respectively (Table 2). The halite leached brines are greatly influenced by the isotopic composition [74]. The saline springs in this study vary from 5.5 to 36.0‰ and from -0.12 to 0.79 ‰, respectively, for the stable isotope $\delta^{11}B$ and $\delta^{37}Cl$ values.

Table 1. Hydrochemical composition of salty groundwater and brines from springs in northern and central Laos.

Samples	Sample Type	TDS	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Li ⁺	Sr ²⁺	B	Si	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	F ⁻	Br ⁻
			g/L				mg/L							mg/L	
Muang Ou Tai	Brine	85.83	31.75	1.26	0.14	355.50	2.65	16.93	1.04	15.61	49.13	0.24	3.12	1.86	21.99
West Moding	Brine	311.27	116.55	1.69	0.37	867.00	3.55	31.73	14.07	17.12	185.54	0.04	3.64		62.95
Mankuang saltworks	Brine	288.92	109.25	1.64	0.11	780.50	3.08	21.43	1.39	51.18	172.86	0.08	2.49		45.09
East Muang Say	Salty water	11.65	3.61	0.56	0.05	152.02	2.67	14.41	1.30	23.43	6.37	0.35	0.45	0.18	2.04
South Pak-Lay	Brine	152.58	57.53	1.74	0.34	569.25	2.23	33.08	1.04	21.85	90.98	0.20	1.73	0.64	50.18
Muang Say 01	Salty water	12.06	3.68	0.63	0.06	133.35	2.60	15.60	1.30	24.79	6.70	0.24	0.53		1.72
Muang Say 02	Salty water	12.62	3.83	0.67	0.06	162.00	2.33	16.96	1.39	25.76	7.01	0.33	0.46		1.60
Thakhek	Brine	76.49	26.46	2.11	0.38	323.80	0.51	11.44	3.12	33.67	42.61	0.07	4.48		19.35

Table 2. Field observations, locations, water types, and isotope date of the saline springs in north and central Laos.

Sample Name	Location	Elevation (m)	Water Type	T (°C)	pH	δD_{V-SMOW}	$\delta^{18}O_{V-SMOW}$	d Value	$\delta^{11}B$	$\delta^{37}Cl$
Muang Ou Tai	N 22°08'30.0" E 101°	718	NaCl	9.5	6.94	-76.14	-9.03	-3.90	20.29	0.14
West Moding	N 21°08'48.0" E 101°	798	Na-Cl	11.0	6.85	-100.97	-12.28	-2.73	36.01	0.79
Mankuang saltworks	N 21°03'42.9" E 101°	807	Na-Cl	10.5	6.90	-82.98	-9.88	-3.94	24.10	-0.12
East Muang Say	N 20°52'08.0" E 102°	456	Na-Cl	10.5	7.00	-78.34	-8.15	-13.14	5.50	0.54
South Pak-Lay	N 17°36'20.9" E 101°	319	Na-Cl	8.5	7.02	-67.85	-6.53	-15.61	33.33	
Muang Say 01	N 20°52'06.0" E 098°	427	Na-Cl	12.1	7.60	-56.40	-7.80	6.00	8.08	
Muang Say 02	N 20°52'06.0" E 098°	416	Na-Cl	11.7	7.40	-50.30	-7.90	12.90	6.77	
Thakhek	N 17°24'40.4" E 104°	127	Na-Cl	14.0	7.20	-42.50	-6.10	6.30	17.05	

5. Discussion

5.1. Origin of the Water Molecules

The $\delta^{18}\text{O}$ versus δD for saline springs from southwestern China and Laos and comparison with the global meteoric water line (GMWL) [11], southeast Asia meteoric water line (RMWL) [75], and southwest Chinese meteoric water line (SW CMWL) are plotted in Figure 3. All the saline spring water samples in the study area and Yunnan of China were slightly below and near the meteoric water line, which indicates they were from local precipitation. The hydrogen and oxygen isotope values of atmospheric origin decrease in the groundwater with an increase in recharge elevation, which can be used to estimate the recharge elevation of atmospheric origin [76,77].

Figure 3. Isotope composition (δD and $\delta^{18}\text{O}$) of the saline springs in north and central Laos plotted against the GMWL, the SW CMWL, and the RMWL, the comparison area date from [67,78].

The δD values are relatively stable during high-temperature hydrolithogenesis due to the low hydrogen content in the rock minerals, and the recharge altitudes and their average values are therefore based on the δD values. As the study area is adjacent to the southwest China, the recharge elevations (H) were estimated by the formula $\delta\text{D} = -0.026\text{H} - 30.2$, which applies to southwest China and its surrounding areas [77]. The mean recharge elevations of the saline spring waters in north and central Laos (1508 m) are close to the mean altitudes of the surrounding mountains (Phu Bia, Phu Lay, Lao Bi, and Phu Miyang), which are above 1500 m. The estimated recharge elevation of the saline springs in this study ranged from 473.9 m to 2722 m, which are 346.1-m to 1924-m higher than the sampling elevation (at 127–807 m). This means that the vertical water head difference between the spring recharge area and the discharge area is large, which may be an important factor in driving the rapid and deep circulation of spring waters under the action of gravity.

Generally, river and lake water does not infiltrate deep geothermal reservoirs under the action of gravity. It can therefore be assumed that the main recharge sources for the saline springs from north and central Laos are likely to be rainfall and/or ice or snow melt from the surrounding mountains. Moreover, the flow rate of the recharge source will increase with increasing hydraulic gradient. The deep and large-scale faults and small-scale faults that were caused by plate collision can however provide migration channels for the deep circulation of saline springs, such as is the case with the Dien Bien Phu fault.

5.2. Solute Sources and Genesis of Spring Waters

5.2.1. Hydrochemistry Evidence

The saline springs can be classified as Na–Cl (based on the Schukalev and Kurilov classification) or as a chloride type (based on the Valyashko classification), respectively [74]. Cl and Na are the major constituents that generate the overall salinity of the springs. The saline springs all have similar chemical characteristics, with $\text{Na} + \text{K} > \text{Ca} > \text{Mg}$ and $\text{Cl} > \text{SO}_4 > \text{HCO}_3$. The classical Gibbs diagram (Figure 4) shows that the saline springs' chemical composition is dominated by evaporation crystallization processes because all the data points plot on the evaporation crystallization end member, similar to the composition of seawater, saline springs, and underground brines in Laos, Thailand, and southwestern Yunnan, China. Halite and potash deposits in Laos are mainly originated from the Cretaceous seawater, with subordinate continental water and possible hydrothermal supplies, there have been cases of flooding by the sea of the Laos territory over the past 145 million years. The halite strata were formed by evaporation from the seawater, which was probably derived from Tethys ocean. These brines also existed during the formation of halite, and residual water flowed into Thailand in subsequent periods. Therefore, the composition of spring water sources is the result of dilution of sea waters and brines by atmospheric precipitation. The rock (evaporites)–water (atmospheric precipitation) interactions and dilution of sea waters are two important factors that controls the chemical composition of saline springs.

The conservative elements (Cl and Br) and the seawater evaporation trajectories (SET) are frequently used to explain the origin and evolution of brines [79,80]. The Cl/Na, Cl/K, Cl/Mg, Cl/Li, Br/Ca, Br/K, and Br/Cl of saline springs and underground brines are therefore plotted onto the SET (see Figure 5). The Na/Cl ratios consistently plot above the SET from Figure 5a, with an approximate 1:1 molar ratio. This means that saline springs originate from the dissolution of halite and typically generate Cl-rich brines with a high ($\approx 1:1$) Na:Cl molar ratio [80]. The K concentrations of saline springs in this study are depleted relative to Cl but enriched relative to Br (except for Muang Say), and the ratios of K/Br and K/Cl are consistent with the SET. Of the K concentrations of the underground brines in the potash mining area, the Thakhek is higher than the peak of the SET (representing the precipitation stage of potash minerals) in the log plot of Cl/K, Br/K, Cl/Br, and Cl/B (see Figure 5). The K^+ concentrations of saline springs in Muang Say are however a deviation from the SET. The partial dissolution of halite and sylvite may have impacted the K content in the saline springs, while the K content in the underground brine comes entirely from the leaching of carnallite and sylvite [66]. According to Cerling et al. [81], Na ions released from clay minerals can be used as exchange ions in cases where the clay minerals are weathered by meteoric water, whereas the adsorption of clay minerals result in Mg depletion. In the saline springs from the study area, Ca is enriched relative to Cl and Br. The dissolution of Ca-bearing minerals (CaSO_4 , CaCO_3 , and $\text{CaMg}(\text{CO}_3)_2$) and the ankeritization of dolomite and calcite in the study area could explain the excess Ca in the saline springs. Mg is depleted relative to Cl, which means that the adsorption of clay minerals in the saline springs is stronger than the dissolution of Mg minerals ($\text{CaMg}(\text{CO}_3)_2$ and MgCO_3). Li does not contribute to diagenesis, and it is enriched in authigenic magnesites and Li-bearing silicates. The enrichment of Li relative to Cl can contribute to the dissolution of authigenic magnesites, which are widely distributed in the salt-bearing clastic layer of the study area. Li^+ concentrations of

underground brine in the potash mining area in central Laos are however lower than the peak of the precipitation stage of the sylvite, which indicates that no Li-bearing minerals are found in the mining area [82]. The SET is constant until halite saturation during seawater evaporation and waters derived from halite dissolution and mixed with marine and meteoric waters experience the enrichment of Cl relative to Br and plot beneath the SET [83]. Therefore, saline springs in this study that plot above and along with the SET (Figure 5g) are likely dominated by meteoric mixtures and halite dissolution. Based on the above, (1) halite dissolution should be a major solute source, (2) the dissolution of sulfate and carbonate rocks may be a minor solute source for saline springs in north and central Laos, and (3) underground brines in the potash mining area, central Laos, are geochemically influenced by the dissolution of carnallite and sylvite. These conclusions are supported by saliferous lithologies in north and central Laos.

Figure 4. Gibbs diagram of the saline springs in north and central Laos, the comparison area data from [66,67,69].

Figure 5. Plot of Cl vs. Na (a), Cl vs. K (b), Cl vs. Mg (c), Cl vs. Li (d), Br vs. Ca (e), Br vs. K (f), and Br vs. Cl (g); SET, HDL, Sw, Gy, HI, HE, E, S, CI, CE, and B represent seawater evaporation trajectory [80], halite dissolution line [84], seawater, gypsum precipitation point, halite precipitation initial point, halite precipitation end point, epsomite precipitation point, sylvite precipitation point, carnallite precipitation initial point, carnallite precipitation end point, and bischofite precipitation point [80], respectively. Date of underground brines and saline springs in potash mining area, central Laos from [66], saline springs in Yunnan from [85], and hot saline springs in Thailand from [69].

The ternary Ca–SO₄–HCO₃ phase diagram (Figure 6a) reflects the evolution of the surface fluid chemical composition. Water samples from the saline springs in the study area fall into the Cl–SO₄ field, which may be related to the dissolution and recycling of buried gypsum/anhydrite in saliferous strata from north and central Laos [86,87]. This may be the main reason for the lack of alkaline HCO₃–CO₃–rich saline springs in north and central Laos. Deep Ca–Cl brines are formed by the interaction of the diagenetic or hydrothermal water with rocks and sediments at high temperatures and deep circulation and return to the surface along faults [88]. If groundwater falls into the Ca–Cl field, this means that the water is mainly influenced by deep Ca–Cl–type waters. Most of the hot saline springs in Krabi province, Thailand, mainly recharge from deep Ca–Cl–type waters that are mixed with meteoric water. Deep Ca–Cl–type waters and the dissolution of sylvite/carnallite may be the main source of solutes in the underground brines from the Longhu potash mining area in Khammouane Province, Central Laos. Additionally, the $\delta^{11}\text{B}$ data (+19.8~+21.0‰) of these underground brines are near those of evaporites (carnallite and sylvite), suggesting that dissolution of carnallite and sylvite by surface water is the major boron origin of these underground brines [66]. Based on the above analyses, the dissolution of halite may be viewed as the main solute source, with the dissolution of marine gypsum/anhydrite and carbonatites being a relatively minor source in saline springs in the study area.

Figure 6. (a). Ternary Ca–SO₄–HCO₃ phase diagram of saline springs from north and central Laos; (b). Na–K–Mg ternary diagram showing saline springs from north and central Laos. Data from [66,69,85].

5.2.2. Evidence–Based on Saturation Index (SI)

The saturation index (SI) of the groundwater is a reflection of the degree of water–rock/mineral reaction. The SI values of the saline springs from north and central Laos were calculated by PHREEQC with temperature. As shown by the trend of mineral saturation (Figure 7a), all saline spring water samples are saturated with aragonite, calcite, dolomite, and talc (and have SI values averaging 1.2, 1.3, 1.8, and 8.5, respectively). These SIs indicate the deposition of carbonate minerals. An oversaturation of any element would lead to the precipitation of that element. The oversaturation of Ca²⁺ and Ca²⁺ + Mg²⁺ is explained by the presence of dolomite and limestone in the Jurassic to Cretaceous sediments in the study area. Only the saline spring water samples of West Moding, the Mankuang saltworks, and Thakhek are saturated in gypsum, while all the saline spring water samples are saturated in anhydrite, except for samples from Muang Say. This means that sulfate minerals in the saline springs of Muang Say are still in the dissolution stage, while those of West Moding, the Mankuang saltworks, and Thakhek are in the deposition stage. Apart from the halite SI being saturated for West Moding (≈ 0), the halite SI for the rest of the saline springs is far

from saturated, indicating that the saline spring waters in the study area are in the halite dissolution stage. The SI values of the carbonate minerals (calcite, aragonite, and dolomite) are independent of TDS, while those of the sulfate minerals (anhydrite and gypsum) and halite tend to increase with an increase in TDS ($R^2 = 0.87$) (Figure 7b), suggesting that the dissolution of halite and gypsum could be the main driver for the increase of salinity. This theory is confirmed by the extensive occurrence of late Cretaceous salt-bearing strata in the study area.

Figure 7. (a). Plot of the saturation indexes of saline spring water samples from north and central Laos. (b). Plot of TDS vs. saturation indexes (SI) of saline spring water samples from north and central Laos.

5.2.3. Inference from Boron Isotopes

In this study, there is no obvious linear relationship ($R^2 = 0.35$) between the $\delta^{11}\text{B}$ value and the pH (Figure 8a), and the pH of saline springs is therefore not the main factor influencing the $\delta^{11}\text{B}$ value, which may be controlled by its source area. We can therefore determine the solute source of the saline springs based on the $\delta^{11}\text{B}$ characteristics. There are three important salt-bearing basins in north and central Laos: the Muong Say, the Vientiane, and the Khammouane Basin, with the late Cretaceous evaporites, clastic deposits, and continental red beds being widely distributed in north and central Laos [2–4]. Carbonates and crustal-derived volcanics from Jurassic to Paleogene are also present in the study area. The characteristics of boron isotopes can be used to distinguish between marine and non-marine sedimentary environments. The $\delta^{11}\text{B}$ value of saline springs (5.50 to 36.01‰, average = 18.89‰) in this study is lower than that of the present-day seawater (36.36 to 45.75‰) [89–91], which differs significantly from continental evaporates (−6.83‰ to −5.79‰). The $\delta^{11}\text{B}$ value of saline springs is however very close to that of salts that have precipitated from evapo-concentrated seawater (10‰ to 36‰) as well as marine carbonates (−5.5‰ to 23‰) (see Figure 8b,c). These data, therefore, support a continental origin for the boron in the saline springs [89,92]. This boron is most likely derived from marine carbonates/salts and crustal-derived volcanics.

The positive correlation between the Cl/B ratios and the $\delta^{11}\text{B}$ values in the brines and the paleo-evaporites worldwide makes it possible to effectively distinguish between marine and terrestrial sources [93,94]. Marine sources are located at the high $\delta^{11}\text{B}$ and high Cl/B end member, while terrestrial sources are characterized by lower $\delta^{11}\text{B}$ and lower Cl/B ratios [95]. We compared our data to that of geothermal systems worldwide and found binary mixing between a continental end member and a marine end member (Figure 9). The hot springs in India, the Dead Sea (Israel), the Izu Peninsula (central Japan), and northeastern Taiwan are all strongly influenced by seawater, which is enriched in ^{11}B . The $\delta^{11}\text{B}$ values in these marine springs are all higher than the saline springs in our study area, which means that saline springs in our study are of terrestrial origin [28,96–98]. Several factors influence the distribution and relationships of $\delta^{11}\text{B}$ –Cl/B in non-marine springs around the world, including the rock type, the presence of any tectonic structures, and the geological setting. The $\delta^{11}\text{B}$ value of geothermal waters may indicate different B

sources (for example, a mantle source for Iceland and the Ngawha geothermal system in New Zealand, magmatic rocks for the Taupo Volcanic Zone in New Zealand [99–101] and the Yellowstone National Park [100,102], groundwater mixing for Java in Indonesia [103], and a granitic source for the Limagne Basin in France [104]). The $\delta^{11}\text{B}$ values of the springs in the marine carbonates (+10‰ to +30‰) [21,105] and halite/potash-associated minerals of the Khammouane potash deposit (19.91‰ to 31.01‰) [7] differs significantly from the continental evaporates (−6.83‰ to −5.79‰), the primitive mantle (−12‰ to −8‰), springs in metamorphic rocks (−9.0‰ to −7.4‰), and igneous rocks (−17‰ to −2‰) [94,106,107] but is very close to that of the saline springs in this study area. The $\delta^{11}\text{B}$ values show that marine carbonate rocks and marine evaporites (gypsum and halite) are the main sources of boron in the saline springs from north and central Laos and are similar to the saline springs of the Nangqen–Qamdo–Simao Salt Basin [108,109]. The higher Cl/B ratios are caused by the dissolution of salt in the saline springs of the study area, which exceed those of other global geothermal systems. The B in thermal waters of the Qamdo–Simao Salt Basin and the Tibet Geothermal Belt is mainly controlled by marine carbonate rocks and B-enriched volcanic rocks, while the springs in the western Yunnan geothermal belt also differs from the B sources of the saline springs in this study [107]. The B in the springs from the western Yunnan geothermal belt has both crustal and mantle sources and is mainly controlled by the leaching of reservoir host rocks (large granitic batholiths and metamorphic rocks) and by magmatic fluids from shallow magma [107,110].

Figure 8. (a). pH vs. $\delta^{11}\text{B}$ of saline springs from north and central Laos; (b). Range of $\delta^{11}\text{B}$ values from different boron sources [7,79,106,111]; (c). $\delta^{11}\text{B}$ vs. B of saline springs and underground brines from the southwestern China and north and central Laos compared with the predicted $\delta^{11}\text{B}$ values based on experimental and measured $\delta^{11}\text{B}$ values in natural systems of marine salts, marine brines, nonmarine salts, and nonmarine brines [93,94].

Figure 9. Correlations between $\delta^{11}\text{B}$ –Cl/B for springs of major geothermal systems around the world.

5.2.4. Inference from Chlorine Isotopes

Stable chlorine isotopes ($\delta^{37}\text{Cl}$) can be used to study dissolved Cl, fluid mixing, water–rock interactions [47,112], and evaporation rates in the salt lake systems [73,113–115]. Chlorine isotope fractionation occurs during evaporation and salt deposition, resulting in ^{37}Cl enrichment within the salt deposits and ^{37}Cl loss in residual brines [116]. Figure 5 shows the characteristics of the Cl isotope for different fluids and saline minerals. In this study, the saturation index of halite (NaCl) in saline springs is less than 0, except for West Moding, which is about 0. There is no correlation between the $\delta^{37}\text{Cl}$ values and the Cl concentrations, indicating that the isotopic composition of chlorine is not controlled by halite precipitation, where halite precipitation is caused by groundwater–rock interaction or by differing flowpaths. The dissolution and recrystallization of halite do not change the Cl/Br ratio of the brine [31]; therefore, the $\delta^{37}\text{Cl}$ value and the Cl/Br ratio reflect the dissolved halite characteristics. The chloride concentration in the halite that is dissolved water is mainly controlled by the solubility of NaCl in the fluid, the fluid temperature, and the flow rate. By comparison, the Cl/Br ratio of the saline springs in this study (ranging from 4076 to 9853, with an average = 6864) is within the halite characteristic value range (>4000) [31,117–119]. The $\delta^{37}\text{Cl}$ values of the saline springs in this study (−0.12 to +0.79, average = 0.34) are consistent with the range of halite eigenvalues (ranging from −1.55‰ to +0.97‰) [120], which is much larger than the $\delta^{37}\text{Cl}$ value of the seawater evaporation stage (see Figure 10b). This means that the saline springs are continental in origin and are possibly mainly be formed by the leaching of the underground halite layer. This interpretation of leaching from an underground halite layer is consistent with the occurrence of late Cretaceous salt-bearing strata within the study area [65]. Stable

hydrogen and oxygen isotopes indicate that the water molecules in saline springs originate from widely distributed meteoric precipitation in north and central Laos. The $\delta^{37}\text{Cl}$ values of the saline springs in this study are consistent with that of global precipitation (ranging from -3.5% to 4.48%) [121]. Atmospheric precipitation is therefore another factor that restricts the change of chlorine isotopes in the saline springs of the study area. Sandstone, mudstone, and volcanic rocks occur widely in the Jurassic to Paleogene strata from north and central Laos. These rocks contain large amounts of biotite and hornblende. Biotite and hornblende have higher Cl/Br ratios and can be regarded as the most important chlorine-containing minerals in nature [122]. The $\delta^{37}\text{Cl}$ compositions of biotite (ranging from -0.26% to 3.4%) and hornblende (ranging from 0.7% to 7%) greatly affect the saline springs in the study area (see Figure 10a). The following conclusions can be drawn from the analysis of the Cl/Br ratios and the $\delta^{37}\text{Cl}$ values: (1) The dissolution of halite layers is the main solute source of brines drained by springs, (2) the water–rock interactions between volcanic rocks, mudstones, and sandstone can cause an increase in the Cl/Br ratios and a positive shift in the $\delta^{37}\text{Cl}$ values for saline springs, and (3) atmospheric precipitation can restrict the $\delta^{37}\text{Cl}$ values in the saline springs.

Figure 10. (a). The range of variation of $\delta^{37}\text{Cl}$ in different fluids and saline minerals. Data sources: Rain water [121]; shallow and deep groundwater [123]; biotite [37]; hornblende and halite [120]. (b) Relationship between the Cl/Br molar ratios and $\delta^{37}\text{Cl}$.

5.3. Reservoir Temperature and Circulation Depth of the Saline Springs

Four mechanisms could explain the heat source of groundwater: (1) deep circulation of the groundwater heating the groundwater, (2) the residual heat of magma heating the groundwater, (3) friction heat from faulting heating the groundwater, and (4) the decay of radioactive elements heating the groundwater [124]. The Jurassic to Cretaceous strata are the main developed strata in the study area and are characterized by sandstone, mudstone, siltstone, limestone, dolomite, and evaporates. There are only a few magmatic rocks in the study area, which are only found sporadically in the Paleogene strata. The residual heat of magma and heat generated by the decay of radioactive elements in granite are therefore not viewed as the main heat sources of the saline springs in this study. Even though the Dien Bien Phu fault was developed in north and central Laos, the heat generated by this fault movement is insufficient to provide a sufficient heat source for the springs [124]. The saline springs in this study must therefore receive heat from heat flow during the deep circulation of groundwater. Reservoir temperature is an important parameter to evaluate the geothermal potential of geothermal fields and to classify the genetic types of geothermal systems, which can be estimated by using chemical geothermometers. Three chemical geothermometers are frequently used, including the silica geothermometer, the cation geothermometer, and the multi-mineral balance chemical geothermometer. These geothermometers are functional expressions of the solute concentration of the geothermal fluid and the reservoir temperature [125,126]. The different geothermometers each have

different restrictive conditions or defects. The cation geothermometers, for example, are only applicable to the reservoir temperature calculation of full equilibrium water and include the Na/K geothermometer, the Na–K–Ca geothermometer, and the K/Mg geothermometer [127–130]. The Na–K–Mg ternary diagram can be used to determine the water–rock equilibrium state, the groundwater type, and the reservoir temperature as estimated by solute geothermometers [127], which shows that all the saline spring water samples in study area are all fall in the full equilibrium area (Figure 6b). Therefore, the reservoir temperatures were calculated using the silica and cation geothermometers [131], and the quartz geothermometer is most suitable for estimating the reservoir temperature (Tr) in this study.

The multi-mineral equilibrium diagram can be used to determine the chemical equilibrium between geothermal fluids and minerals. If a set of minerals in fluids approach saturation ($SI = 0$) over a small temperature range, the saturation temperature is the reservoir temperature [132]. The reservoir temperature range estimated by the multi-mineral equilibrium diagram, which is also the temperature range (36–173 °C) for SI convergence at the zero line in Figure 11. Based on the preceding discussion, the reservoir temperatures (87–137 °C) of the eight saline spring water samples calculated by the quartz geothermometer are more reasonable. This is on average 67 °C higher than the spring outlet temperatures and is in the range of the reservoir temperatures obtained from the multi-mineral equilibrium diagram. If the influence of cold–water mixing is removed, the real reservoir temperature should be slightly higher.

The heat of the saline springs in this study is derived from deep heat flow. The circulation depth can be roughly calculated with the following equation [76]:

$$= G(T - T_0) + Z_0$$

where Z is the circulation depth of the thermal groundwater in m, G is the reciprocal of the geothermal gradient, T is the reservoir temperature in °C, T_0 is the annual average temperature in the study area in °C, and Z_0 is the thickness of the constant temperature zone in m. The G in north and central Laos was selected as 34.5 m/°C, which is similar to the G value of the Simao Basin in southwestern Yunnan, China, that is located adjacent to this study area [133]. The T is 21 °C, and the Z_0 is 25 m. The saline springs in north and central Laos have experienced deep circulation, and that the circulation depths range from 2302 to 4027 m (see Table 3). Based on the estimated circulation depth of the saline springs and the geological conditions in north and central Laos, it is likely that the development of fractures and faults provided migration channels for the deep circulation of the saline spring water. It can also be inferred that the lowest position of saline spring deep water circulation may be the late Cretaceous salt-bearing strata, which are characterized by sandstone, siltstone, conglomerate, red–brown clayey siltstone, marl, beds of salt, gypsum, and anhydrite.

Table 3. Estimated reservoir temperatures of saline spring water samples from north and central Laos.

Sample ID	Water Temperature (°C)	Reservoir Temperature (°C)					Circulation Depth (m)
		Quartz	Na–K	Na–K–Ca	KMg	Multi-Mineral Equilibrium	
Muang Ou Tai	25	87	81.2	126.3	127.6	80–115	2302
West Moding	26	90.4	63.7	125.2	141.4	100–132	2419
Mankuang saltworks	27	137	62.1	122.9	158.8	36–173	4027
East Muang Say	56	102.7	152.4	159.8	117.7	43–134	2844
South Pak–Lay	28	99.9	75.7	127.1	128.8	47–160	2747
Muang Say 01	60	105	143	151.8	111.2	60–125	2923
Muang Say 02	61	106.6	152.7	159.5	116	58–125	2978
Thakhek	29	117.9	85.2	123.8	109.9	108–128	3368

Figure 11. $\log(Q/K)$ – T diagram showing saline springs from the north and central Laos (Q is the ion activity product; K is the equilibrium constant of the mineral at the equilibrium temperature).

5.4. Potassium–Forming Prospect

The $\gamma\text{Na}/\gamma\text{Cl}$ and $\text{Br} \times 10^3/\text{Cl}$ ratio can be used to distinguish brines in salt-bearing basins. Brines can be divided into sedimentary connate brine and salt-dissolution brines [76]. Sedimentary connate brines are the residual connate bitter brine that develops during

evaporation and deposition of a saline basin. The continuous salinization during seepage of surface water or groundwater into the saline strata forms salt–dissolution brines. The $\gamma\text{Na}/\gamma\text{Cl}$ value of the sedimentary connate brines is generally lower than the standard seawater value (0.85), and the $\text{Br} \times 10^3/\text{Cl}$ value is generally greater than the standard seawater value (3.4). The ratio of $\gamma\text{Na}/\gamma\text{Cl}$ in salt–dissolution brines is around 1 or greater, and the $\text{Br} \times 10^3/\text{Cl}$ ratio is generally less than 1 and is caused by the low-level Br content in salt–dissolution brines [134]. The average $\gamma\text{Na}/\gamma\text{Cl}$ ratio of sylvinite–dissolution brines is generally lower than 0.86, and can even be lower. The $\gamma\text{Na}/\gamma\text{Cl}$ ratio and the $\text{Br} \times 10^3/\text{Cl}$ ratio of saline springs in this study varied from 0.84 to 0.99, with an average of 0.93, and from 0.23 to 0.55, with an average of 0.36, respectively. The $\gamma\text{Na}/\gamma\text{Cl}$ ratio is close to 1, except for Muang Say (with an average = 0.85), which is slightly less than 0.86. The $\text{Br} \times 10^3/\text{Cl}$ ratio is less than 1 for all the samples. It can therefore be concluded that the saline springs in this study are salt–dissolution brines (saline water), which undergo salt dissolution processes. The saline springs in Muang Say may also have leached sylvinite and carnallite. Four hydrochemical characteristic coefficients are generally used to indicate the underground dissolution of potassium ores. The $\text{K} \times 10^3/\Sigma_{(\text{Total salinity})}$ and the $\text{K} \times 10^3/\text{Cl}$ ratios are direct indicators for potash exploration, while the $\text{Br} \times 10^3/\text{Cl}$ and the $\text{Mg} \times 10^2/\text{Cl}$ ratios are indirect indicators [135]. During the evaporation of seawater, Br is relatively enriched in the residual seawater during the deposition of NaCl. The $\text{Br} \times 10^3/\text{Cl}$ ratio of brines can therefore determine the degree of concentration and evaporation of saline strata, which can indirectly guide potash exploration. There is a significant sylvite anomaly, which indicates a great possibility for potash exploration when $\text{K} \times 10^3/\Sigma_{(\text{Total salinity})}$ and $\text{K} \times 10^3/\text{Cl}$ ratios exceed 10 and 20, respectively [136]. The average values of indirect indicators (0.25–0.28 for the $\text{Br} \times 10^3/\text{Cl}$ ratio and ≈ 1 for the $\text{Mg} \times 10^2/\text{Cl}$ ratio) of spring waters. These indicators undergo incongruent dissolution of potassium-bearing halite and are greater than values (<0.2 for the $\text{Br} \times 10^3/\text{Cl}$ ratio and <0.5 for the $\text{Mg} \times 10^2/\text{Cl}$ ratio) that only undergo incongruent dissolution of halite [137]. The values of $\text{K} \times 10^3/\Sigma_{(\text{Total salinity})}$, $\text{K} \times 10^3/\text{Cl}$, $\text{Br} \times 10^3/\text{Cl}$ and $\text{Mg} \times 10^2/\text{Cl}$ ratios for the eight saline spring water samples in this study ranged from 2.70–13.05, with an average = 6.82, 4.52–23.88, with an average = 12.15, 0.23–0.55, with an average = 0.36 and 0.06–0.9, and with an average = 0.55, respectively. A comprehensive analysis of the above indicators shows that the characteristic values of saline springs water in Muang Say is abnormal, which means that the prospects are relatively good for potash exploration in the Muang Say basin.

5.5. Conceptual Model of Saline Spring Water Circulation

The Muong Say basin in northern Laos, the Vientiane basin, and the Khammouane basin in southern Laos are important salt-bearing basins. They contain large amounts of saline spring water, late Cretaceous evaporites, and clastic deposits. The origin and evolution of the saline springs in north and central Laos are very complicated. We therefore propose a conceptual model for the circulation of the saline spring water in the study area (see Figure 12). A series of tectonic events after the late Cambrian formed the semi-graben salt-bearing basins in north and central Laos. Many marine salt-bearing strata were formed during the Mesozoic era. Based on water isotope analyses, the most likely recharge sources for saline springs in this study are rainfall and/or ice and snow melt from the surrounding mountains (Phu Bia, Phu Lay, Lao Bi, and Phu Miyang), while the Dien Bien Phu fault and other stretching tensile active faults can serve as favorable conduits for allowing groundwater circulation. The solute sources of the saline springs in this study are mainly be controlled by the dissolution of late Cretaceous marine evaporites (halite, gypsum/anhydrite, and carbonatite). The dissolution of carnallite and sylvite are the principal solute sources that control the chemistry of underground brines in Thakhek. The $\delta^{37}\text{Cl}$ value of the saline springs in this study is controlled by atmospheric precipitation, water–rock interaction, and salt concentration via evaporation, while the $\delta^{11}\text{B}$ is mainly controlled by water–rock interaction. Saline springs have leached from the host rocks and flow along large fracture

zones, through which they have experienced deep circulation, ranging in depth from 2302 to 4027 m. The geothermal system that originates from the magmatic heat source then heats this water, after which further rock–water interaction occurs. The reservoir temperature range from 87–137 °C, as calculated by the quartz geothermometer, which is reasonable for the saline springs in this study.

Figure 12. Conceptual model of saline springs based on hydrochemistry, δD , $\delta^{18}O$, $\delta^{11}B$, and $\delta^{37}Cl$.

6. Conclusions

We used chemical and stable isotopes (δD , $\delta^{18}O$, $\delta^{11}B$, and $\delta^{37}Cl$) of saline springs in north and central Laos to provide constraints on the solute process and recharge sources, the reservoir temperature, the mode of circulation, and the potash exploration prospects. The main findings include the following:

(1) Based on the major ionic components of saline springs in north and central Laos, the saline springs originated from the dissolution of late Cretaceous evaporites (halite, sulfate, and carbonate rocks) and underground brines in the potash mining area. The Thakhek is mainly influenced by the dissolution of carnallite and sylvite. Based on the δD and $\delta^{18}O$ isotopic compositions, the saline springs may recharge by rainfall and/or ice and snow melt from the surrounding mountains, which underwent strong evaporation and intense rock–water interactions.

(2) The Cl/B ratios and $\delta^{11}B$ values (ranging from 5.50 to 36.01‰) for the saline springs in this study vary significantly, confirming their continental origin. The main sources of the B in the saline springs are probably marine carbonate rocks and marine evaporates (gypsum and halite). From the $\delta^{11}B-Cl/B$ diagram of thermal waters around the world, we conclude that the B in saline springs is primarily of a crustal source and does not have any marine or deep mantle sources. It is concluded here that Cl/Br molar ratios (ranging from 4076 to 9853) and the stable Cl isotopes (ranging from -0.12 to $+0.79$)

indicates that atmospheric precipitation and late cretaceous marine halite dissolution are the main halogen sources in the saline springs from north and central Laos.

(3) According to the multi-mineral equilibrium diagram and chemical geothermometers, the reservoir temperatures (ranging from 87–137 °C) for the saline springs calculated by the quartz geothermometer are reasonable. These saline springs have experienced deep circulation (ranging from 2302 to 4027 m deep). Hydrochemical characteristic coefficients show that the saline springs in the Muang Say basin could be dissolved by sylvinite and carnallite. We also suspect that the Muang Say basin has good potash exploration prospects.

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