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MPI-DING reference glasses for in situ microanalysis: New reference values for element concentrations and isotope ratios

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[1] We present new analytical data of major and trace elements for the geological MPI-DING glasses KL2-G, ML3B-G, StHs6/80-G, GOR128-G, GOR132-G, BM90/21-G, T1-G, and ATHO-G. Different analytical methods were used to obtain a large spectrum of major and trace element data, in particular, EPMA, SIMS, LA-ICPMS, and isotope dilution by TIMS and ICPMS. Altogether, more than 60 qualified geochemical laboratories worldwide contributed to the analyses, allowing us to present new reference and information values and their uncertainties (at 95% confidence level) for up to 74 elements. We complied with the recommendations for the certification of geological reference materials by the International Association of Geoanalysts (IAG). The reference values were derived from the results of 16 independent techniques, including definitive (isotope dilution) and comparative bulk (e.g., INAA, ICPMS, SSMS) and microanalytical (e.g., LA-ICPMS, SIMS, EPMA) methods. Agreement between two or more independent methods and the use of definitive methods provided traceability to the fullest extent possible. We also present new and recently published data for the isotopic compositions of H, B, Li, O, Ca, Sr, Nd, Hf, and Pb. The results were mainly obtained by high-precision bulk techniques, such as TIMS and MC-ICPMS. In addition, LA-ICPMS and SIMS isotope data of B, Li, and Pb are presented.

Components: 20,195 words, 5 figures, 21 tables, 1 dataset.

Keywords: MPI-DING glasses; reference values; isotopes; in situ microanalysis.

Index Terms: 1040 Geochemistry: Radiogenic isotope geochemistry; 1065 Geochemistry: Major and trace element geochemistry; 1094 Geochemistry: Instruments and techniques.

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1. Introduction

[2] Jochum et al. [2000] prepared eight geological (MPI-DING) glasses of different natural composi-

tion for the purpose of providing reference materials for geochemical, in situ microanalytical work. The samples cover the entire spectrum from ultramafic to highly siliceous composition and comprise

Table 1. Abbreviations of Analytical Techniques

Abbreviation	Analytical Technique
EPMA	electron probe microanalysis
FTIR	Fourier transform infrared spectroscopy
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICPMS	inductively coupled plasma mass spectrometry
ID	isotope dilution
ID-ICPMS	isotope dilution by inductively coupled plasma mass spectrometry
ID-MC-ICPMS	isotope dilution by multiple collector - inductively coupled plasma mass spectrometry
ID-MIC-SSMS	isotope dilution by multiple ion counting - spark source mass spectrometry
ID-SSMS	isotope dilution by spark source mass spectrometry
ID-TIMS	isotope dilution by thermal ionization mass spectrometry
INAA	instrumental neutron activation analysis
LA-ICPMS	laser ablation - inductively coupled plasma mass spectrometry
LA-MC-ICPMS	laser ablation - multiple collector - inductively coupled plasma mass spectrometry
LIMS	laser plasma ionization mass spectrometry
MC-ICPMS	multiple collector - inductively coupled plasma mass spectrometry
MIC-SSMS	multiple ion counting - spark source mass spectrometry
MS	mass spectrometry
PIXE	proton induced X-ray emission
SIMS	secondary ionization mass spectrometry
SR-XRF	synchrotron radiation induced X-ray fluorescence
SSMS	spark source mass spectrometry
TIMS	thermal ionization mass spectrometry
TOF-SIMS	time of flight - secondary ionization mass spectrometry
XRF	X-ray fluorescence

two basalts (KL2-G, ML3B-G), an andesite (StHS6/80-G), two komatiites (GOR128-G, GOR132-G), a peridotite (BM90/21-G), a rhyolite (ATHO-G) and a quartz-diorite (T1-G). They were analyzed by different bulk and microanalytical methods in various laboratories to obtain preliminary reference values for more than 60 elements. In this paper, numerous abbreviations referring to analytical techniques are used. Table 1 gives an explanation for readers not familiar with these abbreviations.

[3] The MPI-DING glasses found broad acceptance in microanalytical laboratories. Most laboratories use them for calibration of their microanalytical techniques. The komatiite glass GOR132-G was the external reference material for the determination of rare-earth element concentrations in clinopyroxene by SIMS [Hellebrand *et al.*, 2001, 2002; Hellebrand and Snow, 2003; Rankenburg *et al.*, 2004]. Other MPI-DING glasses were also used for calibration of SIMS instruments [Kelley *et al.*, 2003; Johnston and Schwab, 2004; Kita *et al.*, 2004]. The samples were used as reference materials for B, Al and Mg analyses of extraterrestrial materials by SIMS, EPMA and ICPMS [Hoppe *et al.*, 2001; Mostefaoui *et al.*, 2002]. EPMA major element data of mid-ocean ridge basalts and glass shards have been calibrated with MPI-DING glasses by Grevemeyer *et al.* [2002], Horz *et al.*

[2004], and Klein *et al.* [2004]. The accuracy of microscopic synchrotron induced XRF (μ SR-XRF) was verified by analyzing a series of MPI-DING glasses [Smit *et al.*, 2004]. Data accuracy and precision of LA-ICPMS were monitored by analyses of StHS6/80-G [Straub *et al.*, 2004]. Quantification of LA-ICPMS measurements of impurities in glass fibers was performed using the basalt glasses KL2-G and ML3B-G for calibration [Becker *et al.*, 2002].

[4] Some laboratories also use the MPI-DING glasses for their fundamental research in microanalysis. Kempenaers *et al.* [2003] investigated the degree of micro-heterogeneity of some MPI-DING glasses using μ -SR-XRF. Rodushkin *et al.* [2002], Becker *et al.* [2002], and Stoll *et al.* [2003] investigated the matrix-dependent response variations in LA-ICPMS. The potential for high lateral resolution analyses when using sector field instruments for direct sampling was demonstrated with GOR128-G by Latkoczy and Günther [2002].

[5] Since the publication of Jochum *et al.* [2000] many laboratories have provided new major element and trace element data of the MPI-DING glasses. Because there is also an increasing need for isotopic information, the determination of the isotopic composition of stable and radiogenic iso-

topes in the reference glasses is now in progress. Some of these new trace element and isotope results have been recently published, e.g., *Becker et al.* [2000]; *Guillong et al.* [2002]; *Weyer et al.* [2002]; *Raczek et al.* [2003]; *Canil et al.* [2003]; *Badanina et al.* [2004]; *Liu and O'Neill* [2004]; *Villaseca et al.* [2003]; *Willbold and Jochum* [2005]; *Rosner and Meixner* [2004]; and *Jochum et al.* [2005a, 2005b].

[6] Twenty-five laboratories were involved to establish preliminary reference values for about 60 major and trace elements of the MPI-DING glasses [*Jochum et al.*, 2000]. The concentration values for many elements were well established (e.g., major elements, Sr, Ba, rare earth elements (REE)), others (e.g., Cl, Bi, As, Se, Br) were only for information because of the few analytical data available. For some elements (S, Tl, F) no data existed.

[7] During the last five years many new laboratories were invited to analyze the glasses, mainly using EPMA for major elements, and isotope dilution mass spectrometry, SIMS, ICPMS and LA-ICPMS for trace elements.

[8] The aim of this paper is to present new trace and major element results of the MPI-DING glasses, to determine reference values and their uncertainties by following the IAG recommendations for certification of geological reference materials [*Kane et al.*, 2003] and to present new results of the isotopic compositions of H, B, Li, O, Ca, Sr, Nd, Hf and Pb. All data given in this publication can also be found in the GeoReM database (<http://georem.mpch-mainz.gwdg.de>).

2. Analytical Techniques

2.1. Major and Trace Elements

[9] In the following, procedures and most important features of the techniques used in this paper are described briefly. Table 2 lists the codes (C) identifying laboratories, analysts and techniques. Descriptions of the techniques for C = 1–27 have been published earlier by *Jochum et al.* [2000].

2.1.1. Electron Probe Microanalysis (EPMA)

[10] This technique was used by 14 laboratories to provide data for the major element compositions of the MPI-DING glasses. Table 3 lists a compilation of the analytical details of the electron microprobe analyses of this work, *Jochum et al.* [2000], and

two recent publications [*Liu and O'Neill*, 2004; *Badanina et al.*, 2004].

2.1.2. Isotope Dilution by Thermal Ionization Mass Spectrometry (ID-TIMS)

[11] The abundances of Pb, Th and U in the Hawaiian basalt glasses KL2-G and ML3B-G were determined at USGS Denver (C = 53) by isotope dilution using a thermal ionization mass spectrometer.

[12] The glasses were crushed in stainless steel mortar and pestle. Fractions for analysis were transferred to a PFA Teflon vial for dissolution in ultra-pure conc. HF + HNO₃, and heated. Later on they were spiked with a mixed ²³³U-²³⁶U-²³⁰Th-²⁰⁵Pb tracer solution and again heated to achieve equilibration. Lead was separated first using an anion exchange column in an HBr solution and then U and Th in an HNO₃ solution. Analytical blanks for the procedure ranged from 1 to 4 pg each for total U and Th, and were 37 pg for total Pb. Isotopic compositions of U-Th-Pb were measured on a VG Isomass 54R equipped with an ion counting system and the data acquisition ANALYST programming of *Ludwig* [1994], and reduced using PBDAT programming [*Ludwig*, 1993].

2.1.3. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

[13] At the GeoForschungsZentrum Potsdam (C = 33) boron concentrations of three MPI-DING glasses were determined by ICP-AES using a Varian Liberty 200 instrument. Between 260 mg and 130 mg of the powdered glass reference materials were fluxed with K₂CO₃ and boron was chemically separated by cation exchange chromatography using AG 50W-X8 resin as described by *Kasemann et al.* [2001]. The boron recovery for the entire chemical procedure was 95%. Calibration was typically made using a 1 µg ml⁻¹ boron standard solution in 0.05 M HCl. To guarantee precise and reproducible analytical results the boron concentrations in the sample solution were kept between 0.1 and 1 µg g⁻¹.

2.1.4. Inductively Coupled Plasma Mass Spectrometry (ICPMS)

[14] The MPI-DING glasses were cleaned in an ultrasonic bath with deionized water, digested in HF, evaporated to dryness, and consecutively dissolved in aqua regia and HClO₄ before being taken up in 2% HNO₃. The solutions were then analyzed using the upgraded VG PlasmaQuad ICPMS at the

Table 2. Institutions Involved in the Characterization Process of the MPI-DING Reference Glasses^a

C	Institution	Location	Method	Analysts/Reference
1	Max-Planck-Institut für Chemie	Mainz, Germany	(ID)-SSMS	Jochum
2	Max-Planck-Institut für Chemie	Mainz, Germany	(ID)-MIC-SSMS	Stoll, Jochum
3	Max-Planck-Institut für Chemie	Mainz, Germany	LIMS	Seufert, Jochum
4	Max-Planck-Institut für Chemie	Mainz, Germany	ID-TIMS	Raczek
5	Max-Planck-Institut für Chemie	Mainz, Germany	INAA	Spettel
6	Max-Planck-Institut für Chemie	Mainz, Germany	SIMS	Besmehn, Hellebrand, Hoppe
7a	Universität Mainz	Mainz, Germany	EPMA	Jochum
7b	Universität Mainz	Mainz, Germany	XRF	Jochum
8	Universität zu Köln	Köln, Germany	INAA	Weckwerth
9	Universität zu Köln	Köln, Germany	EPMA	Klein
10	Universität zu Köln	Köln, Germany	ICP-AES	Klein et al.
11	Universität zu Köln	Köln, Germany	XRF	Wolf
12	Memorial University of Newfoundland	St. John's, Canada	LA-ICPMS	Jenner
13	Institute of Microelectronics	Yaroslavl, Russia	SIMS	Nikogosian, Simakin, Sobolev
14	Max-Planck-Institut für Kernphysik	Heidelberg, Germany	PIXE	Maetz, Wallianos
15	Forschungszentrum Jülich	Jülich, Germany	LA-ICPMS	Becker, Dietze, Pickhardt
16	Harvard University	Cambridge, USA	LA-ICPMS	Horn, McDonough
17	Harvard University	Cambridge, USA	LA-ICPMS	Horn, McDonough, Straub
18	Hasylab (DESY)	Hamburg, Germany	SR-XRF	Amort et al.
19	Hasylab (DESY)	Hamburg, Germany	SR-XRF	Vincze, Janssens, Amort et al.
20	Hasylab (DESY)	Hamburg, Germany	SR-XRF	Vincze, Janssens, Radtke et al.
21	Hasylab (DESY)	Hamburg, Germany	SR-XRF	Bessette, Haller, Janssens, Jochum, Radtke, Vincze
22a	Universität Heidelberg	Heidelberg, Germany	EPMA	Rocholl, Meier, Ludwig
22b	Universität Heidelberg	Heidelberg, Germany	SIMS	Rocholl, Meier, Ludwig
23	GeoForschungsZentrum Potsdam	Potsdam, Germany	ICPMS (ELAN)	Dulski
24	GeoForschungsZentrum Potsdam	Potsdam, Germany	ICPMS (VG)	Erzinger, Zimmer
25	American Museum of Natural History	New York, USA	EPMA	Mandeville, Straub
26	Universität Münster (Zentrallab. für Geochr.)	Münster, Germany	(ID)-MC-ICPMS	Weyer, Munker, Mezger
27	GeoForschungsZentrum Potsdam	Potsdam, Germany	EPMA	Rocholl, Rhede, Appelt
28	University of Utah	Salt Lake City, USA	EPMA	Nash
29	Max-Planck-Institut für Chemie	Mainz, Germany	TIMS	Pfänder, Amini, Abouchami
30	Max-Planck-Institut für Chemie	Mainz, Germany	TIMS	Raczek et al. [2003]
31	Universität Tübingen	Tübingen, Germany	MS	Vennemann
32	Universität Frankfurt	Frankfurt, Germany	EPMA	Höfer
33	GeoForschungsZentrum Potsdam	Potsdam, Germany	TIMS	Rosner and Meixner [2004]
34	Universität Mainz	Mainz, Germany	EPMA	Amini
35	Max-Planck-Institut für Chemie	Mainz, Germany	(ID)-ICPMS	Willbold
36	Los Alamos National Laboratory	Los Alamos, USA	LA-ICPMS	Wayne
37	ETH Höngrgerberg	Zürich, Switzerland	LA-ICPMS (ELAN)	Guillong et al. [2002]
38	University of Victoria	Victoria, Canada	LA-ICPMS	Canil et al. [2003]
39	Council for Geoscience	Pretoria, South Africa	EPMA	de Bruin
40a	Universität Kiel	Kiel, Germany	EPMA	Horz
40b	Universität Kiel	Kiel, Germany	ICPMS	Horz

Table 2. (continued)

C	Institution	Location	Method	Analysts/Reference
41	Geomar, Kiel	Kiel, Germany	EPMA	Horz
42	Monash University	Clayton, Australia	LA-ICPMS	Aarburg
43	Open University	Milton Keynes, U.K.	LA-ICPMS	Alard
44	Gothenburg University	Göteborg, Sweden	LA-ICPMS	de Hoog, Cornell
45	ETH Höngrgerberg	Zürich, Switzerland	LA-ICPMS(ELEMENT2)	Günther, Guillon, Latkoczy
46	ETH Höngrgerberg	Zürich, Switzerland	LA-ICPMS (ELAN)	Günther, Guillon, Latkoczy
47	Max-Planck-Institut für Chemie	Mainz, Germany	LA-ICPMS	Stoll, Jochum
48	Max-Planck-Institut für Chemie	Mainz, Germany	(ID)-ICPMS	Willbold <i>et al.</i> [2003]
49	Max-Planck-Institut für Chemie	Mainz, Germany	EPMA	Amini
50	University of Melbourne	Melbourne, Australia	EPMA	Aarburg
51	Universität Frankfurt	Frankfurt, Germany	LA-ICPMS	Lahaye
52	Utrecht University	Utrecht, The Netherlands	LA-ICPMS	Mason
53	USGS Denver	Denver, USA	ID-TIMS	Misawa, Premo
54	Bundeskriminalamt	Wiesbaden, Germany	LA-ICPMS	Becker, Dücking
55	Oregon State University	Corvallis, USA	LA-ICPMS	Kent
56	C.N.R.-I.G.G.-Sezione di Pavia	Pavia, Italy	LA-ICPMS (213 nm laser)	Tiepolo, Vannucci
57	C.N.R.-I.G.G.-Sezione di Pavia	Pavia, Italy	LA-ICPMS (266 nm laser)	Tiepolo, Vannucci
58	Max-Planck-Institut für Chemie	Mainz, Germany	LA-ICPMS	Sun
59	Universität Würzburg	Würzburg, Germany	LA-ICPMS	Brätz, Kleind
60	University of Tasmania	Hobart, Australia	LA-ICPMS	Danyushevsky
61	Royal Canadian Mounted Police	Ottawa, Canada	LA-ICPMS	Dalpé
62	Universität Greifswald	Greifswald, Germany	LA-ICPMS	Jacob
63	Max-Planck-Institut für Chemie	Mainz, Germany	EPMA	Stoll, Herwig, Groschopf
64	The University of Melbourne	Melbourne, Australia	MC-ICPMS	Woodhead
65	University of Huelva	Huelva, Spain	LA-ICPMS	Villaseca <i>et al.</i> [2003]
66	Max-Planck-Institut für Chemie	Mainz, Germany	(ID)-ICPMS	Willbold und Jochum [2005]
67	Max-Planck-Institut für Chemie	Mainz, Germany	LA-ICPMS	Stoll, Herwig (Jochum <i>et al.</i> , submitted manuscript, 2005)
68	Australian National University	Canberra, Australia	EPMA	Liu and O'Neill [2004]
69	Forschungszentrum Jülich	Jülich, Germany	LA-ICPMS	Becker <i>et al.</i> [2000]
70	Max-Planck-Institut für Chemie	Mainz, Germany	ICPMS	Willbold, Jochum <i>et al.</i> [2005b]
71	University of Edinburgh	Edinburgh, U.K.	SIMS	Kasemann
72	Max-Planck-Institut für Chemie	Mainz, Germany	LA-ICPMS	Jochum, Stoll, Herwig, Jochum <i>et al.</i> [2005b]
73	Forschungszentrum Jülich	Jülich, Germany	LA-ICPMS	Becker and Dietze [1999]
74	Universität Münster (Zentrallab. für Geochr.)	Münster, Germany	ID-MC-ICPMS	Weyer <i>et al.</i> [2002]
75	Max-Planck-Institut für Chemie	Mainz, Germany	MC-ICPMS	Stracke
76	Thermo Electron	Bremen, Germany	LA-ICPMS	Tiepolo, Boumann
77	Universität Heidelberg	Heidelberg, Germany	SIMS	Zack, Ludwig
78	GeoForschungsZentrum Potsdam	Potsdam, Germany	EPMA	Badanina <i>et al.</i> [2004]
79	Max-Planck-Institut für Chemie	Mainz, Germany	SIMS	Hellebrand <i>et al.</i> [2002], Moeck, Hellebrand
80	Leibniz-Institut für Meereswissenschaften, IFM-GEOMAR	Kiel, Germany	TIMS	Amini, Eisenhauer
81	Carnegie Institution of Washington, Dep. of Terrestrial Magnetism	Washington, USA	SIMS	Hauri
82	Max-Planck-Institut für Chemie	Mainz, Germany	MC-ICPMS	Gao, Snow

^aCode (C) refers to the institute and analysts who provided data for the MPI-DING glasses. The table also contains references for published data. Analytical data for C = 1–27 are published by Jochum *et al.* [2000].

Table 3. Analytical Details of EPMA Analyses

Laboratory	Code C	Electron Microprobe	Accelerating Voltage, kV	Beam Current, nA	Beam Diameter, μm	Counting Time, s	Calibration	Calculation	Additional Information	Number of Analyses per Sample	Reference
University of Utah	28	Cameca SX-50	15	25	20 (defocused)	10 (Na), 20–25 (other elements)	natural obsidian (O, Si, Al, K), natural minerals and synthetic oxides for the other elements	algorithm of <i>Pouchou</i> and <i>Pichoir</i> [1991]	obsidian and unknowns were coated with C simultaneously to assure an equivalent thickness of the C coating [<i>Nash</i> , 1992]	10	this work
Universität Kiel	40a	Cameca Camebax SX	15	12.5	5–10 (defocused)	20 (peaks)–10 (background)	internal synthetic reference materials			3–25	this work
Geomar Kiel	41	Cameca SX-50	15	12.5	5 to 10 (defocused)	20 (peaks)–10 (background)	internal synthetic reference materials			18	this work
Universität Frankfurt	32	JEOL Superprobe JXA 8900RL	20	20	10 (defocused)	20–40	natural and synthetic JEOL silicate and oxide reference samples	PRZ matrix correction with CITZAF [<i>Armstrong</i> , 1991]	reproducibility <1% RSD for all elements at oxide conc. >1% m/m except for Na (about 2% RSD)	11–23	this work
Universität Mainz	34	JEOL JXA 8900 RL	15	12	10 (defocused)	15–20	mineral reference materials	PRZ routine		3	this work and <i>Amini</i> [2003]
Max-Planck- Institut Mainz	49, 63	JEOL JXA 8200	15	12	5–10	15–40	VG-2 glass from Smithsonian Institution, mineral reference materials from P & H Developments	ZAF procedure		3–5	this work and <i>Amini</i> [2003]
University of Melbourne	50	Cameca SX-50	15	10	10–15	5 (Na, Cl), 10 (other elements)	natural minerals, metals and metal oxides	ZAF procedure		53	this work

Table 3. (continued)

Laboratory	Code C	Electron Microprobe	Accelerating Voltage, kV	Beam Current, nA	Beam Diameter, μm	Counting Time, s	Calibration	Calculation	Additional Information	Number of Analyses per Sample	Reference
Council for Geoscience	39	JEOL 733	15	20	10	10	Kakanau- Hornblende, Tiebaghi Mine-Chromite, Rutile and Rhodonite supplied by <i>Jarosewich et al.</i> [1980] and Boyd (Carnegie, unpublished) large number of reference materials	online Fortran program, supplied by JEOL, (FZAFOC)		15	this work
Australian National University	68	Cameca/ JEOL 6400	15	1	1–10			ZAF procedure		56–71	<i>Liu and O'Neill</i> [2004]
GeoForschungs- Zentrum Potsdam	78, 27	Cameca SX-100	15	20	10–40	20	synthetic oxides and natural minerals mineral reference materials	data reduction used the PAP scheme		20–50	<i>Badanina et al.</i> [2004]; <i>Jochum et al.</i> [2000]
Universität Heidelberg	22a	Cameca SX-51	15	20	5–10	10	reference materials			60–100	<i>Jochum et al.</i> [2000]
Universität Mainz	7a	Cameca Camebax	15	12	5	20	11 mineral reference materials	algorithm of <i>Pouchou and Pichoir</i> [1991]		3–10	<i>Jochum et al.</i> [2000]
Universität zu Köln	9	JEOL JXA-8900	15	15	10 (defocused)		mineral reference materials distributed by P & H Developments	ZAF procedure		5	<i>Jochum et al.</i> [2000]
American Museum of National History	25	Cameca SX-100	15	2(Na) – 10 (other elements)	20 (defocused)	20–40	mineral reference materials	ZAF data reductions were carried out by means of the in-built PAP routine.		25	<i>Jochum et al.</i> [2000]

University of Kiel ($C = 40$) following the procedure outlined by *Garbe-Schönberg* [1993]. Various standard solutions were used for calibration. Accuracy was checked against international reference materials [*Govindaraju*, 1994] and was generally better than 5%.

2.1.5. Multiple Collector–ICPMS (MC-ICPMS)

[15] Lithium concentrations were determined at the Max-Planck-Institut für Chemie, Mainz ($C = 82$) by standard bracketing on a Nu Instruments multi-collector ICP-MS following standard separation techniques [*Jeffcoate et al.*, 2004] (cf. description of isotope methods, this study). The lithium recovery was near 100%. Estimated accuracy based on analysis of reference materials is better than 10%.

2.1.6. Multielement Isotope Dilution by Inductively Coupled Plasma-Mass Spectrometry (ID-ICPMS)

[16] High-precision measurements were performed at the Max-Planck-Institut für Chemie Mainz ($C = 35, 48, 66$) using a recently developed multielement isotope dilution ID-ICPMS method [*Willbold et al.*, 2003; *Willbold and Jochum*, 2005]. After the addition of multielement spike solutions, about 100 mg of the samples were dissolved using HF and HNO₃. To correct for mass discrimination effect during measurement a Ru-Re solution was added. The measurements were carried out on a ThermoFinnigan Element 2 double-focusing sector field mass spectrometer. Interferences of polyatomic ions have been avoided by using the high resolution mode of this instrument. Concentrations of 12 trace elements were determined by ID and the overall analytical uncertainty for the ID data is 1–2%. The ID-determined trace elements were used as internal standards for the determination of further 14 (mainly mono-isotopic) trace elements by external calibration by using relative sensitivity factors. The combined standard uncertainty for these data is about 2–3%. ID-ICPMS data for BCR-1, BHVO-1, OU-6, NIST SRM 612 agree with the reference values within about 3% [*Willbold and Jochum*, 2005].

2.1.7. Isotope Dilution by Multiple Collector-ICPMS (ID-MC-ICPMS)

[17] New precise and accurate isotope dilution data for Hf and Ta have been published by *Weyer et al.* [2002]. Analyses were performed on a Micromass Isoprobe MC-ICP mass spectrometer in the Zentral-

labor für Geochronologie, Universität Münster, Germany ($C = 74$). Uncertainties are about 1% for Hf and 3–5% for Ta depending on the concentration.

2.1.8. Secondary Ionization Mass Spectrometry (SIMS)

[18] Lithium concentrations were determined at the University of Edinburgh ($C = 71$) using the Cameca ims 4f ion microprobe. Analytical details are given in section 3.3. Measured lithium concentration was normalized to the NIST SRM 610 reference material using the recommended values from *Pearce et al.* [1997]. The analytical uncertainty for Li determination is less than 5%.

[19] Li, Be and B concentrations were determined at the Universität Heidelberg ($C = 77$) using a Cameca ims 3f secondary ion mass spectrometer. The procedure of *Marschall and Ludwig* [2004] was followed for this study in order to minimize the influence of surface contamination. Analyses were performed using a 14.5 keV/30 nA ¹⁶O[−] primary ion beam. Positive secondary ions were nominally accelerated to 4.5 keV (energy window set to 40 eV) and an energy filtering technique with an offset of 75 eV at $m/\Delta m$ (10%) of ca. 1000 was used. Secondary ion intensities were collected using a 750- μ m field aperture (translating to an imaged field of ca. 15 μ m on the sample surface). Count rates for ⁷Li, ⁹Be and ¹¹B were normalized to the count rate of ³⁰Si. Relative ion yields were calibrated with the NIST SRM 610 glass using the *Pearce et al.* [1997] recommended values. Five spots of the four analyzed MPI-DING glasses were measured. The overall uncertainty is dominated by possible matrix effects [*Ottolini et al.*, 1993].

[20] H₂O, CO₂, F, S and Cl concentrations were determined at the Carnegie Institution of Washington ($C = 81$) using a Cameca IMS6F ion probe, following the methods described by *Hauri et al.* [2002] and *Koga et al.* [2003]. A primary beam of 8 nA Cs⁺ ions was used and negative secondary ions were analyzed at 5 keV (± 50 eV) at a mass resolving power of 2400 (10% definition) with electron-gun charge compensation and no energy filtering. Glass grains were mounted into indium inside an Al-metal disk, and the operating vacuum was 7×10^{-10} torr or better. A single mm-sized grain of each glass was analyzed five times, and the average and reproducibility of the five analyses is reported. Detection limits for the analytical session were 0.0016% m/m H₂O, <3 μ g/g CO₂, and <0.5 μ g/g F, S and Cl as determined by multiple analyses of a synthetic forsterite with 0.00004%

m/m H₂O (see Koga *et al.* [2003] for details). Multiple analyses of ultra-pure Herasil SiO₂ glass gave similar detection limits except for H₂O (0.0088% m/m) and Cl (0.8 µg/g) which are real concentrations resolved from the detection limits. Calibration drift was non-existent, as monitored by interspersed analyses of MORB glass ALV519-4-1 (n = 14); this glass gave concentrations of 0.224% m/m H₂O (±11% 2σ), 143 µg/g CO₂ (±3.2% 2σ), 113 µg/g F (±3.7% 2σ), 831 µg/g S (±5% 2σ) and 43.8 µg/g Cl (±5.7% 2σ). This level of reproducibility is typical for most glasses, including the MPI-DING glasses measured in this study. During our analytical session, we also obtained data for the NIST glasses SRM610 (0.0127% m/m H₂O, 2.2 µg/g CO₂, 413 µg/g F, 693 µg/g S, 438 µg/g Cl), SRM 612 (0.021% m/m H₂O, 2.8 µg/g CO₂, 62 µg/g F, 350 µg/g S, 131 µg/g Cl) and SRM614 (0.0186% m/m H₂O, 4.0 µg/g CO₂, 10 µg/g F, 306 µg/g S, 92 µg/g Cl) with 2σ reproducibilities from 1% to 7%.

[21] For H₂O and CO₂, the SIMS calibration utilized reference glasses whose H₂O contents were determined by both manometry and FTIR. Concentrations of F, S and Cl in reference glasses were determined by EPMA from multiple laboratories. Interlaboratory biases have been examined and eliminated for all SIMS calibration materials. Considering possible matrix effects and errors on calibration slopes, we determine that the combined uncertainties (reproducibility and accuracy) are 15% for H₂O and 10% for CO₂, F, S and Cl.

[22] Some SIMS trace element data of the MPI-DING glasses have been determined using an upgraded Cameca ims-3f ion microprobe at the Max-Planck-Institut für Chemie Mainz (C = 79).

2.1.9. Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)

[23] This method was used in many different laboratories for multielement analyses of the MPI-DING glasses. Altogether 23 LA-ICPMS laboratories were involved in the trace element investigations using different laser ablation systems (266 nm, 213 nm Nd:YAG, and 193 nm ArF excimer lasers) and ICP mass spectrometers (quadrupole, sector field instruments). Table 4 lists the instruments and analytical conditions used in the different laboratories.

2.2. Isotopic Analyses

[24] Different laboratories provided data of the isotopic compositions of H, Li, B, O, Ca, Sr, Nd, Hf and Pb. The results were obtained from high

precision techniques using large sample amounts and from microanalytical techniques.

2.2.1. Hydrogen Isotope and Water Analyses

[25] At the University of Tübingen (C = 31) the water content and hydrogen isotope composition of the MPI-DING glasses StHs6/80-G and T1-G were measured according to a method adapted after the conventional method of *Vennemann and O'Neil* [1993]. Prior to the extraction of water, about 300 to 450 mg of the samples were degassed in a high vacuum (<10⁻⁶ mbar) at 110°C for about 24 hours. Water was extracted by heating the samples to about 800°C (just below the melting point to help facilitate the diffusion of water out of the glass) and held at that temperature for one hour. Thereafter, any remaining water was extracted by melting the sample at temperatures in excess of 1400°C.

[26] Zinc has been used for the quantitative conversion of H₂O to H₂. The product H₂ was analyzed for its isotope composition with a Finnigan MAT 252 mass spectrometer. The reference gas was calibrated using VSMOW (Vienna Standard Mean Ocean Water) and SLAP (Standard Light Antarctic Precipitation). On the basis of replicate analyses of reference materials, the isotopic analyses are precise to within 2 per mil (‰) 2SD.

[27] The quantity of H₂O was determined from calibration curves established by injection of variable amounts of an internal water standard into the same extraction line. The precision of the measurement is about ±0.1‰/m.

2.2.2. Oxygen Isotopes

[28] The oxygen isotope composition (¹⁶O, ¹⁷O, ¹⁸O) of the MPI-DING glasses were measured at the University of Tübingen (C = 31) using a method adapted after that described by *Rumble and Hoering* [1994]. Between 1 to 3 mg of sample was loaded onto a small Pt-sample holder fixed on a stainless steel block and pumped out to a vacuum of less than 10⁻⁶ mbar for a minimum of 2 hours. After prefluorination of the sample chamber with 50 mbars of F₂ overnight, the samples were heated with a 25W CO₂-laser in 50 mbars of pure F₂. Excess F₂ was separated from the O₂ produced by conversion to Cl₂ using KCl held at 150°C. The extracted O₂ was collected on a molecular sieve (13X), desorbed for distillation purposes at -100 to -110°C using an ethanol-liquid nitrogen slush trap and subsequently analyzed as O₂ on a

Table 4 (Representative Sample). Analytical Details of LA-ICPMS Analyses [The full Table 4 is available in the HTML version of this article at <http://www.g-cubed.org>]

Laboratory	Code C	Laser	Wavelength, nm	Spot Repet. Size, μm	Spot Rate, Hz	Total Energy, mJ	Energy Density, J/cm^2	Carrier Gas	Mass Spectrometer	Internal Standard	Calibration (Ref. Material, Ref. Values)	Number of Analyses per Sample	Additional Information	Reference
<i>Trace Element Analysis</i>														
Universität Frankfurt	51	New Wave Nd:YAG LUV-213	213	80	1			Ar-He mixture	Thermo-Finnigan Element 2	⁴⁴ Ca	NIST SRM 612 [Pearce et al., 1997]	mean of 5 line scans		this work
Max-Planck-Institut Mainz	47, 67	New Wave Nd:YAG UP-213	213	120	10	7		He-Ar mixture	Thermo-Finnigan Element 2 (sector field)	⁴³ Ca	NIST SRM 612 (Pearce et al. [1997] and new ID data from Willbold and Jochum [2005] and Jochum et al. (submitted manuscript, 2005c))	mean of 3–6 line and spot analyses	plasma torch conditions: ThO/Th <1–2%; accuracy tested with BCR-2G, BHVO-2G, BIR-1G [Jochum et al., 2005c]	this work and Jochum et al. (submitted manuscript, 2005)
Max-Planck-Institut Mainz	58	New Wave Nd:YAG UP-213	213	160	20	7		He-Ar mixture	Thermo-Finnigan Element 2 (sector field)	⁴³ Ca	NIST SRM 612 [Sylvester and Eggins, 1997]	mean of 3 spot analyses	det. limits of Re, Pt, Au: 0.02, 0.1, 0.2 ng/g, resp.; interfer. of YbO, HfO, TaO on Re, Pt, Au corrected [Sun et al., 2003, 2004]	this work
Los Alamos National Laboratory	36	New Wave Nd:YAG GLU 266X	266	100	20	3			Thermo-Finnigan Element 2 (sector field)	²⁸ Si	NIST SRM 610, 612, 614	mean of 7 individual analyses (beam rastering mode)	P, K, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Rb measurements in moderate resolution mode, others in low resolution mode	this work

Finnigan MAT 252 mass spectrometer. The isotopic composition of the reference gas O₂ has been determined by conversion to CO₂ using a Pt-treated graphite rod and measurement of the isotopic composition of CO₂ relative to a reference gas calibrated against VSMOW. Accuracy controls were done by analyzing NIST SRM 8546 (NBS 28) quartz.

2.2.3. Boron Isotopes

[29] Isotopic compositions of boron were determined by thermal ionization mass spectrometry (TIMS) using the Cs₂BO₂⁺-graphite method at the GeoForschungsZentrum Potsdam (C = 33). A detailed description of the whole analytical procedure has been given by *Rosner and Meixner* [2004]. Boron was extracted from the glasses by alkaline fusion with K₂CO₃ or alternatively by HF attack in the presence of mannitol. In both cases an aliquot sample solution comprising 3 µg boron was separated by sequential ion exchange chromatography. An aliquot comprising 0.5 µg boron, mixed with CsCO₂ solution (1 mol B; 2 mol cesium) and mannitol (1 µg B; 40 µg mannitol), was loaded on a degassed tantalum filament coated with a graphite/ethanol slurry and heated at 0.7 A to dryness. Isotope analyses were carried out on a static multicollector Finnigan MAT 262 mass spectrometer equipped with a special double Faraday cup having a fixed spacing for the dicesium metaborate complexes. The boron was detected as Cs₂BO₂⁺ complexes at masses 308 and 309. Running temperatures were <900°C. B-isotope ratios are reported as δ¹¹B values, i.e., normalized to the mean of concurrently measured NIST SRM 951 standard solutions:

$$\delta^{11}\text{B} = \left[\left\{ \frac{{}^{11}\text{B}}{{}^{10}\text{B}} \right\}_{\text{sample}} / \left\{ \frac{{}^{11}\text{B}}{{}^{10}\text{B}} \right\}_{\text{NIST SRM 951}} - 1 \right] * 1000.$$

Accuracy is controlled by comparison of our δ¹¹B for JB-3, JA-1 and JR-2 [*Rosner and Meixner*, 2004] with literature data. Within error (1.1% 2 SD) our δ¹¹B data overlap the literature values.

[30] The δ¹¹B signature of three MPI-DING glasses (StHs6/80-G, GOR132-G and GOR128-G) has also been determined with laser ablation-multicollector (LA-MC)-ICPMS at Thermo Electron (Bremen) GmbH, Finnigan Advanced Mass Spectrometry, Bremen, Germany (C = 76). Table 4 lists analytical details. Due to the low B content of selected samples the MC-ICPMS was equipped with multiple ion counters instead of the conventional Faraday cups. The “standard-sample-standard”

bracketing approach has been chosen to correct for isotope fractionation effects (mass bias, laser induced fractionation and ion counter drift) and in samples with B at the µg/g level, the method ensures an internal precision of around 2.5‰ (1 RSE). NIST SRM 610 was the external standard reference material and the average value for ¹¹B/¹⁰B of 4.049 [*Le Roux et al.*, 2004] was used. Details on the analytical method are reported by *Tiepolo et al.* [2005a, 2005b].

2.2.4. Lithium Isotopes

[31] Lithium isotopes were measured by MC-ICPMS and SIMS in the Mainz and Edinburgh laboratories, respectively. The data are reported in the conventional δ⁷Li notation relative to LSVEC (NIST SRM 8545).

2.2.4.1. MC-ICPMS

[32] Lithium isotopes were measured by solution MC-ICPMS at the Max-Planck Institut für Chemie (C = 82). Sufficient material (10–60 mg) from each glass was used to provide approximately 0.1–1 µg of Li. Dissolution and separation were carried out using the technique of *Jeffcoate et al.* [2004], with the difference that only a single Methanol-HNO₃ column was used, with tests of pre- and after tail to ensure complete yield. The separation of Na from Li was nonetheless quite good, with Na/Li ratios in solution in all cases less than 5. Total procedural blank was 40 pg. The Li recovery was near 100%.

[33] The solutions were diluted to 100 µg/l for measurement and introduced into the mass spectrometer using a standard CETAC ASX-100 auto-sampler connected to a CETAC Aridus desolvating nebulizer with an ESI teflon PFA microconcentric nebulizer tip. Solution uptake was nominally 50 microliter/min and 4.13 l/min Ar sweep gas. Mass spectrometry was carried out on a standard Nu Plasma double focusing multicollector ICPMS with variable dispersion ion optics. The ⁶Li and ⁷Li beams were measured in the H6 and L5 Faraday collectors at an ion current of 5–7 pA (5–7V with a 10¹² ohm resistor, 50–70V/µg/g). The zoom optics were set as follows: L1:22V; Lin1:250V; Lin2: 250V; all others zero. This provided a relative mass dispersion of 0.058. Three blocks of 10 measurements of 5 seconds each were carried out for each sample, with a 10 second background measurement between each block measured at the half mass. The measurement was followed by 60 seconds wash time in two different wash solutions. This reduced memory effects to <1 mV.

The samples were bracketed with LSVEC reference material at the same concentration. Memory effects were negligible, rising from less than 100 cps of ^7Li at the beginning of the measurement session to as much as 1 mV after an entire day of measurement.

2.2.4.2. SIMS

[34] Samples were analyzed in both lithium concentration and isotope composition, using the single collector secondary ionization mass spectrometer Cameca ims 4f (ion microprobe) at the University of Edinburgh ($C = 71$) following the method detailed by *Kasemann et al.* [2005]. Positive secondary ions of $^6\text{Li}^+$ and $^7\text{Li}^+$ were produced by a 20 nA, 15 kV, $^{16}\text{O}^-$ primary beam focused to a 25 μm spot size. The secondary ions were analyzed with an energy window of 52 eV, a 150 μm image field using the 150 μm contrast and the 1800 μm field apertures and a mass resolution of ~ 1400 . Secondary ions were counted on an electron multiplier in mono collector mode operation. To get an internal precision of $<1\%$ ($1\sigma_{\text{mean}}$), the Li-isotope ratio was measured for 100 cycles, each cycle consisting of 5 and 2 s count times on $^6\text{Li}^+$ and $^7\text{Li}^+$, respectively. Calibration to the international reference material was through BCR-2G ($\delta^7\text{Li} = 4.0 \pm 0.1\%$, 2σ (MC-ICPMS); $4.0 \pm 0.6\%$, 2σ (TIMS) [*Kasemann et al.*, 2005]) and additionally checked against GSD-1G ($\delta^7\text{Li} = 31.1 \pm 0.1\%$, 2σ (MC-ICPMS); $31.7 \pm 0.7\%$, 2σ (TIMS) [*Kasemann et al.*, 2005]) showing an internal uncertainty of 0.8% ($1\sigma_{\text{mean}}$) for a single point analysis and an external uncertainty of about 0.8% (1 SD). At least 10 lithium concentration and isotope measurements (with an average distance of 100–200 μm) were done on two different glass fragments from each sample.

2.2.5. Calcium Isotopes

[35] The Ca isotopic compositions of the MPI-DING glasses and the USGS reference materials BHVO-2 and BIR-1 were determined by thermal ionization mass spectrometry using a double spike technique at the IFM-GEOMAR, Kiel ($C = 80$). After common HF-HNO₃ dissolution, the samples were subjected to a chromatographic clean up by elution with 1.8 mol l^{-1} HCl on cation-exchange columns (BioRad) filled with MCI Gel (75–100 mesh; 0.6 ml). Fractionation effects on the column can be excluded since mixing the sample with an appropriate amount of spike before and after chemical separation resulted in the same isotope ratios within the error limits. Incidentally, Ca was eluted in a yield very close to 100%.

Nonetheless the ^{43}Ca - ^{48}Ca double spike was added to the sample in prior of chromatographic clean-up. After the chemical purification a total amount of about 300 ng Ca was then loaded with a Ta activator onto outgassed Re filaments. The measurements were carried out on a ThermoFinnigan Triton using the routine method of *Heuser et al.* [2002]. Mass fractionation was corrected by exponential law. A total procedure blank of less than 5 ng was determined, so that blank corrections could be neglected. The Ca isotope data are denoted as δ values ($^{44/40}\text{Ca}_{\text{sample}}/^{44/40}\text{Ca}_{\text{standard}} - 1$) $\times 1000$ [*Eisenhauer et al.*, 2004] referred to IAPSO, which is with an average value of 1.86‰ relative to SRM 915a in accordance to the proposed values for seawater [*Hippler et al.*, 2003].

2.2.6. Strontium and Neodymium Isotopes

[36] At the Max-Planck-Institut für Chemie Mainz ($C = 30$) $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios of all MPI-DING glasses were determined by TIMS [*Raczek et al.*, 2003]. The amount of samples used was 50–200 mg (aliquots of the 10 g glass powders [*Jochum et al.*, 2000]) for each analysis. The samples were dissolved in Savillex beakers on a hot plate using 24 mol l^{-1} HF and 7 mol l^{-1} HClO₄. The initial chemical separation of Sr and Nd followed standard ion exchange procedures, employing 5 ml of AG50W-X12 (200–400 mesh) ion exchange resin. The REE fraction was further separated on a 2 ml column of Teflon powder coated with di-2-ethylhexyl phosphoric acid. Neodymium was eluted with 0.18 mol l^{-1} HCl. The isotope ratios were determined on a Finnigan MAT 261 mass spectrometer equipped with a multicollector of seven separate cups. Strontium (about 100 ng) was loaded with TaF₅ on single W filaments, whereas Nd (100 ng, except BM90/21-G: 60 ng) was loaded on double Re filaments and analyzed as metal. During the analytical period, several measurements of NIST SRM 987 Sr and La Jolla Nd reference samples gave the following values: $^{87}\text{Sr}/^{86}\text{Sr} = 0.710203 \pm 0.000034$ (2SD), $^{143}\text{Nd}/^{144}\text{Nd} = 0.511839 \pm 0.000038$ (2SD). Total procedural blanks were about 100 pg Sr and 10 pg Nd.

2.2.7. Hafnium Isotopes

[37] Hafnium isotopes on KL2-G and ML3B-G were measured at the Max-Planck-Institut für Chemie Mainz, Germany ($C = 75$). The chemical separation of Hf followed the procedure described in detail by *Münker et al.* [2001]. Hf isotope ratios were measured on a Nu Plasma multicollector

ICPMS (MC-ICPMS) in static mode using a CETAC Aridus inlet system fitted with an ESI Teflon nebulizer with a 50 μl flow rate. All isotope ratios were corrected with an exponential fractionation law using $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$. Repeated measurements of the JMC 475 Hf reference material averaged $^{176}\text{Hf}/^{177}\text{Hf} = 0.282161 \pm 0.000016$ (2 SD, $n = 361$) over a period of about 2 years, resulting in an overall repeatability of the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of about 60 ppm. Procedural blank was <250 pg. Repeated measurements of international reference materials (e.g., BHVO-1, BCR-1, BIR-1) show excellent reproducibility within 9–24 ppm to calculated average literature values [e.g., Blichert-Toft, 2001; Bizzarro *et al.*, 2003].

2.2.8. Lead Isotopes

[38] Lead isotope ratios were determined by TIMS, MC-ICPMS, solution ICPMS and LA-ICPMS in the Mainz and Melbourne laboratories. The analytical data have been recently published by Jochum *et al.* [2005a, 2005b].

2.2.8.1. TIMS

[39] For the TIMS analyses at the Max-Planck-Institut für Chemie ($C = 29$) the glass chips (20–140 mg) were repeatedly ultrasonicated in cold ultrapure water, and then washed in hot ultrapure water for 30 sec. After rinsing, the chips were dissolved in closed Savillex beakers using hot HF-HNO₃ (about 5: 1) for >48 hours. Lead separation was carried out on Bio-Rad AG1-X8 anion-exchange resin using a HBr-HNO₃ eluent. Measurements were done on a Finnigan MAT 261 mass spectrometer in static mode, applying the highly precise triple spike technique [Galer, 1999]. This technique requires the run of a spiked and unspiked sample aliquot to correct for instrumental mass fractionation, but improves the accuracy of the isotopic ratios significantly. Total procedural blanks were below 50 pg. In-run errors (2RSE) are of the order of 0.004–0.010% for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, and 0.002–0.005% for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ ratios.

2.2.8.2. MC-ICPMS

[40] Pb isotope compositions were determined by MC-ICPMS at the University of Melbourne ($C = 64$). The analytical procedures of the Melbourne laboratory are described in detail by Woodhead [2002]. Pb was separated from the samples by standard ion exchange procedures using BioRad AG1X-8 (200–400 mesh) resin and HBr/HCl.

Total procedural blanks were less than 20 pg. After chemical separation, samples were taken up in ca. 1 ml of 10 ng/g Tl solution in 2% HNO₃. Samples were introduced to a Nu Plasma MC-ICP mass spectrometer via a Cetac Aridus desolvating unit, using a Glass Expansion OpalMist nebulizer operating at an uptake rate of ~ 30 microliters min^{-1} . All analyses were conducted in static mode using Faraday cups. Each analysis consisted of 4 blocks of data, each block comprising a 30 s baseline measurement and 20 scans of 10 s duration. Total Pb beams ranged from 5–10 V, typically consuming 30–60 ng of Pb. Isotope ratios were corrected “on line” for Hg interference on ^{204}Pb . A modified Tl-normalization technique [Woodhead, 2002] was used to correct for mass bias. Within-run precision is typically in the order of 0.003% for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ ratios.

2.2.8.3. ICPMS

[41] Between 50 and 150 mg of glass chips were cleaned in purified water and then dissolved in an HF-HNO₃ mixture. After drying, the samples were treated twice with conc. HCl to eliminate fluorides before they were taken up in 0.4 mol l^{-1} HNO₃. A thallium solution was added for mass fractionation. Procedural Pb blank was 30 pg. Pb isotopes were measured at the Max-Planck-Institut für Chemie Mainz ($C = 70$) with a single-collector sector field ThermoFinnigan Element 2 ICP mass spectrometer equipped with a PFA microconcentric nebulizer and a PFA spray chamber. Ion intensities were measured by fast electric scanning in low mass resolution with flat top peaks. About 2100 scans have been performed for each measurement.

2.2.8.4. LA-ICPMS

[42] To demonstrate the capability of LA-ICPMS for in situ isotopic work, the MPI Mainz laboratory ($C = 72$) has measured Pb isotopes in the MPI-DING glasses using the New Wave UP-213 laser system and the ThermoFinnigan Element 2 ICP mass spectrometer (Table 4). Details are given by Jochum *et al.* [2005a, 2005b]. Three-spot analyses were done with spot diameters of 60–160 μm . Ablation time was about 40 s. To measure the Pb isotope ratios as precise as possible, the electrical scan mode of the mass spectrometer was used. Each run consisted of about 500 ablation measurements. Mass fractionation was determined from the deviation of the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio in NIST SRM 612 measured prior to the MPI-DING glasses from the literature value of 2.3871 [Rosman and Taylor, 1998]. An in-run precision (1 RSE) for Pb > 1 $\mu\text{g/g}$

Figure 1. Concentrations and relative standard deviations (RSD) for elements of different geochemical behavior obtained from LA-ICPMS spot analyses on different locations of the MPI-DING reference glasses ($C = 47$). Also shown is the repeatability field of LA-ICPMS. Most refractory lithophile and siderophile/chalcophile elements lie within this field, indicating that possible chemical heterogeneities are smaller than the combined standard uncertainty of LA-ICPMS, and hence are not detectable. Possible micro-heterogeneities ($<4\%$) are found for Cu, Sn, and Bi.

of less than 0.1% was obtained. External precision is about 0.1–0.2%.

3. Analytical Results and Discussion

3.1. Homogeneity

[43] Homogeneity is a fundamental requirement for any reference material. It is not an inherent property of the material, but is specific to both element and analytical test portion mass [Kane, 2002]. Therefore a reference glass could be homogeneous for most elements at bulk analytical tests and heterogeneous in most cases of microanalysis.

[44] The major and trace element homogeneity of the MPI-DING glasses was studied in detail by Jochum *et al.* [2000] using the microanalytical methods EPMA, SIMS, TOF-SIMS and SR-XRF. Analytical test portion masses for the different techniques range between <1 ng (EPMA) to about 3 µg (LA-ICPMS).

[45] The major element homogeneity was evaluated by means of EPMA profiles. RSD variations (0.3–2%) in all MPI-DING glasses except for the two komatiites GOR128-G and GOR132-G are similar to the ranges of analytical repeatability of EPMA analyses. This indicates that possible chemical heterogeneities are smaller than the analytical uncertainty and hence not detectable. Unequivocal mineralogical and chemical heterogeneities were

observed in a few fragments of GOR128-G and GOR132-G, in which quench olivine crystals formed. However, these crystals are concentrated in small and limited areas, while most of the fragments are glassy throughout.

[46] Trace element investigations showed that RSD variations (0.1–4%) of refractory lithophile elements (e.g., Sr, Ba, REE, Zr, Nb) were well within analytical errors. Heterogeneous distribution had been observed for Cr in ML3B-G (and may also exist in the other glasses) and for a few noble metals (due to variable loss to the platinum crucible during melting). New LA-ICPMS investigations ($C = 47$) confirm the homogeneous distribution of many trace elements. This is shown in Figure 1 where the RSD values of trace elements are plotted versus their concentration. The data were obtained from 3–6 independent analyses performed on different splits of the reference glasses. The figure shows that the RSD values of refractory lithophile elements increase from about 1–3% at concentrations >50 µg/g to about 5–20% at concentrations of 0.003–0.03 µg/g. This RSD field reflects the repeatability of LA-ICPMS analyses ($C = 47$) for homogeneous samples (K. P. Jochum *et al.*, Trace element and isotope analyses of geo- and cosmochemical samples by laser ablation-sector field-ICPMS, submitted manuscript, 2005; hereinafter referred to as Jochum *et al.*, submitted manuscript, 2005). Most siderophile and chalcophile elements are within this field indicating a similar homoge-

neous distribution as the refractory lithophile elements. However, Cu, Sn and Bi show larger variability (RSD of about 4% for high concentrations). Inconsistent results for the noble metals Ir, Pt and Au have also been observed (auxiliary material¹ Tables S1a–S1h). Heterogeneities of these and some other elements are also found in the NIST SRM 610-617 [Eggins and Shelley, 2002] and the USGS GS [Jochum et al., 2005c] glasses. They have been explained by loss of volatile components from the molten glass surface [Eggins and Shelley, 2002] and of siderophile elements to the platinum crucible [Rocholl et al., 1997] during preparation.

[47] Recently, Kempenaers et al. [2003] investigated possible micro-heterogeneity of StHs6/80-G, BM90/21-G, ML3B-G, KL2-G, ATHO-G and T1-G together with USGS BCR2-G and NIST SRM 613 in detail by measuring the elements K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Se, Rb, Sr, Y, Zr, Nb and Mo. They used μ SR-XRF, a non-destructive trace-level microanalytical method with sufficiently low instrumental error. A procedure based on repeated analyses of the reference glass in many locations allowed the minimum sampling mass needed for a representative analysis to be calculated. For ML3B-G at least 5 ng of material must be analyzed in order to obtain a material-related standard deviation below 5%. This corresponds to a sample volume of $13 \times 13 \times 13 \mu\text{m}^3$, i.e., somewhat smaller than what is typically vaporized during a LA-ICPMS pulse series or sampled during a μ SR-XRF experiment that makes use of a micro-beam of 10–15 μm diameter. The results of StHs6/80, BM90/21-G, KL2-G, ATHO-G, T1-G were similar to that of ML3B-G. However, the minimal representative mass differed from element to element in the different glasses. Especially Cu in ATHO-G, T1-G and Zn in T1-G showed higher minimal representative mass values. At least 60 ng of the material must be sampled/analyzed. When Cu and Zn are not considered, the minimal representative mass drops to about 20 ng for all reference glasses. The authors conclude that the MPI-DING glasses appear to be well suited for calibration of trace-level micro analytical methods such as LA-ICP-MS, LIMS, μ -PIXE and μ -SR-XRF.

[48] In summary, many independent investigations showed that individual glass fragments of the MPI-DING glasses are well homogenized with respect to both major and refractory lithophile trace elements at the μm to mm scale using ng - μg analytical test portion masses, and this conclusion

appears to be true also for the entirety of the samples. Minimum test portion masses at which the samples appear homogeneous are about 5–20 ng. Micro-heterogeneities due to quench crystallization of olivine have been observed in small and limited areas of the komatiitic glasses GOR128-G and GOR132-G. Heterogeneities have also been observed for the trace elements Cr, Cu, Zn, Sn, Bi and for the noble metals Ir, Pt, Au.

[49] To determine whether the MPI-DING glasses are also suitable geological reference materials for in situ isotope analysis, we have investigated possible small (within a single fragment) and large scale (different fragments) isotopic heterogeneities. Because of their low analytical uncertainty (0.001–0.1%), large scale isotopic heterogeneities were tested by high-precision TIMS and MC-ICPMS (analytical test portion masses of about 20–100 mg). SIMS and LA-ICPMS (analytical test portion masses of about 5 ng and 3 μg , respectively), where the analytical uncertainty is about 0.1–0.3%, were used to test for possible isotopic micro-heterogeneities of Li, B and Pb. The results of these investigations are discussed in detail for each isotope system in section 3.3.

3.2. Element Abundances

[50] Auxiliary material Tables S1a–S1i list the available major and trace element results for the MPI-DING glasses. Most data are mean values of at least 5 individual analyses (see Tables 3 and 4). Besides of many new data, the tables contain already published concentration values (see Table 2). The data were obtained from more than 60 invited laboratories worldwide using 16 independent analytical methods. Estimated combined standard uncertainties [Eurachem, 2000], given as relative standard deviation in percent, the analytical technique used and the code (Table 2) are also given. Outliers are marked if the data are unacceptable presumably because of technical reasons. Most of the outliers have relatively high overall uncertainties (compared to other techniques) mainly caused by measurements near the detection limits or calibration errors. In the following, the results for the different elements and element groups, respectively, will be discussed in detail.

3.2.1. Major and Minor Elements

[51] Because of the limited sample size of the reference glasses the abundances of major and minor elements (expressed as oxide concentrations) are mainly determined by EPMA. This microanalytical technique is routinely used in geochemical

¹Auxiliary material is available at <ftp://ftp.agu.org/apend/gc/2005GC001060>.

laboratories and yields data with (estimated) uncertainties in the 1–4% (RSD) range depending on element and concentration levels. However, most EPMA results agree within 5–15%, which is higher than the estimated combined standard uncertainties for the EPMA data. Because many investigations showed that the glass samples are well homogenized with respect to major and minor elements (with the exception of some small and limited crystal-bearing areas within the glass shards [Jochum *et al.*, 2000] of the two komatiite glasses (see results for GOR128-G; auxiliary material Table S1d, C = 32)) most discrepancies of the EPMA data may be caused by different correction procedures and calibration samples used. EPMA values are within the few results of bulk analytical techniques, such as XRF and INAA where large sample amounts (0.1–0.8 g) were used for an analysis. Major element data from other microanalytical techniques (LIMS, PIXE, SR-XRF) have higher uncertainties than the EPMA results. LA-ICPMS was used for the determination of some minor element concentrations (e.g., TiO₂, MnO) with good agreement with the EPMA data. A direct oxygen measurement by EPMA was given from the laboratory C = 28. Auxiliary material Tables S1a–S1h contain H₂O data for StHs6/80-G and T1-G using the method of Vennemann and O’Neil [1993]. H₂O data obtained for all eight glasses by SIMS using the methods of Hauri *et al.* [2002] and Koga *et al.* [2003] give H₂O data that are lower than the manometry data by a factor of 2–3. It is thus possible that the manometry data contain additions from non-structural H₂O trapped in micro-inclusions, or (less likely) incorporate water from H₂O-rich heterogeneities in the StHs6/80-G and T1-G glasses. CO₂ data obtained by SIMS are at, or barely above, the detection limit. The combined H₂O and CO₂ data are consistent with air saturation at atmospheric pressure.

3.2.2. Li, Be, B

[52] The database for these light trace elements has been improved compared to Jochum *et al.* [2000]. New data mainly come from LA-ICPMS, MC-ICPMS and SIMS laboratories. At the GeoForschungsZentrum Potsdam laboratory (C = 33) boron concentrations of GOR128-G, GOR132-G and StHs6/80-G were determined using the wet-chemical ICP-AES technique.

3.2.3. F, Cl, Br, S

[53] Auxiliary material Tables S1a–S1h list new chlorine and sulfur data using EPMA, however, with large uncertainties. The Cl values are lower than the detection limits of INAA analyses previ-

ously published. Fluorine, Cl and S data obtained by SIMS are all above the 0.5 µg/g detection limit with uncertainties ranging from 2% to 42% (2RSD); exceptions are Cl in BM90/21-G (~0.7 µg/g) and F and S in ATHO-G (~0.7 µg/g) which are only slightly above the detection limit. The slightly poorer level of reproducibility for F, Cl and S for KL2-G and ML3-B compared to the others may be indicative of micron-scale heterogeneity in these elements. The reasons for the inconsistencies between the Cl data for ATHO-G are unclear. There are no new data for Br.

3.2.4. Sc, V, Cr, Co, Ni, Cu, Zn, Ga

[54] LA-ICPMS has considerably expanded the database for these trace elements. New LA-ICPMS data for Sc are less precise than INAA values; however, most data agree within error limits. LA-ICPMS data for Cr, Co, Ni, Cu, Zn and Ga lie within the concentration ranges obtained from other analytical techniques. However, Co, Ni, Cu, Zn, Ga in some MPI-DING glasses vary widely presumably because of a more heterogeneous distribution of some siderophile and chalcophile trace elements in the glasses compared to refractory lithophile elements, such as Sr, Ba, Yb (see section 3.1).

3.2.5. K, Rb, Cs

[55] The preliminary reference values of Jochum *et al.* [2000] for K and Rb are well constrained because they are mainly based on high precise isotope dilution analyses using TIMS. New EPMA analyses have not changed significantly the accepted mean values for K. Many new ICP-MS and LA-ICPMS data are now available for Rb and Cs.

3.2.6. Ge, As, Se, Mo, Sn, Sb, Cd, In, W, Hg, Tl, Bi

[56] The preliminary reference values for these elements [Jochum *et al.*, 2000] are poorly constrained because of very few analyses. In most cases only information values, upper limits or even no values could be given. Auxiliary material Tables S1a–S1h show new data for these elements; however, in some cases they are inconsistent presumably because of analytical difficulties and possible heterogeneities in the MPI-DING glasses and/or the NIST glasses used for calibration.

3.2.7. Pb

[57] The reliability of the Pb concentration has considerably improved by some new isotope dilution (ID) data using TIMS and ICPMS. New

LA-ICPMS and ICPMS data are less precise; however, they agree with the results of other techniques.

3.2.8. Sr, Ba, REE, Th, U

[58] Partly more than 30 different results per reference glass are available for this group of elements which are of special interest in geochemistry. Analyses were performed by bulk (e.g., TIMS, INAA, SSMS, ICPMS) and microanalytical (e.g., SIMS, LA-ICPMS, SR-XRF) techniques in many laboratories. For most poly-isotopic elements ID data using TIMS, ICPMS, MC-ICPMS, SSMS and MIC-SSMS exist. Because isotope dilution is a definitive method considered to be free from bias [Heumann, 1988] requiring relatively large sample amounts (about 0.1 g), these results are very precise, accurate and representative for the whole glass. The tables contain new data for Sr, Ba, REE, Hf, U from a newly developed multielement ID-ICPMS method ($C = 35, 48$) which agree very well with the ID-TIMS ($C = 4$), ID-SSMS ($C = 1$) and ID-MIC-SSMS ($C = 2$) data. Mean LA-ICPMS values also agree although the results of the different LA-ICPMS laboratories may differ up to 30%. ID-TIMS ($C = 53$) was applied for Th and U measurements of KL2-G and ML3B-G.

3.2.9. Zr, Hf, Nb, Ta

[59] Many analytical data exist for this element group. The concentrations of Zr, Hf and Ta were precisely determined by isotope dilution using MC-ICPMS ($C = 26, 74$). New Zr and Hf ID-ICPMS data for KL2-G and ML3B-G ($C = 35, 48$) and data obtained by other techniques, mainly ICPMS and LA-ICPMS, expand the database for this element group.

3.2.10. Noble Metals, Re

[60] There are only few data for Re and the noble metals. Rhenium abundances in the MPI-DING glasses are very low and therefore difficult to determine. Noble metals differ extremely (up to a factor of 30, e.g., Ir in T1-G). Besides analytical difficulties the major reason for these discrepancies may be a heterogeneous distribution of noble metals in the glass because of contamination by the Pt crucible during glass preparation [Dingwell et al., 1993].

3.3. Isotope Data

3.3.1. Hydrogen Isotopes

[61] The hydrogen isotope composition of the glasses ($C = 31$) is expressed in the conventional

δ -notation relative to VSMOW in ‰ (Table 5). The average precision of the isotopic measurement, on the basis of replicate analyses of standard reference material NBS-30 (biotite, 3.5 ‰m/m water, $\delta D = -65$ ‰) is better than ± 2 ‰ (2σ) and the accuracy is better than 5‰. As only single measurements were possible, given the analytical method used and the amount of material available, the homogeneity of the samples cannot be evaluated at the present time. The measured hydrogen isotope compositions of the glasses are marginally low in D-content compared to those for fresh magmatic glasses [e.g., Kyser, 1986; Taylor, 1986]. This may be a primary feature of the magmatic precursory material, relating to magmatic degassing during crystallization, or indicate hydrothermal alteration of the original sample material and/or exchange of hydrogen with ambient moisture during glass production. Alternatively, the much lower water contents determined by SIMS might mean that the manometry δD values represent that of water trapped in micro-inclusions or heterogeneities in the StHs6/80-G and T1-G glasses.

3.3.2. Oxygen Isotopes

[62] The oxygen isotope compositions of all MPI-DING glasses ($C = 31$) are expressed in the standard δ -notation, relative to VSMOW in ‰ (Table 5). Replicate oxygen isotope analyses of different chips of the same sample and of the reference materials used (NIST SRM 8546 (NBS 28) quartz and UWG-2 garnet [Valley et al., 1995]) had an average reproducibility (2SD) of ± 0.07 ‰ for $\delta^{18}O$ and 0.04‰ for $\delta^{17}O$. The accuracy of both $\delta^{18}O$ and $\delta^{17}O$ values was better than 0.2‰ compared to accepted $\delta^{18}O$ values for NIST SRM 8546 (NBS 28) of 9.64‰ and UWG-2 of 5.8‰ and an accepted $\delta^{17}O$ value for NIST SRM 8546 (NBS 28) of 5.00‰. Hence the glasses have homogeneous isotope compositions on the scale of the measurements made here (equivalent to 1 to 3 mg sample sizes). Compared to fresh peridotites, komatiites and basalts that commonly have $\delta^{18}O$ values between 5 and 6‰, the glasses BM90/21-G, GOR128-G and GOR132-G, ML3B-G and KL2-G, respectively, all have unusually high $\delta^{18}O$ values [Mattey et al., 1994; Harmon and Hoefs, 1995]. This may suggest oxygen isotope exchange between these ultramafic to mafic glasses and atmospheric oxygen (commonly $\delta^{18}O = 23$ ‰) during the preparation of the glasses. Alternatively, the glasses were produced from rocks that have experienced low temperature hydrothermal alteration, a process that can readily lead to an increase

Table 5. Hydrogen and Oxygen Isotope Compositions^a

MPI-DING Glass	δ D	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$
KL2-G		4.31 ± 0.01	8.63 ± 0.09
ML3B-G		4.28 ± 0.08	8.35 ± 0.22
StHs6/80-G	-95 ± 2	3.21 ± 0.10	6.12 ± 0.02
GOR128-G		4.83 ± 0.00	9.43 ± 0.04
GOR132-G		4.34 ± 0.00	8.52 ± 0.08
BM90/21-G		4.27 ± 0.02	8.40 ± 0.01
T1-G	-117 ± 2	3.89 ± 0.01	7.53 ± 0.01
ATHO-G		1.59 ± 0.02	3.20 ± 0.07

^aC = 31. Compositions are expressed in the standard δ -notation, relative to VSMOW in permil. Precision (2σ) of the measurements is also indicated. Average reproducibility (2 SD, obtained from replicate analyses of reference materials) is about 2‰ (δ D), 0.04‰ ($\delta^{17}\text{O}$), and 0.07‰ ($\delta^{18}\text{O}$).

in ^{18}O compared to fresh magmatic rocks [e.g., Muehlenbachs, 1986]. The $\delta^{18}\text{O}$ values of StHs6/80-G (andesite) and T1-G (quartz-diorite) have values that are more typical for fresh magmatic rocks of this type [e.g., Taylor and Sheppard, 1986]. In contrast, ATHO-G (rhyolite) has a $\delta^{18}\text{O}$ value that is low compared to most fresh magmatic rocks of this type which may indicate hydrothermal alteration and isotopic exchange with low- $\delta^{18}\text{O}$ meteoric waters of the rock prior to production of the glass and/or contamination of the magma with a low $\delta^{18}\text{O}$ -component during magma genesis [e.g., Taylor and Sheppard, 1986].

3.3.3. Boron Isotopes

[63] The boron isotope composition of GOR128-G, GOR132-G and StHs6/80-G (Table 6) was determined using TIMS ($C = 33$) and LA-MC-ICPMS ($C = 76$). The boron isotope data are listed as $\delta^{11}\text{B}$ values, i.e., normalized to the reference material NIST SRM 951.

[64] The in-run precision of the TIMS data is typically better than 0.15‰ (2SE), whereas repeatability and reproducibility are up to one order of

magnitude higher indicating the scatter between data from different TIMS measurements and/or independent chemical dissolution/separation aliquots. On the basis of these data and other recently published boron isotope data from the GeoForschungsZentrum Potsdam, the estimated combined standard uncertainty is better than 0.7‰ (1 RSD; for detailed discussion, see Rosner and Meixner [2004]).

[65] The precision of the LA-MC-ICPMS data is significantly lower compared to the TIMS data. However, LA-MC-ICPMS has the advantages of minor sample preparation and high spatial resolution (60–80 μm) [Tiepolo et al., 2005b]. As Figure 2 shows, 88% of the single spot analyses of GOR 128-G overlap the high-precision TIMS value [Rosner and Meixner, 2004] at the 1σ level. All data for GOR128-G, GOR 132-G and StHs6/80-G [Tiepolo et al., 2005b] agree with the TIMS data at the 2σ level indicating uniform distribution of B isotopes.

[66] The $\delta^{11}\text{B}$ value of -4.48‰ for StHs6/80-G is in the range of mantle derived rocks [e.g., Chaussidon and Marty, 1995]. The very high positive values of GOR128-G (13.55‰) and GOR132-G (7.11‰) indicate contamination of the mantle-derived magma, either by seawater altered crustal rocks during magma ascent or directly by assimilation of seawater ($\delta^{11}\text{B} = +39$). Assuming an contaminant (seawater, seawater derived brine or seawater-altered crust) with a seawater like boron composition an increasing contamination would create a series of rocks with relatively low B contents coupled with low $\delta^{11}\text{B}$ values to relatively high B contents coupled with high $\delta^{11}\text{B}$ values. This is exactly displayed by the two komatiites. Moreover, the same systematic between a hypothetical seawater like contaminant and a mantle derived primary magma is shown by Li concentrations and $\delta^7\text{Li}$ values of the GOR glasses.

Table 6. Boron Isotope Data Using TIMS ($C = 33$) and LA-MC-ICPMS ($C = 76$)^a

MPI-DING Glass	TIMS		LA-MC-ICPMS		
	$\delta^{11}\text{B}$, ‰	1 SD, ‰	$\delta^{11}\text{B}$, ‰	1 SE, ‰	Remarks
GOR128-G	13.55	0.11	13.5	1.6	60 μm spots
			14.5	2.8	80 μm spots
GOR132-G	7.11	0.48	6.8	3.0	60 μm spots
StHs6/80-G	-4.48	0.14	-4.3	2.4	80 μm spots

^aTIMS, $C = 33$ [Rosner and Meixner, 2004]; LA-MC-ICPMS, $C = 76$ [Tiepolo et al., 2005b]. 1 SD values of TIMS data are based on 2–3 replicate measurements of the same homogeneous sample solution (GOR132-G, StHs6/80-G) and of two individual processed sample aliquots (GOR128-G), respectively. The 1 SE values of LA-MC-ICPMS data are based on 8 (GOR128-G) and 9 (GOR132-G, StHs6/80-G) replicates on the same glass sample. Data are expressed in the δ -notation (see text) relative to NIST SRM951.

Figure 2. $\delta^{11}\text{B}$ values for the komatiitic glass GOR 128-G obtained from LA-MC-ICPMS analyses using two different spot sizes. Nearly all single spot analyses overlap the high-precision TIMS value [Rosner and Meixner, 2004] at the 1σ level.

However, the high boron concentrations of the GOR glasses require a relatively high boron concentration of the contaminant, which favors a seawater derived brine and/or highly altered crustal rocks and makes unmodified seawater an unlikely contaminant.

3.3.4. Lithium Isotopes

[67] The MC-ICPMS Li isotope data ($C = 82$) are listed in Table 7. The reproducibility is dominated by residual errors in the standard bracketing technique. Repeat bracketed measurements of LSVEC give a total reproducibility for an individual analysis of 0.4 permil (1σ), similar to that achieved by other studies [cf. *Jeffcoate et al.*, 2004]. BHVO-2 (4.5‰) and JG-2 (−0.1‰) analyses agree with published values [*Jeffcoate et al.*, 2004], as do measurements of LSVEC that have been passed through the chemistry. For each dissolution a separate number is assigned, so that the variation between dissolutions of the same sample can be assessed. In some cases, measurements were performed both on the glass and on the sample powder the glass was made from. In the case of T1, no significant difference was found between glass and powder, in the case of BCR2 the difference is close to the analytical uncertainty, with the powder being slightly lighter than the glass. The USGS reference glasses BCR-2G (+5.0‰) and GSD-1G (30.3‰) are close to literature values [*Kasemann et al.*, 2005]. The MPI-DING glasses range from $\delta^7\text{Li}$ of 2.0 to 17.1‰. The uncertainties compared to the

Table 7. Lithium Isotope Data for MPI-DING Glasses and Other Reference Materials Using MC-ICPMS^a

Reference Material	Diss. Number	Run Date	$\delta^7\text{Li}$, ‰
GOR 132-G	H3	21.6.05	8.9
GOR 128-G	H4	21.6.05	14.4
StHs6/80-G	S5	30.5.05	3.7
		30.5.05	3.5
T1-G	H8	17.6.05	2.1
		17.6.05	2.0
ATHO-G	S7	30.5.05	17.1
		30.5.05	17.1
ML3B-G	H1	17.6.05	4.3
		17.6.05	4.4
L-SVEC (NIST SRM 8545)	A3	30.5.05	−0.1
through column		30.5.05	0.0
BCR-2G	H6	17.6.05	5.0
		17.6.05	5.0
GSD-1G	S9	30.5.05	30.4
		30.5.05	30.2
T1 (powder)	H9	17.6.05	2.6
		17.6.05	2.6
BCR-2 (powder)	H7	17.6.05	4.6
		17.6.05	4.2
BHVO-2 (powder)	A1	30.5.05	4.4
		30.5.05	4.1
		30.5.05	4.2
BHVO-2 (powder)	H5	17.6.05	4.9
		17.6.05	4.7
JG-2 (powder)	A2	30.5.05	0.1
		30.5.05	−0.1
		30.5.05	−0.1

^a $C = 82$. Data are relative to LVSEC (NIST SRM 8545). Data are also given for T1, the original rock powder of T1-G. Uncertainty (1 SD) is $\pm 0.4\text{‰}$ based on repeated measurements. Dissolution numbers are given to provide controls on variability between aliquots.

Table 8. Lithium Isotope Data for 5 MPI-DING and 2 USGS Reference Glasses Using SIMS^a

MPI-DING KL2-G	$\delta^7\text{Li}$, ‰		MPI-DING GOR128-G	$\delta^7\text{Li}$, ‰	
	Split 1	Split 2		Split 1	Split 2
Analysis 1 ($\pm$ SE)	4.8 $\pm$ 0.9	3.8 $\pm$ 1.1	Analysis 1 ($\pm$ SE)	12.0 $\pm$ 1.0	10.2 $\pm$ 0.6
Analysis 2 ($\pm$ SE)	3.2 $\pm$ 1.0	5.9 $\pm$ 1.0	Analysis 2 ($\pm$ SE)	12.2 $\pm$ 0.7	13.1 $\pm$ 0.8
Analysis 3 ($\pm$ SE)	6.3 $\pm$ 0.8	1.7 $\pm$ 1.0	Analysis 3 ($\pm$ SE)	13.1 $\pm$ 0.7	14.1 $\pm$ 0.7
Analysis 4 ($\pm$ SE)	3.9 $\pm$ 1.0	4.8 $\pm$ 0.9	Analysis 4 ($\pm$ SE)	12.8 $\pm$ 0.8	13.1 $\pm$ 0.9
Analysis 5 ($\pm$ SE)	3.8 $\pm$ 1.0	2.3 $\pm$ 1.1	Analysis 5 ($\pm$ SE)	12.4 $\pm$ 0.9	12.6 $\pm$ 0.8
Mean ($\pm$ SD)	4.4 $\pm$ 1.2	3.7 $\pm$ 1.8	Mean ($\pm$ SD)	12.5 $\pm$ 0.4	12.6 $\pm$ 1.4
Total mean ($\pm$ SD)	4.1 $\pm$ 1.5		Total mean ($\pm$ SD)	12.6 $\pm$ 1.0	
MPI-DING ML3B-G	$\delta^7\text{Li}$, ‰		MPI-DING GOR132-G	$\delta^7\text{Li}$, ‰	
	Split 1	Split 2		Split 1	Split 2
Analysis 1 ($\pm$ SE)	3.6 $\pm$ 1.1	3.4 $\pm$ 0.9	Analysis 1 ($\pm$ SE)	8.4 $\pm$ 0.8	7.9 $\pm$ 1.0
Analysis 2 ($\pm$ SE)	5.2 $\pm$ 1.4	3.4 $\pm$ 1.1	Analysis 2 ($\pm$ SE)	8.8 $\pm$ 0.8	8.1 $\pm$ 1.0
Analysis 3 ($\pm$ SE)	3.8 $\pm$ 1.2	3.9 $\pm$ 1.2	Analysis 3 ($\pm$ SE)	9.6 $\pm$ 1.0	7.6 $\pm$ 1.0
Analysis 4 ($\pm$ SE)	3.6 $\pm$ 1.0	6.7 $\pm$ 1.3	Analysis 4 ($\pm$ SE)	9.6 $\pm$ 0.9	8.5 $\pm$ 0.9
Analysis 5 ($\pm$ SE)	5.0 $\pm$ 1.3	7.4 $\pm$ 1.1	Analysis 5 ($\pm$ SE)	8.3 $\pm$ 1.0	9.6 $\pm$ 0.9
Analysis 6 ($\pm$ SE)	3.0 $\pm$ 1.2	7.2 $\pm$ 1.1	Analysis 6 ($\pm$ SE)	8.8 $\pm$ 0.8	8.5 $\pm$ 0.8
Analysis 7 ($\pm$ SE)		4.6 $\pm$ 1.2	Analysis 7 ($\pm$ SE)	8.4 $\pm$ 0.9	
Analysis 8 ($\pm$ SE)		5.4 $\pm$ 1.1			
Mean ($\pm$ SD)	4.0 $\pm$ 0.9	5.2 $\pm$ 1.7	Mean ($\pm$ SD)	8.8 $\pm$ 0.6	8.4 $\pm$ 0.7
Total mean ($\pm$ SD)	4.7 $\pm$ 1.5		Total mean ($\pm$ SD)	8.6 $\pm$ 0.6	
MPI-DING T1-G	$\delta^7\text{Li}$, ‰		USGS	$\delta^7\text{Li}$, ‰	
	split 1	split 2		GSD-1G	BCR-2G
Analysis 1 ($\pm$ SE)	0.5 $\pm$ 0.6	−0.3 $\pm$ 0.5	Analysis 1 ($\pm$ SE)	31.2 $\pm$ 0.6	3.7 $\pm$ 0.9
Analysis 2 ($\pm$ SE)	−1.2 $\pm$ 0.6	−0.2 $\pm$ 0.4	Analysis 2 ($\pm$ SE)	30.3 $\pm$ 0.5	4.4 $\pm$ 1.0
Analysis 3 ($\pm$ SE)	−1.6 $\pm$ 0.6	0.8 $\pm$ 0.4	Analysis 3 ($\pm$ SE)	32.1 $\pm$ 0.5	4.7 $\pm$ 1.0
Analysis 4 ($\pm$ SE)	−0.3 $\pm$ 0.6	0.0 $\pm$ 0.6	Analysis 4 ($\pm$ SE)	31.4 $\pm$ 0.4	4.6 $\pm$ 0.8
Analysis 5 ($\pm$ SE)	0.4 $\pm$ 0.6	−0.1 $\pm$ 0.5	Analysis 5 ($\pm$ SE)	31.8 $\pm$ 0.4	2.9 $\pm$ 1.0
Analysis 6 ($\pm$ SE)	0.7 $\pm$ 0.5	0.1 $\pm$ 0.6	Analysis 6 ($\pm$ SE)	30.7 $\pm$ 0.4	3.0 $\pm$ 1.3
			Analysis 7 ($\pm$ SE)	31.0 $\pm$ 0.4	4.2 $\pm$ 0.6
			Analysis 8 ($\pm$ SE)	31.5 $\pm$ 0.4	4.4 $\pm$ 0.8
			Analysis 9 ($\pm$ SE)		4.1 $\pm$ 0.6
Mean ($\pm$ SD)	−0.3 $\pm$ 1.0	0.0 $\pm$ 0.4	Analysis 10 ($\pm$ SE)		5.4 $\pm$ 0.8
Total mean ($\pm$ SD)	−0.1 $\pm$ 0.7		Analysis 11 ($\pm$ SE)		3.4 $\pm$ 0.8
			Analysis 12 ($\pm$ SE)		4.1 $\pm$ 0.7
			Analysis 13 ($\pm$ SE)		3.6 $\pm$ 1.0
			Analysis 14 ($\pm$ SE)		5.2 $\pm$ 0.8
			Analysis 15 ($\pm$ SE)		3.4 $\pm$ 0.9
			Mean ($\pm$ SD)	31.3 $\pm$ 0.6	4.1 $\pm$ 0.8

^aC = 71. Data are given relative to the reference material LSVEC (NIST SRM 8545). Distances between different analyses were about 100 μm . Uncertainty on a single analysis is 1 SE obtained from 100 analytical cycles.

SIMS data (Table 8) are smaller, owing to the larger amount of Li measured. The data are within the range of the SIMS data except for the sample T1-G, which is about 2‰ heavier.

[68] Table 8 lists Li isotope data obtained from SIMS measurements (C = 71). Two different splits were analyzed at 5–8 points. Distances between the points were about 100 μm . $\delta^7\text{Li}$ values of the MPI-DING glasses differ significantly with the exception of the Hawaiian basalt glasses KL2-G and ML3B-G. Some local heterogeneity in Li isotopes could be observed (Figure 3). ML3B-G shows higher $\delta^7\text{Li}$ values in an area of about 200 μm . All $\delta^7\text{Li}$ values for GOR128-G agree with

the exception of the result of one point where $\delta^7\text{Li}$ is 20% lower.

3.3.5. Calcium Isotopes

[69] The TIMS data of the Ca isotopes are listed in Table 9 (C = 80). They are averages of at least four duplicate analyses including separate column chemistry and replicated measurements. Two standard deviations of the mean are less than 0.2‰. At first glance, the data matches with those from the few data available in literature (see compilation by DePaolo [2004]). However, a general convention is needed for the Ca isotope composition in igneous rocks such as an international rock reference

Figure 3. $\delta^7\text{Li}$ values for five MPI-DING glasses. Two different splits were analyzed at 5–8 points by SIMS ($C = 71$). Distances between the points were about 100 μm . Bars indicate ± 1 SD. Slight micro-heterogeneities of Li isotopes could be observed for GOR 128-G and ML3B-G. The figure also contains the MC-ICPMS data ($C = 82$) for four of these glasses.

material. The values of Table 9 are normalized to NIST SRM 915a, which is generally used as standard reference material for carbonates, and to IAPSO, which is a salinity (seawater) reference material.

3.3.6. Strontium and Neodymium Isotopes

[70] Up to three $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotope analyses were performed for each glass (Table 10) using TIMS ($C = 30$). The data for replicate analyses agree within uncertainty limits (repeatability, $2\text{SD} = 0.000034$ for $^{87}\text{Sr}/^{86}\text{Sr}$, 0.000038 for $^{143}\text{Nd}/^{144}\text{Nd}$). Strontium and Nd isotopes were previously determined in the original rock powders of KL-2 and ML3-B [Newsom et al., 1986], which

were used for the preparation of the reference glasses KL2-G and ML3B-G, respectively. The Sr data for the glasses and the powders (KL-2: 0.703497; ML-3B: 0.703817) agree within confidence intervals, whereas the Nd ratios of the original powders (KL-2: 0.512985; ML-3B: 0.512889) are slightly higher compared to those of the reference glasses, presumably because of larger uncertainties of the old data.

3.3.7. Hafnium Isotopes

[71] The Hf isotopic composition of two glasses is listed in Table 11. Replicate MC-ICPMS analyses ($C = 75$) are identical within confidence intervals. The data for KL2-G and ML3B-G, two basalts from

Table 9. Calcium Isotope TIMS Data for the MPI-DING Glasses, the Salinity Standard IAPSO, and the USGS Reference Materials BHVO-2 and BIR-1^a

Reference Materials	$\delta^{44/40}\text{Ca}$ (‰IAPSO)	$\delta^{44/40}\text{Ca}$ (‰NISTSRM915a)	$2\sigma_{\text{mean}}$
KL2-G	-1.18	0.67	0.09 (n = 10)
ML3B-G	-1.18	0.67	0.09 (n = 13)
T1-G	-1.13	0.73	0.13 (n = 9)
StHs6/80-G	-1.12	0.74	0.08 (n = 9)
GOR 128-G	-1.19	0.66	0.04 (n = 5)
GOR 132-G	-1.36	0.49	0.11 (n = 6)
ATHO-G	-1.02	0.84	0.20 (n = 4)
BM90/21-G	-0.56	1.29	0.15 (n = 7)
IAPSO		1.85	0.04 (n = 47)
BHVO-2	-1.18	0.67	0.08 (n = 13)
BIR-1	-1.05	0.80	0.05 (n = 11)

^a $C = 80$. The long-term precision is about 0.15‰ (2SD).

Table 10. Sr and Nd Isotopic Ratios of MPI-DING Reference Glasses^a

MPI-DING Glass	⁸⁷ Sr/ ⁸⁶ Sr	¹⁴³ Nd/ ¹⁴⁴ Nd	MPI-DING Glass	⁸⁷ Sr/ ⁸⁶ Sr	¹⁴³ Nd/ ¹⁴⁴ Nd
KL2-G	0.703517 ± 9	0.512953 ± 9 0.512946 ± 5	GOR132-G	0.707165 ± 7 0.707147 ± 9	0.513282 ± 8
KL2-G (mean)	0.703517	0.512950	GOR132-G (mean)	0.707156	0.513282
ML3B-G	0.703796 ± 10 0.703809 ± 12 0.703809 ± 10	0.512878 ± 8 0.512871 ± 6	BM90/21-G	0.706268 ± 16 0.706284 ± 13	0.512598 ± 10
ML3B-G (mean)	0.703805	0.512875	BM90/21-G (mean)	0.706276	0.512598
StHs6/80-G	0.703500 ± 8 0.703494 ± 7	0.512898 ± 6 0.512890 ± 8	T1-G	0.710094 ± 7 0.710091 ± 9	0.512332 ± 6 0.512320 ± 6
StHs6/80-G (mean)	0.703497	0.512894	T1-G (mean)	0.710093	0.512326
GOR128-G	0.706877 ± 9 0.706898 ± 9	0.513240 ± 6 0.513228 ± 7	ATHO-G	0.703224 ± 9	0.513006 ± 10 0.513011 ± 8
GOR128-G (mean)	0.706888	0.513234	ATHO-G (mean)	0.703224	0.513009

^aC = 30. Uncertainties represent internal errors (2 SE). External precision (2 SD): 0.000035 (⁸⁷Sr/⁸⁶Sr), 0.000030 (¹⁴³Nd/¹⁴⁴Nd). Data from Raczek *et al.* [2003].

Kilauea and Mauna Loa, Hawaii, respectively, are within the range of those reported from other Hawaiian samples [e.g., Blichert-Toft *et al.*, 1999].

3.3.8. Lead Isotopes

[72] Lead isotope ratios have been determined by TIMS (C = 29), MC-ICPMS (C = 64), LA-ICPMS (C = 72) and solution ICPMS (C = 70). The results of these investigations have been recently published by Jochum *et al.* [2005b]. Table 12 shows the average isotope ratios obtained for the different reference glasses. ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb ratios, which are commonly utilized for in situ Pb isotope studies, vary from 2.010 (GOR132-G) to 2.081 (T1-G) and 0.8164 (GOR132-G) to 0.8438 (GOR 128-G), respectively.

[73] Possible heterogeneities of Pb isotopes are found for ML3B-G and KL2-G by high-precision triple spike TIMS and MC-ICPMS measurements using different glass chips (sample amount 20–140 mg). As Figure 4 shows, small but significant differences could be found for ²⁰⁸Pb/²⁰⁶Pb in the different glass fragments, especially for sample ML3B-G. A reason for the discrepancies may be sample heterogeneities superimposed to the samples during glass preparation. However, the differences are small (about 0.02–0.05%) and lower than the reproducibility (0.1–0.3%) obtained from microanalytical techniques, such as LA-ICPMS and SIMS.

4. Geochemical Characterization

[74] Jochum *et al.* [2000] prepared eight MPI-DING glasses for in situ microanalytical work which should fit the International Organisation

for Standardization (ISO) definition of reference materials (ISO Guide 30 [ISO, 1992]), namely a sufficiently homogeneous material to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. They followed the recommendations for the certification of reference materials of Kane and Potts [1997, 1999] and published preliminary reference values and information values.

[75] Recently, the IAG undertook efforts to function as a certifying body and to develop a protocol for the certification of geological and environmental reference materials to comply to the fullest extent possi-

Table 11. Hf Isotope Data^a

MPI-DING Glass	¹⁷⁶ Hf/ ¹⁷⁷ Hf	Analysis Period
KL2-G	0.283114 ± 0.000010	January 2004
	0.283106 ± 0.000004	November 2004
	0.283107 ± 0.000005	January 2005
	0.283109	mean
ML3B-G	0.283067 ± 0.000005	November 2004
	0.283067 ± 0.000009	January 2005
	0.283067	mean
BCR-1	0.282864 ± 0.000009	January 2004
	0.282860 ± 0.000006	January 2004
	0.282874 ± 0.000004	November 2004
	0.282877 ± 0.000005	January 2005
BHVO-1	0.282869	mean
	0.283105 ± 0.000006	January 2004
	0.283106 ± 0.000008	November 2004
	0.283101 ± 0.000008	January 2005
BIR-1	0.283104	mean
	0.283276 ± 0.000005	November 2004
	0.283270 ± 0.000010	November 2004
	0.283273	mean

^aC = 75. Uncertainties represent in-run precision (2 SE). External precision (2 SD) is 0.000017.

Table 12. Pb Isotope Data for the MPI-DING Glasses^a

Reference Material	N	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb
<i>TIMS^b</i>						
KL2-G	4	19.031	15.634	38.528	2.0245	0.82149
ML3B-G	2	18.730	15.607	38.477	2.0543	0.83326
ATHO-G	1	18.387	15.481	38.115	2.0729	0.84196
StHs6/80-G	1	18.900	15.614	38.515	2.0378	0.82611
T1-G	1	18.726	15.679	38.974	2.0813	0.83726
NIST SRM 981		16.942	15.499	36.731	2.1680	0.91485
<i>MC-ICPMS^c</i>						
KL2-G	1	19.026	15.628	38.507	2.0239	0.82141
ML3B-G	1	18.695	15.584	38.397	2.0538	0.83358
ATHO-G	1	18.375	15.473	38.087	2.0727	0.84205
StHs6/80-G	1	18.894	15.609	38.496	2.0375	0.82614
T1-G	1	18.725	15.675	38.953	2.0803	0.83715
GOR128-G	1	18.510	15.618	38.256	2.0668	0.84377
GOR132-G	1	19.245	15.712	38.688	2.0103	0.81644
NIST SRM 981		16.936	15.491	36.701	2.1671	0.91466
Reference Material	N	²⁰⁸ Pb/ ²⁰⁶ Pb	1 SD	²⁰⁷ Pb/ ²⁰⁶ Pb	1 SD	
<i>Solution ICPMS^d</i>						
KL2-G	3	2.021	0.004	0.8203	0.0003	
ML3B-G	3	2.056	0.002	0.8342	0.0014	
ATHO-G	3	2.074	0.005	0.8423	0.0009	
StHs6/80-G	3	2.042	0.001	0.8256	0.0006	
T1-G	3	2.081	0.002	0.8367	0.0008	
GOR128-G	3	2.081	0.001	0.8479	0.0014	
GOR132-G	3	2.007	0.005	0.8156	0.0024	
<i>LA-ICPMS^e</i>						
KL2-G	4	2.024	0.001	0.8225	0.0001	
ML3B-G	4	2.055	0.002	0.8317	0.0042	
ATHO-G	4	2.073	0.001	0.8417	0.0017	
StHs6/80-G	4	2.036	0.006	0.8264	0.0017	
T1-G	5	2.081	0.004	0.8382	0.0017	
GOR128-G	2	2.068	0.006	0.8432	0.0025	
GOR132-G	4	2.011	0.004	0.8179	0.0016	

^aJochum et al. [2005b]. N, number of glass analyses.

^bMean TIMS Pb isotope ratios using different splits (C = 29). In-run precision (2RSE) is 0.002–0.01%.

^cMC-ICPMS (C = 64) measurements of the reference glasses and NIST SRM 981. In-run precision is typically 0.003%.

^dMean Pb isotope ratios by solution ICPMS using the single collector Element 2 ICP mass spectrometer (C = 70). About 2100 scans have been performed for each analysis.

^eMean Pb isotope ratios obtained from three-spot LA-ICPMS analyses of different splits using spot sizes of 60–160 μm and the electrical scan mode of the Element 2 mass spectrometer (C = 72).

ble with recommendations of the ISO [Kane, 2002, 2004; Kane et al., 2003]. In this paper we adapt to these recommendations in order to meet the requirements of the certifying procedure.

4.1. Identification of Qualified Laboratories

[76] Certification can only be accomplished satisfactorily by laboratories having the technical competence to perform measurements that match certification goals for reference values, particularly recognizing the need to minimize interlaboratory

bias and to achieve the appropriate standards of traceability and uncertainty [Kane et al., 2003]. On the basis of ISO Guide 35 [ISO, 1989], at least 15 laboratories are required for interlaboratory programmes. In this interlaboratory programme, 65 laboratories (Table 2) participated in the geochemical characterization of the MPI-DING glasses. Fifty-eight of them are pure geochemistry and the others are applied geochemistry laboratories. More than 95% of the laboratories were invited to analyze the glasses. The remaining laboratories have been self-selecting, partly by publishing analytical data of the samples. All laboratories were

Figure 4. $^{208}\text{Pb}/^{206}\text{Pb}$ ratios measured in two MPI-DING glasses using four splits for TIMS ($C = 29$) and one split for MC-ICPMS ($C = 64$). LA-ICPMS spot analyses ($C = 72$) were performed at different locations of the glasses. The horizontal lines are average values of TIMS/MC-ICPMS and LA-ICPMS data, respectively. The shaded bands represent typical uncertainties (1 SD) of these data. Bars indicate in-run precision (± 1 SE). The figure shows small, but significant, isotopic heterogeneities in the different glass fragments, especially for sample ML3B-G. However, differences are lower than the reproducibility obtained from LA-ICPMS (and SIMS).

considered as “qualified”. According to the IAG protocol [Kane *et al.*, 2003], the competence is assessed for some laboratories by participating in IAG GeoPT™ proficiency testing programme and interlaboratory standard method evaluations. Competence of all laboratories is assessed on the quality of published research data where issues of error investigation and uncertainty estimation have been evaluated satisfactorily. The collaborating laboratories have demonstrated their technical competence in geochemical research by using thoroughly investigated and well established methods, as well as the publication of reports and research papers describing improvements to “state of the practice” analytical techniques. Four laboratories are equipped to perform isotope dilution by TIMS ($C = 4, 53$), MC-ICPMS ($C = 26, 74$) and ICPMS ($C = 35, 48, 66$) using dissolved samples. A special ID-SSMS ($C = 1$) and ID-MIC-SSMS ($C = 2$)

technique was also applied for some elements. ID is considered to be a definitive method with negligible systematic errors. This is demonstrated in auxiliary material Tables S1a, S1b, and S1h, where most ID-ICPMS data agree with the ID-TIMS values within 2 SD.

4.2. Data Assessment

[77] Each laboratory submitted their mean results with the respective standard deviations. Nearly all of the analysts also provided the results of all measurements made. A brief description of the method and the procedure used is given in section 2. References for a detailed description of the techniques used are also given. The analytical data of auxiliary material Tables S1a–S1h are accompanied by estimated combined standard uncertainties [Eurachem, 2000]. These uncertainties comprise all components of variance. Some of the components were evaluated from the statistical distribution of the results of series of measurements and were characterized by relative standard deviations (%). The other components (e.g., calibration error, mass bias), which were also characterized by standard deviations, were evaluated from assumed probability distributions based on experience or other information. As already mentioned, some data are unacceptable presumably because of technical reasons. These outliers were rejected (data are marked). The rejection rates are very low, ranging between 1% to 3% for the different glasses.

4.3. Traceability

[78] Traceability [King, 1997; Potts, 1997] is a key concept in the characterization of reference samples. It links the validity of all analytical measurements to national and international standards through an unbroken chain of comparisons, for each of which an analytical uncertainty is known at a specified level of confidence [Kane, 2002]. In geochemical research, the USGS rock powders BCR-1, BHVO-1, the NIST glasses and other well-known reference materials can be legitimately viewed as important national and international samples that should be accepted as key links in traceability chains. As shown in section 2 and by Jochum *et al.* [2000], traceability was established in the results from the various techniques by the use of such international reference materials, for example, to set up the calibration.

[79] Agreement between two or more independent methods and the use of definitive methods, such as

Table 13a. Summary of Composition Data for KL2-G^a

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value				
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov.	Mean	U	n	
H2O, %m/m									0.015		0.015			0.015		1	Inf
Li, µg/g			5.4				5.0	0.8	5.1	0.7	5.2	0.2	5.1	0.5	9	Ref	
Be, µg/g							0.73	0.11	1.11	0.32	0.92	0.27	0.88	0.34	5	Inf	
B, µg/g							2.69	0.23	2.80	0.28	2.74	0.07	2.73	0.28	5	Inf	
CO2, µg/g									5.2		5.2		5.2		1	Inf	
O, %m/m									44.4		44.4		44.4		1	Inf	
F, µg/g									177		177		177		1	Inf	
Na2O, %m/m					2.24	0.08			2.38	0.13	2.31	0.10	2.35	0.08	14	Ref	
MgO, %m/m					7.35				7.34	0.16	7.35	0.01	7.34	0.09	13	Ref	
Al2O3, %m/m					13.2				13.3	0.3	13.3	0.1	13.3	0.2	13	Ref	
SiO2, %m/m					50.5				50.3	0.6	50.4	0.1	50.3	0.3	13	Ref	
P2O5, %m/m					0.240				0.230	0.034	0.235	0.007	0.232	0.026	8	Ref	
S, µg/g									7.7		7.7		7.7		1	Inf	
Cl, µg/g									26	5	26		26		2	Inf	
K2O, %m/m	0.488				0.472	0.011			0.480	0.020	0.480	0.008	0.480	0.010	14	Ref	
CaO, %m/m					11.0	0.5			10.9	0.4	10.9	0.0	10.9	0.2	16	Ref	
Sc, µg/g			31.0		31.0	1.3	31.7	1.8	33.6	0.8	31.8	1.2	31.8	0.9	15	Ref	
TiO2, %m/m					2.52		2.66	0.28	2.53	0.19	2.57	0.08	2.56	0.09	23	Ref	
V, µg/g							288	33	373	80	330	60	309	38	11	Ref	
Cr, µg/g					285	14	278	22	328	37	297	27	294	27	14	Ref	
MnO, %m/m					0.163	0.002	0.147	0.016	0.171	0.020	0.160	0.012	0.165	0.009	22	Ref	
FeO T, %m/m					10.7	0.4			10.7	0.2	10.7		10.7	0.1	15	Ref	
Co, µg/g			43.0		42.2	1.6	41.1	5.2	39.7	0.5	41.5	1.4	41.2	2.3	17	Ref	
Ni, µg/g			111		120	7	110	12	114	8	114	5	112	5	16	Ref	
Cu, µg/g			97.0				86.4	11.1	89.5	9.2	91.0	5.4	87.9	9.1	11	Ref	
Zn, µg/g			116		113	10	108	14	109	12	111	4	110	10	11	Ref	
Ga, µg/g			22.0		19.5	0.7	20.0	2.2	19.6	2.3	20.3	1.2	20.0	1.2	12	Ref	
Ge, µg/g							1.3	0.6	1.0		1.2	0.2	1.3	0.8	4	Inf	
As, µg/g							0.17	0.08			0.17		0.17		2	Inf	
Se, µg/g							0.07				0.07		0.07		1	Inf	
Br, µg/g					<0.2						<0.2		<0.2		1	Inf	
Rb, µg/g	8.69		8.82	0.46	10.27	0.64	8.47	0.92	7.00		8.65	1.16	8.70	0.40	27	Ref	
Sr, µg/g	366	4	367	29	366	23	346	23	362	23	361	9	356	8	32	Ref	
Y, µg/g			26.8	1.5	31.3	3.3	24.1	1.9	25.9	2.4	27.0	3.1	25.4	1.1	27	Ref	
Zr, µg/g	159	5	159	8	169	20	142	10	159	11	157	10	152	5	34	Ref	
Nb, µg/g			15.4	0.3	16.1		14.8	1.1	15.0	1.2	15.3	0.6	15.0	0.5	27	Ref	
Mo, µg/g			3.6		4.3	1.0	3.3	0.7	4.0		3.8	0.4	3.6	0.6	9	Ref	
Rh, µg/g									37		37		37		1	Inf	
Pd, µg/g					<6						<6		<6		1	Inf	
Ag, µg/g							0.15	0.11			0.15		0.15		2	Inf	
Cd, µg/g							0.09	0.05			0.09		0.09		2	Inf	
In, µg/g							0.24	0.05			0.24		0.24		3	Inf	
Sn, µg/g			1.60		1.90		1.51	0.50	1.40		1.60	0.21	1.54	0.29	13	Ref	
Sb, µg/g			0.16		0.14	0.02	0.11	0.04	0.19		0.15	0.03	0.14	0.03	9	Ref	
Cs, µg/g			0.127	0.011	0.100		0.108	0.021	0.120		0.114	0.012	0.115	0.009	20	Ref	
Ba, µg/g	124	2	125	4	126	5	120	8	126	25	124	3	123	5	32	Ref	
La, µg/g	13.3		13.2	0.4	13.1	0.1	13.0	0.7	13.0	0.9	13.1	0.1	13.1	0.2	32	Ref	
Ce, µg/g	33.2		32.7	1.1	33.4	0.7	32.1	2.2	31.7	2.6	32.6	0.7	32.4	0.7	30	Ref	
Pr, µg/g			4.76	0.1	4.67	0.05	4.54	0.29	4.55	0.21	4.63	0.11	4.60	0.10	25	Ref	
Nd, µg/g	22.0	0.2	21.7	0.8	22.0	1.5	21.4	1.1	21.5	1.9	21.7	0.3	21.6	0.4	30	Ref	
Sm, µg/g	5.69	0.13	5.65	0.34	5.56	0.18	5.48	0.27	5.49	0.40	5.58	0.09	5.54	0.09	31	Ref	
Eu, µg/g	1.99		2.00	0.07	1.91	0.09	1.79	0.10	1.90	0.24	1.92	0.08	1.92	0.04	32	Ref	
Gd, µg/g	6.09	0.05	6.38	0.37	6.50	1.18	5.64	0.38	6.23	0.11	6.17	0.33	5.92	0.20	29	Ref	
Tb, µg/g			0.933	0.040	0.923	0.059	0.851	0.075	0.986		0.923	0.056	0.890	0.031	25	Ref	
Dy, µg/g	5.44	0.06	5.37	0.27	5.34	0.25	5.10	0.38	5.15	0.32	5.28	0.15	5.22	0.12	29	Ref	
Ho, µg/g			0.987	0.038	0.998	0.010	0.941	0.063	0.953	0.046	0.970	0.027	0.961	0.022	26	Ref	
Er, µg/g	2.67	0.09	2.66	0.15	2.67	0.10	2.46	0.17	2.53	0.26	2.60	0.10	2.54	0.07	29	Ref	
Tm, µg/g			0.347	0.011	0.320		0.325	0.020	0.320		0.328	0.013	0.331	0.009	22	Ref	
Yb, µg/g	2.13	0.04	2.15	0.12	2.09	0.03	2.07	0.13	2.16	0.24	2.12	0.04	2.10	0.05	32	Ref	
Lu, µg/g	0.293		0.294	0.010	0.286	0.022	0.279	0.024	0.295	0.078	0.289	0.01	0.285	0.009	30	Ref	

Table 13a. (continued)

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov. Mean	U	n
Hf, µg/g	4.03	0.08	4.38	0.17	4.21	0.01	3.70	0.31	4.19		4.10	0.25	3.93	0.14	26 Ref
Ta, µg/g	0.917	0.009	0.968	0.036	0.987	0.042	0.963	0.066	0.910		0.949	0.034	0.961	0.022	27 Ref
W, µg/g					0.30		0.38	0.06			0.34	0.05	0.37	0.06	7 Inf
Re, µg/g							0.0007	0.0002			0.0007		0.0007		3 Inf
Os, µg/g					<0.3						<0.3		<0.3		1 Inf
Ir, µg/g					0.1						0.1		0.1		1 Inf
Pt, µg/g					7		10		24	21	14	9	16		4 Inf
Au, µg/g					0.1		0.1	0.0	1.2		0.5	0.6	0.4		4 Inf
Hg, µg/g					<0.3						<0.3		<0.3		1 Inf
Tl, µg/g							0.0074	0.0006			0.0074		0.0074		2 Inf
Pb, µg/g	1.97	0.16	2.27	0.10	2.18	0.08	2.04	0.10	2.00		2.09	0.13	2.07	0.10	18 Ref
Bi, µg/g					0.039		0.035	0.007			0.037	0.003	0.036	0.014	3 Inf
Th, µg/g	0.971		1.02	0.05	1.08	0.09	1.01	0.08	0.97	0.13	1.01	0.04	1.02	0.03	32 Ref
U, µg/g	0.525	0.023	0.567	0.035	0.548	0.040	0.551	0.049			0.547	0.017	0.548	0.016	27 Ref

^a All techniques mean: average of 1–5 techn. groups means, Ov. (overall) mean: unweighted mean of all results, Ref: reference value, Inf: information value, SD: standard deviation, U: uncertainty at 95% confidence level, n: number of analyses. BULK T.: XRF, SSMS, MIC-SSMS, MS, INAA, ICP-AES; MICRO T.: EPMA, SIMS, LIMS, SR-XRF, PIXE.

Table 13b. Summary of Composition Data for ML3B-G^a

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov. Mean	U	n
H ₂ O, %m/m									0.015		0.015		0.015		1 Inf
Li, µg/g			4.7	0.2			4.7	0.4	3.9	0.3	4.4	0.5	4.5	0.4	10 Ref
Be, µg/g							0.58	0.10	0.75		0.67	0.12	0.62	0.14	5 Inf
B, µg/g							2.5	0.6	2.2		2.4	0.2	2.5	0.6	5 Inf
CO ₂ , µg/g									4.7		4.7		4.7		1 Inf
O, %m/m									44.7		44.7		44.7		1 Inf
F, µg/g									70		70		70		1 Inf
Na ₂ O, %m/m					2.35	0.04			2.42	0.10	2.38	0.05	2.40	0.06	13 Ref
MgO, %m/m					6.56	0.11			6.59	0.13	6.58	0.02	6.59	0.08	13 Ref
Al ₂ O ₃ , %m/m					13.3	0.4			13.6	0.3	13.5	0.2	13.6	0.2	13 Ref
SiO ₂ , %m/m					50.5	2.2			51.5	0.6	51.0	0.8	51.4	0.6	13 Ref
P ₂ O ₅ , %m/m					0.21	0.00			0.23	0.03	0.222	0.018	0.230	0.025	9 Ref
S, µg/g									1.2		1.2		1.2		1 Inf
Cl, µg/g									7.5		7.5		7.5		1 Inf
K ₂ O, %m/m	0.386				0.382	0.008			0.386	0.006	0.385	0.002	0.385	0.004	14 Ref
CaO, %m/m					10.5	0.20			10.5	0.1	10.5	0.0	10.5	0.1	14 Ref
Sc, µg/g			30.0		30.9		31.6	2.9	33.7		31.5	1.6	31.6	1.6	13 Ref
TiO ₂ , %m/m					2.02	0.06	2.33	0.21	2.04	0.17	2.13	0.18	2.13	0.09	23 Ref
V, µg/g					188		277	29	261	43	242	47	268	23	13 Ref
Cr, µg/g					152	16	179	44	194	23	175	21	177	23	15 Ref
MnO, %m/m					0.169	0.002	0.158	0.014	0.174	0.022	0.167	0.008	0.170	0.009	20 Ref
FeO T, %m/m					11.1	0.5			10.9	0.2	11.0	0.2	10.9	0.1	15 Ref
Co, µg/g					38.4	9.0	42.0	6.0	40.2		40.2	1.8	41.2	3.5	15 Ref
Ni, µg/g			105		125	31	103	9	97		107	12	107	9	15 Ref
Cu, µg/g			121				110	9	117		116	6	112	10	9 Ref
Zn, µg/g			116		111	8	102	21	114	8	111	6	108	14	9 Ref
Ga, µg/g			21.0		19.0		18.5	2.8	23.3		20.4	2.2	19.6	2.1	11 Ref
Ge, µg/g							1.2	0.8	0.9		1.1	0.2	1.1	1.1	4 Inf
As, µg/g							0.28	0.22			0.28		0.28		3 Inf
Se, µg/g							0.06				0.06		0.06		1 Inf

Table 13b. (continued)

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov. Mean	U	n
Br, µg/g									<0.2		<0.2		<0.2		1 Inf
Rb, µg/g	5.81		5.76	0.20			5.82	0.60	5.70		5.77	0.06	5.80	0.21	23 Ref
Sr, µg/g	316	2	312	11	319	16	309	12	319	16	315	4	312	4	30 Ref
Y, µg/g			24.7	1.5	27.6		23.3	1.7	24.6	2.0	25.1	1.8	23.9	0.7	27 Ref
Zr, µg/g	130	4	125	5	137	5	117	8	126	6	127	7	122	3	31 Ref
Nb, µg/g			8.48	0.46	9.03		8.43	0.38	9.38	0.70	8.83	0.46	8.61	0.22	26 Ref
Mo, µg/g			18.0		18.0		16.1	3.4	17.3		17.4	0.9	16.7	2.3	8 Ref
Rh, µg/g															
Pd, µg/g															
Ag, µg/g							0.03				0.03		0.03		1 Inf
Cd, µg/g							0.10	0.04			0.10		0.10		2 Inf
In, µg/g							0.23	0.04			0.23		0.20		3 Inf
Sn, µg/g			1.10				1.15	0.48			1.12	0.03	1.14	0.33	10 Ref
Sb, µg/g			0.13				0.11	0.04			0.12	0.02	0.11	0.05	5 Inf
Cs, µg/g			0.148	0.010			0.137	0.027			0.142	0.008	0.140	0.012	18 Ref
Ba, µg/g	80.8	0.8	88.5	12.2	82.0		79.2	4.1	78.7	8.0	81.8	4.0	80.1	2.2	26 Ref
La, µg/g	9.04		8.92	0.23	9.09	0.30	9.04	0.45	8.80	0.14	8.98	0.12	8.99	0.13	30 Ref
Ce, µg/g	23.4		22.9	0.8	24.3	0.6	23.2	0.9	22.5	1.0	23.3	0.6	23.1	0.3	29 Ref
Pr, µg/g			3.42	0.06	3.37		3.42	0.14	3.54	0.27	3.44	0.07	3.43	0.06	24 Ref
Nd, µg/g	16.9	0.3	16.2	0.7	16.8	0.3	16.9	0.6	16.4	1.1	16.6	0.3	16.7	0.2	29 Ref
Sm, µg/g	4.78	0.02	4.64	0.23	4.78	0.16	4.74	0.24	4.85	0.01	4.76	0.07	4.75	0.07	29 Ref
Eu, µg/g	1.71		1.68	0.06	1.65	0.02	1.67	0.06	1.73	0.02	1.69	0.03	1.67	0.02	29 Ref
Gd, µg/g	5.28	0.08	5.35	0.33	5.10		5.10	0.32	5.10	0.03	5.18	0.12	5.26	0.23	28 Ref
Tb, µg/g			0.811	0.040	0.823	0.011	0.783	0.057	0.805	0.021	0.805	0.016	0.797	0.021	24 Ref
Dy, µg/g	4.90	0.11	4.84	0.23	4.83	0.30	4.84	0.21	4.71	0.24	4.82	0.07	4.84	0.07	28 Ref
Ho, µg/g			0.918	0.035	0.916	0.008	0.901	0.051	0.896	0.020	0.908	0.011	0.906	0.018	25 Ref
Er, µg/g	2.52	0.10	2.45	0.13	2.45		2.41	0.13	2.44	0.28	2.45	0.04	2.44	0.05	27 Ref
Tm, µg/g			0.324	0.008			0.324	0.020	0.330		0.326	0.004	0.324	0.007	21 Ref
Yb, µg/g	2.04	0.02	2.01	0.08	2.15	0.04	2.06	0.12	2.08	0.05	2.07	0.05	2.06	0.04	29 Ref
Lu, µg/g	0.287		0.281	0.010	0.288	0.025	0.287	0.019	0.292	0.002	0.287	0.004	0.286	0.006	28 Ref
Hf, µg/g	3.28	0.08	3.45	0.05	3.51	0.29	3.14	0.20	3.25	0.13	3.32	0.15	3.22	0.08	27 Ref
Ta, µg/g	0.529	0.005	0.570	0.030	0.563		0.552	0.033			0.553	0.018	0.555	0.013	23 Ref
W, µg/g							0.35	0.07			0.35		0.35	0.09	5 Inf
Re, µg/g							0.0007	0.0002			0.0007		0.0007		2 Inf
Os, µg/g															
Ir, µg/g					0.03						0.03		0.03		1 Inf
Pt, µg/g					6.8		9.7		10.0		8.8	1.8	8.8	8.8	3 Ref
Au, µg/g					0.067		0.064	0.034			0.066	0.002	0.065	0.082	3 Inf
Hg, µg/g					<0.3						<0.3		<0.3		1 Inf
Tl, µg/g							0.008	0.004			0.008		0.008		2 Inf
Pb, µg/g	1.32	0.12	1.33	0.10	1.40		1.40	0.15			1.36	0.04	1.38	0.07	16 Ref
Bi, µg/g					0.010		0.004	0.002			0.007	0.004	0.006	0.009	3 Inf
Th, µg/g	0.547		0.534	0.014	0.565	0.021	0.550	0.030			0.549	0.013	0.548	0.011	26 Ref
U, µg/g	0.427	0.014	0.436	0.021	0.438	0.045	0.448	0.055			0.437	0.008	0.442	0.018	26 Ref

^a All techniques mean: average of 1–5 techn. groups means, Ov. (overall) mean: unweighted mean of all results, Ref: reference value, Inf: information value, SD: standard deviation, U: uncertainty at 95% confidence level, n: number of analyses. BULK T.: XRF, SSMS, MIC-SSMS, MS, INAA, ICP-AES; MICRO T.: EPMA, SIMS, LIMS, SR-XRF, PIXE.

ID, provide traceability to the fullest extent possible in these circumstances. As already mentioned 16 different analytical techniques were used for the characterization of the MPI-DING glasses (auxiliary material Tables S1a–S1i). Most of them are independent with respect to the use of different sample preparation techniques based on different principles, the use of different calibrants and dif-

ferent theoretical bases for the measurements [Kane *et al.*, 2003]. To compare more easily the results obtained from the 16 different techniques (auxiliary material Tables S1a–S1i), we created five major groups of analytical methods. Criteria for this grouping are in particular bulk-microanalytical method, definitive-comparative method, and powdered/dissolved samples.

Table 13c. Summary of Composition Data for StHs6/80-G^a

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value				
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov.	Mean	U	n	
H2O, %m/m					0.030				0.020		0.025	0.007	0.025			2	Inf
Li, µg/g			21.4	3.4			21.7	3.8	18.4	0.8	20.5	1.8	20.7	2.3	10	Ref	
Be, µg/g							1.1	0.1	1.3	0.1	1.2	0.1	1.2	0.1	6	Inf	
B, µg/g					11.6		11.9	1.8	11.6	1.3	11.7	0.2	11.8	1.3	7	Ref	
CO2, µg/g									4.4		4.4		4.4			1	Inf
O, %m/m									47.9		47.9		47.9			1	Inf
F, µg/g									320		320		320			1	Inf
Na2O, %m/m					4.59	0.11			4.38	0.25	4.48	0.15	4.44	0.14	13	Ref	
MgO, %m/m					2.01	0.01			1.96	0.06	1.98	0.03	1.97	0.04	13	Ref	
Al2O3, %m/m					17.7	0.2			17.8	0.4	17.7	0.1	17.8	0.2	12	Ref	
SiO2, %m/m					64.0	0.5			63.6	0.8	63.8	0.2	63.7	0.5	12	Ref	
P2O5, %m/m					0.160	0.000			0.166	0.021	0.163	0.004	0.164	0.018	6	Ref	
S, µg/g									2.7		2.7		2.7		1	Inf	
Cl, µg/g									231	39	231		231	50	5	Ref	
K2O, %m/m	1.30				1.27	0.04			1.30	0.04	1.29	0.02	1.29	0.02	14	Ref	
CaO, %m/m					5.19	0.20			5.32	0.11	5.26	0.10	5.28	0.09	15	Ref	
Sc, µg/g			9.6		9.8	0.2	11.9	1.3	11.8	0.4	10.8	1.3	11.5	0.8	15	Ref	
TiO2, %m/m					0.688	0.011	0.746	0.065	0.683	0.026	0.705	0.035	0.703	0.021	22	Ref	
V, µg/g							88.0	8.0	96.0	18.1	92.0	5.7	90.3	6.7	14	Ref	
Cr, µg/g					19.7	9.0	15.5	3.4	17.0	7.0	17.4	2.1	16.9	3.3	15	Ref	
MnO, %m/m					0.075	0.004	0.072	0.004	0.078	0.011	0.075	0.003	0.076	0.004	21	Ref	
FeO T, %m/m					4.37	0.18			4.37	0.12	4.37	0.00	4.37	0.07	15	Ref	
Co, µg/g			13.0		12.7	0.2	13.6	1.6	11.7	4.6	12.8	0.8	13.2	1.1	15	Ref	
Ni, µg/g			22.0		29.5	9.2	23.4	7.1	19.7	4.7	23.7	4.2	23.7	3.8	15	Ref	
Cu, µg/g			40.0				42.0	13.4	40.3	1.1	40.8	1.1	41.5	8.3	10	Ref	
Zn, µg/g			64		65	6	71	10	66	7	66	3	67	7	10	Ref	
Ga, µg/g			21.0		17.5	0.7	22.0	5.1	21.2	0.2	20.4	2.0	20.9	2.7	11	Ref	
Ge, µg/g							1.0	0.7	1.4	0.0	1.2	0.3	1.1	0.7	5	Ref	
As, µg/g					2.10	0.14	2.89	0.66	3.05	0.35	2.68	0.51	2.73	0.48	8	Ref	
Se, µg/g							0.04				0.04		0.04		1	Inf	
Br, µg/g					0.8	0.1			0.7		0.8	0.1	0.8	0.3	3	Inf	
Rb, µg/g	29.5		28.6	0.8	29.0	0.3	31.7	4.4	28.3	4.6	29.5	1.4	30.7	1.7	25	Ref	
Sr, µg/g	506		491	16	482	17	477	21	491	29	489	11	482	8	30	Ref	
Y, µg/g			11.7		10.6	0.4	11.4	1.1	11.4	1.4	11.3	0.5	11.4	0.4	26	Ref	
Zr, µg/g	125		124	6	125	5	115	10	119	9	121	4	118	3	31	Ref	
Nb, µg/g			6.61		8.1	0.01	6.90	0.55	7.00	0.80	7.14	0.63	6.94	0.25	25	Ref	
Mo, µg/g			1.8		2.4	0.8	1.8	0.8			2.0	0.3	2.0	0.6	8	Ref	
Rh, µg/g																	
Pd, µg/g					<6						<6		<6			1	Inf
Ag, µg/g							0.02				0.02		0.02		1	Inf	
Cd, µg/g							0.1				0.1		0.1		1	Inf	
In, µg/g							0.5	0.5			0.5		0.5		2	Inf	
Sn, µg/g			1.0				1.1	0.3	0.7		1.0	0.2	1.1	0.2	10	Ref	
Sb, µg/g			0.2		0.22	0.02	0.18	0.09			0.20	0.02	0.20	0.07	6	Ref	
Cs, µg/g			1.59	0.13	1.96	0.06	1.75	0.23	1.89		1.80	0.16	1.75	0.11	17	Ref	
Ba, µg/g	310		339	52	300	0	298	15	283	28	306	21	298	9	28	Ref	
La, µg/g	12.5		11.9	0.1	11.7	0.7	12.1	0.7	11.8	0.8	12.0	0.3	12.0	0.3	28	Ref	
Ce, µg/g	26.5		25.6	1.3	27.5	5.0	26.3	1.2	24.5	1.2	26.1	1.1	26.1	0.7	28	Ref	
Pr, µg/g			3.22	0.09	3.04		3.21	0.16	3.15	0.05	3.15	0.08	3.20	0.06	22	Ref	
Nd, µg/g	13.5		12.6	0.4	12.8	2.0	13.0	0.6	11.9	2.2	12.8	0.6	13.0	0.3	28	Ref	
Sm, µg/g	2.90		2.81	0.17	2.81	0.10	2.79	0.12	2.63	0.14	2.79	0.10	2.78	0.05	27	Ref	
Eu, µg/g	0.987		0.977	0.093	0.963	0.026	0.954	0.046	0.875	0.078	0.951	0.044	0.953	0.022	26	Ref	
Gd, µg/g	2.73		2.77	0.29	2.75	0.35	2.55	0.20	2.47	0.12	2.65	0.14	2.59	0.09	26	Ref	
Tb, µg/g			0.396	0.029	0.370	0.028	0.367	0.023	0.365	0.014	0.375	0.015	0.371	0.011	22	Ref	
Dy, µg/g	2.32		2.22	0.07	2.41	0.01	2.22	0.15	2.03	0.12	2.24	0.14	2.22	0.06	25	Ref	
Ho, µg/g			0.428	0.011	0.395	0.021	0.421	0.028	0.426	0.006	0.417	0.015	0.420	0.011	22	Ref	
Er, µg/g	1.26		1.22	0.07	0.95		1.19	0.08	1.18	0.07	1.16	0.12	1.18	0.04	25	Ref	
Tm, µg/g			0.173	0.006			0.170	0.015	0.180	0.028	0.174	0.005	0.172	0.007	19	Ref	
Yb, µg/g	1.17		1.11	0.01	1.12	0.02	1.14	0.08	1.09	0.03	1.13	0.03	1.13	0.03	28	Ref	

Table 13c. (continued)

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov. Mean	U	n
Lu, µg/g	0.174		0.170	0.000	0.167	0.006	0.166	0.017	0.179	0.020	0.171	0.005	0.168	0.006	27 Ref
Hf, µg/g	3.23	0.12	3.25	0.04	3.28	0.04	2.98	0.21	3.14	0.05	3.17	0.12	3.07	0.09	24 Ref
Ta, µg/g	0.403	0.004	0.410		0.421	0.001	0.423	0.036			0.414	0.010	0.420	0.015	21 Ref
W, µg/g							0.47	0.17			0.47		0.47	0.18	6 Inf
Re, µg/g							0.0009	0.0006			0.0009		0.0009	0.0017	3 Inf
Os, µg/g					<1						<1		<1		1 Inf
Ir, µg/g					0.02						0.02		0.02		2 Inf
Pt, µg/g							1				1		1		1 Inf
Au, µg/g					0.042	0.000	0.053	0.004			0.048	0.008	0.048	0.032	4 Inf
Hg, µg/g					<0.2						<0.2		<0.2		1 Inf
Tl, µg/g							0.11	0.02			0.11		0.11		3 Inf
Pb, µg/g			9.66	0.36			10.4	1.97	9.95	1.34	10.0	0.4	10.3	0.9	16 Ref
Bi, µg/g					0.13		0.10	0.05			0.11	0.02	0.11	0.07	4 Inf
Th, µg/g			2.27	0.04	2.19	0.06	2.30	0.21	2.21		2.24	0.05	2.28	0.07	25 Ref
U, µg/g			0.98	0.03	1.02	0.13	1.02	0.11			1.01	0.02	1.01	0.04	24 Ref

^aAll techniques mean: average of 1–5 techn. groups means, Ov. (overall) mean: unweighted mean of all results, Ref: reference value, Inf: information value, SD: standard deviation, U: uncertainty at 95% confidence level, n: number of analyses. BULK T.: XRF, SSMS, MIC-SSMS, MS, INAA, ICP-AES; MICRO T.: EPMA, SIMS, LIMS, SR-XRF, PIXE.

Table 13d. Summary of Composition Data for GOR128-G^a

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov. Mean	U	n
H ₂ O, %m/m									0.026		0.026		0.026		1 Inf
Li, µg/g			9.9	0.2			12.2	1.5	7.1	0.4	9.7	2.5	10.4	1.7	11 Ref
Be, µg/g							0.033	0.005	0.037	0.005	0.035	0.003	0.034	0.007	4 Inf
B, µg/g					22.7		24.8	3.1	20.4	2.0	22.6	2.2	23.5	2.8	7 Ref
CO ₂ , µg/g									4.4		4.4		4.4		1 Inf
O, %m/m									44.4		44.4		44.4		1 Inf
F, µg/g									25		25		25		1 Inf
Na ₂ O, %m/m					0.548	0.025			0.588	0.030	0.568	0.028	0.574	0.026	9 Ref
MgO, %m/m					26.1	0.1			25.9	0.5	26.0	0.1	26.0	0.3	10 Ref
Al ₂ O ₃ , %m/m					9.93	0.25			9.90	0.24	9.91	0.02	9.91	0.17	9 Inf
SiO ₂ , %m/m					46.6	0.8			45.9	0.5	46.3	0.5	46.1	0.4	11 Ref
P ₂ O ₅ , %m/m					0.028	0.004	0.020		0.025	0.005	0.024	0.004	0.025	0.005	6 Ref
S, µg/g									4.3		4.3		4.3		1 Inf
Cl, µg/g									12		12		12		1 Inf
K ₂ O, %m/m	0.035				0.037	0.003			0.036	0.010	0.036	0.001	0.036	0.005	11 Ref
CaO, %m/m					6.14	0.23	6.65		6.23	0.11	6.34	0.27	6.24	0.12	12 Ref
Sc, µg/g			30.0		30.2		32.5	1.8			30.9	1.4	32.1	1.4	10 Ref
TiO ₂ , %m/m					0.283	0.004	0.302	0.032	0.279	0.007	0.288	0.013	0.288	0.012	16 Ref
V, µg/g					170		191	17			181	15	189	13	10 Ref
Cr, µg/g					2120	35	2364	222	2210	78	2231	124	2272	171	18 Ref
MnO, %m/m					0.172	0.006	0.183	0.030	0.176	0.014	0.177	0.005	0.176	0.009	14 Ref
FeO T, %m/m					9.82	0.18			9.82	0.19	9.82	0.00	9.81	0.12	11 Ref
Co, µg/g			81.0		78.8	8.2	95.7	9.8			85.2	9.2	92.4	6.2	15 Ref
Ni, µg/g					1070	44	1076	106			1073	4	1074	61	11 Ref
Cu, µg/g			57.0				64.5	17.3			60.8	5.3	63.8	12.5	10 Ref
Zn, µg/g			72.0		75.5	0.7	75.0	4.6			74.2	1.9	74.7	6.7	6 Ref
Ga, µg/g			9.10		8.28		9.04	1.11			8.81	0.46	8.67	1.07	7 Ref
Ge, µg/g							0.96	0.01			0.96		0.96		2 Inf
As, µg/g							<0.1				<0.1		<0.1		1 Inf
Se, µg/g							<0.03				<0.03		<0.03		1 Inf
Br, µg/g					<0.3						<0.3		<0.3		1 Inf
Rb, µg/g	0.373		0.470	0.036			0.395	0.043			0.413	0.051	0.406	0.025	18 Ref

Table 13d. (continued)

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov. Mean	U	n
Sr, µg/g	33.1		30.9	2.7	34.0		29.5	1.9	28.6		31.2	2.3	30.0	1.0	21 Ref
Y, µg/g			12.3	1.0	10.0		11.8	1.2	12.1		11.6	1.1	11.8	0.5	21 Ref
Zr, µg/g	10.1		10.9	1.2	10.4		9.8	1.1	10.3		10.3	0.4	10.0	0.5	23 Ref
Nb, µg/g			0.118	0.017	0.101		0.096	0.012			0.105	0.012	0.099	0.007	18 Ref
Mo, µg/g			0.60				0.73	0.27			0.66	0.09	0.71	0.26	6 Inf
Rh, µg/g															
Pd, µg/g															
Ag, µg/g					<0.5						<0.5		<0.5		1 Inf
Cd, µg/g							0.072	0.003			0.072		0.072		2 Inf
In, µg/g							0.067	0.029			0.067		0.067		3 Inf
Sn, µg/g			0.220				0.225	0.096			0.223	0.004	0.224	0.092	6 Inf
Sb, µg/g			0.020				0.006	0.002			0.013	0.010	0.010	0.021	3 Inf
Cs, µg/g			0.233	0.016	0.290		0.237	0.052			0.253	0.032	0.240	0.025	16 Ref
Ba, µg/g	1.09		1.04				1.06	0.07	1.00		1.05	0.04	1.06	0.03	20 Ref
La, µg/g	0.129		0.130	0.011	0.110		0.118	0.007	0.140		0.125	0.012	0.121	0.004	23 Ref
Ce, µg/g	0.487		0.448	0.039	0.530		0.446	0.028	0.400		0.462	0.049	0.450	0.016	21 Ref
Pr, µg/g			0.110	0.011	0.104		0.098	0.005			0.104	0.006	0.100	0.004	19 Ref
Nd, µg/g	0.881		0.754	0.044	0.789		0.783	0.101	0.790		0.800	0.048	0.784	0.047	22 Ref
Sm, µg/g	0.604		0.535	0.052	0.558	0.085	0.514	0.039	0.530		0.548	0.035	0.525	0.020	23 Ref
Eu, µg/g	0.306		0.264	0.014	0.245	0.006	0.263	0.016	0.290		0.274	0.024	0.264	0.008	24 Ref
Gd, µg/g	1.40		1.19	0.01	1.20	0.42	1.15	0.11			1.23	0.11	1.17	0.04	21 Ref
Tb, µg/g			0.259	0.011	0.235	0.035	0.247	0.025			0.247	0.012	0.248	0.012	17 Ref
Dy, µg/g	2.30		1.96	0.09	1.93	0.01	1.97	0.18	1.89		2.01	0.17	1.98	0.07	23 Ref
Ho, µg/g			0.450	0.021	0.434	0.037	0.443	0.044			0.442	0.008	0.443	0.019	19 Ref
Er, µg/g	1.67		1.41	0.09	1.43		1.40	0.14	1.17		1.42	0.18	1.40	0.06	21 Ref
Tm, µg/g			0.206	0.006	0.180		0.205	0.018			0.197	0.015	0.204	0.009	17 Ref
Yb, µg/g	1.63		1.37	0.06	1.50	0.22	1.41	0.14	1.15		1.41	0.18	1.41	0.06	23 Ref
Lu, µg/g	0.250		0.205	0.009	0.215	0.007	0.203	0.021			0.218	0.022	0.206	0.009	22 Ref
Hf, µg/g	0.353	0.013	0.375	0.047	0.344		0.343	0.036			0.354	0.015	0.349	0.017	20 Ref
Ta, µg/g	0.024	0.000					0.019	0.002			0.021	0.003	0.019	0.001	13 Ref
W, µg/g					14.3		15.7	2.4			15.0	1.0	15.5	2.4	6 Inf
Re, µg/g							0.0006	0.00004			0.0006		0.0006		2 Inf
Os, µg/g															
Ir, µg/g					0.063						0.063		0.063		1 Inf
Pt, µg/g					9.6		12.6				11.1	2.1	11.1		2 Inf
Au, µg/g					0.028		0.021				0.024	0.005	0.024		2 Inf
Hg, µg/g					<0.2						<0.2		<0.2		1 Inf
Tl, µg/g							<0.003				<0.003		<0.003		1 Inf
Pb, µg/g			0.415	0.120	0.340		0.332	0.064			0.362	0.046	0.345	0.043	14 Ref
Bi, µg/g					0.0009						0.0009		0.0009		1 Inf
Th, µg/g			0.010		0.006		0.008	0.002	0.012		0.009	0.003	0.008	0.001	15 Ref
U, µg/g			0.0140	0.0053	0.0140		0.0118	0.0015			0.0133	0.001	0.0123	0.0012	18 Ref

^a All techniques mean: average of 1–5 techn. groups means, Ov. (overall) mean: unweighted mean of all results, Ref: reference value, Inf: information value, SD: standard deviation, U: uncertainty at 95% confidence level, n: number of analyses. BULK T.: XRF, SSMS, MIC-SSMS, MS, INAA, ICP-AES; MICRO T.: EPMA, SIMS, LIMS, SR-XRF, PIXE.

4.3.1. Bulk Analytical Techniques

[80] Isotope dilution (ID using TIMS, MC-ICPMS, ICPMS): ID is a definitive method and delivers data of very high quality with respect to precision and accuracy. ISO Guide 35 [ISO, 1989] specifically encourages use of definitive methods for the characterization of reference materials. Measurements were made directly in terms of base SI units. For ID analysis, samples were spiked and dissolved.

[81] ICPMS methods (ICPMS using single and multicollector instruments): ICPMS is a modern bulk analytical technique, which uses dissolved samples (typically about 50–100 mg sample amount) for analysis. Data were generally calibrated with certified standard solutions.

[82] Other bulk analytical techniques (XRF, SSMS, MIC-SSMS, MS, INAA, ICP-AES): With the exception of ICP-AES these techniques use powdered samples without chemical treatment.

Table 13e. Summary of Composition Data for GOR132-G^a

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value				
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov.	Mean	U	n	
H2O, %m/m									0.026		0.026			0.026		1	Inf
Li, µg/g			9.5	0.6			9.6	1.0	6.9	0.2	8.7	1.5	8.9	1.2	8	Ref	
Be, µg/g							0.10	0.08	0.04		0.07	0.04	0.08		3	Inf	
B, µg/g					15.6		17.6	2.6	17.8		17.0	1.2	17.2	2.6	5	Ref	
CO2, %m/m									5.8		5.8		5.8		1	Inf	
O, %m/m									44.0		44.0		44.0		1	Inf	
F, µg/g									22		22		22		1	Inf	
Na2O, %m/m					0.79	0.03			0.85	0.06	0.82	0.04	0.83	0.04	12	Ref	
MgO, %m/m					22.6	0.2			22.3	0.4	22.4	0.2	22.4	0.2	12	Ref	
Al2O3, %m/m					11.1	0.3			11.0	0.2	11.0	0.1	11.0	0.2	11	Ref	
SiO2, %m/m					46.1	1.0			45.4	0.4	45.7	0.5	45.5	0.4	12	Ref	
P2O5, %m/m					0.037	0.018			0.035	0.005	0.036	0.002	0.036	0.012	5	Inf	
S, µg/g									1.8		1.8		1.8		1	Inf	
Cl, µg/g									6.2		6.2		6.2		1	Inf	
K2O, %m/m	0.0314				0.0323	0.0053			0.0300	0.0053	0.0312	0.0012	0.0308	0.0034	13	Ref	
CaO, %m/m					8.38	0.38			8.48	0.10	8.43	0.07	8.45	0.12	14	Ref	
Sc, µg/g			34.0		34.9	1.2	37.2	1.6			35.4	1.7	36.5	1.2	11	Ref	
TiO2, %m/m					0.309	0.055	0.326	0.024	0.295	0.016	0.310	0.016	0.306	0.013	21	Ref	
V, µg/g					188		219	25	190		199	18	214	17	11	Ref	
Cr, µg/g					2425	87	2640	207	2510	149	2525	108	2528	183	17	Ref	
MnO, %m/m					0.149	0.006	0.147	0.014	0.160	0.015	0.152	0.007	0.154	0.007	18	Ref	
FeO T, %m/m					10.0	0.4			10.2	0.2	10.1	0.1	10.1	0.1	14	Ref	
Co, µg/g			93.0		86.6	6.8	94.5	10.7			91.4	4.2	92.7	5.7	14	Ref	
Ni, µg/g					1168	39	1194	122	1210		1190	21	1187	58	13	Ref	
Cu, µg/g			190		200		208	20			199	9	205	21	8	Ref	
Zn, µg/g			69.0		76.3	11.4	79.9	16.2			75.1	5.6	76.8	12.5	7	Ref	
Ga, µg/g			11.0		10.7	0.1	10.1	1.3			10.6	0.4	10.4	0.9	8	Ref	
Ge, µg/g							0.68	0.12			0.68		0.68		3	Inf	
As, µg/g							0.16	0.01			0.16		0.16		2	Inf	
Se, µg/g							<0.03				<0.03		<0.03		1	Inf	
Br, µg/g					<0.2						<0.2		<0.2		1	Inf	
Rb, µg/g	2.08		2.10		2.12	0.12	2.10	0.22			2.10	0.02	2.10	0.10	17	Ref	
Sr, µg/g	18.0		15.0	0.1			15.1	1.3	15.4		15.9	1.5	15.3	0.6	22	Ref	
Y, µg/g					12.8		13.0	1.0	13.4		12.5	1.3	12.9	0.5	20	Ref	
Zr, µg/g	10.2		10.4	0.6	11.0		9.7	0.8	10.5		10.4	0.5	9.9	0.3	22	Ref	
Nb, µg/g			0.086		0.072		0.069	0.026	0.090		0.079	0.010	0.073	0.013	17	Ref	
Mo, µg/g			32.0		31.1	1.3	29.9	4.0			31.0	1.1	30.5	2.6	8	Ref	
Rh, µg/g																	
Pd, µg/g																	
Ag, µg/g							0.04				0.04		0.04		1	Inf	
Cd, µg/g							0.08	0.01			0.08		0.08		2	Inf	
In, µg/g							0.09	0.04			0.09		0.09		3	Inf	
Sn, µg/g					0.30		0.34	0.09			0.32	0.03	0.34	0.09	7	Inf	
Sb, µg/g			0.06		0.11		0.04	0.02			0.07	0.04	0.06	0.04	5	Ref	
Cs, µg/g			7.46	0.34	8.56	0.08	7.12	1.23	8.86		8.00	0.84	7.45	0.63	16	Ref	
Ba, µg/g	0.860		0.720				0.816	0.144	0.830	0.028	0.807	0.061	0.815	0.062	19	Ref	
La, µg/g	0.0769		0.0930		0.0795	0.0064	0.0843	0.0060	0.0885	0.0021	0.0844	0.0065	0.0842	0.0029	21	Ref	
Ce, µg/g	0.375		0.358				0.397	0.043	0.395	0.013	0.381	0.018	0.393	0.018	21	Ref	
Pr, µg/g			0.093	0.011	0.110		0.087	0.006	0.091		0.095	0.010	0.089	0.004	17	Ref	
Nd, µg/g	0.685		0.695	0.050	0.762		0.679	0.034	0.724	0.012	0.709	0.034	0.689	0.017	21	Ref	
Sm, µg/g	0.509		0.467	0.000	0.536	0.036	0.504	0.032	0.531	0.035	0.509	0.027	0.508	0.015	22	Ref	
Eu, µg/g	0.254		0.258	0.018	0.245	0.005	0.253	0.016	0.283	0.006	0.259	0.014	0.255	0.007	24	Ref	
Gd, µg/g	1.25		1.21	0.01	1.30		1.16	0.09	1.31	0.05	1.24	0.06	1.19	0.04	20	Ref	
Tb, µg/g			0.286	0.020	0.273	0.023	0.262	0.020	0.290		0.278	0.013	0.269	0.011	17	Ref	
Dy, µg/g	2.20		2.13	0.11	2.09	0.11	2.16	0.14	2.22	0.18	2.16	0.05	2.15	0.06	21	Ref	
Ho, µg/g			0.510	0.029	0.555	0.023	0.494	0.035	0.518		0.519	0.026	0.507	0.019	18	Ref	
Er, µg/g	1.68		1.62	0.11	1.77		1.53	0.10	1.50	0.12	1.62	0.11	1.56	0.05	20	Ref	
Tm, µg/g			0.240	0.015			0.233	0.017	0.240		0.237	0.004	0.234	0.009	14	Ref	
Yb, µg/g	1.67		1.56	0.06	1.64	0.08	1.60	0.09	1.62	0.12	1.62	0.044	1.61	0.04	22	Ref	
Lu, µg/g	0.254		0.241	0.013	0.223	0.029	0.237	0.019	0.250		0.241	0.012	0.237	0.009	21	Ref	

Table 13e. (continued)

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov. Mean	U	n
Hf, µg/g	0.352	0.012	0.360	0.057	0.420	0.028	0.349	0.035	0.330		0.362	0.034	0.357	0.018	20 Ref
Ta, µg/g	0.037	0.001	0.040		0.033	0.004	0.030	0.003			0.035	0.004	0.031	0.002	18 Ref
W, µg/g					26.0		25.3	4.8			25.6	0.5	25.4	3.4	8 Inf
Re, µg/g							0.0009	0.0001			0.0009		0.0009		3 Inf
Os, µg/g					<0.2						<0.2		<0.2		1 Inf
Ir, µg/g					1.28	0.03					1.28		1.28		2 Inf
Pt, µg/g					12.4	1.2	13.5				12.9	0.81	13	11	3 Inf
Au, µg/g					0.14	0.00	0.08	0.01			0.11	0.04	0.11	0.09	4 Inf
Hg, µg/g					<0.4						<0.4		<0.4		1 Inf
Tl, µg/g							0.001				0.001		0.001		1 Inf
Pb, µg/g			19.0				19.5	2.8			19.3	0.4	19.5	1.7	12 Ref
Bi, µg/g					0.008		0.007	0.001			0.007	0.001	0.007	0.003	3 Inf
Th, µg/g			0.020		0.016		0.006	0.003	0.020		0.016	0.006	0.009	0.003	15 Ref
U, µg/g			0.046	0.006	0.044	0.005	0.049	0.010			0.046	0.003	0.048	0.005	17 Ref

^a All techniques mean: average of 1–5 techn. groups means, Ov. (overall) mean: unweighted mean of all results, Ref: reference value, Inf: information value, SD: standard deviation, U: uncertainty at 95% confidence level, n: number of analyses. BULK T.: XRF, SSMS, MIC-SSMS, MS, INAA, ICP-AES; MICRO T.: EPMA, SIMS, LIMS, SR-XRF, PIXE.

Table 13f. Summary of Composition Data for BM90/21-G^a

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov. Mean	U	n
H ₂ O, %m/m									0.014		0.014		0.014		1 Inf
Li, µg/g							2.6	0.4	1.4		2.0	0.9	2.2	1.7	3 Inf
Be, µg/g									0.01		0.01		0.01		1 Inf
B, µg/g							5.6		2.8		4.2	2.0	4.2		2 Inf
CO ₂ , µg/g									6.0		6.0		6.0		1 Inf
O, %m/m									45.8		45.8		45.8		1 Inf
F, µg/g									2.6		2.6		2.6		1 Inf
Na ₂ O, %m/m					0.108	0.021			0.120	0.013	0.114	0.009	0.115	0.014	8 Ref
MgO, %m/m					34.8				34.2	0.4	34.5	0.4	34.3	0.5	7 Inf
Al ₂ O ₃ , %m/m					2.44				2.31	0.04	2.37	0.09	2.33	0.05	7 Inf
SiO ₂ , %m/m					53.6				53.1	0.7	53.3	0.4	53.1	0.5	7 Inf
P ₂ O ₅ , %m/m					<0.0004						<0.0004		<0.0004		1 Inf
S, µg/g									1.2		1.2		1.2		1 Inf
Cl, µg/g									0.7		0.7		0.7		1 Inf
K ₂ O, %m/m	0.00375				0.00370						0.00372		0.00372	0.00025	2 Inf
CaO, %m/m					2.12				2.10	0.03	2.11	0.02	2.10	0.02	7 Inf
Sc, µg/g					11.3	0.0	14.3	1.3			12.8	2.1	13.3	2.3	6 Inf
TiO ₂ , %m/m					0.067		0.067	0.005	0.057	0.010	0.064	0.006	0.062	0.007	10 Ref
V, µg/g					37		66	6			52	21	61	15	6 Inf
Cr, µg/g					2073	64	2367	115	2127	225	2189	156	2190	210	9 Ref
MnO, %m/m					0.106	0.005	0.134		0.107	0.005	0.116	0.016	0.109	0.009	9 Ref
FeO T, %m/m					6.77	0.19			6.82	0.17	6.79	0.04	6.80	0.14	9 Ref
Co, µg/g					88.5	3.9	103.0	6.2			95.8	10.2	97.6	7.6	8 Ref
Ni, µg/g					1883	119	1902	178			1893	13	1900	120	9 Ref
Cu, µg/g					36.0		38.4	6.0			37.2	1.7	37.9	7.4	5 Inf
Zn, µg/g					39.3	3.1	41.7				40.5	1.7	39.9	5.9	4 Ref
Ga, µg/g					2.6	0.6	2.0	0.3			2.3	0.4	2.3	1.0	4 Inf
Ge, µg/g							0.44	0.05			0.44		0.44		2 Inf
As, µg/g							<0.03				<0.03		<0.03		1 Inf
Se, µg/g							<0.009				<0.009		<0.009		1 Inf
Br, µg/g					<0.1						<0.1		<0.1		1 Inf
Rb, µg/g	0.391		0.450				0.35	0.03			0.397	0.050	0.374	0.093	6 Ref
Sr, µg/g	0.800		0.880				0.729	0.057	1.030		0.86	0.13	0.78	0.08	11 Ref

Table 13f. (continued)

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov. Mean	U	n
Y, µg/g			2.04		1.44		2.30	0.19	2.10		1.97	0.37	2.18	0.20	11 Ref
Zr, µg/g			20.4		19.3		20.1	2.0	19.5		19.8	0.5	20.0	0.9	11 Ref
Nb, µg/g					0.039		0.037	0.005	0.050		0.042	0.007	0.039	0.005	9 Ref
Mo, µg/g					16.8	0.4	19.6	5.1			18	2	19	4	6 Inf
Rh, µg/g															
Pd, µg/g					<6						<6		<6		1 Inf
Ag, µg/g					<0.3						<0.3		<0.3		1 Inf
Cd, µg/g							0.1	0.1			0.1		0.1		2 Inf
In, µg/g					0.18		0.19	0.05			0.19	0.009	0.19	0.06	4 Inf
Sn, µg/g							0.4	0.4			0.4		0.4		3 Inf
Sb, µg/g					0.052	0.026	0.022	0.011			0.037	0.021	0.037	0.038	4 Inf
Cs, µg/g			1.10		1.31	0.08	0.94	0.04			1.11	0.18	1.07	0.17	7 Ref
Ba, µg/g	0.580						0.528	0.056	0.520		0.543	0.033	0.533	0.032	10 Ref
La, µg/g	0.211		0.205		0.232	0.013	0.219	0.011	0.260		0.225	0.022	0.223	0.009	14 Ref
Ce, µg/g	0.422		0.403		0.510		0.480	0.041	0.460		0.455	0.043	0.471	0.033	13 Ref
Pr, µg/g			0.066		0.097		0.072	0.004			0.078	0.016	0.075	0.009	8 Ref
Nd, µg/g	0.355		0.332		0.408		0.365	0.024	0.390		0.370	0.030	0.367	0.020	11 Ref
Sm, µg/g	0.142		0.133		0.155	0.023	0.146	0.007	0.150		0.145	0.008	0.147	0.009	13 Ref
Eu, µg/g	0.052		0.049		0.054	0.008	0.052	0.006	0.060		0.054	0.004	0.053	0.002	14 Ref
Gd, µg/g	0.243		0.228		0.320		0.249	0.032			0.260	0.041	0.253	0.023	10 Ref
Tb, µg/g			0.044		0.056	0.008	0.050	0.003			0.050	0.006	0.051	0.005	7 Ref
Dy, µg/g	0.352		0.333		0.349	0.016	0.373	0.021	0.350		0.352	0.014	0.361	0.013	13 Ref
Ho, µg/g			0.075		0.085	0.012	0.084	0.006			0.081	0.005	0.083	0.007	8 Ref
Er, µg/g	0.256		0.234		0.302		0.269	0.016	0.230		0.258	0.029	0.264	0.016	11 Ref
Tm, µg/g			0.036				0.043	0.002			0.039	0.005	0.041	0.006	5 Inf
Yb, µg/g	0.275		0.259		0.273	0.008	0.291	0.019	0.250		0.270	0.016	0.280	0.013	13 Ref
Lu, µg/g	0.044		0.040		0.040	0.003	0.048	0.003			0.043	0.004	0.045	0.002	12 Ref
Hf, µg/g			0.490		0.507	0.010	0.528	0.047			0.508	0.019	0.520	0.025	10 Ref
Ta, µg/g							0.0031	0.0008			0.0031		0.0031	0.0009	6 Inf
W, µg/g					0.48	0.03	0.50	0.15			0.49	0.013	0.49	0.13	6 Inf
Re, µg/g							0.0008				0.0008		0.0008		1 Inf
Os, µg/g					<0.3						<0.3		<0.3		1 Inf
Ir, µg/g					0.065	0.000					0.065		0.065		2 Inf
Pt, µg/g					20	1					20		20		2 Inf
Au, µg/g					0.064	0.003					0.064		0.064		2 Inf
Hg, µg/g					<0.3						<0.3		<0.3		1 Inf
Tl, µg/g							0.006				0.006		0.006		1 Inf
Pb, µg/g					0.79		0.54	0.14			0.66	0.18	0.57	0.17	7 Inf
Bi, µg/g					0.0015						0.0015		0.0015		1 Inf
Th, µg/g			0.049		0.038		0.056	0.005	0.060		0.051	0.010	0.054	0.004	11 Ref
U, µg/g			0.073		0.088	0.002	0.085	0.009			0.082	0.008	0.084	0.005	10 Ref

^a All techniques mean: average of 1–5 techn. groups means, Ov. (overall) mean: unweighted mean of all results, Ref: reference value, Inf: information value, SD: standard deviation, U: uncertainty at 95% confidence level, n: number of analyses. BULK T.: XRF, SSMS, MIC-SSMS, MS, INAA, ICP-AES; MICRO T.: EPMA, SIMS, LIMS, SR-XRF, PIXE.

Concentration data were mostly calibrated with international reference materials. A special sample preparation technique was used for the application of ID to SSMS and MIC-SSMS [Jochum *et al.*, 2000].

4.3.2. Microanalytical Techniques

[83] LA-ICPMS: Many trace element data were obtained by this microanalytical technique, which has become one of the most important techniques

for in situ measurements of geochemical samples. Calibration of the data was mainly performed using synthetic NIST reference glasses, such as NIST SRM 612 and NIST SRM 610, and the compiled values of Pearce *et al.* [1997].

[84] Other microanalytical techniques (EPMA, SIMS, LIMS, SR-XRF, PIXE): The methods of this group are comparative and independent with respect to at least two of the three criteria: sample preparation, calibrants, instruments. EPMA is a

Table 13g. Summary of Composition Data for T1-G^a

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value			
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov.	Mean	U	n
H2O, %m/m					0.04				0.012		0.026	0.02	0.026		2	Inf
Li, µg/g			19.8	0.4			20.2	1.6	19.4	1.4	19.8	0.4	19.9	0.9	10	Ref
Be, µg/g							1.9	0.3	2.4		2.2	0.3	2.0	0.6	5	Inf
B, µg/g							4.0	1.0	4.6		4.3	0.5	4.1	1.1	5	Inf
CO2, µg/g									6.3		6.3		6.3		1	Inf
O, %m/m									46.4		46.4		46.4		1	Inf
F, µg/g									321		321		321		1	Inf
Na2O, %m/m					3.13	0.08			3.13	0.15	3.13	0.00	3.13	0.09	13	Ref
MgO, %m/m					3.83	0.02			3.73	0.07	3.78	0.06	3.75	0.04	13	Ref
Al2O3, %m/m					17.1	0.0			17.1	0.4	17.1	0.0	17.1	0.2	12	Ref
SiO2, %m/m					58.6	0.4			58.6	0.9	58.6	0.0	58.6	0.4	13	Ref
P2O5, %m/m					0.175	0.008			0.166	0.037	0.170	0.006	0.168	0.026	8	Ref
S, µg/g									2.6		2.6		2.6		1	Inf
Cl, µg/g									113	24	113		113	37	4	Ref
K2O, %m/m	1.90				1.92	0.06			1.99	0.07	1.94	0.04	1.96	0.04	15	Ref
CaO, %m/m					7.16	0.13			7.09	0.15	7.12	0.05	7.10	0.09	14	Ref
Sc, µg/g			25.0		26.0	0.1	27.1	2.4	27.6	0.6	26.4	1.2	26.9	1.1	17	Ref
TiO2, %m/m					0.721	0.001	0.784	0.035	0.746	0.027	0.750	0.032	0.755	0.017	20	Ref
V, µg/g							190	16	190		190	0	190	11	12	Ref
Cr, µg/g					22.3	2.3	20.3	1.5	21.0	7.1	21.2	1.0	20.9	2.0	14	Ref
MnO, %m/m					0.133	0.003	0.125	0.012	0.125	0.015	0.128	0.004	0.127	0.006	21	Ref
FeO T, %m/m					6.50	0.07			6.42	0.14	6.46	0.05	6.44	0.06	16	Ref
Co, µg/g			19.0		19.6	0.6	19.1	1.8	16.7	1.9	18.6	1.3	18.9	0.8	18	Ref
Ni, µg/g			11.0		8.0		10.7	2.4	12.0		10.4	1.7	10.6	1.3	15	Ref
Cu, µg/g			22.0				18.5	2.2	18.0		19.5	2.2	18.8	2.0	10	Ref
Zn, µg/g					83	15	69	12	68	2	73	9	74	10	11	Ref
Ga, µg/g			20.0		18.0	0.0	19.8	1.5	18.0		18.9	1.1	19.4	0.9	12	Ref
Ge, µg/g							1.8	0.9			1.8		1.8	1.5	4	Inf
As, µg/g					0.72	0.20	1.14	0.59	0.68		0.85	0.26	0.96	0.44	7	Ref
Se, µg/g							0.05				0.05		0.05		1	Inf
Br, µg/g					0.3						0.3		0.3		1	Inf
Rb, µg/g	70.1		81.4	2.9	82.0	5.6	80.5	9.0	73.5	0.7	77.5	5.4	79.7	3.5	23	Ref
Sr, µg/g	292		291	8	293	4	283	16	275	17	287	8	284	6	26	Ref
Y, µg/g			24.3	0.2	21.9		24.1	1.8	23.4	2.7	23.4	1.1	23.9	0.8	25	Ref
Zr, µg/g	154		153	7	149		141	12	146	13	149	6	144	4	28	Ref
Nb, µg/g			8.68	0.11	11.6		8.92	0.53	7.77	1.56	9.24	1.65	8.87	0.43	24	Ref
Mo, µg/g			5.6		5.4	1.9	3.6	2.5			4.8	1.1	4.2	1.8	9	Ref
Rh, µg/g*																
Pd, µg/g*																
Ag, µg/g*							0.1	0.1			0.1		0.1		2	Inf
Cd, µg/g							0.2	0.2			0.2		0.2		4	Inf
In, µg/g							0.3	0.2			0.3		0.3	0.4	3	Inf
Sn, µg/g			3.6				1.8	0.6	1.4		2.3	1.2	2.0	0.5	11	Ref
Sb, µg/g			0.29		0.27	0.00	0.23	0.08	0.27		0.26	0.03	0.25	0.05	8	Ref
Cs, µg/g			2.80	0.08	3.21	0.30	2.58	0.39	2.80		2.85	0.26	2.69	0.19	20	Ref
Ba, µg/g	391		396	25	413	18	393	23	361	33	391	19	388	12	27	Ref
La, µg/g	70.4		69.6	2.0	69.3	6.7	72.1	4.7	66.1	10.7	69.5	2.2	70.4	2.4	29	Ref
Ce, µg/g	126		121	6	133	4	129	6	113	19	124	8	127	4	27	Ref
Pr, µg/g			12.6	0.5	12.6		12.5	0.8	10.4		12.0	1.1	12.4	0.4	21	Ref
Nd, µg/g	42.5		40.8	2.2	42.6	1.9	42.0	2.5	38.1	4.1	41.2	1.9	41.4	1.2	30	Ref
Sm, µg/g	6.75		6.55	0.39	6.72	0.27	6.58	0.33	6.17	0.52	6.55	0.23	6.57	0.14	27	Ref
Eu, µg/g	1.23		1.23	0.15	1.27	0.09	1.20	0.07	1.10	0.03	1.20	0.06	1.21	0.04	28	Ref
Gd, µg/g	5.28		5.29	0.18	5.20		5.32	0.67			5.27	0.05	5.31	0.29	21	Ref
Tb, µg/g			0.807	0.081	0.855	0.039	0.740	0.044	0.848	0.011	0.813	0.05	0.773	0.029	23	Ref
Dy, µg/g	4.62		4.45	0.22	4.72	0.03	4.49	0.30	4.39	0.12	4.53	0.13	4.50	0.12	25	Ref
Ho, µg/g			0.890	0.044	0.843	0.059	0.867	0.067	0.720		0.830	0.076	0.860	0.031	22	Ref
Er, µg/g	2.61		2.56	0.22	2.28	0.16	2.51	0.15	2.42	0.16	2.47	0.13	2.49	0.08	23	Ref
Tm, µg/g			0.364	0.015			0.352	0.032			0.358	0.008	0.354	0.015	18	Ref
Yb, µg/g	2.44		2.35	0.06	2.41	0.15	2.39	0.24	2.21	0.30	2.36	0.09	2.38	0.08	27	Ref
Lu, µg/g	0.361		0.359	0.010	0.356	0.038	0.353	0.035	0.350		0.356	0.004	0.354	0.012	26	Ref

Table 13g. (continued)

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov. Mean	U	n
Hf, $\mu\text{g/g}$	4.21	0.16	4.05	0.09	4.09	0.12	3.80	0.33	3.50		3.93	0.28	3.88	0.15	23 Ref
Ta, $\mu\text{g/g}$	0.436	0.004	0.470		0.485	0.007	0.464	0.038			0.464	0.021	0.464	0.021	22 Ref
W, $\mu\text{g/g}$					0.90		0.63	0.08	0.82		0.78	0.14	0.69	0.12	8 Ref
Re, $\mu\text{g/g}$							0.0018	0.0007			0.0018		0.0018	0.002	3 Inf
Os, $\mu\text{g/g}$															
Ir, $\mu\text{g/g}$					0.2	0.3					0.2		0.2		2 Inf
Pt, $\mu\text{g/g}$							6				6		6		1 Inf
Au, $\mu\text{g/g}$					0.09	0.01	0.11	0.09			0.10	0.01	0.10	0.11	4 Inf
Hg, $\mu\text{g/g}$											<0.3		<0.3		1 Inf
Tl, $\mu\text{g/g}$							0.13	0.06			0.13		0.13	0.08	5 Inf
Pb, $\mu\text{g/g}$			9.68	1.87	11.4		12.0	3.10	10.0		10.8	1.1	11.6	1.5	17 Ref
Bi, $\mu\text{g/g}$					0.09		0.10	0.05			0.10	0.00	0.10	0.05	6 Inf
Th, $\mu\text{g/g}$			31.2	1.5	30.7	2.0	31.2	2.7	34.1		31.8	1.5	31.3	1.0	26 Ref
U, $\mu\text{g/g}$			1.72	0.08	1.67	0.17	1.72	0.26			1.70	0.03	1.71	0.10	24 Ref

^a All techniques mean: average of 1–5 techn. groups means, Ov. (overall) mean: unweighted mean of all results, Ref: reference value, Inf: information value, SD: standard deviation, U: uncertainty at 95% confidence level, n: number of analyses. BULK T.: XRF, SSMS, MIC-SSMS, MS, INAA, ICP-AES; MICRO T.: EPMA, SIMS, LIMS, SR-XRF, PIXE.

routine analytical technique for the determination of major element abundances. The other techniques were used for in situ trace element analyses. Homogeneous geological or NIST SRM glasses were mainly used for calibration.

[85] Tables 13a–13h list the concentration averages for each group with the corresponding SD values. The few outliers of auxiliary material Tables S1a–S1h are not considered. Nearly all mean values of the five groups agree within confidence intervals indicating that possible systematic differences between the techniques used are absent or small. Figure 5 shows a comparison of the mean element concentrations of each group with the reference values (Tables 13a–13h). It contains the data for the glasses KL-2G, ML3B-G, ATHO-G, StHs6/80-G, T1-G having trace element concentrations in the $\mu\text{g/g}$ range. Each point in the figure represents a quite different number of analytical results; for example, in the case of ID: 2–10 data from 1–4 laboratories and LA-ICPMS: 20–90 different data obtained in 4–20 laboratories. Nearly all mean values agree within 5% (relative deviation). With the exception of some elements, agreement of isotope dilution and LA-ICPMS data is even better. Some elements having low concentrations (e.g., Be, Sn, Cs, W) show larger deviations. This is also valid for elements in the trace element poor samples GOR128-G, GOR132-G and BM90/21-G where agreement is about 10% (relative deviation). This means that the results of the different analytical techniques are comparable.

Indications of systematic differences are insignificant. Especially promising are the mean concentration values of each group of analytical methods normalized to the respective reference values and averaged over all elements. These concentration ratios are 1.01 ± 0.04 (SD) for ID, 1.01 ± 0.06 (SD) for ICPMS, 1.02 ± 0.09 (SD) for other bulk analytical techniques, 0.99 ± 0.04 (SD) for LA-ICPMS, and 0.99 ± 0.07 (SD) for other microanalytical techniques. All mean values agree within confidence intervals with the reference values.

4.4. Derivation of Preferred Values and Their Uncertainties

[86] To obtain our preferred values of the MPI-DING glasses, we averaged the results of all contributing laboratories (auxiliary material Tables S1a–S1h). As recommended by the IAG [Kane *et al.*, 2003] we used unweighted means because weighting procedures [Paule and Mandel, 1982] cannot be applied successfully to interlaboratory certification with 20 or more contributing laboratories. Similar to the procedure of Jochum *et al.* [2000] the results are classified in two categories: reference values and information values (Tables 13a–13h).

[87] Reference values were reported when they are derived from at least three laboratories using three or more independent, well-defined techniques that are in statistical agreement [Uriano and Gravatt, 1977]. IAG [Kane, 2004] based certified values on no fewer than 10 individual laboratory results using at least two independent methods of analysis

Table 13h. Summary of Composition Data for ATHO-G^a

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov. Mean	U	n
H ₂ O, %m/m									0.014		0.014		0.014		1 Inf
Li, µg/g			25.1	1.5			28.9	2.6	30.0	2.3	28.0	2.6	28.6	1.8	12 Ref
Be, µg/g							3.04	0.31	3.58	0.11	3.31	0.38	3.20	0.34	7 Inf
B, µg/g							5.9	0.3	5.2	0.8	5.6	0.5	5.7	0.5	7 Inf
CO ₂ , µg/g									3.7		3.7		3.7		1 Inf
O, %m/m									48.7		48.7		48.7		1 Inf
F, µg/g									0.7		0.7		0.7		1 Inf
Na ₂ O, %m/m					4.31	0.25	4.26		3.53	0.48	4.03	0.44	3.75	0.31	14 Ref
MgO, %m/m					0.17		0.11		0.098	0.008	0.126	0.038	0.103	0.010	16 Ref
Al ₂ O ₃ , %m/m					12.0		11.7		12.2	0.5	12.0	0.3	12.2	0.2	17 Ref
SiO ₂ , %m/m					75.9				75.6	1.3	75.7	0.2	75.6	0.7	16 Ref
P ₂ O ₅ , %m/m					0.03		0.020	0.001	0.027		0.025	0.005	0.025	0.004	7 Ref
S, µg/g									0.6		0.6		0.6		1 Inf
Cl, µg/g									2430		2430		2430		7 Inf
K ₂ O, %m/m	2.70				2.65	0.12	2.86		2.62	0.23	2.71	0.11	2.64	0.09	21 Ref
CaO, %m/m					1.67		1.76	0.09	1.69	0.06	1.71	0.04	1.70	0.03	17 Ref
Sc, µg/g			4.9		5.1	0.1	7.6	1.5	6.0		5.9	1.3	7.0	0.9	15 Ref
TiO ₂ , %m/m					0.240		0.282	0.043	0.241	0.031	0.254	0.024	0.255	0.016	27 Ref
V, µg/g							3.80	0.65	4.36	0.27	4.08	0.39	3.91	0.34	16 Ref
Cr, µg/g					11		6.0	2.1	5.3	0.6	7.4	3.1	6.1	1.4	13 Ref
MnO, %m/m					0.102	0.003	0.106	0.009	0.108	0.013	0.105	0.003	0.106	0.005	24 Ref
FeO T, %m/m					3.13	0.15	3.00		3.32	0.20	3.15	0.16	3.27	0.10	20 Ref
Co, µg/g			2.30		2.61	0.06	2.08	1.10	1.91	0.01	2.22	0.30	2.13	0.47	18 Ref
Ni, µg/g			23		20		12	10	12	9	17	6	13	5	17 Ref
Cu, µg/g			18.0				17.7	2.9	21.4	2.0	19.0	2.1	18.6	2.2	13 Ref
Zn, µg/g			118		121	13	143	16	153	13	134	17	141	15	12 Ref
Ga, µg/g			22.0		21.5	0.7	26.9	4.7	25.3	1.3	23.9	2.6	25.3	2.4	13 Ref
Ge, µg/g							1.8	0.8	1.6		1.7	0.2	1.8	0.9	5 Inf
As, µg/g					0.8	0.0	1.6	0.5	1.8		1.4	0.5	1.4	0.5	7 Ref
Se, µg/g							0.10				0.10		0.10		1 Inf
Br, µg/g					1.2	0.1			1.1		1.2	0.1	1.2	0.3	3 Inf
Rb, µg/g	63.8		61.0	3.5	65.0	0.9	66.2	8.5	64.5	7.7	64.1	1.9	65.3	3.0	26 Ref
Sr, µg/g	96.0	0.1	93.6	6.5	108.0		91.1	7.3	99.7	6.8	97.7	6.6	94.1	2.7	34 Ref
Y, µg/g			90.8	4.9			93.7	10.0	97.7	10.9	94.1	3.5	94.5	3.5	31 Ref
Zr, µg/g	519	14	509	9	600		497	58	537	59	532	41	512	20	33 Ref
Nb, µg/g			59.6	7.1			62.5	7.6	63.5	3.0	61.9	2.1	62.4	2.6	27 Ref
Mo, µg/g			5.8		7.0		4.1	0.7	5.5	2.1	5.6	1.2	4.8	1.0	10 Ref
Rh, µg/g															
Pd, µg/g					<20						<20		<20		1 Inf
Ag, µg/g							0.3	0.2			0.3		0.3		2 Inf
Cd, µg/g							0.5	0.6			0.5		0.5		3 Inf
In, µg/g							0.17	0.07			0.17		0.17		3 Inf
Sn, µg/g			4.70				5.54	1.01	5.00		5.08	0.42	5.41	0.73	11 Ref
Sb, µg/g			0.27		0.39	0.16	0.27	0.10	0.46		0.35	0.09	0.32	0.10	8 Ref
Cs, µg/g			1.36		1.40		0.97	0.12	1.15	0.35	1.22	0.20	1.08	0.11	18 Ref
Ba, µg/g	559	12	544	13	540	28	529	47	585	44	551	22	547	16	34 Ref
La, µg/g	56.0		55.2	2.5	56.0	2.8	55.9	4.3	54.8	6.8	55.6	0.6	55.6	1.5	34 Ref
Ce, µg/g	123		118	1	125	10	123	9	118	11	121	3	121	4	34 Ref
Pr, µg/g			15.3	0.5	13.8	1.1	14.7	1.0	13.8	1.0	14.4	0.7	14.6	0.4	26 Ref
Nd, µg/g	63.7	1.4	60.0	1.7	62.9	3.7	60.8	4.6	59.5	6.3	61.4	1.8	60.9	2.0	23 Ref
Sm, µg/g	14.6	0.2	14.2	0.7	15.4	0.6	14.3	1.3	12.8	0.4	14.2	1.0	14.2	0.4	32 Ref
Eu, µg/g	2.89		2.86	0.10	2.84	0.20	2.74	0.27	2.64	0.96	2.79	0.10	2.76	0.10	30 Ref
Gd, µg/g	15.3		15.6	1.2	16.5	0.7	14.9	1.4	16.6	3.4	15.8	0.7	15.3	0.7	28 Ref
Tb, µg/g			2.59	0.10	2.67	0.08	2.49	0.20	2.38	0.29	2.53	0.12	2.51	0.08	23 Ref
Dy, µg/g	16.6	0.2	16.3	0.6	15.5	0.7	16.8	1.4	14.3	0.8	15.9	1.0	16.2	0.7	20 Ref
Ho, µg/g			3.44	0.10	3.42	0.17	3.48	0.30	3.15	0.07	3.37	0.15	3.43	0.11	25 Ref
Er, µg/g	10.6	0.1	10.3	0.6	10.0		10.5	1.0	9.6	1.0	10.2	0.4	10.3	0.5	27 Ref
Tm, µg/g			1.52	0.06			1.55	0.15	1.37	0.10	1.48	0.10	1.52	0.07	20 Ref
Yb, µg/g	10.2	0.4	10.0	0.2	10.3	0.5	10.8	1.0	9.9	0.5	10.2	0.4	10.5	0.4	31 Ref
Lu, µg/g	1.54		1.52	0.05	1.57	0.09	1.56	0.14	1.40	0.09	1.52	0.07	1.54	0.05	28 Ref

Table 13h. (continued)

	ID		ICPMS		BULK T.		LA-ICPMS		MICRO T.		All Techniques		Preferred Value		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Ov. Mean	U	n
Hf, µg/g	13.5	0.5	14.1	0.1	14.1	0.1	13.7	1.4	13.0	0.8	13.7	0.5	13.7	0.5	27 Ref
Ta, µg/g	3.57	0.04	3.66	0.23	3.85	0.23	3.97	0.52	4.10		3.83	0.22	3.90	0.20	23 Ref
W, µg/g					8.2	0.5	9.6	2.0	9.6	0.6	9.1	0.8	9.3	1.2	10 Ref
Re, µg/g							0.0005	0.0001			0.0005		0.0005		3 Inf
Os, µg/g					<2						<2		<2		1 Inf
Ir, µg/g					0.09	0.01					0.09		0.09		2 Inf
Pt, µg/g					12	2	0.2				6	9	8		3 Inf
Au, µg/g					0.02	0.00	0.04	0.02			0.03	0.01	0.03	0.03	4 Inf
Hg, µg/g					<1						<1		<1		1 Inf
Tl, µg/g							0.07	0.01			0.07		0.07		3 Inf
Pb, µg/g	5.57		4.46	0.91			5.64	1.30	7.10	1.27	5.69	1.08	5.67	0.62	20 Ref
Bi, µg/g					0.09		0.03	0.01			0.06		0.05		3 Inf
Th, µg/g			6.76	1.16	6.70	0.93	7.62	0.72	7.49	0.41	7.14	0.48	7.40	0.27	29 Ref
U, µg/g	1.85		2.13	0.07	2.22	0.22	2.46	0.28			2.16	0.25	2.37	0.12	26 Ref

^a All techniques mean: average of 1–5 techn. groups means, Ov. (overall) mean: unweighted mean of all results, Ref: reference value, Inf: information value, SD: standard deviation, U: uncertainty at 95% confidence level, n: number of analyses. BULK T.: XRF, SSMS, MIC-SSMS, MS, INAA, ICP-AES; MICRO T.: EPMA, SIMS, LIMS, SR-XRF, PIXE.

that are in agreement. We used both recommendations for establishment of reference values. The second criterion is of particular importance for some major element data for which too few analytical techniques have been applied. Those elements that were determined by one or two techniques and fewer than ten laboratories are assigned information values rather than reference values. Most data of Tables 13a–13h belong to the category of reference values. Exceptions are some trace elements that are normally not measured in routine geochemical analysis (e.g., Be, Se, Br, Bi).

[88] According to the IAG protocol [Kane *et al.*, 2003] uncertainty “u” of the MPI-DING glass data is mainly based on three components of variance which have been combined in quadrature:

$$u^2 = \text{VAR}(Y_{\text{mean}}/\sqrt{n}) + \text{VAR}_{\text{inhomo}} + \text{VAR}_{\text{bias}}$$

The first component, the standard deviation of the mean Y_{mean} of n contributing laboratory mean data, will be used as the random component of variance. $\text{VAR}_{\text{inhomo}}$ accounts for inhomogeneities in the glasses and VAR_{bias} for between-laboratory biases.

Figure 5. Mean concentrations in KL-2G, ML3B-G, StHs6/80-G, T1-G, and ATHO-G obtained by five different groups of analytical methods (Tables 13a, 13b, 13c, 13g, and 13h) normalized to the respective reference values (overall means). Nearly all values agree within 5%, indicating that all methods are comparable. Elements having low concentrations show generally larger deviations.

Table 14. Compilation of Isotope Data^a

	KL2-G	ML3B-G	StHs6/80-G	ATHO-G	Tl-G	GOR128-G ^b	GOR132-G ^b	BM90/21-G
δD (‰ VSMOW)			−95 ± 2	17.1 ± 0.4	−117 ± 2	14.4 ± 0.4	8.9 ± 0.4	
δ^7Li (‰ NIST SRM8545)	4.1 ± 1.5	4.4 ± 0.4	3.6 ± 0.4		2.1 ± 0.4	13.55 ± 0.11	7.11 ± 0.48	
$\delta^{11}B$ (‰ NIST SRM951)			−4.48 ± 0.14			4.83 ± 0.04	4.34 ± 0.04	4.27 ± 0.04
$\delta^{17}O$ (‰ VSMOW)	4.31 ± 0.04	4.28 ± 0.08	3.21 ± 0.10	1.59 ± 0.04	3.89 ± 0.04	9.43 ± 0.07	8.52 ± 0.08	8.40 ± 0.07
$\delta^{18}O$ (‰ VSMOW)	8.63 ± 0.09	8.35 ± 0.22	6.12 ± 0.07	3.20 ± 0.07	7.53 ± 0.07	0.66 ± 0.15	0.49 ± 0.15	1.29 ± 0.15
$\delta^{44/40}Ca$ (‰ NIST SRM915a)	0.67 ± 0.15	0.67 ± 0.15	0.74 ± 0.15	0.84 ± 0.20	0.73 ± 0.15	0.706888 ±	0.707156 ±	0.706276 ±
$\delta^{87}Sr/^{86}Sr$	0.703517 ±	0.703805 ±	0.703497 ±	0.703224 ±	0.710093 ±	0.000035	0.000035	0.000035
	0.000035	0.000035	0.000035	0.000035	0.000035	0.513234 ±	0.513282 ±	0.512598 ±
$^{143}Nd/^{144}Nd$	0.512950 ±	0.512875 ±	0.512894 ±	0.513009 ±	0.512326 ±	0.000030	0.000030	0.000030
	0.000030	0.000030	0.000030	0.000030	0.000030			
$^{176}Hf/^{177}Hf$	0.283109 ±	0.283067 ±						
	0.000017	0.000017						
$^{206}Pb/^{204}Pb$	19.030 ± 0.009	18.720 ± 0.016	18.900 ± 0.010	18.383 ± 0.004	18.728 ± 0.004	18.52	19.25	
$^{207}Pb/^{204}Pb$	15.632 ± 0.004	15.600 ± 0.014	15.614 ± 0.003	15.480 ± 0.004	15.679 ± 0.004	15.62	15.72	
$^{208}Pb/^{204}Pb$	38.524 ± 0.015	38.454 ± 0.043	38.515 ± 0.010	38.111 ± 0.003	38.973 ± 0.008	38.28	38.71	
$^{208}Pb/^{206}Pb$	2.0243 ± 0.0004	2.0542 ± 0.0017	2.0379 ± 0.0005	2.0730 ± 0.0006	2.0810 ± 0.0005	2.068	2.011	
$^{207}Pb/^{206}Pb$	0.82146 ± 0.00023	0.8334 ± 0.0006	0.82616 ± 0.00014	0.84204 ± 0.00019	0.83724 ± 0.00010	0.8439	0.8166	

^a Bold, preliminary reference values; Others, information values. Uncertainties represent external precision (2 SD; 1 SD for Li, B, Pb isotopes).

^b Pb isotope data for GOR samples; only one high-precision analysis available.

The last two components affect only few element data. There are only some elements (e.g., Cu, Sn, Bi) that are heterogeneously distributed in the glasses (see section 3.1). A RSD of 3% is used to calculate VAR_{inhomo} for Cu, Sn, Bi. Because the collaborating laboratories are qualified, biases are expected to be small and are likely to be normally distributed so that they will be included in the standard deviation of the mean.

[89] The uncertainty U of the reference value at 95% confidence level is

$$U = k u$$

where k is the Student's t factor. It is about 2 for $n > 30$ and larger at small n .

[90] As shown in Tables 13a–13h most reference values agree within confidence intervals with the mean values obtained from the averages of the five groups of analytical techniques. Most data also agree within error limits with the preliminary reference values by Jochum *et al.* [2000]; however, the new data are more reliable because of more data.

[91] Table 14 shows a compilation of the isotope data of the MPI-DING glasses. Most measurements were only done with one analytical method. These results are therefore only for information. However, the data are reliable because they were obtained by well-established high-precision bulk (mainly TIMS) and microanalytical techniques. Boron and Pb isotope measurements were done in different laboratories using TIMS and MC-ICPMS. Mean triple spike Pb values of NIST SRM 981 obtained at Mainz ($^{208}\text{Pb}/^{204}\text{Pb} = 36.7245$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4971$, $^{206}\text{Pb}/^{204}\text{Pb} = 16.9407$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.16782$, $^{207}\text{Pb}/^{206}\text{Pb} = 0.91479$) [see Baker *et al.*, 2004] were used for normalization. The MPI-DING data were confirmed by microanalytical techniques (LA-MC-ICPMS, LA-ICPMS). Boron and Pb isotope data may be assigned to the group of reference values. This may be also the case for some Li isotopes where MC-ICPMS and SIMS values agree within their respective confidence intervals.

5. Conclusions

[92] The MPI-DING glasses are a suitable set of reference materials for in situ microanalytical work. The minimum test portion masses at which the samples appear homogeneous are about 5–20 ng. For each sample reference and information

values for up to 74 major and trace elements have been determined following the recommendations of the IAG. In the geochemical characterization of the MPI-DING glasses more than 60 laboratories were involved using 16 independent methods. For most elements the reference values are established to a high degree of reliability. This is especially true for the major elements and Li, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Cs, Ba, REE, Hf, Ta, Pb, Th and U where generally 10–34 analytical results were available. However, others, such as F, S, Cl, Ge, As, Se, Br, Sb, W, Tl, Bi, were not routinely analyzed by most laboratories. Further analyses are necessary for these trace elements.

[93] The isotopic composition of H, Li, B, O, Ca, Sr, Nd, Hf and Pb was determined by one to four different techniques. The reliability of the isotope data is high because in most cases high-precision bulk techniques were used. Small isotopic heterogeneities of Li, and Pb found in some MPI-DING glasses may be a feature to be taken seriously. However, in the case of Pb they are generally lower than the reproducibility obtained from in situ microanalytical techniques, such as SIMS and LA-ICPMS. However, further microanalytical investigations are needed for all isotope systems.

6. Availability

[94] Small amounts of the MPI-DING reference glasses can be obtained on request (e-mail addresses: kpj@mpch-mainz.mpg.de or stoll@mpch-mainz.mpg.de).

Acknowledgments

[95] Many people were involved in the geochemical characterization of the MPI-DING glasses. We thank all of them who have contributed to the extensive database. The new geochemical database for reference materials and isotopic standards (<http://georem.mpch-mainz.gwdg.de>) was helpful. We thank the reviewers Marion Carpentier and Jean Carignan and the Associate Editor Catherine Chauvel for their valuable comments.

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