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Origin of rare earth element signatures in groundwaters of circumneutral pH from southern Nevada and eastern California, USA

Kevin H. Johannesson [a,*], Xiaoping Zhou [b], Caixia Guo [b], Klaus J. Stetzenbach [b], Vernon F. Hodge [c]

[a] *Department of Ocean, Earth and Atmospheric Sciences, Old Dominion University, Norfolk, VA 23529-0276, USA*
[b] *Harry Reid Center for Environmental Studies, University of Nevada, Las Vegas, Las Vegas, NV 89154-4009, USA*
[c] *Department of Chemistry, University of Nevada, Las Vegas, Las Vegas, NV 89154-4003, USA*

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Abstract

Concentrations of the rare earth elements (REE) were measured in circumneutral pH groundwaters from southern Nevada and Death Valley, CA. Groundwaters from the regional lower Paleozoic carbonate-rock aquifer (Cambrian–Devonian) have flat shale-normalized patterns that closely resemble the shale-normalized patterns of the aquifer rock samples (principally Cambrian). Groundwaters associated with younger carbonate rocks (chiefly Permian) in the study region exhibit heavy REE (HREE) enriched, shale-normalized REE patterns with substantial negative Ce anomalies that also mimic these carbonate rocks. In addition, groundwaters from the felsic volcanic rock aquifers have the same flat to light REE (LREE) enriched shale-normalized patterns with large negative Eu anomalies as the felsic volcanic rocks. The similar REE patterns of all the groundwaters and associated aquifer rocks studied suggest that the groundwaters inherited REE signatures from the host rocks through which they flow. Because negative Ce anomalies are not an uncommon feature of carbonate rocks of marine origin, the negative Ce anomalies reported here for these groundwaters may reflect a Permian marine Ce signature. Previously, we demonstrated that carbonate complexes dominate REE speciation in southern Nevada and Death Valley groundwaters. Moreover, solid–liquid partitioning coefficients (K_d) indicate that the affinity of LREEs to sorb to aquifer surface sites is substantially greater than for the HREEs in the southern Nevada carbonate- and felsic volcanic-rock alluvial aquifers. Consequently, the HREEs enrichments reported here for groundwaters associated with younger Paleozoic carbonate rocks compared to these source rocks is consistent with REE carbonate complexation and preferential removal of LREEs to aquifer surface sites. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Rare earth elements; Groundwater; Water–rock interaction; Hydrogeology; Solution complexation

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1. Introduction

Perhaps one of the most perplexing aspect of understanding the behavior of rare earth elements

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[*] Corresponding author. Fax: +1-757-683-5303; e-mail: kjohanne@odu.edu

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(REE) in natural waters is deciphering those processes that are responsible for controlling their dissolved concentrations and especially identifying the origins of the substantially different REE signatures reported for terrestrial waters of different bulk chemical compositions (Smedley, 1991; Gosselin et al., 1992; Möller and Bau, 1993). Although much has been learned about the important geochemical processes that control REE concentrations and behavior in the oceans (e.g., Elderfield and Greaves, 1982; Elderfield, 1988; Bertram and Elderfield, 1993), there have been far fewer investigations of the REEs in circumneutral pH waters despite the fact that the majority of natural terrestrial waters fall into this broad category. Understanding the geochemistry of REEs in circumneutral pH terrestrial waters, such as groundwaters, is important from both the standpoint of their potential use for investigating water–rock interactions, as well as for tracing groundwater flow (Fee et al., 1992; McCarthy et al., 1998). Moreover, ascertaining the behavior of the REEs in natural terrestrial waters is especially significant in the study of the fate and transport of radioactive transuranics in the environment because of the chemical similarities of the REEs and trivalent transuranics (i.e., Pu^{3+}, Am^{3+}, Cm^{3+}, and Cf^{3+}; Choppin, 1983, 1986, 1989; Brookins, 1986; Krauskopf, 1986; Wood, 1990). Therefore, it is generally well accepted that the ubiquitous and naturally occurring REEs can be used as chemical analogs for studying the behavior of the highly radioactive transuranics in natural waters.

In terms of the origins of aqueous REE patterns, some recent investigations have focused on alkaline terrestrial waters, demonstrating that these waters tend to be enriched in the heavy REEs (HREE) compared to the light REEs (LREE) when normalized to average shale (Möller and Bau, 1993; Johannesson and Lyons, 1994). The HREE enrichments are thought to be due to carbonate complexing and, in particular, the dominance of REE dicarbonato complexes (i.e., $Ln(CO_3)_2^-$; Ln is any lanthanide), whereby the increase in stability constants for REE dicarbonato complexes with increasing atomic number, translates to greater stability for the HREEs in these alkaline waters. On the other hand, acidic natural waters commonly exhibit middle REE (MREE) enriched shale-normalized REE patterns (Gosselin et al., 1992; Johannesson and Lyons, 1995; Nordstrom et al., 1995). In dilute acidic waters, free metal ions (i.e., Ln^{3+}) and aqueous sulfate complexes ($LnSO_4^+$) dominate the REE species, whereas fluoride (LnF^{2+}) and especially chloride ($LnCl^{2+}$) complexes are important in acidic brines (Wood, 1990; Lee and Byrne, 1992; Johannesson and Lyons, 1995). Because stability constants for REE sulfate complexes do not show much variation with atomic number [e.g., $\log\ {}_{SO_4}\beta_1^0(Ln) = 3.2 \pm 0.1$; Millero, 1992] solution complexation does not appear to fractionate REEs in acidic natural waters. Instead, in some cases chemical weathering reactions involving MREE enriched minerals or amorphous phases probably impart a MREE enriched signature to acidic natural waters (e.g., Johannesson and Zhou, 1999).

Previous examination of the REEs in near neutral pH groundwaters ($5.4 < pH < 6.8$), however, indicate that inheritance of rock REE signatures, as a result of solid–liquid exchange reactions such as dissolution/precipitation, cation exchange, weathering reactions, and/or leaching, plays an important role in the origin of the aqueous REE signatures (Smedley, 1991). In this study we investigate the link between the REE signatures of groundwaters of circumneutral pH and aquifer-rock REE signatures in aquifers composed of (1) Paleozoic carbonates and (2) felsic volcanic rocks of rhyolitic and quartz latitic composition from southern Nevada and Death Valley, CA. Our work indicates that both rock source inheritance and the interplay between solution and surface complexation are important in controlling the aqueous REE signatures of these groundwaters.

2. Hydrogeologic setting

The study region is shown in Fig. 1 and occupies much of southern Nevada and parts of Death Valley in eastern California, USA. Interest in the hydrogeology of the region is on the rise owing to the proximity of Las Vegas, NV, the Nevada Test Site, and Yucca Mountain (Fig. 1). Las Vegas is one of the fastest growing metropolitan areas in the USA, while the Nevada Test Site (NTS) and Yucca Mountain represent, respectively, a former nuclear weapons testing facility and a potential future high-level radioactive waste geologic repository. Consequently,

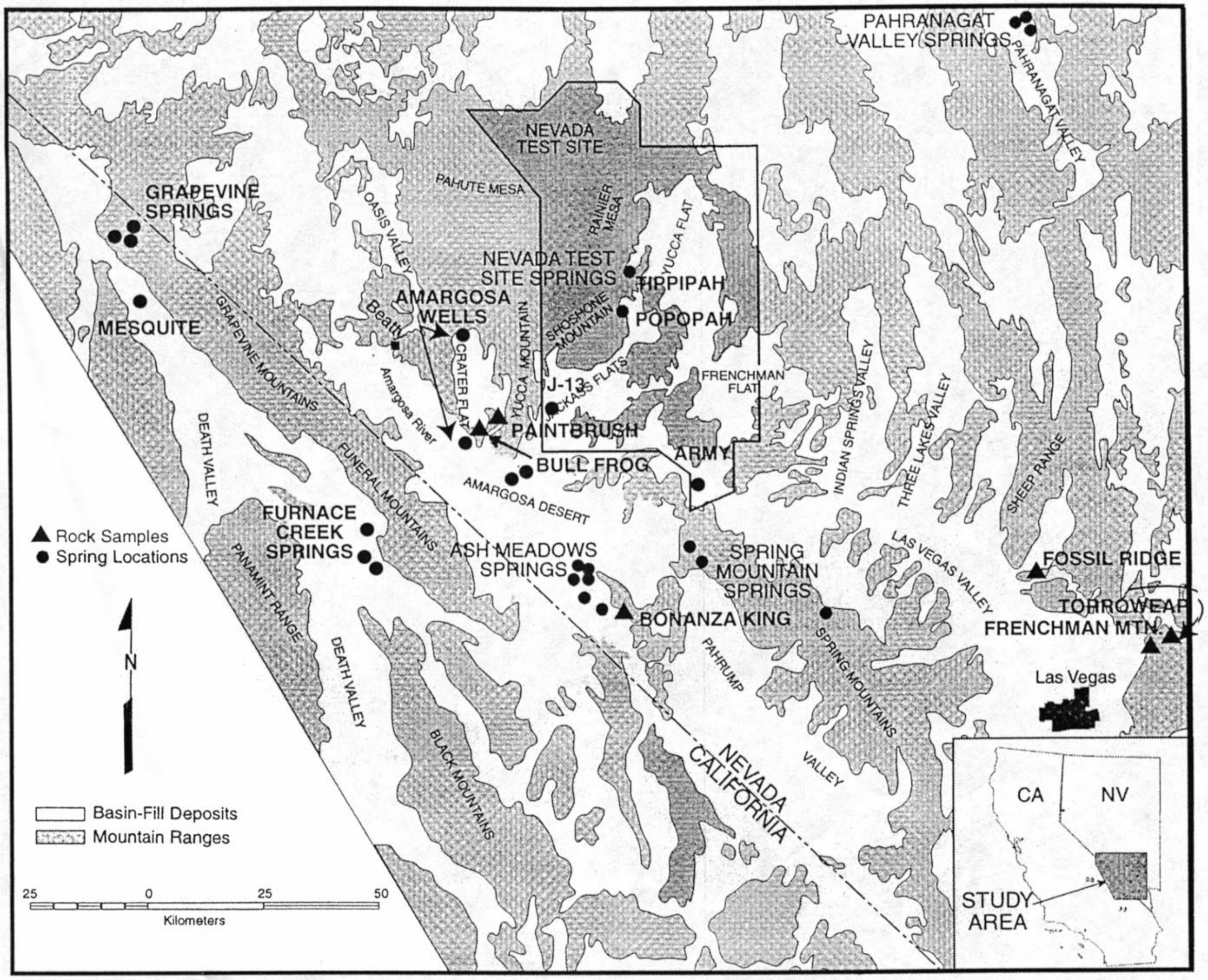

Fig. 1. Sample location map of southern Nevada and Death Valley, California modified from Johannesson et al. (1997a).

both water supply and water quality issues are critical to the region.

The geology of the study area consists of more than 11,000 m of Precambrian through Paleozoic sedimentary rocks that are principally of marine origin. Overlying the Precambrian and Paleozoic strata are roughly 4000 m of rhyolitic and quartz latitic Tertiary volcanic rocks of the Timber Mountain–Oasis Valley caldera complex (e.g., Frizzell and Shulters, 1990; Fridrich et al., 1994). The rocks are themselves overlain by Quaternary basin-fill alluvial and lacustrine sediments (Winograd and Thordarson, 1975). The two principal aquifers in the region are the lower Paleozoic (i.e., Cambrian through Devonian) regional carbonate aquifer, that is locally up to 4600 m thick, and the basin-fill aquifers (Winograd and Thordarson, 1975; Dudley and Larson, 1976; Winograd and Pearson, 1976; Claassen, 1985). The Tertiary felsic volcanic rocks, which occupy much of the NTS and Yucca Mountain region, are also identified as important groundwater bearing units, as is the upper Paleozoic (Pennsylvania through Permian) carbonate aquifer (Winograd and Thordarson, 1975; Dettinger, 1989; Fridrich et al., 1994).

Groundwater flow in the study region is generally thought to be from north to south, with an important component directed southwest towards Death Valley (Winograd and Thordarson, 1975; Dettinger, 1989; Laczniak et al., 1996). The combined annual discharge from the large springs within Ash Meadows is estimated at $10^{7.43}$ m^3, while discharge from the three principal Furnace Creek Springs (i.e., Texas, Nevares, and Travertine Springs) is around $10^{6.78}$ m^3/yr (Winograd and Thordarson, 1975). Precipitation in the region varies from approximately 500 mm/yr at high elevations such as the Spring Mountains, to < 100 mm/yr on the valley floors (Davisson et al., 1999). Because spring discharge from Ash Meadows and the Furnace Creek springs exceeds the amount of water annually recharged to the aquifers, groundwaters from: (1) the surrounding region, (2) the White River Valley to east of the study region, and (3) from central Nevada, are all thought to contribute to the waters issuing from the springs in Ash Meadows and Death Valley (Winograd and Friedman, 1972; Winograd and Thordarson, 1975; Dudley and Larson, 1976; Dettinger, 1989; Thomas et al., 1996; Davisson et al., 1999).

3. Methods

3.1. Sampling and analysis

Groundwater samples were collected from springs in Death Valley National Park, Ash Meadows National Wildlife Refuge, Pahranagat Valley National Wildlife Refuge, the Spring Mountains, and the Nevada Test Site (Fig. 1), by pumping, using a peristaltic pump, from each spring's source through precleaned, acid-washed Teflon® tubing. The water samples were filtered through 0.45 μm Gelman Sciences in-line groundwater filter capsules (polyether sulfone membrane) attached to the Teflon® tubing and transferred directly into acid-washed, high density linear polyethylene bottles (Stetzenbach et al., 1994). The samples were then immediately acidified to $pH < 2$ with ultra-pure nitric acid, placed in acid-washed plastic bags, and transported to the laboratory. Well waters from wells J-13 and Army well on the Nevada Test Site, and four wells from the Amargosa Desert, were sampled identically except that they were initially pumped until the pH stabilized (usually 30 to 40 min) before the water samples were collected to insure that the samples were representative of the local groundwater. Six groundwater samples from Death Valley, six samples from Ash Meadows, three from Pahranagat Valley, three from the Spring Mountains, four samples from the Amargosa Desert, and four samples from the Nevada Test Site (NTS) were collected and analyzed (Fig. 1).

Methods used to measure the REEs in these groundwater samples have been thoroughly described in the literature (Stetzenbach et al., 1994; Johannesson et al., 1997a; Hodge et al., 1998). Briefly, REEs concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer Elan 5000) after 50- or 100-fold preconcentration by cation-exchange (Stetzenbach et al., 1994). We monitored the REE isotopes ^{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 because they are free of elemental isobaric interferences. Introduction of each water sample into the plasma stream was achieved by ultrasonic nebulization, which increased sensitivity and decreased the potential of interferences from oxide formation. Measured $REEO^+/REE^+$ ratios were generally $< 1\%$, and for those which were $> 1\%$, appropriate corrections were made (Stetzenbach et al., 1994). Interference from BaO^+/Ba^+ on Eu was avoided by extraction of Ba from aliquots of each sample using diethylhexylphosphoric acid (Cerrai and Ghersini, 1966; Hodge et al., 1998). In order to calibrate the ICP-MS and verify our sample concentrations, a series of five REE standards of known concentrations (10 ng/kg, 50 ng/kg, 100 ng/kg, 500 ng/kg, and 1000 ng/kg) was included in each sample analysis.

Sampling and analytical techniques used to collect and analyze rock samples are described in detail by Johannesson et al. (1997a) and Johannesson and Zhou (1999). Limestone and dolostone samples were collected from Frenchman Mountain, Fossil Ridge in the Sheep Range, and the Pahrump Hills, while samples of the local felsic volcanic rocks were obtained from the south and west of Yucca Mountain (Fig. 1). All carbonate rock samples were processed by microwave digestion as discussed by Johannesson and Zhou (1999), whereas the volcanic rocks samples were fused by a lithium metaborate flux prior to dissolution in nitric acid solutions (Johannesson et al., 1997a). In both cases the resultant solutions were analyzed for the REEs by ICP-MS. The measured rock REE concentrations were verified against four U.S.G.S. standards (i.e., RGM-1, SCo-1, W-2, and G-2) from which they never varied by more than 10% RSD (Johannesson et al., 1997a; Johannesson and Zhou, 1999). Guo (1996) examined both the microwave digestion technique and the fusion method and found that both procedures resulted in similar and reproducible results.

3.2. REE solution complexation

The solution complexation of the REEs was modelled using standard techniques and stability constants obtained from the literature (Lee and Byrne, 1992, 1993; Millero, 1992; Byrne and Sholkovitz, 1996). Concentrations of free ligands (e.g., $[CO_3^{2-}]_F$) were determined from the measured major solute composition of each groundwater sample using the computer code PHREEQE (Parkhurst et al., 1980). The major solute composition of each groundwater sample was published previously (Hodge et al., 1996; Johannesson et al., 1996, 1997a,b; Stetzenbach et al., 1994). In general, Ash Meadows, Spring Mountain, and Pahranagat Valley groundwaters are classified as Ca–Mg–HCO_3 type waters, the Furnace Creek spring waters are Na–SO_4–HCO_3 waters, the Grapevine springs are Na–Ca–Mg–HCO_3 type waters, the Amargosa Desert groundwaters consist of both Ca–Mg–Na–HCO_3 and Na–K–HCO_3 waters, and the Nevada Test Site groundwaters (i.e., J-13, Tippipah, and Topopah) are Na–K–HCO_3 type waters (Winograd and Thordarson, 1975; Hodge et al., 1996; Johannesson et al., 1997a). Although all groundwater samples were relatively dilute, activity coefficients were ionic strength corrected using the techniques outlined by Millero (1992) in order to obtain speciation results directly comparable to our previous examination of REE complexation in brines (e.g., Johannesson and Lyons, 1994).

4. Results and discussion

4.1. REEs in groundwaters and aquifer rocks

Concentrations (in pmol/kg) of the REEs in groundwaters from southern Nevada and eastern California, that are discussed in this study, are presented in Table 1. The Ash Meadows, Spring Mountains, and Pahranagat Valley REE values in Table 1 represent average values of 6, 3, and 3 springs, respectively, from each site. The REE values for the Furnace Creek springs and Amargosa Desert wells represent the averages of 3 and 4 samples, respectively. The REE concentrations for these 3 Furnace Creek springs, the 4 Amargosa Desert wells, and the Ash Meadows springs were previously reported (Johannesson et al., 1997a). Concentrations of REEs (in ppm) for five samples of Paleozoic (i.e., Cambrian) dolostone representative of the regional lower Paleozoic (Cambrian through Devonian) carbonate aquifer of southern Nevada, three limestones, two of which belong to the Permian Toroweap Formation (Longwell et al., 1965), and are thus roughly characteristic of the upper Paleozoic (Pennsylvanian through Permian) carbonate aquifer (Winograd and Thordarson, 1975), as well as six different felsic Tertiary volcanic rock samples from southern Nevada (Johannesson et al., 1997a) are listed in Table 2. Shale-normalized REE profiles for these groundwa-

Table 1
Rare earth element concentrations in groundwaters from southern Nevada and Death Valley, CA reported in pmol/kg. Also included are shale-normalized Yb/Nd ratios [$(Yb/Nd)_{SN}$], Ce anomalies ($Ce/Ce^* = \log\{2Ce_{SN}/[La_{SN} + Pr_{SN}]\}$), and Eu anomalies ($Eu/Eu^* = \log\{2Eu_{SN}/[Sm_{SN} + Gd_{SN}]\}$)

	Army	Ash Meadows[a]	Furnace Creek[b]	J-13	Amargosa[c]	Spring Mountains[d]	Pahranagat[d]	Tippipah	Topopah	Grapevine	U. Grapevine	M. Grapevine	Mesquite
La	8.39	27	39	17.8	9.4	21	6.2	2322	1008	30	63	42	38
Ce	17.5	48	68	18		4.6	3.1	5053	3213	21	24	40	18
Pr	2.2	6.6	6.8	2.3	2.4	3.6	0.75	468.6	234	5.3	9	4.7	6.4
Nd	9	27	27	8	7.8	16	3.2	1576	863	19	35	17	25
Sm	1.9	5.4	5.3	1.8	1.5	4.6	0.83	396	181	4.1	7.1	3.8	5.3
Eu	0.3	1.1	1		0.5			31	18	0.8	1.5	0.99	0.8
Gd	1.8	5.6	5.5	1.95	1.3	6	0.73	280	185	4.8	9.4	4.3	5.9
Tb	0.3	0.82	0.77	0.38	0.2	0.96	0.11	45	32	0.44	1.1	0.5	0.9
Dy	1.45	4.7	4.2	2.6	1.3	5.7	0.71	141	190	2.7	6.9	3.5	5.9
Ho	0.4	1.1	0.8	0.8	0.4	1.4	0.18	30	36	0.6	1.6	0.8	1.3
Er	1.2	3.1	2.5	2.4	1.2	4.3	0.68	84	139	1.9	5	2.6	4.2
Tm	0.18	0.48	0.37	0.33	0.18	0.57	0.13	11.8	18	0.3	0.71	0.41	0.65
Yb	0.8	3	2.4	2.8	1	3.6	0.69	81	125	1.7	4.5	2.6	4
Lu	0.17	0.53	0.4	0.64	0.15	0.58	0.13	12.5	20.5	0.29	0.69	0.34	0.57
$(Yb/Nd)_{SN}$	1.18	1.47	1.17	4.48	1.63	2.86	2.82	0.669	1.876	1.16	1.67	2.00	2.14
Ce/Ce^*		−0.05	0.01	−0.18		−0.9	−0.47	0.074	0.210	−0.4	−0.63	−0.19	−0.56
Eu/Eu^*	−0.18	−0.09	−0.09		0.13			−0.403	−0.386	−0.13	−0.13	0.01	−0.23
pH	7.07	7.11	7.42	7.36	7.72	7.9	7.21	7.07	6.99	7.47	6.63	6.84	7.36

[a] Average of 6 samples.
[b] Average of 3 samples.
[c] Average of 4 samples (see Johannesson et al., 1997a).
[d] Average of 3 samples (see Johannesson et al., 1997b).

Table 2

Rare earth element concentrations in rocks from southern Nevada reported in ppm. Also included are shale-normalized Yb/Nd ratios [$(Yb/Nd)_{SN}$], Ce anomalies ($Ce/Ce^* = \log\{2Ce_{SN}/[La_{SN} + Pr_{SN}]\}$), and Eu anomalies ($Eu/Eu^* = \log\{2Eu_{SN}/[Sm_{SN} + Gd_{SN}]\}$). FR-1 was collected from Fossil Ridge, NV, French-1, FM1, FM2, and FM3 are lower Paleozoic dolostones from Frenchman Mountain, TW represents limestones of the Toroweap Formation, BF represents Bullfrog Tuffs, and TM stands for Timber Mountain Tuff

	Bonanza King[a]	FR-1[a]	French-1[a]	FM1	FM2	FM3	TW-NC	TW-C	BF-Vitric[a]	BF-Ash Fall[a]	BF-Med.[a]	TM-Nonw.[a]	TM-Weld[a]	Paintbrush[a]
La	1.78	1.93	2.44	5.07	9.84	3.22	1.85	3.24	79.7	44.6	38.5	39	36.1	31.7
Ce	2.79	3.17	1.36	11.3	19.9	6.72	1.37	1.19	150	91.4	78.4	77.3	73.6	71.7
Pr	0.35	0.41	0.34	1.47	2.39	0.9	0.27	0.33	16.4	10.4	9.23	8.41	8.11	8.15
Nd	1.39	1.48	1.41	5.56	8.93	3.31	1.02	1.22	53.1	35.7	32.6	26.2	25.9	26.6
Sm	0.27	0.28	0.26	1.24	1.53	0.65	0.16	0.19	8.40	6.66	6.5	4.81	4.96	7.02
Eu	0.055	0.06	0.05	0.3	0.36	0.16	0.05	0.05	1.08	0.49	0.73	0.38	0.27	0.35
Gd	0.36	0.19	0.31	1.29	1.55	0.64	0.23	0.27	7.09	6.21	5.98	4.39	4.75	6.87
Tb	0.063			0.23	0.23	0.1	0.03	0.04	0.95	0.98	0.97	0.62	0.75	1.15
Dy	0.37	0.24	0.31	1.5	1.3	0.57	0.2	0.25	5.2	5.83	5.45	3.78	4.56	6.79
Ho	0.08	0.05	0.07	0.33	0.27	0.13	0.06	0.08	1.05	1.12	1.12	0.74	0.95	1.39
Er	0.3	0.13	0.25	1.03	0.77	0.37	0.17	0.22	3.1	3.64	3.35	2.18	2.88	3.99
Tm	0.04	0.02	0.04	0.16	0.1	0.05	0.03	0.03	0.43	0.51	0.54	0.34	0.42	0.57
Yb	0.26	0.13	0.18	1.06	0.61	0.36	0.14	0.18	3.12	3.48	3.41	2.3	2.86	3.82
Lu	0.038	0.02	0.03	0.17	0.1	0.05	0.03	0.03	0.48	0.52	0.48	0.34	0.43	0.56
$(Yb/Nd)_{SN}$	1.99	0.91	1.39	2.05	0.74	1.16	1.5	1.59	0.64	1.05	1.13	0.95	1.2	1.55
Ce/Ce*	−0.06	−0.06	−0.45	0.004	0.002	−0.01	−0.34	−0.59	0.005	0.02	0.01	0.02	0.02	0.04
Eu/Eu*	−0.13	0.05	−0.09	0.01	−0.002	0.02	−0.01	−0.03	−0.22	−0.48	−0.3	−0.45	−0.63	−0.67

[a] Data from Johannesson et al. (1997a).

ters and rocks are plotted in Figs. 2–4. The composite shale used to normalize groundwater and the rock REE concentrations (see below) is the average shale used by Elderfield and Greaves (1982) and previously cited by DeBaar et al. (1983) and Sholkovitz (1988).

Concentrations of the REEs in these groundwaters range over two orders of magnitude. Groundwaters

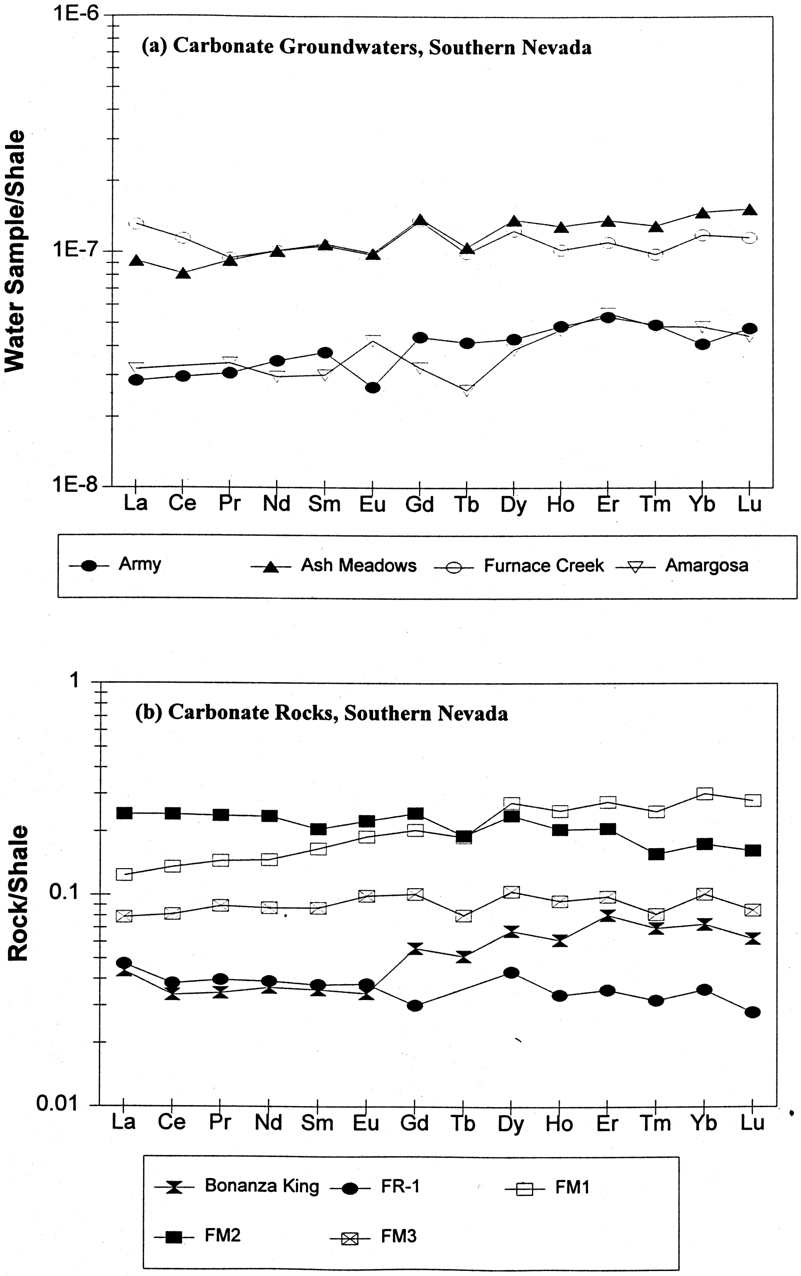

Fig. 2. Shale-normalized REE patterns for (a) groundwaters from the regional lower Paleozoic carbonate aquifer of southern Nevada and Death Valley, CA, and (b) Cambrian dolostones from southern Nevada.

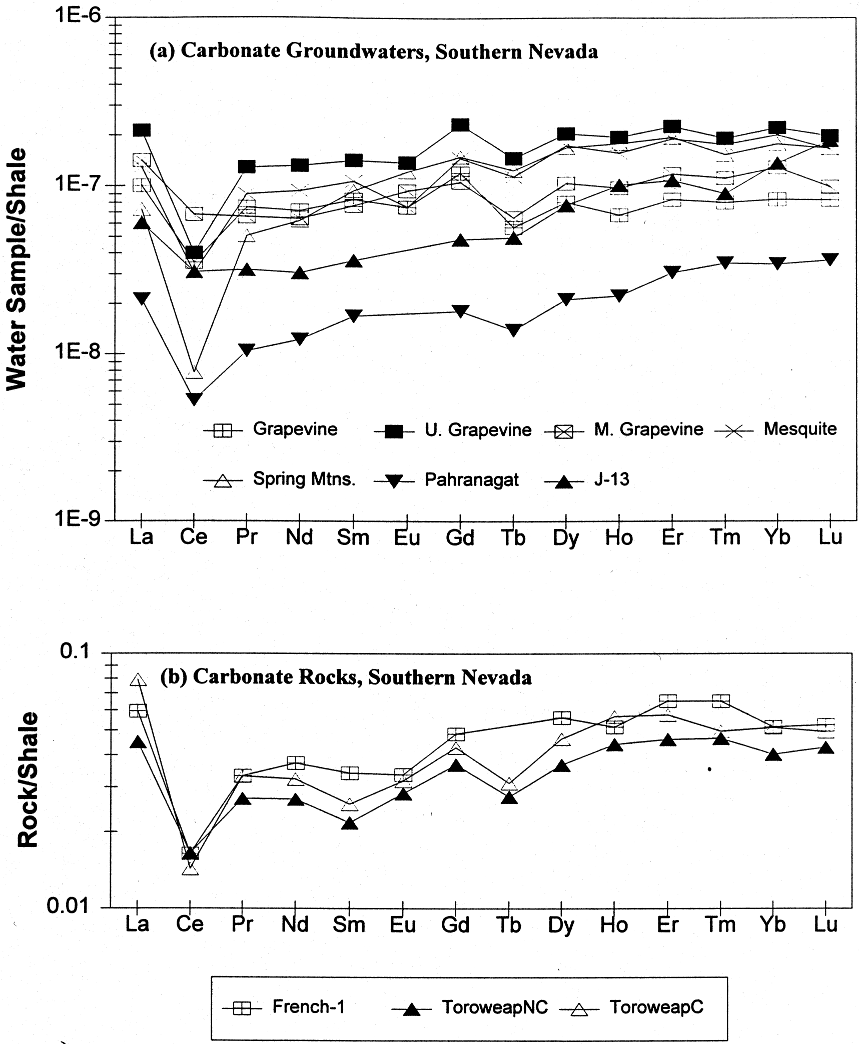

Fig. 3. Shale-normalized REE patterns for (a) groundwaters from younger Paleozoic carbonate-rock aquifers of southern Nevada and Death Valley, CA, and (b) Permian limestones from southern Nevada.

from Army well and the Amargosa Desert have similar concentrations (9 pmol/kg and 8 pmol/kg for Nd, respectively) and shale-normalized patterns (Fig. 2), while Tippipah and Topopah Springs, which emerge at the base of Shoshone Mountain on the Nevada Test Site, have the highest REE concentrations (1576 pmol/kg and 863 pmol/kg for Nd, respectively; Table 1). Army well, Amargosa Desert, and Pahranagat Valley groundwaters exhibit REE concentrations that are also similar in magnitude to seawater values (Elderfield and Greaves, 1982; Elderfield, 1988; Bertram and Elderfield, 1993). Rare earth element concentrations in the rock samples, however, vary by less than an order of magnitude, with the carbonate rock samples having overall lower values for each REE than the volcanic rocks (Table 2).

Shale-normalized patterns for groundwaters from the carbonate- and volcanic-rock aquifers are grossly similar to the shale-normalized patterns of the associated aquifer rocks (Figs. 2–4). Groundwaters and rocks of the carbonate aquifers exhibit two broad pattern types: (1) a relatively flat shale-normalized pattern with slight HREE enrichments [mean and

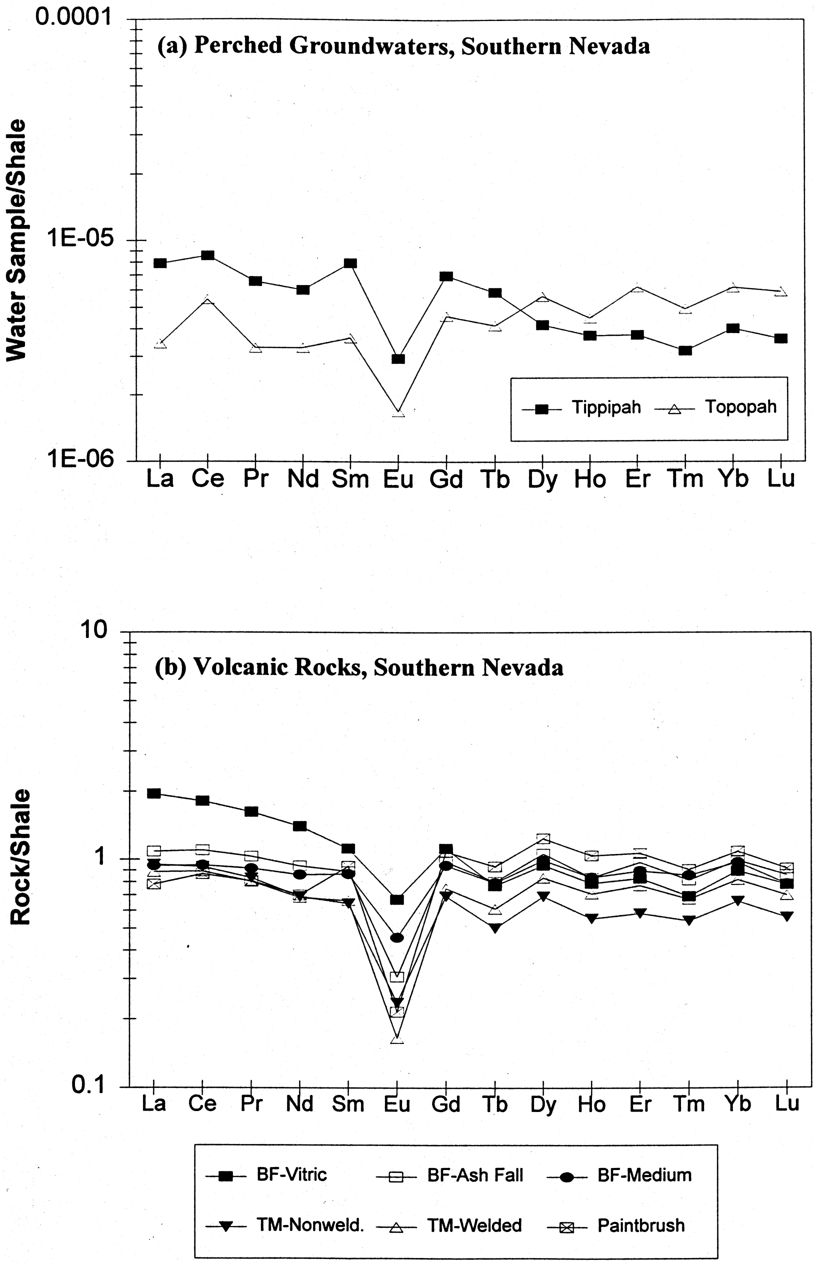

Fig. 4. Shale-normalized REE patterns for (a) groundwaters from perched felsic volcanic-rocks from the Nevada Test Site, and (b) rhyolitic and quartz latitic tuffs from southern Nevada.

standard deviation of groundwater and rock $(Yb/Nd)_{SN}$ ratios $= 1.36 \pm 0.23$ and 1.37 ± 0.61, respectively], and minor or no Ce anomalies (mean and standard deviation of Ce/Ce* of groundwaters and rock $= -0.02 \pm 0.03$ and -0.03 ± 0.03, respectively; Fig. 2); and (2) groundwater and rock samples with more pronounced HREE enrichments [mean and standard deviation of groundwater and rock $(Yb/Nd)_{SN}$ ratios $= 2.45 \pm 1.08$ and 1.49 ± 0.1, respectively], and substantial negative Ce anomalies (mean and standard deviation of Ce/Ce* for groundwaters and rocks = -0.45 ± 0.27 and -0.46 ± 0.13, respectively; Fig. 3). Rocks of the lower Paleozoic carbonate aquifer (Cambrian through Devonian; here dominantly Cambrian) typically have flat REE patterns when normalized to shale, while the younger Paleozoic carbonate rocks of southern Nevada (chiefly Permian) of the upper Paleozoic carbonate aquifer, exhibit seawater-like shale-normalized REE patterns (Figs. 2 and 3). Groundwaters known to discharge from rocks of the lower Paleozoic carbonate aquifer (Ash Meadows and Furnace Creek springs) and wells tapping this aquifer (e.g., Army well), have REE patterns that mimic these lower Paleozoic rocks, whereas groundwaters from regions up gradient of the Ash Meadows and Furnace Creek discharge sites, and those specifically associated with younger Paleozoic carbonate rocks (e.g., Spring Mountains, Pahranagat Valley, Grapevine springs) have REE signatures that resemble these younger carbonate rocks. Interestingly, well J-13 from the Nevada Test Site, which is finished in Tertiary tuffs, has a REE pattern more like the carbonate rocks than the local felsic volcanic rocks. This observation is addressed in a separate study (Stetzenbach et al., in prep.).

Although we only have two groundwater samples from a purely volcanic rock aquifer (i.e., Tippipah and Topopah Springs), it is clear from Fig. 4 that these groundwaters have shale-normalized REE signatures that are more similar to the local volcanic rocks than any of the carbonate rocks. Tippipah and Topopah spring waters, for example, both have substantial negative, shale-normalized Eu anomalies (Eu/Eu* = -0.4 and -0.39, respectively), positive Ce anomalies (Ce/Ce* = 0.07 and 0.21, respectively), and in the case of Tippipah Springs, an enrichment in the LREEs over the HREEs $[(\mathrm{Yb}/\mathrm{Nd})_{\mathrm{SN}} = 0.67]$. These features are shared by the felsic volcanic rocks (mean and standard deviation of Eu/Eu* = -0.46 ± 0.01), although the positive Ce anomalies of the rock samples (mean and standard deviation of Ce/Ce* = 0.02 ± 0.01) are less than observed for these spring waters.

Again the striking feature of these data is that groundwaters from these aquifers have REE signatures that closely resemble the REE patterns of the rocks through which they flow (Figs. 2–4). The compositions, therefore, strongly suggest that the REE signatures of the aquifer rocks exert important controls on the REE signatures of the associated groundwaters. These observations are in agreement with the conclusions of Smedley (1991) for groundwaters from southwest England.

4.2. Origin of Ce anomalies in carbonate groundwaters

Rare earth elements are expected to exist in the trivalent state in low-temperature aqueous solutions such as groundwaters (e.g., Brookins, 1989). The only exceptions include Eu which can be reduced to Eu^{2+}, and Ce which can be oxidized to Ce^{4+}. In low-temperature aqueous solutions, however, Eu^{2+} is not generally stable (Sverjensky, 1984), and as a consequence, the negative Eu anomalies that have been reported for some groundwaters likely reflect the upper crustal origin of the majority of rocks through which the groundwater flows (e.g., Banner et al., 1988). Oxidative processes involving Ce are, however, important in seawater, resulting in Ce removal and subsequent formation of negative, shale-normalized Ce anomalies (Elderfield and Greaves, 1982; Moffett, 1990, 1994; Sholkovitz and Schneider, 1991; Bertram and Elderfield, 1993; Byrne and Sholkovitz, 1996).

The negative Ce anomalies reported here for some groundwaters from carbonate-rock aquifers of southern Nevada could reflect oxidative removal processes involving Ce, to the aquifer substrate, dissolution of Ce depleted aquifer rocks (Fig. 3), or be related to the slightly higher pH of these groundwaters compared to those from the volcanic rocks (Table 1). The pH values of all the carbonate groundwaters examined in this study are, however, relatively similar. Consequently, it is difficult to explain the lower overall Ce concentrations reported for the groundwaters associated with the younger Paleozoic rocks as resulting from differences in pH values of these waters. On the other hand, Winograd and Robertson (1982) demonstrated that groundwaters from these carbonate-rock aquifers are typically well oxygenated. This observation lends support to the possibility that the negative Ce anomalies reported here for some southern Nevada groundwaters reflect the generally oxic conditions of these groundwaters. However, it is also difficult to explain why only some carbonate groundwaters from southern Nevada have negative Ce anomalies while others do not (Fig. 2a). In other words, if Ce oxidation and subsequent removal from solution is responsible for the negative Ce anomalies in these oxic groundwaters, we might expect to see similar negative Ce anomalies in all oxic groundwaters from southern Nevada carbonate-rock aquifers. Instead, only groundwaters collected up gradient from the Ash Meadows and Furnace Creek regional discharge zones, and specifically, those groundwaters associated with younger Paleozoic carbonate rocks, or alluvial deposits composed of these rocks, exhibit significant negative Ce anomalies (Fig. 3). These observations strongly suggest that the negative Ce anomalies reported for some southern Nevada groundwaters do not reflect redox conditions in the aquifers, but are instead related to the REE signature of the source rock through which they flow. Similar conclusions were obtained by Smedley (1991) in her study of groundwaters from southwestern England.

Fig. 5 presents shale-normalized REE patterns of Cretaceous limestones from the southern Alps (Bellanca et al., 1997) and Devonian dolostones and limestones from western Canada (Qing and Mountjoy, 1994). These data demonstrate that negative, shale-normalized Ce anomalies and slight HREE enrichments are not uncommon features of marine carbonate rocks. Bellanca et al. (1997) argued that the carbonate rocks they studied obtained their seawater-like REE signatures by uptake of dissolved REEs during calcite formation in seawater. The negative Ce anomalies and general enrichment in the HREEs of the southern Nevada carbonate rocks (Fig. 3b), therefore, likely reflects the REE signature of the seawater from which they precipitated. These rock data suggest that Permian seawater had relatively similar REE signatures to modern seawater. Others have also maintained that Permian seawater had major solute compositions like modern seawater (Horita et al., 1991). Wright et al. (1987) presented REE data for fossil, biogenic apatite from Phanerozoic sediments and argued that the negative, shale-normalized Ce anomalies exhibited by Permian biogenic apatites reflects the prevalence of oxidizing conditions in the Permian oceans. Thus the same may be true of the Permian carbonate rocks of southern Nevada. Consequently, the negative Ce anomalies and HREE enrichments of the groundwaters that flowed through these upper Paleozoic rocks of southern Nevada may ultimately be representative of Permian seawater REE signatures. Other studies of carbonate groundwaters from southern Nevada and Death Valley, California also reveal remarkable similarities between groundwater trace element concentrations and those of modern seawater (e.g., Hodge et al., 1996, 1998).

Interestingly, the carbonate groundwaters of the lower Paleozoic carbonate aquifer, as well as the Cambrian dolostones through which they flow, do not have shale-normalized REE patterns that resemble modern seawater (Fig. 2). Currently, it is unclear whether the shale-like patterns of these carbonate rocks reflect differences in the distribution of REEs in Cambrian seas or redistribution of REEs in these rocks during dolomitization. Wright et al. (1987) demonstrated that lower Palezoic biogenic apatites had either no Ce anomalies or slight positive anomalies owing to the ocean-wide anoxia characteristic of much of the lower Paleozoic. On the other hand, Banner et al. (1988) demonstrated that REEs can be mobilized in carbonate rocks by dolomitization. Hence, more study is necessary to sort out the importance of these processes on the REE concentrations of southern Nevada carbonate rocks.

4.3. REE fractionation patterns

Although the REE data presented here strongly suggest that groundwaters inherit REE signatures from aquifer materials, the data also indicate that other processes are important. For example, the shale-normalized Yb/Nd ratios [i.e., $(\mathrm{Yb/Nd})_{\mathrm{SN}}$] for groundwaters discharging directly from the lower Paleozoic carbonate aquifer (Fig. 2; mean and standard deviation for groundwaters and rocks $= 1.36 \pm 0.23$ and 1.37 ± 0.61, respectively), and the volcanic groundwaters and rocks (Fig. 4; 1.27 ± 0.85 and 1.09 ± 0.3, respectively) are similar; however, the $(\mathrm{Yb/Nd})_{\mathrm{SN}}$ ratios for the groundwaters associated with the younger Paleozoic carbonate rocks are generally greater than the ratios for these rocks (Fig. 3; mean and standard deviation for groundwaters and rocks $= 2.45 \pm 0.66$ and 1.49 ± 0.1, respectively). The $(\mathrm{Yb/Nd})_{\mathrm{SN}}$ ratios (a measure of fractionation) indicate that the groundwaters associated with younger Paleozoic carbonate rocks in the study re-

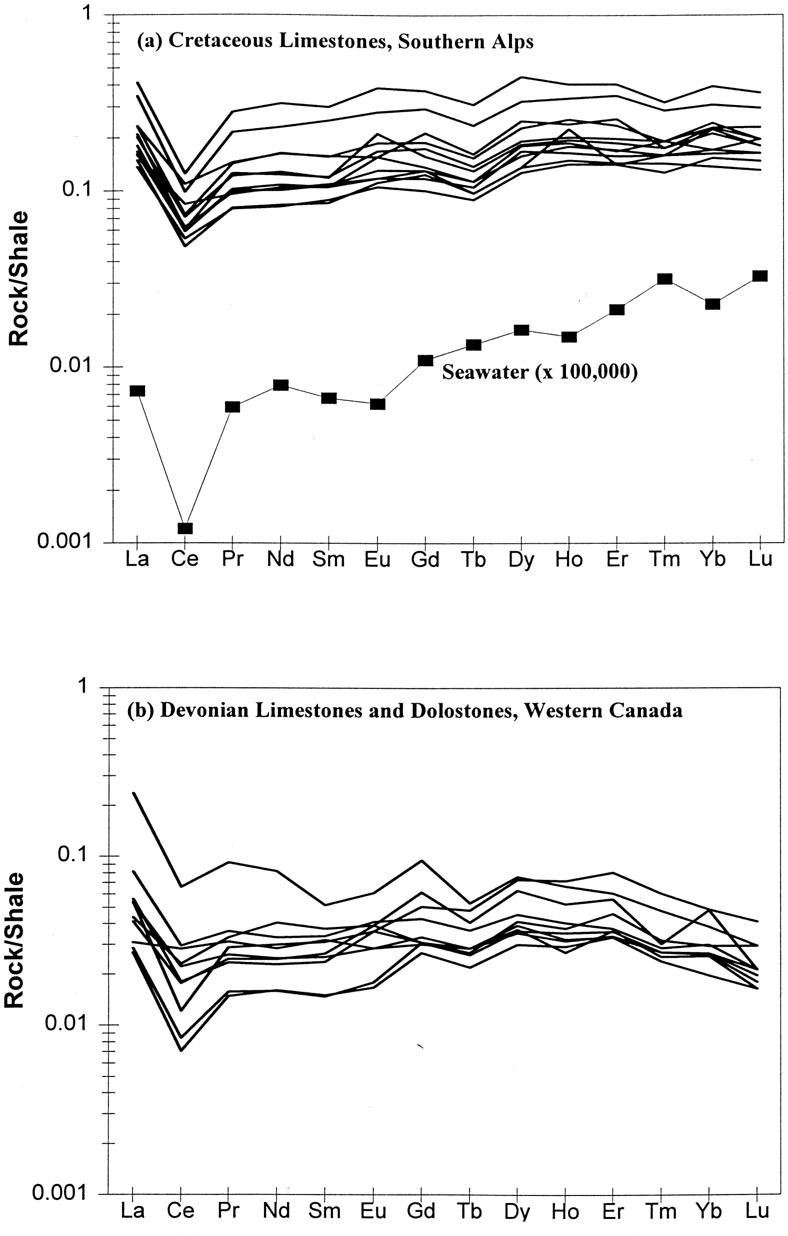

Fig. 5. Shale-normalized REE patterns for (a) Cretaceous limestones from the southern Alps (Bellanca et al., 1997), and (b) Devonian limestones and dolostones from western Canada (Qing and Mountjoy, 1994). Seawater values are those from Brewer (1975).

gion are, in general, more fractionated than the rocks through which they flow.

One explanation for the greater HREE enrichments of these groundwaters compared to the younger Paleozoic carbonate aquifer rocks is solution complexation reaction involving the REEs. Previously, we modelled the solution complexation of REEs in southern Nevada and Death Valley groundwaters and demonstrated that carbonate complexes ($LnCO_3^+$ and $Ln(CO_3)_2^-$) are the dominate dissolved form of these metals, accounting for at least 50%, and up to $> 99\%$ of each REE in solution (Johannesson et al., 1996, 1997b). Phosphate complexes and the free metal species ($LnPO_4^0$ and Ln^{3+}, respectively) were also shown to be of significance in some of these groundwaters (Johannesson et al., 1996, 1997b). The free metal ion species, for example, can account for between 12% to 20% of the lightest REEs (La, Ce, Pr) in Ash Meadows groundwaters, and as much as 40% of La in groundwaters of Tippipah and Topopah Springs (Johannesson et al., 1996, 1997b). As an example, Fig. 6 presents results of speciation calculations for La, Nd, Gd, and Yb for the three Grapevine springs (Grapevine, Middle Grapevine, and Upper Grapevine Springs) from Death Valley. It is clear from Fig. 6 that carbonate complexes dominate the speciation of the REEs in the three Grapevine springs, accounting for between 94% of La to $>99\%$ of Yb in Grapevine Spring waters, 76% of La to 99% of Yb in Middle Grapevine Spring water, and 65% of La to 98% of Yb in Upper Grapevine Spring waters. Bicarbonate and sulfate complexes are also expected to be of importance for the LREEs in Middle and Upper Grapevine Springs (Fig. 6). Therefore, the greater $(\mathrm{Yb}/\mathrm{Nd})_{\mathrm{SN}}$ ratios of groundwaters associated with the younger Paleozoic carbonate rocks compared to these rocks is consistent with the predicted dominance of REE carbonate complexes in these groundwaters. Stability constants describing the formation of REE carbonate complexes increase with increasing atomic number across the REE suite (e.g., Cantrell and Byrne, 1987; Millero, 1992; Lee and Byrne, 1993). Consequently, carbonate complexes of the HREEs are more stable in solution than those of the LREEs.

Complexation of REEs with organic ligands is probably important in natural waters where naturally occurring organic matter concentrations are high, or where anthropogenic organic acids with strong affinities for the REEs are abundant (e.g., EDTA; Wood, 1993; Byrne and Li, 1995; McCarthy et al., 1998). Experimentally determined stability constants for the REEs with some simple organic acids do increase with increasing atomic number (Wood, 1993; Byrne and Li, 1995). Current models, however, are unable to predict the speciation of REEs with naturally occurring organic matter owing to the complex nature of these materials, and the absence of a valid method to evaluate the activity coefficients and stoichiometric stability constants of REE complexes with humic and fulvic acids. Undoubtedly, more attention is necessary to satisfactorily assess complexation of REEs with naturally occurring organic ligands in natural waters.

Another possible explanation for the enrichment of HREEs over LREEs in these groundwaters compared to the younger Paleozoic carbonate rocks is preferential removal of LREEs to aquifer surfaces. Generally, surface complexation reactions involving the REEs are difficult to model in groundwaters owing to the paucity of data concerning surface complexation constants, and the numbers of surface sites within any given aquifer that are available for sorption of trace metals. Benedict et al. (1997), however, recently determined solid–liquid partitioning coefficients (K_{d}) for REEs with a variety of aquifer materials from southern Nevada. Specifically, saturation paste extract major ion compositions were determined for compositionally different alluvial basin-fill materials from southern Nevada, and subsequently used as representative ‘‘groundwaters’’ for REE sorption experiments (Benedict et al., 1997). The REE solid–liquid partitioning coefficients of Benedict et al. (1997) for the carbonate- and volcanic-rock alluvial aquifer materials are presented in Fig. 7. Shown are the K_{d}’s for particle size composites of carbonate and felsic volcanic rock alluvium as they were collected in the field (Fig. 7a), as well as the K_{d}’s determined for particles >2 mm for each bulk-rock composition (Fig. 7b). It is clear from Fig. 7 that the K_{d}’s for the carbonate rock materials are always greater than for the felsic volcanic rock materials, indicating that the REEs exhibit a greater affinity to sorb to the carbonate-rock aquifer materials (including alluvium composed of fragments of these carbonate rocks) than to the volcanic-rock aquifer materials. In addition, the K_{d}’s typically decrease with increasing atomic number across the REE suite for both bulk-rock compositions, demonstrating that the LREEs have a greater affinity for aquifer surface sites than the HREEs in both the carbonate- and felsic volcanic-rock aquifers of southern Nevada (Fig. 7). The only exceptions are Ce and Gd in the ‘‘as collected’’ particle size composite for southern Nevada carbonate-rock aquifer materials, which exhibit positive K_{d} anomalies compared to their nearest neighbors in the REE suite (Fig. 7a). The positive K_{d} anomalies for Ce and Gd indicate that these REEs have a greater affinity to sorb to aquifer surface sites in carbonate-rock alluvial deposits of

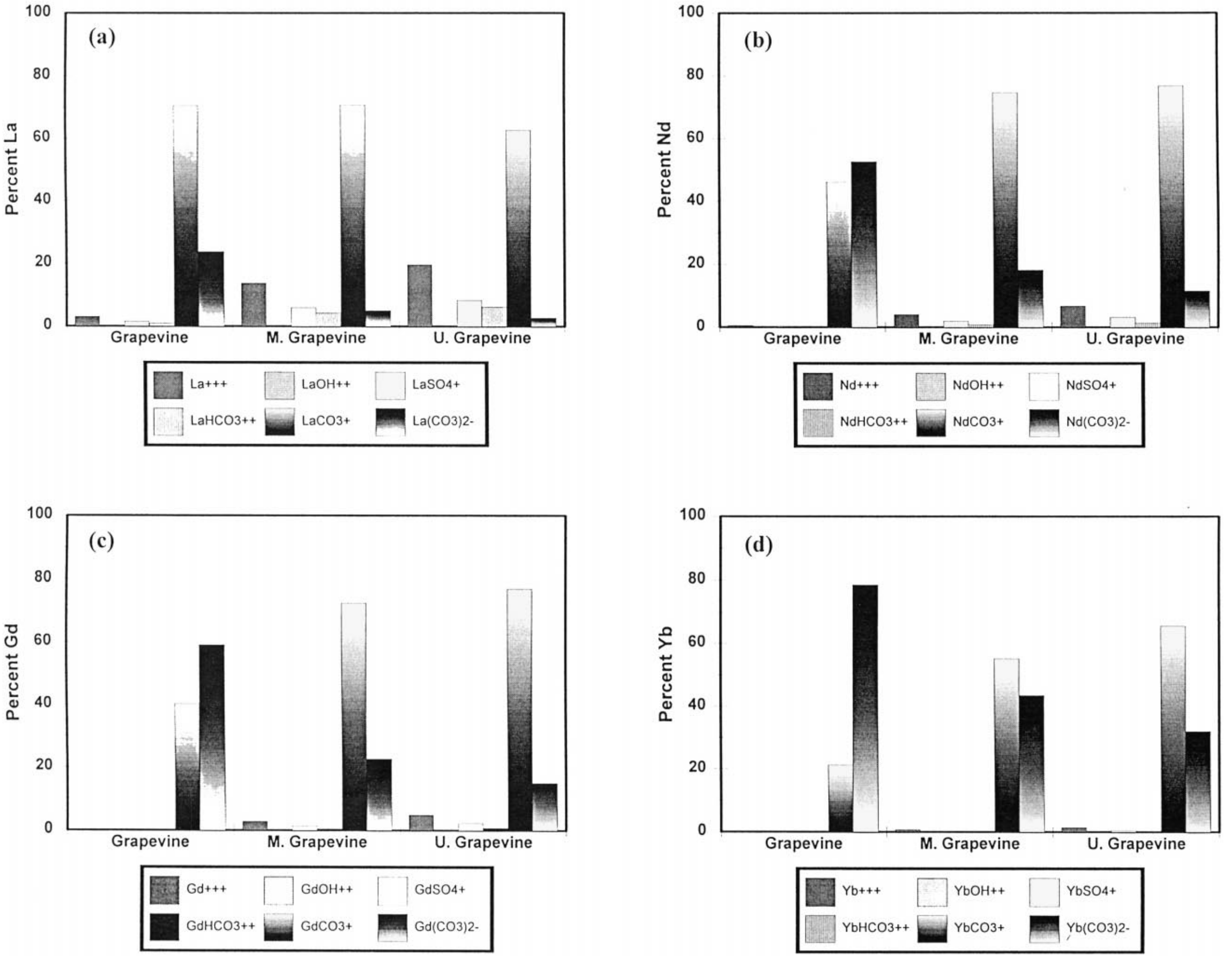

Fig. 6. Results of REE speciation calculations for (a) La, (b) Nd, (c) Gd, and (d) Yb for Grapevine, Middle Grapevine (M. Grapevine), and Upper Grapevine (U. Grapevine) Springs in Death Valley, California. La+++ = La^{3+}; LaOH++ = $LaOH^{2+}$; LaSO4+ = $LaSO_4^+$; LaHCO3++ = $LaHCO_3^{2+}$; LaCO3+ = $LaCO_3^+$; La(CO3)2− = $La(CO_3)_2^-$.

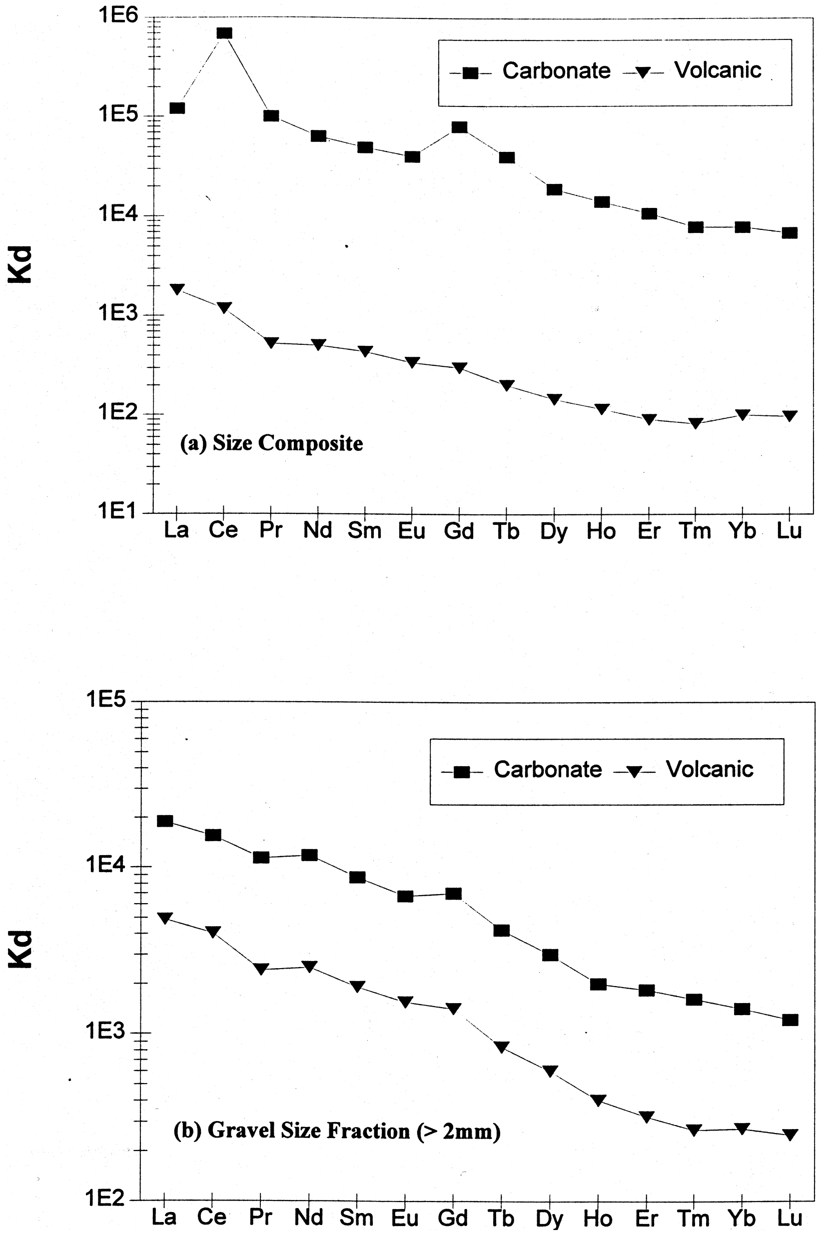

Fig. 7. Solid–liquid partitioning coefficients (K_d) for REEs for basin-fill alluvium composed of carbonate rocks and felsic volcanic rocks from southern Nevada for (a) particle size composites of alluvium as collected in the field and (b) particles size > 2 mm. Data from Benedict et al. (1997).

mixed particle size from the study region compared to their nearest elemental neighbors (Benedict et al., 1997).

Although the solid–liquid partitioning coefficients shown in Fig. 7 were determined using alluvial materials and thus may not be directly applicable to fracture flow in the carbonate- and felsic volcanic-rock aquifers of southern Nevada, these K_d's are consistent with the results of our previous solution complexation studies of southern Nevada and Death

Valley groundwaters (e.g., Johannesson et al., 1996; Hodge et al., 1998). Previous investigations demonstrated that in the absence of important inorganic and organic complexing ligands, the proclivity for REEs to adsorb to surface sites increases with increasing atomic number (Aagaard, 1974; Roaldset, 1974). However, for the groundwaters associated with younger Paleozoic carbonate rocks from southern Nevada and Death Valley, the HREEs are enriched relative to the LREEs when compared to the source rocks. These HREE enrichments indicate that the HREEs have a greater affinity for the solution phase in these groundwaters relative to the LREEs, which instead exhibit a greater propensity to sorb to aquifer surface sites. Because carbonate complexes dominate the speciation of the REEs in these groundwaters, and inasmuch as the stability constants for REE carbonate complexes increase with increasing atomic number (Cantrell and Byrne, 1987; Wood, 1990; Millero, 1992; Lee and Byrne, 1993), the greater affinity of the HREEs to remain in solution relative to the LREEs in these groundwaters likely reflects the importance of complexation of REEs with carbonate ions in solution.

Again, an especially interesting feature of the REE K_d's for the ‘‘as collected’’ carbonate alluvial materials of Benedict et al. (1997) is the positive Ce anomaly. The positive K_d anomaly for Ce suggests that the negative Ce anomalies reported here for many groundwaters of the carbonate-rock aquifers of southern Nevada (Fig. 3a) may reflect stronger adsorption of Ce to carbonate-rock aquifer surface sites compared to La and Pr. A similar K_d anomaly for Ce is not, however, observed for carbonate rock particles > 2 mm (Fig. 7b). Moreover, the experimental data of Benedict et al. (1997) suggests that the positive K_d anomaly for Ce may reflect particle size and not necessarily particle composition. A similar positive K_d anomaly for Ce was reported for < 53 μm size fraction of compositionally mixed (i.e., Paleozoic carbonate rocks, Paleozoic quartzite, Tertiary tuff) alluvial, basin-fill materials, and a substantially smaller positive K_d anomaly for Ce was described for the same size particles of the Paleozoic carbonate alluvium (Benedict et al., 1997). Further investigation is required, however, in order to clarify the relationships between the observed negative Ce anomalies in these groundwaters and preferential adsorption of Ce to the aquifer substrate implied by the work of Benedict et al. (1997). For example, it is interesting to note that although the K_d for Gd for the ‘‘as collected’’ carbonate alluvial materials suggests that preferential adsorption of Gd to the aquifer substrate ought to be observed, negative Gd anomalies are not a feature of these groundwater REE data (Figs. 2 and 3).

5. Conclusions

Concentrations of REEs were determined in groundwaters from regional carbonate aquifers in southern Nevada and Death Valley, CA, and a more localized felsic volcanic rock aquifer system in southern Nevada. The groundwater REE signatures were compared to the REE signatures of rocks collected from, or representative of, these aquifer systems in order to investigate the relationship between groundwater and aquifer-rock REE signatures. Our work indicates that groundwaters from the carbonate aquifers and the felsic volcanic rock system have REE signatures that closely resemble the REE signatures of the respective rocks through which the groundwaters flow. Of particular interest in this respect are the shale-normalized negative Ce anomalies reported for groundwaters associated with younger (principally Permian) Paleozoic carbonate rocks. We suggest that the groundwater and rock data are consistent with these carbonate groundwaters inheriting their negative Ce anomalies from the Ce depleted carbonate rocks through which they flow. Previously measured partitioning coefficients (K_d) demonstrate that LREEs exhibit a greater propensity to sorb to aquifer surface sites compared to the HREEs in the southern Nevada aquifers composed of both carbonate- and felsic volcanic-rock materials. Moreover, our investigations of REE solution complexation in southern Nevada and Death Valley groundwaters have shown that carbonate complexes consistently dominate REE speciation. Consequently, the observed fractionation of the REEs in groundwaters associated with younger Paleozoic carbonate rocks of southern Nevada compared to these source rocks is consistent with the formation of carbonate complexes in solution, and the greater affinity of LREEs to sorb to aquifer surface sites.

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