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Standard reference water samples for rare earth element determinations

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Abstract

Standard reference water samples (SRWS) were collected from two mine sites, one near Ophir, CO, USA and the other near Redding, CA, USA. The samples were filtered, preserved, and analyzed for rare earth element (REE) concentrations (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) by inductively coupled plasma-mass spectrometry (ICP-MS). These two samples were acid mine waters with elevated concentrations of REEs (0.45–161 µg/l). Seventeen international laboratories participated in a ‘round-robin’ chemical analysis program, which made it possible to evaluate the data by robust statistical procedures that are insensitive to outliers. The resulting most probable values are reported. Ten to 15 of the participants also reported values for Ba, Y, and Sc. Field parameters, major ion, and other trace element concentrations, not subject to statistical evaluation, are provided. Published by Elsevier Science Ltd.

1. Introduction

For over 30 years, rare earth elements (REEs) have been used successfully to interpret many geological processes including the evolution of the earth’s mantle and crust, magma genesis, sedimentary petrology, and ore genesis (Haskin and Paster, 1979; McLennan, 1989; Henderson, 1984). More recently REEs have been used to interpret hydrogeochemical processes (Banner et al., 1989; Smedley, 1991; Fee et al., 1992; Johannesson et al., 1994,

1997a, b; Auque et al., 1994; Gimeno et al., 1996) and to identify in-stream processes (Sholkovitz, 1995). In addition, the increase in industrial applications for REEs has led to increased releases of REEs to the environment (Kramer et al., 1999). With the advent of ICP-MS, determinations of REE concentrations in natural waters and aqueous solutions have become more routine. A number of REE solid standard reference materials are currently available including suites of rock standards prepared by the US Geological Survey (Gladney et al., 1983, 1991) and the Japanese Geological Survey (Ando et al., 1987; Terashima et al., 1990), and new REE calibration standards with environmental matrices (mussel tissue and aquatic plant composites) are being evaluated (Kramer et al., 1999). No SRWS or ‘round-robin’ comparison analyses for REEs dissolved in aqueous solutions are currently available. Calibration standards are usually produced by mix-

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ing individual REEs from gravimetrically prepared stock solutions at each laboratory. Other than using standard addition techniques, the accuracy is not well known. Furthermore, the matrix of the water sample can vary considerably from the standard matrix, and the standard is not traceable to an independent source.

Determining REE concentrations in waters is difficult because concentrations are typically in the ng/l range, except for some geothermal and acid waters that have REE concentrations in the µg/l range. In addition, the similar chemical nature of these elements can pose analytical problems because of oxide formation in the plasma.

Prior to the advent of the ICP-MS, REE concentrations in waters were determined using either neutron activation analysis (NAA) or isotope-dilution thermal ionization mass spectrometry (ID-TIMS). The first reported study of rare earth element concentrations in water was the analysis of seawater using NAA (Goldberg et al., 1963). To determine REEs by NAA, preconcentration of the REEs and separation from elements that cause interferences are required (De Baar et al., 1983, 1985; Gosselin et al., 1992). Losses occurring during these steps must be accounted for. With great effort, 12 of the naturally-occurring REEs can be satisfactorily determined by NAA (Laul et al., 1988). Analysis of REEs by ID-TIMS requires not only preconcentration and separation of the REEs (Greaves et al., 1989), but also the addition of an enriched isotope for each element to be determined. Enriched isotopes are commercially available for only 10 REEs. This method continues to be the most precise technique for REE determinations (Byrne and Sholkovitz, 1996; Taylor et al., 1998).

Advantages of determining REE concentrations by the ICP-MS technique include: the ability to determine concentrations of the full suite of REEs; to analyze and reduce data for a large number of samples (50) in a few days; and to simultaneously determine the concentrations of other trace elements (Hall et al., 1995; Byrne and Sholkovitz, 1996). With no preconcentration or separation, detection limits for the REEs are 0.01–0.02 µg/l with an analytical uncertainty of approximately 5% (Jarvis, 1989; Balaram, 1996).

With the greatly increased use of the ICP-MS for determining REE concentrations in water samples, a SRWS for the REEs is needed to improve interlaboratory consistency and accuracy. This paper presents the results of a REE interlaboratory comparison of two well-characterized and carefully prepared natural waters that can fill the need for standard reference water samples for REEs. Seventeen international laboratories participated in a 'round-robin' analysis for which the 'most probable values' (MPVs) for the 14

naturally-occurring lanthanides (La–Lu) were determined. A subset of these laboratories determined the concentrations of other elements, including Ba, Y, and Sc.

It seemed appropriate to present these results in this journal because of the frequent publication of articles on aqueous REE geochemistry.

2. Sample description

The 2 reference waters were selected because they have relatively high REE concentrations (µg/l range) and have well-characterized hydrogeochemistry. Sample PPREE1 is an acid mine water from the Paradise Portal, San Juan Mountains. The San Juan Mountains of southwestern Colorado consist of a sequence of middle to late Tertiary lavas and pyroclastic rocks (Larsen and Cross, 1956). Paradise Portal, at an elevation of 3245 m, is located 1.5 km SE of the Ophir Pass along the Middle Fork of Mineral Creek in the western San Juan Mountains. No history of production from the mine could be located. The mine effluent discharges from a caved portal at the upper edge of a dump pile that rests on a steep slope 20 m above the Middle Fork Mineral Creek. The dump primarily consists of pyritized and propylitically altered San Juan tuff. The portal effluent cascades down the dump pile coating the rocks with white precipitate, an amorphous Al hydroxysulfate. Beneath the 1–10 mm-thick white precipitate is a mass of Fe oxyhydroxide precipitates.

Sample SCREE1 is from Spring Creek in the West Shasta mining district of northern California. The sample was collected at the Spring Creek Debris Dam (SCDD), approximately 8 km downstream of the Iron Mountain site. The bedrock geology consists of a Devonian bimodal volcanic suite, the Copley Greenstone capped by the Balakala Rhyolite. Detailed descriptions of the units and the mineral deposits can be found in Kinkel et al. (1956). Massive sulfide deposits, mined for Ag, Au, Cu, Zn, and pyrite (for H₂SO₄ production), are oxidizing and producing acid mine drainage (AMD; Nordstrom and Alpers, 1999). The AMD is being treated such that approximately 80–95% of the metal loading does not reach the Sacramento River. The water at SCDD represents AMD from Iron Mountain that has been partially treated. This treatment likely removes some of the REEs such that the reported concentrations do not represent the primary mine effluent.

3. Methodology

A total of 50 l of Paradise Portal effluent was col-

lected within 1 m of the collapsed adit on 4 August 1997. Water temperature, pH, specific conductance, and Eh were determined on site. The Eh and pH were measured by placing electrodes in a flow-through-cell through which the sample was pumped with a portable peristaltic pump (Ball et al., 1976). The pH electrode was calibrated on-site with pH buffers, 4.01 and 7.00, that bracketed the sample pH value. Additional water samples filtered with a 142-mm diameter, 0.1- μ m pore-size, tortuous path, filter membrane were collected for major, minor, and trace element determinations. Filtration of the 50 l reference water began within 3 h of collection in an US Geological Survey (USGS) mobile field laboratory truck. Two parallel, 0.1- μ m, acid-

cleaned, all-plastic plate filters (Kennedy et al., 1976) with 293-mm and 142-mm diameters were used with the filtrates composited into a 50-l acid-washed carboy. Filtration was completed within 1 h, and the pH of the reference water was adjusted to less than 2 with concentrated HNO_3 .

A total of 50 l of Spring Creek water was collected on 24 September 1997. Field and filtration procedures were the same as those used for PPREE1.

At the USGS laboratory in Boulder, CO, each reference water was split into 250-ml aliquots with a 10-position, PTFE cone splitter. The aliquots were capped in acid-cleaned polyethylene bottles, sealed with parafilm, and numbered sequentially. The participating lab-

Table 1
Results of water analyses

Sample name	PPREE1	SCREE1
Date	4/8/97	24/9/97
State	CO	CA
County	San Juan	Shasta
Temp ($^{\circ}\text{C}$) at intake	4.8	21.5
pH (in situ/laboratory)	5.29/5.08	3.35/3.31
Eh (volts)	0.378	0.668
Conductance, $\mu\text{S}/\text{cm}$ (in situ/laboratory)	1950/1853	904/936
Sample density @ 20°C (g/cm^3)	1.00155	0.99865
Alkalinity (mg/l as HCO_3^-)	5.44	NA
Acidity (mM (free/total))	NA	0.28/0.35
Ca (mg/l)	369	84.4
Mg (mg/l)	37.4	24.5
Na (mg/l)	7.79	10.5
K (mg/l)	0.89	3.92
Li (mg/l)	0.006	0.014
SO_4 (mg/l)	1250	423
F (mg/l)	< 0.05	< 0.05
Cl (mg/l)	0.63	0.54
SiO_2 (mg/l)	30.2	35.9
Al (mg/l)	11.7	10.7
Fe(T) (mg/l)	62.7	4.12
Fe(II) (mg/l)	62.1	1.19
Mn (mg/l)	5.23	1.93
B (mg/l)	0.17	0.10
Sr (mg/l)	2.67	0.11
Ba (mg/l)	< 0.01	0.032
Cu (mg/l)	0.0005	0.87
Zn (mg/l)	0.54	1.69
Cd (mg/l)	0.0003	0.012
Co (mg/l)	0.10	0.03
Cr (mg/l)	< 0.045	< 0.045
Ni (mg/l)	0.019	0.014
Pb (mg/l)	< 0.001	0.030
V (mg/l)	< 0.006	< 0.006
As (mg/l)	0.005	0.002
Sum cations (meq/l)	18.3	6.8
Sum anions (meq/l)	18.8	6.7
Charge imbalance (%)	-2.4	1.4

oratories were sent two aliquots of each reference water with no laboratory receiving sequential numbers. Samples spanning the entire range of aliquot numbers were analyzed to allow the recognition of any sub-sampling biases.

Water analyses (Table 1) were obtained for both samples. These determinations include Ca, Mg, SiO₂, Al, B, Sr, Ba, Mn, Zn, Pb, Cr, and Co by inductively-coupled plasma-optical emission spectroscopy using a Leeman Labs Plasma-Spec III SO₄, F, and Cl by ion chromatography using a Dionex model 2010i, Na, K, and Li by flame atomic-absorption spectrometry using a Perkin-Elmer AAnalyst 300, As, Ni, Cu, and Cd by graphite-furnace atomic-absorption spectrometry using a Perkin-Elmer 4110 ZL, and Fe (T) and Fe (II) by the FerroZine colorimetric method as described in To et al. (1999). Using an Orion 940/960 autotitrator, alkalinity was determined by titration with standardized H₂SO₄, and acidity was determined by titration with NaOH to pH 7. All analyses were performed at the USGS laboratories, Boulder, CO.

Concentrations of individual REEs, measured at the USGS laboratories in Boulder, CO, were determined by ICP-MS using a Perkin-Elmer Model 5000 instrument utilizing a ‘cone-spray’ pneumatic nebulizer for sample introduction (Garbarino and Taylor, 1995). Samples were determined in triplicate using a direct calibration curve quantification technique with ¹⁰³Rh, ¹¹⁵In, and ¹⁹³Ir used as internal standards. Calibration standards were gravimetrically prepared from high purity salts, dissolved in HNO₃-acidified deionized water. Corrections for spectral interferences were made when necessary. All REEs with masses greater than Sm were routinely corrected for isobaric interferences because Ba and the light REEs are prone to form isobaric oxides during analysis.

Specific equipment, procedures, and methods for ICP-MS determinations varied amongst other participants. Table 2 summarizes the specific instrument models and nebulizers used by the participating laboratories that reported this information. Table 3 summarizes the distribution of REE isotopes that were used by

Table 2
Laboratory participants in reference water round robin

Laboratory	Instrument	Nebulizer
US Geological Survey, Boulder, CO	Perkin Elmer/Sciex ELAN 5000	“Cone-spray” pneumatic nebulizer
US Geological Survey, Denver, CO	Perkin Elmer/Sciex ELAN 6000	Modified Lichte nebulizer
US Geological Survey, Menlo Park, CA	Perkin Elmer/Sciex ELAN 6000	Ryton cross-flow nebulizer and spray chamber
US Geological Survey, Reston, VA	Perkin Elmer/Sciex ELAN 6000	Cross-flow nebulizer
Geological Survey of Canada, Ottawa, Ontario	Perkin Elmer/Sciex ELAN 5000	Cross-flow nebulizer
Department of Geological Sciences, University of Capetown, South Africa	Perkin Elmer/Sciex ELAN 6000	Cross-flow nebulizer
Geological Survey of Finland, FIN-02151 ESPOO	Perkin Elmer/Sciex ELAN 6000	Scott type cross-flow nebulizer
Geofluids, Bassins, Eau, Montpellier, France	VG PQ2 ⁺ Turbo	Meinhardt continuous nebulizer
SMN/PEA/ISO, BRGM, Orleans, France	VG PQ2 ⁺	Meinhardt continuous nebulizer
Geochimie. UMR, Toulouse, France	Perkin Elmer/Sciex ELAN 6000	Not reported
British Geological Survey, Keyworth, Nottingham, UK	VG PQ2 ⁺	De Galan V-groove nebulizer
Centre for Environmental Technology, Imperial College, Berkshire, UK	VG PQ2 ⁺ STE	De Galan nebulizer
Institute of Geography and Earth Sciences, University of Wales, Aberystwth, UK	VG PQ2 ⁺	Not reported
Norwegian Geological Survey, Trondheim, Norway	Finnegan MAT	Not reported
University of Bristol, Department of Geology, Bristol, UK	VG PQ2 ⁺	Not reported
Department of Marine Sciences, University of South Florida, St. Petersburg, FL, USA	Fisons PQS	Not reported
Elemental Research Inc., North Vancouver, BC Canada	Not reported	Not reported

the round-robin participants. For all the elements except Gd, there was a ‘most preferred’ isotope that was selected by the participants for analytical use. Each laboratory was asked to analyze the two aliquots of each reference water in triplicate and report the results of all the analyses.

The reported REE determinations of the individual REEs in the two aliquots of each reference water were averaged. The uncertainty, represented by the error

bars in Figs. 1 and 2, is calculated as the maximum of the standard deviation of the two aliquot measurements and the pooled standard deviation (Walpole and Myers, 1985) from the reported individual standard deviations.

The MPVs for the REEs from the interlaboratory comparison are reported in Table 4. The MPVs were determined using a non-parametric statistical treatment which is insensitive to the presence of outliers (Hoaglin

Table 3
Rare earth element isotopes used for ICP-MS elemental determinations by ‘round robin’ participants

Element	Isotope	Number of Laboratories ^a
La	139*	15/15
Ce	140*	15/15
Pr	141*	15/15
Nd	143	1
	145	1
	146*	11
	143, 145, 146	1
	143, 145, 150	1
Sm	147*	9
	149	1
	152	1
	147 and 149	3
	147 and 152	1
Eu	151*	9
	153	4
	151 and 153	2
Gd	155	1
	157	5
	158*	2
	160	4
	157 and 160	1
	158 and 160	1
	156, 157, 158	1
Tb	159*	15/15
Dy	162	1
	163*	10
	164	2
	161 and 163	2
Ho	165*	15/15
Er	166	10
	167*	3
	166 and 167	1
	167 and 169	1
Tm	169*	15/15
Yb	172	5
	173	1
	174*	8
	172 and 174	1
Lu	175*	14
	175 and 176	1

^a 15 of the 17 participants reported which isotopes were used for elemental determinations.

* Isotope used at the USGS, Boulder, CO.

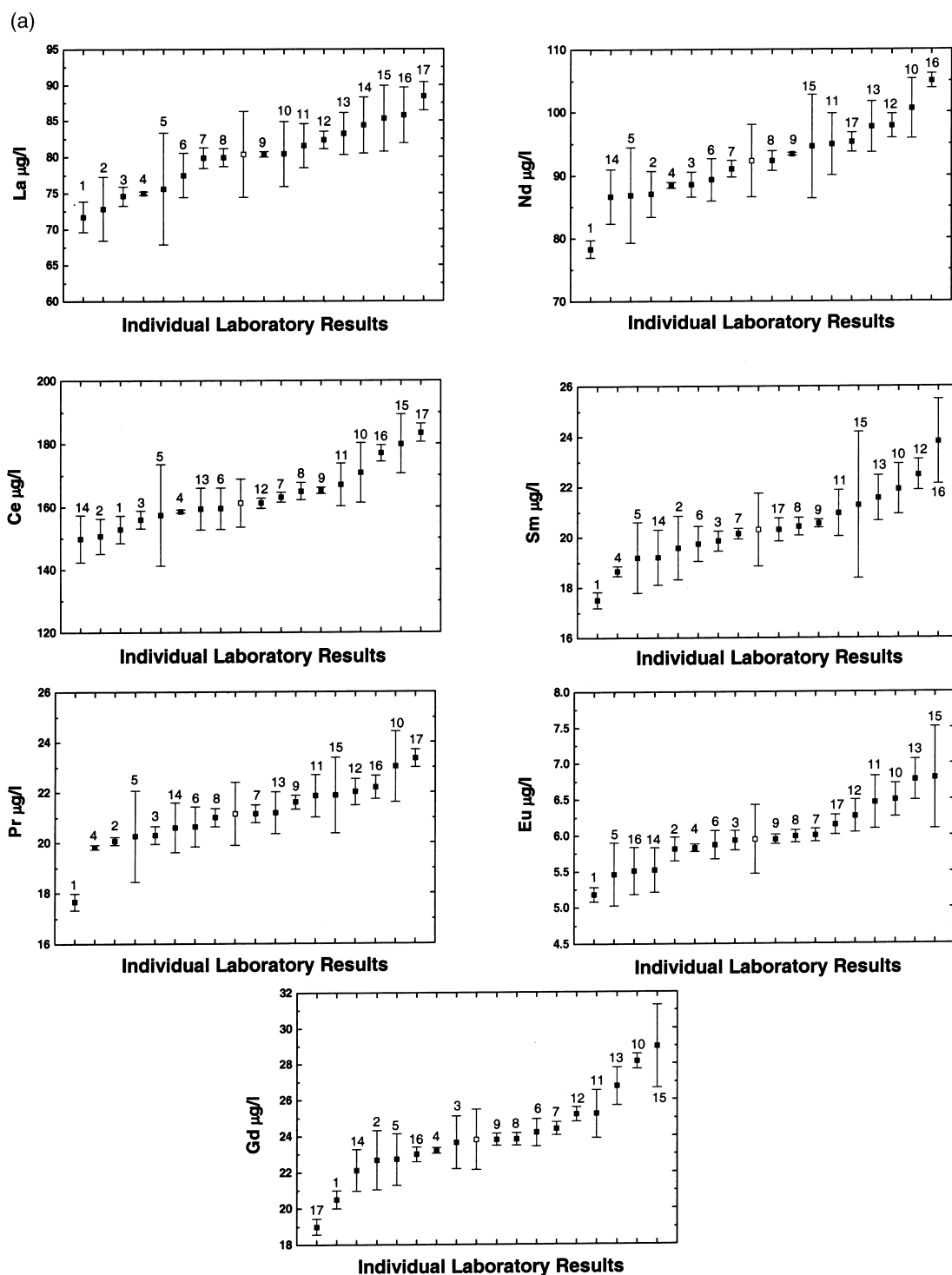


Fig. 1. (a) PPREE1 La through Gd determinations from individual laboratories plotted by increasing concentration; (b) PPREE1 Tb through Lu determinations from individual laboratories plotted by increasing concentration. (■), average concentration of two aliquots analyzed by each participant with uncertainty as described in text; (□), median value and MAD. Numbers above symbols correspond to an individual laboratory.

(b)

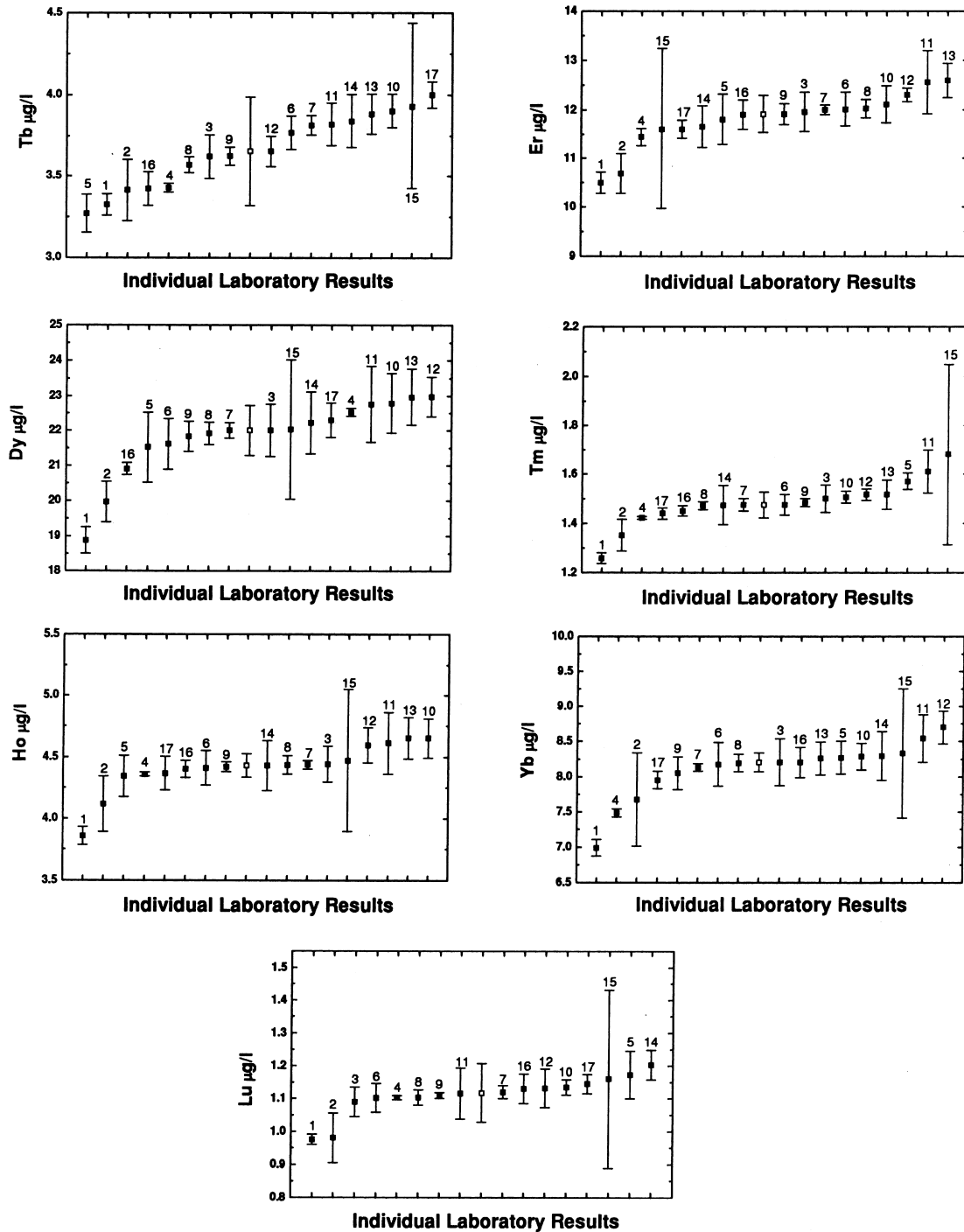


Fig. 1 (continued)

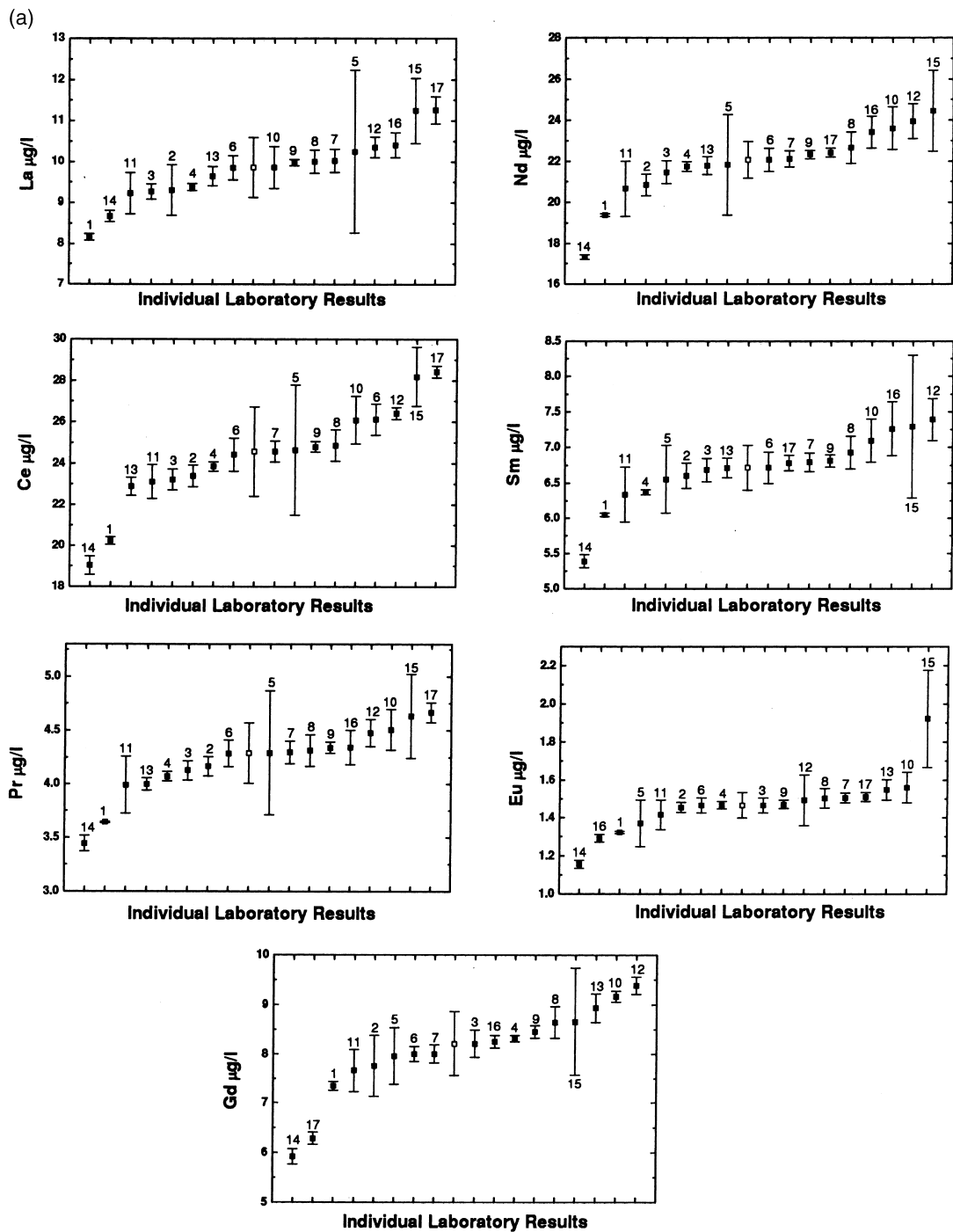


Fig. 2. (a) SCREE1 La through Gd determinations from individual laboratories plotted by increasing concentration; (b) SCREE1 Tb through Lu determinations from individual laboratories plotted by increasing concentration. (■), average concentration of two aliquots analyzed by each participant with uncertainty as described in text; (□), median value and MAD. Numbers above symbols correspond to an individual laboratory and are the same as in Fig. 1a.

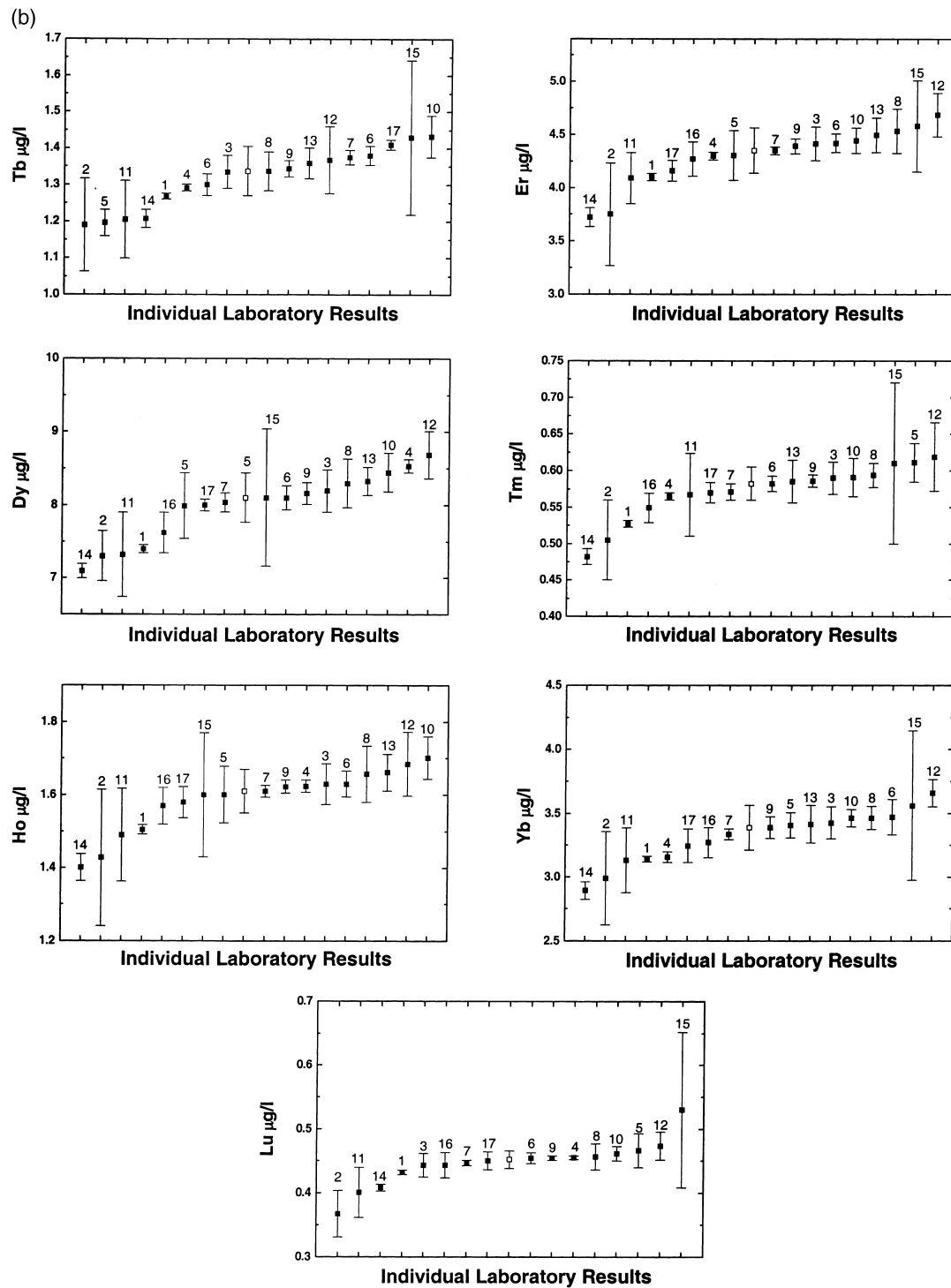


Fig. 2 (continued)

et al., 1983; Farrar and Long, 1997; Peart et al., 1998). With this treatment, the MPV is the median of all reported values, and the uncertainty of the MPV is the median absolute deviation (MAD; Rousseeuw, 1990). The advantage of using these statistical methods is the ability to incorporate the results from all the laboratories in the calculation of the MPV and MAD, without the need to determine and eliminate outliers (Peart et al., 1998).

Estimated values for non-REEs are reported in Table 5 and are calculated in the same statistical manner as the MPVs and MADs. Because the number of laboratories that reported determinations for many of these elements is small, the values should be used only as estimates of the elemental concentrations.

4. Results and discussion

The REE analytical results from the interlaboratory comparison are graphically presented on Figs. 1–4 with the MPVs reported in Table 4. Water analyses are reported in Table 2 (determinations by techniques other than ICP-MS) and the estimated values of non-REEs are reported in Table 5.

In general, the REE determinations by the participating laboratories were similar. The range in determinations is not correlated with aliquot number (Fig. 3) suggesting that no biases were imposed during splitting. For PPREE1 and SCREE1, 85 and 83%, respectively, of the individual laboratories' results overlap with the MPVs, within the uncertainties. Gadolinium had the greatest number of determinations outside of

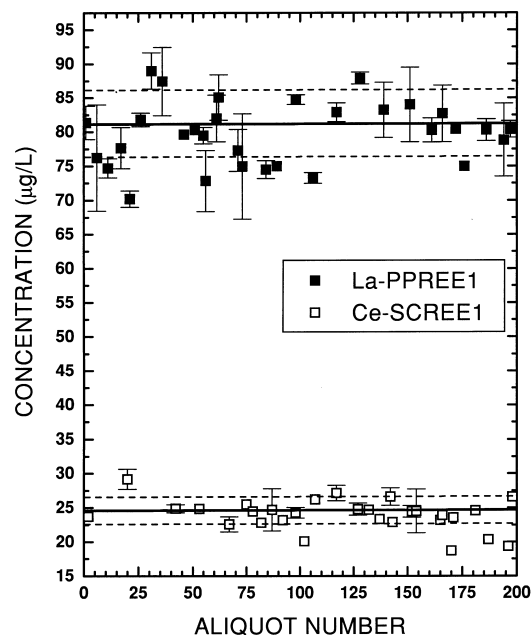


Fig. 3. La (PPREE1) and Ce (SCREE1) vs aliquot number for each sample analyzed by round-robin participants. (—), MPV for each element; and (---), MAD for each element. Error bars represent the standard deviation as reported by the participating laboratories. Error bars not shown if the range in the standard deviation was smaller than the symbol.

Table 4

Most probable values (MPV) and mean average deviation (MAD) for standard reference water samples (µg/l)

Element	PPREE1			SCREE1		
	<i>n</i>	MPV	MAD	<i>n</i>	MPV	MAD
La	17	80.4	5.9	17	9.85	0.73
Ce	17	161.	8.	17	24.6	2.2
Pr	17	21.2	1.3	17	4.29	0.28
Nd	17	92.3	5.7	17	22.1	0.9
Sm	17	20.3	1.5	17	6.71	0.31
Eu	17	5.95	0.48	17	1.47	0.07
Gd	17	23.8	1.7	17	8.21	0.65
Tb	17	3.65	0.33	17	1.34	0.07
Dy	17	22.0	0.7	17	8.10	0.34
Ho	17	4.43	0.09	17	1.61	0.06
Er	17	11.9	0.4	17	4.35	0.21
Tm	17	1.48	0.05	17	0.582	0.023
Yb	17	8.20	0.13	17	3.39	0.17
Lu	16	1.12	0.03	16	0.452	0.014

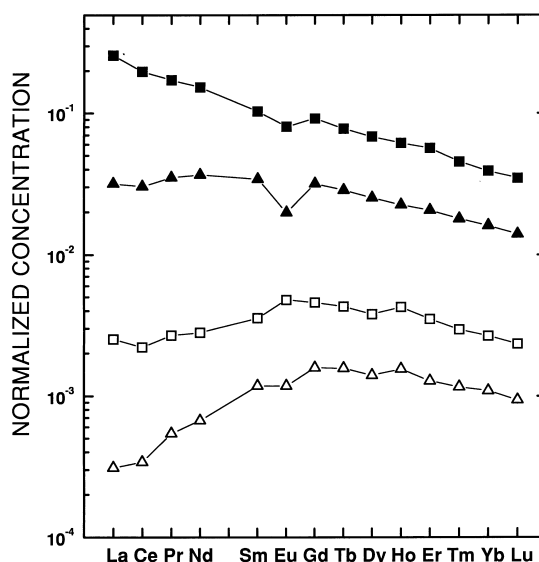


Fig. 4. Rare earth element most probable values normalized to C1 chondrite (Anders and Ebihara, 1982) and North American Shale Composite (Haskin et al., 1968; Gromet et al., 1984). Squares, PPREE1; and triangles, SCREE1. Open symbols, water normalized to NASC, and filled symbols, water normalized to chondrite.

the range of the uncertainties, 5 for each reference water. A possible reason for this is that Gd had the largest number of different isotopes (5) used for concentration determinations by the participants (Table 3). A few laboratories consistently reported determinations out of the range of uncertainty (Figs. 1 and 2). This variation does not correlate with instrument

model, but likely results from the calibration standards used.

The MPVs for PPREE1 range from 1.12 µg/l for Lu to 161 µg/l for Ce (Fig. 1, Table 4) and for SCREE1 from 0.452 µg/l for Lu to 24.6 µg/l for Ce (Fig. 2, Table 4). The REE concentrations in PPREE1 are from 3 to 8 times higher than the concentrations in

Table 5
Estimated values for non-rare earth elements for PPREE1 and SCREE1

Element	<i>n</i>	PPREE1 Estimated value	Uncertainty ^a	<i>n</i>	SCREE1 Estimated value	Uncertainty ^a
(mg/l)						
Al	4	11.5	0.8	4	11.2	1.2
Ca	4	348	44	4	82.3	2
Fe	2	68.3	(2.9)	2	3.76	(0.62)
K	2	0.94	(0.14)	2	5.39	(0.44)
Mg	4	34.6	2.3	4	24.8	1.8
Mn	2	5.3	(0.4)	3	1.46	0.16
Na	3	8.1	0.2	3	11.5	0.7
SiO ₂	3	27.8	1.1	3	40.9	0.2
(µg/l)						
Ag	1	< 0.8		1	< 0.8	
As	2	1.5	(0.1)	1	0.2	
Ba	14	7.1	0.8	14	34.5	3.7
Be	1	2.5		1	0.4	
Br	1	6.4		1	< 5	
Cd	3	0.41	0.04	3	10.3	0.2
Co	2	98	(11)	2	29	(3)
Cr	1	< 0.4		1	< 0.4	
Cs	2	1.2	(0.1)	2	0.16	(0.01)
Cu	3	0.4	0.4	4	733	127
Hf	2	0.15	(0.03)	2	0.050	(0.030)
Li	3	6.0	0.1	3	15.3	1.1
Mo	2	0.22	(0.01)	2	< 0.4	
Nb	1	0.03		1	0.03	
Ni	3	22.3	5.8	3	12.8	0.6
P	1	179		1	< 50	
Pb	3	0.14	0.02	3	12.2	0.8
Rb	3	2.5	0.0	3	7.1	0.3
Re	1	0.36		1	0.030	
Sb	1	0.014		1	0.013	
Sc	10	4.3	1.8	10	6.1	2.6
Se	1	3.4		1	2.6	
Sn	1	0.033		1	0.061	
Sr	4	2680	250	4	121	3
Ta	2	0.064	(0.060)	2	0.023	(0.024)
Te	1	< 0.01		1	0.022	
Th	6	0.11	0.02	6	0.014	0.003
Ti	2	4.7	(2.9)	2	3.4	(1.4)
Tl	1	0.021		1	0.47	
U	5	0.11	0.01	5	0.26	0.01
V	3	2.7	0.1	2	< 0.4	
Y	15	134	6	15	47.0	4.1
Zn	5	490	48	5	1680	180
Zr	2	0.12	(0.13)	2	< 0.3	

^a Uncertainty for samples with two determinations in parentheses.

SCREE1 with the light REEs being more enriched than the heavy REEs. The % uncertainty for PPREE1 ranges from 2 (Yb) to 9 (Tb) % and for SCREE1 from 4 (Nd, Dy, Ho, and Tm) to 9 (Ce) %. The % uncertainty does not appear to be a function of absolute concentration.

A chondrite-normalized REE plot of PPREE1 displays light REE enrichment relative to the heavy REEs and a small negative Eu anomaly (Fig. 4). In contrast, the chondrite-normalized REE plot of SCREE1 displays a nearly flat pattern with a more pronounced negative Eu anomaly. The North American Shale Composite (NASC) normalized plots of the reference waters display convex upward patterns with the SCREE1 pattern having a steeper positive slope in the light REE. The convex upward pattern has been observed in a number of acid waters and likely reflects the REE pattern of the lithologies along the flow path (Auque et al., 1994; Johannesson et al., 1996).

For elements other than the REEs, the estimated values (Table 5) and the elemental concentrations determined by other techniques are similar (Table 1). With the exception of K, SiO₂, and Mn in SCREE1, the concentrations determined by techniques other than ICP-MS fall within the uncertainty or are within approximately 10% of the estimated values. Many of the estimated values in Table 5 are calculated from a limited data set and should be used as approximations.

Three elements, Ba, Y, and Sc, were determined by the majority of the participants. These elements are of particular interest, because Ba oxides form interferences with Eu isotopes, and Y and Sc have chemical properties similar to the REEs and many geochemical studies include these elements with the REEs. Fourteen laboratories reported Ba determinations, and the estimated values for PPREE1 and SCREE1 are 7.1 and 34.5 µg/l, respectively, with an uncertainty of 11%. Fifteen laboratories reported Y concentrations, and the estimated values for PPREE1 and SCREE1 are 134 and 47.0 µg/l, respectively, with an uncertainty of 4.5 and 9%. Scandium concentrations were reported by 10 laboratories and the estimated values for PPREE1 and SCREE1 are 4.3 and 6.1 µg/l, respectively, with an uncertainty greater than 40%. The large MAD most likely results from the fact that Sc is monoisotopic and is isobaric with ²⁹Si¹⁶O and ²⁸Si¹⁶O¹H.

5. Conclusions

This study has evaluated the REE determinations of 2 reference water samples in the first interlaboratory comparison for REEs in waters. The 17 participating laboratories used the ICP-MS technique to determine the elemental concentrations. The MPVs were deter-

mined using robust statistical procedures that are insensitive to outliers. Uncertainty in the MPVs range from 2 to 9%. The shale-normalized REE patterns of both waters display a smooth, convex upward pattern with the SCREE1 pattern having a slight negative Eu anomaly.

Although little change in the REE concentrations of these SRWS is expected, periodic analyses of the reference waters will be conducted to determine the long-term stability of their constituents. After 1 year no change in concentration has been observed. These new SRWS are available from the authors upon request.

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