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Geochemistry of the rare-earth elements in hypersaline and dilute acidic natural terrestrial waters: Complexation behavior and middle rare-earth element enrichments

Kevin H. Johannesson [a,*], W. Berry Lyons [b], Mary A. Yelken [c], Henri E. Gaudette [d], Klaus J. Stetzenbach [a]

[a] *Harry Reid Center for Environmental Studies, University of Nevada, Las Vegas, Las Vegas, NV 89154, USA*
[b] *Department of Geology, University of Alabama, Tuscaloosa, AL 35487, USA*
[c] *Water Resources Management Program, Department of Geosciences, University of Nevada, Las Vegas, Las Vegas, NV 89154, USA*
[d] *Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham, NH 03824, USA*

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Abstract

Rare-earth element (REE) speciation was modelled in acid ($2.9 \leq \mathrm{pH} \leq 3.5$), hypersaline groundwaters from Australia and from the Palo Duro Basin in Texas, USA, using a combined specific ion interaction (Pitzer model) and ion pairing model. The free metal ion species (i.e. Ln^{3+}) is the dominant form of dissolved REEs in these systems, accounting for 40–70% of the dissolved metal in groundwater from Lake Tyrrell (Victoria, Australia), 50–90% of the REEs in groundwater from Lake Gilmore (Western Australia), and always > 90% of each REE in the Texas groundwaters. (Lakes Tyrrell and Gilmore are actually dry lakes that act as groundwater discharge zones.) The abundance of the free metal ion species increases in these waters with increasing ionic strength and with decreasing pH. The free metal ion species is followed in abundance by REE-sulfate and REE-chloride complexes that account for: 20–50% and 10–15%, respectively, of the dissolved REEs in the groundwaters from Lake Tyrrell; 15–30% and 5–20%, respectively, in the groundwaters from Lake Gilmore; and < 3% and < 7%, respectively, in the Palo Duro Basin groundwaters.

The groundwaters of the Lake Tyrrell system and the Palo Duro Basin are enriched in the middle REEs (MREEs) compared to both the light REEs (LREEs) and the heavy REEs (HREEs). (Only Nd, Sm, and Dy were determined in the Lake Gilmore groundwaters and, consequently, it is unclear whether these acid groundwaters are also enriched in the MREEs.) Previous investigators suggested that Fe-rich organic flocs, REE-phosphate complexation, and solid–liquid exchange reactions between terrestrial waters and MREE-enriched surface Fe–Mn coatings, suspended particulates, or secondary mineral phases within aquifer materials, may promote the development of MREE enrichments in natural waters. We propose that organic colloids and REE-phosphate complexes are insignificant in acidic natural waters in regards to MREE enrichments. Instead, solid–liquid exchange reactions or dissolution of surface coatings, suspended particulates, and/or secondary phases as well as sulfate complexation, more likely controls the development of MREE enrichments in acidic natural terrestrial waters.

Keywords: Rare-earths; Hypersaline; Dilute; Acid waters; Metal speciation; Australia; North America

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[*] Corresponding author.

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1. Introduction

The study of rare-earth elements (REEs) in natural waters has primarily involved the examination of their occurrence in seawater (e.g., Goldberg et al., 1963; Elderfield and Greaves, 1982; DeBaar et al., 1983; Elderfield, 1988; Bertram and Elderfield, 1993; Sholkovitz et al., 1994; German et al., 1995, and references therein) and rivers and estuaries (Hoyle et al., 1984; Sholkovitz and Elderfield, 1988; Elderfield et al., 1990; Sholkovitz, 1993, 1995). Recently, however, investigators have been concerned with REE distributions and chemical behavior in natural terrestrial waters such as lakes (Möller and Bau, 1993; Johannesson and Lyons, 1994, 1995; Johannesson et al., 1994a), and groundwaters (Banner et al., 1989; Smedley, 1991; Fee et al., 1992; Gosselin et al., 1992; Johannesson et al., 1994b,1995a,1996) because, among other things, the REEs behave similar chemically to the trivalent actinides (i.e. Am^{3+}, Cm^{3+}, and Cf^{3+}) (Choppin, 1983; Krauskopf, 1986; Wood, 1990; Runde et al., 1992), and, consequently, may prove useful for predicting the behavior of these actinides in terrestrial waters. Studies of REEs in terrestrial waters indicate that although these waters may inherit their REE signatures via interaction with rocks and/or other aquifer materials (e.g., Smedley, 1991), solution complexation can significantly affect the dissolved REE signature (Elderfield et al., 1990; Gosselin et al., 1992; Johannesson and Lyons, 1994; Sholkovitz, 1995).

Investigations of the complexation behavior of the REEs in natural terrestrial waters have demonstrated the importance of carbonate ion complexes in neutral- to high-pH surface- and groundwaters (Wood, 1990; Lee and Byrne, 1992; Millero, 1992; Möller and Bau, 1993; Johannesson and Lyons, 1994; Johannesson et al., 1994a,1995a,b,1996) and the free metal ion species (e.g., La^{3+}) and REE-sulfate complexes in an acidic, freshwater lake (Johannesson and Lyons, 1995). Gosselin et al. (1992) calculated the complexation behavior of REEs in the acidic brines of the Palo Duro Basin in Texas (ionic strength, $I = 3.4$–5.7 mol/kg) using stability constants appropriate for seawater ($I = 0.7$ mol/kg) but, until the present study, the speciation of the REEs in acid brines have not been appropriately examined using activity coefficients and stability constants suitable for the ionic strength of such brines. In this study, we have modelled the speciation of the REEs in the acid, saline to hypersaline groundwaters ($I = 0.65$–3.3 mol/kg) that discharge at Lake Tyrrell and Lake Gilmore in Australia, using a combined specific ion interaction (i.e. Pitzer theory) and ion pairing model that accounts for the high ionic strengths of these groundwater brines (Millero, 1992; Johannesson and Lyons, 1994). In addition, we re-examined the speciation of the REEs in the acid, saline groundwaters of the Palo Duro Basin, Texas, using appropriate stability constants and activity coefficients determined by using the specific ion interaction/ion pairing model from the data of Fisher and Kreitler (1987) and Gosselin et al. (1992).

We also present shale-normalized REE plots for the Lake Tyrrell waters, replotted from Fee et al. (1992). These replotted data reveal a shale-normalized middle REE (MREE) enrichment compared to both the light REEs (LREEs) and the heavy REEs (HREEs). Such patterns have recently been referred to as hump-shaped patterns (Schaltegger et al., 1994) and have been observed in other natural acid waters (Gosselin et al., 1992; Johannesson and Lyons, 1995; D.K. Nordstrom, pers. commun., 1995). The origin of MREE enrichments patterns in natural terrestrial waters is currently not well understood and, consequently, in order to identify those chemical processes important in controlling REE behavior in terrestrial waters it is necessary to determine the origin of these MREE enrichments. Previous investigators have suggested colloidal associations (Elderfield et al., 1990), water–rock and/or secondary mineral interactions (Gosselin et al., 1992), and phosphate complexation (Sholkovitz, 1995) to explain MREE-enriched waters. Here we review these mechanism and sulfate complexation in terms of MREE enrichments.

2. Hydrogelogic settings

Lake Tyrrell is located within the River Murray basin in northern Victoria, Australia, and Lake Gilmore is in southern Western Australia within the semi-arid Yilgarn Block (Fig. 1). The hydrologic, geologic, and geochemical settings of both Lake Tyrrell and Lake Gilmore have been discussed at length in a series of previous studies (e.g., Teller et

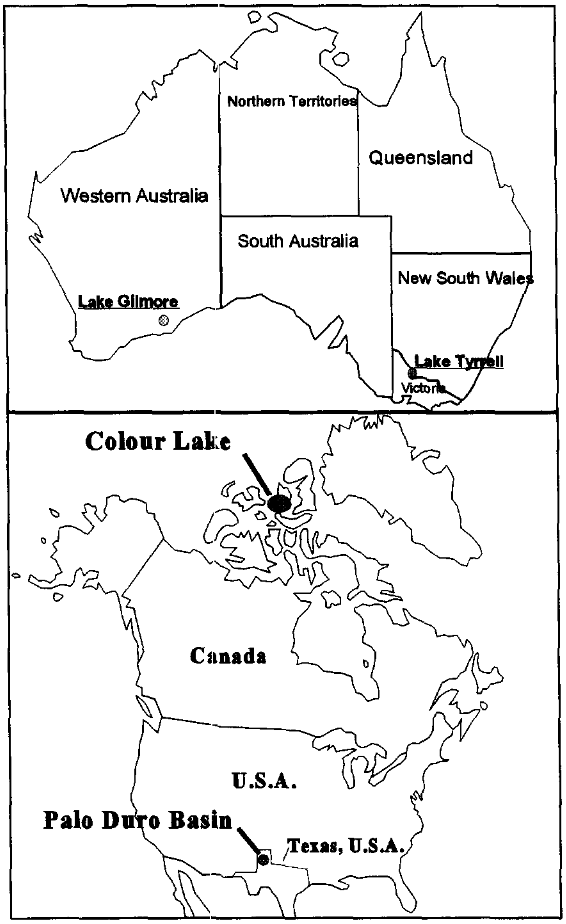

Fig. 1. Highly schematic maps of Australia and North America showing the approximate locations of: Lake Tyrrell in Victoria, Australia; Lake Gilmore in Western Australia; Colour Lake on Axel Heiberg Island, Northwest Territories, Canada; and the Palo Duro Basin, Texas, U.S.A.

al., 1982; Macumber, 1983, 1991, 1992; Mann, 1983; Long et al., 1987, 1992; McArthur et al., 1989, 1991; Lyons et al., 1990, 1992, 1995; Chivas et al., 1991; Dickson and Herczeg, 1992; Fee et al., 1992; Fegan et al., 1992; Hines et al., 1992). Briefly, Lakes Tyrrell and Gilmore occur within arid to semi-arid regions where evaporation greatly exceeds the typically yearly precipitation of ≤ 300 mm (Macumber, 1983; McArthur et al., 1989, 1991; Fee et al., 1992). Lake Tyrrell and Lake Gilmore are playas and actually represent discharge sites for regional groundwaters (Macumber, 1983, 1992; McArthur et al., 1989, 1991). Both playa lakes seldom contain water and Lake Tyrrell, for example, has been reported to be dry for at least 9 months of the year (Bowler, 1986). The regional groundwaters, examined in this study and that discharge onto the Lake Tyrrell and Lake Gilmore playas, are acidic (pH ranges from 2.9 to 3.4) and hypersaline (ionic strength ranges from 0.65 to 3.3 mol/kg) (Teller et al., 1982; Macumber, 1983, 1992; McArthur et al., 1989, 1991; Lyons et al., 1992; Fee et al., 1992). Lake Gilmore is located in the Yilgarn Block in Western Australia which is composed of Archean rocks of granitic composition as well as greenstones (Williams, 1975; McArthur et al., 1989, 1991). On the other hand, the major aquifer beneath Lake Tyrrell is the Miocene to Pliocene Parilla Sand which is up to 100 m thick and consists primarily of quartz sand but also contains heavy minerals including ilmenite, rutile, and zircon (Macumber, 1983; Fee et al., 1992; Long et al., 1992). The Parilla Sand is underlain by the Geera Clay and overlain by the Blanchetown Clay (Macumber, 1983).

The Palo Duro Basin, located in the Texas Panhandle, is described in detail by Fisher and Kreitler (1987) and Gosselin et al. (1992) and references therein. The groundwater samples analyzed by these authors and re-examined here were collected from wells in the Deep Basin Brine aquifer of the basin. The aquifer consist of Pennsylvanian arkosic sandstones and carbonate rocks which are overlain by Permian carbonate rocks (Gosselin et al., 1992). The Palo Duro Basin groundwaters are Na–Cl brines with ionic strengths from 3 mol/kg up to as high as 6.72 mol/kg and total dissolved solids that range between 140 and 290 g/kg (Fisher and Kreitler, 1987). The Na concentrations range from 2 up to 4 mol/kg and account for between 70% and 90% of the cations, whereas Cl concentrations are between 2.4 and 5 mol/kg in these brines and typically accounts for $> 98\%$ of the anions (Fisher and Kreitler, 1987). The pH and water temperature of the Palo Duro Basin brines discussed ranged from 4.4 to 6 and 32° to 41°C, respectively (Appendix A) (Fisher and Kreitler, 1987; Gosselin et al., 1992).

We will also briefly discuss the REE geochemistry of the dilute ($I = 0.01$ mol/kg) acidic waters of Colour Lake (pH ~ 3.6) located in the Canadian High Arctic within a natural basin composed primarily of upper Mississippian through lower Tertiary sandstones and shales (Fricker, 1963; Allan et al., 1987). The geologic setting and lake water chemistry have been discussed in detail by Allan et al. (1987), English et al. (1991), Schiff et al. (1991), Boike et al. (1992), Doran (1993), and Johannesson and Lyons (1995).

3. Sampling and analytical methods

The REE data presented here for groundwaters that discharge at the Lake Tyrrell playa are from Fee et al. (1992) and for groundwaters collected beneath the Lake Gilmore playa surface are taken from Johannesson et al. (1994b). The sampling and analytical techniques have been discussed in detail by McArthur et al. (1991), Fee et al. (1992), and Johannesson et al. (1994b) and will not be repeated here to the same degree. Briefly, all groundwater samples were filtered in the field through 0.45-μm Millipore membrane filters, acidified to pH < 2 with Ultrar HCl, and stored in precleaned, acid-washed high-density linear polyethylene bottles. Measurements of the pH were also obtained in the field. The groundwater samples from the Lake Tyrrell playa were collected from shallow wells using an acid-washed Teflon® bailer and the groundwater samples from the Lake Gilmore playa were collected by digging or augering into the playa surface sediments to a maximum depth of 4.3 m. For Lake Gilmore, the saturated zone was within 50–100 cm of the playa surface (McArthur et al., 1991). No Fe precipitated from solution during sample collection of these oxygenated and acidic groundwaters (Fee et al., 1992; Johannesson et al., 1994b).

The REEs for the Lake Tyrrell and Lake Gilmore groundwaters were determined at the Massachusetts Institute of Technology using inductively coupled plasma mass spectrometry (ICP–MS) (VG® 12-12S SIMS Quadrapole Plasmaquad) on preconcentrated samples (Fee et al., 1992; Johannesson et al., 1994b). The REEs were preconcentrated via ferric hydroxide coprecipitation (Weisel et al., 1984; Welch et al., 1990) and separated from other potentially interfering cations by cation exchange (Fee et al., 1992). Concentrations of Nd, Sm, and Dy were verified with thermal ionization isotope dilution mass spectrometry at the University of New Hampshire for the Lake Tyrrell and Lake Gilmore samples. Nd and Sm were separated from the other REEs before analysis by anion-exchange chromatography (Cheatham, 1985; Hayward, 1989; Fee et al., 1992) and Dy was separated from the other REEs using an adaptation of the method of Hooker et al. (1975).

4. Speciation modelling

Because the groundwaters that discharge into Lake Tyrrell and Lake Gilmore are brines as are the groundwaters of the Palo Duro Basin, it was necessary to calculate the activity coefficients for the individual REEs, the important complexing ligands, and the REE–ligand ion pairs (see Appendix A), as well as the stability constants for the complexation reactions in these brines. The activity coefficients and appropriate stability constants were calculated using a combined specific ion interaction (i.e. Pitzer theory) and ion pairing model developed for the REEs by Millero (1992). The model was modified (Johannesson and Lyons, 1994) to account for the possible formation of REE-phosphate complexes (i.e. stability constant data from Lee and Byrne, 1992) and updated with more recently determined stability constant data for REE carbonate complexes (Lee and Byrne, 1993). The formation of inorganic REE complexes with OH^-, Cl^-, F^-, HCO_3^-, SO_4^{2-}, CO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} were considered in the calculations and the importance of Ln^{3+}, $LnOH^{2+}$, $LnCl^{2+}$, LnF^{2+}, $LnSO_4^+$, $LnHCO_3^{2+}$, $LnCO_3^+$, $Ln(CO_3)_2^-$, $LnH_2PO_4^{2+}$, $LnHPO_4^+$, $Ln(HPO4)_2^-$, and $LnPO_4^0$ species were evaluated (where Ln stands for all the REEs [lanthanide series elements = Ln]).

The free concentration of each phosphate species ($[H_2PO_4^-]_F$, $[HPO_4^{2-}]_F$, and $[PO_4^{3-}]_F$) was determined from the total phosphate concentration following the techniques outlined in Millero and Schreiber (1982). Carbonate species (HCO_3^- and CO_3^{2-}) were determined from alkalinity measurements where appropriate (i.e. the groundwater from the Palo Duro Basin, Texas (Fisher and Kreitler, 1987; Gosselin et al., 1992)), or from estimated carbonate alkalinity values (i.e. Lake Tyrrell, Lake Gilmore, and Colour Lake) (see Johannesson et al., 1995b) using the geochemical model PHRQPITZ (Plummer et al., 1989).

Free sulfate ion concentrations were calculated using the methods of Millero and Schreiber (1982).

Water temperatures for the groundwaters from the Lake Tyrrell system averaged 20°C (W.B. Lyons, unpublished data) and water temperatures for the Palo Duro Basin groundwaters ranged between 32° and 41°C (Gosselin et al., 1992) (see Appendix A). Unfortunately, the temperature of the groundwaters from the Lake Gilmore system were not measured at the time of sampling and, consequently, we have assumed that these groundwaters have similar temperatures to the groundwaters from the Lake Tyrrell system. The model used to calculate the speciation of the REEs in these groundwaters was developed for solutions at 25°C (Millero, 1992). However, because the actual temperatures in these groundwaters do not vary tremendously from 25°C, especially for the Lake Tyrrell groundwaters, the speciation of these groundwaters was modelled keeping all parameters constant and assuming the water temperature was 25°C. In addition, the speciation of the REEs in the groundwater from the Palo Duro Basin with the highest temperature (M1Z1, Appendix A), i.e. 41°C, was also modelled at 25°C to examine differences in the results. These differences were determined to be minor or negligible (e.g., the percentage of La that occurs as the free metal species, i.e. La^{3+}, in this groundwater was calculated to be 98.69% at 41°C and 98.78% at 25°C). These results suggest that ionic strength plays a more important role in determining the speciation of the REEs in brines than small differences in solution temperature.

5. Results and discussion

5.1. Speciation of the REEs in acid, hypersaline groundwaters

The major-ion data used in this study to determine the speciation of the REEs in Lake Tyrrell groundwater are from Giblin and Dickson (1992), Long et al. (1992), and W.B. Lyons (unpublished data) and for Lake Gilmore groundwater are from McArthur et al. (1989, 1991). The major-ion data used to calculate the complexation of the REEs in the groundwaters from the Palo Duro Basin in Texas are those of Fisher and Kreitler (1987) and Gosselin et al. (1992). The REE data for the Lake Tyrrell and Lake Gilmore groundwaters are taken from Fee et al. (1992) and Johannesson et al. (1994b), respectively. The major-ion data for the Lake Tyrrell and Lake Gilmore groundwater are reproduced in Table 1 and the REE data are presented in Table 2. Because the major solute and REE data for the Palo Duro Basin groundwaters were sampled at different times, we have assumed for our calculations that the respective con-

Table 1
Major-ion concentrations (in mmol/kg) in groundwaters from Lake Tyrrell (LT-54 and LT-86) and Lake Gilmore (LG-0 through LG-6)

	Lake Tyrrell		Lake Gilmore					
	LT-54	LT-86	LG-0	LG-1	LG-3	LG-4	LG-5	LG-6
Ca	7.37	2.54	3	3.66	5.03	12.2	12.4	18.1
Mg	106	43.1	39.3	62.8	111	189	186	198
Na	1065	743	500	444	1345	2274	2315	2464
K	6.1	4.69	3.52	5.13	7.39	13.4	12.7	13.8
Cl	1153	675	566	887	1517	2884	2325	2812
SO_4	60.9	59.4	17.9	25.8	46.3	150	152	76.3
HCO_3^{a}	0.59	1.1	0.85	1	0.64	0.56	0.33	0.34
PO_4^{b}	0.35	< 0.06	~ 0.05	~ 0.05	~ 0.05	~ 0.05	~ 0.05	~ 0.05
pH	3.0	3.3	3.3	3.5	3.0	2.9	3.0	2.9
I	1.46	0.917	0.655	0.852	1.76	3.02	3.29	3.23

Values for HCO_3^{2-} are in pmol/kg and represent estimates determined using PHRQPITZ (Plummer et al., 1989). The phosphate data are in μmol/kg amd ionic strength (I) is given in mol/kg. Data for Lake Tyrrell are from Giblin and Dickson (1992), Long et al. (1992), and W.B. Lyons (unpublished data) and for Lake Gilmore the data are from McArthur et al. (1989, 1991).

[a] Estimated using PHRQPITZ (Plummer et al., 1989).

[b] W.B. Lyons (unpublished data).

centrations have remained constant with time. The reader is referred to Fisher and Kreitler (1987), McArthur et al. (1989, 1991), Fee et al. (1992), Giblin and Dickson (1992), Gosselin et al. (1992), Long et al. (1992), Macumber (1992), Johannesson et al. (1994b), and Johannesson and Lyons (1995) for more thorough discussions of the hydrogeology and geochemistry of Lake Tyrrell, Lake Gilmore, and Palo Duro Basin groundwater.

5.1.1. Lake Tyrrell and Lake Gilmore groundwater

The results of the speciation modelling for the Lake Tyrrell and Lake Gilmore groundwaters are presented in Figs. 2 and 3, respectively. Because F^- concentrations were measured in the Lake Tyrrell groundwaters (Giblin and Dickson, 1992), the LnF^{2+} complex is included in the speciation results for Lake Tyrrell groundwaters but not for the Lake Gilmore groundwaters.

For the Lake Tyrrell groundwaters the two dominant species are the free metal ion species (Ln^{3+}) and sulfate complexes ($LnSO_4^+$) (Fig. 2). For groundwater sample LT-54, the free metal species is the primary form of the dissolved REEs and always accounts for more than half of each REE in solution and up to 70% of the concentration of the dissolved HREEs (Fig. 2a). Following the free metal species is the sulfate complex which is responsible for between 20% and 35% of each REE. Rare-earth element complexes with the chloride ion are also important in this groundwater accounting for between 8% and 15% of the REEs. Finally, fluoride complexes are of minor importance and never represents more than 5% of each REE. All other inorganic REE complexes, including REE-carbonate, REE-phosphate, and REE-hydroxyl complexes, are negligible and never account for more that 0.001% of each dissolved REE.

The complexation of the REEs in Lake Tyrrell LT-86 is different than for LT-54 in that the free metal species and sulfate complexes account for roughly the same amount of the LREEs (i.e. 40–50%) (Fig. 2b). For the HREEs, the importance of the free metal ion for LT-86 increases whereas the sulfate complex decreases in importance. The percentage of each REE complexed with chloride is essentially the same as for LT-54, however, more of the HREEs are complexed as fluoride complexes than was observed for LT-54. Again, all other REE complexes are negligible in LT-86 groundwater.

The same general complexation behavior of the REEs observed in the Lake Tyrrell groundwaters are predicted for the Lake Gilmore groundwaters. For Lake Gilmore groundwaters, for example, the free metal ion species is always predicted to be the dominant form of each REE in solution followed by REE-sulfate and REE-chloride complexes in decreasing importance (Fig. 3a–f). The major differences of

Table 2
Rare-earth element concentrations (in nmol/kg) for groundwaters from Lake Tyrrell and Lake Gilmore, Australia

	Lake Tyrrell						Lake Gilmore					
	LT-54A	LT-54B	LT-78A	LT-78	LT-86	LT-BIM6	LG-0	LG-1	LG-3	LG-4	LG-5	LG-6
La	134.9	179	105	113.4	648	195.4						
Ce	465.7	617	415.2	556	1193	652						
Pr	74.4	99.9	57.4	94.5	280.8	105.6						
Nd	314.3	425.3	229.2	361	1061	447.5	804.2	762.6	409	797.3	783.4	762.6
Sm	80.7	109.5	43.2	91.9	212.5	110.3	126.3	99.7	59.8	119.7	93.1	106.4
Eu	18.8	27.4	11.9	20.1	52.1	27.2						
Gd	93.2	108.8	80.5	133.3	319.2	118.6						
Tb	11	14.1	10.8	17	34	15.6						
Dy	52.3	66.1	82.1	122.1	249.5	81.1	80	73.9	36.9	98.5	80	83.1
Ho	11.3	12.9	10.9	20.2	28.4	13.2						
Er	30.4	39	22.5	55.1	81.9	38.3						
Tm	6.04	6.6	3.7	6.4	10.7	5.9						
Yb	33.2	38.7	21.5	40.6	40	34.3						
Lu	4.8	4.8	4.2	6.9	4.2	5.5						

Lake Tyrrell data are from Fee et al. (1992) and Lake Gilmore data are from Johannesson et al. (1994b).

the REE complexation behavior between the Lake Gilmore groundwaters are the relative proportions of the free metal species, and sulfate and chloride complexes. The two extremes are represented by Lake Gilmore groundwater samples LG-1 and LG-6; the relative proportions of each REE species in the other Lake Gilmore groundwater samples fall within the variation exhibited by these two samples (Fig. 3a–f). In LG-1, for example, the free metal species accounts for between 50% and 70% of each REE and is similar in its percentages of all three species (Ln^{3+}, $LnSO_4^+$, $LnCl^{2+}$) to LT-54 (compare Fig. 2a with Fig. 3b). On the other hand, the free metal ion species represents between 80% and 90% of each REE in LG-6 (Fig. 3f). The REE-sulfate and REE-chloride complexes account for typically $\leq$ 10% of each REE in this groundwater sample.

The differences in the importance of the free REE ion species in these groundwater is most strongly associated with the Ca^{2+} concentration (Fig. 4a). The lowest Ca^{2+} concentration occurs in sample LT-86 (2.54 mmol/kg) for which the percentage of each REE present in solution as the free metal ion, $[Nd^{3+}]_F$ (e.g., 45.8% of total Nd), is the lowest of all the groundwater samples. In contrast, LG-6, which exhibits the highest percentage of each REE as free metal ions (e.g., 83.5% of total Nd), has the highest Ca^{2+} concentration (18.1 mmol/kg). A similar positive relationship is observed for the total cation concentration and the ionic strength (Fig. 4b). Moreover, the percentage of the total Nd concentration that occurs in solution as the free metal species is also positively correlated with the anion concentrations in these brines. (Because the same pattern is observed for the total cation, total anion, and ionic strength, we have chosen to show only ionic strength in Fig. 4b.) There also exists an inverse relationship between the percentage of REE complexed with sulfate and chloride ions and the ionic strength (Fig. 4b).

The percentage of each REE present as the free metal ion in these groundwaters is inversely related to the pH. In general, the groundwaters with lower pH values (e.g., LG-6 and LG-4) typically have higher percentages of REEs present in solution as the free metal ion, whereas the opposite is observed for the higher-pH groundwaters (LT-86, LG-0, and LG-1) (Table 1; Figs. 2 and 3). Because the difference in pH between these samples is less than one pH unit, the inverse relationship between pH and percentage of each REE present as the free metal ion in these groundwaters should be viewed with caution. It is important to point out, however, that it is reasonable to expect such an inverse relationship based on the previous work of Wood (1990) and Lee and Byrne (1992) who demonstrated the importance of the free metal REE ion species in a low-pH, model groundwater.

The differences in the percentage of free metal ion in solution for the REEs appears to be more closely related to the ionic strength of these groundwater brines than to pH, although it is likely that a

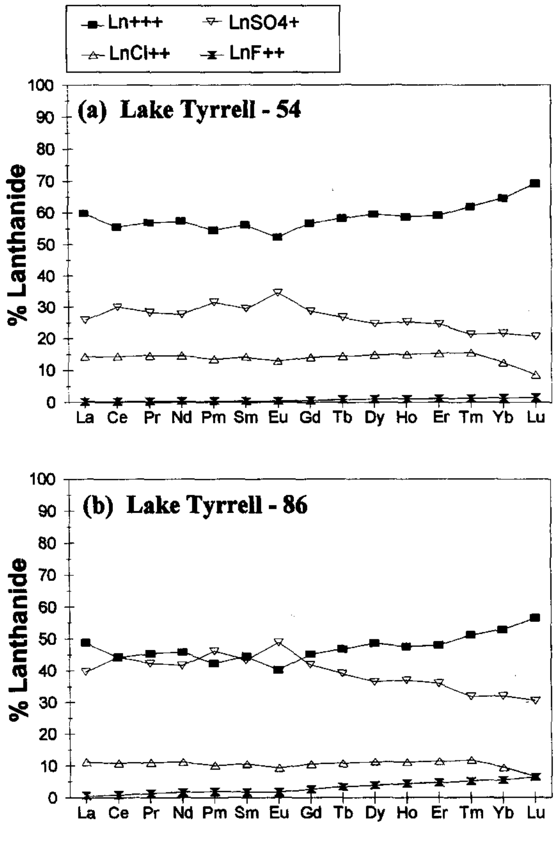

Fig. 2. Results of speciation modelling plotted as percent dissolved rare earths (i.e. *% lanthanides*) vs. atomic number for groundwater samples: (a) LT-54 and (b) LT-86, from Lake Tyrrell (*LT*), Victoria, Australia. (*Ln + + +* = Ln^{3+}, *LnSO4 +* = $LnSO_4^+$, *LnCl + +* = $LnCl^{2+}$, and *LnF + +* = LnF^{2+}, where *Ln* = lanthanide series elements.)

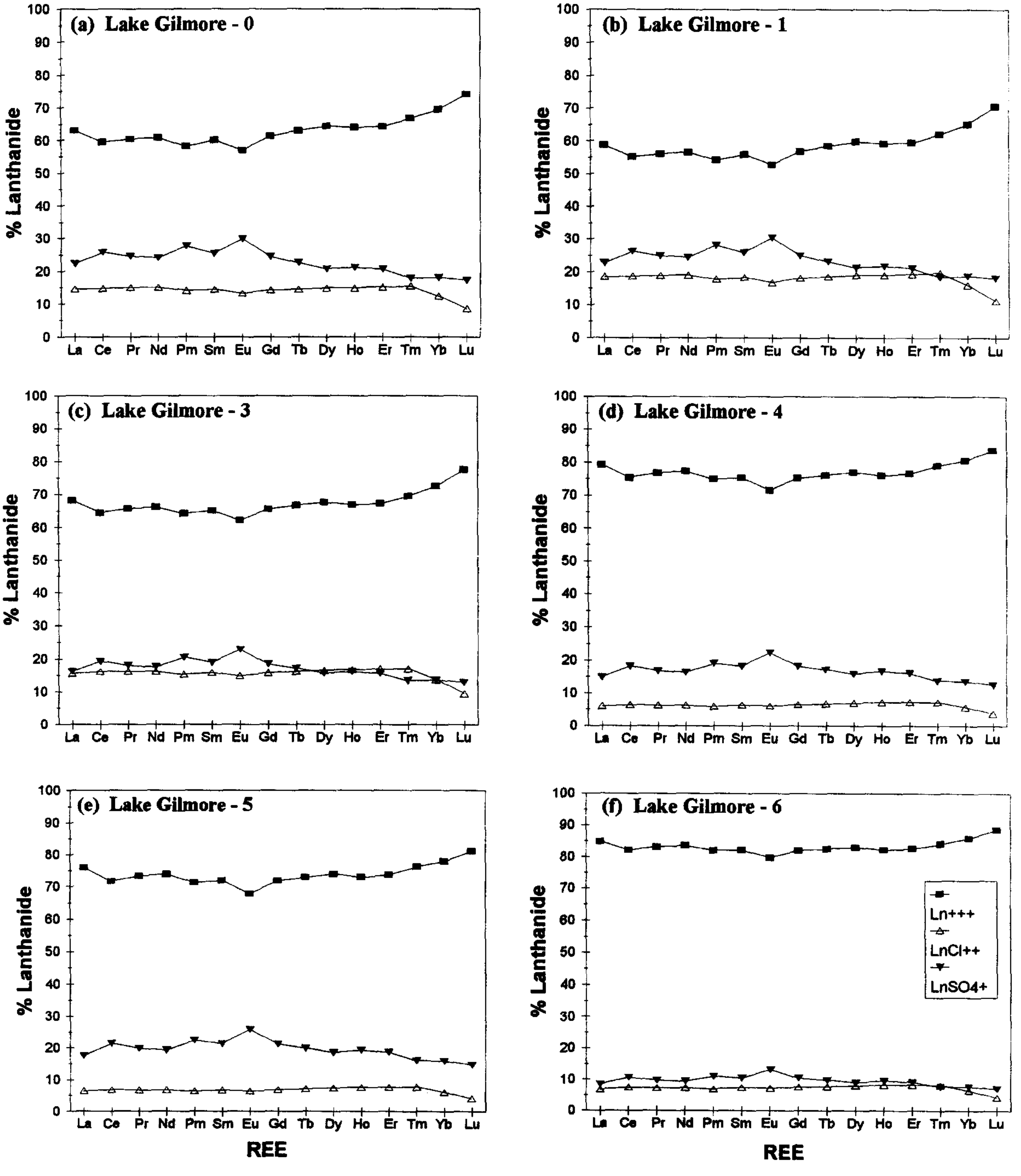

Fig. 3. Results of speciation modelling plotted as percent dissolved rare earths vs. atomic number for Lake Gilmore (i.e. *LG*) groundwater samples: (a) LG-0, (b) LG-1, (c) LG-3, (d) LG-4, (e) LG-5, and (f) LG-6. (*Ln* + + + = Ln^{3+}, *LnSO4* + = LnSO$_4^+$, and *LnCl* + + = LnCl^{2+}, where *Ln* = lanthanide series elements.)

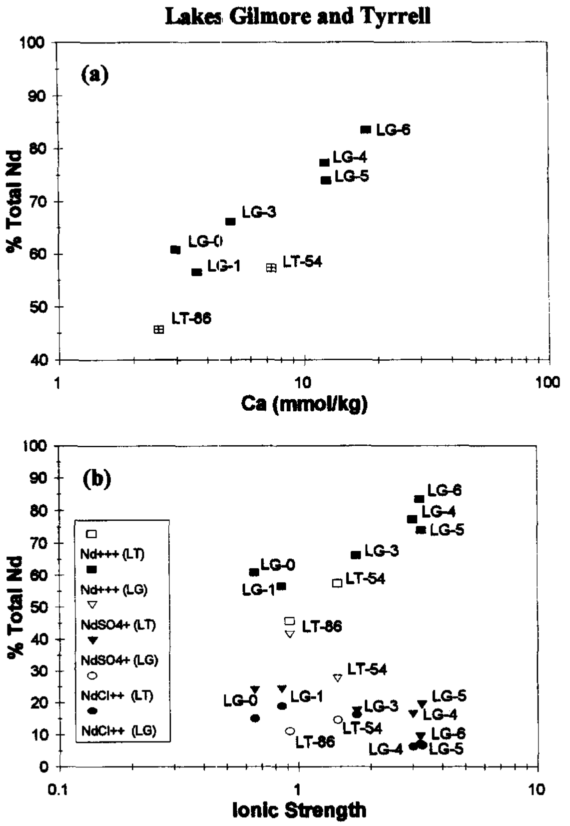

Fig. 4. Percent of Nd that occurs as: (a) the free metal ion species (i.e. *Nd*$^{3+}$) in the groundwaters of Lake Tyrrell (*LT*) and Lake Gilmore (*LG*) vs. Ca^{2+} concentration (in mmol/kg); and (b) the percent of the total Nd concentration that occurs as the free metal ion species (*Nd*$^{3+}$), sulfate complex (*NdSO*$_4^+$), and chloride complex (*NdCl*$^{2+}$) in the same groundwaters vs. ionic strength (in mol/kg). (*Nd* + + + = Nd^{3+}, *NdSO4* + = $NdSO_4^+$, and *NdCl* + + = $NdCl^{2+}$.)

combination of both are important. Our observations suggest that ionic strength plays a prominent role in REE speciation in low-pH brines. Ion pair formation between the major cations, such as Ca^{2+} and Mg^{2+}, and the major complex forming anions, is expected to increase with increasing ionic strength (e.g., Garrels and Christ, 1965; Morel and Hering, 1993; Nordstrom and Munoz, 1994) such that at higher ionic strengths there will be lower free ligand concentrations available to form complexes with the REEs. Consequently, the percentage of uncomplexed REEs in solution, i.e. free metal ions, is also expected to rise with increasing ionic strength in low-pH waters. On the other hand, because the concentration of free ligands will decrease with increasing ionic strength due to formation of ion pairs with the concomitant increase in available major cations in these low-pH brines, the percentage of REE complexed with complexing ligands will also decrease. The results of the speciation modelling for the Lake Tyrrell and Lake Gilmore groundwaters are in agreement with these arguments.

5.1.2. Palo Duro Basin groundwater

The results of our speciation calculations for mildly acidic ($4 < pH < 6$), hypersaline groundwaters from the Palo Duro Basin, Texas, are shown in Fig. 5. The speciation of these same groundwaters and three other samples was previously calculated by Gosselin et al. (1992) using stability constants appropriate for seawater ($I = 0.7$ mol/kg). The ionic strength, however, for the three samples presented here range from 3.36 to 5.67 mol/kg and for the three other samples examined by Gosselin et al. (1992), the ionic strength ranges up to 6.72 mol/kg. As discussed, we have accounted for the differences in ionic strength of these groundwaters in our speciation calculations and have used stability constants and activity coefficients that are appropriate for the high ionic strengths (Appendix A).

Gosselin et al. (1992) predicted that the $LnCl^{2+}$ complex would dominate the speciation of the REEs in these groundwaters and would account for between 42% and 75% of the dissolved REEs in the three samples discussed here and between 64% and 80% in the other three groundwater samples they analyzed. They estimated that the free metal species was responsible for between 23% and 53% of the REEs in the three samples discussed here and from 20% to 35% in the three other groundwater samples. The $LnSO_4^+$ complex was predicted to represent up to 3.7% of the dissolved REEs but was typically shown to account for < 1% whereas carbonato complexes ($LnCO_3^+$) always accounted for < 1% (Gosselin et al., 1992).

The results of our speciation calculations using appropriate activity coefficients and stoichiometric stability constants for these brines are strikingly different. For all three groundwaters, the overwhelming majority of each REE is predicted to occur as free metal ions (Fig. 5). The $LnCl^{2+}$ complex is only predicted to account for 7% of the dissolved REEs in groundwater from Sawyer No. 1, Zone 5 (S1Z5), and 1% and < 1% in the Mansfield No. 1, Zone 1 (M1Z1) and Sawyer No. 1, Zone 4 (S1Z4) samples, respectively. The LnSO$_4^+$ complex accounts for upwards of 3% of Eu in the S1Z5 groundwater, ~ 0.1% of each REE for M1Z1 groundwaters and < 0.01% in the S1Z4 groundwater. Similar to the results of Gosselin et al. (1992), our calculations indicate that REE-carbonate complexes always account for < 1% of the dissolved REEs in these groundwaters (Fig. 5).

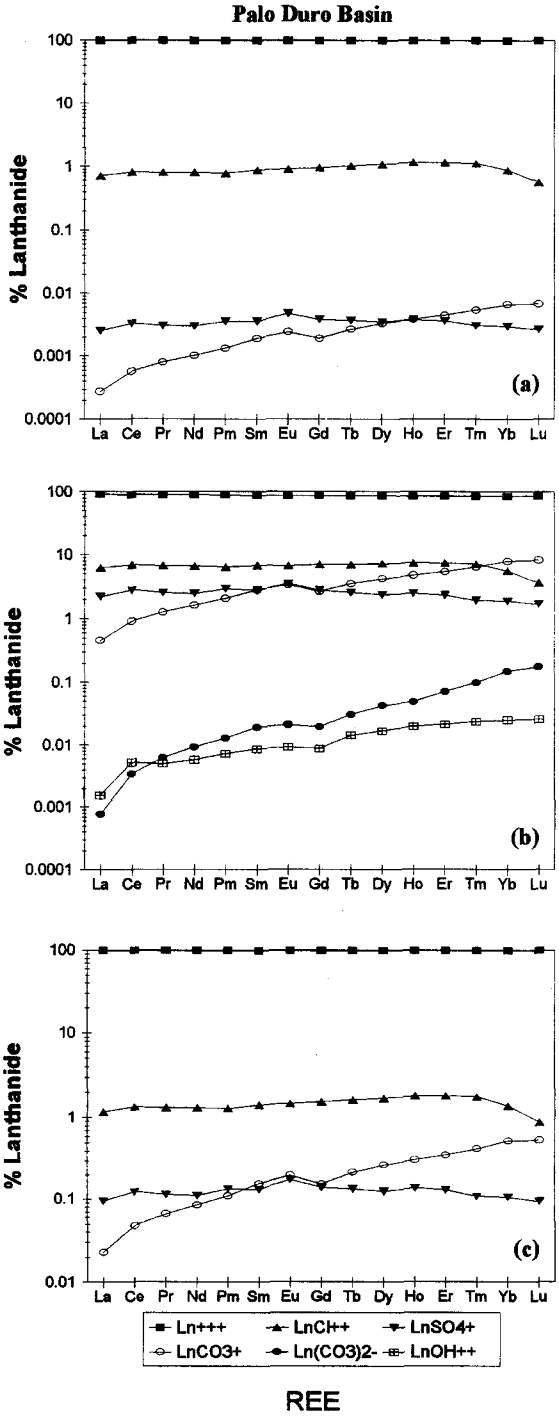

Fig. 5. Results of speciation modelling using our modified version (Johannesson and Lyons, 1994) of Millero's (1992) REE speciation model for groundwater from the Palo Duro Basin, Texas, U.S.A., for: (a) Sawyer No. 1, Zone 4; (b) Sawyer No. 1, Zone 5; and (c) Mansfield No. 1, Zone 1. Major-ion data used to calculate REE speciation are from Fisher and Kreitler (1987). (*Ln* + + + = Ln^{3+}, *LnSO4* + = LnSO$_4^+$, *LnCl* + + = LnCl^{2+}, *LnCO3* + = LnCO$_3^+$, *Ln(CO3)2* − = Ln(CO$_3$)$_2^-$, and *LnOH* + + = LnOH^{2+}, where *Ln* = lanthanide series elements.)

The percentage of each REE present in solution as the free metal ion in the Palo Duro Basin groundwaters is greater than for any of the hypersaline groundwaters from the Lake Tyrrell system or the Lake Gilmore system presented in this study. The ionic strength of the Palo Duro Basin groundwaters are also much higher than the Lake Tyrrell or Lake Gilmore groundwaters. The general correlation between ionic strength and the percentage of each REE in the free metal ion form is preserved when these groundwaters are compared with the lower ionic strength groundwater brines of Lake Tyrrell and Lake Gilmore (Fig. 6a). The inverse relationship between the free metal ion percentage and the pH reported for the Lake Tyrrell and Lake Gilmore groundwater, however, does not hold when the Palo Duro Basin groundwaters are included (Fig. 6b). Instead, the Palo Duro Basin groundwaters plot separately from both the Lake Tyrrell and Lake Gilmore groundwaters in Fig. 6b. However, a general decrease in the percentage of the free metal ion species is also observed with increasing pH in the Palo Duro Basin groundwaters.

5.2. *Shale-normalized* REE *patterns*

The concentrations of the REEs in seawater are typically normalized to shale in order to examine the fractionation of the REEs in seawater compared to

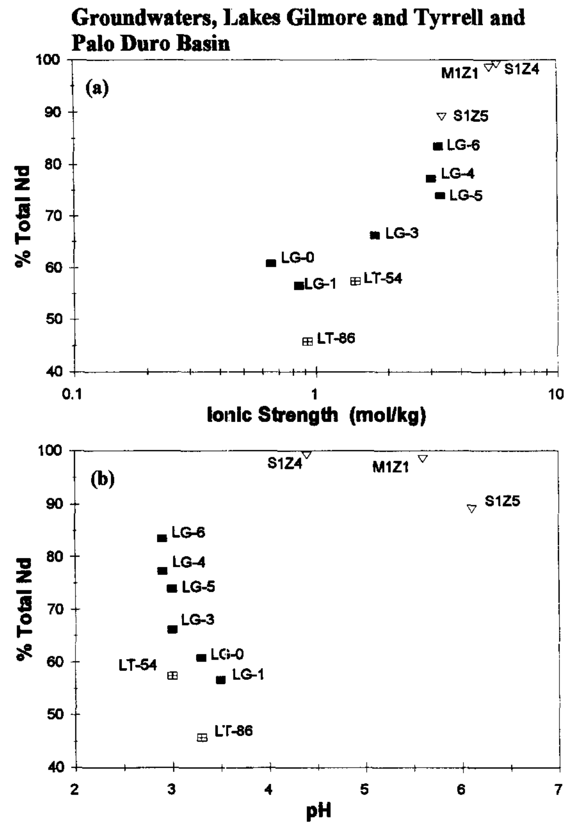

Fig. 6. Percent of the total Nd concentration that occurs as the free metal ion species (i.e. Nd^{3+}) in the acid, hypersaline groundwaters of Lake Tyrrell (*LT*), Lake Gilmore (*LG*), and the Palo Duro Basin, Texas vs. (a) ionic strength (in mol/kg) and (b) pH. *Labels* for the Palo Duro Basin groundwaters are: *S1Z4* = Sawyer No. 1, Zone 4; *S1Z5* = Sawyer No. 1, Zone 5; and *M1Z1* = Mansfield No. 1, Zone 1.

their source, i.e. continental weathering and transport of the REEs to the oceans via rivers and estuaries (Elderfield and Greaves, 1982; Elderfield, 1988; Sholkovitz, 1988, 1993, 1995; Elderfield et al., 1990). The resultant REE signature of the materials originating on the continents and entering the oceans is a composite of the continental crustal sources and typically exhibits a shale signature (Taylor and McLennan, 1985; Elderfield, 1988; Sholkovitz, 1988). On the other hand, terrestrial waters have been normalized to shale in past studies for a variety of reasons, one of which is to be able to compare the REE signatures of terrestrial waters to seawater. Terrestrial waters, however, may interact with a variety of rock types with REE signatures that differ from shales. Consequently, the ideal normalizing standard for terrestrial waters does not exist because such a standard would be required to vary in composition depending on the rocks with which the waters reacted via, for example, weathering or dissolution. Therefore, in order to best evaluate the geochemical processes responsible for the fractionation of the REEs in terrestrial waters, it is most appropriate to normalize the waters to the rocks with which they react. However, because terrestrial waters may react with many different rock types with different REE signatures, developing normalizing standards for every system under study is a monumental task.

The rocks within the Colour Lake Basin are predominantly sandstones, siltstones, and shales and therefore normalizing the Colour Lake waters to shale is justified. Likewise, the geologic materials

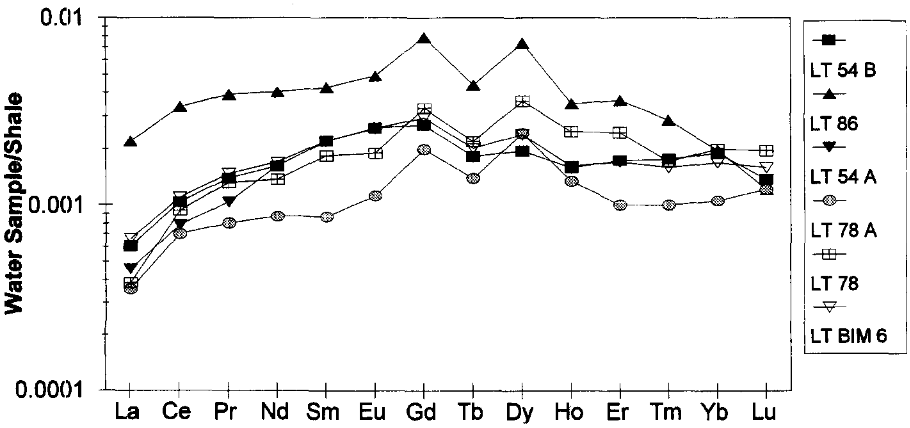

Fig. 7. Shale-normalized REE patterns for groundwaters from the Lake Tyrrell system. REE data are from Fee et al. (1992).

through which the Lake Tyrrell groundwaters flow are composed principally of sands and clays and, as a result, normalizing these groundwaters to shale is also warranted. Moreover, Gosselin et al. (1992) normalized their Palo Duro Basin groundwaters to Post-Archean Average Shale (PAAS; McLennan, 1989) because the dominant aquifer material (arkosic sandstones) had REE concentrations that were very similar to PAAS. Because the concentrations of the REEs in PAAS and the shale used in this study are similar (compare Sholkovitz, 1988 and McLennan, 1989), we have also normalized the Palo Duro Basin groundwaters to shale.

Shale-normalized REE patterns for the Lake Tyrrell groundwater are presented in Fig. 7 using the shale standard reported in Sholkovitz (1988). These same REE data were previously presented as shale-normalized plots by Fee et al. (1992); however, the earlier versions were misplotted such that the REE patterns appeared substantially flatter in Fee et al. (1992) [compare Fig. 7 with Fig. 5a of Fee et al. (1992)]. The shale-normalized REE profiles of the Lake Tyrrell groundwaters reported in Fig. 7 are correct for the data presented in Fee et al. (1992) and in Table 2.

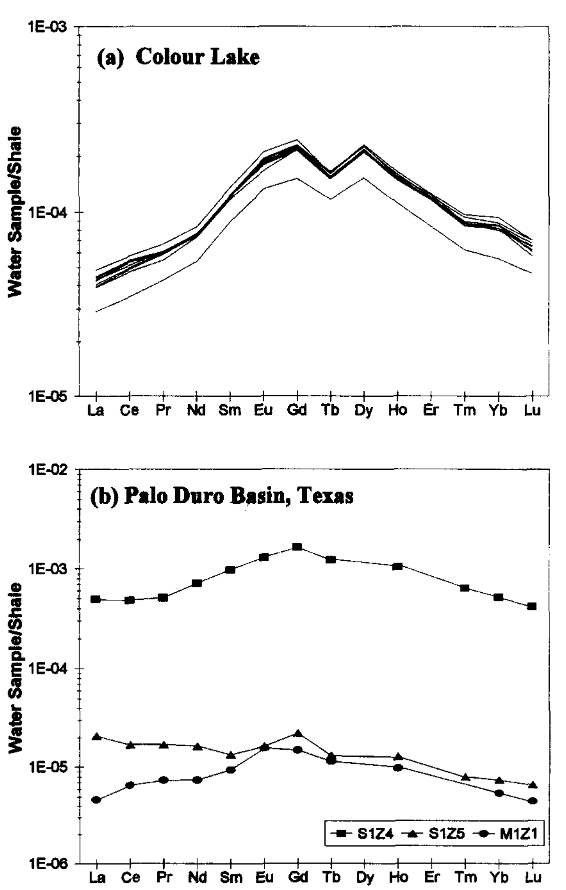

Fig. 8. Shale-normalized REE patterns from: (a) acid (pH = 3.6), dilute ($I = 0.01$ mol/kg) lake waters of Colour Lake in the Canadian High Arctic (Johannesson and Lyons, 1995); and (b) groundwater from the Palo Duro Basin, Texas (Gosselin et al., 1992). *Labels* for the Palo Duro Basin groundwaters are the same as in Fig. 6.

The striking feature of the normalized REE profiles for these groundwaters is that, in general, the groundwaters are enriched in the MREEs (i.e. Eu, Gd, Tb, Dy) over both the LREEs and the HREEs (Fig. 7). The shale-normalized ratios for both Gd and Dy, for example, are greater than for all of the other REEs, followed by Eu, Sm, and Tb; La generally has the lowest ratios. The enrichments in the MREEs over the LREEs is typically greater than the enrichment of the MREEs compared to the HREEs. Three of the groundwaters, samples LT-54A, LT-54B, and LT-BIM-6, exhibit relatively flat normalized REE patterns for the HREEs compared to the other groundwater samples, although the shale-normalized ratios for the HREEs are less than for the MREEs (Fig. 7). There are not enough data for the Lake Gilmore groundwaters to determine if the shale-normalized REE patterns for these groundwaters are also enriched in the MREEs or if they possess different shale-normalized REE patterns.

5.3. *Shale-normalized* MREE *enrichments in natural terrestrial waters*

The origins of shale-normalized MREE enriched patterns in natural terrestrial waters as reported here are currently not sufficiently understood. Because the REEs may prove to be useful tracers for investigating water–rock interactions (e.g., Smedley, 1991) as well as the fact that understanding the behavior of the REEs in terrestrial waters may facilitate predictions of actinide series element behavior in natural waters (Choppin, 1983; Krauskopf, 1986), it is important that the origins of these MREE enrichments are identified.

MREE-enriched patterns have been recognized before in a variety of different terrestrial waters including some river waters (Hoyle et al., 1984; Elderfield et al., 1990; Sholkovitz, 1995), an acid lake (Johannesson and Lyons, 1995), and low-pH groundwaters and surface waters (Gosselin et al., 1992; Yelken et al., 1995; D.K. Nordstrom, pers. commun., 1995). MREE-enriched shale-normalized REE plots for the acidic Colour Lake waters and the Palo Duro Basin brines are presented in Fig. 8. Moreover, MREE enrichments have also been reported for acid-leachates of metasedimentary rocks (Schaltegger et al., 1994), leachates from sandstone (Zhou et al., 1995), pre-Cretaceous biogenic apatite (Wright et al., 1987; Grandjean-Lécuyer et al., 1993), Fe–Mn-rich coatings on foraminfera tests (Palmer, 1985; Palmer and Elderfield, 1986), and a variety of secondary and/or vug-filling minerals within carbonate rocks (Banner et al., 1988; Gosselin et al., 1992). In terms of natural waters, MREE-enriched patterns are commonly associated with low-pH waters (D.K. Nordstrom, pers. commun., 1995) and have not been observed in high-pH systems such as modern seawater (e.g., Elderfield and Greaves, 1982; DeBaar et al., 1983; Elderfield, 1988) or alkaline lakes (e.g., Möller and Bau, 1993; Johannesson and Lyons, 1994; Johannesson et al., 1994a). Previous investigators have suggested a number of possible processes that may be responsible for MREE enrichments in natural waters including fractionation by colloid-borne REEs (Hoyle et al., 1984; Elderfield et al., 1990), solid–liquid exchange reactions such as adsorption/desorption and/or ion exchange between the groundwaters and MREE-enriched surface coatings, suspended particles, or secondary minerals (Gosselin et al., 1992; Sholkovitz, 1995), dissolution of MREE-enriched mineral surface coatings by acid waters (Gosselin et al., 1992; Johannesson and Lyons, 1995), and phosphate complexation (Sholkovitz, 1995). In the following sections, we will briefly examine some of the possible processes responsible for these MREE-enriched patterns in natural acidic waters with the goal of eliminating the number of possibilities.

5.3.1. Iron-rich organic colloids and flocs

Hoyle et al. (1984) and Elderfield et al. (1990) reported MREE-enriched patterns for flocs formed during the mixing of river water and seawater. Moreover, Elderfield et al. (1990) recognized that shale-normalized REE patterns of river waters represent the combination of colloidal and dissolved populations. Because Fe can exist as organically stabilized colloids in river waters (Elderfield et al., 1990), and because a definite relationship exists between dissolved Fe and REEs in river waters (Goldstein and Jacobsen, 1988; Elderfield et al., 1990; Sholkovitz, 1995), it is likely that colloids are also important to the geochemistry of REEs in rivers. It is unlikely, however, that organic colloids are important in the groundwaters of Lake Tyrrell and Lake Gilmore due to the very low pH values of these groundwaters. In addition, Johannesson and Lyons (1995) argued that for the acid waters of Colour Lake, which also exhibit MREE enrichments (Fig. 8) and where dissolved organic carbon (DOC) concentrations are very low (DOC = 8–67 μmol/kg; Allan et al., 1987), organic colloids are also not expected to be important. Consequently, although MREE enrichments in some estuarine and river waters may be due to organic-rich colloids or flocs, such colloids and/or flocs cannot be universally invoked to explain MREE enrichments in natural waters.

5.3.2. Fe–Mn-rich particulates and surface coatings

Inorganic particulates, surface coatings, and secondary mineral phases within aquifer materials may be especially important contributors to MREE enrichments in natural waters. Grandjean-Lécuyer et al. (1993), for example, demonstrated that the progressive removal of the LREEs from river waters by Fe-oxyhydroxides can produce inorganic precipitates enriched in the MREEs. Middle REE enrichments have been recognized for the reactive fraction of particulates in river waters (Elderfield et al., 1990; Sholkovitz, 1995), Fe–Mn-oxyhydroxide coatings on foraminefera tests (Palmer, 1985; Palmer and Elderfield, 1986), Fe–Mn nodules within the oceans (Addy, 1979; Elderfield et al., 1981; Alpin, 1984; DeCarlo and McMurtry, 1992) and coatings on these nodules (Ingri and Pontér, 1987). More recently Lyons and Lechler (1995) have observed MREE enrichments with strong positive Eu anomalies in riverine sediments from New Zealand, while Ross et al. (1995) have observed similar profiles from riverine particulate matter from Argentina. If it is assumed that similar MREE-enriched Fe-rich, inorganic particulates, Fe-rich surface coatings on particulates, and/or MREE-enriched phosphate minerals (e.g., Weber et al., 1995) are present in the groundwaters and/or aquifer material substrate of the Lake Tyrrell system, then the MREE enrichments could be explained by dissolution of the particulates and/or surface coatings by the acid groundwaters. Similarly, dissolution of MREE-enriched suspended particles and/or coatings on the sedimentary rocks within the Colour Lake basin may be responsible for the MREE enrichments reported for Colour Lake water (Johannesson and Lyons, 1995). At the low pH values of these waters it is reasonable to expect that Fe-rich particulates and surface coatings would readily dissolve (Zinder et al., 1986).

Secondary minerals associated with aquifer materials may also contribute to the MREE enrichment of groundwaters and lake waters in these systems. Gosselin et al. (1992) has invoked solid–liquid exchange reactions such as adsorption/desorption and ion exchange between the groundwaters of the Palo Duro Basin, Texas, and secondary minerals within the local aquifer materials in order to explain the MREE enrichments of the local groundwater. Many investigators have demonstrated that secondary phases such as Fe-rich vug-filling calcites and fracture filling pyrite as well as Fe-clay-rich dolomites, argillaceous carbonates, and Fe–Mn coatings can be enriched in the MREEs (Palmer, 1985; Palmer and Elderfield, 1986; Banner et al., 1988; Gosselin et al., 1992).

5.3.3. *REE-phosphate complexation*

Complexation of the REEs by phosphate ions has recently been suggested as another possible mechanism responsible for MREE enrichments in natural terrestrial waters (Sholkovitz, 1995). Previous investigators have argued that phosphate in river waters may be controlled by an Fe-phosphate solid–solution phase within Fe-oxyhydroxides particles or surface coatings (Fox et al., 1986; Fox, 1989, 1990, 1991; Sholkovitz, 1995) and that because of the strong relationship between Fe and REEs in river waters (Hoyle et al., 1984; Elderfield et al., 1990), the REE chemistry of terrestrial waters may also be closely associated with phosphate. A strong relationship between phosphate and the REEs in natural terrestrial waters has also been reported by Johannesson et al. (1995b) who observed that neutral- to high-pH waters are approximately saturated with respect to REE-phosphate salts. These authors argued that phosphate ions may be responsible for the removal of REEs from solution in natural terrestrial waters through the precipitation of phosphate salts.

Recently, it was suggested that the reactivity and speciation of phosphorus in Amazon River waters may be closely associated with the MREE enrichments reported for these waters (Sholkovitz, 1995). Previous REE speciation calculations, using a model groundwater composition (Wood, 1990), suggest that REE phosphate complexes may dominate over carbonate complexes for the HREEs when the pH is between 7 and 9 (Lee and Byrne, 1992). Johannesson et al. (1996) have demonstrated, however, that in real groundwaters with pH between 7 and 9, phosphate complexes are negligible and REE-carbonate complexes dominate the REE speciation. Moreover, Johannesson and Lyons (1994) and Johannesson et al. (1994a) showed that even in high-pH lakes with very high total phosphate concentrations (i.e. ΣPO_4^{3-} up to 1000 μmol/kg), the REE-phosphate complexes were negligible compared to carbonate complexes. Phosphate ions cannot compete with carbonate ions for the REEs in neutral- to high-pH natural terrestrial waters because of the relatively low total phosphate concentrations compared to the carbonate ion concentrations and because of the even lower free phosphate ion concentrations (i.e. $[PO_4^{3-}]_F$) that results from ion pair formation of PO_4^{3-} with Ca^{2+} and Mg^{2+} (Johannesson et al., 1996). Perhaps of more importance, however, is that in no instances are phosphate complexes predicted to be of any consequence in these acid waters (e.g., see Wood, 1990; Lee and Byrne, 1992; Johannesson and Lyons, 1995; Johannesson et al., 1995b). The fact that MREE enrichments are reported in many acid terrestrial waters, therefore, argues strongly against phosphate complexation as an important mechanism responsible for MREE enrichments. The importance of REE removal by phosphate salts to the development of MREE enrichments, however, cannot be ruled out due to our incomplete understanding of the nature of these REE-phosphate phases.

5.3.4. *REE-sulfate comlpexation*

In contrast to REE-phosphate complexes, REE-sulfate complexes have previously been predicted to be important in low-pH terrestrial waters (Wood,

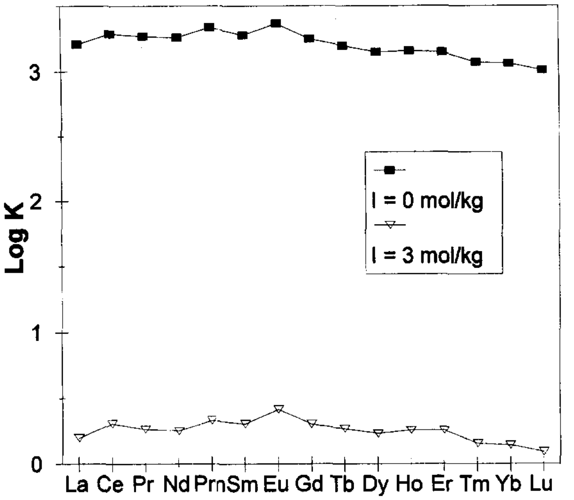

Fig. 9. Plot of the log K (stability constant) for the formation of REE-sulfate complexes vs. atomic number for different ionic strength solutions ($I = 0$ and 3.0 mol/kg). Data for log K at $I = 0$ mol/kg are from Millero (1992), whereas values of log K for $I = 3.0$ mol/kg where calculated following the methods outlined in Millero and Schreiber (1982) and Millero (1992).

1990; Lee and Byrne, 1992; Johannesson and Lyons, 1995; Johannesson et al., 1995b). Speciation of the REEs in low-pH waters is typically dominated by the free metal ion, Ln^{3+}, followed by sulfate complexes (Wood, 1990; Lee and Byrne, 1992; Johannesson and Lyons, 1995). Because the sulfate ion tends to be the most important inorganic complexing ligand in acidic natural terrestrial waters, REE-sulfate complexes may exert some control on the development of MREE-enriched patterns.

Fig. 9 is a plot of the stability constants (Millero, 1992) for the formation of the $LnSO_4^+$ species in an infinitely dilute aqueous solution ($I = 0$ mol/kg) and a solution where $I = 3.0$ mol/kg. It is clear from Fig. 9 that the stability constants for MREE-sulfate complexes are greater than for the LREEs and the HREEs. The stability constants describing the formation of $EuSO_4^+$ and $PmSO_4^+$, for example, exceeds the stability constants for sulfate complexes with all of the other REEs. In the acid, hypersaline groundwaters of Lake Tyrrell, Lake Gilmore, and the Palo Duro Basin (e.g., $I = 3.0$ mol/kg), the actual stability constant values will be lower than the infinite dilution values; however, the same general pattern will be preserved, i.e. stability constants for the formation of $LnSO_4^+$ complexes with the MREEs will exceed the stability constant for the formation of the same complex with the LREEs and HREEs. Based on the fact that MREEs form stronger complexes with sulfate ions and because the sulfate ion is the most important complexing inorganic ligand in these low-pH waters, it is possible that formation of REE-sulfate complexes contributes to the development of MREE enrichments in these acid waters. The possibility that REE-sulfate complexation is the sole mechanism responsible for MREE enrichments is not likely, however, because the MREE enrichments of the natural waters typically center around Gd and not Eu and because the enrichments in the MREEs in natural waters compared to the LREEs are generally greater than compared to the HREEs which is opposite to the observed trend for the stability constants (Fig. 9). Consequently, it is more likely that sulfate complexation in conjunction with dissolution of MREE-enriched Fe–Mn surface coatings or suspended particles or solid–liquid exchange reactions such as adsorption/desorption and/or ion exchange between such phases or secondary minerals within aquifer materials, are responsible for MREE enrichments in natural acid waters. More work is required, however, to verify or refute these mechanisms and to examine, in detail, the significance of sulfate complexation vs. dissolution and/or solid–liquid reactions in the development of MREE enrichments in acid waters.

6. Conclusions

Our work indicates that the free metal ion (Ln^{3+}) is the dominant form of the dissolved REEs in acid, hypersaline groundwaters and that the free metal ion species increases in importance with increasing ionic strength. The sulfate ion is the dominant inorganic complexing ion in these waters and the sulfate complex (i.e. $LnSO_4^+$) follows the free metal ion as the second most important form of dissolved REEs in these acidic, hypersaline groundwaters. Chloride and fluoride complexes ($LnCl^{2+}$ and LnF^{2+}), on the other hand, are much less significant.

Shale-normalized REE patterns for acid, hypersaline groundwaters typically exhibit enrichments in the MREEs as do the acid fresh waters of Colour Lake. Development of these MREE enrichments as a function of the existence of Fe-rich organic colloids or complexation of the REEs with phosphate ions have been ruled out because of the low pH of these waters, the low organic carbon concentrations, and the insignificance of phosphate complexes in these waters. Instead, dissolution by the acid waters of Fe–Mn surface coatings or suspended particles or solid–liquid reactions between such phases or secondary phases within the aquifer materials as well as sulfate complexation are more likely mechanisms responsible for the MREE enrichments.

Acknowledgements

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Appendix A

Activity coefficients for the individual rare-earth elements, complexing anions, and rare-earth element ion pairs for groundwater brines from Lake Tyrrell (LT), Australia, Lake Gilmore (LG), Australia, and the Palo Duro Basin, Texas, U.S.A. (S1Z4, S1Z5, and M1Z1) calculated using a specific ion interaction–ion pairing model (Millero, 1992). Ionic strength (I) is given in mol/kg.

	Lake Tyrell		Lake Gilmore						Palo Duro Basin		
γ	LT-54	LT-86	LG-0	LG-1	LG-3	LG-4	LG-5	LG-6	S1Z4	S1Z5	M1Z1
La^{3+}	0.143	0.115	0.106	0.112	0.165	0.371	0.318	0.357	1.63	0.386	1.26
Ce^{3+}	0.149	0.118	0.108	0.115	0.173	0.399	0.341	0.384	1.78	0.416	1.38
Pr^{3+}	0.144	0.115	0.106	0.112	0.166	0.378	0.323	0.364	1.71	0.393	1.32
Nd^{3+}	0.143	0.114	0.106	0.112	0.164	0.374	0.32	0.36	1.71	0.389	1.31
Pm^{3+}	0.143	0.114	0.106	0.112	0.164	0.374	0.32	0.36	1.71	0.389	1.31
Sm^{3+}	0.149	0.117	0.108	0.114	0.172	0.407	0.346	0.391	1.96	0.424	1.49
Eu^{3+}	0.152	0.119	0.109	0.116	0.177	0.427	0.361	0.41	2.12	0.445	1.6
Gd^{3+}	0.153	0.119	0.109	0.116	0.178	0.437	0.369	0.42	2.24	0.456	1.69
Tb^{3+}	0.156	0.121	0.11	0.118	0.183	0.457	0.384	0.439	2.44	0.478	1.83
Dy^{3+}	0.157	0.122	0.111	0.118	0.185	0.471	0.395	0.452	2.58	0.493	1.92
Ho^{3+}	0.161	0.123	0.111	0.12	0.189	0.49	0.409	0.469	2.76	0.513	2.05
Er^{3+}	0.158	0.122	0.111	0.119	0.186	0.478	0.4	0.458	2.69	0.5	1.99
Tm^{3+}	0.158	0.121	0.11	0.118	0.185	0.476	0.398	0.456	2.7	0.498	2
Yb^{3+}	0.157	0.121	0.11	0.118	0.185	0.473	0.396	0.454	2.7	0.496	1.99
Lu^{3+}	0.157	0.121	0.11	0.118	0.184	0.472	0.395	0.453	2.69	0.495	1.99
Cl^-	0.654	0.657	0.667	0.658	0.66	0.73	0.713	0.726	0.95	0.735	0.902
F^-	0.535	0.574	0.604	0.581	0.52	0.477	0.482	0.478	0.46	0.476	0.462
OH^-	0.672	0.665	0.673	0.666	0.638	0.797	0.771	0.79	1.16	0.804	1.08

SO_4^{2-}	0.081	0.113	0.139	0.118	0.071	0.042	0.046	0.043	0.03	0.042	0.03
CO_3^{2-}									0.05	0.068	0.054
$LnCl^{2+}$	0.891	0.436	0.337	0.406	1.4	20.1	12.2	17.9	2064	22.9	943
LnF^{2+}	0.891	0.436	0.337	0.406	1.4	20.1	12.2	17.9	2064	22.9	943
$LnOH^{2+}$	0.891	0.436	0.337	0.406	1.4	20.1	12.2	17.9	2064	22.9	943
$LnSO_4^+$	2.67	1.53	1.2	1.44	3.68	20.7	15.1	19.2	343	22.4	215
$LnCO_3^+$									343	22.4	215
$Ln(CO_3)_2^-$									343	22.4	215
Temp. [a] (°C)	20	20							38	32	41
I	1.46	0.917	0.654	0.852	1.76	3.29	3.02	3.23	5.67	3.36	5.28

[a] Temperature data for Lake Tyrrell groundwaters is from W.B. Lyons (unpublished data) and for the Palo Dur Basin is from Gosselin et al. (1992).

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