

A Reappraisal of Rb, Y, Zr, Pb and Th Values in Geochemical Reference Material BHVO-1

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The geochemical reference material BHVO-1 was analysed by a variety of techniques over a six year period. These techniques included inductively coupled plasma-mass spectrometry and atomic emission spectroscopy (ICP-MS and ICP-AES, respectively), laser ablation ICP-MS and spark source mass spectrometry. Inconsistencies between the published consensus values reported by Gladney and Roelandts (1988, *Geostandards Newsletter*) and the results of our study are noted for Rb, Y, Zr, Pb and Th. The values reported here for Rb, Y, Zr and Pb are generally lower, while Th is higher than the consensus value. This is not an analytical artefact unique to the University of Notre Dame ICP-MS facility, as most of the BHVO-1 analyses reported over the last ten to twenty years are in agreement with our results. We propose new consensus values for each of these elements as follows: Rb = $9.3 \pm 0.2 \mu\text{g g}^{-1}$ (compared to $11 \pm 2 \mu\text{g g}^{-1}$), Y = $24.4 \pm 1.3 \mu\text{g g}^{-1}$ (compared to $27.6 \pm 1.7 \mu\text{g g}^{-1}$), Zr = $172 \pm 10 \mu\text{g g}^{-1}$ (compared to $179 \pm 21 \mu\text{g g}^{-1}$), Pb = $2.2 \pm 0.2 \mu\text{g g}^{-1}$ (compared to $2.6 \pm 0.9 \mu\text{g g}^{-1}$) and Th = $1.22 \pm 0.02 \mu\text{g g}^{-1}$ (compared to $1.08 \pm 0.15 \mu\text{g g}^{-1}$).

Keywords: geochemical reference materials, BHVO-1, basalt geochemistry, inductively coupled plasma-mass spectrometry, laser ablation, trace elements.

*Le matériau certifié de référence BHVO-1 a été analysé par différentes techniques sur une période de six années. Ces techniques incluaient les couplages entre source plasma et spectrométrie de masse et spectroscopie d'émission (ICP-MS et ICP-AES respectivement), le couplage ICP-MS - laser et la spectroscopie de masse à étincelle. Des incohérences ont été trouvées entre les résultats de notre étude et les données généralement admises reportées par Gladney et Roelandts (1988, *Geostandards Newsletter*), ceci pour les éléments Rb, Y, Zr, Pb et Th. Nos valeurs pour Rb, Y, Zr et Pb sont en général plus basses et celles de Th b-plus élevées que les valeurs généralement admises. Ce ne peut pas être un artefact analytique lié à notre service ICP-MS puisque la majorité des valeurs publiées ces dix à vingt dernières années sont en accord avec les nôtres. Nous proposons donc les valeurs recommandées suivantes: Rb = $9.3 \pm 0.2 \mu\text{g g}^{-1}$ (à comparer à $11 \pm 2 \mu\text{g g}^{-1}$), Y = $24.4 \pm 1.3 \mu\text{g g}^{-1}$ (à comparer à $27.6 \pm 1.7 \mu\text{g g}^{-1}$), Zr = $172 \pm 10 \mu\text{g g}^{-1}$ (à comparer à $179 \pm 21 \mu\text{g g}^{-1}$), Pb = $2.2 \pm 0.2 \mu\text{g g}^{-1}$ (à comparer à $2.6 \pm 0.9 \mu\text{g g}^{-1}$) et Th = $1.22 \pm 0.02 \mu\text{g g}^{-1}$ (à comparer à $1.08 \pm 0.15 \mu\text{g g}^{-1}$).*

Mots-clés : matériaux géochimiques de référence, BHVO-1, géochimie des basaltes, ICP-MS, ablation laser, éléments en trace.

Geochemical reference materials (GRMs) are used in the analysis of geological samples as a test of analytical accuracy to provide a means of demonstrating traceability of measurements, and through repeated analyses, analytical precision. For many established reference materials, a consensus value for elemental concentrations for each GRM has been reached through distribution of aliquots to various analytical laboratories to be analysed by a variety of techniques

(cf. Gladney and Roelandts 1988, Govindaraju 1989, 1994, Pearce *et al.* 1997). The practice established in earlier years was for the results to be averaged, with spurious results omitted, to derive "working concentrations" (other terms include recommended, proposed, informational and preferred values, the use of which has often depended on the reproducibility and number of analyses) for each element in the GRM. Once consensus has been reached, however, these values

Table 1.
 Current "working" values ($\mu\text{g g}^{-1}$) for the
 geochemical reference material BHVO-1
 as reported by Govindaraju (1994)

Element	Concentration ($\mu\text{g g}^{-1}$)
Li	4.6
Be	1.1
Sc	31.8
V	317
Cr	289
Co	45
Ni	121
Cu	136
Zn	105
Ga	21
Rb	11
Sr	403
Y	27.6
Zr	179
Nb	19
Cs	0.13
Ba	139
La	15.8
Ce	39
Pr	5.7
Nd	25.2
Sm	6.2
Eu	2.06
Gd	6.4
Tb	0.96
Dy	5.2
Ho	0.99
Er	2.4
Tm	0.33
Yb	2.02
Lu	0.291
Hf	4.38
Ta	1.23
Pb	2.6
Th	1.08
U	0.42

are generally not modified and become the "accepted" values, regardless of their overall precision and accuracy. This has been the case for Kilauean basalt BHVO-1 (Flanagan *et al.* 1976). It is commonly used as a GRM in the analysis of basalts (e.g., Rhodes *et al.* 1996, Neal *et al.* 1997, 2002). BHVO-1 consensus values for elements of geological importance were published by Gladney and Roelandts (1988) and are shown in Table 1. The Gladney and Roelandts (1988) data were re-compiled with other data by Govindaraju (1989, 1994), but as the BHVO-1 data are the same in both, we will only use the Gladney and Roelandts reference henceforth. Subsequent analyses of this GRM have suggested that values of Rb, Y, Zr, Pb and Th may differ from the consensus values by as much as 20% (e.g., Xie *et al.* 1994) (Table 1). Even isotope dilution procedures do not produce results that are entirely

consistent (Jochum *et al.* 1990, Mahoney *et al.* 1998, 2000, Raczek *et al.* 2001). However, these elements are extremely important in geochemical modelling: Rb is important as an indicator of partial melting and crustal contamination (e.g., DePaolo 1981), can be an important element in defining source region characteristics (e.g., Hofmann *et al.* 1986) and is integral to the Rb-Sr isotopic system; Y, often grouped with the heavy rare earth elements (HREEs), is used as an indicator of garnet influence and both Y and Zr are commonly used as reference elements in geochemical discrimination plots (e.g., Brügmann *et al.* 1993, Fitton *et al.* 1997); Pb and Th are highly incompatible elements and are, of course, fundamental to the U-Th-Pb isotopic system. They are commonly used in ratios that differentiate source regions (e.g., E-MORB vs. N-MORB sources) and as indicators of crustal contamination (Jochum *et al.* 1983, Hofmann *et al.* 1986, Halliday *et al.* 1995). In this study, we re-examine the concentrations of Rb, Y, Zr, Pb and Th in BHVO-1 in an effort to improve both their accuracy and uncertainty. The study was prompted by the compilation of data from the Notre Dame inductively coupled plasma-mass spectrometry (ICP-MS) facility over a six year period. We compare these data with those from other ICP-MS laboratories, as well as data derived using different analytical techniques [e.g., ICP-AES, spark source mass spectrometry (SSMS) and isotope dilution thermal ionisation mass spectrometry (ID-TIMS)].

Analytical methods

Sample preparation

A typical sample preparation involved dissolving approximately 50 mg of powdered BHVO-1 in screw-top Teflon[®] containers (Savillex[®]) using 2 ml of 16 mol l⁻¹ HNO₃ and approximately 2.25 ml of 60% v/v HF. The sample was then left on a hot plate at 100 °C for 48 hours and subsequently evaporated to dryness and reacidified with 1.5 ml of 16 mol l⁻¹ HNO₃. The sample was then recapped and left at 100 °C overnight before being dried down again. Another 1.5 ml of 16 mol l⁻¹ HNO₃ was added to the sample and immediately dried down. The repetitive HNO₃ treatments were designed to remove as much fluorine as possible. The final residue was then redissolved in 5% v/v HNO₃, transferred to a 125 ml Nalgene bottle and brought up to 100 g in 5% v/v HNO₃. All nitric acid used was double-distilled in-house using quartz sub-boiling stills, and 5% v/v HNO₃ was prepared using 18 MΩ H₂O. The sample powder and final solution were all prepared gravimetrically. Standardisation and spiking protocols

for the ICP-MS analyses were modified from Jenner *et al.* (1990) and are described in Neal (2001).

For laser ablation analyses, ~ 0.5 g of BHVO-1 powder was fused without a fluxing agent on a molybdenum strip in a nitrogen atmosphere (modified from Brown 1977). Subsequent electron microprobe and laser ablation ICP-MS analyses demonstrated the homogeneity of the glass produced with respect to most elements. Notable exceptions included Zr and Hf, which are discussed later.

Sample digestion for Y determination by ICP-AES was accomplished in much the same fashion as for the ICP-MS. Two 100 mg aliquots of sample powder were dissolved using the same method as above, combined, and diluted to a ~ 30 g solution. This final solution was then spiked via standard addition before being run on the ICP-AES. The Y spikes were designed to be 0, 0.1, 0.2, 0.4 and 0.6 $\mu\text{g g}^{-1}$ in the final solution, which were added to the sample that was ~ 0.2 $\mu\text{g g}^{-1}$ Y after dilution. The data reduction and regression analysis for the standard additions were modified from Ely and Neal (2002).

Instrumentation

A Fisons PlasmaQuad 2+ ICP-MS connected to a Gilson 221-222 autosampler was used to conduct the ICP-MS analyses. Typical operation settings and conditions for an analytical run are displayed in Table 2a. During the analyses, a wash procedure between each sample included a 90 second wash of two drops (0.5 μl) of 60% v/v HF per 300 ml of 10% v/v HNO_3 , followed by a 90 second wash of 10% v/v HNO_3 and finally a 90 second wash of 5% v/v HNO_3 to reduce memory effects (see McGinnis *et al.* 1997, for details).

The ICP-AES used in these analyses was a Perkin Elmer Optima 3300 XL attached to a Perkin Elmer As-90 autosampler. Typical operation settings and conditions for an analytical run are displayed in Table 2b. A 90 second wash of 10% v/v HNO_3 was run between each sample.

Laser ablation (LA) ICP-MS analyses were conducted using a Spectron SL282 Nd:YAG laser quadrupled to 266 nm. Spot size was ~ 25 μm with a laser power of ~ 1 mJ per pulse. Calcium was used as the internal standard, which is ideal for Rb, Y, Zr and Th, as they exhibit similar fractionation behaviour during LA-ICP-MS analysis (Fryer *et al.* 1995). Lead can potentially be

Table 2.
(a) Typical settings for the Notre Dame pneumatic nebulisation ICP-MS. (b) Typical settings for the Notre Dame ICP-AES

(a) ICP-MS

Instrument	Fisons PlasmaQuad 2+
Autosampler	Gilson 221-222
Incident power	1350 W
Reflected power	2-10 W
Cool gas	15 l min ⁻¹
Auxiliary gas	2.1 l min ⁻¹
Nebulizer gas	0.85 l min ⁻¹
Nebulisation	Meinhardt
Spray chamber temperature	4.9 °C
Sampler cone orifice	1 mm
Skimmer cone orifice	0.75 mm
Expansion chamber vacuum	150 Pa
Intermediate chamber vacuum	0.01 Pa
Analyser chamber vacuum	5E-4 Pa
Detector	PC mode, Peak jumping mode
Dwell time	10 ms
Sample acquire time	40 s
Replicates per analysis	3-4

(b) ICP-AES

Instrument	Perkin Elmer Optima 3300 XL
Autosampler	As-90
Mode	Axial
Detector	Sequential
Incident power	1300 W
Cool gas	15 l min ⁻¹
Auxiliary gas	0.5 l min ⁻¹
Nebulizer gas	0.8 l min ⁻¹
Nebulisation	Babington
Sample flow rate	1.25 ml min ⁻¹
Acquire time	10 s
Replicates per analysis	3
Y wavelengths analysed	371.029 nm
	324.227 nm
	360.073 nm
	361.104 nm

fractionated from Ca during analysis (again, see Fryer *et al.* 1995), but this can be minimized by carefully controlling the laser frequency (Norman *et al.* 1996). For this study, such fractionation was at a minimum with a laser frequency of ~ 5 Hz. Fractionation effects far outweigh any matrix effects, so by carefully controlling inter-element fractionation, LA-ICP-MS calibration was essentially matrix independent (Jackson *et al.* 1997). Analyses were conducted in peak jumping mode with one peak per mass quantified, and were quantified using the NIST SRM 612 reference material glass (Pearce *et al.* 1997) and the data reduction software LAMTRACE (S. Jackson, Macquarie University, Sydney, Australia). The NIST glasses have been shown to be homogenous and are currently widely used as reference materials for silicate materials ranging from

Table 3.
 Results from pneumatic nebulisation ICP-MS and LA-ICP-MS analyses of BHVO-1 undertaken at the University of Notre Dame

Technique Number of analyses	Gladney and Roelands (1988), Govindaraju (1989, 1994) Compilation consensus	1 s	ICP-MS 92	1 s	% of working value	LA-ICP-MS average 7	% of working value	This study ICP-AES 4
Li	4.6	1.5	4.6	0.3	100%	-	-	-
Be	1.1	0.3	0.93	0.10	85%	1.3	118%	-
Sc	31.8	1.3	31.7	1.5	100%	31.9	100%	-
V	317	12	323	21	102%	345	109%	-
Cr	289	22	293	22	101%	314	109%	-
Co	45	2	47	2	105%	43	96%	-
Ni	121	2	124	6	102%	-	104%	-
Cu	136	6	148	11	109%	141	-	-
Zn	105	5	119	11	113%	-	-	-
Ga	21	2	21.7	1.0	103%	21.8	104%	-
Rb	11	2	9.35	0.56	85%	9.4	85%	-
Sr	403	25	406	20	101%	402	100%	-
Y	276	1.7	24.0	1.1	87%	23.2	84%	24
Zr	179	21	171	7	96%	154	86%	-
Nb	19	2	18.9	1.2	100%	19.2	101%	-
Cs	0.13	0.06	0.10	0.03	78%	0.17	130%	-
Ba	139	14	134	4	96%	132	95%	-
La	15.8	1.3	15.5	0.5	98%	15.0	95%	-
Ce	39	4	39.4	1.9	101%	38.7	99%	-
Pr	5.7	0.4	5.53	0.24	97%	5.2	91%	-
Nd	25.2	2.0	24.73	0.69	98%	24.3	96%	-
Sm	6.2	0.3	6.17	0.27	100%	5.3	86%	-
Eu	2.06	0.08	2.11	0.09	102%	2.08	101%	-
Gd	6.4	0.5	6.36	0.46	99%	6.0	93%	-
Tb	0.96	0.08	0.95	0.07	99%	0.89	93%	-
Dy	5.2	0.3	5.36	0.19	103%	5.1	99%	-
Ho	0.99	0.08	0.97	0.07	98%	0.92	93%	-
Er	2.4	0.2	2.54	0.12	106%	2.4	98%	-
Tm	0.33	0.04	0.33	0.04	99%	0.33	99%	-
Yb	2.02	0.20	2.07	0.10	103%	1.90	94%	-
Lu	0.291	0.026	0.27	0.03	92%	0.29	99%	-
Hf	4.38	0.22	4.48	0.18	102%	3.90	89%	-
Ta	1.23	0.13	1.22	0.11	99%	1.19	97%	-
Pb	2.6	0.9	2.21	0.34	85%	2.3	89%	-
Th	1.08	0.15	1.20	0.11	111%	1.20	111%	-
U	0.42	0.06	0.41	0.05	98%	0.47	111%	-
Zr/Hf	40.9	-	38.2	-	-	39.5	-	-

Table 3 (continued). Results from pneumatic nebulisation ICP-MS and LA-ICP-MS analyses of BHVO-1 undertaken at the University of Notre Dame

Technique Number of Analyses	Jochum (pers. comm.) MIC-SSMS 3	M. Godard (unpubl. data) ICP-MS ?	Kalfoun (2002) ICP-MS 16	Dulski (2001) ICP-MS 6	Raczek et al. (2001) ID-TIMS/MIC-SSMS 2	Jochum et al. (2000) MIC-SSMS ?	Jochum et al. (2000) RNAA ?	Mahoney et al. (1998, 2000) ID-TIMS, ICP-MS ?	Makishima et al. (1999) FI-ICP-MS n=4-6	Robinson et al. (1999) HR-ICP-MS/XRF 19	Campbell et al. (1996) Micro-PIXE 5
Li	-	-	-	-	-	-	-	-	-	-	-
Be	-	-	-	-	-	-	-	-	-	-	-
Sc	-	-	-	-	-	-	-	-	-	31	-
V	-	-	-	-	-	-	-	-	-	-	-
Cr	-	-	-	-	-	-	-	-	-	-	-
Co	-	-	-	-	-	-	-	-	-	-	-
Ni	-	-	-	-	-	-	-	-	-	-	119
Cu	-	-	-	-	-	-	-	-	-	-	160
Zn	-	-	-	-	-	-	-	-	-	-	113
Ge	-	-	-	-	-	-	-	-	-	-	22
Rb	-	9.1	9.3	9.7	9.31	-	-	9.4	-	-	9
Sr	-	3670	368	406	396	-	-	416	-	-	398
Y	-	25.14	-	25.3	-	27	-	25.8	-	24	23.5
Zr	-	161.6	167	183	-	181	-	181	169	-	170
Nb	-	18.07	18.7	-	-	18.1	-	18.6	16	-	18
Cs	-	0.1	0.101	0.094	-	-	-	-	-	-	-
Ba	-	128.1	129.5	132	133	-	-	136	-	-	-
La	-	14.96	15.1	15.5	15.5	-	-	15.7	-	15.5	-
Ce	-	37.39	38.2	38.1	38	-	-	40.3	-	38	-
Pr	-	5.17	5.2	5.59	5.33	-	-	5.21	-	5.5	-
Nd	-	24.46	24.8	24.5	24.8	-	-	24.7	-	25	-
Sm	-	5.8	5.9	6.0	6.12	-	-	6.17	-	6.23	-
Eu	-	2.05	2.07	2.1	2.1	-	-	2.14	-	2.14	-
Gd	-	6.3	6.4	6.6	6.26	-	-	6.51	-	6.35	-
Tb	-	0.89	0.92	0.94	0.954	-	-	-	-	0.94	-
Dy	-	5.35	5.5	5.4	5.3	-	-	5.24	-	5.28	-
Ho	-	0.97	0.99	0.98	0.99	-	-	0.85	-	1.01	-
Er	-	2.41	2.5	2.55	2.56	-	-	2.48	-	2.57	-
Tm	-	0.32	0.33	0.34	-	-	-	0.30	-	0.34	-
Yb	-	1.92	1.9	2.1	2.04	-	-	2.05	-	2	-
Lu	-	0.28	0.29	0.28	0.271	-	-	0.28	-	0.28	-
Hf	4.38	4.16	4.45	4.7	-	4.21	-	-	4.35	-	-
Ta	1.24	1.18	1.22	-	-	1.14	1.18	-	1.17	-	-
Pb	2.49	2.08	2.0	2.2	-	-	-	2.051	-	-	-
Th	1.24	1.24	1.25	1.22	-	-	-	1.233	-	-	-
U	0.410	0.41	0.43	0.42	-	-	-	0.41	-	-	-
Zr/Hf	-	38.8	37.5	38.9	-	-	-	-	38.9	-	-

Table 3 (continued).
 Results from pneumatic nebulisation ICP-MS and LA-ICP-MS
 analyses of BHVO-1 undertaken at the University of Notre Dame

Technique Number of Analyses	Hollocher <i>et al.</i> (1995) ICP-MS 4-14	Xie <i>et al.</i> (1994) ICP-MS 8	Jenner <i>et al.</i> (1990) ICP-MS 8	Jochum <i>et al.</i> (1990) ID-SSMS 1	Watkins and Nolan (1990) ICP-AES	Norman <i>et al.</i> (1989) INAA Variable by element	Roelandts (1987) ICP-AES
Li	-	-	4.9	-	-	-	-
Be	-	-	-	-	-	-	-
Sc	-	32.7	31	-	33.3	30.5	-
V	-	334	-	-	-	-	-
Cr	-	-	-	-	-	278	-
Co	-	-	-	-	-	43.7	-
Ni	-	-	-	-	-	134	-
Cu	143	-	-	-	-	-	-
Zn	127	-	-	-	-	-	-
Ga	-	-	-	-	-	-	-
Rb	9.1	9.38	9.2	11.4	-	-	-
Sr	384	407	409	394	-	410	-
Y	23.2	22.2	25.6	29.5	24.5	-	-
Zr	166	178	190	182	-	-	-
Nb	24	21.2	19	19.8	-	-	-
Cs	0.10	0.093	0.11	0.113	-	0.3	-
Ba	132	131	133	143	-	166	-
La	15.4	16	15.1	14.5	15.9	15.2	15.93
Ce	39	39.3	37.7	36.3	39.5	38.1	38.83
Pr	-	5.6	5.25	5.36	5.43	-	-
Nd	24.7	24.6	24.4	23.6	25.1	-	25.43
Sm	6.1	6.01	6	5.68	6.48	6.24	6.20
Eu	2	2.14	2.2	1.85	2.12	2.04	2.10
Gd	6.4	6.55	6.2	5.96	6.46	-	6.44
Tb	0.96	0.895	0.96	0.864	-	0.95	-
Dy	-	5.37	5.4	5.17	5.40	-	5.18
Ho	0.98	0.958	1.05	1	1.06	-	-
Er	2.5	2.56	2.54	2.63	2.64	-	-
Tm	0.3	0.331	0.32	-	-	-	-
Yb	1.9	2.01	2.01	1.93	2.06	2.01	2.06
Lu	0.25	0.288	0.28	0.311	0.30	0.3	0.29
Hf	4.3	4.39	4.6	4.6	4.4	4.3	-
Ta	1.5	1.35	1.2	-	-	1.08	-
Pb	-	2.11	2	2.12	-	-	-
Th	1.2	1.4	1.2	1.43	-	1.2	-
U	0.44	0.424	0.43	0.422	-	0.3	-
Zr/Hf	38.6	40.5	41.3	39.6	-	-	-

Values are in $\mu\text{g g}^{-1}$. Included are the 1s values for the ICP-MS, a comparison of the ICP-MS value against the working value, and compiled values from 1987-2001 for BHVO-1. Note that this table is not intended to include all results from that time period.

quartz to various types of basalt glasses. (e.g. Horn *et al.* 1994, Pearce *et al.* 1997, Chen *et al.* 2001, Flem *et al.* 2002, Gao *et al.* 2002) but taking note of the localised occurrence of "cords" (Eggins and Shelley 2002). The ICP-MS was set up in a similar manner to that summarised in Table 2a, except that the nebulizer flow rate was typically 1.1 to 1.3 l min⁻¹.

Results

Results for thirty six elements analysed over the past six years by pneumatic nebulisation ICP-MS and

the thirty one elements analysed by LA-ICP-MS are presented in Table 3. The standard deviation of the mean of most elements is less than 10%. Notable exceptions are Cs, Tm, Lu and U, which, after dilution of the sample to reduce the total dissolved solids entering the ICP-MS, are analysed in the pg g^{-1} range. These concentrations are close to or at the instrumental detection limits of an ICP-MS using standard pneumatic (Meinhardt) nebulisation. Generally, elemental concentrations are within error of the consensus values given by Gladney and Roelandts (1988), with the exception of Rb, Y, Zr, Pb and Th for which the consensus

values fall outside the calculated uncertainty (1s) on our average data for these elements (Tables 1 and 3). One standard deviation (1s) is used to express the uncertainty for all averages calculated in this paper, as not only are these uncertainties directly comparable to the values of Gladney and Roelandts (1988), but are conservative given that the number of analyses (n) is large for each element. Thus, a confidence interval of 95% ($1.96s/\sqrt{n}$) is actually smaller than 1s where n is greater than or equal to 4. The average values for Rb, Y, Zr, Pb and Th analysed by LA-ICP-MS are consistent with the solution data, but larger uncertainties are associated with this smaller statistical population, with the resultant values for Pb and Th being within error of the consensus values (Gladney and Roelandts 1988). Only Y was quantified by ICP-AES and the results ($24 \mu\text{g g}^{-1}$, Table 3) match those using ICP-MS techniques. Spark-source data for Pb ($2.49 \pm 0.10 \mu\text{g g}^{-1}$) and Th ($1.24 \pm 0.02 \mu\text{g g}^{-1}$) are also within error of our ICP-MS data (K.P. Jochum, personal communication 2002; Table 3). The spark-source datum is an average of two aliquots of BHVO-1 Split 4 from Notre Dame and BHVO-1 Split 15 from the laboratory at the Max Planck Institute. Details of the spark-source method can be found in Jochum *et al.* (1994, 1997).

When compared with data reported since 1987, which, subsequently, we shall refer to as "recently reported", our average BHVO-1 Rb values of $9.35 \pm 0.56 \mu\text{g g}^{-1}$ (solution ICP-MS) and $9.4 \pm 0.3 \mu\text{g g}^{-1}$ (LA-ICP-MS) are similar to the range determined by other laboratories (9.1 to $9.7 \mu\text{g g}^{-1}$; Table 3), but lower than the consensus value of $11 \mu\text{g g}^{-1}$ and a value of $11.4 \mu\text{g g}^{-1}$ reported by Jochum *et al.* (1990). Yttrium abundances for BHVO-1 determined by other laboratories range from 22.2 to $25.8 \mu\text{g g}^{-1}$, with the Notre Dame ICP-MS laboratory averages being $24.0 \pm 1.1 \mu\text{g g}^{-1}$ (solution ICP-MS), $24 \pm 3 \mu\text{g g}^{-1}$ (ICP-AES) and $23.2 \pm 0.4 \mu\text{g g}^{-1}$ (LA-ICP-MS) (Table 3). Again, these values are consistently lower than the consensus value of $27.6 \mu\text{g g}^{-1}$ and the value of $29.5 \mu\text{g g}^{-1}$ reported by Jochum *et al.* (1990) (Table 3). The solution mode ICP-MS Zr values ($171 \pm 7 \mu\text{g g}^{-1}$) are also slightly lower than the consensus value ($179 \pm 21 \mu\text{g g}^{-1}$) and are in agreement with recently reported values that are $\sim 170 \mu\text{g g}^{-1}$.

Recently reported values for Pb are generally in the range 2.0 - $2.5 \mu\text{g g}^{-1}$ (Table 3), with the Notre Dame ICP-MS averages being $2.2 \pm 0.3 \mu\text{g g}^{-1}$ (solution) and $2.3 \pm 0.2 \mu\text{g g}^{-1}$ (laser ablation). Both solution ICP-MS and LA-ICP-MS averages are statistically

distinct from the consensus value of $2.6 \mu\text{g g}^{-1}$ (Gladney and Roelandts 1988).

Thorium abundances recently reported for BHVO-1 are in the range 1.20 - $1.43 \mu\text{g g}^{-1}$ (Table 3), with the Notre Dame ICP-MS averages being $1.2 \pm 0.1 \mu\text{g g}^{-1}$ (solution) and $1.20 \pm 0.05 \mu\text{g g}^{-1}$ (laser ablation). These values are higher than the consensus value of $1.08 \mu\text{g g}^{-1}$ (Gladney and Roelandts 1988).

We do note some problems with the Notre Dame BHVO-1 data derived by LA-ICP-MS, notably Zr ($154 \pm 5 \mu\text{g g}^{-1}$) and Hf ($3.9 \pm 0.2 \mu\text{g g}^{-1}$) both of which are significantly lower than the consensus values of 179 and $4.38 \mu\text{g g}^{-1}$, respectively. This may be due to heterogeneity in the fused BHVO-1 glasses for these elements, inappropriate standardisation or poor ablation (although we feel the latter two options are unlikely given the good agreement of other elements in the same analyses). Fedorowich *et al.* (1993) also noticed inconsistencies in these elements in certain glasses and attributed them to mild glass heterogeneity.

Discussion

Rubidium

The range of Rb values for BHVO-1 in the original dataset of Gladney and Roelandts (1988) is 0.147 - $23 \mu\text{g g}^{-1}$, although only the values ranging from 7.96 - $16.0 \mu\text{g g}^{-1}$ were used to calculate the consensus value of $11 \mu\text{g g}^{-1}$. Data derived from wavelength dispersive XRF and instrumental thermal neutron activation (ITNA) techniques cover the entire range of Rb values (0.147 - $23.0 \mu\text{g g}^{-1}$) gathered by Gladney and Roelandts (1988), including all of the values rejected by those authors (i.e., not included in their average). Other techniques (e.g., isotope dilution thermal ionisation mass spectrometry or ID-TIMS, energy dispersive XRF, instrumental neutron activation or INAA, and both flame and electrothermal atomic absorption) generally fall between 9 and $11 \mu\text{g g}^{-1}$. This last grouping is similar to abundances defined by three of the techniques (solution ICP-MS, LA-ICP-MS and ID-TIMS) presented in Table 3 (9 - $9.7 \mu\text{g g}^{-1}$), which suggest that the current published consensus value for Rb in BHVO-1 could be high by as much as 20%. If we average the Rb values in Table 3 (excluding the result of Jochum *et al.* 1990 and the compiled values of Gladney and Roelandts 1988), an estimate of $9.3 \pm 0.2 \mu\text{g g}^{-1}$ (1s) is obtained. The data point of 11.4 (Jochum *et al.* 1990) is rejected via a Q test at a greater than 99% confidence

Table 4.
 Original consensus average values, preferred average values from this study and average values generated using all data and the data assessment method of Gladney and Roelandts (1988)

	Consensus values		Preferred values		Gladney and Roelandts (1988) method	
	Average	1s	Average	1s	Average	1s
Rb	11	2	9.3	0.2	9.9	0.9
Y	27.6	1.7	24.4	1.3	25.7	1.3
Zr	179	21	172	10	174	8
Pb	2.6	0.9	2.2	0.2	2.2	0.2
Th	1.08	0.15	1.22	0.02	1.13	0.09

All data are presented with 1s and are in $\mu\text{g g}^{-1}$.

level. The Q test (Harris 1995) checks to see if a data point is an outlier by dividing the gap between the value and its nearest neighbour by the total range in values. If the observed value is greater than the tabulated value, then the point is not considered part of the same population as the rest of the data and is omitted. It should be noted that the ID-TIMS values presented in Gladney and Roelandts (1988) are 9.25 and 9.38 $\mu\text{g g}^{-1}$, respectively (note that Gladney and Roelandts 1988 used the acronyms IDMS and MS in their paper). While we prefer the value of $9.3 \pm 0.2 \mu\text{g g}^{-1}$ for Rb in BHVO-1, we feel some may not be inclined to discount all previous data. Using all of the data and the iterative data exclusion method of Gladney and Roelandts (1988) produces a value $9.9 \pm 0.9 \mu\text{g g}^{-1}$ for Rb. The old consensus values, our preferred values and the values generated by the Gladney and Roelandts (1988) method for Rb, Y, Zr, Rb and Th are presented in Table 4.

Yttrium

XRF, AAS and DC arc optical emission spectroscopy are the predominant techniques that determined BHVO-1 elemental abundances used in the Gladney and Roelandts (1988) consensus value for Y. Like Rb, Y values determined for BHVO-1 in this and other recent studies (Table 3) are consistently lower than the consensus value of 27.6 $\mu\text{g g}^{-1}$. Robinson *et al.* (1999) have detailed this aberration in BHVO-1 and several other GRMs and attributed the problem to the instrumental Y bias of XRF. Specifically, the problem is the interference of the Rb K_{β} on the Y K_{α} peak. If the interference of Rb on Y is similar in magnitude to that indicated by Longerich and Dulski (2002), such that $0.2 * \text{Rb} (\mu\text{g g}^{-1})$ is added to Y, then at the very least Y would be ~ 8% high in XRF data. In fact, of the twenty two results factored into the consensus value of Gladney and Roelandts (1988), eight were XRF values

and only one is less than 27 $\mu\text{g g}^{-1}$. The Y values for ICP-MS (21 $\mu\text{g g}^{-1}$, excluded from the Gladney and Roelandts 1988 average) and ICP-AES (24.2 and 25.7 $\mu\text{g g}^{-1}$), however, were low and comparable to the more recent data (Table 3). We suggest a revision of the consensus value for Y in BHVO-1 to be $24.4 \pm 1.3 \mu\text{g g}^{-1}$. This Y value is an average of those in Table 3, excluding the value of 29.5 $\mu\text{g g}^{-1}$ (Jochum *et al.* 1990), which was eliminated via a Q test at a greater than 95% confidence interval and the compiled data (Gladney and Roelandts 1988). The Gladney and Roelandts (1988) method yields a result of $25.7 \pm 1.3 \mu\text{g g}^{-1}$ when all XRF data are excluded from the average.

Zirconium

The average Zr abundance in BHVO-1 from the Notre Dame ICP-MS laboratory is $171 \pm 7 \mu\text{g g}^{-1}$ and is slightly lower than the consensus value of Gladney and Roelandts (1988) of $179 \pm 21 \mu\text{g g}^{-1}$, although they are statistically no different. It is unlikely that the low Zr value is due to incomplete dissolution of trace zircon (if present), as this would likely also result in low Hf values, which is not the case (our average Hf value is $4.48 \pm 0.18 \mu\text{g g}^{-1}$ compared to the consensus value of $4.38 \mu\text{g g}^{-1}$). Blank levels are insignificant and cannot account for this slight difference. The work in Gladney and Roelandts (1988) upon which the consensus value is based gives a large range for Zr, ranging from 145 to 230 $\mu\text{g g}^{-1}$ (81-444 $\mu\text{g g}^{-1}$ before subjective value elimination). However, more recent studies often indicate Zr concentrations of ~ 170 (e.g. this study, Hollocher *et al.* 1995, Makishima *et al.* 1999, Jochum *et al.* 2000). It is therefore possible that the consensus value is too high. Both Zr and Hf abundances ($154 \pm 5 \mu\text{g g}^{-1}$ and $3.9 \pm 0.2 \mu\text{g g}^{-1}$, respectively) from LA-ICP-MS are significantly lower than both the consensus value and those in the more recent studies. This could indicate fractionation of Zr and Hf

during ablation (although this is considered unlikely, see Fryer *et al.* 1995), or that some of the Zr and Hf reacted with the Mo strip, lowering the overall abundances in the glass. It is also possible that whatever phase houses these elements in BHVO-1 (trace zircon?) was refractory during the fusion process and was not completely homogenized with the other elements. Zirconium/hafnium ratios cannot be used to assist in diagnosing the cause of this variation; the range presented in Table 3 for BHVO-1 alone covers our Zr/Hf ratio and all of them fall within the range given for ocean island basalts (36.9-43.9; David *et al.* 2000). When the statistical method of Gladney and Roelandts (1988) is applied to the entire list of Zr values, the LA-ICP-MS datum is removed during the second iteration for being outside one sigma of the initial average. The final average using this method for Zr in BHVO-1 is $174 \pm 8 \mu\text{g g}^{-1}$. However, the LA-ICP-MS value of $154 \pm 5 \mu\text{g g}^{-1}$ cannot be eliminated via a Q test and is therefore included in our average. Our preferred value for Zr of $172 \pm 10 \mu\text{g g}^{-1}$ is therefore an average of all data presented in Table 3.

Lead

Over the years that BHVO-1 has been analysed in the Notre Dame ICP-MS facility, the consistent differences in Pb abundances between our data and the consensus values have become increasingly apparent. The Pb consensus average value of $2.6 \pm 0.9 \mu\text{g g}^{-1}$ is an average of only seven values from atomic absorption spectroscopy (AAS), wavelength dispersive XRF, DC arc optical emission spectroscopy, ICP-AES and anodic stripping voltammetry (Gladney and Roelandts 1988). The AAS data produced an average value of $2.2 \pm 0.3 \mu\text{g g}^{-1}$, but the other techniques are extremely variable and range from 1.22 - $12 \mu\text{g g}^{-1}$. While only the values ranging from 1.22 - $3.8 \mu\text{g g}^{-1}$ were used in the consensus average, the variability is clear. More recent analyses of BHVO-1 for Pb cover a more limited (but still significant) range of 2.0 - $2.49 \mu\text{g g}^{-1}$; the common feature is that they are all low relative to the current consensus average value of $2.6 \mu\text{g g}^{-1}$. Calibration and matrix effects were significant problems for these earlier techniques, especially when dealing with the then relatively low concentrations. While fractionation of Pb from the other elements may have occurred during our LA-ICP-MS analyses, the lower power and pulse frequency settings resulted in flat time-resolved Pb counts, minimizing any fractionation effects and resulting in Pb values that are similar to the solution

ICP-MS results. We suggest a revision of the consensus value for Pb to $2.2 \pm 0.2 \mu\text{g g}^{-1}$; this average includes all Pb values from Table 3 except the value from Gladney and Roelandts (1988). When applied to entire dataset of both older and recent values, the Gladney and Roelandts (1988) method also results in a Pb value of $2.2 \pm 0.2 \mu\text{g g}^{-1}$.

Thorium

As with Pb determinations, the difference between the consensus value for Th in BHVO-1 and that determined at Notre Dame has become increasingly apparent (Table 3). Recent results from other laboratories also indicate that Th may be higher by as much as ~ 13% than the current consensus value (Gladney and Roelandts 1988). The consensus value is an average of data generated by ITNA, instrumental epithermal neutron activation, wavelength dispersive XRF, direct gamma ray counting and SSMS (Gladney and Roelandts 1988). Of these, neutron activation analyses account for most of the data, producing an average of $1.10 \pm 0.16 \mu\text{g g}^{-1}$; other techniques were more varied, with values ranging from 0.91 to $1.8 \mu\text{g g}^{-1}$. All of the values reported in Table 3 are higher than the consensus value of $1.08 \mu\text{g g}^{-1}$. If Q test analysis (at greater than 95% confidence) is performed, the high values of Xie *et al.* (1994) and Jochum *et al.* (1990) (1.4 and $1.43 \mu\text{g g}^{-1}$, respectively) are excluded and the range in values for Th becomes 1.20 - $1.25 \mu\text{g g}^{-1}$. The average of these data and our suggested new consensus value for Th in BHVO-1 is $1.22 \pm 0.02 \mu\text{g g}^{-1}$. The Gladney and Roelandts (1988) method retains a large amount of Th data of ~ $1 \mu\text{g g}^{-1}$, resulting in a lower average value of $1.13 \pm 0.09 \mu\text{g g}^{-1}$.

Conclusions

Recent data from a variety techniques show that the values for Rb, Y, Zr, Pb and Th may be significantly different from those values compiled and reported in Gladney and Roelandts (1988). These newer data (1987 to the present) show a marked decrease in the range and thus $1s$ values when compared with the earlier compilation values. These results are not surprising; as early techniques are refined and newer, more sophisticated techniques are developed, the accuracy and precision of sample analyses should increase. As such, we suggest new consensus values for each of these elements: Rb = $9.3 \pm 0.2 \mu\text{g g}^{-1}$, Y = $24.4 \pm 1.3 \mu\text{g g}^{-1}$, Zr = $172 \pm 10 \mu\text{g g}^{-1}$, Pb = $2.2 \pm 0.2 \mu\text{g g}^{-1}$ and Th = $1.22 \pm 0.02 \mu\text{g g}^{-1}$.

Acknowledgements

We would like to thank Jim Ely, James Seidler, Cathleen McMahon and Amy Van Dyke for their work analysing BHVO-1 over the years. Thanks also to Larry Taylor and Allen Patchen at the University of Tennessee, Knoxville, for preparing the fused glass of BHVO-1 and to Klaus Peter Jochum for his analyses of BHVO-1 by SSMS. This research was partially supported by NASA grants NAG5-8099 and NAG5-12076 and National Science Foundation grants ECS92-14596, EAR93-15930 and EAR96-28252 and grants from the United States Science Support Programme of the Ocean Drilling Programme.

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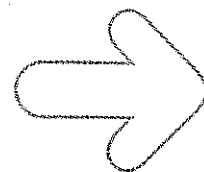
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