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Rare-earth elements in geothermal waters from Oregon, Nevada, and California

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Abstract

The concentrations of rare-earth elements (REE) were determined in thermal waters from hot springs in the Oregon Cascades and southeastern Oregon, and from wells in the Beowawe (NV), Dixie Valley (NV) and Heber (CA) geothermal fields. The waters are all near-neutral to slightly alkaline, and dominated by sodium chloride or sodium bicarbonate. Concentrations of REE range from $<10^{-6}$ to approximately 10^{-3} times chondrite. In general, filtered aliquots of the fluids contain substantially less REE (sometimes by an order of magnitude or more) than corresponding unfiltered aliquots, suggesting a considerable particulate contribution to the total REE. Concentrations of REE in the waters from Beowawe and Dixie Valley are generally quite low, possibly owing to loss of REE on boiling. Most of the waters exhibit LREE-enriched, chondrite-normalized REE patterns, with slight or non-existent Eu anomalies. The main exceptions are the waters from Heber, which exhibit a concave-upward pattern with a prominent, positive Eu anomaly ("Mexican hat" pattern). The behavior of REE in waters from continental geothermal systems is a useful indicator of water–rock interaction and holds promise as a potential tool for exploration.

Keywords: Rare earth elements; Geothermal systems; Water-rock interaction

1. Introduction

Improved knowledge of the behavior of the rare-earth elements (REE) in thermal waters has possible applications in the exploration for geothermal resources and the study of water–rock interactions in geothermal systems. To this end, we have embarked on a program to determine REE contents in waters from a wide variety of continental geothermal systems. We have previously reported results from geothermal systems in New Zealand [1,2] and Idaho [3]. In this paper we report results from geothermal systems in Oregon, Nevada and California. Samples were procured from natural hot springs located (Fig. 1) in the Oregon Cascades (Bagby, Breitenbush, Bigelow, Bellknap, Terwilliger, Wall Creek, McCredie and Umpqua) and southeastern Oregon (Crystal Crane, Mickey, Alvord, Borax Lake, Whitehorse Ranch, Snively), in June 1998 and October 1998, respectively. In addition, samples were taken from wells in producing geothermal fields in Nevada (Dixie Valley and Beowawe; Fig. 2) in November 1998, and California (Heber) in June 1999, but two samples were also taken from a natural hot spring (carbonate mounds) near the Dixie Valley geothermal field.

2. Experimental section

At each site, the following samples were taken: (1) a 1-L unfiltered sample for REE determination; (2) a 1-L filtered sample for REE determination; (3) a 250-mL filtered sample for non-REE cation determination; and (4) a 250-mL filtered sample for anion determination. All filtered samples were obtained by forcing the sample through a 0.45-μm polysulfone membrane with a hand-operated peristaltic pump. The first three samples were preserved with 2% high-purity HNO_3 and the last sample was unadulterated. Samples were stored in carefully cleaned, high-density polyethylene containers until analysis. At thermal springs, samples were procured with a polypropylene ladle with a 12-ft handle. Wells were sampled at the surface after phase separation, using a length of coiled stainless steel tubing cooled

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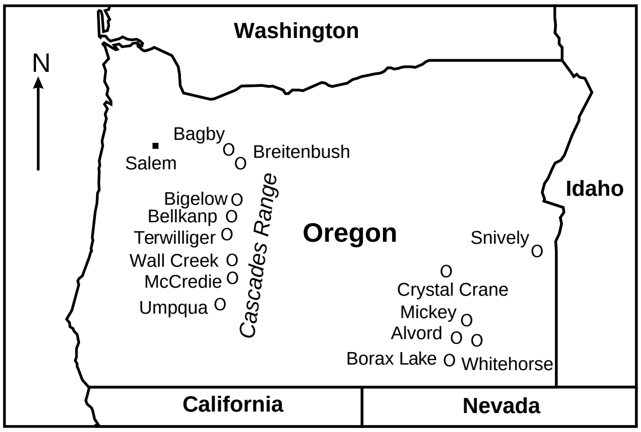

Fig. 1. Map showing the location of thermal springs in Oregon investigated in this study.

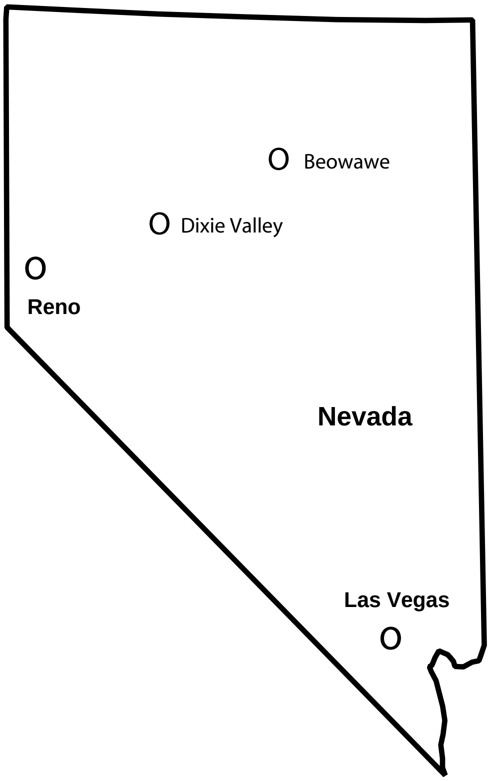

Fig. 2. Map showing the location of the Dixie Valley and Beowawe geothermal fields.

with water. Temperature, conductivity, and pH were determined in the field at each site. Alkalinity was determined by titration as soon, after sampling, as possible, usually within 72 h.

The REE were determined by inductively coupled plasma-mass spectrometry (ICP-MS) after pre-concentration via co-precipitation with ferric hydroxide. A Hewlett Packard (HP) 4500 ICP-MS was employed. Oxide formation, as measured by ^{156}[CeO]/^{140}Ce, was typically less than 0.5%. Corrections for isobaric oxide interferences were applied for BaO on Eu and Sm, PrO on Gd, and NdO on Tb. Cobalt, Ru, In, Re, and Bi were employed as internal standards. For more details on the analytical protocol for the REE see Ref. [4]. The results of the REE determinations are given in chondrite-normalized form in Figs. 3–8.

The elements Ag, Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sr, Ti, V, Zn were routinely determined via inductively coupled plasma-atomic emission spectrometry (ICP-AES) using Be, Sc, and In as internal standards. Fluoride, chloride, bromide, nitrate, phosphate, and sulfate were determined using ion chromatography. No attempt has been made to correct the compositions of thermal waters from wells for liquid–vapor phase separation. The pH and the concentrations of major components (Ca, K, Mg, Na, Si, F^-, Cl^-, HCO_3^-, and SO_4^{2-}) of the thermal waters are given in Table 1.

3. Results and discussion

3.1. *Oregon cascades*

Geologic, geophysical, geochemical and hydrological data suggest that the hot springs in the Western Cascades (Fig. 1) represent hydrothermal circulation directly related to recent igneous activity [5]. The rocks in the Western Cascades are predominantly volcaniclastic rocks and lava flows, comprising rhyodacites, dacites, andesites and basaltic andesites. The thermal fluids from this area may be characterized as dilute, near-neutral to alkaline, sodium chloride-dominated waters (Table 1). The fluid from Bagby is an exception in that it is a bicarbonate-dominated water; it is also the most alkaline and dilute of all the thermal waters studied from the Cascades.

The REE concentrations in the thermal waters from the Cascades (Fig. 3) range from $\sim 10^{-6}$ to 10^{-3} times chondrite. However, the filtered aliquots typically contain considerably less REE than the unfiltered aliquots, suggesting that much of the REE is present as particulate matter. A notable observation is that the water from Bagby, which has the highest pH and lowest total dissolved solids content, also has the lowest REE content, in both the filtered and unfiltered aliquots. With the exception of the fluid from Umpqua, the chondrite-normalized patterns exhibit an overall negative slope (LREE-enrichment). The pattern for the fluid from Umpqua has an overall positive slope. Moreover, the pattern has an “S” shape, being concave up from La to Gd and concave down from Gd to Lu. None of the fluids exhibit a strong Eu anomaly, although several appear to show very weak negative Eu anomalies.

The reason for the anomalous “S-shaped” REE pattern for the fluid from Umpqua is not clear. However, it is interesting that both the filtered and

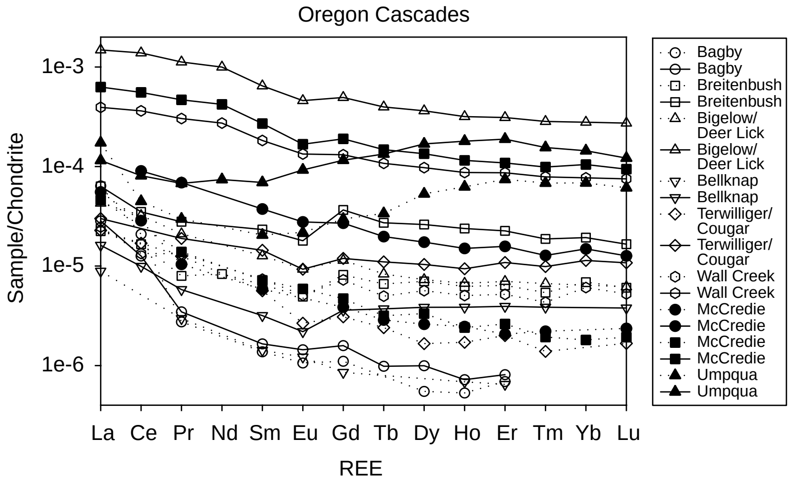

Fig. 3. Chondrite-normalized REE contents of samples from thermal springs from the Oregon Cascades. Note that in this and all subsequent diagrams, data for unfiltered samples are connected by solid lines and those for filtered samples are connected by dotted lines. REE concentrations for chondrite are taken from [13].

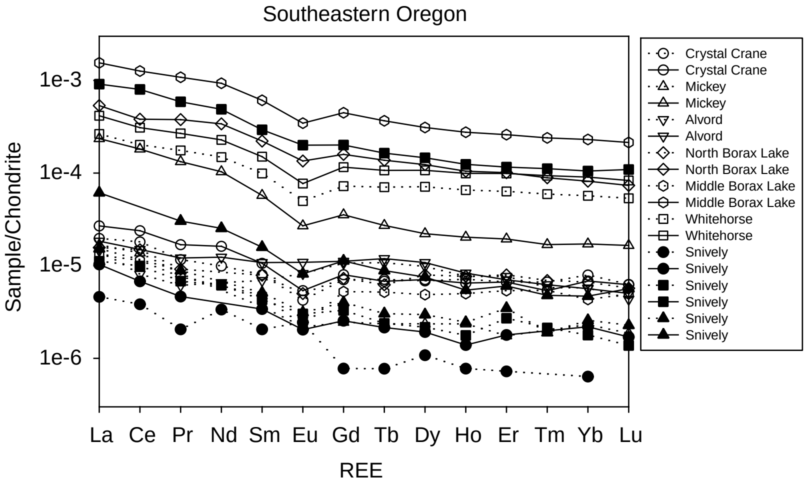

Fig. 4. Chondrite-normalized REE contents of samples from thermal springs from southeast Oregon.

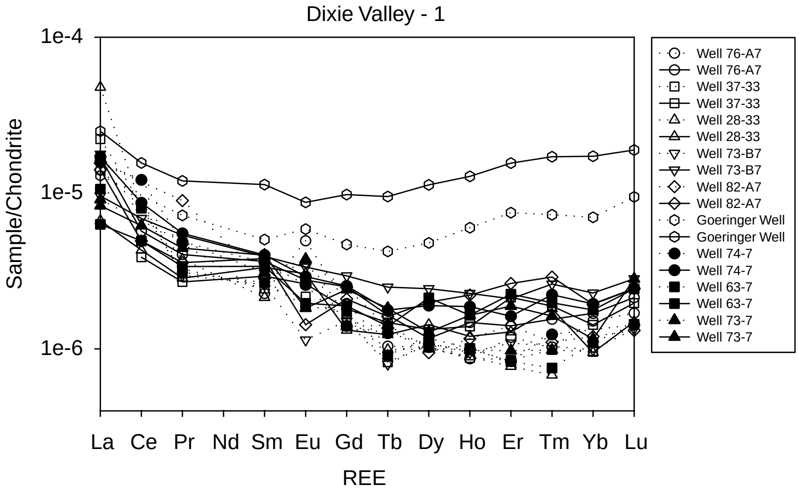

Fig. 5. Chondrite-normalized REE contents of samples from wells from the Dixie Valley geothermal field in Nevada.

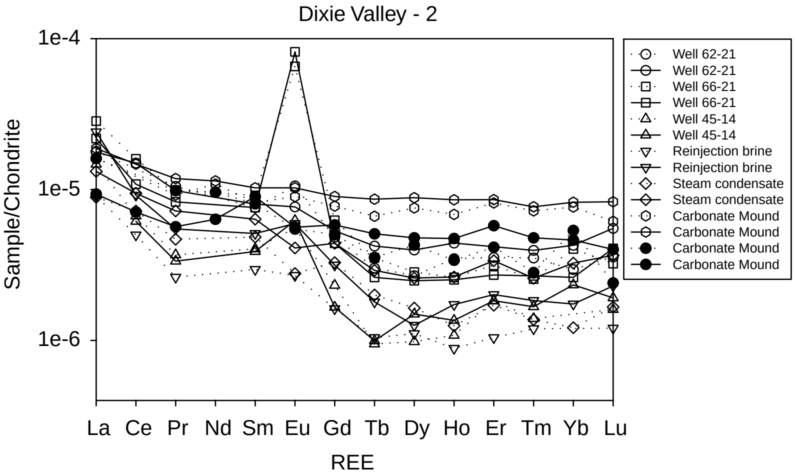

Fig. 6. Chondrite-normalized REE contents of samples from wells and a thermal spring from the Dixie Valley geothermal field in Nevada. Also shown are the REE contents of the reinjection brine and steam condensate.

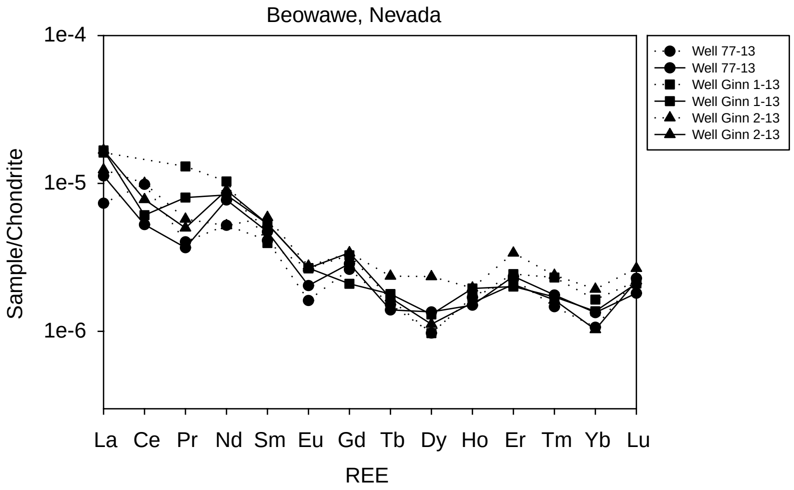

Fig. 7. Chondrite-normalized REE contents of samples from wells from the Beowawe geothermal field in Nevada.

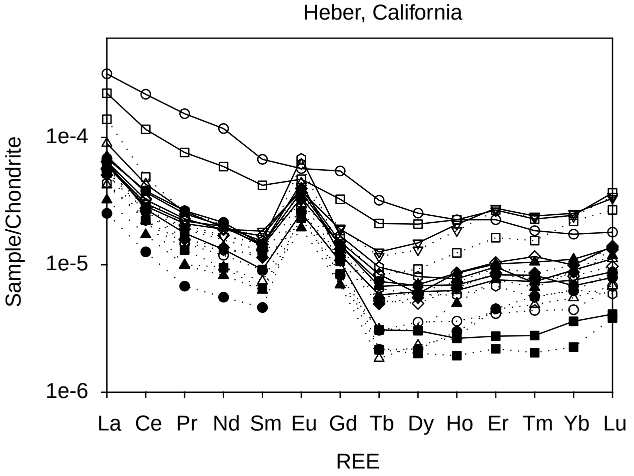

Fig. 8. Chondrite-normalized REE contents of samples from wells from the Heber geothermal field in California.

unfiltered aliquots have the same shape, although the absolute REE concentrations of the latter are about a half a log unit higher than those of the former. The fluid from Umpqua is the most acidic of those sampled from the Oregon Cascades, and it has the highest total dissolved solids content. The fluid from Umpqua is also distinguished by having the highest Mg concentration, by a factor of 40. The unusual REE pattern for Umpqua and other aspects of its anomalous chemistry probably reflect either mixing with a cooler, more saline ground water, a much lower reservoir temperature, or interaction with a rock type different from those involved in the evolution of the other thermal waters from the Cascades. Our studies of thermal waters from New Zealand [1,2] and Idaho [3] suggest that the REE patterns of thermal waters commonly reflect the patterns of their reservoir rocks.

Table 1
Chemical characteristics of thermal waters from selected areas in Oregon, Nevada, and California. All concentrations are in mg L^{-1}

Sample	pH	Ca	K	Mg	Na	Si	HCO$_3^-$	F$^-$	Cl$^-$	SO$_4^{2-}$
Bagby	9.5	3.1	1.0	0.02	51.5	32	72.5	0.5	14.2	44.7
Breitenbush	7.0	82.8	43.9	0.93	620.0	65.1	143	1.9	1030.0	123.0
Bigelow (Deer Lick)	7.0	160.0	23.4	1.06	560.0	29.8	36.5	0.3	1120.0	132.0
Bellknap	7.6	200.0	27.5	0.35	638.0	38.8	26.6	0.1	1480.0	173.0
Terwilliger (Cougar)	8.7	198.0	10.6	0.14	358.0	19.1	48.2	0.3	807.0	254.0
Wall Creek	7.4	101.0	13.8	0.37	304.0	26.3	49.7	3.4	609.0	138.0
McCredie	7.3	447.0	42.7	1.15	1030.0	32.1	38.0	2.0	2550.0	269.0
McCredie	7.4	464.0	42.7	1.10	1010.0	31.8	45.4	2.0	2550.0	271.0
Umpqua	6.4	328.0	96.0	43.40	2570.0	37.5	1507	1.2	3840.0	210.0
Crystal Crane	8.2	4.8	5.1	nd	161.0	40.6	753	9.1	70.1	73.0
Crystal Crane	8.2	4.7	11.1	nd	113.0	46.0	924	9.6	69.7	71.9
Mickey Hot Springs	8.7	0.8	45.0	nd	560.0	115.0	1639	15.1	0.0	18.1
Alvord Hot Springs	6.8	16.4	90.7	2.07	969.0	68.3	1227	10.0	430.0	201.0
North Borax Lake	7.3	15.4	36.3	nd	428.0	78.9	1605	6.1	237.0	280.0
Middle Borax Lake	7.0	24.6	37.6	0.69	414.0	80.6	1507	6.2	243.0	282.0
Whitehorse Ranch	7.7	7.4	8.9	nd	238.0	37.8	1468	19.0	46.0	80.3
Snively	9.4	3.1	1.5	nd	105.0	46.2	371	15.2	16.0	77.7
Snively	8.9	4.8	4.2	nd	114.0	72.7	371	14.0	21.3	81.2
Snively	9.3	na	na	na	na	na	na	na	na	na
Dixie Valley Well #76–A7	9.1	10.0	72.6	nd	475.3	300.0	262	11.5	561.0	227.0
Dixie Valley Well #37–33	9.2	7.8	66.0	nd	407.3	305.0	252	13.6	469.0	208.0
Dixie Valley Well #28–33	8.9	8.2	65.9	nd	409.1	316.0	257	13.6	473.0	211.0
Dixie Valley Well #73–B7	9.1	10.3	72.2	nd	487.2	318.0	212	12.9	580.0	242.0
Dixie Valley Well #82A–7	8.8	10.3	69.3	nd	482.2	280.0	222	12.9	575.0	244.0
Goeringer Well	7.4	53.9	24.9	45.60	235.6	30.2	414	0.7	294.0	201.0
Dixie Valley Well #74–7	9.1	9.5	70.1	nd	494.3	339.0	234	12.2	572.0	233.0
Dixie Valley Well #63–7	9.0	9.7	69.5	nd	487.7	333.0	217	12.8	578.0	241.0
Dixie Valley Well #73–7	9.1	9.5	68.5	nd	484.1	322.0	208	13.0	581.0	239.0
Dixie Valley Well #62–21	6.7	16.4	22.0	0.60	505.1	87.1	1107	4.9	80.8	231.0
Dixie Valley Well #66–21	6.0	45.0	89.1	0.33	874.0	144.0	216	12.3	1410.0	86.7
Dixie Valley Well #45–14	6.7	24.4	44.2	0.03	396.4	138.0	148	5.5	499.0	217.0
Dixie Valley injection brine	9.6	10.3	75.1	nd	506.7	362.0	234	14.3	564.0	252.0
Dixie Valley steam condensate	6.9	0.2	0.3	0.04	0.5	0.8	34.4	nd	0.5	18.7
Carbonate Mound	6.7	46.6	20.1	11.41	335.5	31.8	957	5.7	43.1	128.0
Carbonate Mound	7.0	41.8	19.4	10.00	328.3	29.1	925	5.9	42.0	121.0
Beowawe Well #77–13	9.7	3.4	22.3	nd	207.0	141.2	382	13.1	54.8	111.0
Beowawe Well Ginn 1–13	9.8	3.4	21.6	nd	203.7	138.4	376	13.2	55.4	110.0
Beowawe Well Ginn 2–13	9.8	3.4	21.4	nd	202.4	145.6	365	12.8	54.2	109.0
Heber HGU#7	7.7	835	359	2.27	4000	209.4	na	2.7	8360	96.1
Heber HGU#9	6.7	762	348	3.03	4040	209.4	na	2.4	7770	91.4
Heber HGU#11	8.1	729	342	4.36	4220	209.4	na	2.1	8250	85.2
Heber HGU#13	7.8	772	363	3.25	4390	209.4	na	2.5	8760	85.8
Heber HGU#16	7.8	742	331	4.22	4130	186.9	na	2.3	8180	84.4
Heber HGU#14	8.0	815	356	4.24	4110	160.0	na	2.2	8370	85.4
Heber HGU#12	7.4	784	351	3.32	4200	209.4	na	2.4	8700	87.1
Heber HGU#10	7.4	846	363	2.37	4080	209.4	na	2.6	8580	94.9
Heber HGU#8	7.1	836	343	2.09	4020	193.0	na	2.5	8600	114.0
Heber injection brine	8.1	898	379	3.29	4480	209.4	na	2.4	9200	97.4

nd = not detected; na = not analyzed.

3.2. Southeastern Oregon

The Alvord Valley is a north-northeast-trending graben in the northeastern Basin and Range Province, Harney County, southeastern Oregon. Thermal areas investigated from this area are Borax Lake, Alvord and Mickey hot springs (see [6,7] for detailed descriptions of the geology and hydrochemistry of these springs). The graben is bounded on the west by tilted fault-block mountains of the Steens and Pueblo Ranges, which attain elevations up to 2975 m. A large playa (the Alvord desert) covers approximately 250 km^2 in the north-central part of the valley. The basement in the area consists of Permian and Triassic metamorphic rocks (quartzite, greywacke, greenstone, sericite schist, quartz-muscovite schist, argillite and minor marble) and Cretaceous granitic rocks (gneissic granodiorite and quartz diorite) which intrude the older metamorphic rocks. These are overlain by Miocene and younger volcanic rocks successively comprising rhyolite and dacite flows and tuffs, andesite and basalt flows, and finally minor rhyolite and dacite flows and tuffs. The basin is filled with Plio-Pleistocene and Holocene alluvium. It is believed that the area underwent regional extension during the Cenozoic. Geophysical data suggest that each hot spring is associated with a fault. The system is probably recharged by meteoric water along the Steens Mountain–Pueblo Mountain fault block [7].

The other hot springs from SE Oregon studied here occur outside of the Alvord Valley proper, but the geotectonic setting is similar. Crystal Crane hot springs occurs in the Harney Basin, about 100 km north of the Alvord Valley, and White Horse Ranch hot springs is located about 30 km due west of Fields, Oregon (a town at the southernmost extent of the Alvord Valley). Snively hot springs is found in the Owyhee River Canyon, approximately 200 km northeast of the Alvord Valley. The waters from all the SE Oregon thermal areas studied can be described as dilute, near-neutral to slightly alkaline, sodium-bicarbonate waters with significant sulfate and chloride.

In general, the REE systematics of fluids from SE Oregon (Fig. 4) are very similar to those of fluids from the Oregon Cascades (Fig. 3). Unfiltered aliquots consistently contain more REE than the filtered aliquots (commonly by more than an order of magnitude), the slopes are generally negative (LREE-enriched), and the concentrations span a range from 10^{-6} to 10^{-3} times chondrite. The main differences between fluids from SE Oregon and those from the Cascades are that the former have somewhat more prominent negative Eu anomalies and more consistent chondrite-normalized patterns. The only fluid from SE Oregon with an obviously different REE pattern is that from Alvord hot springs, which has a nearly flat chondrite-normalized REE pattern. This fluid also has the highest Mg and Cl concentration of the thermal waters from SE Oregon (Table 1). Another interesting observation is that, in the three unfiltered samples from Snively hot springs (taken from three different vents all within a few hundred meters of one another), the chondrite-normalized patterns are roughly parallel, but the absolute REE concentrations vary over almost two orders of magnitude. This finding indicates that substantial spatial variation is possible within a closely related group of hot springs.

3.3. *Dixie Valley and Beowawe*

Dixie Valley and Beowawe geothermal areas are both located in the Basin and Range Province of northern Nevada (Fig. 2) and both are the sites of geothermal power plants. Dixie Valley is located about 95 km northeast of Fallon, Nevada, and Beowawe is 32 km southeast of Battle Mountain, Nevada. There is no evidence of a shallow magmatic heat source for either of these systems. Rather, they likely derive their heat via conduction from rocks at depth in a regional zone of elevated heat flow and geothermal gradients [8]. Like the Alvord Valley, Dixie Valley is a graben, and the geothermal reservoir is related to a major normal fault(s) that separates Dixie Valley from the Stillwater Range to the west. The rocks in the area consist of Mesozoic sedimentary and igneous rocks overlain by Tertiary volcanic rocks [9]. The Beowawe system occurs along a range-front normal fault (the Malpais fault system) and is thought to be among the highest-temperature systems in Nevada (maximum temperature of 215°C) [8]. The basement geology in the Beowawe area consists of strongly deformed and thrust-faulted Paleozoic clastic and carbonate sedimentary rocks. The sedimentary rocks are overlain by basaltic-andesite and dacite lava flows with minor tuffs. These volcanic rocks are related to a rift located just a few km west of Beowawe, which is part of 700-km long belt of extensional faulting that extends from central Oregon to central Nevada [9]. This belt includes the Alvord Valley thermal springs discussed in the previous section.

Fluids from Dixie Valley and Beowawe are relatively dilute, near-neutral to mildly alkaline waters. Waters from Beowawe wells are dominated by bicarbonate. Those from Dixie Valley wells usually are dominated by chloride, with the exception of the Goeringer well and well 62-21 which are dominated by bicarbonate. However, restoration of fluid compositions to pre-flash conditions shows that bicarbonate and chloride are actually about equal in importance in the deep fluid at Dixie Valley [10]. Thermal waters from the Carbonate Mounds thermal springs in Dixie Valley are bicarbonate-dominated.

In general, the fluids from Dixie Valley (Figs. 5 and 6) and Beowawe (Fig. 7) contain low concentrations of REE (near or below 10^{-5} times chondrite). Almost all the samples exhibit LREE-enriched chondrite-normalized patterns with slight to non-existent Eu anomalies. The exceptions to these general observations are the samples from the Goeringer and 66-21 wells at Dixie Valley. The former has an MREE-depleted, concave-upward pattern (and higher absolute REE than any other sample) and the latter has a prominent, positive Eu anomaly. For most samples, there does not appear to be large differences between filtered and unfiltered aliquots, but this may be an artifact of proximity to the detection limit.

At Dixie Valley, there is no obvious difference in REE patterns for the steam condensate, the reinjectate, the vast majority of the well waters, and waters from the nearby springs (carbonate mounds). Although it is possible that the relatively low REE concentrations observed in fluids from Beowawe and Dixie Valley simply reflect low solubility of REE in the deep fluid, we suspect that the low concentrations may result in part from loss of REE to scale as the thermal waters separate into liquid and vapor phases on ascent to the surface. Such a process was proposed for thermal waters from wells in New Zealand [1,2]. This conclusion was based on the following observations: (1) fluids that have undergone phase separation (e.g., from wells and geysers) typically have much lower REE concentrations than related thermal springs that have not undergone boiling; (2) samples taken from down hole in wells prior to phase separation tend to contain higher REE contents than those taken after boiling; (3) scale and sinter samples contain significant REE concentrations; and (4) theoretical considerations suggest that increase in pH of the liquid phase upon loss of water vapor and acidic gases (e.g., CO_2, H_2S) should result in decreased solubility of REE.

That the REE content in the steam condensate at Dixie Valley apparently contains approximately the same REE content as the liquids from the wells is curious, especially in light of the much larger differences in the concentrations of other constituents (Table 1). It is interesting that the only sample with a prominent, positive Eu anomaly, comes from a shut-in, non-flowing well (Dixie Valley 66-21). Well 66-21 also has the highest concentrations of total dissolved solids of all the fluids from Dixie Valley, and the lowest pH. The other anomalous sample, the one from the Goeringer well, has by far the highest Mg (similar to Umpqua), the highest Ca, the lowest Si and F, and one of the lowest K contents of the Dixie Valley waters. Thus, waters with anomalous REE systematics also appear to be anomalous in other aspects of their chemistry. The low Si and high Mg of the Goeringer well suggest a much lower-temperature fluid at depth. Indeed this well is not a production well but is used to supplement reinjection at Dixie Valley (Stu Johnson, pers. comm. 1998).

3.4. *Heber, California*

Located in the southern part of the Imperial Valley of California, on the margins of the Salton Trough and 7 km from Mexico, the Heber geothermal field supports a 47-MW geothermal power plant. The fluid is chloride-dominated, with a relatively high total dissolved solids content ($\sim$13,000 ppm) and an average deep temperature of about 195°C [11]. The Salton Trough is an active continental rift, which has been filled with deltaic sediments of the Colorado River, resulting in a thick sequence of interbedded sandstones and shales [11]. Formation and evaporation of saline lakes has led to the common occurrence of lacustrine evaporite deposits throughout the deltaic sequence. These evaporites are probably the source of the high dissolved solid contents of the Heber brines. There is no clear relationship of the Heber field to volcanic activity, and the thermal brines are probably generated by heating and convection of groundwater near block-faulted basement rocks [11].

The Heber fluids exhibit REE patterns (Fig. 8) that are unique among those reported here and can generally be described as a “Mexican hat”. They are generally concave upward from La to Lu, but with a distinct positive Eu anomaly. Only two unfiltered aliquots do not show the “Mexican hat” pattern, but even for these samples, the filtered aliquots do. The unfiltered aliquots generally have slightly higher REE concentrations than do the filtered samples, again suggesting a significant proportion of the REE occur in particulate form. In some cases, positive Eu anomalies in geothermal fluids can be attributed to relatively high temperatures in the geothermal aquifer [12] combined with comparatively rapid flow to the surface. This was proposed for some geothermal fluids from New Zealand which exhibited positive Eu anomalies [1,2]. However, the deep aquifer temperatures at Heber appear to be less than 200°C, so high temperatures cannot be the explanation for the positive Eu anomalies here. It has been pointed out that the Heber brines are more reduced than the relatively oxidized brines from the nearby Salton Sea geothermal field [11]. It is possible that the positive Eu anomaly at Heber is a reflection of these more reduced conditions. Alternatively, the Eu anomaly may be inherited from an Eu-enriched lithology in the geothermal reservoir. For example, Ca-bearing phases such as gypsum occurring in the evaporites in the Salton Trough might be enriched in Eu^{2+} relative to other REE.

4. Conclusions

The major findings in this study are similar to those from our previous investigations [1–3]. We consistently find that near-neutral to alkaline thermal waters tend to have relatively low REE concentrations ($<10^{-6}$–10^{-3} times chondrite), higher REE concentrations in unfiltered compared to filtered aliquots, and generally negatively sloping (LREE-enriched) chondrite-normalized patterns. In contrast, acidic fluids ($pH<4$), for which we have no representatives in this study, but which were investigated in our New Zealand studies [1,2], tend to have much higher REE concentrations (occasionally more than 10^{-1} times chondrite), near-identical REE concentrations in unfiltered and filtered aliquots, and distinctive “gull-wing” chondrite-normalized patterns. For near-neutral to alkaline thermal waters, deviation from a LREE-enriched pattern appears to be rare. Moreover, some of the examples of fluids with deviant REE behavior in this study, i.e., Umpqua in the Oregon Cascades, Alvord hot springs in southeastern Oregon, and the Goeringer well at Dixie Valley, also have anomalously high Mg concentrations in common. This relationship bears further investigation. The samples from Heber also have REE patterns that differ from the LREE-enriched norm; these samples have a "Mexican hat" pattern with a prominent, positive Eu anomaly. Such positive Eu anomalies were observed rarely in fluids from New Zealand, and were attributed in part to higher than usual reservoir temperatures [1,2]. However, elevated temperatures do not appear to be the explanation for the Heber samples.

The results of this study are also consistent with our previous finding [1,2] that samples of thermal waters taken from wells at the surface, and therefore that have experienced vapor loss, tend to have very low REE concentrations. Although further testing is required, this finding may be a result of loss of REE to scale or other solid phases upon boiling. If so, the potential for REE loss may require down-hole sampling of wells to obtain fluid samples prior to boiling, so that the true REE content of the deep fluid may be determined.

Our results, combined with previous studies, clearly demonstrate the utility of the REE as probes into processes of water–rock interaction in continental geothermal systems. Further work will be required before REE systematics can be considered a reliable exploration tool, but results so far hint that efforts in this direction ultimately will be rewarded.

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