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Rare-earth element geochemistry of Colour Lake, an acidic freshwater lake on Axel Heiberg Island, Northwest Territories, Canada

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Abstract

A lake column profile was collected in 24 m of water from Colour Lake, Axel Heiberg Island, Northwest Territories, Canada, in early June of 1991 beneath 1.8 m of lake-ice. The rare-earth element (REE) concentrations of the acidic, fresh waters of Colour Lake were analyzed, along with the major solute chemistry, in order to investigate REE distribution and speciation in the low-pH waters. Previous studies indicate the lake is dominated by Ca^{2+}, Mg^{2+} and SO_4^{2-}, and has no measurable carbonate alkalinity.

Shale-normalized REE patterns for the lake waters are all enriched in the middle REE's (MREE's) as compared to the light REE's (LREE's) and heavy REE's (HREE's). Dissolved REE concentrations in Colour Lake (e.g., 2.3–22 nmol kg^{-1} for Nd, mean value of 20 nmol kg^{-1}) are typically less than values obtained for the acid, saline waters of the Lake Tyrrell playa system in Australia as well as the slightly acidic groundwaters of the Carnmenellis region of England but greater than REE concentrations measured in the alkaline, saline waters of Mono Lake, California, U.S.A.

The speciation of the REE's in Colour Lake was modelled based on the major solute chemistry, using a combined specific ion interaction and ion pairing model. These calculations suggest that in the relatively high-sulfate, low-pH waters of Colour Lake, the REE's exist as either free metal, SO_4^{2-}, or F^- complexes. Our calculations indicate that SO_4^{2-} complexes dominate over the free metal and fluoride species for the majority of the REE's in the lake water and that, in general, for acidic, high-sulfate waters, sulfate complexes with the REE's may increase the dissolved concentrations of the REE's over natural waters where relatively low sulfate concentrations prevail.

1. Introduction

Rare-earth elements (REE's) are important trace elements that are routinely used in the petrogenetic study of magmatic rocks (e.g., Hanson, 1980) and have also been employed as tracers of geochemical processes in seawater (e.g., Elderfield and Greaves, 1982; DeBaar et al., 1983). More recently the REE concentrations of terrestrial waters, such as groundwaters and lakes, have been examined as potential tracers of processes affecting their geochemical evolution (e.g., Banner et al., 1989; Smedley, 1991; Fee et al.,

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1992; Gosselin et al., 1992). These studies indicate that groundwaters can obtain REE signatures from the rocks or aquifer material with which they interact.

Interest in the chemistry of the REE's in natural waters also stems from the potential release of long-lived radioisotopes to the environment (e.g., Choppin, 1986, 1989; Wood, 1990; Millero, 1992; Rai and Felmy, 1993). Radioactive isotopes of the REE's are common products of the fission of U and Pu fuels (Wood, 1990). In addition, the naturally occurring trivalent REE's may be used as analogues for modelling the behavior of trivalent actinides (e.g., Am^{3+} and Cm^{3+}) in natural waters (Choppin, 1986, 1989; Wood, 1990; Millero, 1992). Therefore, understanding the behavior of the REE's in natural waters has important consequences for ensuring such activities as the safe burial of high-level radioactive waste.

Many workers have demonstrated with models, the importance of speciation and complexing of the REE's with various ligands in controlling their dissolved concentrations (Choppin, 1986, 1989; Wood, 1990; Lee and Byrne, 1992, 1993). These studies indicate that REE complexation with carbonate ions will predominate in most natural waters of moderate to high pH where carbonate is a major component. Only in waters where T_{CO_2} is <0.001 M will the free Ln^{3+} species effectively compete with carbonate complexes (Millero, 1992). For example, we have modelled the speciation of the REE's in the alkaline, saline waters of Mono Lake in eastern California, U.S.A. Mono Lake has CO_3^{2-} concentrations more than 1000 times greater than seawater and, consequently, dicarbonato complexes of the REE's (i.e. $Ln(CO_3)_2^-$) were predicted to account for >99% of all of the REE's in solution in the lake (Johannesson and Lyons, 1994).

The majority of the REE speciation studies have been conducted in seawater or other natural waters of moderate to high pH and less work has been focused on acid waters. In this study we present REE concentrations for a lake profile from Colour Lake, an acidic freshwater lake on Axel Heiberg Island in the Canadian High Arctic. The concentrations of REE's in the lake waters are discussed in terms of their source and the major solute chemistry is employed to model the speciation of the REE's following the techniques of Millero (1992).

2. Hydrogeologic setting

Colour Lake is a naturally occurring acidic lake (mean pH ~3.6) located on Axel Heiberg Island, Northwest Territories, Canada (Fig. 1). The geology of the region consist of Paleozoic rocks of the Franklinian geosyncline deformed during the late Devonian, which are overlain by a thick sequence of predominantly clastic sedimentary rocks deposited in the Sverdrup basin from late Mississippian through early Tertiary (Fricker, 1963; Allan et al., 1987). This sedimentary rock sequence is especially thick in the Colour Lake region, extending up to 11,000 m (Fricker, 1963). The sedimentary rocks surrounding Colour Lake consist chiefly of sandstone, shale and siltstone with the lake underlain primarily by shale (Fricker, 1963; Allan et al., 1987). A relatively large gypsum dome of early Pennsylvanian age outcrops immediately to the south, between the lake and the Expedition River (Hoen, 1964).

Colour Lake is small with a surface area of 10.2 ha and an approximate maximum depth of 25 m and mean depth of 10.1 m (Adams et al., 1989). The lake occupies a small basin carved out by a tongue of the nearby White Glacier approximately 9000 yr B.P. (Allan et al., 1987). The watershed is ~0.56 km^2 (Allan et al., 1987). The majority of precipitation in the region occurs as snowfall during the winter months through mid- or even late June (Allan et al., 1987). Between 50% and 60% of the watershed drains into the lake by streamflow in several ephemeral streams (Allan et al., 1987). The remainder of the inflow to the lake occurs by way of subsurface seeps that predominate during the fall of the year (English et al., 1991; Schiff et al., 1991).

The process responsible for generation of the lake water acidity is complex and, at present, not

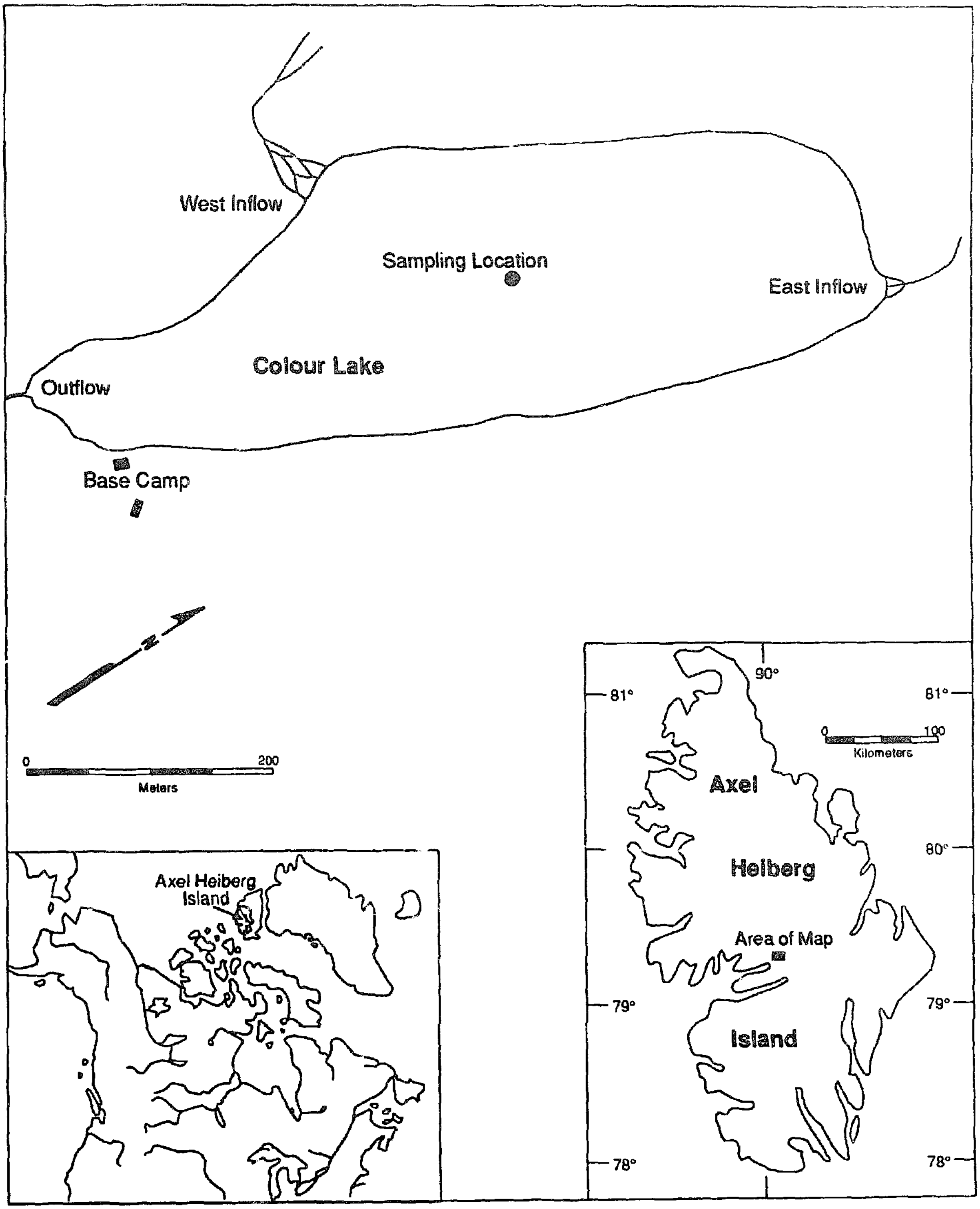

Fig. 1. Location map of Axel Heiberg Island and Colour Lake modified from Schiff et al. (1991) and Boike et al. (1992).

clearly understood. Schiff et al. (1991) have identified three potential sources of acidity to the lake: (1) nearshore groundwater seepage during the summer; (2) acidic flux from the lake sediments; and (3) reoxygenation of the small anoxic hypolimnion along with precipitation of Fe-hydroxides (i.e. ferrolysis). This third source of acidity apparently exerts the most control on generating and maintaining the low pH-values of the lake (Schiff et al., 1991). Ferrolysis has also been suggested as the major contributing process to strong acid generation in some Australian shallow groundwater systems (McArthur et al., 1991).

3. Methods

3.1. Sampling collection and processing

Samples were collected at Colour Lake in early June of 1991. High-density linear polyethylene sample bottles were acid cleaned as described in Johannesson and Lyons (1994). All labware was cleaned and all reagent were prepared following the methods outlined in Johannesson and Lyons (1994).

The lake profile was obtained in ~24 m of water after drilling through 1.8 m of ice with an electric powered steel auger (Fig. 1). Samples were collected at 0, 0.5, 1, 2, 5, 10, 15, 17, 20, 21 and 22 m below the ice–water interface by use of a peristaltic pump. [Samples are referred to in the text, tables and figures by their true depth which can be obtained by adding 1.8 m (ice thickness) to the below-ice sampling depths.] The pump was equipped with polyethylene tubing that was lowered to the specific sample depth. At each sampling depth, the pump was run for ~1 min to flush the tubing of any water from the previous sampling depth. Water was pumped directly from the lake into an acid, precleaned polycarbonate filtering device and filtered through 0.4-μm Nuclepore® filters. The filtering device was flushed with ~250 ml of filtered lake water from each sampling depth before the sample water was collected. An aliquot of filtered lake water was used to rinse the sample bottles before the actual filtered water sample was placed in the sample bottles. Filtered lake samples were then double bagged with plastic bags and placed into an ice cooler and transported back to Reno where they were acidified to pH < 2 with Baker Ultrex® HNO_3 approximately 10 days after collection. Except for the lake bottom sample, the loss of REE's from solution during transport was unlikely in these oxygenated, acid waters (see below).

Water temperature was measured in situ before water samples were collected with a downhole thermometer and measurements of pH were made in the laboratory at Colour Lake from samples that were allowed to warm to ~25°C. Dissolved oxygen (DO) was also determined in situ.

3.2. Analytical techniques

Major solutes were measured by a variety of methods. Dissolved silica and total Fe were measured by colorimetric techniques with a Milton® Roy *21D* spectrophotometer. Cations (Na, K, Ca and Mg) were determined by inductively coupled plasma (ICP) using a Perkin-Elmer® Plasma II emission spectrometer. Alkalinity was measured by titration using an Orion® *520A* pH meter and either 1 *N* or 0.1 *N* Baker® Analyzed HCl. Sulfate was determined by ion chromatography on a Dionex® *2000* i/sp and Cl^- was measured using an Orion® ion-specific electrode.

The REE's were concentrated by a factor of 5 from the filtered and acidified water samples using the ferric hydroxide coprecipitation method modified by Welch et al. (1990) from the previous work of Weisel et al. (1984). The coprecipitation technique allows essentially complete removal of the major cations that can produce spectral interference when analyzing concentrated samples (Fee et al., 1992). In addition, Fee et al. (1992) report that inductively coupled plasma–mass spectrometry (ICP–MS) analyses of coprecipitated and unprecipitated SPEX-pure REE mix 1.0 $\mu g\ l^{-1}$ standards produced excellent agreement and indicate virtually complete recovery of REE's by the coprecipitation method. Moreover, Buchanan and Hannaker (1984) reported recoveries for the REE's as high as 99% when the pH was adjusted to ≥8.6. Accordingly, we adjusted the pH of acidified Colour Lake samples to ≥8.6.

In addition, we prepared two aliquots of each lake sample to monitor the recoveries of the coprecipitation technique. One of these aliquots was concentrated by a factor of 5 and the other was not preconcentrated. The 5-fold concentration was obtained by coprecipitating a 25-ml sample and then redissolving the precipitate in a 5-ml, 10% v/v Baker Ultrex® HNO_3 solution

(Welch et al., 1990). Recovery comparisons between the two aliquots were better than 90% for all the REE's except Lu which exhibited recoveries of ~88%. The recoveries for the other REE's were commonly better than 93% and for Gd we obtained agreements of 95%. On the other hand, Ba recoveries were typically 65% (Johannesson and Lyons, 1994).

REE concentrations were determined by ICP-MS on acidified aliquots of the metal solution recovered through the ferric hydroxide coprecipitation method discussed above. The 1.0-ml aliquots were diluted 50 times with 10% v/v ultrapure HNO_3 and analyzed by ICP-MS on a Perkin-Elmer® Elan *5000* ICP-MS. Analysis was repeated five times for each sample. A series of five REE standards of known concentrations (i.e. 0.1, 0.25, 0.5, 1.0 and 1.5 $\mu g\ l^{-1}$) and laboratory blanks were routinely analyzed along with the samples to monitor instrument drift which never varied by more than ±10%. All data were corrected for instrument drift following the analysis.

The following REE isotopes were chosen to minimize the effects of isobaric interferences: ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{149}Sm, ^{151}Eu and ^{153}Eu (mean value), ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb and ^{175}Lu. These REE isotopes are free of isobaric interferences and, as a result, no corrections were required (Jarvis et al., 1989; Smedley, 1991).

Of particular importance in this study were the formation of oxides of Ba and the light REE's (LREE's) which can cause interferences with the middle REE's (MREE's) and the heavy REE's (HREE's) (Litche et al., 1987; Longerich et al., 1987; Jarvis et al., 1989; Smedley, 1991). A nebulizer gas flow rate of 0.7 l min^{-1} was employed at a power setting of 1005 W to minimize potential oxide and hydroxide interferences (Table 1).

Ba^{2+} concentrations in uncoprecipitated Colour Lake samples were low and ranged from 159 to 163 nmol kg^{-1} with a mean value of 161 nmol kg^{-1}. Measured BaO^+/Ba^+ ratios for the Colour Lake analyses were ≤0.03%. Therefore, interference of oxides of Ba on the REE's was not significant and no corrections were made.

Oxides of the LREE's can also cause interferences with the HREE's which can be problematic especially for materials with LREE concentrations that are considerably higher than the HREE concentrations. Measured $REEO^+/REE^+$ ratios for the LREE's in Colour Lake were small, i.e. $LaO^+/La^+ = 0.74\%$, $CeO^+/Ce^+ = 1.03\%$, $PrO^+/Pr^+ = 1.18\%$, $NdO^+/Nd^+ = 1.16\%$, $SmO^+/Sm^+ = 0.2\%$, $EuO^+/Eu^+ = 0.05\%$, $GdO^+/Gd^+ = 0.5\%$ and $TbO^+/Tb^+ = 0.5\%$. However, $LREEO^+/REE^+$ ratios of >1% can lead to significant interferences on the MREE's and HREE's (E.R. Sholkovitz, pers. commmun., 1993). Consequently, we have corrected the REE concentrations to account for interferences from oxides of the LREE's.

Table 1
Instrument operating conditions

Plasma settings:	
Power	1,005 W
Gas flow (Ar)	
plasma flow	12 l min^{-1}
nebulizer flow	0.7 l min^{-1}
auxiliary flow	1 l min^{-1}
Ion lens settings:	
B lens	45 V
P lens	45 V
E-*1* lens	25 V
S-*2* lens	45 V

The detection limit for the REE's using ICP-MS was 6.5 pmol kg^{-1}. Field blanks and laboratory blanks were analyzed in this study and the concentrations of REE's in these blanks were typically below the detection limits of the technique. Those blanks that had REE concentrations higher than the detection limits were subtracted from the lake samples.

3.3. Analytical precision

The results of 5 replicate analyses of each Colour Lake sample indicate that the precision of the REE measurements for the majority of the samples was typically 10% (RSD) or better for all REE's except Tm, Yb and Lu for which the precision was between ±8% and ±15% (RSD). In addition, duplicates of each sample were coprecipitated and analyzed separately to examine the reproducibility. In this case, precision was generally better than ± 10% (RSD) for all the REE's except Eu and Lu which occasionally exhibited lower precision, e.g. ±22% (RSD) for Eu for the 6.8-m-depth sample. The lowest precision for all the lake samples was observed for the 6.8- and 22.8-m-depth samples. For the 6.8-m sample, precision was ±10% (RSD) or better for all of the REE's except La, Ce, Eu and Lu which exhibited precision of ±12%, ±16%, ±22% and ±19% (RSD), respectively. Precision for the 22.8-m sample was better than ±12% (RSD) for all the REE's except Tm and Lu for which the precision was ±13% and ±18% (RSD), respectively.

3.4. Speciation modelling

Recent determination of stability constants for the inorganic REE complexes now allow speciation calculations to be performed in complex natural waters. For the Colour Lake waters, speciation calculations were performed using a model developed for the REE's by Millero (1992). The method integrates the specific ion interaction model formulated by Pitzer and coworkers (e.g., Pitzer, 1979 and references therein) and the ion pairing model developed by Garrels and Thompson (1962) and more recently described by Millero and Schreiber (1982). We have subsequently modified the program to account for phosphate species, which are potentially important in freshwater systems, by the addition of the infinite dilution stability constants for $LnPO_4^0$ complexes determined by Lee and Byrne (1992). In addition, we updated the model by incorporating the new stability constants for the REE-carbonate species determined by Lee and Byrne (1993).

The concentration of each phosphate species (i.e. $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) was calculated using the phosphoric acid dissociation constants determined by the model (see Johannesson and Lyons, 1994). Free concentrations of phosphate and sulfate species were determined by the product of the free fractions of each species and their measured concentrations. The free concentrations were then used in the speciation calculations for the REE's (Millero, 1992).

4. Results

4.1. Major ions

Major ions including dissolved silica, total dissolved Fe, pH, DO and temperature for each sample of the lake profile are presented in Table 2. The lake water chemistry is dominated by Ca^{2+}, Mg^{2+} and SO_4^{2-}. Individual sample depths are also given in Table 2.

Ionic balances have been calculated for all of the lake profile samples with typically very good agreement, i.e. less than 10% differences. Owing to the low pH of the lake waters, Fe and Al data are included in the charge-balance calculations. Because we did not analyze for dissolved Al concentrations, we used the average water column value (i.e. 248 μmol kg^{-1}) reported by Schiff et al. (1991) for our calculations. Iron was assumed to be Fe^{2+} for the charge-balance analysis and thus provides a conservative estimate of the contribution of dissolved Fe to the charge balance. [Lyons et al. (1992) have shown that ferric iron does exist in Fe-rich, acid waters systems from eastern Australia.] The 11.8-m-depth sample exhibited a charge-balance error of > 20%. The Ca^{2+} value for this sample is, however, much larger than for the other samples and is likely in error.

4.2. Rare-earth elements (REE's)

REE concentration (in nmol kg^{-1}) are presented in Table 3 along with shale-normalized Gd/La, Gd/Ce, Gd/Yb and Gd/Lu ratios. Dissolved REE concentrations for Colour Lake are generally lower than values reported by others working in acidic waters. For example, Nd concentrations in Colour Lake range from a low value of 2.3 up to 22 nmol kg^{-1}. The sample collected at the ice-water interface, 1.8-m depth, exhibits the next lowest Nd concentration at 14 nmol kg^{-1}. The remaining samples all have similar Nd concentrations that average 20 nmol kg^{-1}

Table 2
Major solute concentrations (in mmol kg^{-1}) for Colour Lake samples [Fe and dissolved oxygen (DO) are in μmol kg^{-1}]

	Depth (m)										
	1.8	2.3	2.8	3.8	6.8	11.8	16.8	18.8	21.8	22.8	23.8
Ca^{2+}	1.02	1.45	1.43	1.35	1.40	2.54	1.44	1.43	1.47	1.50	1.36
Mg^{2+}	0.44	0.59	0.61	0.61	0.60	0.75	0.62	0.65	0.63	0.68	0.58
Na^{+}	0.32	0.39	0.37	0.31	0.32	0.32	0.33	0.39	0.34	0.34	0.39
K^{+}	0.07	0.12	0.12	0.10	0.10	0.12	0.11	0.14	0.13	0.14	0.19
SO_4^{2-}	2.15	2.64	2.83	2.64	2.81	2.87	2.84	2.93	2.69	2.95	3.69
Cl^{-}	0.13	0.054	0.047	0.043	0.044	0.044	0.041	0.044	0.042	0.042	0.022
Fe	8.24	9.31	10.21	9.67	10.03	9.31	8.23	7.34	6.27	6.8	269
Si	0.097	0.095	0.099	0.098	0.098	0.097	0.10	0.101	0.109	0.116	0.119
pH	3.8	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	4.7
DO	406	394	394	400	394	394	381	356	309	266	72
T (°C)	0.1	0.2	1.5	2.2	2.2	2.4	2.9	3.1	3.3	3.8	4.2

Samples are identified by their depth in meters.

Table 3
Rare-earth element concentrations in nmol kg^{-1} for the Colour Lake samples — shale-normalized Gd/La, Gd/Ce, Gd/Yb and Gd/Lu ratios are also tabulated

	Depth (m)										
	1.8	2.3	2.8	3.8	6.8	11.8	16.8	18.8	21.8	22.8	23.8
La	8.56	11.58	11.93	12.61	11.50	12.87	13.10	13.03	14.23	12.48	2.30
Ce	20.6	28.87	29.26	30.26	27.84	31.79	32.13	32.26	34.08	31.53	4.15
Pr	3.04	4.21	4.28	4.37	3.91	4.24	4.28	4.34	4.78	4.29	0.50
Nd	14.16	19.59	19.77	19.58	19.24	19.58	20.12	20.05	21.95	19.44	2.25
Sm	4.44	6.12	6.14	6.14	5.88	6.00	5.96	6.12	6.74	6.06	0.59
Eu	1.41	1.9	1.93	2.05	1.77	1.94	1.99	2.03	2.22	1.96	0.22
Gd	6.13	8.68	9.14	9.26	8.76	8.68	8.85	9.16	9.82	9.06	1.16
Tb	0.91	1.18	1.25	1.28	1.18	1.16	1.18	1.20	1.26	1.18	0.14
Dy	5.15	7.23	7.64	7.58	7.37	7.11	7.24	7.28	7.76	7.19	0.84
Ho	0.90	1.26	1.27	1.30	1.23	1.24	1.23	1.24	1.34	1.21	0.14
Er	1.8	2.66	2.78	2.71	2.59	2.60	2.63	2.69	2.81	2.61	0.32
Tm	0.23	0.33	0.33	0.35	0.32	0.31	0.33	0.32	0.36	0.32	0.04
Yb	1.13	1.62	1.67	1.77	1.66	1.66	1.72	1.72	1.90	1.72	0.20
Lu	0.16	0.23	0.23	0.25	0.20	0.22	0.23	0.22	0.25	0.21	0.03
$(Gd/La)_{SN}$	5.24	5.48	5.60	5.37	5.57	4.93	4.94	5.14	5.04	5.30	3.69
$(Gd/Ce)_{SN}$	4.37	4.41	4.58	4.49	4.62	4.00	4.04	4.17	4.23	4.21	4.12
$(Gd/Yb)_{SN}$	2.72	2.70	2.76	2.62	2.65	2.63	2.58	2.68	2.60	2.64	2.89
$(Gd/Lu)_{SN}$	3.29	3.28	3.46	3.26	3.78	3.45	3.27	3.55	3.46	3.71	3.05

Samples are identified by their depth in meters.

(Table 3). By comparison, Smedley (1991) working with the mildly acidic groundwaters of the Carnmenellis region of England, reported Nd concentrations between 3.5 and 478 nmol kg^{-1} with an average value of 80 nmol kg^{-1}, whereas Fee et al. (1992) observed Nd concentrations of

229 to 1061 nmol kg^{-1} (mean value of 487 nmol kg^{-1}) in the acidic, saline to hypersaline groundwaters of the Lake Tyrrell playa system in Australia. On the other hand, Nd concentrations in Colour Lake are higher than those measured in the alkaline, saline waters of Mono Lake in eastern California, where the values ranged from 444 to 776 pmol kg^{-1} (Johannesson and Lyons, 1994).

The lake profile samples are presented as shale-normalized plots in Fig. 2. The shale data are from Sholkovitz (1988, table 5.I). Because the rocks of the watershed are composed primarily of sandstone, shale and siltstones, the composite shale is the best normalizing factor for these waters.

All of the samples have similar shale-normalized REE patterns that exhibit enrichment of the MREE's over both the LREE's and HREE's (Fig. 2). This pattern has been recently referred to as a hump-shaped pattern (Schaltegger et al., 1994). In all cases the shale-normalized MREE/LREE and the MREE/HREE ratios are greater than unity, demonstrating the enrichment of the MREE's over both the LREE's and the HREE's (Table 3). In addition, the MREE/LREE ratios are larger than the MREE/HREE ratios, indicating a larger enrichment of the MREE over the LREE's than the HREE's.

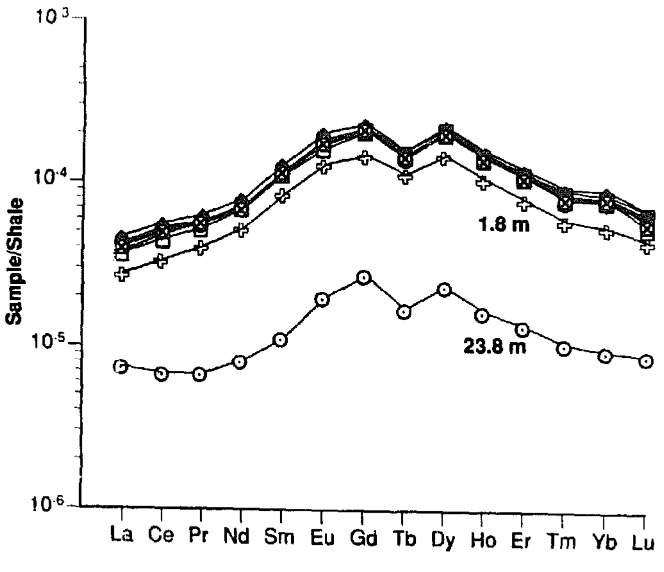

Fig. 2. Shale-normalized plot of the rare-earth elements for Colour Lake water. Because the majority of the lake samples plot the same they are not individually identified on the plot. The only exceptions are the ice–water interface sample (1.8-m depth) and the lake bottom sample (23.8-m depth) which have lower rare-earth concentrations.

The majority of lake samples, i.e. 2.3–22.8-m depth, plot identically as a group in Fig. 2. Both the ice–water interface sample (1.8 m) and the lake bottom sample, however, plot below these samples. For example, the shale-normalized REE values for the lake bottom sample are a factor of 8 lower than the mid-lake group of samples and the REE values for 1.8-m depth are roughly 1.5 times lower.

5. Discussion

5.1. pH, REE*'s and dissolved iron*

The highest pH-values for the lake samples are exhibited by the lake bottom sample (pH = 4.74) and the ice–water interface sample (pH = 3.78). The lake samples were collected during the spring melt and, consequently, the higher pH-value at the ice–water interface may be due to introduction of meltwater from the inflow streams (P. Doran, pers. commun., 1993). Meltwaters enter and leave the lake rapidly during the melt period and, as a result, much of the alkalinity gained from the meltwater streams is lost from the lake before it can be utilized to neutralize the lake's acidity (Allan et al., 1987). Therefore, the rapid flux of meltwater through the lake apparently does not significantly affect the water chemistry below the ice–water interface. The observed increase in pH at the lake bottom is likely due to sulfate reduction and/or groundwater input since the pH-value of the bottom water is very similar to groundwaters beneath the lake (Schiff et al., 1991; Boike et al., 1992). The remaining samples all have essentially the same pH (~3.6), similar major solute chemistry and similar REE concentrations (Table 3). The REE concentrations at the ice–water interface and the lake bottom are lower than the mid-lake samples. These relationships are more clearly demonstrated in Fig. 3 which shows the variation in Sm and Yb concentrations with depth in the lake. Identical profiles are observed for the other REE's with depth.

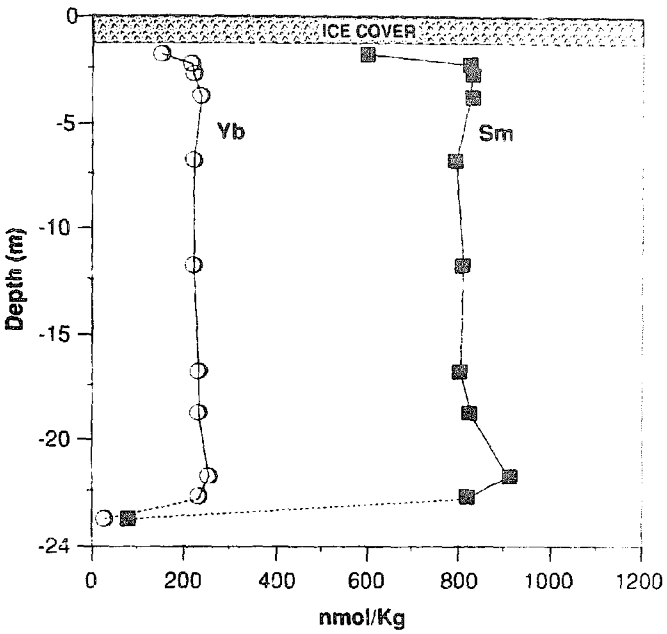

Fig. 3. Samarium and ytterbium profiles vs. depth for Colour Lake in nmol kg^{-1}. The same pattern is observed for the other rare-earth elements.

These data suggest an inverse relationship between pH and the total dissolved REE concentrations in the lake similar to that observed by other workers for river waters (e.g., Keasler and Loveland, 1982; Goldstein and Jacobsen, 1987; Elderfield et al., 1990) and acid groundwater systems (Fee et al., 1992; Johannesson et al., 1994). However, this cannot be demonstrated conclusively with the present data due to the similar pH-values exhibited by the majority of the samples. In addition, the lower Fe and REE concentrations that we measured in the lake bottom water may reflect loss of these elements during the collection and processing of this sample. More specifically, we observed greater than 20% error in the ionic balance of the bottom sample due to a negative charge surplus. Because we measured considerably lower DO concentrations at the lake bottom than for the overlying water column (Table 2) and because our Fe values for the lake bottom are less than values reported by Allan et al. (1987) for the same depth, we believe the lack of positive charge is due to loss of Fe as a result of oxidation of the water during sample collection and filtering. An additional 836 μmol kg^{-1} (1.7 meq l^{-1}) of Fe are required for charge balance. This would give a total dissolved Fe value of 1105 μmol kg^{-1} (2.2 meq l^{-1}) which is similar to reported dissolved Fe values for anoxic deep groundwaters beneath the lake (Boike et al., 1992).

DO concentrations along with the Fe data for the lake profile are presented in Fig. 4. The DO data indicate that the water column is well oxygenated except for the lake bottom water which exhibits significantly lower oxygen concentrations (Fig. 4). Neglecting the bottom water sample, the DO concentrations range from 406 μmol kg^{-1} at the ice–water interface to 266 μmol kg^{-1} at a depth of 22.8 m and have a mean value of 369 μmol kg^{-1}. By comparison, the DO concentration in the lake bottom water sample was 72 μmol kg^{-1}.

Other workers have reported a small layer (~ 1 m) of anoxic water at the lake bottom (e.g., Allan et al., 1987; Schiff et al., 1991; Doran, 1993). Doran (1993) presents evidence that indicates that for years when the lake remains ice-covered during the summer, a small anoxic layer persists at the lake bottom. However, for summers when the lake is ice-free, the entire water column is better mixed and the anoxic layer is not observed (Doran, 1993). Colour Lake remained ice-covered during the summer of 1991 and, consequently, low-oxygen to anoxic waters were

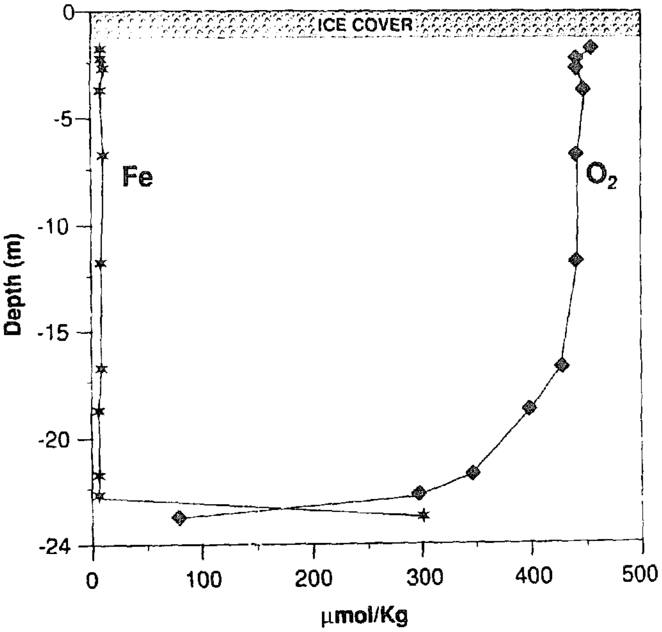

Fig. 4. Dissolved oxygen and iron profiles vs. depth in Colour Lake in μmol kg^{-1}.

expected at the lake bottom. Although we did not observe anoxic conditions (i.e. measurable O_2), it is reasonable to expect, based on the previous work, that anoxic waters may persist locally at the lake bottom.

Fe concentrations are relatively constant for the entire water column and, neglecting the bottom water, exhibit a mean value of 8.5 μmol kg^{-1} (Fig. 4). The Fe concentration in the bottom water is considerably higher, presumably due to the resolubilization of Fe^{2+} in the low-oxygen bottom water. As discussed above, the difference in the Fe values recalculated based on charge-balance considerations, i.e. 1105 μmol kg^{-1}, and our measured value, 269 μmol kg^{-1}, provides a rough estimate of the amount of Fe lost from solution during filtration and processing of the sample.

During collection and filtration of the bottom water sample, we observed a reddish colored precipitate that collected on the filter. This precipitate was likely Fe-hydroxide. We believe that a portion of the dissolved REE's at this lowest water depth may have coprecipitated along with Fe-hydroxide by oxidation of this low-oxygen bottom water during the filtration process. The precipitate, however, was not observed during the collection, filtering, or transport of any of the other lake samples. Consequently, the well-oxygenated, acidic overlying lake waters, relatively constant Fe values with depth and lack of observed precipitate in the other samples indicate that, except for the lake bottom sample, Fe was not precipitated from solution during sample collection and handling. This is similar to our experiences with other oxygenated, acidic waters such as those at Lake Tyrrell (Fee et al., 1992; Lyons et al., 1992). Similarly, except for the lake bottom sample, we believe that the REE's were not lost from solution during collection and processing of the overlying oxygenated, acidic lake waters.

5.2. *Shale-normalized* REE *patterns*

Other workers have reported convex patterns for river waters (Hoyle et al., 1984; Elderfield et al., 1990) and chloride-rich groundwaters (Gosselin et al., 1992) similar to what we have observed in Colour Lake (Fig. 2). Elderfield et al. (1990) observed that shale-normalized REE patterns for river waters reflects the combination of the colloidal and dissolved populations (Elderfield et al., 1990). Iron can exist in river waters as organically stabilized colloids and the relationship between Fe and REE concentrations in river water suggests that the colloidal population of the REE's is important (Elderfield et al., 1990). However, Fe-rich colloids are unlikely to be important in the low-pH waters of Colour Lake and, consequently, the contribution of such colloids to the total REE concentrations is expected to be small. Moreover, the contribution of organic colloids to the REE concentrations is also expected to be small due to the very low concentrations of dissolved organic carbon (DOC) (8-67 μmol l^{-1}) in the lake (Allan et al., 1987).

MREE-enriched patterns have also been reported for chloride-rich groundwater from the Palo Duro Basin in the Texas Panhandle, U.S.A. (Gosselin et al., 1992). These authors argue that the MREE-enriched or hump-shaped patterns of these waters are the result of water–rock interactions such as ion-exchange and/or adsorption/desorption on mineral surfaces including Fe–Mn coatings on sedimentary particles, alumino-silicate detritus-rich carbonate rocks, and secondary minerals in fractures and vugs within the local carbonate rocks (Gosselin et al., 1992). Other workers have examined REE concentrations of Fe–Mn coatings, iron–clay-rich dolomites and argillaceous carbonates, and secondary phases like Fe-rich vug-filling calcites and fracture-filling pyrite (Palmer, 1985; Banner et al., 1988; Gosselin et al., 1992). These surface coatings, detritus-rich carbonates and secondary mineral phases all exhibit shale-normalized enrichments in the MREE's (see Gosselin et al., 1992, fig. 4).

Palmer and Elderfield (1986) have shown that the MREE's tend to be mobilized, compared to the LREE's and HREE's in Fe–Mn surface coatings, by post-burial reactions such that the fluid phase is enriched in the MREE's as are any secondary mineral phases that may precipitate from these fluids (Gosselin et al., 1992). Both diagenetic fluids and groundwaters were likely involved in solid–liquid exchange reactions with surface coatings and secondary phases within the carbonate rocks of the Palo Duro Basin (Gosselin et al., 1992). Consequently, based on these arguments and the similarity between MREE-enriched patterns for Palo Duro Basin groundwaters and Fe–Mn coatings, detritus-rich carbonates and secondary phases, Gosselin et al. (1992) proposed that such reactions between these surface coatings, secondary mineral phases and the fluid phase are responsible for the REE concentrations in the groundwater. Other minerals such as apatite and glauconite may also contribute to the observed MREE-enriched groundwaters because both phases exhibit such enrichments. In fact, recent work on acid leachates from low-grade metamorphic rocks (i.e. shales) from Morocco also exhibit a similar MREE-enriched (hump-shaped) pattern (Schaltegger et al., 1994). These authors attribute this pattern to the presence of apatite in the shales that has been solubilized by their acid leach procedure. However, they do not rule out that the solubilization of the REE's associated with Fe/Mn-oxides could also explain the observed normalized patterns. However, solubilization of apatite and especially glauconite probably does not contribute significantly to the overall REE patterns in many geologic settings because of their typically low abundances (Banner et al., 1988; Gosselin et al., 1992).

The Colour Lake drainage basin is dominated by sandstones with minor amounts of siltstone, shale and impure limestones (Fricker, 1963; Allan et al., 1987). Similar to the conclusions of Gosselin et al. (1992), we propose that the MREE-enriched patterns of the Colour Lake water may be due to solid–liquid exchange processes like adsorption/desorption and ion exchange between the local acid waters and MREE-enriched Fe–Mn-oxyhydroxide coatings on clastic sedimentary particles, minor carbonate minerals, and with secondary mineral phases as well as dissolution of these coatings and secondary minerals. Certainly, at the observed low pH-values of these waters, the surface coatings would readily dissolve (Zinder et al., 1986). In addition, the Savik Formation, which outcrops on the northern and eastern side of Colour Lake, contains minor impure limestones along with shales and siltstones (Fricker, 1963). As with the groundwaters in the Palo Duro Basin in Texas, partitioning of the REE's into the fluid phase from MREE-enriched Fe–Mn coatings on carbonate mineral and/or secondary vug- and fracture-filling minerals in these local limestones may contribute to the MREE-enriched lake patterns. Shallow groundwaters entering the lake during the melt season most likely contributes the majority of REE's to the lake system because of the demonstrated gain of water to the lake by such groundwaters (Boike et al., 1992).

5.3. Speciation of the REE*'s in Colour Lake*

Speciation calculations were performed for the ice–water interface sample, the bottom water sample and the sample collected at 16.8-m depth. The formation of complexes of the REE's with OH^-, Cl^-, F^-, 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-}, $LnSO_4^+$, $LnCO_3^+$, $Ln(CO_3)_2^-$, $LnH_2PO_4^{2-}$, $LnHPO_4^+$, $Ln(HPO_4)_2^-$ and $LnPO_4^0$ species were evaluated.

Because we did not measure phosphate in Colour Lake we employed the phosphate data of Allan et al. (1987) in our modelling. All of the phosphate concentrations they measured for the entire water column are identical (i.e. 10.5 nmol kg^{-1}) except for the sample they collected 0.5 m below the ice–water interface where they obtained 63.2 nmol kg^{-1} and the lake bottom sample for which they report a value of 600.2 nmol kg^{-1}. Consequently, in our modelling we have used a phosphate concentration of 10.5 nmol kg^{-1} except for the lake bottom waters where we used the corresponding phosphate concentration.

In addition, we did not measure fluoride concentrations in Colour Lake and, as a result, the fluoride values of Allan et al. (1987) have been used in our modelling. In this case, they report fluoride values of 0.012 mmol kg^{-1} for the entire water column except at 22- and 23.5-m depth where the values are 0.146 and 0.096 mmol kg^{-1}, respectively. We have used the fluoride concentration of 0.012 mmol kg^{-1} in our modelling except for the lake bottom sample where we used a concentration of 0.096 mmol kg^{-1} because it represents the deepest measured value of fluoride in the lake (Allan et al., 1987).

Because the major anion in the lake is SO_4^{2-} we expected complexes of the form $LnSO_4^+$ to be important. In addition, for low-pH water like Colour Lake, other workers have predicted that the free metal species, Ln^{3+}, may be very important (Wood, 1990; Lee and Byrne, 1992). The lack of carbonate alkalinity in the lake indicates, however, that carbonate complexes with the REE's are not important and the low total phosphate concentrations in the lake (10.5 nmol kg^{-1}) suggest that complexes of the REE's with phosphate species are also not likely to be important. In addition, because of the very low DOC concentrations (8–67 μmol l^{-1}; Allan et al., 1987), REE-organic complexes are not expected to be of major importance in the lake. Currently, we are unable to account for speciation of the REE's with complex humic and fulvic acids due to the lack of a rigorous method to calculate activity coefficients and stoichiometric stability constants for these complexes.

The results of the speciation calculations are presented in Fig. 5 for the ice–water interface water, 16.8-m-depth sample and the lake bottom water. The calculations indicate that essentially all of the dissolved REE's in Colour Lake water can be accounted for by Ln^{3+}, LnF^{2-} and $LnSO_4^+$ species. Our modelling suggests that $LnSO_4^+$ complexes are more important for the LREE's than the free metal species, but for atomic numbers of >63 (i.e. Eu), $LnSO_4^+$ complexes decrease in importance and the free metal species, Ln^{3+}, becomes progressively more important (Fig. 5). The LnF^{2-} species is of minor significance for the majority of the lake water where it accounts for $<5\%$ of the total metal for each REE. The only exception may be the bottom waters where the fluoride ion may be an important complexer of the HREE's. However, because we have not measured fluoride concentrations for the lake bottom waters (i.e.

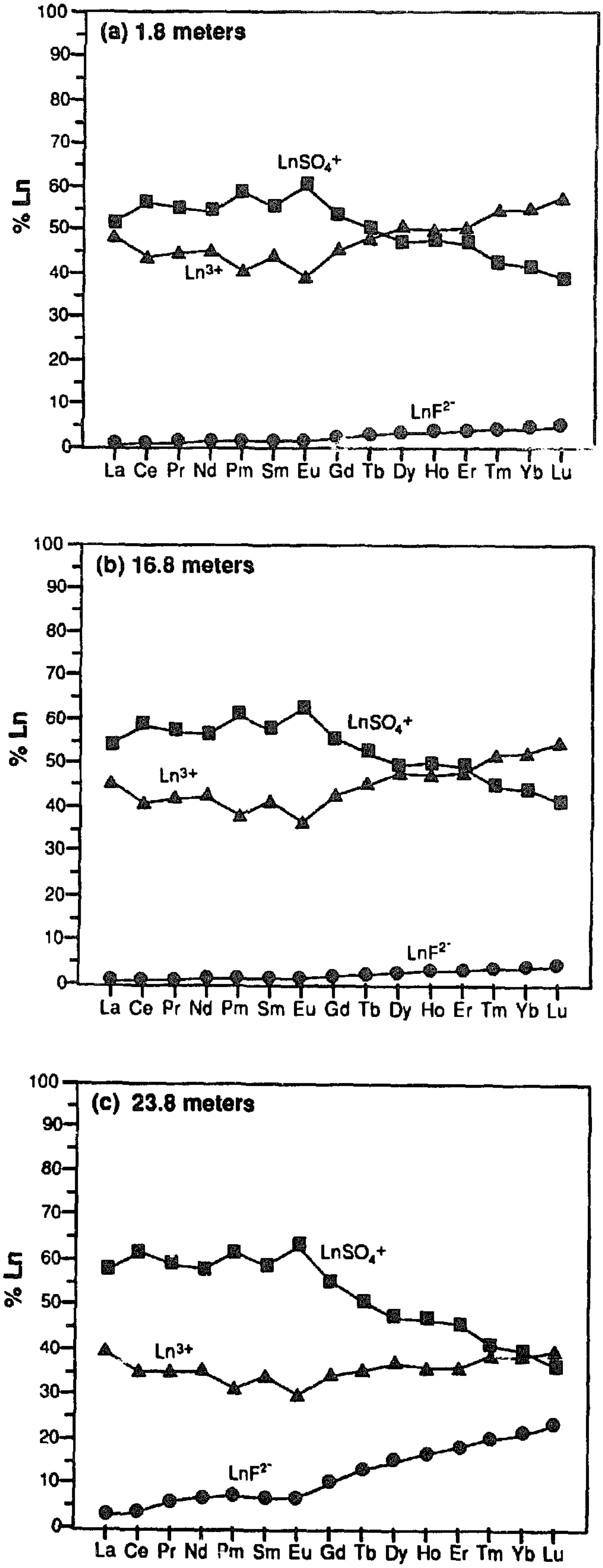

Fig. 5. Speciation of the rare-earth elements in Colour Lake as percent metal at: (a) 1.8-m depth; (b) 16.8-m depth; and (c) 23.8-m depth.

23.8 m) and instead have used the concentration at 23.5-m depth reported by Allan et al. (1987), the actual percentage of metal complexed with fluoride may be different.

At the ice–water interface, the free metal species for the HREE's dominates over the $LnSO_4^+$ and LnF^{2-} complexes. This predominance of the free metal species for the HREE's is predicted to decrease with depth in the lake, such that the REE's dissolved in the bottom waters should be primarily complexed with SO_4^{2-} (Fig. 5). Therefore, based on the major solute chemistry of Colour Lake, our speciation calculations indicate that the REE's exist in solution as free metal species or as complexes with sulfate and fluoride, and that with the exception of the surface waters, the dominate species for the majority of the REE's in the lake are sulfate complexes.

Our speciation calculations support the earlier work of Wood (1990) and Lee and Byrne (1992), who predicted that at low pH-values, like those measured in Colour Lake, the free metal (Ln^{3+}) and $LnSO_4^+$ species are expected to dominate. These workers based their speciation calculations on a model groundwater with a total sulfate concentration of 10^{-4} *m* (Wood, 1990). In Colour Lake, however, $LnSO_4^+$ complexes with the REE's are the dominant species primarily because of the relatively high sulfate concentrations (i.e. $10^{-2.5}$ *m*) as compared to the model groundwater of Wood (1990).

In support of our earlier suggestion, the speciation calculations indicate that other factors besides complexation of the REE's, such as dissolution of Fe–Mn coatings on mineral grains in the rocks of the watershed as well as adsorption/desorption and/or ion-exchange reactions with these coatings, exert more control on the dissolved REE concentrations and, hence, the MREE-enriched patterns of the lake waters. The infinite-dilution stability constants for the REE complexes with sulfate are similar for the entire suite of REE's differing only by a factor of 2.3 (Millero, 1992). As a result, the formation of complexes with sulfate is not expected to fractionate the REE's as significantly as carbonate complexes, where the difference in stability constants between the HREE's and LREE's of dicarbonato species (i.e. $Ln(CO_3)_2^-$) for example, differs by greater than two orders of magnitude (Wood, 1990; Lee and Byrne, 1993; Johannesson and Lyons, 1994). In contrast, in alkaline waters, the formation of strong, predominantly dicarbonato complexes with the REE's, results in large enrichments in the HREE's as compared to the LREE's (Lee and Byrne, 1992, 1993; Millero, 1992; Johannesson and Lyons, 1994).

6. Conclusions

Colour Lake water is dominated by Ca^{2+}, Mg^{2+} and SO_4^{2-} and has no measurable carbonate alkalinity. The sulfate concentration is high at $10^{-2.5}$ *m*. Speciation modelling indicates that, based on the major solute chemistry of Colour Lake, all of the REE's occur as Ln^{3+}, LnF^{2-} and $LnSO_4^+$ species with the sulfate complexes being the dominant species for the majority of the REE's. These observations suggest that for low-pH waters dominated by the sulfate anion, REE concentrations may increase compared to waters where sulfate concentrations are relatively low because of formation of more stable complexes of the REE's with sulfate. The stability constants for the REE-sulfate complexes only vary by a factor of 2.3, which indicates that, compared to carbonate complexes where the stability constants can vary by a factor of >200, the formation of complexes with sulfate does not fractionate the REE's as much as carbonate ions. As a result, the MREE enrichment of the lake waters may be controlled by other factors in addition to the speciation of the REE's. Water–rock interactions involving ion exchange and/or adsorption/desorption between the local acid waters and MREE-enriched Fe–Mn coatings and secondary mineral phases as well as dissolution of these coatings are proposed as possible mechanisms responsible for the observed enrichments in the MREE's.

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