

Distribution of Rare Earth Elements and Their Applications as Tracers for Groundwater Geochemistry - A Review

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Abstract: Several studies investigating the behavior and environmental distribution of rare earth elements (REEs) have been reviewed to determine the geochemical processes that may affect their concentrations and fractionation patterns in groundwater and whether these elements can be used as tracers for groundwater-rock interactions and groundwater flow paths in small catchments. Inductively coupled plasma-mass spectrometry (ICP-MS), equipped with an ultrasonic nebulizer and active-film multiplier detector, is routinely used as an analytical technique to measure REEs in groundwater, facilitating the analysis of dissolved REE geochemistry. This review focuses on the distribution of REEs in groundwater and their application as tracers for groundwater geochemistry. Our review of existing literature suggests that REEs in ice cores can be used as effective tracers for atmospheric particles, aiding the identification of source regions.

Keywords: rare earth element, groundwater-rock interaction, groundwater flow paths, ice core study

Introduction

With the development of new energy and energy storage technologies, the consumption of critical elements is increasing rapidly (Zou et al., 2020). In addition, rare earth element (REE) geochemistry is a useful complementary tool in trying to elucidate chemical variations in geological systems due to their generally coherent and predictable behavior (Henderson, 1984; Bau and Dulski, 1996). This coherent behavior of the REE, combined with their sensitivity to changes in pH, redox potential and adsorption/desorption reactions, make the REE particularly useful in groundwater geochemistry studies (Johannesson et al., 1996a; McCarthy et al., 1998; Dia et al., 2000; Noack et al., 2014). However, the low concentrations of these elements in waters (ppb level or less) had been prevented their use either as witness of water/rock interaction processes or as hydrological tracers. These

problems have been alleviated by the advent of analytical methods, in particular, inductively coupled plasma-mass spectrometry (ICP-MS) (Stetzenbach et al., 1994; Verplanck et al., 2001). With more chemical data available for each groundwater sample, it becomes possible to fingerprint groundwaters accurately based on their unique trace elements signatures. The analyses of multiple trace elements in groundwater samples can thus provide more information concerning a groundwater sample than was possible with traditional analyses of the major solutes. For example, the use of the multivariate statistical method (principal component analysis; PCA) was explored by many workers as a means of rapidly searching for chemical similarities between many different groundwater samples. They employed a large data set consisting REE that was measured in each groundwater sample by inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS) (Stetzenbach et al., 1999; Stetzenbach et al., 2001; Worrall and Pearson, 2001a) and inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) (Chung et al., 2009; Rousseau et al., 2013).

Rare earth element (REE) pattern can record subtle geochemical processes in natural systems (Nesbitt et al., 1979; Elderfield and Greaves, 1982; Zhang et al.,

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1998; Moller et al., 2000; Smedley, 1991). Because of lithophilic nature of REE, the source in groundwaters is dominantly the surrounding strata, and hence the potential REE have to be tracers of groundwater mixing, source regions, and water-rock interactions (Banks et al., 1999; Stetzenbach et al., 1999; Serrano et al., 2000; Stetzenbach et al., 2001; Lee et al., 2003; Tweed et al., 2006; Yan et al., 2013; Liu et al., 2016). Some works have proposed that the REEs may approach conservative in some groundwater (Johannesson et al., 1997; Feng et al., 2001). Other studies have tended to focus on the probable complexation behavior of the REEs in different groundwater environments (Johannesson et al., 1996b; Tricac et al., 1999; Takahashi et al., 2002). These studies suggest, therefore, that, depending on the system, both rock source and solution chemistry can play important roles in controlling and determining the dissolved REE signatures of natural waters (Johannesson et al., 1994; Johannesson et al., 1995; Johannesson et al., 1999; Leybourne et al., 2000).

The primary objective of this paper are: 1) to suggest precise measurement of REE concentrations in groundwaters 2) determine geochemical processes that likely exert controls on the REE concentrations and fractionation patterns in groundwaters and 3) to test whether these elements can be useful tracers of groundwater-rock interaction and groundwater flow paths in small size catchments.

Methodology

Sampling and analytical techniques

The methods used to sample groundwater from the springs and wells have been thoroughly discussed in the literature (Stetzenbach et al., 1994). In brief, groundwater samples were pumped from the springs using a peristaltic pump or bailer equipped with acid-washed Teflon[®] tubing, subsequently passed through an inline Gelman Sciences filtering capsules (pore size 0.45 μm ; polyether sulfone membrane), and collected in acid-washed, high-density polyethylene sample bottles (Nalgene). After the well and spring water

samples were filtered, they were immediately acidified to pH <2 with ultrapure nitric acid.

REE concentrations were measured by inductively coupled plasma-mass spectrometry (ICP-MS) with ultrasonic nebulization (Stetzenbach et al., 1994; Verplanck et al., 2001). The ultrasonic nebulization (Cetac Technologies Model U-5000) increased the sensitivity of the instrument by roughly a factor of 30 over cross-flow nebulization and decreased the potential interferences from oxide formation in the plasma stream (Stetzenbach et al., 1994). The ICP-MS was also equipped with the active film multiplier ion detector (ETP Scientific) that, along with the ultrasonic nebulizer, further increased the sensitivity of the instrument by roughly 100 times (Stetzenbach et al., 1994). The REEs were preconcentrated 50-fold by cation exchange and quantified by ICP-MS using the REE isotopes (Stetzenbach et al., 1994).

Principal component analysis (PCA)

Principal component analysis is an ideal technique for analyzing multivariate data such as REE patterns. This method can be used to simplify data, to explore groups in data, and to visualize underlying controls in a multivariate data set. PCA recalculates the data in terms of multivariate components that better explain the variation in the data than the original variables (Worral and Pearson, 2001b). In using PCA, a large data matrix can be reduced to two smaller matrices, one consisting of principal component (PC) scores and the other containing the loadings (Stetzenbach et al., 1999). The PC scores (s) are linear combinations of the standardized data (x) with the loadings (l) as the coefficients:

$$s_{n,c} = \sum x_{n,e} \times l_{e,c} \quad (1)$$

where n identifies the samples spring or well water, e is the chemical measurement (e.g., different trace element), and c identifies the principal component (Stetzenbach et al., 1999; Stetzenbach et al., 2001). The maximum amount of variance is explained in the first PC, with decreasing variance explained in each

subsequent component. All PCs are uncorrelated (i.e. orthogonal) to one another.

Rare Earth Elements in Groundwater Geochemistry

The distribution of rare earth elements in groundwaters

Recently, REEs have been employed to investigate the geochemistry of groundwater system and other low temperature aqueous system (Brookins, 1989; Smedley 1991; Alibo and Nozaki, 1999; Lee et al., 2002). These studies have demonstrated that groundwater and some surface waters can inherit their REE signatures from the rocks or aquifer material with which they flowed (Smedley, 1991; Stetzenbach et al., 2001; Worrall and Pearson, 2001a). Unfortunately, the significance of rock inherited aqueous REE signature as compared to control of REE signatures by solution and/or surface complexation has not been completely unraveled (Lee and Byrne, 1993; Johannesson et al., 1996a; Dia et al., 2000).

All REE patterns were chondrite-normalized or shale-normalized to values reported in Anders and Ebihara (1982) and Gromet et al. (1984), respectively

(See Table 1 and 2). Smedley (1991) reported that groundwaters from the metasediments have a notable depletion in Ce which is distinct from waters in the granite. This depletion is problematic in that it is difficult to see how redox processes could be the dominant control, since groundwaters from the metasediments are unlikely to be more oxidizing than those from the granite. It is therefore suggested that the Ce contents are largely source-related rather than process-related. Johannesson and Hendry (2000) have conducted that rare earth elements were determined in groundwater samples collected from a thick till and clay-rich aquitard sequence located in southern Saskatchewan, Canada. Shale-normalized REE patterns for the site groundwaters were used in the study. Shallow groundwaters have heavy REE (HREE)-enriched shale-normalized patterns, whereas the REE patterns of the deep groundwaters are relatively flat.

The REE are especially useful because they exhibit similar chemical properties to the highly radioactive actinides owing, in the case of the trivalent actinides (e. g., Pu^{3+} , Am^{3+} , Cm^{3+} , Cf^{3+}), to their identical valence and similar ionic radii (Johannesson et al., 1996a). Studies of REEs in terrestrial waters was described that although these waters may inherit their

Table 1. Analysis results for the "North American shale composite (NASC)" from and Gromet et al. (1984)

	Neutron activation analyses	Mass spectrometry isotope dilution analyses
La	31.1	---
Ce	66.7	67.8
Pr	---	---
Nd	27.4	34.4
Sm	5.59	6.69
Eu	1.18	1.39
Gd	---	5.60
Tb	0.85	---
Dy	---	5.75
Ho	---	---
Er	---	3.34
Tm	---	---
Yb	3.06	3.21
Lu	0.456	---
Sample wt. (mg)	107.41	229.88

*Weight basis is for shale including H_2O and CO_2 ; values in $\mu\text{g/g}$.

Table 2. Abundance of REE in chondrites from Anders and Ebihara (1982)

Element	Unfractionated pattern ppb
La	236
Ce	616
Pr	92.9
Nd	457
Sm	149
Eu	56.0
Gd	197
Tb	35.5
Dy	245
Ho	54.7
Er	160
Tm	24.7
Yb	159
Lu	24.5

REE signatures through interaction with rocks and/or other aquifer materials, solution complexation can significantly affect the dissolved REE signature by several workers (Johannesson et al., 1996a; Johannesson et al., 1996b). Lee and Byrne (1993) and Johannesson et al. (1999, 2000a, 2000b), for example, have demonstrated that REE-carbonate complexes dominate and typically account for more than 99% of each REE in circumneutral pH ($7 \leq \text{pH} \leq 9$) groundwaters from south-central Nevada. In acid ($2.9 \leq \text{pH} \leq 3.5$), hypersaline groundwater from Australia, the striking feature of the normalized REE profiles is that, in general, the groundwaters are enriched in the MREEs (i.e. Eu, Gd, Tb, Dy) over both the LREEs and the HREEs. Although MREE-enriched patterns have been recognized in a variety of different terrestrial waters, the origins of shale-normalized MREE enriched patterns are currently not sufficiently understood. In addition, several studies have shown that free ions and complexes with carbonates generally dominate the aqueous speciation of REE in groundwaters (Elbaz-Poulichet and Dupuy, 1999; Biddau et al., 2002). The speciation of REE was calculated by the EQ3Nr or MINEQL computer program (Liang et al., 2021), using the given database of thermodynamic constants

for the inorganic complexes of the REE. The carbonate complexes dominate the REE speciation at pH between 6.7 and 8.6, REECO_3^+ being prevalent for the LREE, and $\text{REE}(\text{CO}_3)_2^{2-}$ being increasingly important with increasing atomic number. The free ion REE^{3+} is the main aqueous species for the LREE at pH < 6.7. The REE^{3+} ions, and the complexes with SO_4^{2-} , F^- , and HCO_3^- become negligible (<1%) at pH > 7.0. These results of the REE speciation in the waters are consistent with those observed in previous mentioned studies.

Rare earth elements as groundwater geochemistry tracers

Stetzenbach et al. (1999) have proposed that PCA may provide rapid and relatively cost-effective methods to assess possible groundwater flow regimes in systems that have not been previously investigated. In addition, the PCA of REE suggested that groundwaters from felsic volcanic rocks in the vicinity of Yucca Mountain, previously thought to have interacted only with the volcanic rocks, have a significant component that is characteristic of the underlying carbonate aquifer (Stetzenbach et al., 2001) because the PCA indicates that wells from Yucca Mountain have trace element signatures that are statistically more similar to the regional carbonate groundwaters discharging from Ash Meadows, the Pahrana Valley and the Spring Mountains than to the strictly volcanic rock groundwater characterized by Tippipah and Topopah Springs. Again, these results can be interpreted as indicating that groundwaters from these wells are mixtures of regional carbonate groundwaters and local volcanic groundwaters.

Johannesson et al. (1997) have investigated that the groundwater sources and mixing ratios determined directly with dissolved REE concentrations in the regional groundwaters of south-central Nevada as well as with the La-normalized REE patterns expected to persist in solution as a function of surface and solution complexation are remarkably similar are those determined with more traditionally accepted conservative tracers, such as deuterium, U, and Na. Their work is highly suggestive of the practical use of REEs as

geochemical tools for tracing groundwater sources, deciphering mixing proportions of different groundwaters, and for investigating groundwater- rock interactions.

In addition, Johannesson et al. (1999) has examined fractionation patterns and concentration variations of REE along a groundwater flow path within a specific aquifer. Aqueous REE concentrations sampled along a groundwater flow path decrease along the direction of flow. The removal of REEs from solution is attributed to their sorption to aquifer surface sites. Groundwater REE data, in conjunction with K_d 's, support strong sorption of aqueous REEs to aquifer surface sites as the primary removal mechanism of REEs from these groundwaters.

REE are also a useful geochemical tool for estimating source regions in the ice core studies due to their conservative behavior in the environment and their transport mostly in the atmosphere in the particle phase (Gabrielli et al., 2006; Zhang et al., 2009; Wegner et al., 2012). Gabrielli et al. (2006) present a direct ultrasensitive method for determination of REE in less than 1 mL of molten ice layer collected in Antarctica by ICP-SFMS using a micro-flow nebulization equipped with a desolvation sample introduction system. The system was used to overcome spectroscopic interferences during the direct determination of REE. The determination of REE has enabled studies for paleoclimate/paleoenvironment reconstruction in ice core samples such as change in dust variability and of potential sources areas and so on.

Summary and Closing Thought

Thanks to their properties and to their consistent chemical behavior, rare earth elements (REE) are considered important trace elements in the study and understanding of various hydrogeochemical processes. Previous investigations have shown that, groundwaters typically exhibit REE signatures (i.e., normalized to a common rock standard) that closely resemble the rocks through which they have interacted, whereas others have examined their inorganic solution complexation behavior. The previously reported

similarities between aquifer-rock REE patterns and those of some groundwaters strongly suggest that the REEs can be useful tracers of groundwater-rock interactions. However, several authors argued that solution complexation plays an important role whereby formation of strong complexes with ligands, acts to inhibit REE uptake onto sorptive surface sites within an aquifer. In addition, in ice core studies, the determination of REE has enabled studies for paleoclimate/paleoenvironment reconstruction using ice core samples such as change in dust variability and of potential sources areas and so on.

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