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5
6 **Abstract:** To evaluate ion origins and fluid behavior, the chemical properties of
7 thermal water sampled from the Eocene reservoir in the Yitong Basin (YB), Northeast
8 China, were investigated. The thermal water samples are classified as Na-HCO₃-type
9 water and were fully equilibrated, except for Sijixiangkang (SJXK) and Yitong (YT).
10 The cations originate mainly from water-rock interactions (e.g. albitization and
11 weathering of plagioclase), while the anions originate from magmatic volatiles and
12 leaching of limestone and granite, which were heated by hot magmatic volatiles and
13 exhibited an evaporation-like pattern in the Gibbs's diagrams. The existence of
14 magmatic volatiles was verified by the high ion ratio, the minor element origins, $\delta^{13}\text{C}$
15 values of HCO₃, and $\delta^{34}\text{S}$ of SO₄ values, which flowed upward along lithospheric
16 faults, with higher fluxes in the northeast than in the southwest (the $\delta^{13}\text{C}$ value of the
17 Chaluhe depression (CD) is 0.93‰ lower than that of the Moliqing depression (MD
18 1.63‰)). Furthermore, according to the Br/Cl and HCO₃⁻/Cl ratios and the $\delta^{13}\text{C}$
19 values, we speculate that a deep Permian limestone reservoir exists below the granitic
20 unit. Based on the ion origins and fluid potentials, we conclude that the CD and MD
21 are open systems rather than closed systems. The recharged water migrates from the
22 margin to the center in the plane, and in the vertical direction, it migrates from the

23 Yongji (E_2y) and Sheling (E_2sh) strata to the overlying strata and underlying
24 Shuangyang (E_2s) strata along faults. By summarizing all of the available data, we
25 proposed a conceptual model of fluid migration.

26 **Keywords:** Thermal waters; Geochemical properties; Water-rock interaction;
27 Fluid potential; Yitong Basin

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1 Introduction

High-temperature formation waters, a type of geothermal water, can be derived from Holocene meteoric water, from “old” meteoric water, or from mixing with other types of water, such as connate water of marine origin (Chen et al., 2014; Kharaka and Hanor, 2004). Thermal waters of different origins have different ion characteristics, and later circulation can also alter the chemical properties due to water-rock interactions. These processes can lead to thermal waters that have high concentrations of certain elements, which may be beneficial or harmful to human health (Ellis and Mahon, 1967; Freeze and Cherry, 1979; Wang et al., 2016; White, 1957a, b). Therefore, research on the origin and controlling factors of the chemical components in thermal water is critical for thermal water exploration and/or future geothermal resource utilization.

The Chaluhe depression (CD) and the Moliqing depression (MD), which are located in the northeast and southwest of the Yitong Basin (YB), respectively, have a low exploration potential in terms of oil (Zhou et al., 2010), but they have become an exploration zone for thermal springs (formation water). Previous studies on the formation water in the CD and MD areas are scarce, and published data are reported only in summary form and have mainly been used for hydrocarbon estimation purposes (Jia et al., 2008; Hou et al., 2009). The first study of the geothermal activity, performed in 2010 (Li, 2010), focused on the CD area. In that study, the characteristics of the Eocene sandstone reservoir, geothermal reservoir temperatures and water type were studied in detail, and an analysis of the δD , $\delta^{18}O$ and tritium

values of thermal water demonstrated that the Eocene reservoir to be a closed environment. More recently, Liu (Liu et al., 2014) analyzed the characteristics of the burial conditions and the geothermal field characteristics of Shengdequan in the CD and concluded that the fluid existed in a closed environment. However, according to the ion combination coefficients, such as $\gamma(\text{Na})/\gamma(\text{Cl})$, the preservation ability of the Eocene reservoir from the interior to the northeastern slope of the CD gradually decreased (Jia et al., 2008). In this study, a detail geochemical investigation was conducted on the thermal water in the CD and MD of the YB. Through analysis of the ion and stable isotopic characteristics of the thermal waters, this study aimed to (i) investigate the origin of chemical component in thermal waters and (ii) investigate the fluid behavior.

[Figure 1 near here]

2 Geology of the Yitong Basin

2.1 Geological setting

The CD and MD are part of a secondary structural belt in the YB on the northern margin of the North China Plate (Fig. 1). The YB is located in the Jiamusi-Yitong faulted area in the western part of the northern Tanlu Fault Zone which formed due the subduction of the Pacific Plate after the arc area of the Eurasian Plate (Zhou et al., 1993; Hou et al., 2009). The northwestern and southeastern boundaries of the basin correspond to lithospheric faults that are part of the Yishu Fault Zone; the southwestern and northeastern boundaries correspond to the Dongliaohe fault and the secondary Songhuajiang fault, respectively (Fig. 1). Since the Cenozoic period, the

subduction of the Pacific Plate leading to basin-bounding lithospheric activity has continued, providing access to magma upwelling. K-Ar and Ar-Ar dated four magma eruption stages, with distribution along the basin-bounding fault in the YB (Hou et al., 2009): the late Cretaceous (82-57 Ma); Eocene-Miocene (40.5-21 Ma); Miocene (13.9-8.7 Ma); and Pliocene-Pleistocene (4.3-1.2 Ma). Following the main stage of the subduction of the Pacific Plate beneath the Eurasian Plate, the formation of the YB began in response to Cretaceous rifting, which can be divided into three stages: the initial rift stage (Jurassic-Cretaceous), the rift stage (Eocene-Oligocene), and the basin inversion stage (Ren et al., 1999; Zhou et al., 1993).

The Cenozoic basin-fill successions of the CD and MD consist of alluvial fans, braided river deltas, lacustrine and fluvial deposits that mainly formed during the rift stage (Ren et al., 1999). The reservoir formed during the Eocene period and consists of the units E_{2s} , E_{2sh} and E_{2w} , which are composed of muddy siltstones intercalated with siltstones and shales (Fig. 1). The basement of the YB comprises Yanshanian and Variscan granite with many NE-trending normal faults (Hou et al., 2009). This granite mainly consists of quartz (50.1%), plagioclase (approximately 25.7%) and potassium feldspar (approximately 16.6%) (Wang et al., 2015). Before the Cenozoic era, the YB formed on the northern margin of the North China Plate, which existed as a marine sedimentary environment prior to the Triassic period; a limestone formation may exist below the basin, similar to the one identified in 2015 in the well Chang-27 in the Xianpu Depression, which is also located in the middle of the YB (Wang et al., 2015). therefore, we speculate that limestone may underlie the entire YB (Fig. 1).

2.2 Hydrogeology

The collision between the Pacific Plate and the Eurasian Plate has resulting in the formation of a central pacific tropical zone with the high temperature magma chamber and high geothermal gradient. The YB as one geothermal field of the central pacific tropical zone has a high geothermal gradient (3.49 °C/100m, average), forming numerous thermal springs, including the thermal springs of Jinda (JD), Ziyu (ZY), Shennong (SN), Qiaotun (QT), Sijixiangkang (SJXK), Aolong (AL) and Yitong (YT), which are located in the CD and MD (Fig. 1).

The study area is located in the Songnen Plain in the Changbaishan Mountain area of the transition zone and slopes to the northwest gradually along the Songhuajiang River, which is a large river originating from the highest mountain Changbaishan, of the northeast area. The YB features a continental monsoon climate with four distinct seasons. According to meteorological station data from Jilin City (Geological environment monitoring station of Jilin Province, 2004), the annual mean precipitation is 639.2 mm, and the average annual evaporation is 1423.8 mm, which is obviously greater than the precipitation. However, the Changbaishan area has enough water to recharge the study area and the Tianchi, with a total storage capacity of 20.04 billion cubic meters (Zhu et al., 1981). The geothermal reservoir of the YB is mainly Eocene sandstone, which is supplied by precipitation through basin-bounding faults from the surrounding mountains (Li, 2010; Liu et al., 2014). The surface lithology of the YB is relatively simple and is mainly constituted by exposure to O_q sandy mudstone; only the northeastern region is covered by Quaternary alluvium (Fig. 1).

116 3 Sampling and analytical results

117 3.1 Sampling and analytical methods

118 Nine thermal water samples were collected from the YB in February and May
119 2017 (see sampling locations in Fig. 1). Temperature and pH were measured in the
120 field, while alkalinity, as HCO_3^- and CO_3^{2-} , was determined by Gran titration in the
121 laboratory on the day of sampling. Water samples collected for analysis were stored in
122 clean polyvinyl fluoride bottles and sealed with wax. Samples for major and trace
123 element analysis were acidified with concentrated HNO_3 (0.5 ml and 1 ml for 100-ml
124 samples), which were analyzed using inductively coupled plasma optical emission
125 spectrometry (ICP-OES Optima 2100 DV, which has a lower limit of $0.01 \text{ mg}\cdot\text{L}^{-1}$)
126 and ion chromatography (IC, which has a lower limit of $0.01 \text{ mg}\cdot\text{L}^{-1}$), respectively, in
127 the Jilin University Test Center, China. The precision of the IC and ICP-OES analyses
128 is less than $\pm 5\%$ for major ions. Water samples for analysis of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
129 values of HCO_3^- waters and the $\delta^{34}\text{S}$ values of SO_4 waters were collected in
130 polyethylene bottles using Na-OH and Ba-OH to form BaCO_3 and BaSO_4 ; for the
131 detailed procedure, refer to S. Halas and Wolacewicz (1982). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
132 values for HCO_3^- waters were determined using a Multiflow-Isoprime 100 with a
133 precision of less than 0.2‰. The $\delta^{34}\text{S}$ values for water were determined using a vario
134 PYRO cube with a precision of less than 0.2‰. This analysis was performed at the
135 Jilin University Stable Isotope Research Center. The carbon isotope compositions are
136 reported in ‰ relative to the PDB standard, and the sulfur isotope compositions are
137 reported in ‰ relative to the CDT standard.

138 **3.2 Analytical results**

139 The geochemical compositions of the water samples from the YB are shown in
140 Table 1. The hydrothermal waters have temperatures ranging from 43.2 °C (AL) to
141 74.2 °C (QT) at the mouth of the well. The pH values of the hydrothermal waters vary
142 from 7.82 (SN-1) to 8.44 (ZY-1), indicating that the waters are neutral to slightly
143 alkaline. Relative to the hydrothermal waters, the groundwater has a relatively lower
144 pH value (6.8). The Na⁺, HCO₃⁻ and Cl⁻ concentrations in the thermal waters range
145 from 235.29 mg·L⁻¹ to 2332 mg·L⁻¹, 617.28 mg·L⁻¹ to 5369.76 mg·L⁻¹ and 6.14
146 mg·L⁻¹ to 97.98 mg·L⁻¹, respectively, and the MD exhibited much higher values than
147 the CD (Table 1, Fig. 3b). The waters from the Eocene reservoir are homogeneously
148 classified as Na-HCO₃-type water, which is very different from that of the
149 groundwater and the water from the Second Songhuajiang River, as shown in the
150 Piper diagram (Fig. 2, Table 1). The total dissolved silica content in the thermal
151 waters varies from 34.86 mg·L⁻¹ to 51.64 mg·L⁻¹. The minor elements in the thermal
152 waters are shown in Table 2; Sr, Ba, B and Fe have higher concentration than the
153 other minor elements, which are all below 0.1 mg/L. The δ¹³C and δ³⁴S values in the
154 MD, i.e., approximately 1.63‰ and 1.5‰, respectively, are different from those in the
155 CD, which range from -1.04‰ to -0.84‰ and 2.3‰ to 3.7‰, respectively (Table 1).

156 **[Table 1, 2 and Figure 2, 3 near here]**

157 **4 Discussion**

158 **4.1 Hydrochemical characteristics**

159 According to White (1957a), the Br/Cl, I/Cl, K/Na and Li/Na ratios of the water
160 samples in the YB reflect oil-field brines; the SO_4/Cl and B/Cl ratios of the water
161 samples indicate volcanic hot spring waters; and the $(\text{Ca}+\text{Mg})/(\text{Na}+\text{K})$ values of the
162 water samples are within the fields of both oil-field brines and volcanic hot springs.
163 Moreover, the HCO_3/Cl and F/Cl ratios of most samples are in fields beyond those
164 defined by all three of these criteria; however, the F/Cl ratio of YT sample is within
165 the volcanic hot spring range (Table 3). The Na-K-Mg diagram (Fig. 3a) shows that
166 all the thermal water samples, except for those of SJXK and YT, are located in a fully
167 equilibrated area with an equilibrated temperature of approximately 100°C, which
168 implies that the geothermal system needs a long time to arrive at equilibrium
169 (Giggenbach, 1988). Moreover, due to the low equilibrium temperature, the
170 dissolution of rock may be very low; thus, the equilibrium of the thermal water may
171 be mainly controlled by water-rock interaction (Giggenbach, 1988). The fully
172 equilibrated nature of the water indicates that no cold water mixed with hot water
173 before arriving at the surface and that no meteoric water locally infiltrates into the
174 reservoir. The Schoeller semi-logarithmic diagram (Fig. 3b) shows that there are
175 significant differences between the thermal water and the groundwater and river water,
176 a finding that is further supported by the fluid potential (Fig. 1). The exception of the
177 SJXK and YT samples may be due to immature water recharge, as indicated by the
178 tritium value, which was 2.45 tritium units (TU) in 2014 (Liu et al., 2014) but now
179 ranges from 5.3 TU to 7.47 TU in 2017 (Zhao et al., 2017). Therefore, the water

180 arrived at equilibrium in the Eocene reservoir through some mechanism other than
181 migration.

182 **[Table 3 and Figure 3 near here]**

183 To understand the main controlling factors of the hydrogeochemical processes
184 during water circulation, two Gibbs's diagrams were used (Fig. 4). In these diagrams,
185 the weight ratios of cations ($\text{Na}^+:\text{Na}^+ + \text{Ca}^{2+}$) and anions ($\text{Cl}^+:\text{Cl}^- + \text{HCO}_3^-$) are plotted
186 against TDS. Fig. 4 shows that the cations and anions have different controlling
187 factors: the main controlling factor for cations is water-rock interactions according to
188 the Na-K-Mg diagram, while the main controlling factor for anions is evaporative
189 crystallization. These factors are very different from those of the groundwater ions,
190 which are mainly derived from dissolved rock (Xiao et al., 2016). Furthermore, the
191 cations of the YT water sample from the MD showed a seawater character, which
192 probably due to contamination by water reinjection from the MD area. Generally,
193 cations and anions show the same hydrogeochemical processes during circulation, and
194 the differences in the thermal water in the study area may be due to the injection of
195 peculiar chemical components, which will be discussed in detail below.

196 **[Figure 4 near here]**

197 **4.2 Main element characteristics of the thermal water**

198 **4.2.1 Cations**

199 The abundance of cations in the thermal water in the YB is as follows: $\text{Na}^+ > \text{K}^+ >$
200 $\text{Ca}^{2+} > \text{Mg}^{2+}$. This pattern is mainly controlled by water-rock interactions. Therefore,
201 the chemical activity represents a useful approach for analyzing the mineral-solution

equilibria and for determining the stability of the solid-solution system to identify the origins of the cations (Freeze and Cherry, 1979; Wang et al., 2016). The lithology of the reservoir in the study area is muddy siltstone intercalated with siltstone and shale, which overlies granite and Permian limestone and is overlain by Quaternary alluvium. Therefore, the ion composition of the fluid is mainly controlled by these strata. In this study, we assume that Al in the solid phase is conservative, so chemical activity plots were then used to analyze the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, $\text{CaO}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, and $\text{MgO}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ systems (Fig. 5a-d). The secondary potential minerals are defined as kaolinite, muscovite, albite, gibbsite, kaolinite, paragonite, Ca-montmorillonite, and Mg-montmorillonite, among others (Wang et al., 2016).

Na^+ is the main cation in the thermal water of the YB and accounts for more than 97% of the major cations. In sedimentary basins, water-rock interaction involving Na^+ include albitization of plagioclase, weathering of plagioclase, halite dissolution or precipitation, and clay mineral alteration (Garrels and Mackenzie, 1967). Fig. 5a shows that the Na^+ in the YB thermal water is related to the Na – silicates, e.g., albitization and plagioclase. As the CO_2 level increases the Na – silicates undergo hydrolysis (Boschetti et al., 2015; Venturelli et al., 2003; Toran and Saunders 1999), and this process releases Na^+ , Ca^{2+} , and HCO_3^- and is accompanied by calcite precipitation. This can be described by the following reactions (Davisson et al., 1994; Garrels and Mackenzie, 1967): $1.77\text{Na}_{0.62}\text{Ca}_{0.58}\text{Al}_{1.38}\text{Si}_{2.62}\text{O}_8 + 2.44\text{CO}_2 + 3.67\text{H}_2\text{O} = 1.23\text{Al}_2\text{Si}_2\text{O}_3(\text{OH})_4 + 1.1\text{Na}^+ + 0.68\text{Ca}^{2+} + 2.44\text{HCO}_3^- + 2.2\text{SiO}_2$ (plagioclase);

224 $\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{SiO}_2 + \text{Na}^+ + 4\text{H}^+ = \text{NaAlSi}_3\text{O}_8 + \text{Ca}^{2+} + \text{Al}^{3+} + 2\text{H}_2\text{O}$ or $\text{CaAl}_2\text{Si}_2\text{O}_8 +$
 225 $4\text{SiO}_2 + 2\text{Na}^+ = 2\text{NaAlSi}_3\text{O}_8 + \text{Ca}^{2+}$ (albitization of plagioclase 1:1 and 1:2,
 226 respectively). The low Ca^{2+} concentration and the high of Na^+ concentration in the
 227 thermal water implies that the weathering of plagioclase played a dominant role in the
 228 reactions in the YB. The concentrations of Ca^{2+} and SiO_2 in the HCO_3 -Na-type water
 229 are mainly controlled by the pH, as pH values higher than 7 lead to precipitation. The
 230 pH of the thermal water in the study area ranges from 7.95 to 8.44. Therefore, the
 231 Ca^{2+} produced by the albitization of plagioclase may precipitate as CaCO_3 (Fig. 5c).
 232 This hypothesis is consistent with the low concentrations of SiO_2 in the thermal water,
 233 as SiO_2 is also controlled by the pH. The analysis of cements in the Eocene reservoir
 234 indicates that two periods of feldspar dissolution and carbonate cementation took
 235 place (Zhou et al. 2010). Furthermore, the cement mainly consists of quartz and
 236 carbonate, with the carbonate cement accounting for 80% of the composition (Hou et
 237 al., 2009). Moreover, the Ca^{2+} concentrations are also influenced by the alteration of
 238 clay as follows (Xiao et al., 2016): $0.5\text{Ca}/(\text{K}^+)\text{-Clay}_2 + \text{Na}^+ \rightleftharpoons 0.5\text{Ca}^{2+}/(\text{K}^+) +$
 239 Na-Clay (Fig. 5c). The K^+ concentration is mainly related to the weathering of
 240 muscovite rather than K-feldspar (Fig. 3b), but the K^+ concentration was very low,
 241 which may be due to absorption by clay minerals (Venturelli et al., 2003). The Mg^{2+}
 242 content is mainly related to the weathering of biotite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$) in silicate
 243 units, dolomite ($\text{CaMg}_3(\text{CO}_3)_4$) in carbonate units or both (Connolly et al., 1990;
 244 Robert and Fred, 1967). A molar ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ of less than 2 indicates
 245 dissolution of carbonate, whereas a ratio greater than 2 indicates the dissolution of

246 silicate minerals (Katz et al., 1997; Mayo and Loucks, 1995). The $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios of
247 the YB thermal water samples ranges from 2.4 to 31, which are greater than 2,
248 implying that the ions of the thermal water are mainly controlled by interactions with
249 silicate rocks and that the low concentrations of Mg^{2+} are due to the conversion of
250 clay minerals (Fig. 5d), which also corresponds to the Late A diagenetic stage (Zhou
251 et al. 2010).

252 **[Figure 5 near here]**

253 Plots of Na (the most abundant cation in the waters) versus other elements can
254 provide a more accurate indication of the mixing relationships in the thermal water
255 and can reveal the sample that is least affected by diagenetic alteration (Connolly et
256 al., 1990). A mixture of two different waters with different compositions will produce
257 a good linear relationship on an x-y plot, with a non-zero intercept. In contrast, the
258 mixing of three end-member waters will produce a triangle-shaped array of points
259 (Connolly et al., 1990; Lowry et al., 1988). In Fig. 6, all the samples exhibit good
260 linearity with non-zero intercepts for all the major elements, suggesting that the
261 thermal water has more than one source. Therefore, the especially high concentration
262 of Na^+ may have another origin. The most common hypotheses on the origin of Na
263 can be summarized as (Venturelli et al., 2003; Toran and Saunders, 1999): 1) the
264 dissolution of silicate minerals; 2) ion exchange in Na-rich clay; and 3) the addition of
265 an NaCl component. From the above discussion, we know that the hydrolysis of Na –
266 silicate minerals predominates, but we cannot exclude ion exchange or leaching of
267 alkali-rich volcanic rock. The low K^+ and Mg^{2+} contents imply ion exchange of clay

minerals (Fig. 5b, 5d). The positive correlation between Na and Cl (Fig. 6) indicates the addition of an NaCl component, which may reflect (Connolly et al., 1990; Venturelli et al., 2003; White, 1957a) 1) the dissolution of halite, and 2) the desorption of magmatic volatiles. No halite-bearing stratum is present in the study area, and the addition of an NaCl component in the thermal water is therefore likely due to the desorption of magmatic volatiles, which are transported as a dense vapor through condensation of the magma emanations, and NaCl and other alkali halides are become very soluble near the critical point of water (White, 1957a, b). Additionally, Venturelli et al., 2003) proposed that the fluid inclusions can also release an NaCl component during water-rock interactions, such as granite. Certainly, the laboratory leaching experiments show that approximately 160 g of Cl⁻ is available per m³ of the basement rock inclusions (<5 μm) due to available in chloride ions rather than an NaCl component, the Na⁺ formed mainly through later water circulation (Michard et al., 1996). In fact, regardless of the predominant factor, we can conclude that water circulation from the bottom recharges the Eocene reservoir.

According to Odum (1951), the Sr/Ca ratio (μM/mM) of fresh water varies between 0.5 (corresponding to water from regions with carbonate rocks) and 5 or greater (corresponding to water from volcanic areas). Moreover, the average Sr/Ca ratio of representative rivers around the world is 2.2 (Odum, 1951). In the YB thermal water samples, the Sr/Ca ratios range from 9.3 to 92, indicating that the water flowed through volcanic rocks. Additionally, the positive correlation between Sr²⁺ and SO₄²⁻, with a calculated regression coefficient of 0.902 (Fig. 6), implies that a portion of Sr²⁺

is derived from the dissolution of carbonates (as no evaporites are present in the study area). From the above discussion, we speculate that a limestone reservoir exists below the granite unit and that high-temperature water flows upward along the fault through the granite and into the Eocene sandstone reservoir.

[Figure 6 near here]

4.2.2 The origin of CO₂

The presence of CO₂ is critical to the weathering of rock and the formation of HCO₃⁻ (Davisson et al., 1994; Garrels and Mackenzie, 1967; Nesbitt, 1985). Therefore, the origin of CO₂ gas in a system is essential for understanding the formation of sodium-bicarbonate water. CO₂ of different origins has different $\delta^{13}\text{C}$ values. Therefore, $\delta^{13}\text{C}$ values can be used to trace the origin of HCO₃⁻ (Becker et al., 2008; Liu et al., 2000; Wang et al., 2016). Previous studies have reported that the typical $\delta^{13}\text{C}$ value of magmatic CO₂ is $\sim -4\text{‰}$ (Javoy et al., 1982), that most marine carbonates have an average $\delta^{13}\text{C}$ value of 0‰ (Clarke and Fritz, 1997), and that organic matter in recent sediment features $\delta^{13}\text{C}$ values ranging from -10‰ to -30‰ (Wang et al., 2016).

The $\delta^{13}\text{C}$ values in the CD of the YB thermal water samples are -0.84‰ to -1.24‰ (Table 1), imply that the carbon in CO₂ may derive from magmatic volatiles or from leaching of marine carbonates. Thermal water mixed with magmatic volatiles tends to have abnormally high ion ratios that are not easily affected by dilution or concentration processes (Ellis and Mahon, 1964; White, 1957a, b). The SO₄/Cl, B/Cl, HCO₃/Cl and F/Cl ratios of the CD thermal water were abnormally high, and the

HCO₃/Cl and F/Cl ratios were greater than those of even volcanic hot springs (Table 2), implying that magmatic volatiles dissolve in thermal water. Due to continuous subduction of the Pacific Plate, the northwestern and southeastern basin-bounding lithospheric faults are still active today (Hou et al., 2009). Such faults can act as channels between the mantle and the surface, allowing magmatic volatiles to migrate upwards. Therefore, the $\delta^{13}\text{C}$ composition is most likely related to magmatic volatiles, but we cannot exclude the possibility of carbonate leaching due to the abnormally high HCO₃/Cl ratios and the presence of carbonate strata in the center of the YB (Wang et al., 2015). The MD has a higher $\delta^{13}\text{C}$ value (1.63‰) than the CD (-0.93‰, average), implying that the $\delta^{13}\text{C}$ composition is mainly controlled by limestone leaching, as evidenced by the cations in the Gibbs's diagram (Fig. 4). However, magmatic volatiles still likely exert some effect, as the $\delta^{13}\text{C}$ values are much lower than those of the Permian limestone in the Changbaishan area (4.3‰, Zhao et al., 2017). Furthermore, the F/Cl ratio corresponds to the volcanic hot springs field of the White criterion (Table 3). The different $\delta^{13}\text{C}$ values of the CD and MD water samples suggest that the activity of the basin-bounding lithospheric faults is stronger in the northeast than in the southwest.

4.2.3 Anions

The abundance of the main anions in the thermal water is as follows: HCO₃⁻ > Cl⁻ > SO₄²⁻ > F⁻. The Gibbs diagram (Fig. 3) shows that the anion composition exhibits characteristics typical of evaporation, but the Eocene-to-present climate in the Jilin Province has been mild and rainy (Wan et al., 2014; Wang, 2003). Therefore, the

334 formation of the anion composition is not due to evaporation, and it is instead due to
335 other factors, such as heating by magmatic volatiles. The concentrations of Cl^- and Br ,
336 which are conservative elements, are plotted in Fig. 7 and are compared to the
337 seawater evaporation trend (SET), which has been extensively used to determine the
338 origin of salinity in sedimentary basins (Kharaka et al., 1987; Rittenhouse, 1967).
339 Normally, evaporated waters plot along the SET, whereas waters affected by halite
340 dissolution and mixing between evaporated seawater and other waters plot above and
341 below the SET, respectively. The Cl^- and Br concentrations of the YB thermal water
342 samples plot near the extended SET line and exhibit a very good mixing or dilution
343 trend (Fig. 7) resulting from the interaction between water and a marine reservoir
344 (Carpenter, 1978; Chen et al., 2014). Additionally, the molar Br/Cl ratio of the thermal
345 water ranges from 1.6×10^{-3} to 4.1×10^{-3} , suggesting that water leachate from the
346 granite basement also exists (e.g., Michard et al., 1996).

347 The concentration of SO_4^{2-} in the MD is higher than that in the CD area, and the
348 activity of the faults is stronger in the northeast than in the southwest. Therefore, this
349 SO_4^{2-} probably formed through oxidation of H_2S gas (Valentino and Stanzione, 2003).
350 To further verify this conclusion, we measured the ^{34}S of SO_4^{2-} in the thermal water of
351 the two areas. The gas of volcanic thermal water, which originates from magmatic
352 volatiles, always ranging from -4.6‰ to 5.6‰ (Xiao et al., 2016). The $\delta^{34}\text{S}$ value
353 ranges from 2.3‰ to 3.7‰ in the CD area, and it is 1.5‰ in the MD, probably due to
354 the supply of magmatic volatiles, and it is consistent with the result of $\text{SO}_4^{2-}/\text{Cl}^-$ ratio
355 (Table 3). The formation of SO_4^{2-} in this process may be accompanied by a pH

356 decrease. However, in the study area, the pH was mainly neutral to alkaline, and it
357 may be buffered by water-rock interactions in the Eocene reservoir (Valentino and
358 Stanzione, 2003).

359 Based on ^{13}C , ^{34}S data and the results of Table 3 (SO_4/Cl , B/Cl , HCO_3/Cl and
360 F/Cl ratios), we know that the thermal waters were influenced by hot magmatic
361 volatiles. Therefore, the anion compositions exhibiting evaporation-like
362 characteristics are most likely due to the heating of the water by magmatic volatiles
363 and the resulting alteration of the ion composition of the water.

364 **[Figure 7 near here]**

365 The introduction of dissolved magmatic volatiles may lead to high F/Cl ratios
366 because F^- is believed to be one of the major components in magmatic volatiles
367 (Capaccioni et al., 2011; White 1957a, b). However, the F/Cl ratio of the study area
368 was higher than the typical values of volcanic hot springs (0.0005-1). Therefore, other
369 factors may have influenced the F concentration. The reservoirs in the YB are
370 composed of Eocene sandstones that overlie Yanshanian granite. F^- concentrations are
371 generally higher in granite than in sandstone, and F can be easily leached by water
372 (Ellis and Mahon, 1967). The concentration of F in thermal waters is mainly limited
373 by the solubility of calcium fluoride (Ellis and Mahon, 1967), as described by the
374 following reaction at temperatures below 230°C : $\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$. Using
375 PHREEQC, we calculated the saturation index (SI) of fluorite, which was the main
376 fluorine-containing mineral in the rock. The SI varied between -0.64 and -1.64 (Table
377 1). Moreover, the concentration of F in thermal waters is also controlled by pH as

alkaline environments favor the enrichment of F in the water (Ellis and Mahon, 1967; Liu et al., 2000). The Eocene reservoir temperature generally ranges from 51.11°C to 147.22°C (Liu, 2014), and the pH ranges from 7.95 to 8.44. Additionally, Ca^{2+} largely precipitated as CaCO_3 . These conditions all favor forcing the reaction to the right. Therefore, the high F/Cl ratio in the thermal water is mainly due to magmatic volatile dissolution and granite leaching.

4. 3 Minor element characteristics of the thermal water

The geochemical patterns of different sediments always display regular combinations of minor element characteristics (Yu et al., 1990). Therefore, R-model cluster analysis can be used to identify these combinations based on the correlations among minor elements (Guo and Wang, 2012; Wang et al., 2011; Yu et al., 1990). Therefore, we used this method to identify the origin of the minor elements. Here, we used SPSS software to determine Pearson correlation coefficient and to perform R-mode cluster analysis of the minor elements (the YT water sample was not included due to the contamination by water reinjection) (Fig. 8).

[Figure 8 near here]

Fig. 8 shows that the minor elements can be divided into three groups at the 15 level: the first group includes Ba, Sr, Li, Cr, Cu, B, Co, Se, Al, Cs and Ag; the second group includes Fe, Mn and As; and the third group includes Pb, Zn, Ni, Sb, Mo, Ge, Hg and Cd. At the 20 level, the first and second groups combine into a single group, which is negatively correlated with the third group, possibly due to different ion sources. The first group represents the main mineral constituents of the thermal water

400 in the YB. The Ba and Sr correlation coefficient is 0.995, and these elements are
401 negatively correlated with Pb. These characteristics are typical of continental fresh
402 water (Yu et al., 1990), and the first group may therefore represent sandstone reservoir
403 water. However, the positive correlations between Ba and B and between Ba and Co
404 are suggestive of seawater characteristics, which may be due to the leaching of
405 limestone. The high B/Cl ratio indicates water from a volcanic source (Table 3) as B
406 frequently derives from one of three sources (Arnórsson and Andréðsdóttir, 1995;
407 Valentino and Stanzione, 2003): 1) seawater intrusion; 2) recharge by enriched deep
408 fluids deriving from magma degassing; and 3) rock dissolution. We can use Fig. 9 to
409 determine the main process affecting the B/Cl ratio of the thermal water. The samples
410 corresponding to waters with the lowest Cl/B ratio (14.4-38.7), except for YT sample,
411 indicate interactions with volcanic rock (42.3). As we know, B is incompatible with
412 geothermal systems above 150°C, similar to Cl⁻ at all temperatures (Ellis and Mahon,
413 1964). On the other hand, B can be effectively removed from water at low
414 temperatures by clay minerals, particularly illite (Arnórsson and Andréðsdóttir, 1995;
415 Harder, 1970). As reservoir temperatures reach approximately 99°C (Zhao et al.,
416 2017), the Cl/B ratio will become higher. Contrary to the facts, we concluded that
417 magmatic volatiles were present in the thermal water. The high Cl/B ratio of the YT
418 sample is probably due to contamination by water reinjection rather leaching of
419 volcanic rock, and the stronger activity of the basin-bounding faults in the northeast
420 compared to that in the southwest will lead a lower Cl/B in the YT thermal water than
421 other samples. Moreover, As, Fe and Mn generally represent deeply sourced materials

422 (Cronan et al., 1997; Lin et al., 1999). Therefore, the elements of the first and second
423 groups exhibit characteristics typical of sandstone and limestone leaching under the
424 influence of magmatic volatiles. The third group is a basic combination and contains
425 Mo, which displayed lower mobility relative to B and is a characteristic element of
426 granite (Wang et al., 2011; Yu et al., 1990). Therefore, this group may be related to the
427 leaching of granite.

428 [Figure 9 near here]

429 **4.4 Fluid behavior characteristics**

430 **4.4.1 Thermal water in a closed or open system?**

431 Fluid behavior can be divided into closed system behavior and open system
432 behavior (Ma et al., 2015; Li et al., 2013; Pedersen and Bjørlykke, 1994). From Fig.
433 3a, we know that immature water has mixed with fully equilibrated water in the
434 Eocene reservoir. Therefore, the thermal water of the YB is part of an open system.
435 This conclusion is consistent with the results of the ion combination coefficient
436 analysis (Jia et al., 2008). The cation analysis results imply that the cation patterns are
437 mainly due to water-rock interactions, but the interaction could have occurred without
438 CO₂, which was mainly from the magmatic volatiles migrating upward along the
439 lithospheric faults. Furthermore, the anion analysis demonstrated that both major and
440 minor elements showed characteristics typical of the leaching of granite and limestone
441 in association with magmatic volatile dissolution. Therefore, we conclude that the
442 immature water is recharging the Eocene reservoir from the bottom rather than from
443 overlying groundwater. Moreover, both the Schoeller plot (Fig. 3b) and the fluid

potential diagram (Fig. 1) imply that no hydraulic connection exists between the shallow groundwater and the Eocene thermal water, which further supports our conclusion. The correlations between Br and Cl, Sr^{2+} and SO_4^{2-} , and the $\delta^{13}\text{C}$ values suggest that a deep limestone reservoir exists and may be the reservoir of the immature recharge water (Fig. 1).

4.4.2 Fluid pathway

Fluid pathways are mainly controlled by the fluid potential, as fluids migrate from high fluid potential to low fluid potential (Li et al., 2013; Pedersen and Bjørlykke, 1994). Fig. 1 shows a centrifugal flow pattern in map view, in which the fluid migrates from low-lying areas to the slopes due to the release of fluids during mudstone compaction. Additionally, multiple migration centers are observed (Hou et al., 2009). In the diagram of the modern vertical fluid potential (Fig. 1), the fluid potential is obviously higher in the middle strata (E_{2y} and E_{2sh}) than in the uppermost strata (E_3 and Q) and in the bottom strata (E_{2s}) in the reservoir. Moreover, an obviously low fluid potential belt exists along the fault at the bottom. These patterns imply that the fluid mainly flows from E_{2y} and E_{2sh} to the upper and lower strata via the fault. This conclusion is also verified by the TDS values and vertical pressure distribution, which are higher in the middle section than at the top or the bottom (Fig. 10). Fig. 10 shows that the TDS values increase from low-lying areas to the slopes (Botai to Gudian), whereas the preservation ability decreases (Jia et al., 2008), implying that the immature recharge water has a much higher TDS than the preexisting water in the Eocene reservoir. In map view, the lowest TDS value occurs

466 in the LD, while the highest value occurs in the CD, with the values in the MD falling
467 in between (Hou et al., 2009). Therefore, the recharge water migrates from the margin
468 to the center, which can be regarded as centripetal flow, but the recharge ability of the
469 MD is lower than that of the CD. Therefore, based on the anion characteristics and
470 fluid potential data, we propose a conceptual model of fluid migration (Fig. 11).

471 **[Figure 10 and 11 near here]**

472 **5 Conclusions**

473 (1) The thermal water in the Eocene sandstone reservoirs in different depressions
474 is homogeneously classified as Na-HCO₃-type water in the Piper diagram. Due to
475 immature recharge water, the Sijixiangkang (SJXK) and Yitong (YT) water samples
476 plot in the partially equilibrated or mixed water fields, while the other samples plot in
477 the fully equilibrated field of the Na-K-Mg ternary equilibrium diagram. This
478 difference indicates the existence of immature recharge water.

479 (2) The cations in the studied water are mainly from water-rock interaction, such
480 as the albitization and weathering of plagioclase and the transformation of clay
481 minerals in the Eocene sandstone reservoir. The anion compositions were affected by
482 heating due to magmatic volatiles, creating geochemical patterns typical of
483 evaporation. The anions themselves were sourced from the magmatic volatiles and
484 from the leaching of granite and limestone.

485 (3) The origins of the major and minor elements imply that the Eocene reservoir
486 is an open system rather than a closed system. This conclusion is also verified by the
487 high SO₄²⁻/Cl, B/Cl, F/Cl and HCO₃⁻/Cl ratios and by the $\delta^{13}\text{C}$, $\delta^{34}\text{S}$ values, which

488 indicate that magmatic volatiles dissolved into thermal water and that a limestone
489 reservoir exists below the granitic unit underlying the basin sediments. An R-model
490 cluster analysis also illustrates this point.

491 (4) The thermal water in the Eocene reservoir is recharged by a limestone
492 reservoir via the migration of fluid upward along the northwestern and southeastern
493 basin-bounding lithospheric faults. In map view, this fluid then migrates from the
494 margins to the center, which can be regarded as a centripetal flow, and the fluid flows
495 vertically from E_2y and E_2sh to the upper strata and the underlying E_2s strata along the
496 faults. These flow patterns are based on the horizontal and vertical variations in fluid
497 potential, TDS and pressure. Understanding the ion origin and fluid behavior of the
498 Eocene reservoir thermal water is not only important for geothermal resource
499 utilization but also for facilitating the exploration of geothermal systems in the future.

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Tables

Table 1 General hydrochemical properties and isotopic compositions of thermal water collected from the Yitong Basin (mg/L)

Sample ID	T (°C)	pH	Main component								TDS	SI	$\Delta^{13}\text{C}$	$\Delta^{34}\text{S}$
			Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	F		Fluorite	(‰)	(‰)
JD ^a	62.4	8.1	462	5.56	5.12	0.10	1310	1.63	6.14	2.58	1843	-1.49	-	-
ZY-1 ^a	64.2	8.4	470	4.86	4.41	0.15	1296	1.63	10.53	5.66	1854	-0.95		-
ZY-2 ^a	62.4	8.1	575	5.37	3.23	0.15	1474	9.80	22.81	7.84	2148	-0.66	-	-
SN-1 ^a	61.0	7.8	1004	7.22	3.47	0.85	2633	6.53	35.10	6.44	3730	-1.04	-1.04	2.4
SN-2 ^a	63.0	8.0	951	7.24	3.63	0.87	2620	6.53	33.34	6.44	3662	-1.02	-0.93	2.3
QT ^a	74.2	7.9	822	8.63	3.28	0.11	2208	4.90	24.57	3.14	3129	-1.64	-0.92	2.8
SJXK ^a	54.7	8.2	443	4.61	5.49	0.22	1234	1.63	10.53	6.04	1760	-0.71	-0.84	3.7
AL ^a	43.2	7.9	235	1.51	3.10	0.06	617	1.63	14.04	7.65	917	-0.64	-	-
YT	60.5	8.3	2332	20.98	12.36	2.44	5369	97.98	229.80	2.07	8103	-1.70	1.63	1.5

Groundwater ^b	-	6.8	27	4.50	71.70	35.70	168	107.00	53.20	0.36	409	-	-	-
River ^c	-	7.4	376	63.48	429.00	165.40	853	229.00	220.30	-	133	-	-	-

Note: The major and ¹³C values of a are cited from Zhao et al. (2017); b is cited from Xiao et al. (2016); c is cited from Liu et al. (2013); River refers to the Second Songhuajiang.

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Table 2 Minor element contents of the thermal water collected from the Yitong**Basin (µg/L)**

Sample		Minor component								
ID	Cs	Sr	Ba	B	As	Sb	Al	Fe	Mn	Co
JD	1.6	235.8	211.9	313.1	0.7	0.5	32.2	238.0	6.3	0.1
ZY-1	1.2	296.6	239.7	732.0	0.4	0.7	37.2	87.0	7.8	0.1
ZY-2	1.6	332.4	286.3	832.2	0.8	0.7	33.7	194.8	6.0	0.2
SN-1	1.5	702.1	701.9	907.0	0.7	0.2	85.4	83.4	6.5	0.2
SN-2	1.4	693.6	692.3	915.5	0.4	0.2	94.6	76.0	6.1	0.2
QT	3.3	421.5	425.0	795.8	0.3	0.3	79.3	74.4	0.0	0.1
SJXK	1.4	237.6	205.2	627.9	0.7	0.6	74.3	420.8	19.3	0.1
AL	0.3	63.4	73.7	328.6	0.2	0.2	75.8	44.8	0.0	0.1
YT	-	2014.0	4060.0	1031.0	0.6	0.2	52.9	780.0	22.0	0.1

Continues

Sample		Minor component								
ID	Ni	Se	Hg	Cu	Pb	Cd	Cr ⁶⁺	Zn	Ge	Mo
JD	0.2	1.7	0.6	25.3	0.0	0.2	2.6	5.5	6.3	1.1
ZY-1	2.1	1.7	0.8	31.4	0.5	0.2	3.5	11.9	12.8	10.8
ZY-2	3.6	2.2	0.6	51.6	3.4	0.3	5.5	78.7	15.7	6.8
SN-1	0.4	2.3	0.4	73.7	0.0	0.2	6.9	7.2	8.3	2.9
SN-2	0.4	2.5	0.5	88.6	0.0	0.0	6.0	8.9	8.0	1.7
QT	0.6	1.9	0.6	78.0	0.0	0.1	5.4	10.6	16.0	8.0

SJXK	0.5	1.8	0.6	57.8	0.0	0.1	3.7	14.0	11.3	9.8
AL	0.8	1.7	0.8	37.4	0.0	0.5	2.7	15.1	15.6	3.9
YT	0.8	1.7	0.8	37.4	0.0	0.5	2.7	15.1	-	-

Table 3 A comparisons of ion ratios of thermal water from the Yitong Basin with other water mass

Ratios (weight)	Ocean ^a	Oil-field brines ^a	Volcanic hot springs ^a	YB thermal water
HCO ₃ /Cl	0.0074	0.0001-1	0.01-3	23.6-213.3
SO ₄ /Cl	0.14	0-1	0.01-0.5	0.116-0.43
F/Cl	0.00007	0.00001-0.001	0.0005-0.1	0.009-0.574
Br/Cl	0.0034	0.0001-0.01	0.0001-0.001	0-0.0041
I/Cl	0.000003	0.00003-0.02	0.00001-0.0005	0.00081-0.0029
B/Cl	0.00024	0.00001-0.02	0.01-0.1	0.0234-0.07
K/Na	0.036	0.001-0.03	0.003-0.03	0.00642-0.012
Li/Na	0.00001	0.0001-0.003	0.003-0.03	0.0001-0.000164
Ca+Mg/Na+K	0.153	0.01-5	0.001-0.2	0.0043-0.0133

Note: The values of a are cited from White (1957a).

Figure Captions

Fig. 1 Geological map of the Yitong Basin, its location, stratigraphic column and fluid potential evolution (modified after Hou et al., 2009). (1) Quaternary alluvial fan, (2) Pliocene clastic rock, (3) Oligocene clastic rock, (4) Eocene clastic rock, (5) Cretaceous clastic rock, (6) Jurassic granite, (7) Permian clastic rock interbedded with limestone, (8) Permian lava interbedded with limestone, (9) Yanshanian granite, (10) Variscan granite, (11) river and lake, (12) Compressional fault, (13) Compresso-shear fault.

Fig. 2 Piper diagram for the studied water samples from the Yitong Basin.

Fig. 3 Na-K-Mg trilinear equilibrium diagram (a) and Schoeller plot (b) of thermal water samples collected from the Yitong Basin.

Fig. 4 Gibbs's diagrams showing the mechanisms governing groundwater chemistry in the Yitong Basin (modified from Xiao et al., 2016).

Fig. 5 Activity plots of (a) $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, (b) $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, (c) $\text{CaO}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, and (d) $\text{MgO}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 25 °C (solid line) and 100 °C (dashed line). The saturation lines of calcite are also shown at 25 °C (horizontal solid line) and 100 °C (horizontal dashed line) under a pCO_2 of 1 atm. This figure is modified from Wang et al. (2016).

Fig. 6 Plots of Na vs. K, Ca, Mg, Cl, and HCO_3^- and Sr vs. SO_4^{2-} for the thermal water in the Yitong Basin. The unit mg/L of all elements has been transformed into to mmol/L (mM) in the diagram.

Fig. 7 Br vs. Cl concentrations of the thermal waters from the Yitong Basin. The

seawater evaporation trend (SET, solid line) from Carpenter (1978) is also shown. The dashed line is the extended SET line, drawn through all the Yitong Basin thermal waters.

Fig. 8 R-model cluster analysis dendrogram for elements.

Fig. 9 Correlations between B and Cl in studied waters. This figure is modified from Valentino and Stanzione (2003).

Fig. 10 The vertical distributions of TDS and pressure. The TDS and pressures data are cited from Jia et al. (2008) and Hou et al. (2009), respectively.

Fig. 11 Conceptual model of fluid migration in the YB. Fault and strata information modified from Ren et al. (1999) and Hou et al. (2009).

Figure 1 Geologic map of the Changbaishan area, Jilin Province, China. The figure includes a location map of China, a detailed geological map, a stratigraphic column, a fluid potential evolution diagram, and a photograph of the study site.

Geological Map: The map shows the distribution of various geological units (Q, Ns, E_j, E_g, k₂q, J_y, P₃y, P₃l, P₃z) and faults (Dongchuan, Luxiang, Chaluhe, Southwest tithospheric). Key locations marked include Xinanpu, Wanchang, Botai, and Gudianzi Slope. The map also indicates the migration direction of fluids and the formation boundaries.

Stratigraphic Column: The column lists the geological units and their corresponding descriptions and thicknesses (m).

Period Epoch	Formation	Lithology	Thick-ness (m)	Description	Hydroge-ological units
Pleistocene			80	alluvium	Cap
Pliocene			300	clay rock, sand-shale interbed	
Oligocene	O _q		600	muddy siltstone with lamina conglomeration	Cap
	O _w		190	thin sand-mud interbed	
Eocene	E _{2y}		210	muddy siltstone intercalated with siltstone and shale	Sandstone reservoir
	E _{2sh}		250	muddy siltstone intercalated with siltstone and shale	
	E _{2s}		310	muddy siltstone intercalated with mudstone	
			230	granite, albite-rich	
Permian?			600	speculate limestone	Deep reservoir?

Fluid Potential Evolution (0 Ma): The diagram shows the fluid potential contours (0.35, 0.6, 0.9) and the migration direction of fluids. The potential contours are labeled with values 0.35, 0.6, and 0.9. The migration direction is indicated by arrows.

Photograph: A photograph showing the study site, which is a wellhead or similar structure, with a red arrow pointing to the location of the study area on the geological map.

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11