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The Solubility Control of Rare Earth Elements in Natural Terrestrial Waters and the Significance of PO_4^{3-} and CO_3^{2-} in Limiting Dissolved Rare Earth Concentrations: A Review of Recent Information

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Abstract. Rare earth element (REE) concentrations in alkaline lakes, circumneutral pH groundwaters, and an acidic freshwater lake were determined along with the free carbonate, free phosphate, and free sulfate ion concentrations. These parameters were used to evaluate the saturation state of these waters with respect to REE phosphate and carbonate precipitates. Our activity product estimates indicate that the alkaline lake waters and groundwaters are approximately saturated with respect to the REE phosphate precipitates but are significantly undersaturated with respect to REE carbonate and sulfate precipitates. On the other hand, the acidic lake waters are undersaturated with respect to REE sulfate, carbonate, and phosphate precipitates. Although carbonate complexes tend to dominate the speciation of the REEs in neutral and alkaline waters, our results indicate that REE phosphate precipitates are also important in controlling REE behavior. More specifically, elevated carbonate ion concentrations in neutral to alkaline natural waters tend to enhance dissolved REE concentrations through the formation of stable REE-carbonate complexes whereas phosphate ions tend to lead to the removal of the REEs from solution in these waters by the formation of REE-phosphate salts. Removal of REEs by precipitation as phosphate phases in the acid lake (pH = 3.6) is inconsequential, however, due to extremely low $[PO_4^{3-}]_F$ concentrations (i.e., $\sim 10^{-23}$ mol/kg).

Key words: rare earth elements, lakes, groundwaters, activity products, solubility products, solubility controls, complexation.

1. Introduction

In addition to the dominant adsorptive scavenging processes effecting trace elements in the oceans (e.g., Balistrieri *et al.*, 1981; Byrne and Kim, 1990; DeBaar *et al.*, 1985; Koeppenkastrop and De Carlo, 1993), dissolved rare earth elements (REE) are also likely removed from seawater, at least in part, by precipitation (Jonasson *et al.*, 1985) or coprecipitation (Byrne and Kim, 1993) of rare earth elements (REE) phosphate phases. These studies suggest that precipitates and coprecipitates of REE phosphates are important in controlling REE concentrations in seawater and may, in fact, play an important role in limiting their concentrations (Byrne and Kim, 1993). Similar processes are also likely to be important in terrestrial natural waters. However, due to the limited number of studies of REE behavior in such waters, REE cycling in natural terrestrial waters is poorly understood compared to seawater.

Previous studies have emphasized the importance of REE carbonate complexes in seawater (Cantrell and Byrne, 1987; Choppin, 1989; Lee and Byrne 1992; Millero, 1992; Turner *et al.*, 1981), groundwaters (Lee and Byrne, 1992; Wood 1990), and alkaline lakes (Johannesson *et al.*, 1994; Johannesson and Lyons, 1994; Möller and Bau, 1993), and other workers have demonstrated that REE phosphate complexes are of potential significance in terrestrial waters (Byrne *et al.*, 1991; Lee and Byrne, 1992). Moreover, Byrne and Kim (1993) argue that an understanding of the manner in which pH, phosphate, and carbonate ion concentrations affect dissolved REE concentrations is necessary in order to discern the complex geochemical processes controlling the REEs in natural waters. Recent work suggests that carbonate complexes dominate the speciation of the REEs in most natural waters whereas the percentage of metal complexed with phosphate is negligible, despite the large stability constants for $LnPO_4^0$ species (Johannesson and Lyons, 1994; Lee and Byrne, 1992). Typically, the importance of REE phosphate coprecipitates in removing REEs from seawater has been stressed, in part, because of their low solubility (e.g., the solubility product for REE phosphates ranges from 10^{-26} to 10^{-24}) (Byrne and Kim, 1993; Firsching and Byrne, 1991; Jonasson *et al.*, 1985). Rare earth carbonate precipitates and coprecipitates are also highly insoluble, with solubility products between 10^{-35} and 10^{-29} (Firsching and Mohammadzadel, 1986; Smith and Martell, 1976). Due to the potential significance of both phosphate and carbonate coprecipitates in natural waters, we present in this work the first comparative examination of REE solubility controls by phosphate and carbonate ions.

REE data are evaluated for a wide variety of natural terrestrial waters including alkaline lakes from the western U.S.A., circumneutral pH groundwaters from southern Nevada, Death Valley, California, and the Carnmenellis region of England, Smedley (1991), and an acidic freshwater lake from the Canadian High Arctic (Colour Lake). In this study we present for the first time recently evaluated activity products for light REE (LREE) phosphate and carbonate precipitates for groundwaters from the Nevada Test Site, Yucca Mountain, Nevada (Yucca Mountain is currently being investigated as a potential future high-level nuclear waste repository), the Carnmenellis region of England, water from Colour Lake as well as activity products for alkaline lakes of the western U.S.A. These new estimated activity products are presented along with previously determined values for groundwaters from Ash Meadows National Wildlife Refuge in Nevada and Death Valley National Park in California (Johannesson *et al.*, in review), and La and Ce phosphate activity products for the alkaline lakes (Johannesson *et al.*, 1994). In addition to the estimation of activity products for REE carbonate and phosphate precipitates, we have evaluated activity products for REE sulfate precipitates in the relatively high sulfate waters of Colour Lake.

2. Overview of Natural Waters Sampled

The alkaline lakes examined in this study include Mono Lake in eastern California, Summer Lake, Goose Lake, and Lake Abert in south-central Oregon, and Walker Lake in western Nevada. Samples were collected from the lake surfaces except for the Mono Lake sample which represents the average of six samples collected at 5 m depth intervals in 36 m of water (Johannesson and Lyons, 1994). The acidic lake, Colour Lake, is naturally occurring and is located on Axel Heiberg Island in the Canadian High Arctic. The Colour Lake sample was collected at approximately 17 m depth in the 24 m deep lake (Johannesson and Lyons, 1995).

Groundwaters were collected from Fairbanks and Jackrabbit Springs in Ash Meadows National Wildlife Refuge and from Texas, Nevares, Travertine, Scotty's, Surprise, Mesquite, and Upper Brier Springs in Death Valley National Park. The groundwaters collected from Ash Meadows discharge from Paleozoic carbonate rocks as do the groundwaters discharging from Texas, Nevares, and Travertine Springs in Death Valley (Winograd and Thordarson, 1975). The other Death Valley springs issue from Tertiary felsic volcanics except Mesquite Springs which discharges from alluvial basin-fill deposits (Kreamer *et al.*, in review; Winograd and Thordarson, 1975). Groundwaters were also collected from Well 5C on the Nevada Test Site and Well J-13 which is approximately 3 miles east of Yucca Mountain in southern Nevada. Well 5C is completed in Paleozoic carbonate rocks whereas Well J-13 is completed in the local Tertiary felsic tuffaceous rocks (E. P. Busrick, 1994, written comm.).

Although the groundwaters from the Nevada Test Site and Yucca Mountain region are similar to the groundwaters discharging from the nearby springs in Ash Meadows and Death Valley, the Nevada Test Site and Yucca Mountain groundwaters are typically more dilute and have lower REE concentrations (Tables I and II). For example, groundwaters from the Nevada Test Sites tend to exhibit higher concentrations of Na and K than the Ash Meadows groundwaters, which are by comparison, enriched in Ca and Mg, and the Nevada Test Site groundwater have lower sulfate concentrations than the Death Valley groundwaters (Winograd and Thordarson, 1975).

We also present data for previously collected and analyzed (Smedley, 1991) groundwater samples from the Carnmenellis region of England (Tables I and II). Groundwater sample 2393 was collected from an aquifer composed of granitic rocks whereas samples 2376 and 2563 were collected from metasedimentary rocks. Of the 11 samples analyzed by Smedley (1991), only three have been employed in this study because of their measureable phosphate concentrations. For the eight remaining samples, Smedley (1991) reported that the phosphate values were below 0.3 μmol/kg.

TABLE I. Concentrations of rare earth elements (in pmol/kg) for alkaline lakes from the western U.S.A., groundwaters from springs in Southern Nevada, U.S.A., Death Valley, California, U.S.A., groundwaters from the Carnmenellis region of England, and an acidic lake from the Canadian High Arctic.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Alkaline Lakes:														
Mono	158	699	106	596	226	53	413	113	1046	285	1010	172	1127	183
Abert	511	2355	156	707	193	59	305	63	560	164	789	178	1647	343
Summer	634	1106	177	617	160	39	153	25	166	36	114	18	104	17
Walker	202	435	43	118	27	9	26	5	31	8	17	6	32	9
Goose	346	528	64	236	53	13	45	13	62	18	60	12	81	11
Groundwaters, U.S.A.														
Fairbanks	28	50	8.6	33	7.2	0.7	6.4	1	5.8	1.2	3.3	0.5	3	0.5
Jackrabbit	36	65	8.7	35	6.5	0.7	6.9	0.9	4.9	1.2	3.2	0.5	3.2	0.6
Texas	38	56	6.4	25	5	0.8	4.9	0.7	4.1	0.8	2.6	0.4	2.3	0.4
Nevares	33	67	7.2	28	5.6	1.2	6	0.8	4.1	0.8	2.3	0.4	2.3	0.4
Travertine	45	80	6.7	27	5.3	1.1	5.6	0.8	4.3	0.9	2.5	0.3	2.6	0.4
Upper Brier	264	208	78	354	87	14	95	15	97	25	82	13	82	14
Scotty's	76	235	13	51	9.5	2	9.3	1.4	8	1.8	6.4	1	6.7	1.1
Surprise	44	73	8.2	27	7	1	7.5	1.3	7.8	1.7	4.9	0.7	3.9	0.6
Mesquite	47	58	9	36	7	1.2	6.6	1	5.6	1.1	3.3	0.5	3	0.5
Well 5C	6	10	1	8										
J-13		35												
Groundwaters, England[a]														
2393	6983	18127	2910	10815	3059	553	2989		2092	352	1016		982	
2376	3312	657	1065	5962	997	408	2289		985	279	496		<405	
2563	13822	1142	2271	9221	2128	415	1653		800	<182	<416		<289	
Acid Lake														
Colour Lake	13100	32130	4280	20120	5960	1990	8850	1180	7240	1230	2630	330	1720	230

[a] From Smedley (1991).

TABLE II. Calculated free carbonate ($\log[CO_3^{2-}]_F$), free phosphate ($\log[PO_4^{3-}]_F$), ionic strength (I), (all in moles/kg) and measured pH values for lake waters and groundwaters discussed in this study. The log $[SO_4^{2-}]_F$ concentration (in moles/kg) for Colour Lake is -2.62.

	I	pH	$\log[CO_3^{2-}]_F$	$\log[PO_4^{3-}]_F$
Alkaline Lakes:				
Mono	1.84	9.78	–0.63	-4.68
Abert	1.64	9.71	–0.61	-5.08
Summer	0.009	8.48	–4.02	-9.74
Walker	0.210	9.52	–1.97	-8.73
Goose	0.088	9.61	–1.87	-8.14
Groundwaters, U.S.A.				
Fairbanks	0.0095	7.05	–5.86	–14.74
Jackrabbit	0.0108	6.99	–5.91	–14.93
Texas	0.0124	7.61	–5.18	–13.23
Nevares	0.0286	7.34	–5.31	–13.58
Travertine	0.0133	7.37	–5.31	–13.85
Upper Brier	0.0028	7.37	–5.97	–13.81
Scotty's	0.0077	7.62	–5.10	–12.86
Surprise	0.0076	7.62	–5.17	–13.31
Mesquite	0.0154	7.36	–5.19	–13.55
Well 5C	0.0053	8.60	–4.28	–11.17
J-13[a]	0.0028	7.36	–6.03	–14.11
J-13[b]	0.0076	7.00	–5.86	–13.84
Groundwaters, England[c]				
2393	0.0016	6.07	–8.28	–15.32
2376	0.0048	6.78	–7.03	–14.52
2563	0.0017	5.54	–8.86	–16.12
Acid Lake				
Colour Lake	0.01	3.6	N.A.	-22.92

[a] Our data.

[b] Determined with the data from Nitsche *et al.* (1992).

[c] From Smedley (1991).

3. Analytical and Calculational Procedures

Sampling and analytical techniques have been discussed in detail elsewhere (Johannesson and Lyons, 1994; Stetzenbach *et al.*, 1994). Briefly, samples for REEs were collected in acid-washed high density polyethylene sample bottles after filtering through Nuclepore® (0.4 μm) or Gelman Sciences (0.45 μm) filters and then acidified to pH < 2 with ultra pure nitric acid. The major cations were determined by atomic adsorption spectroscopy and anions were measured by ion chromatography. (The complete chemical analyses are reported in Johannesson and Lyons (1994), Johannesson and Lyons (1995), Johannesson *et al.* (1994), and Johannesson *et al.* (in review).) The pH was measured in the field using a Hach One portable pH meter and alkalinity was determined on site by titration (Stetzenbach *et al.*, 1994). The REEs were measured by inductively coupled plasma mass spectrometry (ICP-MS) after either coprecipitation with ferric hydroxide or after a 50-fold preconcentration by cation exchange (Johannesson and Lyons, 1994; Stetzenbach *et al.*, 1995). The following REE isotopes were chosen to minimize 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. The effects of interferences from Ba oxide on Eu and oxides of the LREEs on the heavy REEs (HREE) were corrected (Johannesson and Lyons, 1995; Stetzenbach *et al.*, 1994). Precision for the REE analyses was typically better than 10% relative standard deviation (RSD) (Johannesson and Lyons, 1994).

Concentrations of HCO_3^- and CO_3^{2-} were calculated from alkalinity titrations involving either PHREEQE (Parkhurst *et al.*, 1980) or PHRQPITZ (Plummer *et al.*, 1989) depending on the ionic strength of the water. PHRQPITZ was used for the high ionic strength alkaline lake waters of Mono, Abert, Summer, Goose, and Walker Lakes, and PHREEQE was employed for the more dilute waters of Colour Lake and the groundwaters of southern Nevada, Death Valley, and England.

Activity coefficients for uncomplexed (free) REEs as well as $[PO_4^{3-}]_F$, $[CO_3^{2-}]_F$, and $[SO_4{}^{2-}]_F$, were estimated using the techniques of Millero and Schreiber (1982). These techniques employ the specific ion interaction model of Pitzer (1973, 1979) and Pitzer and Mayorga (1973) to estimate the activity coefficients of metals and ligands over a wide range of ionic strengths (i.e., from pure water to highly concentrated brines). The waters in this study exhibited ionic strengths that ranged from I = 0.0016 mol/kg (e.g., groundwater from the Carnmenellis region, England) to the highly concentrated waters of Mono Lake (I = 1.84 mol/kg) and Lake Abert (I = 1.64 mol/kg) (Johannesson and Lyons, 1994; Johannesson *et al.*, 1994; Smedley, 1991). Speciation of total phosphate among total $H_2PO_4{}^-$, $HPO_4{}^{2-}$, and $PO_4{}^{3-}$ concentrations was evaluated using a Pitzer model developed by F. J. Millero (Millero, 1993, pers. comm.). Free concentrations of carbonate, phosphate, and sulfate ions (e.g., $[PO_4{}^{3-}]_F$, $[CO_3{}^{2-}]_F$, and $[SO_4{}^{2-}]_F$) were then calculated from total concentrations $[H_2PO_4{}^-]_T$, $[HPO_4{}^{2-}]_T$, and $[PO_4{}^{3-}]_T$ as discussed by Millero and Schreiber (1982).

The speciation of the REEs in these waters was modelled using the combined specific ion interaction and ion-pairing model developed for the REEs by Millero (1992) and the results are presented elsewhere (Johannesson and Lyons, 1994; Johannesson and Lyons, 1995, Johannesson *et al.*, 1994; Johannesson *et al.*, in review). The modelling indicates that carbonate complexes of the REEs are the primary forms of dissolved REEs in all of these waters except Colour Lake where sulfate complexes dominate.

We did not account for the speciation of the REEs with complex humic and fulvic acids in these waters due to the lack of a rigorous technique to calculate the activity coefficients and stoichiometric stability constants for humic and fulvic REE complexes. However, the dissolved organic carbon (DOC) concentrations in the groundwaters from southern Nevada and Death Valley, California (83 and 150 μmol/kg for two springs (Winograd and Pearson, 1976) and in Colour Lake (8–67 μmol/kg (Allan *et al.*, 1987), are low and, consequently, REE-organic complexes are not expected to be of major importance in these waters. On the other hand, in the alkaline lakes, DOC can exhibit high concentrations as in Mono Lake where DOC levels range from 6 to 7 mmol/kg (Domagalski *et al.*, 1990). Speciation calculations in seawater and the WIPP brines (Waste Isolation Project Program) indicate that all of the known organic ligands cannot compete with carbonate complexes at the observed concentrations of these organic ligands (Millero, 1992). For Mono Lake, where the carbonate ion concentration is a factor of 1000 larger than in seawater, stability constants for REE-organic complexes would have to be much greater than the stability constants for the carbonate complexes to effectively compete (Johannesson and Lyons, 1994). Stability constants for REE complexes with simple organic acids at infinite dilution are typically much lower than the stability constants for REE carbonate complexes. Exceptions include polydentate ligands such as EDTA, for which the REE stability constants are larger than for REE-carbonate complexes (Lee and Byrne, 1993; Wood, 1993). EDTA, however, is not expected to occur at high concentrations in natural aqueous organic matter (Wood, 1993). Other strongly complexing polydentate ligands are also not expected to occur in natural waters at high concentrations and, as a result, are not likely to effectively compete with carbonate ions. Clearly, more research is required before the importance of REE complexes with organic ligands is fully understood.

Despite the high concentrations of total phosphate in some of the alkaline lakes (e.g., 600 μmol/kg in Lake Abert (Philips and Van Denburgh, 1971) and 800–1000 μmol/kg in Mono Lake (Jellison and Melack, 1988), as well as the demonstrated large stability constants for REE phosphate complexes (Lee and Byrne, 1992), REE phosphate species were of minor importance in all of the waters studied. Phosphate complexes with the REEs can not effectively compete with the carbonate complexes in these waters because of the relatively higher carbonate ion concentrations (e.g., Johannesson and Lyons, 1994). However, Byrne and Kim (1993) argued that even at the low phosphate concentrations of seawater (1–3 μmol/kg), coprecipitation behavior of the REEs with phosphate may play an important role in the removal of dissolved REEs from the oceans. Consequently, REE phosphate coprecipitation may also be important in these terrestrial waters.

3.1. ACTIVITY PRODUCT CALCULATIONS

Because REE phosphate, carbonate, and sulfate phases are actually coprecipitates, it is unclear how to accurately determine saturation states. Rare earth element solubility products have been evaluated for individual rare earths, but effective solubility products for rare earths synergistically precipitating to form phases consisting of all REEs have not been experimentally evaluated (such studies are presently in progress at the University of South Florida). In the absence of solubility products directly appropriate to REE coprecipitation an alternative approach is to estimate activity products for individual REE phosphates, carbonates, and sulfates and compare these values with the appropriate individual solubility products. Alternatively, activity products for these phases can also be roughly evaluated by summing the concentrations of the REEs. Typically, the summation is conducted over the LREEs because of the similarity of the magnitude of their solubility products and because in most natural waters, LREE concentrations are typically greater than the heavy REEs (HREE) concentrations (e.g., DeBaar *et al.*, 1983; DeBaar *et al.*, 1985; Elderfield and Greaves, 1982; Klinkhammer *et al.*, 1983; Smedley, 1991). Because of the similarity of the solubility products of the LREEs they can be treated, to a first approximation, as isotopes of the same element in the activity product calculations (Byrne and Kim, 1993). These authors estimated activity products for REE phosphate coprecipitates by summation from La to Gd using the following expression

$$\mathrm{AP} = \sum_{\mathrm{La}}^{\mathrm{Gd}} \{M_i^{3+}\}\{\mathrm{PO}_4^{3-}\}. \tag{1}$$

We have chosen to evaluate the individual activity products of REE phosphate precipitates in these waters for the five LREEs, La, Ce, Pr, Nd, and Sm, as described above. For this approach activity products were calculated as AP = $\{M_i{}^{3+}\}\{\mathrm{PO}_4{}^{3-}\}$, where $\{M_i{}^{3+}\}$ represents the activity of the free metal ion and $\{\mathrm{PO}_4{}^{3-}\}$ is the activity of the free phosphate ion. Accounting for the appropriate stoichiometry of the precipitates, activity products for the individual REE carbonates and sulfates were calculated in a similar manner.

4. Results and Discussion

The complete results of the REE measurements and major solute analyses are presented elsewhere (Smedley, 1991; Johannesson and Lyons, 1994; Johannesson *et al.*, 1994; Johannesson and Lyons, 1995; Johannesson *et al.*, in review). Here we present data for the REEs (Table I) and the free concentrations for phosphate and carbonate ions in these waters (Table II). In addition, because of the relatively large sulfate concentrations in Colour Lake (which has no measurable carbonate alkalinity) the free sulfate concentration for Colour Lake is presented in Table II.

We did not measure total phosphate concentrations in the lakes and, consequently, values obtained from the literature have been used in the activity product calculations (e.g., see Allan *et al.*, 1987; Jellison and Melack, 1988; Phillips and Van Denburgh, 1971). We did, however, measure the total phosphate concentrations in the groundwaters of southern Nevada and Death Valley, California (Johannesson *et al.*, in review).

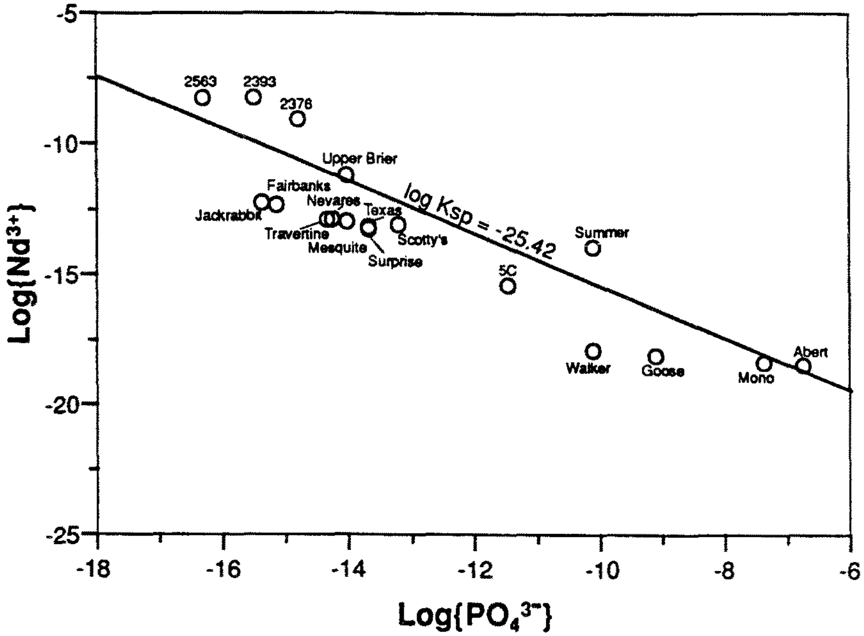

Fig. 1. Activities of free Nd^{3+} and free $PO_4{}^{3-}$ plotted as log quantities for alkaline lake waters from the western U.S.A., groundwaters from southern Nevada (including the Nevada Test Site, Yucca Mountain, and Ash Meadows National Wildlife Refuge) and Death Valley, California, and groundwaters from the Carnmenellis region of England. The curve for the solubility product of $NdPO_4 \cdot nH_2O$ (Ksp = $10^{-25.42}$) determined by Firsching and Brune (1991) has been plotted for corresponding Nd^{3+} and PO_4^{3-} activities. The proximity of these waters to the solubility product curve suggests that all of these waters are approximately saturated with respect to Nd phosphate precipitates (see text for discussion). Groundwater data from the Carnmenellis region of England is from Smedley (1991).

Solubility products for REE phosphate and carbonate salts (i.e., $LnPO_4 \cdot nH_2O$ and $Ln_2(CO_3)_3 \cdot nH_2O$) are presented in Tables III and IV. Solubility products for REE phosphates at zero ionic strength (Table III) are those of Byrne and Kim (1993) plus recalculated, (Byrne and Kim, 1993) solubility product values from Tananaev and Vasil'eva (1963), Jonasson *et al.* (1985), and Firsching and Brune (1991). Solubility products for REE carbonates are from Smith and Martell (1976) and Firsching and Mohammadzadel (1986).

4.1. ALKALINE LAKES AND CIRCUMNEUTRAL pH GROUNDWATERS

Figure 1 is a plot of the log{Nd^{3+}} versus the log{$PO_4{}^{3-}$} for the alkaline lake waters, the groundwaters of southern Nevada and Death Valley, California, and the groundwaters of the Carnmenellis region of England. The solubility product curve for $NdPO_4 \cdot nH_2O$ determined by Firsching and Brune (1991) has been plotted

TABLE III. Solubility products for light rare earth element phosphates at zero ionic strength and 25°C reported as log K^0_{sp}.

Reference	log K^0_{sp} $LaPO_4 \cdot nH_2O$	$CePO_4 \cdot nH_2O$	$PrPO_4 \cdot nH_2O$
Byrne and Kim (1993)		–24.26	
*Firsching and Brune (1991)	–25.44		–25.40
*Jonasson *et al.* (1985)	–24.74		–26.41
*Tananaev and Vasil'eva (1963)	–24.99		
Reference	**$NdPO_4 \cdot nH_2O$**	**$SmPO_4 \cdot nH_2O$**	
Byrne and Kim (1993)			
*Firsching and Brune (1991)	–25.42	–25.31	
*Jonasson *et al.* (1985)			
*Tananaev and Vasil'eva (1963)			

* Recalculated by Byrne and Kim (1993).

TABLE IV. Solubility products for light rare earth element carbonates at zero ionic strength and 25°C reported as log K^0_{sp}.

Reference	log K^0_{sp} $La_2(CO_3)_3 \cdot nH_2O$	$Ce_2(CO_3)_3 \cdot nH_2O$	$Pr_2(CO_3)_3 \cdot nH_2O$
Smith and Martel (1976)	–33.4		
Firsching and Mohammadzadel (1986)	–29.91		–33.19
Reference	**$Nd_2(CO_3)_3 \cdot nH_2O$**	**$Sm_2(CO_3)_3 \cdot nH_2O$**	
Smith and Martel (1976)	–33.0	–32.5	
Firsching and Mohammadzadel (1986)	–34.10	–34.41	

along with the activity values. Waters that plot on the solubility curve are saturated with respect to Nd phosphate precipitates whereas waters that plot above or below are either supersaturated or undersaturated, respectively. The alkaline lake waters and circumneutral pH groundwaters discussed in this study plot on or close to the solubility product curve indicating that these waters are all approximately saturated with respect to Nd phosphate precipitates. These same relationships are observed for the other LREEs when their activities are plotted against the activity of free $PO_4{}^{3-}$ and compared to the appropriate solubility product curve. The approximate saturation of these waters with respect to LREE phosphate precipitates is also demonstrated by comparison of the solubility product values in Table III with the estimated individual activity product (i.e., $\{M_i^{3+}\}\{PO_4^{3-}\}$) values for these waters presented in Table V.

TABLE V. Activity products (AP = $\{M^{3+}\}\{PO_4^{3-}\}$) for light rare earth element phosphates reported as log (AP) in alkaline lakes of the western U.S.A., groundwaters from southern Nevada and Death Valley, California, U.S.A., and groundwaters from the Carnmenellis region of England. Activity product calculations for Ce phosphates for Well J–13 were conducted with our REE data and both the major solute data we measured and the values determined by Nitsche *et al.* (1992). Groundwaters from the Carnmenellis region of England are from Smedley (1991). Sample 2392 represents groundwater grom granitic rocks whereas 2376 and 2563 are groundwaters from metasedimentary rocks.

	$\{La^{3+}\}$ $\{PO_4^{3-}\}$	$\{Ce^{3+}\}$ $\{PO_4^{3-}\}$	$\{Pr^{3+}\}$ $\{PO_4^{3-}\}$	$\{Nd^{3+}\}$ $\{PO_4^{3-}\}$	$\{Sm^{3+}\}$ $\{PO_4^{3-}\}$
Alkaline Lakes					
Mono[a]	–25.3	–25.3	–26.4	–25.8	–26.5
Abert	–24.4	–24.3	–25.8	–25.3	–26.2
Summer	–23.1	–23.4	–24.5	–24.1	–25.0
Goose	–26.1	–26.5	–27.7	–27.3	–28.3
Walker	–26.8	–27.1	–28.4	–28.1	–29.1
Groundwater, U.S.A.					
Fairbanks	–27.1	–27.1	–28.0	–27.6	–28.4
Jackrabbit	–27.1	–27.1	–28.2	–27.7	–28.6
Texas	–26.1	–26.3	–27.4	–27.0	–27.9
Nevares	–26.5	–26.6	–27.7	–27.3	–28.2
Travertine	–26.5	–26.6	–27.8	–27.4	–28.3
Upper Brier	–24.9	–25.3	–25.9	–25.4	–26.2
Scotty's	–25.5	–25.4	–26.9	–26.4	–27.4
Surprise	–26.1	–26.3	–27.4	–27.0	–27.9
Mesquite	–26.3	–26.6	–27.6	–27.1	–28.1
Well 5C	–26.1	–26.4	–27.7	–27.0	
J-13[b]		–26.3			
J-13[c]		–26.8			
Groundwater, England[d]					
2393	–24.0	–23.6	–24.4	–23.9	–24.6
2376	–24.0	–24.8	–24.7	–24.0	–25.0
2563	–24.4	–25.6	–25.3	–24.7	–25.4

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[a] Johannesson and Lyons (1994) average of six samples.

[b] Phosphate data determined at the Harry Reid Center for Environmental Studies, University of Nevada, Las Vegas.

[c] Phosphate data from Nitsche *et al.* (1992).

[d] From Smedley (1991).

The Nd phosphate activity products for the investigated natural waters are scattered about the line defined by the Nd phosphate solubility product suggesting that these waters are generally saturated with respect to LREE phosphate precipitates. Although many points plot below the equilibrium line, suggesting undersaturation, considering the potential uncertainties inherent in calculations of rare earth and

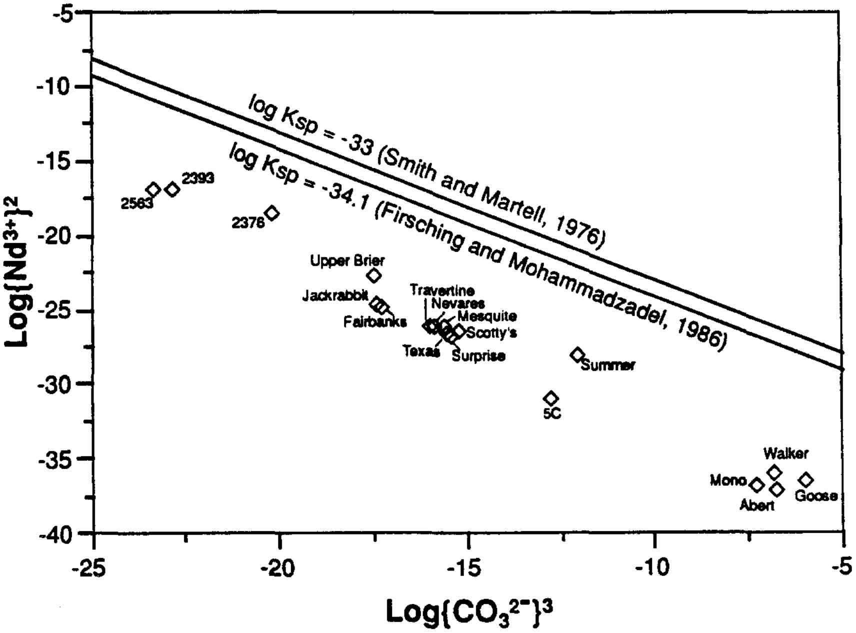

Fig. 2. Activities for free Nd^{3+} and free CO_3^{2-} (accounting for stoichiometry) for the same natural waters plotted in Figure 1. Solubility product curves for $Nd_2(CO_3)_3 \cdot nH_2O$ are from Smith and Martell (1976) ($Ksp = 10^{-33}$) and Firsching and Mohammadzadel (1986) ($Ksp = 10^{-34.1}$). All of the waters examined plot below both solubility product curves by many orders of magnitude (see text for discussion).

phosphate activities in these waters (especially the high ionic strength alkaline lake waters) and, in particular, the uncertainties in the selection of appropriate solubility products, the calculated individual activity products for these waters are remarkably similar to the solubility products (compare Tables III and IV and Figure 1). Byrne and Kim (1993) demonstrated that the solubility products of aged REE phosphate coprecipitates are lower than the solubility products of fresh precipitates. For example, using radiotracers of the REEs (i.e., ^{144}Ce, ^{152}Eu, ^{153}Gd, and ^{169}Yb), they showed that the solubility products for each REE phosphate decreased with time such that after 20 and 40 days the solubility products were roughly a factor of 2.6 and 1.7 times larger, respectively, than their final 80 day values (Byrne and Kim, 1993). Moreover, activity products determined by summation of the LREEs would result in larger values than the estimates presented in Table V and are likely closer approximations of the effective activity product values. These larger summed activity products values suggest that the alkaline lakes and circumneutral pH groundwaters are all close to saturation with respect to aged REE phosphate precipitates. Consequently, these results provide evidence that REE phosphate precipitates may exert substantial controls on the total dissolved concentrations of the REEs in these natural waters and may limit the maximum dissolved REE concentrations in these waters.

Compared to the calculated activity products and solubility products for the REE phosphate precipitates in these natural waters, the calculated activity products for REE carbonate precipitates (i.e., $\{M_i^{3+}\}^2\{CO_3{}^{2-}\}^3$) are substantially lower than the corresponding solubility products (Tables IV and VI). Figure 2 is a plot of the activities of free Nd^{3+} versus the activities of free $CO_3{}^{2-}$ in these alkaline lakes and circumneutral groundwaters along with the solubility product lines appropriate for $Nd_2(CO_3)_3 \cdot nH_2O$ solubility products of Smith and Martell (1976) and Firsching and Mohammadzadel (1986). Figure 2 demonstrates that all of the waters studied are highly undersaturated (by many orders of magnitude) with respect to REE carbonate precipitates. It is very unlikely that REE carbonate precipitates exert significant controls on dissolved concentrations of the REEs in these natural waters. Instead, high dissolved carbonate ion concentrations in these waters result in elevated concentrations of the REEs (especially the HREEs in the alkaline lakes) due to the formation of strong REE carbonate complexes (Johannesson and Lyons, 1994; Johannesson *et al.*, 1994).

4.2. ACIDIC WATERS OF COLOUR LAKE

Calculated individual activity product values of REE phosphate precipitates in Colour Lake are presented in Table VII. Because Colour Lake is a dilute acidic lake (ionic strength = 0.01 mol/kg; pH = 3.6) where free sulfate ion concentrations are relatively high ($10^{-2.6}$ mol/kg), the importance of REE sulfates precipitates was also examined and calculated individual activity products for REE sulfate precipitates are included in Table VII.

The calculated individual activity products for the REE phosphate precipitates in Colour Lake are substantially lower than the solubility products for these phases (Tables III and VII). The total phosphate concentrations in Colour Lake are low (10.5 nmol/kg, Allan *et al.* (1987)) which in addition to the low pH of the waters, results in extremely low $[PO_4{}^{3-}]_F$ concentrations of approximately 10^{-23} mol/kg. Typically, the $LnPO_4$ activity products are between 6 and 7 orders of magnitude less than the corresponding solubility products for each REE phosphate. Activity products for REE carbonates were not determined because carbonate alkalinity was not detected in the low pH waters of Colour Lake. Considering, however, the total $HCO_3{}^-$ concentration in the lake to be much less than 10^{-4} mol/kg, the $CO_3{}^{2-}$ concentration is certainly smaller than 10^{-11} mol/kg. Consequently, REE carbonate activity products for $Nd_2(CO_3)_3 \cdot nH_2O$ are no greater than 10^{-41}, and Colour Lake is very highly undersaturated with respect to REE carbonate phases. In addition, the activity products for the REE sulfate precipitates are much lower than solubility products for these phases. Although the data are limited, Rard (1990) reports a thermodynamic solubility product value for aqueous $Lu_2(SO_4)_3 \cdot 8H_2O$ of $10^{-9.64}$. The calculated activity products for REE sulfate precipitates in Colour

TABLE VI. Activity products (AP = $\{M^{3+}\}^2\{CO_3^{2-}\}^3$) for light rare earth element carbonates reported as log (AP) in alkaline lakes of the western U.S.A., groundwaters from southern Nevada and Death Valley, California, U.S.A., and groundwaters from the Carnmenellis region of England.

	$\{La^{3+}\}^2\{CO_3^{2-}\}^3$	$\{Ce^{3+}\}^2\{CO_3^{2-}\}^3$	$\{Pr^{3+}\}^2\{CO_3^{2-}\}^3$	$\{Nd^{3+}\}^2\{CO_3^{2-}\}^3$	$\{Sm^{3+}\}^2\{CO_3^{2-}\}^3$
Alkaline Lakes					
Mono[a]	–43.2	–43.1	–45.3	–44.2	–45.6
Abert	–42.0	–41.9	–44.8	–43.9	–45.6
Summer	–38.0	–38.7	–40.8	–40.1	–41.8
Goose	–40.0	–40.8	–43.2	–42.4	–44.3
Walker	–40.3	–40.8	–43.4	–42.9	–44.7
Groundwater, U.S.A.					
Fairbanks	–41.1	–41.2	–43.0	–42.1	–43.9
Jackrabbit	–41.0	–41.0	–43.0	–42.1	–44.0
Texas	–40.3	–40.7	–43.0	–42.1	–44.0
Nevares	–40.4	–40.8	–42.8	–41.9	–43.8
Travertine	–40.2	–40.4	–43.0	–42.1	–44.0
Upper Brier	–39.2	–40.0	–41.3	–40.2	–41.8
Scotty's	–39.7	–30.5	–42.5	–41.6	–43.6
Surprise	–40.2	–40.5	–42.9	–42.1	–43.8
Mesquite	–40.1	–40.7	–42.7	–41.8	–43.7
Well 5C	–42.0	–42.7	–43.2	–43.7	
J-13[b]		–41.7			
J-13[c]		–43.5			
Groundwater, England[d]					
2393	–39.8	–39.1	–40.7	–39.7	–40.9
2376	–38.4	–40.2	–39.9	–38.6	–40.5
2563	–39.6	–41.8	–41.3	–40.1	–41.6

[a] Johannesson and Lyons (1994) average of six samples.

[b] Alkalinity data measured in the field by titration (Harry Reid Center for Environmental Studies, University of Nevada, Las Vegas).

[c] Alkalinity data from Nitsche *et al.* (1992).

[d] From Smedley (1991).

TABLE VII. Activity products for light rare earth element phosphates (AP = $\{M^{3+}\}\{PO_4^{3-}\}$) and sulfates (AP = $\{M^{3+}\}^2\{SO_4^{2-}\}^3$) for acid waters of Colour Lake, N.W.T., Canada, reported as log (AP).

	$\{Ln^{3+}\}\{PO_4^{3-}\}$	$\{Ln^{3+}\}^2\{SO_4^{2-}\}^3$
La	−31.9	−25.1
Ce	−31.6	−24.4
Pr	−32.5	−26.1
Nd	−31.8	−24.8
Sm	−32.3	−25.9

Lake are at least 15 orders of magnitude less than this solubility product. We calculated an activity product of $10^{-28.4}$ for Lu sulfate precipitates in Colour Lake which is approximately 19 orders of magnitude less than the solubility product of Rard (1990) for this phase. Consequently, the Colour Lake waters are substantially undersaturated with respect to REE phosphate, REE carbonate, and REE sulfate precipitates. In contrast to the alkaline lakes and circumneutral pH groundwaters, REEs in Colour Lake are not subject to solubility controls.

5. Conclusions

Our work indicates that similar to the oceans, REE phosphate phases are important in controlling dissolved REE concentrations in neutral to high pH natural terrestrial waters. Because these waters are all substantially undersaturated with respect to REE carbonate precipitates, solubility control by REE carbonate phases is negligible. Our work indicates that elevated carbonate ion concentrations serve only to enhance dissolved REE concentrations in natural waters through formation of dissolved REE carbonate complexes, while elevated phosphate ion concentrations reduce dissolved REE concentrations in natural waters through precipitation of REE phosphate salts.

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