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Separation of Lanthanide Series Elements in Marine Fe-Mn Crusts by Ion-Exchange Chromatography and Determination by ICP/AES

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Abstract

A method is described for the separation of lanthanide series elements (REE) from major matrix components of deep-sea ferromanganese crusts using cation-exchange chromatography. The samples are digested in concentrated mineral acids, evaporated to near dryness, and redissolved in 0.5 *N* HCl. Solutions are passed through Bio-Rad AG50W-X8 strong cation-exchange resin in the H^+ form. Major (Fe and Mn) and minor constituents (Al, Co, Cu, Ni, Ca, and Mg) are eluted with 1.7 or 2.0 *N* HCl; the REE are then eluted from the resin with 4.0 or 6.0 *N* HCl. Only Ba is not separated and coelutes from the resin with the REE. The method quantitatively separates the lanthanides from most matrix constituents and greatly facilitates their rapid sequential analysis by ICP/AES. The method has been shown to yield accurate and precise analyses of ferromanganese minerals for their REE content in the U.S. Geological Survey standard Fe-Mn nodule A-1 and has been applied to Fe-Mn crusts from our collection.

INTRODUCTION

The analysis of lanthanide series or rare earth elements (REE) in geologic materials has received considerable attention due to the utility of this coherent group of elements in petrogenetic studies of igneous systems and sedimentary deposits (*1*). Concentrations and fractionation patterns of REE in marine ferromanganese nodules, underlying sediments and, more recently, seawater have been widely used to infer processes governing the formation, abundance, and distribution of Fe-Mn deposits on the seafloor (*2–12*).

Geological studies of the REE, often present as trace elements in natural samples, require their accurate and precise determination (*1, 13*). Direct instrumental analysis of the REE in geologic materials without prior separation from major matrix constitutents is often plagued with poor sensitivities or interelement interferences which require tedious calculations to correct for spectral overlap. Analytical difficulties arise primarily from the low concentrations of REE in common geologic materials relative to the principal components of the matrix. Methods that minimize these problems have been described in the literature (*13–26*) and are generally based on combinations of ion-exchange or liquid chromatography with atomic, ICP/mass, mass, or x-ray spectrometry. Neutron activation analysis (*27*) and isotope dilution mass spectrometry (*28*) also yield reliable results, but both methods are expensive, time consuming, and also require chemical separations prior to analysis.

Analytical procedures for REE in geologic materials are typically characterized by matrix dissolution in concentrated mineral acids followed by cation- and/or anion-exchange chromatographic group separations. Gradient elution with HCl and/or HNO_3 is commonly used to separate major constituents from the REE (*13, 20, 21, 24, 26*), but mixed solvents have also been successfully applied (*29, 30*). Techniques described in the literature have usually been developed for specific matrices (siliceous rocks such as basalts and granites and/or sediments, monazite and uranium ores, or alloys) and often require modifications before they can be applied to other samples with significantly different compositions; furthermore, not all methods report the determination of all the lanthanides. Because the REE are present in relatively high concentrations in marine Fe-Mn deposits, Fries and Lamothe described a method for the direct determination of the REE in manganese nodules by ICP/AES after digestion with mineral acids (*31*).

A method combining a closed-system single-column cation-exchange chromatographic separation followed by inductively coupled plasma atomic emission spectrometry (ICP/AES) has been applied to the determination of La and 13 REE in marine Fe-Mn crusts. The technique provides a quantitative separation from the major constituents in these deposits, and permits reliable analysis of a few hundred milligrams of iron- and manganese-rich oxides for their REE content.

EXPERIMENTAL SECTION

Apparatus and Equipment

Sample dissolutions were carried out in a Toshiba ERS-8620 household microwave oven by using CEM Corporation (Matthews, North Carolina) digestion vessels and/or Teflon HP beakers on a hot plate. A Millipore vacuum filtration apparatus was used to separate insoluble residues from the digested solutions. Ion-exchange separations were performed in closed systems (Fig. 1) consisting of 57 mL capacity columns (11 mm i.d. × 600 mm) prepared in our laboratory equipped with a Teflon sample/solvent delivery system modified after Kingston et al. (*32*). A Leeman Labs (Lowell, Massachusetts) Plasma Spec I ICP/AES system operated in the rapid-sequential mode was employed for elemental analyses. Operating conditions and analytical wavelengths employed for atomic emission measurements are presented in Table 1.

Reagents

Analytical reagent-grade mineral acids were used for sample dissolutions and eluent preparation. Aqueous solutions were prepared with water purified in a Barnstead glass still followed by a 5-cartridge Nanopure ion-exchange and particulate removal system. Resistivity of the distilled deionized (dd) water was always greater than 15 MΩcm. Standard multielement REE solutions were prepared by dilution of 10 mg/mL single-element Plasma-Pure standards from Leeman Labs. The standards are certified to contain less than 0.1 mg/L of other REE and elements commonly encountered as matrix components in geologic materials.

Cation-exchange columns were prepared with a 35-mL bed of Bio-Rad AG50W-X8 resin (100–200 mesh) in the H^+ form prequilibrated in 1 *N* HCl. The columns were stripped of residual metals with 200 mL 4 *N* HCl and rinsed with 75 mL 1 *N* HCl immediately prior to the loading of samples.

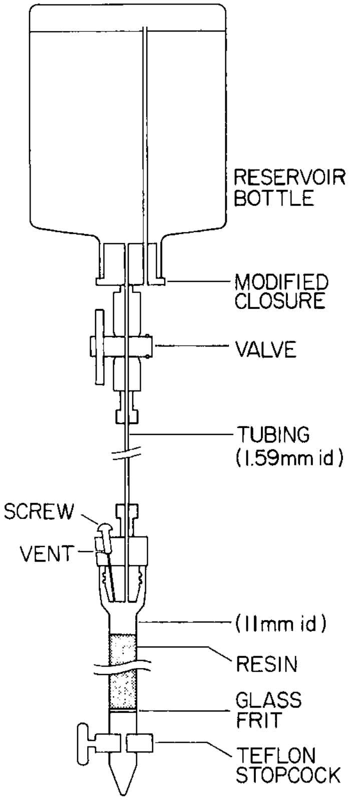

FIG. 1. Apparatus used for delivery of sample and eluents at a controlled rate to resin; the system is modified after Kingston et al. (*32*). Column height is 700 mm and contains 35 mL (wet) Bio-Rad AG50W-X8 (100–200 mesh) resin in the H^+ form. Reservoir can be interchanged to provide a variable capacity of 100 to 1000 mL.

Analytical Procedure

A Fe-Mn-rich solution was prepared from laboratory reagents and standards to simulate the solution resulting from the digestion of approximately 300 mg of an average Hawaiian Archipelago Fe-Mn crust (*11*). The solid phase composition of an average Hawaiian crust, the desired model simulated crust composition, and actual metal concentrations (determined by ICP/AES analysis) in the test solution are given in Table 2.

TABLE 1
Analytical Operating Conditions

Power:	0.98 kW
Coolant flow rte:	14.5 L/min
Nebulizer flow:	0.4 L/min
Auxiliary flow:	None
Integrations:	3 X 3 s

Element	Wavelength (nm)
La	379.48
Ce	418.66
Pr	410.09
Nd	430.36
Sm	442.43
Eu	368.84
Gd	342.25
Tb	350.92
Dy	353.17
Ho	345.60
Er	390.63
Tm	346.22
Yb	369.42
Lu	261.54

TABLE 2
Composition of Crusts and Test Solution

	Hawaiian Crust[a]	Synthetic crust[b]	Test solution[c]
Fe	15.6	20.0	2440
Mn	23.3	20.0	2380
Co	0.90	1.0	120
Cu	0.06	0.5	60.4
Ni	0.44	1.0	118
Al	1.15	3.0	332
Ca	2.38	2.0	232
Mg	1.19	1.0	130
Ba	0.18	0.5	60
REE[d]	Variable	0.05	6.0

[a] Concentrations in dry weight percent for average Hawaiian Archipelago crust after De Carlo et al (*11*).

[b] Concentrations in dry weight percent selected to simulate the average composition of Pacific Ocean crusts.

[c] Concentrations in mg/L of test solution loaded on columns; determined by ICP/AES analysis.

[d] Concentration of 14 lanthanide elements.

Reagent-grade Fe and Mn chloride salts were dissolved in dilute mineral acids and single element standards (Fisher Scientific, Tustin, California) added in approximate amounts to yield the desired composition. The high-purity REE standards were added to result in a final solution concentration of 6 mg/L of each REE. The mixture was reduced on a hot plate to drive off HNO_3 and diluted to volume in 0.5 *N* HCl.

Pacific Ocean Fe-Mn crusts from our collection were ground to pass through 100 mesh standard U.S. sieves and stored in glass vials until needed. Samples were dried at 110°C for a minimum of 24 h, cooled in a desiccator, and weighed to the nearest 0.1 mg prior to dissolution. Splits (~150–300 mg) of Fe-Mn crusts were placed in microwave digestion vessels and 5 mL of 1:1 aqua regia added, or placed in Teflon HP beakers and 20 mL aqua regia added. The microwave bombs were sealed in plastic bags, placed in the microwave oven, and full power applied for 30–45 s. After a cooling period, samples were transferred to Teflon HP beakers and treated as described below. Samples in open vessels were covered with a ribbed watch glass, digested over medium heat to near dryness, and 10 mL concentrated HCl added carefully; digestion was continued until the Fe-Mn oxides were completely dissolved. Samples were again taken to near-dryness and 5 mL of 4 *N* HCl added. They were allowed to cool, filtered through 0.22 μm membranes to remove any remaining undissolved aluminosilicates, and rinsed with a small amount of dd water. Samples were then transferred to glass beakers and diluted to yield 30–50 mL of solution 0.5 *N* in HCl. No noticeable difference was observed in the efficacy of either digestion procedure, although the microwave technique consumes less reagent and requires less time. Splits (approximately 200 mg) of the U.S. Geological Survey standard nodule A-1 (USGS A-1) were treated in an analogous manner.

Thirty-milliliter aliquots of the test solution were loaded on the ion-exchange columns at a flow rate of 1–1.5 mL/min. Matrix constituents of the test solutions were eluted from the column with 1.7 or 2.0 *N* HCl. The volumes of eluent used in each separation scheme are given in Table 3. Eluate fractions (~25 mL) were collected and stored for ICP/AES analysis. The REE were eluted with 4 or 6 *N* HCl and 25 mL fractions also collected as above. Three replicate separations of the elements in the test solution were carried out by using each elution sequence. Because three columns were used in this study, a single replicate of the test solution was also separated by the first scheme on each column to ascertain the reproducibility of separations on the different columns.

Chromatograms were derived by plotting relative emission intensities (obtained by ICP/AES analysis) versus cumulative fraction volume.

TABLE 3
Chromatographic Conditions

Procedure	Eluent	Volume (mL)
1	1.7 *N* HCl	400
	4.0 *N* HCl	500
2a	2.0 *N* HCl	300
	6.0 *N* HCl	200
2b	2.0 *N* HCl	275
	6.0 *N* HCl	375

Emission intensities were ratioed to those obtained by direct analysis of the major constituents in the test solution and reported as recovered percentage of original; a pure mixed-REE standard containing equivalent amounts of each element loaded on the columns was also analyzed by ICP/AES and emission intensity ratios calculated as above. Overall recovery of the REE from the test solution was evaluated by dividing the cumulative ICP/AES emission intensity for all fractions by the intensity of each REE in the mixed-REE standard.

Digested samples of a reference material (USGS A-1) and selected crust samples were loaded on the columns as described above. Eluates from the loading step and the 1.7 *N* HCl fraction were combined in a 500-mL Erlenmeyer flask for subsequent major element analysis. The REE fraction (4 *N* HCl) was eluted into a 500-mL flask, reduced on a hot plate to near dryness, redissolved in a small amount of 4 *N* HCl, filtered, and volumetrically diluted to 10 or 25 mL with 0.5 *N* HCl. Solutions were transferred to Nalgene vials and stored at 4°C until analyzed by ICP/AES. The recovery of REE from USGS nodules A-1 was evaluated by comparison of our analytical results with those published elsewhere (*31, 33–36*).

RESULTS AND DISCUSSION

Procedure 1

The elution behavior of Fe, Mn, Al, Co, Cu, Ni, Ca, Mg, and Ba is presented in the chromatograms of Fig. 2(A). Copper and Fe are the first transition metal cations to elute (after 50 mL) and are completely stripped from the column with 125 mL of 1.7 *N* HCl. The other transition metal ions (Co, Fe, Mn, and Ni) exhibit a slightly greater retention and coelute quantitatively with 150 mL of 1.7 *N* HCl. Aluminum elutes after the transition metals from 150–250 mL.

Three alkaline earths (Mg, Ca, Ba) were also studied. Magnesium coelutes with the transition metals for 75–125 mL. Retention of the other alkaline earth cations increases with atomic number; Ca elutes as a band between 150 and 275 mL of 1.7 *N* HCl, whereas Ba is only stripped after 225 mL of 4 *N* HCl and coelutes with the light REE. The elution behavior of Ca, which is completely separated from the REE in this study, is closer to that described by Strelow and Jackson (*14*) than others (*20*). This is to be expected as Procedure 1 resembles the former scheme more than the other reported methods. Crock et al. (*20*) obtained similar separation trends with HCl, although their retention volumes are considerably different. In a more recent method using a mixed HCl/HNO_3 elution, Crock et al. (*26*) observed a slight tailing of Ca into the REE fraction.

Representative chromatograms of the REE from Procedure 1 are shown in Fig. 2(B). The REE are eluted from the column in order of decreasing atomic number. Lutetium, Yb, and Tm coelute between 50 and 75 mL of 4 *N* HCl, with the latter exhibiting a significantly higher concentration in the 75-mL fraction than the former two. These elements are followed by Er and Ho which also begin to elute after 50 mL but require 100 and 125 mL, respectively, to completely strip from the column. Dysprosium displays a slightly broader band, begins to elute with Er and Ho, but exhibits nearly equal concentrations in the 75 and 100 mL fractions. Terbium elutes predominantly with Dy but tails (<5% of total) into the 150 mL fraction The elution of Gd occurs from 75 to 175 mL of 4 *N* HCl eluent. A broad peak is observed for Eu with its first appearance occurring after 75 mL and continuing to 225 mL. The elution behavior of Sm is nearly identical to that of Eu. From Nd through La the peak width increases progressively, and the onset of elution occurs over a greater volume of acid. Neodymium elution is observed between 100–250 mL, whereas that of Pr appears to begin earlier and occurs over a larger volume (50–300 mL). A slightly narrower band is seen for Ce (125–325 mL) relative to Nd and Pr. Lanthanum is the last REE stripped from the column (125–400 mL) and displays the greatest tailing. Under the conditions described above, complete elution of the REE is achieved with 400 mL of 4 *N* HCl; the additional 100 mL of eluent used in this scheme are apparently not required.

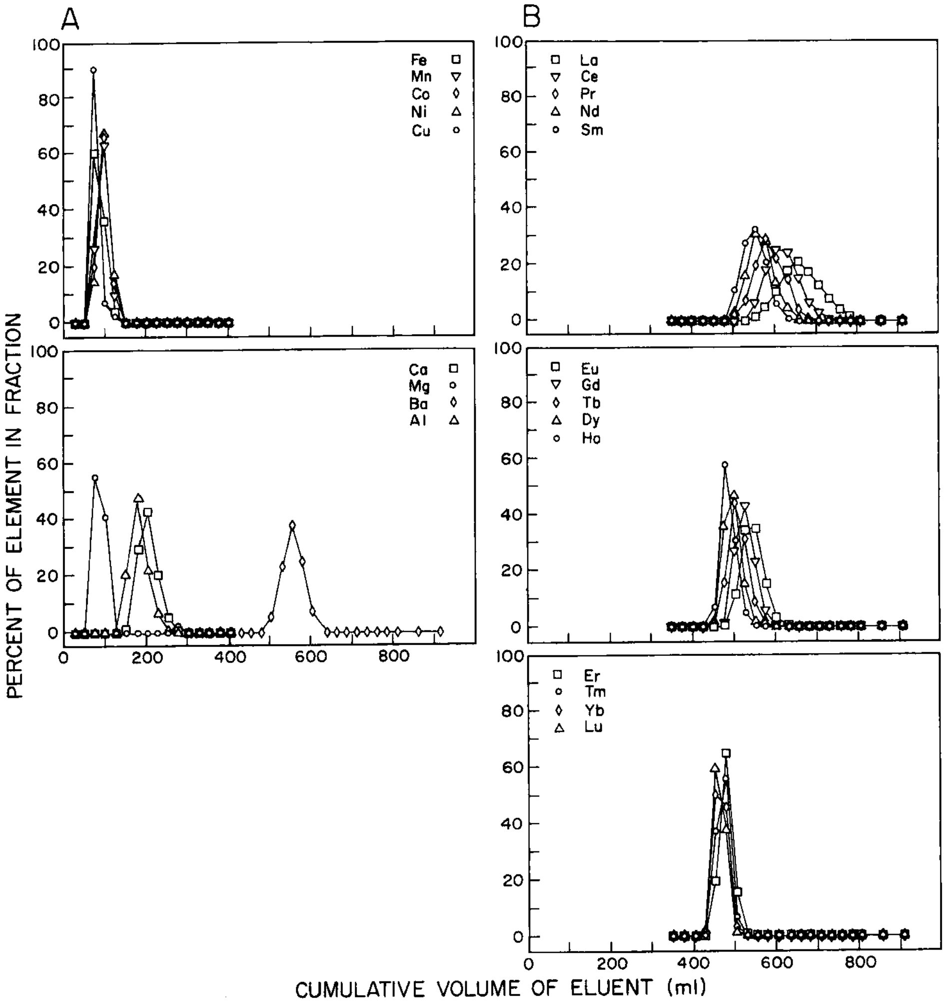

FIG. 2. Chromatogram obtained by elution with 400 mL of 1.7 *N* HCl followed by 500 mL of 4 *N* HCl. Curves represent relative recovery of each element in individual fractions as a function of cumulative volume of eluent in milliliters. (A) Aluminum, alkaline earths, and transition metal ions. (B) Lanthanide series elements.

Procedure 2

The general behavior of the transition metals shown in Fig. 3(A) is quite similar to that observed in Procedure 1. The first two metals (Cu and Fe) to elute from the column with 2 *N* HCl appear in the 50-mL fraction and only trace amounts are found in the 100-mL fraction. The other transition metals, Co, Mn, and Ni, coelute from 75 to 100 mL. Aluminum is found from 100 to 200 mL, and displays a broader elution peak than the transition metals.

The elution of Mg from the column coincides with that of Co, Mn, and Ni within the resolution of our methods. However, only traces of Mg appear in the 50-mL fraction and the majority elutes in the 100-mL fraction. This indicates that Mg is more strongly retained on AG50W-X8 resin in 2 *N* HCl than Co, Mn, or Ni. Calcium elution occurs from 125 to 250 mL of 2 *N* HCl, whereas Ba only elutes between 100 and 225 mL of 6 *N* HCl (375–500 mL total volume).

The behavior observed in Procedure 2 is generally consistent with the distribution coefficients (K_d) in 2 *N* HCl published by Strelow et al. (*38*), which predict the elution order: Cu(II) > Fe(III) > Mn(II) = Mg(II) = Co(II) > Ni(II) ≫ Ca(II) = Al(III) > Sr(II) ≫ Ba(II). The only exceptions to the predicted behavior are the slightly greater retention of Mg than Co and Ni and the onset of elution of Al 25 mL prior to Ca. This Al elution sequence is also observed with 1.7 *N* HCl and suggests that the Al K_d is slightly lower than that of Ca. As predicted by theory, elution of all cations is more readily achieved with 2.0 *N* HCl than with 1.7 *N* HCl and requires less (≈25–50 mL) eluent.

A chromatogram of the REE elution is presented in Fig. 3(B). As observed for the major constituents of the test solution, elution of the REE also requires less acid. The use of 300 mL of 2 *N* HCl followed by 200 mL of 6 *N* HCl was initially evaluated for the separation of REE from major constituents. Low but significant quantities of Lu appeared in the last fraction of the 2 *N* HCl eluent, suggesting that a reduced volume of this eluent should be used to prevent a premature removal of Lu from the column; additionally, quantitative recovery of La and Ce could not be achieved with 200 mL of 6 *N* HCl. Subsequent separations employed 275 mL of 2 *N* HCl and 375 mL of 6 *N* HCl.

The elution order of the REE in 6 *N* HCl is identical to the previous procedure (4 *N* HCl) but results in compression of the chromatogram (Fig. 3). Lanthanum and Ce, which were not quantitatively recovered with the procedure employing 300 mL of 2 *N* HCl/200 mL of 6 *N* HCl, are completely stripped from the column after 275 and 325 mL of 6 *N* HCl, respectively.

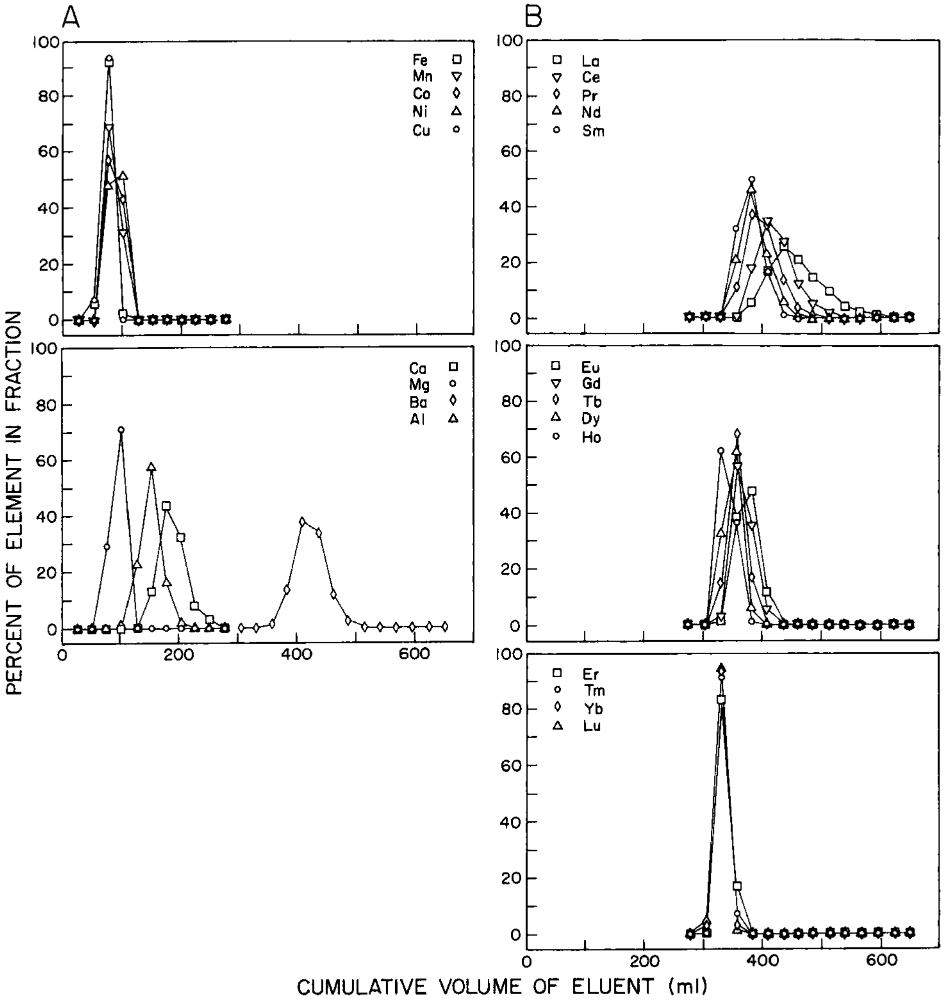

FIG. 3. Chromatogram obtained by elution with 275 mL of 2 *N* HCl followed by 375 mL of 6 *N* HCl. Curves represent relative recovery of each element in individual fractions as a function of cumulative volume of eluent in milliliters. (A) Aluminum, alkaline earths, and transition metal ions. (B) Lanthanide series elements.

The last 50 mL of eluent are apparently not necessary, hence elution may be terminated after 325 mL.

The elution order observed for the REE can be attributed to periodic trends. It is well know that ionic size decreases with increasing atomic number within a row of the periodic table. For the trivalent REE a gradual contraction of the 4f subshell leads to slight differences in chemical properties as a function of atomic number, and is particularly reflected in the stability of their aqueous complexes. Recent studies have shown that the heavy REE form significantly stronger oxalate and carbonate complexes than the intermediate and light REE (*37*, and references therein). Thus a greater tendency of the heavy REE to form chloro complexes leads to the variations in K_d with increasing atomic number observed on AG50W-X8 in HCl media.

Both procedures evaluated in this study lead to the complete separation of Ca from the REE not achieved by Crock et al. (*20*). One must bear in mind that a complete separation of alkaline earth cations (Mg, Ca, Sr, Ba) from the REE was achieved by Strelow and Jackson using HNO_3 but that under such conditions Fe coeluted with the REE. The methods described herein quantitatively separate all metals tested except Ba, which remains in the REE fraction. In samples composed primarily of Fe and Mn oxides and small amounts of carbonate fluorapatite, separation of the REE from Fe is more desirable than separation from Ba. Barium is generally present at concentrations well below 0.5% w/w in the deep-sea Fe-Mn crusts; thus it is less likely to cause spectral interferences than Fe. The combined volume of eluent required for our separations are 900 and 600 mL for Procedures 1 and 2, respectively. Although this is considerably larger than used in mixed HNO_3 and HCl separation schemes (e.g., Ref. *26*), a cleaner separation from potential interferents in the ICP/AES analysis is achieved. Separation of the REE from Ca is particularly important because of the likelihood of spectral overlap with some of the REE lines (La, Lu, Nd, Sm, Tm, and Yb) used in this study. The separation sequence employing the more concentrated acids (2 and 6 *N*) seems preferable because the decreased volumes of eluents result in a time saving of nearly 2 h. In samples containing large quantities of calcite or apatite it is possible that Ca will tail into the REE fraction when using the 2 *N*/6 *N* HCl procedure. This has been noted previously by Zachmann (*25*) and Crock et al. (*26*); hence a combination of the weak (1.7 *N* HCl) elution from the longer first separation procedure and elution of the REE with 325 mL 6 *N* HCl is suggested for such samples.

Recovery of REE from Reference Materials

A comparison of the concentrations of the REE is USGS nodule A-1 determined in our laboratory and other published values is presented in Table 4. A generally good agreement exists between all laboratories; the standard deviation of the interlaboratory mean is less than 10% for Ce, Pr, Nd, Gd, Dy, Tm, and Lu; it is between 11 and 14% for La, Sm, Eu, Ho, Er, and Yb. Only Tb exhibits a large standard deviation (32%) which is, however, based upon only three determinations. Overall, the REE concentrations determined in this work are within 10% of the interlaboratory mean except for Tb (32%) and to a lesser extent Ho (18% deviation). Our value for Tb is considerably lower than that reported by Flanagan and Gottfried (*33*) by neutron activation and by Rankin and Glasby (*35*) by mass spectrometry. It deviates by 32% from the mean of the three reported values; it is probable that our determination is the least accurate and is a result of determination near the limit of quantitation of our spectrometer. A similar argument can be used for Ho (18% deviation from interlaboratory mean); the analyzed solution concentrations of these two elements were approximately 15 and 24 μg/L, respectively. Lutetium, although present at the lowest concentration of all REE in Fe-Mn deposits, does not suffer from the above problem since it, as well as Yb, has detection limits on the Leeman ICP/AES system well below the concentrations in the analyzed solutions. The REE concentrations determined in our laboratory appear to fall randomly within the range defined by all reported values (except Tb and Ho which are odd atomic number REE present at very low concentrations and for which no emission lines of greater sensitivity are available on our ICP/AES systems).

Precision of duplicate determinations of the REE in nodule A-1 are below 5% relative except for Eu and Lu (8.5%), Er (13%), and Tm (20%). Day-to-day reproducibility of analysis by ICP/AES is below 10% for all REE except Pr (17%); the latter is due to the use of a week emission line near stronger lines of other, more abundant REE.

Preliminary studies indicated that spectral interferences can still arise even after separation of the REE from major matrix constitutents. Initial Eu determinations resulted in low values compared to those found by other investigators; this had been attributed to an unidentified interference at the wavelength employed for the determination, but further analyses revealed that background correction had been applied incorrectly and overlapped with another REE emission line. Subsequent re-

TABLE 4
Interlaboratory Comparison of REE in USGS Nodule A-1[a]

Element	(1)	(2)	(3)	(4)	(5)	(6)	Average
La	115	112	133	130	93	104	114 ± 15
Ce	682	676	668	<300	620	760	681 ± 51
Pr	23.2	—	—	23	—	<30	23.1 ± 0.1
Nd	102	105	85.3	94	93	81	93.4 ± 9.3
Sm	—	24.7	20.9	21	22.0	18	21.3 ± 2.4
Eu	4.8	6.1	4.48	4.8	5.0	4.3	4.9 ± 0.6
Gd	24.9	23.6	26.5	22	26.0	29	25.3 ± 2.4
Tb	2.5	—	4.87	3.7	—	<10	3.7 ± 1.2
Dy	22.1	22.4	—	22	26.0	20	22.5 ± 2.2
Ho	4.2	4.7	—	5.3	—	5.8	5.0 ± 0.7
Er	12.1	14.4	—	15	11.7	14.6	13.6 ± 1.5
Tm	1.6	—	1.72	—	—	<5	1.7 ± 0.1
Yb	12.2	11.8	16.3	13.5	12.0	13.2	13.1 ± 1.7
Lu	2.0	1.92	2.16	—	2.56	2.8	2.3 ± 0.4

[a] All concentrations reported in μg/g in the original nodule. Column identifications:

(1) This work.
(2) ICP/AES values reported by Ingri and Ponter (*34*).
(3) INAA values reported in Flanagan and Gottfried (*33*).
(4) Spark source MS values reported by Rankin and Glasby (*35*).
(5) ICP/AES values by Govindaraju (*36*), Geostandards Laboratory, Nancy, France.
(6) Direct analysis results reported by Fries and Lamothe (*31*).

analysis of the A-1 solutions under the appropriate conditions resulted in a Eu concentration of 4.8 μg/g, in agreement with others (Table 4). Although we are readily able to determine Sm in synthetic solutions, we have been unable to obtain reliable values for this element in natural samples. This also appears to be due to an unidentified, yet inconsistent, spectral interference at the chosen wavelength. It may result from another constituent of the nodule matrix that is not completely separated by the ion-exchange procedures and which is not compensated for by standardization with a pure mixed REE solution. Attempts to identify a suitable interference-free wavelength for Sm have been unsuccessful to date.

The above results suggest that a quantitative recovery of the REE from the reference material is achieved by using our separation procedure and that our ICP/AES analysis results in reliable determinations of the REE in marine Fe-Mn deposits. Although the direct determination of the REE in USGS nodules reported by Fries et al. (*31*) generally yields reliable results for most elements, it is also a labor-intensive method and indicates that separation of the REE prior to analysis is still recommended for accurate and precise determinations. The long digestion procedures employed in the former method, the complex interelement interference correction calculations undertaken to account for spectral overlap of major constituents (and other REE) on individual REE emission lines, and the fact that several REE (Pr, Tb, Tm) are below their limit of quantitation whereas others (Sm, Dy, Ho, and Lu) are only determined with relative precisions of 11 to 25% all support this contention.

An important implication of our studies is that the bulk of the REE in marine Fe-Mn deposits is contained within the Fe-Mn phase of the sample (and other material, such as apatite and calcite, which is readily solubilized with HCl and HNO_3). Because the aqua-regia digestion used for the USGS standard and our crusts does not quantitatively attack the aluminosilicates which are also present in the samples, it is reasonable to assume that detrital aluminosilicates, which generally constitute only a small part of our samples, contain a negligible fraction of the REE.

Analysis of Deep-Sea Fe-Mn Crusts

A thick (~8 cm) Fe-Mn crust dredged from Schumann Seamount in the exclusive economic zone (EEZ) of the Hawaiian Archipelago was subsampled into layers as part of a geochemical study of marine Fe-Mn deposits. Results of the REE determinations in selected layers within this crust are shown as shale-normalized REE abundance patterns in Fig. 4; the shale normalized pattern for the USGS A-1 nodule is also included for comparison. Normalization to shales is a common procedure (in the geosciences) which eliminates the natural even/odd atomic number variations in abundances of the REE in geologic materials and readily allows the identification of unusual features in the REE pattern of investigated samples. Typical features commonly observed in hydrogenous marine Fe-Mn deposits include a positive Ce anomaly which results from the oxidative scavenging of Ce^{3+} to Ce^{4+} onto MnO_2 and a smaller positive Gd anomaly. The significance of such features are described elsewhere (*12*).

CONCLUSIONS

The separation methods described in this paper provide the means to quantitatively separate major constituents in marine Fe-Mn mineral

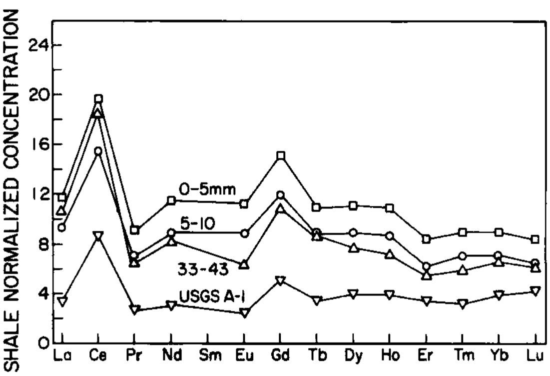

FIG. 4. Shale normalized concentrations of REE in marine Fe-Mn deposits including USGS A-1 and various layers from a thick crust, RD50-S1B, recovered from Schumann Seamount in the Hawaiian EEZ. Depth intervals of layers are expressed in millimeters from the outer surface of the sample.

deposits from the lanthanide series elements. Minor (<2% w/w) amounts of Ca and Mg present in crusts and nodules are also quantitatively separated from the REE, although it is possible that some tailing of Ca into the REE fraction will occur in crusts containing elevated concentrations of Ca (*25*) by using the more concentrated eluent separation. Barium is not separated and coelutes with the light REE. The concentration of Ba commonly found in marine Fe-Mn deposits is sufficiently low (<0.5% w/w) so as not to cause significant spectral interferences in the determination of the REE by ICP/AES. Quantitative recovery of all lanthanides is achieved by using both procedures.

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