

High-precision Pb-Sr-Nd-Hf isotopic characterization of USGS BHVO-1 and BHVO-2 reference materials

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[1] The recent development of multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and increasing use of the technique have created the need for well-characterized rock standards, especially for isotopic systems where no internal fractionation correction can be applied. This paper presents a careful leaching experiment on the U.S. Geological Survey (USGS) reference materials BHVO-1 and BHVO-2 (Hawaiian basalts) and documents the evidence for contamination of the rock powders during processing. This contamination accounts for the difference in Pb isotopic ratios of BHVO-1 and BHVO-2 as well as for their lack of homogeneity both in Pb isotopic compositions and in some trace element contents.

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1. Introduction

[2] The Pacific Centre for Isotopic and Geochemical Research (PCIGR) at the University of British Columbia has undertaken a systematic analysis of isotopic compositions (Pb, Sr, Nd, Hf) and concentrations of a broad compositional range of United States Geological Survey (USGS) reference materials. In doing so, and confirming previous Pb isotopic studies [Woodhead and Hergt, 2000; Baker et al., 2004], we discovered that there were systematic differences, especially in Pb, between the first

(e.g., BHVO-1) and second (e.g., BHVO-2) generation of these reference materials. Some of the reference materials (BHVO-2) display anomalously poor reproducibility, particularly considering the high precision of the analytical techniques. To investigate the origin of this problem, a systematic experiment that involved two different leaching methods [Weis and Frey, 1996; McDonough and Chauvel, 1991] and high-precision trace element analysis of the rock powders was undertaken. The results are especially important as analyses by multiple-collector inductively coupled plasma mass

spectrometry (MC-ICP-MS) allow for a faster sample throughput, with increased precision, compared to conventional TIMS analyses. However, the accuracy of the MC-ICP-MS results is strongly dependent on the careful monitoring of known isotopic standards or reference materials. It is therefore critical to have homogenous, well-characterized rock standards, which have a matrix comparable to the studied samples.

2. Leaching Procedures

[3] For the analysis of oceanic basalts and for the removal of secondary phases or potential contamination, it is clearly demonstrated that leaching of the sample powder or chip is critical. Various methods are used by different researchers and we picked two different ones [Weis and Frey, 1991, 1996; McDonough and Chauvel, 1991] to compare the results.

2.1. Weis and Frey [1991, 1996] Method

[4] This procedure was modified from Mahoney [1987] to ensure the maximum removal of secondary phases that may be present in altered basalt.

[5] 1. About 0.3–0.4 g of rock powder is weighed into an acid-washed 15 mL Savillex[®] beaker.

[6] 2. Ten mL of 6N sub-boiled HCl are added.

[7] 3. The suspension is ultra-sonicated for 20 min.

[8] 4. The supernatant is decanted.

[9] 5. Steps 2–4 are repeated 5 to 6 times until the supernatant is clear and pale yellow to colorless.

[10] 6. Steps 2–4 are repeated 2 more times with milli-Q H₂O (i.e., water that is 18.2 megohm (ion free), pyrogen free, with reduced organic contamination as well as with bacterial and particulate removal) in place of 6N sub-boiled HCl to eliminate the excess HCl.

[11] 7. The leached rock powder is dried on a hot plate at ~120°C.

[12] 8. The leached rock powder is weighed after cooling.

2.2. McDonough and Chauvel [1991] Method

[13] In this leaching procedure, the authors designed an experiment to remove a foreign Pb component that was incorporated in Rurutu island

basalts, most probably prior to the initiation of isotopic analyses.

[14] 1. About 0.3–0.4 g of sample rock powder is weighed into an acid-washed 15 mL Savillex[®] beaker.

[15] 2. Ten mL of 6N sub-boiled HCl are added.

[16] 3. The beaker is capped and put on the hot plate, under boiling conditions, for two hours.

[17] 4. The supernatant is decanted.

[18] 5. Steps 2–4 are repeated with a mixture of 6N HCl and concentrated HF (2 mL of each). The beakers are removed from the hot plate as soon as a foam appears, i.e., after about 30 min, to avoid complete sample dissolution.

[19] 6. The supernatant is decanted right away and the residues are rinsed with milli-Q H₂O at least four times.

[20] 7. The leached rock powder is dried on a hot plate at ~120°C.

[21] 8. The leached rock powder is weighed after cooling.

[22] During each of the leaching steps (3 to 5), the leachates are collected. The leachates are dried down and processed through chemistry for isotopic analysis.

[23] In this study, samples were dissolved in a mixture of sub-boiled HF and HNO₃ acids using sealed Teflon vessels on a hot plate over a period of ~48 hours at ~130°C. The separation techniques are described by Weis and Frey [1996] and Blichert-Toft *et al.* [2003]. A detailed description of each of the individual steps is given in a recent systematic study of the isotopic compositions of USGS reference materials (D. Weis *et al.*, High-precision isotopic characterization of USGS reference materials by TIMS and MC-ICP-MS, submitted to *Geochemistry, Geophysics, Geosystems*, 2004; hereinafter referred to as Weis *et al.*, submitted manuscript, 2004).

3. Analytical Procedure

3.1. Mass Spectrometry

[24] Isotopic composition measurements were determined on a Finnigan Triton thermo-ionization mass spectrometer (TIMS; Sr, Nd) and on a Nu Instruments (Nu 021) multiple collector inductively coupled plasma mass spectrometer (MC-ICP-MS;

Hf, Pb) at the Pacific Centre for Isotopic and Geochemical Research (PCIGR) at the University of British Columbia.

[25] Sr and Nd compositions were measured in static mode multicollection with relay matrix rotation (the “virtual amplifier” of Finnigan) on a single Ta and double Re-Ta filament, respectively. The data were corrected for mass fractionation using $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, respectively. Fifty-five analyses of the NIST SRM 987 Sr standard and seventy-six analyses of the La Jolla Nd standard made during the course of this study have mean values of $^{87}\text{Sr}/^{86}\text{Sr} = 0.710250 \pm 12$ (2SD) and $^{143}\text{Nd}/^{144}\text{Nd} = 0.511853 \pm 16$ (2SD), respectively. A single analysis typically consists of 135 cycles (9 blocks of 15) to allow a full rotation of the virtual amplifier.

[26] Pb and Hf isotopic compositions were analyzed by static multicollection. The collector array on the Nu Plasma is fixed and a zoom lens is employed to position the masses in the collectors. For Pb and Hf, the central collectors (H4-L2) are 1 amu apart while the outer collectors (H6, H5, L3, L4 and L5) are 2 amu apart. For Pb, masses 208 to 202 are measured in collectors H4 to L2, and for Hf, masses 180 to 172 are measured in collectors H4 to L3.

[27] The configuration for Pb isotopic analyses enables simultaneous collection of Pb (208, 207, 206 and 204) together with Tl (205 and 203), which is used to monitor and correct for instrumental mass discrimination and Hg (202), which is used to correct mass 204 for the presence of ^{204}Hg . The ^{204}Hg correction was made using natural abundances ($^{202}\text{Hg} = 0.29863$ and $^{204}\text{Hg} = 0.06865$) adjusted for instrumental mass fractionation using $^{205}\text{Tl}/^{203}\text{Tl}$. Mercury levels were always below 0.8 mV (below 0.3 mV, all runs except 2) of 202 corresponding to a correction of less than 0.2 (0.07) mV on the 204 peak.

[28] To improve the reproducibility of the analytical conditions for the Pb isotopic analyses, and thus the precision, all sample solutions were analyzed with the same Pb/Tl ratios as the NIST SRM 981 standards. To accomplish this, a small aliquot of each sample was analyzed using an Element 2 HR-ICP-MS to determine the exact amount of Pb available for isotopic analyses. Doing this ensures that the correct amount of Tl can be added to each sample to achieve a Pb/Tl ratio of ~ 4 and thus match the Pb/Tl of the standards. Seventy-two

analyses of the NIST SRM 981 Pb standard during the course of this investigation gave mean values of $^{208}\text{Pb}/^{204}\text{Pb} = 36.7157 \pm 78$ (2SD), $^{207}\text{Pb}/^{204}\text{Pb} = 15.4967 \pm 25$ (2SD), and $^{206}\text{Pb}/^{204}\text{Pb} = 16.9413 \pm 34$ (2SD), which is in agreement with the TIMS triple spike values [Galer and Abouchami, 1998]. In light of the reproducibility of the data, there was no need to adjust the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio and a value of 2.3885 was used for all runs. Depending on the amount of Pb available in each sample, the samples were either analyzed by wet or dry (DSN = Nu desolvator) plasma, which corresponds to standard analyses of either 250 ppb or 50 ppb of NIST SRM 981. Except where sample material was insufficient, all samples were run with a ^{208}Pb beam of $>2\text{V}$. The standard was run every two samples and, even though the NIST SRM 981 results were within error of the triple spike values after online correction for fractionation by Tl addition, the USGS reference results were further corrected by the bracketing method as described by White *et al.* [2000] and Blichert-Toft *et al.* [2003].

[29] The Hf isotope analyses were carried out following a modified analytical procedure from Patchett and Tatsumoto [1980] and Blichert-Toft *et al.* [1997]. The configuration used to measure Hf isotopes enables simultaneous collection of Hf (180, 179, 178, 177, 176 and 174) together with monitoring of Lu at mass 175 and Yb at mass 172, which allows interference corrections to be applied to masses 174 and 176. Hf isotope measurements were normalized internally to a $^{179}\text{Hf}/^{177}\text{Hf}$ ratio of 0.7325 using an exponential correction.

[30] The ^{176}Lu , ^{176}Yb and ^{174}Yb corrections were made using natural abundances ($^{175}\text{Lu} = 0.97416$, $^{176}\text{Lu} = 0.02584$, $^{172}\text{Yb} = 0.2183$, $^{174}\text{Yb} = 0.3138$, $^{176}\text{Yb} = 0.1276$) corrected for instrumental mass discrimination as monitored by the $^{179}\text{Hf}/^{177}\text{Hf}$ ratio. The configuration used does not permit correction of mass 180 for the presence of ^{180}Ta , because ^{181}Ta cannot be monitored. Although a ^{180}W correction could be applied through monitoring of ^{182}W or ^{184}W , this was not done because in the absence of a ^{180}Ta correction only a partial correction can be made. The presence of ^{180}Ta and ^{180}W can be assessed by comparing $^{180}\text{Hf}/^{177}\text{Hf}$ values of samples to the mean ($\pm 2\text{SD}$) values measured on the standards. None of the USGS reference materials were affected by Ta and W interferences (28 USGS reference materials analyzed: $^{180}\text{Hf}/^{177}\text{Hf} = 1.886984 \pm 45$ (2SD) and 60 JMC-475 analyses: $^{180}\text{Hf}/^{177}\text{Hf} = 1.886976 \pm 100$ (2SD)).

Table 1. Sr, Nd, Pb, and Hf Isotopic Compositions of BHVO-1 and BKVO-2^a

	⁸⁷ Sr/ ⁸⁶ Sr	2σ _m	n	¹⁴³ Nd/ ¹⁴⁴ Nd	2σ _m	n	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ _m	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ _m	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ _m	n	¹⁷⁷ Hf/ ¹⁷⁶ Hf	2σ _m	n
<i>Unleached^b</i>																
BHVO-1	0.703475	17	8	0.512986	9	19	18.6927	54	15.5727	29	38.3618	147	2	0.283100	3	2
BHVO-2	0.703481	20	10	0.512983	10	9	18.6173	465	15.5355	54	38.2108	384	6	0.283096	20	2
<i>Leached Using Weis and Frey [1991, 1996] Method</i>																
<i>Residue</i>																
BHVO-1	0.703468	8		0.512983	5		18.6466	6	15.4856	6	38.1975	21				
BHVO-2	0.703466	8		0.512974	11		18.6167	15	15.4702	13	38.1567	36				
<i>Leached Using McDonough and Chauvel [1991] Method</i>																
<i>Residue</i>																
BHVO-1 (1)	0.703470	8		0.512982	8		18.5217	544	15.4813	468	38.0730	1174				
BHVO-1 (2)	0.703481	8		0.512986	5		18.6392	23	15.4825	20	38.1869	51				
BHVO-2 (1)	0.703480	8		0.512982	8		18.6638	13	15.4899	12	38.2060	33				
BHVO-2 (2)	0.703481	7		0.512986	5		18.6714	47	15.4940	41	38.2113	126				
<i>Leachate</i>																
Leachate BHVO-1 (1)	0.703485	8		0.512989	9		18.6982	15	15.5825	13	38.3757	34				
Leachate BHVO-1 (2)	0.703490	7		0.512984	6		18.7076	13	15.5836	12	38.3799	34				
Leachate BHVO-2 (1)	0.703482	7		0.512981	6		18.6963	7	15.5844	6	38.2937	17				
Leachate BHVO-2 (2)	0.703488	8		0.512986	5		18.6576	9	15.5628	8	38.2724	35				
Pestle							18.1410	31	15.5871	28	38.6692	95				
Mortar							19.1954	16	15.6937	15	38.8687	31				

^a Reported 2σ_m applies to the last decimal place. Italics indicate a poor analysis because too little Pb was available; only 13 cycles were obtained, and values are reported for information, but should only be taken as indicative.

^b The numbers correspond to the mean of analyses of the unleached BHVO-1 and BHVO-2 powders as part of a high-precision isotopic characterization of ten USGS reference materials (Weis et al., submitted manuscript, 2004).

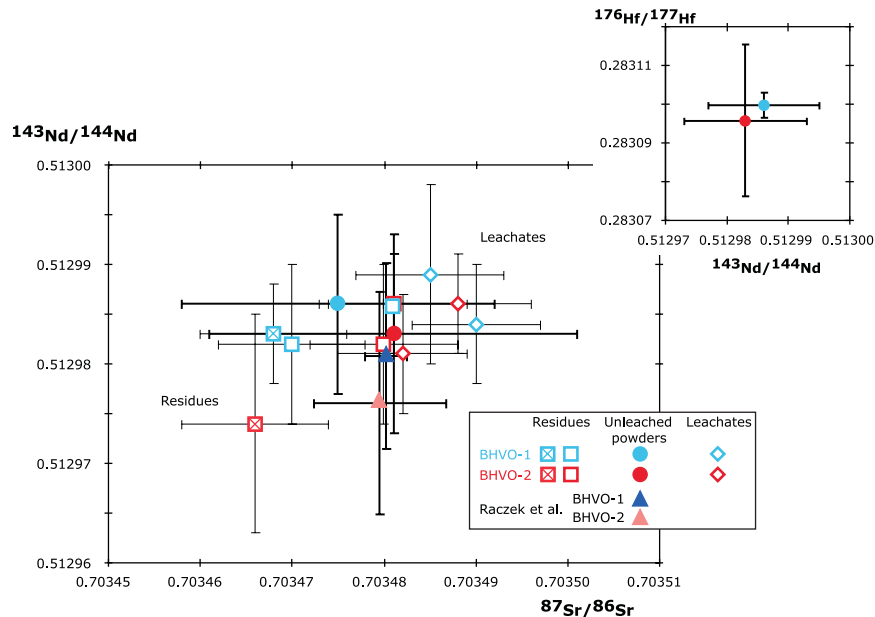


Figure 1. Sr-Nd isotopic diagram showing the results of BHVO-1 (blue symbols) and BHVO-2 (red symbols) leaching experiments. The circle symbols correspond to the mean of the unleached powders (Weis et al., submitted manuscript, 2004). For the mean, the error bars correspond to two standard deviations (thicker lines), while for the other results they are the $2\sigma_m$ of the individual mass spectrometric analyses. Residues after leaching are represented by the square symbols (crosses: Weis and Frey method; plain symbols: McDonough and Chauvel method), while the leachates (only McDonough and Chauvel method) are represented by diamonds. The means of the analyses of *Raczek et al.* [2003] are also reported as triangles in this figure for comparison.

[31] During the period of data collection, the JMC-475 Hf standard gave an unweighted mean for $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.282152 ± 0.000017 (2SD ; $n = 175$). The standard was run every two samples to monitor machine performance. The results in Table 1 have been normalized to a $^{176}\text{Hf}/^{177}\text{Hf}$ value of JMC-475 of 0.282160.

3.2. Elemental Abundances

[32] Samples of BHVO-1 and BHVO-2 were digested in concentrated HNO_3 -HF for 48 hours at 130°C on a hotplate in sealed 7 to 15 mL Savillex[®] Teflon sample beakers. After digestion, samples were dried and diluted 2000 times in 1% HNO_3 , and spiked with 1 part per billion (ppb) of In. The addition of In as internal standard facilitates correction for sensitivity drift (i.e., matrix effects). A low abundance multielement standard, analyzed after every 3–5 samples, was used to correct for mass drift of pertinent elements throughout the course of each analysis session. Samples were analyzed in medium resolution mode on a Finnigan Element 2 high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS), except for Cd, Sb, Sn, Ta, W, Pb and U, which were determined in low resolution mode. Sample con-

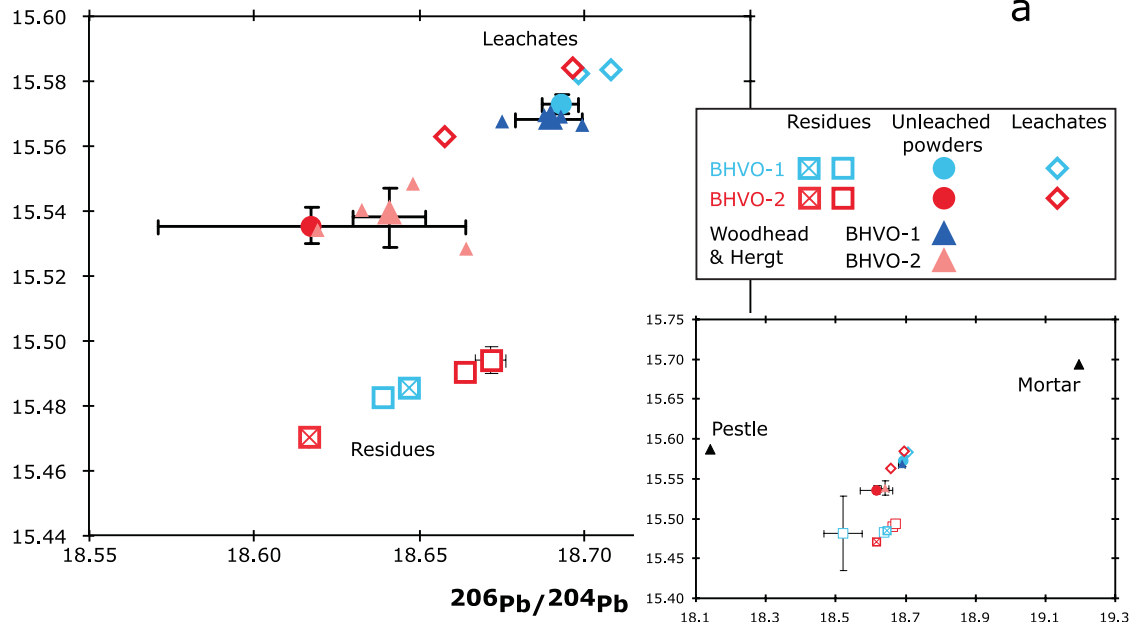
centrations were determined using external calibration after in-house preparation of multielement standards, prepared from 1000 ppm stock Spex Certiprep[®] single element standards. To reduce memory effects, trace elemental analyses were performed using a Teflon sample introduction system coupled to the HR-ICP-MS (i.e., PFA spray chamber, Microflow PFA self aspirating nebulizer, Elemental Scientific (Omaha, USA) and PFA take-up tubes), using a wash solution of 4% Aqua Regia (+ trace of HF).

[33] Analytical precision and accuracy, evaluated by replicate analysis of the reference materials, is typically $<10\%$ RSD and overlaps within error with certified reference values. Undiluted blanks for all elements measured in low and medium resolution are typically <0.05 ppb, except for V, Cu and Zn, which may be as high as 0.5 ppb. At the high dilution factors for solutions analyzed in this study, all blanks are inconsequential to final concentrations.

4. Results and Discussion

[34] The isotopic results are reported in Table 1 and in Figures 1 and 2. The $^{87}\text{Sr}/^{86}\text{Sr}$ of the residues of

$^{207}\text{Pb}/^{204}\text{Pb}$



$^{208}\text{Pb}/^{204}\text{Pb}$

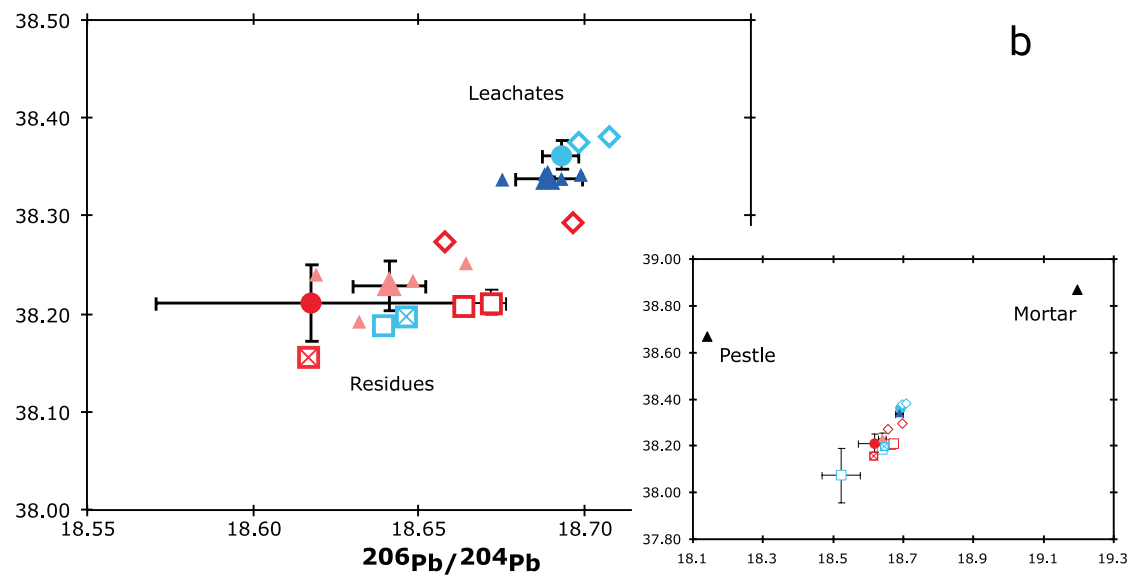


Figure 2. Pb-Pb isotopic systematics of the leaching experiments of BHVO-1 and BHVO-2: (a) $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ and (b) $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$. The errors on individual runs are smaller than are symbol sizes, unless indicated. Symbols and color-coding as in Figure 1, with the mortar and pestle results (inset) shown in black triangles and data from *Woodhead and Hergt* [2000] for double spike analyses in smaller symbols for individual analyses (no error bars, except for the mean).

both leaching experiments (0.703466 to 0.703481) are slightly lower than those of the unleached powders (0.703475–0.703481), which are in turn slightly lower than the leachates (0.703482–0.703490). The recent Sr and Nd isotopic data of *Raczek et al.* [2003] on unleached BHVO-1 and BHVO-2 have been normalized to our values for

NIST SRM 987 and La Jolla and are reported for comparison in Figure 1; they overlap within error with our results.

[35] In Figure 1, the differences between the unleached powder, the residue and the leachate are minor, at the limit of the analytical error, and

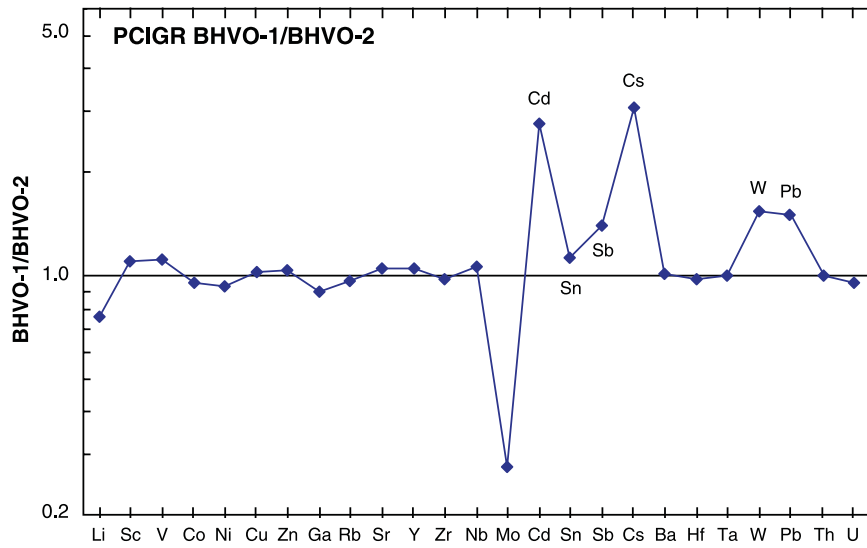


Figure 3. Comparison of trace element concentrations of BHVO-1 and BHVO-2 powders (reported as a ratio of BHVO-1/BHVO-2 concentrations in $\mu\text{g/g}$) analyzed at the Pacific Centre for Isotopic and Geochemical Research (PCIGR).

reflect the minor degree of alteration of this Hawaiian basalt. Despite being within error, the *Weis and Frey* [1991, 1996] method of leaching appears to be more efficient in removing alteration phases than that of *McDonough and Chauvel* [1991]. There is no difference in Nd isotopic composition for any of these analyses as they all overlap within error. In the light of this observation, we chose not to continue on the leaching experiment for Hf isotopes.

[36] The Pb isotopic results are reported in Figure 2, together with a comparison of recent double spike data on unleached BHVO powders [*Woodhead and Hergt*, 2000]. The agreement between the two different methods (double spike and MC-ICP-MS with Tl correction for fractionation) is excellent. Our data confirm the observation of these authors that the first generation of USGS reference materials has more radiogenic Pb ratios and most probably suffered some contamination during sample preparation. Recent publications of trace element contents [*Raczek et al.*, 2000; *Ila and Frey*, 2000] of USGS reference materials do not provide Pb concentrations, but our own analyses by HR-ICP-MS give $1.96 \pm 0.31 \mu\text{g/g}$ for BHVO-1 and $1.30 \pm 0.10 \mu\text{g/g}$ for BHVO-2; i.e., BHVO-1 is $\sim 40\%$ enriched in Pb in comparison to BHVO-2 (Figure 3).

[37] The residues of both leaching experiments are significantly less radiogenic in Pb isotopic compositions than the unleached rock powders, while the leachates are distinctly more radiogenic. This observation is valid for both BHVO-1 and BHVO-2,

but the differences are smaller for BHVO-2. The residues show much more homogeneous isotopic ratios than the unleached whole rocks [*Woodhead and Hergt*, 2000; *Baker et al.*, 2004; Weis et al., submitted manuscript, 2004]. In addition, the differences between BHVO-1 and BHVO-2 are significantly reduced after leaching and there is no significant difference between the two leaching methods employed in this study.

[38] In Figure 2, we also report analyses of samples of the steel percussion mortar and pestle used in the crushing of Hawaiian basalts for the Hawaiian Scientific Drilling Program (HSDP). The mortar and pestle are made of high-purity carbon steel and were carefully selected to minimize contamination during sample processing. The mortar and pestle material analyzed here is not the same as that used to process the first or second generation of USGS reference materials. Unfortunately, actual samples of the mortar and pestle used in the original preparation of the USGS reference materials were unobtainable for this study, so these results should be taken as a reference for the contamination possible during sample preparation. Of note in Figure 2 is the large difference between the isotopic compositions of these two potential contaminants, with the mortar having significantly higher $^{206}\text{Pb}/^{204}\text{Pb}$ than the pestle. Both have much higher $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ than BHVO values. The mortar and pestle also have higher Pb isotopic ratios than both the most common petrol-derived leads (Mississippi Valley-type and Broken Hill, Australia) and lead in environmental studies [e.g.,

Table 2. Trace Element Concentrations (in $\mu\text{g/g}$) of BHVO-1 and BHVO-2 and Comparison With Compilation Consensus and MIC-SSMS Values

	BHVO-1					BHVO-2				
	USGS ^a	MIC-SSMS ^b	This Study Average (n = 5)	stdev	%RSD	USGS ^a	MIC-SSMS ^b	This Study Average (n = 5)	stdev	%RSD
Li	4.6		4.42	0.07	1.53			5.86	0.41	7.02
Sc	31.8		31.3	0.6	2.05	32		28.6	2.1	7.26
V	317		344	5	1.38	317		310	45	14.67
Co	45		44.2	1.10	2.50	45		46.5	0.98	2.12
Ni	121		112	1	0.98	119		121	4	3.45
Cu	136		120	3	2.40	127		117	2	1.85
Zn	105		98	3	2.99	103		95	11	11.58
Ga	21		18.9	1.0	5.55	21.7		21.2	1.2	5.72
Rb	11		9.3	0.2	2.05	9.8		9.6	0.2	2.42
Sr	403		400	7	1.76	389		381	42	10.94
Y	28	30	24.3	0.4	1.81	26	29	23.1	0.4	1.60
Zr	179	175	169	3	1.60	172	170	174	6	3.44
Nb	19	18.2	18.3	0.2	0.83	18	18	17.2	1.9	11.15
Mo	1.02		1.14	0.05	4.00	nd		4.15	0.63	15.15
Cd	0.069		0.17	0.01	6.26	nd		0.06	0.01	12.96
Sn	2.1		1.91	0.01	0.58	1.9		1.70	0.02	1.18
Sb	0.16		0.14	0.01	4.51			0.10	0.01	6.97
Cs	0.13		0.11	0.02	18.57			0.03	0.01	34.61
Ba	139		134	4	2.76	130	129	133	2	1.24
Hf	4.38	4.3	4.15	0.08	1.84	4.1	4.2	4.28	0.11	2.55
Ta	1.23	1.18	1.06	0.02	1.65	1.4	1.14	1.06	0.11	10.16
W	0.27		0.21	0.01	2.83			0.13	0.00	2.58
Pb	2.6	2.56	1.96	0.31	15.69		2.09	1.30	0.10	8.07
Bi	0.018		<lod ^c	<lod	<lod			0.13	0.00	0.82
Th	1.08	1.22	1.03	0.18	17.16	1.2	1.16	1.03	0.25	24.38
U	0.42	0.41	0.36	0.05	12.89		0.404	0.38	0.07	19.76

^aUSGS values [Wilson, 1997], except for U and Pb, compilation consensus values [Gladney and Roelandts, 1988].

^bMulti-ion counting spark-source mass spectrometry (MIC-SSMS) [Jochum et al., 2001].

^clod, limit of detection.

Weiss *et al.*, 2004], which are distinctly less radiogenic than the values in question here. As described by Flanagan [1967], the processing of BHVO samples involved four stages using a steel jaw crusher, steel roller mill, porcelain ball mill, and a stainless steel blender. It is probable that contamination from one (or a blend) of the pieces of equipment involved in the crushing and homogenization of these reference materials occurred during processing. A mixture of the mortar and pestle material analyzed here would be a suitable contaminant to explain the shift toward more radiogenic ratios in BHVO-1, and in BHVO-2 to a lesser extent. Such a contaminant could also account for the differences observed between BCR-1 and BCR-2, and between AGV-1 and AGV-2 [Woodhead and Hergt, 2000].

[39] To investigate the issue further, high-precision trace element analyses of BHVO-1 and BHVO-2 powders are reported in Table 2 and in Figure 3. There are no significant differences between the trace elemental compositions of BHVO-1 and BHVO-2, except for the elements Li, Mo, Cd, Sb, Cs, W and Pb (Figure 3). All of these latter elements, apart from Li and Mo, are enriched by between ~50–300% in BHVO-1. The lack of certified USGS and additional literature values for some of the latter elements prevents a direct comparison with the data obtained in this study. However, the concurrent enrichment of elements such as Cd, Sn, Sb, W and Pb is consistent with contamination from one or a combination of steel sample preparation devices used during the homogenization and preparation of BHVO-1. BHVO-2 appears to be enriched in Mo in comparison to BHVO-1. The relative enrichment of Mo in BHVO-2 is coherent with other literature data [Lin *et al.*, 2000], and although it may also be the result of contamination, additional analyses are needed to identify its origin.

5. Conclusions

[40] Isotopic and trace elemental results for BHVO-1 and BHVO-2 in this study document clear contamination in the first generation of USGS Hawaiian basalt reference materials during sample preparation. Contamination accounts for the high concentration in some specific trace elements in the basalts. The second generation of reference materials also appears to have suffered contamination, apparent in less homogeneous isotopic compositions. The source of the contamination was likely from the steel-type sample grinding equipment

used to prepare the USGS reference material at the time. It is reasonable to infer that the difference in Pb isotopic ratios of other first and second generation USGS reference materials, such as between BCR-1 and BCR-2, and between AGV-1 and AGV-2 [Woodhead and Hergt, 2000; Baker *et al.*, 2004; Weiss *et al.*, submitted manuscript, 2004], is also the result of contamination. A systematic isotopic and trace elemental investigation of additional USGS reference materials is suggested to further constrain the potential source of contamination.

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