

Oxygen and hydrogen stable isotopes as indicators of geothermal water recharge

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Abstract

Confined groundwater, unconfined groundwater and spring water were taken in the Guide basin, P.R. China. Chemical and isotopic characteristics of these water samples were investigated. Relatively higher temperature was observed in confined groundwater from deep aquifers than in unconfined groundwater from shallow aquifers. Both hot spring and cold springs occurred in the study area. Confined groundwater generally had relatively lower TDS with Cl-HCO₃-SO₄-Na water type than unconfined groundwater with HCO₃-Cl-SO₄-Ca-Na water type. $\delta^{18}\text{O}$ and δD of all samples mostly lay in or near the LMWL, indicating that precipitation was the major sources of groundwater in the basin. Geothermal waters were more depleted in ¹⁸O and D in relative to cold waters, suggesting that geothermal water had older ages and recharged from mountain ranges with higher altitudes. The recharge altitudes of geothermal water ranged between 2210 and 3270 m.

Introduction

Geothermal groundwater has been observed in deep aquifers of the Guide basin, which is believed to be the result of the high geothermal gradients (Lang et al., 2016). In the basin, confined groundwater had temperature between 18.5 and 41°C at depths between 200 and 600 m below land surface (bls), which is believed to be low temperature geothermal source (Fang et al., 2009). Most of geothermal wells are artesian, with the water heads between 9.5 and 32.9 m above the land surface (als) (Li et al., 2016). However, chemical characteristics and source of these confined groundwater are less understood, which are important for sustainable usage of these geothermal water. The major objectives of this abstract are to (1) investigate chemical and isotopic characteristics of confined groundwater and unconfined groundwater, and (2) evaluate source of geothermal water.

Methods

The Guide Basin is located between the Laxiwa Gorge and Songba Gorge on the upper reaches of the Yellow River in Qinghai Province (northwestern China), which is surrounded by mountains region composed of hardrock strata before tertiary periods. There are East River in the east, and West River in the west of the study area. Widely distributed Quaternary sandy gravel layers are aquifers hosting shallow groundwater, the middle Pliocene group, being composed of light grey mudstone, sandy mudstone and green gray sandstone at depths 310 m, hosts confined groundwater. Groundwater is recharged from the mountain ranges and flows from the south to the Yellow river in the south and from the north to the yellow river in the north. The Yellow River, which deeply incises the basin, is the discharge area for groundwater in the basin. The speculative reverse fault along the river could be the channel for discharge of confined groundwater.

In July 2015, forty-four groundwater samples were collected from various locations in the basin, including thirty unconfined water samples, nine confined water samples, and five spring water

samples (one hot spring water and four cold spring water) (Fig. 1). The unconfined water samples were collected at depths from 3 to 40 m, and confined water samples were taken at depths between 160 and 600 m.

During sampling, water temperature (T), EC, pH, TDS, and ORP were on-site monitored in an in-line flow cell using a multi-parameter portable meter (HI 9828, HANNA), which was calibrated using standard solution before use. Concentrations of S^{2-} , Fe(II), NO_2^- , and NH_4^+ of groundwaters were measured in the field using a portable spectrophotometer (DR2800, HACH). Alkalinity was measured with bromocresol green-methyl red indicator using a Model 16900 digital titrator (HACH). Prior to sampling, all samples were filtered through 0.22 μm membrane filters in the field. Samples for determining major cations and trace elements were collected in 125 mL polyethylene bottles and acidified to pH <1 by adding 6 M ultrapure HNO_3 . Samples for analyzing anions were not acidified. Groundwaters for analysis of hydrogen and oxygen isotopes were stored in polyethylene bottles without headspace. All groundwater samples were stored at 4°C and transported to the laboratory.

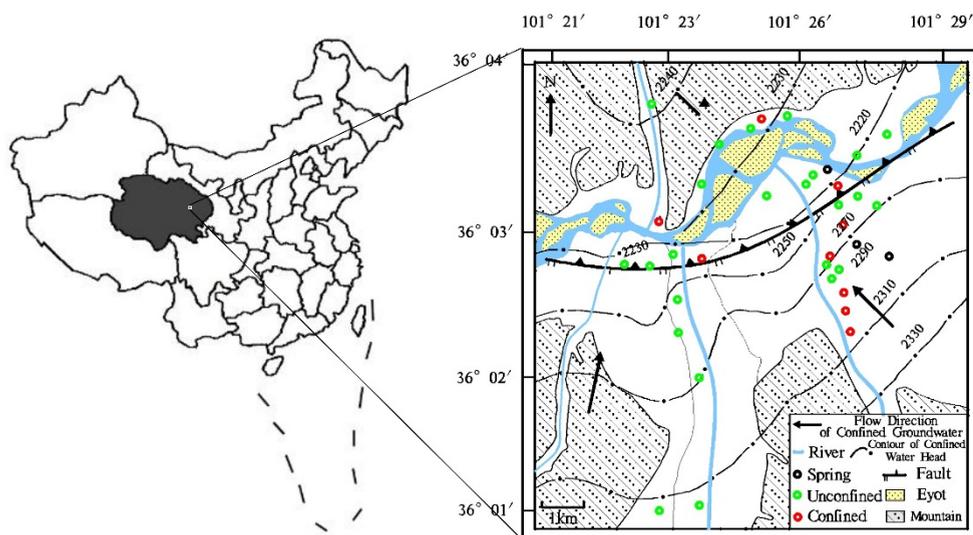


Fig. 1. Study area and locations of water sampling

Concentrations of major cations and trace elements were measured by ICP-AES (iCAP6300, Thermo) and ICP-MS (7500CE, Agilent), respectively. Concentrations of anions (including F^- , Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-}) were analyzed with an Ion Chromatography (DX-120, Dionex). For most water samples, analytical ion charge imbalances was less than 5%. Hydrogen and oxygen stable isotopes were determined using Picarro L2120-I analyzer. The isotopic ratios of D/H and $^{18}O/^{16}O$ are expressed relative to the Vienna Standard Mean Ocean Water international standard. Analytical precisions of $\delta^{18}O$ and δD were $\pm 0.1\text{‰}$ and $\pm 1\text{‰}$, respectively.

Results & Discussion

Water chemistry

Unconfined groundwater had pH between 7.1 and 8.0, while confined groundwater between 8.4 and 9.1. Higher temperature was observed for confined groundwater (with the range between 15.7 and

24.9°C; average 19.2°C) than unconfined groundwater (with the range between 10.0 and 13.8°C; average 11.8°C). Relatively higher TDS were observed in unconfined groundwater (262-1350 mg/L, average 622 mg/L) than confined groundwater (290-639 mg/L, average 451 mg/L). Confined groundwater were mainly of Cl-HCO₃-SO₄-Na type with Na⁺ as the dominant cation, and Cl⁻ and HCO₃⁻ as the predominant anions. The unconfined groundwater were mainly of HCO₃-Cl-SO₄-Ca-Na type, with Ca²⁺ as the dominant cation, and HCO₃⁻ and Cl⁻ as the predominant anions. Two kinds of springs were observed in the study area: hot spring and cold spring. Hot spring had temperature of 51.1°C, while average temperature of cold springs was 13.1°C. Chemical characteristics of cold springs were quite similar to unconfined groundwater, indicating recharge of shallow groundwater. Hot spring was plotted near confined groundwater in the piper plot, showing the connection between hot spring and confined groundwater (Fig. 2).

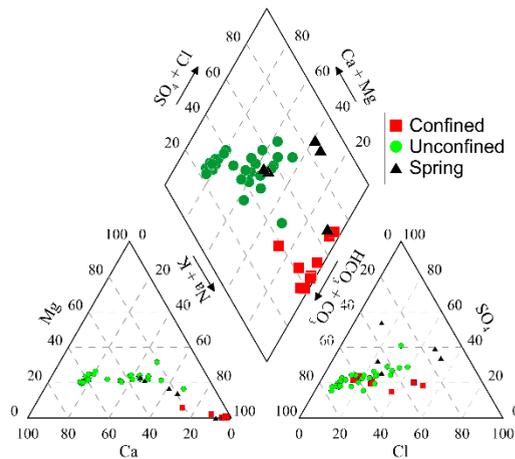


Fig. 2. Piper plots of confined groundwater, unconfined groundwater and spring water

Hydrogen and oxygen isotopes

Confined groundwater were more depleted in ¹⁸O and D than shallow groundwater. δ¹⁸O of confined groundwater ranged between -12.3 and -11.0‰ (average -11.7‰), and δD between -86.6 and -75.8‰ (average -81.7‰), which are lower than those unconfined groundwater (δ¹⁸O: -10.8 to -7.6‰, average -9.3‰; δD: -78.9 to -51.1‰, average -63.7‰). Hot spring had lower δ¹⁸O and δD in relative to confined groundwater. δ¹⁸O and δD of cold spring water were around the averages of unconfined groundwater.

All samples lay in or near the LMWL (Fig. 3), which indicates that precipitation was the major sources of groundwater in the basin. However, the wide range in δ¹⁸O and δD values reflects various recharge processes. Unconfined groundwater and cold springs had similar δ¹⁸O and δD to river water (Wu et al., 2014), showing that unconfined aquifer was directly recharged by river. Confined water samples and hot spring were more depleted in ¹⁸O and D, which indicates that confined groundwater had older ages and was recharged from mountain ranges with higher altitudes (Guo et al., 2014). It indicated that confined groundwater and hot spring underwent long-distance circulation (Tan et al., 2014; Qin et al., 2005).

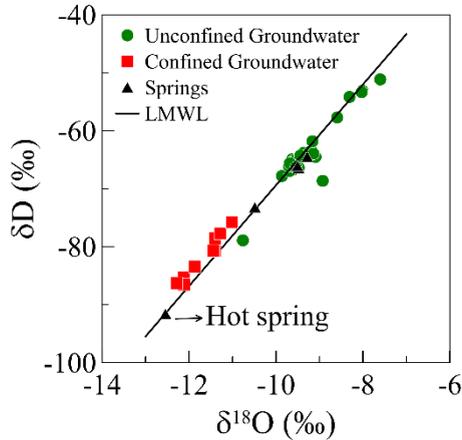


Fig. 3. $\delta^{18}\text{O}$ versus δD in confined groundwater, unconfined groundwater and spring water

Relationship between water temperature and isotopes

A good correlation between water temperature and δD (or $\delta^{18}\text{O}$) was observed (Fig. 4), indicating that groundwater depleted in ^{18}O and D generally had high temperature. This observation is consistent with those in Tibetan plateau (Tan et al., 2014). The depletion can be attributed to the deep circulation of hot spring and geothermal groundwater within geothermal reservoirs (Fusari et al., 2017). According to the altitude effect on ^{18}O (Clark & Fritz, 1997), the recharge elevation of hot spring and confined groundwater can be calculated. For ^{18}O , the depletion was -0.36‰ per 100 m rise in altitude in the study area (Li, 2015). Results showed that recharge altitudes of confined groundwater ranged between 2210 and 2290 m, while that of the hot spring was 3270 m. The highest altitude of the mountains to the south of the study area is around 5011 m. After recharged from high altitude areas, groundwater was heated along the flow path due to the high geothermal gradient (around $7^\circ\text{C}/100\text{ m}$, Lang et al., 2016). No apparent ^{18}O shift was observed in both confined groundwater and hot spring water (Fig. 3), possibly due to short residence time in deep reservoirs (Tan et al., 2014). The short residence time of confined groundwater would be the cause of the relatively lower TDS of geothermal water than shallow groundwater and cold springs.

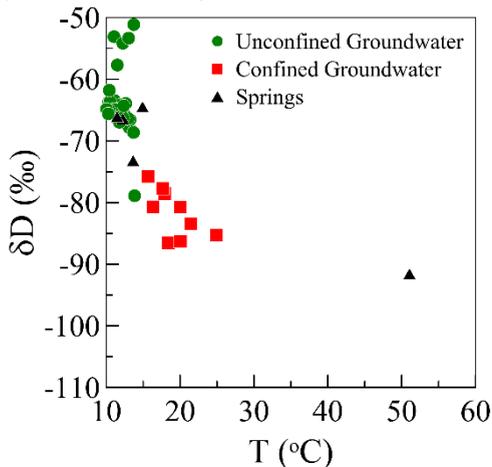


Fig. 4. Temperature versus δD in confined groundwater, unconfined groundwater and spring water

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