Eh-pH diagrams for the rare earth elements at 25° C and one Bar Pressure

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INTRODUCTION

Rare earth geochemistry has received a great deal of attention for the last fifteen years or so, and use of the abundance and distribution of the rare earths has proven to be a most useful approach to geochemical problems. Rare earth studies in sea waters and in bottom sediments, however, have been primarily limited to analytical studies (PIPER, 1974; ELDERFIELD and GREAVES, 1982, and others). No Eh-pH diagram has been presented previously for the rare earth elements, however, and it is purpose of this communication to provide such diagrams.

The rare earths in solids in the earth's crust are usually present as simple M(III) species. Cerium, however, occurs as both Ce(III) and Ce(IV), while Eu occurs as Eu(II) and Eu(III).

Variation of Eu(II)/Eu(III) has received a great deal of attention to petrogenetic problems, but the Ce(III)/Ce(IV) ratio has received only slight study.

In this paper I will attempt to show that the distribution of the rare earth elements in the ocean environment is easily explainable in terms of simple Eh-pH diagrams, and that empirical data for various REE species can be readily calculated from the literature to supplement the available experimental data.

CALCULATION OF THERMODYNAMIC DATA

Data for many species of the various lanthanides have been given by SCHUMM *et al.* (1973) and are tabulated in Table 1. Unfortunately, the experimental data for M(OH)₃

Table 1. Summary of rare earth elements ΔG_f° (-kcal/mol) data

Element	M ³⁺	M(OH) ₃	M ₂ O ₃	M ₂ (CO ₃) ₃
La	163.4	(305.8)	407.7	750.9
Ce*	160.6	(303.6)	407.8	(744.1)
Pr	162.3	307.1	—	(747.1)
Nd	160.5	(305.2)	411.3	741.4
Sm	159.3	(306.9)	414.6	741.4
Eu**	137.2	285.5	372.2	(697.3)
Gd	158.	(306.9)	—	(738.9)
Tb	155.8	(303.4)	—	(734.5)
Dy	159.	(307.2)	423.4	739.3
Ho	161.0	(310.1)	428.1	(744.9)
Er	159.9	(309.5)	432.3	(742.7)
Tm	158.2	(307.8)	428.9	(739.3)
Yb	153.9	(303.9)	412.6	729.1
Lu	150.	(300.3)	427.6	(722.9)
Y	165.8	308.6	434.2	752.4

Data in parentheses ( ) calculated; other data from SCHUMM *et al.* (1973), and SMITH and MARTELL (1976). * ΔG_f° for Ce⁴⁺ = -120.44 kcal/mol; ΔG_f° for CeO₂ = -244.9 kcal/mol (SCHUMM *et al.*, 1973). ** ΔG_f° for Eu²⁺ = -129.1 kcal/mol (SCHUMM *et al.*, 1973).

and $M_2(CO_3)_3$ species are available for only a few of the lanthanides, and it is necessary to calculate the values for the others.

Solubility data for many of the lanthanides are given in BAES and MESMER (1976). These are tabulated in Table 2. For reactions of the type:

the ΔG_f° for $M(OH)_3$ can be calculated from knowledge of the ΔG_f° values for M^{3+} and H_2O and ΔG_R° (calculated from K values). This

the ΔG_R° can be calculated for La, Nd and Sm as +45.2, +44.6 and +43.9 kcal/mol, respectively. Now from the data for other lanthanide M^{3+} species and an average $\Delta G_R^\circ = +44.5$ kcal/mol, the ΔG_f° values for the remaining $M_2(CO_3)_3$ lanthanides can be calculated. An estimate of the accuracy of this empirical method can be obtained by comparing the ΔG_f° values for $M_2(CO_3)_3$ determined experimentally with those calculated. The values are

Table 2. Solubility data for $M(OH)_3$ rare earth elements

Lanthanide	$\log K_{s10}^*$	$\Delta G_f^\circ (M(OH)_3)$ (–kcal/mol)
La	20.3	305.8
Ce	19.9	303.6
Pr	19.5	305.8
Nd	18.6	305.2
Sm	16.5	306.9
Eu	17.5	283.4
Gd	15.6	306.8
Tb	16.5	303.4
Dy	15.9	307.4
Ho	15.4	310.1
Er	15.0	309.5
Tm	15.0	307.8
Yb	14.7	303.9
Lu	14.5	300.3
Y	17.5	312.0

*Data for K_{s10} (solubility product constant) values from BAES and MESMER (1976). See text for details of calculation of ΔG_f° values for $M(OH)_3$.

has been done for all the lanthanides, and the data for all but $Eu(OH)_3$, $Pr(OH)_3$, and $Y(OH)_3$ are given in Table 1. An estimate of the accuracy of the calculated values can be obtained by comparing the calculated *versus* experimental values for the hydroxides of Pr, Eu and Y (ΔG_f° in kcal/mol); these are: Pr: –307.1 (exp.) *vs.* –305.8 (calc.); Eu: –285.5 (exp.) *vs.* –283.4 (calc.); and Y: –308.6 (exp.) *vs.* –307.6 (calc.). These comparisons indicate that the calculated value is within 1 – 1.5 kcal of the experimental values.

For $M_2(CO_3)_3$ values a different approach is used. For the reaction:

(in kcal/mol): La: –750.9 (exp.) *vs.* –749.7 (calc.); Nd: –744.5 (exp.) *vs.* –743.9 (calc.); Sm: –741.4 (exp.) *vs.* –741.5 (calc.); and Y: –752.4 (exp.) *vs.* –754.2 (calc.); Dy: –739.3 (exp.) *vs.* –740.2 (calc.); Yb: –729.1 (exp.) *vs.* –730.1 (calc.). This indicates that the calculated values are different from the experimentally determined values by less than 2 μ kcal in all instances.

The importance of the estimated $M(OH)_3$ and $M_2(CO_3)_3$ data (Table 1) is that these values are, in all likelihood, within 1–2 μ kcal of the true values and can thus be used for construction of Eh-pH diagrams and for other

general purposes where such estimated data must be used in the absence of experimentally determined data.

CALCULATION OF THE Eh-pH DIAGRAMS

Standard methods have been used for the calculation of Eh-pH diagrams for the lanthanides (See GARRELS and CHRIST, 1965; VERINK, 1979; BROOKINS, 1980). The diagrams for Eu and Ce species involve both Eh and pH as variables while pH is the only variable for the remaining lanthanides. The diagrams are shown as Figs. 1–15. It is important to note that in all diagrams M^{3+} ion is used instead of hydrolysis products. BROOKINS (unpub.) has shown

Figs. 1–15 Eh-pH diagrams for yttrium and the rare earth elements at 25°C and one bar pressure. Activities of ions are: M^{2+} , M^{3+} , M^{4+} , $= 10^{-6}$, $\Sigma CO_2 = {}^aH_2CO_3 + {}^aHCO_3^- + {}^aCO_3^{2-} = 10^{-3}$.

that $M(OH)^{2+}$, $M(OH)_2^+$ and other species are important for very low pH values (i.e. less than 2.5–3.0), but in the range of 6–10, M^{3+} ion predominates. Similarly, the simple $M(OH)_3$ hydroxides as opposed to the sesquioxides (M_2O_3) are the species that form under natural conditions.

For the trivalent rare earth elements, the activity of M^{3+} is taken as 10^{-6} . Activity of dissolved CO_2 is taken as 10^{-3} because this is a reasonable value for many crustal waters.

DISCUSSION AND CONCLUSIONS

The REE are depleted in sea water (PIPER, 1974) owing to the extreme insolubility of $M(OH)_3$ compounds and, for Ce, insolubility of CeO_2 . Yet Ce is much more depleted than the other REE in most sea water which, if considered just in light of solubility product constants, should not necessarily be the case.

ELDERFIELD and GREAVES (1982) have also shown that Ce is highly depleted in most ocean waters relative to the other REE, which they attribute to the probable oxidation of Ce(III) to Ce(IV) with removal as CeO_2 . The diagram presented here (Fig. 3) clearly supports this interpretation, although the diagrams for the REE (Figs. 2–14) fail to provide any information for the relative enrichment of surface waters in the REE relative to deeper waters (See discussion in ELDERFIELD and GREAVES, 1982). Further, their work also shows a lack of correlation with the REE with either P or Si. This is important since P-ligands as transporting agents for the REE (as $M_2P_2O_7^{2-}$?) have been discussed by the writer (BROOKINS, 1980) that may compete with the simple M^{3+} ions for typical ocean water P concentrations. Yet total P increases from surface waters with depth while total REE decrease, which suggests that P-ligands are not the prime species responsible for the REE behavior (See also ELDERFIELD and GREAVES, 1982). Surface water enrichment in colloids, organic life, amorphous coatings, or other factors may be responsible for the difference in between surface water and deeper

water (ELDERFIELD and GREAVES, 1982).

Inspection of the Eh-pH diagram for Ce relative to the other REE shows that the boundary between Ce^{3+} and CeO_2 effectively reduces the Eh-pH limits of Ce^{3+} relative to other M^{3+} -REE species. Very simply, this means that any Ce^{3+} available from weathering or any other source will be oxidized to Ce(IV) and removed as CeO_2 , over virtually any slight pH shift, whereas M(III) REE removal is restricted to pH values of about 7.5 and higher. The field for $M_2(CO_3)_3$ is important for the REE as it argues for REE removal at pH values less than that indicated by the simple M^{3+} ; $M(OH)_3$ boundary. The REE are commonly described as precipitating in oxide-hydroxide phases on the sea floor bottom, but the data and diagrams presented here suggest the possibility of incorporation into carbonate phases as well.

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