



Article Reservoirs and Hydrogeochemical Characterizations of the Yanggao Geothermal Field in Shanxi Province, China

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Abstract: Geothermal water is the product of deep circulation within the crust, and the understanding of its hydrogeochemical process can provide effective information for integrated research on its circulation pattern and formation mechanism. Based on the geothermal geological conditions of the Yanggao geothermal field, this study analyzed water samples from thermal springs and geothermal wells in the geothermal field, ascertaining their hydrochemical components, along with their hydrogen and oxygen isotopes. Using methods like piper diagrams, ionic component ratio characterization, Na-K-Mg equilibrium diagrams, and reverse path simulations, this study elucidated the recharge source of geothermal water in the study area, revealed the water-rock interactions the geothermal water experienced, and evaluated the geothermal reservoir temperatures. The results show that the geothermal water has hydrochemical types of Na-Cl-HCO₃ and Na-HCO₃-Cl, and is primarily recharged by the atmospheric precipitation in the northern mountainous area. The geothermal water has experienced extended water runoff and deep thermal circulation, and its hydrochemical composition primarily results from the weathering and dissolution of silicate rocks and evaporites. The major hydrogeochemical processes of the geothermal water involve the dissolution of calcite, dolomite, gypsum, and kaolinite. In addition, the canon-exchange also changes the chemical component of the geothermal water. The SiO₂ Geothermometer, a multimineral equilibrium diagram, and the silica-enthalpy model reveal the presence of deep and shallow geothermal reservoirs in the study area, which exhibit temperatures of 73 °C and ranging from 125 to 150 °C, respectively. The open geothermal reservoir environment results in the mixing of geothermal water and cold water, with shallow and deep geothermal water mixing with cold water at ratios of 57% and 76%, respectively.

Keywords: geothermal water; hydrochemistry; water–rock interaction; hydrogen and oxygen isotopes; reservoir temperature; evaporite minerals

1. Introduction

Geothermal resources, as renewable and clean energy sources within the Earth, are characterized by low carbon emissions, great exploitation and utilization potential, and wide applications [1,2]. With the increasingly prominent global energy crisis, there is an urgent need for the exploitation and utilization of renewable, clean energy to replace or reduce the use of conventional energy [3,4]. Since geological settings play a vital role in the exploitation of geothermal energy, it is especially essential to understand the formation mechanism of geothermal energy for its sustainable and effective exploitation [5,6]. As a product of deep circulation within the Earth's crust, geothermal water reflects abundant hydrogeochemical information, which provides valuable insights into the comprehensive research on the circulation pattern and formation mechanism of deep geothermal water. The commonly employed methods for geothermal water include hydrogeochemical and



Citation: Yan, X.; Wei, S.; Zhang, W.; Liu, F.; Liao, Y. Reservoirs and Hydrogeochemical Characterizations of the Yanggao Geothermal Field in Shanxi Province, China. *Water* **2024**, *16*, 669. https://doi.org/10.3390/ w16050669

Academic Editors: Elias Dimitriou and Juan José Durán

Received: 30 November 2023 Revised: 21 February 2024 Accepted: 21 February 2024 Published: 24 February 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). isotopic methods [7,8]. Hydrogeochemical methods focus on identifying the evolutionary process of geothermal water, while isotopic methods are primarily employed to determine the source and the storage and transport duration of geothermal water [9,10].

The study area lies in the northwestern part of Shanxi Province, China. Tectonically, it is located in the northwestern part of the Yanggao–Tianzhen fault [11]. With abundant geothermal resources, the study area is an important research focus for moderate- to low-temperature geothermal resources [12–15]. The geothermal resources produced in this area exhibit temperatures of 28–45 °C, indicating moderate- to low-temperature geothermal resources, which are primarily used for thermal spring bathing. Previous studies mainly focused on the formation background and the structural and hydrochemical characteristics of the Yanggao geothermal field, while rarely involving the interrelationships among these aspects [16–18].

Controlled by unique geological conditions, the surface geothermal manifestation and genetic mechanisms of geothermal systems show specific characteristics. Geothermal systems can be divided into convective hydrothermal systems and conduction hydrothermal systems, according to the movement conditions and heat source mechanism. In convective hydrothermal systems, hot water flows up along the high-permeability zone formed by the intersection of tectonic faults and emerges as hot springs. In conductive hydrothermal systems, the heat source is simply vertical heat conduction through the Earth's crust [4].

Shanxi Province, situated in the Loess Plateau in the western portion of Northern China, boasts abundant geothermal resources with a relatively concentrated spatial distribution. These geothermal resources primarily occur in the Fen-Wei rift zone [19] and are "Low medium temperature geothermal systems of conduction type", serving as a major target in the research on low- to moderate-temperature geothermal resources. The Yanggao geothermal field, located in the Datong Basin, northern Shanxi Province, has produced geothermal resources with temperatures ranging from 28 to 45 °C. These resources are Neogene and Quaternary low-temperature geothermal resources, and are primarily used for bathing. Based on the analysis of geological conditions, seismic activity, volcanic activity, terrestrial heat flow, and thermal springs, as well as geophysical exploration, it is proposed that the Datong Basin enjoys favorable geological conditions for geothermal resources and exhibits significant research value [18,20]. As regards the Yanggao geothermal field, its geological, structural, and cap rock distribution characteristics have been identified through geophysical exploration [19], and the hydrochemical characteristics and other general properties of its geothermal water have been analyzed [16,17]. However, limited studies have been conducted on the hydrogeochemical characteristics of geothermal water in the study area, along with their formation and evolution. Furthermore, there is a lack of unified understanding of the occurrence environment, migration patterns, and genetic mechanism of geothermal fluids. All these hinder the rational and effective exploitation and utilization of geothermal resources.

Based on water samples from the Yanggao geothermal field, this study has qualitatively analyzed the mineral sources and water–rock interactions of the geothermal water during its circulation. In addition, it has quantitatively analyzed the mineral transfer of the geothermal water, providing a theoretical basis for further investigating the formation mechanism of the Yanggao geothermal field. This study will assist in the exploration and exploitation of geothermal resources in the study area and in gaining a deep understanding of the origin of geothermal resources in North China.

2. Geological Background

The Datong Basin is located in the central portion of the North China Craton, at the intersection of the central zone of the North China Block and the Inner Mongolia suture zone. It is a Cenozoic faulted basin [21] that has undergone multi-stage tectonic movements since the Late Mesozoic, subjected to local lithospheric modification and thinning. The Yanggao geothermal field resides in the Yanggao–Tianzhen basin, a sub-basin in the northeastern Datong Basin. The entire sub-basin extends in the NEE direction. The structures in the

sub-basin are dominated by faults, followed by folds, with a dominant tectonic direction of NE. The Yanggao geothermal field, the study area, is located in the northeastern part of the Cathaysian Block. The geothermal field lies in the Yanggao–Tianzhen Basin in northern Shanxi Province. It is a secondary basin in the northern Datong Basin, distributed in a NEE direction [12–15,19].

The NE-trending Yunmen piedmont fault, also known as the Yanggao fracture zone, which is composed of several parallel high-angle normal faults, is the primary fault in the study area. Controlling the Yanggao geothermal field, this fault is a transpressive fault extending for about 35 km within Shanxi Province [12]. This fault serves as a boundary between a rift basin and the bedrock, with large-area Cenozoic strata extending to the south and the exposed bedrock of the Archaean Sanggan Group occurring to the north. Owing to fracturing, the fault zone commonly exhibits kaolinization and limonitization [22]. According to field observations, the Quaternary sediments in the study area, dominated by alluvial sediments, include sandy gravel layers consisting of sandy loam soil, clay loam, and clayey soil, with thicknesses ranging from 40 to 98 m. The Tertiary sediments are dominated by mudstones and limestones, with thicknesses ranging from 50 to 535 m and multiple reticulate gypsum layers interbedded. The Archean Sanggan Group, dominated by plagioclase gneisses, shows moderately to thickly laminated textures and contains minerals dominated by plagioclase, biotite, and quartz. The study area has experienced intense magmatic activity, with relatively developed magmatic rocks dominated by Archean diabase dykes and Yanshanian quartz porphyries, followed by pre-Sinian metamorphic granites and a few pyroxene dykes.

The Datong Volcanic Group, which formed during the Quaternary and is situated 35 km southwest of the study area, is derived from the upwelling of molten materials in the upper mantle. Non-erupting magma migrated to the northeast along tectonic fissures, providing a heat source for the geothermal water in Yanggao County.

Thermal springs are primarily located in the vicinity of the Yunmen piedmont fault, indicating that this fault plays a significant role in the formation of the Yanggao geothermal zone [18]. A thermal spring is exposed in the study area, showcasing a geothermal water temperature of 39.5 °C and a flow rate of 8 m³/h. The geothermal wells exhibit depths between 106 and 600 m, with wellhead water temperatures ranging from 28.7 to 37.2 °C and single-well water yields between 30 and 60 m³/h, suggesting low- to moderate-temperature geothermal resources. Besides this, there is no correlation between the well depth and temperature.

3. Sampling and Methods

This study conducted a sampling campaign in 2022, with 15 sets of water samples collected, including five sets from geothermal wells, one set of thermal spring water, five sets of shallow groundwater, two sets of spring water, and one set of rainwater (Table 1). Additionally, three sets from geothermal wells collected in a previous study were obtained. Figure 1 and Table 1 depict the sampling locations and the hydrochemical characteristics of the water samples, respectively.

Physicochemical parameters of water, including temperature, pH, and total dissolved solids (TDS) content, were measured in the field using a handheld instrument (HQ40D, manufactured by Hach in Loveland, CO, USA). This device was calibrated using a standard solution prior to use.

All the samples were filtered through 0.45 μ m membranes and stored in high-density polyethylene bottles rinsed with groundwater. For SiO₂ analyses, the water samples were diluted to 10% of their initial concentrations using deionized water. For metallic and cation element analyses, samples were acidified using HNO₃ until the pH was 1. As a result, the rate of biological or chemical reactions was reduced. Inorganic anions in the samples were analyzed before adding reagents. All samples were stored at 4 °C and tested within two weeks.

Wator Tupo	Sampla	DU	Ca ²⁺	Mg ²⁺	K+	Na ⁺	Cl+	SO4 ²⁻	HCO ₃ -	NO ₃ -	\mathbf{F}^{-}	Hydrochemical
water Type	Sample	PH	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	Туре
Thermal spring water	WQ01	8.21	13.43	2.25	11.82	177.9	145.7	103.9	135.2	4.1	5.17	Na-Cl-HCO ₃
	DR02	8.36	13.3	2.28	5.48	109.5	75.28	63.62	129	1.79	3.79	Na-Cl-HCO ₃
	DR01	8.87	6.49	0.62	4.38	79.17	39.92	34.02	98.31	2.47	4.4	Na-HCO ₃
Geothermal well water	DR03	8.18	17.5	1.25	5.23	111	69.7	67	155	0.53	2.87	Na-HCO ₃ -Cl
wen water	DR04	8.37	14.4	1.87	4.29	112	69.7	70.9	133	0.56	2.87	Na-HCO ₃ -Cl
	DR05	8.29	25.4	6.06	8.16	81.2	57.4	70	145	4.02	1.1	Na-HCO ₃ -Cl
	GW01	8.06	71.62	19.58	2.87	16	26.61	47.33	221.2	38.07	0.29	Ca–Mg–HCO ₃
	GW02	7.37	31.82	26.19	1.19	15.87	8.05	22.5	209.5	18.18	0.64	Ca–Mg–HCO ₃
Well water	GW03	7.85	41.14	31.98	1.91	47.11	30.81	34.03	288.8	28.64	0.97	Ca–Mg–HCO ₃
	GW04	7.88	38.49	29.81	2.02	47.41	26.61	32.94	279.6	26.01	1.11	Na–Ca–HCO ₃
	GW05	7.83	53.1	20.88	2.7	98.98	51.12	53.17	374.2	2.14	1.36	Na–Ca–HCO ₃
Contine a susation	Q01	7.52	72.48	24.71	3.48	12.58	5.95	97.62	240.3	13.82	0.3	Ca–HCO ₃
Spring water	Q02	8.47	25.45	54.7	2.88	16.46	5.6	75.34	271.6	5.31	0.47	Ca–HCO ₃
Rain water	YS01	7.15	20.1	1.97	2.54	1.56	4.2	23.96	30.72	14.56	0.55	Ca-HCO ₃

Table 1. Geochemical compositions of water samples from the Yanggao geothermal field.



Figure 1. Tectonic sketch map of the Cathaysian Block and geological map of the Yanggao geothermal field [16,19].

The sample tests were conducted following the guidelines of the Methods for Examination of Drinking Natural Mineral Water [23] and Groundwater Test Methods [24] at the Key Laboratory of Groundwater Sciences and Engineering of the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences. The cations and trace elements in the samples were detected using ICP-AES (ICAP6300) and ICP-MS (7500C, manufactured by Agilent in Santa Clara, CA, USA). Anions and HCO₃⁻ in the samples were detected through ion chromatography (DX120) and alkalinity titration, respectively. The charge balance error was less than 3%. The hydrogen and oxygen isotopes in the samples were measured using the MAT 253 stable isotope ratio mass spectrometer(manufactured by Beijing Aotao Science & Technology Co., Ltd., Beijing, China) with analytical precisions of $\pm 0.1\%$ and $\pm 1\%$, respectively, for δ^{18} O and δ^{2} H.

4. Results and Discussion

4.1. Hydrochemical Characteristics

Water samples from geothermal wells exhibited temperatures of 28.7–40 °C, TDS contents of 282–486 mg/L, and pH levels of 8.18–8.87, indicating weakly alkaline–alkaline water; thermal spring water samples had a temperature of 39.5 °C, TDS contents of 580 mg/L, and pH levels of 8.21, indicating weakly alkaline water; shallow groundwater samples had temperatures of 10.3–15 °C and pH levels of 7.37–8.06; spring water samples showed pH levels of 7.52–8.47 and TDS contents of 358–480 mg/L.

As shown in Figure 2, compared to geothermal water samples, the geothermal water samples showed significantly higher Na⁺, Cl⁻, and F⁻ contents but lower Mg²⁺, Ca²⁺, SO₄²⁻, and HCO₃⁻ contents. As revealed by the Piper diagram (Figure 3), the geothermal water samples primarily fall within the lower right zone, with cations dominated by Na and K⁺ and anions primarily consisting of Cl⁻. Furthermore, the cold water samples (including samples of well water, spring water, and rainwater) mainly fall within the left zone, with ions dominated by Ca²⁺, Mg²⁺, and HCO₃⁻. As indicated by the composition of primary elements, the geothermal water samples primarily showed hydrochemical types of Na–Cl–HCO₃ and Na–HCO₃–Cl, while the cold water samples exhibited a hydrochemical type of Ca–HCO₃.



Figure 2. Schoeller-Berkaloff diagram of water samples from the Yanggao geothermal field.



Figure 3. Piper diagrams of water samples from the Yanggao geothermal field.

The results show that the geothermal water samples had significantly lower Ca²⁺ contents than the cold water samples. This is mainly due to the low solubility of Ca²⁺ and the strong exchange and adsorption of cations in geothermal water. Additionally, the geothermal water samples had significantly higher Na⁺ and Cl⁻ contents than the cold water samples, indicating that the geothermal water underwent relatively adequate leaching during migration.

Although trace elements do not determine the type of groundwater, they can provide insights into the water–rock interactions and sources of groundwater. The dissolved silica content was 27.46–51.85 mg/L in the geothermal water samples and 6.66–18.45 mg/L in the water samples from wells and springs. The F^- content was 1.1–5.17 mg/L in the geothermal water samples and 0.29–1.11 mg/L in the samples from wells and springs. The Li⁺ content was 0.05–0.16 mg/L in geothermal water samples and 0.006–0.008 mg/L in the water samples from wells and springs. The Sr^{2+} content was 0.08–0.69 mg/L in the geothermal water samples and 0.43–0.67 mg/L in the water samples from wells and springs. The cold water samples yielded extremely low contents of trace elements. Hydrothermal activity and water–rock interactions jointly enhanced the reactions between geothermal water and the surrounding rocks of reservoirs, thus enriching trace elements [25]. The low Sr^{2+} content in geothermal water may be related to the lithology (metamorphic rocks with few strontium-bearing minerals) of geothermal reservoirs in the study area [26].

Gibbs charts can help to intuitively and qualitatively determine the sources and origins of hydrochemical components [27–29]. Samples falling within the lower right, upper right, and middle zones of the Gibbs chart imply that the sources of hydrochemical components were primarily regional precipitation, evaporation and concentration, and water–rock interactions. In this study, both geothermal and cold water samples fell within the zone controlled by water–rock interactions, indicating that the hydrochemical components were derived mainly from water–rock interactions (Figure 4).

The hydrochemical parameters of groundwater can reflect its sealing degree and metamorphism (Table 2). The $\gamma(Na^+)/\gamma(Cl^-)$ ratio is commonly used to determine the origin of groundwater. A $\gamma(Na^+)/\gamma(Cl^-)$ ratio of close to or greater than 1 suggests a leaching origin, while a $\gamma(Na^+)/\gamma(Cl^-)$ ratio less than 0.86 indicates a sedimentary origin [30–32]. In this study, all samples had $\gamma(Na^+)/\gamma(Cl^-)$ ratios of greater than 1, which were 1.88–3.06, 2.3–2.98, and 3.26–4.54 for the geothermal water samples, the water samples from pumping and domestic wells, and spring water samples, respectively. These ratios suggest a dominant leaching origin. Besides halite, other Na⁺ sources, such as the dissolution of sodium minerals including albite (NaAlSi₃O₈), and reverse cation exchange and adsorption, also affect geothermal areas.

The desulfurization coefficient, $\gamma SO_4^{2-} \times 100/\gamma Cl^-$, can reveal the oxidizing-reducing conditions of deep geothermal water, and then determine the sealing performance of the geothermal reservoir environment [33]. Generally, the $\gamma SO_4^{2-} \times 100/\gamma Cl^-$ value is inversely proportional to the sealing degree of the geothermal fluid environment. In this study, the $\gamma SO_4^{2-} \times 100/\gamma Cl^-$ values of the geothermal water samples, water samples from wells, and spring water samples were 25.8–44.2, 37.7–64.4, and 487–594, respectively, indicating an open geothermal water environment.

The calcium–magnesium coefficient, $\gamma Ca^{2+}/\gamma Mg^{2+}$, can reflect the metamorphic degree of deep geothermal fluids. Generally, this coefficient correlates positively with the retention time of the geothermal fluids. A longer geothermal fluid retention time corresponds to a higher metamorphic degree, and thus, a higher $\gamma Ca^{2+}/\gamma Mg^{2+}$ ratio [34]. This study shows that the geothermal water samples and cold water samples exhibited $\gamma Ca^{2+}/\gamma Mg^{2+}$ ratios of less than 3 or greater than 3, respectively. These results suggest that the geothermal water exists in a reducing geothermal reservoir environment, and is characterized by a long retention time and intense cation exchange and adsorption.



Figure 4. Gibbs diagrams of groundwater in the Yanggao geothermal field. (a) $Na^+/(Na^+ + Ca^{2+})$ vs. TDS; (b) $Cl^-/(Cl^- + HCO_3^-)$ vs. TDS content.

Water Type	Sample	$\gamma Na^+/\gamma Cl^-$	$\gamma SO_4{}^{2-} \times 100/\gamma Cl^-$	$\gamma Ca^{2+}/\gamma Mg^{2+}$
Thermal water	WQ01	1.88	25.83	3.58
	DR02	2.25	30.61	3.5
-	DR01	3.06	30.87	6.28
Geothermal well water	YG1	2.46	34.82	8.4
-	YG2	2.48	36.85	4.62
-	YG6	2.18	44.18	3.5 6.28 8.4 4.62 2.51 2.19 0.77 0.77 1.53 1.76
	GW01	0.93	64.43	2.19
-	GW03	2.36	40.01	0.77
Well water	GW04	2.75	44.84	0.77
-	GW05	2.99	37.68	1.53
Spring water	Q01	3.26	594.33	1.76
Spring water -	Q02	4.54	487.35	0.28
Rain water	YS	0.57	206.65	6.12

Table 2. $\gamma Na/\gamma Cl^-$, $rSO_4^{2-} \times 100/rCl$, and rCa^{2+}/rMg^{2+} ratios of water samples from the Yanggao geothermal field.

The Ca²⁺/Na⁺, Mg²⁺/Na⁺, and HCO₃⁻/Na⁺ ratios are commonly used to investigate water–rock interactions (Figure 5), reflecting the source relationships of different materials involved in groundwater processes such as migration, evaporation, and concentration [35,36]. The geothermal water in the study area is primarily controlled by the



weathering and dissolution of silicate rocks and evaporite rocks, while the cold water is mainly influenced by the weathering and dissolution of silicate rocks and carbonate rocks.

Figure 5. Relationships of Ca^{2+}/Na^+ vs. HCO_3^-/Na^+ and Ca^{2+}/Na^+ vs. Mg^{2+}/Na^+ in the Yanggao geothermal field.

Evaporite rocks are a type of precipitate formed by the evaporation of saline water. The significant correlation (r = 0.96) between Na⁺ and Cl⁻ indicates the dissolution of evaporate minerals, such as halite. Thus, a high concentration of Na⁺ in geothermal water in the studied area might be the result of the dissolution of evaporite rocks, and evaporative rocks are mainly composed of halites [37–39].

Chloro-alkaline indices 1 and 2 (i.e., CAI-1 and CAI-2) can be employed to assess the role of cation exchange and adsorption [40,41]. They are calculated as follows:

$$CAI1 = \frac{CI^{-} - (Na^{+} + K^{+})}{CI^{-} - (Na^{+} + K^{+})}$$

$$CAI2 = \frac{CI^{-} - (Na^{+} + K^{+})}{HCO_{3}^{-} + SO_{4}^{2} - + CO_{3}^{2} - + NO_{3}^{-}}$$
(1)

Negative CAI-1 and CAI-2 values indicate positive cation exchange and absorption in groundwater, whereas positive values reflect reverse cation exchange and absorption. Most of the water samples from the study area fell within the lower left zone of Figure 6, indicating that positive cation exchange and adsorption predominate hydrochemical reactions. This finding implies that the Ca²⁺ and Mg²⁺ dissolved in water were replaced by the Na⁺ and K⁺ in surrounding rocks, increasing the Na⁺ and K⁺ contents in water. Furthermore, Ca²⁺ and Mg²⁺ were adsorbed on the surfaces of water-bearing medium particles, decreasing their contents and concentrations in water. This result suggests that Ca²⁺ and Mg²⁺ at the sampling sites exchanged with Na⁺ and K⁺ in surrounding rocks during the runoff process, releasing Na⁺ and K⁺ in plagioclase and potassium feldspar minerals into the water.

4.2. Geothermometer-Based Temperature Estimates

In research on the origin mechanism and potential evaluation of geothermal resources, geothermal reservoir temperature is a crucial parameter for classifying the genetic mechanism of geothermal systems and for assessing the geothermal resource potential [42–46]. One of the most cost-effective and efficient methods used to determine this parameter is chemical geothermometers. The most widely used geothermal geothermometers consist of two types: SiO₂ geothermometers (quartz and chalcedony geothermometers) and cation geothermometers (Na–K, K–Mg, and Na–K–Ca geothermometers).



Figure 6. Plot of CAI1 vs. CAI2 in the Yanggao geothermal field.

4.2.1. Geothermometer Selection

A cation geothermometer estimates the temperatures of deep geothermal reservoirs based on the relationship between the soluble chemical composition of groundwater and the temperature of geothermal water. Its theoretical basis lies in the fact that deep geothermal reservoirs and surrounding rock minerals reach chemical equilibrium under certain temperature conditions. Therefore, it is necessary to ascertain the equilibrium state of geothermal water and surrounding rocks and test the reliability of the selected geothermometers before estimating the temperatures of deep geothermal reservoirs using geothermometers. This study employed a Na–K–Mg ternary diagram [45], which incorporates Na/K and K^2/Mg geothermometers, to determine the equilibrium condition of samples. Cation geothermometers are not applicable to samples that are not in equilibrium (or at least partially in equilibrium). The Na-K-Mg ternary diagram allows for a more intuitive comparison of the calculated results obtained using Na-K and K²-Mg geothermometers. In the Na-K-Mg ternary diagram, the K-Mg and Na-K oblique lines represent the temperatures obtained using K^2 –Mg and Na–K geothermometers, respectively. This diagram can be used to estimate the maximum geothermal reservoir temperature. The hot water points located in the partially equilibrated water zone exhibited overall high K^2 -Mg geothermometerderived temperatures between 100 and 120 °C, which were much higher than the Na-K geothermometer-derived temperatures, between 160 and 180 °C. When projecting the Na^+ , K^+ , and Mg^{2+} contents in the geothermal water samples into the Na-K-Mg ternary diagram, all the geothermal water samples fell within the immature water zone (Figure 7). This indicates the possible participation of meteoric water. Therefore, the temperatures of geothermal reservoirs in the study area estimated by cation geothermometers would be subjected to deviations, which can be used as reference for this study [47].

4.2.2. SiO₂ Geothermometers

SiO₂ geothermometers can predict reservoir temperatures based on the dissolution balance of SiO₂ in geothermal water. The solubility of silica minerals is a function of temperature, and the changes in pressure and salinity slightly affect the solubility of quartz and amorphous silicon below 300 °C. Therefore, the silica concentration in geothermal water can be used as a geothermometer to calculate the temperatures of geothermal reservoirs [48].

Various silica minerals arise in nature, with quartz, chalcedony, and amorphous silica frequently involved in geothermal research (Table 3). According to the log (SiO₂) vs. log (K^2/Mg) chart, these silica minerals can help identify the minerals controlling the mass concentration of SiO₂ in geothermal fluids [49].



Figure 7. Na-K-Mg ternary diagram for thermal water samples from Yanggao geothermal field [45].

Geothermometer	Empirical Formula
Quartz (conduction cooling)	T = [1309/(5.19 - lgS)] - 273
Chalcedony	T = [1032/(4.69 - lgS)] - 273

Table 3. Formulae of geothermometers for geothermal reservoir temperature.

According to the calculation results of SiO₂ geothermometers, the temperatures estimated using a quartz geothermometer in the Yanggao geothermal field were 73–97 °C, which are 47–68 °C higher than the wellhead temperatures. In contrast, temperatures estimated using a chalcedony geothermometer were 53–65 °C, which are 13–36 °C higher than the wellhead temperatures.

As shown in Figure 8, data points of geothermal water were distributed between the lines of quartz and chalcedony, indicating that both quartz and chalcedony species occurred in geothermal water. The reservoir temperatures indicated by the plot of log (SiO_2) versus log (K^2/Mg) data for geothermal water and thermal water were mainly distributed in the range of 70–100 °C, which overlaps with the temperature calculated by quartz geothermometers. Hence, the measurement of quartz geothermometers may provide more reliable results than other silica geothermometers [50].

Above, *T* is the reservoir temperature acquired using a chalcedony geothermometer (°C) and *S* is the silica (SiO₂) (mg/kg).

4.2.3. Multimineral Equilibrium Diagram

To enhance the calculation accuracy of geothermal reservoir temperatures, this study estimated the heat exchange equilibrium temperatures of non-fully equilibrated water using the multimineral equilibrium method [51]. This study simulated the saturation indices [log(Q/K)] of 10 common hydrothermal minerals under different temperatures using the PHREEQC 3.6.2 software, establishing the relationships between the log(Q/K) and temperature of multiple minerals [52,53]. As revealed by the curves of these relationships, geothermal water in the study area reached equilibrium with minerals in surrounding rocks including quartz, chalcedony, calcite, plagioclase, fluorite, kaolinite, and dolomite, exhibiting high convergence. These curves also show that the geothermal reservoirs in the Yanggao geothermal field have temperatures of 80–90 °C(Figure 9), which are slightly higher than the calculated results yielded by SiO₂ geothermometers, and might be related to the mixing of cold water.



Figure 8. Plot of log (SiO₂) vs. log (K^2/Mg). The lines indicate the temperature dependence of the variables for silica minerals [49].



Figure 9. SI vs. temperature diagrams of minerals in geothermal waters from typical geothermal reservoirs in the Yanggao geothermal field.

4.2.4. Mixing Fraction of Shallow Groundwater

According to the above analysis, the geothermal water in the study area may be affected by the mixing of cold water. The silica–enthalpy model can be employed to estimate the fraction of mixed cold water, and to correct the estimation reservoir temperature [54,55].

The equations used are presented below:

$$S_{c}x + S_{h}(1 - x) = S_{s}$$
 (2)

$$\operatorname{SiO}_{2c} x + \operatorname{SiO}_{2h}(1 - x) = \operatorname{SiO}_{2s}$$
(3)

where S_c is the enthalpy of the shallow groundwater, S_h is the initial enthalpy of geothermal water, S_s is the final enthalpy of geothermal water mixed with shallow groundwater, SiO_{2c} is the SiO_2 concentration of the shallow groundwater, SiO_{2h} is the initial SiO_2 concentration of geothermal water, SiO_{2s} is the final SiO_2 concentration of geothermal water mixed with shallow groundwater, and x is the fraction of mixed shallow groundwater.

In Equations (2) and (3), only the fraction of shallow groundwater mixture and the fraction of initial enthalpy of the deep geothermal water are unknown. The diagrammatic method can be used to simplify the calculation procedure. According to Equations (2) and (3), the solutions of the shallow groundwater mixing fraction X can be obtained as follows [56]:

$$X_1 = (S_h - S_s) / (S_h - S_c)$$
(4)

$$X_{2} = (SiO_{2h} - SiO_{2s}) / (SiO_{2h} - SiO_{2c})$$
(5)

where X_1 and X_2 are the two solutions of the mixture fraction of groundwater to deep geothermal water. The point of intersection shows the initial temperature of the reservoir and the mixed fraction of groundwater.

The shallow groundwater had a temperature of 20 °C and a SiO₂ concentration of 7 mg/L, according to the measurements of the cold water samples from the study area. Each of the enthalpies and SiO₂ concentrations corresponding to the various temperatures in Table 4 were substituted into Equations (4) and (5) to produce the mixing proportion of groundwater and to plot the diagram in Figure 10. The intersection points are the solutions of Equations (4) and (5), showing the reservoir temperature and groundwater mixing faction of corresponding geothermal water.

Temperature (°C)	Pressure (Bars)	Enthalpy (cal/g)	SiO ₂ Content (mg/L)
50	0.12	50	13.5
75	0.39	75	26.6
100	1.01	100.1	48
125	2.32	125.4	80
150	4.76	151	125
175	8.92	177	185
200	15.54	203.6	265
225	25.48	230.9	365
250	39.73	259.2	486

Table 4. Enthalpies of liquid water and the corresponding quartz solubility.

As shown in Figure 10, two temperature ranges can be obtained using the silicon– enthalpy model. The curves of the plot of thermal spring water-dissolved silica and enthalpy intersect at the point with a groundwater mixing ratio of 57% and a temperature of 73 °C, indicating the temperature of the shallow reservoir. The curves of other plots of geothermal water-dissolved silica and enthalpy intersect at points with a cold water mixing ratio of 76% and a temperature of 125–150 °C, indicating the temperature of the deep reservoir.

As presented in Table 5, the reservoir temperatures of the geothermal water calculated using the multimineral equilibrium model and silica–enthalpy model differ from each other. The multimineral equilibrium model did not consider that groundwater could mix during the rise of geothermal water. The estimated temperature corresponds to the new equilibrium after groundwater mixing. On the contrary, the silica–enthalpy model removed the effect of groundwater mixing, yielding a more reasonable temperature for the deep reservoir. The results show that the shallow heat storage temperature was 73 °C and the deep heat storage temperature was 125–175 °C.

Table 5. Calculated geothermal reservoir temperatures of the geothermal field in the study area (T in $^{\circ}$ C).

	T _{gw}	T _Q	T _C	T _{Mul}	T _{S-E}
WQ-01	39.5	73.79	53.36	85	80
DR-02	40	87.52	68.49	98	120

Table 5. Cont.

	T _{gw}	T _Q	T _C	T _{Mul}	T _{S-E}
DR-01	38.4	91.26	73.21	72	135
YG1	28.7	95.02	78.42	90	175
YG2	30	92.54	74.91	79	172
YG6	34	89.56	71.01	82	145

Note(s): T_{gw} denotes the temperature of geothermal water from wells. T_Q denotes the temperature determined by a Quartz geothermometer. T_C denotes the temperature determined by a Chalcedony geothermometer. T_{Mul} denotes the temperature estimated according to the solubility equilibrium of the mineral–geothermal water system. T_{S-E} denotes the reservoir temperature determined using the silica–enthalpy model.



Figure 10. Dissolved silica-enthalpy graphs for the Yanggao geothermal water.

4.3. Recharge Sources of Geothermal Water

Table 1 shows the analytical results of stable isotopes. The geothermal water samples yielded δ^2 H and δ^{18} O values of -10.6--9.5% and -82--74%, respectively. As shown in the δ^2 H vs. δ^{18} O plot (Figure 11), all the geothermal and cold water samples fell along the meteoric water line (δ^2 H = 5.938 δ^{18} O - 17.14) [46], indicating that all kinds of water in the study area originate from meteoric water [46].



Figure 11. $\delta^2 H vs. \delta^{18} O$ of water samples from the Yanggao geothermal field.

The effect of elevation on δ^{18} O can be used to evaluate the recharge elevation of groundwater according to the following equation:

$$H = (\delta G w - \delta P w) / K + E w$$
(6)

where *H* is the elevation of a geothermal water recharge area (m); Ew is the elevation of a geothermal water sampling site (m); δ Gw is the δ^{18} O (or δ^{2} H) value of the geothermal water (‰); δ Pw is the δ^{18} O (or δ^{2} H) value of the meteoric water near the sampling site (‰); K is the gradient of the δ^{18} O (or δ^{2} H) value of meteoric water, varying with the elevation. Based on the relationships between the elevation and the stable hydrogen and oxygen isotopes in meteoric water, this study determined the K value of δ^{18} O as -0.26% /100 m. The δ^{2} H and δ^{18} O values of river samples were -54.31% and -6.39%, respectively [57]. Based on regional geographical characteristics, the recharge elevations in the Yanggao geothermal field were about 1129–1156 m (Table 6), and the recharge meteoric water might originate from the Beishan Mountain, which is 5 km to the north.

Table 6. δ^2 H and $\delta 1^8$ O values of water samples from the Yanggao geothermal field.

Water Type	Sample	δ ² H _{VSMOW} (‰)	δ ¹⁸ Ο _{VSMOW} (‰)	Elevation (m a.s.l.)	Recharge Elevation (m a.s.l.)
Thermal water	WQ-01	-81	-10.4	1069	1134
	DR-02	-82	-11	1069	1136
	DR-01	-86	-11.7	1087	1157
Geothermal well water	YG1	-80	-10.4	1065	1130
	YG2	-82	-10.6	1064	1129
	YG6	-74	-9.5	1083	1144

4.4. Water-Rock Interactions

The PHREEQC software is effective in building a water–rock interaction model. Using this software, this study established a model that could be used to invert the geochemical characteristics of geothermal water in the study area [58–60]. For this model, rainwater was taken as the starting point, while a thermal spring and the deepest geothermal well (WQ01 and DR01) acted as the starting and ending parts, respectively.

Potential mineral phases were determined based on the above analysis results of water-rock interactions and the stratum lithologies in the study area. The Quaternary strata in the study area primarily include sandy gravel layers consisting of sandy loam soil and clayey soil. The Tertiary strata are dominated by mudstones and limestones, interbedded with multiple reticulate gypsum layers. Their primary minerals include halite, gypsum, mica, calcite, and dolomite. The primary minerals of plagioclase gneiss include albite, potassium feldspar, biotite, chalcedony, and quartz, accompanied by kaolinite due to varying degrees of alterations. Hence, the rocks in the study area are dominated by albite, potassium feldspar, calcite, chalcedony, dolomite, muscovite, gypsum, halite, and kaolinite, all of which participated in the simulated reaction. Based on the rock mineral composition and geothermal conditions in the study area, the optimal solution was selected from the PHREEQC simulation results (Table 7). As the recharge water migrated and transitioned into geothermal water, its hydrochemical composition changed due to the precipitation of minerals such as calcite, dolomite, gypsum, and kaolinite, and the dissolution of albitite, potassium feldspar, chalcedony, halite, and muscovite. Meanwhile, cation exchange occurred, with Na⁺ from the solution replacing the Ca²⁺ in surrounding rocks.

Table 7. Inversed hydrogeochemical simulation results.

	Albite	Calcite	Chalcedony	Dolomite	Gypsum	K-Feldspar	Halite	Kaolinite	Muscovite
WQ01	$4.05 imes 10^{-3}$	$-2.23 imes10^{-3}$	$8.02 imes 10^2$	-5.74×10^{-4}	-9.69×10^{-4}	$-4.01 imes10^2$	$3.14 imes 10^{-3}$	$-4.01 imes10^2$	$4.01 imes 10^2$
DR01	$2.56 imes10^{-3}$	$-1.01 imes10^{-3}$	$4.09 imes 10^2$	$-3.54 imes10^{-4}$	$-8.15 imes10^{-4}$	$-2.05 imes10^2$	$5.71 imes 10^{-4}$	$-2.05 imes10^2$	$2.05 imes 10^2$

4.5. Conceptual Model

The interpretation of the hydrochemical information and stable isotope data from the geothermal water can yield (1) the reservoir temperature and the hydrogeochemical characteristics of the geothermal and cold water in the study area; (2) recharge areas and circulation depth; (3) water–rock interactions along the path of geothermal water runoff, as reversely simulated using PHREEQC.

Based on the above results, this study built a conceptual model of the origin of the Yanggao geothermal field to account for the formation mechanism of geothermal water in the study area (Figure 12). According to this model, the geothermal water in the study area was formed as follows: (1) The meteoric water infiltrated deep underground along the piedmont fault in the northern mountainous area. (2) Then, the meteoric water migrated through bedrock fractures and was heated under the background of high terrestrial heat flow as it moved from the recharge area to the discharge area in the central basin. Meanwhile, the hydrochemical composition of the water changed due to the weathering and dissolution of silicate rocks and evaporates. (3) Finally, under the influence of the highpressure hydraulic head, the underground hot water upwelled along the high-permeability pathways at the intersection of the dominant faults of new structures in the uplift area of the metamorphic basement. Consequently, the hot water was exposed in the Quaternary fissured geothermal reservoirs. The continuous mixing of the hot water with cold water during the upwelling of the former led to moderate- to low-temperature geothermal water resources (28–45 °C) being formed. During the migration, heating, and recharge of meteoric water, water-rock interactions led to the precipitation of calcite, dolomite, gypsum, and kaolinite, and the dissolution of albite, potassium feldspar, chalcedony, halite, and mus-



covite, thus changing the hydrochemical composition of the recharge water. In addition, cation exchange occurred, increasing the Na^+ concentration in the geothermal water.

Figure 12. Conceptual genetic geothermal system model of the study area [18,19].

5. Conclusions

Based on the hydrochemical characteristics, the test results of stable isotopes, and the geological setting, this study investigated the hydrogeochemical evolution mechanism of the Yanggao geothermal system through H and O isotope analysis, hydrochemical analysis, and inverse modeling. The findings allow to the following conclusions:

(1) The geothermal water in the Yanggao geothermal field has temperatures of 28.7–40 °C and TDS contents of 282–580 mg/L. It is mainly of the Na–Cl–HCO₃ or Na–HCO₃–Cl type, suggesting lightly alkaline to alkaline water. Furthermore, it has δD and $\delta^{18}O$ values from -82% to -74% and from -10.6% to -9.5%, respectively;

(2) The combination of suitable classical geothermometers and geothermal simulation calculations proves to be an effective means of evaluating the temperature of geothermal reservoirs. The geothermal water in the study area has not reached equilibrium due to the mixing of cold water in a relatively open environment. A SiO₂-chalcedony geothermometer and a multimineral equilibrium diagram indicate the existence of deep and shallow reservoirs in the study area. The shallow reservoirs exhibit a temperature of 73 °C, with a cold water mixing ratio of approximately 57%. The deep reservoirs display temperatures ranging from 125 to 150 °C, with a cold water mixing ratio of approximately 76%;

(3) As indicated by the hydrochemical composition analysis, the hydrochemical composition of geothermal water in the Yanggao area primarily results from the weathering and dissolution of silicate rocks and evaporites, accompanied by reverse cation exchange and adsorption. This study evaluated the origin of major ions in the geothermal water through inverse modeling using PHREEQC. The major hydrogeochemical processes in the geothermal water involve the dissolution of calcite, dolomite, gypsum, and kaolinite, and weak cation exchange, which together change the hydrochemical composition of the groundwater;

(4) The isotopic compositions (δD and $\delta^{18}O$) suggest that the geothermal water in the study area originates from meteoric water recharge at elevations ranging from 1129 to

1144 m. The meteoric water recharge might originate from the Beishan Mountain, which is about 5 km to the north.

Author Contributions: Conceptualization, X.Y.; Methodology, X.Y. and W.Z.; Investigation, X.Y., S.W., F.L. and Y.L.; Data curation, S.W.; Writing—original draft, X.Y.; Writing—review & editing, X.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by geothermal survey projects of the China Geological Survey grant numbers DD2021676, DD20221676-1, DD20190128, the Foundational Research Fund of the Chinese Academy of Geological Sciences, grant number sk202212, and the Shanxi Geoscience Think Tank Development Fund, grant number 2023-001.

Data Availability Statement: All data analyzed in this study are available from the corresponding authors upon reasonable request.

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

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