Chapter 6

ORIGIN OF RARE EARTH ELEMENT SIGNATURES IN GROUNDWATERS OF SOUTH NEVADA, USA: IMPLICATIONS FROM PRELIMINARY BATCH LEACH TESTS USING AQUIFER ROCKS

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1. Introduction

Rare earth elements (REE) have been used extensively to study petrologic and mineralogic processes, as well as trace element cycling in the oceans since the late 1970's and early 1980's (e.g., Hanson, 1980; Elderfield and Greaves, 1982; DeBaar et al., 1983; Cullers and Graf, 1984). More recently, with the improvement of analytical instrumentation, REEs can be readily measured at the low parts-per-trillion level in natural waters using, for example, inductively coupled plasma mass spectrometry (ICP-MS; Stetzenbach et al., 1994; Graham et al., 1996; Halicz et al., 1999). One consequence of the improvements in analytical instrumentation is the increase in the numbers of investigations of the REEs in groundwaters (Smedley, 1991; Fee et al., 1992; Gosselin et al., 1992; Halicz et al., 1999). Many of these studies indicate that groundwaters commonly have REE patterns that closely mimic the REE patterns of the rocks through which they flow. The similarities between groundwater and aquifer rock REE patterns suggest that the REEs may be useful tracers of groundwater-aquifer rock interactions. Many investigations have already demonstrated the utility of the REEs as chemical tracers of numerous geochemical weathering processes and possibly biogeochemical redox processes (Hanson, 1980; Moffett, 1990, 1994). Although previous studies have demonstrated that in many cases the REE concentrations observed in groundwaters mimic those of rocks through which they flowed, quantitative, controlled investigations of the REE signatures aqueous solutions acquire by reacting with different types of rocks at low temperatures have not been completed. In order to gain a better understanding of how different rock types can affect the concentrations of REEs in aqueous solutions that react with the rocks and to obtain additional information concerning REE behavior during rock-water reactions, we conducted a series of batch reactor experiments involving compositionally different rock types, and two aqueous solutions (i.e., distilled deionized water and an acidic solution). It should be noted that the current study represents the results of a preliminary investigation within a larger study that includes the PhD dissertation research of the lead author.

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2. Analytical Methods

2.1. ROCK SAMPLE COLLECTION

We chose the Paleozoic stratigraphic section at Frenchman Mountain near Las Vegas, Nevada as our major sampling location because: (1) the stratigraphic sequence in this section is very similar to the lower part of the regional carbonate aquifer of southern Nevada (e.g., Winograd and Thordarson, 1975); and (2) information gained by studying the REE signatures of these rocks and their resulting leachate solutions can be applied to our studies of REEs in groundwaters from this aquifer (e.g., Stetzenbach et al., 1994; Johannesson et al., 1997). In addition, the stratigraphic section is exposed on the eastern edge of the city of Las Vegas, which allows for easy access and detailed sampling. The Paleozoic strata exposed at the site consist of shales, sandstones, and especially abundant carbonate rocks (e.g., dolomite, dolomitic limestone, and limestone) that range in age from Cambrian up to Permian (Rowland, 1987; Rowland et al., 1990). Ordovician and Silurian rocks are, however, missing from this section. Sixteen out of 19 rock samples used for the batch tests in this study were collected from the lower portion of the Frenchman Mountain section, including samples from the Tapeats Sandstone (Tapeats1), Bright Angel Formation (shale or sandstone) [BAS(SS)1, BAS(SL)2, BAS3, and BAS6], and Bonanza King Formation (dolomite) (BKD1, BKD2, BKD3, BKD4, BKD5, BKD6, BKD7, BKD8, BKD9, BKD10, and BKD11). In addition, one sample (FR8Oaal) was collected from the Aysees Member of the Lower Ordovician Antelope Valley Limestone at Fossil Ridge; 20 miles northwest of Las Vegas, Nevada (see Johannesson et al., 2000a). One rhyolitic rock sample (Surprise1) was also examined in the batch tests. Therefore, the samples used in the batch tests represent five different rock types, including shale [BAS(SL)2, BAS(SL)3, BAS6), fine- and medium-grained sandstone (BAS(SS)1, Tapeats1], limestone (FR8Oaal), dolomite (BKD1 through BKD11), and felsic volcanic rock (Surprise1).

2.2. BATCH TESTS

2.2.1. *Preparation and leachates*

Approximately 5 - 10 kg of rock was collected from each sample location. Rock samples were subsequently broken into 0.5-1.0 cm size fragments using a sledge hammer. Fragments without weathering rinds, calcite veins, and obvious signs of alteration were carefully selected until approximately 500 to 1000 grams of fragmental material were obtained for each rock sample. The fragmental rock samples were further crushed to ~70 mesh in size, which were subsequently used in three batch tests employing different solutions and variable reaction times (Table 1). In addition, an aliquot of each crushed rock sample was preserved for REE analysis of the bulk rock (see below).

For Batch Tests 1 and 2, 60 to 220 g of distilled-deionized water (pH=7; 18 MΩ-cm) was added to between 30 g to 80 g of each of the crushed rock samples within acid-washed, high-density linear polyethylene bottles (mass ratio of solution to rock sample ranged from 2:1 to 3:1; Table 1). The crushed rock samples and distilled-deionized water was allowed to react at room temperature (~ 25^{o}C) for 40 days (Batch Test 1) and 67 days (Batch Test

2), respectively. In Batch Test 3, a dilute nitric acid solution (pH=4) was prepared from ultrapure HNO_3 (Seastar, Inc. double sub-boiling, distilled in quartz) and distilled-deionized water, and subsequently reacted with the crushed rock samples for 42 days at room temperature (~ 25°C; Table 1). During each batch test period, all sample bottles containing the crushed rock - leaching solution mixtures were agitated for 5 minutes each day to allow a complete reaction between rock sample and leaching solution. Following completion of the reaction period, the leachate solutions were separated from the crushed rock using a centrifuge, and then filtered through 0.45 μm Nuclepore® filters (Johannesson and Zhou, 1999).

2.2.2. *REE analysis of leachates*

All leachate samples were acidified, subsequent to filtration, using ultrapure nitric acid (Seastar, Inc. double sub-boiling, distilled in Teflon®), and analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Perkin-Elmer® Elan 5000) with ultrasonic nebulization. The ultrasonic nebulization increased the analytical sensitivity and decreased the potential interferences from oxide formation in the plasma stream (Hodge et al., 1998). Due to the small amount of leachate from each batch test, pre-concentration by cation-exchange was not employed. The following REE isotopes were selected for analysis since they have no or less elemental isobaric interferences: ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{149}Sm, ^{151}Eu and ^{153}Eu (mean value), ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, and ^{175}Lu. During ICP-MS analysis, a series of 5 standards of known concentrations (i.e., 0.1μg/kg, 0.5 μg/kg, 1.0 μg/kg, 5.0 μg/kg, and 10.0 μg/kg) were prepared and routinely monitored in order to calibrate the instrument, check the calibration, and calculate the sample REE concentrations. The REE values determined in the Method Blanks were subtracted from the leachate solutions to obtain the leachate concentrations.

2.3. ANALYSIS OF REE IN ROCK SAMPLES

The REEs were measured in 17 rock samples using ICP-MS (Perkin-Elmer® Elan 5000) as discussed in Johannesson and Zhou (1999). Briefly, approximately 0.25 grams of each rock (i.e., powder) sample were placed in precleaned Teflon®-lined microwave digestion bombs, followed by 5 mL of ultrapure HF (Seastar, Inc. double sub-boiling, distilled in Teflon®) and 5 mL of ultrapure HNO_3 (Seastar, Inc. double sub-boiling, distilled in quartz). The Teflon®-lined microwave digestion bombs were then sealed and placed in a microwave oven (CEM Corporation MDS-2100) and heated to 189°C and pressurized to 8.62×10^5 Pa (125 p.s.i.) for 25 minutes. After 25 minutes, the samples were allowed to cool before 30 mL of a saturated boric acid solution was added to each sample. The samples were subsequently heated again in the microwave for 5 minutes at 100°C and 6.9×10^4 Pa - 1.38×10^5 Pa (10 - 20 p.s.i.). The dissolved rock samples were then decanted into clean polyethylene bottles and diluted by a factor of 180 before analysis by ICP-MS. The U.S. Geological Survey rock standard W-2 (diabase) was included as a check standard during the analysis from which our measurements never deviated by more than 10% (Guo, 1996, Guo et al., this volume).

Table 1. Parameters used for three batch tests.

Parameters	Batch Test 1	Batch Test 2	Batch Test 3
Rock Types	shale, sandstone, limestone, dolomite, rhyolite	shale, sandstone, dolomite	shale, sandstone, limestone, dolomite, rhyolite
Solutions	distilled-deionized water	distilled-deionized water	acidic water solution
Sample Weight (g)	30	75 - 82	50
Solution Weight (g)	60	200 - 220	100
Solution/Rock Weight Ratio	2 : 1	3 : 1	2 : 1
pH (starting)	7	7	4
Temperature (^{0}C)	~ 25	~ 25	~ 25
Reaction Time (days)	40	67	42

3. Analytical Results

3.1. REE CONCENTRATIONS OF SOUTHERN NEVADA ROCKS

The REE concentrations (in ppm) for the 16 different sedimentary rock samples and one rhyolite (Surprise 1) examined in this study are presented in Table 2. Again, these same rock samples were used in the different batch leach tests of this study. The chondrite-normalized REE patterns for these rock (both silicate and carbonate rocks) samples are plotted in Fig. 1. The chondrite-normalizing factor that was employed for the normalization calculations is that tabulated by Hanson (1980).

The silicate rocks (Fig. 1a) have REE concentrations that are, on average, about a factor of 10 greater than the carbonate rocks examined in the study (Fig. 1b; Table 2). Moreover, every rock analyzed exhibits enrichment in the light REEs (LREE) over the heavy REEs (HREE) compared to chondrite (Fig. 1). The chondrite-normalized Nd/Yb ratios [$(Nd/Yb)_{CN}$, where CN = chondrite-normalized) range from 1.7 for one of the Bonanza

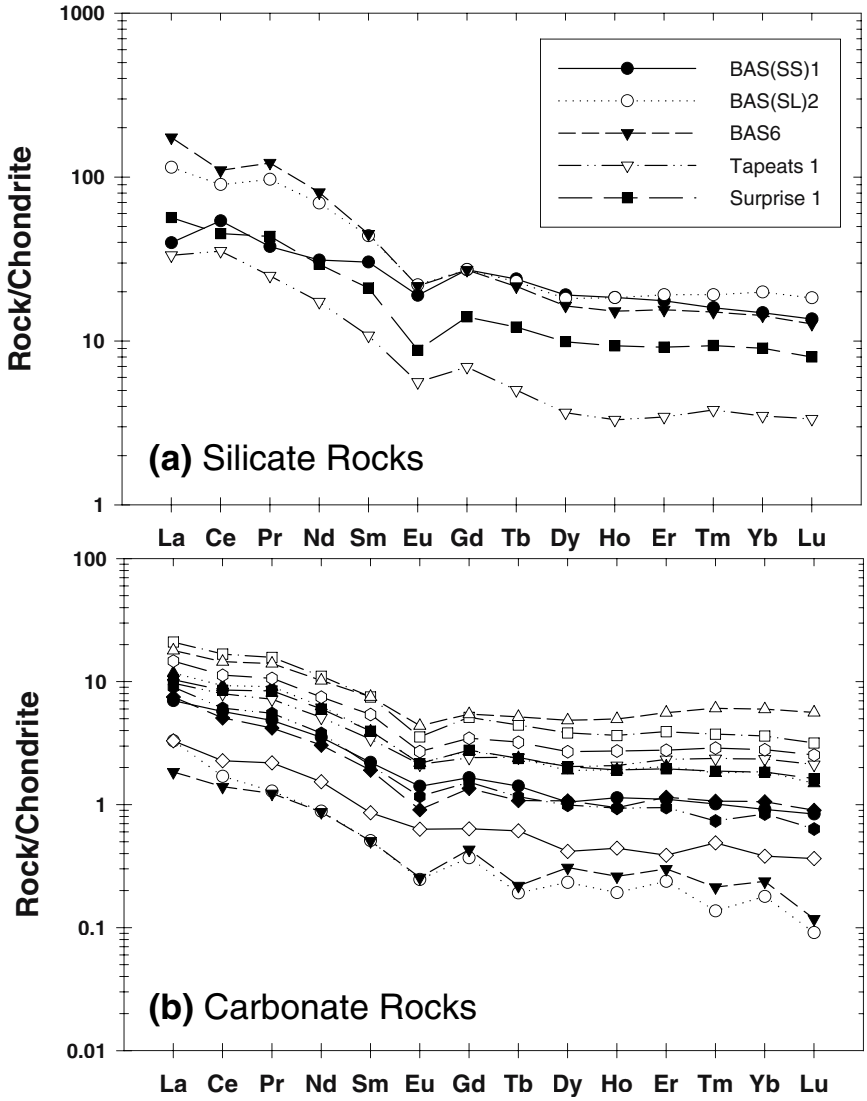


Figure 1. Chrondrite-normalized REE plots of (a) silicate rocks from Frenchman Mountain, Nevada and Death Valley, California, and (b) carbonate rocks (i.e., Bonanza King Dolomite) from Frenchman Mountain and Fossil Ridge (filled circle), Nevada. BAS = Bright Angel Shale. "Surprise" sample is from Death Valley. These rock samples were prepared and used in the batch tests.

King dolostone samples, up to 5.6 for sample BAS6 from the Bright Angel Formation (Table 2). All of the carbonate rocks have chondrite-normalized negative Ce anomalies, whereas the silicate rocks exhibit both negative and positive Ce anomalies (Fig.1). When the rock samples are normalized to Average Shale, they exhibit relatively flat patterns (not shown) as demonstrated by their $(Yb/Nd)_{SN}$ ratios (where SN = shale-normalized), which are generally close to 1 (Table 2). The Average Shale values used to calculate these shale-normalized ratios is the composite "Average Shale" previously used by oceanographic researchers (e.g., Elderfield and Greaves, 1982; DeBaar et al., 1983; Sholkovitz, 1988), and in our previous investigations (Johannesson et al., 1997, 2000a).

The chondrite-normalized REE patterns for the silicate and carbonate rocks of southern Nevada demonstrate that the carbonate rocks contain lower abundances of all of the REEs than the silicate rocks (Fig. 1). The spiky HREE patterns exhibited by some of the carbonate rocks (i.e., BKD1 and BKD2) reflect the difficulty encountered in quantifying the HREEs in these two rock samples using the digestion and analytical methods employed in this study. Many of the HREE for BKD1 and BKD2 approach or are below the method detection limits for our ICP-MS using the above described digestion techniques (e.g., Guo, 1996; Guo et al, this volume).

3.2 REES OF THE LEACH SOLUTIONS

3.2.1. *Leachable fraction using distilled water*

The REE data for each batch test are presented in Table 3. The data show that individual REE concentrations in the leachate solutions from Batch Test 1 are generally low, ranging from 1.4 pmol/kg to 2,570 pmol/kg (Table 3). In Batch Test 1, the solution that reacted with rhyolitic pumice (Surprise1) had the highest REE concentrations, whereas the solutions that reacted with Ordovician limestone (FR8Oaal), and with Cambrian dolomite (BKD3) exhibit the lowest REE concentrations (Table 3).

Rare earth element concentrations for each of the leachate solutions from Batch Test 1 are plotted in Fig. 2, where each leachate has been normalized to the REE concentrations determined in the respective rock with which each reacted. All of the leach solutions from Batch Test 1 have substantially lower REE concentrations than the respective rocks (e.g., between a factor of 10^5 to 10^6 lower). Interestingly, except for Eu in each case, and La for the leachates that reacted with BKD3 and FR8Oaal, the rock-normalized REE patterns for the leachate are relatively flat (Fig. 2). These flat rock-normalized pattern is best developed for the leachates that reacted with the rhyolitic rock sample, Surprise 1, with shale BAS(SL)2, and with fine sandstone BAS (SS)1 [(Yb/Nd)RN = 1.21, 1.04, 1.10, respectively; Table 3]. These flat patterns indicate that REEs were leached from these rocks in essentially the same relative proportions in which they occur in their respective rock samples. There is evidence for a slight enrichment in the HREEs in the Surprise 1 leach solutions, as the rock-normalized pattern for this leach solution exhibits a shallow positive slope between Tb and Lu (Fig. 2). There may also be some enrichment in the HREEs of the leachate solution that reacted with FR8Oaal, however insufficient data exists for the HREEs in this leachate (e.g., only Dy and Yb were quantified by our method). On the other hand, the leachates that reacted with dolomite (BKD3) and the

Table 2. Concentrations of rare earth elements (ppm) in aquifer materials (rocks) used for batch tests. CN = chondrite-normalized, SN = shale-normalized.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	$(Nd/Yb)_{CN}$	$(Yb/Nd)_{SN}$	Ce/Ce*	Eu/Eu*
BAS(SS)1	13.1	47.6	4.2	18.7	5.5	1.3	6.8	1.1	6.2	1.3	3.5	0.5	3.0	0.5	2.1	1.7	0.2	0.0
BAS(SL)2	37.8	79.4	10.9	41.6	8.0	1.5	6.8	1.1	5.9	1.3	3.8	0.6	4.0	0.6	3.5	1.0	0.0	-0.1
BAS6	57.7	97.0	13.7	48.5	8.2	1.5	6.8	1.0	5.4	1.1	3.1	0.5	2.9	0.4	5.6	0.6	-0.1	-0.1
Tapeats 1	11.0	31.3	2.8	10.4	2.0	0.4	1.7	0.2	1.2	0.2	0.7	0.1	0.7	0.1	5.0	0.7	0.1	0.0
Surprise 1	18.7	39.8	4.9	17.7	3.8	0.6	3.5	0.6	3.2	0.7	1.8	0.3	1.8	0.3	3.3	1.1	0.0	-0.1
FR8Oaal	2.3	5.1	0.5	2.1	0.4	0.1	0.4	0.1	0.3	0.1	0.2	0.0	0.2	0.0	3.8	0.9	0.0	0.0
BKD1	1.1	1.5	0.1	0.5	0.1	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	5.0	0.7	-0.1	-0.1
BKD2	0.6	1.2	0.1	0.5	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.0	0.0	3.7	1.0	0.0	-0.1
BKD3	3.2	7.0	0.8	3.1	0.6	0.1	0.6	0.1	0.7	0.1	0.5	0.1	0.5	0.1	2.2	1.7	0.0	0.0
BKD4	3.4	7.5	0.9	3.6	0.7	0.1	0.7	0.1	0.7	0.1	0.4	0.1	0.4	0.1	3.3	1.1	0.0	0.0
BKD5	6.9	14.7	1.8	6.7	1.4	0.2	1.3	0.2	1.2	0.3	0.8	0.1	0.7	0.1	3.1	1.2	0.0	-0.1
BKD6	2.5	4.5	0.5	1.8	0.3	0.1	0.3	0.1	0.3	0.1	0.2	0.0	0.2	0.0	2.9	1.3	0.0	-0.1
BKD7	1.1	2.0	0.2	0.9	0.2	0.0	0.2	0.0	0.1	0.0	0.1	0.0	0.1	0.0	4.0	0.9	0.0	0.1
BKD8	3.9	8.2	1.0	3.8	0.7	0.2	0.7	0.1	0.6	0.1	0.4	0.1	0.4	0.1	3.4	1.1	0.0	0.0
BKD9	5.9	12.8	1.6	6.1	1.4	0.3	1.4	0.2	1.6	0.3	1.1	0.2	1.2	0.2	1.7	2.1	0.0	0.0
BKD10	3.0	5.4	0.6	2.3	0.4	0.1	0.4	0.1	0.3	0.1	0.2	0.0	0.2	0.0	4.5	0.8	0.0	0.0
BKD11	4.9	9.9	1.2	4.5	1.0	0.2	0.9	0.2	0.9	0.2	0.6	0.1	0.6	0.1	2.9	1.3	0.0	-0.3

$Ce/Ce^* = \log \{2Ce_{SN}/[La_{SN} + Pr_{SN}]\}$.
$Eu/Eu^* = \log \{2Eu_{SN}/[Sm_{SN} + Gd_{SN}]\}$.

Table 3. Concentrations of rare earth elements (pmol/kg) in leachates from three batch tests. RN = rock-normalized. Ratios are shale-normalize

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Yb/Nd)	Ce/Ce*	Eu/E
Test 1																	
BKD3	179.3	135.6	18.1	78.7	19.9	43.9	19.0	1.4	11.5	1.5	4.5	0.0	5.3	0.0	0.5	-0.3	1.0
Surprise 1	1594.6	2574.2	320.8	1201.8	216.1	95.1	232.1	30.0	174.2	37.7	117.5	18.7	124.1	19.8	1.2	-0.1	0.4
BAS(SL)2	185.0	464.6	59.7	226.4	47.1	26.5	50.3	7.2	38.0	6.3	20.1	3.5	18.7	3.4	1.0	0.1	0.4
BAS(SS)1	199.4	498.1	56.3	270.0	98.7	50.0	145.3	21.1	116.9	21.0	50.9	7.3	39.5	5.0	1.1	-0.1	0.3
FR8Oaal	194.4	28.0	6.6	17.6	1.5	4.3	3.2	0.0	1.7	0.0	0.0	0.0	1.8	0.0	1.4	-0.9	0.9
Test 2																	
Tapeats 1	122.5	213.7	22.1	79.6	21.9	146.3	15.4	2.0	8.8	2.1	6.9	1.4	2.1	0.7	0.5	-0.1	1.6
BAS6	506.5	475.8	77.2	341.7	72.5	27.6	91.2	12.3	58.3	9.9	33.6	3.0	36.7	5.3	2.2	-0.2	0.2
BKD1	43.9	120.4	11.2	54.9	22.1	22.1	24.5	4.2	22.9	2.8	9.6	1.8	7.1	0.9	2.3	0.1	0.7
BKD2	41.4	51.1	5.2	21.8	7.4	56.0	8.0	0.6	2.4	0.5	2.4	0.4	1.5	0.2	0.9	-0.1	1.6
BKD4	15.5	19.7	3.1	12.6	3.3	7.9	4.8	0.4	4.2	0.6	1.7	0.5	1.0	0.2	0.9	-0.2	1.0
BKD5	22.3	34.0	5.3	15.1	3.9	23.7	4.9	0.5	2.1	0.9	2.3	0.8	3.7	0.4	2.7	-0.1	1.5
BKD6	28.0	20.7	3.2	8.9	2.8	15.3	1.7	0.0	2.7	0.6	0.7	0.5	0.5	0.1	0.6	-0.3	1.6
BKD7	17.4	26.1	4.1	12.5	6.2	8.5	2.4	0.2	3.3	0.2	1.6	0.5	1.3	0.3	1.5	-0.1	0.8
BKD8	20.0	16.1	1.6	7.0	2.8	18.2	2.7	1.0	0.9	0.5	1.1	0.5	0.9	0.4	1.5	-0.2	1.5
BKD9	28.5	39.2	4.9	15.7	6.2	19.5	4.4	0.3	5.7	0.2	1.7	0.3	1.6	0.2	0.6	-0.1	1.2
BKD10	20.4	29.7	3.6	12.1	4.3	12.7	2.8	1.3	2.9	0.7	0.9	1.3	3.1	0.9	4.2	-0.1	1.2
BKD11	399.2	821.6	104.3	392.0	77.2	27.4	67.9	10.5	60.1	12.2	29.8	4.3	29.3	4.4	0.7	0.0	0.3
Test 3																	
FR8Oaal	221.7	245.5	43.5	183.7	37.2	15.0	37.5	6.6	24.7	5.8	22.3	1.4	11.4	1.4	0.9	-0.3	0.2
BAS6	334.0	1829.1	67.1	242.0	80.5	60.6	76.9	10.3	42.4	14.5	20.7	4.7	29.9	5.7	2.5	0.5	0.6
BKD1	138.9	2635.6	56.8	153.2	13.9	27.8	6.2	3.8	16.8	1.8	16.2	0.0	12.8	1.4	1.5	0.8	0.8
Tapeats 1	63.7	1513.0	16.1	88.7	11.0	223.1	19.7	0.0	4.8	0.0	2.1	0.0	3.0	0.0	0.6	0.9	1.8

$Ce/Ce^* = \log \{2Ce_{RN}/[La_{RN} + Pr_{RN}]\}$.

$Eu/Eu^* = \log \{2Eu_{RN}/[Sm_{RN} + Gd_{RN}]\}$.

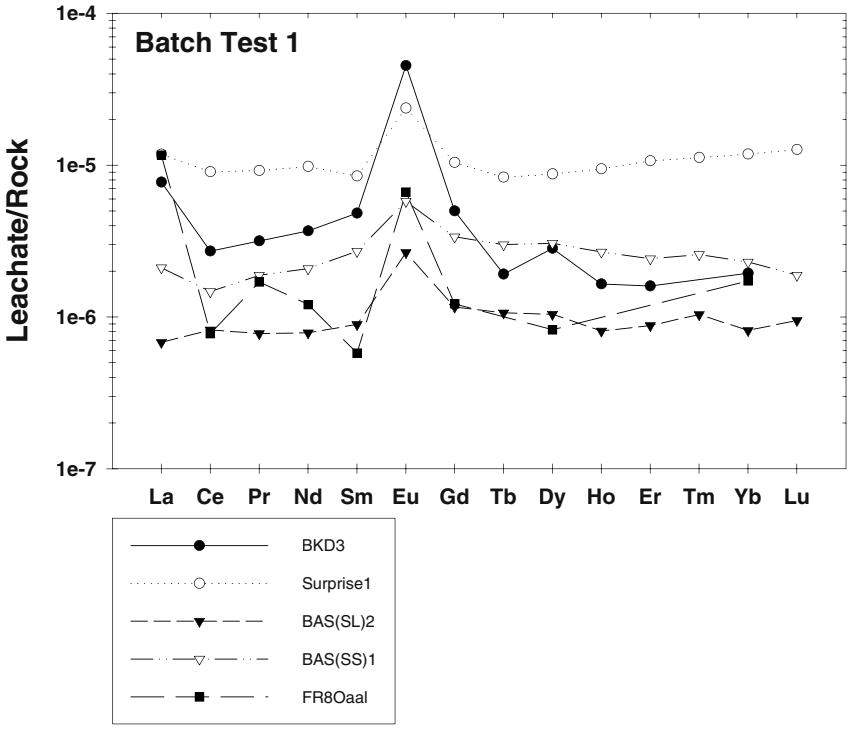


Figure 2. Rock-normalized REE patterns of the leachate solutions from Batch Test 1.

sandstone [BAS(SS)1] may have slight enrichments in the middle REEs (MREE) compared to their respective rocks. The Batch Test 1 leachates have variously enriched and depleted Ce concentrations. The leachate that reacted with BAS(SL)2 exhibits weak positive Ce anomaly (Ce/Ce* = 0.05; Table 3), whereas Surprise 1, BKD3, FR8Oaal, and BAS(SS)1 have negative Ce anomalies (Ce/Ce* = -0.07, -0.30, -0.93, -0.07, respectively; Table 3). On the other hand, the Eu concentration in each leachate is higher than expected based on the rock-normalized values for Sm and Gd ($0.28 \leq Eu/Eu^* \leq 0.97$; Table 3).

Table 3 contains rare earth element concentrations for each of the leachate solutions from Batch Test 2. The solutions that reacted with one of the Cambrian dolomites (BKD11), and the shale (BAS6) had the highest REE concentrations, whereas the solutions that reacted with other Cambrian dolomites (e.g. BKD4 and BKD8) exhibit the lowest REE concentrations (Table 3). The chief difference in Batch Test 2 compared to Batch Test 1 is the greater solution/rock sample ratio (by weight, 3:1 vs. 2:1, respectively; Table 1), and the greater duration of Batch Test 2 (67 days vs. 40 days for Batch Test 1; Table 1).

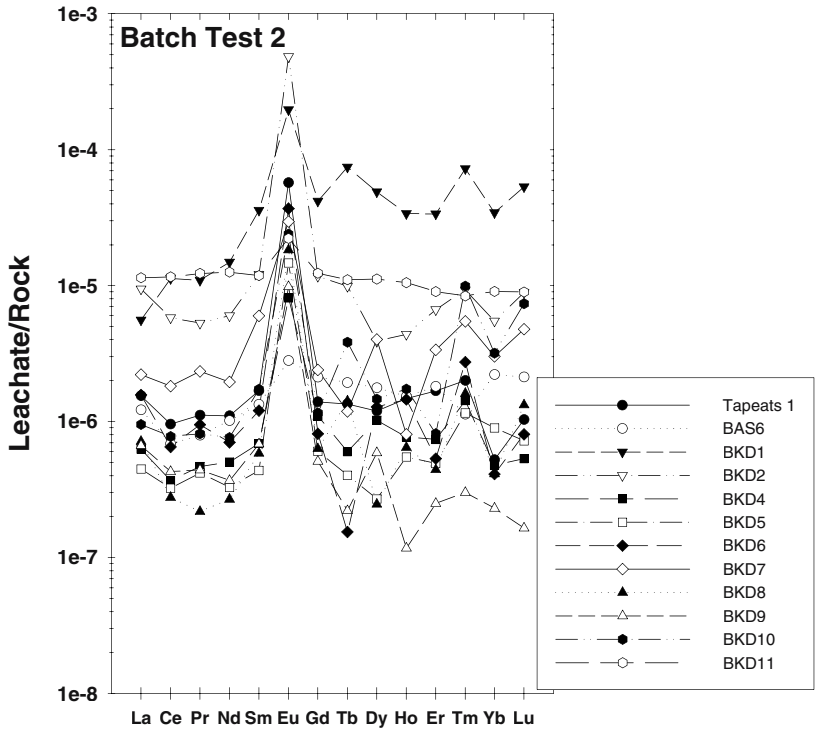


Figure 3. Rock-normalized REE patterns of leachate solutions from Batch Test 2.

Figure 3 is a rock-normalized REE plot of the leachate solutions from Batch Test 2 where each leach solution has been normalized to the respective rock with which it reacted. In general, the shapes of these rock-normalized leachate patterns resemble those from Batch Test 1 in that they are all relatively flat, and have large positive Eu anomalies ($0.21 \leq Eu/Eu^* \leq 1.61$; Table 3). Only two leachate samples do not exhibit the same degree of positive enrichment in Eu compared to Sm and Gd; BAS6 and BKD11 have Eu/Eu* of 0.21 and 0.27, respectively (Table 3). These leachates also exhibit weak negative Ce anomalies ($-0.29 \leq Ce/Ce^* \leq -0.01$), except for the leachate that reacted with BKD1 ($Ce/Ce^* = 0.13$; Table 3). The chief differences between the results of these two batch tests are the smoother LREE patterns and more variability in the HREE patterns of the Batch Test 2 leachates compared to the Batch Test 1 leachates.

3.2.2. *Leachable fraction using acidic water solution*

Table 3 also lists the REE concentrations of leach solutions from Batch Test 3, in which crushed rock samples were reacted with a weak nitric acidic solution (pH = 4) for 42 days. Similar to the other batch tests, the REE concentrations of these leachates are also low, ranging from 1.1 pmol/kg to 2,630 pmol/kg (Table 3). The solution that reacted with

Cambrian dolomite (BKD1) had the highest REE concentrations, whereas the solution that reacted with Tapeats Sandstone (Tapeats1) had the lowest REE concentrations (Table 3).

Rock-normalized REE ratios of these weak nitric acid leach solutions are plotted in Fig. 4. These leachates have similar (i.e., order of magnitude) REE concentrations to those of Batch Test 1 (Table 3) and also exhibit similar rock-normalized ratios. Again, all of the leachates of Batch Test 3 exhibit positive Eu anomalies that range from a low of Eu/Eu* = 0.22 up to Eu/Eu* = 1.82 (Table 3). In addition, all but the leachate that reacted with the Ordovician Limestone (i.e., FR8Oaal) have large positive Ce anomalies (Fig. 4). The leachate that reacted with FR8Oaal instead exhibits a small negative Ce anomaly (Ce/Ce* = -0.26; Table 3). Neglecting the Ce and Eu anomalies, the leachates that reacted with FR8Oaal, BAS6, and Tapeats1 have relatively flat rock-normalized REE patterns. However, the rock-normalized REE pattern for the leachate that reacted with BKD1 exhibits an irregular shape (Fig. 4).

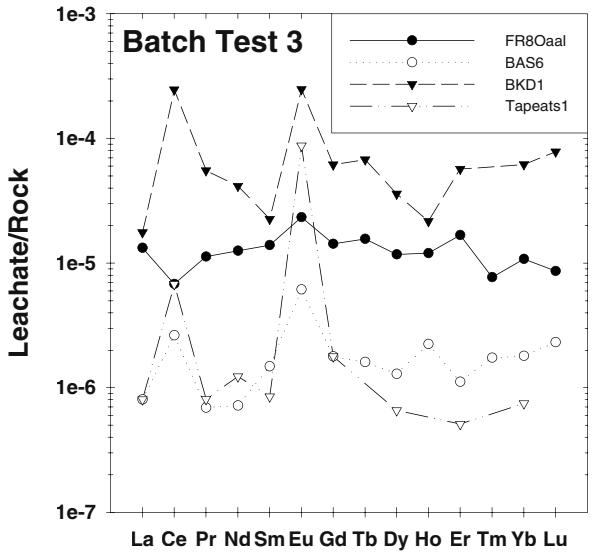


Figure 4. Rock-normalized REE patterns of leachate solutions from Batch Test 4.

4. Discussion

4.1. REE SIGNATURES OF LEACHATES

Many of the leachate solutions have REE signatures that are not substantially fractionated compared to the rock samples with which they reacted, and hence, do not differ from the source of the dissolved REEs in the leachates (Figs. 2 - 4). The similarities in the relative proportions of REEs between rock samples and leachates are especially apparent for the distilled-deionized water leachates (i.e., Batch Tests 1 and 2; Figs. 2 and 3). These data indicate that, in general, the REEs in these rocks must be in readily leachable sites. Although, overall the distilled-deionized water leachates exhibit relatively flat REE patterns when normalized to their respective rock sample, there are some subtle deviations that suggest minor fractionation of the REEs during the leaching process. For example, the leachate with perhaps the flattest rock-normalized pattern (i.e., Surprise 1, rhyolite) also exhibits a smooth increase in rock-normalized HREE values with increasing atomic number (Fig. 1). This smooth increase between Tb and Lu suggests that either (1) heavier REEs are located within progressively more readily leachable sites within the source rocks than the LREEs, or (2) solution complexation reactions in the distilled-deionized leachate become important as the water reacts with the rocks leading to preferential leaching and stabilization of HREEs within solution. Many investigators have argued that during the weathering process, LREEs released are subsequently captured by secondary clay minerals formed by weathering reactions, whereas the HREEs are preferentially liberated from the rock and removed from the site of weathering by solution complexation reactions involving inorganic and/or organic ligands (Nesbitt, 1979; Duddy, 1980; Schau and Henderson, 1983; Braun et al., 1993). It is well known that stability constants for REE complexes with carbonate ions increase with increasing atomic number (Cantrell and Byrne, 1987; Lee and Byrne, 1993). Moreover, production of bicarbonate and carbonate ions are a common product of weathering reactions involving silicate rocks and dissolution of carbonate rocks, respectively (e.g., Garrels and MacKenzie, 1967; Langmuir, 1971). Bicarbonate ions were likely produced in our Batch Test 1 and 2 as distilled-deionized water reacted with the crushed rock samples as vessels were initially open to the atmosphere.

Some of the leachates from the dolomites (Batch Test 2; Fig. 3) also exhibit enrichments in the HREEs relative to the LREEs, although the same, relatively smooth progressive increase in rock-normalized values reported for the Surprise 1 leachate is not observed. Instead, these dolostone leachates have a step-like rock-normalized REE pattern, with relatively lower LREE normalized values that step up to higher values between Nd and Sm, and are relatively constant from Tb through Lu (BKD1, Fig. 3).

Another subtle fractionation pattern of the rock-normalized leachate profiles is slight enrichments in the middle REEs. This subtle fractionation is only observed in leachates that reacted with the clastic sedimentary rock samples of the Bright Angel Formation [i.e., BAS(SS)1, BAS(SL)2; Fig. 2]. Johannesson and Zhou (1999) reported similar, albeit more pronounced, rock-normalized MREE enriched patterns for strong acid leach solutions that reacted with clastic sedimentary rocks containing Fe-Mn oxide/oxyhydroxide phases. Moreover, using a leach solution that specifically targets Fe-Mn oxide/oxyhydroxide phases (i.e., 0.04 M $NH_2OH{\cdot}HCl$ in 25% (v/v) CH_3COOH), these authors reported MREE enriched, rock-normalized REE patterns for those leachates that reacted with the clastic

sedimentary rocks containing petrographically identifiable Fe-Mn oxide/oxyhydroxide phases. Johannesson and Zhou (1999) suggested that the MREE enriched patterns of the leachates reflected the distribution of the REEs in the Fe-Mn oxide/oxyhydroxide phases within these rocks. Others have shown that such oxide phases commonly exhibit MREE enrichments (Gosselin et al., 1992). Consequently, the slight MREE enrichments of the distilled-deionized water leachates for the two Bright Angel Formation samples compared to their respective rocks may reflect the presence of Fe-Mn oxide/oxyhydroxide phases within these clastic sedimentary rocks that supply MREEs to the leachate solutions. Further investigation may involve leaching these rocks with a hydroxylamine hydrochloride solution to specifically examine the possible contributions of Fe-Mn oxide/oxyhydroxide phases to their readily leachable REE fractions.

Interestingly, the distilled-deionized water leachate of Batch Test 1 that reacted with BKD3 exhibits higher rock-normalized LREE values than observed for the HREEs (Fig. 2). The REE pattern of this leach solution suggests that the LREEs occur in sites in BKD3 that are more readily leached by distilled-deionized water than the HREEs, or alternatively, the LREEs are preferentially leached from the rock owing to the formation of stronger LREE complexes with some ligand(s) than for the HREEs. It is difficult to identify a ligand that could occur in distilled-deionized water that more strongly complexes the LREEs in solution than the HREEs. Because BKD3 is a dolomite, carbonate ions are expected to increase in the distilled-deionized water leachate as a result of the dolomite reacting with the neutral pH solution. As a consequence, we would expect that the HREEs would be more stable in the leachate than LREEs owing to complexation of the REEs with carbonate ions. Therefore, the enrichment of the LREEs in this leachate likely reflects that the LREEs occur in more easily leached sites than the HREEs in BKD3.

The most interesting feature of Batch Test 3 is that all of the leachates except for the one that reacted with the Ordovician limestone, FR8Oaal, exhibit positive, rock-normalized Ce anomalies (Fig. 3). Batch Test 3 involved reacting each of the rock samples with a weak nitric acid solution (pH = 4), and hence was different than the other batch tests where distilled-deionized water (pH ≈ 7) was used. The Tapeats Sandstone sample is enriched in Ce relative to La and Pr when normalized to chondrite. Consequently, the positive Ce anomaly of the leachate sample that reacted with the Tapeats Sandstone indicates that the weak nitric acid leachate preferentially liberated Ce from the Tapeats Sandstone compared to both La and Pr. The same preferential leaching of Ce from the rocks can be argued for both BAS6 and BKD1 as a result of reacting these rocks with the weak acid solution (Fig. 4). Relatively more Ce must have been leached from the Tapeats Sandstone, however, for the leachate solution to be enriched in Ce with respect to La and Pr when normalized to the Ce enriched Tapeats Sandstone (compare Figs.1 and 4). The difference in the behavior of Ce between the distilled-deionized leachate solutions and the weak nitric acid solutions indicates that a Ce enriched mineral or amorphous phase, that is susceptible to the weak acid leach but not the distilled-deionized water solutions, is present in these southern Nevada sedimentary rocks.

As mentioned above, all of the leachates exhibit positive Eu anomalies when normalized to their respective rocks. These positive Eu anomalies may reflect either BaO^+ interference on the two naturally occurring Eu isotopes (i.e., ^{151}Eu and ^{153}Eu) during mass quantification by ICP-MS (i.e., Jarvis et al., 1989), or simply the fact that the rocks are depleted in Eu with

respect to their chondrite-normalized Sm and Gd values (Fig. 1; Table 2). We suggest that for the vast majority of the leachates, the large positive Eu anomalies reflect Ba interference during quantification (i.e., false positive). For groundwater samples, the majority of the Ba is removed from the sample by extraction using diethylhexylphosphoric acid (Cerrai and Ghersini, 1966; Hodge et al., 1998). Typically, at least a 500 mL aliquot of each groundwater sample is required to quantify Eu after Ba is extracted from the sample. Unfortunately, insufficient leachate volumes were recovered during the batch tests in the current study (Table 1) to conduct the diethylhexylphosphoric acid extraction of Ba from these solutions, and subsequently correct the measured dissolved Eu concentrations.

Nonetheless, it is important to point out that for some of the leachate solutions; the Eu data suggests that false positives during mass quantification from Ba interferences may not be responsible for the positive Eu anomalies. These leachate solutions include those that reacted with BAS(SL)2, BAS(SS)1 of Batch Test 1, BAS6, BKD11 of Batch Test 2, and FR8Oaal and BAS6 of Batch Test 3. For the case of these leachate solutions, the positive Eu anomalies that are characteristic of the leachates are likely due, in part, to the large negative Eu anomalies of the rocks. In other words, because of the depletion in Eu (i.e., negative Eu anomalies) that is characteristic of the sedimentary (and felsic igneous) rocks from southern Nevada, normalization of leachate Eu values to the rock values leads, in part, to the positive rock-normalized Eu anomalies of the leachates. For example, the Eu concentration of the leachate that reacted with Surprise 1 rhyolitic pumice (i.e., 95.1 pmol/kg) is substantially lower than either the Sm or Gd concentrations (216 pmol/kg and 232 pmol/kg, respectively) in the leachate. Indeed, the Eu concentration of this leachate is 2.3 times lower than the corresponding Sm value, and 2.4 times lower than the Gd concentration. Moreover, the Eu concentration of the rhyolitic source rock is a factor of 6.3 lower than Sm, and 5.7 times lower than the Gd concentrations in this rock (Table 2). Hence, because the Eu concentration of the leachate in substantially lower than the corresponding Sm and Gd concentrations, the positive Eu anomaly or the rock-normalized leachate probably reflects the large Eu depletion of the rhyolitic rock, Surprise 1.

4.2. IMPLICATIONS OF BATCH TESTS

The results of our batch leaching tests are in general agreement, in terms of the similarities between the REE distributions of the leachates and the rock samples, with previous field investigations that report groundwaters with REE signatures that closely mimicked the REE signatures of the aquifer rocks through which they flowed (e.g., Smedley, 1991; Gosselin et al., 1992; Fee et al., 1992; Leybourne et al., 2000). In addition, the measured REE concentrations in the leachates from our batch tests are grossly similar, in magnitude, to those reported for groundwaters, including groundwaters from southern Nevada (Johannesson et al., 1997; 2000a). Consequently, the batch test data suggest that aquifer rocks are the primary source of REEs to groundwaters, and more importantly, REEs are leached from aquifer rocks by aqueous solutions in proportions similar to those found in the rock/aquifer materials. Consequently, the similarities between the results of our batch leach tests (i.e., REE concentrations and rock-normalized patterns) and reported observations of REE concentrations and patterns in actual groundwater-aquifer systems strongly suggests that groundwaters can inherit aquifer-rock like REE signatures via leaching reactions with the aquifer rocks without incurring significant fractionation of the REEs during the process.

It is generally well accepted that the acquisition of REEs by natural terrestrial waters from rock weathering reactions depends upon many factors including: (1) the distribution and abundance of REE-bearing minerals within the rocks; (2) the chemical composition of the natural water/weathering solution (e.g., major solute concentrations, pH, pe, concentrations of inorganic and organic complexing ligands, temperature); (3) the solubility of the REE-bearing minerals in the rocks with respect to the composition of the natural water/weathering solution; and (4) the ability of secondary minerals formed during water-rock reactions to accept REEs leached from the primary minerals of the unweathered rock (Humphris, 1984; Braun et al., 1990; Johannesson and Zhou, 1999). Moreover, previous investigators have examined REE fractionation as a function of chemical weathering of different types of parent rocks (e.g., Balashov et al., 1964; Ronov et al., 1967; Ludden and Thompson, 1978, 1979; Nesbitt, 1979; Duddy, 1980; Schau and Henderson, 1983; Humphris, 1984; Middelburg et al., 1988; Braun et al., 1990, 1993, 1998). Many of these studies indicate that weathered residual materials become enriched in LREEs and depleted in the HREEs compared to the parent rock during water-rock reactions owing, in part, to preferential mobilization of the HREEs (Balashov et al., 1964; Ronov et al., 1967; Nesbitt, 1979; Duddy, 1980). More specifically, LREEs are retained by secondary clay minerals formed by water-rock reactions, whereas HREEs are preferentially removed from the reaction site by solution complexation reactions involving inorganic and/or organic ligands (e.g., CO_3^{2-}, PO_4^{3-}, humic and/or fulvic acids) that are present in natural waters, including groundwaters (Nesbitt, 1979; Duddy, 1980; Schau and Henderson, 1983; Braun et al., 1993; Johannesson and Zhou, 1999). Therefore, solution and surface (i.e., adsorption) complexation can play important roles in fractionating REEs during water-rock reactions by enriching the aqueous solutions in the HREEs, and preferentially concentrating the LREEs in the residual phases (e.g., clay minerals). On the other hand, in the absence of important inorganic and organic complexing ligands, the REEs exhibit greater tendencies to sorb to surface sites as a function of increasing atomic number (e.g., Roaldset, 1974; Aagaard, 1974; Tang and Johannesson, in prep.).

The fact that the leachates resulting from the batch leach tests do not exhibit significant fractionation of the REEs compared to the aquifer rocks suggests that solution and surface complexation reactions involving these heavy metals were not important in the batch tests. More importantly, the observations reporting that many groundwaters have similar REE signatures to the aquifer rocks through which they flow implies that, at least in some cases, REEs are not fractionated during the weathering/leaching process whereby groundwater acquire their REE signatures. The results of our batch leaching tests and the reported REE patterns of actual groundwaters appear to contradict the observations and models of the behavior of REEs during the weathering process which argue for enrichment of the HREEs in the weathering solutions, and hence fractionation of the REEs. In other words, our batch tests suggest that, at least in some cases, preferential removal of HREEs compared to the LREEs from the site of active chemical weathering of aquifer rocks by groundwaters does not appear to be important. Instead, these leachates and real groundwaters appear to inherit REE distributions that closely resemble the source (i.e., aquifer) rocks.

However, more recent investigations have reported groundwaters with highly fractionated REE patterns compared to the aquifer/aquitard patterns (Johannesson et al., 1999, this volume; Johannesson and Hendry, 2000; Leybourne et al., 2000). For example, groundwaters from a shallow, basin-fill aquifer in southern Nevada, a till and clay-rich

aquitard in Saskatchewan, and a rhyolitic aquifer in central México, all exhibit large enrichments in HREEs compared to LREEs when normalized to the REE concentration in their respective aquifer materials (Johannesson et al., 1999, 2000a, this volume; Johannesson and Hendry, 2000). The fractionation of REEs in these groundwaters is consistent with the formation of carbonato and dicarbonato complexes in solution. More specifically, the LREEs exhibit a greater affinity to sorb to aquifer/aquitard materials than the HREEs because they chiefly occur in these circumneutral pH groundwaters as positively charged, solution species (i.e., $LnCO_3^+$, Ln^{3+}, $LnSO_4^+$), whereas the HREEs occur as negatively charged dicarbonato species (Johannesson and Hendry, 2000). Consequently, solution and surface complexation reactions do exert controls on REEs in groundwater-aquifer systems. Therefore, it is conceivable that during the initial weathering of aquifer rocks by relatively acidic aqueous solutions (e.g., meteoric waters augmented by soil-zone CO_2), the REEs are leached from aquifer rocks in roughly the same proportion with which they occur in the rock. However, with flow within the aquifer and as more rock is weathered, solution complexation becomes progressively more important (e.g., production of HCO_3 during weathering raises the pH and increases the significance of carbonate complexes) leading to strong fractionation of the REEs (Johannesson et al., 2000b, this volume).

Although the current batch study shows some interesting results for REEs in the leachates during rock/water interactions, more leaching tests with systematic design parameters are needed to better constrain the leaching processes. The design parameters, such as pH values of solutions, particle sizes of crushed rock samples, water-rock batch contact time, and amount ratios of solution to rock sample, must be carefully controlled to learn more about these processes that occur as REEs transition from source (i.e., aquifer) rocks to natural waters. Such systematic leaching studies using different types of rocks and solutions will help us to understand the relationship between aquifer rock and groundwater REE signatures, the leaching mechanisms and kinetics of REEs during water/rock interaction, and the controlling factors on REE signatures and fractionation in natural waters.

5. Conclusions

Laboratory batch tests were conducted in order to study the affect that compositionally different rocks have on the behavior and concentration of rare earth elements (REEs) in low-temperature aqueous solutions. Different rock types (i.e., shale, sandstone, limestone, dolomite, and rhyolitic pumice) were reacted with distilled deionized water (pH=7; 18 MΩ-cm), and/or acidic aqueous solutions (pH=4). Rock samples were crushed to about 70 mesh in size. Different amounts of distilled deionized water or acidic aqueous solutions were mixed with 20 to 80 grams of individual crushed rock samples within acid-washed, pre-clean polyethylene bottles (mass ratio of aqueous solution to rock sample ranged from 2:1 to 3:1). The crushed rock samples and aqueous solutions were allowed to react for 40 to 65 days at room temperature (~25°C). The sample slurry was subsequently centrifuged and the supernatant filtered (0.45 μm poly-carbonate membrane) before quantification of dissolved REEs by ICP-MS. Concentrations of REEs in the leachate solutions are low, ranging from 0.05 pmol/kg to 2,570 pmol/kg. Solutions that reacted with rhyolitic pumice exhibit the highest REE concentrations, whereas the solutions that reacted with Ordovician limestone, and especially with Cambrian dolomite, have the lowest REE concentrations. When the

leachates are normalized to the respective rock with which they reacted, they exhibit relatively flat REE patterns, except for large positive Eu anomalies. Interestingly, the solution that reacted with the pumice sample is slightly enriched in HREE, and the solution leached from Cambrian sandstone shows a weak MREE enrichment. These batch studies suggest that different types of rocks can play important roles in imparting REE signatures to natural waters, and in particular, groundwaters where rock/water ratios are high.

The results of our batch tests using aquifer materials and solutions allowed us to characterize REE signatures released from rock samples to leachates and to determine the easily exchangeable fractions of REEs during water/rock interaction under standard conditions. Moreover, this study provides information that may be applicable to REE behavior during low-temperature water/rock interaction in general. However, we should apply these batch test results to real groundwater systems with great caution because other factors, such as the filter size used, possible secondary minerals in rock samples and variations of laboratory conditions, could also affect REE patterns of the leachate solutions. More systematic batch tests are needed to better control the leaching processes during rock/water interactions.

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