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Distribution Characteristics and Enrichment Mechanism of Fluorine Icons in Geothermal Water in Beijing

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Abstract: Beijing boasts abundant geothermal resources, however, the exploitation of its subterranean hot water is often limited by significant levels of fluorine ions. To gain a better understanding of the distribution characteristics and enrichment mechanism of fluorine ions in the geothermal water surrounding Beijing, this study analyzed both normal and trace components of the geothermal water. The findings reveal that: 1) The concentration of fluorine ions in underground hot water in Beijing averages 8.59 mg/L, with Yanqing exhibiting the highest concentration and Miyun the lowest; 2) The hydrochemical types include HCO_3-Ca•Mg•Na type, SO_4-Na type, SO_4-Na•Ca type, Cl-Na type, SO_4•CO_3-Na type, and SO_4•Cl-Na type. Notably, the fluoride ion concentration is directly proportional to the pH value, which exerts some influence on the fluoride ion concentration. These findings have practical implications for preventing potential harm caused by excessive fluoride ions and guiding the development and exploitation of pertinent resources.

1. Introduction

As an emerging clean energy source, geothermal energy plays a critical role in adjusting the energy structure and protecting the environment, attracting increasing attention worldwide. [1-3]China boasts rich geothermal resources, including a vast reserve and extensive distribution, and Beijing is no exception.[4] However, the geothermal water in Beijing typically contains high levels of fluorine ions, exhibiting distinct distribution characteristics. Fluorine-rich geothermal resources have long been a research focus in China. Previous studies investigated the high-fluorine display of typical geothermal fields in Tibet and pointed out the impact of geothermal wastewater discharge. In Northern China, Ruoxi Yuan et al. examined the significance of fluorine indications in the medium-low temperature convection geothermal system in the northeast of Hebei Province.[5-9] However, few studies have focused on the content of fluoride ions in Beijing and its surrounding areas. This paper takes the underground hot water in Beijing as the research object, aiming to address the problem of high fluorine content in the underground hot water. By conducting data processing and analysis, this study reveals the distribution characteristics and enrichment mechanism of fluorine ions in the underground hot water in Beijing, which has practical implications for the development and utilization of geothermal resources in Beijing.

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2. Geological Settings

Beijing is situated on the northwest edge of the North China Plain, with the exception of certain areas in the southeast that are adjacent to Tianjin, while the other areas are adjacent to Hebei. It is surrounded by mountains to the east, west, and north, and slopes down into a plain to the southeast. Numerous rivers and artificial canals flow through Beijing, including the Yongding River and Chaobai River. The geographic coordinates of Beijing are E 115°25'~117°30' and N 39°28'~41°05'. The city's annual precipitation averages approximately 527.1mm.

Beijing is administratively divided into 16 districts (counties), including the urban area comprised of Dongcheng District and Xicheng District, the inner suburb consisting of Chaoyang District, Haidian District, Fengtai District, and Shijingshan District, and the outer suburb comprising Mentougou District, Fangshan District, Tongzhou District, Shunyi District, Daxing District, Pinggu District, Huairou District, Changping District, Miyun District, and Yanqing District. The total area of Beijing covers 16,800 km^2.

The geothermal resources in Beijing are primarily situated within the Beijing Plain, which encompasses the Yanqing Basin. The carbonate formation constitutes the primary thermal reservoir layer, while argillaceous carbonate rock and glutenite represent secondary thermal reservoirs. Among these reservoirs, the Jixian thermal reservoir is of significant value due to its extensive distribution and substantial thickness.

The geological strata in the Beijing area are classified from the most recent to the oldest as Quaternary (Q), which primarily consists of loose sediments. The Neogene (N) stratum consists mainly of argillaceous rock with sandy rock, while the Paleogene (E) stratum contains sandy mudstone, sandy gravel, basalt, and tuffaceous basalt in certain areas. The Cretaceous (K) stratum comprises mudstone and volcanic clastic rock, and the Jurassic (J) stratum includes andesite, tuff, and mudstone. The Permian-Triassic (C-P) stratum is composed of sandstone and shale, and the Ordovician-Cambrian (O-C) stratum primarily consists of dolomite and limestone. The Qingbaikou system (Qn) includes shale, sandstone, and marl, while the Jixian system (Jx), Tieling formation (Jxt), and Hongshuizhuang Formation (Jxh) contain dolomite, shale, and sandstone, respectively. The Wumishan Formation is primarily composed of dolomite. The Great Wall System (Ch) consists of sandstone, mudstone, shale, dolomite, and other rock types. Lastly, the Archean Miyun Group (Ar) comprises metamorphic rock.

The Beijing plain area is extensively covered by carbonate strata that have undergone multiple structural transformations, corrosion, and fissure and karst development. These carbonate formations provide an excellent storage space for groundwater. The Mesozoic-Cenozoic strata, with a thickness of hundreds of meters or even several kilometers, have been deposited on top of these carbonates, creating a relatively impervious and thermally insulating cover.

3. Data and Methods

This paper analyzes a total of 20 water samples collected from the Geothermal Records of China (Northeast and Northwest region of North China), which include 5 hot springs and 15 geothermal wells. The data were mainly concentrated in the urban area of Beijing and its surroundings. Basic statistical analysis, correlation coefficient analysis, and Gibbs chart analysis were performed on the collected data.

Table 1: Statistical results of physical parameters, major and minor elements concentration of geothermal water in Beijing

Parameter	Min	Median	Mean	Max	SD
T(°C)	20	45.5	46.378	97	16.23
pH	7.49	7.84	7.95	8.6	0.3378
TDS	332	588	949.62	6700	1341.78
Na^+	47.1	124	248.46	2330	483.01
K^+	0.82	4.1	31.18	66.1	20.42
Ca^{2+}	4.6	22	31.18	66.1	20.42
Mg^{2+}	0.2	9.1	11.01	26.7	8.70
HCO_3^-	29.3	268	384.57	3057	630.48
SO_4^{2-}	1.6	68	132.38	586	163.87
Cl^-	3.1	50	215.24	3380	727.03
F^-	1.4	6.95	8.59	19	4.65

4. Results and discussions

4.1. Spatial distribution characteristics of fluorine ions

The present study examined 20 sets of hydrochemical data obtained from underground water samples, comprising 5 sets of hot spring data and 15 sets of geothermal water data. The pH test results, as presented in Table 1, reveal that the pH value of groundwater in the study area ranges from 7.49 to 8.6, with an average value of 7.95. The pH values of all the water points are alkaline, with Yanqing recording the highest value of 8.6 and Shunyi recording the lowest value of 7.49.

The underground hot water wells (springs) in the study area exhibit temperatures ranging from 20 to 77 °C, with an average of 46 °C. The highest temperature is observed in Daxing, while the lowest temperature is recorded in Miyun. The distribution of hot water temperature tends to increase gradually from the northwest hilly area to the southeast plain area. Additionally, the water temperature in the area east of Junling Mountain is slightly lower than that in the area east of Xishan Mountain in the south.

The concentration of Total Dissolved Solids (TDS) in the tested area ranges from 332 mg/L to 6700 mg/L, with an average of 949 mg/L. The highest concentration of TDS is observed in Daxing, at 6700 mg/L, while the lowest concentration is recorded in Huairou, at 332 mg/L. From a spatial perspective, the concentration of TDS gradually increases from the suburbs of Beijing to the center of Beijing, influenced by human activities. Moreover, the low altitude area exhibits slightly lower TDS concentrations than the high-altitude area.

The hydrochemical types present in the groundwater of the study area include HCO_3-Ca•Mg•Na type, SO_4-Na type, SO_4-Na• Ca type, Cl-Na type, SO_4•CO_3-Na type, and SO_4•Cl-Na type. The dominant type is the HCO_3-Na type, followed by the SO_4-Na type. The pH value is directly proportional to the concentration of fluoride ions, indicating that the pH value affects the concentration of fluoride ions to some extent. According to the Gibbs distribution map, the groundwater in the sampling area is of rock weathering type or evaporation concentration type, and there is no precipitation infiltration type. Therefore, although there are a large number of rivers in Beijing and the annual precipitation is high, the groundwater receives limited recharge from oxygen-containing surface water due to evaporation concentration and low precipitation in the dry season. The groundwater is mostly in a reducing environment, which favors the enrichment of fluoride ions.

In summary, the fluorine ion concentration of underground hot water in Beijing is highest in Yanqing and lowest in Miyun, and the hydrochemical types and spatial distribution characteristics of fluoride ion, Ca^{2+}, and Mg^{2+} in the study area are closely related.

4.2. Hydrochemical characteristics

Based on the Shukalev classification rule, the hydrochemical types of groundwater in the study area include HCO_3-Ca•Mg•Na type, SO_4-Na type, SO_4-Na•Ca type, Cl-Na type, SO_4•CO_3-Na type, and SO_4•Cl-Na type. Among them, HCO_3-Na type is the dominant type, accounting for approximately 36.4%, followed by SO_4-Na type, which accounts for about 18.2% (Figure 1). The hydrochemistry in the Beijing area exhibits distinct zonal characteristics. Chaoyang, located in the urban area of Beijing with a flat terrain, mainly has HCO_3-Na type and HCO_3-Na•Ca type hydrochemistry. Huairou, Miyun, and other areas near Jundu Mountain have SO_4-Na type, HCO_3-Na type, and HCO_3•SO_4-Na type hydrochemistry, which fully reflects the recharge characteristics and frequent water replacement and exchange characteristics of groundwater in the piedmont area.

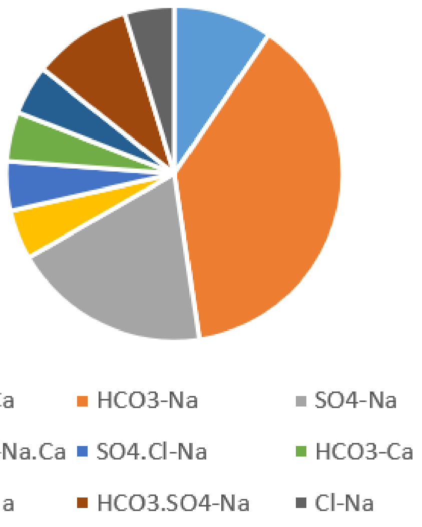

Figure 1: Geothermal water hydrochemical types in Beijing

4.3. Genesis analysis of fluorine ion

4.3.1. Effect of pH value on fluorine ion enrichment

Upon comparing the obtained pH values and fluoride ion concentrations, it was observed that areas with higher pH values, such as Yanqing, also exhibited higher fluorine ion concentrations. Conversely, areas with lower pH values exhibited lower fluoride ion concentrations, indicating that the pH value of the solution can affect the enrichment of fluoride ions to a certain extent. As the pH value increases, the concentration of OH^- also increases, thereby reducing the adsorption of F^- by the environment through competitive adsorption. For example, OH^- can replace the fluorine ion on the surface of fluorine-containing minerals, subsequently releasing F^- into the underground water and increasing the concentration of fluoride ions.

4.3.2. Effect of redox environment on fluorine ion enrichment

Additionally, the Gibbs distribution map (Figure 2) shows that the groundwater in the sampling area is predominantly of rock weathering type or evaporation concentration type, with no precipitation infiltration type. This indicates that despite the presence of numerous rivers in Beijing and the high annual precipitation, the groundwater is unlikely to receive significant recharge from oxygen-containing surface water. Instead, the groundwater in the region is largely influenced by evaporation concentration and the reduced amount of precipitation during the dry season, resulting in a reducing environment that is favorable for the enrichment of fluoride ions.

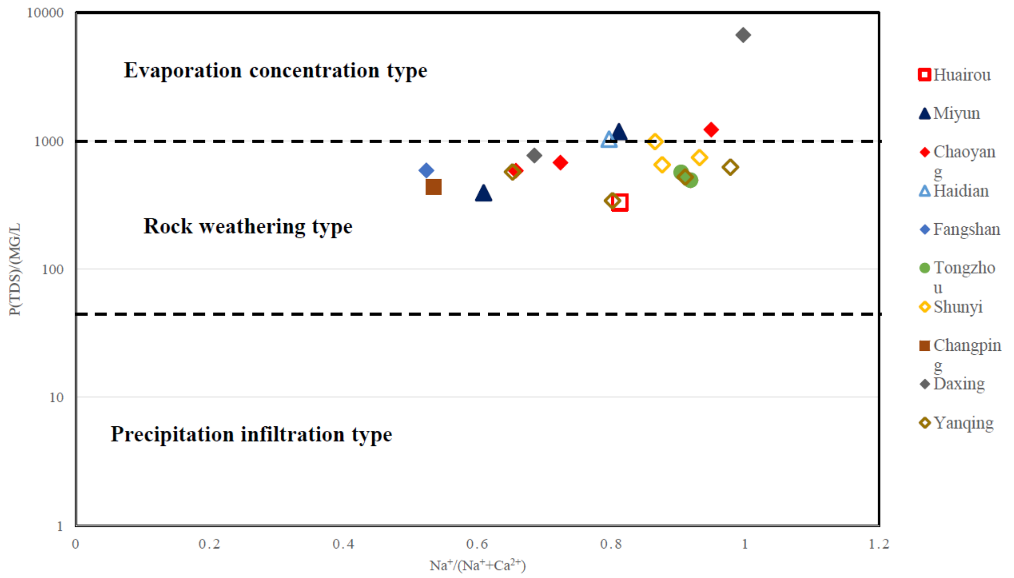

Figure 2: Gibbs distribution of TDS of the groundwater in the study area

5. Conclusions

In conclusion, the study found that the concentration of fluoride ions in underground hot water in Beijing ranges from 1.4mg/L to 19mg/L, with the highest concentration observed in Yanqing and the lowest in Miyun. The hydrochemical types identified in the groundwater include HCO_3-Ca•Mg•Na type, SO_4-Na type, SO_4-Na•Ca type, Cl-Na type, SO_4•CO_3-Na type, and SO_4•Cl-Na type, with the HCO_3-Na type being the dominant type, followed by the SO_4-Na type.

The fluoride-containing geothermal water in Beijing is primarily of rock weathering type or evaporative concentration type, as shown by the Gibbs distribution map. The study also found that the pH value of the water is directly proportional to the concentration of fluoride ions. Areas with higher pH values, such as Yanqing, exhibit higher concentrations of fluoride ions, while areas with lower pH values have lower concentrations of fluoride ions. This indicates that the pH value of the solution affects the enrichment of fluoride ions to a certain extent.

Overall, this study provides valuable insights into the hydrochemistry and fluoride distribution in groundwater in Beijing, which can be useful for managing and protecting water resources in the region.

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