Chapter K

Rare earth elements by inductively coupled plasma-mass spectrometry

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Principle

The rare earth elements (REE) La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb are determined by inductively coupled plasma-mass spectrometry (ICP-MS) in geologic materials (Lichte, et al., 1987). The REE are made soluble in the sample material by sintering with sodium peroxide, leaching with water, and acidifying with nitric acid. Lutetium is added as an internal standard for oxide correction. Rhodium and Iridium are added on line as internal standards to correct for matrix effects and instrument instability. Calibration for each of the REE is made by using the average intensity of blanks taken through the entire procedure and the intensities acquired on a solutions of rock standards containing known concentrations of each REE.

Interferences

Interferences in ICP-MS come from matrix effects, instrumental drift, and isobaric overlap of some elemental isotopes and molecular ions formed in the plasma resulting in suppression or enhancement of measured ion intensity. Rock standards are used so samples and standards are matrix matched. Internal standards are used to minimized matrix effects and instrumental drift as well as oxide correction. The isotopes measured are selected to minimize isobaric overlap from other elements and molecular species that might be present. The production of oxides in the plasma is minimized by reducing the amount of water vapor reaching the plasma through desolvation. Oxide overlaps from the lighter REE on the heavier REE are subtracted by measuring the ratio of oxide to element for single element standards and the oxide ratio of Lutetium oxide to lutetium in each run and applying this ratio to each sample to correct for oxide contribution.

Scope

Rocks and sediments can be analyzed by this method from lower reporting limits of 0.2 La, 0.3 Ce, 0.04 Pr, 0.2 Nd, 0.04 Sm, 0.03 Eu, 0.03 Gd, 0.02 Tb, 0.02 Dy, 0.02 Ho, 0.02 Er, 0.03 Tm, and 0.03 Yb ppm, to upper limits of approximately 32,000 La, 34,000 Ce, 25,000 Pr, 130,000 Nd, 170,000 Sm, 50,000 Eu, 100,000 Gd, 20,000 Tb, 75,000 Dy, 20,000 Ho, 65,000 Er, 20,000 Tm, and 100,000 Yb ppm in the sample. Approximately 40 samples per person day can be analyzed using this method.

Apparatus

- Inductively coupled plasma-mass spectrometer (Perkin Elmer Elan 6000)
- Desolvator (Cetac AT-5000)
- Muffle furnace
- Zirconium crucibles or high-density carbon crucibles, 5 mL
- Teflon screw capped bottles, thick walled, from Savellex
- 7-mL disposable polypropylene tubes

Reagents

- Deionized water (DI)
- Sodium peroxide, Na_2O_2, reagent grade ground in a shatter box to pass an 80-mesh screen (<180 µm) or commercially available in powered form from Fluka Chemika (71880).
- Nitric acid HNO_3, conc. reagent grade

Nitric acid 25 percent: Dilute 250 mL conc. HNO_3 to 1,000 mL with DI water.

Nitric acid 1 percent: Dilute 10 mL conc. HNO_3 to 1,000 mL with DI water.

500 µg/mL Lu internal standard stock solution: Dissolve 0.5690 g lutetium oxide, Lu_2O_3, in a minimum volume of HNO_3. Dilute to 1000 mL with 1 percent HNO_3.

Safety precautions

All laboratory personnel must wear safety glasses, a lab coat or apron, and gloves. Digestion and flux preparations should be performed in chemical fume and dust hoods, respectively. All personnel must read the *CHP* and *MSDS* for each procedure.

Procedure

1. Weigh 0.100 g sample into zirconium or carbon crucible. Three appropriate rock standards, duplicates, and an in-house reference material, TMB+, a natural basalt spiked with REE which is used for calibration must all be taken through the digestion procedure.
2. Add 0.6 g dry Na_2O_2. Mix sample and peroxide thoroughly. (Keep under a heat lamp until samples and flux are placed into the muffle furnace.)
3. Place crucibles into a preheated muffle furnace (450°C for zirconium crucibles) and (500°C for carbon crucibles). Heat for 30 min and remove from furnace. Cool the crucibles.
4. Place each crucible into a Teflon bottle.
5. Add 10 mL DI water, cap and mix by inverting a few times, let sit overnight or a minimum of 4 hours (may be stored capped until analysis).
6. Mix and add 0.100 mL Lu Internal Standard Solution (500 µg/mL Lu).
7. Add 10 mL 25 percent HNO_3, let stand until reaction has stopped (about 15 min), and then mix thoroughly.
8. Take a 1 mL aliquot and dilute with 1 percent HNO_3 to 5 mL for ICP-MS analysis.
9. Determine REE by ICP-MS using the instrumental operating conditions in table 49. The standard concentrations, dwell times, and masses measured for the rare earth elements are listed in table 50.

Table 1.—Operating conditions for determination of REE by ICP-MS

Sweeps/replicate	35
Number of replicates	1
Points/peak	1
Resolution	0.7
Plasma RF power	1,100 W
Nebulizer flow	0.85 L/min
Plasma flow	16.0 L/min
Nebulizer pressure	60.0 psi
Sample uptake rate	0.8 mL/min
Internal Standard uptake rate	0.8 mL/min
Sample delay time	50 s
Sample read delay	50 s
Sampler wash time	60 s
Auto lens	ON, max across mass range
Dual detector	On
Desolvator heater	25°C
Desolvator cooler	0°C

Table 2.—Standard concentrations, dwell times, and masses measured for REE

Element	*Symbol*	*Mass*	*Repetition, ms*	*Dwell, ms*	*TMB+ µg/g*
Barium	Ba	138	350	10	1080
Lanthanum	La	139	350	10	60
Cerium	Ce	140	350	10	116
Praseodymium	Pr	141	350	10	42
Neodymium	Nd	146	350	10	50
Samarium	Sm	149	350	10	39
Europium	Eu	151	700	20	31
Gadolinium	Gd	160	700	20	34
Terbium	Tb	159	700	20	30
Dysprosium	Dy	164	700	20	32
Holmium	Ho	165	700	20	28
Erbium	Er	166	700	20	30
Thulium	Tm	169	700	20	30
Ytterbium	Yb	172	350	10	34
Lutetium	Lu	175	350	10	500
Lutetium	Lu	175	1750	50	500
Hafnium	Hf	180	1400	40	27
Background	Bg	220	1750	50	-

Calculation

A 0.100 g sample is diluted to 100 mL. Dilution factor = 1000

$$\text{Concentration (ppm)} = \frac{\text{sample volume}}{\text{sample wt (g)}} \times \text{ICP-MS reading (ppm)}$$

Assignment of uncertainty

Table 3 is the rare earth element analytical results for selected reference materials, duplicate samples, and method blanks by ICP-MS.

Table 3.—Analytical performance summary for REE (ppm)

(*A pv* (proposed value)from Govandaraju, 1994 and B pv from Wilson, 1997, C pv Wilson, 1998, D pv Wilson, 1998 E pv Wilson, 1998). See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Cerium, Ce							
BIR-1	basalt	12	2.1	0.36	1.95 A	17	107
BHVO-1	basalt	13	37.8	1.09	39.0 A	2.9	97
BHVO-2	basalt	12	37.4	0.74	38.0 B	2.0	98
BCR-1	basalt	12	53.4	0.79	53.7 A	2.9	97
BCR-2	basalt	12	53.0	0.47	53.0 C	0.9	100
AGV-1	andesite	12	68.6	1.39	67.0 A	2.0	102
AGV-2	andesite	12	68.8	0.96	68.0 D	1.4	101
G-2	granite	12	151.0	5.80	160 A	3.8	94
G-3	granite	10	156.0	5.86	160 A	3.7	98
GSP-2	granodiorite	14	400	21	410 E	5.3	97
SY-3	syenite	12	2,110	48	2,230 A	2.3	95
Dysprosium, Dy							
BIR-1	basalt	12	2.7	0.1	2.50	3.8	103
BHVO-1	basalt	13	5.2	0.1	5.3	2.0	99
BHVO-2	basalt	12	5.2	0.1	5.28	1.5	99
BCR-1	basalt	12	6.4	0.1	6.34	1.2	100
BCR-2	basalt	12	6.4	0.1	6.54	1.6	98
AGV-1	andesite	12	3.6	0.1	3.60	1.9	100
AGV-2	andesite	12	3.5	0.1	3.60	2.5	98
G-2	granite	12	2.2	0.03	2.4	1.4	90
G-3	granite	10	2.1	0.1	2.4	3.8	88
GSP-2	granodiorite	14	5.9	0.2	6.1	3.0	96
SY-3	syenite	12	122	2.5	118	2.1	103
Erbium, Er							
BIR-1	basalt	12	1.7	0.09	1.70	5.2	99
BHVO-1	basalt	13	2.5	0.05	2.47	2.1	99
BHVO-2	basalt	12	2.5	0.04	2.68	1.6	91
BCR-1	basalt	12	3.5	0.02	3.63	0.6	98
BCR-2	basalt	12	3.6	0.04	3.45	1.1	103
AGV-1	andesite	12	1.8	0.04	1.70	2.0	107
AGV-2	andesite	12	1.8	0.03	1.79	1.9	100
G-2	granite	12	0.89	0.03	0.92	3.1	96
G-3	granite	10	0.86	0.02	0.92	2.7	94
GSP-2	granodiorite	14	2.4	0.08	2.2	3.6	107
SY-3	syenite	12	78	1.1	68	1.4	114

Table 3.—Analytical performance summary for REE (ppm) ---Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Europium, Eu							
BIR-1	basalt	12	0.58	0.11	0.54	18	108
BHVO-1	basalt	13	2.1	0.06	2.18	2.9	96
BHVO-2	basalt	12	2.1	0.03	2.19	1.2	96
BCR-1	basalt	12	2.0	0.02	1.95	.9	103
BCR-2	basalt	12	2.0	0.03	2.0	1.3	101
AGV-1	andesite	12	1.7	0.04	1.64	2.2	102
AGV-2	andesite	12	1.6	0.03	1.54	2.1	103
G-2	granite	12	1.4	0.03	1.40	1.9	100
G-3	granite	10	1.4	0.06	1.40	4.2	101
GSP-2	granodiorite	14	2.3	0.08	2.30	3.2	102
SY-3	syenite	12	17	0.3	17.0	1.9	101
Gadolinium, Gd							
BIR-1	basalt	12	2.0	0.12	1.85	5.9	107
BHVO-1	basalt	13	6.5	0.14	6.80	2.1	95
BHVO-2	basalt	12	6.5	0.09	6.30	1.4	103
BCR-1	basalt	12	7.0	0.10	6.68	1.4	105
BCR-2	basalt	12	7.0	0.09	6.8.	1.3	103
AGV-1	andesite	12	5.0	0.13	5.0	2.6	101
AGV-2	andesite	12	4.8	0.11	4.69	2.3	103
G-2	granite	12	4.1	0.08	4.3	1.9	96
G-3	granite	10	4.2	0.15	4.3	3.4	98
GSP-2	granodiorite	14	13.4	0.5	12.0	3.8	111
SY-3	syenite	12	120	2.5	105	2.1	114
Holmium, Ho							
BIR-1	basalt	12	0.59	0.10	0.57	16.5	104
BHVO-1	basalt	13	0.94	0.02	0.90	1.7	105
BHVO-2	basalt	12	0.93	0.02	1.04	1.7	90
BCR-1	basalt	12	1.24	0.01	1.26	1.1	98
BCR-2	basalt	12	1.25	0.01	1.33	1.1	94
AGV-1	andesite	12	0.65	0.02	0.67	2.5	98
AGV-2	andesite	12	0.64	0.01	0.71	1.5	90
G-2	granite	12	0.34	0.01	0.40	2.2	85
G-3	granite	10	0.33	0.01	0.40	3.8	84
GSP-2	granodiorite	14	0.92	0.02	1.00	2.5	92
SY-3	syenite	12	25.5	0.4	29.5	1.6	86
Lanthanum, La							
BIR-1	basalt	12	0.71	0.19	0.62	26	114
BHVO-1	basalt	13	15.6	0.50	17.0	3.2	91
BHVO-2	basalt	12	15.5	0.31	15.0	2.0	103
BCR-1	basalt	12	25.7	0.39	24.9	1.5	103
BCR-2	basalt	12	25.4	0.31	25.0	1.2	102
AGV-1	andesite	12	38.9	0.88	38.0	2.3	102
AGV-2	andesite	12	38.4	0.64	38.0	1.7	101
G-2	granite	12	87.5	2.3	89.0	2.6	98
G-3	granite	10	89.4	2.8	89.0	3.1	100
GSP-2	granodiorite	14	171.7	8.6	180.0	5.0	95
SY-3	syenite	12	1229	24	1340	2.0	92

Table 3.—Analytical performance summary for REE (ppm) ---Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Neodymium, Nd							
BIR-1	basalt	12	2.5	0.15	2.50	6.3	98
BHVO-1	basalt	13	25	0.7	24.8	2.8	100
BHVO-2	basalt	12	25	0.4	25.0	1.4	99
BCR-1	basalt	12	29	0.5	28.8	1.7	102
BCR-2	basalt	12	29	0.3	28.0	0.9	104
AGV-1	andesite	12	33	0.8	33.0	2.3	99
AGV-2	andesite	12	31	0.5	30.0	1.4	105
G-2	granite	12	55	1.0	55.0	1.9	99
G-3	granite	10	55	1.8	55.0	3.3	101
GSP-2	granodiorite	14	206	7.0	200.0	3.4	103
SY-3	syenite	12	672	24	670.0	3.5	100
Praseodymium, Pr							
BIR-1	basalt	12	0.42	0.13	0.38	32	111
BHVO-1	basalt	13	5.1	0.15	5.20	2.9	97
BHVO-2	basalt	12	5.0	0.09	5.57	1.7	90
BCR-1	basalt	12	6.5	0.11	6.8	1.6	96
BCR-2	basalt	12	6.5	0.06	6.8	1.0	95
AGV-1	andesite	12	8.1	0.18	7.60	2.3	106
AGV-2	andesite	12	7.8	0.11	8.3	1.5	94
G-2	granite	12	16	0.34	18.0	2.1	88
G-3	granite	10	16	0.53	18.0	3.3	89
GSP-2	granodiorite	14	51	1.9	51.0	3.7	101
SY-3	syenite	12	190	2.7	223	1.4	85
Samarium, Sm							
BIR-1	basalt	12	1.1	0.12	1.10	11	103
BHVO-1	basalt	13	6.1	0.18	6.08	3.0	100
BHVO-2	basalt	12	6.10	0.11	6.2	1.8	98
BCR-1	basalt	12	6.6	0.14	6.59	2.0	101
BCR-2	basalt	12	6.6	0.16	6.7	2.3	99
AGV-1	andesite	12	5.9	0.16	5.9	2.7	100
AGV-2	andesite	12	5.6	0.18	5.7	3.1	99
G-2	granite	12	7.2	0.15	7.2	2.1	100
G-3	granite	10	7.3	0.29	7.2	3.9	101
GSP-2	granodiorite	14	26	0.97	27.0	3.7	97
SY-3	syenite	12	116	2.3	109	2.0	107
Terbium, Tb							
BIR-1	basalt	12	0.43	0.11	0.36	25	120
BHVO-1	basalt	13	0.97	0.02	0.99	2.3	98
BHVO-2	basalt	12	0.96	0.01	0.90	1.4	107
BCR-1	basalt	12	1.1	0.01	1.05	1.2	104
BCR-2	basalt	12	1.1	0.02	1.07	1.4	103
AGV-1	andesite	12	0.68	0.02	0.70	2.6	97
AGV-2	andesite	12	0.66	0.01	0.64	1.7	103
G-2	granite	12	0.47	0.01	0.48	2.3	99
G-3	granite	10	0.48	0.02	0.48	4.8	99
GSP-2	granodiorite	14	1.4	0.06	1.27	4.0	110
SY-3	syenite	12	20	0.47	18.0	2.3	113

Table 3.—Analytical performance summary for REE (ppm) ---Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Thulium, Tm BIR-1	basalt	12	0.33	0.11	0.26	34.1	128
BHVO-1	basalt	13	0.36	0.01	0.29	2.2	124
BHVO-2	basalt	12	0.36	0.01	0.42	1.61	85
BCR-1	basalt	12	0.57	0.01	0.56	1.29	102
BCR-2	basalt	12	0.57	0.05	0.54	1.68	106
AGV-1	andesite	12	0.28	0.01	0.34	2.11	84
AGV-2	andesite	12	0.28	0.01	0.26	3.17	108
G-2	granite	12	0.13	0.01	0.18	4.26	71
G-3	granite	10	0.12	0.01	0.18	4.01	69
GSP-2	granodiorite	14	0.32	0.01	0.29	3.56	107
SY-3	syenite	12	12.2	0.18	11.6	1.49	105
Ytterbium, Yb							
BIR-1	basalt	12	1.7	0.11	1.65	6.4	104
BHVO-1	basalt	13	2.0	0.04	2.02	2.1	100
BHVO-2	basalt	12	2.0	0.05	2.0	2.6	99
BCR-1	basalt	12	3.4	0.05	3.38	1.4	101
BCR-2	basalt	12	3.4	0.05	3.50	1.4	97
AGV-1	andesite	12	1.7	0.05	1.72	2.8	98
AGV-2	andesite	12	1.7	0.05	1.60	2.9	106
G-2	granite	12	0.73	0.02	0.80	3.3	91
G-3	granite	10	0.72	0.03	0.80	3.6	90
GSP-2	granodiorite	14	1.7	0.05	1.60	3.2	105
SY-3	syenite	12	65	1.5	62.0	2.3	105

Table 3.--Continued--Duplicate samples results

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No of < (total)*	*No of <(pairs)*
Ce	24	2	157	18	11	0.28 to 2,436	0	0
Dy	24	2	14	2	14	0.018 to 202	0	0
Er	24	2	9	1	13	0.01 to 120	0	0
Eu	24	2	3	0.2	7	0.002 to 24	0	0
Gd	24	2	15	3	17	0.03 to 211	0	0
Ho	24	2	3	0.4	11	0.002 to 38	0	0
La	24	2	88	14	16	0.13 to 1446	0	0
Nd	24	2	82	14	17	0.11 o 1368	0	0
Pr	24	2	21	3	15	0.03 to 338	0	0
Sm	24	2	16	3	20	0.02 to 244	0	0
Tb	24	2	3	0.34	11	0.003 to 32	0	0
Tm	24	2	2.2	0.18	8	0.002 to 24	0	0
Yb	24	2	8	1	12	0.01 to 119	0	0

Table 3.–Continued--Method blank results 3s values are considered the lower limit of detection (LOD), and 5s values are considered the lower limits of determination (LLD)

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Ce	30	0.02039	0.0577	0.1732	0.2886
Dy	30	0.00038	0.0033	0.0098	0.0164
Er	30	0.00041	0.0035	0.0105	0.0175
Eu	30	0.00037	0.0042	0.0125	0.0209
Gd	30	0.00150	0.0042	0.0127	0.0211
Ho	30	0.00019	0.0036	0.0109	0.0181
La	30	0.00799	0.0245	0.0736	0.1227
Nd	30	0.00905	0.0258	0.0773	0.1289
Pr	30	0.00236	0.0067	0.0202	0.0337
Sm	30	0.00019	0.0077	0.0232	0.0387
Tb	30	0.00005	0.0034	0.0101	0.0169
Tm	30	0.00019	0.0044	0.0132	0.0220
Yb	30	0.00166	0.0058	0.0174	0.0291

Bibliography

Govandaraju, K., ed., 1994, 1994 Compilation of Working Values and Sample Description for 383 Geostandards: Geostandards Newsletter, v. 18, Special Issue July 1994.

Lichte, Frederick E., Meier, Allen L., and Crock, James G., 1987, Determination of the rare earth elements in geological materials by inductively coupled plasma-mass spectrometry: Analytical Chemistry, v. 59, no. 8, p. 1,150-1,157.

Wilson, S. A., 1997, The collection, preparation and testing of USGS reference material BCR-2, Columbia River, Basalt, USGS Open File report 98-00x.

Wilson, S. A., 1997, Data compilation for USGS reference material BHVO-2, Hawaiian Basalt, US Geological Survey Open-file Report xxx..

Wilson, S. A., 1998, Data compilation and statistical analysis of intralaboratory results for AGV-2, U.S. Geological Survey Open-File Report (in progress).

Wilson, S. A., 1998, Data compilation for USGS reference material GSP-2, Granoditite, Silver Plume, Colorado, U.S. Geological Survey Open-File Report (in progress).