



## Geochemical behaviors of rare earth elements in groundwater along a flow path in the North China Plain



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### ABSTRACT

Rare earth element (REE) geochemistry is a useful tool in delineating hydrogeochemical processes and tracing solute transport, which can be used to reveal groundwater chemical evolution in the complexed groundwater systems of the North China Plain (NCP). Groundwaters and sediments were collected approximately along a flow path in shallow and deep aquifers of the NCP to investigate REE geochemistry as a function of distance from the recharge zone. Groundwater REE concentrations are relatively low, with ranges from 81.2 to 163.6 ng/L in shallow groundwaters, and from 65.2 to 133.7 ng/L in deep groundwaters. Speciation calculation suggests that dissolved REEs mainly occur as dicarbonato ( $\text{Ln}(\text{CO}_3)_2$ ) and carbonato ( $\text{LnCO}_3^+$ ) complexes. Although along the flow path groundwater REE concentrations do not vary substantially, relatively lower HREEs are observed in central plain (Zone II) compared to recharge area (Zone I) and discharge plain (Zone III). Shale-normalized REE patterns are characterized by different degrees of enrichment in the HREEs, as indicated by the variation in average  $(\text{Er}/\text{Nd})_{\text{NASC}}$  value. The similar REE compositions and shale-normalized REE patterns of shallow and deep groundwaters demonstrate that interactions of groundwaters between shallow and deep aquifers possibly occur, which is likely due to the long-term groundwater over-exploration. Cerium anomalies ( $\text{Ce}/\text{Ce}^* = \text{Ce}_{\text{NASC}}/(\text{La}_{\text{NASC}} \times \text{Pr}_{\text{NASC}})^{0.5}$ ) generally increase from Zone I, through Zone II, to Zone III, with trends from 0.79 to 3.58, and from 1.22 to 2.43 in shallow groundwaters and deep groundwaters, respectively. This is consistent with the variations in oxidation–reduction potential and redox sensitive components (i.e., dissolved Fe, Mn,  $\text{NO}_3^-$  and As concentrations) along the flow path. Positive Ce anomaly and redox indicators suggest that redox conditions progressively evolve from oxic to moderate anaerobic in the direction of groundwater flow. In the recharge zone (Zone I), groundwater low positive Ce anomalies are likely due to partially oxidative scavenging of Ce(III) to Ce(IV), and HREE enrichment would result from preferential scavenging of the LREEs relative to the HREEs during Fe/Mn oxides/oxyhydroxides precipitations, which is well supported by the low concentrations of dissolved Fe and Mn. In the down-gradient (Zone II and Zone III), reductive dissolution of Fe/Mn oxides/oxyhydroxides increases positive Ce anomalies along the flow path. The positive correlations between  $(\text{Er}/\text{Nd})_{\text{NASC}}$  values and dissolved Fe/Mn concentrations suggest that reductive dissolution of Fe/Mn oxides/oxyhydroxides, as well as read-sorption, are the geochemical controls on groundwater REE fractionation patterns. Groundwaters mostly have positive Eu anomalies ( $\text{Eu}/\text{Eu}^* = \text{Eu}_{\text{NASC}}/(\text{Sm}_{\text{NASC}} \times \text{Gd}_{\text{NASC}})^{0.5}$ ), which would be the result of chemical weathering of feldspars (e.g., plagioclase) detected in aquifer sediments by XRD technique.

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### 1. Introduction

The North China Plain (NCP) is the largest alluvial plain in eastern Asia with serious water shortage problems, which poses great

restrictions on its economic development (Wang et al., 2008). Since 1970s, groundwater has been used as major water sources for agriculture irrigation, industrial production, as well as domestic usage (Zhang et al., 1997, 2000). Over-exploitation of groundwater has induced groundwater level falling and caused numerous depression cones leading to water quality deterioration due to the changes of groundwater flow conditions and groundwater

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chemistry (Chen et al., 2005a). Prior to large-scale exploitation of groundwater (around 1960), naturally occurring groundwater was characterized by shallow groundwater table, well-developed surface water system and strong evaporation, and discharge of deep groundwater to shallow groundwater in the central and coastal plains (Zhang et al., 1997). Under extensive extraction (since 2000), both shallow and deep groundwater tables have fallen sharply, forming numerous depression cones and consequently leading to recharge of shallow groundwater into deep groundwater (Shao et al., 2013; Cui et al., 2014; Shi et al., 2014). Furthermore, areas with  $\text{HCO}_3^-$ -dominant water extend from the piedmont area to central and coastal areas, while  $\text{Cl}^-$ -dominant water areas extensively regress (Zhang and Fei, 2009; Zhan et al., 2014). Therefore, a tremendous number of investigations have been carried out to study groundwater flow systems and evaluate chemical and hydrogeochemical processes controlling groundwater chemistry in the flow system (Yin and Sun, 1995; Fan, 1998; Xue et al., 2000; Chen et al., 2003; Xia et al., 2004; Chen et al., 2005a,b; Xing et al., 2013; Zhan et al., 2014). Conclusions showed that groundwater hydrochemical characteristics and geochemical processes within specific aquifers changed severely due to the declines in groundwater level under the influence of human activities. The NCP is well characterized as three zones, which correspond to piedmont zone, central zone and coastal zone (Liu et al., 1997; Chen et al., 2005b). Groundwater major components showed an obvious zonation trend from piedmont area to coastal area (Zhang and Fei, 2009; Xing et al., 2013). Steep increases in some major ions (e.g.,  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) were observed in the area of the depression cones, and seawater intrusion was found in the coastal aquifers due to excessive withdrawal (Xue et al., 2000; Han et al., 2011), which significantly changed the previously established hydrogeochemical zones. More recently, based on groundwater major components in combination with hydrochemical modeling, Xing et al. (2013) suggested that mineral precipitations including dolomite and calcite primarily occur in piedmont zone of both deep and shallow groundwater systems, and cation exchange take place along the entire flow path. However, none investigations have been done from the perspective of rare earth elements (REEs) to unravel the changes in groundwater chemistry and flow conditions. No information is available about groundwater REE geochemical characteristics as well as their relations and implications for geochemical processes along the flow path of the NCP, which are useful in studying groundwater chemistry and geochemical processes in the systems.

Rare earth elements (REEs), which have well-noted coherent properties and geochemical behaviors, are extensively used in groundwater study, especially for understanding groundwater-aquifer rock interactions, groundwater flow system and groundwater mixing in nature (Smedley, 1991; Lee et al., 2003; Ojiambo et al., 2003; Tang and Johannesson, 2006; Steinmann and Stille, 2008; Willis and Johannesson, 2011; Zhan et al., 2013; Noack et al., 2014; Vázquez-Ortega et al., 2015; Chevis et al., 2015), since REEs in groundwaters are generally believed to be derived initially from the rock which they flow through (Smedley, 1991) and conservatively transported in solution (Johannesson et al., 1997a,b). Thereafter, REE mobilization and relatively conservative performance have brought investigators to focus on studying the consistency of the element solution complexation behaviors and assess the significance of different solution ligands, including carbonate (Cantrell and Byrne, 1987; Johannesson et al., 1999), phosphate (Lee and Byrne, 1992), fluoride (Haas et al., 1995) and humic and fulvic substances (Pouret et al., 2007; Goyné et al., 2010). Other ligands, including bacteria (Martinez et al., 2014), Mn and Fe oxides (Pouret and Davranche, 2013; Schijf and Marshall, 2011), and siderophores (Christenson and Schijf, 2011), have recently been shown to complex with REEs. Moreover, researches showed

that, within some aquifers, groundwater REEs transported in forms of complexes with inorganic and/or organic ligands (Shock et al., 1997; Johannesson et al., 1999; Guo et al., 2010). In such a scenario, solution complexes essentially act as an “umbrella” to protect REEs from being uptaken by aquifer minerals which have great affinity of, in particular, negatively charged complexes (Johannesson et al., 1999). Through modeling and speciation calculations, it is commonly recognized that dissolved REEs in natural waters are strongly complexed with carbonate species. However, a wide range of REE fractionation patterns in groundwater, including “aquifer rock-like” and “seawater-like”, and in between, have been extensively discussed (Sholkovitz et al., 1994; Johannesson et al., 1999; Banks et al., 1999; Leybourne et al., 2000; Dia et al., 2000; Biddau et al., 2002; Gruau et al., 2004; Tang and Johannesson, 2006; Pouret et al., 2007, 2010). In spite of the well-known REE patterns, it is still a controversial issue as to what and how geochemical processes occurring over a groundwater flow system lead to distinguishing REE concentrations and shale-normalized REE patterns and their relations to aquifer sediments. Early studies indicated that REE signatures in groundwaters obtained toward the discharge area represented water-host-rock interactions at a late stage (Banner et al., 1989). However, Willis and Johannesson (2011) concluded that, although groundwaters inherited “rock-like” REE signatures in the recharge zone, they were modified by sorption, solution complexation, redox conditions and major solute along the length of the flow path. Furthermore, as pH was believed to be an indicator of groundwater maturity (Banks et al., 1999; Johannesson et al., 1999) and, to a certain degree, reflected the aquifer rock composition that groundwaters encountered during flowing, changes in pH values along a flow path were also expected to modify REE distribution patterns in groundwaters. It has been reported that with lower pH values, the fractionation patterns of groundwater would approach more closely the maternal rock patterns (Smedley, 1991; Johannesson et al., 1997a,b, 1999). More recently, Duvert et al. (2015) found that waters that interacted with different rock types had different REE concentrations and normalized patterns. Overall, in natural groundwater flow system, aqueous REE concentrations and fractionation patterns in aquifers yield a mass of information about geochemical reactions and/or interactions groundwater was experienced.

In this investigation, we try to examine whether groundwater REE geochemistry (e.g., concentrations and fractionation patterns) could be efficiently applied as tracers of changes of groundwater chemistry and groundwater environment as well as the related geochemical processes in different aquifer systems (e.g., shallow and deep) under the great influences of human activities. Rare earth element concentrations and normalized REE patterns are thought to be closely related to hydrogeochemical processes under various conditions (Tang and Johannesson, 2006; Laveuf et al., 2008; Guo et al., 2010; Delgado et al., 2012; Vázquez-Ortega et al., 2015). In oxic conditions, precipitation of Fe(III) oxides/oxyhydroxides causes preferential scavenging and/or co-precipitation of the LREEs over the HREEs, and leads to enrichment of the HREEs in groundwaters (Steinmann and Stille, 2008; Willis and Johannesson, 2011). Besides, Ce behaves differently from other REEs because of its greater sensitivity to redox conditions. Accordingly, Ce anomalies could serve as indicators tracing the present and the past redox states of the system (Leybourne et al., 2000; Guo et al., 2010).

To accomplish our goals, a series of groundwater samples and sediment samples were collected from shallow and deep aquifers along a selected hydrochemical profile proximately along a groundwater flow path. The detailed objectives of the study are: (i) to investigate REE concentrations in groundwaters from different aquifers, (ii) to characterize the geochemical behaviors of REEs along the flow path in the shallow and deep aquifers, and (iii) to

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