

Determination of Lanthanides in Soil and Sediment Reference Samples by ICP-MS: Comparison of Fusion and Acid Digestion Methods

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INTRODUCTION

There are 15 rare earth elements (REEs) with atomic numbers from 57 through 71 of which one element, promethium (Pm), is radioactive and does not exist in nature. REEs are found in many soils in concentrations of up to tens of parts per million with organic soils usually richer in lanthanides than mineral soils (1). Traditionally, REEs are divided into two sub groups: light rare earth elements (LREEs) from La to Eu and heavy rare earth elements (HREEs) from Gd to Lu (2-3).

Soil erosion is a global environmental problem which is often easy to observe but hard to measure. One monitoring technique is tagging of soil with tracers. The REE oxides have been successfully used as a multi-sediment tracers (4-6). REEs have also been used to explain many geochemical processes in the environment, such as natural surface weathering processes, origin of some sediments, identification of anthropogenic impact, and palaeo-environmental and palaeo-oceanic changes (3, 7-15). The importance of REEs in geochemistry for modelling the earth's crustal and mantle evolutionary processes and dating the age of rocks is beyond any doubt.

Samples are brought into solution before their determination by instrumental methods. Complete dissolution is a fundamental factor for obtaining precise and accurate analytical data (16). Fusion and acid digestion with different combina-

ABSTRACT

The determination of lanthanides in six soil and six sediment reference materials was investigated by inductively coupled plasma mass spectrometry (ICPMS) using fusion and acid digestion. In the present study, the samples were fused with lithium metaborate (LiBO_2) and lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$). In the case of acid decomposition, the samples were digested with a mixture of hydrofluoric acid (HF) and perchloric acid (HClO_4). For both cases, 1:1 HNO_3 was used for extraction of the decomposed samples. The internal standard (10 ppb indium) was used to take care of the signal drift of the instrument. The measurement was done using a 1 ppb matrix-matched calibration standard prepared from lanthanide salts. The effect of different combinations of fusion flux was investigated. A detailed study was also made taking a different isotopic mass for measurement of the lanthanides.

Both dissolution techniques were evaluated. Uniform and good recovery of the lanthanides was observed using a fusion mixture containing 35% lithium tetraborate and 65% lithium metaborate. The accuracy of the methodology was excellent. Extraction of the lanthanides from the soil and sediment samples by acid digestion method varied from 80–105%. Precision and accuracy in case of the fusion method was very good. The limit of quantitation (10 σ) for the determination of the lanthanides in soil and sediment samples was in the ppb range.

tions are normally adopted for complete dissolution of geological samples. Some workers have used open vessel acid digestion for dissolution of rock samples with or without fusion of any insoluble residue and then direct determination of the REEs by inductively coupled plasma mass spectrometry (ICP-MS) (17-19).

Because the crustal abundance of REEs is very low, pre-concentration procedures such as solvent extraction, co-precipitation or ion-exchange separation are used by some workers to achieve a lower limit of detection (20-24). Fudyunina et al. (25) determined REEs in rock samples using lithium metaborate fusion followed by the pre-concentration on Pol-DETATA, and reported less than 15% difference between the certified and observed values. The present authors used a mixture of lithium metaborate and lithium tetraborate which reduces the melting point of the fusion mixture and also dissolves the acidic and basic oxides easily (26). The pre-concentration procedures are time-consuming and labor-intensive. Sengupta et al. (27) reported that direct ICP-MS determination of lanthanides in common rocks and sediments is possible with acceptable accuracy and precision after the decomposition of the samples by microwave digestion with acids and the complexation of excess HF and fluoride with boric acid and EDTA. Begum et al. (28) applied an open and closed vessel dissolution technique with HF, HClO_4 and HNO_3 for the determination of REEs in marine sediment samples by ICP-MS and reported a better yield with closed vessel dissolution. Microwave digestion or closed vessel dissolution with a

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mixture of acids requires evaporation of HF and HClO₄ or complexation of HF for the elemental determination by instrumental techniques.

The instrumental techniques used for the determination of REEs in rock samples are mainly neutron activation (NA), isotope dilution mass spectrometry, ICP-AES and ICP-MS, of which ICP-MS is the most widely used technique for the determination of REEs in different types of rock samples (29). It is a rapid multi-elemental detection technique with very low detection limits, high sensitivity, high sample throughput, fewer interferences, and a wide range of detection (30). The REEs in chondrite and meteorite were determined using the acid dissolution procedure and found ICP-MS to be a better and more precise measurement technique (31-32).

In the present study, a comparison of two dissolution methods, namely fusion and acid digestion, was made for the direct determination of REEs in soil and sediment reference materials and samples

analyzed by ICP-MS. Six sediment and six soil reference samples were used to validate the analytical methodology for the determination of rare earth elements. There are very few studies available on the determination of REEs in soil and sediment samples, which requires an accurate and simple method for routine determination. The objective of the present study was to establish a simple, fast, precise, accurate, and less labor-intensive method for the determination of REEs in soil and sediment samples with detection limits much below the crustal abundance.

EXPERIMENTAL

Instrumentation

All analyses were performed using a model ELAN® DRCTM-e ICP-MS instrument (PerkinElmer, Inc., Shelton, CT, USA). The instrumental parameters are listed in Table I. The data acquisition parameters and isotopes used for measurement are listed in Tables II and III, respectively.

TABLE I
ICP-MS Instrumental Parameters

RF Power	1125 W	Plasma Gas Flow	15.50 L/min
Nebulizer Gas Flow	0.85 L/min	Lens Voltage	7.75 V
Auxiliary Gas Flow	1.20 L/min	Sample Uptake Rate	1.0 mL/min

TABLE II
Data Acquisition Parameters

Measuring Mode	Peak Hopping	Integration Time	2500 ms
Points per Peak	1	Replicates	3
Number of Sweeps	50	Internal Standard	¹¹⁵ In
Dwell Time	50 ms		

TABLE III
Isotopes for ICP-MS Analysis

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Mass Number	136.906	139.905	140.907	142.910	146.915	150.920	157.924	158.925	162.925	164.930	166.932	168.930	171.937	174.941

Reagents and Standard Solutions

Reagents

The following reagents were used: Ultrapure HF, Emsure® ACS HClO₄, and distilled (sub-boiling) Emsure® ACS HNO₃ (Merck Millipore Corporation). GR Li₂B₄O₇ and Spectromelt® LiBO₂ were from Merck. Deionized water (18MΩ) was obtained with a Milli-Q® 116 apparatus.

Calibration Standards

The lanthanide standards were prepared from their salts and were obtained from Johnson and Matthey Chemical Ltd., Royston, U.K.

1000 ppm Lanthanide Solution

Lanthanide salts were dissolved using 60 mL 1:1 HNO₃, except the cerium salt which was dissolved in 60 mL 1:1 H₂SO₄. Both solutions were evaporated to a pasty mass, and the volumes made up to 500 mL in volumetric flasks made of borosilicate glass maintaining 2% HNO₃ concentration. The compounds of the lanthanides and their weight taken for preparation of 1000 ppm standard solution are listed in Table-IV.

Mixed Calibration Standard

An amount of 10 ppb mixed calibration standard solution of all lanthanides was prepared by successive serial dilution of the 1000-ppm stock solution.

Certified Reference Materials (CRMs)

For this study, 12 CRMs were obtained from the China National Analysis Centre for Iron and Steel, Beijing, P.R. China. Six certified sediment samples of GSD-4, GSD-5, GSD-6, GSD-7, GSD-10, and GSD-11

and six soil reference samples of GSS-1, GSS-2, GSS-3, GSS-5, GSS-6, and GSS-7.

Sample Dissolution

Acid Digestion Method

A quantity of 0.2 g sample was accurately weighed into a Teflon® beaker, to which 8 mL HF and 3 mL HClO₄ were added. The beaker was covered with a lid and heated slowly on hot plate for one hour to about 110 °C. The lid was removed to evaporate HF. Then the sample was heated to about 220 °C under covered conditions for about one hour to obtain a clear solution. The solution was then evaporated to a pasty mass. The residue was dissolved by heating with 30 mL 8% HNO₃. After cooling to room temperature, the volume was made up to 100 mL in a volumetric flask. The indium concentration of the solution was maintained at 10 ppb using 2 mL of 500 ppb In solution which acts as internal standard. Procedural blanks were prepared similarly.

Fusion Method

To start, 0.1 g of sample, 0.15 g of Li₂B₄O₇, and 0.2 g of LiBO₂ were accurately weighed into a platinum crucible and mixed homogeneously. It was then placed into a muffle furnace and heated in stages up to 1000 °C for two and half hours. The heating rate was 6 °C/min up to 250 °C, then 7 °C/min up to 700 °C, and finally 6 °C/min up to 1000 °C, allowing 10 minutes resi-

dency period at each stage. After cooling to room temperature, the oily melt residue obtained was dissolved with 30 mL 8% HNO₃ by stirring at 720 rpm for 30 minutes with a Teflon®-coated magnetic bar until a clear solution was obtained. The volume was made up to 250 mL in a volumetric flask. The indium concentration in the solution was maintained at 10 ppb using 5 mL of 500 ppb In solution which acts as internal standard. Procedural blanks were prepared similarly.

RESULTS AND DISCUSSION

This work analyzed 12 certified reference materials using both dissolution techniques for comparative study. Indium was added as an internal standard to take care of the signal drift of the instrument caused by changes in nebulizer efficiency, gradual clogging of the injector and cones, and matrix-induced suppression and enhancement effects. Spectroscopic interferences arise mainly due to isobaric overlaps which have been minimized by choosing an isotope having minimum isobaric interferences and applying isobaric correction factors, when required. Of the 14 lanthanides, Pr, Tb, Ho, and Tm consist of only a single isotopic mass, whereas for La, Eu, and Lu two isotopes exist. The isotopic ratio for Eu is almost 1, but in the case of La and Lu, only one isotope is predominant. For the rest of the seven elements, the isotope was selected based on the natural abun-

dance and potential interferences. A correction factor of -0.004016 * Dy 163 was used for measurement of Gd only. The CeO/Ce ratio was maintained at <2.5% throughout the instrumental analysis with a view to minimize the formation of elemental oxides. Matrix-matched calibration standards and blanks were used for this study.

The results of six stream sediment reference samples are listed in Tables V(A) and V(B), and the six soil reference samples are listed in Tables VI(A) and VI(B). The observed values for all of the elements of the sediment and soil samples were in very close agreement with the certified values using the lithium metaborate and lithium tetraborate fusion technique. In the case of the acid dissolution technique, the observed values for the lighter rare elements (LREEs) were within the range of the certified values, but the heavier rare earth elements (HREEs) gave lower values.

The percent recovery of six stream sediment samples and six soil reference samples are listed in Tables VII(A) and VII(B), respectively. The lanthanide recovery for the sediment samples was very good using the fusion technique, except for Tm and Ho. In the case of acid digestion, good recovery was observed from La to Gd, but for Tb to Lu the recovery was not satisfactory. The three main mineral sources of lanthanides are monazite, xenotime, and euxenite. These minerals contain all the members of the series. However, monazite contains mostly lighter lanthanides and xenotime contains mostly heavier lanthanides. For the lanthanides, the basicity series is La³⁺ > Ce³⁺ > Pr³⁺ > Nd³⁺ > Pm³⁺ > Sm³⁺ > Eu³⁺ > Gd³⁺ > Tb³⁺ > Dy³⁺ > Ho³⁺ > Er³⁺ > Tm³⁺ > Yb³⁺ > Lu³⁺. It shows that LREEs are more basic than HREEs. This property may affect the solubility of the lanthanides in the acid digestion procedure.

TABLE IV
Elements, Compounds, and Weight
Taken for 1000 ppm Lanthanide Solution

Elements	La	Ce	Pr	Nd	Eu	Sm	Gd
Compounds	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Eu ₂ O ₃	Sm ₂ O ₃	Gd ₂ O ₃
Weight (g)	0.5864	0.6142	0.6041	0.5832	0.5790	0.5798	0.5763
Elements	Tb	Dy	Ho	Er	Tm	Yb	Lu
Compounds	Tb ₄ O ₇	Dy ₂ O ₃	Ho ₂ O ₃	Er ₂ O ₃	Tm ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃
Weight (g)	0.5881	0.5738	0.5717	0.2858	0.5693	0.5685	0.6349

TABLE V(A)
Results of Stream Sediment Samples

Elements	CRM GSD-4			CRM GSD- 5			CRM GSD- 6		
	A	B	C	A	B	C	A	B	C
La	42.03	42.23	40±9	39.72	44.11	46±7	33.00	40.79	39±8
Ce	73.02	77.57	78±4	74.15	85.34	89±8	55.01	65.95	68±8
Pr	8.68	9.37	9.3±1.3	8.47	9.43	9.9±0.9	7.18	8.72	8.4±0.6
Nd	33.69	36.40	32±4	32.40	37.24	35±5	28.69	34.78	33±6
Sm	5.51	6.40	6.2±0.5	5.26	5.81	6.6±0.5	4.67	5.70	5.6±0.6
Eu	1.23	1.25	1.31±0.13	1.20	1.29	1.4±0.2	1.30	1.51	1.5±0.13
Gd	5.81	6.07	5.0±0.8	5.79	7.75	6.4±1.1	5.05	5.35	5.5±0.9
Tb	0.63	0.86	0.90±0.16	0.59	0.84	0.89±0.17	0.53	0.73	0.69±0.15
Dy	3.24	5.19	4.6±0.4	2.90	4.99	5±0.5	2.60	4.04	3.8±1
Ho	0.64	0.84	1.0±0.2	0.58	0.81	0.95±0.15	0.52	0.66	0.76±0.12
Er	1.68	2.70	2.5±0.4	1.48	2.91	2.8±0.5	1.32	2.25	2.2±0.5
Tm	0.23	0.39	0.46±0.05	0.20	0.38	0.46±0.05	0.17	0.29	0.35±0.07
Yb	1.67	3.08	2.9±0.4	1.47	2.88	2.9±0.3	1.22	2.17	2.1±0.4
Lu	0.25	0.44	0.47±0.13	0.22	0.41	0.46±0.05	0.18	0.32	0.34±0.08

A: Acid Digestion Method.
B: Fusion Method
C: Certified Values.

TABLE V(B)
Results of Stream Sediment Samples

Elements	CRM GSD-7			CRM GSD-10			CRM GSD-11		
	A	B	C	A	B	C	A	B	C
La	40.02	46.07	45± 6	11.58	13.22	13±1.4	31.30	27.88	30±3
Ce	65.80	79.56	78± 7	29.87	38.76	38±5	52.37	53.90	58±5
Pr	8.84	9.94	9.6±1.1	2.53	2.93	3.2±0.4	6.99	6.09	7.4±0.6
Nd	32.06	37.86	37±6	10.50	11.76	11.8±1.6	27.44	26.18	27±3
Sm	5.06	5.57	6.1±0.5	1.86	2.40	2.4±0.2	5.76	5.60	6.2±0.4
Eu	1.13	1.30	1.3±0.2	0.38	0.44	0.47±0.05	0.54	0.58	0.6±0.08
Gd	5.19	6.03	5.8±0.8	2.34	2.50	2.2±0.3	6.35	7.52	5.9±0.5
Tb	0.58	0.77	0.76±0.14	0.31	0.38	0.42±0.11	0.83	1.04	1.13±0.1
Dy	2.99	4.56	4.2±0.7	1.84	2.27	2.2±0.3	5.16	7.31	7.2±0.8
Ho	0.60	0.72	0.96±0.21	0.34	0.38	0.45±0.08	0.97	1.21	1.4±0.2
Er	1.61	2.65	2.3±0.2	1.08	1.34	1.3±0.2	3.05	4.65	4.6±0.6
Tm	0.22	0.34	0.44±0.09	0.14	0.17	0.2±0.04	0.43	0.66	0.74±0.11
Yb	1.53	2.58	2.6±0.4	0.98	1.28	1.2±0.3	3.47	5.11	5.1±0.8
Lu	0.24	0.44	0.39±0.07	0.14	0.18	0.19±0.04	0.46	0.77	0.78±0.08

A: Acid Digestion Method.
B: Fusion Method.
C: Certified Values.

Table VI(A)
Results of Soil Samples

Elements	CRM GSS-1			CRM GSS-2			CRM GSS-3		
	A	B	C	A	B	C	A	B	C
La	37.80	35.84	34±3	148.49	160.22	164±16	20.17	21.31	21±2
Ce	72.02	71.64	70±5	385.09	408.67	402±25	37.44	39.39	39±6
Pr	8.04	7.32	7.5±0.5	51.22	57.53	57±6	4.67	4.68	4.8±0.4
Nd	30.52	29.15	28±3	196.30	224.68	210±22	18.10	17.26	18.4±2.4
Sm	5.35	5.09	5.2±0.4	15.24	18.23	18±3	2.79	2.85	3.3±0.3
Eu	1.04	0.97	1.0±0.1	2.87	2.95	3.0±0.3	0.75	0.70	0.72±0.06
Gd	5.00	4.41	4.6±0.3	8.45	8.67	7.8±0.6	2.85	2.80	2.9±0.4
Tb	0.73	0.80	0.75±0.09	1.06	1.28	0.97±0.40	0.35	0.45	0.49±0.09
Dy	3.74	4.32	4.6±0.3	3.65	4.33	4.4±0.3	1.91	2.45	2.6±0.2
Ho	0.75	0.91	0.87±0.08	0.67	0.85	0.93±0.15	0.38	0.44	0.53±0.07
Er	1.86	2.52	2.6±0.2	1.45	2.19	2.1±0.4	1.09	1.49	1.5±0.3
Tm	0.29	0.45	0.42±0.07	0.19	0.33	0.42±0.13	0.17	0.22	0.28±0.06
Yb	1.90	2.59	2.7±0.4	1.27	2.11	2.0±0.3	1.10	1.76	1.7±0.3
Lu	0.30	0.44	0.41±0.06	0.20	0.31	0.32±0.06	0.17	0.26	0.29±0.03

A: Acid Digestion Method.
 B: Fusion Method.
 C: Certified Values.

Table VI(B)
Results of Soil Samples

Elements	CRM GSS-5			CRM GSS-6			CRM GSS-7		
	A	B	C	A	B	C	A	B	C
La	32.95	32.77	36±6	29.54	29.96	30±3	39.17	43.16	46±7
Ce	88.81	85.04	91±15	57.43	60.27	66±8	90.16	92.12	98±16
Pr	6.43	6.50	7±1.3	5.90	5.77	5.8±0.6	9.81	10.17	11±1
Nd	23.01	23.78	24±2	21.52	21.03	21±3	40.69	41.48	45±3
Sm	3.62	3.90	4±0.6	3.34	4.28	3.8±0.6	8.79	9.14	10.3±0.6
Eu	0.75	0.68	0.82±0.06	0.62	0.64	0.66±0.06	3.32	3.41	3.4±0.3
Gd	3.57	3.48	3.5±0.3	3.04	3.57	3.4±0.3	8.66	9.64	9.6±1
Tb	0.47	0.58	0.7±0.2	0.44	0.53	0.61±0.12	0.87	1.13	1.3±0.3
Dy	2.55	3.16	3.7±0.6	2.65	3.30	3.3±0.3	4.67	6.26	6.6±0.8
Ho	0.53	0.68	0.8±0.2	0.48	0.64	0.69±0.06	0.69	0.83	1.1±0.2
Er	1.82	2.25	2.4±0.3	1.68	2.20	2.2±0.3	1.87	2.61	2.7±0.6
Tm	0.29	0.38	0.41±0.05	0.28	0.31	0.40±0.07	0.20	0.32	0.42±0.06
Yb	1.87	2.43	2.8±0.5	1.98	2.65	2.7±0.5	1.54	2.27	2.4±0.6
Lu	0.27	0.37	0.42±0.07	0.30	0.41	0.42±0.06	0.19	0.29	0.35±0.08

A: Acid Digestion Method.
 B: Fusion Method.
 C: Certified Values.

TABLE VII(A)
Percent Recovery of Stream Sediment Samples

Elements	CRM GSD-4		CRM GSD-5		CRM GSD-6		CRM GSD-7		CRM GSD-10		CRM GSD-11	
	A	B	A	B	A	B	A	B	A	B	A	B
La	105	106	86	96	85	105	89	102	89	102	104	93
Ce	94	99	83	96	81	97	84	102	79	102	90	93
Pr	93	101	86	95	85	104	92	104	79	92	94	82
Nd	105	114	93	106	87	105	87	102	89	100	102	97
Sm	89	103	80	88	83	102	83	91	78	100	93	90
Eu	94	95	86	92	87	101	87	100	81	94	90	97
Gd	116	121	90	121	92	97	89	104	106	114	108	127
Tb	70	96	66	94	77	106	76	101	74	90	73	92
Dy	70	113	58	100	68	106	71	109	84	103	72	102
Ho	64	84	61	85	68	87	63	75	76	84	69	86
Er	67	108	53	104	60	102	70	115	83	103	66	101
Tm	50	85	43	83	49	83	50	77	70	85	58	89
Yb	58	106	51	99	58	103	59	99	82	107	68	100
Lu	53	94	48	89	53	94	62	113	74	95	59	99

A: Acid Digestion Method.
B: Fusion Method.

TABLE VII(B)
Percent Recovery of Soil Samples

Elements	CRM GSS-1		CRM GSS-2		CRM GSS-3		CRM GSS-5		CRM GSS-6		CRM GSS-7	
	A	B	A	B	A	B	A	B	A	B	A	B
La	111	105	91	98	96	101	92	91	98	100	85	94
Ce	103	102	96	102	96	101	98	93	87	91	92	94
Pr	107	98	90	101	97	98	92	93	102	99	89	92
Nd	109	104	93	107	98	94	96	99	102	100	90	92
Sm	103	98	85	101	85	86	91	98	88	113	85	89
Eu	104	97	96	98	104	97	91	83	94	97	98	100
Gd	109	96	108	111	98	97	102	99	89	105	90	100
Tb	97	107	109	132	71	92	67	83	72	87	67	87
Dy	81	94	83	98	73	94	69	85	80	100	71	95
Ho	86	105	72	91	72	83	66	85	70	93	63	75
Er	72	97	69	104	73	99	76	94	76	100	69	97
Tm	69	107	45	79	61	79	71	93	70	78	48	76
Yb	70	96	64	106	65	104	67	87	73	98	64	95
Lu	73	107	63	97	59	90	64	88	71	98	54	83

A: Acid Digestion Method.
B: Fusion Method.

The lanthanum recovery for the sediment samples was found better using the fusion method in comparison to the acid digestion method. The results showed that the recovery of the heavier rare earth

elements were non-uniform for the acid dissolution technique.

The recovery of lanthanides for the soil samples follows a similar trend as for the sediment samples. But in the case of lanthanum, acid

recovery was observed to be better than fusion recovery. Heavier rare earth element recovery is not only non-uniform using the acid digestion technique but is also much less in comparison to the fusion technique.

The percentage relative standard deviation (standard deviation \times 100 / mean concentration) for the determination of the lanthanides was less than 4%, confirming good precision of these methods. The limit of quantitation (LOQ, 10 times the standard deviation of the digestion procedure blank solution) was expressed as the concentration in the samples, thereby accounting for the dilution factor used. The LOQ observed for the lanthanides was in ppb level using the fusion method. Though the observed LOQ in the acid dissolution technique was lower than the fusion method, the recovery of HREEs was non-uniform.

CONCLUSION

The fusion technique using a mixture of lithium metaborate and tetraborate in the ratio of 35:65 allowed complete and uniform extraction of all of the lanthanides from soil and sediment samples. The advantage of the mixture of lithium metaborate and lithium tetraborate in the above ratio was in lowering the fusion temperature. The extraction for LREEs using the acid dissolution technique is very good, whereas for the HREEs it is incomplete. The recovery of lanthanum from soil samples was better than from sediment samples.

The present study established that the fusion technique is superior to acid dissolution. Acid dissolution is good for only LREEs of soil and sediment samples. The fusion technique for soil and sediment samples using lithium metaborate and lithium tetraborate followed by ICP-MS measurement is a simple, rapid, less strenuous, precise, and accurate method for the determination of REEs. The LOQ for lanthanides using the fusion method was in the 30 to 100 ppb range and for the acid dissolution technique it was in the 15 to 50 ppb range.

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REFERENCES

1. B. Merkert, *Phytochem.* 26(12), 3167 (1987).
2. P. Henderson, General geochemical properties and abundances of the rare earth elements. *Rare earth element geochemistry* (P. Henderson ed.), Elsevier, New York, USA, 2 (1984).
3. M. Ravichandran, *Mar. Pollut. Bull.* 32, 719 (1996).
4. G. Matisoff, M.E. Ketterer, C.G. Wilson, R. Layman, and P.J. Whiting, *Environ. Sci. Technol.* 35, 3356 (2001).
5. S. Wei, L. Puling, Y. Mingyi, and X. Yazhou, *J. Rare Earths.* 21, 587 (2003).
6. X.C. Zhang, M.A. Nearing, V.O. Polyakov, and J.M. Friedrich, *Soil. Sci. Soc. Am. J.* 67, 279 (2003).
7. I. Olmez, E.R. Sholkovitz, D. Hermann, and R.P. Eganhouse, *Environ. Sci. Technol.* 25, 310 (1991).
8. W.T. Holser, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 132, 309 (1997).
9. R. Ramesh, A.L. Ramanathan, R. A. James, V. Subramanian, S.B. Jacobsen and H.D. Holland, *Hydrobiologia* 397, 89 (1999).
10. G.E. Webb, and B.S. Kamber, *Geochim. Cosmochim. Acta* 64, 1557 (2000).
11. Y. Nozaki, D. Lerche, D.S. Albibo, and M. Tsutsumi, *Geochim. Cosmochim. Acta* 64, 3975 (2000).
12. S.Y. Yang, H.S. Jung, M.S. Choi, and C.X. Li, *Earth Planet. Sci. Lett.* 201, 407 (2002).
13. Y. I. Lee, H.S. Lim, and H.I. Yoon, *Geochim. Cosmochim. Acta* 68, 4319 (2004).
14. V.G. Caccia and F.J. Millero, *Mar. Chem.* 104, 171 (2007).
15. K. Tanaka, F. Akagawa, K. Yamamoto, Y. Tani, I. Kawabe, and T. Kawai, *Quaternary Sci. Rev.* 26, 1362 (2007).
16. T.T. Chao and R.F. Sazolone, *J. Geochem. Explor.* 44, 65 (1992).
17. W. Doherty and A. Vander Voet, *Can. J. Spectrosc.* 30, 135 (1985).
18. A.R. Date and D. Hutchinson, *J. Anal. At. Spectrom.* 2, 269 (1987).
19. K.E. Jarvis, *Chem. Geol.* 68, 31 (1988).
20. M.B. Shabani and A. Masuda, *Anal. Chem.* 63, 1 (1991).
21. J.G. Sengupta, *Talanta* 31, 1045 (1984).
22. J.G. Sengupta, *Talanta* 32, 1 (1985).
23. J.G. Sengupta, *Talanta* 8, 93 (1993).
24. G.N. Eby, *Anal. Chem.* 44, 2137 (1972).
25. N.N. Fedyunina, K. B. Ossipov, I.F. Seregina, M.A. Bolshov, M.A. Statkus, and G.I. Tsysin, *Talanta* 102, 128 (2012).
26. F. Claisse, "Fusion and Fluxes", *Comprehensive Analytical Chemistry: Sample Preparation for Trace Element Analysis*, Vol. 41, Elsevier, pp. 301-311 (2003).
27. J.G. Sengupta, *Talanta* 42, 269 (1995).
28. Z. Begum, V. Balaram, S.M. Ahmad, M. Satyanarayanam, and T. Gnaneshwar Rao, *At. Spectrosc.* 28(2), 41 (2007).
29. B. Zawisza, K. Pytlakowska, B. Feist, M. Polowniak, A. Kita, and R. Sitka, *J. Anal. At. Spectrom.* 26, 2373 (2011).
30. V. Balaram, *Tr. Anal. Chem.* 15, 475 (1996).
31. L. Haichen, L. Ying, and Z. Zhanxia, *Spectrochim. Acta, Part B*, 53(10), 1399 (1998).
32. K. Shinotsuka and M. Ebihara, *Anal. Chim. Acta* 338(B), 237 (1997).