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Characteristics of rare earth elements of geothermal water from Fengshun-Tangkeng geothermal field and its affecting factors

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ABSTRACT

Geothermal resources and multi-phases granites are widely developed in igneous rock regions of South China and they have close relationships. Studies on differentiation properties and enrichment mechanism of rare earth elements (REE) of granite rock have been done a lot while that for geothermal water is seldom. Taking Fengshun-Tangkeng geothermal field as the study area, this paper discusses properties and species of REE of geothermal water and its affecting factors. Results show that geothermal water has lower REE content of 0.020-0.204 μg/L comparing with shallow groundwater and Rongjiang River water, average concentrations of which are 0.275 μg/L and 0.183 μg/L, respectively and it is enriched by MREE. It exhibits REE distribution pattern of positive Eu anomaly and negative Ce anomaly with reference to PAAS, which are caused by silicate minerals dissolution of parent rock under alkaline conditions. REE content show positive correlations with pH and also its species are controlled by pH. Calculations by PHREEQC indicate that inorganic species of REE in alkaline geothermal water are dominated by bicarbonate complex of $Ln(CO_3)^{2-}$ and monocarbonate complex of $LnCO_3^{+}$ with minor content of LnF^{2+} and Ln^{3+} (Ln refers to REE). Total proportions of $Ln(CO_3)^{2-}$ and $LnCO_3^{+}$ can exceed 95%. In contrast, REE species in neutral Rongjiang River water and slightly acid shallow groundwater are mainly composed of $LnCO_3^{+}$ and Ln^{3+} with certain content of $LnSO_4^{+}$, respectively, average proportions of $LnCO_3^{+}$ can be up to 86.8%. Besides, with increase of atomic number, concentrations of Ln^{3+} complex decrease until becoming 0.

1. INTRODUCTION

Rare earth elements (REE) are a group of trace elements with very similar physical and chemical properties located in the third subfamily of the periodic table of elements. They are lanthanide elements with atomic number 57-71 and yttrium (Y) and scandium (Sc) closely related to lanthanide. There are often used to identify magmatic melting process, mantle evolution, sedimentary evolution mechanism and weathering process and main sources are carbonate rocks and alkaline igneous rocks (Liu, 2018; Verplanck et al., 2014). The study of REE in groundwater began in the 1980s and its concentration is related to the rock and soil flowing through. At present, it is mainly used in water-rock interaction process, mixing process and redox environment tracing (Francis et al., 2020; Wang et al.2021).

For the surface water system, the differentiation of REE is mainly controlled by two mechanisms, (1) pH-induced changes in the stability of water-soluble organic or anaerobic complexes and (2) heavy REE preferentially adsorbs to the hydroxides of Fe or Mn at low pH (Larsen et al., 2021). In addition, temperature has a significant effect on REE differentiation, and Eu and Ce anomalies are related to the abundance in surrounding rocks, mixing and water-rock interactions (Fiket et al., 2015; Temizel et al., 2020). REE and Eu anomaly of geothermal water in Tengchong area are mainly controlled by surrounding rock properties while Ce anomaly is related to oxidation process or precipitation and adsorption of Fe hydroxide, and pH controls the distribution of REE inorganic forms (Wang et al., 2020). Generally, the content and characteristics of REE in water are mainly controlled by the water-rock interactions and the adsorption-desorption of hydroxides such as Fe and Mn.

Multi-stage granites and abundant geothermal resources are widely developed in the igneous rock areas of South China. REE in granite and its weathering zones is high. Previous studies mainly focus on the REE differentiation and enrichment mechanisms, e.g., some rare earth ore in South China is controlled by the leaching of REE-bearing minerals in the vadose zone and the adsorption of REE ions in the saturated zone with high pH and relatively stable environment (Wu et al., 2003; Huang et al., 2021). But there are few studies on REE content, differentiation characteristics and formation mechanism of geothermal water. In this paper, we take Tangkeng geothermal field as the study area where the first low-medium temperature geothermal power station in China established, to carry out studied on properties, sources and forms of inorganic REE in geothermal water and their indicative significances based on hydrochemical and geochemical simulation methods.

2. GEOLOGICAL SETTINGS OF THE STUDY AREA

The TangKeng geothermal field is located in eastern Guangdong Province (Fig.1a). Only Mesozoic and Cenozoic strata are outcropped, especially Quaternary sediments and Mesozoic igneous rocks (Fig.1b). Quaternary sediments are mainly distributed on both sides of the RongJiang River and its tributaries in forms of fluvial alluvial deposits. The Mesozoic Jurassic strata are widely distributed, including rhyolite-andesite-andesite erupted from continental volcanic rocks, which are composed of acidic-neutral lava, volcanic clastic rocks and a small amount of sedimentary rock interlayers with total thickness greater than 3358 m (Li, 2017).

Faults are controlled by the Neocathaysian system and mainly are NE, EW and NW orientations (Fig.1b). Related deep faults include the NE-trending Lianhuashan fault, the EW-trending Fogang-Fengliang fault and the NW-trending Xingning-Shantou fault (Luo, 2020). Due to the strong extrusion, the granite body in the area was strongly schistoseized resulting in crushed rock and developed joints.

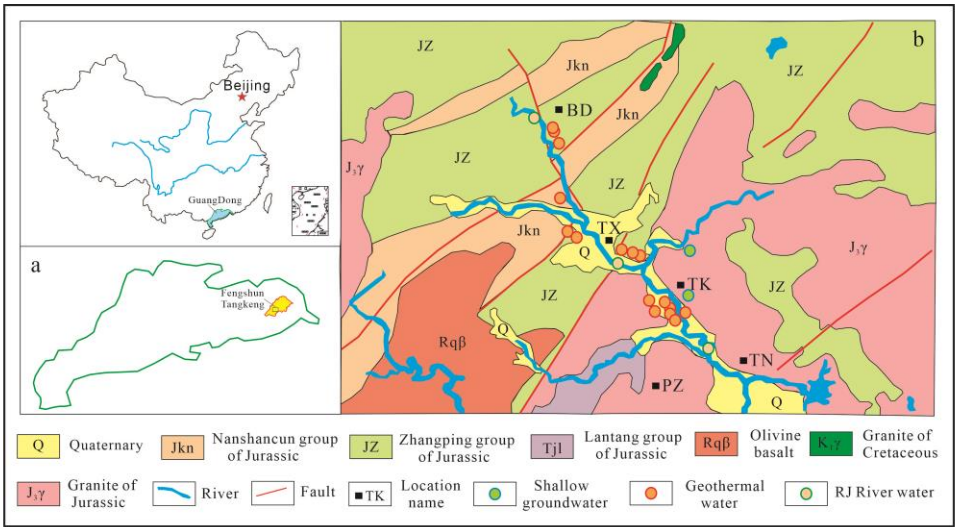

Figure 1 Geological settings of Fengshun Tangkeng geothermal field，a-location of the study area; b-geological settings and sampling locations

3. SAMPLING AND ANALYSIS

A total of 17 geothermal water samples, 2 shallow groundwater samples and 3 RongJiang river water samples were collected in 2020 in Feng Shun area of Guangdong province. Locations of samples were shown in Fig.1. Sampling temperature of geothermal water is 35 - 94 °C, with an average value of 63.8 °C. Surface water was collected from the upper, middle and lower reaches of the RongJiang River and shallow groundwater was collected from the cold spring in Dongxiu village and well in Datongpan village.

All the samples were collected in high density polyethylene plastic bottles (HDPE) which were washed three times before collection. For samples from wells, they were not collected until the well was pumped continuously for at least 20 min. pH, temperature, conductivity, redox potential, sulfide content and ferrous ion content of water samples were measured in situ. Samples for REE analysis were first filtered by 0.45 μm membrane and then acidified to pH <2 by adding 6N ultrapure HNO_3 solution. REE were analyzed at the analysis and testing center of Beijing Institute of Geology using ICP-MS. The analytical accuracy and detection limit were ±0.5% and 2 ng/L respectively. In addition, samples for water chemistry and isotopic analysis were also collected and tested (Luo et al., 2022).

4. RESULTS

4.1 REE concentrations in different water bodies

Statistical characteristics of REE concentration in geothermal water are shown in Fig.2. The total REE concentration (ΣREE) is 20-204 ng/Land the average value is 73 ng/L. The content of Eu is higher than that of other elements. The range of ΣREE of RongJiang River water was 131-264 ng/L and the contents of La and Eu were relatively higher. The ΣREE of shallow groundwater were 64 and 275 ng/L, respectively. ΣREE in groundwater from well that close to Rongjiang River is similar to that from lower Rongjiang River. It can be seen that the ΣREE of geothermal water is significantly lower than that of RongJiang River water, indicating difference in the source and main forms of REE.

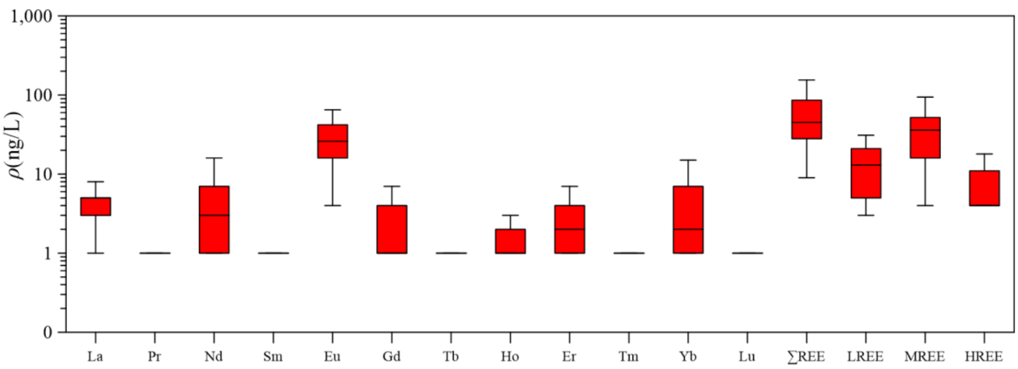

Figure 2 REE concentrations in geothermal water of Tangkeng area

4.2 Standardized distribution of REE

Generally, the concentration of REE needs to be standardized to eliminate the odd-even effect when mapping. In this paper, PAAS model is selected and results were shown in Fig.3. It is found that REE in all the three types of water showing a consistent right leaning distribution pattern while REE in granite shows a relatively smooth pattern. In addition, typical differentiation parameters of REE include Eu anomaly index (Eu/Eu*), Ce anomaly index (Ce/Ce*), (La/Sm) standard, (Gd/Yb) standard, (Yb/Nd) standard and (Gd /Nd) standard. (La/Sm) standard of geothermal water is 0.2- 2.2 with an average of 0.6; (Gd /Nd) value was 1.8 -29.1 with an average of 6.2; (Yb / Nd) value was 2.8- 96.2 with an average of 17.4. The Eu anomaly index and Ce anomaly index were 18.8 - 197 and 0.1-1.1, respectively while that of granite were 0.1-0.4 and 1.0, respectively.

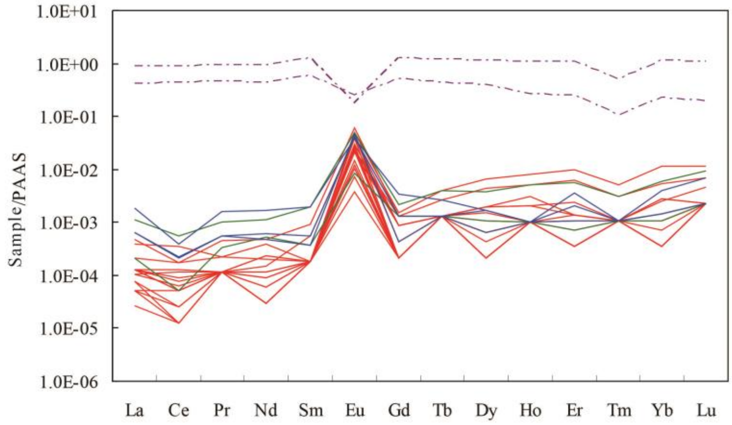

Figure 3 Standardized distribution patterns of REE in different water bodies (red-geothermal water, blue-Rongjiang river water, green-shallow groundwater, purple dotted line-Local granite)

5. DISCUSSIONS

5.1 Sources and dominant forms of REE

Previous studies show that REE in groundwater are usually derived from the chemical weathering and dissolution of rock minerals. (Yb/Nd)p of geothermal water is greater than 1 and most of the samples locate in the heavy REE enrichment area (Fig.4(a) and 4(b)). Ce/Ce* shows negative anomaly while Eu/Eu* shows positive anomaly. REE of geothermal water is resulted from dissolution of silicate minerals in alkaline fluid, showing MREE enrichment with Eu positive anomaly and Ce negative anomaly pattern. As investigated, geothermal reservoir is mainly composed by microcline, quartz, plagioclase and biotite with seldom amount of hornblende and pyroxene but its Ce shows no anomaly. Field analysis of ORP of most geothermal water indicates oxidation environment but there was no significant correlation between ORP and Ce/Ce * (Fig.4 (c)). However, Ce is in forms of insoluble CeO_2 in oxidation conditions or in water with pH of 5.0-8.5 and will precipitate on the wreathing zones, leading to the negative Ce anomaly in geothermal water. Therefore, negative Ce anomaly in geothermal water is mainly affected by dissolution of primary rock limited by pH and oxidation-reduction. All the water show obvious positive Eu anomalies, while granite thermal storage shows negative Eu anomalies. As showed in Fig.4 (d), Eu/Eu* value positively correlated with ORP. Since geothermal water occurs in the granite reservoir, the positive Eu anomaly is mainly related to the dissolution process and oxidation reduction of feldspar minerals.

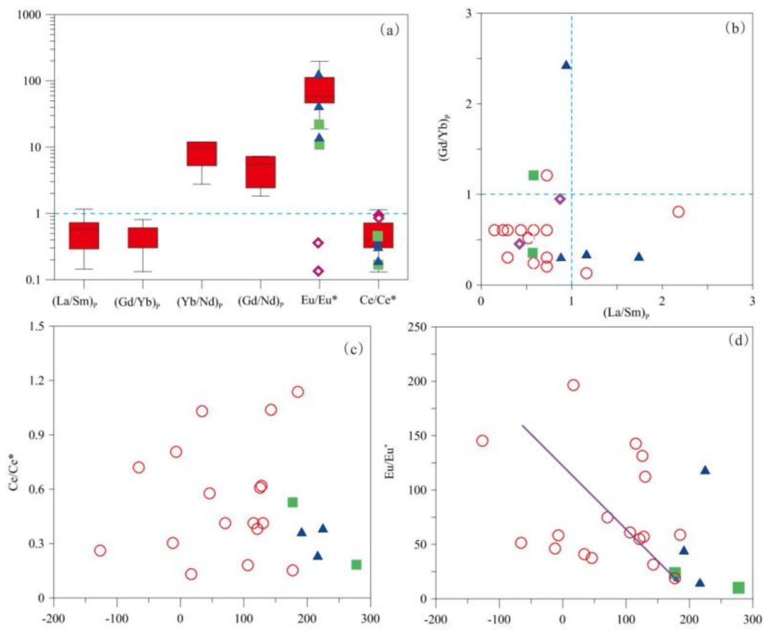

Figure 4 Statistics of typical differential parameters of geothermal water （red circle-geothermal water; blue triangle-RJ River water; green square-shallow groundwater; purple diamond-Granite）

Geochemical simulations by PHREEQC indicate that inorganic forms of REE in geothermal water, shallow groundwater and Rongjiang River water are significantly different. The main inorganic forms of REE in geothermal water are dicarbonate complex Ln $(CO_3)^{2-}$ and monocarbonate complex $LnCO_3^+$ with small amount of LnF^{2+} and Ln^{3+} (Ln is REE). Ln $(CO_3)^{2-}$ of most of the elements takes more than 50% and for Er, Dy, Gd, Ho, Pr, Sm, Tb, Tm and Yb, it exceeds 70%. $LnCO_3^+$ takes 10.9-49.4 % of the total, indicating it was mainly controlled by HCO_3^- and CO_3^{2-}. Main forms of Eu are $EuOHCO_3$, EuOH $(CO_3)_2^{2-}$ and Eu $(OH)_2CO_3^-$. Inorganic forms of REE in Rongjiang River water are mainly $LnCO_3^+$ with small amount of Ln $(CO_3)^{2-}$ and Ln^{3+}. Inorganic forms of REE in shallow groundwater are mainly $LnCO_3^+$ and $Ln^{3+}$with small amount of LnF_2^+, Ln $(CO_3)^{2-}$, $LnSO_4^+$ and $LnOH^+$.

5.2 Analysis of influencing factors on REE

Concentrations of REE of geothermal water with higher pH is lower than that of RongJiang River water and shallow groundwater with lower pH value (Fig.5 (a)) and this is because weathering of REE is more easily occurring in lower pH conditions. Datongpan Village is located in the middle reaches of the RongJiang River and the pH value of shallow groundwater is 6.3 and the REE concentration is the highest. Geothermal water is slightly alkaline with pH higher than 8.0 and dissolved REE are mainly in forms of Ln $(CO_3)^{2-}$ and $LnCO_3^+$. The RongJiang River water is relatively neutral (pH = 7.5) and REE concentration is higher than that of geothermal water and main form is $LnCO_3^+$ which takes more than 70 % of the total. For acidic shallow groundwater with the lowest pH, it has the highest REE concentration and with the increase of atomic number, concentration of Ln^{3+} decreases while $LnCO_3^+$ and LnF^{2+} increase.

Generally, REE concentration in water is negative with pH. For alkaline fluid like geothermal water, REE is mainly in forms of Ln $(CO_3)^{2-}$ and $LnCO_3^+$ while that in neutral fluid is mainly in forms of $LnCO_3^+$. REE in acidic fluid like shallow groundwater is mainly in forms of Ln^{3+} with certain amount of $LnSO_4$. Besides, concentrations of complex Ln^{3+} gradually decreases to disappear with the increase of atomic number.

Anion of all the samples is mainly HCO_3^- and it is significantly higher in geothermal water than that in RongJiang River water and shallow groundwater but it has much lower REE concentration. For RongJiang River water and shallow groundwater, the HCO_3^- content was low but REE concentration is relatively high. Generally, REE in samples with higher HCO_3^- content are more likely to exist in the form of Ln $(CO_3)^{2-}$. Taking geothermal water as example, more than 40% of the inorganic forms of REE is Ln $(CO_3)^{2-}$ and with the increase of atomic number, the proportion increases. In contrast, REE proportions in RongJiang River water and shallow groundwater show negative correlations with HCO_3^-.

6. CONCLUSIONS

The REE concentrations and inorganic forms in different water bodies of Tangkeng geothermal field in Fengshun area are significantly different. Comparing with RongJiang River water and shallow groundwater, REE of geothermal water is much lower which is resulted from silicate minerals dissolution in alkaline fluid and it shows characteristics of enrichment of middle REE, Eu positive anomaly and Ce negative anomaly.

Inorganic forms of REE of geothermal water are mainly dicarbonate complex Ln $(CO_3)^{2-}$ and monocarbonate complex $LnCO_3^+$. With the increase of HCO_3^-, concentrations of Ln $(CO_3)^{2-}$ decreases but $LnCO_3^+$ increases. REE with larger atomic number has higher concentrations of Ln $(CO_3)^{2-}$. RongJiang River water is dominated by $LnCO_3^+$ with small amount of Ln $(CO_3)^{2-}$ while shallow groundwater is dominated by $LnCO_3^+$ or Ln^{3+} and contains an appropriate amount of LnF^{2+} and $LnSO_4^+$ complexes.

REE concentration was positively correlated with pH. REE in alkaline and neutral fluid are dominated by Ln $(CO_3)^{2-}$ & $LnCO_3^+$ and $LnCO_3^+$ respectively while that in acidic fluid are dominated by Ln^{3+} but with certain amount of $LnSO_4^+$. For neutral-acidic fluid, concentration of complex Ln3+ decrease to 0 with the increase of atomic number.

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