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Hydrochemical characteristics and geothermometry applications of thermal groundwater in northern Jinan, Shandong, China



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ABSTRACT

Carbonate rock thermal reservoirs are important geothermal resources but lack systematical study on a regional scale. This paper integrated hydrochemical and isotopic data to outline thermal water resources in carbonate rock aquifers as part of deep regional groundwater flow system. Hydrochemical characteristics of thermal groundwater in northern Jinan geothermal field, where Ordovician carbonate rocks are the main thermal reservoir, were examined and characterized by SO₄-Ca, SO₄-Ca·Na, SO₄·Cl-Ca·Na and Cl-SO₄-Na-Ca types. Hydrochemical evolution was revealed by analyzing correlation between different chemical constituents and their relative changes in various waters, Isotopic data allowed the origin of thermal water to be determined and presented different recharge elevations. Thermal groundwater was originated from precipitation in the northern piedmont of Tai Mountain with elevation of 708–1493 m.a.s.l.. Reservoir temperature was estimated by chemical geothermometry and validated by fluid-mineral equilibria calculations. The feasibility of different geothermometers was verified, indicating that quartz geothermometers were more suitable for the geothermal system and yielded reservoir temperatures of 60-80 °C. Finally, a conceptual hydrogeological model of the geothermal field was proposed: thermal groundwater was derived from regional flow system with high recharge areas, deep circulation depth and slow flow velocities, confirmed by its depleted stable isotopic contents, high chloride and TDS concentrations and long residence time. The improved understanding of this geothermal system is fundamental for the better management of this karst geothermal resource.

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1. Introduction

Deep carbonate rock aquifers, most of which are to some degree karstified, are probably the most important thermal water resources outside volcanic areas (Goldscheider et al., 2010). For example, both the European largest and second-largest thermal and mineral springs, in Budapest, Hungary (Erőss et al., 2012) and Stuttgart, Germany (Goldscheider, 2008), respectively, are discharging from carbonate rocks, as is the thermal water system in northern Jinan, China in this study. While many publications deal with fresh or drinking water from karst aquifers, few available studies systematically investigated the role of carbonate rock aquifers as thermal water resources and the possible use of these aquifers for geothermal energy production.

Groundwater circulation at different scales can be understood within a conceptual framework of hierarchical flow systems, consisting of local, intermediate, and regional flow systems (Tóth, 2009a). Thermal water resources in continental carbonate aquifers outside volcanic zones are related to deep, regional flow systems, characterized by cross-formational hydraulic continuity (Frumkin and Gvirtzman, 2006; Tóth, 1995). Given the strong geological heterogeneity generated by the karst system in which fractures and conduits are often developed and hard to quantify, conventional hydrogeological investigation and numerical model of groundwater flow are difficult to provide a primary sound hydrogeological description (Lauber and Goldscheider, 2014; Pavlovskiy and Selle, 2015). In such cases, a multiparametric approach integrating hydrochemical and isotopic data is always useful to diagnose the groundwater flow system (Pavlovskiy and Selle, 2015; Wang et al., 2013).

Subsurface thermal reservoir temperature, as a crucial parameter in evaluating the potential of a geothermal field to be utilized

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as a possible source of energy, can be estimated by chemical geothermometers (Fournier, 1977; Giggenbach, 1988; Verma and Santoyo, 1997). But different geothermometers have strict apply conditions, so special attention should be paid when using them. The results of these chemical geothermometers can be validated by applying multicomponent chemical equilibria calculations in thermal water. Some secondary processes (e.g., mineral re-equilibrium, mixing and boiling) during the ascent of thermal water can also be ascertained by this approach (Gemici and Tarcan, 2002; Pang and Reed, 1998; Tarcan and Gemici, 2003).

The present study was conducted in northern Jinan geothermal field, where Ordovician carbonate rocks are the main thermal reservoir. Since the 1970s, geothermal resources in this area have been gradually explored and exploited. Some previous studies related to hydrogeological issues in this area mainly focused on the geological structure of the geothermal field, using geophysical method, to assist geothermal exploration (Li et al., 2005; Sui et al., 2013). But few, if any, researches are conducted to study the formation and evolution of geothermal water from a viewpoint of regional groundwater flow system.

The main objective of this study was to outline thermal water resources in carbonate rock aquifers as part of deep regional groundwater flow system. Within this context, this paper presented hydrochemical and isotopic characterization of thermal groundwater in northern Jinan geothermal field with emphasis on: (1) thermal reservoir temperature, based on chemical geothermometry and mineral saturation indices; (2) regional hydrogeological conceptual model. The feasibility of different temperature estimation methods was verified, which may provide references when applying them to other similar geothermal systems. Groundwater system in a regional scale proposed in this paper can help understand thermal water origin and evolution in the geothermal system, which is fundamental for the better management of this karst geothermal resource.

2. Geological setting

The geothermal field is located in the deep through flow zone of Jinan karst aquifer system (Fig. 1), which is a monoclinic structure and gradually lowered in elevation from south to north: from mountainous and hilly land to a piedmont inclined plain and to the Yellow River alluvial plain. The study area lies between longitudes 116°45′ to 117°20′E and latitudes 36°40′ to 37°00′N, with an area of 1800 Km² and an average annual precipitation of 673 mm.

Ordovician carbonate rocks with strong water yield property are the main thermal reservoir in this area. It is composed by thick-bedded limestone, argillaceous limestone and dolomitic limestone, and outcrops in the mountain areas to the south with dip direction of NE20° and dip angle ranging from 5 to 10° (Kang et al., 2011).

Faults which can act as channels for convective circulation of hydrothermal fluids are well developed in the study area. Thick cap rocks (194–2500 m thickness; Sui et al., 2013) above Ordovician carbonate rocks, consisting of Quaternary, Neogene, Permian and Carboniferous strata, are good thermal insulation layers for the geothermal field. Archean metamorphic rocks and Cambrian interbeds of limestone and shale constitute the basement below Ordovician strata. Igneous rocks (diorite and gabbro), which formed in the Mesozoic Yanshan Orogeny, are distributed in the south of geothermal field.

As shown in Fig. 1, karst groundwater is generally flowing from south to north, basically coinciding with the dip direction of strata and topography. The impermeable Mesozoic igneous rocks resist large amount of cold groundwater to move to the geothermal field, which would cool down the thermal groundwater. Consequently, the geological setting creates favorable conditions for the forma-

tion of thermal groundwater in this area. The temperature of water extracted from the geothermal field ranges from 30 to 60 $^{\circ}$ C, classified as low to medium temperature.

3. Sampling and analysis

Water samples were collected from wells in the study area during three site visits in 2013, including 10 thermal samples and 4 non-thermal samples. The non-thermal water flows from Ordovician carbonate aquifer except one (sample No. DW1) from igneous fractured aquifer and were selected to represent upstream of thermal groundwater and for comparison as well. Three additional thermal groundwater were also included in this study and their chemical analysis results were cited from previous study (Li et al., 2005; Sui et al., 2013) since they were unaccessible for sampling. The sampling locations and information of geothermal wells were shown and listed in Fig. 1 and Table 1, respectively.

Temperature, pH and electrical conductivity (EC) were measured in the field using portable pH and EC meters (HACH HQ40d) that had been calibrated beforehand, while alkalinity was determined by titration with 0.05 mol/L HCl on the day of sampling. Water samples were filtered on site through 0.45 µm membranes prior to collection in pre-washed polyethylene bottles. Samples for cation and trace element analysis were acidified (with ultrapure HNO₃ to pH < 2). Anions (SO₄, Cl, F) were determined using ion chromatography (Dionex ICS-1100), while cations (K, Na, Ca, Mg) and minor elements (e.g., Sr, B, Li) were determined by ICP-OES (Thermo Fisher ICAP-6300) in the Environmental Chemistry Laboratory of School of Environmental Studies, China University of Geosciences (Wuhan) within two weeks of sampling. Charge balance errors of water samples were generally less than 5% which is within the limits of acceptability. The stable isotope compositions (²H and ¹⁸O) in water samples were measured by LGR IWA-35-EP in the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences (Wuhan). δ^2 H and δ^{18} O values were referred to VSMOW (Vienna Standard Mean Ocean Water) and reported in the conventional δ (%) notation, with precisions of \pm 0.6 and \pm 0.2%, respectively.

 14 C activities of dissolved inorganic carbon (DIC) were measured radiometrically by liquid scintillation spectrometer (PE 1220 QUANTULUS) after conversion to benzene in the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, to determine the residence time of thermal groundwater. 14 C results were given in the standard notation as percent modern carbon (PMC). Radiocarbon ages were calculated using a 5730-year half-life of 14 C and expressed in years BP (before present), where 1950 is taken as the starting year. Greater accuracy in the age estimates could possibly be attained by using a correction scheme for matrix carbon (e.g., Clark and Fritz, 1997). However, δ^{13} C contents were not measured, and given that absolute age determinations were not critical to the aims of this study, the uncorrected 14 C ages may provide reasonable enough residence time estimates of thermal groundwater.

4. Results and discussion

4.1. Hydrochemical characteristics of thermal groundwater

The chemical analysis results of water samples from northern Jinan geothermal field were presented in Table 2. As shown in the Piper diagram (Fig. 2), thermal groundwater sampled in the same region had similar hydrochemical characteristics, reflecting local variations in geological conditions and hydrochemical processes governed the quality of groundwater.

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