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Partitioning of REE between solution and particulate matter in natural waters: a filtration study

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Abstract

Rare earth element (REE) concentrations were determined in filtered and unfiltered fractions of one stream water and five shallow ground waters from springs and wells from the Palouse region of Idaho/Washington to characterize the contribution of suspended, colloidal, and solution fractions to the REE contents of each water sample. Similar characteristics were observed in the shallow ground waters as reported in the literature for rivers. In almost all cases the LREE were depleted substantially in filtered fractions relative to the unfiltered fractions, indicating substantial partitioning of LREE onto particulate matter. In some, but not all samples, the HREE were far less depleted, indicating greater mobility of the REE as dissolved species or small colloidal particles. Increased solubility of HREE relative to LREE in these neutral to slightly alkaline waters may be due to preferential complexation of the HREE with ligands such as carbonate, hydroxide, fluoride or organic anions. In one water studied, filtration through a finer pore-size filter resulted in markedly more pronounced Ce anomalies. Cerium anomalies are likely controlled by preferential sorption of Ce^{4+} onto Fe–Mn particle coatings.

1. Introduction

Over the past few decades, rare earth elements (REE) have grown in importance as geochemical tracers of the chemical evolution of the Earth because of their unique chemical properties [1]. The rare earths have been used to study weathering of rocks and soil [2,3], as well as the low-temperature evolution of waters in ground [4–7], river [8–11], and oceanic settings [12,13]. Research in estuarial zones also has intensified in recent years as scientists study how continental waters contribute to the composition of ocean waters [14,15]. Several studies of REE in river water (e.g., [9,11,18]) have dealt with the partitioning of the REE among dissolved species, colloidal particles and suspended particulates, but few such studies [16] have been conducted on ground waters.

In this study we focus on the fractionation of the REE as they are partitioned among particulate, colloidal and solution fractions of ground water. Samples have been collected from the Palouse Basin in Moscow, ID and Pullman, WA. The Palouse aquifer system is comprised of two basalt aquifers overlain by rolling hills of loess. It has been suggested that the basalt aquifers are recharged by infiltration at Moscow Mountain, which is composed of granite. Shallow ground water samples from springs and wells were collected from the loess as well as the upper basalt (Wanapum Formation) and granite (Moscow Mountain) aquifers. In addition to ground water from springs and wells, one stream (Paradise Creek, PAR-0713) was also sampled. This stream begins as a series of springs, one of which was sampled (WLSP1-1018).

In natural waters the REE can be partitioned among three fractions distinguished on the basis of size: solution (dissolved species), colloidal particles, and suspended particles. Fractionation of the REE from one another may or may not occur as a result of this partitioning. The operational division of colloidal particles from suspended solids has generally been considered to be $<0.45\,\mu m$. For the purposes of this study the fraction of REE included in the filtrate that had passed through a 0.1-μm filter was considered to be "dissolved" in solution, although it is recognized that

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Table 1
Major ion chemistry of waters in this study (mg/L)

Sample (0.45-μm filtrates)	Temp. (°C)	pH	Alkalinity ($CaCO_3$)	F^-	Cl^-	PO_4^{3-}	Br^-	NO_3^-	SO_4^{2-}	B	Ca	Fe	K	Mg	Mn	Na	Si
PAR-0713	20.5	7.73	113.69	0.50	39.86	0.73	0.15	4.82	14.48	0.12	43.34	0.12	6.31	15.19	0.17	35.74	28.89
TSSP-1022	6.7	6.29	149.40	0.25	0.98	0.17	0.00	0.51	1.45	0.01	3.73	0.00	1.59	0.65	0.00	4.09	13.88
WLSP1-1018	13.0	7.15	74.14	0.29	2.61	0.23	0.00	25.57	8.95	0.00	20.58	0.00	0.72	6.44	0.01	13.06	25.40
LOES1-0814	13.1	7.46	152.55	0.29	2.90	0.31	0.00	29.28	21.72	0.02	26.02	0.00	1.25	7.78	0.00	29.06	17.34
GRS2-0720	12.8	7.27	191.79	0.23	59.00	0.80	0.00	13.58	68.32	0.11	166.14	0.00	6.50	52.30	0.17	51.89	24.96
GRS1-0713	11.6	7.26	605.08	0.26	33.95	0.06	0.20	40.63	26.71	0.16	67.32	0.00	3.02	21.89	0.00	21.71	27.75

smaller colloidal particles probably pass through such a filter. Furthermore, the fraction of REE passing a 0.45-μm filter but not a 0.1-μm filter was designated the "colloidal" fraction. The purpose of this study was to determine which fraction is most important for transport of rare earth elements in shallow ground waters and to determine whether or not partitioning results in fractionation of the REE.

2. Experimental and analytical methods

Filtration protocol is perhaps the most important element of this study to ensure that results and interpretations of data are reliable. To reach conclusive geochemical interpretations it is critical that contamination does not occur. To ensure clean and consistent sampling the following measures were taken during the field season (July–October 2001):

(1) Prior to each sampling campaign, four 1-L Nalgene polypropylene bottles were acid washed and then rinsed thoroughly with deionized water. Twenty milliliters of Optima-grade nitric acid were dispensed into the bottles, which were then capped tightly and sealed with parafilm.
(2) Samples were collected in a designated sample bottle in the fastest flowing part of the stream or spring. In the case of shallow ground water, two borehole volumes of water were evacuated from each well prior to sample collection using a bailer, and samples were poured into a designated sample bottle.
(3) Samples were then filtered on site using a peristaltic hand pump to transfer the water from the designated sampling bottle through a filter membrane into a pre-labeled, 1 L, acid-washed Nalgene polypropylene bottle. Samples were filtered individually with one of three filters: a 3.0-μm Versapor supported membrane filter, a 0.45-μm Metricel membrane filter, or a 0.1-μm Supor membrane filter (all membranes were 47 mm in diameter). If the filter became clogged during filtration, it was carefully replaced and filtration resumed.
(4) Sample bottles were then sealed tightly and transported back to the lab for pre-concentration and analysis.

Upon return to the lab, acidified water samples were analyzed to determine the concentrations of major cations, including Al, Fe, and Mn, using a *Perkin-Elmer, Optima 3000XL* Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) equipped with an axial torch. Unacidified samples were analyzed for anions by ion chromatography. Temperature and pH measurements were made in the field, and alkalinity was determined as soon as possible in the laboratory. The general chemical characteristics of the waters investigated (0.45-μm filtrate) are given in Table 1.

Because REE occur at very low concentrations (ng/L), a preconcentration method was necessary to ensure that samples would be well above the instrument detection limit. In all cases a ferric-hydroxide coprecipitation technique was used (see [17] for full details) for a ~50× effective concentration. REE concentrations were determined at Washington State University using a *Hewlett-Packard Model 4500* Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). Blanks were used to monitor contamination. These showed that contamination was generally not an issue for most of the REE. The exceptions were Nd and Yb, which occasionally were anomalously high.

3. Results and discussion

3.1. General observations

The REE data are reported in Table 2. Fig. 1a–f depicts REE patterns of the three filtrates, normalized by the respective unfiltered sample. The primary observation from the filtration experiments is that there is partitioning of REE among the three fractions:

Table 2
REE contents of waters in this study (μg/L)

Filtrate (μm)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
I. Surface Water														
Paradise Creek (PAR-0713)														
Unfiltered	0.171	0.313	0.041	0.181	0.037	0.009	0.042	0.006	0.036	0.008	0.030	0.005	0.046	0.010
3.00	0.139	0.250	0.033	0.209	0.031	0.007	0.036	0.005	0.031	0.007	0.028	0.005	0.047	0.010
0.45	0.053	0.090	0.012	0.064	0.012	0.003	0.016	0.002	0.014	0.004	0.018	0.004	0.137	0.009
0.10	0.058	0.112	0.013	0.075	0.013	0.003	0.016	0.002	0.015	0.004	0.019	0.004	0.037	0.008
II. Spring Waters														
Granite-derived (TSSP-1022)														
Unfiltered	0.030	0.063	0.011	0.048	0.015	0.003	0.015	0.003	0.017	0.003	0.010	0.002	0.011	0.002
3.00	0.025	0.276	0.010	0.045	0.011	0.003	0.012	0.002	0.013	0.003	0.008	0.001	0.009	0.001
0.45	0.018	0.036	0.007	0.031	0.010	0.002	0.011	0.002	0.011	0.002	0.007	0.001	0.008	0.001
0.10	0.011	0.030	0.004	0.022	0.007	0.002	0.007	0.001	0.008	0.002	0.005	0.001	0.007	0.001
Loess-derived (WLSP1-1018)														
Unfiltered	0.506	0.988	0.123	0.518	0.109	0.025	0.109	0.015	0.092	0.018	0.051	0.007	0.046	0.007
3.00	0.105	0.200	0.025	0.113	0.024	0.006	0.023	0.003	0.020	0.004	0.012	0.002	0.016	0.002
0.45	0.024	0.041	0.006	0.032	0.008	0.002	0.006	0.001	0.005	0.001	0.004	0.001	0.007	0.001
0.10	0.014	0.020	0.003	0.020	0.006	0.002	0.004	0.001	0.003	0.001	0.003	0.000	0.005	0.001
III. Groundwaters														
Loess-derived (LOES1-0814)														
Unfiltered	0.793	1.460	0.196	0.758	0.131	0.015	0.101	0.014	0.076	0.015	0.049	0.008	0.062	0.012
3.00	0.313	0.612	0.078	0.297	0.049	0.005	0.036	0.005	0.028	0.006	0.024	0.004	0.039	0.008
0.45	0.098	0.167	0.024	0.097	0.016	0.002	0.013	0.002	0.013	0.004	0.017	0.003	0.033	0.007
0.10	0.186	0.351	0.046	0.175	0.029	0.003	0.022	0.003	0.018	0.004	0.016	0.003	0.028	0.006
Alluvium-derived (GRS2-0720)														
Unfiltered	10.433	30.856	2.680	11.672	2.368	0.533	2.332	0.336	2.046	0.392	1.112	0.153	0.993	0.148
3.00	3.675	10.594	0.958	4.114	0.830	0.189	0.812	0.118	0.720	0.141	0.400	0.056	0.366	0.056
0.45	0.027	0.073	0.007	0.037	0.006	0.001	0.009	0.001	0.010	0.003	0.011	0.002	0.016	0.003
0.10	0.048	0.134	0.012	0.093	0.011	0.004	0.016	0.003	0.020	0.005	0.020	0.003	0.030	0.006
Alluvium/Basalt-derived (GRS1-0713)														
Unfiltered	0.007	0.005	0.001	–	0.002	0.001	0.002	0.000	0.003	0.001	0.004	0.001	0.007	0.002
3.00	0.006	0.006	0.001	–	0.001	0.000	0.003	0.000	0.003	0.001	0.004	0.001	0.008	0.002
0.45	0.005	0.003	0.001	–	0.001	0.000	0.002	0.000	0.003	0.001	0.004	0.001	0.008	0.002
0.10	0.004	0.001	0.001	–	0.001	0.000	0.002	0.000	0.003	0.001	0.004	0.001	0.007	0.001

solution, colloidal, and suspended solids, i.e., there are generally different concentrations of REE in the various fractions. Some samples show substantial REE fractionation, but others do not. Also, there are significant differences in the Ce anomalies of the three fractions in some samples.

3.2. Surface water

The normalized 3.0-μm filtrate REE pattern from Paradise Creek (PAR-0713) shows a relatively smooth increase from the LREE to the heaviest REE, lutetium. The LREE are depleted compared to the unfiltered sample, but the HREE are less depleted. In fact, there is essentially no difference in the Yb and Lu concentrations between the unfiltered and the 3.0-μm filtered sample. On the other hand, roughly 20% of the LREE are present as particles larger than 3.0 μm. A similar pattern is seen in the 0.45- and 0.1-μm filtrates. The concentrations of the LREE in these two fractions are much lower than that in the unfiltered fraction, and the relative proportions are similar for La to Tb. The concentrations of the HREE increase from Dy to Lu, and the concentrations of Yb and Lu in these filtrates is within 80% of those of the unfiltered fraction. Clearly, in Paradise Creek, the HREE appear to be more soluble than the LREE.

There is a wide gap with respect to LREE concentrations in the fine filtrates (0.1 M μm and 0.45 μm) and the coarse filtrates (3.0 μm and unfiltered). Hence, filtration through smaller pore-size filters results in decreased concentrations of the LREE. However, there is very little difference in the REE concentrations between the 0.45- and 0.1-μm filtrates. This suggests that larger colloidal particles may not play an important role in REE transport in this environment. Transport via small colloidal particles (<0.1 μm) or in solution is increasingly important for the HREE; such transport is responsible for >80% of the Lu. LREE are primarily transported via particles larger than 0.45 μm. It is

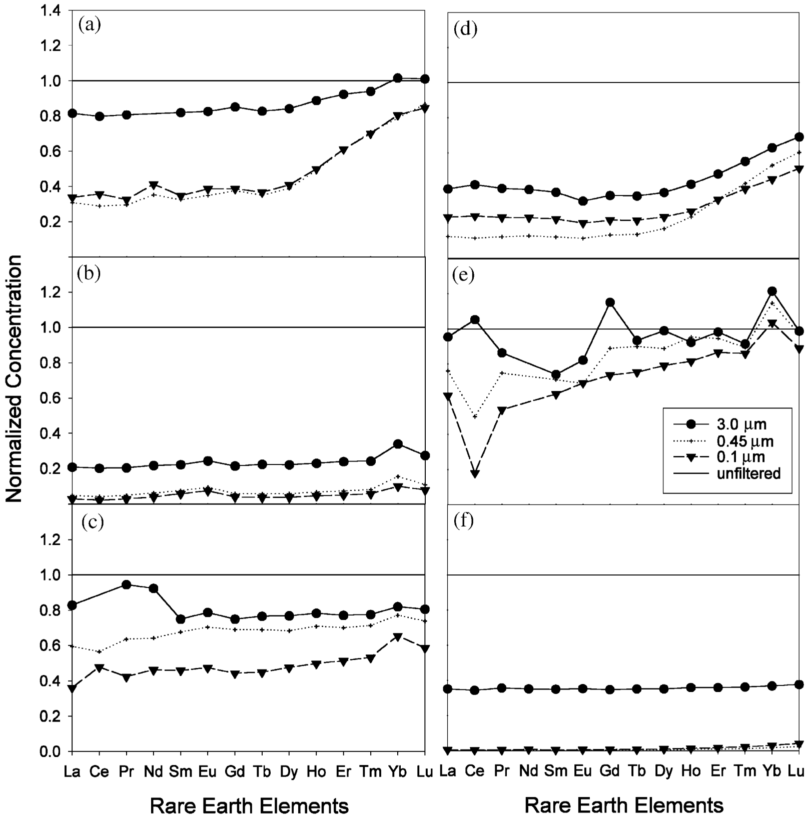

Fig. 1. Normalized REE Patterns for sampled waters. (a) Paradise Creek (PAR-0713), (b) Loess-derived spring (WLSP1-1018), (c) Granite-derived spring (TSSP-1022), (d) Loess-derived ground water (LOES1-0814), (e) Basalt-derived ground water (GRS1-0713), (f) Loess-derived ground water (GRS2-0720).

unknown whether the LREE in the particulate fractions are sorbed onto a foreign material (Fe–Mn oxide or organic material), or contained in particles of host rock or individual REE minerals.

3.3. Shallow ground water: springs

The two spring waters show very different results. The first spring emerges from loess (WLSP1-1018) and represents the headwaters of Paradise Creek. The normalized patterns for all fractions are nearly flat with much lower REE concentrations than the unfiltered sample. A slight positive slope is observed, showing some preferential dissolution of the HREE. A small positive Eu anomaly is exhibited in all three filtrates. The apparent Yb anomalies in these patterns and others may represent laboratory contamination. Partitioning of the REE shows a very different picture for this loess spring compared to Paradise Creek. In this case REE transport is almost entirely ($>90\%$) via particles larger than 0.45 μm. This finding is probably a result of the very fine-grained nature of the loess, which facilitates its suspension in ground water.

Tamarack Spring (TSSP-1022) emerges from granitic bedrock and had very little sediment in solution visible to the naked eye. The spring's REE pattern is relatively flat with a gentle positive slope and significant Ce anomalies. A positive Ce anomaly is observed for the finest filtrate (0.1 μm), suggesting Ce^{4+} is either dissolved in solution, or more likely incorporated into small colloidal particles. Tamarack Spring also exhibits partitioning of the REE into size fractions. In this case, dissolved and colloidal species play an important role in REE transport, together accounting for $>60\%$ of the rare earth element concentration.

3.4. Shallow ground water: wells

The 3.0-μm filtrate of the loess-derived well water (LOES-0814) is slightly depleted in Eu with respect to the unfiltered sample. These filtrate patterns show similar characteristics to Paradise creek, which flows primarily through a loess landscape. Again, filtration through finer pore size leads to lower rare earth concentrations, especially with respect to the light rare earths. The heavy rare earths are more readily dissolved in solution (nearly 50% for Lu). The 0.45-μm fraction appears to have lower LREE concentrations than the 0.1-μm fraction in this sample. However, the difference is probably within analytical uncertainty, so the concentrations of REE in these two fractions should be considered to be the same. The major difference seen in this loess-derived well water, as opposed to the loess spring (WLSP1-1018), is stronger LREE-HREE fractionation.

The basalt-derived ground water (GRS1-0713) pattern is quite noisy, which may be attributed in part to analytical uncertainty. In addition, the Nd concentrations in the filtered fractions were anomalously high, which we attribute to laboratory contamination. Thus, Nd data are not reported for this sample. The anomalous Yb may also be a result of contamination, but the Ce anomalies appear to be real. This sample was collected a few feet below the loess-basalt contact and the well water is also connected via fracture to Paradise Creek (~25 ft away). Again a positive slope is observed for the 0.45- and 0.1-μm filtrates, showing LREE-depletion in the solution and colloidal fractions. Of greatest interest in this sample are the Ce anomalies, first positive in the 3.0-μm filtrate, and then increasingly negative for the solution phase. Perhaps sorption onto Fe–Mn particle coatings is responsible for these deviations.

The final loess-derived ground water (GRS2-0720) is also located in close proximity to Paradise Creek, but has a very different pattern. Filtration through smaller pore-size results in lower rare earth concentrations, but very little interelemental fractionation. The distribution of the REE among the size fractions shows that there is almost no REE transport via colloidal or solution fractions, with only 35% of the REE attributable to particles smaller than 3.0 μm.

3.5. *Importance of the colloidal fraction*

As seen in Fig. 1, the importance of the colloidal fraction varies greatly from sample to sample. Overall, rare earth transport via large colloidal particles, as operationally defined, is most important in the Tamarack Spring (TSSP-1022). However, in most of the other samples, there is very little difference in the REE concentrations of the 0.1- and 0.45-μm fractions, indicating that in most of these waters, either colloidal transport is not important, or the colloidal particles are sufficiently small to pass through a 0.1-μm filter.

4. Conclusions

This study supports previous findings in river water that the solution, colloidal, and suspended fractions can be significantly and systematically different in REE composition [8,9,18]. These findings have now been extended to springs and shallow ground water derived from loess, basalt, and granite. In nearly every case, the LREE were depleted in the various filtered fractions with respect to the unfiltered fraction. However, in some of the waters, the HREE were less depleted in the filtered fractions compared to the unfiltered fraction, suggesting that the HREE are more mobile (either in true solution or as very fine colloids) than the LREE. Heavy REE form stronger complexes than light REE with inorganic ions common in natural waters such as CO_3^{2-}, OH^-, F^- [18, 19], as well as with organic anions [20], which may account for the increased mobility of the HREE in some of the waters.

The negative Ce anomaly observed in the basalt-derived ground water (GRS1-0713), is likely due to preferential removal of Ce^{4+} onto Fe–Mn coatings of particles [18], which also occurs in marine environments [21]. This process is common at slightly alkaline to alkaline pHs. REE-organic complexes may also be important in locations with high organic matter content (i.e., Paradise Creek (PAR-0713) and the loess spring (WLSP1-1018)) [20,22].

Shallow ground waters experience similar controls on REE solution chemistry as rivers.

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