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Rare earth element complexation behavior in circumneutral pH groundwaters: Assessing the role of carbonate and phosphate ions

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Abstract

Rare earth element (REE) concentrations were determined in circumneutral pH ($7 \leq pH \leq 9$) groundwaters from south-central Nevada and the Mojave Desert in eastern California, U.S.A. The inorganic speciation of the REEs in these water were evaluated primarily to assess the relative importance of carbonate ($LnHCO_3^{2+}$, $LnCO_3^+$ and $Ln(CO_3)_2^-$) and phosphate ($LnH_2PO_4^{2+}$, $LnHPO_4^+$, $Ln(HPO_4)_2^-$ and $LnPO_4^0$) complexes. Other REE complexes with sulfate, hydroxyl, chloride, and fluoride ions were also assessed, as was the significance of the free metal ion species (i.e., Ln^{3+}). Our speciation calculations indicate that REE–carbonate complexes dominate and typically account for more than 99% of each REE in solution. Moreover, carbonato complexes ($LnCO_3^+$) were predicted to be the dominant species for the light REEs and dicarbonato complexes ($Ln(CO_3)_2^-$) were predicted to increase in importance with increasing atomic number. All other complexes were predicted to be negligible. Furthermore, the combined percentage of all REE–phosphate complexes never accounted for more than 0.1% of the dissolved REEs, and generally much less than 0.1%. Phosphate complexes can not compete with carbonate complexes in these groundwaters because of the low ΣPO_4^{3-} concentrations (<0.3–1.58 μmol/kg), the much lower concentrations of the free phosphate ion (i.e., $[PO_4^{3-}]_F = 10^{-9}$–10^{-6} μmol/kg), due to ion pair formation with Ca^{2+} and Mg^{2+}, and the much higher free carbonate ion concentrations ($[CO_3^{2-}]_F = 0.32$–87 μmol/kg).

Keywords: Nevada; Mojave Desert; ground water; rare earths; phosphate ion; carbonate ion; bicarbonate ion

1. Introduction

The complexation behavior of trace elements in natural waters is of great interest due to potential differences in metal toxicity and effective solubility that can vary among dissolved species [1–3]. Moreover, because of the well established chemical similarities between the rare earth elements (REE) and the trivalent actinide series elements (e.g., Am^{3+}, Cm^{3+} and Cf^{3+}) [4,5], understanding the speciation behavior of the ubiquitous and naturally occurring REEs in groundwater can facilitate predictions of actinide complexation behavior. Such investigations may assist in the evaluation of actinide solubility in natural waters of different compositions.

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Many investigators have examined the probable complexation behavior of the REEs in seawater and have suggested that the observed shale-normalized enrichments in the heavy REEs (HREE) compared to the light REEs (LREE), first observed by Goldberg et al. [6], are probably the result of formation of carbonate complexes with the HREEs that are stronger than those with the LREEs [7,8]. Much less work has been conducted on terrestrial waters and especially on determining the speciation of REEs in groundwaters. Gosselin et al. [9] have examined REE concentrations in saline groundwaters from the Palo Duro Basin in Texas, and, using stability constants appropriate for seawater, predicted that REE complexes with chloride ions dominate REE speciation in the saline Palo Duro Basin groundwaters. (Our calculations, using stability constants and activity coefficients appropriate for these brines, suggests that the free ion, e.g., La^{3+}, is the dominant form of dissolved REEs [10].) Moreover, Wood [5] estimated the speciation of the REEs in a dilute model groundwater and found that, in the absence of unnaturally high dissolved phosphate concentrations, free metal ions dominate the speciation of the REEs in low pH waters ($pH < 6.5$) and REE–carbonate complexes account for essentially all of the dissolved concentration for each REE in neutral to high pH waters ($pH > 6.5$). Lee and Byrne [11] reassessed the values for the stability constants for REE–phosphate complexes and, using their new values and the major anion concentrations of Wood's model groundwater, concurred that, for low pH waters (i.e., $pH < 7.5$ for La and $pH < 6.5$ for Lu), free metal ions are the most likely form of each dissolved REE. For neutral to high pH waters, however, the $LnPO_4^0$ species (where Ln = any REE, i.e., lanthanide series element) was predicted to be important and may even dominate the speciation of the HREEs for pH 7–9 waters [9,11]. In our previous work examining REE speciation in both high pH [13,14] and low pH [10,15] natural terrestrial waters, phosphate complexes with the REEs were found to be negligible for all cases compared to carbonate complexes. We were careful to use only the free concentrations of the important phosphate and carbonate species (i.e., $[H_2PO_4^-]_F$, $[HPO_4^{2-}]_F$, $[PO_4^{3-}]_F$, and $[CO_3^{2-}]_F$) in our previous and present modelling efforts. Here we present REE data and the results of speciation calculations for circumneutral pH groundwaters ($7 \leq pH \leq 9$) from south-central Nevada, and eastern California, U.S.A., to evaluate REE complexes in these groundwaters and to assess the significance of REE–carbonate and REE–phosphate complexes.

Previous investigators have suggested that groundwaters probably inherit their dissolved REE signatures from the rocks and/or aquifer materials through which they flow and, consequently, REE patterns for the groundwaters should resemble the REE patterns of the rocks and/or aquifer materials [16]. However, solution complexation is also important in controlling the dissolved REE signatures in natural waters. Johannesson and Lyons [13] and Johannesson et al. [14], for example, have demonstrated that the substantial enrichments in the HREEs observed in alkaline lakes from the western U.S.A. were probably the result of the formation of strong HREE–carbonate complexes in these carbonate-rich waters, whereas the reported negative Eu anomalies were a rock weathering signature. Recent studies of river waters [12] also demonstrate the importance of solution chemistry compared to the rock source on the dissolved REE signatures. These studies suggest, therefore, that, depending on the system, both rock source and solution chemistry can play important roles in controlling and determining the dissolved REE signatures of natural waters. The results of the REE speciation calculations presented here, therefore, represent the next step towards sorting out and constraining the sources and geochemical processes responsible for the REE signatures of groundwaters.

2. Methods

2.1. Sampling and analytical techniques

Spring samples from Ash Meadows National Wildlife Refuge in Nevada, Death Valley National Park, California, the eastern Mojave Desert, and the western side of the dry Soda Lake playa near Baker, California (Fig. 1), were collected from their source by pumping the sample through precleaned, acid-washed teflon tubing attached to a peristaltic pump, through acid-washed, in-line (0.45 μm) Gelman Sciences groundwater filtering capsules, and into the precleaned acid-washed low density linear polyethylene sample bottles [17,18]. Identical collection techniques were used for the well waters from the Amargosa Desert of Nevada and the Owens Lake playa in California (Fig. 1), except that the wells were initially allowed to flow until constant pH measurements were obtained (usually 30–40 min) to ensure that the samples were representative of the local groundwaters. Samples were immediately acidified to pH < 2 with ultrapure nitric acid and placed in clean plastic bags until analysis.

The pH of each sample was measured in the field using a Hach One portable pH meter on unfiltered and unacidified aliquots of each sample. In addition, the alkalinity of each sample was measured on site by titration using another unfiltered and unacidified aliquot of the sample [17]. Major cations were determined by atomic adsorption spectroscopy and the anions were measured by ion chromatography at the University of Nevada, Las Vegas [19].

The REE concentrations were determined by inductively coupled plasma mass spectrometry (ICP–MS) (Perkin-Elmer Elan 5000) with ultrasonic nebulization after preconcentration by cation exchange [13–15,17,18]. The ultrasonic nebulization increased the sensitivity and decreased the potential interferences from oxide formation in the plasma stream. A series of five REE reference standards of known concentrations (10 ng/kg, 50 ng/kg, 100 ng/kg, 500 ng/kg and 1000 ng/kg) were included with our sample analyses to verify our measurements and to calibrate the ICP–MS (see [17] for more details).

The following REE isotopes were chosen for analysis because they are free of elemental isobaric interferences: ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{149}Sm, ^{151}Eu

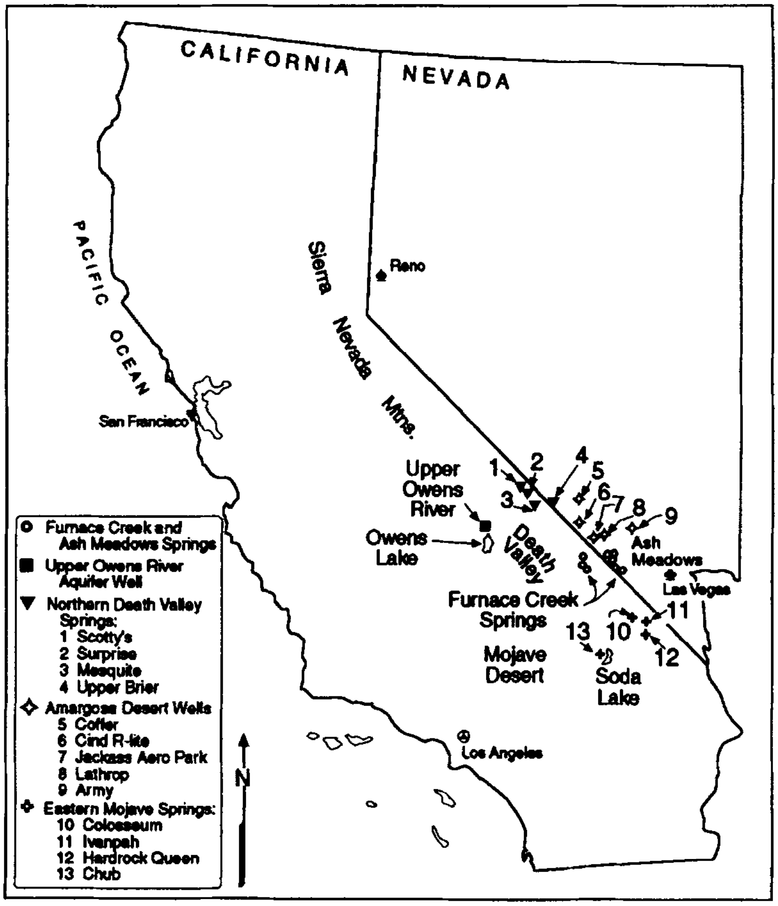

Fig. 1. Map of Nevada and California showing the spring and well locations sampled in this study.

and ^{153}Eu (mean value), ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb and ^{175}Lu. Measured $REEO^+/REE^+$ and BaO^+/Ba^+ ratios for our analyses were generally < 1%: $LaO^+/La^+ = 0.74\%$; $CeO^+/Ce^+ = 0.94\%$; $PrO^+/Pr^+ = 1.18\%$; $NdO^+/Nd^+ = 1.16\%$; $SmO^+/Sm^+ = 0.2\%$; $EuO^+/Eu^+ = 0.05\%$; $GdO^+/Gd^+ = 0.5\%$; $TbO^+/Tb^+ = 0.5\%$; and $BaO^+/Ba^+ = 0.03\%$. The REE concentrations were corrected to account for potential interferences [14,18].

Analytical precision for Ce, Pr, Gd, Tb, Dy, Ho, Er and Yb was better than 5% relative standard deviation (RSD). For La, Nd and Tm the precision was 7% (RSD) or better, for Eu the precision was 10% (RSD) or better, and for Sm and Lu the precision was 11% and 12% (RSD), respectively. Replicate analyses of water from Fairbanks Spring indicate that the measurement reproducibility was 10% (RSD) or better for the REEs, except Sm and Er, for which the reproducibility was 14% (RSD) or better, and Ce, Tm, and Lu which were reproducible within 20% (RSD) [17].

2.2. Speciation modelling

Inorganic speciation of REEs in these groundwaters was modelled using the combined specific ion interaction and ion pairing model developed for the REEs by Millero [8]. We used a modified version of the model [13] that incorporates the stability constants for REE carbonate and phosphate species determined by Lee and Byrne [7,11]. The importance of Ln^{3+}, $LnOH^{2+}$, $LnCl^{2+}$, LnF^{2+}, $LnSO_4^+$, $LnHCO_3^{2+}$, $LnCO_3^+$, $Ln(CO_3)_2^-$, $LnH_2PO_4^{2+}$, $LnHPO_4^+$, $Ln(HPO_4)_2^-$, and $LnPO_4^0$ species in these groundwaters were evaluated in this study. The free concentration of each phosphate species ($H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) and carbonate species (HCO_3^- and CO_3^{2-}) were determined following the techniques of Millero and Schreiber [20] and Millero [8], by accounting for the formation of phosphate and carbonate ion pairs with Ca^{2+} and Mg^{2+}. Measurable phosphate was below the detection limit of 0.3 μmol/kg for Rogers, Longstreet, and Bradford Springs in Ash Meadows, as well as all of the Amargosa Desert and Mojave Desert groundwater samples. The detection limit value for total phosphate was used to model the speciation in these groundwaters and, consequently, the percent of each REE complexed with phosphate ions predicted by the model represents the maximum possible amount.

3. Results

3.1. Rare earth elements

Concentrations of the REEs in the groundwaters from south-central Nevada and eastern California are presented in Appendix A. The major ion chemistry of these groundwaters have previously been discussed at length and are presented elsewhere ([19,21,22]and references therein). Total $[CO_3^{2-}]$ and $[HCO_3^-]$ concentrations were calculated from alkalinity measurements using PHREEQE [23,24].

Shale-normalized plots of the REEs in these groundwaters are shown in Fig. 2. The composite shale data used to normalize the groundwater data are from Sholkovitz ([25], table 5.I). Shale-normalized REE plots for these groundwaters are flat to slightly enriched in the HREEs. Shale-normalized Yb/Nd and Er/Nd ratios are typically larger than unity for these groundwaters. The major exception is the groundwater from the Upper Owens River Aquifer, which exhibits an enrichment in the LREE over the majority of the HREEs (e.g., $(Er/Nd)_{SN} = 0.89$; SN = shale-normalized). The degree of HREE enrichment is similar for the majority of the other groundwaters presented in this study, with both $(Yb/Nd)_{SN}$ and $(Er/Nd)_{SN}$ ratios between approximately 1 and 2. The exceptions include Rogers Spring in Ash Meadows with the largest HREE enrichment [$(Yb/Nd)_{SN} = 4.33$], Upper Brier Spring [$(Yb/Nd)_{SN} = 3.01$], Hardrock Queen Spring [$(Yb/Nd)_{SN} = 2.21$, $(Er/Nd)_{SN} = 2.82$], and Colosseum Spring [$(Yb/Nd)_{SN} = 2.86$, $(Er/Nd)_{SN} = 3.63$].

The Nd concentrations in these groundwaters are lower than for mildly acidic groundwaters from southwestern England, for which Smedley [16] reported Nd values between 3,500 pmol/kg and 478,000 pmol/kg, and lower than Nd values reported in acid, hypersaline groundwaters from Australia, that ranged from 120,000 pmol/kg to 1,061,000 pmol/kg [26,27]. The REE concentrations reported here are also lower than the values measured by Gosselin et al. [9] in acid, saline groundwaters from the Palo Duro Basin in Texas. These investigators report Nd concentrations between 367 pmol/kg and 187,890 pmol/kg (mean value ~ 33,000 pmol/kg) for these brines. The REE samples in all these studies were filtered using 0.45 μm filters, except for Palo Duro Basin groundwaters for which some samples were filtered with 0.8 μm

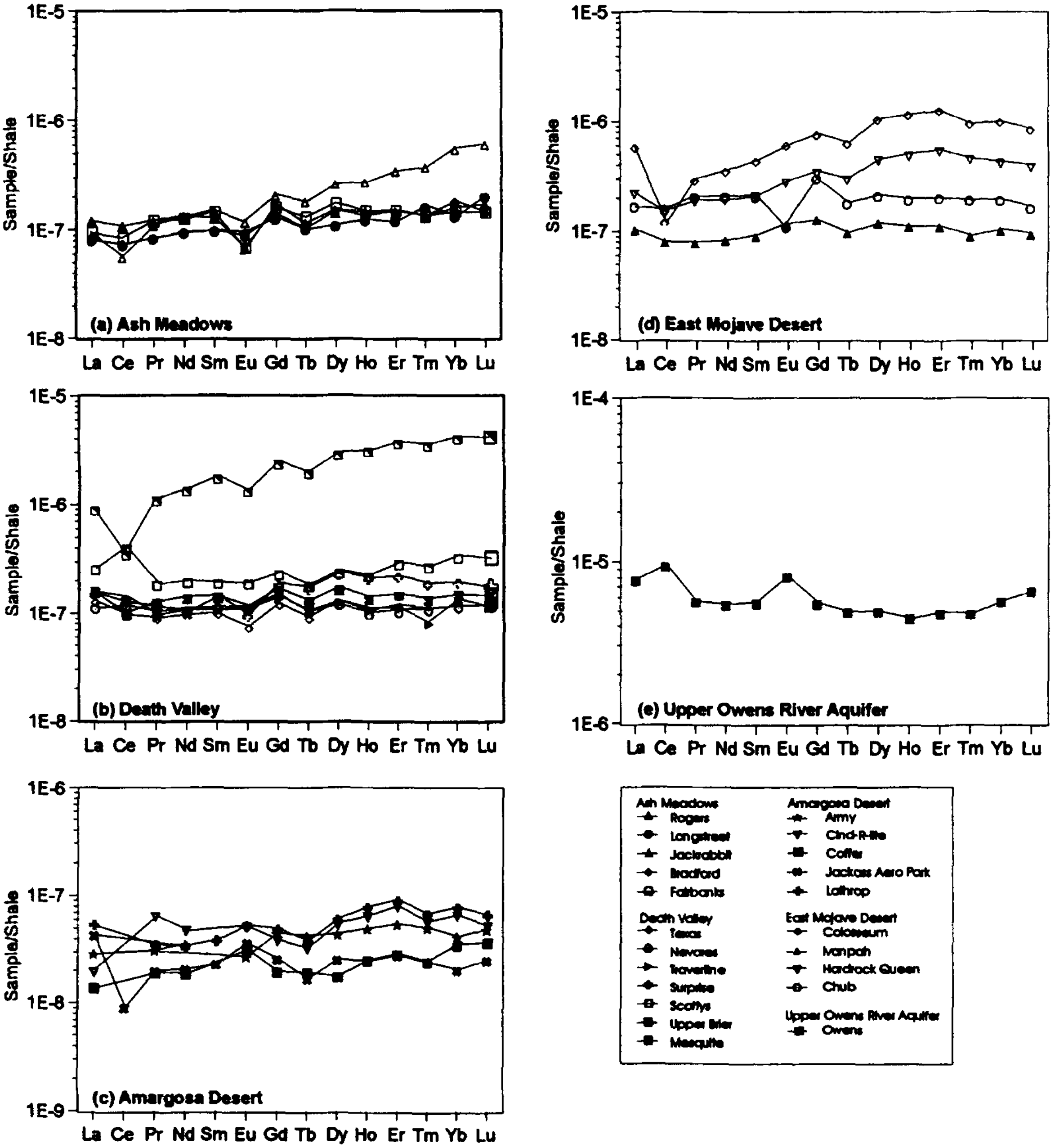

Fig. 2. Shale-normalized REE patterns for groundwater from (a) Ash Meadows National Wildlife Refuge; (b) Death Valley National Park; (c) the Amargosa Desert; (d) the east Mojave Desert; and (e) the Upper Owens River Aquifer. Although the log scales are the same, note that the shale-normalized values for the Amargosa Desert groundwaters are lower than the other groundwaters of this study.

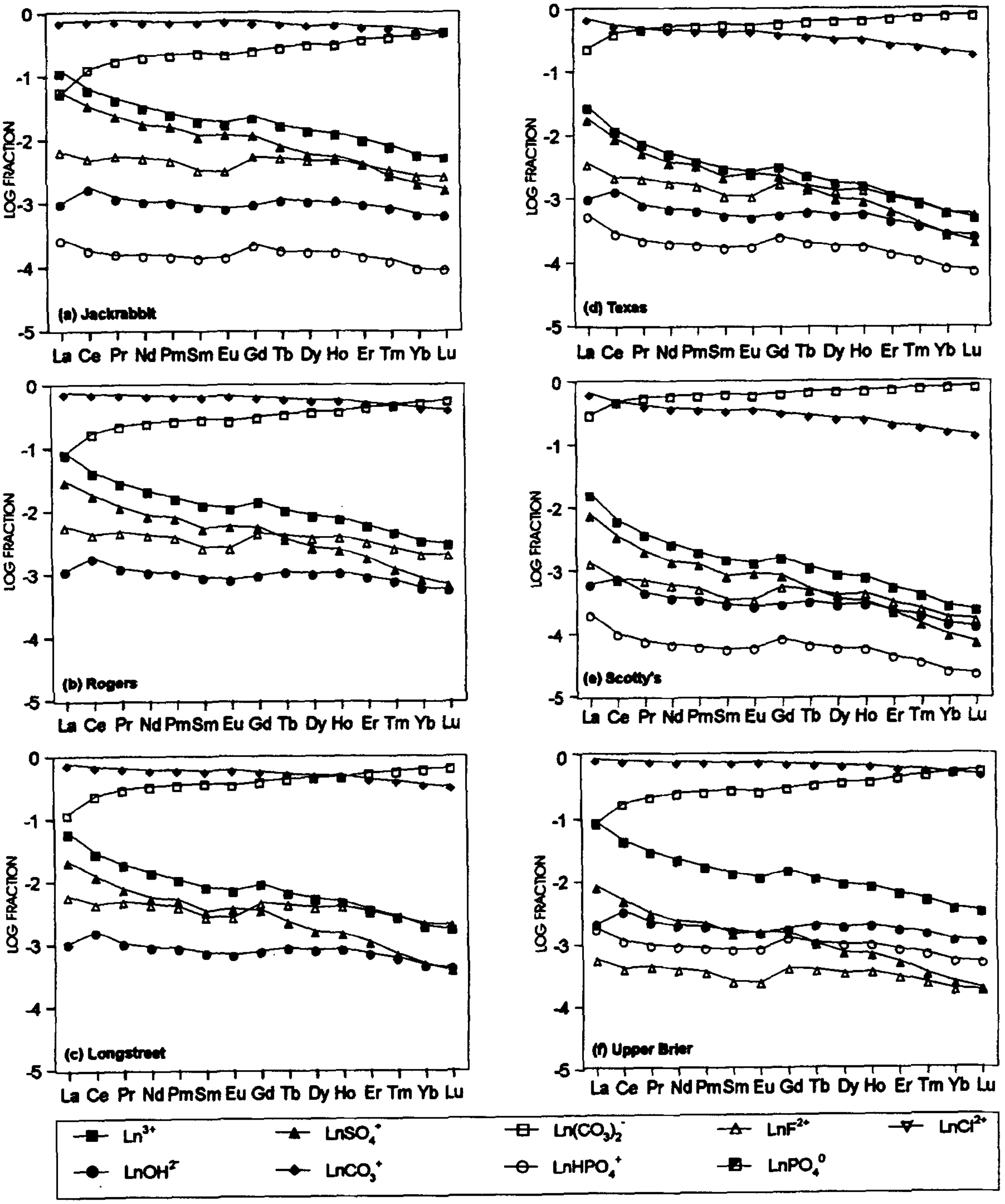

Fig. 3. Results of speciation calculations plotted as the log fraction of dissolved rare earths versus atomic number for the Ash Meadows springs: (a) Jackrabbit Spring, (b) Rogers Spring, and (c) Longstreet Spring; and the Death Valley springs: (d) Texas Spring, (e) Scotty's Spring and (f) Upper Brier Spring. Log (fraction) value of zero is equivalent to 100%, log (fraction) = -1 is equivalent to 10%, log (fraction) = -2 is equivalent to 1%, log (fraction) = -3 is equivalent to 0.1%, log (fraction) = -4 is equivalent to 0.01%, and log (fraction) = -5 is equivalent to 0.001%.

filters [9]. The REE concentrations of the Palo Duro Basin groundwaters are not as high as those reported for southwestern England and for Australia. Consequently, it is unlikely that high REE concentrations are related to differences in filter pore size. The presence of colloids, however, has been suggested to explain the high REE concentrations of some of the groundwaters from southwestern England [16],

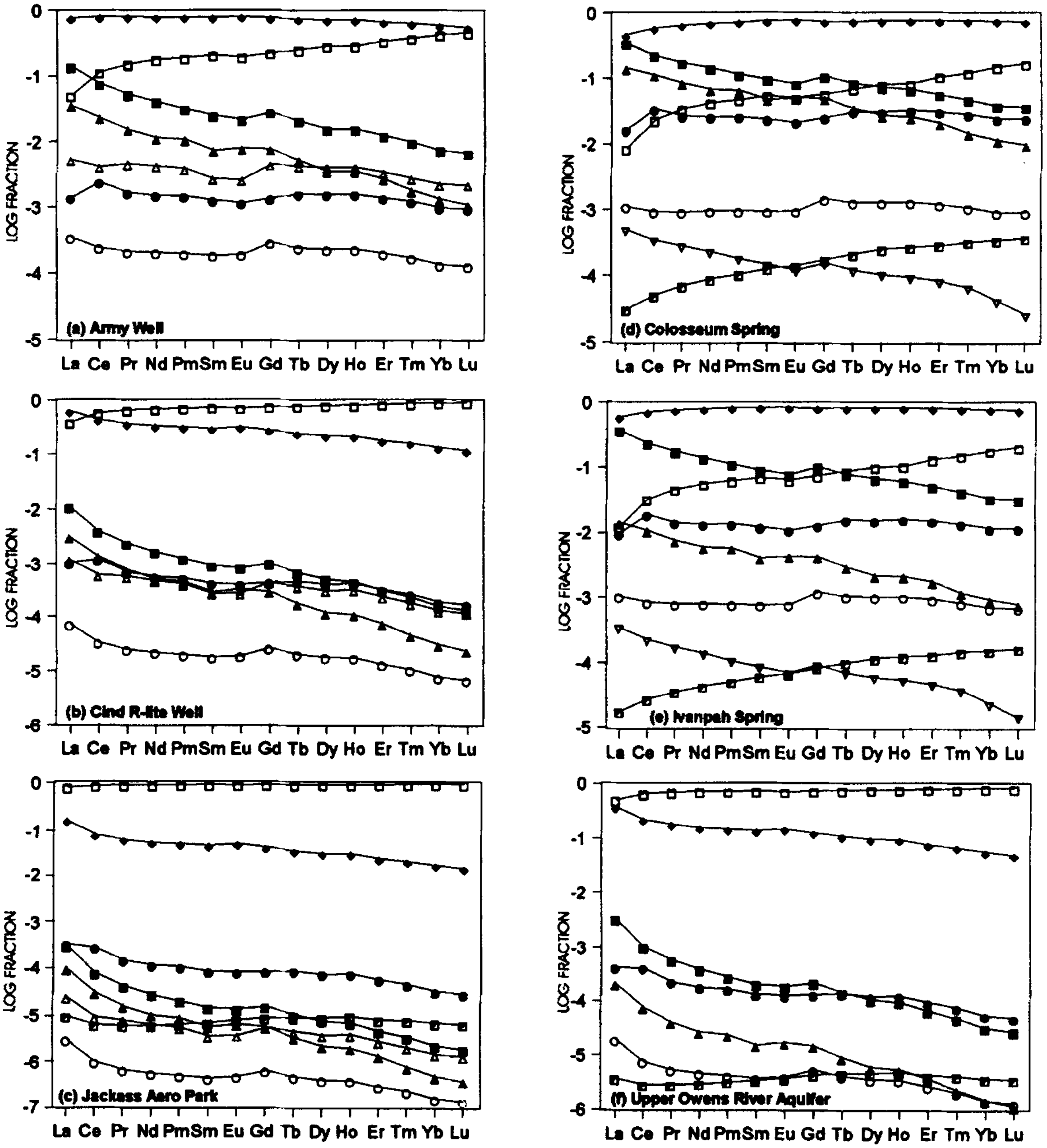

Fig. 4. Results of speciation calculations plotted as the log fraction of dissolved rare earths versus atomic number for the Amargosa Desert well waters from: (a) Army Well, (b) Cind R-lite Well, and (c) Jackass Aero Park Well; and Mojave Desert groundwater samples from: (d) Colosseum Spring, (e) Ivanpah Spring; and (f) the Upper Owens River Aquifer. Symbols as in Fig. 3.

whereas colloids were determined to be insignificant in the Palo Duro Basin groundwaters [9]. The effect of colloids on REE concentrations cannot, however, be ruled out for the Australian groundwaters.

3.2. Speciation modelling

Results of inorganic speciation modelling of the Ash Meadows and Death Valley spring waters are presented in Fig. 3, and for Amargosa Desert and Mojave Desert groundwaters in Fig. 4, as the log of the fraction of the total metal. The calculated free fractions and free concentrations for the carbonate and phosphate species in these groundwaters that are used in the speciation calculations are presented in Tables 1 and 2, respectively.

Speciation modelling indicates that the REEs are complexed primarily with carbonate ions in these groundwaters (Figs. 3 and 4), which have pH values from 6.97 to 9.05 (mean = 7.55 ± 0.47) (see Appendix). For the LREEs, the percentage of total metal in solution complexed with carbonate ions is always greater than 60%. The percentage of La, for example, complexed with carbonate ions ranges from a low of 60% in Ivanpah Spring to more than 99%, in Jackass Aero Park and Upper Owens River Aquifer groundwaters. For the HREEs, typically more than 99% of the metal is complexed with carbonate ions in these groundwaters. In addition, carbonato complexes ($LnCO_3^+$) tend to dominate the complexation of the LREEs, whereas dicarbonato complexes ($Ln(CO_3)_2^-$) are more important for the HREEs (Figs. 3 and 4). Dicarbonato complexes are the dominant REE species in all of the Death Valley groundwaters,

Table 1
Free fractions of important carbonate and phosphate species in south-central Nevada and eastern California groundwaters. The free fractions were determined by the methods outlined by Millero and Schreiber [20] and Millero [8]

	$[CO_3^{2-}]_F / [CO_3^{2-}]_T$	$[H_2PO_4^-]_F / [H_2PO_4^-]_T$	$[HPO_4^{2-}]_F / [HPO_4^{2-}]_T$	$[PO_4^{3-}]_F / [PO_4^{3-}]_T$
ASH MEADOWS				
Fairbanks	0.498	0.985	0.663	0.0008
*Rogers	0.495	0.985	0.662	0.0008
*Longstreet	0.494	0.985	0.662	0.0008
*Bradford	0.471	0.982	0.624	0.0007
Jackrabbit	0.496	0.985	0.657	0.0008
AMARGOSA DESERT				
*Army	0.463	0.984	0.635	0.0007
*Cind R-lite	0.719	0.995	0.839	0.0021
*Coffer	0.346	0.961	0.449	0.0005
*Jackass Aero Park	0.892	0.999	0.959	0.005
*Lathrop	0.759	0.997	0.892	0.0019
DEATH VALLEY				
Texas	0.579	0.988	0.719	0.0014
Nevares	0.642	0.989	0.753	0.0014
Travertine	0.576	0.988	0.716	0.0011
Upper Brier	0.717	0.996	0.867	0.0017
Scotty's	0.926	0.999	0.970	0.0080
Surprise	0.898	0.999	0.958	0.0056
Mesquite	0.653	0.991	0.776	0.0016
MOJAVE DESERT				
*Chub	0.854	0.997	0.911	0.0044
*Hardrock Queen	0.461	0.985	0.656	0.0006
*Colosseum	0.392	0.978	0.566	0.0005
*Ivanpah	0.381	0.975	0.537	0.0005
*Owens	0.7	0.993	0.791	0.0020

[*] Total phosphate values were below 0.3 μmol/kg. The estimated free fractions for phosphate species in the samples were determined assuming $\Sigma PO_4 = 0.3$ μmol/kg and, consequently, the estimated free fractions represent maximum values.

except for Upper Brier Spring where carbonato complexes are predicted to be more abundant. Dicarbonato complexes are also dominant in groundwaters from the Cind R-lite and Jackass Aero Park wells in the Amargosa Desert, and for groundwater from the Upper Owens River Aquifer. Carbonato complexes dominate the speciation of the REEs in all of the remaining groundwaters sampled.

After the carbonate species, the free metal species (i.e., Ln^{3+}), is typically the next most abundant form of dissolved REE in these groundwaters, accounting for up to 12% of the dissolved La concentrations in some of the Ash Meadows springs, 13% of dissolved La in Army Well groundwater, and as high as 36% of the dissolved La in Ivanpah Spring waters (Figs. 3 and 4). The importance of the free metal ion species in these waters decreases dramatically with increasing atomic number, to as little as 0.02% for the HREEs in the Death Valley groundwaters. Following the carbonate ion, the sulfate ion is the second most important complexing ion in these groundwaters, although compared to carbonate the percentage of REE complexed with sulfate is negligible (Figs. 3 and 4). The remaining amount of each REE in these groundwaters (i.e., < 1%) is complexed with hydroxyl, biphosphate, phosphate, fluoride and chloride ions.

Although the stability constants for $LnPO_4^0$ are larger than for carbonato complexes and of the same order of magnitude as dicarbonato complexes, the $LnPO_4^0$ complex is always less than 0.001% of each REE, and even lower for the Death Valley and Ash Meadows groundwaters (Figs. 3 and 4). Because we have used an upper limit for the total phosphate

Table 2
Calculated free carbonate (log $[CO_3^{2-}]_F$) and free phoshate species (log $[H_2PO_4^-]_F$, log $[HPO_4^{2-}]_F$ and log $[PO_4^{3-}]_F$

	log $[CO_3^{2-}]_F$	log $[H_2PO_4^-]_F$	log $[HPO_4^{2-}]_F$	log $[PO_4^{3-}]_F$
ASH MEADOWS				
Fairbanks	-5.86	-6.71	-6.83	-14.74
*Rogers	-5.74	-6.91	-6.90	-14.68
*Longstreet	-5.59	-6.99	-6.85	-14.52
*Bradford	-5.95	-6.82	-7.00	-14.95
Jackrabbit	-5.91	-6.81	-6.98	-14.93
AMARGOSA DESERT				
*Army	-5.98	-6.84	-7.01	-15.00
*Cind R-lite	-4.95	-7.50	-6.65	-13.40
*Coffer	-5.57	-7.29	-6.96	-14.28
*Jackass Aero Park	-4.06	-8.51	-6.55	-11.94
*Lathrop	-5.53	-7.11	-6.70	-13.99
DEATH VALLEY				
Texas	-5.18	-6.54	-6.03	-13.23
Nevares	-5.31	-6.68	-6.32	-13.58
Travertine	-5.31	-6.69	-6.42	-13.85
Upper Brier	-5.97	-6.49	-6.27	-13.81
Scotty's	-5.10	-6.90	-6.31	-12.86
Surprise	-5.17	-7.20	-6.62	-13.31
Mesquite	-5.19	-6.54	-6.23	-13.55
MOJAVE DESERT				
*Chub	-5.42	-7.62	-6.57	-12.83
*Hardrock Queen	-6.29	-7.47	-6.73	-13.92
*Colosseum	-6.52	-7.34	-6.82	-14.16
*Ivanpah	-6.48	-7.12	-6.89	-14.47
*Owens	-4.65	-7.64	-6.64	-13.21

All values in mol/kg. * Total phosphate concentrations were below 0.3 μmol/kg. Free phosphate species concentrations have been estimated using $\Sigma PO_4 = 0.3$ μmol/kg. Free phosphate species concentrations therefore represent maximum possible values.

concentration in the Amargosa and Mojave Desert groundwaters, the fraction of each REE complexed with phosphate ions in these groundwater is actually less than predicted by the model.

At present, we are unable to address REE–organic complexes quantitatively because of the lack of appropriate methods to determine the activity coefficients and stoichiometric stability constants for these complexes and because of our incomplete understanding of complex humic and fulvic acids in these groundwaters. Total dissolved organic carbon concentrations for groundwaters from Ash Meadows are typically low (e.g., 83 μmol/kg and 150 μmol/kg for two springs [28]). Moreover, speciation calculations in seawater and the Waste Isolation Pilot Plant (WIPP) brines, for example, indicate that no known organic ligand competes with carbonate complexes at the observed concentrations of the organic ligands in seawater and the WIPP site brines [8]. Stability constants for REE complexes with simple organic acids at infinite dilution are generally substantially lower than the stability constants for REE carbonate complexes. Wood [29], for example, presents stability constants (i.e., $\log \beta_1$(REE)) for REE complexes with simple organic ligands at infinite dilution that range from 1.53, for the La complex with formate, up to 6.04, for the Dy complex with malonate. These values are lower than stability constants for the REE carbonate complexes, which range from 7.12 to 8.29 for $\log \beta_1$ and from 12.01 to 14.28 for $\log \beta_2$ [11]. The exceptions include polydentate ligands such as EDTA, which may have stability constants for REE complexes that are similar or greater than that for REE carbonate complexes [7,29]. Polydentate ligands, like EDTA, however, do not occur in natural organic material [29] and are, consequently, not expected to be important in the dilute groundwaters of southern Nevada and eastern California. Moreover, in order for REE–EDTA complexes to compete effectively with REE–dicarbonato complexes in these groundwaters, the EDTA concentrations would have to be as high as $10^{-4.3}$ mol/l, which is approximately a factor of 1000 larger that EDTA concentrations typically reported for municipal sewage (i.e., 10^{-7} mol/l) in the United States [2]. Such high concentrations of EDTA are unlikely in these dilute groundwaters and, consequently, it is doubtful that EDTA is an important complexer of the REEs.

4. Discussion

4.1. *Phosphate and carbonate complexes: The evidence from previous studies*

Complexation of the REEs in seawater is thought to involve primarily carbonate ions. The observed enrichments in the HREEs compared to the LREEs are believed to result from formation of stronger REE–carbonate complexes with increasing atomic number [2,7,8]. Phosphate complexes are not thought to be important complexers of the REEs in seawater compared to the carbonate complexes [7,11]; however, phosphate appears to exert significant control on dissolved REE concentrations by possible removal from solution as REE–phosphate salts ([30], and references therein). The average total carbonate ion concentration in seawater is 270 μmol/kg, whereas total phosphate concentrations are between 1 μmol/kg and 3 μmol/kg [30].

In terrestrial waters even less is known about REE speciation and the importance of phosphate and carbonate complexes. Much of the previous work in real systems has primarily focused on surface waters, including alkaline lakes [13,14] and an acidic lake [15], although some work has been conducted in acidic groundwaters [9,10]. In these systems, speciation calculations indicate that dicarbonato complexes ($Ln(CO_3)_2^-$) are effectively the only important REE species in the alkaline lakes [13,14] and that sulfate complexes ($LnSO_4^+$) and the free metal ion species (Ln^{3+}) dominate in the acid lake [15]. Phosphate complexes were not observed to be significant in these systems. In the alkaline lakes, even though total phosphate concentrations were as high as, for example, 1000 μmol/kg in Mono Lake, the free carbonate ion concentrations ($[CO_3^{2-}]_F$) were always at least 4 orders of magnitude greater and up to 6 orders of magnitude greater than the free phosphate concentrations ($[PO_4^{3-}]_F$) [13,24]. In the acidic, hypersaline groundwaters from the Palo Duro Basin in Texas, Gosselin et al. [9] predicted that REE–chloride complexes would dominate. On the other hand, the free metal species was predicted to be the primary form of the dissolved REEs in acidic, hypersaline groundwaters associated with the groundwater discharge zone playa lakes (Lake Tyrrell and Lake Gilmore) in Australia [10].

Other investigators have examined REE speciation in a model groundwater [5] of constant major solute concentration (i.e., $\Sigma Cl^- = 10^{-3.7}$ mol/kg; $\Sigma SO_4^{2-} = 10^{-4}$ mol/kg; $\Sigma CO_3^{2-} = 10^{-4}$ mol/kg; $\Sigma NO_3^- = 10^{-4}$ mol/kg; $\Sigma PO_4^{3-} = 10^{-6}$ mol/kg; $\Sigma F^- = 10^{-6}$ mol/kg) and varying pH. Wood [5], for example, calculated the percentage of Eu complexed with different inorganic ligands in this model groundwater and predicted, for pH between 2 and 6.5, that the free metal ion species (Eu^{3+}) and sulfate complexes ($EuSO_4^+$) would predominate, carbonato complexes ($EuCO_3^+$) would dominate in groundwaters with pH between 6.5 and 9.5, and that dicarbonato complexes ($Eu(CO_3)_2^-$) would be most important for groundwaters with pH > 9.5. Phosphate only became important as a complexer of the REEs when the pH was less than 6 and the total phosphate concentration was increased to 0.01 *M* in conjunction with a decease in the total sulfate concentration [5]. Wood [5] only considered the formation of $LnH_2PO_4^{2+}$ complexes and therefore concluded that, in acid waters with elevated phosphate concentrations (i.e., 0.01 *M*) due to anthropogenic inputs, the $EuH_2PO_4^{2+}$ complex would dominate over $EuSO_4^+$.

Lee and Byrne [11] considered the formation of $LnPO_4^0$ species in their modelling using their estimated stability constants for this complex. They used the same model groundwater [5] in their calculations and predicted, for pH between 7 and 9, that $LnPO_4^0$ complexes with the HREEs would predominate over carbonate complexes [11]. The potential dominance of the $LnPO_4^0$ species can be attributed to the large stability constants for the complex, log β between ~ 11 and 13 [11], which is of the same order of magnitude as the stability constants for REE–dicarbonato complexes [7,11]. It should be pointed out, however, that these models, including the model we have used to calculate REE speciation, do not account for mixed ligand complexes nor to they address fractionation that may result from adsorption onto particles or colloids [12].

4.2. Phosphate and carbonate complexes: The evidence from real groundwaters

The inorganic speciation modelling for the REEs in the circumneutral pH groundwaters of south-central Nevada and eastern California indicate that, for all cases, carbonate complexes are the dominant form of the dissolved REEs and that all other REE species are negligible, including all phosphate complexes. The only exception is the free metal species (Ln^{3+}) of some of the LREEs in groundwaters from Ash Meadows, Amargosa Desert, and the eastern Mojave Desert. Under no circumstances are phosphate complexes with the REEs predicted to be significant compared to the carbonate complexes (Figs. 3 and 4). Moreover, in those groundwaters for which the phosphate concentration is below the 0.3 μmol/kg experimental detection limit, phosphate complexes are still negligible using the detection limit phosphate value in the speciation calculations (Fig. 4). Of the potential REE–phosphate complexes that could have formed, the $LnHPO_4^{2-}$ complex is predicted to be more important than either $LnH_2PO_4^-$ or $LnPO_4^0$ in these groundwaters.

Because previous investigations have predicted that $LnPO_4^0$ complexes may dominate REE complexation for the HREEs in groundwaters with pH between 7 and 9 [11], we have also modelled the speciation of the model groundwater of Wood [5] using our modified version of Millero's [8] model for these pH values. The results are shown in Fig. 5a–c for pH = 7, pH = 8 and pH = 9. Similar to Wood [5], we chose world concentration averages for river water [31,32] for the major cations in order to account for ion pairing with phosphate and carbonate ions.

For all three pH values for the model groundwater, our calculations indicate that carbonate complexes are the dominant form of the dissolved REEs (Fig. 5a–c). The only exceptions are La and Ce for pH = 7, where the model predicts that the free metal ions, La^{3+} and Ce^{3+}, are more important than carbonate complexes. The speciation modelling indicates that carbonato complexes ($LnCO_3^+$) are foremost for pH = 7 and 8, whereas dicarbonato complexes ($Ln(CO_3)_2^-$) surpass the carbonato complex as the principal HREE complex for pH = 9 (Fig. 5a–c). Phosphate complexes, on the other hand, are predicted to only account for approximately 4% of the dissolved Lu for the model groundwater at pH = 7. These percentages drop to < 1% for pH = 8 and 9 (Fig. 5a–c). In addition, our calculations indicate that the $LnHPO_4^+$ species is the primary REE–phosphate complex for pH = 7 and 8, except for Yb and Lu, where the $LnPO_4^0$ complex accounts for more Yb and Lu than the $LnHPO_4^+$ complex. Only at pH = 9 does the $LnPO_4^0$ complex account for more of each REE than the $LnHPO_4^+$ complex. Moreover, our calculations indicate that the total phosphate concen-

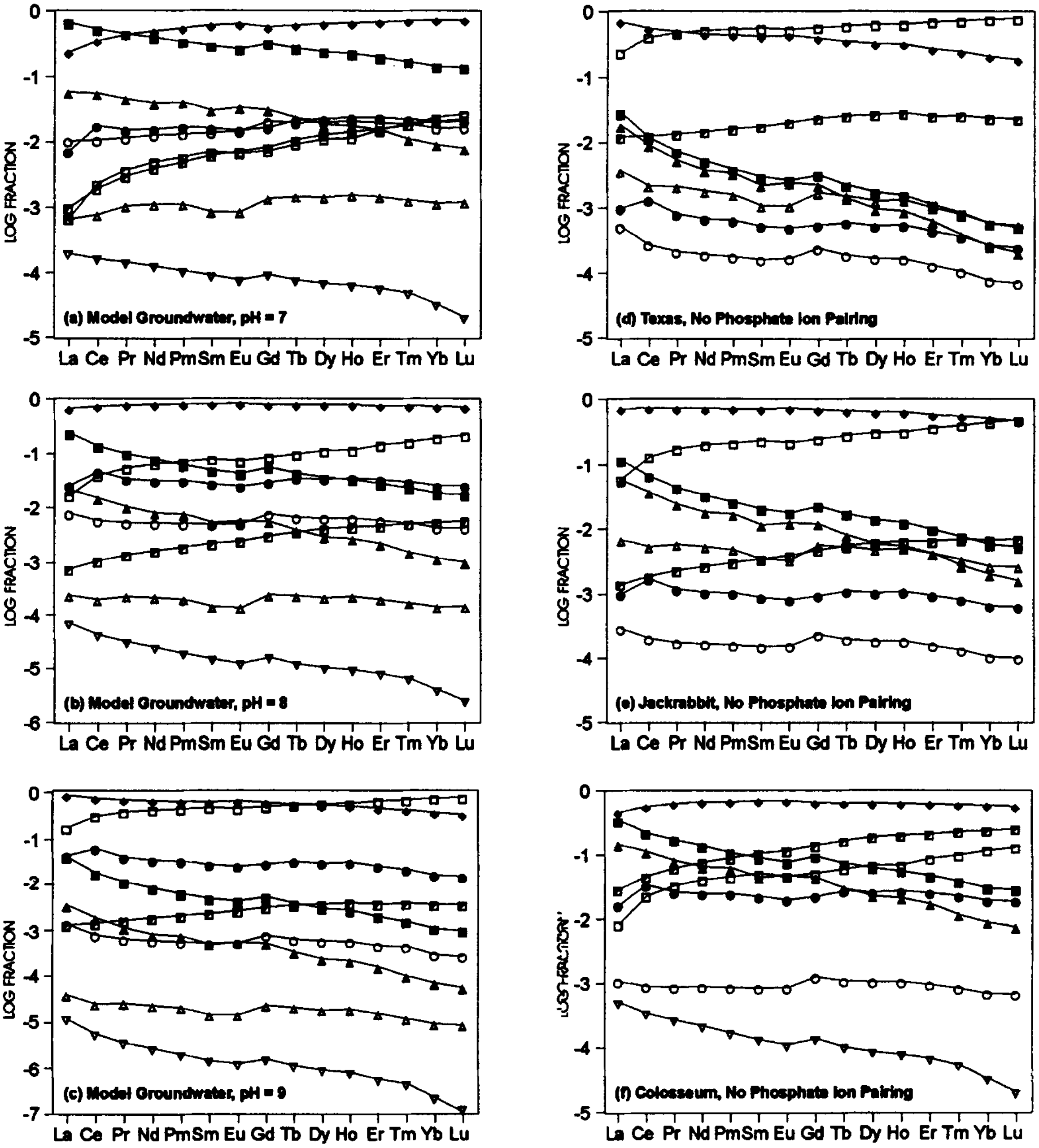

Fig. 5. Results of speciation calculations plotted as the log fraction of dissolved rare earths versus atomic number for the model groundwater of Wood [5] using our modified version [13] of Millero's [8] REE speciation model for (a) pH = 7, (b) pH = 8, and (c) pH = 9, and results of speciation calculations for (d) Texas Spring, (e) Jackrabbit Spring, and (f) Colosseum Spring, assuming that ion pair formation between Ca^{2+}, Mg^{2+} and PO_4^{3-} does not occur and ion pair formation between Ca^{2+}, Mg^{2+} and CO_3^{2-} does occur in these groundwaters. See text for explanation. Symbols as in Fig. 3.

tration must be at least 100 μmol/kg for the $Ln(HPO_4)_2^-$ complex and 10,000 μmol/kg for the $LnPO_4^0$ complex to compete with carbonate complexes for the REEs. These elevated total phosphate concentrations are in agreement with the estimate of Wood [5].

One possible discrepancy between our modelling efforts and previous endeavors may lie in the differences between the free phosphate ion concentrations ($[H_2PO_4^-]_F$, $[HPO_4^{2-}]_F$ and $[PO_4^{3-}]_F$) and the total phosphate ion concentrations ($[H_2PO_4^-]_T$, $[HPO_4^{2-}]_T$ and $[PO_4^{3-}]_T$). The free phosphate ion concentrations represent the amount of each phosphate ion available to form complexes with trace elements after ion pair formation with Ca^{2+} and Mg^{2+} (see [20] for a discussion of the techniques used to calculate the free ion concentration). Our estimates of the free fractions, in percent of the total, for $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} ions in the model groundwater, at all three pH values considered, are 99.5%, 83% and 0.14%, respectively. Consequently, in all cases the $[PO_4^{3-}]_F$ was typically between 2.5 and 3 orders of magnitude lower than the $[PO_4^{3-}]_T$ concentrations. By comparison with the $[PO_4^{3-}]_F$ concentrations presented in Table 2, the $[PO_4^{3-}]_T$ concentrations for the three springs Texas, Jackrabbit, and Colosseum Springs are $10^{-10.47}$ mol/kg, $10^{-12.06}$ mol/kg and $10^{-11.21}$ mol/kg, respectively. If we assume that phosphate does not form ion pairs with Ca^{2+} and Mg^{2+}, and consequently use the $[PO_4^{3-}]_T$ values to calculate REE–phosphate complexation, then the $LnPO_4^0$ complexes dramatically increases in importance. Fig. 5d–f shows the results of the speciation modelling without accounting for ion pair formation between Ca^{2+}, Mg^{2+} and phosphate for Texas, Jackrabbit and Colosseum Springs. (Colosseum Springs was chosen because it has the lowest CO_3^{2-} concentration of all of the groundwaters examined, Texas Spring has among the highest CO_3^{2-} concentrations and Jackrabbit has an intermediate CO_3^{2-} concentration — Table 2). In all three cases, however, even though the importance of the $LnPO_4^0$ complexes has increased, it never exceeds the carbonate complexes as the primary REE complex (Fig. 5d–f). For Texas Spring, for example, the $LnPO_4^0$ complex would only account for between 1.2% and 2.4% of the REEs with no ion pairing for the PO_4^{3-} ion, whereas carbonate complexes would be responsible for 93% to ~ 98% of the REEs. In Jackrabbit Spring, carbonate complexes would account for 79–98% of the REEs, in contrast to 0.1–0.7% for the $LnPO_4^0$ complex. Only for groundwater from Colosseum Springs, where we have already assumed a detection limit total phosphate concentration of 0.3 μmol/kg, could $LnPO_4^0$ potentially overtake $Ln(CO_3)_2^-$ in importance, if the total phosphate concentration is close to the detection limit, and attain significant percentages of dissolved HREEs (e.g., 25% of the dissolved Lu is predicted to occur as $LuPO_4^0$) (Fig. 5f). The $LnCO_3^+$ complexes, however, would still predominate (Fig. 5f), such that carbonate complexes would account for between 47% and 69% of the REEs and the $LnPO_4^0$ complex would be responsible for 2.8–25%. Consequently, even if ion pair formation with Ca^{2+} and Mg^{2+} is neglected for the phosphate ions, but not for the carbonate ion, REE carbonate complexes are still predicted to dominate over phosphate complexes in circumneutral pH groundwaters.

5. Conclusions

Our work indicates that REE–carbonate complexes are the dominant form of dissolved REEs in circumneutral pH ($7 \leq pH \leq 9$) groundwaters. Rare earth carbonate complexes are followed in importance by the free metal ion (Ln^{3+}), sulfate or hydroxyl complexes, fluoride complexes, and then phosphate complexes. Carbonato complexes ($LnCO_3^+$) typically predominate over dicarbonato complexes ($Ln(CO_3)_2^-$) in the majority of the groundwaters analyzed. However, the dicarbonato complex is especially significant for the HREEs in these groundwaters. Despite earlier predictions, we did not observe substantial contributions from phosphate complexation and especially not from the $LnPO_4^0$ complex. The insignificance of phosphate complexes is due to the overall low total phosphate concentrations in these groundwaters, the even lower free phosphate concentration (i.e., $[PO_4^{3-}]_F$), which is a consequence of ion pair formation of phosphate with Ca^{2+} and Mg^{2+}, and the higher free carbonate ion concentrations. If ion pair formation is not considered important for phosphate ions, then the model predicts that phosphate complexes become significant but still do not surpass carbonate complexes as the dominant form of the dissolved REEs in these groundwaters. Total phosphate concentrations must be at least 100 μmol/kg for $Ln(HPO_4)_2^-$ and 10,000 μmol/kg for $LnPO_4^0$ for these complexes to compete with carbonate complexes for dissolved REEs. Although phosphate ions are apparently not important in stabilizing dissolved REE concentrations in these groundwaters, and consequently enhancing REE concentrations, as is the case with carbonate ions, earlier work [24,30] indicates that phosphate ions may act in an opposite sense by removing REEs as phosphate salts.

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Appendix A

Rare earth element concentrations (in pmol/kg) for groundwater from south-central Nevada and eastern California. Shale-normalized Yb/Nd ratios are also tabulated

	Fair-banks	Rogers	Longst.	Brad.	Jack-rabbit	Texas	Nevares	Traver-tine	Upper Brier	Scotty's	Surprise	Mesquite	Army	Cind R-lite	Coffer	Jackass Aero Park	Lathrop	Chub	Hardrock Queen	Collos-seum	Ivanpah	Owens
La	28	26	24	24	36	38	33	45	260	76	44	47	8.4	5.6	4	12	16	49	65	171	30	2250
Ce	50	33	43	45	65	56	67	80	210	235	73	58				5.2		93	86	71	48	5540
Pr	8.6	7.9	6	6.1	8.7	6.4	7.2	6.7	78	13	8.2	9	2.2	4.5	1.3	1.4	2.4	15	13	21	5.6	410
Nd	33	33	25	25	35	25	28	27	350	51	27	36	9.1	12.3	4.8	5.3	8.7	54	51	93	22	1400
Sm	7.2	7.4	4.9	5	6.5	5	5.6	5.3	87	9.5	7	7				1.1	1.9	10	10	22	4.5	280
Eu	0.7	1.3	1	0.9	0.7	0.8	1.2	1.1	14	2	1	1.2	0.3	0.5	0.3	0.4	0.5	1.2	3	6.5	1.2	86
Gd	6.4	8.3	5.1	5.7	6.9	4.9	6	5.6	95	9.3	7.5	6.6	1.8	1.5	0.8	1	1.9	12	14	31	5.2	220
Tb	1	1.4	0.8	0.8	0.9	0.7	0.8	0.8	15	1.4	1.3	1	0.3	0.2	0.1	0.1	0.3	1.4	2.3	4.9	0.8	38
Dy	5.8	8.9	3.7	5.1	4.9	4.1	4.1	4.3	97	8	7.8	5.6	1.5	1.8	0.6	0.8	2	7	15	36	4	170
Ho	1.2	2.2	1	1.1	1.2	0.8	0.8	0.9	25	1.8	1.7	1.1	0.4	0.5	0.2	0.2	0.6	1.6	3.9	9.5	0.9	36
Er	3.3	7.7	2.7	3.3	3.2	2.6	2.3	2.5	82	6.4	4.9	3.3	1.2	1.7	0.6	0.6	2	4.4	12	29	2.5	110
Tm	0.5	1.4	0.6	0.5	0.5	0.4	0.4	0.3	13	1	0.7	0.5	0.2	0.2	0.1		0.2	0.7	1.7	3.6	0.3	18
Yb	3	11	2.7	3.7	3.2	2.3	2.3	2.6	82	6.7	3.9	3	0.8	1.3	0.7	0.4	1.5	3.9	8.6	20	2.1	120
Lu	0.5	2.1	0.7	0.5	0.6	0.4	0.4	0.4	14	1.1	0.6	0.5	0.2	0.2	0.1	0.1	0.2	0.6	1.4	3	0.3	23
$(Yb/Nd)_{SN}$	1.18	4.33	1.40	1.92	1.19	1.19	1.07	1.25	3.01	1.71	1.88	1.08	1.18	1.37	1.88	0.99	2.28	0.93	2.21	2.86	1.24	1.06
$(Er/Nd)_{SN}$	1.17	2.74	1.27	1.55	1.07	1.22	0.97	1.09	2.72	1.47	2.13	1.08	1.54	1.66	1.54	1.36	2.65	0.99	2.82	3.63	1.34	0.89
pH	7.05	7.19	7.30	6.97	6.99	7.61	7.34	7.37	7.37	7.62	7.62	7.36	7.04	7.98	7.50	9.05	7.48	7.95	7.92	7.74	7.47	8.14

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