

Geochemical characteristics of trace elements of hot springs in the Xianshuihe-Xiaojiang Fault Zone

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Abstract: Trace elements in hot spring waters are the indicators for tracing the hydrochemical processes, such as the deep circulation of geothermal water and the contamination of shallow water by thermal water. In this study, 74 hot springs in the Xianshuihe-Xiaojiang Fault Zone (XSHF-XJF) were chosen for investigation of geochemical characteristics of trace elements using classic geochemical tools and multivariate statistical analysis. The results indicated: (1) the hot spring waters were mainly derived from atmospheric precipitation as indicated by δD and $\delta^{18}O$ values that generally increased with decreasing elevations. Variations of dissolved compositions were mainly controlled by the dissolution of carbonate, evaporite, and silicate minerals, as well as cation exchange, (2) the high concentrations of B, As, Fe, and Mn in the waters as well as the values of WQI indicated that the water quality was spatially heterogeneous and hot spring waters were not entirely suitable for drinking, and (3) B/Cl ratios showed that the presence of two different heat sources at the XSHF and XJF, respectively. The leaching of the surrounding rock during water circulation contributed predominantly to the ions of trace elements in the waters. The diversity of lithology was the main factor affecting their concentrations. In addition, deep circulation controlled by the fault could influence trace element enrichment. Our results offer a guide for the exploration and use of the geothermal resources.

Keywords: trace element; hot springs; water quality assessment; XSH-XJ fault zone

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1. Introduction

Hot springs are the surface manifestation of deep hydrothermal fluids, which frequently present in the regions of active volcanism and intense tectonic activity [1,2]. In the past decade, geothermal energy has been increasingly emphasized because of its advantages like renewable and large reserves, and widely exploited for power generation, tourism, physiotherapy, heating, etc.[3–5].

In comparison with groundwater or surface water, trace elements, including typical elements (As, B, Li, etc.) and heavy elements (Fe, Mn, Cd, etc.), usually show enrichment in hot spring waters, which play a crucial role in determining the genesis of hot springs and explaining the process of thermal water circulation[6,7]. The high concentrations of

F, As, B, Li and heavy metals, as found in geothermal water in Turkey[7], Chile[8], Tibet[9], Tengchong[10], and Taiwan[6], are usually constrained by multiple factors such as the type of host rock in water-rock reaction, magmatic fluids, and secondary processes. On the other hand, mixing of geothermal waters, which contain high concentrations of trace elements, with surface waters can result in problems linking to drinking water quality and environmental contamination[11–14]. Therefore, researches on the source and enrichment patterns of trace elements in hot spring waters favor understanding the genesis and development of geothermal systems and assessing the pollution situation of water sources caused by deep thermal water.

The XSHF-XJF is located at the eastern edge of the Sichuan-Yunnan rhombic block[15]. It is continuously active with plenty of geothermal resources owing to the continuous northeastward thrusting of the Indian Plate and eastward subduction of the Myanmar Plate[16,17]. In this region, a series of investigations of the hydrochemical features of the hot springs[18–20], gas isotope characteristics[21], the genesis of geothermal water[22], and the relationship between fluids and seismic activity[23,24] were conducted by the approaches of hydrogeochemistry and isotopes and the methods of geophysical exploration. Besides, high concentrations of B, Li, and F in the Kangding area were reported[25]. However, the geochemical characteristics of trace elements in the hot springs throughout the fault zone and their environmental effects so far are lack. Therefore, this paper aims at analyzing the source and enrichment mechanism of trace elements in hot springs, and evaluating the water quality of thermal waters in terms of trace elements to provide a new reference for the exploitation of hot springs in the XSHF-XJF.

2. Geological Setting

The study area is on the eastern margin of the Tibetan Plateau (Figure 1a). Due to the predominantly plateau-type monsoon climate, precipitation is annually concentrated from May to September. The surface water system is well developed by atmospheric precipitation and ice meltwater. The groundwater in solidified host rocks can be classified into bedrock fissure water in granite, clastic fissure water with sandstone as the dominant water-bearing lithology, and carbonate fissure water[26].

The XSHF-XJF includes Xianshuihe Fault (XSHF), Anninghe Fault (ANHF), Zemuhe Fault (ZMHF) and Xiaojiang Fault (XJF) (Figure 1b). The XSHF is a NW-SE-trending left-slip fault, which is located between Ganzi and Shimian in Sichuan province. The regional stratum includes Triassic sedimentary strata composed of sandstone, siltstone, and mudstone, Precambrian rocks composed of metamorphic rocks, and Mesozoic intrusive rocks dominated by granite and diorite[27]. The ANHF is NS trending, with dip directions of the east or west. And ZMHF is NNW trending, dipping the northeast. Metamorphic sedimentary rocks of Aurignacian, muddy siltstone of Jurassic, and early-middle Paleozoic granite are mainly exposed in the ANHF. While the ZMHF is exposed from the Aurignacian to Triassic constructed of marine carbonates and clastic rocks. The Cenozoic strata mainly consist of mudstone and sandstone interbedded with thin layers of coal[19]. The XJF is a SN-trending, left-slip active fault. The rocks of fault walls are mostly carbonate rocks and sedimentary rocks[28].

In the study area, most hot springs occur along the XSHF-XJF, and the geothermal resources are most developed in the XSHF. The hot springs geographically look like the scatted beads in the Tertiary strata and Yanshanian-Himalayan granites, they are mostly medium-high temperatures. The hot springs in the south part of XSHF-XJF (ANHF-XJF) are unevenly distributed, mainly developed in carbonate and sedimentary rock strata, with temperatures generally below 60°C, belonging to the medium-low temperature hot springs[29].

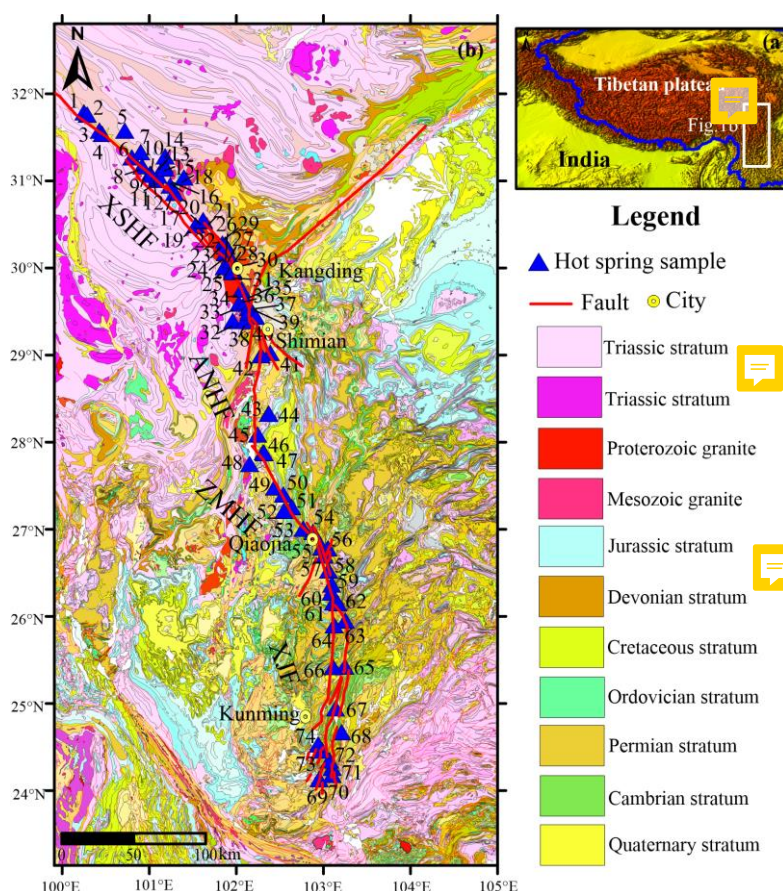


Figure 1. (a) Localization of the area of this study; (b) geological map with the sampling sites.

3. Sampling and Methods

3.1. Sampling and analysis methods

74 water samples were obtained from hot springs in the XSHF-XJF during the 2018–2019. After filtrating with a 0.45 µm membrane, the samples were collected in polyethylene terephthalate (PET) bottles (50 mL) for laboratory analysis. A portable equipment was used to monitor the pH, EC, and temperature of the waters in the field. The major elements were tested using a Dionex ICS-900 ion chromatograph fitted with an AS40 automatic sampler in the Key Laboratory of Earthquake Prediction, China Earthquake Administration, with a detection limit of 0.01 mg/L[30]. The concentrations of HCO_3^- and CO_3^{2-} were titrated with a ZDJ-100 potentiometric titrator using the 0.05 mol/L HCl titration 0.1% methyl orange and 1% phenolphthalein procedures (reproducibility within $\pm 2\%$). The following equation was used to compute the ion balance error in water samples (Equation 1):

$$\% \text{difference} = \frac{\sum \text{cations} - \sum \text{anions}}{(\sum \text{cations} + \sum \text{anions}) * 0.5} * 100 \quad (1)$$

Trace element analysis was conducted with an element type inductively coupled plasma mass spectrometer (ICP-MS) at the Test Center of the Institute of Nuclear Industry Geology[31]. The concentration of As was determined with LC-6500 atomic fluorescence photometer, with the detection limit of 0.60 µg/L. The $\delta^{18}\text{O}$ and δD were analyzed with a Finnigan MAT253 mass spectrometer using the TC/EA method. And they are expressed as permille standardized by V-SMOW, with analytical uncertainty of $\pm 0.2\%$ and $\pm 1\%$ respectively[32].

3.2. Water quality index

The Water Quality Index (WQI), a comprehensive pollution indicator, was applied to assess the cumulative impacts of trace elements in hot springs. It can be calculated by follows (Equation 2, 3)[33]:

$$PI = C_i / Q_i \quad (2)$$

$$WQI = \frac{1}{n} \sum_{i=1}^n PI = \frac{1}{n} \sum_{i=1}^n C_i / Q_i \quad (3)$$

where C_i is the concentration of trace elements analyzed in the water sample, Q_i is the limit value of the water quality standard of the elements, and PI stands for the exceedance index of a trace element i , relative to the standard limit value. Considering the geological location of the study area, the trace element concentrations were assessed by China Standards for Drinking Water Quality (GB 5749-2022). The comprehensive pollution indicator is divided into four categories: $WQI \leq 1$ (practically unpolluted); $1 < WQI \leq 2$ (slightly polluted); $2 < WQI \leq 3$ (moderately polluted); and $WQI > 3$ (heavily polluted)[34].

3.3. Statistical analysis

Using the different water parameters, descriptive statistical analysis, correlation analysis, and factor analysis (FA) was performed using SPSS 22.0 software. For FA, the data were verified for suitability by the KMO (Kaiser-Meyer-Olkin) and Bartlett tests. The value of the KMO test in this study is 0.540, and the significance level of Bartlett test is less than 0.01, suggesting that the data have a certain correlation and are suitable for FA.

4. Results

4.1. Hydrochemical compositions

The results of physicochemical parameters of the water samples were given in Table S1. The outlet temperatures of the thermal waters range from 11.3 °C to 77.0 °C, EC values are in a range of 6–57600 µS/cm, and pH values range from 6.49 to 9.50. TDS values of the water samples range from 113.45 to 2247.98 mg/L, 134.69 to 6331.29 mg/L, and 115.27 to 1486.79 mg/L in the XSHF, AZF (ANHF-ZMHF), and XJF, respectively. HCO_3^- is the most prominent anion in the XSHF and AZF, and the main cation is Na^+ . The thermal waters in the XSHF are $\text{HCO}_3\text{-Na}$, while those in AZF are $\text{HCO}_3\text{-Ca}$ (Mg) and $\text{HCO}_3(\text{SO}_4)\text{-Na}$ (Ca)[19,20]. In the XJF, the main anion is SO_4^{2-} and HCO_3^- , and Mg^{2+} is the dominant cation in the thermal waters, resulting in water types of $\text{SO}_4\text{-Ca}$ (Mg) and $\text{HCO}_3\text{-Ca}$ (Mg)[18].

The statistical results of trace elements of the water samples were shown in Table S2 and Figure 2 with data of surface water[35,36] for comparison. The concentrations of Co, Cu, Ni, Pb, and Tl in the water samples are generally low. In contrast, the concentrations of B, Fe, Li, and Mn in the ranges of 5.6–6366 µg/L, 0.66–10520 µg/L, 1.29–4547 µg/L, 0.07–1754 µg/L, respectively, which are much higher than those in surface water. As concentrations range from <0.60 to 530 µg/L. Compared with the typical magmatic geothermal waters[37,38], the concentrations of B, Li, and As in the water samples are relatively low, indicating that the input of magmatic fluids into the hot spring waters is limited.

The δD and $\delta^{18}\text{O}$ values of the water samples were listed in Table S1. δD and $\delta^{18}\text{O}$ values in the XSHF range from -115‰ to -82‰ and -19.20‰ to -11.40‰, δD and $\delta^{18}\text{O}$ values in the AZF from -118‰ to -84‰ and -15.60‰ to -11.50‰, and δD and $\delta^{18}\text{O}$ values in the XJF from -117‰ to -81‰ and -15.40 to -11.10‰, respectively.

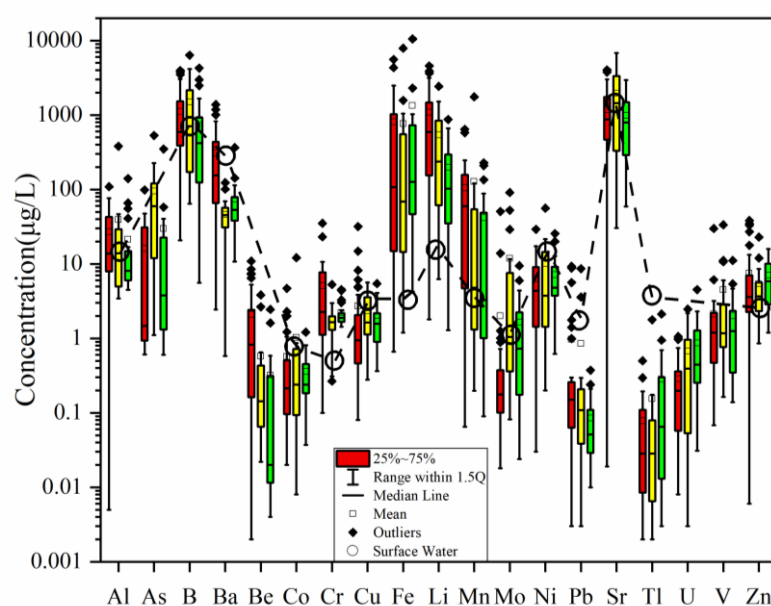


Figure 2. Trace element concentrations in the water samples in the XSHF-XJF. The red color stands for the samples from the XSHF, yellow color for the samples from the AZF, and green color for the samples from the XJF.

4.2. Water quality assessment

The results of the water quality evaluation were shown in Table S3 and **Figure 3**. Apparently, high concentrations of As, Mn, B, and Fe are found in the hot spring waters in the XSHF-XJF, greatly exceeding the standard values and hinting they are potentially polluting elements. Additionally, high concentrations of Be, Ba, and Ni are also found in portions of hot spring waters. The WQI values of water samples in the XSHF-XJF range from 0.0 to 5.4 (Table S3). In the XSHF, WQI values of the water samples of Nos.1,4,8,19 and 20 are above 1, indicating that those waters are slightly contaminated. In the ANHF-XJF, hot spring waters are generally contaminated to a higher degree, the water sample 67 and 46 being moderately contaminated, and the water samples of Nos. 42, 51, and 65 being heavily contaminated, with exception of the water samples 45 and 54 being slightly contaminated.

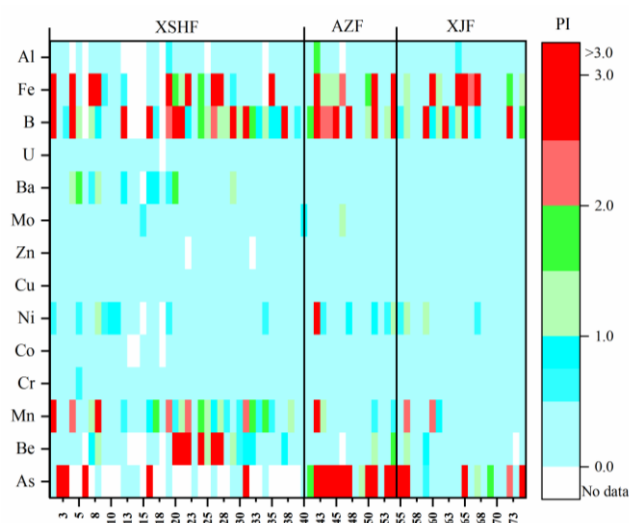


Figure 3. Heat map of risk assessment of trace elements in hot spring waters.

5. Discussion

5.1. Origin and isotopic characteristics of hot spring water

The isotopic compositions of hydrogen and oxygen in the hot spring waters are recognized as an efficient proxy for tracing the origin and geochemical evolution of water[39]. The data of δD and $\delta^{18}O$ for the hot springs and surface waters in the study area were plotted in **Figure 4**, along with Global Meteoric Water Line (GMWL, $\delta D = 8\delta^{18}O + 10$)[40] and Local Meteoric Water Line in the Tibetan Plateau (LMWL, $\delta D = 8.41\delta^{18}O + 16.72$)[41]. Both hot spring water samples and surface water samples are scattered around the GMWL and LMWL, indicating that the source of their recharge is all atmospheric precipitation. However, the values of $\delta^{18}O$ and δD are generally lower in the thermal waters compared to surface waters at the same or nearby locations, indicating that the surface water and surrounding atmospheric precipitation are not the direct source of recharge to the hot springs, which are recharged by the infiltration of distant atmospheric precipitation transported through fractures and the pipes beneath the surface.

Additionally, an obvious phenomenon is that the δD and $\delta^{18}O$ values of the water samples in the XSHF are more negative compared to those in the AZF and XJF. The East Asian monsoon is a key source of water vapor, and as it passes through the high terrain, the heavy isotopes of water (^{18}O and D) are prioritized for removal based on a Rayleigh fractionation mode[42]. There is a gradual decrease in the topographic elevation from northwest to southeast in the study area, resulting in a more depleted isotope composition in the thermal waters in the XSHF. This explanation is supported by the fact that the recharge elevation in the XSHF is higher than that in the AZF and XJF[19,20]. Besides, most of the hot spring samples shift to the right of LMWL, namely positive $\delta^{18}O$ drift, which can be attributed to water-rock interactions influenced by higher thermal storage temperatures, longer circulation time, or higher rock-to-water ratios[43]. A few of the water samples show a $\delta^{18}O$ left shift that may be caused by the ^{18}O exchange during the dissolution of CO_2 from a deep source.

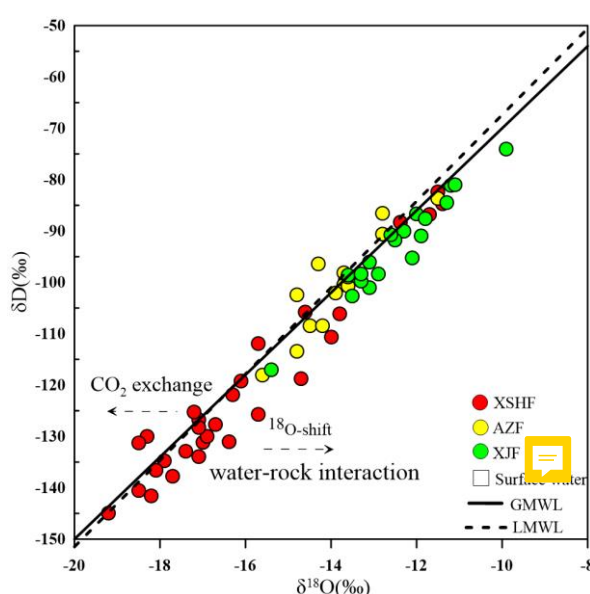
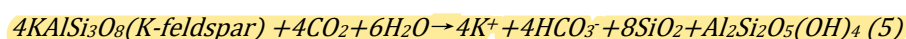
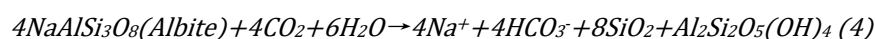


Figure 4. Plot of δD and $\delta^{18}O$ of the hot springs and surface waters in the XSHF-XJF. Dotted line stands for the LMWL and solid line for the GMWL. The data of surface waters from[44].

5.2. Hydrogeochemical characteristics of hot springs

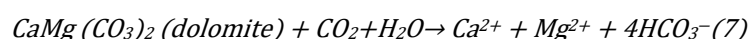
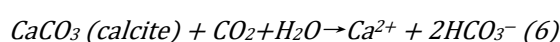
5.2.1. water-rock reaction and major ion

The ion compositions of groundwater depend mainly on the dissolution of mineral components during the water-rock interactions[45,46]. The molar ratio of $\text{Na}^+\text{+K}^+/\text{Cl}^-$ generated by the halite dissolution is generally equal to 1. However, most of the water samples fall below $y = x$ (**Figure 5a**), indicating that they mainly originate from the weathering and dissolution of silicate minerals (Equation 4, 5). Some of the samples (Nos. 42, 49, 52, 54, and 71) from AZF and XJF fall on the line of halite dissolution, indicating that the ions may have the origin of halite.

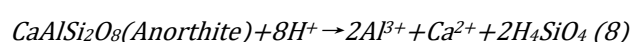


In addition to halite dissolution, seawater and deep fluids can also be sources of Cl^- [46]. Most of the Cl^- concentrations of the water samples are higher ($>3\text{mg/L}$), especially in the high temperature hot springs (Table S1), so Cl^- contribution of seawater is neglected because the mean value of Cl^- contribution is 0.92 mg/L in continental meteoric water and TDS is generally less than 20 mg/L [45]. Therefore, the high concentrations of Cl^- in water samples can be attributed to the deep fluids mixing and water-rock reaction.

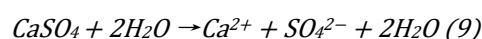
Ca^{2+} , Mg^{2+} , and HCO_3^- are commonly obtained by the dissolution of carbonate minerals (Equation 6, 7), resulting in $\text{Ca}^{2+}/\text{HCO}_3^-$ and $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$ molar ratios of 1:2[47].



In this study, most of the water samples in the XSHF almost are close to the y-axis side (**Figure 5c, d**). Previous studies have found that many gases spilled from the hot springs in the XSHF-AZF, which are mainly mantle-derived CO_2 . Thus, excess HCO_3^- may be the dissolution of sodium silicate minerals promoted by CO_2 (Equation 4, 5)[21]. Some of the water samples in the AZF and XJF are located below the $y=x$, suggesting that excess Ca^{2+} and Mg^{2+} are likely to derive from the dissolution of Ca-Mg materials (Equation 8), rather than carbonate dissolution alone. The **Figure 5d** displays that majority of the water samples are scattered above $y=x$, indicating that dissolution of silicate minerals is the main hydrogeochemical process controlling the ion concentration of the hot spring waters.



Besides, dissolution of gypsum in groundwater could also contribute to Ca^{2+} (Equation 9). The **Figure 5e** illustrates that gypsum may be the source of Ca^{2+} in the hot spring waters. However, some of samples in the AZF and XJF are scattered above the gypsum dissolution line, indicating that the excess SO_4^{2-} may originate from the hydrolysis of sulfides in the strata.



In the $\text{Na}^+\text{+K}^+\text{--Cl}^-$ vs $(\text{Ca}^{2+}\text{+Mg}^{2+}) - (\text{SO}_4^{2-}\text{+HCO}_3^-)$ diagram (**Figure 5f**), most of the samples are scattered along the 1:1 line (except for the water sample of No.46), hinting that cation-exchange process between deep fluids and rocks may affect the chemical composition of the water.

5.2.2. mineral saturation index

The mineral saturation index (SI) could be used to qualitatively recognize the minerals that tend to precipitate or dissolve during water-rock interactions[48]. A positive or negative values of the SI can indicate whether the water is saturated or unsaturated with a particular mineral. The PHREEQC software was utilized to determine the mineral saturation indices of potential minerals in circulation path of thermal waters, considering the temperature and pH. The results were presented in Table S4

Almost all the water samples are undersaturated with respect to albite, anorthite, Ca-montmorillonite, K-feldspar, halite, carbonate minerals (rhodochrosite, siderite, witherite), and sulfate minerals (anhydrite, barite, celestite, gypsum), indicating that dissolution of those minerals could not be the main processes for the hydrochemical formation of the hot spring waters. In contrast, the thermal waters exhibit an oversaturation of aragonite, calcite, and dolomite, indicating contribution of deep-earth fluids enriched in CO_2 that degassed with the decrease of hydrostatic pressure during upwelling. Oxides and hydroxides, such as manganite and pyrolusite, show either oversaturation or undersaturation in the water samples, which may reflect the variations of the surrounding rock and Fe and Mn origins.

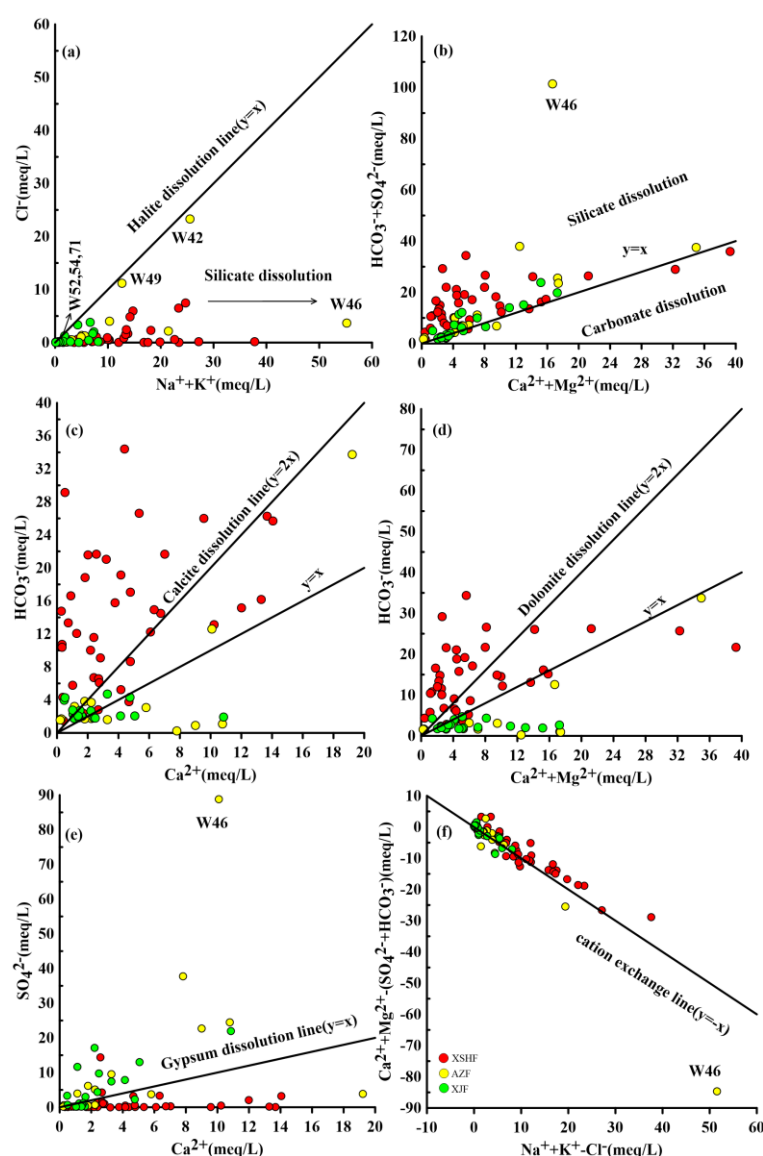


Figure 5. The plots of major ions for the water samples, (a) $(\text{Na}^+ + \text{K}^+)$ vs Cl^- ; (b) $(\text{Ca}^{2+} + \text{Mg}^{2+})$ vs $(\text{SO}_4^{2-} + \text{HCO}_3^-)$; (c) Ca^{2+} vs HCO_3^- ; (d) $(\text{Ca}^{2+} + \text{Mg}^{2+})$ vs HCO_3^- ; (e) Ca^{2+} vs SO_4^{2-} ; (f) $(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$ vs $((\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{SO}_4^{2-} + \text{HCO}_3^-))$.

5.3. Geochemistry of trace element

As aforementioned, B, As, Fe, and Mn could be potential contaminating elements in hot spring waters in the XSHF-XJF, and Li and Sr are also typical trace components in geothermal systems. In the following section, the source characterizations of trace elements (B, Li, As, Sr, Fe, Mn) in the hot spring waters are discussed by using multivariate

statistical methods. According to the results of the factor analysis (**Figure 6a**), the first four eigenvalues together accounted for 73.4% of the total variability of the hydrochemical processes. F1 explains 37.1 % of the total variation with strong positive loading on Li, K⁺, Na⁺, B, T, Cl⁻, and HCO₃⁻. It shows a general trend in hydrochemical characterization, probably reflecting the mixture of the surface water (**Figure 2**) and deep-earth fluids, as well as the dissolution of silicate. F2, explaining 15.4% of the variance, is related to Mn, Ca²⁺, HCO₃⁻, Cl⁻, and Fe. It characterizes the effect of Fe, Mn, and carbonite dissolution. F3, explaining 13.6% of the variance, is related to SO₄²⁻, As, and Sr and characterizes the effect of sulfate. F4, explaining only 7.3% of the variance, is positively correlated with Mg²⁺, NO₃⁻ and negatively correlated with pH and mainly characterizes the anthropogenic effect. Noteworthily, most of the samples from the XSHF are with high scores for F1 and F2, while most of the samples in the AZF and XJF (except for sample of No.42) are with high scores for F3 and F4, as indicated by the factor scores result (**Figure 6b**). Therefore, it is inferred that trace elements in the hot springs in the XSHF-XJF have different sources and controlling factors.

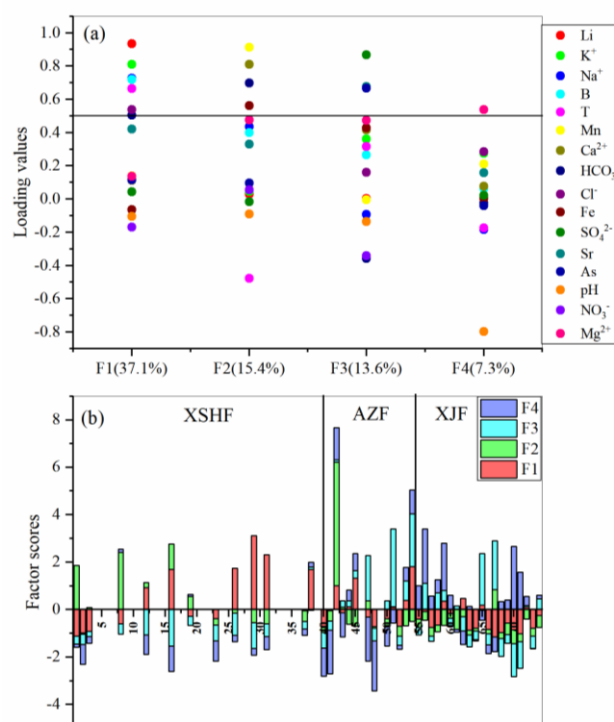


Figure 6. (a) Results of factor analysis of hydrochemical parameters; (b) distribution of factor scores of water samples in the XSHF-XJF.

5.3.1. Sources and controlling factors of trace elements in the XSHF

In the XSHF, the concentrations of trace elements (B, Li, Fe, and Mn) in the hot spring waters are generally higher (**Figure 2**). Multi-period granites are the main thermal reservoir in this area, and F1 also shows that silicate mineral dissolution influences the chemical compositions of hot springs. B concentrations in water samples range from 20.7 to 3943 µg/L, with the mean value of 1045.33 µg/L. B in thermal waters is usually controlled by leaching from the host rocks and the input of deep fluids owing to its soluble and incompatible nature[49]. B correlates positively with Na⁺($r=0.63$), K⁺($r=0.76$), and Cl⁻($r=0.64$) (**Figure 7**), indicating that their sources are similar. Previous studies indicate that felsic igneous rocks (granites and rhyolites) in the Tibetan Plateau usually have greater B contents than sedimentary and metamorphic rocks[50]. High concentrations of B

(>1mg/L) are found in the Kangding segment developed by Cenozoic granite and in water samples of Nos.1, 4, 12, 16, 19, and 20 exposed to Cretaceous and Tertiary granites in the northern part of the fault. Therefore, the dissolution of granites should be the important source of B in the hot springs. Also, B and Cl are conservative components of thermal waters, and their ratios are often used to determine a common reservoir[51]. In the **Figure 8**, the values of B/Cl ratio in the water samples in the southern parts of the XSHF (Kangding-moxi segment) are lower than that in the north, which reflect that the hot springs are controlled by two different heat sources. Based on previous studies, the Kangding hydrothermal system is likely to be influenced by magma on the hot springs, with a high concentration of Cl[52]. So, the contribution of deep-earth fluids to B in hot spring waters cannot negligible. Additionally, B in the hot spring waters correlate positively with HCO_3^- ($r=0.36$) (**Figure 7**), which may reveal the influence of deep water- CO_2 -rock reactions on concentrations of B. Since most water samples have pH values of below 8 (Table S1), it is likely that B is present as H_3BO_3 [53]. The experiments on the leaching of borate minerals demonstrate that when CO_2 concentration rises, the solubility of B in waters increases, producing H_3BO_3 [54]. So, the strong release of deep CO_2 gas may promote the enrichment of B in the hot springs.

Li concentrations range from 1.79 to 4547 $\mu\text{g/L}$, with the mean value of 1009.65 $\mu\text{g/L}$. Li belongs to alkali metals that tends to be more enriched in acidic rocks[55]. Li correlates positively with K^+ ($r=0.37$) and B ($r=0.70$) (**Figure 7**), indicating that they have the similar material sources. The Li concentrations of granite in the XSHF range from 10.70 to 48.00 ppm[50], which can provide abundant Li for the hot spring waters. So, hydrolysis of silicate minerals (lepidolite) may be the main source of Li.

The concentrations of Fe and Mn in the hot springs show large variability, ranging from 0.662 to 5569 $\mu\text{g/L}$, and 0.065 to 6424 $\mu\text{g/L}$, respectively. No.4 water sample contains the highest Fe concentration (5569 $\mu\text{g/L}$) and No.8 has the highest Mn concentrations(642 $\mu\text{g/L}$). High concentration of Fe in water samples may related to groundwater flowing through iron deposits in the Triassic strata in the area[56,57]. The water samples are supersaturated for goethite and hematite also support the high content of Fe in the hot springs. Mn correlates positively with Fe ($r=0.65$) (**Figure 7**), indicating that they may be concomitant. The concentrations of Sr range from 0.019 to 4016 $\mu\text{g/L}$. Sr correlates positively with Ca^{2+} ($r=0.47$), Mg^{2+} ($r=0.32$), HCO_3^- ($r=0.65$), and Na^+ ($r=0.40$) (**Figure 7**), suggesting that the dissolution of Sr-bearing minerals in granite and carbonate rocks may provide a large amount of Sr to the hot spring waters.

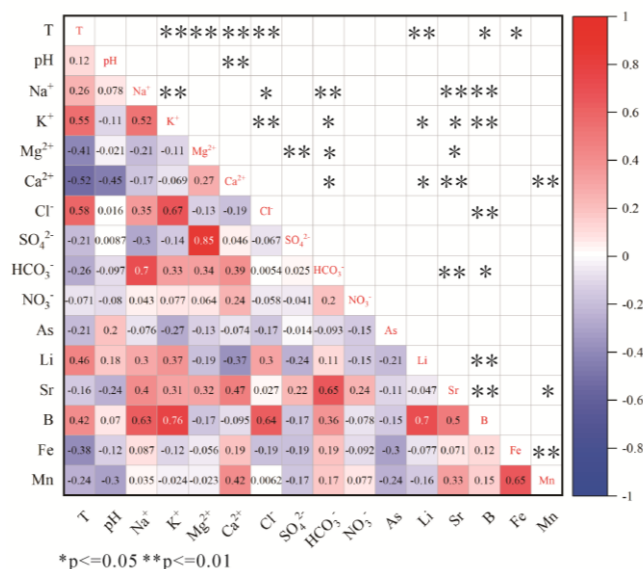


Figure 7. Pearson correlation diagram for trace elements and major ions in the XSHF.

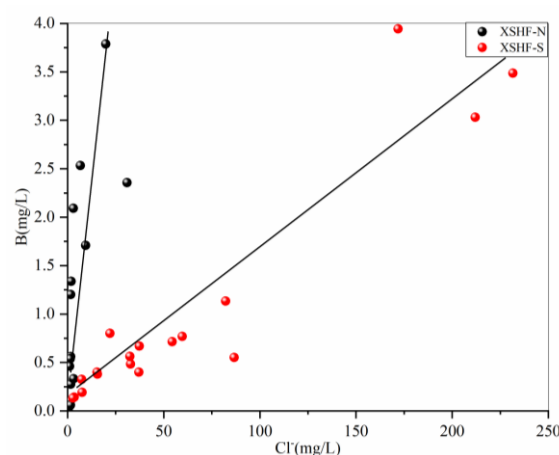


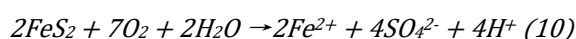
Figure 8. Plot of B vs. Cl in the hot spring waters in the XSHF.

5.3.2. Sources and controlling factors of trace elements in the AZF and XJF

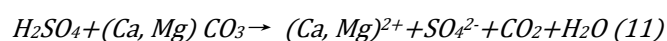
The concentrations of As and Sr in hot springs in the ANHF-XJF are **higher** (Figure 2). Sr is positively correlated with Ca^{2+} , Mg^{2+} , Na^{+} , and SO_4^{2-} in the AZF and XJF (Figure 9, 10). Sr can form sulfate and carbonate minerals, and also be integrated into carbonates, sulphates, and aluminum silicates to replace calcium, so it is more abundant in rocks with high calcium content[58]. The ZMHF is dominated by Cambrian and Ordovician dolomite and limestone, whereas the XJF is surrounded by carbonate rocks, limestone, and sandstone. Therefore, the concentrations of Sr in hot springs in the ANHF-XJF are much higher than that in the XSHF, which is caused by the former flowing through a large distribution of carbonate rocks.

As concentrations in water samples in the AZF and XJF range from 1.11 to 530 $\mu\text{g/L}$, 0.6 to 349 $\mu\text{g/L}$, respectively. As is significantly and positively correlated with Mg^{2+} ($r=0.55$), Ca^{2+} ($r=0.67$) in the AZF (Figure 9), and with K^{+} ($r=0.50$), Sr ($r=0.53$) in the XJF (Figure 10), suggesting that it also may originate from water-rock interactions. High concentrations of As are related to dissolution of pyrite and arsenopyrite in shale, siltstone, and interbedded Tertiary lignite. However, As is **not significant** with SO_4^{2-} in the AZF and not correlated with SO_4^{2-} in the XJF (Figure 9, 10), which indicates that sulfide minerals are not the major mediators of As migration in the hot spring waters. The hydrated iron oxide in the aquifer has a high As adsorption capability owing to its large specific surface area[7]. Goethite and hematite have a tendency to precipitate ($\text{SI}>0$), implying that large amounts of As can be adsorbed. As is significantly and positively correlated with Fe (Figure 9, 10), further illustrating that it may be sorbed to the surfaces of iron-bearing minerals. Therefore, As is most likely released by the reductive breakdown of iron oxides under the high temperature and alkaline environments.

The concentrations of Fe in hot springs range from 8.25 to 7867 $\mu\text{g/L}$, and 4.23 to 10520 $\mu\text{g/L}$, respectively. Fe is positively correlated with Mg^{2+} ($r=0.75$) and Ca^{2+} ($r=0.72$) in the AZF (Figure 9) and correlated with Ca^{2+} ($r=0.58$) and SO_4^{2-} ($r=0.54$) in the XJF (Figure 10), which is inferred to be derived from the dissolution of pyrite of the lignite (Equation 10)



Besides, because carbonates are present in the strata, the free sulfuric acid produced by the oxidation of pyrite will react with carbonates (Equation 11), which may also be a reason for the high concentration of Fe, SO_4^{2-} , Ca^{2+} , and Mg^{2+} in hot springs in the XJF.



The concentration ranges of B and Li in the AZF are 11.1–6366 $\mu\text{g/L}$, 6.49–2425 $\mu\text{g/L}$, respectively. The ionic components of hot springs were influenced by a combination of

silicates, carbonates, and evaporites in the AZF[19]. B correlate positively with K^+ ($r=0.75$), Mg^{2+} ($r=0.6$), Cl^- ($r=0.59$), and Li correlate positively with Na^+ ($r=0.74$), Ca^{2+} ($r=0.62$), HCO_3^- ($r=0.7$), SO_4^{2-} ($r=0.78$), Cl^- ($r=0.66$) (Figure 9). So, B and Li may be derived from water-rock interactions between thermal water and granite, dolomite, and other sedimentary rocks. In the XJF, B and Li concentrations range from 5.6 to 4262 $\mu g/L$, and 1.29 to 872 $\mu g/L$, respectively, and the dissolution of carbonate minerals has the greatest impact on the hot springs[18]. However, B and Li are weakly correlated with Ca^{2+} , Mg^{2+} and HCO_3^- , but are significantly positively correlated with Na^+ , K^+ and Cl^- in the water samples (Figure 10), suggesting that they are likely derived from the leaching of reservoir rocks in deep and magma contribution. Additionally, The B/Cl ratio of water samples of No.55 to No.60(mean value of 0.016) in the northern segment of the XJF is lower than that in the southern (mean value of 0.1), hinting that two different heat sources may exist. According to earlier research, a molten mass underneath the northern portion of the XJF. It has a significant concentration of Cl-containing magma vapor in addition to providing heat for the geothermal water[59]. Besides, F4 implies that human activities may also have an influence on the components of hot springs in the AZF-XJF.

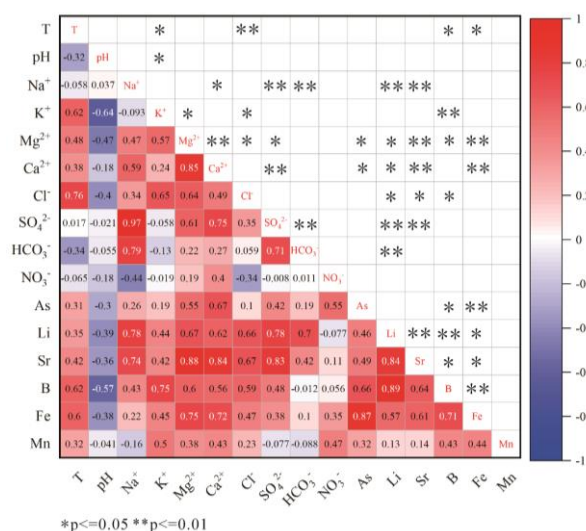


Figure 9. Pearson correlation diagram for trace elements and major ions in the AZF.

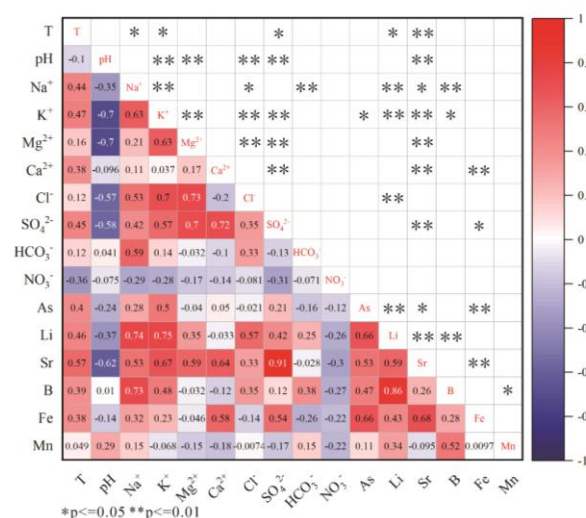


Figure 10. Pearson correlation diagram for trace elements and major ions in the XJF.

5.3.3. Influence of fault-controlled circulation depth on trace elements

The concentrations of trace element in geothermal waters are usually influenced by the circulation depth controlled by faults, resulting in a vertical distribution[60]. **Figure 11** illustrates the relationship between circulation depth and trace element concentration. B and Li concentrations increase with increasing circulation depth of hot spring waters. Sr concentrations show a positive trend with circulation depth in the XJF, while it has a negative trend with circulation depth in the XSHF. There are two structural thermal reservoirs in the XSHF, including granite in the deep and Permian carbonate in the shallow[25]. Therefore, with shallower circulation depth, the chemical composition is significantly influenced by carbonate rocks, and Sr concentrations are higher owing to the stronger affinity between Sr and Ca. As for the concentration of Fe, Mn, and As, they are not significantly controlled by the circulation depth, except in the XJF, which may be affected by dissolution and precipitation of minerals, redox processes, and adsorption and desorption[61]. The circulation depth of hot springs in the AZF is generally low, and the concentrations of trace element are highly variable because of the complex geological conditions in this area. As mentioned above, the circulation depth of hot springs can affect the trace element concentration, especially B and Li. Deep circulation of thermal waters would promote the upwelling of deep geothermal fluids and enhance water-rock interactions, which in turn affects their concentrations.

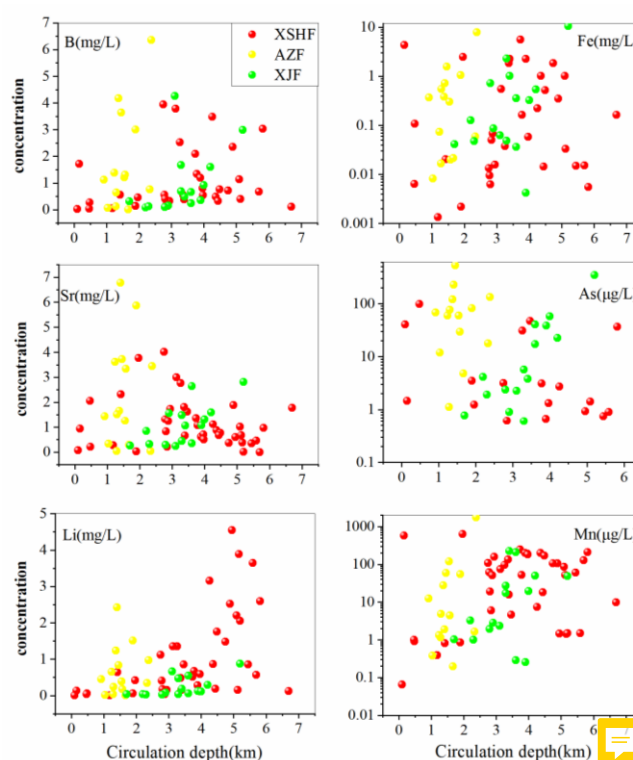


Figure 11. Scatter plot of circulation depth[18–20] vs. trace element concentration

5.4. Conceptual model of hot springs in the XSF-XJF

Deep and large fault zones and secondary fractures play an important role in the convective transfer of geothermal water, which can control the circulation path of geothermal water[62]. The emergence and circulation of hot springs in the study area are controlled by the XSHF-XJF and the secondary fractures (**Figure 12**). The values of δD and $\delta^{18}O$ show recharge by meteoric water, with recharge elevations of 1.8–4.8 km[18–20]. The deep heat source for geothermal water is related to the frictional heat generation from active faults, decay of radioactive elements, and high conductivity and low-velocity zones associated with partial melting of the upper crust[59]. Due to the constrain imposed by the lithology of thermal reservoir and the degree of water-rock interaction, the

composition of hot spring waters appears to be controlled by a specific geologic environment. In the XSHF, the hot springs are mainly influenced by deep granite and shallow carbonate rocks, with high circulation depth (mean value of 3.58km). High concentrations of B and Li mainly originate from leaching of granite and are controlled by circulation depth. Deep-earth fluids input may also contribute to them, especially in the Kangding area. Interaction with surrounding rocks containing Fe and Mn minerals at high temperatures during the upwelling of hot spring water, resulting in high concentrations of Fe and Mn. In the XJF, the surrounding rocks of the hot springs are mostly carbonates, limestone, and sedimentary rocks, and the circulation depth (mean value of 3.30km) is lower compared to XSHF. Sedimentary rocks and Tertiary lignite provide an important source of Fe and As in hot springs, and B may originate from deep thermal reservoir. Trace element concentrations are significantly controlled by circulation depth. The hot spring waters in the AZF has a much lower circulation depth (mean value of 1.44km), and the chemical composition of hot spring waters vary significantly owing to complex stratigraphic lithology.

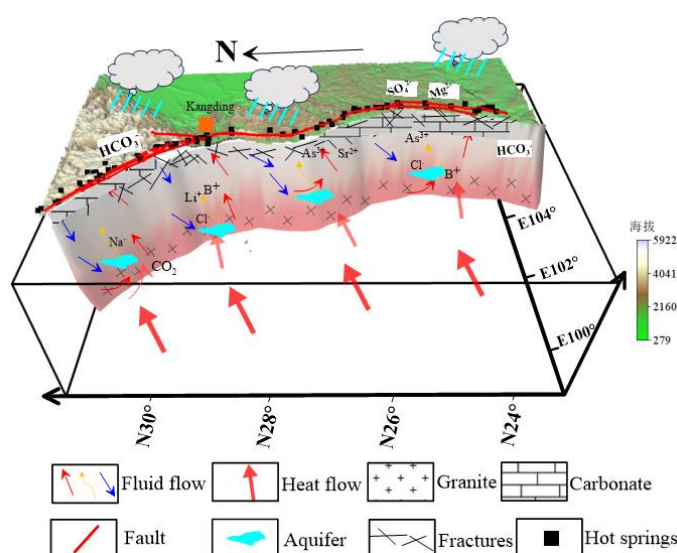


Figure 12. Conceptual model of hot spring water formation pattern in the XSHF-XJF.

6. Conclusions

In this study, the geochemical characteristics of trace elements in hot spring waters were investigated in the XSHF-XJF, and the conclusions were as follows:

- (1) The hot spring water was recharged by atmospheric precipitation, and the isotope compositions were more depleted in the XSHF owing to the elevation effect. Variations of dissolved compositions were mainly controlled by the dissolution of silicate minerals, carbonate minerals, and evaporites, as well as cation exchange.
- (2) The high concentrations of B, Fe, Mn, and As were found in the XSHF-XJF, which greatly exceeded the Chinese standards for drinking water. The values of WQI indicated that the water quality was spatially heterogeneous and the hot spring waters were not entirely suitable for drinking.
- (3) The leaching of the surrounding rock during water-rock interaction was the main source of trace elements, and the diversity of stratigraphic lithology was the main factor affecting their concentration in hot spring waters. High concentrations of B and Li were mainly derived from the dissolution of granite, and magmatic fluid contributions were

not neglected. The major cause of high As concentration is reductive breakdown of iron oxides. In addition, B/Cl ratios indicated that there were two different heat sources at the XSHF and XJF, respectively, and circulation depth can influence the trace element concentrations.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Table S1: Field and analytical data of major elements and stable isotopes (δD , $\delta^{18}O$) on water samples.; Table S2: Analytical data of trace elements on hot spring water sample; Table S3: The results of the water quality assessment using the measurements of trace elements.; Table S4: Saturation indices values of thermal water samples with respect to minerals.

Author Contributions: Conceptualization, Y.B. and Z.X.; methodology, Y.B.; software, Y.B.; validation, Z.Z., W.Y. and Y.Y.; formal analysis, X.G., C.S.; investigation, Z.X., L.Y.; resources, Q.D., Z.F.; data curation, H.M., T.J., D.J., and L.J.; writing—original draft preparation, Y.B.; writing—review and editing, Z.X.; visualization, Y.B.; supervision, Z.X., D.J.; funding acquisition, Z.X. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Martínez-Florentino, T.A.K.; Esteller-Alberich, M.V.; Expósito, J.L.; Domínguez-Mariani, E.; Morales-Arredondo, J.I. Hydrogeochemistry and geothermometry of thermal springs in the eastern Trans-Mexican Volcanic Belt. *Geothermics* **2021**, *96*, 102176. <https://doi.org/10.1016/j.geothermics.2021.102176>.
- Welch, A.H.; Westjohn, D.B.; Helsel, D.R.; Wanty, R.B. Arsenic in groundwater of the United States: Occurrence and geochemistry. *Groundwater* **2000**, *38*, 589–604. <https://doi.org/10.1111/j.1745-6584.2000.tb00251.x>.
- Cacciapuoti, S.; Luciano, M.A.; Megna, M.; Annunziata, M.C.; Napolitano, M.; Patruno, C.; Scala, E.; Colicchio, R.; Pagliuca, C.; Salvatore, P.; et al. The role of thermal water in chronic skin diseases management: A review of the literature. *J. Clin. Med.* **2020**, *9*, 3047. <https://doi.org/10.3390/jcm9093047>.
- Chandrajith, R.; Barth, J.A.C.; Subasinghe, N.D.; Merten, D.; Dissanayake, C.B. Geochemical and isotope characterization of geothermal spring waters in Sri Lanka: Evidence for steeper than expected geothermal gradients. *J. Hydrol.* **2013**, *476*, 360–369. <https://doi.org/10.1016/j.jhydrol.2012.11.004>.
- Wang, J.; Pang, Z.; Cheng, Y.; Huang, Y.; Jiang, G.; Lu, Z.; Kong, Y. Current state, utilization and prospective of global geothermal energy. *Science & Technology Review* **2023**, *41*, 5–11.
- Maity, J.P.; Chen, C., Y.; Bundschuh, J.; Bhattacharya, P.; Mukherjee, A.; Chang, Y., F. Hydrogeochemical reconnaissance of arsenic cycling and possible environmental risk in hydrothermal systems of Taiwan. *Groundw. Sustain. Dev.* **2017**, *5*, 1–13. <https://doi.org/10.1016/j.gsd.2017.03.001>.
- Okan, Ö.; Kalender, L.; Çetindag, B. Trace-element hydrogeochemistry of thermal waters of Karakocan (Elazığ) and Mazgirt (Tunceli), eastern Anatolia, Turkey. *J. Geochem Explor* **2018**, *194*, 29–43. <https://doi.org/10.1016/j.gexplo.2018.07.006>.
- Daniele, L.; Taucare, M.; Viguier, B.; Arancibia, G.; Aravena, D.; Roquer, T.; Sepúlveda, J.; Molina, E.; Delgado, A.; Muñoz, M.; et al. Exploring the shallow geothermal resources in the Chilean southern Volcanic Zone: Insight from the Liquine thermal springs. *J. Geochem Explor* **2020**, *218*, 106611. <https://doi.org/10.1016/j.gexplo.2020.106611>.

9. Liu, M.L.; Guo, Q.H.; Luo, L.; He, T. Environmental impacts of geothermal waters with extremely high boron concentrations: Insight from a case study in Tibet, China. *J. Volcanol. Geotherm. Res.* **2020**, *397*, 106887. <https://doi.org/10.1016/j.jvolgeores.2020.106887>. 509 510 511
10. Wang, M.M.; Zhou, X.; Liu, Y.; Xu, H.F.; Wu, Y.Q.; Zhuo, L.Y. Major, trace and rare earth elements geochemistry of geothermal waters from the Rehai high-temperature geothermal field in Tengchong of China. *Appl. Geochemistry* **2020**, *119*, 104639. <https://doi.org/10.1016/j.apgeochem.2020.104639>. 512 513 514
11. Bundschuh, J.; Maity, J.P. Geothermal arsenic: Occurrence, mobility and environmental implications. *Renew. Sust. Energ. Rev.* **2015**, *42*, 1214-1222. <https://doi.org/10.1016/j.rser.2014.10.092>. 515 516
12. He, P.; Zhang, H.; Li, S.; Zhou, X.; Zhou, X.; He, M.; Tian, J.; Zhang, Y.; Wu, Z.; Chen, T.; et al. Geological and hydrochemical controls on water chemistry and stable isotopes of hot springs in the three parallel rivers region, southeast Tibetan Plateau: The genesis of geothermal waters. *Sci. Total Environ.* **2023**, *906*, 167648-167648. <https://doi.org/10.1016/j.scitotenv.2023.167648>. 517 518 519
13. Mukherjee, I.; Singh, U.K. Fluoride abundance and their release mechanisms in groundwater along with associated human health risks in a geologically heterogeneous semi-arid region of east India. *Microchem. J.* **2020**, *152*, 104304. <https://doi.org/10.1016/j.microc.2019.104304>. 520 521 522
14. Sun, Y.T.; Zhou, X.C.; He, M.; Yan, Y.C.; Tian, J.; Li, J.C.; Dong, J.Y.; Zhang, Y. Geochemical characteristics and water quality assessment of trace elements in geothermal springs in the Gulu-Yadong rift, Tibetan Plateau. *Geothermics* **2023**, *111*, 102720. <https://doi.org/10.1016/j.geothermics.2023.102720>. 523 524 525
15. Allen, C.R.; Luo, Z.L.; Qian, H.; Wen, X.Z.; Zhou, H.W.; Huang, W.S. Field study of a highly active fault zone: The Xianshuihe fault of southwestern China. *Geol. Soc. Am. Bull.* **1991**, *103*, 1178-1199. [https://doi.org/10.1130/0016-7606\(1991\)103<1178:FSOAHA>2.3.CO;2](https://doi.org/10.1130/0016-7606(1991)103<1178:FSOAHA>2.3.CO;2). 526 527 528
16. Liu, W.; Guan, L.F.; Liu, Y.; Xie, X.A.; Zhang, M.L.; Chen, B.Y.; Xu, S.; Sano, Y. Fluid geochemistry and geothermal anomaly along the Yushu-Ganzi-Xianshuihe fault system, eastern Tibetan Plateau: Implications for regional seismic activity. *J. Hydrol.* **2022**, *607*, 127554. <https://doi.org/10.1016/j.jhydrol.2022.127554>. 529 530 531
17. Tapponnier, P.; Xu, Z.Q.; Roger, F.; Meyer, B.; Arnaud, N.; Wittlinger, G.; Yang, J.S. Geology-Oblique stepwise rise and growth of the Tibet platea. *Science* **2001**, *294*, 1671-1677. 532 533
18. Li, C.H.; Zhou, X.C.; Yan, Y.C.; Ouyang, S.P.; Liu, F.L. Hydrogeochemical characteristics of hot springs and their short-term seismic precursor anomalies along the Xiaojiang Fault Zone, southeast Tibet Plateau. *Water* **2021**, *13*, 2638. <https://doi.org/10.3390/w13192638>. 534 535 536
19. Tian, J.; Zhou, X.C.; Yan, Y.C.; He, M.; Li, J.C.; Dong, J.Y.; Liu, F.L.; Ouyang, S.P.; Li, Y.; Tian, L.; et al. Earthquake-induced impulsive release of water in the fractured aquifer system: Insights from the long-term hydrochemical monitoring of hot springs in the southeast Tibetan Plateau. *Appl. Geochemistry* **2023**, *148*, 105553. <https://doi.org/10.1016/j.apgeochem.2022.105553>. 537 538 539 540
20. Yan, Y.C.; Zhou, X.C.; Liao, L.X.; Tian, J.; Li, Y.; Shi, Z.M.; Liu, F.L.; Ouyang, S.P. Hydrogeochemical characteristic of geothermal water and precursory anomalies along the Xianshuihe Fault Zone, southwestern China. *Water* **2022**, *14*, 550. <https://doi.org/10.3390/w14040550>. 541 542 543
21. Liu, W.; Zhang, M.L.; Chen, B.Y.; Liu, Y.; Cao, C.H.; Xu, W.; Zheng, G.D.; Zhou, X.C.; Lang, Y.C.; Sano, Y.; et al. Hydrothermal He and CO₂ degassing from a Y-shaped active fault system in eastern Tibetan Plateau with implications for seismogenic processes. *J. Hydrol.* **2023**, *620*, 129482. <https://doi.org/10.1016/j.jhydrol.2023.129482>. 544 545 546
22. Cheng, Y.Z.; Pang, Z.H.; Kong, Y.L.; Chen, X.B.; Wang, G.J. Imaging the heat source of the Kangding high-temperature geothermal system on the Xianshuihe fault by magnetotelluric survey. *Geothermics* **2022**, *102*, 102386. <https://doi.org/10.1016/j.geothermics.2022.102386>. 547 548 549

23. Du, J.G.; Cheng, W.Z.; Zhang, Y.L.; Jie, C.L.; Guan, Z.J.; Liu, W.; Bai, L.P. Helium and carbon isotopic compositions of thermal springs in the earthquake zone of Sichuan, southwestern China. *J Asian Earth Sci* **2006**, *26*, 533-539. <https://doi.org/10.1016/j.jseaes.2004.11.006>.
24. Liang, J.L.; Yu, Y.; Shi, Z.M.; Li, Z.P.; Huang, Y.; Song, H.; Xu, J.Y.; Wang, X.Y.; Zhou, X.C.; Huang, L.Y.; et al. Geothermal springs with high $\delta^{13}\text{C}_{\text{CO}_2\text{-DIC}}$ along the Xianshuihe fault, western Sichuan, China: A geochemical signature of enhanced deep tectonic activity. *J. Hydrol.* **2023**, *623*, 129760. <https://doi.org/10.1016/j.jhydrol.2023.129760>.
25. Zhang, Y.H.; Xu, M.; Li, X.; Qi, J.H.; Zhang, Q.; Guo, J.; Yu, L.L.; Zhao, R. Hydrochemical characteristics and multivariate statistical analysis of natural water system: A case study in Kangding county, southwestern China. *Water* **2018**, *10*, 80. <https://doi.org/10.3390/w10010080>.
26. Li, X.; Huang, X.; Liao, X.; Zhang, Y.H. Hydrogeochemical characteristics and conceptual model of the geothermal waters in the Xianshuihe Fault Zone, southwestern China. *Int. J. Environ. Res. Public Health* **2020**, *17*, 500. <https://doi.org/10.3390/ijerph17020500>.
27. Liu, Z.H.; Yuan, D.X.; He, S.Y.; Zhang, M.L.; Zhang, J.G. Geochemical features of the geothermal CO_2 -water-carbonate rock system and analysis on its CO_2 sources-Examples from Huanglong Ravine and Kangding, Sichuan, and Xiage, Zhongdian, Yunnan. *Sci. China Earth Sci.* **2000**, *43*, 569-576.
28. Sun, Y.T.; Zhou, X.C.; Yan, Y.C.; Li, J.C.; Fang, W.Y.; Wang, W.L.; Liu, Y.M. Soil degassing from the Xianshuihe-Xiaojiang Fault system at the eastern boundary of the Chuan-Dian rhombic block, southwest China. *Front. Earth Sci.* **2021**, *9*, 635178. <https://doi.org/10.3389/feart.2021.635178>.
29. Wang, Y.; Zhao, C., P.; Liu, F.; Cheng, K., H.; Ran, H. Research on relationship between geochemical characteristics of thermal springs and seismic activities in the Xiaojiang Fault Zone and its adjacent areas. *Journal of Seismological Research* **2014**, *37*, 228-243+323(In Chinese with English abstract).
30. Chen, Z.; Zhou, X.; Du, J.; Xie, C.; Liu, L.; Li, Y.; Yi, L.; Liu, H.; Cui, Y. Hydrochemical characteristics of hot spring waters in the Kangding district related to the Lushan $M=7.0$ earthquake in Sichuan, China. *Nat. Hazards Earth Syst. Sci.* **2015**, *15*, 1149-1156. <https://doi.org/10.5194/nhess-15-1149-2015>.
31. Zhang, Y., H.; Zhang, L., S.; Chang, Y.; Fan, Z., W.; Guo, D., F. Determination trace elements in rock samples containing refractory minerals by pressurization-microwave inductively coupled plasma mass spectrometry. *Uranium Geology* **2018**, *34*, 105-111(In Chinese with English abstract).
32. Liu, H., B.; Jing, G., S.; Li, J., J.; Han, J.; Zhang, J., F.; Zhang, J.; Zhong, F., W.; Guo, D., Q. Determination of stable isotope composition in uranium geological samples. *World Nuclear Geoscience* **2013**, *30*, 174-179(In Chinese with English abstract).
33. Qu, B.; Zhang, Y.; Kang, S.; Sillanpää, M. Water quality in the Tibetan Plateau: Major ions and trace elements in rivers of the "Water Tower of Asia". *Sci. Total Environ.* **2019**, *649*, 571-581. <https://doi.org/10.1016/j.scitotenv.2018.08.316>.
34. Ma, Y., Q; Shi, Y.; Qin, Y., W; Zheng, B., H; Zhao, Y., M; Zhang, L. Temporal-spatial distribution and pollution assessment of heavy metals in the upper reaches of Hunhe River (Qingyuan section), northeast China. *Environ. Sci.* **2014**, *35*, 108-116.
35. Huang, X.; Sillanpää, M.; Duo, B.; Gjessing, E.T. Water quality in the Tibetan Plateau: Metal contents of four selected rivers. *Environ. Pollut.* **2008**, *156*, 270-277. <https://doi.org/10.1016/j.envpol.2008.02.014>.
36. Qu, B.; Zhang, Y.L.; Kang, S.C.; Sillanpää, M. Water quality in the Tibetan Plateau: Major ions and trace elements in rivers of the "Water Tower of Asia". *Sci. Total Environ.* **2019**, *649*, 571-581. <https://doi.org/10.1016/j.scitotenv.2018.08.316>.
37. Guo, Q.; Planer-Friedrich, B.; Liu, M.; Li, J.; Zhou, C.; Wang, Y. Arsenic and thioarsenic species in the hot springs of the Rehai magmatic geothermal system, Tengchong volcanic region, China. *Chem. Geol.* **2017**, *453*, 12-20. <https://doi.org/10.1016/j.chemgeo.2017.02.010>.
38. Yuan, J.; Guo, Q.; Wang, Y. Geochemical behaviors of boron and its isotopes in aqueous environment of the Yangbajing and Yangyi geothermal fields, Tibet, China. *J Geochem Explor* **2014**, *140*, 11-22. <https://doi.org/10.1016/j.gexplo.2014.01.006>.

39. Bénard, B.; Famin, V.; Agrinier, P.; Aunay, B.; Lebeau, G.; Sanjuan, B.; Vimeux, F.; Bardoux, G.; Dezayes, C. Origin and fate of hydrothermal fluids at Piton des Neiges volcano (Réunion Island): A geochemical and isotopic (O, H, C, Sr, Li, Cl) study of thermal springs. *J. Volcanol. Geotherm. Res.* **2020**, *392*, 106682. <https://doi.org/10.1016/j.jvolgeores.2019.106682>.
40. Craig, H. Isotopic variations in meteoric waters. *Science* **1961**, *133*, 1702-1703. DOI: 10.1126/science.133.3465.1702.
41. Kong, Y.L.; Wang, K.; Li, J.; Pang, Z.H. Stable isotopes of precipitation in China: A consideration of moisture sources. *Water* **2019**, *11*, 1239. <https://doi.org/10.3390/w11061239>.
42. Xu, Q.; Hoke, G.D.; Jing, L.Z.; Ding, L.; Wang, W.; Yang, Y. Stable isotopes of surface water across the Longmenshan margin of the eastern Tibetan Plateau. *Geochemistry, Geophys. Geosystems* **2014**, *15*, 3416-3429. <https://doi.org/10.1002/2014GC005252>.
43. Pang, Z.; Kong, Y.; Li, J.; Tian, J. An isotopic geoinicator in the hydrological cycle. *Procedia Earth and Planetary Science* **2017**, *17*, 534-537. <https://doi.org/10.1016/j.proeps.2016.12.135>.
44. Zhang, L.; Guo, L.; S.; liu, S.; W.; Yang, Y.; Shi, D., Y. Characteristics of hydrogen and oxygen stable isotopes of hot springs in Xianshuihe-Anninghe fault zone, Sichuan, Province, China. *Acta Petrol.* **2021**, *37*, 589-598.
45. Cui, Y., J.; Sun, F.X.; Du, J., G. Methods for identification of seismic geochemical precursors and source partitioning of hot spring fluids in eastern Chinese Mainland. *Journal of Seismological Research* **2022**, *45*, 199-216(In Chinese with English abstract).
46. Cui, Y.J.; Sun, F.X.; Liu, L.; Xie, C.; Li, J.; Chen, Z.; Li, Y.; Du, J.G. Contribution of deep-earth fluids to the geothermal system: A case study in the Arxan volcanic region, northeastern China. *Front. Earth Sci.* **2023**, *10*, 996583. <https://doi.org/10.3389/feart.2022.996583>.
47. Zhu, X.Q.; Liu, L.; Lan, F.N.; Li, J.; Hou, S.T. Hydrogeochemistry characteristics of groundwater in the Nandong Karst water system, China. *Atmosphere* **2022**, *13*, 604. <https://doi.org/10.3390/atmos13040604>.
48. Davraz, A.; Nalbantçilar, M.T.; Önden, I. Hydrogeochemical characteristics and trace element of geothermal systems in central Anatolia, Turkey. *J African Earth Sci* **2022**, *195*, 104666. <https://doi.org/10.1016/j.jafrearsci.2022.104666>.
49. Liu, M.; Guo, Q.; Wu, G.; Guo, W.; She, W.; Yan, W. Boron geochemistry of the geothermal waters from two typical hydrothermal systems in southern Tibet (China): Daggyai and Quzhuomu. *Geothermics* **2019**, *82*, 190-202. <https://doi.org/10.1016/j.geothermics.2019.06.009>.
50. Lai, S.C.; Qin, J.F.; Long, X.P.; Li, Y.F.; Ju, Y.J.; Zhu, R.Z.; Zhao, S.W.; Zhang, Z.Z.; Zhu, Y.; Wang, J.B. Neoproterozoic gabbro-granite association from the Micangshan area, northern Yangtze Block: Implication for crustal growth in an active continental margin. *Geol. J.* **2018**, *53*, 2471-2486. <https://doi.org/10.1002/gj.3082>.
51. Tassi, F.; Aguilera, F.; Darrah, T.; Vaselli, O.; Capaccioni, B.; Poreda, R.J.; Huertas, A.D. Fluid geochemistry of hydrothermal systems in the Arica-Parinacota, Tarapaca and Antofagasta regions (northern Chile). *J. Volcanol. Geotherm. Res.* **2010**, *192*, 1-15. <https://doi.org/10.1016/j.jvolgeores.2010.02.006>.
52. Li, J.; Yang, G.; Sagoe, G.; Li, Y. Major hydrogeochemical processes controlling the composition of geothermal waters in the Kangding geothermal field, western Sichuan Province. *Geothermics* **2018**, *75*, 154-163. <https://doi.org/10.1016/j.geothermics.2018.04.008>.
53. Bernard, R.; Taran, Y.; Pennisi, M.; Tello, E.; Ramirez, A. Chloride and boron behavior in fluids of Los Humeros geothermal field (Mexico): A model based on the existence of deep acid brine. *Appl. Geochemistry* **2011**, *26*, 2064-2073. <https://doi.org/10.1016/j.apgeochem.2011.07.004>.
54. Erdogan, Y.; Aksu, M.; Demirbas, A.; Abali, Y. Analyses of boronic ores and sludges and solubilities of boron minerals in CO₂-saturated water. *Resour Conserv Recycl* **1998**, *24*, 275-283. [https://doi.org/10.1016/S0921-3449\(98\)00045-7](https://doi.org/10.1016/S0921-3449(98)00045-7).
55. Li, J.; Wang, X.; Ruan, C.; Sagoe, G.; Li, J. Enrichment mechanisms of lithium for the geothermal springs in the southern Tibet, China. *J. Hydrol.* **2022**, *612*, 128022. <https://doi.org/10.1016/j.jhydrol.2022.128022>.

56. Zhang, Z.; Hou, T.; Santosh, M.; Li, H.; Li, J.; Zhang, Z.; Song, X.; Wang, M. Spatio-temporal distribution and tectonic settings of the major iron deposits in China: An overview. *Ore Geol. Rev.* **2014**, *57*, 247–263. <https://doi.org/10.1016/j.oregeorev.2013.08.021>.
57. Xie, Y.; Li, Y.; Hou, Z.; Cooke, D.R.; Danyushevsky, L.; Dominy, S.C.; Shuping, Y. A model for carbonatite hosted REE mineralisation — the Mianning–Dechang REE belt, Western Sichuan Province, China. *Ore Geol. Rev.* **2015**, *70*, 595–612. <https://doi.org/10.1016/j.oregeorev.2014.10.027>.
58. Kaasalainen, H.; Stefánsson, A. The chemistry of trace elements in surface geothermal waters and steam, Iceland. *Chem. Geol.* **2012**, *330*, 60–85. <https://doi.org/10.1016/j.chemgeo.2012.08.019>.
59. Bai, D.H.; Unsworth, M.J.; Meju, M.A.; Ma, X.B.; Teng, J.W.; Kong, X.R.; Sun, Y.; Sun, J.; Wang, L.F.; Jiang, C.S.; et al. Crustal deformation of the eastern Tibetan plateau revealed by magnetotelluric imaging. *Nat. Geosci.* **2010**, *3*, 358–362. <https://doi.org/10.1038/ngeo830>.
60. Zhang, H., X.; Zhang, W.; Wang, G., L.; Zhao, J., Y.; Yue, G., F. Distribution and genetic mechanism of high arsenic geothermal water in the Batang area, Western Sichuan. *Geothermics* **2021**, *97*, 102232. <https://doi.org/10.1016/j.geothermics.2021.102232>.
61. Negri, A.; Daniele, L.; Aravena, D.; Muñoz, M.; Delgado, A.; Morata, D. Decoding fjord water contribution and geochemical processes in the Aysen thermal springs (Southern Patagonia, Chile). *J. Geochem. Explor.* **2018**, *185*, 1–13. <https://doi.org/10.1016/j.gexplo.2017.10.026>.
62. Wu, Y.; Zhou, X.; Zhuo, L.; Tao, G.; Ma, J.; Wang, Y. Structural controls of the northern Red River Fault Zone on the intensity of hydrothermal activity and distribution of hot springs in the Yunnan–Tibet geothermal belt. *Geothermics* **2023**, *109*, 102641. <https://doi.org/10.1016/j.geothermics.2022.102641>.