



RESEARCH ARTICLE

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Key Points:

- Pb-Sr-Nd-Hf isotopic and trace element data set of mafic-ultramafic rock reference materials
- First report of isotopic compositions for many reference materials
- Assessment of leaching effects on basalts

Supporting Information:

- Supporting Information S1
- Table S1

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Comprehensive Pb-Sr-Nd-Hf isotopic, trace element, and mineralogical characterization of mafic to ultramafic rock reference materials

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Abstract Controlling the accuracy and precision of geochemical analyses requires the use of characterized reference materials with matrices similar to those of the unknown samples being analyzed. We report a comprehensive Pb-Sr-Nd-Hf isotopic and trace element concentration data set, combined with quantitative phase analysis by XRD Rietveld refinement, for a wide range of mafic to ultramafic rock reference materials analyzed at the Pacific Centre for Isotopic and Geochemical Research, University of British Columbia. The samples include a pyroxenite (NIM-P), five basalts (BHVO-2, BIR-1a, JB-3, BE-N, GSR-3), a diabase (W-2), a dolerite (DNC-1), a norite (NIM-N), and an anorthosite (AN-G); results from a leucogabbro (Stillwater) are also reported. Individual isotopic ratios determined by MC-ICP-MS and TIMS, and multielement analyses by HR-ICP-MS are reported with 4–12 complete analytical duplicates for each sample. The basaltic reference materials have coherent Sr and Nd isotopic ratios with external precision below 50 ppm (2SD) and below 100 ppm for Hf isotopes (except BIR-1a). For Pb isotopic reproducibility, several of the basalts (JB-3, BHVO-2) require acid leaching prior to dissolution. The plutonic reference materials also have coherent Sr and Nd isotopic ratios (<50 ppm), however, obtaining good reproducibility for Pb and Hf isotopic ratios is more challenging for NIM-P, NIM-N, and AN-G due to a variety of factors, including postcrystallization Pb mobility and the presence of accessory zircon. Collectively, these results form a comprehensive new database that can be used by the geochemical community for evaluating the radiogenic isotope and trace element compositions of volcanic and plutonic mafic-ultramafic rocks.

1. Introduction

Quality assurance, quality control, and metrological traceability during the chemical analysis of geological samples require the characterization of reference materials [e.g., Kane and Potts, 1997; Kane, 2000; Goldstein et al., 2003; Weis et al., 2006; Jochum and Nohl, 2008; Barwick and Wood, 2010; Jochum and Enzweiler, 2014]. When measuring radiogenic isotope ratios, instrumental mass bias is corrected by using stable isotopic ratios (e.g., $^{146}\text{Nd}/^{144}\text{Nd}$, $^{179}\text{Hf}/^{177}\text{Hf}$) and by analyzing “matrix-free” standards with known values (e.g., JNdi for Nd [Tanaka et al., 2000]; JMC 475 for Hf [Patchett and Tatsumoto, 1980; Vervoort and Blichert-Toft, 1999]). After chemical purification and the separation of the elements of interest via ion exchange, the remaining sample matrix may still affect the instrumental mass bias in multiple collector-inductively coupled plasma-mass spectrometers (MC-ICP-MS) and result in inaccurate and irreproducible isotopic ratios [e.g., Woodhead and Hergt, 2000; Albarède and Beard, 2004; Barling and Weis, 2008, 2012]. The analysis of well-characterized matrix-matched reference materials is therefore necessary to monitor the accuracy of results [Woodhead and Hergt, 2000; Weis et al., 2005, 2006; Chauvel et al., 2011].

There are ~600 rock reference materials currently available [Jochum and Enzweiler, 2014], the most commonly used are volcanic rocks, ranging from basaltic to andesitic compositions [Chauvel et al., 2011; Jochum and Enzweiler, 2014]. There are relatively few characterized plutonic rock reference materials, especially for rocks of ultramafic composition (i.e., high MgO, low SiO₂). Quality control is particularly important during the analysis of mafic to ultramafic plutonic rocks. Due to the combination of their low to very low levels of trace elements, coarse grain textures, potential presence of refractory accessory minerals (e.g., chromite, zircon), and high contents of MgO, FeO, CaO, or Al₂O₃, these materials are more susceptible to both matrix effects [Barling and Weis, 2008] and to sample heterogeneity that may make them difficult to completely

Table 1. Summary of Major Compositional Characteristics and Pb, Sr, Nd and Hf Elemental Concentrations of Mafic and Ultramafic Rock Reference Materials Analyzed in This Study^a

Reference Material	Rock Type	Issuing Organization	Locality	wt%					μg/g			
				SiO ₂	MgO	CaO	Al ₂ O ₃	Fe ₂ O ₃ ^T	Pb	Sr	Nd	Hf
NIM-P	Pyroxenite	MINTEK	Bushveld Complex, South Africa	51.10	25.33	2.66	4.18	12.7	1.42 ^a	32	1.86	<0.2 ^a
BE-N	Melilite-bearing Nephelinite	SARM	Essey-la-côte, France	38.2	13.15	13.87	10.07	12.84	4	1370	67	5.6
DNC-1	Dolerite	USGS	Braggtown Quarry, North Carolina	47.15	10.13	11.49	18.34	9.97	6.3	144	5.2	1.04 ^a
BIR-1a	Olivine Tholeiite	USGS	Reykjavik, Iceland	47.96	9.7	13.3	15.5	11.3	3	110	2.5	0.582 ^b
GSR-3	Olivine Basalt	IGGE	Hebei, China	44.64	7.77	8.81	13.83	13.4	5 ^a	1100	54	6.5
NIM-N	Norite	MINTEK	Bushveld Complex, South Africa	52.64	7.5	11.5	16.50	8.97	2.2 ^a	260	3	0.38 ^a
BHVO-2	Basalt	USGS	Halemaumau Crater, Hawaii	49.9	7.23	11.4	13.5	12.3	1.65 ^b	389	25	4.1
W-2	Diabase	USGS	Bull Run Quarry, Virginia	52.68	6.37	10.86	15.45	10.83	9.3	190	13	2.44 ^b
JB-3	High-alumina Basalt	GSJ	Fuji volcano, Japan	50.96	5.19	9.79	17.2	11.82	5.58	403	15.6	2.67
ST05-03	Leucogabbro	PCIGR	Stillwater Complex, Montana	48.83	3.06	14.9	26.69	3.39				
AN-G	Anorthosite	SARM	Fiskenaeset, Greenland	46.3	1.8	15.9	29.8	3.36	2	76	2.4	0.38

^aAll data are from the issuing organization, except when noted: (a) *Dulski* [2001], (b) *Jochum et al.* [2015]. Significant figures follow the reported uncertainty for certificates and published values.

dissolve by conventional acid digestion techniques [e.g., *Yokoyama et al.*, 1999; *Tanaka et al.*, 2003; *Nakamura and Chang*, 2007; *Ulrich et al.*, 2012; *Sun et al.*, 2013; *Chu et al.*, 2014].

In this study, we provide the mineralogical characterization, trace element concentrations, and Pb-Sr-Nd-Hf isotopic reference values for 10 reference materials of mafic to ultramafic composition. These materials include a pyroxenite (NIM-P), five basalts (BHVO-2, BIR-1a, JB-3, BE-N, GSR-3), a diabase (W-2), a dolerite (DNC-1), a norite (NIM-N), and an anorthosite (AN-G) (Table 1). The composition of a leucogabbro from the Stillwater complex is also reported as this sample contains zircon that is a potential new reference material for U-Pb dating of Archean rocks [*Wall and Scoates*, 2014]. Trace element contents and isotope compositions were measured on unleached and leached powders of the basaltic materials to evaluate the effect of leaching on their reproducibility. Mineralogical compositions were determined to assess the potential role of the phases during leaching of basaltic samples and the potential relationship between mineral content and isotopic heterogeneity of the plutonic samples. The analytical instrumentation utilized at the Pacific Centre for Isotopic and Geochemical Research (PCIGR), University of British Columbia, Vancouver (Canada), included three MC-ICP-MS (Nu Instruments Ltd., Nu 021, NP 214, and Nu 1700), two thermal ionization mass spectrometers (TIMS, Thermo Scientific (formerly Finnigan) Triton and Nu TIMS), and a high resolution-ICP-MS (HR-ICP-MS, Thermo Scientific Element II). This paper presents recommendations for the appropriate basaltic and mafic-ultramafic plutonic rock reference material to be used depending on the isotopic system of interest, the sample matrix, and whether the samples are leached. These results form a comprehensive new data set essential for the isotopic investigation of mafic-ultramafic volcanic and plutonic rocks from a wide range of tectonic settings and highlight some of the analytical challenges encountered during their analysis.

2. Reference Materials

Complete descriptions of the reference materials examined in this study are given in Table 1, including rock type, supplier, locality, and relevant major element oxide and trace element concentrations. Below, the key mineralogical and compositional characteristics of the 11 samples are addressed based on information provided both in the original reference to each material and by new XRD Rietveld refinements (Table 2) determined at the Electron Microbeam/X-Ray Diffraction Facility at the Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia.

For quantitative X-ray analysis, the samples were reduced to the optimum grain-size range (<10 μm) by grinding under ethanol in a vibratory McCrone Micronizing Mill for 10 min. Continuous-scan X-ray powder-diffraction data were collected over a 2θ range of 3–80° with CoKα radiation on a Bruker D8 Advance Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye-XE detector. The long fine-focus Co X-ray tube was

Table 2. Mineralogical Composition of Mafic-Ultramafic Rock Reference Materials Determined by Rietveld Refinement of XRD Results^a

Reference Material		NIM-P	BE-N	DNC-1	BIR-1a	GSR-3	NIM-N	BHVO-2	W-2	JB-3	ST05-03	AN-G
Rock Type		Pyroxenite	Melilite-bearing Nephelinite	Dolerite	Olivine Tholeiite	Olivine Basalt	Norite	Basalt	Diabase	High- alumina Basalt	Leucogabbro	Anorthosite
Group	Mineral ^a	Modal composition (wt%) ^b										
Olivine	Forsterite	1.0	13.8					1.4				
	Forsterite, ferrian			16.3	13.6	9.4				1.8		
Feldspar	Andesine			31.7	22.3	21.7		42.9				
	Andesine An48									59.1		
	Bytownite 30933											84.0
	Bytownite An80 34667											
	Labradorite An66	8.5		25.7	24.9		53.3		45.6		64.0	
	Microcline intermediate					11.9						
	Orthoclase								3.1			
Pyroxene	Augite	6.4	49.1	18.4	36.6	31.6	23.9	39.4	28.3	18.2		0.7
	Diopside										9.4	
	Enstatite, ferroan	75.7		1.9			19.5		13.2	2.5		
	Pigeonite							11.0		14.0		
Amphibole	Actinolite						0.7		1.5		2.6	11.7
	Pargasite	2.2										
Feldspathoid	Leucite low					0.9						
	Nepheline 97294		15.2									
	Nepheline 65961					12.3						
Oxide	Hematite							0.4				
	Ilmenite			0.6		0.8		1.5	1.7			0.2
	Magnesiochromite	4.3										
	Magnetite			0.6								
	Titanomagnetite		6.5			5.3						
	Ulvöspinel				2.0			3.1		3.7		
Carbonate	Calcite		1.3									
Chlorite group	Chamosite 1M1b					2.1						
	Clinocllore 11b-4 68942			2.9			0.5		1.5		4.5	1.0
Epidote group	Clinozoisite										11.3	1.2
	Zoisite										3.9	
Melilite	Akermanite		2.3									
Phosphate	Apatite-(CaOH)		2.8									
	Fluorapatite					2.7						
Phyllosilicate	Biotite 1M	0.6	2.0						0.7			
	Talc 1A	0.5		1.5			0.5					
Zeolite	Analcime		0.6			1.3						
	Gonnardite		6.5									
Quartz	Quartz low	0.7		0.4	0.5		1.6	0.4	4.4	0.7	4.3	1.2

^aMineral names and modality are the results of quantitative phase analysis by Rietveld refinements of X-ray powder-diffraction data of the mafic-ultramafic rock reference materials. The Rietveld refinement plots are shown on supporting information Figures S1–S11.

^bModal compositions represent the relative amounts of crystalline phases in wt% normalized to 100%.

operated at 35 kV and 40 mA, using a take-off angle of 6°. The X-ray diffractograms were analyzed using the International Centre for Diffraction Database PDF-4 and Search-Match software by Bruker. X-ray powder-diffraction data of the samples were refined with Rietveld program Topas 4.2 (Bruker AXS) and mineralogical content is reported in wt%. Associated Rietveld refinement plots may be found in supporting information Figures S1–S11.

2.1. Pyroxene-Rich Ultramafic Reference Material

NIM-P [Russell *et al.*, 1968] is a pyroxenite collected from the Critical Zone of the ca. 2056 Ma Bushveld Complex in South Africa (age from Scoates and Wall [2015]) and it has the highest MgO content (25.3 wt%) of the reference materials in this study (Table 1). The XRD results show that the pyroxenite consists mainly of enstatite (76 wt%), labradorite (9%), augite (6%), and magnesiochromite (4%) (Table 2), a mineral composition that agrees with the description provided by MINTEK (Council for Mineral Technology, South Africa) [Russell *et al.*, 1968].

2.2. Basaltic Reference Materials

Five basaltic reference materials, with MgO contents ranging from 5.2 to 13.2 wt%, were selected for this study: BE-N, BIR-1a, GSR-3, BHVO-2, and JB-3 (Table 1). BE-N is a 27.6 Ma melilite-bearing nephelinite [Lippolt

et al., 1976] sampled from a volcano near Essey-la-Côte, Meurthe-et-Moselle (France). The nephelinite contains phenocrysts of olivine and augite in a crystalline matrix [Govindaraju, 1980]. The mineralogy of this alkali rock consists of 49% augite, 15% nepheline, 14% forsterite, 7% titanomagnetite, 3% apatite, and 2% akermanite (Table 2). BIR-1a is a coarse-grained olivine tholeiite collected from the Reykjavik dolerite lava flows in Iceland and it contains 37% augite, 25% labradorite, 22% andesine, 14% forsterite, and 2% ulvöspinel (Table 2). GSR-3 is an olivine basalt from Changjiakou, Hebei (China) and contains plagioclase, olivine, magnetite, and augite according to the original reference [Govindaraju, 1994]. The new XRD results indicate that GSR-3 is a feldspathoid-bearing alkaline rock with 32% augite, 22% andesine, 12% nepheline, 12% microcline, 9% forsterite, 3% apatite, and 2% secondary chamosite as main phases (Table 2). BHVO-2 is a basalt collected by the United States Geological Survey (USGS) from a pahoehoe lava flow erupted at Halemau mau crater, Kilauea volcano (Hawaii, USA), in 1919; it contains 43% andesine, 40% augite, 11% pigeonite, and 3% ulvöspinel (Table 2). JB-3 is a high-alumina basalt collected by the GSJ (Geological Survey of Japan) from the Aokigahara lava flow of Fuji volcano (Japan) that erupted in the year 864 [Govindaraju, 1994]. Ando *et al.* [1987] describes this basalt as consisting of hypersthene, augite, and olivine; the new XRD results indicate that the mineralogical composition is 59% andesine, 18% augite, 14% pigeonite, 4% ulvöspinel, and 3% enstatite (Table 2).

2.3. Gabbroic Reference Materials

The three plutonic gabbroic reference materials examined in this study (DNC-1, NIM-N, W-2) range from 6.4 to 10.2 wt% MgO (Table 1). DNC-1 is a Triassic-Jurassic dolerite from the Braggtown quarry, North Carolina (USA), and consists mainly of olivine, plagioclase, and augite [Ragland *et al.*, 1968]. The XRD results for this material give 57% plagioclase (31% andesine + 26% labradorite), 18% augite, 16% forsterite, and 3% secondary clinocllore (Table 2). NIM-N is a norite sampled from the Main Zone of the Bushveld Complex, South Africa. It consists mainly of orthopyroxene, plagioclase, magnetite, ilmenite, and clinopyroxene with minor amounts of quartz and alteration products [Russell *et al.*, 1968]; the XRD analysis confirms this mineralogical composition (53% labradorite, 24% augite, 20% enstatite; Table 2). W-2 is a diabase sampled in the Bull Run quarry, Virginia (USA), and is described as being mainly composed of augite and plagioclase with minor amounts of quartz, potassium feldspar, biotite, and opaque minerals [Chayes, 1951]. The mineralogy of W-2 determined by Rietveld refinement of the XRD results is 46% labradorite, 28% augite, 11% pigeonite, and 3% ulvöspinel (Table 2).

2.4. Plagioclase-Rich Reference Materials

AN-G is a metamorphosed anorthosite from the ca. 2.97 Ga Fiskenaesset basic complex in Greenland [Polat *et al.*, 2010] and consists of 84% plagioclase (bytownite) and 12% actinolite [Govindaraju, 1980, Table 2]. ST05-03 is a leucogabbro sampled from the Anorthosite-II (AN-II) zone of the Middle Banded Series in the ca. 2.71 Ga Stillwater Complex [Premo *et al.*, 1990; Wall and Scoates, 2014]. It is evaluated here as a potential new plagioclase-rich reference material for isotopic compositions. The Stillwater leucogabbro contains cumulus plagioclase and interstitial pigeonite with minor K-feldspar and quartz. The XRD results yield 64% plagioclase (bytownite), 9% diopside, and 4% quartz with abundant secondary minerals, including 11% clinzoisite, 5% clinocllore, 4% zoisite, and 4% actinolite (Table 2).

3. Analytical Techniques

3.1. Laboratory Environment and Reagents

Chemical digestion and separation were carried out in class 100 fume hoods located in a class 1000 clean laboratory, with concentration and isotopic analyses carried out in class 10 000 laboratories, at the Pacific Centre for Isotopic and Geochemical Research (PCIGR), University of British Columbia (Vancouver, Canada). Acids used for digestion, leaching and Pb separation were subboiling distilled in Teflon® bottles. HNO₃ and HF were also subboiling distilled in Teflon® bottles for Sr, Nd and Hf separations, whereas HCl was quartz distilled. Acid blanks were below 10 ppt in subboiled and quartz distilled acids for all elements, except Cr, Ni, Cu, Zn, Sr, Sb, Ba, and Zr, whose values range from 35 ppt to 1.2 ppb. All acid dilutions were made with ultrapure Milli-Q® water (18.2 MΩ·cm). Savillex® Teflon beakers were acid-cleaned between uses, following four steps: (1) batch cleaning in Extran® or Citranox®, (2) batch cleaning in 50% HCl solution (Trace metal grade), (3) batch cleaning in 50% HNO₃ solution (Trace metal grade), and finally, (4) fluxing in 50% HNO₃–10% HF solution. These cleaning steps were 24 h each on a hotplate at 120°C.

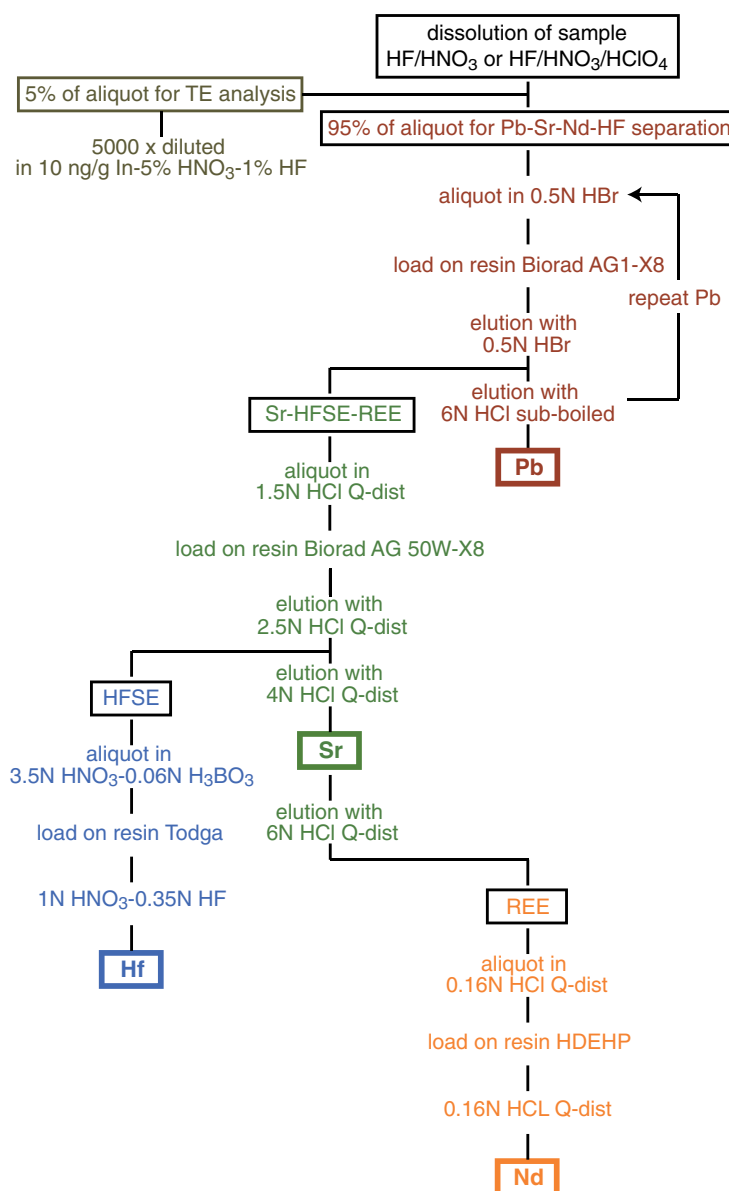


Figure 1. Flow chart summarizing the sample processing and analytical steps leading to the measurement of trace element concentrations and Pb-Sr-Hf-Nd isotopic ratios of mafic-ultramafic rock reference materials. TE: Trace elements; Q-dist: quartz-distilled.

the hafnium separation is adapted from the method described by Connelly *et al.* [2006]. Solutions were passed twice through the Pb exchange resin to ensure Pb purification [e.g., Nobre Silva *et al.*, 2009]. For samples with heavy matrices and low levels of Sr (NIM-P, AN-G, ST05-03), an additional Sr purification step was done using the method described in Deniel and Pin [2001].

3.3. Mass Spectrometry

Trace element concentrations were measured on an Element II High Resolution ICP-MS (HR-ICP-MS) (Thermo Scientific). Aliquots were diluted by a factor of 4000–5000 with a 10 ng/g In-5% HNO₃–1% HF solution; the instrument signal was calibrated using the BCR-2 reference material (USGS) (supporting information Table S12 and Table 3). Correction for instrumental drift was done by sample-standard bracketing where BCR-2 was measured typically every six samples [e.g., Carpentier *et al.*, 2013]. Procedural blanks were measured for each set of analysis; they were negligible compared to the concentrations measured in the reference materials, except in a few cases (supporting information Tables S1–S11). Analytical precision for

3.2. Sample Preparation

Duplicates ($n = 4–12$) of each reference material as sent by the issuing organization (i.e., without extra drying) were digested individually and analyzed at PCIGR; replicates are analyses of the same solution. The preparation of samples for concentration analysis is detailed in Weis *et al.* [2006], Carpentier *et al.* [2013], and Schudel *et al.* [2015]. Briefly, 100–250 mg of rock powder was digested either in concentrated HF-HNO₃ on a hotplate at 130°C in screw-top Savillex® beakers for basaltic rocks, or in concentrated HF-HNO₃-HClO₄ at 190°C in steel-jacketed high-pressure PTFE bombs for all other rock types [Pretorius *et al.*, 2006]. Five duplicates of each basaltic reference material were leached with HCl following the procedure of Weis and Frey [1996] to monitor for contamination, which has been demonstrated for the BHVO-2 reference material [e.g., Weis *et al.*, 2006].

After digestion, a 5% aliquot was taken for concentration measurements while the remaining 95% went through ion exchange chromatography to separate Pb, Sr, Hf and Nd (Figure 1). The procedures for Pb, Sr and Nd separation are detailed in Weis *et al.* [2006];

Table 3. Typical Instrument Settings for Trace Element and Isotopic Analyses of Mafic-Ultramafic Rock Reference Materials at PCIGR^a

Instrument	Element 2 HR-ICP-MS	MC-ICP-MS (Nu 021, NP11 214, NP1700)	Triton TIMS	Nu-TIMS
Element/Isotope	all trace elements	Pb, Hf, Nd	Sr	Sr
RF power	1200 W	1300 W		
Argon flow:				
Cooling gas	16 L/min	13 L/min		
Auxiliary gas	0.9 L/min	0.7–0.8 L/min		
Sample gas	0.9–1.1 L/min	tune daily		
Sample introduction		DSN-100	Ta filament	Re filament + Ta activator
Sample uptake rate	~100 μ L/min	~100–160 μ L/min		
Nebulizer type	PFA nebulizer	PFA nebulizer		
Interface cones	Aluminum	Nickel		
Mass resolution	LR, MR, HR	LR		
Voltage of analysis:		²⁰⁸ Pb: 4V, ¹⁷⁷ Hf: 2–2.2V, ¹⁴⁴ Nd: 3.5V	⁸⁸ Sr: 4V	⁸⁸ Sr: 4.5V
Sampling mode	3 runs of 6 scans	3 blocks of 20 cycles	10 blocks of 13 cycles	4 blocks of 33 cycles
Integration time	LR: 0.12s, MR: 0.18s, HR: 0.46s	10s	16.8s	16.8s
Baseline determination	1) Blank measured at beginning of day of analysis 2) Background measured typically every 7 samples	30s every block	30s every block	120s every block
Internal standard	Indium	Ta for Pb analysis (²⁰⁵ Ta: 1.3V)		
Data processing	SSB (Standard: BCR-2)	SSB (Pb, Hf, Nd) or daily average (Hf, Nd) (Standards: SRM981, JMC475, Rennes, JNdi)	Wheel average (Standard: SRM987)	Wheel average (Standard: SRM987)

^aLR: Low resolution; MR: medium resolution; HR: high resolution; SSB: sample-standard bracketing.

the trace element concentrations, evaluated by duplicate analysis, is typically <5% RSD for the rare earth elements, Ba, Zr, Hf, Cs, Nb, Rb, Ga, Cu, Ni, Co, and V, and <10% RSD for Li, Mo, Cd, Sn, Sb, Ta, W, Bi, Th, Sr, Pb, U, Sc, Y (Tables 4–6) and Figure 2).

Lead, Nd, and Hf isotopic compositions were measured on three different Nu Instruments MC-ICP-MS (Nu 021, NP11 214, Nu1700) and were cross-calibrated by the repeated analyses of reference materials and standards (SRM981, Nd Rennes, JNdi, La Jolla, JMC 475), which ensured the comparability of the results after data processing. Strontium isotopic compositions were measured on two thermal ionization mass spectrometer (TIMS): a Thermo Scientific Triton and a Nu Instruments TIMS. Using the Nu TIMS, run of ~130 cycles of ⁸⁷Sr/⁸⁶Sr can be done for samples as small as 50 ng, which was required for the low levels of Sr in several samples (NIM-P, AN-G, ST05-03). Repeated analysis of reference materials and standards (SRM987) were done to compare the results of the PCIGR TIMS instruments. For the low to very low trace element concentrations of the reference materials AN-G, NIM-P, and NIM-N, and the leucogabbro ST05-03 (Tables 4 and 6), Pb-Nd-Hf isotopic analyses were possible with the enhanced interface of the Nu Plasma 214 MC-ICP-MS resulting in a sensitivity of 660 V/ppm for Pb, 190 V/ppm for Hf, and 105 V/ppm for Nd (flow rate of ~100 μ L/min) [Weis *et al.*, 2013, <http://www.nu-ins.com/wp-content/uploads/AN27-NP11-ES.pdf>]. The conditions of analysis are summarized in Table 3. The isotopic results were corrected on-line for mass fractionation using natural stable ratios (Sr, Hf, Nd) or using TI spike for Pb. In addition, the isotopic results were normalized to established standard values (Pb-Sr-Nd-Hf). For TIMS, Sr isotope data were normalized using the average measured SRM987 of the corresponding barrel. For MC-ICP-MS, different data processing techniques were tested: sample-standard bracketing, log-log correction, and normalization to the average standard value of the day [e.g., Albarède *et al.*, 2004]. The sample-standard bracketing correction yielded more reproducible replicates and was the least sensitive to residual matrix effects. Use of this correction provides results for the reference materials that can be used for comparison with other laboratories.

During the 3 years of data acquisition of this study, the average of the measured Pb standard SRM981, corrected on-line for mass fractionation using ²⁰⁵Tl/²⁰³Tl = 2.3885, was ²⁰⁸Pb/²⁰⁴Pb = 36.7189 \pm 0.0049, ²⁰⁷Pb/²⁰⁴Pb = 15.4994 \pm 0.0018, ²⁰⁶Pb/²⁰⁴Pb = 16.9421 \pm 0.0017 (2SD, *n* = 41) on the Nu Instruments Plasma 214 and ²⁰⁸Pb/²⁰⁴Pb = 36.7207 \pm 0.0096, ²⁰⁷Pb/²⁰⁴Pb = 15.4989 \pm 0.0039, ²⁰⁶Pb/²⁰⁴Pb = 16.9425 \pm 0.0034 (2SD, *n* = 94) on the Nu 021 MC-ICP-MS. The Hf standard JMC 475 average ¹⁷⁶Hf/¹⁷⁷Hf = 0.282151 \pm 0.000018 (2SD, *n* = 75) on the NP 214 and ¹⁷⁶Hf/¹⁷⁷Hf = 0.282170 \pm 0.000044 (2SD, *n* = 80) on the Nu 021. The average for the Nd standard Rennes was ¹⁴³Nd/¹⁴⁴Nd = 0.511941 \pm 0.000046 (2SD, *n* = 61) on the Nu 021 and 0.511972 \pm 0.000011 (*n* = 12) on the

Table 4. Trace Element Concentrations of the Pyroxene-Rich and Plagioclase-Rich Rock Reference Materials Measured by HR-ICP-MS^a

Trace Elements (μg/g)	NIM-P Pyroxenite			AN-G Anorthosite				ST05-03 Leucogabbro	
	n = 4	% RSD	[Dulski, 2001] n = 1	n = 8	% RSD	[Carignan et al., 2001] n = 25		n = 5	% RSD
Li	4.14	1.3		-	-			-	-
V	242	1.6		63	2.1	74.3	4.6	60.8	0.7
Co	106	1.1		11.6	3.1	25.5	1.3	15.0	1.1
Ni	514	1.3		33	3.1	38	8.8	50	2.3
Cu	15.0	1.4		17.0	2.7	17.7	1.0	41.9	0.9
Zn	108	2.7		-	-	22.4	1.6	18.2	1.1
Ga	7.22	1.3		16.6	2.5	20.9	3.6	14.94	0.5
Rb	2.52	0.4	2.80	0.7	15.3	0.95	17	0.379	2.3
Nb	0.52	3.8		0.77	2.6	0.74	6.4	0.23	4.4
Mo	* ₋	* ₋		* ₋	* ₋	0.22	40.1	* ₋	* ₋
Cd	*	*		* ₋	* ₋	0.05	54.6	*	*
Sn	*	*		* ₋	* ₋	0.3	30.4	* ₋	* ₋
Sb	*	*		-	-	0.11	62.8	* ₋	* ₋
Cs	0.140	2.0	0.131	0.039	10.6	0.098	149.3	0.0271	1.6
Hf	0.29	6.3	<0.2	0.35	5.2	0.34	0.05	0.162	3.4
Ta	0.030	7.0		0.063	6.4	0.19	0.01	0.0129	2.5
W	0.11	15.4		-	-	112	5.2	1.89	1.4
Bi	-	-		-	-	0.015	101.3	0.0060	10.7
Th	0.31	4.3	0.260	0.022	13.1	0.025	69.5	0.07	14.2
Sr	32.4	1.5	34.2	52	7.1	78.9	4.1	134	2.1
Zr	9.8	7.0	8.84	9.6	5.9	11.0	12.8	5.2	2.8
Ba	31.4	1.1	31.1	21	6.8	31.9	4.4	19.1	1.0
Pb	1.01	3.5	1.42	1.59	5.4	1.9	16.7	0.53	2.8
U	0.23	6.5	0.275	0.025	15.3	0.05	159.6	0.0245	2.9
Sc	-	-		2.2	7.8			3.1	4.2
Y	3.29	2.2	3.11	5.8	4.3	7.8	3.7	2.4	5.5
La	1.77	4.0	1.88	1.6	7.7	2.27	4.0	0.687	1.3
Ce	3.92	1.2	3.93	3.8	7.2	4.83	3.7	1.70	1.6
Pr	0.447	1.3	0.497	0.46	5.8	0.59	5.0	0.203	1.8
Nd	1.87	1.0	1.86	2.1	5.6	2.49	6.4	1.00	1.8
Sm	0.429	2.1	0.427	0.62	4.8	0.73	0.06	0.316	2.1
Eu	0.128	1.7	0.131	0.30	3.3	0.378	0.027	0.265	1.7
Gd	0.461	0.5	0.461	0.82	3.7	0.97	7.2	0.410	1.5
Tb	0.0788	1.0	0.076	0.157	3.4	0.172	6.1	0.077	2.2
Dy	0.514	0.9	0.500	1.06	3.1	1.19	5.6	0.51	2.8
Ho	0.115	1.3	0.110	0.247	2.8	0.268	6.0	0.116	2.7
Er	0.359	1.4	0.351	0.72	2.0	0.751	5.5	0.341	2.7
Tm	0.058	2.1	0.051	0.112	1.6	0.121	7.3	0.053	2.4
Yb	0.396	1.6	0.39	0.72	2.5	0.8	6.3	0.336	2.2
Lu	0.0644	0.6	0.065	0.108	2.8	0.123	7.4	0.050	2.9

^aAll concentrations are in μg/g. Concentrations where the RSD was higher than 20% are not reported and are marked with a dash. No values are reported when the blank represented more than 5% of the element measured in the samples; these elements are marked with *. Relative standard deviation, %RSD = (standard deviation/average)*100.

NP214. Averages for $^{143}\text{Nd}/^{144}\text{Nd}$ for the JNdi standard were 0.512105 ± 0.000020 (2SD, $n = 23$) on the NP1700 and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512070 \pm 0.000030$ ($n = 39$) on the NP214. The Sr standard SRM987 average was $^{87}\text{Sr}/^{86}\text{Sr} = 0.710236 \pm 0.000018$ (2SD, $n = 35$) on the Thermo Scientific TIMS and $^{87}\text{Sr}/^{86}\text{Sr} = 0.710242 \pm 0.000027$ ($n = 9$) on the Nu-TIMS. The data were corrected on-line for mass fractionation using $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$, $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, and $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. For Pb, the isotopic ratios reported were normalized to $^{208}\text{Pb}/^{204}\text{Pb} = 36.7219$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4963$, and $^{206}\text{Pb}/^{204}\text{Pb} = 16.9405$ [Galer and Abouchami, 1998]. For the other isotopic systems, the ratios were normalized to $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160$ [Vervoort and Blichert-Toft, 1999], to $^{143}\text{Nd}/^{144}\text{Nd} = 0.511973$ [Weis et al., 2006] for the Rennes Nd standard and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512116$ for JNdi [Tanaka et al., 2000], and to $^{87}\text{Sr}/^{86}\text{Sr} = 0.710248$ [Weis et al., 2006] for SRM987. Potential contamination was carefully monitored during chemistry by measuring multiple blanks for the four radiogenic isotopic systems. The concentrations in column blanks (i.e., amount of contamination added during column chemistry) yielded an average of Pb = 55 pg, Nd = 117 pg, Hf = 3 pg, and Sr = 113 pg ($n = 7-9$) and were negligible compared to their concentrations in the samples. Procedural blanks (i.e., amount of each element added during the course of the entire chemical procedure) were also processed through column chemistry with averages of 65 pg Pb, 145 ng Nd,

Table 5. Trace Element Concentrations of the Basaltic Rock Reference Materials Measured by HR-ICP-MS^a

Trace elements μg/g	BE-N			BE-N Leached			BIR-1a			GSR-3			Leached			BHVO-2			JB-3			JB-3 Leached				
	Melilitite-bearing Nephelinite			Olivine Tholeiite			Olivine-Basalt			GSR-3			Leached			Basalt			High-Alumina Basalt							
	n = 7	% RSD	Jochum et al., [2015]	n = 1-35	% RSD	Jochum et al., [2015]	n = 5	% RSD	Jochum et al., [2015]	n = 5	% RSD	Dulski [2001]	n = 3	% RSD	Jochum et al., [2015]	n = 5	% RSD	Jochum et al., [2015]	n = 5	% RSD	Jochum et al., [2015]	n = 5	% RSD	Jochum et al., [2015]		
Li	12.3	1.7	12.9	1.6	4.9	10.2	2.5	16.5	3.203	2.2	9.4	4.7	3.1	11.4	4.5	9.9	4.500	1.9	7.35	1.2	7.28	3.0	6.8	3.1		
V	232	2.4	231.9	2.0	121	7.0	324	0.4	320.6	0.9	167	3.0	129	9.8	306	2.7	318	0.7	387	0.9	384	7.3	256	5.4		
Co	583	1.0	59.0	2.5	35	9.1	51.6	0.7	52.22	1.1	47.4	1.6	22	10.6	43	2.6	44.9	0.7	35.0	0.9	35.1	5.7	30.4	3.0		
Ni	275	1.1	269.7	2.5	179	11.2	178	1.9	168.9	1.1	150	1.5	65	11.5	118	2.5	120	1.0	38.1	0.7	37.0	4.1	30.9	3.0		
Cu	71.0	1.3	68.8	3.3	46	5.0	122	2.0	120.7	1.3	49.3	2.0	21	10.8	129	2.5	129	1.1	202	0.6	179	2.9	55	3.4		
Zn	109	2.4	122.9	2.8	36	10.4	61	4.7	70.4	1.6	146	2.8	42	12.7	90	7.7	104	1.0	99	1.8	114	8.2	83	3.0		
Ga	179	1.0	17.2	7.6	9.3	6.1	14.84	4.2	15.46	1.5	25.4	2.5	17	9.2	21.6	2.4	21.37	0.9	21.5	1.1	20.7	4.9	19.5	2.8		
Rb	48.1	0.5	47.61	1.7	7.0	3.8	-	-	0.2100	3.9	39	2.6	38.2	1.7	17	10.3	8.9	2.7	9.261	1.0	14.0	1.9	13.9	2.3		
Nb	111	3.8	113.2	2.0	148	6.1	0.531	1.5	0.553	2.5	74	2.5	96	13.4	18.6	4.5	18.10	1.1	2.00	0.8	2.03	2.7	2.03	2.7		
Mo	2.62	2.2	2.75	13.8	0.74	4.7	0.10	13.2	0.068	30.9	2.94	2.1	0.9	16.3	-	-	4.070	3.9	1.10	2.7	0.72	5.1	0.72	5.1		
Cd	0.21	11.4	0.2	0.14	9.5	0.18	7.0	0.077	22.1	0.23	5.8	6.1	0.16	14.8	0.23	17.5	0.152	33.2	0.20	5.6	0.188	3.9	0.188	3.9		
Sn	1.5	6.7	1.68	19.0	1.4	9.4	0.65	3.4	0.701	9.6	1.8	6.1	1.4	8.9	-	-	1.776	3.3	0.85	2.9	0.67	5.8	0.67	5.8		
Sb	0.17	19.6	0.269	7.4	0.126	3.7	-	-	0.462	6.9	*	*	*	*	-	-	0.1034	7.6	0.120	3.8	*	*	*	*		
Cs	0.714	1.1	0.729	3.2	0.161	2.2	-	-	0.006	11.1	0.426	2.3	0.42	6.3	0.057	10.9	0.091	0.096	2.2	0.884	1.1	0.928	1.5	0.87	3.5	
Hf	5.8	2.5	5.72	1.9	8.2	4.8	0.55	3.0	0.5822	1.5	6.5	4.4	6.7	6.4	8.0	10.7	4.3	4.470	0.6	2.67	1.7	2.43	2.9	2.43	2.9	
Ta	4.7	13.8	5.64	3.4	7.3	6.6	0.039	4.2	0.041	4.8	3.7	7.6	5.1	9.9	1.2	15.5	1.154	1.6	0.128	1.9	0.127	4.9	0.127	4.9		
W	1.27	6.8	28	1.23	8.0	*	*	*	0.027	55.6	0.41	2.8	0.38	14.1	0.24	5.1	0.251	13.9	1.42	3.6	0.89	6.0	0.89	6.0		
Bi	0.0064	4.9	0.01	*	*	*	-	-	0.005	27.5	0.0059	6.3	-	-	0.0095	9.2	0.0148	29.1	0.0124	5.0	0.0154	7.7	0.0069	5.6		
Th	10.5	1.6	10.58	1.3	5.16	1.1	0.026	9.7	0.033	4.6	6.3	7.6	5.9	2.7	1.7	14.8	1.12	1.224	1.3	1.22	2.3	1.30	1.0	0.92	6.0	
Sr	1437	1.5	1392	1.4	430	5.5	73	25.9	108.6	0.6	1121	2.5	1146	4.7	943	9.8	389	2.9	394.1	0.4	421	0.8	414	2.4	401	2.2
Zr	268	1.2	272.9	1.4	351	4.5	14.2	1.7	14.80	1.5	293	4.0	349	9.3	164	4.2	171.2	0.8	91	2.0	239	1.8	219	2.7		
Ba	1054	1.2	1039	1.3	580	6.2	6.2	2.5	6.75	1.9	546	2.4	656	9.3	126	2.4	130.9	0.8	236	0.6	239	1.8	219	2.7		
Pb	4.40	1.3	4.081	2.1	0.4	26.9	2.9	5.4	3.037	1.6	4.9	2.7	5	20.4	1.4	10.7	1.7	16.5	1.653	2.3	5.3	3.0	4.85	2.5	4.6	2.8
U	2.58	1.0	2.440	1.6	2.00	2.9	0.0107	4.5	0.011	3.9	1.53	3.2	1.44	1.8	0.58	11.6	0.409	2.0	0.412	8.5	0.49	3.0	0.480	0.6	0.41	4.2
Sc	22.8	0.8	22.55	2.7	32	6.5	-	-	43.21	1.4	14.4	2.0	20	8.0	32	7.5	31.83	1.1	33.8	0.9	34.2	6.9	38	2.7		
Y	30	5.5	29.44	1.9	25	7.0	16.4	4.8	15.60	1.1	25.7	2.4	21.8	2.1	349	9.3	27.7	3.3	25.91	1.1	28.3	2.3	23.1	3.7	14.9	1.8
La	82	1.7	82.55	0.9	29	3.8	0.54	5.4	0.627	1.9	58	4.7	53.9	1.3	12	9.7	14.5	2.7	15.20	0.5	8.2	2.1	8.12	0.8	2.27	1.5
Ce	158	1.6	153.0	1.4	76	4.6	1.88	5.2	1.92	1.2	114	4.3	103	1.2	30	8.9	36.9	2.6	37.53	0.5	21.6	1.5	20.9	0.7	5.6	2.4
Pr	17.5	0.9	17.39	1.3	9.6	5.5	0.36	5.1	0.372	1.3	12.8	2.8	12.7	2.1	4.4	8.4	5.1	2.3	5.339	0.5	3.22	0.4	3.14	0.8	0.84	2.7
Nd	70.0	0.9	66.35	1.4	41	5.3	2.28	2.0	2.397	1.8	54	2.2	48.9	2.9	21	9.2	23.9	2.5	24.27	1.0	15.5	1.2	15.9	0.5	4.3	3.0
Sm	12.39	0.8	12.03	1.0	8.7	6.0	1.08	2.0	1.113	1.6	10.5	1.9	9.8	2.2	5.3	7.5	5.9	2.7	6.023	0.9	4.29	1.3	4.17	0.8	1.44	3.2
Eu	3.74	1.4	3.679	1.8	2.8	6.5	0.50	3.4	0.52	0.9	3.31	2.1	3.2	3.1	2.2	9.9	2.04	3.0	2.043	0.6	1.34	2.0	1.31	1.6	0.97	3.3
Gd	9.9	2.0	10.09	2.6	7.7	5.4	1.8	6.2	1.809	1.2	8.7	2.7	8.6	3.4	4.9	9.1	6.1	3.0	6.207	0.6	4.65	1.2	4.77	0.9	1.82	3.4
Tb	1.31	2.1	1.303	2.8	1.06	5.6	0.36	3.4	0.362	1.4	1.14	2.5	1.09	4.4	0.67	8.9	0.94	2.6	0.9392	0.6	0.76	2.3	0.741	0.9	0.345	2.5
Dy	6.7	1.9	6.48	1.7	5.4	5.0	2.49	2.8	2.544	1.1	5.7	1.9	5.3	3.7	3.6	8.2	5.2	2.9	5.280	0.5	4.62	1.6	4.66	0.6	2.25	3.7
Ho	1.09	1.8	1.084	1.9	0.92	6.2	0.56	5.3	0.572	0.8	0.90	2.0	0.84	5.6	0.57	9.1	0.95	3.0	0.9887	0.5	0.925	1.0	0.949	0.9	0.49	4.0
Er	2.68	1.5	2.605	1.9	2.3	7.3	1.67	3.2	1.680	0.9	2.01	2.3	1.9	5.7	1.3	8.2	2.48	3.0	2.511	0.6	2.70	1.5	2.69	1.8	1.56	2.9
Tm	0.32	5.5	0.3216	1.8	0.30	8.5	0.25	5.5	0.256	1.6	0.234	2.6	0.225	1.9	0.18	7.0	0.34	4.3	0.3349	0.9	0.403	1.8	0.380	0.6	0.263	2.2
Yb	1.82	2.3	1.817	1.2	1.9	8.3	1.60	3.8	1.631	0.9	1.20	2.8	1.18	3.6	1.00	9.9	1.99	2.8	1.994	1.4	2.54	1.8	2.50	0.8	1.77	3.1
Lu	0.251	2.3	0.2489	2.1	0.28	7.4	0.246	3.9	0.243	1.3	0.16	6.6	0.165	3.8	0.14	8.4	0.280	3.3	0.2754	0.9	0.371	2.2	0.377	1.4	0.270	3.4

^aAll concentrations are in μg/g. Concentrations where the RSD was higher than 20% are not reported and are marked with a dash. No values are reported when the blank represented more than 5% of the element measured in the samples; these elements are marked with *. Relative standard deviation, %RSD = (standard deviation/average)*100.

Table 6. Trace Element Concentrations of the Gabbroic Rock Reference Materials Measured by HR-ICP-MS^a

Trace Elements ($\mu\text{g/g}$)	DNC-1 Dolerite				NIM-N Norite				W-2 Diabase			
	n = 11	% RSD	[Dulski, 2001] n = 3		n = 9	% RSD	[Dulski, 2001] n = 3		n = 9	% RSD	[Jochum et al., 2015] n = 3-58	
Li	5.2	11.7			5.1	4.9			9.5	12.1	9.21	2.1
V	145	5.8			212	4.5			249	5.3	265.8	1.1
Co	58	5.1			26	4.4			42	5.5	44.37	1.5
Ni	276	4.2			122	3.7			69	5.0	72.0	1.4
Cu	102	5.5			11.0	4.2			105	3.9	105.9	1.4
Zn	65	9.0			55	6.2			72	7.6	77.7	2.1
Ga	14.7	5.4			17.6	2.8			17.8	5.0	17.88	1.7
Rb	3.1	10.0	3.7	8.3	3.3	9.7	3.84	4.2	18.9	4.6	20.23	1.3
Nb	1.53	6.1			0.45	6.9			7.1	5.7	7.51	2.0
Mo	*_	*_			*	*			*_	*_	0.465	6.5
Cd	*	*			0.149	5.8			*_	*_	0.074	18.9
Sn	*_	*_			*	*			*	*	1.92	6.3
Sb	-	-			0.067	6.7			*_	*_	0.809	8.5
Cs	0.18	7.6	0.194	1.3	0.23	8.5	0.254	3.5	0.82	4.4	0.915	1.7
Hf	0.8	18.7	1.04	8.5	0.32	10.2	0.38	4.0	2.5	5.8	2.444	16.8
Ta	0.085	7.4			-	-			0.43	5.2	0.489	2.9
W	0.050	14.9			0.124	5.8			0.281	4.5	0.29	17.2
Bi	0.0070	12.7			0.0058	8.4			0.019	7.5	0.032	34.4
Th	0.19	13.5	0.24	14.1	0.30	7.8	0.34	4.0	2.05	4.2	2.179	1.4
Sr	144	7.7	144	3.8	272	3.0	259	2.4	187	6.9	195.4	0.8
Zr	29	14.5	37	3.1	10.2	7.6	12.5	3.5	89	6.4	93.3	1.5
Ba	100	4.2	103	3.6	82	3.5	81	4.9	162	5.0	172.8	1.1
Pb	7.2	8.9	7.5	10.1	2.5	8.4	2.20	4.6	8.3	6.9	7.83	2.4
U	0.059	5.7	0.06	19.5	0.33	9.9	0.30	6.2	0.50	6.9	0.5048	1.4
Sc	-	-			26	11.6			36	8.7	35.86	1.1
Y	19	5.8	16.4	3.6	6.2	4.5	6	0.7	22.7	3.8	21.82	1.5
La	3.3	3.4	3.6	4.5	2.6	4.6	2.85	2.8	9.9	6.0	10.63	1.1
Ce	8.1	3.4	7.9	4.2	5.8	4.4	5.8	2.8	23.1	3.4	23.21	0.7
Pr	1.06	3.9	1.12	6.8	0.71	4.3	0.76	3.9	2.9	5.0	3.018	1.1
Nd	4.9	3.8	4.8	5.6	3.2	4.0	3.17	2.0	12.4	4.2	13.09	0.9
Sm	1.43	3.0	1.4	4.7	0.83	4.1	0.794	1.2	3.2	4.9	3.3	3.9
Eu	0.60	4.4	0.59	4.4	0.58	4.0	0.59	3.1	1.06	5.2	1.091	1.0
Gd	2.04	6.1	2.04	1.0	0.93	4.1	0.98	1.3	3.6	5.0	3.713	1.1
Tb	0.40	6.8	0.373	1.9	0.162	4.6	0.162	4.6	0.61	4.7	0.6270	1.3
Dy	2.8	7.6	2.7	5.1	1.06	4.1	1.06	4.1	3.8	5.3	3.806	0.8
Ho	0.64	4.7	0.61	5.0	0.230	4.1	0.230	4.1	0.77	5.4	0.7908	0.8
Er	2.0	6.2	1.9	3.8	0.68	3.9	0.68	3.9	2.21	5.0	2.208	1.1
Tm	0.31	5.0	0.28	3.8	0.105	4.6	0.100	2.2	0.32	4.2	0.3315	1.9
Yb	2.0	5.5	1.89	3.0	0.69	4.0	0.67	1.9	2.04	4.2	2.054	0.8
Lu	0.32	7.3	0.3	6.5	0.104	4.5	0.104	1.0	0.31	6.2	0.3090	1.1

^aAll concentrations are in $\mu\text{g/g}$. Concentrations where the RSD was higher than 20% are not reported and are marked with a dash. No values are reported when the blank represented more than 5% of the element measured in the samples; these elements are marked with *. Relative standard deviation, %RSD = (standard deviation/average)*100.

0.3 pg Hf, and 1459 pg Sr ($n = 2-3$), which represent less than a maximum of 2 ‰ of the most depleted samples. Details of the instrument settings and analysis conditions (e.g., number of ratios per each analysis, voltages, etc.) are given in Table 3.

4. Results

Average trace element concentrations for the reference materials are given in Tables (4–6); individual concentration analyses are available in supporting information Tables S1–S11. The individual isotopic measurements are reported in Tables 7 (Pb) and 8 (Hf, Nd, Sr), and the average isotopic ratios in Table 9 (Pb) and Table 10 (Hf, Nd, and Sr). A few outliers (<10% of the isotopic analyses) were excluded from the average isotopic ratios following application of Dixon tests on the duplicates [Dixon, 1953]. The criterion of rejection obeys the critical values given in Gopal [1993] with a level of significance $\alpha = 0.05$. Tables 4–6, 9, and 10 also report published values for the reference materials to compare with this study. Published trace element concentrations cited in Tables (4–6) are from the most recent studies that specifically focus on trace element characterization of the given reference materials. Isotopic ratios from the literature were reported

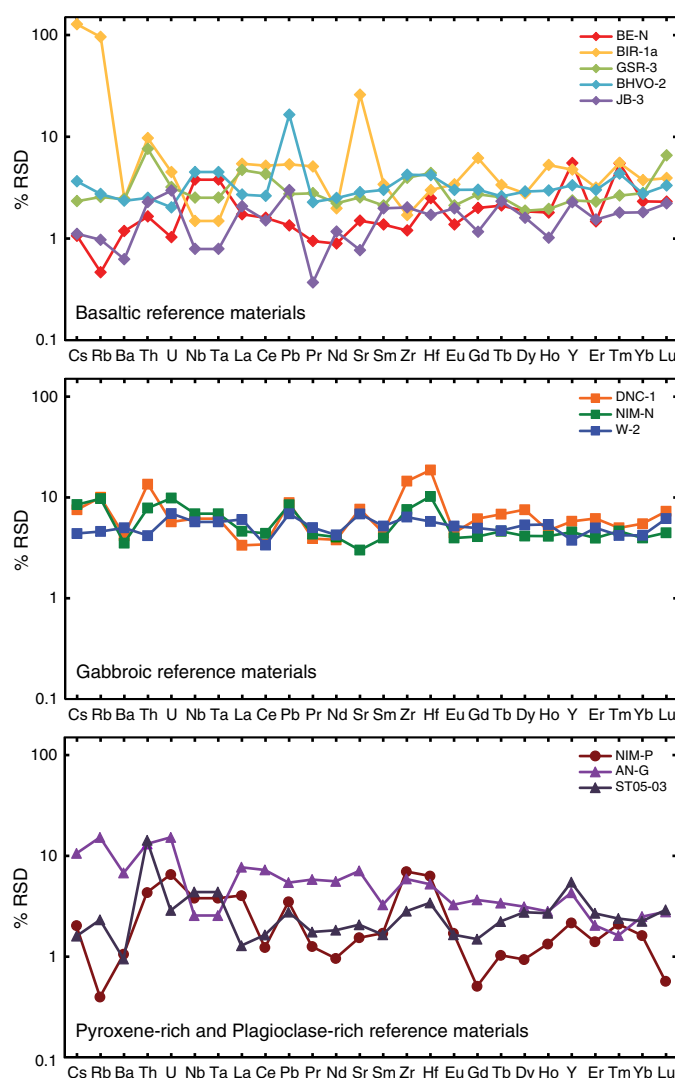


Figure 2. Multielement %RSD of the analyzed mafic-ultramafic rock reference materials. Note that most of the %RSD are below 10% and that the %RSD for the gabbroic reference materials appear to be the most homogeneous.

and Figure 4). Sr and Nd isotopic ratios reproduce well with 2SD = 36 ppm for $^{87}\text{Sr}/^{86}\text{Sr}$ and 14 ppm ($n = 3$) for $^{143}\text{Nd}/^{144}\text{Nd}$, whereas the reproducibility for Hf isotopic ratios is 100 ppm ($n = 2$) (Table 10 and Figure 5–7). After age-correction to 2056 Ma [Scoates and Friedman, 2008; Scoates and Wall, 2015], the initial Sr–Nd isotopic ratios are in the range for whole rock analyses reported from the Critical Zone [e.g., Harmer et al., 1995; Maier et al., 2000; Prevec et al., 2005; Chutas et al., 2012] and the initial $^{176}\text{Hf}/^{177}\text{Hf}$ matches that of zircon from the Critical Zone analyzed by Zirakparvar et al. [2014].

4.2. Basaltic Reference Materials

The five basaltic reference materials present a wide range of trace element concentrations (Figure 3). The nephelinite BE-N has the highest concentrations for most elements, especially the light REE (LREE) and large ion lithophile elements (LILE) (e.g., La = 82 $\mu\text{g/g}$; RSD = 1.7%, $n = 7$), whereas the Icelandic basalt BIR-1a has the lowest concentrations (e.g., La = 0.54 $\mu\text{g/g}$; RSD = 5.4%, $n = 5$). Despite this variation, most analyses present a good reproducibility with %RSD lower than 5% (Table 5 and Figure 2). JB-3 is the most homogeneous material with %RSD lower than 3% ($n = 5$) for all the elements, except for Cd (5.6%), Sb (3.8%), W (3.6%), and Bi (5%) (Table 5 and Figure 2). With a few exceptions, the reported concentrations overlap to better than 10% with published values (Table 5).

only when the number of duplicates was greater than one, when possible. More reference values are available on the GeoREM database [Jochum et al., 2005, <http://georem.mpch-mainz.gwdg.de/>].

4.1. Pyroxene-Rich Ultramafic Reference Material

The pyroxenite NIM-P is characterized by very low concentrations of rare earth elements (REE, Tm = 0.058 to Ce = 3.92 $\mu\text{g/g}$), high field strength elements (HFSE, Ta = 0.030 to Zr = 9.8 $\mu\text{g/g}$), and Sr (32.4 $\mu\text{g/g}$) (Table 4 and Figure 3). Despite these low concentrations, all trace elements present good reproducibility with %RSD ($n = 4$) lower than 4% for most, and all lower than 7%, except for W (15.4%) (Figure 2). Average concentrations are in agreement with results reported by Dulski [2001] (Table 4).

We report the first Pb–Sr–Nd–Hf isotopic ratios for NIM-P. With respect to Pb isotopes, this pyroxenite is one of the least reproducible reference materials analyzed in this study with uncertainties of 1784 ppm (parts per million) for $^{208}\text{Pb}/^{204}\text{Pb}$, 1163 ppm for $^{207}\text{Pb}/^{204}\text{Pb}$, and 6310 ppm for $^{206}\text{Pb}/^{204}\text{Pb}$ (2 standard deviations, 2SD, $n = 4$, where ppm = (average/ $2 \times \text{standard deviation}$) $\times 10^6$) (Table 9

Table 7. Pb Isotopic Analyses of the Mafic-Ultramafic Rock Reference Materials^a

Sample	Run Number	²⁰⁸ Pb/ ²⁰⁴ Pb	2SE/SD	²⁰⁷ Pb/ ²⁰⁴ Pb	2SE/SD	²⁰⁶ Pb/ ²⁰⁴ Pb	2SE/SD
NIM-P	NIM-P 1	37.4605	32	15.4713	9	17.6755	10
	NIM-P 1 rep	37.4562	31	15.4698	9	17.6742	11
	NIM-P 2	37.4696	37	15.4585	11	17.6420	14
	NIM-P 3	37.3970	24	15.4507	9	17.5689	10
	NIM-P 4	37.4253	20	15.4542	7	17.5624	8
	Average NIM-P	37.4381	668	15.4587	180	17.6122	1111
BE-N	ppm, n = 4		1784		1163		6310
	BE-N 1	39.0173	23	15.6013	8	19.1928	12
	BE-N 2	39.0134	26	15.5994	8	19.1924	12
	BE-N 3	39.0151	28	15.6008	10	19.1929	12
	BE-N 4	39.0141	25	15.6002	9	19.1953	11
	BE-N 5	39.0187	28	15.5998	11	19.1994	14
	BE-N 5 rep	39.0116	38	15.5968	12	19.1946	16
	BE-N 22/11	39.0178	26	15.5996	10	19.1962	9
	BE-N 6/05/14	39.0205	25	15.6012	11	19.1982	10
	BE-N 10/07/14	39.0143	28	15.6005	9	19.1946	17
	BE-N 4/11/14	39.0167	53	15.6005	15	19.2004	24
	Average BE-N	39.0164	48	15.6004	13	19.1958	59
	ppm, n = 9		122		86		308
BE-N L	BE-N La	40.0300	21	15.6470	7	20.2227	10
	BE-N Lb	39.9354	24	15.6444	9	20.1614	11
	BE-N Lc	40.1040	26	15.6506	9	20.3061	12
	BE-N Ld	40.1492	42	15.6505	15	20.3638	20
	BE-N Le	40.1316	28	15.6518	10	20.3082	13
	Average BE-N L	40.0700	1759	15.6489	62	20.2725	1599
DNC-1	ppm, n = 5		4390		393		7887
	DNC-1a	38.3728	38	15.6484	13	18.6851	14
	DNC-1b	38.3800	23	15.6479	9	18.6974	10
	DNC-1c	38.3632	37	15.6460	15	18.6826	18
	DNC-1c rep	38.3617	39	15.6453	15	18.6812	17
	DNC-1 1	38.3705	25	15.6479	9	18.6875	10
	DNC-1 2	38.3761	25	15.6486	9	18.6962	10
	DNC-1 3	38.3706	26	15.6483	13	18.6840	14
	DNC-1 4	38.3757	23	15.6484	9	18.6949	10
	DNC-1 5	38.3785	24	15.6497	11	18.6925	10
	DNC-1 5 rep	38.3765	34	15.6504	14	18.6892	16
	DNC-1 6	38.3689	18	15.6462	7	18.6905	9
	DNC-1 7	38.3688	18	15.6467	6	18.6860	7
	DNC-1 8	38.3637	22	15.6460	8	18.6790	10
	DNC-1 8 rep	38.3616	31	15.6465	7	18.6793	8
	DNC-1 9	38.3631	23	15.6459	8	18.6826	9
	DNC-1 18/11	38.3696	26	15.6478	8	18.6864	10
	DNC-1 6/05/14	38.3630	23	15.6464	8	18.6789	9
	DNC-1 4/11/14	38.3667	27	15.6481	12	18.6799	14
	Average DNC-1	38.3701	113	15.6475	24	18.6869	123
	ppm, n = 15		295		153		659
BIR-1a	BIR-1a 1	38.4986	30	15.6600	11	18.8504	12
	BIR-1a 2	38.4938	28	15.6583	10	18.8474	12
	BIR-1a 2 rep	38.4937	27	15.6585	9	18.8476	10
	BIR-1a 3	38.4963	21	15.6587	8	18.8496	9
	BIR-1a 4	38.4977	22	15.6599	8	18.8508	9
	BIR-1a 4 rep	38.4938	19	15.6582	9	18.8506	9
	BIR-1a 5	38.5013	28	15.6609	11	18.8513	13
	Average BIR-1a	38.4975	55	15.6595	22	18.8499	31
BIR-1a L	ppm, n = 5		143		139		163
	BIR-1a La	38.2912	142	15.5080	37	18.6611	90
	BIR-1a Lb	38.3814	89	15.5297	35	18.6667	48
	BIR-1a Lc	38.2808	98	15.5003	38	18.6893	41
	BIR-1a Ld	38.3109	106	15.4966	40	18.6668	51
	BIR-1a Le	38.3436	106	15.5045	31	18.6873	34
GSR-3	Average BIR-1a L	38.3216	823	15.5078	260	18.6742	262
	ppm, n = 5		2147		1675		1400
	GSR-3 1	37.8559	26	15.4813	9	17.7612	11
	GSR-3 1 rep	37.8579	21	15.4826	7	17.7621	8
	GSR-3 2	37.8565	27	15.4813	9	17.7606	10
	GSR-3 3	37.8546	27	15.4810	9	17.7557	10
	GSR-3 4	37.8565	29	15.4813	10	17.7600	11
GSR-3	GSR-3 5	37.8573	27	15.4820	9	17.7603	10
	Average GSR-3	37.8562	20	15.4814	8	17.7595	45
	ppm, n = 5		53		48		251

Table 7. (continued)

Sample	Run Number	$^{208}\text{Pb}/^{204}\text{Pb}$	2SE/SD	$^{207}\text{Pb}/^{204}\text{Pb}$	2SE/SD	$^{206}\text{Pb}/^{204}\text{Pb}$	2SE/SD
GSR-3 L	GSR-3 La	37.8512	25	15.4727	9	17.7969	11
	GSR-3 Lb	37.8467	26	15.4707	9	17.7961	11
	GSR-3 Lc	37.8537	31	15.4740	12	17.7979	12
	GSR-3 Ld	37.8564	32	15.4729	11	17.7985	13
	GSR-3 Le	37.8548	21	15.4752	8	17.7909	9
	Average GSR-3 L	37.8526	75	15.4731	33	17.7961	61
NIM-N	ppm, n = 5		199		213		341
	NIM-N 1	37.5969	20	15.6702	9	17.6516	9
	NIM-N 2	37.5311	36	15.6702	9	17.6414	16
	NIM-N 3	37.5543	24	15.6821	9	17.7082	11
	NIM-N 4	37.4838	24	15.6634	16	17.5750	11
	NIM-N 5	37.4012	18	15.6503	7	17.4496	7
	NIM-N 6	37.7115	20	15.6909	7	17.7981	8
	NIM-N 6 rep	37.7120	21	15.6908	7	17.7978	7
	NIM-N 7	37.5055	22	15.6601	9	17.5731	9
	NIM-N 8	37.5953	24	15.6757	8	17.6804	9
	NIM-N 9	37.5548	20	15.6658	7	17.6097	8
	NIM-N 10	37.5639	23	15.6722	9	17.6630	9
	Average NIM-N	37.5482	800	15.6700	140	17.6378	971
	ppm, n = 8		2130		892		5507
BHVO-2	BHVO-2	38.1663	24	15.5371	8	18.5364	9
	BHVO-2 rep	38.1635	22	15.5358	9	18.5349	10
	BHVO-2 2	38.2500	32	15.5387	13	18.6441	15
	BHVO-2 7/01/13	38.2481	21	15.5338	8	18.6673	11
	BHVO-2 7/01/13 rep	38.2519	24	15.5347	9	18.6692	11
	BHVO-2 30/05	38.3136	24	15.5540	9	18.7421	9
	Average BHVO-2	38.2445	1270	15.5409	179	18.6475	1701
	ppm, n = 4		3156		1153		9121
BHVO-2 L	BHVO2 La	38.2120	24	15.4909	9	18.6408	10
	BHVO2 Lb	38.2091	28	15.4902	9	18.6449	11
	BHVO2 Lb rep	38.2013	26	15.4864	10	18.6413	12
	BHVO2 Lc	38.2101	25	15.4904	10	18.6510	11
	BHVO2 Ld	38.2074	24	15.4904	9	18.6480	15
	BHVO2 Le	38.2077	27	15.4897	10	18.6492	11
	BHVO2 Le rep	38.2080	24	15.4898	9	18.6487	10
	BHVO2 Lf	38.2126	28	15.4897	9	18.6447	10
	BHVO2 Lg	38.2045	28	15.4871	11	18.6450	13
	BHVO2 Lh	38.2092	26	15.4869	10	18.6436	11
	BHVO2 Li	38.1992	39	15.4870	14	18.6446	10
	BHVO2 Li rep	38.2007	24	15.4878	9	18.6451	11
	BHVO2 Lj	38.2012	29	15.4874	10	18.6425	12
	Average BHVO2 L	38.2073	88	15.4890	33	18.6454	62
	ppm, n = 9		231		212		334
W-2	W-2a	38.6315	29	15.6636	11	18.7512	13
	W-2b	38.6316	25	15.6624	8	18.7502	12
	W-2c	38.6235	29	15.6593	12	18.7468	13
	W-2c rep	38.6248	44	15.6595	15	18.7480	14
	W-2 1	38.6328	22	15.6634	8	18.7508	9
	W-2 2	38.6316	34	15.6618	13	18.7460	11
	W-2 3	38.6388	28	15.6631	11	18.7516	11
	W-2 4	38.6139	24	15.6621	8	18.7603	9
	W-2 4rep	38.6176	24	15.6630	10	18.7611	10
	W-2 5	38.6357	38	15.6635	16	18.7514	17
	W-2 6	38.6363	14	15.6626	6	18.7513	7
	W-2 7	38.6303	23	15.6637	8	18.7519	8
	W-2 8	38.6355	25	15.6629	9	18.7465	12
	W-2 9	38.6333	14	15.6619	8	18.7511	9
	Average W2	38.6321	89	15.6623	30	18.7497	45
	ppm, n = 11		232		191		238
JB-3	JB-3 1	38.2513	32	15.5357	11	18.2946	12
	JB-3 2	38.2520	38	15.5367	10	18.2957	17
	JB-3 3	38.2449	20	15.5336	7	18.2918	10
	JB-3 4	38.2556	23	15.5369	8	18.2965	11
	JB-3 5	38.2443	37	15.5343	17	18.2925	20
	Average JB-3	38.2496	97	15.5355	29	18.2942	40
	ppm, n = 5		254		189		221

Table 7. (continued)

Sample	Run Number	$^{208}\text{Pb}/^{204}\text{Pb}$	2SE/SD	$^{207}\text{Pb}/^{204}\text{Pb}$	2SE/SD	$^{206}\text{Pb}/^{204}\text{Pb}$	2SE/SD
JB-3 L	JB-3 La	38.2467	25	15.5335	9	18.2931	10
	JB-3 Lb	38.2476	30	15.5346	11	18.2943	12
	JB-3 Lc	38.2490	22	15.5346	8	18.2934	10
	JB-3 Lc rep	38.2526	22	15.5362	8	18.2956	9
	JB-3 Ld	38.2523	29	15.5358	10	18.2945	12
	JB-3 Le	38.2525	28	15.5364	9	18.2952	11
	Average JB-3 L	38.2496	54	15.5350	23	18.2941	17
ST05-03	ppm, n = 5		140		146		92
	ST05-03 1	35.7846	21	15.3645	7	15.8943	7
	ST05-03 2	35.7654	17	15.3632	6	15.8833	6
	ST05-03 3	35.7542	34	15.3741	13	15.9291	13
	ST05-03 4	35.9311	35	15.3810	11	16.0284	11
	ST05-03 5	35.7951	24	15.3660	9	15.9008	8
	Average ST05-03	35.7748	369	15.3670	98	15.9018	391
AN-G	ppm, n = 4		1031		638		2459
	AN-G 1	33.6568	18	14.6428	7	14.0491	6
	AN-G 1rep	33.6543	17	14.6422	7	14.0476	5
	AN-G 2	33.5712	25	14.6294	10	14.0012	8
	AN-G 2rep	33.5667	20	14.6277	7	14.0001	7
	AN-G 3	33.5720	23	14.6251	9	13.9834	8
	AN-G 3rep	33.5696	17	14.6251	7	13.9847	6
	AN-G 4	33.5263	19	14.6127	6	13.9273	7
	AN-G 5	33.5257	17	14.6174	7	13.9512	7
	AN-G 5rep	33.5200	16	14.6154	7	13.9495	6
	AN-G 6	33.6176	13	14.6347	5	14.0266	4
	AN-G 7	33.9186	19	14.6935	7	14.3014	7
	AN-G 7rep	33.9194	19	14.6940	8	14.3022	8
	AN-G 8	33.5279	20	14.6124	8	13.9274	9
	AN-G 9	33.5261	21	14.6297	7	14.0283	7
	AN-G 10	33.5583	17	14.6234	7	13.9764	6
	Average AN-G	33.5647	929	14.6253	202	13.9856	890
	ppm, n = 9		2769		1384		6362

^aDuplicates analyses are from different digestions. Outliers (five out of a total of 113 analyses) are indicated in italics and calculated according to the Dixon test; [Gopal, 1993; replicates are indicated as "rep." Averages do not include outlier and replicate analyses. 2SE is the 2 standard error of the individual analysis (internal error) and 2SD is the 2 standard deviation on the mean of the individual analysis; they are both reported as times 10^4 .

To better characterize what elements are removed during the leaching procedure and the impact of leaching on isotopic ratios, trace element concentrations were measured after leaching for three of the basaltic reference materials: BE-N, GSR-3, and JB-3 (Table 5 and Figure 8). Throughout the acid-leaching procedure, the basalts lost 40–70% of their initial weights. Even with this high variability in weight loss, the trace element concentrations in leached samples present a good reproducibility with an average of 7% RSD (range from 1.1% to 26%) (Figure 8 and Table 5). *Nobre Silva et al.* [2010] also observed this reproducibility in trace element concentrations after leaching in their leaching experiments of oceanic island basalts. During leaching, the trace elements were variably washed out with 90% of the Pb content removed for BE-N (Figure 8a), 54% for GSR-3 (Figure 8b), and only 8% for JB-3 (Figure 8c). Similarly, BE-N lost 70% of its Sr content, whereas JB-3 and GSR-3 only lost 5% during leaching (Figures 8a and 8c). Leaching also removed 40% of the Nd content for BE-N (Figure 8a), 60% for GSR-3 (Figure 8b), and 70% for JB-3 (Figure 8c). BE-N and GSR-3 did not lose Hf during leaching, however JB-3 lost 2.5% of its Hf content (Figure 8).

The basaltic reference materials reproduce well in the four isotopic systems measured (Tables 9 and 10; Figures 9 and 10). The precision is better than 260 ppm for $^{208}\text{Pb}/^{204}\text{Pb}$, 215 ppm for $^{207}\text{Pb}/^{204}\text{Pb}$, and 340 ppm for $^{206}\text{Pb}/^{204}\text{Pb}$ (2SD), and better than 30 ppm for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$. The reproducibility for Hf isotopic ratios is below 80 ppm (2SD), except for BIR-1a (120 ppm, $n = 5$) and JB-3 (100 ppm, $n = 5$) (Table 10). Average Pb, Hf, Sr and Nd isotopic compositions are all within error of published values [e.g., *Chauvel et al.*, 2011; *Yang et al.*, 2011b; *Li et al.*, 2014; *Pin et al.*, 2014; *GeoREM database*] (Tables 9 and 10; Figures 4–7). To our knowledge, the Pb and Nd isotopic compositions in this study are the first reported for GSR-3.

The Pb isotopic ratios of leached BE-N are more radiogenic and more heterogeneous than those for unleached BE-N (e.g., $^{208}\text{Pb}/^{204}\text{Pb}$ unleached = 39.0164 ± 0.0048 and $^{208}\text{Pb}/^{204}\text{Pb}$ leached = 40.0700 ± 0.1759) (Figure 4 and Table 9). Leached BIR-1a is less radiogenic than unleached, but it is not reproducible (Figure 4 and Table 9) (e.g., 2147 ppm for $^{208}\text{Pb}/^{204}\text{Pb}$, 2SD, $n = 5$), and is consistently

Table 8. Hf-Nd-Sr Isotopic Analyses of Mafic-Ultramafic Rock Reference Materials^a

Sample	Run Number	¹⁷⁶ Hf/ ¹⁷⁷ Hf	2SE/SD	¹⁴³ Nd/ ¹⁴⁴ Nd	2SE/SD	⁸⁷ Sr/ ⁸⁶ Sr	2SE/SD
NIM-P	NIM-P 1						
	NIM-P 2	0.282454	8	0.511503	8	0.711854	8
	NIM-P 2 rep			0.511490	7		
	NIM-P 3	0.282473	5	0.511503	8	0.711869	7
	NIM-P 4	0.282524	4	0.511497	9	0.711844	7
	Average NIM-P	0.282463	27	0.511501	7	0.711856	25
BE-N	ppm	n = 2	96	n = 3	14	n = 3	36
	BE-N 1	0.282932	4	0.512889	8	0.703790	7
	BE-N 2	0.282939	6	0.512873	8	0.703798	7
	BE-N 3	0.282947	6	0.512892	6	0.703792	7
	BE-N 3rep					0.703794	8
	BE-N 4	0.282937	13	0.512880	6	0.703788	8
	BE-N 5	0.282922	6	0.512884	6	0.703804	7
	BE-N 22/11	0.282921	5	0.512885	6	0.703794	8
	BE-N 6/05/14	0.282922	5	0.512885	7		
	BE-N 6/05/14 rep	0.282922	5				
	BE-N 10/07/14	0.282911	10	0.512871	6		
	BE-N 10/07/14 rep			0.512878	7		
	BE-N 4-11-14	0.282928	6	0.512879	6	0.703793	7
	BE-N 4-11-14 rep			0.512882	9	0.703791	7
	Average BE-N	0.282929	22	0.512882	14	0.703794	11
	ppm	n = 9	79	n = 9	27	n = 7	16
BE-N L	BE-N La	0.282945	6	0.512890	7	0.703276	8
	BE-N La rep	0.282924	5				
	BE-N Lb	0.282936	10	0.512888	7	0.703302	8
	BE-N Lb rep	0.282923	5				
	BE-N Lc	0.282927	6	0.512878	6	0.703271	8
	BE-N Ld	0.282939	6	0.512888	8	0.703283	7
	BE-N Ld rep	0.282941	7				
	BE-N Le	0.282938	5	0.512883	6	0.703263	8
	Average BE-N L	0.282937	13	0.512885	9	0.703279	30
	ppm	n = 5	46	n = 5	18	n = 5	43
DNC-1	DNC-1 a	0.282820	15			0.705824	8
	DNC-1 b	0.282842	11			0.705820	9
	DNC-1 c	0.282869	12			0.705821	8
	DNC-1 1	0.282844	6	0.512480	7	0.705823	8
	DNC-1 2	0.282864	7	0.512472	6	0.705816	8
	DNC-1 3	0.282857	5	0.512460	7	0.705816	8
	DNC-1 4	0.282847	6	0.512472	8	0.705828	8
	DNC-1 5	0.282858	7	0.512482	10	0.705830	8
	DNC-1 6	0.282848	6	0.512468	10	0.705822	8
	DNC-1 7	0.282853	7	0.512475	9	0.705822	9
	DNC-1 8	0.282852	6	0.512475	9	0.705815	7
	DNC-1 9	0.282850	6	0.512473	6	0.705817	8
	DNC-1 18/11	0.282853	6	0.512471	9	0.705830	7
	DNC-1 6/05/14	0.282851	6	0.512470	6	0.705805	8
	DNC-1 6/05/14 rep	0.282855	10				
	DNC-1 4-11-14	0.282856	7	0.512473	8	0.705829	8
	DNC-1 4-11-14 rep	0.282861	5	0.512463	7		
	DNC-1 4-11-14 rep2			0.512465	10		
	Average DNC-1	0.282853	15	0.512473	11	0.705821	14
	ppm	n = 14	52	n = 12	22	n = 15	20
BIR-1a	BIR-1a 1	0.283259	12	0.513097	8	0.703108	8
	BIR-1a 2	0.283225	16	0.513111	6	0.703118	9
	BIR-1a 2rep					0.703102	8
	BIR-1a 3	0.283245	13	0.513110	6	0.703123	16
	BIR-1a 4	0.283260	8	0.513107	8	0.703099	8
	BIR-1a 5	0.283226	14	0.513106	6	0.703102	7
	Average BIR-1a	0.283243	34	0.513106	11	0.703110	21
	ppm	n = 5	120	n = 5	22	n = 5	29
BIR-1a L	BIR-1a La	0.283211	11	0.513109	5	0.703062	12
	BIR-1a Lb	0.283129	8	0.513095	6	0.703085	11
	BIR-1a Lc	0.283131	11	0.513106	6	0.703056	12
	BIR-1a Ld	0.283229	11	0.513094	7	0.703054	10
	BIR-1a Le	0.283157	14	0.513099	8	0.703067	10
	Average BIR-1a L	0.283172	92	0.513101	13	0.703065	25
	ppm	n = 5	326	n = 5	26	n = 5	35

Table 8. (continued)

Sample	Run Number	$^{176}\text{Hf}/^{177}\text{Hf}$	2SE/SD	$^{143}\text{Nd}/^{144}\text{Nd}$	2SE/SD	$^{87}\text{Sr}/^{86}\text{Sr}$	2SE/SD
GSR-3	GSR-3 1	0.282986	5	0.512903	7	0.704069	8
	GSR-3 2	0.282991	4	0.512899	7	0.704083	7
	GSR-3 2 rep			0.512913	8		
	GSR-3 3	0.282980	7	0.512907	7	0.704079	8
	GSR-3 4	0.282981	6	0.512893	6	0.704084	8
	GSR-3 5	0.282986	7	0.512905	7	0.704063	8
	Average GSR-3	0.282985	9	0.512901	11	0.704076	18
	ppm	n = 5	32	n = 5	22	n = 5	26
	GSR-3 L						
	GSR-3 La	0.282988	5	0.512906	7	0.703863	7
GSR-3 L	GSR-3 Lb	0.282978	6	0.512899	8	0.703866	8
	GSR-3 Lb rep	0.282978	4				
	GSR-3 Lc	0.282986	7	0.512904	7	0.703867	8
	GSR-3 Ld	0.282984	7	0.512900	8	0.703876	8
	GSR-3 Le	0.282983	6	0.512903	7	0.703869	8
	Average GSR-3 L	0.282984	7	0.512902	6	0.703868	10
	ppm	n = 5	25	n = 5	11	n = 5	14
	NIM-N 1	0.282813	10	0.511748	8	0.709371	9
	NIM-N 2	0.282839	12	0.511759	8	0.709366	8
	NIM-N 2 rep			0.511758	8		
NIM-N	NIM-N 3	0.282723	7	0.511744	6	0.709372	8
	NIM-N 4	0.282741	9	0.511740	7	0.709378	9
	NIM-N 5	0.282846	11	0.511744	10	0.709363	8
	NIM-N 6	0.282819	7	0.511750	7	0.709375	7
	NIM-N 7	0.282899	7	0.511761	7	0.709378	11
	NIM-N 7 rep			0.511757	6		
	NIM-N 8	0.282879	6	0.511775	9	0.709374	7
	NIM-N 9	0.282844	9	0.511773	7	0.709382	7
	NIM-N 10	0.282838	6	0.511768	7	0.709375	7
	Average NIM-N	0.282847	57	0.511756	25	0.709373	11
BHVO-2	ppm	n = 8	202	n = 10	50	n = 10	16
	BHVO-2 2	0.283091	6			0.703462	8
	BHVO-2 2rep	0.283102	7				
	BHVO-2 7/01/13	0.283105	6	0.513000	6	0.703461	8
	BHVO-2 7/01/13 rep	0.283111	6				
	BHVO-2 29/05	0.283095	5	0.512987	7	0.703473	8
	BHVO-2 29/05 rep	0.283094	5				
	Average BHVO-2	0.283097	14	0.512994	17	0.703465	14
	ppm	n = 3	50	n = 2	34	n = 3	20
	BHVO-2 L						
BHVO-2 L	BHVO2 La	0.283109	7	0.512985	9	0.703484	8
	BHVO2 La rep			0.512991	7		
	BHVO2 Lb	0.283090	7	0.512975	7	0.703466	8
	BHVO2 Lc	0.283103	7	0.512989	6	0.703465	7
	BHVO2 Ld	0.283101	8	0.512989	9	0.703473	8
	BHVO2 Le	0.283097	6	0.512991	8	0.703472	9
	BHVO2 Lf	0.283107	7	0.512982	7	0.703462	8
	BHVO-2 Lf rep			0.512983	7		
	BHVO2 Lg			0.512996	6	0.703469	8
	BHVO2 Lh			0.512991	6	0.703464	8
BHVO2 L	BHVO2 Li	0.283103	8	0.512989	7	0.703461	7
	BHVO2 Li rep	0.283100	8				
	BHVO2 Lj	0.283106	9	0.512992	7	0.703464	7
	BHVO2 Lj rep					0.703451	8
	Average BHVO2 L	0.283102	12	0.512988	12	0.703468	14
	ppm	n = 8	44	n = 10	24	n = 10	20
	W-2						
	W-2 a	0.282733	6			0.706974	7
	W-2 b	0.282739	7			0.706983	8
	W-2 c	0.282731	15			0.706991	8
W-2	W-2 1	0.282732	6	0.512532	7	0.706979	10
	W-2 2	0.282723	6	0.512523	6	0.706983	6
	W-2 3	0.282714	9	0.512528	6	0.706979	7
	W-2 4	0.282727	7	0.512545	6	0.706990	8
	W-2 5	0.282732	9	0.512535	6	0.706963	20
	W-2 4 rep			0.512508	8		
	W-2 6	0.282731	4	0.512525	9	0.706972	8
	W-2 6 rep					0.706985	15
	W-2 7	0.282670	7	0.512536	11	0.706967	10
	W-2 8	0.282663	5	0.512529	7	0.706973	8
W-2	W-2 9	0.282730	6	0.512529	7	0.706976	7
	Average W2	0.282729	14	0.512531	13	0.706977	17
	ppm	n = 10	48	n = 9	26	n = 12	24

Table 8. (continued)

Sample	Run Number	$^{176}\text{Hf}/^{177}\text{Hf}$	2SE/SD	$^{143}\text{Nd}/^{144}\text{Nd}$	2SE/SD	$^{87}\text{Sr}/^{86}\text{Sr}$	2SE/SD
JB-3	JB-3 1	0.283206	5	0.513052	7	0.703424	7
	JB-3 2	0.283194	4	0.513050	6	0.703407	8
	JB-3 3	0.283188	5	0.513061	6	0.703415	8
	JB-3 4	0.283220	8	0.513053	7	0.703418	8
	JB-3 5	0.283217	7	0.513054	8	0.703411	8
	Average JB-3	0.283205	28	0.513054	8	0.703415	13
	ppm	n = 5	100	n = 5	16	n = 5	18
	JB-3 La	0.283211	6	0.513062	7	0.703413	8
	JB-3 Lb	0.283005	5	0.513056	10	0.703421	8
	JB-3 Lc	0.283234	6	0.513070	9	0.703409	8
JB-3 L	JB-3 Ld	0.283240	7	0.513060	8	0.703417	8
	JB-3 Le	0.283238	6	0.513056	7	0.703425	8
	Average JB-3 L	0.283231	27	0.513061	12	0.703417	12
	ppm	n = 4	94	n = 5	23	n = 5	18
	ST05-03 1	0.283760	9	0.512334	6	0.702795	9
	ST05-03 2	0.283646	8	0.512338	8	0.702787	8
	ST05-03 3	0.283073	5	0.512336	6	0.702787	10
ST05-03	ST05-03 4	0.283729	4	0.512336	6	0.702796	8
	ST05-03 5	0.283691	7	0.512340	9	0.702796	8
	Average ST05-03	0.283706	98	0.512337	5	0.702792	9
	ppm	n = 4	345	n = 4	10	n = 5	13
	AN-G 1	0.283482	10	0.512342	5	0.702531	12
	AN-G 1 rep	0.283482	10	0.512350	7	0.702531	12
	AN-G 2	0.283180	11	0.512340	7	0.702444	8
AN-G	AN-G 3	0.283502	6	0.512338	6	0.702448	10
	AN-G 4	0.283451	9	0.512339	6	0.702448	10
	AN-G 5	0.283349	8	0.512348	8	0.702445	7
	AN-G 5 rep	0.283349	8	0.512346	8	0.702445	8
	AN-G 6	0.283356	15	0.512339	7	0.702434	10
	AN-G 7	0.283392	11	0.512336	9	0.702448	10
	AN-G 8	0.283552	10	0.512345	6	0.702445	7
	AN-G 9	0.283505	6	0.512348	7	0.702445	8
	AN-G 10	0.283316	7	0.512354	7	0.702445	8
	Average AN-G	0.283434	166	0.512343	11	0.702443	11
	ppm	n = 8	585	n = 10	22	n = 5	15

^aDuplicates analyses are from different digestions. Outliers are indicated in italics and calculated according to the Dixon test; [Gopal, 1993] (outliers include 9 for Hf on 104 analyses, and 1 for Sr on 101 analyses); replicates are indicated as "rep." Averages do not include outlier and replicate analyses. 2SE is the 2 standard error on the mean of the individual analysis (internal error) and 2SD is the 2 standard deviation of the individual analysis; they are both reported as times 10⁶.

associated with high individual analysis errors (2SE) (Table 7). The leached BIR-1a has higher 2SE (Table 8) for Pb isotopic ratios due to low Pb contents that prevented analyzing the samples under optimal conditions; the duplicates were analyzed at low voltage (1.1–1.5V), instead of the usual 4V, and only 30 cycles were measured instead of 60 (Table 3). The average compositions of leached and unleached GSR-3 are similar for $^{208}\text{Pb}/^{204}\text{Pb}$, and leached GSR-3 has less radiogenic $^{207}\text{Pb}/^{204}\text{Pb}$ and more radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ (Table 9 and Figures 4 and 9). The precision is not as good for leached GSR-3 (199 ppm, instead of 53 ppm for $^{208}\text{Pb}/^{204}\text{Pb}$ unleached, Table 9). JB-3 and BHVO-2 are both much more reproducible leached (91–334 ppm, $n = 5$ –10) than unleached (189–9121 ppm, $n = 4$ –5) (Table 9 and Figure 4) [Weis *et al.*, 2006]. The Pb isotopic ratios of JB-3 do not change with leaching (Table 9, Figure 4 and 9), whereas BHVO-2 is less radiogenic leached than unleached (Table 9; Figures 4 and 9) as discussed in Weis *et al.* [2005] and Todd *et al.* [2015].

For the five basaltic reference materials, the $^{143}\text{Nd}/^{144}\text{Nd}$ results of the leached samples are within error of the unleached samples with similar precisions (Table 10 and Figure 6). BE-N, GSR-3, JB-3, and BHVO-2 have the same Hf isotopic compositions and reproducibility (<100 ppm, $n = 4$ –9), both leached and unleached (Figure 5 and Table 10). The results for leached BIR-1a are slightly lower, and more heterogeneous, with an average $^{176}\text{Hf}/^{177}\text{Hf} = 0.283172 \pm 0.000092$ ($n = 5$), compared to the unleached result (0.283243 ± 0.000034 , $n = 5$) (Table 10 and Figure 5). The Sr isotopic ratios of leached and unleached BHVO-2 and JB-3 are similar (Table 10 and Figure 7). The average $^{87}\text{Sr}/^{86}\text{Sr}$ are less radiogenic after leaching for BE-N, BIR-1a, and GSR-3 (Table 10 and Figure 7). For BIR-1a and GSR-3, the reproducibility does not change with leaching, however, for BE-N, the precision is not as good for leached samples (43 ppm, $n = 5$) as for unleached samples (16 ppm, $n = 7$) (Table 10 and Figure 7).

Table 9. Compilation of Pb Isotopic Compositions of Mafic-Ultramafic Reference Materials^a

Sample	²⁰⁸ Pb/ ²⁰⁴ Pb	2SD	ppm	²⁰⁷ Pb/ ²⁰⁴ Pb	2SD	ppm	²⁰⁶ Pb/ ²⁰⁴ Pb	2SD	ppm	n
NIM-P	37.4381	668	1784	15.4587	180	1163	17.6122	1111	6310	4
BE-N	39.0164	48	122	15.6004	13	86	19.1958	59	308	9
<i>Pin et al. [2014]</i>	38.9930	13	33	15.6060	3	19	19.1720	11	57	2
<i>Chauvel et al. [2011]</i>	39.060	60	145	15.602	60	363	19.236	200	1029	2
<i>Schuth et al. [2011]</i>	39.013	290	731	15.592	100	618	19.224	150	792	3
<i>Albarède et al. [2004]</i>	39.0380	16	41	15.5994	50	321	19.2363	49	255	6
<i>Baker et al. [2004]</i>	39.062	200	501	15.601	30	207	19.247	410	2107	5
BE-N Leached	40.0700	1759	4390	15.6489	62	393	20.2725	1599	7887	5
DNC-1	38.3701	113	295	15.6475	24	153	18.6869	123	659	15
BIR-1a	38.4975	55	143	15.6595	22	139	18.8499	31	163	5
<i>Todd et al. [2015]</i>	38.4995	110	290	15.6600	33	210	18.8498	97	510	6
<i>Pin et al. [2014]</i>	38.4968	11	29	15.6585	7	45	18.8533	21	111	3
<i>Schuth et al. [2011]</i>	38.4960	27	70	15.6578	23	145	18.8518	21	113	2
<i>Baker et al. [2004]</i>	38.4979	60	156	15.6585	10	64	18.8498	50	265	3
BIR-1a Leached	38.3216	823	2147	15.5078	260	1675	18.6742	262	1400	5
<i>Todd et al. [2015]</i>	38.3310	83	210	15.5570	626	4000	18.7304	529	2800	2
GSR-3	37.8562	20	53	15.4814	8	48	17.7595	45	251	5
GSR-3 Leached	37.8526	75	199	15.4731	33	213	17.7961	61	341	5
NIM-N	37.5482	800	2130	15.6700	140	892	17.6378	971	5507	8
BHVO-2	38.2445	1207	3156	15.5409	179	1153	18.6475	1701	9121	4
<i>Weis et al. [2006]</i>	38.2367	182	476	15.5334	94	605	18.6474	242	1298	5
BHVO-2 Leached	38.2073	88	231	15.4890	33	212	18.6454	62	334	10
<i>Todd et al. [2015]</i>	38.2029	86	239	15.4910	62	400	18.6394	108	580	4
<i>Weis et al. [2006]</i>	38.1901	290	760	15.4826	115	740	18.6407	84	452	3
<i>Baker et al. [2004]</i>	38.2142	0	1	15.4930	4	20	18.6446	40	210	2
W-2	38.6321	89	232	15.6623	30	191	18.7497	45	238	11
<i>Li and Niu [2003]</i>	38.6969	320	827	15.6798	70	446	18.7606	40	213	5*
JB-3	38.2496	97	254	15.5355	29	189	18.2942	40	221	5
<i>Pin et al. [2014]</i>	38.2506	12	31	15.5356	10	64	18.2952	6	33	3
<i>Halldorsson et al. [2008]</i>	38.2559	164	429	15.5387	69	444	18.2972	84	459	3
<i>Makishima et al. [2007]</i>	38.2518	56	147	15.5355	18	117	18.2951	17	90	6
<i>Kuritani and Nakamura [2003]</i>	38.254	310	800	15.534	110	717	18.295	120	668	3
<i>Kuritani and Nakamura [2002]</i>	38.2526	65	170	15.5366	23	148	18.2966	18	98	5
JB-3 Leached	38.2496	54	140	15.5350	23	146	18.2941	17	92	5
ST05-03	35.7748	369	1031	15.3670	98	638	15.9018	391	2459	4
AN-G	33.5647	929	2769	14.6253	202	1384	13.9856	890	6362	9

^a2SD is the 2 standard deviation on the mean of the individual analysis. 2SD and 2SE are reported as times 10⁴. * replicates of the same solution (one digestion).

4.3. Gabbroic Reference Materials

The three gabbroic reference materials present intermediate trace element concentrations between the basaltic and the plagioclase-rich reference materials (Figure 3). Diabase W-2 has the highest concentrations (e.g., La = 9.9 µg/g) with enrichment in incompatible elements and a positive anomaly in Pb with respect to mantle-normalized concentrations. Dolerite DNC-1 is depleted in the LREE and has a strong positive Pb anomaly. Norite NIM-N has the lowest concentrations for most elements (e.g., La = 2.6 µg/g) and is characterized by positive Eu and Sr anomalies (Figure 3 and Table 6). Reproducibilities are good with %RSD below 10% for most elements, except Li (12.1%, *n* = 9) for W-2, Zr (14.5%), Th (13.5%), Bi (12.8%), W (14.9%), Hf (18.7%), and Li (11.7%) for DNC-1 (*n* = 11), and Sc (11.6%, *n* = 9) for NIM-N (Table 6 and Figure 2). All reported concentrations agree with recent published values (Table 6).

W-2 and DNC-1 show good isotopic reproducibility for radiogenic isotopic compositions (Figures 9 and 10). The precision is better than 295 ppm for ²⁰⁸Pb/²⁰⁴Pb, 191 ppm for ²⁰⁷Pb/²⁰⁴Pb, and 700 ppm for ²⁰⁶Pb/²⁰⁴Pb, better than 25 ppm for ⁸⁷Sr/⁸⁶Sr, and better than 52 ppm for ¹⁴³Nd/¹⁴⁴Nd and ¹⁷⁶Hf/¹⁷⁷Hf (2SD, *n* = 9–15) (Tables 9 and 10; Figures 9 and 10). Isotopic ratios of Sr, Hf, and Nd for W-2 are similar to previously published results (Table 10 and Figures 5–7) and Pb isotope ratios much lower than reported in *Li and Niu* [2003] (Table 9 and Figure 4). For DNC-1, we report the first Pb isotopic reference values (²⁰⁸Pb/²⁰⁴Pb = 38.3701 ± 0.0113, ²⁰⁷Pb/²⁰⁴Pb = 15.6475 ± 0.0024, and ²⁰⁶Pb/²⁰⁴Pb = 18.6869 ± 0.0123). Our Nd and Sr isotopic ratios for DNC-1 are in agreement with *Li et al.* [2011a] and *Yang et al.* [2012], however ¹⁷⁶Hf/¹⁷⁷Hf (0.282853 ± 0.000015, *n* = 14) is significantly lower than reported in *Le Fèvre and Pin* [2001] (0.283252 ± 0.000064, *n* = 3) (Table 10 and Figure 5).

Table 10. Compilation of Hf-Nd-Sr Isotopic Compositions of Mafic-Ultramafic Rock Reference Materials^a

Sample	¹⁷⁶ Hf/ ¹⁷⁷ Hf	2SD	ppm	n	¹⁴³ Nd/ ¹⁴⁴ Nd	2SD	ppm	n	⁸⁷ Sr/ ⁸⁶ Sr	2SD	ppm	n
NIM-P	0.282463	27	96	2	0.511501	7	14	3	0.711856	25	36	3
BE-N	0.282929	22	79	9	0.512882	14	27	9	0.703794	11	16	7
Chauvel et al. [2011]	0.282940	27	96	3	0.512875	35	68	3	0.703791	4	6	1
Martin et al. [2010]	0.282915	82	290	2								
Bizzarro et al. [2003]	0.282932	4	15	2								
Münker et al. [2001]	0.282928	20	70	3								
BE-N Leached	0.282937	13	46	5	0.512885	9	18	5	0.703279	30	43	5
DNC-1	0.282853	14	52	14	0.512473	11	22	12	0.705821	14	20	15
Yang et al. [2012]									0.705837	23	33	1
Li et al. [2011a]					0.512471	31	61	2				
Le Fèvre and Pin [2001]	0.283252	64	226	3								
BIR-1a	0.283243	34	120	5	0.513106	11	22	5	0.703110	21	29	5
Li et al. [2014]	0.283288	13	45	2	0.513101	16	30	2	0.703116	4	6	2
Pin et al. [2014]					0.513099	5	10	3	0.703111	5	7	3
Li et al. [2012]					0.513094	13	25	6				
Ali and Srinivasan [2011]					0.513088	3	6	2				
Li et al. [2011a]					0.513098	24	46	6				
Li et al. [2011b]					0.513098	12	23	8				
Yang et al. [2011a]					0.513112	7	14	3				
Li et al. [2007]					0.513064	15	29	4				
Jochum et al. [2006]	0.283273	8	30	2								
Elburg et al. [2005]									0.703109	11	16	4
Hanyu et al. [2005]	0.283265	45	160	2								
Le Fèvre and Pin [2005]	0.283247	79	278	4	0.513108	48	93	3				
Bizzarro et al. [2003]	0.283277	13	47	3								
Blichert-Toft [2001]	0.283266	17	60	2								
Le Fèvre and Pin [2001]	0.283268	42	148	3								
Münker et al. [2001]	0.283252	10	35	2								
BIR-1a Leached	0.283172	92	326	5	0.513101	13	26	5	0.703065	25	35	5
GSR-3	0.282985	9	32	5	0.512901	11	22	5	0.704076	18	26	5
Yang et al. [2011b]	0.282985	13	46	3								
Richardson et al. [1996]									0.70408	20	28	2
GSR-3 Leached	0.282984	7	25	5	0.512902	6	11	5	0.703868	10	14	5
NIM-N	0.282847	57	202	8	0.511756	25	50	10	0.709373	11	16	10
BHVO-2	0.283097	14	50	3	0.512994	17	34	2	0.703465	14	20	3
Weis et al. [2007]	0.283105	11	39	9								
Weis et al. [2006]					0.512990	10	19	8	0.703479	19	27	12
BHVO-2 Leached	0.283102	12	44	8	0.512988	12	24	10	0.703468	14	20	10
Weis et al. [2006]					0.512986	2	5	3	0.703471	23	33	3
W-2	0.282729	14	48	10	0.512531	13	26	9	0.706977	17	24	12
Li et al. [2014]	0.282733	27	95	2	0.512523	6	11	2	0.706990	20	28	2
Sánchez-Lorda et al. [2013]					0.512520	8	16	4				
Li et al. [2012]					0.512521	6	11	6	0.706965	15	21	2
Li et al. [2011b]					0.512527	3	6	2				
Yang et al. [2011b]	0.282715	8	28	4								
Yang et al. [2010]	0.282726	7	25	3	0.512518	22	43	3	0.706964	36	51	3
Le Fèvre and Pin [2001]	0.282715	60	212	6								
JB-3	0.283205	28	100	5	0.513054	8	16	5	0.703415	13	18	5
Pin et al. [2014]					0.513068	12	23	3	0.70343	9	13	3
Guo et al. [2013]	0.283222	10	35	5								
Huang et al. [2013]	0.283234	2	7	6								
Li et al. [2012]					0.513051	17	33	6	0.703432	16	22	2
Wang et al. [2011]	0.283230	11	39	2	0.513063	13	25	2				
Marín-Cerón et al. [2010]	0.283227	3	11	4								
Yang et al. [2010]	0.283224	12	43	3	0.513040	36	71	3	0.703394	36	51	3
Makishima et al. [2008]					0.513085	20	38	4	0.703456	11	16	5
Li et al. [2007]					0.513057	19	37	3				
Lu et al. [2007]	0.283223	7	25	8								
Hanyu et al. [2005]	0.283245	34	120	2								
Pin and Zalduegui [1997]					0.513071	82	160	2				
JB-3 Leached	0.283231	27	94	4	0.513061	12	23	5	0.703417	12	18	5
ST05-03	0.283706	98	345	4	0.512337	5	10	4	0.702792	9	13	5
AN-G	0.283434	166	585	9	0.512343	11	22	10	0.702443	11	15	5
Blichert-Toft [2001]	0.283903	5	18	1								
Pin and Bassin [1992]									0.70248	40	57	1

^a2SD is the 2 standard deviation on the mean of the individual analysis. For the literature data, when n = 1, the error reported is the 2SE, standard error of individual analysis. 2SD and 2SE are reported as times 10⁶.

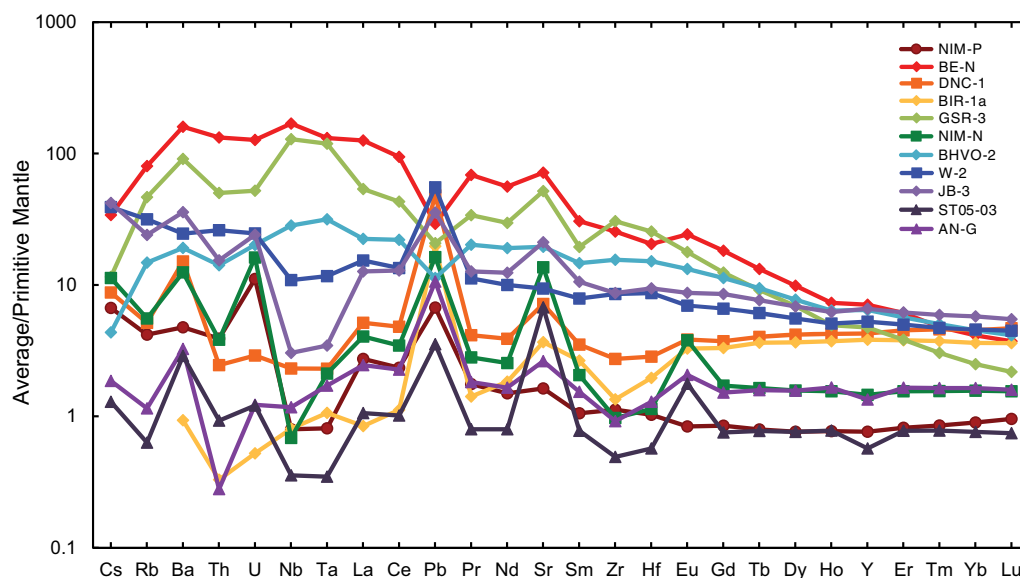


Figure 3. Multielement concentrations of the mafic-ultramafic rock reference materials normalized to Primitive Mantle [McDonough and Sun, 1995]. Note the wide range in total concentrations, slopes, and anomalies (e.g., Nb-Ta, Pb, Sr, Eu, Zr-Hf).

We report the first radiogenic isotopic ratios for the reference material NIM-N. Nd and Sr isotopic ratios of this norite reproduce very well with precision equal to 50 ppm and 16 ppm for $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, respectively ($n = 10$, 2SD) (Table 10; Figures 6 and 7). The Sr and Nd isotopic ratios of NIM-N match published results for samples from the Main Zone of the Bushveld Complex [e.g., Harmer *et al.*, 1995; Maier *et al.*, 2000; Prevec *et al.*, 2005; Chutas *et al.*, 2012]. The Pb and Hf isotopic ratios have relatively low precision: 2130 ppm (2SD, $n = 8$) for $^{208}\text{Pb}/^{204}\text{Pb}$ and 202 ppm for $^{176}\text{Hf}/^{177}\text{Hf}$ (Tables 9 and 10; Figures 4 and 5).

4.4. Plagioclase-Rich Reference Materials

The low trace element concentrations of the two plagioclase-rich samples AN-G and Stillwater ST03-05 are notable (Figure 3). Both have similar primitive mantle-normalized patterns with negative Y anomalies and positive Eu, Sr, and Pb anomalies, but with different magnitudes and concentrations (Figure 3 and Table 4). The reproducibility is good for AN-G with RSD lower than 8% ($n = 8$) for all elements, except for Cs (10.6%), U (15.3%), Th (13.1%), and Rb (15.3%). Compared to Carignan *et al.* [2001], the measured concentrations are lower for most elements (Table 4 and Figure 2). Stillwater ST05-03 presents very good reproducibility with RSD better than 5% ($n = 5$) for all elements, except Th (14.2%) and Bi (10.7%).

Anorthosite AN-G reproduces well for Nd and Sr isotopic ratios with precisions equal to 22 ppm ($n = 10$) for $^{143}\text{Nd}/^{144}\text{Nd}$ and 15 ppm ($n = 5$) for $^{87}\text{Sr}/^{86}\text{Sr}$ (2SD, Table 10). However, the precision for Hf and Pb isotopic ratios is relatively poor with uncertainties equal to 585 ppm ($n = 9$) for $^{176}\text{Hf}/^{177}\text{Hf}$ and 2769 ppm ($n = 9$) for $^{208}\text{Pb}/^{204}\text{Pb}$ (Tables 9 and 10; Figures 4 and 5). The results for ST05-03 are similar with excellent precision determined for Nd (10 ppm, $n = 4$) and Sr isotopic ratios (13 ppm, $n = 5$), and relatively poor reproducibility for Hf (345 ppm, $n = 4$) and Pb (1031 ppm, $n = 4$) (Tables 9 and 10; Figures 4 and 5). We report the first Nd isotopic value for AN-G of $^{143}\text{Nd}/^{144}\text{Nd} = 0.512343 \pm 0.000011$ (2SD, $n = 10$). The Sr isotopic composition for AN-G ($^{87}\text{Sr}/^{86}\text{Sr} = 0.702443 \pm 0.000011$, $n = 5$) agrees with the value reported by Pin and Bassin [1992] ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70248 \pm 0.00004$, $n = 1$), however the difference in $^{176}\text{Hf}/^{177}\text{Hf}$ from this work and Blichert-Toft [2001] is equivalent to three times the external precision (Table 10).

5. Discussion

For some of the reference materials, few to no isotopic data were previously published and we report the first Pb-Sr-Nd-Hf isotopic compositions for NIM-P and NIM-N, the first Pb and Nd isotopic ratios for GSR-3 and AN-G, and the first Pb isotopic data for DNC-1. The results supplement published trace element compilations [e.g., Dulski, 2001; Carignan *et al.*, 2001; Chauvel *et al.*, 2011; Jochum *et al.*, 2015] with values for 40 trace elements from individual samples (Tables (4–6)). Seven of the reference materials show excellent

reproducibility for most element concentrations and isotopic systems (Tables 9 and 10). Below, we address the trace element and isotopic reproducibility of the mafic-ultramafic reference materials, the effects of sample matrix and leaching, the challenge of using plutonic rocks as reference materials, and provide recommendations for the use of these samples.

5.1. Trace Element Concentrations and the Effect of Sample Matrix

The accuracy and reproducibility of trace element concentrations in the reference materials were evaluated by measuring BHVO-2 as an unknown sample during each analytical session [Carpentier *et al.*, 2013] (supporting information Table S7) and by processing and measuring complete analytical duplicates. Trace element concentrations for the four basaltic reference materials BE-N, BIR-1a, GSR-3, and JB-3 are very reproducible with an average %RSD = 4% (Table 5 and Figure 2) and, for most elements, they agree within

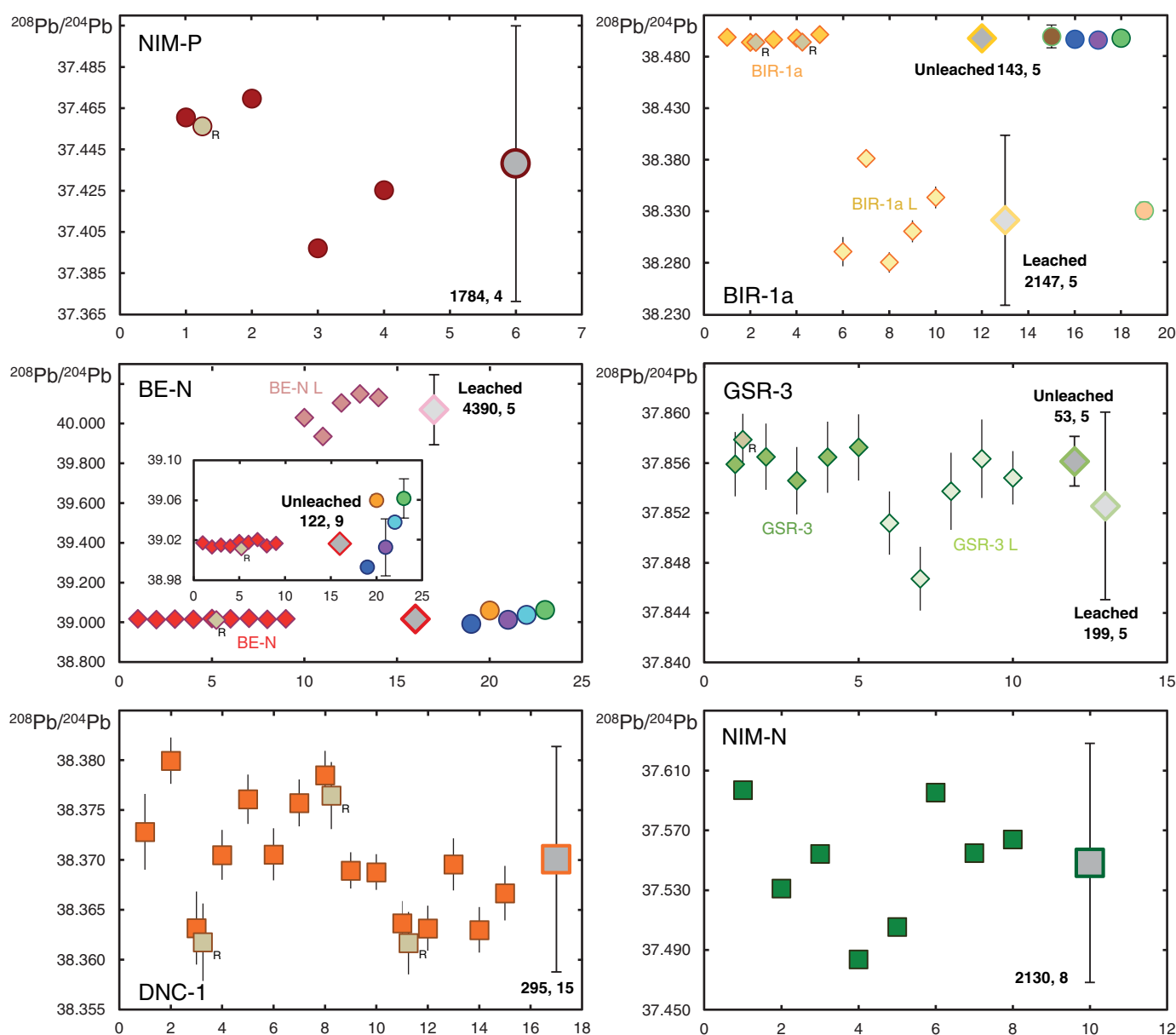


Figure 4. Measured $^{208}\text{Pb}/^{204}\text{Pb}$ for mafic-ultramafic rock reference materials. Replicate (R) analyses are in beige; average ratios are in dark grey (unleached) and light grey (leached). Numbers next to the average are the precision (2SD in ppm) and number of duplicates. Open error bars are 2SE and closed errors bars are 2SD (absolute); when not visible, error bars are smaller than symbols.

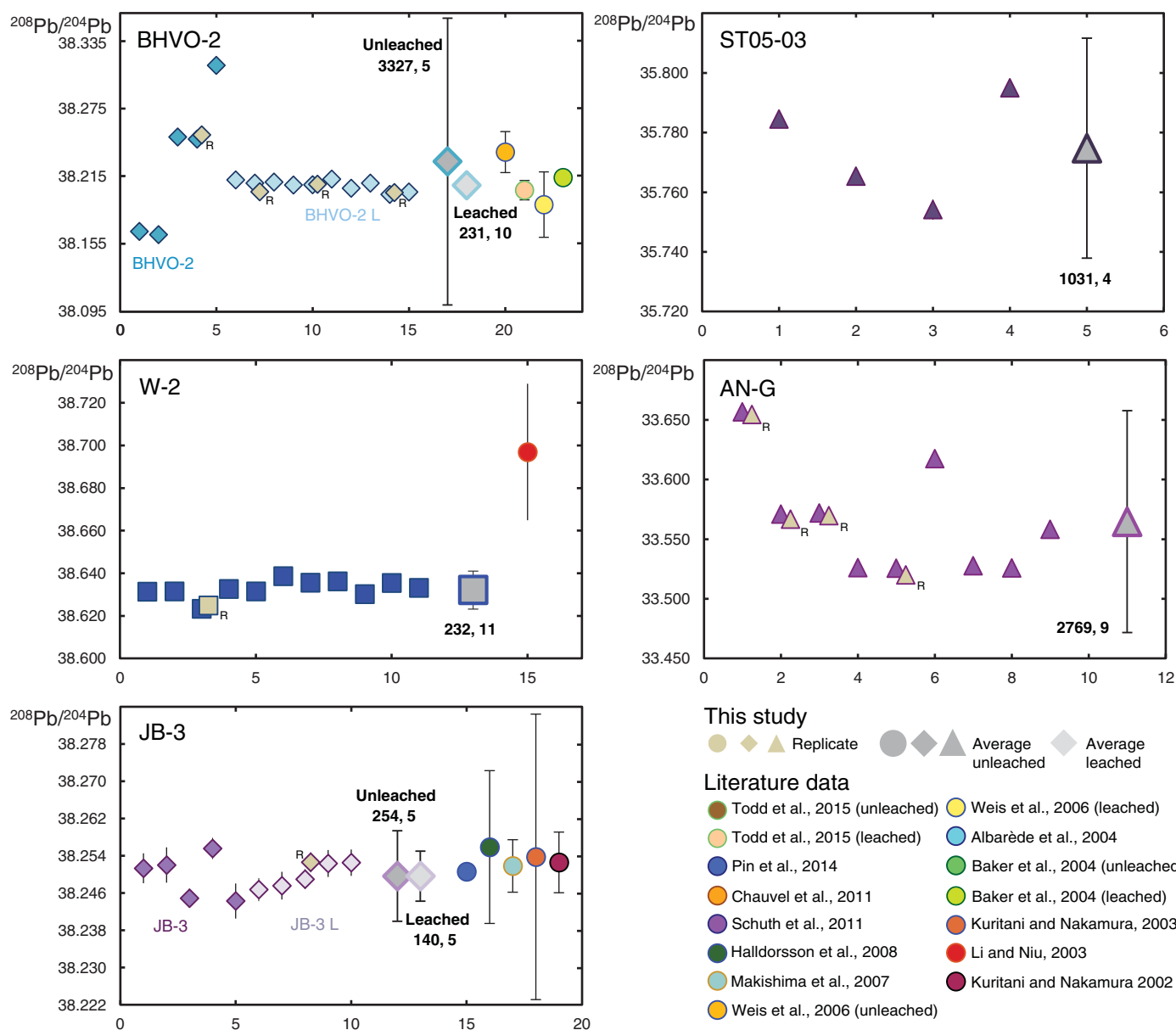


Figure 4. (continued)

10% of the results from previous studies for BE-N, BIR-1a, and BHVO-2 [Jochum et al., 2015], for GSR-3 [Dulski, 2001], and for JB-3 [Makishima and Nakamura, 2006] (Table 5).

Trace element concentrations of the leached basalts (Table 5 and Figure 8) are reproducible (average %RSD = 7%) [Nobre Silva et al., 2010]. In the basalts, the LREE are preferentially leached compared to the HREE (Figure 8), which is consistent with the relative mobility of the REE, and especially LREE, during weathering and concentration in secondary minerals [e.g., Ludden and Thompson, 1979; Price et al., 1991; Verma, 1992; Nobre Silva et al., 2010]. The positive Eu and Sr anomalies in leached GSR-3 and JB-3 indicate that the residues consist of plagioclase [e.g., Koppers et al., 2003; Nobre Silva et al., 2010]; the anomalies are stronger for JB-3, which contains 59% plagioclase in unleached samples compared to 47% combined feldspar + feldspathoids for GSR-3 (Table 2). The positive HFSE anomaly in the leached basaltic samples signals the resistance of titanomagnetite and ulvöspinel to leaching [e.g., Hanano et al., 2009; Nobre Silva et al., 2010]. Together with previous studies on leaching effects [e.g., Koppers et al., 2003; Hanano et al., 2009; Nobre Silva et al., 2010], these results demonstrate that leaching may change the original mineral

proportions in the samples and thus leaching is not appropriate for determining the trace element concentrations of unknown samples.

The ultramafic and mafic plutonic rocks have more complex matrices with low to very low trace element abundances (e.g., 63 $\mu\text{g/g}$ V to 0.022 $\mu\text{g/g}$ Th for AN-G, Figure 3), thus it is a significant challenge to obtain good reproducibility. The high-pressure digestion method is generally effective based on the results from W-2 (diabase), NIM-N (norite), NIM-P (pyroxenite), AN-G (anorthosite), and ST05-03 (leucogabbro) (Tables 4 and 6). The pyroxene-rich and plagioclase-rich reference materials, which present the lowest elemental concentrations (Figure 3), do not have higher RSD than the other samples (Figure 2). Precisions range from 0.4% RSD (2.52 $\mu\text{g/g}$ Rb in NIM-P, $n = 4$) to 18.7% (0.8 $\mu\text{g/g}$ Hf for DNC-1, $n = 11$) with an average of 5% RSD for the 38 elements (Figure 2). Their RSD vary significantly depending on the elements, especially for Zr and Hf, which have higher RSD than the other elements in NIM-P and ST05-03, and for Cs, Rb, Th and U in AN-G

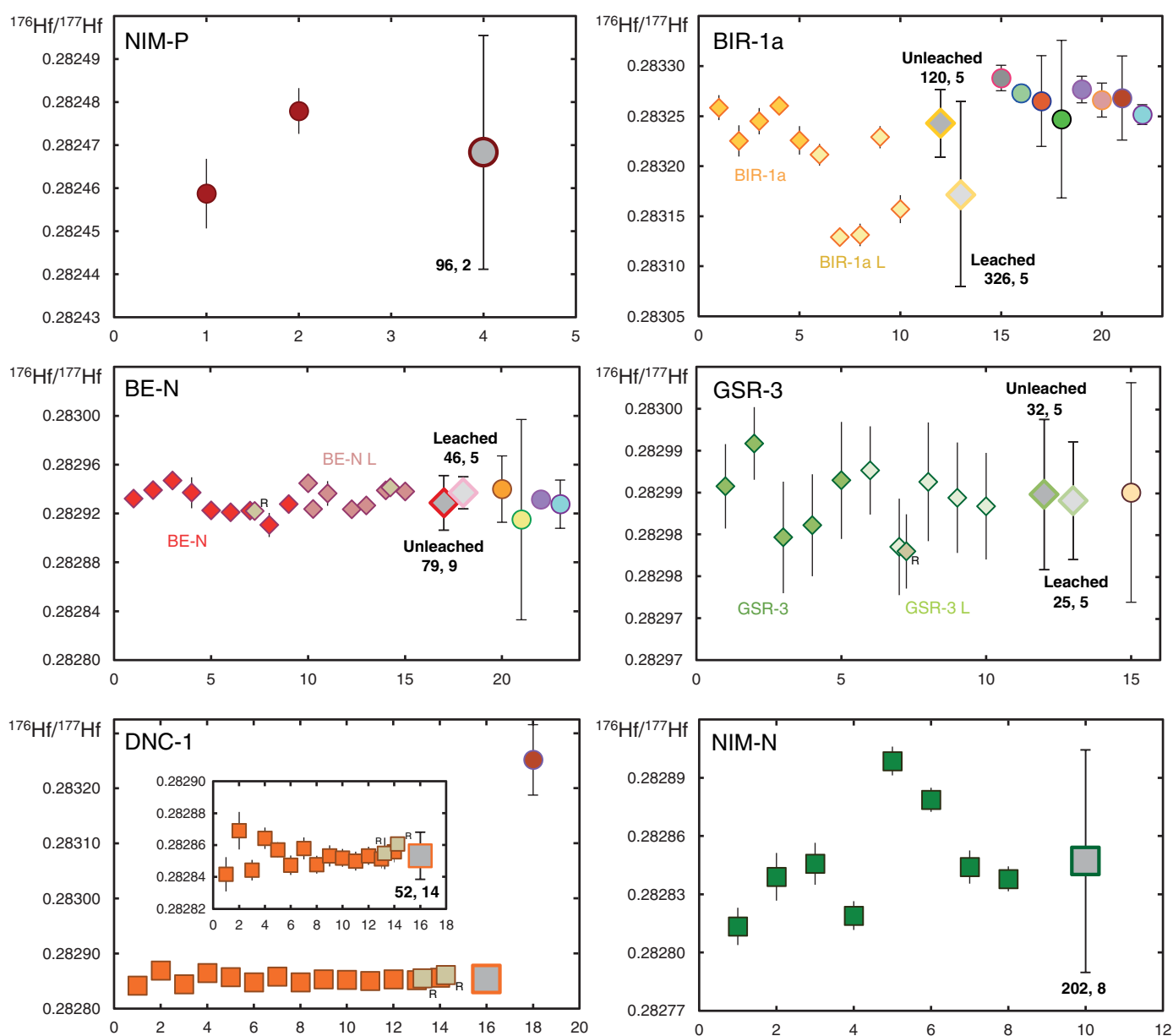


Figure 5. Measured $^{176}\text{Hf}/^{177}\text{Hf}$ for mafic-ultramafic rock reference materials. Replicate (R) analyses are in beige; average ratios are in dark grey (unleached) and light grey (leached). Numbers next to the average are the precision (2SD in ppm) and number of duplicates. Open error bars are 2SE and closed errors bars are 2SD (absolute); when not visible, error bars are smaller than symbols.

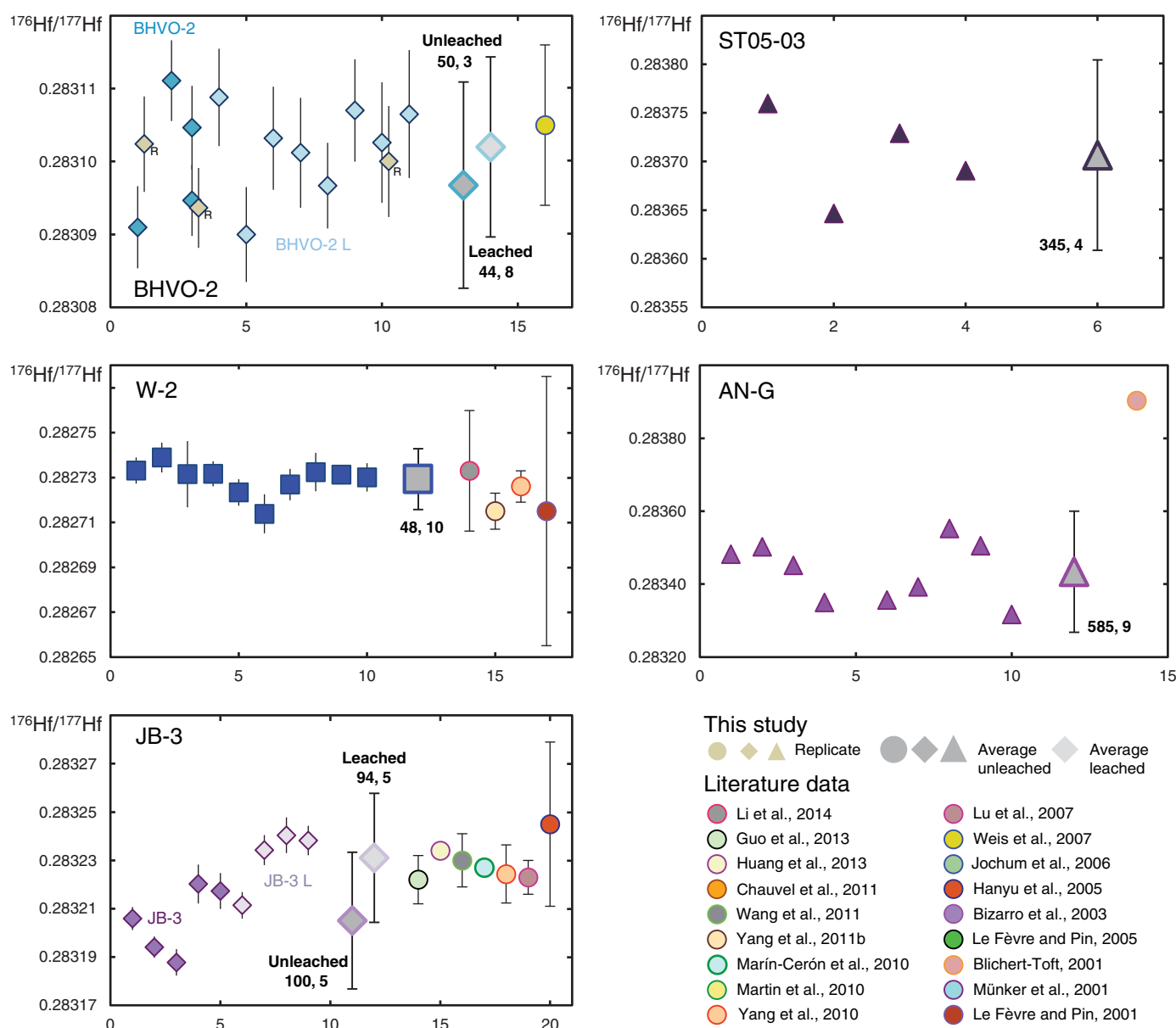


Figure 5. (continued)

(Figure 2). The variations in %RSD appear to be mostly related to variations in elemental concentrations (Figures 2 and 3). For AN-G, the systematic differences in concentrations determined in this study and those reported by Carignan et al. [2001] indicate that further studies are necessary for this material. On average, the gabbroic samples have the highest RSD for most of the elements (Figure 2). Even after high-pressure digestion, the dolerite DNC-1 presents variable Hf and Zr contents (Table 6 and Figure 2), which indicates incomplete dissolution or heterogeneous distribution of accessory minerals, such as zircon, and highlights the difficulty of analyzing plutonic rocks.

5.2. Variable Effects of Acid Leaching of Basaltic Rocks

Leaching allows for better precision on measured Pb isotopic ratios by removing contaminants from basaltic rocks [e.g., McDonough and Chauvel, 1991; Abouchami et al., 2000; Regelous et al., 2003; Koppers et al., 2003; Baker et al., 2004; Weis et al., 2005, 2006; Nobre Silva et al., 2009, 2010; Jweda et al., 2015; Todd et al., 2015]. The leaching experiments in this study on the five basaltic reference materials (BE-N, BIR-1a, GSR-3, BHVO-2, JB-3)

yielded variable results depending on the specific isotopic system and the presence of secondary alteration minerals or contamination.

Leaching improves the precision on Pb isotopic ratios for BHVO-2 [e.g., Baker *et al.*, 2004; Weis *et al.*, 2006; Todd *et al.*, 2015] and JB-3 without changing their average ratios, but surprisingly, has the opposite effect on BE-N, GSR-3, and BIR-1a [Todd *et al.*, 2015] (Table 9). For leached BE-N, two observations suggest that the measured Pb heterogeneity between the duplicates results from nonreproducible amounts of leaching of Pb. First, the Pb concentrations for the leached duplicates of BE-N have a high RSD (26.9%, $n = 5$) (Table 5). Second, there is a correlation between Pb isotopic ratios and weight loss of the BE-N duplicates during leaching: $^{207}\text{Pb}/^{204}\text{Pb} = 15.6444 \pm 0.0009$ (2SD) when 35% of the powder was lost, whereas $^{207}\text{Pb}/^{204}\text{Pb} = 15.6518 \pm 0.0010$ (2SD) when 56% was leached. A similar, but weaker, relation is observed for leached GSR-3 duplicates ($^{207}\text{Pb}/^{204}\text{Pb} = 15.4752 \pm 0.0008$ for 29% weight loss; $^{207}\text{Pb}/^{204}\text{Pb} = 15.4727 \pm 0.0009$ for 57% weight loss) despite reasonable reproducibility (10.7% RSD, $n = 5$).

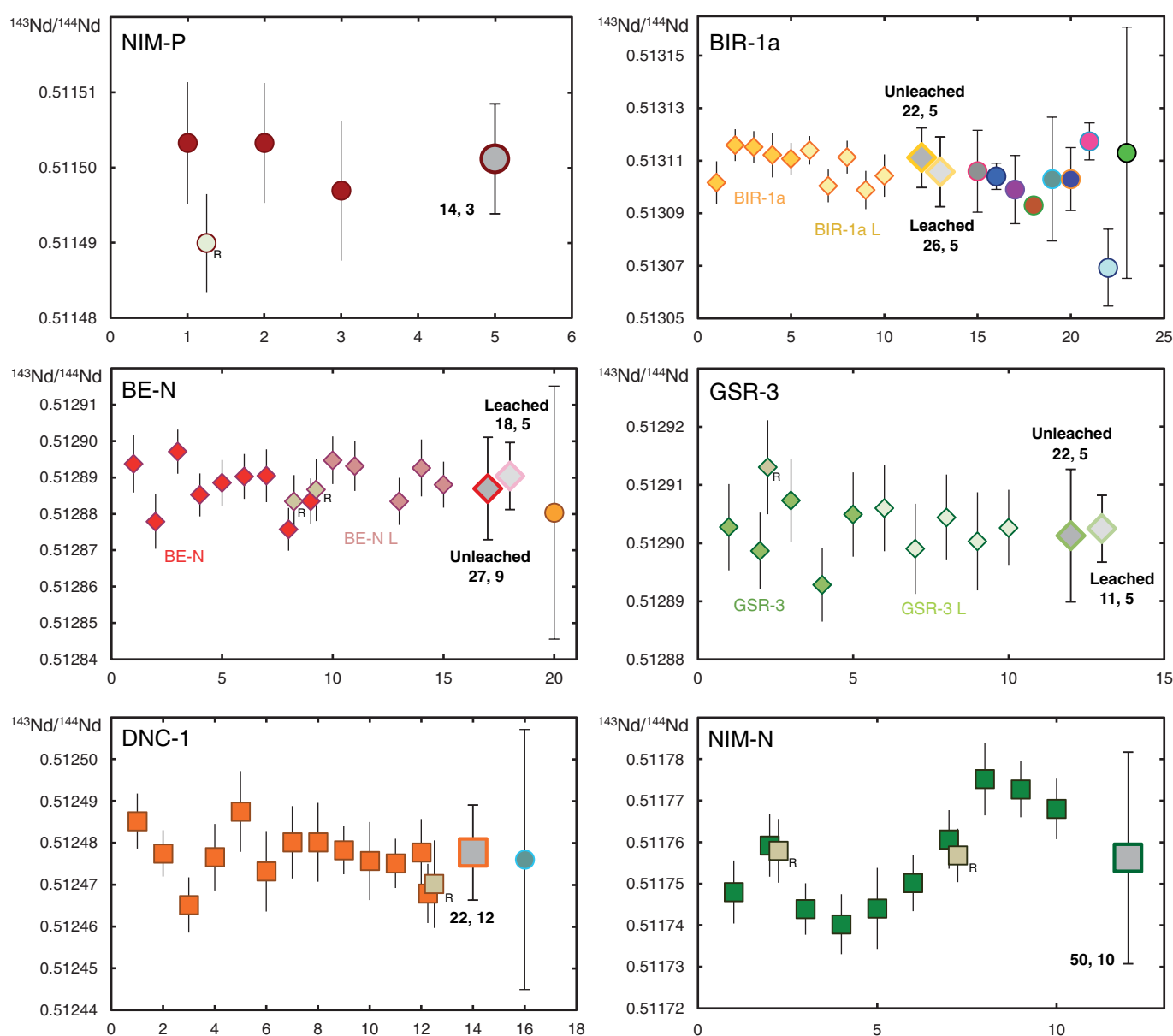


Figure 6. Measured $^{143}\text{Nd}/^{144}\text{Nd}$ for mafic-ultramafic rock reference materials. Replicate (R) analyses are in beige; average ratios are in dark grey (unleached) and light grey (leached). Numbers next to the average are the precision (2SD in ppm) and number of duplicates. Open error bars are 2SE and closed errors bars are 2SD (absolute); when not visible, error bars are smaller than symbols.

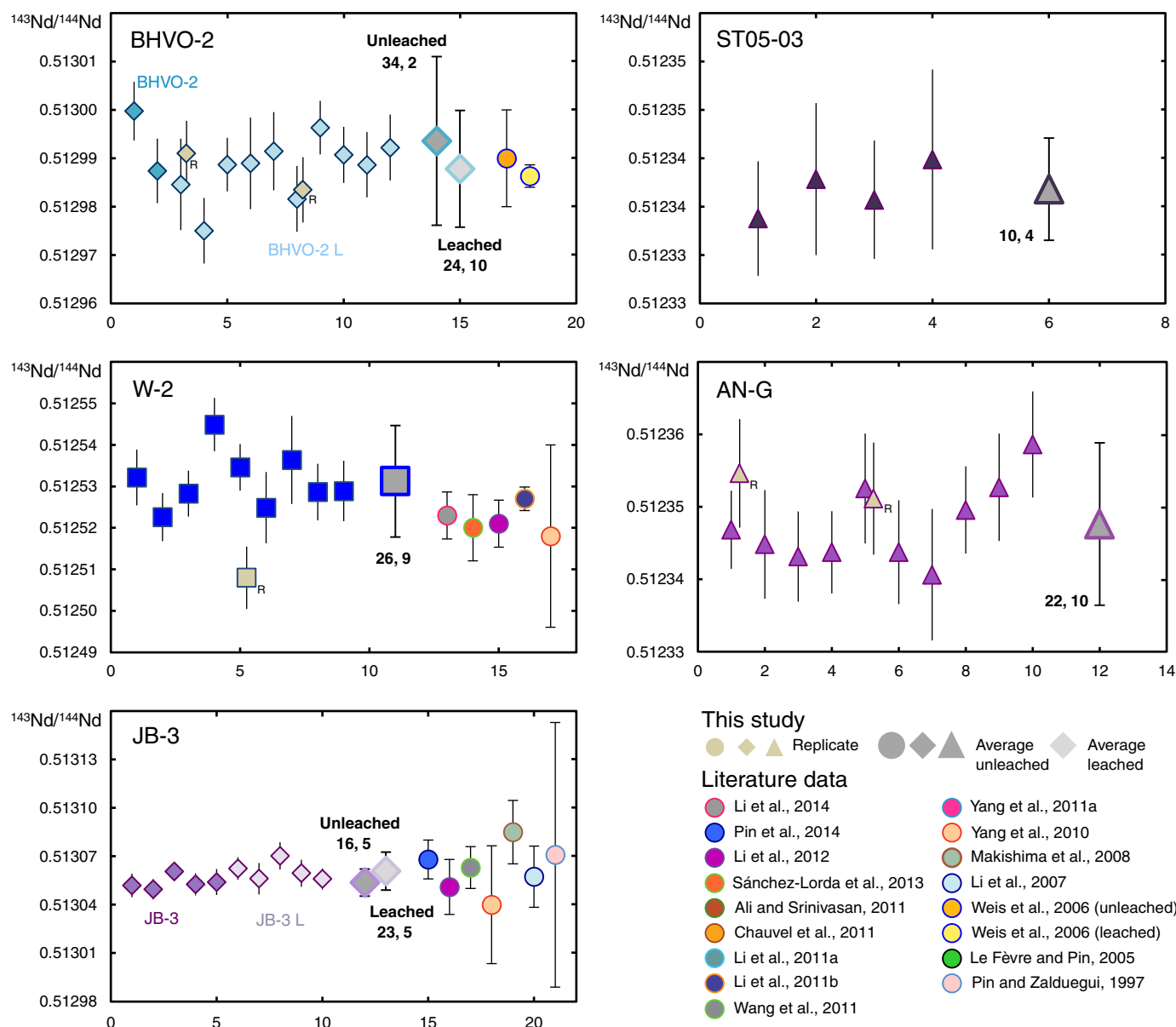


Figure 6. (continued)

for Pb concentrations (Table 5). *Todd et al.* [2015] reported Pb isotopic heterogeneity for leached BIR-1a (2SD, $n = 2$: 210 ppm for $^{206}\text{Pb}/^{204}\text{Pb}$; 4000 ppm for $^{207}\text{Pb}/^{204}\text{Pb}$; 2800 ppm for $^{208}\text{Pb}/^{204}\text{Pb}$), results that were considered as inconclusive due to the low number of duplicates [*Todd et al.*, 2015]. Similar results are obtained in this study (2SD, $n = 5$: 1400 ppm for $^{206}\text{Pb}/^{204}\text{Pb}$; 1675 ppm for $^{207}\text{Pb}/^{204}\text{Pb}$; 2147 ppm for $^{208}\text{Pb}/^{204}\text{Pb}$) despite a higher number of duplicates ($n = 5$) and a stronger leaching method (Figure 4). These observations indicate that the heterogeneity in Pb isotopic ratios cannot be resolved by leaching for BE-N, GSR-3, and BIR-1a even with a multistep leaching procedure (7–10 steps) [e.g., *Abouchami et al.*, 2000; *Eisele et al.*, 2003; *Albarède et al.*, 2005; *Hanano et al.*, 2009; *Todd et al.*, 2015] due to selective leaching of mineral phases that affect the Pb isotopic compositions.

Leaching can also improve Sr isotopic ratios measurements [e.g., *Dasch et al.*, 1973; *Alibert et al.*, 1983; *Hemond et al.*, 1993; *Stracke and Hegner*, 1998; *Koppers et al.*, 2003; *Weis et al.*, 2006; *Nobre Silva et al.*, 2010]. In this study, the leaching experiments have different results depending on which basaltic reference material was analyzed. The Sr isotopic compositions of JB-3 and BHVO-2 do not vary significantly with leaching, whereas leached GSR-3, BE-N, and BIR-1a have less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ than their unleached duplicates

(Table 10 and Figure 10). Neither JB-3 nor BHVO-2 contain secondary minerals (Table 2), which indicates that the contamination responsible for the Pb isotopic variability was either very small or that it was introduced during sampling [Weis *et al.*, 2005, 2006]. If any alteration was involved, it did not affect Sr, which is preferentially hosted in plagioclase in JB-3 and BHVO-2 [Price *et al.*, 1991]. In contrast, secondary minerals are present in both GSR-3 (chlorite, zeolite) and BE-N (calcite, zeolite) (Table 2), thus the less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ in leached BE-N, GSR-3, and most likely BIR-1a, indicates that leaching removes the crustal contamination or alteration signature in these samples [e.g., Alibert *et al.*, 1983; Hanano *et al.*, 2009; Nobre Silva *et al.*, 2009, 2010]. For example, Alibert *et al.* [1983] measured Sr isotopic ratios in leached and unleached melilite (similar to BE-N) and noted lower $^{87}\text{Sr}/^{86}\text{Sr}$ associated with the removal of calcite and zeolite during leaching. For the basaltic reference materials in this study, leaching yielded good precision for Sr isotopic measurements (2SD = 14–43 ppm, $n = 5$) (Table 10).

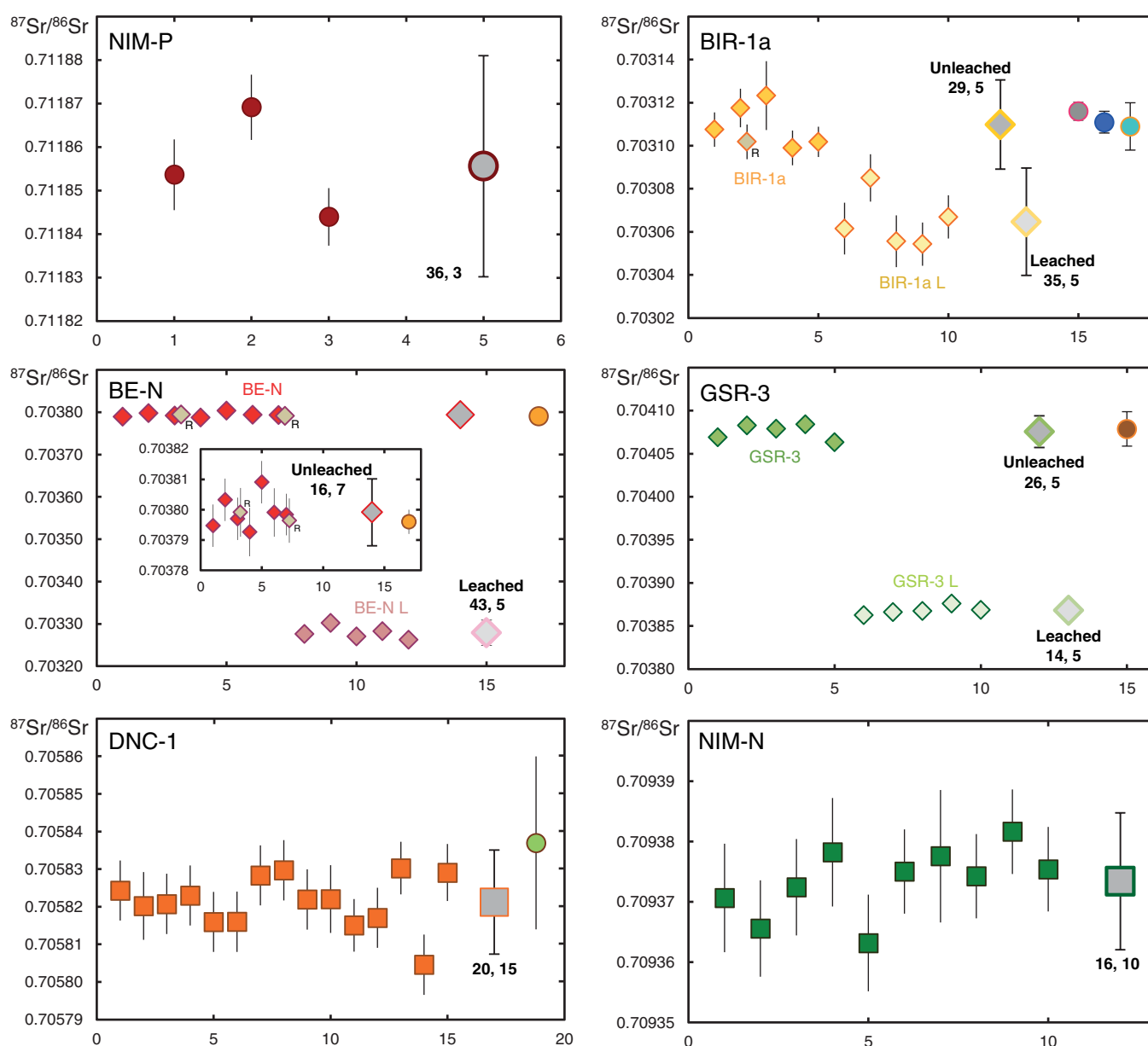


Figure 7. Measured $^{86}\text{Sr}/^{87}\text{Sr}$ for mafic-ultramafic rock reference materials. Replicate (R) analyses are in beige; average ratios are in dark grey (unleached) and light grey (leached). Numbers next to the average are the precision (2SD in ppm) and number of duplicates. Open error bars are 2SE and closed errors bars are 2SD (absolute); when not visible, error bars are smaller than symbols.

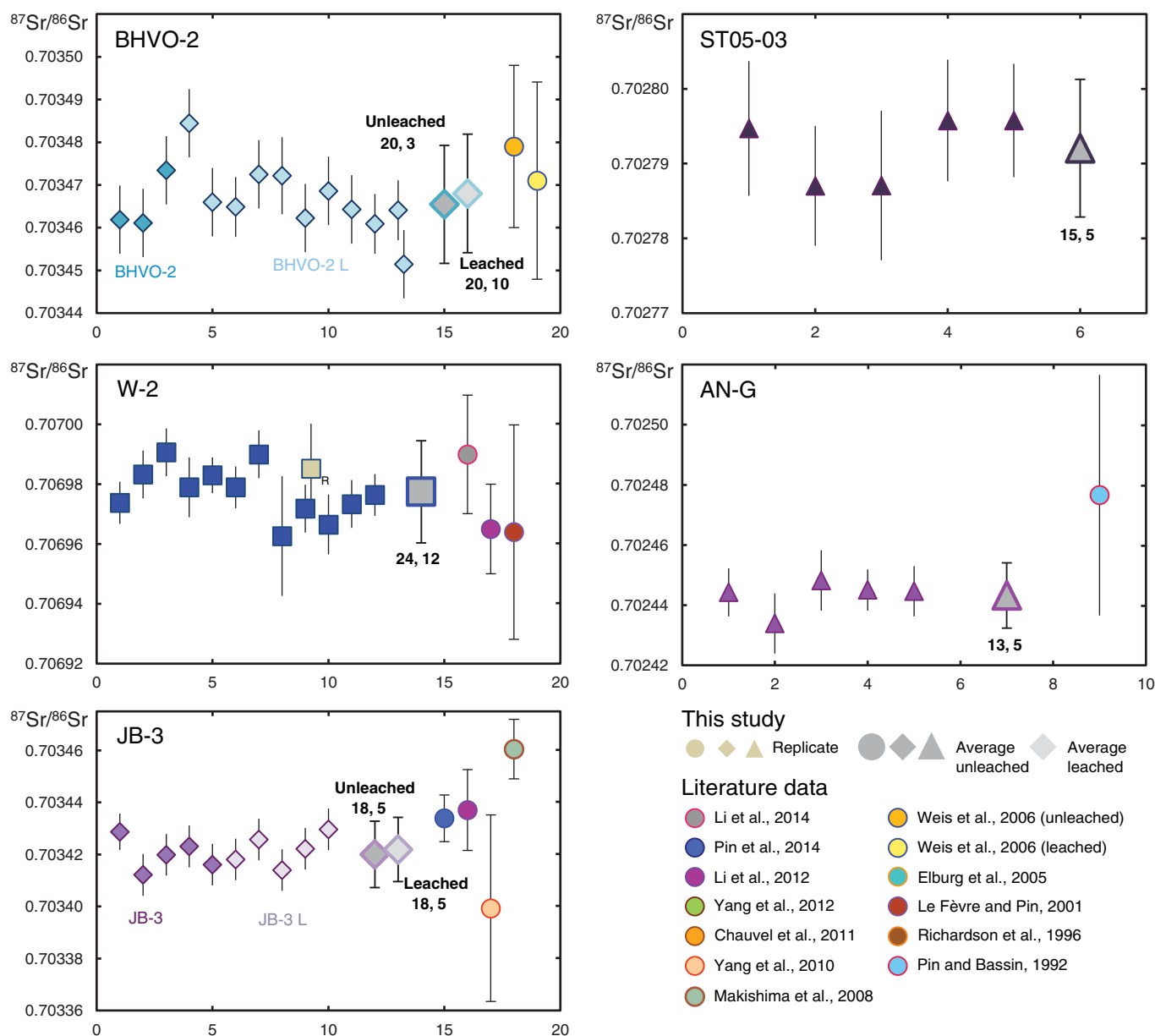


Figure 7. (continued)

Finally, for all five basaltic reference materials, Nd and Hf isotopic ratios for unleached and leached samples are within error (Tables 9 and 10; Figures 5 and 6). These results indicate that these two isotopic systems were not affected by the low degree of alteration or contamination that perturbed the Pb and Sr isotopic compositions.

5.3. Reproducible Pb and Hf Isotopic Ratios: A Challenge for Plutonic Rocks

The heterogeneity of Pb and Hf isotopic ratios observed for some plutonic rocks (Tables 9 and 10; Figures 9 and 10) cannot be explained by incomplete digestion as most trace elements present good reproducibility (average 5% RSD, Tables 4 and 6), or by contamination during chemistry as the blanks are negligible. None of the reference materials show evidence for contamination in elements that can be added during sample processing, such as W and Ta (Figures 2 and 3). The plagioclase-rich rocks, AN-G (Fiskenæsset) and ST05-03 (Stillwater), are heterogeneous with respect to Pb and Hf isotopes (Tables 9 and 10). Both contain significant abundances of secondary minerals, including clinozoisite (+zoisite) and actinolite [e.g., McCallum, 1996;

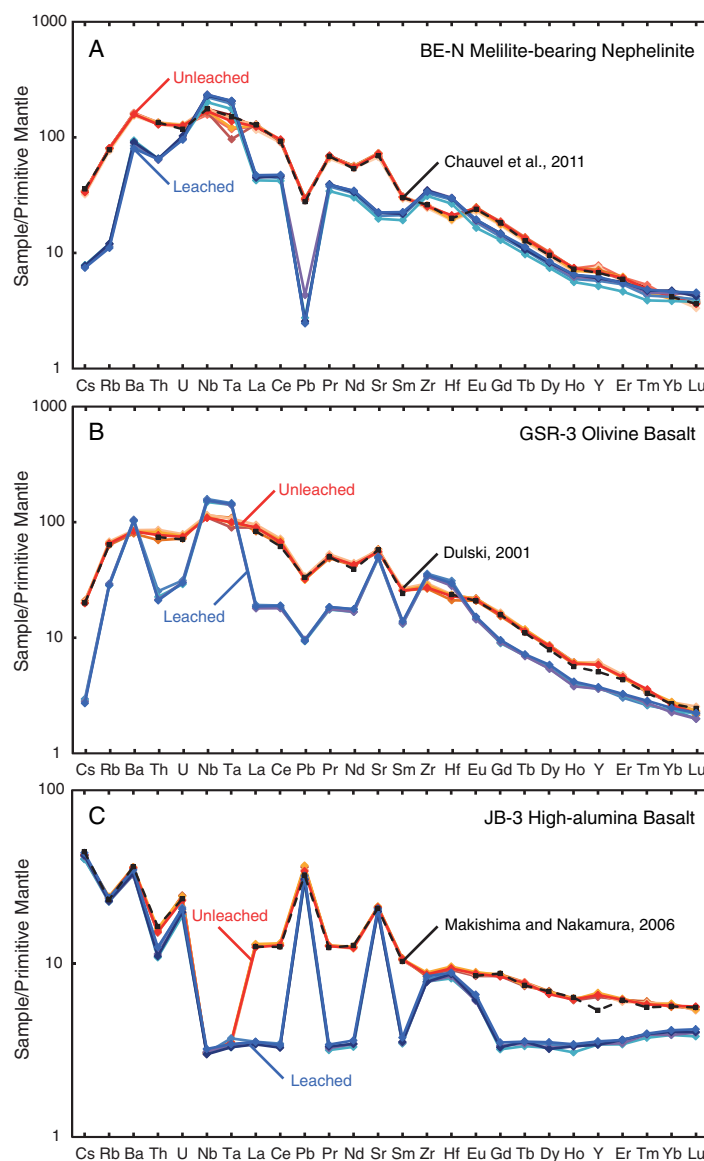


Figure 8. Multielement concentrations for basaltic reference materials BE-N (panel A), GSR-3 (panel B), and JB-3 (panel C), comparing leached and unleached values normalized to Primitive Mantle [McDonough and Sun, 1995]. Cold colors indicate leached samples and warm colors indicate unleached samples. Black dashed lines represent previously published values from Chauvel *et al.* [2011] for BE-N, from Dulski [2001] for GSR-3, and from Makishima and Nakamura [2006] for JB-3.

2005, 2006], or inherent heterogeneity in these rocks due to hydrothermal alteration during cooling of the complex [e.g., Harmer *et al.*, 1995; Mathez and Kent, 2007], or to the mineral-scale isotopic variation reported in samples from the Bushveld Complex [e.g., Prevec *et al.*, 2005; Chutas *et al.*, 2012; Roelofse and Ashwal, 2012; Yang *et al.*, 2013]. A follow-up study is recommended to uncover the exact reason for the Pb isotopic heterogeneity in NIM-P and NIM-N from the Bushveld Complex.

5.4. Recommended Reference Materials for Mafic-Ultramafic Rocks

The reference materials examined in this study may be used to monitor the analysis of trace element concentrations of unknown mafic-ultramafic rocks. With the lowest %RSD, JB-3 is the most appropriate basaltic reference material, whereas W-2 is the most suited for gabbroic samples (Figure 2). Additional studies are required to evaluate the use of AN-G for plagioclase-rich samples as our values differ from those reported in Carignan *et al.* [2001]. For plagioclase-rich rocks, we recommend using NIM-N or W-2, which are both

Polat *et al.*, 2009] (Table 2), and there is geochemical evidence for isotopic disturbance in both intrusions. In the Stillwater Complex, Pb isotopic variations between sulfides and plagioclase [McCallum *et al.*, 1999] and between leached and unleached plagioclase [Bosch *et al.*, 1991; Wooden *et al.*, 1991] are interpreted to result from Pb mobility during a low-grade metamorphic event. At Fiskensæset, Polat *et al.* [2010] observed that during metamorphism the U-Pb system has been disturbed in rocks containing more than 10% mafic minerals (AN-G has ~12 wt% actinolite, Table 2). ST05-03 also contains relatively abundant interstitial zircon [Wall and Scoates, 2014], thus the poor precision on the Hf isotopic composition (345 ppm, $n = 4$) might reflect a nugget effect caused by a heterogeneous distribution of this accessory mineral. AN-G is also heterogeneous with respect to Hf isotopes (585 ppm, $n = 9$) (Figure 10) and may reflect the same mechanism.

Both of the reference materials from the Bushveld Complex, NIM-P and NIM-N, are heterogeneous with respect to their Pb isotopic compositions (Table 9). Possible explanations for this heterogeneity are either contamination introduced during sample preparation [e.g., McDonough and Chauvel, 1991; Woodhead and Hergt, 2000; Weis *et al.*,

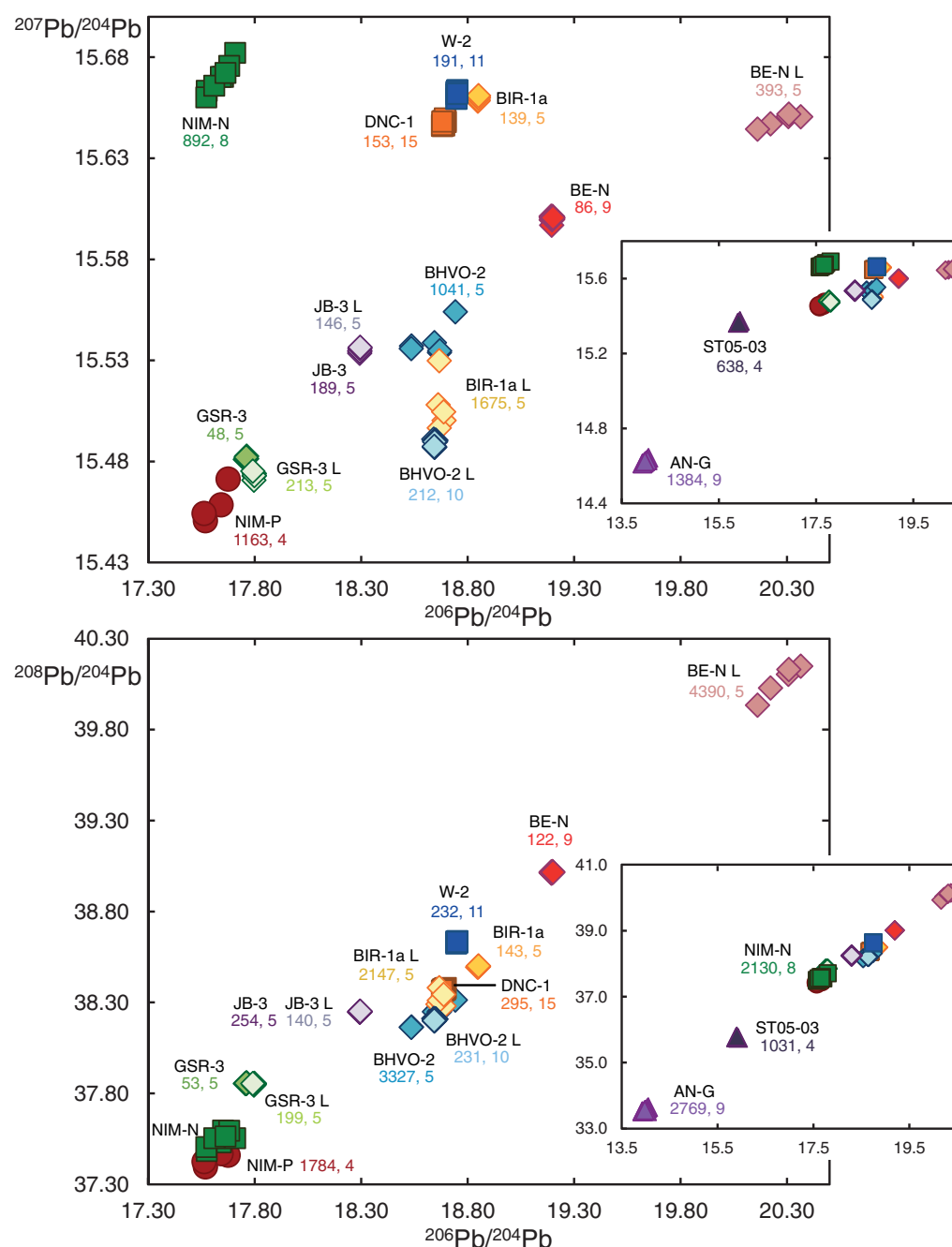


Figure 9. Comparison of the Pb isotopic variations in mafic-ultramafic rock reference materials. A. $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, B. $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$. The insets highlight the relatively unradiogenic ratios of the plagioclase-rich samples AN-G and ST05-03; dashed boxes correspond to the areas covered by the main figures. Numbers below the reference material names are the reproducibility in ppm (2SD) and the number of duplicates. Error bars are smaller than the symbols.

plutonic rocks with relatively high plagioclase contents (Table 2). Leached basaltic samples are not appropriate for evaluating the quality of trace element analyses of unknown samples, however they may be useful for verifying the efficiency of a leaching procedure.

Our recommendations for the use of the mafic-ultramafic reference materials for Pb-Sr-Nd-Hf isotopic analyses are summarized in Table 11 and depend on the type of sample being analyzed and the isotopic system of interest. Briefly, BE-N, BIR-1a, GSR-3, and JB-3 are all appropriate reference materials for monitoring the Sr-Nd-Hf analysis of leached and unleached basaltic rocks. BHVO-2 and JB-3 are good reference materials for controlling the quality of Pb isotopic measurements of leached basalts, whereas BE-N, BIR-1, and GSR-3

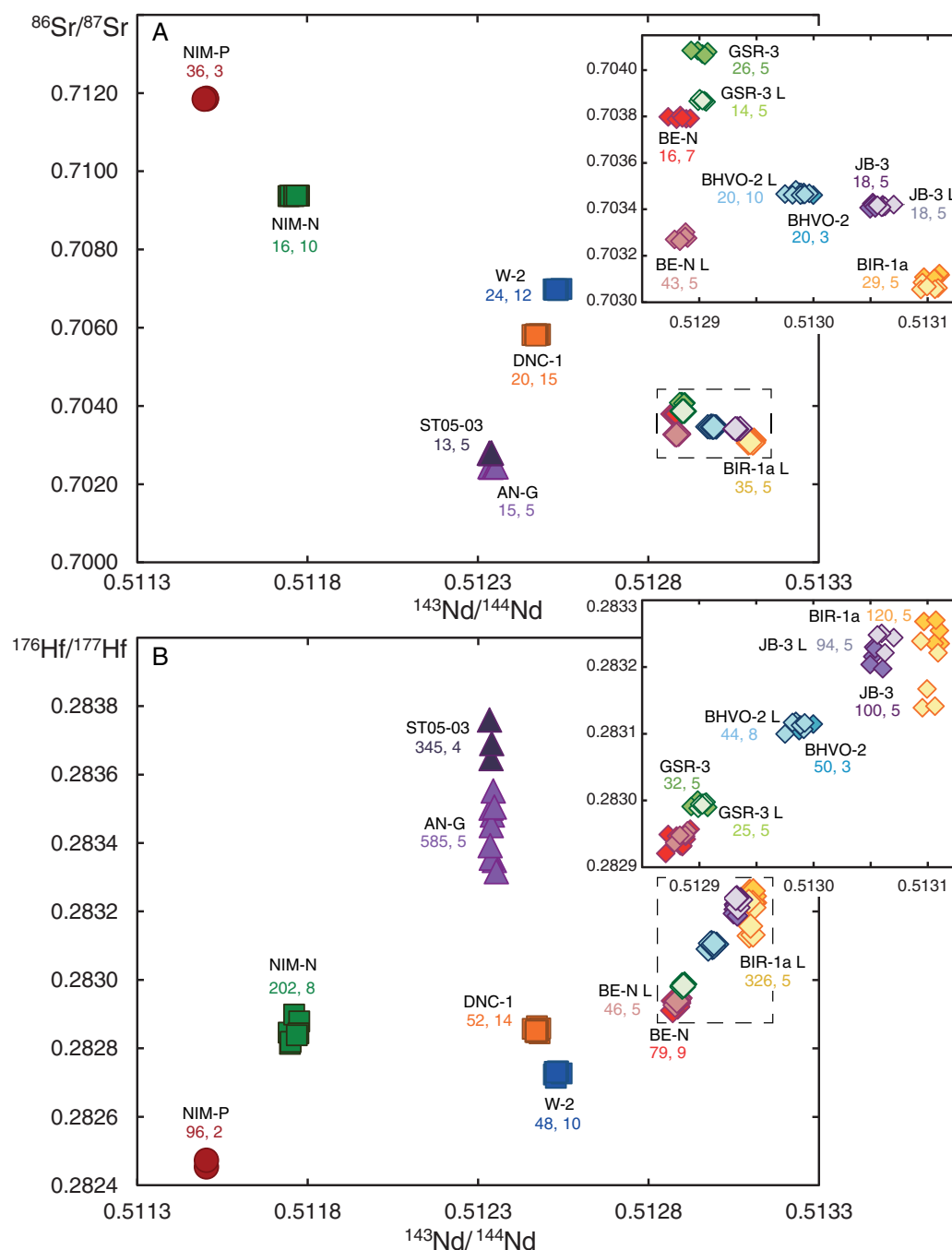


Figure 10. Comparison of the Sr-Nd-Hf isotopic variation in mafic-ultramafic rock reference materials. A. $^{86}\text{Sr}/^{87}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$, B. $^{176}\text{Hf}/^{177}\text{Hf}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$. The insets highlight the basaltic reference materials; the dashed boxes in the main figures correspond to the areas covered by the insets. Numbers below the reference material names are the reproducibility in ppm (2SD) and the number of duplicates for (a) Sr and (b) Hf. Error bars are smaller than the symbols.

are better suited for unleached basaltic samples (Tables 9 and 10; Figures 9 and 10). These recommendations apply to the use of these basaltic standards as glasses for Pb isotopic analyses by laser-ablation-(MC)-ICP-MS; the BHVO-2 powder should be leached before being used to make a glass standard. BE-N, which has the second highest MgO content (13.2 wt%) in this study, is recommended for monitoring the quality of Pb isotopic analyses of ultramafic rocks; NIM-P is not appropriate due to its heterogeneity in Pb isotopic ratios. For the same reason, DNC-1 and W-2 are recommended for the Pb and Hf isotopic analysis of plagioclase-rich rocks rather than AN-G and ST05-03.

Table 11. Recommended Reference Materials for Mafic-Ultramafic Rocks

Reference Material	Rock Type	Appropriate for	Isotopic system ^{a,b}			
			Pb	Hf	Nd	Sr
NIM-P	Pyroxenite	Ultramafic rocks	N	Y	Y	Y
BE-N	Melilite-bearing Nephelinite	Basaltic rocks ^c , ultramafic rocks	Y	Y	Y	Y
DNC-1	Dolerite	Gabbroic rocks, plagioclase-rich rocks ^d	Y	~ ^d	Y	Y
BIR-1a	Olivine Tholeiite	Basaltic rocks ^c	Y	N	Y	Y
GSR-3	Olivine Basalt	Basaltic rocks ^c	Y	Y	Y	Y
NIM-N	Norite	Gabbroic rocks	N	N	Y	Y
BHVO-2	Basalt	Basaltic rocks ^c	Y	Y	Y	Y
W-2	Diabase	Gabbroic rocks, plagioclase-rich rocks	Y	Y	Y	Y
JB-3	High-alumina Basalt	Basaltic rocks ^c	Y	Y	Y	Y
ST05-03	Leucogabbro	Plagioclase-rich rocks	N	N	Y	Y
AN-G	Anorthosite	Plagioclase-rich rocks	N	N	Y	Y

^aY = "Yes, recommended," based on the good reproducibility of the materials with respect to this isotopic system.

^bN = "No, not recommended," based on the poor reproducibility of the materials with respect to this isotopic system.

^cSee text for precision regarding recommendation for leaching.

^dDNC-1 has good reproducibility (48 ppm, n = 10), however the average $^{176}\text{Hf}/^{177}\text{Hf}$ of this study is significantly different than that reported by *Le Fèvre and Pin* [2001].

6. Conclusions

This study provides a complete data set of trace element concentrations and Pb-Sr-Nd-Hf isotopic compositions for 10 mafic-ultramafic rock reference materials. Five volcanic reference materials (BE-N, BIR-1a, GSR-3, BHVO-2, JB-3), which range from nephelinite to high-alumina basalt, present excellent reproducibility for most of the trace elements and isotopic ratios. The analytical accuracy of unleached basalts can be monitored with BE-N, BIR-1a, and GSR-3, which have homogeneous isotopic compositions. Leaching experiments reproducibly remove trace elements, but cannot always resolve Pb isotopic heterogeneity. Leached BHVO-2 and JB-3 are now characterized for all four radiogenic isotopic systems and they can be used for quality control during the isotopic analysis of leached basalts. For mafic-ultramafic plutonic reference materials ranging from pyroxenite to anorthosite (NIM-P, DNC-1, NIM-N, W-2, AN-G), this study provides many new isotopic results. W-2 and DNC-1 are both adequate reference materials for the analysis of Pb-Sr-Hf-Nd isotopic ratios of gabbroic samples. NIM-P and NIM-N are suitable ultramafic and gabbroic reference materials, respectively, for Sr-Nd-Hf isotopic analysis, and the plagioclase-rich AN-G for Nd and Sr isotopic values. Due to the heterogeneous Pb and Hf isotopic compositions of AN-G, NIM-N, and NIM-P, we recommend the use of W-2 or DNC-1 for plagioclase-rich rocks and BE-N for ultramafic rocks for these two isotopic systems. These reference materials will be useful for future Pb-Sr-Nd-Hf isotopic investigations of mafic-ultramafic rocks in volcanic (e.g., mid-ocean ridge basalt, ocean island basalt, arc basalt, continental flood basalt, lunar mare basalt) and plutonic (e.g., lower oceanic crust, ophiolites, mantle xenoliths, layered intrusions, anorthosite complexes, lunar ferroan anorthosite) settings.

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