



## High-precision isotopic characterization of USGS reference materials by TIMS and MC-ICP-MS

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[1] The Pacific Centre for Isotopic and Geochemical Research (PCIGR) at the University of British Columbia has undertaken a systematic analysis of the isotopic (Sr, Nd, and Pb) compositions and concentrations of a broad compositional range of U.S. Geological Survey (USGS) reference materials, including basalt (BCR-1, 2; BHVO-1, 2), andesite (AGV-1, 2), rhyolite (RGM-1, 2), syenite (STM-1, 2), granodiorite (GSP-2), and granite (G-2, 3). USGS rock reference materials are geochemically well characterized, but there is neither a systematic methodology nor a database for radiogenic isotopic compositions, even for the widely used BCR-1. This investigation represents the first comprehensive, systematic analysis of the isotopic composition and concentration of USGS reference materials and provides an important database for the isotopic community. In addition, the range of equipment at the PCIGR, including a Nu Instruments Plasma MC-ICP-MS, a Thermo Finnigan Triton TIMS, and a Thermo

Finnigan Element2 HR-ICP-MS, permits an assessment and comparison of the precision and accuracy of isotopic analyses determined by both the TIMS and MC-ICP-MS methods (e.g., Nd isotopic compositions). For each of the reference materials, 5 to 10 complete replicate analyses provide coherent isotopic results, all with external precision below 30 ppm (2 SD) for Sr and Nd isotopic compositions (27 and 24 ppm for TIMS and MC-ICP-MS, respectively). Our results also show that the first- and second-generation USGS reference materials have homogeneous Sr and Nd isotopic compositions. Nd isotopic compositions by MC-ICP-MS and TIMS agree to within 15 ppm for all reference materials. Interlaboratory MC-ICP-MS comparisons show excellent agreement for Pb isotopic compositions; however, the reproducibility is not as good as for Sr and Nd. A careful, sequential leaching experiment of three first- and second-generation reference materials (BCR, BHVO, AGV) indicates that the heterogeneity in Pb isotopic compositions, and concentrations, could be directly related to contamination by the steel (mortar/pestle) used to process the materials. Contamination also accounts for the high concentrations of certain other trace elements (e.g., Li, Mo, Cd, Sn, Sb, W) in various USGS reference materials.

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## 1. Introduction

[2] The recent development of multiple collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) for high-precision isotopic analyses of a large number of elements and the ability of the Ar-ICP source to ionize most elements in the periodic table, has made these instruments critical to the advancement of research in geochemical, environmental and medical fields [Halliday et al., 1998; Albarède et al., 2004]. The precision achieved on isotopic analyses of Nd, Hf and Pb is significantly better than 100 ppm due to the fact that most of the analyses can be run in static mode. Quality control protocols that monitor accuracy and precision demand well-characterized, homogenous reference materials. In addition, matrix effects can significantly affect the accuracy of the results, contrary to what was initially believed [e.g., Belshaw et al., 1998; Woodhead, 2002]. Therefore the reference material basis must also encompass the entire compositional range of studied samples. Similarly, recent technical improvements in thermo-ionization mass spectrometers (TIMS) have also led to the ability to produce more precise analyses on these instruments [e.g., Caro et al., 2003].

[3] We have carried out a systematic study of some of the most commonly used USGS reference materials: BCR-1, BCR-2, BHVO-1, BHVO-2, AGV-1, AGV-2, STM-1, STM-2, RGM-1, G-2, G-3 and GSP-2. Due to the heterogeneous nature of some of the basaltic samples, both in terms of concentrations and isotopic compositions, leaching experiments were carried out on BHVO-1, BHVO-2, AGV-1, AGV-2, BCR-1 and BCR-2 to further extend the study of Weis et al. [2005a].

[4] The availability of both a TIMS (Thermo Electron, Finnigan Triton) and a MC-ICP-MS (Nu Instruments Plasma) in the same laboratory allowed us to carry out a parallel study of Sr and Nd isotopic compositions on the TIMS, and Nd, Hf and Pb isotopic compositions on the MC-ICP-MS. To improve the comparison and reproducibility of the MC-ICP-MS analyses, we also measured Hf and Pb isotopic ratios on two different instruments in two different laboratories (Nu Plasma serial #015 in Brussels and Nu Plasma serial #021 in Vancouver) when possible.

[5] The results are presented and discussed for each separate isotopic system, except where it is relevant to combine two systems. This paper focuses on Sr, Nd and Pb isotopes. Hf isotopic results will be presented in a separate paper, because of interesting developments related to the

**Table 1a.** Nu Plasma MC-ICP-MS Operating Conditions

	Dry Plasma	Wet Plasma
RF power	1350 W	1350 W
Acceleration voltage	~4000 V	~4000 V
Mass analyzer pressure	$\sim 2 \times 10^{-9}$ mbar	$\sim 2 \times 10^{-9}$ mbar
Desolvating system	DSN-100	n/a
Nebulizer	ESI $\mu$ flow	GE Micromist
Sample uptake rate	170–190 $\mu$ L/min	50–100 $\mu$ L/min
Spray chamber temperature	110°C	5°C
Membrane temperature	110°C	n/a
Hot gas flow	0.2 L/min	n/a
Membrane gas flow	2.5–3.5 L/min	n/a

role of labware composition [Weis *et al.*, 2005b] and different separation issues.

## 2. Analytical Techniques

[6] This study aims to present accurate high-precision isotopic compositions for USGS reference materials. We therefore describe our analytical procedures in some detail to provide the reader with sufficient information to evaluate and apply our methods. Cleaning protocols for high-pressure PTFE bombs and other labware are discussed by Pretorius *et al.* [2006]. All of the acids used for sample digestion and chemical separation were sub-boiling distilled in Teflon<sup>®</sup> bottles, whereas the acids used for cleaning columns were quartz-distilled.

### 2.1. Sample Dissolution Protocol

[7] First, a series of tests was carried out to determine the appropriate digestion method for each reference material. This investigation demonstrated that it is critical to use high-pressure PTFE bomb dissolutions to achieve full recovery of trace elements from felsic rocks containing refractory accessory phases [Pretorius *et al.*, 2006]. Full trace element recovery from mafic compositions and volcanic rock types, however, was achieved with a standard hotplate dissolution, in a Savillex<sup>®</sup> beaker.

### 2.1.1. Felsic Samples

[8] Approximately 100 to 150 mg of sample rock powder is loaded into a steel-jacketed acid-washed high-pressure PTFE bomb with 5.0 mL of 48% HF and 1.0 mL of  $\sim 14$  N HNO<sub>3</sub>, and then dissolved for 5 days at 190°C. Digested samples are dried down on a hotplate overnight at  $\sim 130$ °C, reconstituted in 6.0 mL of 6 N HCl and re-bombed for 24 hours at 190°C. Afterward, samples are taken to dryness on a hotplate prior to re-dissolution for ion exchange purification of Pb, Hf, Sr and Nd.

### 2.1.2. Mafic Samples

[9] For mafic samples the rock powders (100 to 250 mg) are placed in 15 mL screw-top Savillex<sup>®</sup> beakers with 10.0 mL of 48% HF and 1.0 mL of  $\sim 14$  N HNO<sub>3</sub>, and then dissolved on a hotplate for 48 hours at 130°C. During this step samples are periodically placed in an ultrasonic bath to ensure complete digestion. After digestion, samples are dried down overnight on a hotplate at  $\sim 130$ °C, reconstituted in 6.0 mL of 6 N sub-boiled HCl and re-dissolved for 24 hours at 130°C, before commencing ion exchange chemistry.

## 2.2. Ion Exchange Chemistry

### 2.2.1. Pb Column Chemistry

[10] Pb, Hf, Sr and Nd are all purified from the same sample solution. The first stage is the sepa-

**Table 1b.** Nu Plasma MC-ICP-MS Nd and Pb Collector Configurations<sup>a</sup>

Element	H6	H5	H4	H3	H2	H1	Ax	L1	L2	L3	L4	L5	Integration Time, s
Nd		150	148	147	146	145	144	143	142	140			10
Pb			208	207	206	205	204	203	202				10

<sup>a</sup>Baselines were half-mass zeros and were taken over 30 s, every block.

**Table 2.** USGS Reference Materials: Sr Isotopic Analyses (TIMS)<sup>a</sup>

Sample	Run Number	<sup>87</sup> Sr/ <sup>86</sup> Sr	Error (2σ)	<sup>87</sup> Sr/ <sup>86</sup> Sr Norm <sup>b</sup>	2 SD <sup>c</sup>	
<i>Basalt</i>						
BCR-1	BCR-1 a S6 <sup>d</sup>	0.705024	6	0.705014		
	BCR-1 b S7 <sup>d</sup>	0.705038	7	0.705028		
	BCR-1 b S7 <sup>d</sup> (5 months later)	0.705039	7	0.705025		
	BCR-1 (1) 06/05/03	0.705023	9	0.705017		
	BCR-1 (2) 06/05/03	0.705022	8	0.705016		
	<i>BCR-1 (1) 08/08/03</i>	<i>0.705015</i>	<i>7</i>	<i>0.705010</i>		
	<i>BCR-1 (2) 08/08/03</i>	<i>0.705013</i>	<i>7</i>	<i>0.705011</i>		
	<i>BCR-1 S10<sup>d</sup></i>	<i>0.705024</i>	<i>7</i>	<i>0.705023</i>		
	<b>Mean (2 SD)</b>	<b>0.705025</b>	<b>19</b>	<b>0.705018</b>	<b>13</b>	
BCR-2	BCR-2 24/03/03	0.705018	6	0.705014		
	BCR-2 (1) 19/04/03	0.705028	9	0.705024		
	BCR-2 04/01/03	0.705025	9	0.705016		
	BCR-2 (1) 08/08/03	0.705030	7	0.705016		
	BCR-2 (2) 08/08/03	0.705033	9	0.705019		
	BCR-2 (3) 08/08/03	0.705019	9	0.705005		
	<i>BCR-2 (1) 05/12/03</i>	<i>0.705017</i>	<i>9</i>	<i>0.705017</i>		
	<i>BCR-2 (2) 05/12/03</i>	<i>0.705011</i>	<i>7</i>	<i>0.705009</i>		
	<i>BCR-2 19/12/03</i>	<i>0.705012</i>	<i>7</i>	<i>0.705012</i>		
	<i>BCR-2 HA</i>	<i>0.705012</i>	<i>7</i>	<i>0.705008</i>		
	<i>BCR-2 (1) 24/09/03</i>	<i>0.705009</i>	<i>7</i>	<i>0.705008</i>		
	<i>BCR-2 (2) 24/09/03</i>	<i>0.705013</i>	<i>8</i>	<i>0.705012</i>		
	<i>BCR-2 9/05/05</i>	<i>0.705020</i>	<i>7</i>	<i>0.705009</i>		
		<b>Mean (2 SD)</b>	<b>0.705019</b>	<b>16</b>	<b>0.705013</b>	<b>10</b>
	BHVO-1	BHVO-1 a S1 <sup>d</sup>	0.703483	6	0.703473	
BHVO-1 a A8 <sup>d</sup>		0.703502	6	0.703488		
BHVO-1 b S2 <sup>d</sup>		0.703486	7	0.703476		
BHVO-1 24/03/03		0.703471	6	0.703467		
BHVO-1 19/04/03		0.703470	10	0.703464		
BHVO-1 08/08/03		0.703489	7	0.703475		
BHVO-1 Ca <sup>d</sup>		0.703487	7	0.703473		
BHVO-1 c S3 <sup>d</sup>		0.703487	6	0.703486		
		<b>Mean (2 SD)</b>	<b>0.703484</b>	<b>21</b>	<b>0.703475</b>	<b>17</b>
BHVO-2	BHVO-2 Cb <sup>d</sup>	0.703481	9	0.703469		
	BHVO-2 24/03/03	0.703484	6	0.703480		
	BHVO-2 19/04/03	0.703483	8	0.703474		
	BHVO-2 19/04/03 Dble	0.703500	6	0.703499		
	BHVO-2 (1) 08/08/03	0.703494	8	0.703480		
	BHVO-2 (1) 08/08/03 (rerun)	0.703509	7	0.703495		
	<i>BHVO-2 HA</i>	<i>0.703484</i>	<i>7</i>	<i>0.703484</i>		
	<i>BHVO-2 (2) 05/12/03</i>	<i>0.703485</i>	<i>6</i>	<i>0.703483</i>		
	<i>BHVO-2 (1) 05/12/03</i>	<i>0.703474</i>	<i>7</i>	<i>0.703470</i>		
	<i>BHVO-2 19/12/03</i>	<i>0.703481</i>	<i>7</i>	<i>0.703477</i>		
	<i>BHVO-2 9/05/05</i>	<i>0.703482</i>	<i>7</i>	<i>0.703471</i>		
	<i>BHVO-2 9/05/05</i>	<i>0.703482</i>	<i>7</i>	<i>0.703471</i>		
		<b>Mean (2 SD)</b>	<b>0.703487</b>	<b>19</b>	<b>0.703479</b>	<b>20</b>
	<i>Andesite</i>					
AGV-1	AGV-1 a A1 <sup>d</sup>	0.703986	13	0.703984		
	AGV-1 b A2 <sup>d</sup>	0.704001	8	0.703989		
	AGV-1 a S4 <sup>d</sup>	0.704006	7	0.703988		
	AGV-1 b S5 <sup>d</sup>	0.703990	7	0.703980		
	AGV-1 RMF <sup>d</sup>	0.703993	6	0.703983		
	AGV-1 24/03/03	0.703992	6	0.703988		
	AGV-1 19/04/03	0.704004	8	0.703998		
	AGV-1 19/04/03 Dble	0.704014	10	0.704008		
	<i>AGV-1 a S1<sup>d</sup></i>	<i>0.703987</i>	<i>6</i>	<i>0.703985</i>		
	<i>AGV-1 D10<sup>d</sup></i>	<i>0.703985</i>	<i>7</i>	<i>0.703985</i>		
		<b>Mean (2 SD)</b>	<b>0.703996</b>	<b>20</b>	<b>0.703989</b>	<b>17</b>
AGV-2	AGV-2 b A7 <sup>d</sup>	0.703988	5	0.703978		
	AGV-2 (1) 19/04/03	0.703988	8	0.703979		
	AGV-2 (2) 19/04/03	0.703993	10	0.703984		

**Table 2.** (continued)

Sample	Run Number	$^{87}\text{Sr}/^{86}\text{Sr}$	Error ( $2\sigma$ )	$^{87}\text{Sr}/^{86}\text{Sr}$ Norm <sup>b</sup>	2 SD <sup>c</sup>
	<i>AGV-2 a A6<sup>d</sup></i>	<i>0.703979</i>	<i>6</i>	<i>0.703977</i>	
	<i>AGV-2 (2) 05/12/03</i>	<i>0.703984</i>	<i>8</i>	<i>0.703980</i>	
	<i>AGV-2 (1) 05/12/03</i>	<i>0.703973</i>	<i>7</i>	<i>0.703973</i>	
	<i>AGV-2 19/12/03</i>	<i>0.703983</i>	<i>9</i>	<i>0.703983</i>	
	<i>AGV-2 (1) 08/08/04</i>	<i>0.703986</i>	<i>8</i>	<i>0.703985</i>	
	<i>AGV-2 LT9 03/22/05</i>	<i>0.703997</i>	<i>7</i>	<i>0.703987</i>	
	<i>AGV-2 LT10 03/22/05</i>	<i>0.703998</i>	<i>7</i>	<i>0.703988</i>	
	<b>Mean (2 SD)</b>	<b>0.703987</b>	<b>16</b>	<b>0.703981</b>	<b>9</b>
		<i>Syenite</i>			
<b>STM-2</b>	<i>STM-2 D10<sup>d</sup></i>	<i>0.703701</i>	<i>8</i>	<i>0.703697</i>	
	<i>STM-2 L8<sup>d</sup></i>	<i>0.703704</i>	<i>7</i>	<i>0.703703</i>	
	<i>STM-2 L9<sup>d</sup></i>	<i>0.703708</i>	<i>7</i>	<i>0.703704</i>	
	<i>STM-2 L10<sup>d</sup></i>	<i>0.703703</i>	<i>8</i>	<i>0.703699</i>	
	<i>STM-2 D1<sup>d</sup></i>	<i>0.703707</i>	<i>9</i>	<i>0.703703</i>	
	<b>Mean (2 SD)</b>	<b>0.703705</b>	<b>6</b>	<b>0.703701</b>	<b>6</b>
		<i>Rhyolite</i>			
<b>RGM-1</b>	RGM-1 A10 <sup>d</sup>	0.704228	6	0.704214	
	RGM-1 (1) 19/04/03	0.704219	9	0.704210	
	RGM-1 (2) 19/04/03	0.704217	8	0.704208	
	RGM-1 A5 <sup>d</sup>	0.704218	9	0.704203	
	RGM-1 S2 <sup>d</sup>	0.704220	6	0.704206	
	<i>RGM-1 (2) 19/12/03</i>	<i>0.704218</i>	<i>7</i>	<i>0.704214</i>	
	<i>RGM-1 (3) 19/12/03</i>	<i>0.704206</i>	<i>7</i>	<i>0.704202</i>	
	<i>RGM-1 (1) 19/12/03</i>	<i>0.704208</i>	<i>7</i>	<i>0.704204</i>	
	<i>RGM-1 D9<sup>d</sup></i>	<i>0.704227</i>	<i>8</i>	<i>0.704215</i>	
	<i>RGM-1 03/03/05</i>	<i>0.704227</i>	<i>8</i>	<i>0.704215</i>	
	<b>Mean (2 SD)</b>	<b>0.704219</b>	<b>15</b>	<b>0.704210</b>	<b>14</b>
		<i>Granite</i>			
<b>G-2</b>	<i>G-2 A5<sup>d</sup></i>	<i>0.709783</i>	<i>8</i>	<i>0.709781</i>	
	<i>G-2 04/01/04 + HClO<sub>4</sub></i>	<i>0.709775</i>	<i>6</i>	<i>0.709775</i>	
	<i>G-2 04/01/04 No HClO<sub>4</sub></i>	<i>0.709760</i>	<i>9</i>	<i>0.709760</i>	
	<i>G-2 L5<sup>d</sup></i>	<i>0.709766</i>	<i>8</i>	<i>0.709766</i>	
	<i>G-2 L6<sup>d</sup></i>	<i>0.709765</i>	<i>7</i>	<i>0.709765</i>	
	<i>G-2 D8<sup>d</sup></i>	<i>0.709774</i>	<i>7</i>	<i>0.709774</i>	
	<i>G-2 D9<sup>d</sup></i>	<i>0.709766</i>	<i>8</i>	<i>0.709766</i>	
	<b>Mean (2 SD)</b>	<b>0.709770</b>	<b>16</b>	<b>0.709770</b>	<b>14</b>
		<i>Granodiorite</i>			
<b>GSP-2</b>	GSP-2 (1) B5 <sup>d</sup>	0.765112	4	0.765096	
	GSP-2 (2) B6 <sup>d</sup>	0.765122	9	0.765102	
	<i>GSP-2 D2<sup>d</sup></i>	<i>0.765171</i>	<i>7</i>	<i>0.765167</i>	
	<i>GSP-2 D3<sup>d</sup></i>	<i>0.765175</i>	<i>7</i>	<i>0.765171</i>	
	<i>GSP-2 D5<sup>d</sup></i>	<i>0.765160</i>	<i>8</i>	<i>0.765156</i>	
	<i>GSP-2 D5<sup>d</sup> (rerun)</i>	<i>0.765156</i>	<i>7</i>	<i>0.765152</i>	
	<i>GSP-2 D6<sup>d</sup></i>	<i>0.765202</i>	<i>8</i>	<i>0.765198</i>	
	<i>GSP-2 D7<sup>d</sup></i>	<i>0.765111</i>	<i>7</i>	<i>0.765107</i>	
	<b>Mean (2 SD)</b>	<b>0.765151</b>	<b>66</b>	<b>0.765144</b>	<b>75</b>

<sup>a</sup>“Dble”: same digestion but different columns. Italic: measured after change of one of the Faraday cups. (rerun): sample measured twice with same filament load. The  $2\sigma$  error is the absolute error value of the individual sample analysis (internal error) and reported as times  $10^6$ .

<sup>b</sup>Measured ratio normalized to SRM 987  $^{87}\text{Sr}/^{86}\text{Sr} = 0.710248$ .

<sup>c</sup>Here, 2 SD is the 2 standard deviation on the mean of the individual reference material analyses.

<sup>d</sup>High-pressure dissolution (the coding corresponds to the pressure-vessel number).

ration of Pb from other elements using an anion exchange column. The discard from this column is then dried down and reconstituted for cation exchange separation of Sr from the rare earth ele-

ments (REE) and Hf. The bulk REE fraction is then processed through exchange column to separate Nd from the remaining REE. The Hf fraction requires two further purification steps [Blichert-Toft *et al.*,

**Table 3.** USGS Reference Materials: Nd Isotopic Analyses (TIMS)<sup>a</sup>

Sample	Run Number	<sup>143</sup> Nd/ <sup>144</sup> Nd	Error (2σ)	<sup>145</sup> Nd/ <sup>144</sup> Nd	Error (2σ)	<sup>143</sup> Nd/ <sup>144</sup> Nd Norm <sup>b</sup>	2 SD <sup>c</sup>	
<i>Basalt</i>								
<b>BCR-1</b>	BCR-1 A <sup>d</sup>	0.512625	8	0.348395	2	0.512640		
	BCR-1 A <sup>d</sup> (rerun)	0.512626	4	0.348402	4	0.512641		
	BCR-1 B <sup>d</sup>	0.512622	6	0.348400	3	0.512637		
	BCR-1 B <sup>d</sup> (rerun)	0.512623	6	0.348401	3	0.512638		
	BCR-1 302-6 <sup>d</sup>	0.512621	8	0.348396	9	0.512636		
	BCR-1 302-7 <sup>d</sup>	0.512624	6	0.348399	9	0.512639		
	BCR-1 (2) 06/05/03	0.512635	4	0.348410	6	0.512633		
	BCR-1 (1) 06/05/03	0.512643	6	0.348409	3	0.512641		
	<i>BCR-1 (1) 08/08/03</i>	<i>0.512629</i>	<i>6</i>	<i>0.348404</i>	<i>3</i>	<i>0.512637</i>		
	<i>BCR-1 a S6<sup>d</sup></i>	<i>0.512632</i>	<i>5</i>	<i>0.348411</i>	<i>3</i>	<i>0.512636</i>		
	<i>BCR-1 b S7<sup>d</sup></i>	<i>0.512639</i>	<i>5</i>	<i>0.348407</i>	<i>3</i>	<i>0.512643</i>		
	<i>BCR-1 S10<sup>d</sup></i>	<i>0.512631</i>	<i>5</i>	<i>0.348400</i>	<i>3</i>	<i>0.512635</i>		
	<i>BCR-1(2) 08/08/03</i>	<i>0.512626</i>	<i>5</i>	<i>0.348408</i>	<i>3</i>	<i>0.512633</i>		
	<b>Mean (2 SD)</b>	<b>0.512629</b>	<b>14</b>			<b>0.512638</b>	<b>6</b>	
	<b>BCR-2</b>	BCR-2 (1) 19/04/03	0.512639	5	0.348408	3	0.512636	
BCR-2 24/03/03		0.512640	5	0.348410	3	0.512637		
BCR-2 04/01/03		0.512639	4	0.348409	3	0.512636		
BCR-2 (1) 08/08/03		0.512643	5	0.348408	3	0.512648		
BCR-2 (3) 08/08/03		0.512638	6	0.348407	3	0.512643		
BCR-2 (2) 08/08/03		0.512631	6	0.348401	3	0.512639		
<i>BCR-2 HA</i>		<i>0.512631</i>	<i>6</i>	<i>0.348407</i>	<i>3</i>	<i>0.512643</i>		
<i>BCR-2 19/12/03</i>		<i>0.512631</i>	<i>5</i>	<i>0.348403</i>	<i>4</i>	<i>0.512635</i>		
<i>BCR-2 (1) 05/12/03</i>		<i>0.512627</i>	<i>5</i>	<i>0.348410</i>	<i>4</i>	<i>0.512631</i>		
<i>BCR-2 (2) 05/12/03</i>		<i>0.512633</i>	<i>5</i>	<i>0.348402</i>	<i>3</i>	<i>0.512637</i>		
<i>BCR-2 24/09/03</i>		<i>0.512623</i>	<i>7</i>	<i>0.348407</i>	<i>4</i>	<i>0.512627</i>		
<b>Mean (2 SD)</b>		<b>0.512634</b>	<b>12</b>			<b>0.512637</b>	<b>12</b>	
<b>BHVO-1</b>		BHVO-1 Aa <sup>d</sup>	0.512972	4	0.348395	2	0.512987	
		BHVO-1 Aa <sup>d</sup> (rerun)	0.512977	4	0.348399	3	0.512992	
	BHVO-1 Ab <sup>d</sup>	0.512969	8	0.348401	3	0.512984		
	BHVO-1 Ab <sup>d</sup> (rerun)	0.512971	6	0.348401	3	0.512986		
	BHVO-1 Ba <sup>d</sup>	0.512972	8	0.348394	5	0.512987		
	BHVO-1 Bb <sup>d</sup>	0.512972	6	0.348399	3	0.512987		
	BHVO-1 Bb <sup>d</sup> (rerun)	0.512965	6	0.348398	4	0.512980		
	BHVO-1 Ca <sup>d</sup>	0.512971	8	0.348400	2	0.512986		
	BHVO-1 Cb <sup>d</sup>	0.512967	6	0.348397	3	0.512982		
	BHVO-1 b <sup>d</sup>	0.512978	10	0.348394	5	0.512993		
	202-6 <sup>d</sup>	0.512973	2	0.348399	3	0.512988		
	BHVO-1 302-8 <sup>d</sup>	0.512967	8	0.348404	3	0.512982		
	BHVO-1 24/03/03	0.512981	5	0.348410	2	0.512978		
	BHVO-1 19/04/03	0.512986	6	0.348405	6	0.512983		
	BHVO-1 08/08/03	0.512977	6	0.348410	3	0.512982		
	BHVO-1 a A8 <sup>d</sup>	0.512977	7	0.348408	4	0.512984		
	BHVO-1 a S1 <sup>d</sup>	0.512988	5	0.348409	3	0.512995		
	BHVO-1 c S3 <sup>d</sup>	0.512985	6	0.348397	4	0.512992		
	BHVO-1 b S2 <sup>d</sup>	0.512980	5	0.348406	3	0.512987		
	<b>Mean (2 SD)</b>	<b>0.512975</b>	<b>13</b>			<b>0.512986</b>	<b>9</b>	
	<b>BHVO-2</b>	BHVO-2 24/03/03	0.512983	5	0.348412	3	0.512981	
BHVO-2 19/04/03 Dble		0.512982	4	0.348408	3	0.512980		
BHVO-2 19/04/03		0.512987	6	0.348419	4	0.512985		
BHVO-2 (1) 08/08/03		0.512982	6	0.348410	3	0.512987		
BHVO-2 HA		0.512981	5	0.348405	3	0.512993		
<i>BHVO-2 (1) 05/12/03</i>		<i>0.512972</i>	<i>7</i>	<i>0.348406</i>	<i>5</i>	<i>0.512976</i>		
<i>BHVO-2 (2) 05/12/03</i>		<i>0.512977</i>	<i>10</i>	<i>0.348402</i>	<i>5</i>	<i>0.512981</i>		
<i>BHVO-2 19/12/03</i>		<i>0.512978</i>	<i>6</i>	<i>0.348408</i>	<i>4</i>	<i>0.512982</i>		
<i>BHVO-2 19/12/03 (rerun)</i>		<i>0.512976</i>	<i>5</i>	<i>0.348405</i>	<i>3</i>	<i>0.512980</i>		
<i>BHVO-2 Dec04-Jan05</i>		<i>0.512981</i>	<i>6</i>	<i>0.348409</i>	<i>3</i>	<i>0.512985</i>		
<i>BHVO-2 Dec04-Jan05</i>		<i>0.512983</i>	<i>6</i>	<i>0.348406</i>	<i>4</i>	<i>0.512987</i>		
<i>BHVO-2 Dec04-Jan05</i>		<i>0.512992</i>	<i>6</i>	<i>0.348408</i>	<i>4</i>	<i>0.512996</i>		
<i>BHVO-2 Dec04-Jan05</i>		<i>0.512979</i>	<i>7</i>	<i>0.348397</i>	<i>4</i>	<i>0.512983</i>		
<b>Mean (2 SD)</b>		<b>0.512981</b>	<b>10</b>			<b>0.512984</b>	<b>11</b>	

**Table 3.** (continued)

Sample	Run Number	$^{143}\text{Nd}/^{144}\text{Nd}$	Error (2 $\sigma$ )	$^{145}\text{Nd}/^{144}\text{Nd}$	Error (2 $\sigma$ )	$^{143}\text{Nd}/^{144}\text{Nd}$ Norm <sup>b</sup>	2 SD <sup>c</sup>	
<i>Andesite</i>								
AGV-1	AGV-1 <sup>d</sup>	0.512774	4	0.348391	2	0.512791		
	AGV-1 A <sup>d</sup>	0.512773	8	0.348393	4	0.512790		
	AGV-1 A <sup>d</sup>	0.512781	8	0.348398	3	0.512798		
	AGV-1 B <sup>d</sup>	0.512776	6	0.348395	3	0.512793		
	AGV-1 24/03/03	0.512787	5	0.348405	3	0.512785		
	AGV-1 19/04/03 Dble	0.512788	5	0.348410	3	0.512786		
	AGV-1 19/04/03	0.512791	5	0.348406	4	0.512789		
	AGV-1 D10 <sup>d</sup> 11/01/04	0.512789	5	0.348408	3	0.512793		
	AGV-1 a S4 <sup>d</sup>	0.512801	8	0.348412	6	0.512805		
	AGV-1 b S5 <sup>d</sup>	0.512778	7	0.348400	4	0.512782		
	<b>Mean (2 SD)</b>	<b>0.512784</b>	<b>18</b>			<b>0.512791</b>	<b>13</b>	
AGV-2	AGV-2 (2) 19/04/03	0.512805	7	0.348411	4	0.512802		
	AGV-2 (1) 19/04/03	0.512783	5	0.348406	3	0.512780		
	AGV-2 (A) A6 <sup>d</sup>	0.512798	5	0.348411	4	0.512798		
	AGV-2 (B) A7 <sup>d</sup>	0.512788	6	0.348408	4	0.512788		
	AGV-2 (1) 05/12/03	0.512788	6	0.348407	3	0.512792		
	AGV-2 (2) 05/12/03	0.512783	6	0.348405	4	0.512787		
	AGV-2 08/08/03	0.512787	6	0.348404	3	0.512791		
	AGV-2 19/12/03	0.512785	6	0.348403	3	0.512792		
		<b>Mean (2 SD)</b>	<b>0.512790</b>	<b>16</b>			<b>0.512791</b>	<b>13</b>
	<i>Syenite</i>							
STM-2	STM-2 D10 <sup>d</sup>	0.512912	5	0.348406	3	0.512917		
	STM-2 L8 <sup>d</sup>	0.512902	5	0.348408	3	0.512907		
	STM-2 L9 <sup>d</sup>	0.512913	5	0.348407	3	0.512918		
	STM-2 L10 <sup>d</sup>	0.512907	5	0.348405	4	0.512912		
	STM-2 D1 <sup>d</sup>	0.512914	6	0.348409	3	0.512911		
		<b>Mean (2 SD)</b>	<b>0.512910</b>	<b>10</b>			<b>0.512913</b>	<b>9</b>
<i>Rhyolite</i>								
RGM-1	RGM-1 (2) 19/04/03	0.512800	5	0.348407	3	0.512797		
	RGM-1 A10 <sup>d</sup>	0.512797	7	0.348408	3	0.512797		
	RGM-1 D9 <sup>d</sup>	0.512802	5	0.348405	3	0.512806		
	RGM-1 A5 <sup>d</sup>	0.512799	6	0.348404	5	0.512803		
	RGM-1 b A4 <sup>d</sup>	0.512798	5	0.348404	3	0.512802		
	RGM-1 (1) 19/12/03	0.512790	5	0.348404	3	0.512794		
	RGM-1 (2) 19/12/03	0.512794	5	0.348403	3	0.512798		
	RGM-1 (3) 19/12/03	0.512797	5	0.348410	3	0.512801		
	RGM-1 05/04/05 <sup>d</sup>	0.512817	8	0.348408	6	0.512820		
		<b>Mean (2 SD)</b>	<b>0.512799</b>	<b>15</b>			<b>0.512802</b>	<b>15</b>
<i>Granite</i>								
G-2	G-2 <sup>d</sup>	0.512218	6	0.348398	6	0.512233		
	G-2 04/01/04 No HClO4	0.512222	6	0.348404	4	0.512227		
	G-2 04/01/04 + HClO4	0.512226	5	0.348408	3	0.512231		
	G-2 D8 <sup>d</sup>	0.512222	6	0.348410	3	0.512227		
	G-2 D9 <sup>d</sup>	0.512218	5	0.348406	3	0.512223		
	G-2 L6 <sup>d</sup>	0.512224	5	0.348409	3	0.512229		
	G-2 L5 <sup>d</sup>	0.512227	6	0.348401	5	0.512232		
	G-2 Dec04-Jan05	0.512222	5	0.348402	6	0.512226		
	G-2 Dec04-Jan05	0.512223	8	0.348412	4	0.512227		
		<b>Mean (2 SD)</b>	<b>0.512222</b>	<b>6</b>			<b>0.512228</b>	<b>6</b>
	<i>Granodiorite</i>							
GSP-2	GSP-2 D2 <sup>d</sup>	0.511368	6	0.348400	4	0.511373		
	GSP-2 D3 <sup>d</sup>	0.511369	6	0.348403	4	0.511374		
	GSP-2 D5 <sup>d</sup>	0.511368	5	0.348407	4	0.511373		
	GSP-2 D6 <sup>d</sup>	0.511369	8	0.348408	4	0.511374		
	GSP-2 D7 <sup>d</sup>	0.511372	6	0.348405	4	0.511377		
		<b>Mean (2 SD)</b>	<b>0.511369</b>	<b>3</b>			<b>0.511374</b>	<b>3</b>

1997]. Elution volumes used for the column procedures are not given as resin properties vary from lot to lot and thus require individual calibration. Exact details are available on request.

[11] A standard, low-blank, Pb chemistry is used in which the sample is loaded on a 200  $\mu\text{L}$  column of Biorad AG1-X8 100–200 mesh resin. The column is washed with two cycles of 18 mega ohm water/0.5 N HBr/6 N HCl, and conditioned with 18 mega ohm water followed by 0.5 N HBr. The sample is taken up in 0.5 N HBr with complete dissolution ensured by heating (10 min) and ultrasonication (10 min). The solution is then centrifuged at 14500 RPM for 6 min and the supernatant is loaded onto the column. Sr, Hf, and the REE are washed from the column with 0.5 N HBr, after which Pb is eluted in 6 N HCl. The resin is discarded after each Pb chemical separation.

### 2.2.2. First (Sr+REE) Column Chemistry

[12] A standard cation exchange column of Biorad AG50W-X8 resin (100–200 mesh) is used to separate Sr from Hf and the REE. Columns are made of Pyrex or PFA depending on the type of sample and isotopes of interest; samples with Hf and/or Nd concentrations <10 ppm are processed through PFA columns and all others are processed on Pyrex columns [Weis *et al.*, 2005b]. Before use the resin is equilibrated with 1.5 N HCl. The Sr-, Hf- and REE-bearing fraction from the Pb column is dried down and redissolved in 1.5 N HCl by heating at 110°C and ultrasonication for 10 min. The solution is then centrifuged for 10 min at 3400 RPM and the supernatant carefully loaded onto the column so as to disturb the resin bed as little as possible. The column is then washed with 1.5 N HCl. Hf collection starts immediately after the sample is loaded and continues for the first few mL of 1.5 N HCl. Further washing with 2.5 N HCl removes sample matrix components, including Rb, prior to Sr elution in 2.5 N HCl. Further washing with 4.0 N HCl removes more sample matrix before the REE are eluted. The Sr and REE fractions are dried on a hotplate at  $\sim 130^\circ\text{C}$ . Columns are cleaned with  $\sim 100$  mL of 6 N HCl prior to re-equilibration with  $\sim 100$  mL of 1.5 N HCl.

### 2.2.3. Second Column (REE Separation) Chemistry

[13] Nd is separated from the other REE on a column using HDEHP (di-2ethylhexyl-orthophosphoric acid)-coated Teflon powder as the ion exchange medium [Richard *et al.*, 1976]. The purification of Nd is especially critical for mass spectrometric analysis due to the presence of isobaric interferences from Sm and Ce on  $^{144}\text{Nd}$  and  $^{142}\text{Nd}$ , respectively. HDEHP columns cannot separate Ce and Nd efficiently, which is not as critical for the measurement of  $^{143}\text{Nd}/^{144}\text{Nd}$  as it is for  $^{142}\text{Nd}/^{144}\text{Nd}$  [Boyet *et al.*, 2003]. The presence of other REE will also reduce the yield of Nd on ionization during TIMS analysis.

[14] The column is conditioned with 0.16 N HCl. The dried REE separate from the first cation exchange column is dissolved in 0.16 N HCl and loaded onto the column. The column is then carefully washed with 0.16 N HCl to remove Ba, La and most of the Ce. Nd together with a small fraction of the Ce and Pr is then eluted in 0.16 N HCl. Sm is eluted more than 10 mL after Nd, thereby avoiding any presence of Sm in the Nd cut. All of the heavier REE remain on the column and are subsequently removed with 6 N HCl prior to re-use of the column.

### 2.3. Mass Spectrometry Analytical Procedure

[15] Isotopic composition measurements were performed either on a Thermo Finnigan TIMS (Sr, Nd) or on a Nu Instruments Plasma (Nu 021) MC-ICP-MS (Nd, Pb) at the Pacific Centre for Isotopic and Geochemical Research (PCIGR) at the University of British Columbia. In addition, Pb isotopic compositions for some of the USGS reference materials were also measured on the Nu Instruments Plasma MC-ICP-MS (Nu 015) at the Department of Earth and Environmental Sciences of the Université Libre de Bruxelles for interlaboratory comparison.

[16] Due to drift in the Sr isotopic ratio of SRM 987 prior to October 2003, which was attributed to a problem with one of the Faraday cups on the TIMS, we have normalized the measured isotopic ratios of the USGS reference materials to SRM 987

#### Notes to Table 3.

<sup>a</sup>“Dble”: same digestion but different columns. *Italic*: measured after change of one of the Faraday cups. The  $2\sigma$  error is the absolute error value of the individual sample analysis (internal error) and reported as times  $10^6$ .

<sup>b</sup>Measured ratio normalized to La Jolla  $^{143}\text{Nd}/^{144}\text{Nd} = 0.511858$  (based on the mean of the wheel).

<sup>c</sup>Here, 2 SD is the 2 standard deviation on the mean of the individual reference material analyses.

<sup>d</sup>High-pressure PTFE digestion bomb (the coding corresponds to the bomb number).



**Table 4.** USGS Reference Materials: Nd Isotopic Analyses (MC-ICP-MS)<sup>a</sup>

Sample	Run Number	<sup>143</sup> Nd/ <sup>144</sup> Nd	Error (2σ)	<sup>145</sup> Nd/ <sup>144</sup> Nd	Error (2σ)	<sup>143</sup> Nd/ <sup>144</sup> Nd Norm <sup>b</sup>	2 SD <sup>c</sup>	<sup>145</sup> Nd/ <sup>144</sup> Nd Norm <sup>b</sup>	
<i>Basalt</i>									
<b>BCR-1</b>	BCR-1 (A) S6 <sup>d</sup>	0.512657	12	0.348410	6	0.512659		0.348398	
	BCR-1 (A) S6 <sup>d</sup> (rerun)	0.512655	13	0.348421	7	0.512657		0.348409	
	BCR-1 (B) S7 <sup>d</sup>	0.512641	15	0.348414	7	0.512643		0.348403	
	BCR-1 (B) S7 <sup>d</sup> (rerun)	0.512649	11	0.348422	8	0.512650		0.348410	
	BCR-1 (2) 08/08/03	0.512642	11	0.348410	7	0.512644		0.348398	
	BCR-1 (2) 08/08/03 (rerun)	0.512641	11	0.348418	6	0.512642		0.348406	
	BCR-1 S10 <sup>d</sup>	0.512636	11	0.348421	6	0.512637		0.348409	
	BCR-1 S10 <sup>d</sup> (rerun)	0.512639	12	0.348428	6	0.512640		0.348416	
	<b>Mean (2 SD)</b>	<b>0.512645</b>	<b>16</b>			<b>0.512646</b>	<b>16</b>		
<b>BCR-2</b>	BCR-2 HA	0.512654	10	0.348418	5	0.512652		0.348412	
	BCR-2 HA (rerun)	0.512642	11	0.348419	5	0.512640		0.348413	
	BCR-2 (1) 05/12/03	0.512635	7	0.348421	5	0.512637		0.348409	
	BCR-2 (1) 05/12/03 (rerun)	0.512644	9	0.348418	5	0.512646		0.348406	
	BCR-2 (2) 05/12/03	0.512636	11	0.348416	5	0.512638		0.348404	
	BCR-2 (2) 05/12/03 (rerun)	0.512635	12	0.348416	5	0.512636		0.348404	
	BCR-2 19/12/03	0.512635	10	0.348420	7	0.512637		0.348409	
	BCR-2 19/12/03 (rerun)	0.512640	10	0.348417	5	0.512642		0.348405	
	BCR-2 24/09/03	0.512632	8	0.348416	6	0.512634		0.348403	
	BCR-2 24/09/03 (rerun)	0.512622	10	0.348425	6	0.512623		0.348412	
		<b>Mean (2 SD)</b>	<b>0.512637</b>	<b>17</b>			<b>0.512638</b>	<b>15</b>	
<b>BHVO-1</b>	BHVO-1 (A) A8 <sup>d</sup>	0.512988	9	0.348423	5	0.512991		0.348413	
	BHVO-1 (A) A8 <sup>d</sup> (rerun)	0.512990	11	0.348421	5	0.512992		0.348411	
	BHVO-1 (A) S1 <sup>d</sup>	0.512988	12	0.348418	7	0.512991		0.348408	
	BHVO-1 (A) S1 <sup>d</sup> (rerun)	0.512977	10	0.348415	7	0.512980		0.348404	
	BHVO-1 (C) S3 <sup>d</sup>	0.512986	13	0.348417	7	0.512987		0.348405	
	BHVO-1 (C) S3 <sup>d</sup> (rerun)	0.512984	11	0.348421	7	0.512985		0.348408	
		<b>Mean (2 SD)</b>	<b>0.512986</b>	<b>9</b>			<b>0.512988</b>	<b>10</b>	
<b>BHVO-2</b>	BHVO-2 HA	0.512983	10	0.348418	6	0.512989		0.348410	
	BHVO-2 HA (rerun)	0.512986	9	0.348423	5	0.512992		0.348414	
	BHVO-2(1) 05/12/03	0.512982	10	0.348420	7	0.512983		0.348407	
	BHVO-2(1) 05/12/03 (rerun)	0.512994	11	0.348422	7	0.512995		0.348409	
	BHVO-2(2) 05/12/03	0.512990	11	0.348429	7	0.512992		0.348416	
	BHVO-2(2) 05/12/03 (rerun)	0.512983	11	0.348411	5	0.512985		0.348398	
	BHVO-2 19/12/03	0.512995	11	0.348422	8	0.512996		0.348410	
	BHVO-2 19/12/03 (rerun)	0.512984	9	0.348429	6	0.512985		0.348417	
		<b>Mean (2 SD)</b>	<b>0.512987</b>	<b>10</b>			<b>0.512990</b>	<b>10</b>	
	<i>Andesite</i>								
<b>AGV-1</b>	AGV-1 (A) S4 <sup>d</sup>	0.512784	59	0.348440	38	0.512789		0.348422	
	AGV-1 (A) S4 <sup>d</sup> (rerun)	0.512804	60	0.348438	32	0.512808		0.348420	
	AGV-1 (B) S5 <sup>d</sup>	0.512807	14	0.348423	6	0.512812		0.348405	
	AGV-1 (B) S5 <sup>d</sup> (rerun)	0.512796	11	0.348419	7	0.512801		0.348401	
	AGV-1 D10 <sup>d</sup> 11/01/04	0.512801	9	0.348424	6	0.512806		0.348406	
	AGV-1 D10 <sup>d</sup> 11/01/04 (rerun)	0.512778	10	0.348428	5	0.512783		0.348410	
		<b>Mean (2 SD)</b>	<b>0.512795</b>	<b>23</b>			<b>0.512800</b>	<b>23</b>	
<b>AGV-2</b>	AGV-2 (1) 05/12/03	0.512780	13	0.348426	7	0.512785		0.348408	
	AGV-2 (1) 05/12/03 (rerun)	0.512789	12	0.348414	8	0.512794		0.348397	
	AGV-2 (2) 05/12/03	0.512791	12	0.348430	8	0.512795		0.348412	
	AGV-2 (2) 05/12/03 (rerun)	0.512767	10	0.348420	6	0.512772		0.348402	
	AGV-2 19/12/03	0.512790	11	0.348421	5	0.512795		0.348403	
	AGV-2 19/12/03 (rerun)	0.512791	9	0.348423	7	0.512796		0.348405	
	AGV-2 (1) 08/08/03 BK13	0.512787	12	0.348428	6	0.512788		0.348415	
	AGV-2 (1) 08/08/03 BK13 (rerun)	0.512792	11	0.348415	6	0.512793		0.348402	
		<b>Mean (2 SD)</b>	<b>0.512786</b>	<b>17</b>			<b>0.512790</b>	<b>17</b>	
<i>Syenite</i>									
<b>STM-2</b>	STM-2 D10 <sup>d</sup>	0.512912	11	0.348420	7	0.512909		0.348409	
	STM-2 D10 <sup>d</sup> (rerun)	0.512915	11	0.348422	7	0.512912		0.348411	
	STM-2 L8 <sup>d</sup>	0.512929	9	0.348421	5	0.512926		0.348410	
	STM-2 L8 <sup>d</sup> (rerun)	0.512923	9	0.348427	5	0.512920		0.348416	

**Table 4.** (continued)

Sample	Run Number	$^{143}\text{Nd}/^{144}\text{Nd}$	Error ( $2\sigma$ )	$^{145}\text{Nd}/^{144}\text{Nd}$	Error ( $2\sigma$ )	$^{143}\text{Nd}/^{144}\text{Nd}$ Norm <sup>b</sup>	2 SD <sup>c</sup>	$^{145}\text{Nd}/^{144}\text{Nd}$ Norm <sup>b</sup>
	STM-2 L9 <sup>d</sup>	0.512928	9	0.348423	6	0.512925		0.348412
	STM-2 L9 <sup>d</sup> (rerun)	0.512916	8	0.348425	5	0.512913		0.348415
	STM-2 L10 <sup>d</sup>	0.512911	8	0.348417	4	0.512907		0.348406
	STM-2 L10 <sup>d</sup> (rerun)	0.512912	8	0.348419	5	0.512908		0.348408
	STM-2 D1 <sup>d</sup>	0.512914	11	0.348426	6	0.512910		0.348416
	STM-2 D1 <sup>d</sup> (rerun)	0.512905	8	0.348424	6	0.512902		0.348414
	<b>Mean (2 SD)</b>	<b>0.512917</b>	<b>16</b>			<b>0.512913</b>	<b>16</b>	
				<i>Rhyolite</i>				
<b>RGM-1</b>	RGM-1 (2) 19/12/03	0.512813	10	0.348426	5	0.512815		0.348415
	RGM-1 (2) 19/12/03 (rerun)	0.512809	9	0.348427	5	0.512812		0.348417
	RGM-1 (3) 19/12/03	0.512798	9	0.348425	7	0.512801		0.348415
	RGM-1 (3) 19/12/03 (rerun)	0.512810	11	0.348436	6	0.512812		0.348425
	RGM-1 (1) 19/12/03	0.512796	13	0.348431	7	0.512798		0.348420
	RGM-1 (1) 19/12/03 (rerun)	0.512804	12	0.348424	7	0.512807		0.348414
	RGM-1 D9 <sup>d</sup>	0.512780	12	0.348423	8	0.512783		0.348413
	RGM-1 D9 (rerun)	0.512787	14	0.348409	7	0.512789		0.348399
	RGM-1 b A4 <sup>d</sup> DSN	0.512795	5	0.348418	4	0.512805		0.348418
	RGM-1 b A4 <sup>d</sup> DSN (rerun)	0.512803	7	0.348423	4	0.512813		0.348423
	RGM-1 A5 <sup>d</sup> DSN	0.512791	5	0.348410	3	0.512801		0.348410
	RGM-1 A5 <sup>d</sup> DSN (rerun)	0.512795	9	0.348413	4	0.512805		0.348413
	<b>Mean (2 SD)</b>	<b>0.512799</b>	<b>19</b>			<b>0.512804</b>	<b>20</b>	
				<i>Granite</i>				
<b>G-2</b>	G-2 04/01/04	0.512242	10	0.348423	7	0.512241		0.348417
	G-2 04/01/04 (rerun)	0.512235	10	0.348415	7	0.512234		0.348409
	G-2 D8 <sup>d</sup>	0.512233	9	0.348426	6	0.512232		0.348420
	G-2 D8 <sup>d</sup> (rerun)	0.512241	8	0.348424	4	0.512239		0.348418
	G-2 D9 <sup>d</sup>	0.512236	10	0.348425	5	0.512234		0.348418
	G-2 D9 <sup>d</sup> (rerun)	0.512232	14	0.348423	7	0.512230		0.348417
	G-2 L5 <sup>d</sup>	0.512235	10	0.348426	7	0.512233		0.348420
	G-2 L6 <sup>d</sup>	0.512250	12	0.348433	6	0.512249		0.348427
	G-2 L6 <sup>d</sup> (rerun)	0.512245	11	0.348424	7	0.512243		0.348418
	G-2 HClO <sub>4</sub>	0.512226	10	0.348422	8	0.512225		0.348416
	G-2 HClO <sub>4</sub> (rerun)	0.512225	10	0.348425	8	0.512223		0.348419
	G-2 D9 <sup>d</sup> 3rd analysis	0.512235	10	0.348422	5	0.512233		0.348416
	<b>Mean (2 SD)</b>	<b>0.512236</b>	<b>15</b>			<b>0.512235</b>	<b>15</b>	
				<i>Granodiorite</i>				
<b>GSP-2</b>	GSP-2 D2 <sup>d</sup>	0.511360	10	0.348415	4	0.511366		0.348407
	GSP-2 D2 <sup>d</sup> (rerun)	0.511366	9	0.348415	4	0.511372		0.348407
	GSP-2 D3 <sup>d</sup>	0.511375	9	0.348415	5	0.511380		0.348407
	GSP-2 D3 <sup>d</sup> (rerun)	0.511373	11	0.348414	5	0.511378		0.348405
	GSP-2 D5 <sup>d</sup>	0.511362	9	0.348422	5	0.511368		0.348414
	GSP-2 D5 <sup>d</sup> (rerun)	0.511367	8	0.348419	5	0.511373		0.348410
	GSP-2 D6 <sup>d</sup>	0.511366	7	0.348418	4	0.511372		0.348410
	GSP-2 D6 <sup>d</sup> (rerun)	0.511376	9	0.348423	5	0.511381		0.348415
	GSP-2 D7 <sup>d</sup>	0.511370	9	0.348419	5	0.511376		0.348411
	GSP-2 D7 <sup>d</sup> (rerun)	0.511370	8	0.348425	5	0.511376		0.348416
	GSP-2 B5 <sup>d</sup>	0.511375	10	0.348417	5	0.511381		0.348409
	GSP-2 B5 <sup>d</sup> (rerun)	0.511368	11	0.348420	6	0.511374		0.348412
	GSP-2 B6 <sup>d</sup>	0.511364	8	0.348415	5	0.511369		0.348407
	GSP-2 B6 <sup>d</sup> (rerun)	0.511360	8	0.348417	7	0.511366		0.348408
	<b>Mean (2 SD)</b>	<b>0.511368</b>	<b>11</b>			<b>0.511374</b>	<b>11</b>	

<sup>a</sup> (Rerun): ran back-to-back with the 1st analysis.  $^{145}\text{Nd}/^{144}\text{Nd} = 0.348403$  (based on the daily mean of the La Jolla or Rennes analyses). DSN: Nu desolvator, i.e., dry plasma (all other analyses are wet plasma). The  $2\sigma$  error is the absolute error value of the individual sample analysis (internal error) and reported as times  $10^6$ .

<sup>b</sup> Measured ratio normalized to La Jolla  $^{143}\text{Nd}/^{144}\text{Nd} = 0.511858$  or to Rennes  $^{143}\text{Nd}/^{144}\text{Nd} = 0.511973$  and  $^{145}\text{Nd}/^{144}\text{Nd} = 0.348403$  (based on the daily mean of the La Jolla or Rennes analyses).

<sup>c</sup> Here, 2 SD is the 2 standard deviation on the mean of the individual reference material analyses.

<sup>d</sup> High-pressure PTFE digestion bomb (the coding corresponds to the bomb number).

**Table 5.** USGS Reference Materials: Pb Isotopic Analyses (MC-ICP-MS)<sup>a</sup>

Sample	Run Number	<sup>206</sup> Pb/ <sup>204</sup> Pb <sup>b</sup>	Error (2σ)	<sup>207</sup> Pb/ <sup>204</sup> Pb <sup>b</sup>	Error (2σ)	<sup>208</sup> Pb/ <sup>204</sup> Pb <sup>b</sup>	Error (2σ)	Wet/Dry	Nu Plasma	
<i>Basalt</i>										
<b>BCR-1</b>	BCR-1	18.8215	0.0011	15.6379	0.0010	38.7340	0.0029	W	015	
	BCR-1	18.8247	0.0011	15.6375	0.0011	38.7355	0.0032	W	015	
	BCR-1	18.8213	0.0008	15.6345	0.0008	38.7315	0.0024	W	015	
	BCR-1 S10 <sup>c</sup>	18.8223	0.0009	15.6352	0.0008	38.7272	0.0022	W	021	
	<b>Mean (2 SD)</b>	<b>18.8225</b>	<b>0.0031</b>	<b>15.6363</b>	<b>0.0033</b>	<b>38.7321</b>	<b>0.0073</b>			
<b>BCR-2</b>	BCR-2	18.7487	0.0006	15.6252	0.0007	38.7136	0.0023	W	015	
	BCR-2	18.7468	0.0020	15.6233	0.0018	38.7090	0.0042	W	015	
	BCR-2	18.7623	0.0009	15.6298	0.0010	38.7467	0.0031	W	015	
	BCR-2	18.7575	0.0009	15.6247	0.0010	38.7326	0.0028	W	015	
	BCR-2/1 ~100 ppb	18.7511	0.0031	15.6218	0.0024	38.7211	0.0055	W	021	
	BCR-2/2 ~120 ppb	18.7657	0.0026	15.6240	0.0015	38.7514	0.0049	W	021	
	BCR-2/3 ~100 ppb	18.7629	0.0013	15.6240	0.0011	38.7350	0.0039	W	021	
	BCR-2a	18.7553	0.0009	15.6247	0.0009	38.7334	0.0024	D	021	
	BCR-2b	18.7364	0.0009	15.6257	0.0008	38.6912	0.0023	D	021	
	BCR-2a	18.7570	0.0006	15.6249	0.0005	38.7343	0.0016	W	015	
	BCR-2b	18.7379	0.0008	15.6258	0.0008	38.6918	0.0022	W	015	
	<b>Mean (2 SD)</b>	<b>18.7529</b>	<b>0.0195</b>	<b>15.6249</b>	<b>0.0040</b>	<b>38.7237</b>	<b>0.0405</b>			
	<b>BHVO-1</b>	BHVO-1	18.6889	0.0012	15.5707	0.0012	38.3514	0.0031	W	015
		BHVO-1	18.6965	0.0013	15.5748	0.0012	38.3721	0.0032	W	015
BHVO-1		18.7123	0.0044	15.5767	0.0041	38.3600	0.0098	W	021	
BHVO-1		18.6963	0.0006	15.5719	0.0005	38.3597	0.0013	D	021	
<b>Mean (2 SD)</b>		<b>18.6985</b>	<b>0.0197</b>	<b>15.5735</b>	<b>0.0055</b>	<b>38.3608</b>	<b>0.0171</b>			
<b>BHVO-2</b>	BHVO-2	18.6299	0.0015	15.5362	0.0012	38.2320	0.0035	W	015	
	BHVO-2	18.6411	0.0017	15.5387	0.0015	38.2293	0.0040	W	015	
	BHVO-2	18.6609	0.0010	15.5333	0.0009	38.2492	0.0025	D	021	
	BHVO-2	18.6541	0.0017	15.5262	0.0014	38.2294	0.0034	W	015	
	BHVO-2	18.6509	0.0007	15.5328	0.0006	38.2435	0.0016	D	021	
	<b>Mean (2 SD)</b>	<b>18.6474</b>	<b>0.0242</b>	<b>15.5334</b>	<b>0.0094</b>	<b>38.2367</b>	<b>0.0182</b>			
<i>Andesite</i>										
<b>AGV-1</b>	AGV-1	18.9433	0.0008	15.6552	0.0007	38.5668	0.0022	W	015	
	AGV-1	18.9398	0.0008	15.6512	0.0008	38.5575	0.0024	W	015	
	AGV-1	18.9415	0.0007	15.6549	0.0006	38.5623	0.0018	W	015	
	AGV-1	18.9398	0.0006	15.6530	0.0007	38.5584	0.0018	W	015	
	AGV-1 D10 <sup>c</sup>	18.9349	0.0007	15.6512	0.0008	38.5544	0.0042	W	021	
	<b>Mean (2 SD)</b>	<b>18.9399</b>	<b>0.0063</b>	<b>15.6531</b>	<b>0.0038</b>	<b>38.5599</b>	<b>0.0096</b>			
<b>AGV-2</b>	AGV-2	18.8714	0.0006	15.6182	0.0006	38.5476	0.0023	W	015	
	AGV-2	18.8629	0.0016	15.6114	0.0014	38.5318	0.0036	W	015	
	AGV-2	18.8671	0.0011	15.6230	0.0009	38.5509	0.0026	W	015	
	AGV-2a	18.8684	0.0009	15.6166	0.0008	38.5420	0.0028	D	021	
	AGV-2b	18.8718	0.0008	15.6187	0.0008	38.5501	0.0020	D	021	
	AVG-2a	18.8713	0.0009	15.6182	0.0007	38.5472	0.0019	W	015	
	AVG-2b	18.8685	0.0011	15.6151	0.0009	38.5405	0.0026	W	015	
	<b>Mean (2 SD)</b>	<b>18.8688</b>	<b>0.0063</b>	<b>15.6173</b>	<b>0.0071</b>	<b>38.5443</b>	<b>0.0135</b>			
	<i>Syenite</i>									
<b>STM-1</b>	STM-1	19.5163	0.0006	15.6304	0.0006	39.1886	0.0017	W	015	
	STM-1	19.5234	0.0013	15.6312	0.0011	39.1964	0.0034	W	015	
	STM-1	19.5228	0.0008	15.6296	0.0007	39.1954	0.0021	W	015	
	STM-1	19.4956	0.0006	15.6356	0.0005	39.1693	0.0014	D	021	
	<b>Mean (2 SD)</b>	<b>19.5145</b>	<b>0.0260</b>	<b>15.6317</b>	<b>0.0053</b>	<b>39.1874</b>	<b>0.0252</b>			
<b>STM-2</b>	STM-2	19.7240	0.0009	15.6174	0.0008	39.4226	0.0021	W	015	
	STM-2 replicate	19.7192	0.0019	15.6135	0.0015	39.4132	0.0042	W	015	
	STM-2	19.7220	0.0011	15.6163	0.0011	39.4199	0.0032	W	015	
	STM-2 D1 <sup>c</sup>	19.7224	0.0010	15.6150	0.0016	39.4150	0.0049	W	021	
	STM-2 L10 <sup>c</sup>	19.7154	0.0015	15.6139	0.0011	39.4087	0.0032	W	021	
	STM-2 D10 <sup>c</sup>	19.7105	0.0012	15.6138	0.0011	39.4019	0.0024	W	021	
	STM-2 L9 <sup>c</sup>	19.7060	0.0009	15.6118	0.0010	39.3912	0.0036	W	021	
	STM-2a	19.7135	0.0013	15.6148	0.0011	39.4105	0.0028	D	021	
	STM-2b	19.7302	0.0010	15.6189	0.0008	39.4295	0.0023	D	021	

**Table 5.** (continued)

Sample	Run Number	$^{206}\text{Pb}/^{204}\text{Pb}^b$	Error ( $2\sigma$ )	$^{207}\text{Pb}/^{204}\text{Pb}^b$	Error ( $2\sigma$ )	$^{208}\text{Pb}/^{204}\text{Pb}^b$	Error ( $2\sigma$ )	Wet/Dry	Nu Plasma
	STM-2 L8 <sup>c</sup>	19.7051	0.0008	15.6051	0.0007	39.3815	0.0018	D	021
	STM-2a	19.7107	0.0009	15.6125	0.0008	39.4050	0.0025	W	015
	STM-2b	19.7255	0.0009	15.6144	0.0006	39.4164	0.0022	W	015
	<b>Mean (2 SD)</b>	<b>19.7170</b>	<b>0.0161</b>	<b>15.6140</b>	<b>0.0068</b>	<b>39.4096</b>	<b>0.0268</b>		
	<b>Mean bomb digestion</b>	<b>19.7136</b>	<b>0.0140</b>	<b>15.6136</b>	<b>0.0026</b>	<b>39.4042</b>	<b>0.0204</b>		
	<b>Mean Savillex<sup>®</sup> digestion</b>	<b>19.7207</b>	<b>0.0136</b>	<b>15.6154</b>	<b>0.0045</b>	<b>39.4167</b>	<b>0.0162</b>		
				<i>Rhyolite</i>					
<b>RGM-1</b>	RGM-1	19.0036	0.0007	15.6315	0.0007	38.6925	0.0022	W	015
	RGM-1	18.9962	0.0007	15.6457	0.0008	38.6550	0.0025	W	015
	RGM-1	18.9949	0.0007	15.6430	0.0008	38.6487	0.0025	W	015
	RGM-1 D9 <sup>c</sup>	19.0042	0.0009	15.6293	0.0008	38.6969	0.0023	W	021
	RGM-1	19.0027	0.0006	15.6310	0.0005	38.6971	0.0013	D	021
	<b>Mean (2 SD)</b>	<b>19.0003</b>	<b>0.0089</b>	<b>15.6361</b>	<b>0.0153</b>	<b>38.6780</b>	<b>0.0481</b>		
				<i>Granite</i>					
<b>G-2</b>	G-2	18.3783	0.0008	15.6341	0.0008	38.9144	0.0027	W	015
	G-2	18.4049	0.0007	15.6394	0.0009	38.8987	0.0024	W	015
	G-2	18.4026	0.0007	15.6359	0.0008	38.8892	0.0023	W	015
	G-2 D8 <sup>c</sup>	18.4156	0.0010	15.6374	0.0010	38.9133	0.0026	W	021
	G-2 D9 <sup>c</sup>	18.3991	0.0011	15.6342	0.0010	38.8951	0.0029	W	021
	G-2 D9/2 <sup>c</sup>	18.3987	0.0012	15.6345	0.0010	38.8966	0.0026	W	021
	G-2 HClO <sub>4</sub>	18.4089	0.0008	15.6388	0.0007	38.9085	0.0020	W	021
	G-2a	18.3851	0.0008	15.6337	0.0009	38.8946	0.0020	D	021
	G-2b	18.3953	0.0006	15.6362	0.0006	38.9020	0.0015	D	021
	G-2 L5 <sup>c</sup>	18.4094	0.0008	15.6354	0.0007	38.9025	0.0020	D	021
	G-2 L6 <sup>c</sup>	18.4101	0.0010	15.6354	0.0009	38.9031	0.0026	D	021
	G-2a	18.3873	0.0009	15.6346	0.0008	38.8958	0.0020	W	015
	G-2b	18.3942	0.0006	15.6338	0.0007	38.8940	0.0017	W	015
	<b>Mean (2 SD)</b>	<b>18.3992</b>	<b>0.0219</b>	<b>15.6357</b>	<b>0.0038</b>	<b>38.9006</b>	<b>0.0154</b>		
	<b>Mean bomb digestion</b>	<b>18.4019</b>	<b>0.0209</b>	<b>15.6353</b>	<b>0.0025</b>	<b>38.9010</b>	<b>0.0130</b>		
	<b>Mean Savillex<sup>®</sup> digestion</b>	<b>18.3960</b>	<b>0.0233</b>	<b>15.6361</b>	<b>0.0049</b>	<b>38.9001</b>	<b>0.0190</b>		
<b>G-3</b>	G-3	18.4379	0.0006	15.6401	0.0006	38.9185	0.0019	W	015
	G-3	18.3444	0.0009	15.6342	0.0009	38.8316	0.0028	W	015
	G-3	18.3398	0.0007	15.6293	0.0007	38.8200	0.0022	W	015
	G-3a	18.3816	0.0009	15.6354	0.0009	38.8558	0.0024	D	021
	G-3 B <sup>c</sup>	18.4242	0.0010	15.6368	0.0009	38.8686	0.0019	D	021
	G-3b	18.4218	0.0009	15.6339	0.0008	38.8587	0.0022	W	015
	G-3a	18.3776	0.0009	15.6307	0.0009	38.8426	0.0022	W	015
	<b>Mean (2 SD)</b>	<b>18.3896</b>	<b>0.0787</b>	<b>15.6343</b>	<b>0.0073</b>	<b>38.8565</b>	<b>0.0640</b>		
				<i>Granodiorite</i>					
<b>GSP-2</b>	GSP-2 D2 <sup>c</sup>	17.6092	0.0018	15.5109	0.0017	50.8849	0.0061	W	021
	GSP-2 D2 <sup>c</sup> (rerun)	17.6108	0.0023	15.5103	0.0023	50.8886	0.0074	W	021
	GSP-2 D6 <sup>c</sup>	17.6224	0.0015	15.5126	0.0014	50.9599	0.0048	W	021
	GSP-2 D5 <sup>c</sup>	17.6113	0.0011	15.5125	0.0010	50.9308	0.0035	W	021
	GSP-2 D3 <sup>c</sup>	17.6270	0.0017	15.5147	0.0016	50.7956	0.0053	W	021
	GSP-2 D7 <sup>c</sup>	17.6096	0.0014	15.5114	0.0013	50.5748	0.0044	W	021
	GSP-2a	17.5246	0.0011	15.5050	0.0011	51.0666	0.0037	D	021
	GSP-2b	17.5281	0.0010	15.5064	0.0009	51.1354	0.0037	D	021
	GSP-2a	17.5244	0.0008	15.5048	0.0007	51.0736	0.0026	W	015
	GSP-2b	17.5301	0.0013	15.5078	0.0011	51.1419	0.0037	W	015
	<b>Mean (2 SD)</b>	<b>17.5797</b>	<b>0.0919</b>	<b>15.5096</b>	<b>0.0069</b>	<b>50.9452</b>	<b>0.3483</b>		
	<b>Mean bomb digestion</b>	<b>17.6151</b>	<b>0.0153</b>	<b>15.5121</b>	<b>0.0031</b>	<b>50.8391</b>	<b>0.2818</b>		
	<b>Mean Savillex<sup>®</sup> digestion</b>	<b>17.5268</b>	<b>0.0056</b>	<b>15.5060</b>	<b>0.0028</b>	<b>51.1044</b>	<b>0.0795</b>		

<sup>a</sup>(Rerun): same sample, duplicate analysis. a and b: same chemistry series, separate dissolutions. W/D: W: analyses with wet plasma, D: analyses with dry plasma (DSN: Nu desolvator).

<sup>b</sup>All Pb isotopic ratios have been normalized to the SRM 981 triple spike values of *Abouchami et al.* [2000]; see Table 6 for SRM 981 values.

<sup>c</sup>Bomb digestion (the coding corresponds to the bomb number).

**Table 6.** SRM 981 Pb Isotopic Analyses (MC-ICP-MS): Averages for Individual Days

Instrument	Date of Analysis	Wet/Dry	$^{206}\text{Pb}/^{204}\text{Pb}$	2 SD <sup>a</sup>	ppm <sup>b</sup>	$^{207}\text{Pb}/^{204}\text{Pb}$	2 SD <sup>a</sup>	ppm <sup>b</sup>	$^{208}\text{Pb}/^{204}\text{Pb}$	2 SD <sup>a</sup>	ppm <sup>b</sup>	$^{208}\text{Pb}/^{206}\text{Pb}$	2 SD <sup>a</sup>	ppm <sup>b</sup>	$^{207}\text{Pb}/^{206}\text{Pb}$	2 SD <sup>a</sup>	ppm <sup>b</sup>
<b>Nu 015</b>	September 30, 2003	W	36.7191	0.0094	255	15.4977	0.0040	260	16.9403	0.0046	269	2.16756	0.00013	59	0.91483	0.00003	33
	November 10, 2003	W	36.7184	0.0083	226	15.4976	0.0034	219	16.9410	0.0031	180	2.16744	0.00019	89	0.91480	0.00005	53
	December 19, 2003	W	36.7136	0.0118	321	15.4963	0.0043	280	16.9398	0.0044	261	2.16729	0.00021	96	0.91479	0.00006	71
	February 16, 2004	W	36.7190	0.0084	229	15.4978	0.0029	190	16.9410	0.0037	216	2.16745	0.00014	67	0.91481	0.00004	44
	August 9, 2004	W	36.7195	0.0075	203	15.4979	0.0036	230	16.9413	0.0037	218	2.16747	0.00013	62	0.91480	0.00002	25
	September 12, 2003	W	36.7137	0.0034	93	15.4965	0.0012	76	16.9400	0.0016	96	2.16730	0.00009	43	0.91480	0.00003	28
	September 19, 2003	W	36.7165	0.0041	111	15.4976	0.0014	87	16.9408	0.0012	73	2.16733	0.00005	24	0.91480	0.00001	15
	March 24, 2004	D	36.7129	0.0079	215	15.4958	0.0033	210	16.9400	0.0036	212	2.16721	0.00013	59	0.91474	0.00005	53
	July 1, 2004	W	36.7181	0.0078	212	15.4974	0.0027	173	16.9421	0.0030	176	2.16726	0.00013	58	0.91472	0.00003	33
	July 2, 2004	W	36.7145	0.0062	168	15.4965	0.0024	156	16.9418	0.0026	155	2.16712	0.00013	61	0.91470	0.00003	33
<b>Nu 021</b>	July 7, 2004	W	36.7161	0.0080	217	15.4968	0.0032	204	16.9410	0.0033	193	2.16730	0.00017	79	0.91475	0.00006	67
	July 9, 2004	W	36.7170	0.0070	189	15.4971	0.0027	174	16.9415	0.0034	203	2.16729	0.00008	37	0.91474	0.00003	30
	July 27, 2004	D	36.7183	0.0072	197	15.4975	0.0030	192	16.9433	0.0030	176	2.16716	0.00010	46	0.91467	0.00004	43
	July 28, 2004	D	36.7177	0.0046	126	15.4969	0.0019	124	16.9423	0.0021	124	2.16723	0.00009	44	0.91469	0.00003	33
	August 6, 2004	D	36.7114	0.0059	126	15.4958	0.0021	124	16.9392	0.0021	124	2.16725	0.00014	44	0.91479	0.00004	33
	September 15, 2004	D	36.7131	0.0100	272	15.4961	0.0034	219	16.9398	0.0026	155	2.16726	0.00030	138	0.91477	0.00006	67
	September 22, 2004	W	36.7138	0.0060	162	15.4965	0.0016	102	16.9398	0.0025	145	2.16734	0.00007	31	0.91481	0.00006	63
	September 24, 2004	D	36.7108	0.0074	200	15.4955	0.0025	158	16.9392	0.0023	138	2.16722	0.00016	74	0.91477	0.00004	41
	September 28, 2004	D	36.7115	0.0111	303	15.4956	0.0036	235	16.9398	0.0031	184	2.16721	0.00021	97	0.91476	0.00005	56
	<b>Average Nu 015</b>			<b>0.0121</b>	<b>328</b>	<b>15.4968</b>	<b>0.0047</b>	<b>303</b>	<b>16.9400</b>	<b>0.0049</b>	<b>287</b>	<b>2.16744</b>	<b>0.00025</b>	<b>114</b>	<b>0.91481</b>	<b>0.00005</b>	<b>56</b>
<b>Average Nu 021</b>			<b>0.0088</b>	<b>240</b>	<b>15.4964</b>	<b>0.0029</b>	<b>188</b>	<b>16.9407</b>	<b>0.0036</b>	<b>215</b>	<b>2.16724</b>	<b>0.00019</b>	<b>86</b>	<b>0.91475</b>	<b>0.00009</b>	<b>97</b>	

<sup>a</sup>The 2 standard deviation on the mean of the SRM 981 analyses on a given day (n varies between 12 and 20).

<sup>b</sup>The ppm error.

**Table 7.** Leaching Experiment: Pb Isotopic Analyses (MC-ICP-MS) and Sr and Nd Isotopic Analyses (TIMS) for BHVO, BCR, and AGV USGS Reference Materials<sup>a</sup>

Sample	<sup>206</sup> Pb/ <sup>204</sup> Pb <sup>b</sup>	Error (2σ)	<sup>207</sup> Pb/ <sup>204</sup> Pb <sup>b</sup>	Error (2σ)	<sup>208</sup> Pb/ <sup>204</sup> Pb <sup>b</sup>	Error (2σ)	<sup>87</sup> Sr/ <sup>86</sup> Sr <sup>c</sup>	Error (2σ)	<sup>143</sup> Nd/ <sup>144</sup> Nd <sup>c</sup>	Error (2σ)
<i>BHVO</i>										
BHVO-1 (1) residue	18.6460	0.0007	15.4852	0.0006	38.1954	0.0017	0.703464	0.000008	0.512989	0.000006
BHVO-1 (2) residue	18.6435	0.0010	15.4786	0.0008	38.1733	0.0025	0.703467	0.000006	0.512981	0.000007
BHVO-1 (3) residue	18.6150	0.0013	15.4847	0.0007	38.1723	0.0018	0.703476	0.000007	0.512989	0.000006
BHVO-2 (1) residue	18.6455	0.0009	15.4892	0.0011	38.2055	0.0034	0.703484	0.000007	0.512987	0.000005
BHVO-2 (2) residue	18.6378	0.0008	15.4789	0.0009	38.1881	0.0027	0.703467	0.000007	0.512987	0.000005
BHVO-2 (3) residue	18.6387	0.0006	15.4797	0.0007	38.1767	0.0021	0.703462	0.000007	0.512985	0.000006
BHVO-1 (1) leachate	18.7061	0.0007	15.6291	0.0008	38.4393	0.0021	0.703493	0.000007	0.512983	0.000008
BHVO-1 (3) leachate	18.7311	0.0006	15.6390	0.0005	38.4721	0.0015	0.703494	0.000007	0.512981	0.000006
BHVO-2 (2) leachate	18.5649	0.0008	15.5987	0.0007	38.2213	0.0022	0.703508	0.000007	0.512992	0.000006
BHVO-2 (3) leachate	18.5628	0.0010	15.6015	0.0008	38.2307	0.0020	0.703496	0.000007	0.512994	0.000006
<i>BCR</i>										
BCR-1 (1) residue	18.7995	0.0009	15.6234	0.0008	38.8219	0.0022	0.704981	0.000007	0.512644	0.000005
BCR-1 (2) residue	18.8013	0.0006	15.6230	0.0006	38.8228	0.0018	0.704982	0.000008	0.512645	0.000007
BCR-2 (1) residue	18.8007	0.0007	15.6241	0.0006	38.8256	0.0019	0.704992	0.000007	0.512641	0.000004
BCR-2 (2) residue	18.7993	0.0010	15.6230	0.0009	38.8232	0.0029	0.705012	0.000008	0.512644	0.000007
BCR-2 (3) residue	18.6646	0.0010	15.6265	0.0009	38.5279	0.0025	0.705019	0.000013	0.512639	0.000005
BCR-1 (1) leachate	18.8232	0.0006	15.6302	0.0005	38.6047	0.0014	0.705118	0.000007	0.512647	0.000006
BCR-1 (2) leachate	18.8390	0.0009	15.6469	0.0008	38.6518	0.0020	0.705095	0.000009	0.512641	0.000008
BCR-2 (1) leachate	18.6473	0.0009	15.6209	0.0007	38.4955	0.0020	0.705085	0.000008	0.512643	0.000007
BCR-2 (3) leachate	18.7951	0.0006	15.6146	0.0007	38.7996	0.0024				
<i>AGV</i>										
AGV-1 (1) residue	18.9060	0.0006	15.6164	0.0005	38.5985	0.0015	0.703957	0.000007	0.512753	0.000006
AGV-1 (2) residue	18.9047	0.0007	15.6165	0.0006	38.5765	0.0015	0.703948	0.000008	0.512808	0.000006
AGV-1 (3) residue	18.8894	0.0010	15.5984	0.0011	38.5181	0.0037	0.703946	0.000008	0.512800	0.000006
AGV-2 (1) residue	18.9067	0.0005	15.6137	0.0005	38.5692	0.0014	0.703948	0.000007		
AGV-2 (2) residue	18.9078	0.0005	15.6157	0.0004	38.5764	0.0013	0.703966	0.000008	0.512794	0.000005
AGV-1 (1) leachate	18.9443	0.0006	15.6584	0.0005	38.5480	0.0015	0.704025	0.000008	0.512800	0.000005
AGV-1 (3) leachate	18.9525	0.0005	15.6670	0.0004	38.5587	0.0011	0.704084	0.000007	0.512795	0.000005
AGV-2 (1) leachate	18.8126	0.0007	15.6251	0.0012	38.5089	0.0018	0.704060	0.000008	0.512798	0.000005
AGV-2 (2) leachate	18.8055	0.0006	15.6232	0.0006	38.4951	0.0017	0.704054	0.000008	0.512797	0.000006

<sup>a</sup>All isotopic measurements of the leaching experiment were carried out over four days in September 2004. The 2σ error is the absolute error value of the individual sample analysis (internal error).

<sup>b</sup>All Pb isotopic ratios have been normalized to the SRM 981 triple-spike values of *Abouchami et al.* [2000]; see Table 6 for SRM 981 values.

<sup>c</sup>Measured ratio normalized to SRM 987 <sup>87</sup>Sr/<sup>86</sup>Sr = 0.710248 and to La Jolla <sup>143</sup>Nd/<sup>144</sup>Nd = 0.511858 (based on the mean of the wheel).

<sup>87</sup>Sr/<sup>86</sup>Sr = 0.710248 relative to the barrel average. For each barrel of 21 filaments, 4 or 5 positions were occupied by a reference material (SRM 987 for Sr and La Jolla or Rennes for Nd). The average of these 4 or 5 analyses corresponds to the barrel average. The normalization procedure has been applied to the Nd isotopic ratios for the La Jolla and Rennes reference materials, with a normalization value of <sup>143</sup>Nd/<sup>144</sup>Nd = 0.511858 [*Lugmair et al.*, 1983] and 0.511973 [*Chauvel and Blichert-Toft*, 2001], respectively.

[17] Sr and Nd isotopic compositions were measured in static mode 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 by normalizing to

<sup>86</sup>Sr/<sup>88</sup>Sr = 0.1194 and <sup>146</sup>Nd/<sup>144</sup>Nd = 0.7219, using an exponential law. Replicate analyses of the La Jolla Nd reference material on the Triton TIMS gave 0.511850 ± 15 (n = 73, where n corresponds to the number of analyses) and then 0.511853 ± 12 (n = 118) after one of the Faraday cups was changed. We also analyzed the Rennes Nd reference material [*Chauvel and Blichert-Toft*, 2001] and obtained <sup>143</sup>Nd/<sup>144</sup>Nd = 0.511970 ± 10 (n = 10). Replicate analyses of the Sr reference material SRM 987 yielded <sup>87</sup>Sr/<sup>86</sup>Sr values of 0.710256 ± 16 (n = 145) and then 0.710252 ± 13 (n = 88) after one of the Faraday cups was changed. Usually, a single analysis consisted of minimum of 135 ratios (9 blocks of 15 cycles) to allow for a full rotation of the virtual amplifier.

**Table 8.** Pb Concentrations by Isotope Dilution for USGS Reference Materials<sup>a</sup>

Sample	Pb, ppm	2 $\sigma$	Sample	Pb, ppm	2 $\sigma$
<b>BCR-1</b>			<b>BCR-2</b>		
BCR-1 A	13.16	0.22	BCR-2 A	10.31	0.15
BCR-1 B	13.36	0.16	BCR-2 B	12.35	0.15
BCR-1 C	13.07	0.15	BCR-2 C	10.11	0.08
BCR-1 D	13.79	0.14	BCR-2 C (rerun)	10.14	0.08
<b>Mean</b>	<b>13.34</b>	<b>0.64</b>	BCR-2 D	12.21	0.13
			<b>Mean</b>	<b>11.02</b>	<b>2.30</b>
<b>AGV-1</b>			<b>AGV-2</b>		
AGV-1 A	33.01	1.47	AGV-2 A	13.39	0.20
AGV-1 B	37.79	1.18	AGV-2 B	12.53	0.20
AGV-1 C	40.52	0.81	AGV-2 C	13.59	0.13
AGV-1 D	40.46	0.76	AGV-2 D	13.07	0.13
AGV-1 E	37.11	0.68	<b>Mean</b>	<b>13.15</b>	<b>0.93</b>
AGV-1 F	35.26	0.60			
<b>Mean</b>	<b>37.36</b>	<b>5.88</b>			
<b>BHVO-1</b>			<b>BHVO-2</b>		
BHVO-1 A	2.46	0.01	BHVO-2 A	1.62	0.01
BHVO-1 B	1.98	0.01	BHVO-2 B	1.54	0.01
BHVO-1 C	2.02	0.01	BHVO-2 C	1.32	0.01
BHVO-1 D	1.99	0.01	BHVO-2 D	1.48	0.01
BHVO-1 E	2.04	0.01	BHVO-2 E	1.42	0.01
BHVO-1 F	2.05	0.02	BHVO-2 F	1.62	0.01
<b>Mean</b>	<b>2.09</b>	<b>0.37</b>	BHVO-2 F (rerun)	1.63	0.01
			<b>Mean</b>	<b>1.52</b>	<b>0.24</b>

<sup>a</sup>(Rerun): same filament.

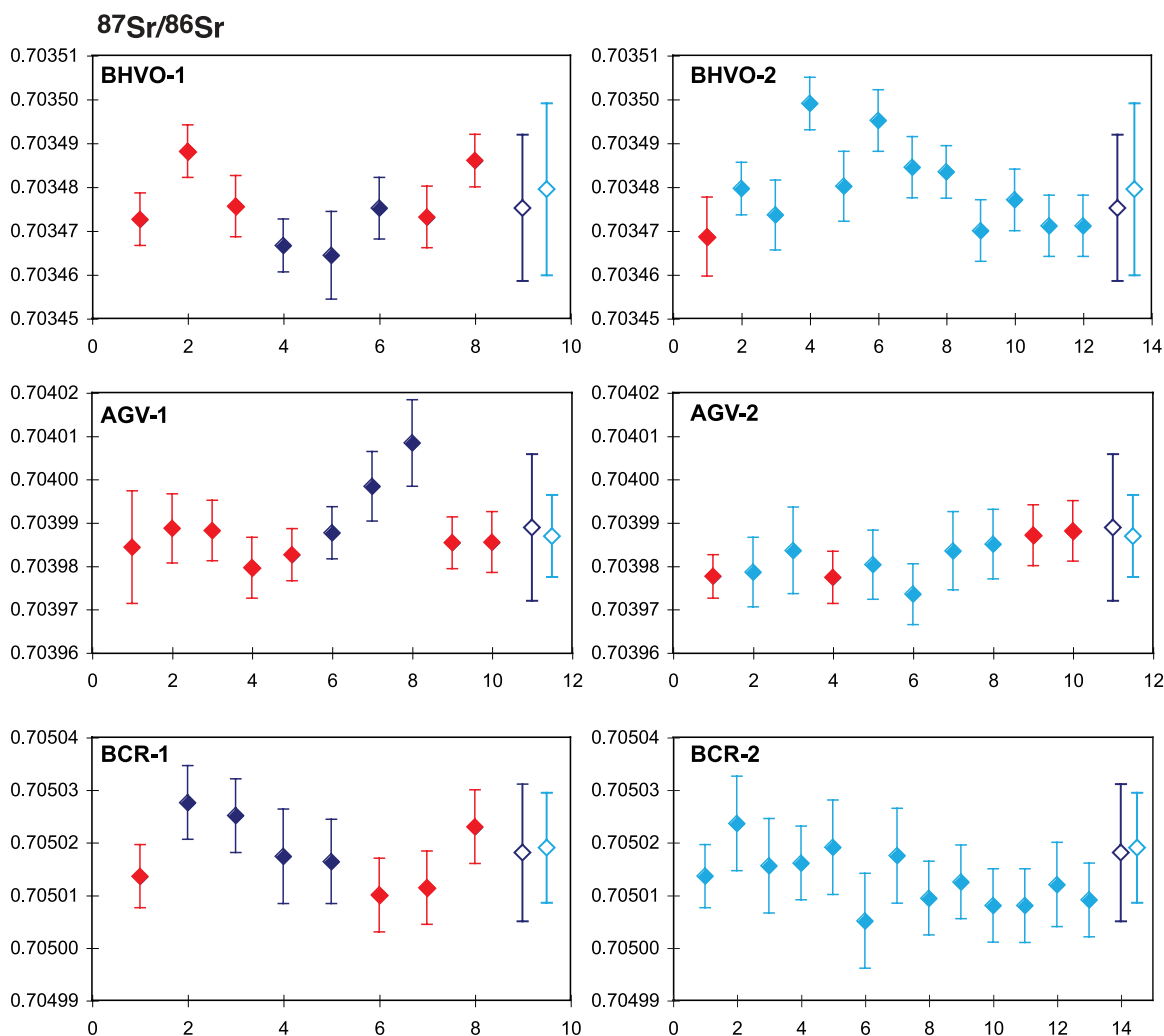
Note that with the new version of the Finnigan software (version 3.0 and higher), the number of blocks must match the number of collectors used, i.e., 5 for Sr and 8 for Nd. Four or five standards are loaded per 21 sample barrel.

[18] Nd isotopic compositions were also measured on the Nu Plasma, by static multicollection with Faraday cups on aliquots of the same sample solutions used for TIMS analyses and on separate dissolutions. Instrument parameters and collector configurations are summarized in Tables 1a, 1b, and 2. Each analysis consisted of 60 ratios (3 blocks of 20 cycles), resulting in a 12–13 minute duration of data collection for each individual analysis. Wash-out time and time for standard replicates after every second sample resulted in an average instrument time of 30 min per sample. All Nd isotopes (150, 148, 146, 145, 144, 143, 142) were measured, while simultaneously monitoring masses 147 (Sm) and 140 (Ce) (Table 1b), allowing for interference corrections on masses 144, 148 and 150 (Sm) and 142 (Ce). Except for Ce, all other interference corrections were entirely negligible (e.g., fraction of a mV on <sup>147</sup>Sm). Nd isotope measurements were normalized internally to the values reported above for the Triton TIMS measurements, on the basis of the daily mean of

the La Jolla or Rennes reference material analyses. The <sup>144</sup>Sm, <sup>148</sup>Sm, <sup>150</sup>Sm and <sup>142</sup>Ce corrections were made using natural isotopic abundances (<sup>144</sup>Sm = 0.030734, <sup>147</sup>Sm = 0.149934, <sup>148</sup>Sm = 0.112406, <sup>150</sup>Sm = 0.073796, <sup>140</sup>Ce = 0.88449, <sup>142</sup>Ce = 0.11114 [Rosman and Taylor, 1998]) corrected for instrumental mass discrimination using an exponential law as monitored by the <sup>146</sup>Nd/<sup>144</sup>Nd ratio.

[19] During the period of data collection, the average value measured for the La Jolla reference material on the Nu Plasma was  $0.511856 \pm 15$  (n = 59) for <sup>143</sup>Nd/<sup>144</sup>Nd and the average for the Rennes Nd reference material was  $0.511969 \pm 13$  (n = 45). This demonstrates the excellent agreement between the MC-ICP-MS and the TIMS instruments. To achieve comparable precision, the amount of material needed for Nd isotopic analyses on the MC-ICP-MS is about double (200–400 ng) for a wet plasma analysis than that for a TIMS or dry plasma analysis (100–150 ng).

[20] Pb 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, the central collectors (H4-L2) are 1 amu apart and the outer collectors (H6, H5, L3, L4 and L5) are 2 amu



**Figure 1.** Individual  $^{87}\text{Sr}/^{86}\text{Sr}$  analyses by TIMS of BHVO-1, BHVO-2, AGV-1, AGV-2, BCR-1, BCR-2, STM-2, RGM-1, G-2, and GSP-2. Note the much larger variations for GSP-2 (see text for discussion). On this page, the left-hand panels report results for the first-generation USGS reference materials (BHVO-1, AGV-1, and BCR-1), and the right-hand panels report results for the second-generation materials (BHVO-2, AGV-2, and BCR-2). Red symbols indicate high-pressure digestion PTFE in a bomb. All blue symbols indicate hotplate SavilleX<sup>®</sup> digestion. For comparison, on the far right side of each figure, open symbols represent the mean and 2 standard deviations of replicate analyses for both generations (dark blue for first generation, light blue for second generation). For individual analyses, the error bar corresponds to the 2 sigma error on the measured isotopic ratio.

apart. Therefore masses 208 to 202 are measured in collectors H4 to L2 (Table 1b). The configuration for Pb isotopic analyses enables simultaneous collection of Pb (208, 207, 206 and 204) together with Tl (205 and 203) and Hg (202). Tl is used to monitor and correct for instrumental mass discrimination and Hg is used to correct for the isobaric overlap of  $^{204}\text{Hg}$  on  $^{204}\text{Pb}$ . The  $^{204}\text{Hg}$  correction was made using natural abundances ( $^{202}\text{Hg} = 0.29863$  and  $^{204}\text{Hg} = 0.06865$ ) adjusted for instrumental mass fractionation as monitored by the  $^{205}\text{Tl}/^{203}\text{Tl}$  ratio. Ion beam intensities for  $^{202}\text{Hg}$

were always below 0.3 mV for all runs (except two), corresponding to a correction of less than 0.2 (0.07) mV on the 204 mass (always >53 mV).

[21] To improve the reproducibility of the analytical conditions for the Pb isotopic compositions, and thus the precision and the accuracy (i.e., better precision on  $^{205}\text{Tl}/^{203}\text{Tl}$  and less interference on  $^{204}\text{Pb}$ ), all sample solutions were analyzed with the same [Pb]/[Tl] ratio ( $\sim 4$ ) as the NIST SRM 981 reference material. To accomplish this, a small aliquot of each sample was analyzed using the Thermo Finnigan Element2 HR-ICP-MS to deter-



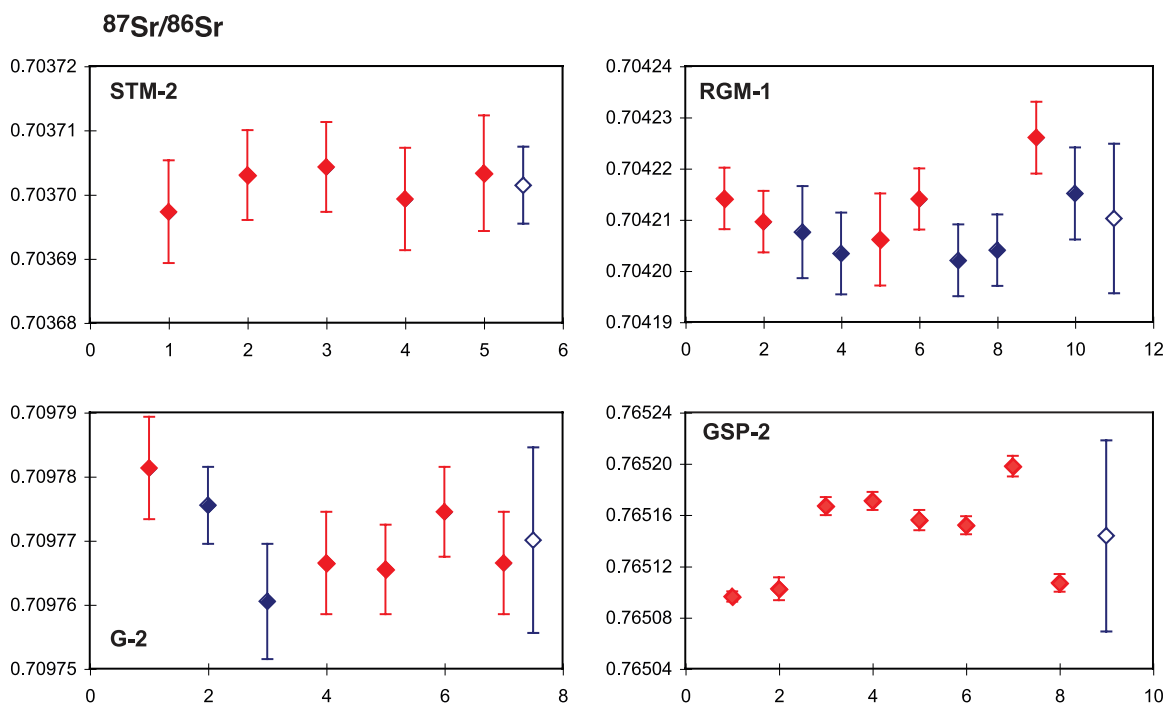
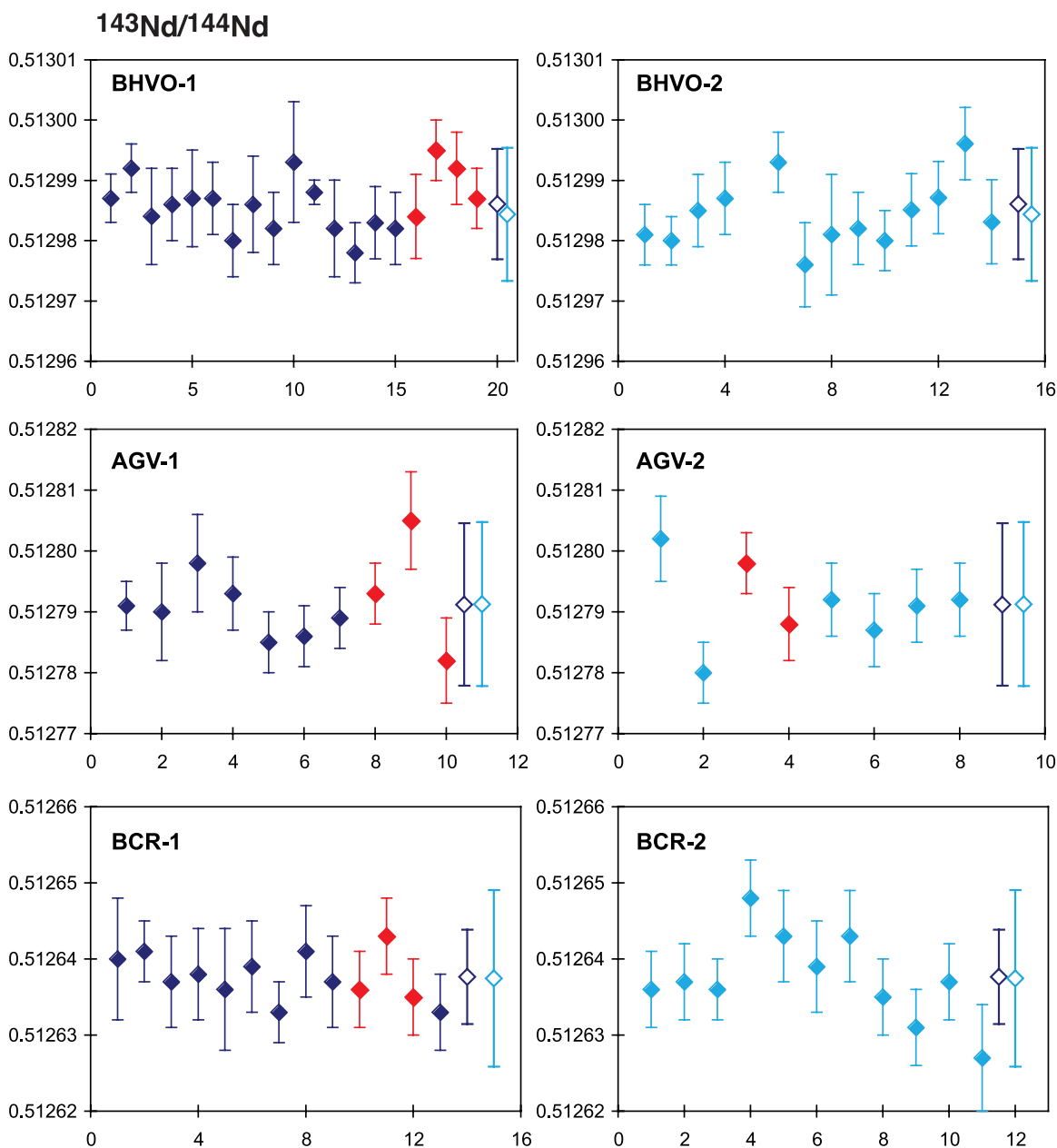


Figure 1. (continued)

mine the exact amount of Pb available for isotopic analysis. During the course of this investigation, 65 analyses of the NIST SRM 981 Pb reference material performed in wet plasma mode on the Nu 015 gave mean values of  $^{208}\text{Pb}/^{204}\text{Pb} = 36.7163 \pm 121$  (2 SD),  $^{207}\text{Pb}/^{204}\text{Pb} = 15.4968 \pm 47$  (2 SD), and  $^{206}\text{Pb}/^{204}\text{Pb} = 16.9400 \pm 49$  (2 SD), while 167 analyses on the Nu 021 gave mean values of  $36.7145 \pm 88$ ,  $15.4964 \pm 29$  and  $16.9407 \pm 36$ , respectively (Table 6, Figure 4). No significant difference was observed in the values of the SRM 981 reference material measured in the two laboratories. These values are in agreement with previously reported TIMS triple-spike values [Galer and Abouchami, 1998], but with slightly lower  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios ( $\sim 60$  ppm lower). This difference in  $^{208}\text{Pb}/^{204}\text{Pb}$  is comparable, albeit smaller, to other MC-ICP-MS analyses of SRM 981 [Vance and van Calsteren, 1999]. In light of the reproducibility and accuracy of the Pb isotopic compositions determined on the two Nu Plasma instruments in this study, there was no need to adjust the  $^{205}\text{Tl}/^{203}\text{Tl}$  ratio from day-to-day; a value of 2.3885 was used for all runs as it yields SRM 981 Pb isotopic compositions within error of the triple-spike values. Depending on the amount of Pb available in each sample, the samples were analyzed in either wet or dry (using a Nu Instruments DSN-100 desolvator) plasma mode,

corresponding to a NIST SRM 981 reference material concentration of 200 ppb (wet) or 40 ppb (dry). Except where the amount of sample material was insufficient, all samples were run with a  $^{208}\text{Pb}$  ion beam of  $>2$  V. The reference material was run every two samples. Even though the NIST SRM 981 results were within error of the triple-spike values after online correction for instrumental mass bias by Tl addition, the USGS reference results were further corrected by the sample-standard bracketing method or the ln-ln correction method as described by White *et al.* [2000] and Blichert-Toft *et al.* [2003].

[22] As  $\sim 100$  nanograms of Pb are needed for the analysis of Pb concentrations (load sizes vary between 72 and 140 ng) by isotope dilution using a  $^{205}\text{Pb}$  spike ( $\sim 5$  ppb  $^{205}\text{Pb}$ ), 3.0 to 65.0 mg of sample rock powder was weighed. The Pb column separation is comparable to that outlined in section 2.2 above, except that it was carried out twice to ensure clean separations. Samples, as well as procedural blanks and SRM 981 Pb reference materials, were loaded on degassed, 99.995% 4-pass zone-refined H. Cross Re filaments using the SiGel ( $\text{SiCl}_4$ ) –  $\text{H}_3\text{PO}_4$  technique and were analyzed with a VG54R single collector TIMS instrument in peak-switching mode at  $1450^\circ\text{C}$ . A mass fractionation correction of



**Figure 2.** Individual  $^{143}\text{Nd}/^{144}\text{Nd}$  analyses by TIMS of BHVO-1, BHVO-2, AGV-1, AGV-2, BCR-1, BCR-2, STM-2, RGM-1, G-2, and GSP-2. Symbols and color coding as in Figure 1.

0.12%/amu was applied on the basis of repeated SRM 981 analyses conducted throughout the course of the study. An average procedural blank of 75 pg is based on 5 determinations during the course of the study, negligible in comparison to the sample Pb concentration. Individual blanks ranged from 56–84 pg, with  $^{208}\text{Pb}/^{204}\text{Pb} = 37.73$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.59$  and  $^{206}\text{Pb}/^{204}\text{Pb} = 18.33$ , all  $\pm 3\%$  (1 SD). Reported concentrations are spike- and blank-corrected (0.06–0.12% of the total) (Table 8).

## 2.4. Leaching Experiment

[23] A preliminary study of BHVO-1 and BHVO-2 [Weis et al., 2005a] showed clear differences in Pb isotopic composition and trace metal concentrations between the two generations of USGS reference materials, confirming the earlier findings of Woodhead and Hergt [2000]. The differences could be ascribed to contamination of the rock powders during processing (crushing, pulverization). We repeated these careful experiments here, on

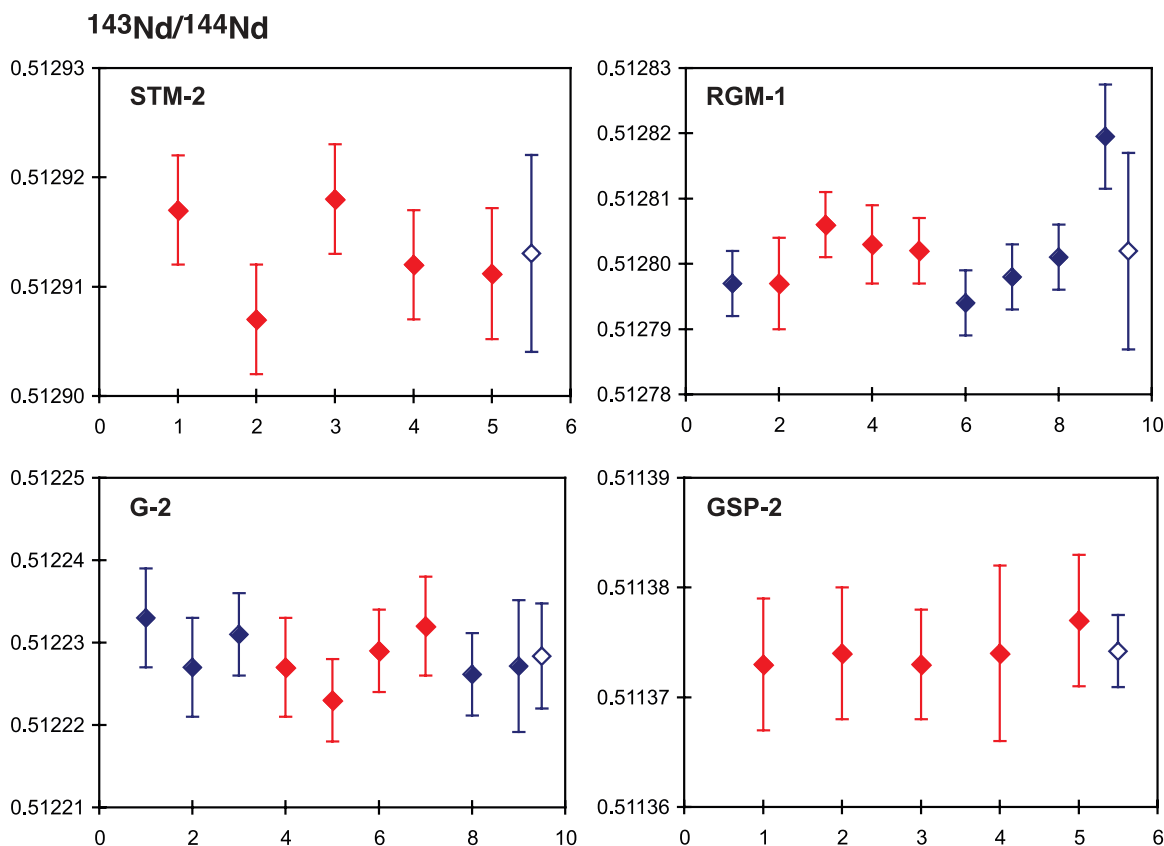


Figure 2. (continued)

BHVO-1, BHVO-2, AGV-1, AGV-2, BCR-1 and BCR-2. The leaching procedure of *Weis and Frey* [1991, 1996] was used, as this method, which was developed to remove secondary alteration phases from old oceanic basalts, has been shown to be more efficient in obtaining reproducible ratios than that of *McDonough and Chauvel* [1991] [*Weis et al.*, 2005a].

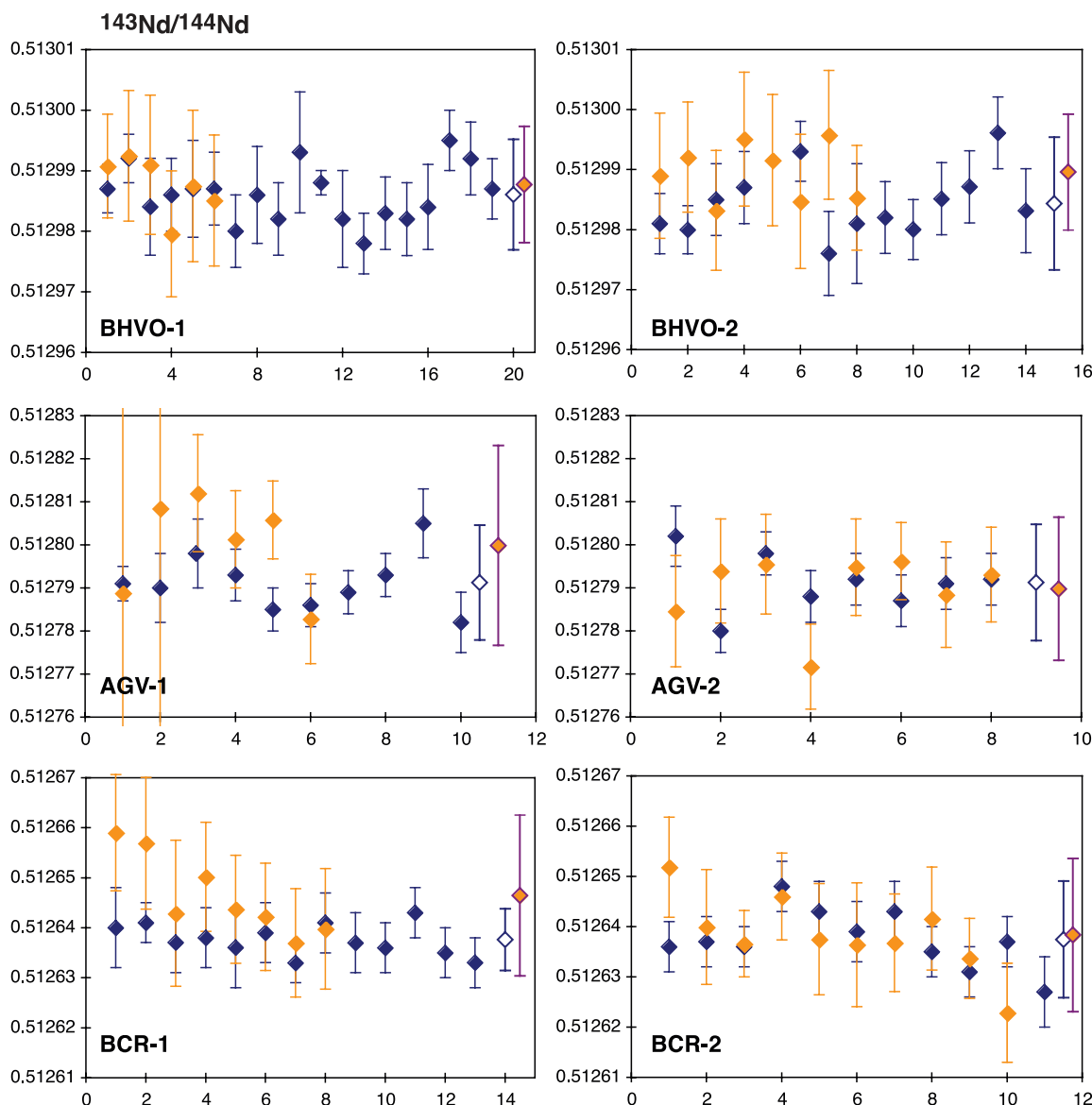
### 3. Results and Discussion

[24] Sr isotopic results are reported in Table 2, Nd isotopic results in Table 3 (TIMS) and Table 4 (MC-ICP-MS), and Pb isotopic results in Tables 5 and 6. The leaching experiment results are reported in Table 7 and the Pb isotope dilution concentrations in Table 8.

#### 3.1. Sr Isotopic Compositions

[25] The Sr isotopic compositions for all analyzed USGS reference materials were obtained with a precision better than 30 ppm (2 SD [ $n = 5$  to 13]), a precision barely larger than the in-run errors (2 SE), which were generally better than  $\pm 0.000010$

absolute on the measured value (average =  $0.000007 \pm 3$  [ $n = 91$ ]). This reflects the homogeneity of all these materials. The precision of Sr isotopic ratios of GSP-2, however, was close to 100 ppm, despite careful digestion in high-pressure PTFE digestion bombs (Table 2, Figure 1). This large range of variation for GSP-2 has previously been documented by *Raczek et al.* [2003], who indicated heterogeneity of GSP-2 with respect to Sr isotopic ratios for aliquots in the 100 mg size range. The precision for Sr concentrations determined on an equivalent sample size (100 mg) and sample matrix (e.g., G-2) was much better (4% RSD) than that found for GSP-2 (8% RSD) using the HR-ICP-MS instrument in the *Pretorius et al.* [2006] study. GSP-2 has also been found to be inhomogeneous with respect to Li contents, likely related to a nugget effect [*Pretorius et al.*, 2006]. The nugget effect for Li and relatively poor reproducibility of Sr concentrations in GSP-2 compared to G-2 suggests that the Sr isotopic heterogeneity for GSP-2 found in this study may also be partly related to the inhomogeneous distribution of an accessory phase in GSP-2, in addition to incom-



**Figure 3.** Individual  $^{143}\text{Nd}/^{144}\text{Nd}$  analyses by MC-ICP-MS of BHVO-1, BHVO-2, AGV-1, AGV-2, BCR-1, BCR-2, STM-2, RGM-1, G-2, and GSP-2 (orange symbols) compared to the TIMS analyses (dark blue symbols; see Figure 2). In each panel the mean and 2 standard deviations of the replicate analyses are indicated for both MC-ICP-MS (orange-filled purple diamond) and TIMS (blue empty diamond) analyses for comparison.

plete recovery of Sr. Thus GSP-2 is a somewhat poor choice for a reference material for Sr.

[26] The largest difference for Sr isotopic ratios is 11 ppm between AGV-1 and AGV-2, whereas it is 7 ppm between BCR-1 and BCR-2 and 6 ppm between BHVO-1 and BHVO-2 (Figure 1). Taking into account the difference in NIST SRM 987 standard values (e.g.,  $0.710203 \pm 34$  ( $n = 24$ ) for *Raczek et al.* [2003] versus  $0.710256 \pm 16$  ( $n = 145$ ) and  $0.710252 \pm 13$  ( $n = 88$ ) after the change of one of the Faraday cups in this study), our

results agree entirely with those of *Raczek et al.* [2003].

### 3.2. Nd Isotopic Compositions

[27] For Nd isotopic compositions analyzed by TIMS (Table 3, Figure 2), the in-run errors (2 SE) are more comparable (average =  $0.000006 \pm 3$  [ $n = 103$ ]) than for Sr. For  $^{143}\text{Nd}/^{144}\text{Nd}$ , the 2 standard deviations are all below 30 ppm. Nd isotopic ratios of GSP-2 are as reproducible as those of the other USGS reference materials. We

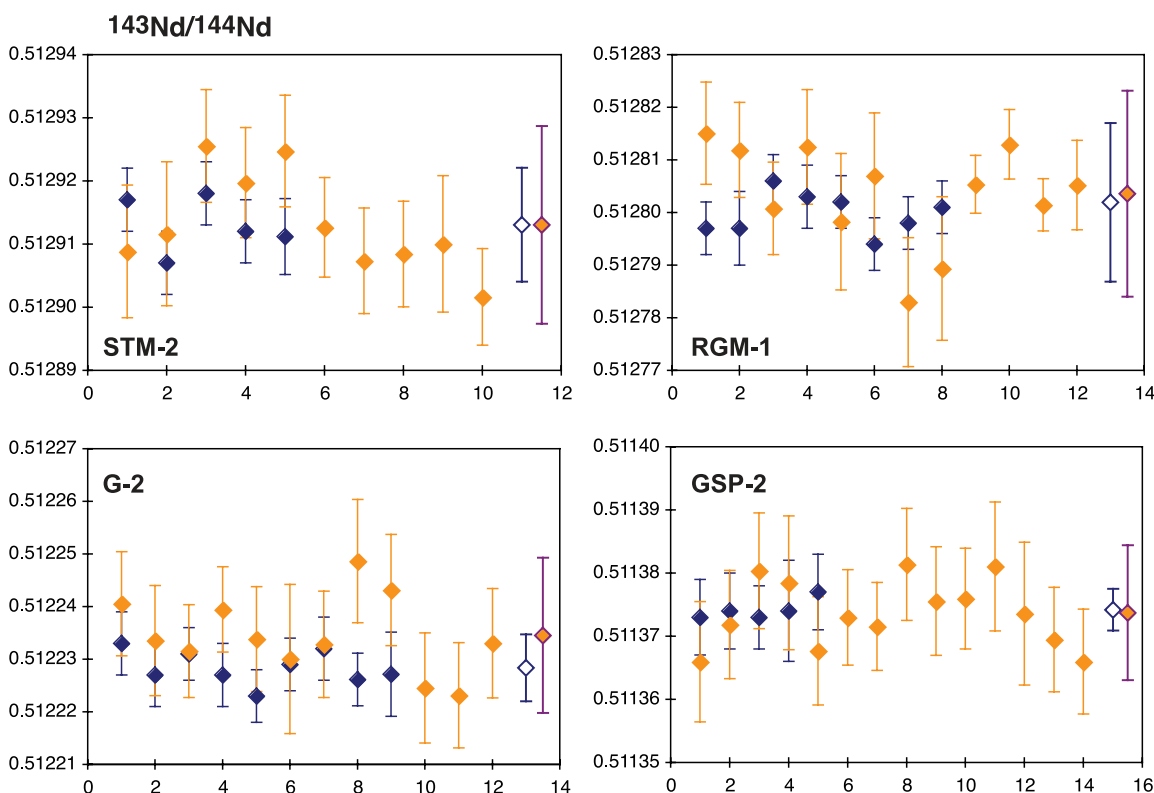
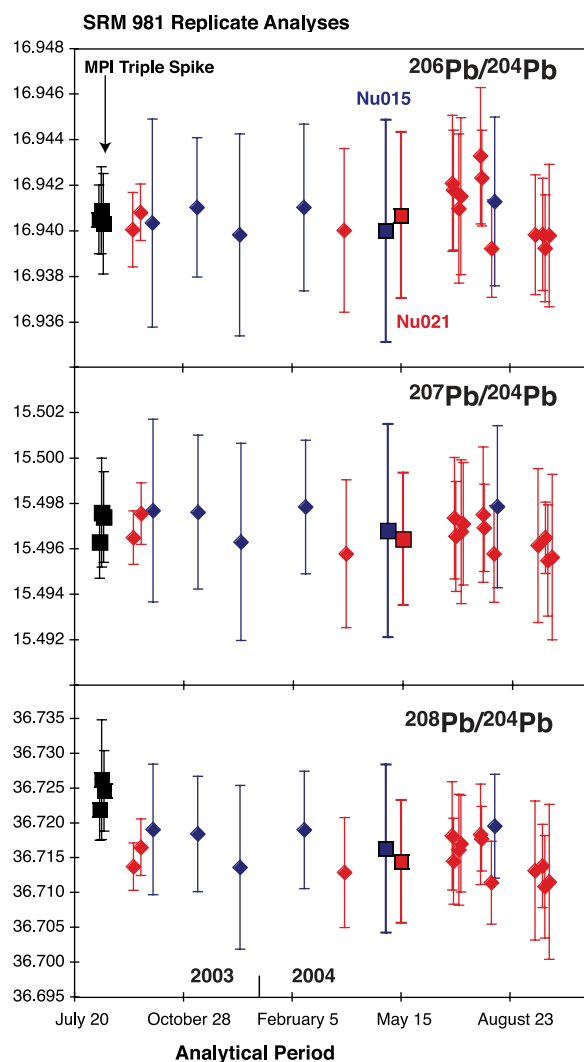


Figure 3. (continued)

have detected no difference between generations 1 and 2 of the analyzed reference materials for BHVO, AGV and BCR (relative difference <3 ppm; Figure 2). The agreement with the results of *Raczek et al.* [2003] is excellent after normalization of both data sets to the accepted La Jolla  $^{143}\text{Nd}/^{144}\text{Nd}$  values ( $0.511839 \pm 38$  [n = 38] versus  $0.511850 \pm 15$  [n = 73] and  $0.511853 \pm 12$  [n = 118] for this study).

[28] The Nd isotopic compositions measured by MC-ICP-MS (Table 4, Figure 3) agree very well with the TIMS values for all USGS reference materials analyzed (relative differences up to 17 ppm). However, sample analysis time by MC-ICP-MS is about 4–6 times less than by TIMS [Luais et al., 1997], bearing in mind that most of the time and effort lie in the chemistry in both cases. The in-run errors are slightly higher than for the TIMS analyses with an average of  $\pm 0.000011 \pm 15$  (n = 94), which has been reduced during the course of this study by using the desolvator (i.e., increase in sensitivity and decrease in sample size). Replicate analyses of the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio are better than 45 ppm (2 SD [n = 6 to 14]). The precision and the accuracy of Nd isotopic analyses by MC-ICP-

MS are also documented by the long-term reproducibility of La Jolla and Rennes Nd reference materials, which have a precision on the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of 29 and 25 ppm, respectively, comparable to the TIMS results. The accuracy of both reference values is better than 10 ppm relative to the accepted value. This indicates that for the Nu Plasma MC-ICP-MS there is no need either to adjust the normalization ratio, as documented earlier for other instruments [Vance and Thirlwall, 2002], or to carry out multidynamic analysis [Thirlwall and Anczkiewicz, 2004] to achieve accurate and precise Nd isotopic analyses. The  $^{145}\text{Nd}/^{144}\text{Nd}$  average for all the USGS reference materials is  $0.348421 \pm 12$  [n = 94], in agreement with the values recently published by *Pearson and Nowell* [2005] for data acquired using a Thermo Finnigan Neptune MC-ICP-MS and within error of the multidynamic MC-ICP-MS analysis [see *Thirlwall and Anczkiewicz*, 2004, Table 9]. Our results support the recent conclusion of *Pearson and Nowell* [2005] that deviations from exponential mass bias behavior during isotope measurements by MC-ICP-MS might be instrument specific.



**Figure 4.** Comparison of the daily averages of SRM 981 for the Nu 015 (blue diamonds) and Nu 021 (red diamonds), with 2 standard deviation bars during the course of this study. The overall average of each instrument is indicated by the square symbols. For comparison, three published values of the SRM 981 measured by the triple-spike method are also indicated as solid black squares in the far left of each diagram [Galer and Abouchami, 1998; Eisele et al., 2003; Regelous et al., 2003].

### 3.3. Pb Isotopic Compositions

[29] Pb isotopic compositions measured on the two different MC-ICP-MS instruments are in good agreement (Figure 4) and both within error of

compositions measured by the double-spike technique [Woodhead and Hergt, 2000; Baker et al., 2004]. The only exception is AGV-1 measured by TIMS by Woodhead and Hergt [2000], which appears to be from a different batch (Table 5, Figures 5a). Comparison between the first and second generations of BHVO, BCR and AGV shows significant differences in Pb isotope ratios (Figures 5a and 5b) and concentrations (Table 8 and W. Pretorius et al. (Complete trace elemental characterization of volcanic rock (USGS BHVO-1, BHVO-2, BCR-1, BCR-2, AGV-1, AGV-2, RGM-1, STM-2) reference materials by high resolution inductively coupled plasma-mass spectrometry, manuscript in preparation, 2006); hereinafter referred to as Pretorius et al., manuscript in preparation, 2006), well outside of analytical errors. The reproducibility of repeated analyses of the volcanic USGS reference materials documented in this study varies between 164 to 1298 ppm. Heterogeneous Pb isotope compositions, and significantly higher Pb concentrations (Pretorius et al., manuscript in preparation, 2006), in first-generation reference materials confirm earlier studies [Woodhead and Hergt, 2000; Baker et al., 2004] and indicate that these reference materials are heterogeneous, at least for Pb. This is probably a result of contamination during processing, as documented by the analysis of mortar and pestle material and leaching of some of the reference materials (see Weis et al. [2005a] for discussion).

[30] For felsic compositions (STM-1, STM-2, RGM-1, GSP-2, G-2 and G-3), the reproducibility of the Pb isotopic compositions (Table 5, Figure 5c) is strongly related to whether or not the rock powder was completely and properly digested. This is reflected by the difference in isotopic composition between the samples dissolved by hotplate digestion in Savillex<sup>®</sup> beakers versus those dissolved in high-pressure PTFE digestion bombs. In the case of GSP-2 and G-2, Pb isotopic compositions for hotplate-dissolved samples are less radiogenic than for samples digested in high-pressure bombs. The opposite is observed for STM-2. The average Pb isotopic compositions of hotplate and high-pressure bomb digestions nevertheless overlap within 2 standard

**Figure 5a.** Comparison of Pb isotopic analyses of BHVO-1, BHVO-2, AGV-1, AGV-2, BCR-1, and BCR-2 by MC-ICP-MS (this study, blue diamonds), by TIMS double-spike [Woodhead and Hergt, 2000] (pale pink triangles) and by MC-ICP-MS double-spike [Baker et al., 2004] (dark pink triangles). For each group of analyses, the average and 2 standard deviation error bars are also plotted. Also shown for BCR-1 are the values obtained by the slightly modified Tl-normalization method of Woodhead [2002] (brown circles). All data have been normalized to the SRM 981 triple-spike values of Abouchami et al. [2000].

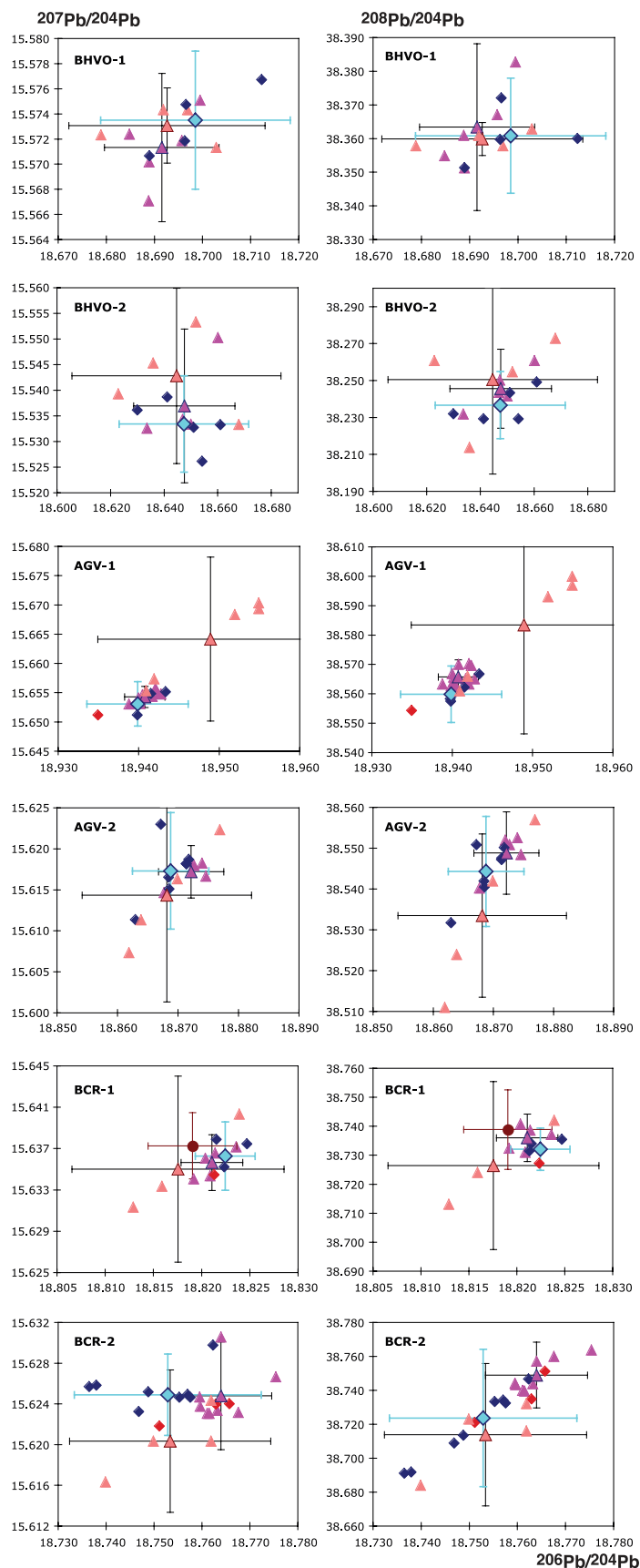
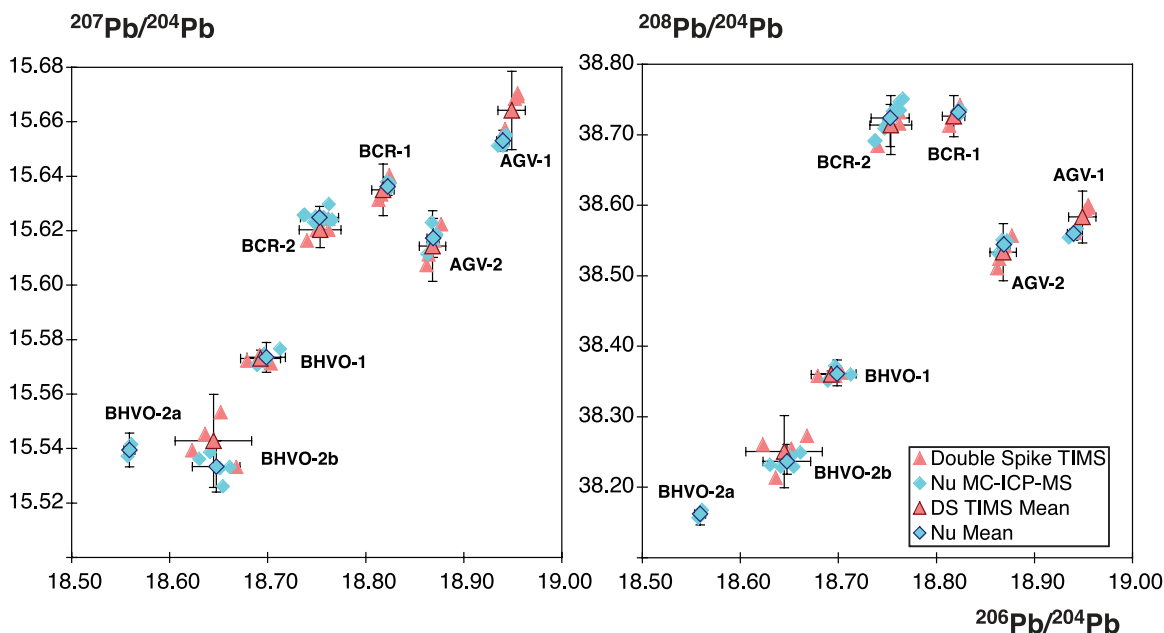


Figure 5a



**Figure 5b.** Overall comparison of Pb isotopic analyses of BHVO-1, BHVO-2, AGV-1, AGV-2, BCR-1, and BCR-2 by MC-ICP-MS (this study, light blue diamonds) and by TIMS double-spike [Woodhead and Hergt, 2000] (light pink triangles). In each case the individual data points are plotted as well as their means and 2 standard deviation error bars. For BHVO-2, there were two different powder splits, 2a and 2b. DS, double spike.

deviations for both G-2 and STM-2, but not for GSP-2. The Pb concentrations for GSP-2 digested in bombs are also significantly higher (13%) than those obtained when digestions are performed on a hotplate [Pretorius *et al.*, 2006] and there is clearly a nugget effect involved. Felsic compositions should always be dissolved under high-pressure conditions.

[31] There are also large differences between first- and second-generation reference materials, as STM-2 is distinctly more radiogenic in all Pb isotopic ratios than STM-1, whereas G-2 is more radiogenic than G-3 (Table 5). We interpret this to be likely due to the chemical composition of these rocks and the presence of accessory minerals whose proportion can vary from one sample to another. The significantly higher Pb concentrations in the first-generation reference materials (STM-1 (18 ppm), G-2 (44 ppm) and GSP-1 (55 ppm)) compared to the same second-generation reference materials (STM-2 (10.2 ppm), G-3

(29 ppm) and GSP-2 (42 ppm) [Pretorius *et al.*, 2006]) seem to indicate that contamination during sample processing also affected the felsic compositions.

### 3.4. Leaching Experiments

[32] To investigate the issue of contamination for the mafic volcanic USGS reference materials further, we undertook leaching experiments on BHVO-1, BHVO-2, AGV-1, AGV-2, BCR-1 and BCR-2. The results are reported in Table 7. In each case, the leachates, the residues and the unleached powders were analyzed (Figures 6 and 7). For BHVO-1 and BHVO-2, the residues have less radiogenic Pb isotopic compositions than the unleached rock powders, whereas the leachates are distinctly more radiogenic (Figure 6). The same observation is valid for AGV-1 and BCR-1 (except for  $^{208}\text{Pb}/^{204}\text{Pb}$ ), although the opposite is true for AGV-2 and BCR-2 (the residues are more radiogenic than the unleached rock powders). Corre-

**Figure 5c.** Comparison of Pb isotopic compositions of felsic compositions (STM-2, RGM-1, G-2, G-3, and GSP-2 by MC-ICP-MS). The left-hand panels show  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$ , and the right-hand panels show  $^{208}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$ . Red symbols indicate high-pressure digestion in PTFE bombs, and blue symbols indicate hotplate Savillex<sup>®</sup> digestion.



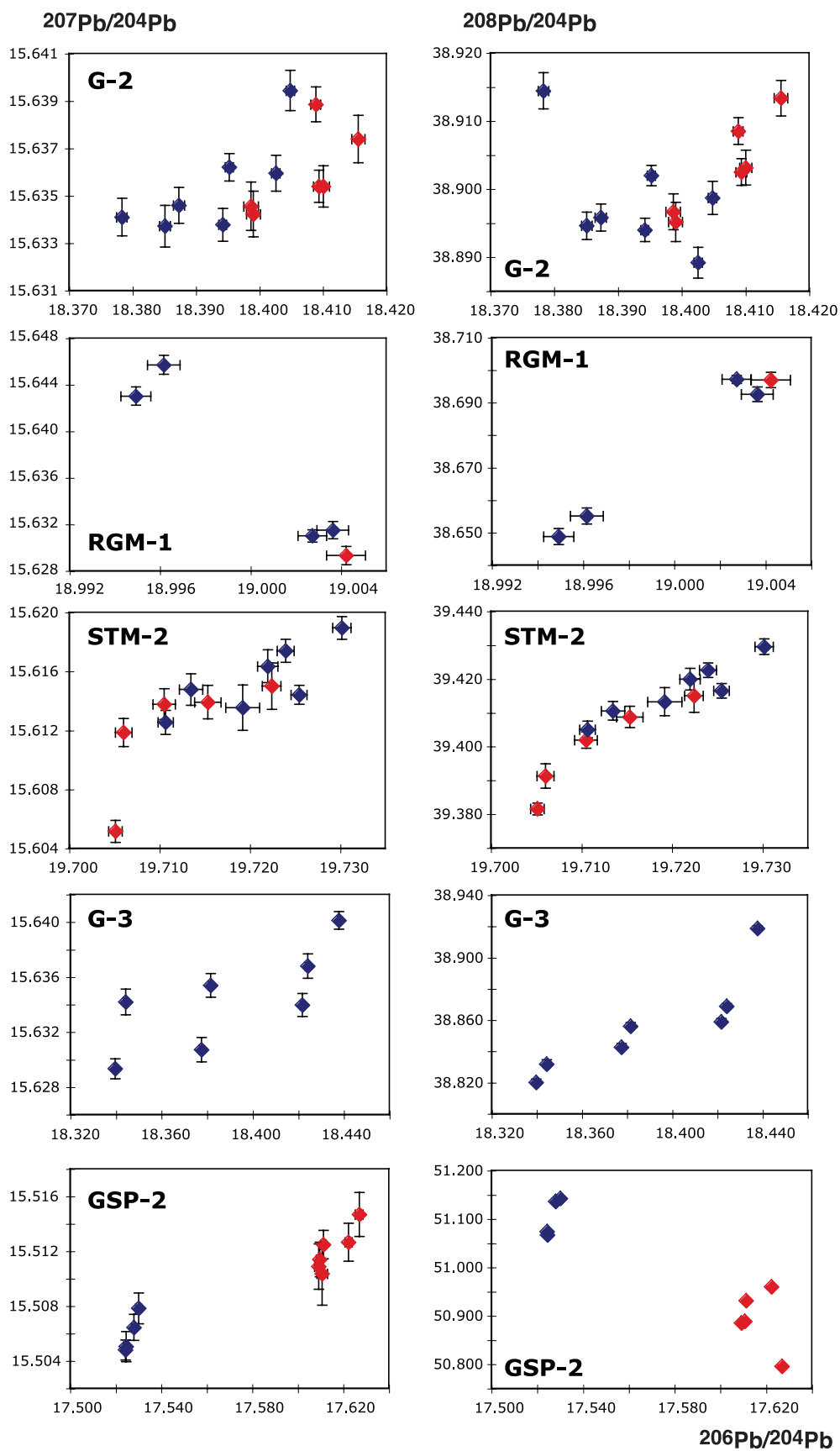
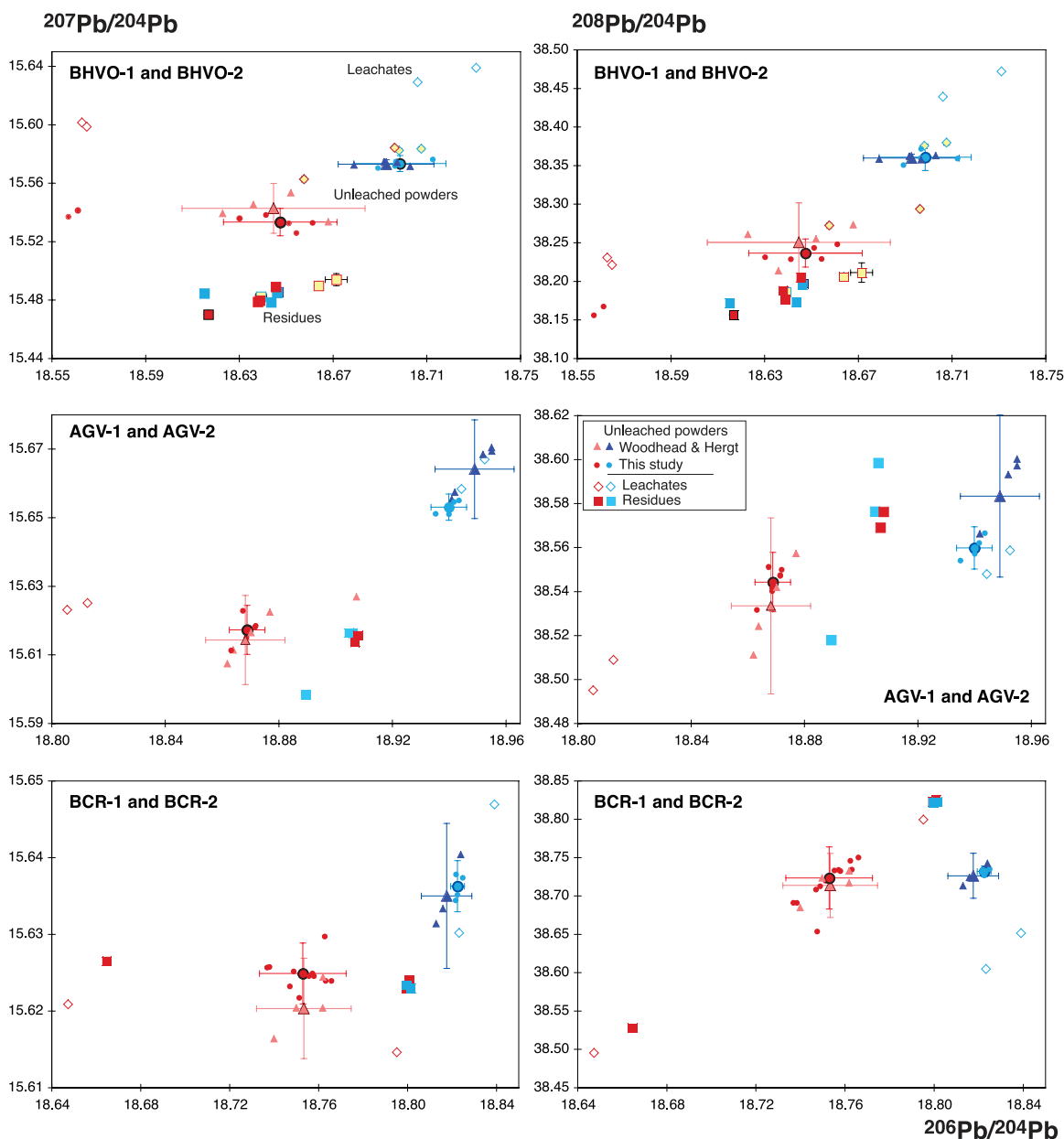


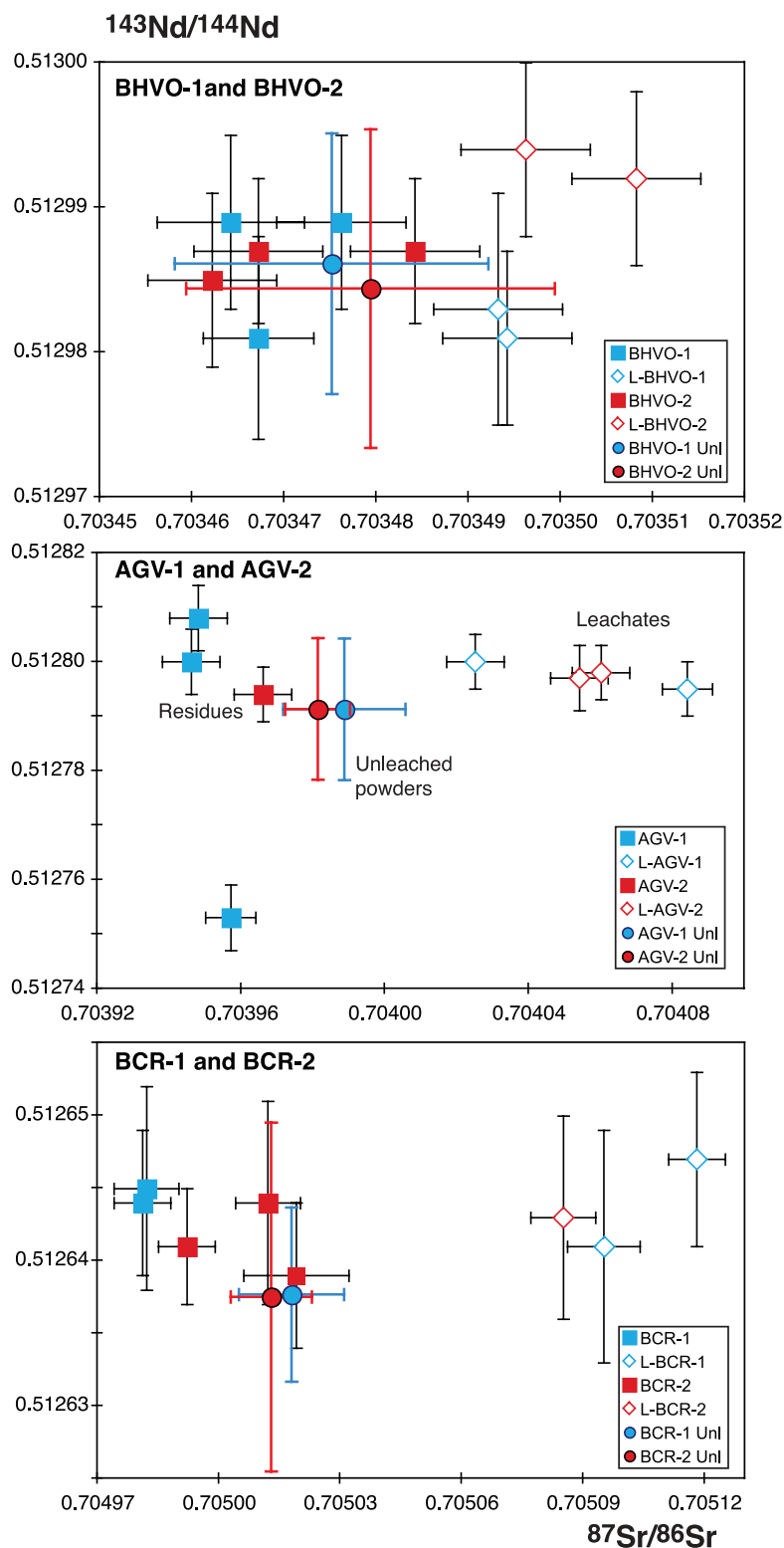
Figure 5c



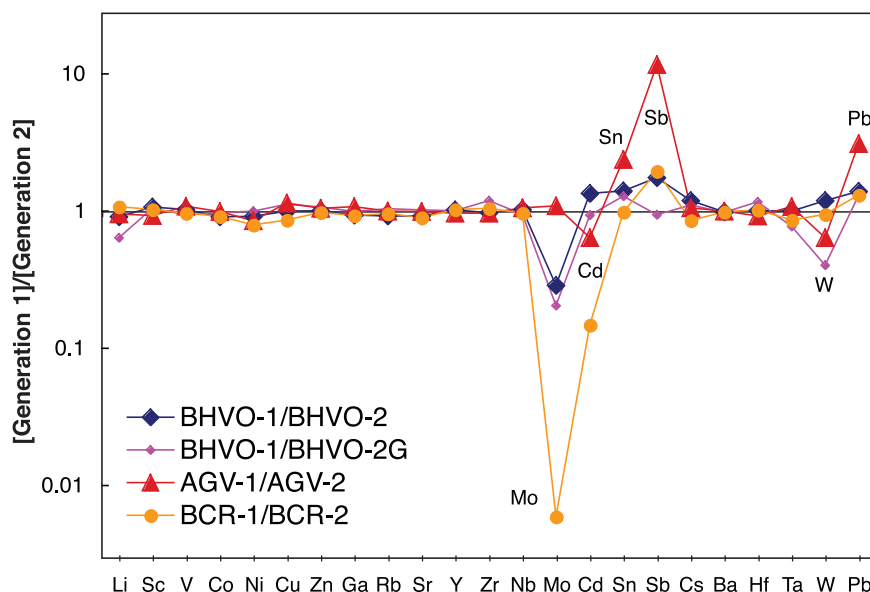
**Figure 6.** Pb isotopic results of the leaching experiments of BHVO-1, BHVO-2, AGV-1, AGV-2, BCR-1, and BCR-2 analyzed by MC-ICP-MS. For a detailed discussion of this experiment, see *Weis et al.* [2005a]. Blue symbols indicate the first-generation USGS reference materials (BHVO-1, AGV-1, and BCR-1), whereas results from the second generation (BHVO-2, AGV-2 and BCR-2) are reported in red. The errors on individual runs are smaller than symbol sizes, unless otherwise indicated. Whole rock powder data are represented by circles. Residues after leaching are represented by square symbols, and diamonds indicate the corresponding leachates. Data from *Weis et al.* [2005a] for BHVO-1 and BHVO-2 (yellow color) and data from *Woodhead and Hergt* [2000] for double-spike TIMS analyses (triangles) are shown for comparison. In all cases, smaller symbols are for individual analyses of the unleached whole rock powders, and the larger symbols are used for their means and 2 standard deviations.

spondingly, the leachates of AGV-2 and BCR-2 have distinctly less radiogenic Pb isotopic compositions than the unleached powders. In Figure 8, the trace element concentrations of the first- and second-generation reference materials for BHVO, AGV and BCR, as well as for BHVO-1/BHVO-2G

(the USGS reference glass), are compared (Pretorius et al., manuscript in preparation, 2006). The only significant differences between the trace element compositions of the two generations of reference materials are for the elements Li, Mo, Cd, Sn, Sb, Cs, W and Pb. The magnitude, the



**Figure 7.**  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  of the leaching experiments on BHVO-1, BHVO-2, AGV-1, AGV-2, BCR-1, and BCR-2 by TIMS. Blue symbols represent first-generation USGS reference materials (BHVO-1, AGV-1, and BCR-1), and the second-generation materials (BHVO-2, AGV-2 and BCR-2) are reported in red. The in-run 2 sigma errors are indicated. Individual analyses of residues after leaching are represented by the square symbols and by diamonds for the leachates. Whole rock unleached powder data (circles) is plotted as the mean of duplicates with their 2 standard deviations (see Tables 2 and 3).



**Figure 8.** Ratio of the trace element concentration of generation 1 compared to generation 2 USGS reference materials for BHVO (powder and glass), AGV, and BCR. See text for discussion of important deviations.

relative enrichment of the first-generation versus the second-generation reference materials, and their individual patterns are not consistent among the BHVO, BCR and AGV series materials, supporting the notion of different sources of contamination. For example, BHVO-2 and BCR-2 are clearly contaminated in Mo, whereas AGV-1 is clearly contaminated in Sn, Sb and Pb. All reference materials show differences in Pb concentrations by a factor of 2 to 5, as also documented here by the isotope dilution concentration measurements (Table 8). This has important implications for laser-ablation studies that use fused (i.e., glass) versions of these reference materials prepared from the original powders. The homogeneity of the glasses relative to the size of the typical laser-ablation spot may thus be questionable and should be thoroughly assessed in future studies.

[33] The residues after leaching show much more homogeneous Pb isotopic compositions than the unleached whole rocks (Figure 6). Additionally, the differences in Pb isotopic compositions between the first and second generations are significantly reduced after leaching, indicating that this is indeed contamination rather than sample heterogeneity or a leaching issue as observed in some Hawaiian basalts [Abouchami *et al.*, 2000]. The presence of outliers (Figure 6, AGV-1 and BCR-2) among the residues indicates that leaching is not always successful at entirely eliminating contamination from the powders. We have

recently carried out systematic leaching experiments (up to 17 steps) on basalts from Hawaii and Kerguelen to assess the reproducibility of Pb analyses by MC-ICP-MS [Nobre Silva *et al.*, 2005] and achieved external reproducibility lower than 200 ppm. This indicates that sample preparation plays a crucial role in obtaining high-precision Pb isotopic ratios and that MC-ICP-MS can achieve comparable levels of reproducibility as double- or triple-spike TIMS analyses [Eisele *et al.*, 2003; Albarède *et al.*, 2005; Baker *et al.*, 2005].

[34] There are also slight differences in  $^{87}\text{Sr}/^{86}\text{Sr}$  between the residues and the unleached powders of BHVO, AGV and BCR (Table 7, Figure 7). The unleached powders are slightly more radiogenic, although only by about twice the external error. The largest differences between residues and unleached powders for  $^{87}\text{Sr}/^{86}\text{Sr}$  are for AGV-1 and BCR-1 (54 and 51 ppm, respectively). This most probably reflects the presence of minor alteration in these volcanic rocks. The leaching has no effect on  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios.

#### 4. Conclusions

[35] Our study of a broad compositional range of USGS reference materials provides the first complete Sr-Nd-Pb isotopic characterization of 13 of these samples. We highlight the importance of an integrated analytical approach, which allows for a better understanding of the potential issues that

arise during sample processing and analysis, from crushing and pulverization, to trace element and isotopic analysis. There is no difference in Sr and Nd isotopic compositions between first- and second-generation USGS reference materials analyzed in this study. The isotopic ratios in Tables 2, 3, and 4 can then be used as recommended  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  values. Nd isotopic compositions can be measured, with comparable accuracy and precision, either by TIMS or MC-ICP-MS. The situation is somewhat more delicate for Pb isotopic ratios where leaching appears to be necessary to remove any potential contamination introduced during the original preparation of the samples. This compromises the use of the materials as glass reference materials for laser-ablation studies involving Pb concentrations or compositions.

## Acknowledgments

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