Determination of Reference Values for NIST SRM 610–617 Glasses Following ISO Guidelines

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We present new reference values for the NIST SRM 610–617 glasses following ISO guidelines and the International Association of Geoanalysts’ protocol. Uncertainties at the 95% confidence level (CL) have been determined for bulk- and micro-analytical purposes. In contrast to former compilation procedures, this approach delivers data that consider present-day requirements of data quality. New analytical data and the nearly complete data set of the GeoReM database were used for this study. Data quality was checked by the application of the Horwitz function and by a careful investigation of analytical procedures. We have determined quantitatively possible element inhomogeneities using different test portion masses of 1, 0.1 and 0.02 g. Although avoiding the rim region of the glass wafers, we found moderate inhomogeneities for several chalcophile/siderophile elements and gross inhomogeneities of Ni, Se, Pd and Pt at small test portion masses. The extent of inhomogeneity was included in the determination of uncertainties. While the new reference values agree with the NIST certified values with the one exception of Mn in SRM 610, they typically differ by as much as 10% from the Pearce et al. (1997) values in current use. In a few cases (P, S, Cl, Ta, Re) the discrepancies are even higher.

Keywords: microanalysis, glass reference materials, NIST, characterisation, sample inhomogeneity.

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Nous présentons des nouvelles valeurs de référence pour les verres NIST SRM 610–617 en suivant les recommandations de l’ISO et le protocole de l’IAG. Les incertitudes au niveau de confiance de 95% ont été déterminées à des fins d’analyse totale et de micro-analyse. Contrairement aux procédures de compilation précédentes, cette approche fournit des données qui tiennent compte des exigences actuelles dans la qualité des données. De nouvelles données analytiques et le jeu de données presque complet de la base de données GeoReM ont été utilisés pour cette étude. La qualité des données a été vérifiée par l’application de la fonction de Horwitz et par un examen minutieux des procédures analytiques. Nous avons déterminé quantitativement les possibles inhomogénéités d’élément en utilisant des prises d’essai de masses différentes correspondant à 1, 0.1 et 0.02 g. Bien que nous ayons évité les zones de bordure des disques de verre, nous avons trouvé des inhomogénéités modérées pour plusieurs éléments chalcophiles/sidérophi les et des inhomogénéités flagrantes de Ni, Se, Pd et Pt pour les prises d’essai de petites masses. La mesure d’inhomogénéité a été incluse dans la détermination des incertitudes. Alors que les nouvelles valeurs de référence sont en accord avec les valeurs NIST certifiées à la seule exception du Mn dans SRM 610, elles sont généralement différentes, avec des écarts de près de 10%, des valeurs de Pearce et al. (1997) qui ont été vérifiées. Dans quelques cas (P, S, Cl, Ta, Re), les écarts sont encore plus élevés.

Mots-clés : microanalyse, verre de référence, NIST, caractérisation, inhomogénéité de l’échantillon.
Reference material glasses play an important role in micro-analytical techniques such as laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), secondary ionisation mass spectrometry (SIMS) and synchrotron radiation induced X-ray fluorescence (XRF) (Jochum and Stoll 2008). They are used as samples in geo- and cosmochemistry, environmental research, biogeochemistry and forensics for calibration, development of methods, quality control and for inter-laboratory comparisons. For the purposes of calibration of LA-ICP-MS and other micro-analytical techniques, the National Institute of Standards and Technology (NIST) reference materials of the SRM 61x series (SRM 610–617) are used most frequently. NIST SRM 610–611 and 612–613 have the advantage that they contain many trace elements, whose concentrations are uniform and sufficiently high for a precise primary calibration (ca. 400 μg g⁻¹ for NIST SRM 610–611, ca. 40 μg g⁻¹ for NIST SRM 612–613). The disadvantages are that the NIST glasses – with the exception of a few elements – have not been certified and were not designed for micro-analytical purposes. Because of this, several authors (e.g., Pearce et al. 1997, Rocholl et al. 1997) compiled published data to derive consensus values. The possibility of micro-inhomogeneity in the NIST glasses has been investigated in many publications (e.g., Carpenter 1972, Sylvester and Eggins 1997, Hinton 1999, Eggins and Shelley 2002, Kuratsawa et al. 2002). The most widely used compilation of NIST SRM 610–611 and SRM 612–613 concentration data is that of Pearce et al. (1997), who used literature data published up to 1996 to derive reference values and their uncertainties by simply calculating standard deviations (s). This procedure was regarded as best practice at that time, but does not comply with ISO Guide 34 (2009) and ISO Guide 35 (2006) of the International Organization for Standardization (ISO). However, because of the great need for the best possible reference values for the NIST glasses, in this paper we act in a similar way as the International Association of Geoanalysts (IAG) would proceed in re-certifying a reference material. Improving micro-analytical data can only be achieved by improving the quality of reference materials.

Since 1997, analytical techniques such as multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) and LA-ICP-MS have been applied for bulk and in situ analysis and have provided many new high-precision data for the NIST SRM glasses. However, since that time, the requirements for data quality have changed. In particular, the determination of the uncertainty budget (Kane et al. 2003, Jochum et al. 2006, Luo et al. 2007) has received wide attention within the analytical community. Therefore, a revision of the reference values of Pearce et al. (1997) is necessary.

The aims of this paper are:

1. To provide new data and quantify possible element inhomogeneities in the NIST glasses for different test portion masses using electron probe microanalysis (EPMA) (0.01 μg) and LA-ICP-MS (1, 0.1, 0.02 μg).
2. To present the currently best possible reference (‘true’) values, which may be useful for inter-laboratory comparisons from now on, by following ISO guidelines and the IAG protocol for certifying reference materials similar to the certification programmes recently performed for rock powders (Kane 2004, 2010, Cotta and Enzweiler 2008, Kane et al. 2009) and geological reference glasses (Jochum et al. 2006).
3. To determine uncertainties at the 95% CL for bulk- and micro-analytical purposes by considering the main sources of error.

Samples

A detailed history of the development of the NIST glasses SRM 610–617 has been given by Kane (1998). The base glass, consisting of high purity quartz sand, alumina, soda ash and calcium carbonate, was fused in a Pt/Rh-lined electrically heated furnace. About 100 kg of NIST SRM 610–611, 612–613, 614–615 and 616–617 were prepared by doping with sixty-one trace elements to nominal concentrations of 500, 50, 1 and 0.02 μg g⁻¹. Each glass is available as either 3 mm (NIST SRM 610, 612, 614, 616) or 1 mm (NIST SRM 611, 613, 615, 617) wafers, hence the eight reference glasses have only four glass compositions. Loss of volatile species during high temperature fusion and sequestration of highly siderophile elements into the noble metal furnace components led to possible inhomogeneities in the final NIST glasses. Eggins and Shelley (2002) demonstrated, by compositional profiling and mapping using LA-ICP-MS, that extensive compositional inhomogeneity affects at least twenty-five of the doped trace elements in the NIST SRM 610–617 glasses.

New data and inhomogeneity

To obtain new data for the NIST SRM glasses and to quantify possible inhomogeneity of major and trace elements in these samples, we analysed different wafers using LA-ICP-MS, ID-TIMS, (ID)-ICP-MS and EPMA. The following sections provide short descriptions of each of the techniques employed by the different participating laboratories.
LA-ICP-MS at the MPI Mainz

A detailed documentation of the LA-ICP-MS procedure at the MPI Mainz has been given by Jochum et al. (2007). For the investigations of possible inhomogeneities of the NIST glasses, we used a New Wave UP-213 laser ablation system, where ablation in the New Wave Large Format Cell was carried out in a He atmosphere. Spot analyses were performed at different times using crater diameters of 80, 40 and 25 μm at energy densities of about 7–11 J cm⁻² (determined at the sample surface), whereas laser energy was uniform within one experiment. Ablation times were 95 s (80 μm spot), 50 s (40 μm) and 35 s (25 μm), washout time between spots was 30 s and blank count rates were measured for 15 s prior to ablation. Ion intensities were measured in the low mass resolution mode of a Thermo Scientific Element2 sector field mass spectrometer. Important instrumental parameters were: RF power = 1200 W, plasma gas flow rate = 1.5 l min⁻¹, auxiliary gas flow rate = 1 l min⁻¹, sample gas flow rate (Ar) = 0.5 l min⁻¹, carrier gas flow rate (He) = 0.8 l min⁻¹.

The mass spectrometer was tuned to give maximum, stable signals at low oxide formation (ThO/Th < 1%). Molecular interferences on the investigated isotopes from oxides were low, as shown by measurements of different isotopes of one element. In the case of the low abundance ¹⁰³Rh, ¹⁰⁹Pd and ¹⁹⁵Pt (element concentrations: about 1–3 μg g⁻¹) in NIST SRM 610, possible interferences of argides and oxides from high abundance Cu, Gd and Hf (about 450 μg g⁻¹) isotopes were less than 1–2% (CuAr, GdAr) and 7% (HFO), respectively, of the element peaks of the noble metals as determined at a high mass resolution of 10000. About 60–80 single spot analyses (80, 40, 25 μm; crater depths similar to the spot sizes) were performed at 200 μm spacing across the diameters of the NIST wafers. To correct for possible signal drift, the ion intensities were measured at one fixed position of the sample after every ten spot analyses to minimise potential calibration bias caused by compositionally different spots, similar to the procedure of Eggins and Shelley (2002). Data reduction was done by calculating the blank corrected count rates of the isotopes relative to the internal standard ⁴³Ca. The low abundance ⁴³Ca peak (isotopic abundance = 0.135%) may be subject to interference by the ²⁷Al¹⁶O peak. However, in the case of NIST glasses, where Al₂O₃/CaO < 0.2, the interference of ²⁷Al¹⁶O on ⁴³Ca is less than 1% (Regnery et al. 2010).

For the determination of NIST SRM 616 data (Table 3), we used the UP-213 system and NIST SRM 612 (Table 9) for calibration. The spot size used was 100 μm. The crater depth was less than 100 μm to avoid elemental fractionation associated with ablating at a single spot (Mank and Mason 1999, Gaboardi and Humayun 2009). USGS and MPI-DING reference glasses were included in the measurements as quality control samples. We also determined concentrations of some rarely determined trace elements (e.g., Cl, S, Cd) in NIST SRM 610, 612 and 614 using UP-193SS (spot size = 75 μm) and UP-213 (spot size = 80 μm) laser ablation systems, respectively, and the certified BAM-S005-B glass (final certification report BAM-S005-A and BAM-S005-B; http://www.rm-certificates.bam.de) of the Federal Institute for Materials Research and Testing (BAM), Germany, for calibration. The BAM glass is homogeneous, has a similar matrix to the NIST glasses and is therefore suitable as a calibration material in microanalysis (Yang et al. 2011). Analytical data for refractory (e.g., Ti, Zr) and volatile elements (e.g., Se, Sn, Cd) of the NIST glasses obtained by the 193 and 213 nm Nd:YAG lasers (Table 4), respectively, agree well.

LA-ICP-MS at the University of Mainz

LA-ICP-MS measurements were carried out in the New Wave Large Format Cell of a New Wave UP-213 laser ablation system coupled with an Agilent 7500ce quadrupole ICP-MS. Helium was used as the carrier gas at a flow rate of ca. 0.7 l min⁻¹ mixed with Ar sample gas at 0.7 l min⁻¹. The NIST SRM 616 glass was ablated in nine single spot analyses, irregularly spaced in the centre of the wafer, at 10 Hz and 1.9 J cm⁻² with crater sizes of 100 μm. Analyses were undertaken with the ICP-MS in standard mode (RF power = 1200 W) at ThO/Th ratios of less than 0.5%. General information on the system and detection limits is given in Jacob (2006). Each measurement consisted of 30 s background followed by 60 s of signal collection.

⁴³Ca was the internal standard (Regnery et al. 2010) and NIST SRM 612 was used as the external calibration material using the new reference data (Table 9). The USGS reference glass BCR-2G (six single spot analyses) was measured as an unknown. A second data set of five single spot analyses, also spaced randomly across the centre of the wafer, was produced with Si as the internal standard and NIST SRM 612 as the external reference material under otherwise identical conditions. In this session, the MPI-DING glass BM90/21-G (eight single spot analyses) was measured as an unknown, using the same isotope as internal standard. Data reduction was carried out with the software GLITTER 4.0 (Macquarie University, Sydney, Australia). Table 5 lists the new data for NIST SRM 616.
ID-TIMS data at the MPI Mainz

Highly precise and accurate isotope dilution (ID) determinations of K, Rb, Sr, Ba and the multi-isotopic rare earth elements (REEs) in NIST SRM 612 by TIMS were performed at the MPI Mainz. Two different glass splits (ca. 60–70 mg) were used. The NIST glasses were dissolved together with spikes using HCl and HClO₄. The separation procedure used for the alkalis, Sr, REE and Ba was the same as that of Raczek et al. (2001). Up to four measurements were performed on a Finnigan MAT 261 mass spectrometer equipped with a multi-collector consisting of seven Faraday cups. Preliminary data (I. Raczek, unpublished data) of these investigations were already given in Jochum et al. (2005). Table 6 lists the ID-TIMS data. Relative standard deviations (RSDs) ranged between about 0.1% and 0.5%.

(ID)-ICP-MS at the ETH Zürich

The ICP-MS analyses followed the multi-element (ID)-ICP-MS method described by Willbold and Jochum (2005), but with some modifications. A total of thirty-two elements were determined, fifteen by ID (Cr, Ni, Sr, Zr, Mo, Ba, Nd, Sm, Gd, Dy, Er, Yb, Hf, Pb and U) and seventeen (Sc, V, Co, Rb, Y, Nb, Cs, La, Ce, Pr, Eu, Tb, Ho, Tm, Lu, Ta and Th) by calculating unknown concentrations using relative sensitivity factors (RSF) with the ID elements as internal standard elements. The RSF is the ratio of a non-ID element (e.g., Rb) and an ID element (e.g., Sr) measured in a 1 ng ml⁻¹ solution prepared from a 1000 ng ml⁻¹ standard solution (Specpure™ Alfa Aesar, Ward Hill, MA, USA; stated uncertainty = 0.3%). With the ID concentration (e.g., Sr concentration), the measured RSF (Rb/Sr ratio in the standard solution) and the known concentrations in the 1 ng ml⁻¹ standard solution (Rb and Sr), the concentration of the non-ID element (Rb) in the sample could be calculated. The RSF accounts for differences in the response between the element of interest (Rb) and the internal standard element (Sr) owing to the differences in ionisation potential, transmission, mass-dependent sensitivity of the detector system etc. See Willbold and Jochum (2005) for a more detailed discussion.

An aliquot of about 20–30 mg glass chips of NIST SRM 610 and SRM 612 was dissolved in HF-HNO₃ at 160 °C for about 3 days. After evaporation the samples were redissolved in aqua regia (3:1 HCl:HNO₃, about 2 days), HCl (about three times), and finally converted to 2 ml of 7 mol 1⁻¹ HNO₃ with trace amounts of HF. Aliquots of the solution were spiked with different spike-sample ratios and the trace element measurements were performed on an Element² ICP-MS at the Laboratory of Inorganic Chemistry, ETH Zürich, using a CETAC, Omaha, NE, USA Aridus I sample introduction system. NIST SRM 614 was spiked prior to dissolution and subjected to the same digestion and dissolution procedure as NIST SRM 610 and 612. An appropriate aliquot of the spiked sample solution was diluted to 4 ml 1 mol 1⁻¹ HNO₃ to achieve a concentration of about 1 ng ml⁻¹ in the analyte solution. The sample was introduced into the Aridus desolvation system with a micro-concentric polypropylene nebuliser with a nominal uptake rate of 50 μl min⁻¹ and typical sample and auxiliary gas flows of 0.72 and 0.84 l min⁻¹. Using Ar sweep gas and N₂ gas flow rates in the Aridus system of 3–6% for the transition metals (Sc, V, Cr, Co, Ni) and of about 1–2% for the REE, Hf, Zr, Sr, Ba and U, and of about 3–6% for the transition metals Sc, V, Cr, Co and Ni and Y, Nb, Ta, Th and Rb. Most element concentrations were within 2–3% of the USGS reference values given in the GeoReM database.

USGS reference materials BCR-2, BHVO-2 and BIR-1 were analysed routinely with every batch of samples as quality control samples to assess accuracy, i.e., trueness, and precision. Multiple measurements of the reference materials (n of about 50) yielded an average RSD of better than 1–2% for the REE, Hf, Zr, Sr, Ba and U, and of about 3–6% for the transition metals Sc, V, Cr, Co and Ni and Y, Nb, Ta, Th and Rb. Most element concentrations were within 2–3% of the USGS reference values given in the GeoReM database.

For determination of the concentrations (Table 7), at least four different splits of NIST SRM 610 and SRM 612 were measured with different spike-sample ratios to be able to measure all elements with error magnification factors (Albarède 1995) of less than 2–3. Whenever error magnification factors were greater than 3–5, the ID and corresponding non-ID element concentrations were not taken into account (e.g., Zr (ID) and Nb (non-ID) in NIST SRM 614). During measurement of NIST SRM 612 and 614, the RSF factors for Th (Th/Sm), Eu (Eu/Sm), Tm (Tm/Eu) and Lu (Lu/Yb) changed significantly compared with previous measurement sessions, leading to a constant offset of the Th, Eu, Tm and Lu concentrations in the NIST, but not in the USGS reference materials used as analytical control samples (BCR-2, BHVO-2 and BIR-1). The reason for this effect is unknown and hence, no Th, Eu, Tm and Lu concentrations for NIST SRM 612 and 614 are reported.
EPMA at the MPI Mainz

Electron probe microanalysis at MPI Mainz was used to determine the major element composition of the NIST glasses (Table 1) and to test homogeneity. Analyses were performed in the wavelength-dispersive detection mode of the Jeol JXA-8200 electron microprobe using an accelerating voltage of 15 kV and a beam current of 12 nA. The electron beam was defocused to 20 μm. Distances between spots were 30 and 50 μm respectively. Data were corrected using the routine ZAF procedure. Peak counting times were 30 s for Na and 60 s for the other major elements. Sets of reference materials, i.e., natural and synthetic oxides, minerals and glasses (P&H Developments Ltd., Calibration Standards for Electron Probe Microanalysis, Standard Block GEO; Smithsonian Institution standard set for electron microprobe analysis, Jarosewich 2002) were used for calibration and instrument stability monitoring. We used the USNM 111240/52 VG2 basaltic and 72854 VG-568 alkaline rhyolite glasses (Jarosewich 2002) as quality control samples.

Element inhomogeneity and test portion

The determination of the element inhomogeneity in the NIST glasses at the large-scale (mg sample range) and at the small-scale (ng–μg range) is important for micro-analytical purposes. Because the NIST glasses were originally designed for bulk-analytical work, the NIST certified values and their uncertainties are only valid if the entire wafer is used for analysis. Highly precise ID measurements on different glass wafers also demonstrate element homogeneity for smaller samples of about 2–50 mg, based on better than 1% precision (e.g., Rochall et al. 2000, Nebel et al. 2009). Nuclear track and ID data by Carpenter (1972) show an excellent axial homogeneity for B and U over the entire length of the 600 feet of glass canes. These results have particular significance with regard to using the glasses as reference materials for microanalysis (Kane 1998). The main application of the glasses is currently their use as calibration material in microanalysis. Eggins and Shelley (2002) demonstrated that at least twenty-five elements (e.g., Ag, As, Au, B, Cd, Cr, Cs, Cu, Mo, Pb, Pt, Re, Rh, Sb, Se, Te, Ti, W) are inhomogeneously distributed at the 30–65 μm scale. These authors found that Ti is an excellent marker for compositionally inhomogeneous domains within the NIST glasses. This inhomogeneity appears to affect all NIST glasses, where severe depletions of some elements (Ti, Au, Re, B) are found in the rim region of the wafers. However, the majority of elements, including Be, Mg, Ca, Sc, Ti, V, Cr, Ni, Zn, Ga, Rb, Sr, Y, Zr, Nb, In, Sn, Ba, REE, Hf, Ta, Th and U shows no evidence of significant compositional inhomogeneity. Kurosawa et al. (2002) investigated NIST SRM 614 and 616 by LA-ICP-MS at a larger sampling scale (80 μm spot size) and found no evidence for trace element inhomogeneities within the observed precision of 5% and 15% respectively.

In this paper we quantify possible inhomogeneities of four major and fifty-four trace elements in all NIST SRM 61x glasses using EPMA and LA-ICP-MS, undertaken at MPI Mainz. This was done by measuring element distributions in 1–2 wafers with electron beams of 20 μm (EPMA) and spot sizes up to 25 μm (LA-ICP-MS). Because of the

|                      | NIST SRM 610 |                      | NIST SRM 612 |                      | NIST SRM 614 |                      |
|----------------------|--------------|----------------------|--------------|----------------------|--------------|----------------------|
|                      | Core         | Rim                  | Core         | Rim                  | Core         | Rim                  |
| Number of analyses   | 194          | 80                   | 135          | 71                   | 154          | 90                   |
| SiO₂                 | 69.4 ± 0.2   | 69.3 ± 0.2           | 71.7 ± 0.2   | 72.0 ± 0.3           | 72.0 ± 0.2   | 72.0 ± 0.2           |
| Al₂O₃                | 1.98 ± 0.03  | 2.01 ± 0.04          | 2.06 ± 0.02  | 2.07 ± 0.04          | 2.056 ± 0.026| 2.07 ± 0.03          |
| MnO                  | 0.051 ± 0.017|                      | 0.057 ± 0.014|                      |              |                      |
| MgO                  | 0.057 ± 0.014|                      |              |                      |              |                      |
| CaO                  | 11.59 ± 0.06 | 11.54 ± 0.07         | 11.93 ± 0.05 | 11.98 ± 0.06         | 11.98 ± 0.06 | 12.04 ± 0.06         |
| Na₂O                 | 136 ± 0.1    | 13.5 ± 0.1           | 14.0 ± 0.1   | 13.8 ± 0.2           | 13.9 ± 0.1   | 13.9 ± 0.2           |
| K₂O                  | 0.048 ± 0.015|                      |              |                      |              |                      |
| P₂O₅                 | 0.10 ± 0.02  |                      |              |                      |              |                      |
| S                    | 0.050 ± 0.011|                      |              |                      |              |                      |
| Cl                   | 0.033 ± 0.004|                      | 0.027 ± 0.010|                      | 0.023 ± 0.010|                      |
| Ti                   | 0.046 ± 0.002|                      | 0.011 ± 0.004|                      | 0.008 ± 0.004|                      |
| Zr                   | 0.045 ± 0.003|                      |              |                      |              |                      |

Uncertainties are 1 s.
small number of investigated wafers and the possibility that all wafers manufactured are not identically homogeneous we also used the results of other publications (e.g., Hinton 1999, Eggins and Shelley 2002).

For the evaluation of element inhomogeneity, the ‘test portion’ is of particular importance. After the International Union of Pure and Applied Chemistry (IUPAC; McNaught and Wilkinson 1997) a test portion is defined as the amount or volume of the test sample taken for analysis.

The test portion mass for bulk-analytical work is typically in the mg range (e.g., aliquots of 5–50 mg were used for solution ICP-MS and TIMS analysis). In the non-destructive EPMA technique, interaction processes between electrons and target are important. Using our measurement conditions the penetration depth was about 2 μm and the test portion mass for our EPMA analysis was about 0.01 μg for the NIST glasses. For the LA-ICP-MS measurements three different spot sizes (80, 40, 25 μm) were used. The ablation rate of NIST glasses was about 0.1 μm pulse⁻¹ using the 213 nm laser ablation system. From these data we obtained test portion masses (here: ablated material for one spot analysis) of about 1 μg (crater size = 80 μm), 0.1 μg (40 μm) and 0.02 μg (25 μm), when considering the different ablation times per crater diameter and the difference in fluence.

**Major element profiles**

Previous studies have shown that the major elements of the NIST glasses are homogeneously distributed (e.g., Rocholl et al. 1997, Hinton 1999). Our EPMA measurements confirmed these results. This is shown in Figure 1, where several profile measurements of SiO₂ are plotted in different parts of NIST SRM 610, 612 and 614 wafers using 20 μm electron beams corresponding to a test portion mass of 0.01 μg. Within uncertainty limits all data agree. There is no indication for any inhomogeneity on the scale of precision of these measurements, in particular not in the rim regions when compared with the core. The same is true for other major elements, which is demonstrated in Table 1, where the mean values of SiO₂, Al₂O₃, Na₂O and CaO and some minor elements in the core and rim locations are listed. Uncertainties of the data were similar to the repeatability of EPMA (about 0.5–2%). Core and rim data were also identical within those repeatability limits.

**Trace element profiles**

The measurements were carried out using LA-ICP-MS with different spot sizes. As demonstrated by Kroslakova and Günther (2007), an increase of the mass load of the ICP by a factor of sixteen (crater diameter from 30 to 120 μm) leads to a decrease in Cu/Ca, Zn/Ca, Cd/Ca and Pb/Ca ratios. In addition, Gaboardi and Humayun (2009) documented that volatile elements were enhanced relative to Ca with their set-up. This may affect the inhomogeneity investigations. However, our measurements were normalised to the corresponding crater diameters to avoid different element response based on plasma effects. As a consequence, experiments with NIST SRM 610 showed that there was no significant decrease (less than about 5%) in the intensity ratios (crater diameter from 25 to 80 μm). In addition, fractionation indices calculated from the different element/Ca ratios agree within uncertainty limits of about 5% for the different crater sizes.

Figure 2 shows rim to rim profiles of typical elements for NIST SRM 610. As already noted by Eggins and Shelley (2002), some elements, such as Ti and Au, are strongly depleted in the rims. The reason for this is loss of volatile and siderophile elements during glass preparation (Kane 1998). Our LA-ICP-MS results confirm the data of Eggins and Shelley (2002). Consequently, the trace element depleted rims (about 1–1.5 mm) of the NIST glasses have to be avoided for microanalysis, especially for the elements Ti, Au and Se (Figure 2). Because the other NIST SRM 61x glasses show similar depletions, we do not recommend the rim region of NIST glass wafers for microanalysis and, hence, our discussion on inhomogeneity refers to the core region of the reference glasses.

The ability to detect inhomogeneity is dependent on the test portion mass and the repeatability of the technique.
(LA-ICP-MS) used. The smaller the test portion mass (spot size), the more readily inhomogeneity can be detected. This effect is shown in Figure 3, showing a modified sampling diagram from Ingamells and Pitard (1986) for Pt in NIST SRM 610. The sampling error increases by a factor of 100 with decreasing test portion mass. To determine local trace element inhomogeneities in the core regions, we calculated the RSD values of about 60–80 independent spot analyses of fifty-four elements in NIST SRM 610, 612, 614 and 616. Significantly higher values for a given test portion mass and concentration can be interpreted as inhomogeneities.

In Figures 4a–d, we have plotted the element inhomogeneity, expressed as RSDinhom (%) for the NIST SRM 610 (a), NIST SRM 612 (b), NIST SRM 614 (c) and NIST SRM 616 (d) obtained by LA-ICP-MS analyses using different spot sizes (80, 40, 25 µm). Most trace elements (e.g., lithophile elements) were homogeneously distributed (RSDinhom < 2%). Some siderophile and chalcophile elements, especially Ni, Se, Pt, Pd were inhomogeneously distributed at low test portion masses.

Figure 2. Rim to rim profiles of element concentrations across a single NIST SRM 610 glass wafer obtained by LA-ICP-MS using different spot sizes (spacing = 200 µm). Because of the lower amount of sample ablated and transported, the scatter of the data increases with smaller spot sizes. Se, Tl and Au were depleted in the rim regions.

Figure 3. Modified sampling diagram from Ingamells and Pitard (1986). This diagram shows the variation of sampling error with test portion mass for Pt in NIST SRM 610. Both curves represent the expected maximum and minimum analytical results. The ‘true’ value determined by ID and the LA-ICP-MS data at large spot sizes (200 µm corresponding to a test portion mass of about 10 µg) are from Sylvester and Eggins (1997). Also shown is the repeatability field of LA-ICP-MS.
RSD\textsubscript{inhom} = \sqrt{(RSD\textsuperscript{2}\textsubscript{r-meas} - RSD\textsuperscript{2}\textsubscript{r-rep})} \quad (1)

where RSD\textsubscript{r-meas} is the RSD of the element concentration of interest (%) determined in the core region of the NIST glass and RSD\textsubscript{r-rep} is the repeatability (expressed as % RSD) of LA-ICP-MS. The repeatability varied between about 1.5\% and 15\% for 80–25 \mu m spot analyses (corresponding to test portion masses of 1–0.02 \mu g) and concentrations of about 0.02–400 \mu g \textsuperscript{g}\textsuperscript{-1}. Using this procedure, uncertainties of RSD\textsubscript{inhom} caused by counting statistics are excluded to a large extent.

Table 2.
Summary of element inhomogeneity in NIST SRM 610, 612, 614 and 616

| Geochemical behaviour | Homogeneous | Moderately inhomogeneous | Grossly inhomogeneous |
|-----------------------|-------------|--------------------------|-----------------------|
| Major lithophile      | RSD\textsubscript{inhom} (1–0.02 \mu g) ≤ 1\% | RSD\textsubscript{inhom} (1–0.02 \mu g) = 1–20\% | RSD\textsubscript{inhom} (1–0.02 \mu g) = 5% to > 20\% |
| Lithophile            | Li (610), Be (610), Si (610), Al (610), Ca (610), Na (610), Mg (610), Fe (610), Mn (610), Sr (610), Ba (610), Tb (610), Eu (610), Ce (610), Pr (610), Nd (610), Sm (610), Eu (610), Gd (610), Tb (610) | Li (610), Be (610), Si (610), Al (610), Ca (610), Na (610), Mg (610), Fe (610), Mn (610), Sr (610), Ba (610), Tb (610), Eu (610), Ce (610), Pr (610), Nd (610), Sm (610), Eu (610), Gd (610), Tb (610) | Li (610), Be (610), Si (610), Al (610), Ca (610), Na (610), Mg (610), Fe (610), Mn (610), Sr (610), Ba (610), Tb (610), Eu (610), Ce (610), Pr (610), Nd (610), Sm (610), Eu (610), Gd (610), Tb (610) |
| Moderately chalcophile/siderophile | Ni (610), Cu (610), Ag (610), Pt (610), Au (610), Rh (610), Pd (616), Pt (616), Au (616) | Ni (610), Cu (610), Ag (610), Pt (610), Au (610), Rh (610), Pd (616), Pt (616), Au (616) | Ni (610), Cu (610), Ag (610), Pt (610), Au (610), Rh (610), Pd (616), Pt (616), Au (616) |
| Highly siderophile     | Pu (610), Pu (612), Pu (614), Pu (616) | Pu (610), Pu (612), Pu (614), Pu (616) | Pu (610), Pu (612), Pu (614), Pu (616) |
| Others (Eggins and Shelley 2002) | Br, I, K, R, F | Br, I, K, R, F | Br, I, K, R, F |

Elements are grouped according to their geochemical behaviour. The inhomogeneity of some elements may be different in some glasses (sample names in brackets). Elements not investigated in this paper are from Eggins and Shelley (2002). The table also contains approximate values for RSD\textsubscript{inhom} (1–0.02 \mu g) for test portion masses varying between 1 and 0.02 \mu g (corresponding to spot sizes between 80 and 25 \mu m in LA-ICP-MS).

Whereas RSD\textsubscript{inhom} of a grossly inhomogeneous trace element (e.g., Pt in NIST SRM 610; Figures 3, 4a) is about 3–4\% for 1 \mu g test portion masses, it is 35–45\% for 0.02 \mu g test portion masses but not detectable in bulk analyses.

Table 2 lists a summary of the investigations on inhomogeneity. We categorised the behaviour of the elements into three groups according to their RSD\textsubscript{inhom} values obtained from the LA-ICP-MS analyses using different spot sizes: homogeneous, moderately inhomogeneous and grossly inhomogeneous. Nearly all lithophile elements and the major elements were homogeneously distributed in all NIST SRM 61x glasses, even for test portion masses of 0.02 \mu g. Excluding Ni, Se, Pd and Pt the maximum inhomogeneity of moderately chalcophile/siderophile elements in NIST SRM 610 was less than 3\% (1 \mu g test portion mass), 4\% (0.1 \mu g) and 10\% (0.02 \mu g), and 5\% (1 \mu g), 15\% (0.1 \mu g) and 30\% (0.02 \mu g) for NIST SRM 612 respectively (Figures 4a, b). This means that these glasses are – in spite of some inhomogeneously distributed elements – suitable as calibration materials for most microanalytical purposes. The results of Table 2 are in agreement with the observations reported by Eggins and Shelley (2002). In contrast to this study, Tl was found to be relatively homogeneously distributed; however, it must be noted that our data only refer to the core section of the NIST glasses (not considering the approximately 1 mm Tl depleted rim).

Reference and information values following ISO guidelines

The ISO Reference Materials Committee (ISO/REMCO) develops guidelines regarding proper reference materials terminology, production, certification and use. According to the rules of these guides, especially of ISO Guide 34 (2009), the production of a reference material includes all...
necessary activities and tasks leading to a reference material supplied to customers. It can include characterisation, but necessarily assignment of and decision on property values and relevant uncertainties, authorisation and issue of certificates. In order to determine updated reference and information values of NIST glasses we adopt ISO Guide 35 (2006): Reference materials – general and statistical principles for certification. Furthermore, the IAG has prepared a protocol to promote best practice in the certification of new geological reference materials (Kane et al. 2003, 2007) following ISO guidelines as completely as possible.

Among other attributes, ISO Guide 35 (2006) defines a reference material (RM) as a sufficiently homogeneous material to be used in a measurement process, while a certified reference material (CRM) is a RM characterised by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability.

The importance of the NIST SRM 61x glasses arises from their use for calibration in many LA-ICP-MS and other micro-analytical laboratories. In general, uncertainties associated with values of calibration should be smaller than uncertainties with values for other applications, such as method validation (ISO Guide 35 2006). Analytical instruments in microanalysis are calibrated with reference materials. So, stated and preferably small uncertainties associated with the reference values are essential to avoid introducing error into analyses (Kane 2002). The situation is made more difficult by the added concern for homogeneity on a micro-scale.

Certifying body

We are aware that we are unable to act as a certifying body for the NIST SRM 61x glasses. The management of a collaborative recertification study is primarily the responsibility of the organisation that performed the original certification. However, in view of the increasing studies using LA-ICP-MS we have proceeded as the IAG would in recertifying an existing material (e.g., Kane et al. 2009). We therefore consider these values to be equal in status to certified values, because of the validity of the metrological procedure used in deriving both the reference values and their uncertainties.

Data

In contrast to a certification programme, where guidelines of the collaborative study have to be developed, which should account for establishing and demonstrating traceability, we used two different kinds of elemental data. These are:

1. New data: major element abundances using EPMA at the MPI Mainz (Table 1), trace element data obtained by LA-ICP-MS at MPI Mainz (Tables 3, 4) and University of Mainz (Table 5), high-precision ID-TIMS data from MPI-Mainz (Table 6), new (ID)-ICP-MS trace element data from the ETH Zürich (Table 7), and RSDinhom values obtained by LA-ICP-MS analyses using different spot sizes.

2. GeoReM data: The GeoReM database contains about 5000 concentration data for the NIST glasses mainly published between 1995 and 2010 in analytical, geoanalytical and geological journals. Therefore, we are confident that we have access to a nearly complete data set from the last 15 years. Tables S1–S6 list the literature values, which are available in Application Version 12 (March 2011) of GeoReM.

Identification of qualified laboratories and data quality

According to ISO Guide 35 (2006), a minimum number of laboratories is required for a certification programme. If well-established measurement methods exist, the number of laboratories involved can be as small as two or three. A typical example is the use of primary methods, such as ID. When the statistical and metrological control is less, but still adequate to accept every technically valid result, the minimum number of laboratories involved is typically six to eight. Finally, if there is a non-negligible chance of having statistically and technically invalid results, the minimum number should be at least ten and preferably fifteen. This minimum number allows data to be scrutinised with the aid of outlier treatment techniques.

The number of methods available has also to be taken into consideration. ISO Guide 35 (2006) proposes, in the case where no primary methods are available, that ideally about three methods should be used by six competent laboratories. The IAG (Kane et al. 2003) based certified values on no fewer than ten individual laboratory results using at least two methods of analysis that are in agreement.

In contrast to certification procedures using the IAG protocol (Kane et al. 2003, Jochum et al. 2006, Cotta and Enzweiler 2008) competence of the laboratories could not be judged based on participation in a programme such as the GeoPT. However, the IAG protocol also allows
qualification to be based on published geochemical research reports that focus on detailed method validation and/or the quantification of uncertainty (Kane et al. 2007).

Metrological traceability (King 1997, Potts 1997, ISO Guide 35 2006) is a key concept in the characterisation of reference samples. It links the validity of all analytical measurements to national and international standards through an unbroken chain of calibrations, each contributing to the measurement uncertainty. Traceability was established in the results by the use of international reference materials.

Data quality was checked in several different ways: the calibration procedures and analytical techniques used were verified, and the Horwitz function (Horwitz and Albert 1995) was employed to identify data ‘outliers’. As a first step, we excluded all concentration data of the NIST glasses that were obtained by using the same NIST sample for external calibration (e.g., NIST SRM 610 data using NIST SRM 610 for calibration), because a single reference material cannot be used for both calibration and validation of results in the same measurement procedure. These data are marked with ‘**’ in Tables S1–S4.

To test the quality of the remaining data we used the Horwitz function for the identification of ‘outliers’:

\[ H_a = k \times X_a^{0.8495} \]  

where \( H_a \) is the target standard deviation, which is the precision value appropriate for the contributing laboratory, \( X_a \) is the assigned value (the best estimate of the ‘true’ value), the concentration of the element expressed as a fraction, and the factor \( k = 0.01 \) or \( 0.02 \) refers to pure and applied geochemistry or analytical laboratories respectively.

Because of the high number of laboratories involved in quite different research fields, we used \( k = 0.02 \). After the IAG protocol for the operation of the GeoPT proficiency testing scheme (Thompson 2002) the assigned value is the mean of the results if the data are roughly symmetrically distributed, and the median of the results if the distribution is clearly skewed. In some instances it is not possible to estimate a satisfactory assigned value, e.g., for an unusually wide or multi-modal dispersion or when the number of results is low. Z-scores were calculated for each concentration value from

\[ z = (X - X_a)/H_a \]  

where \( X \) is the contributed concentration value. Z-score results in the range \(-2 < z < 2\) are considered to be ‘satisfactory’. This procedure is recommended by the IAG protocol (Kane et al. 2003). If the z-score falls outside this range, it would be advisable to examine the procedures of the laboratory and, if necessary, take action to ensure that determinations are not subject to unsuspected analytical bias. The number of ‘outliers’ rejected by this procedure in this

| Element | Isotope used | NIST SRM 616 | Conc. | SE | U (95% CL) |
|---------|-------------|-------------|-------|----|---------|
| Ag      | 107         | 0.047       | 0.001 | 0.002 |
| As      | 75          | 0.125       | 0.004 | 0.0066 |
| Au      | 197         | 0.21        | 0.01  | 0.03  |
| B       | 11          | 1.20        | 0.03  | 0.32  |
| Ba      | 137         | 2.53        | 0.01  | 0.15  |
| Bi      | 209         | 0.020       | 0.001 | 0.008 |
| Cd      | 111         | 0.047       | 0.006 | 0.014 |
| Co      | 140         | 0.030       | 0.001 | 0.001 |
| Cr      | 59          | 0.030       | 0.002 | 0.004 |
| Cs      | 133         | 0.028       | 0.001 | 0.002 |
| Cu      | 65          | 0.73        | 0.01  | 0.11  |
| Dy      | 163         | 0.019       | 0.001 | 0.002 |
| Er      | 167         | 0.017       | 0.003 | 0.007 |
| Ga      | 71          | 0.441       | 0.003 | 0.027 |
| Ge      | 74          | 0.30        | 0.01  | 0.05  |
| Hf      | 178         | 0.019       | 0.001 | 0.002 |
| Ho      | 165         | 0.015       | 0.001 | 0.001 |
| In      | 115         | 0.033       | 0.001 | 0.004 |
| La      | 139         | 0.031       | 0.001 | 0.002 |
| Li      | 7           | 0.949       | 0.008 | 0.094 |
| Lu      | 175         | 0.014       | 0.001 | 0.001 |
| Mo      | 95          | 0.101       | 0.004 | 0.014 |
| Nb      | 93          | 0.022       | 0.001 | 0.003 |
| Nd      | 146         | 0.024       | 0.001 | 0.002 |
| Ni      | 62          | 0.52        | 0.05  | 0.11  |
| Pb      | 208         | 1.85        | 0.01  | 0.07  |
| Pd      | 105         | 1.73        | 0.03  | 0.45  |
| Pr      | 141         | 0.016       | 0.001 | 0.001 |
| Rb      | 85          | 0.105       | 0.002 | 0.005 |
| Rh      | 103         | 0.95        | 0.01  | 0.05  |
| Sb      | 121         | 0.077       | 0.002 | 0.012 |
| Se      | 77          | 0.22        | 0.03  | 0.06  |
| Sn      | 118         | 1.25        | 0.01  | 0.11  |
| Sr      | 88          | 44.2        | 0.1   | 0.7   |
| Ta      | 181         | 0.028       | 0.001 | 0.003 |
| Tb      | 159         | 0.015       | 0.001 | 0.001 |
| Th      | 232         | 0.026       | 0.001 | 0.001 |
| Tl      | 203         | 0.0098      | 0.0004| 0.0015 |
| Tm      | 169         | 0.016       | 0.001 | 0.001 |
| U       | 238         | 0.076       | 0.001 | 0.003 |
| V       | 51          | 0.242       | 0.004 | 0.021 |
| W       | 182         | 0.045       | 0.001 | 0.004 |
| Y       | 89          | 0.032       | 0.001 | 0.003 |
| Yb      | 173         | 0.020       | 0.001 | 0.002 |
| Zn      | 66          | 1.28        | 0.02  | 0.15  |
| Zr      | 90          | 0.094       | 0.002 | 0.008 |

SE, standard error; U, Uncertainty at the 95% confidence level (CL) (containing the main sources of error, such as inhomogeneity of the calibration material NIST SRM 612).
The work was low (5–7% (NIST 612–617), 12% (NIST 610–611)). Figure 5 shows as an example the analytical data for Ba in NIST SRM 610 together with their calculated z-score results.

We also tested data quality by the analytical technique applied, because the results obtained from different techniques may show systematic differences. We grouped the data into five categories according to the technique used:

Table 4.
Element concentrations (in µg g⁻¹) for NIST SRM 610, 612 and 614 obtained by LA-ICP-MS at the MPI Mainz using UP-193SS and UP-213 ablation systems

| Element | Isotope used | NIST SRM 610 | NIST SRM 612 | NIST SRM 614 |
|---------|--------------|-------------|-------------|-------------|
|         |              | UP-193SS    | UP-213      | UP-193SS    | UP-213      | UP-193SS    | UP-213      |
| As      | 75           | 348.5       | 36.8        | 0.74        | 0.02        |
| Ba      | 137          | 449.8       | 39.8        | 2.97        | 0.02        | 3.06        | 0.04        |
| Cd      | 111          | 283.8       | 280.5       | 0.51        | 0.03        | 0.49        | 0.06        |
| Cl      | 35           | 229.14      | 179.40      | 1.4         | 1.2         | 1.2         |
| Co      | 59           | 380.7       | 179.40      | 177.8       |             |
| Cr      | 53           | 378.6       | 356.01      | 1.4         | 1.2         | 1.2         |
| Cu      | 63           | 411.6       | 387.02      | 4.02        |             |
| Fe      | 57           | 460.7       | 512.04      | 0.72        | 1.64        | 1.3         |
| Mn      | 55           | 441.7       | 394.03      | 0.9         | 1.3         | 1.0         |
| Mo      | 95           | 425.7       | 387.07      | 0.72        | 0.5        |
| Ni      | 61           | 411.5       | 379.13      | 0.7         | 0.49        | 0.1         |
| Pb      | 208          | 385.9       | 37.56       | 0.7         | 0.4         |
| S       | 34           | 614.9       | 389.14      | 1.79        | 0.4         |
| Sb      | 121          | 421.8       | 364.04      | 0.7         | 0.4         |
| Se      | 77           | 150.2       | 195.01      | 1.91        | 0.4         |
| Sn      | 117          | 443.6       | 409.06      | 1.4         | 0.7         |
| Ti      | 47           | 446.6       | 397.05      | 0.7         |
| V       | 51           | 453.7       | 399.04      | 0.7         |
| Zn      | 67           | 486.11      | 412.09      | 0.7         |
| Zr      | 90           | 473.12      | 383.04      | 0.7         |

Data were calibrated with the certified values of the BAM-S005-B reference glass.

Table 5.
Element concentrations (in µg g⁻¹) for NIST SRM 616, BCR-2G and BM90/21-G obtained by LA-ICP-MS at the University of Mainz using NIST SRM 612 (Table 9) for calibration

| Element | Isotope used | NIST SRM 616 | BCR-2G | BM90/21-G |
|---------|--------------|-------------|--------|-----------|
|         |              | Conc. s     | Conc. s | Conc. s  |
| Ag      | 107          | 0.042       | 0.006  |
| Ba      | 137          | 2.47        | 0.21   |
| Co      | 59           | 0.052       | 0.004  |
| Cr      | 53/52        | 0.307       | 0.06   |
| Ga      | 69           | 0.50        | 0.02   |
| K       | 39           | 32.0        | 4.2    |
| Li      | 7            | 0.927       | 0.06   |
| Mg      | 26           | 32.1        | 0.6    |
| Mn      | 55           | 0.666       | 0.064  |
| Ni      | 60           | 0.51        | 0.10   |
| P       | 31           | 13.7        | 2.4    |
| Pb      | 208          | 1.91        | 0.15   |
| Rb      | 85           | 0.107       | 0.016  |
| Sn      | 118          | 1.21        | 0.08   |
| Sr      | 88           | 41.4        | 0.8    |
| Ti      | 205          | 0.008       | 0.002  |
| U       | 238          | 0.099       | 0.008  |
| V       | 51           | 0.21        | 0.02   |
| Zn      | 66           | 1.44        | 0.21   |

Data were calibrated with the certified values of the BAM-S005-B reference glass.
1. ID by TIMS, MC-ICP-MS and ICP-MS.
2. Solution ICP-MS.
3. Other bulk-analytical techniques, such as XRF, INAA, SSMS, ICP-OES, AAS.
4. LA-ICP-MS.
5. Other micro-analytical techniques, such as SIMS, EPMA, PIXE.

Data of category 1 have the highest level of confidence. ID by TIMS and (MC)-ICP-MS is considered to be a primary method of measurement, whose operation can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units (ISO Guide 35 2006). Isotope dilution data of 30, 25, 22 and 4 trace elements are available for NIST SRM 610–611, 612–613, 614–615 and 616–617 respectively (Tables 8–11, S1–S4). However, the ID results for some elements (e.g., Tl) may be questionable for the characterisation of the core when parts of the depleted rim were included.

Data of category 2 were obtained by solution ICP-MS, and certified standard solutions were generally used for calibration. Because of this, data of this category have a high level of confidence. For nearly all elements in NIST SRM 610–611, 612–613 solution ICP-MS data exist.

Data of category 3 were obtained by quite different analytical techniques. Whereas calibration of ICP-OES and AAS data was generally performed using standard solutions, this is not the case for INAA, XRF and SSMS, where solid reference materials were used.

Published LA-ICP-MS data of the NIST SRM 61x glasses were calibrated by using the same glasses (e.g., NIST SRM 610 data using NIST SRM 610 for calibration), which were excluded in this paper as explained above, other (than those measured) NIST SRM 61x glasses, geological reference glasses of the USGS, MPI-DING and other procedures. Because of some unsatisfactory calibration procedures, data of category 4 were carefully checked (e.g., type of laser, detection limit, uncertainty) and several outliers were rejected and not further considered in our calculation of reference values.

Data of category 5 were obtained by other micro-analytical techniques, mainly EPMA and SIMS. The accuracy of SIMS data may suffer from matrix effects; however, new technique developments and calibration procedures have improved the reliability of trace element data considerably (Hervig et al. 2006).

### Table 6.
Element concentrations (in µg g⁻¹) for NIST SRM 612 obtained by ID-TIMS at the MPI Mainz

| Element | Split 1   | Split 2   | Mean ± ±  |
|---------|-----------|-----------|-----------|
| K       | 60.65     | 60.61     | 60.63 ± 0.03 |
| Rb      | 31.79     | 31.80     | 31.79 ± 0.01 |
| Sr      | 78.28     | 78.43     | 78.36 ± 0.09 |
| Ba      | 39.69     | 39.69     | 39.69 ± 0.01 |
| La      | 35.83     | 35.92     | 35.85 ± 0.06 |
| Ce      | 38.78     | 38.71     | 38.73 ± 0.04 |
| Nd      | 35.97     | 35.93     | 35.95 ± 0.03 |
| Sm      | 38.08     | 38.05     | 38.07 ± 0.02 |
| Gd      | 36.54     | 36.83     | 36.67 ± 0.19 |
| Dy      | 36.19     | 36.27     | 36.28 ± 0.09 |
| Er      | 38.78     | 38.77     | 38.70 ± 0.10 |
| Yb      | 39.08     | 39.33     | 39.16 ± 0.15 |
| Lu      | 39.06     | 36.89     | 36.93 ± 0.05 |

Whereas typical sample amounts needed for analytical techniques of categories 1–3 are 2–100 mg, they are much less for micro-analytical techniques of category 4 (several µg) and of category 5 (ng range).

Tables 8–11 list the concentration averages for each group with the corresponding standard deviation values. Nearly all mean values of the five groups agree within uncertainty limits indicating that possible systematic differences between the analytical techniques are absent or small, making a bias component of uncertainty unnecessary.

### Reference and information values

To obtain the present best estimates of the ‘true’ values of the NIST SRM 61x glasses, we averaged the data of Tables 8–11 (= overall mean). As mentioned above, some data were not used for these calculations because they were inappropriately calibrated (marked by ‘*’ in Tables S1–S4) or they did not fulfil the Horwitz requirement and/or had low precision (marked by ‘**’). As recommended by the IAG (Kane et al. 2003) we used unweighted means because weighting procedures (Paule and Mandel 1982) cannot be applied successfully with many contributing laboratories. For some elements, two to five
independently determined ID values exist and according to ISO Guide 35 (2006) this is a sufficient number of laboratories involved in a characterisation process. However, in these special cases we also determined the preferred values from all available data. As Tables 8–11 show, the overall mean values agreed very well with the ID values. The overall means were divided in two kinds of values: reference values and information values. The reference values are comparable with ‘certified’ values in a certification programme (Kane et al. 2003, 2007). We report reference values when they were derived from at least six laboratories, where at least three laboratories published data of category 1 (ID) or 2 (solution-ICP-MS). Where fewer data exist, data of at least three methods of categories 1–5 determined in at least ten laboratories were necessary to establish a reference value. Those elemental abundances that were determined by only one or two techniques, by fewer than three techniques or less than ten laboratories were assigned information values rather than reference values.

Table 7. Element concentrations (in µg g⁻¹) for NIST SRM 610, 612 and 614 obtained by ID-ICP-MS (bold type) and ICP-MS at the ETH Zürich

| Element | NIST SRM 610 | Conc. | % RSD | N   | Conc. | % RSD | N   | Conc. |
|---------|-------------|-------|-------|-----|-------|-------|-----|-------|
| Ba      | 458.2       | 1.9   | 8     |     | 39.37 | 1.2   | 3   | 3.281 |
| Ce      | 449.4       | 1.0   | 6     | 37.25 | 2.4   | 6    | 0.790 |
| Cr      | 411.2       | 1.8   | 4     | 36.26 | 1.6   | 3    | 0.999 |
| Cs      | 361.5       | 0.5   | 4     | 42.14 | 2.2   | 1    | 0.655 |
| Co      | 411.4       | 0.8   | 4     | 34.83 | 3.1   | 3    | 0.780 |
| Dy      | 444.3       | 1.7   | 9     | 36.15 | 1.8   | 4    | 0.780 |
| Er      | 466.5       | 1.2   | 7     | 38.86 | 1.1   | 4    | 0.781 |
| Eu      | 454.8       | 1.7   | 3     |     |       |       |     |       |
| Hf      | 437.5       | 2.0   | 9     | 37.13 | 1.4   | 4    | 0.739 |
| Gd      | 461.1       | 1.6   | 9     | 38.56 | 1.7   | 4    | 0.801 |
| Ho      | 462.4       | 1.7   | 7     | 38.69 | 1.0   | 4    | 0.779 |
| La      | 432.2       | 1.3   | 12   | 34.65 | 2.3   | 6    | 0.686 |
| Lu      | 450.3       | 1.6   | 2     |     |       |       |     |       |
| Mo      | 400.1       | 1.9   | 7     | 35.79 | 1.7   | 4    | 0.792 |
| Nb      | 485.9       | 0.3   | 6     | 41.54 | 2.6   | 3    |       |
| Nd      | 432.3       | 1.1   | 12    | 34.96 | 1.8   | 6    | 1.082 |
| Ni      | 469.3       | 2.2   | 4     | 37.66 | 3.0   | 3    |       |
| Pb      | 433.3       | 1.2   | 9     | 38.6  | 3.7   | 3    | 2.510 |
| Pr      | 448.0       | 1.1   | 12    | 37.31 | 1.9   | 6    | 0.772 |
| Rb      | 417.1       | 1.2   | 5     | 31.07 | 1.0   | 1    | 0.824 |
| Sc      | 451.8       | 3.7   | 5     | 36.71 | 1.4   | 3    |       |
| Sm      | 452.5       | 0.6   | 9     | 37.15 | 1.5   | 4    | 0.761 |
| Sr      | 525.3       | 2.7   | 10    | 78.51 | 1.2   | 3    | 46.59 |
| Ta      | 448.3       | 2.7   | 6     | 38.17 | 0.3   | 3    |       |
| Tb      | 475.8       | 2.6   | 9     | 39.96 | 1.2   | 4    | 0.805 |
| Th      | 464.1       | 1.6   | 4     |     |       |       |     |       |
| Ti      | 436.9       | 0.1   | 2     |     |       |       |     |       |
| U       | 474.5       | 2.2   | 11    | 37.68 | 0.7   | 5    | 0.893 |
| V       | 447.9       | 2.5   | 4     | 39.92 | 1.6   | 3    | 1.084 |
| Y       | 479.7       | 2.5   | 9     | 40.14 | 1.7   | 3    | 0.799 |
| Yb      | 473.1       | 1.5   | 7     | 39.84 | 0.9   | 4    | 0.788 |
| Zr      | 473.7       | 1.5   | 9     | 40.36 | 1.7   | 3    |       |

N, number of analyses.

Figure 5. Data distribution chart for Ba in NIST SRM 610. Horizontal lines show the limits of the z-score results for \(-2 < z < 2\) (Horwitz and Albert 1995). Z-score results in this range are considered satisfactory.
As already mentioned, some trace elements have been certified by NIST for bulk-analytical purposes. With the exception of Mn in NIST SRM 610 (Table 8), we did not find any systematic difference between the certified values and the new data. Therefore, there is no need to revise the certified values. However, it must be remembered that the uncertainty of the data given by NIST is only valid for bulk analysis and cannot be extended automatically to microanalytical use.

Uncertainty of reference values and a discussion of the results

The reference values and most information values are accompanied with uncertainties at the 95% CL for the different test portion masses (Tables 8–11). These values were calculated using the IAG protocol (Kane et al. 2003), where the uncertainty, \( u \), is based mainly on three components of variance which were combined in quadrature:

\[
U^2 = \text{VAR}(Y_{\text{mean}})/\sqrt{N} + \text{VAR}_{\text{inhom}} + \text{VAR}_{\text{bias}}
\]  

(4)

The first component, the standard deviation of the mean of \( N \) contributing laboratories’ mean data, was used as the random component of variance. The second and the third components account for inhomogeneities in the NIST glasses and between-laboratory biases. \( \text{VAR}_{\text{inhom}} \) affects elements that are inhomogeneously distributed in the glasses. For such elements the \( \text{RSD}_{\text{inhom}} \) values (Figure 4a–d) for test portion masses of 1, 0.1 and 0.02 \( \mu \)g were used. Because the laboratories were qualified, biases were already included in the standard deviation of the mean, so that \( \text{VAR}_{\text{bias}} = 0 \).

The uncertainty \( U \) of the reference value at the 95% CL is

\[
U = t \times u
\]  

(5)

where \( t \) is the coverage factor. Student’s \( t \) distribution was used to assign \( t \), which is about 2 for \( N > 30 \) and much larger at small values of \( N \). As shown in Tables 8–11, the uncertainty \( U \) is constant regardless of test portion mass for elements that are homogeneously distributed. This allowed us to use the uncertainty determined by NIST for all homogeneously distributed elements, whose concentrations are certified, unchanged. However, inhomogeneities lead to higher values of \( U \) as test portion mass decreases. Because we found them to be large for Ni at test portion masses \( \leq 0.1 \mu \)g, the uncertainty for Ni reference values must be higher at small test portion mass.

In the following, the reference and information values and their uncertainties for the different elements and element groups, respectively, will be discussed in detail. Of particular interest are possible differences between our data for NIST SRM 610–611 and SRM 612–613 with those of the frequently used compilation values of Pearce et al. (1997) (Figure 6).

Major elements

The NIST glasses were prepared from a single support matrix whose nominal concentration is 72% m/m SiO\(_2\), 12% m/m CaO, 14% m/m Na\(_2\)O and 2% m/m Al\(_2\)O\(_3\) (Kane 1998). However, the nominal composition of the matrix does not exactly represent the major oxide composition of the final glasses due to the spiking processes with trace elements and volatilisation losses. Given the measured concentrations of trace elements, the oxide total, based on major elements alone, should be different from about 100% m/m in NIST SRM 616–617 to about 96.7% in NIST SRM 610–611 (Hinton 1999). Our values for major elements (Tables 8–11) agreed very well with these considerations: total oxide = 99.99% m/m (NIST SRM 616–617), 99.8% m/m (NIST SRM 614–615), 99.7% m/m (NIST SRM 612–613) and 96.5% m/m (NIST SRM 610–611). The measured H\(_2\)O and CO\(_2\) contents were low (\( \leq 0.02\)% m/m; Tables 8–11).

As shown in this paper (Figure 1) and other publications (e.g., Hinton 1999) the major elements are homogeneously distributed at both the small- and the large-scale. Because results from fewer than ten laboratories and only two different analytical techniques (EPMA, LA-ICP-MS) were available, mean values are only for information. However, all published data agree well and therefore the information values have a high level of confidence.

Refractory lithophile trace elements

Such elements with high condensation temperatures include Ba, Sr, Y, Zr, Hf, Nb, Ta, REEs, Th, U, Sc and Ti. As shown by LA-ICP-MS analyses in this work (Figures 4a–d) and Eggins and Shelley (2002) as well as by ion microprobe measurements (Hinton 1999) these trace elements are homogeneously distributed at all scales. Even for small spot sizes there is no indication of inhomogeneities. This means that uncertainties are the same for all test portion masses. Strontium is over-abundant in the NIST glasses because of the Sr base glass composition of 50 \( \mu \)g g\(^{-1}\) (Kane 1998). Bulk- and micro-analytical techniques, including the highly precise and accurate ID technique, are able to determine precisely the concentrations of most refractory
| Analyte | Ov. mean | Type of data | Uncertainty (U) at 95% CL | Test portion mass | Category | N | No. techn. | t | Literature | Other comp. (see Geo-ReM) |
|---------|---------|--------------|--------------------------|------------------|-----------|---|-----------|---|------------|--------------------------|
| Ag      | 251     | IV           | 9 ± 0.1 µg               | 1 µg             | 1         | 2  | 3         | 4 | 5          | NIST Pearce et al. (1997) |
| A2O3    | 1.95    | IV           | 0.04 µg                  | 0.02 µg          | 1         | 2  | 3         | 4 | 5          | 4239                     |
| As      | 325     | IV           | 18 ± 0.2 µg              | 1 µg             | 1         | 2  | 3         | 4 | 5          | 238 ± 2.57               |
| Au      | 23.6    | IV           | 2.2 ± 0.2 µg             | 0.1 µg           | 1         | 2  | 3         | 4 | 5          | 239 ± 2.37               |
| Bi      | 350     | IV           | 56 ± 3.0 µg              | 0.02 µg          | 1         | 2  | 3         | 4 | 5          | 239 ± 1.7               |
| Ba      | 452     | RV           | 9 ± 0.1 µg               | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Br      | 476     | RV           | 31 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Br      | 384     | RV           | 26 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Br      | 93      | IV           | 120 ± 150 (2)            | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| CO2     | 11.4    | IV           | 02 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Cd      | 270     | RV           | 16 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Ce      | 452     | RV           | 8 ± 0.1 µg               | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Cl      | 274     | RV           | 67 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Co      | 410     | RV           | 10 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Cr      | 408     | RV           | 10 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Cs      | 366     | RV           | 9 ± 0.1 µg               | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Cu      | 441     | RV           | 15 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Dy      | 437     | RV           | 11 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Er      | 455     | RV           | 14 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Eu      | 447     | RV           | 12 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| F       | 304     | IV           | 9 ± 0.1 µg               | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Fe      | 458     | CV           | 9 ± 0.1 µg               | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Ga      | 433     | RV           | 13 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Gd      | 449     | RV           | 12 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |
| Ge      | 447     | IV           | 78 ± 0.2 µg              | 0.00002 µg       | 1         | 2  | 3         | 4 | 5          | 424 ± 2.13               |

Table 8. Summary of compositional data for NIST SRM 610–611. Data are grouped into five categories of analytical techniques (see text).
Table 8 (continued).
Summary of compositional data for NIST SRM 610–611. Data are grouped into five categories of analytical techniques (see text).

| Analyte | Ov. mean | Type of data | Test portion mass | Uncertainty (U) at 95% CL | Category | N | No. tech. | NIST | Pearce et al. (1997) | Other comp. (see Geo-ReM) |
|---------|----------|--------------|-------------------|-----------------------------|----------|---|----------|------|----------------------|-----------------------------|
|         |          |              | mg range          | 1 µg | 0.1 µg | 0.02 µg | ID | ICP-MS | Bulk tech. | LA-ICP-MS | Microanal. |
| H       | 15       | IV           | 12 12 12 12 12    | 438 ± 1 (2) | 437 ± 11 (6) | 428 ± 2 (2) | 439 ± 37 (7) | 423 ± 31 (2) | 423 ± 31 (2) | 420 ± 40 (7) |
| Hf      | 435      | RV           | 12 12 12 12 12    | 441 ± 17 (12) | 466 ± 26 (2) | 456 ± 43 (8) | 457 (1) | 401 ± 27 (1) | 19 7 2.10 | 4177 | 4212–432 |
| Ho      | 449      | RV           | 12 12 12 12 12    | 447 ± 19 (3) | 436 ± 6 (2) | 436 (1) | 447 (1) | 497 (1) | 29 7 2.05 | 4414 | 415–441 |
| H2O     | 0.013    | IV           | 19 19 19 19 19    | 447 ± 19 (3) | 436 ± 6 (2) | 436 (1) | 447 (1) | 497 (1) | 29 7 2.05 | 4414 | 415–441 |
| In      | 464      | RV           | 21 21 21 21 21    | 463 ± 3 (2) | 449 ± 10 (2) | 429 ± 46 (2) | 480 ± 40 (7) | 497 (1) | 29 7 2.05 | 461 | 486 | 466–525 |
| la      | 440      | RV           | 10 10 10 10 10    | 440 ± 1 (2) | 445 ± 9 (6) | 447 ± 35 (10) | 477 (1) | 13 7 2.18 | 4846 | 428–485 |
| Li      | 468      | IV           | 24 24 24 24 24    | 455 ± 3 (2) | 441 ± 40 (2) | 450 ± 20 (7) | 405 (1) | 24 6 2.07 | 4347 | 420–435 |
| Lu      | 439      | RV           | 8 8 8 8 8          | 432 ± 3 (3) | 441 ± 40 (2) | 450 ± 20 (7) | 405 (1) | 24 6 2.07 | 4347 | 420–435 |
| Mg      | 432      | RV           | 29 29 29 29 29    | 488 (1) | 449 ± 45 (4) | 400 ± 40 (7) | 23 10 2.07 | 485 ± 10 | 4333 | 440–464 |
| Mn      | 444      | RV           | 13 13 13 13 13    | 440 (1) | 434 ± 36 (4) | 450 ± 15 (8) | 440 ± 40 (7) | 23 10 2.07 | 485 ± 10 | 4333 | 440–485 |
| Mo      | 417      | RV           | 21 23 27 27 27    | 400 (1) | 411 ± 15 (3) | 419 (1) | 429 ± 28 (8) | 433 ± 33 (2) | 15 6 2.15 | 3768 | 410 |
| Na2O    | 14.3     | IV           | 03 03 03 03 03    | 134 ± 0.2 (3) | 134 ± 0.5 (5) | 8 2 | 2.37 | 14 13332 | 134–1382 |
| Nb      | 465      | RV           | 34 34 34 34 34    | 473 ± 36 (3) | 462 ± 51 (6) | 9 2 | 2.31 | 4194 | 419–497 |
| Nd      | 430      | RV           | 8 8 8 8 8          | 434 ± 5 (3) | 425 ± 16 (11) | 429 (1) | 430 ± 22 (8) | 460 (1) | 26 8 | 4308 | 427–431 |
| Ni      | 458.7    | CV           | 4 4 25 184        | 469 (1) | 436 ± 13 (2) | 445 ± 24 (9) | 477 ± 42 (4) | 19 9 | 2.10 | 4439 | 443–4587 |
| P       | 413      | IV           | 46 46 46 46 46    | 363 ± 82 (2) | 420 ± 57 (2) | 8 2 | 2.37 | 14 13332 | 134–1382 |
| Pb      | 426      | CV           | 1 1 1 1 1          | 434 (1) | 421 ± 13 (9) | 414 ± 29 (3) | 417 ± 36 (6) | 22 6 | 2.08 | 426 ± 1 | 4133 | 417–428 |
| Pd      | 121      | IV           | 044 048 065 2.7   | 105 (1) | 130 ± 0.15 (2) | 415 (1) | 418 ± 19 (9) | 426 ± 28 (8) | 400 ± 65 (2) | 23 6 | 2.07 | 425.7 ± 0.8 | 4311 | 386–4257 |
| Pt      | 448      | RV           | 7 7 7 7 7          | 448 ± 17 (12) | 451 (1) | 447 ± 13 (5) | 458 (1) | 19 5 | 2.10 | 4298 | 430–454 |
| Pr      | 312      | IV           | 008 046 097 5.5   | 513 (1) | 310 ± 0.01 (2) | 3 2 | 4.30 | 3425 | 343–427 |
| Rb      | 4257     | CV           | 1 1 1 1 1          | 415 ± 17 (1) | 418 ± 19 (9) | 426 ± 28 (8) | 400 ± 65 (2) | 23 6 | 2.07 | 425.7 ± 0.8 | 4311 | 386–4257 |
| Re      | 499      | IV           | 37 37 37 37 11    | 499 (1) | 53 (1) | 483 ± 13 (2) | 4 3 | 3.18 | 1037 | 37 |
| Rh      | 129      | IV           | 007 007 023 0.87  | 131 (1) | 128 ± 0.03 (2) | 3 2 | 4.30 | 3425 | 343–427 |
| S       | 575      | IV           | 32 32 44 307      | 597 ± 32 (5) | 548 ± 34 (8) | 9 3 | 2.31 | 456 | 456 |
Table 8 (continued). Summary of compositional data for NIST SRM 610–611. Data are grouped into five categories of analytical techniques (see text).

| Analyte | Ov. mean | Type of data | Uncertainty (U) at 95% CL | Category | N | No. techn. | I | Literature |
|---------|----------|--------------|---------------------------|----------|---|-----------|---|-----------|
|         |          | Test portion mass | | | | | | NIST Pearce et al. (1997) | Other comp. (see Geo-ReM) |
|         |          | mg range | 1 µg | 0.1 µg | 0.02 µg | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Sb 396  | RV       | 19        | 19 | 19 | 22 | 3404 ± 1 (1) | 410 ± 5 (3) | 400 ± 25 (5) | 392 (1) | 10 | 4 | 2.26 | 3685 | 369–405 |
| Sc 455  | RV       | 10        | 10 | 10 | 10 | 450 ± 17 (7) | 454 ± 20 (5) | 468 ± 22 (3) | 15 | 4 | 2.15 | 4411 | 441–452 |
| Sr 138  | IV       | 42        | 42 | 43 | 91 | 95 (1) | 152 ± 2 (2) | 147 ± 36 (2) | 5 | 4 | 2.78 | 109 | 1105–1183 |
| SiO₂ 69.7| IV       | 0.5       | 0.5 | 0.5 | 0.5 | 69.7 (1) | 69.7 ± 06 (6) | 1 | 2 | 4.25 | 69795 | 6906–70 |
| Sm 453  | RV       | 11        | 11 | 11 | 11 | 452 ± 5 (3) | 442 ± 15 (11) | 457 ± 27 (4) | 532 (1) | 29 | 8 | 2.05 | 4505 | 449–454 |
| Sn 430  | IV       | 29        | 29 | 31 | 69 | 505 ± 11 (7) | 473 ± 20 (2) | 467 ± 43 (10) | 599 ± 1 (2) | 23 | 8 | 2.07 | 4794 | 477–516 |
| Sr 515.5| CV       | 1         | 1 | 1 | 1 | 521 ± 6 (2) | 392 ± 3 (4) | 475 ± 20 (3) | 430 ± 1 (2) | 6 | 2 | 2.57 | 3963 | 396–427 |
| Te 446  | RV       | 33        | 33 | 33 | 33 | 429 (1) | 439 ± 13 (3) | 424 ± 21 (6) | 443 (1) | 22 | 5 | 2.08 | 4766 | 452–476 |
| Tb 437  | RV       | 9         | 9 | 9 | 9 | 443 ± 21 (12) | 439 ± 13 (3) | 424 ± 21 (6) | 443 (1) | 22 | 5 | 2.08 | 4428 | 438–443 |
| Th 302  | IV       | 1         | 1 | 1 | 1 | 451 ± 38 (10) | 450 ± 42 (5) | 453 ± 27 (8) | 478 ± 131 (2) | 25 | 6 | 2.06 | 4572 ± 1.2 | 4506 | 442–4572 |
| Ti 59.6 | RV       | 10        | 10 | 10 | 10 | 440 ± 3 (2) | 440 ± 4 (2) | 461 ± 16 (4) | 455 ± 18 (6) | 14 | 6 | 2.16 | 437 | 434–4460 |
| Tm 435  | RV       | 10        | 10 | 10 | 10 | 431 ± 20 (12) | 454 ± 32 (2) | 432 ± 22 (6) | 470 (1) | 21 | 4 | 2.09 | 4201 | 420–447 |
| U 461.5 | CV       | 1         | 1 | 1 | 1 | 475 (1) | 461 ± 25 (8) | 484 ± 64 (2) | 464 ± 18 (7) | 19 | 5 | 2.1 | 4571 | 447–4615 |
| V 450   | RV       | 9         | 9 | 9 | 9 | 439 ± 10 (5) | 435 (1) | 455 ± 18 (9) | 465 ± 8 (3) | 15 | 7 | 2.12 | 4417 | 442–462 |
| W 444   | IV       | 29        | 29 | 29 | 29 | 4466 (1) | 415 (1) | 465 ± 61 (2) | 447 (1) | 7 | 5 | 2.45 | 4533 | 428–445 |
| Y 462   | RV       | 11        | 11 | 11 | 11 | 453 ± 17 (6) | 480 (1) | 467 ± 27 (6) | 484 ± 7 (2) | 18 | 5 | 2.11 | 4499 | 450–478 |
| Yb 450  | RV       | 9         | 9 | 9 | 9 | 459 ± 13 (3) | 446 ± 15 (9) | 455 ± 35 (3) | 451 ± 26 (8) | 23 | 7 | 2.07 | 4615 | 440–4457 |
| Zn 460  | RV       | 18        | 21 | 33 | 79 | 457 ± 35 (3) | 415 ± 18 (3) | 469 ± 34 (9) | 497 ± 26 (2) | 18 | 6 | 2.11 | 433 | 4563 | 456–505 |
| Zr 448  | RV       | 9         | 9 | 9 | 9 | 460 ± 19 (2) | 447 ± 21 (8) | 435 (1) | 449 ± 29 (10) | 446 ± 8 (3) | 24 | 7 | 2.07 | 4399 | 423–440 |

RV*: NIST certified value for Mn = 485 ± 10 µg g⁻¹.
NIST certified (CV), reference (RV) and information (IV) values are indicated.
Uncertainties (U) at the 95% confidence level (CL) determined for different test portion masses; t coverage factor. Trace elements in µg g⁻¹, oxides in % m/m.

Ov. (overall) mean, unweighted mean of all results; N, number of laboratory means; No techn., number of techniques used.
| Analyte | Type of data | Uncertainty (u) at 95% CL | Category | N | No. tech. | Literature |
|---------|--------------|--------------------------|----------|---|----------|------------|
| Ag      | 0.1 mg 0.02 μg | 22.0 CV 0.3 0.3 2.6 3.0 | 21 ± 2 (3) | 23 ± 3 (5) | 8 2 2.37 22.0 ± 0.3 21.92 22 | 
| Al2O3   | mg | 2.03 CV 0.04 0.04 0.04 0.04 | 2.07 ± 0.02 | 2.01 ± 0.04 | 6 2 2.09 2.01 2.09 | 
| As      | mg | 35.7 CV 5.5 5.5 5.5 8.9 | 48.1 (1) | 43 ± 0.42 | 5 12 35.7 ± 0.4 | 
| Au      | mg | 4.77 CV 1.7 1.7 1.7 1.7 | 121 (1) | 49 ± 1.2 | 8 12 4.77 ± 1.2 | 
| B       | mg | 34.3 CV 0.09 0.09 0.09 0.09 | 35 ± 0.42 | 35 ± 0.44 | 10 2 34.3 ± 0.42 | 
| Ba      | mg | 39.3 RV 0.9 0.9 0.9 0.9 | 40 ± 0.1 | 40 ± 0.1 | 21 6 39.3 ± 0.1 | 
| Be      | mg | 37.5 CV 1.5 1.5 1.5 1.5 | 38 ± 0.1 | 38 ± 0.1 | 12 3 37.5 ± 0.1 | 
| Bi      | mg | 30.2 RV 2.3 2.3 2.3 2.3 | 38 ± 0.1 | 38 ± 0.1 | 5 2 30.2 ± 0.1 | 
| CaO     | mg | 28.1 RV 1.1 1.1 1.1 1.1 | 38 ± 0.1 | 38 ± 0.1 | 35 ± 0.1 | 
| Cd      | mg | 28.4 CV 0.07 0.07 0.07 0.07 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Co      | mg | 18.4 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Cr      | mg | 35.4 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Cs      | mg | 42.7 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Cu      | mg | 35.8 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Dy      | mg | 35.5 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Er      | mg | 38.0 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Eu      | mg | 35.6 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| F       | mg | 8.0 CV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Fe      | mg | 35.6 CV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Ga      | mg | 40.3 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Gd      | mg | 36.9 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Ge      | mg | 37.3 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Hf      | mg | 36.3 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Ho      | mg | 35.5 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| In      | mg | 37.3 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Ir      | mg | 38.0 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| K       | mg | 36.1 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| La      | mg | 36.7 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 | 
| Lu      | mg | 37.3 RV 0.09 0.09 0.09 0.09 | 38 ± 0.1 | 38 ± 0.1 | 38 ± 0.1 |
Table 9 (continued). Summary of compositional data for NIST SRM 612–613. Data are grouped into five categories of analytical techniques (see text)

| Analyte | Ov. mean | Type of data | Uncertainty (U) at 95% CL | Category | N | No. techn. | t | Literature |
|---------|----------|--------------|---------------------------|----------|---|-----------|---|------------|
|         |          |              |                           | Test portion mass | 1 | 2 | 3 | 4 | 5 |         |           |           |
|         |          |              |                           | mg range | 1 μg | 0.1 μg | 0.02 μg | ID | ICP-MS | Bulk techn. | LA-ICP-MS | Microanal. |
| Ho      | 38.3     | RV           | 0.8                       | 0.8      | 0.8  | 0.8     | 38 ± 1 (10) | 39 ± 2 (12) | 22 | 2 | 208 | 37.87 | 38–40.2 |
| H₂O     | 0.021    | IV           | 0.1                       | 0.2      | 0.2  | 0.2     | 38 ± 2 (4)  | 38 ± 2 (4)  | 20 | 1 | 1 | 4293 | 43       |
| In      | 38.9     | RV           | 2.1                       | 2.1      | 2.1  | 2.1     | 38 ± 2 (10) | 38 ± 2 (10) | 36 | 6 | 204 | 36 | 35.77 | 35.8–36.5 |
| K       | 36.0     | RV           | 0.7                       | 0.7      | 0.7  | 0.7     | 35 ± 1 (12) | 35 ± 1 (12) | 32 | 6 | 204 | 36 | 35.77 | 35.8–36.5 |
| Li      | 402      | RV           | 1.3                       | 1.3      | 1.3  | 1.3     | 40 ± 2 (8)  | 41 ± 1 (10) | 13 | 3 | 2.18 | 41.4 | 42       |
| Lu      | 37.0     | RV           | 0.9                       | 0.9      | 0.9  | 0.9     | 36 ± 2 (9)  | 37 ± 2 (12) | 25 | 5 | 206 | 37.1 | 36.9–396 |
| Mg      | 68.0     | IV           | 0.1                       | 0.1      | 0.1  | 0.1     | 68 ± 3 (2)  | 68 ± 3 (2)  | 10 | 2 | 2.26 | 77.4 | 77       |
| Mn      | 38.7     | RV           | 0.9                       | 0.9      | 0.9  | 0.9     | 39 ± 2 (10) | 39 ± 2 (10) | 19 | 5 | 2.10 | 39.6 ± 0.8 | 38.4 ± 38 |
| Mo      | 37.4     | RV           | 0.3                       | 0.3      | 0.3  | 0.3     | 37 ± 2 (5)  | 38 ± 3 (8)  | 14 | 3 | 2.16 | 38.3 | 38       |
| N₂O⁵    | 137      | RV           | 0.3                       | 0.3      | 0.3  | 0.3     | 136 ± 0.5 (4) | 136 ± 0.5 (4) | 8  | 2 | 2.37 | 14 | 1398 | 14–1402 |
| Nb      | 38.9     | RV           | 2.1                       | 2.1      | 2.1  | 2.1     | 40 ± 3 (3)  | 39 ± 3 (10) | 13 | 2 | 2.18 | 38.06 | 40–42    |
| Nd      | 35.5     | RV           | 0.7                       | 0.7      | 0.7  | 0.7     | 35 ± 3 (3)  | 35 ± 1 (9)  | 25 | 5 | 2.06 | 35 | 35.24 | 35.3–36.2 |
| N       | 38.8     | CV           | 0.2                       | 3.7      | 2.82 | 45.3     | 377 ± 1 (10) | 377 ± 1 (10) | 12 | 3 | 2.20 | 38.8 ± 0.2 | 38.44 | 36.8–38.8 |
| P       | 466      | RV           | 6.9                       | 6.9      | 6.9  | 6.9     | 90 ± 1 (1)  | 50 ± 2 (4)  | 383 | 1 | 2.18 | 38.6 ± 0.2 | 38.96 | 36.9–38.6 |
| Pb      | 38.57    | CV           | 0.20                      | 0.20     | 0.20 | 0.20    | 386 ± 1 (6) | 39 ± 3 (16) | 23 | 3 | 2.07 | 38.57 ± 0.2 | 38.96 | 36.9–38.6 |
| Pd      | 105      | RV           | 0.10                      | 0.10     | 0.10 | 0.10    | 109 (1)     | 10 ± 1 (5)  | 4  | 2 | 3.18 | 3716 | 372–38    |
| Pr      | 379      | RV           | 1.0                       | 1.0      | 1.0  | 1.0     | 38 ± 1 (10) | 38 ± 3 (11) | 21 | 2 | 2.09 | 37.5 | 37.5 |
| Pt      | 2.51     | RV           | 0.01                      | 0.41     | 1.84 | 3.11    | 259 (1)     | 2.48 ± 0.03 (3) | 4  | 2 | 3.18 | 2.59 |
| Rb      | 31.4     | CV           | 0.4                       | 0.4      | 0.4  | 0.4     | 318 ± 1 (8) | 33 ± 2 (8)  | 18 | 4 | 2.11 | 31.4 ± 0.4 | 3163 | 267–32    |
| Re      | 663      | RV           | 0.61                      | 0.61     | 0.25 | 0.25    | 62.9 ± 0.05 (4) | 62.9 ± 0.05 (4) | 6  | 2 | 2.57 | 8.12 | 6.57    |
| Rh      | 0.91     | RV           | 0.02                      | 0.06     | 0.20 | 0.49    | 0.9 ± 0.001 (6) | 0.9 ± 0.001 (6) | 4  | 2 | 3.18 | 0.91 |
| S       | 377      | RV           | 0.7                       | 0.85     | 1.97 | 4.61    | 411 ± 10 (4) | 411 ± 10 (4) | 6  | 3 | 2.57 | 38.4 | 38       |
| Sb      | 347      | RV           | 1.8                       | 1.8      | 1.8  | 1.8     | 36 ± 2 (2)  | 34 ± 2 (7)  | 9  | 2 | 2.31 | 38.44 | 38       |
| Sc      | 399      | RV           | 2.5                       | 2.5      | 2.5  | 2.5     | 40 ± 3 (5)  | 40 ± 3 (6)  | 12 | 3 | 2.20 | 41.05 | 39–41    |
| Se      | 163      | RV           | 1.9                       | 2.7      | 7.8  | 19.0    | 156.1 ± 148 (17) | 17 ± 2 (4)  | 7  | 4 | 2.45 |
| SO₂⁵    | 72.1     | RV           | 0.6                       | 0.6      | 0.6  | 0.6     | 72 ± 1 (3)  | 72 ± 1 (3)  | 9  | 2 | 2.31 | 71.9 | 71.9    |
| Sm      | 37.7     | RV           | 0.8                       | 0.8      | 0.8  | 0.8     | 377 ± 0.07 (9) | 38.8 ± 0.8 (7) | 385 | 1 | 2.06 | 36 | 36.72 | 38–38.1 |

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Table 9 (continued).

Summary of compositional data for NIST SRM 612–613. Data are grouped into five categories of analytical techniques (see text).

| Analyte | Ov. mean | Type of data | Uncertainty (U) at 95% CL | Category |
|---------|----------|--------------|---------------------------|----------|
|         |          | Test portion mass | 1  | 2  | 3  | 4  | 5  | N | No. techn. |
|         |          | mg range | 1 µg | 0.1 µg | 0.02 µg | ID | ICP-MS | Bulk techn. | LA-ICP-MS | Micro-techn. | NIST | Pearce et al. (1997) | Other comp. (see GeoReM) |
| Sn      | 38.6     | IV       | 1.3  | 1.3  | 4.6  | 80 | 38 ± 2 (2) | 39 ± 2 (6) | 77 ± 4 (15) | 10 | 2          | 2.26 | 37.96  | 38 |
| Sr      | 78.4     | IV       | 0.2  | 0.2  | 0.2  | 0.2 | 78 ± 4 ± 6 | 73 (1)    | 37 ± 2 (4) | 25 | 5          | 2.06 | 74 ± 0.2 | 46.15 | 77–88.4 |
| Ta      | 37.6     | RV       | 1.9  | 1.9  | 1.9  | 1.9 | 359 ± 1 (1) | 39 ± 1 (3) | 37 ± 3 (9) | 13 | 3          | 2.18 | 30.77  | 39–41.4 |
| Tb      | 37.6     | RV       | 1.1  | 1.1  | 1.1  | 1.1 | 37 ± 1 (9) | 38 ± 1 (1) | 38 ± 3 (11) | 21 | 3          | 2.09 | 35.99  | 36 |
| Th      | 37.79    | CV       | 0.08 | 0.08 | 0.08 | 0.08 | 37 ± 1 (6) | 38 ± 1 (8) | 38 ± 3 (12) | 19 | 3          | 2.10 | 37.79 ± 0.08 | 37.23 | 37.82–39.8 |
| Ti      | 44.0     | RV       | 2.3  | 2.3  | 2.3  | 2.3 | 45 ± 6 (3) | 45 ± 6 (6) | 43 ± 4 (10) | 16 | 5          | 2.13 | 50.2 ± 0.8 | 48.41 | 40–48 |
| Tl      | 14.9     | RV       | 0.5  | 2.2  | 3.2  | 4.6 | 157 ± 1 (1) | 147 ± 0.7 (4) | 148 ± 0.4 (3) | 8  | 3          | 2.37 | 157 ± 0.3 | 15.07 | 151 |
| Tm      | 36.0     | RV       | 0.6  | 0.6  | 0.6  | 0.6 | 37 ± 1 (9) | 37 ± 2 (10) | 19 ± 2 (10) | 19 | 2          | 2.10 | 37.55  | 38 |
| U       | 37.38    | CV       | 0.08 | 0.08 | 0.08 | 0.08 | 377 ± 1 (1) | 37 ± 1 (4) | 35 ± 3 (11) | 20 | 4          | 2.09 | 37.38 ± 0.08 | 37.15 | 332–37.4 |
| V       | 38.8     | RV       | 1.1  | 1.1  | 1.1  | 1.1 | 38 ± 1 (1) | 36 ± 1 (1) | 39 ± 1 (1) | 16 | 3          | 2.13 | 39.22  | 332–39 |
| W       | 38.0     | IV       | 1.1  | 1.1  | 1.1  | 1.1 | 380 ± 1 (1) | 39 ± 1 (1) | 38 ± 1 (4) | 5  | 2          | 2.17 | 39.55  | 40 |
| Y       | 38.3     | RV       | 1.4  | 1.4  | 1.4  | 1.4 | 38 ± 3 (9) | 40 ± 1 (4) | 38 ± 3 (10) | 20 | 3          | 2.09 | 38.25  | 38–42 |
| Yb      | 39.2     | RV       | 0.9  | 0.9  | 0.9  | 0.9 | 40 ± 1 (5) | 38 ± 1 (7) | 42 ± 1 (10) | 25 | 6          | 2.06 | 39.95  | 39–402 |
| Zn      | 39.1     | RV       | 1.7  | 1.7  | 1.7  | 1.7 | 169 ± 1 (5) | 40 ± 2 (5) | 32 ± 5 (4) | 40 ± 2 (8) | 16 | 4          | 2.15 | 37.92  | 349–38 |
| Zr      | 37.9     | RV       | 1.2  | 1.2  | 1.2  | 1.2 | 39 ± 2 (2) | 38 ± 3 (8) | 37 ± 3 (11) | 22 | 5          | 2.08 | 35.99  | 38–419 |

Ov. (overall) mean, unweighted mean of all results; N, number of laboratory means; No. techn., number of techniques used.
NIST certified (CV), reference (RV) and information (IV) values are indicated.
Uncertainties (U) at the 95% confidence level (CL) determined for different test portion masses; t coverage factor. Trace elements in µg g⁻¹; oxides in % m/m.
| Analyte | Ov. mean | Type of data | Uncertainty (U) at 95% CL | Category | N | No. techn. | t | Literature |
|---------|----------|--------------|---------------------------|----------|---|-----------|---|-----------|
|         |          | Test portion mass |              | 1         | 2 | 3         | 4 | 5         | NIST | other comp. (see GeoReM) |
|         |          | mg range | 1 µg | 0.1 µg | ID | ICP-MS | Bulk tech. n. | LA-ICP-MS | Microanal. |         | |
| Ag      | 0.42     | RV       | 0.04 | 0.04 | 0.38 | 0.41 ± 0.03 | (4) | 4 | 1 | 3.18 | 0.42 ± 0.04 | 0.42 |
| Al₂O₃   | 2.04     | RV       | 0.05 | 0.05 | 0.05 | 2.06 ± 0.05 | (4) | 7 | 2 | 2.45 | 2.01 ± 0.06 | 1.99 |
| As      | 0.74     | RV       | 0.23 | 0.25 | 0.42 | 0.74 ± 0.13 | (4) | 4 | 1 | 3.18 | 0.66 |
| Au      | 0.48     | RV       | 0.07 | 0.10 | 0.23 | 0.46 ± 0.09 | (6) | 8 | 3 | 2.37 | 0.5 | 0.45 |
| B       | 1.49     | RV       | 0.19 | 0.19 | 1.39 | 3.35 ± 0.08 | (3) | 16 | 2 (6) | 3.02 | 21 | 4 | 2.09 | 3.2 |
| Be      | 0.753    | RV       | 0.051 | 0.051 | 0.51 | 0.75 ± 0.08 | (10) | 0.76 | (1) | 11 | 2 | 2.23 | 0.67 |
| Bi      | 0.581    | RV       | 0.043 | 0.043 | 0.043 | 0.57 | (1) | 0.58 ± 0.05 | (7) | 8 | 2 | 2.37 | 0.58 |
| CO₂     | 0.0004   | RV       | 0.0 | 0.0 | 0.0 | 0.0004 (1) | 1 | 1 | 1 | 1.19 | 11 |
| Co      | 11.9     | RV       | 0.2 | 0.2 | 0.2 | 0.48 (1) | 0.55 (1) | 0.57 | (1) | 11.9 ± 0.2 (5) | 5 | 2 | 2.78 | 12 |
| Cd      | 0.56     | RV       | 0.05 | 0.13 | 0.39 | 0.48 (1) | 0.55 (1) | 0.57 | (1) | 11.9 ± 0.2 (5) | 5 | 2 | 2.78 | 12 |
| Ce      | 0.813    | RV       | 0.025 | 0.025 | 0.025 | 0.805 (1) | 0.80 ± 0.03 (4) | 0.82 ± 0.06 (18) | 0.76 (1) | 24 | 4 | 2.07 | 0.81 |
| Cl      | 102      | RV       | 84 | 84 | 84 | 1.0 ± 0.4 (2) | 0.73 (1) | 0.72 | (1) | 0.75 ± 0.05 (4) | 0.99 (1) | 101 |
| Cr      | 1.19     | RV       | 0.12 | 0.31 | 1.11 | 0.999 (1) | 0.999 (1) | 0.99 | (1) | 0.75 ± 0.05 (4) | 0.99 (1) | 101 |
| Cs      | 0.664    | RV       | 0.034 | 0.048 | 0.561 | 0.66 ± 0.05 | 0.66 ± 0.05 | 0.66 | (13) | 0.74 ± 0.04 (16) | 0.60 (1) | 0.60 |
| Cu      | 1.37     | RV       | 0.07 | 0.27 | 1.57 | 1.86 (1) | 1.86 (1) | 1.5 | (9) | 1.75 ± 0.04 (16) | 0.74 (1) | 21 | 5 | 2.09 | 0.74 |
| Dy      | 0.746    | RV       | 0.02 | 0.02 | 2.02 | 0.77 ± 0.01 (2) | 0.77 ± 0.01 (2) | 0.72 | (1) | 0.74 ± 0.04 (16) | 0.60 (1) | 0.60 |
| Er      | 0.740    | RV       | 0.017 | 0.017 | 0.017 | 0.77 ± 0.01 (2) | 0.77 ± 0.01 (2) | 0.72 | (1) | 0.77 ± 0.04 (16) | 0.60 (1) | 0.60 |
| Eu      | 0.770    | RV       | 0.016 | 0.016 | 0.016 | 0.763 (1) | 0.763 (1) | 0.77 | (1) | 0.75 (1) | 0.75 (1) | 21 | 4 | 2.09 | 0.99 ± 0.04 |
| F       | 6.2      | RV       | 18.8 | 18.8 | 18.8 | 24 (1) | 13.3 (1) | 0.9 ± 0.07 | 0.22 | 13.3 ± 1 | 4 | 2 | 2.09 | 6.2 |
| Fe      | 1.31     | RV       | 0.09 | 0.09 | 0.09 | 0.13 (1) | 0.13 (1) | 0.13 | (1) | 0.13 ± 0.01 (10) | 11 | 2 | 2.23 | 1.3 |
| Ge      | 1.31     | RV       | 0.09 | 0.09 | 0.09 | 0.13 (1) | 0.13 (1) | 0.13 | (1) | 0.13 ± 0.01 (10) | 11 | 2 | 2.23 | 1.3 |

Table 10. Summary of compositional data for NIST SRM 614–615. Data are grouped into five categories of analytical techniques (see text).
Table 10 (continued).
Summary of compositional data for NIST SRM 614–615. Data are grouped into five categories of analytical techniques (see text)

| Analyte | Ov. mean | Type of data | Uncertainty (U) at 95% CL | Category | N | No. techn. | t | Literature |
|---------|---------|--------------|---------------------------|----------|---|-----------|---|-----------|
|         |         |              | Test portion mass         |          |   |           |   |           |
|         |         |              | mg range                  | 1 µg     | 0.1 µg | ID | ICP-MS | Bulk techn. | LA-ICP-MS | Microanal. | NIST | other comp. (see GeoReM) |
| Gd      | 0.763   | RV           | 0.021                     | 0.021    | 0.021 | 0.79 ± 0.01 (2) | 0.79 ± 0.04 (3) | 0.76 ± 0.05 (16) | 0.74 (1) | 22 | 5 | 2.08 | 0.75 |
| Ge      | 0.942   | RV           | 0.096                     | 0.208    | 0.585 | 0.79 ± 0.01 (2) | 0.79 ± 0.04 (3) | 0.84 ± 0.10 (7) | 0.66 (1) | 20 | 4 | 2.09 | 0.089 |
| Hf      | 0.711   | RV           | 0.022                     | 0.022    | 0.022 | 0.79 ± 0.01 (2) | 0.79 ± 0.04 (3) | 0.72 ± 0.04 (15) | 0.66 (1) | 21 | 3 | 2.09 | 0.074 |
| Ho      | 0.749   | RV           | 0.015                     | 0.015    | 0.015 | 0.74 ± 0.03 (4) | 0.74 ± 0.03 (4) | 0.75 ± 0.03 (16) | 0.73 (1) | 20 | 4 | 2.09 | 0.074 |
| HfO     | 0.019   | RV           | 0.05                      | 0.05     | 0.05  | 0.72 ± 0.01 (1) | 0.72 ± 0.01 (1) | 0.80 ± 0.06 (16) | 0.80 ± 0.06 (16) | 1 | 1 | 2.31 | 0.088 |
| In      | 0.79    | RV           | 0.002                     | 0.002    | 0.002 | 0.79 ± 0.01 (2) | 0.79 ± 0.01 (2) | 0.79 ± 0.01 (2) | 0.79 ± 0.01 (2) | 1 | 1 | 2.31 | 0.088 |
| K       | 30      | RV           | 1                         | 1        | 1    | 0.79 ± 0.01 (2) | 0.79 ± 0.01 (2) | 0.79 ± 0.01 (2) | 0.79 ± 0.01 (2) | 1 | 1 | 2.31 | 0.088 |
| La      | 0.720   | RV           | 0.013                     | 0.013    | 0.013 | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
| Li      | 1.69    | RV           | 0.09                      | 0.09     | 0.09  | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
| Lu      | 0.732   | RV           | 0.018                     | 0.018    | 0.018 | 0.70 ± 0.03 (3) | 0.70 ± 0.03 (3) | 0.74 ± 0.04 (16) | 0.74 ± 0.04 (16) | 21 | 4 | 2.09 | 0.073 |
| Mg      | 33.8    | RV           | 19                        | 19       | 19   | 0.70 ± 0.03 (3) | 0.70 ± 0.03 (3) | 0.74 ± 0.04 (16) | 0.74 ± 0.04 (16) | 21 | 4 | 2.09 | 0.073 |
| Mn      | 1.42    | RV           | 0.007                     | 0.007    | 0.007 | 0.70 ± 0.03 (3) | 0.70 ± 0.03 (3) | 0.74 ± 0.04 (16) | 0.74 ± 0.04 (16) | 21 | 4 | 2.09 | 0.073 |
| Mo      | 0.80    | RV           | 0.003                     | 0.006    | 0.028 | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
| Na2O    | 13.7    | RV           | 0.3                       | 0.3      | 0.3   | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
| Nb      | 0.824   | RV           | 0.003                     | 0.003    | 0.003 | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
| Nd      | 0.752   | RV           | 0.014                     | 0.014    | 0.014 | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
| Ni      | 1.1     | RV           | 0.1                       | 1.0      | 1.3   | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
| P       | 11.4    | RV           | 3.9                       | 3.9      | 3.9   | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
| Pb      | 2.32    | RV           | 0.04                      | 0.04     | 0.04  | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
| Pd      | 2.05    | RV           | 0.01                      | 0.06     | 0.124 | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
| Pr      | 0.768   | RV           | 0.015                     | 0.015    | 0.015 | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
| Pt      | 2.36    | RV           | 0.12                      | 0.225    | 0.375 | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
| Rb      | 0.855   | RV           | 0.005                     | 0.005    | 0.005 | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 0.72 ± 0.04 (4) | 23 | 4 | 2.07 | 0.072 |
Table 10 (continued).
Summary of compositional data for NIST SRM 614–615. Data are grouped into five categories of analytical techniques (see text)

| Analyte | Ov. mean | Type of data | Uncertainty (U) at 95% CL | Test portion mass | Category | N | No. techn. | t | Literature |
|---------|----------|-------------|---------------------------|------------------|----------|---|-----------|---|-----------|
|         |          |             |                           | mg range | 1 µg | 0.1 µg | ID | ICP-MS | Bulk techn. | LA-ICP-MS | Micro- anal. |
|         |          |             |                           |          |      |       |    |        |             |           |               |
|         |          |             |                           | mean ± s (N) |         |       |    |        |             |           |               |
| Re      | 0.170    | RV          |                           | 0.008 | 0.012 | 0.142 | 0.179 (1) |         |       |    |        |               |
| Rh      | 1.54     | RV          |                           | 0.18   | 0.18  | 0.18  | 1.67 (1)  |         |       |    |        |               |
| S       | 0.79     | RV          |                           | 0.064  | 0.064 | 0.11  | 0.067 (1) |         |       |    |        |               |
| Sb      | 0.74     | RV          |                           | 0.08   | 0.24  | 0.56  | 0.09 (1)  |         |       |    |        |               |
| Sc      | 0.40     | RV          |                           | 0.08   | 0.24  | 0.56  | 0.03 (1)  |         |       |    |        |               |
| Se      |          | RV          |                           | 0.075  | 0.074 | 0.074 | 0.043 (1) |         |       |    |        |               |
| SO₃     | 0.40     | RV          |                           | 0.099  | 0.099 | 0.099 | 0.097 (1) |         |       |    |        |               |
| Sm      | 0.754    | RV          |                           | 0.013  | 0.013 | 0.013 | 0.075 (1) |         |       |    |        |               |
| Sn      | 0.808    | RV          |                           | 0.026  | 0.026 | 0.026 | 0.076 (1) |         |       |    |        |               |
| Sr      | 0.739    | RV          |                           | 0.020  | 0.020 | 0.020 | 0.077 (1) |         |       |    |        |               |
| Ta      | 0.748    | RV          |                           | 0.006  | 0.006 | 0.006 | 0.074 (1) |         |       |    |        |               |
| Tb      | 0.361    | RV          |                           | 0.025  | 0.025 | 0.025 | 0.034 (1) |         |       |    |        |               |
| Th      | 0.273    | RV          |                           | 0.020  | 0.020 | 0.020 | 0.023 (1) |         |       |    |        |               |
| Tm      | 0.732    | RV          |                           | 0.020  | 0.020 | 0.020 | 0.073 (1) |         |       |    |        |               |
| U       | 0.823    | RV          |                           | 0.002  | 0.002 | 0.002 | 0.087 (1) |         |       |    |        |               |
| V       | 1.01     | RV          |                           | 0.04   | 0.04  | 0.04  | 0.110 (1) |         |       |    |        |               |
| W       | 0.806    | RV          |                           | 0.071  | 0.071 | 0.071 | 0.081 (1) |         |       |    |        |               |
| Y       | 0.790    | RV          |                           | 0.032  | 0.032 | 0.032 | 0.087 (1) |         |       |    |        |               |
| Yb      | 0.777    | RV          |                           | 0.021  | 0.021 | 0.021 | 0.076 (1) |         |       |    |        |               |
| Zn      | 2.79     | RV          |                           | 0.38   | 0.38  | 0.38  | 0.28 (1)  |         |       |    |        |               |
| Zr      | 0.848    | RV          |                           | 0.028  | 0.028 | 0.028 | 0.088 (1) |         |       |    |        |               |

Ov. (overall) mean, unweighted mean of all results; N, number of laboratory means; No. techn., number of techniques used. NIST certified (CV), reference (RV) and information (IV) values are indicated. Uncertainties (U) at the 95% confidence level (CL) determined for different test portion masses; t coverage factor. Trace elements in µg g⁻¹; oxides in % m/m.
| Analyte | Ov. mean | Type of data | Uncertainty (U) at 95% CL | Category | N | No. techn. | t | Literature |
|---------|----------|--------------|--------------------------|----------|---|------------|---|------------|
|         |          |              | Test portion mass         |          |   |            |   |            |
|         |          |              | mg range | 1 μg | 0.1 μg | ID | ICP-MS | Bulk techn. | LA-ICP-MS | Micro-anal. | NIST value |
| Hg      | 0.048    | N            | 0.020 | 0.020 | 0.020 | 0.048 ± 0.013 | 4 | 1 | 3.18 |
| Al₂O₃   | 1.99     | N            | 0.089 | 0.089 | 0.089 | 0.194 ± 0.018 | 3 | 1 | 4.30 |
| Ag      | 0.20     | N            | 0.020 | 0.020 | 0.020 | 0.194 ± 0.018 | 2 | 1 | 12.71 |
| B       | 0.189    | N            | 0.024 | 0.024 | 0.024 | 0.194 ± 0.018 | 6 | 3 | 2.57 |
| Ba      | 2.31     | N            | 0.12  | 0.12  | 0.12  | 0.194 ± 0.018 | 4 | 2 | 3.18 |
| Be      | 0.028    | N            | 0.025 | 0.025 | 0.025 | 0.194 ± 0.018 | 9 | 2 | 2.31 |
| Bi      | 0.021    | N            | 0.006 | 0.006 | 0.006 | 0.194 ± 0.018 | 3 | 2 | 4.30 |
| CaO     | 11.8     | N            | 0.1   | 0.1   | 0.1   | 11.79 ± 0.05  | 4 | 1 | 3.18 |
| Cd      | 0.036    | N            | 0.0011 | 0.0011 | 0.0011 | 0.024 ± 0.024 | 7 | 2 | 12.71 |
| Co      | 0.0297   | N            | 0.0016 | 0.0016 | 0.0016 | 0.0045 ± 0.001 | 7 | 2 | 2.45 |
| Co      | 0.051    | N            | 0.0016 | 0.0016 | 0.0016 | 0.0045 ± 0.001 | 7 | 1 | 2.45 |
| Cr      | 0.40     | N            | 0.013 | 0.013 | 0.013 | 0.027 ± 0.002 | 6 | 1 | 2.57 |
| Cr      | 0.027    | N            | 0.0011 | 0.0011 | 0.0011 | 0.027 ± 0.002 | 6 | 2 | 2.57 |
| Cu      | 0.30     | N            | 0.0014 | 0.0014 | 0.0014 | 0.081 ± 0.010 | 3 | 3 | 4.30 |
| Dy      | 0.0173   | N            | 0.00014 | 0.00014 | 0.00014 | 0.066 ± 0.010 | 6 | 2 | 0.80 ± 0.09 |
| Er      | 0.0157   | N            | 0.00013 | 0.00013 | 0.00013 | 0.016 ± 0.001 | 6 | 2 | 2.57 |
| Eu      | 0.0146   | N            | 0.00007 | 0.00007 | 0.00007 | 0.015 ± 0.001 | 5 | 2 | 2.78 |
| Fe      | 16       | N            | 0.008 | 0.008 | 0.008 | 0.005 ± 0.001 | 5 | 2 | 2.78 |
| Ga      | 0.50     | N            | 0.0013 | 0.0013 | 0.0013 | 0.005 ± 0.001 | 5 | 1 | 2.78 |
| Gd      | 0.0162   | N            | 0.0024 | 0.0024 | 0.0024 | 0.005 ± 0.001 | 5 | 2 | 2.78 |
| Ge      | 0.283    | N            | 0.0039 | 0.0039 | 0.0039 | 0.026 ± 0.003 | 5 | 1 | 2.78 |
| Hf      | 0.0154   | N            | 0.0018 | 0.0018 | 0.0018 | 0.026 ± 0.003 | 7 | 2 | 2.45 |
| Hg      | 0.0169   | N            | 0.0031 | 0.0031 | 0.0031 | 0.018 ± 0.004 | 9 | 3 | 2.31 |
Table 11 (continued).
Summary of compositional data for NIST SRM 616–617. Data are grouped into five categories of analytical techniques (see text).

| Analyte | Ov. mean | Type of data | Uncertainty (U) at 95% CL | Category | N | No. techn. | t |
|---------|----------|--------------|--------------------------|----------|---|------------|---|
|         |          |              | Test portion mass        |          |   |            |   |
|         |          |              | mg range | 1 µg | 0.1 µg | 1 | ICP-MS | Bulk techn. | LA-ICP-MS | Micro-anal. |
| In      | 0.0302   | N           |          |       |       | 0.0035 | 0.0035 | 0.0035 | 0.0024 | 0.031 ± 0.002 | 0.031 ± 0.002 | 6 | 2 | 257 |
| K       | 29       | CV          |          | 1     | 1     | 1   |       |       |       | 31 ± 2.2 | 31.6 (1) | 3 | 2 | 430 |
| La      | 0.0298   | N           |          |       |       | 0.0032 | 0.0032 | 0.0032 | 0.0034 (1) | 0.029 ± 0.004 | 0.029 ± 0.004 | 8 | 3 | 237 |
| Li      | 0.895    | N           |          |       |       | 0.0059 | 0.0059 | 0.0059 | 0.0013 (1) | 0.89 ± 0.076 | 0.91 (1) | 7 | 2 | 245 |
| Lu      | 0.0145   | N           |          |       |       | 0.0020 | 0.0020 | 0.0020 | 0.0013 (1) | 0.015 ± 0.001 | 0.014 (1) | 8 | 3 | 237 |
| Mg      | 34.7     | N           |          | 2.8   | 2.8   | 2.8  |       |       | 35 ± 3 | 35.4 (1) | 5 | 2 | 278 |
| Mn      | 0.609    | N           |          | 0.027 | 0.027 | 0.027 |       |       | 0.61 ± 0.02 | 0.61 ± 0.02 | 5 | 1 | 278 |
| Mo      | 0.0879   | N           |          | 0.013 | 0.047 | 0.066 |       |       | 0.084 ± 0.010 | 0.113 (1) | 7 | 2 | 245 |
| Na₂O    | 13.7     | N           |          | 0.09  | 0.09  | 0.09  |       |       | 13.7 ± 0.4 | 13.7 ± 0.4 | 3 | 1 | 430 |
| Nb      | 0.0194   | N           |          | 0.0015 | 0.0015 | 0.0015 |       |       | 0.020 ± 0.005 | 0.019 (1) | 6 | 2 | 257 |
| Nd      | 0.0227   | N           |          |       |       | 0.0031 | 0.0031 | 0.0031 | 0.023 ± 0.005 | 0.023 ± 0.005 | 6 | 2 | 257 |
| Ni      | 0.435    | N           |          | 0.10  | 0.81  | 1.11 |       |       | 0.44 ± 0.06 | 14 (1) | 122 (1) | 2 | 2 | 1371 |
| P       | 13       | N           |          | 10    | 10    | 10   |       |       | 18 ± 0.1 | 18 ± 0.1 | 8 | 2 | 237 |
| Pb      | 1.85     | CV          |          | 0.04  | 0.04  | 0.04  |       |       | 1.8 ± 0.1 (7) | 1.6 (1) | 8 | 2 | 237 |
| Pd      | 1.77     | N           |          | 0.13  | 0.13  | 0.13  | 1.75 (1) |       | 1.78 ± 0.07 | 1.78 ± 0.07 | 3 | 2 | 430 |
| Pr      | 0.0150   | N           |          | 0.009 | 0.009 | 0.009 | 0.0015 (1) |       | 0.015 ± 0.001 | 0.014 (1) | 6 | 2 | 257 |
| Pt      | 1.77     | N           |          | 0.25  | 0.25  | 0.25  | 1.79 (1) |       | 1.75 (1) | 1.75 (1) | 2 | 2 | 1371 |
| Rb      | 0.104    | N           |          | 0.004 | 0.004 | 0.004 | 0.1 (1) |       | 0.105 ± 0.004 | 0.105 ± 0.004 | 8 | 2 | 237 |
| Re      | 0.0036   | N           |          | 0.0013 | 0.0025 | 0.0032 | 0.0035 (1) |       | 0.0037 (1) | 0.007 (1) | 2 | 2 | 1371 |
| Rh      | 0.98     | N           |          | 0.34  | 0.34  | 0.34  | 0.078 (1) |       | 0.098 ± 0.004 | 0.075 ± 0.008 | 2 | 1 | 1371 |
| Sb      | 0.076    | N           |          | 0.008 | 0.019 | 0.040 |       |       | 0.078 (1) | 0.078 (1) | 6 | 2 | 257 |
| Sc      | 0.026    | N           |          |       |       | 0.0004 | 0.0004 | 0.0004 | 0.026 (1) | 0.026 (1) | 1 | 1 | 0.026 ± 0.012 |
| Se      | 0.22     | N           |          |       |       | 0.0004 | 0.0004 | 0.0004 | 0.026 (1) | 0.026 (1) | 1 | 1 | 0.026 ± 0.012 |
| SO₂₅    | 72.5     | N           |          | 0.7   | 0.7   | 0.7   |       |       | 72 ± 0.3 | 72 ± 0.3 | 3 | 1 | 430 |
| Sm      | 0.0164   | N           |          | 0.0029 | 0.0029 | 0.0029 | 0.00165 ± 0.0004 | 0.0016 (1) | 0.016 ± 0.003 | 0.016 ± 0.003 | 5 | 2 | 278 |
| Sn      | 1.18     | N           |          | 0.08  | 0.73  | 0.81  |       |       | 1.2 ± 0.1 | 1.07 (1) | 7 | 2 | 245 |
Table 11 (continued).
Summary of compositional data for NIST SRM 616–617. Data are grouped into five categories of analytical techniques (see text)

| Analyte | Ov. mean | Type of data | Uncertainty (U) at 95% CL | Category |
|---------|----------|--------------|---------------------------|----------|
|         |          |              | Test portion mass          | 1        | 2        | 3        | 4        | 5        | N  | No. techn. | t | Literature |
|         |          |              | mg range | 1 µg | 0.1 µg | ID | ICP-MS |Bulk techn.| LA-ICP-MS| Microanal.| | | |
| Sr      | 41.72    | CV           | 005      | 0.05 | 0.05  | 41.95 (1) | 41 ± 2 (10) | 399 (1) | 9    | 3   | 2.00 | 41.72 ± 0.05 |
| Ta      | 0.0299   | N            | 000555   | 0.0055| 0.0055| 0028 (1) | 0031 ± 0.008 (7)| 0022 (1) | 7    | 3   | 2.31 |
| Tb      | 0.0145   | N            | 00021    | 0.0021| 0.0021| 0019 (1) | 0014 ± 0.001 (8)| 0012 (1) | 7    | 3   | 2.45 |
| Th      | 0.0252   | CV           | 0007     | 0.007 | 0.007 | 0014 (1) | 0026 ± 0.003 (7)| 0026 (1) | 8    | 2   | 2.37 |
| Ti      | 2.65     | N            | 029      | 0.29 | 0.29  | 00082 (1) | 25 (1) | 2.6 ± 0.2 (3) | 2.92 (1) | 5    | 3   | 2.78 |
| U       | 0.0081   | N            | 00012    | 0.0042| 0.0059| 00007 (1) | 0008 ± 0.002 (8)| 0001 (1) | 8    | 2   | 2.37 |
| Tm      | 0.0144   | N            | 00012    | 0.0012| 0.0012| 0016 (1) | 0014 ± 0.001 (8)| 0013 (1) | 7    | 3   | 2.45 |
| U       | 0.0721   | CV           | 00013    | 0.0013| 0.0013| 0084 (1) | 0074 ± 0.006 (8)| 0063 (1) | 10   | 3   | 2.26 |
| V       | 0.228    | N            | 0015     | 0.015 | 0.015 | 003 (1) | 023 ± 0.002 (7)| 0036 (1) | 7    | 1   | 2.45 |
| W       | 0.043    | N            | 0004     | 0.033 | 0.055 | 0045 ± 0.002 (8)| 0036 (1) | 6    | 2   | 2.57 |
| Y       | 0.0288   | N            | 00024    | 0.0024| 0.0024| 0094 (1) | 009 ± 0.002 (8)| 009 (1) | 6    | 2   | 2.57 |
| Zr      | 1.33     | N            | 027      | 0.27 | 0.27  | 0101 (1) | 013 ± 0.2 (6) | 0101 (1) | 7    | 1   | 2.45 |
| Z       | 0.0951   | N            | 00080    | 0.0080| 0.0080| 008 | 0.004 ± 0.010 (7)| 0.001 (1) | 8    | 2   | 2.37 |

Ov. (overall) mean, unweighted mean of all results; N, number of laboratory means; No techn., number of techniques used.

NIST certified (CV) and information (IV) values are indicated.

Uncertainties (U) at the 95% confidence level (CL) determined for different test portion masses; t coverage factor. Trace elements in µg g⁻¹, oxides in % m/m.
lithophile elements. Therefore, many published data for NIST SRM 610–611, SRM 612–613, SRM 614–615 exist. Our new reference values are of high quality with relative uncertainties of less than 3% (Figure 7) and agree well with existing ID measurements. Many values agree within the stated uncertainties [this work: about 2–3% (95% CL relative); Pearce et al. (1997): about 3–10% (RSD)] (Figure 6). Notable exceptions are Nb and Ta in SRM 610–611, where our reference values (Nb $465 \text{ g}^{-1}$, Ta $446 \text{ g}^{-1}$), the ID value of Ta ($429 \text{ g}^{-1}$) and most other recently published data were significantly higher than the Pearce et al. (1997) value (Nb $419.4 \text{ g}^{-1}$, Ta $376.6 \text{ g}^{-1}$). The NIST certified Sr, Th and U concentrations agree well with published bulk- and micro-analytical

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**Figure 6.** Deviation of the reference and information values from the compilation data of Pearce et al. (1997).

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**Figure 7.** Diagram illustrating the relative uncertainties at the 95% confidence level for the reference and information values of NIST SRM 610–611 and 612–613 at different test portion masses.
data. As Figure 4a–d demonstrate, these elements are homogeneously distributed in all NIST SRM 61x glasses, even for very low test portion masses. This means that the uncertainty at the 95% CL of the NIST certified Sr, Th and U values is valid to test portion masses as low as 0.02 µg.

**Other lithophile elements**

The alkali elements Li, Rb, Cs were found to be homogeneously distributed in all NIST glasses. This is in contrast to the investigations of Eggins and Shelley (2002) who report slight to moderate inhomogeneities for these elements. Potassium appears to be grossly contaminated and over-abundant in the NIST SRM glass series by about 30 µg g⁻¹, which is consistent with reported base glass compositions of 5–100 µg g⁻¹ (Eggins and Shelley 2002). Caesium is a volatile element and may therefore be subject to loss during high temperature fusion. This, however, had no influence on the homogeneity of Cs in the NIST SRM 61x glasses; all measurements yielded a RSD < 2% (Figure 4a–d). The NIST certified values of Rb are nearly identical to the mean values calculated from recently published data. Rubidium was homogeneously distributed in the glass wafers and therefore, the uncertainty given by NIST is also valid for micro-analytical applications.

The NIST certified value for Mn (485 ± 10 µg g⁻¹) in NIST SRM 610 does not agree with our overall mean value (444 ± 13 µg g⁻¹) determined from recent publications. Because the values determined by different techniques (Table 8) agree and are much lower than the certified value, this requires that the NIST Mn reference value for SRM 610 be revised. Manganese values lower than the certified value were also proposed by Pearce et al. (1997) (433 µg g⁻¹) and Rocholl et al. (2000) (443 µg g⁻¹).

Magnesium is homogeneously distributed in the NIST glasses (Eggins and Shelley 2002). The new reference values for NIST SRM 610 and 612 were found to be lower than the Pearce et al. (1997) data by about 10%. The discrepancies for P are even higher; the new reference values for NIST SRM 610 and SRM 612 were 21% higher and 16% lower than the Pearce et al. (1997) values respectively.

Because of the many published data for NIST SRM 610–615 the reference values for Be and V analyses are reliable. They agree within uncertainty limits with the Pearce et al. (1997) values. There are only a few, but somewhat consistent, data for the halogens F, Cl, Br, and none for I. The information values have, therefore, high uncertainties.

**Chalcophile/siderophile trace elements**

Members of this group include Ag, As, Bi, Cd, Co, Cr, Cu, Fe, Ga, Ge, In, Mn, Mo, Ni, Pb, Re, S, Sb, Sn, Se, Te, Tl, W and Zn. Because of their volatility and their chalcophile/siderophile behaviour some of them are inhomogeneously distributed in the glass wafers. Such inhomogeneities have been explained by loss of volatile components from the molten glass surface (Eggin and Shelley 2002) and of siderophile elements to the platinum furnace (Rocholl et al. 1997) during preparation. Typical examples are Tl, Cr, Ni and Se (Figure 4a–d). Eggins and Shelley (2002) established the order of relative depletion: Tl > Te > Re > Au > As > Se > Cr > Ag > Cd > B > Mo > Sb > Bi > Pb > W > Cs, which is notable for closely matching the relative order of bulk composition in NIST glasses relative to the nominal concentration levels. Our investigations demonstrated that inhomogeneities for most of the chalcophile/siderophile elements exist, but they are low (< 5% and < 7% for NIST SRM 610 and 612, respectively, at a test portion mass of 0.1 µg) in the core parts of the glass wafers (Table 2, Figure 4a–d). Exceptions are Cr, Ni, Se and Tl with higher degrees of inhomogeneity.

Because of analytical difficulties the number of published data for some chalcophile/siderophile elements (e.g., Ge, Se, Te) is low. Therefore, uncertainties are significantly higher than for lithophile trace elements. Exceptions are the concentrations of Ag in SRM 612–613 and SRM 614–615, Fe and Ni in SRM 610–611 and SRM 612–613, Cu in SRM 614–615 as well as Pb in all NIST glasses, which have been certified by NIST. For Co, Cr, Cu sufficient literature data for SRM 610–611, 612–613 and 614–616 exist to establish reliable reference values. For some chalcophile/siderophile trace elements in the depleted SRM 616–617 glass we report first information values mainly obtained by LA-ICP-MS.

Our Cr reference value (36.4 ± 1.7 µg g⁻¹ (95% CL for a test portion mass of 1 µg)) for NIST SRM 612–613 is similar to the Pearce et al. (1997) value [39.88 ± 15.17 µg g⁻¹ (1s for bulk analysis)], but has a much lower uncertainty. There are large discrepancies in Ga data for NIST SRM 616–617. LA-ICP-MS (0.54 ± 0.13 µg g⁻¹, Table 11) and SIMS values (1.25 µg g⁻¹, Table S4) were significantly higher than the NAA value (0.23 µg g⁻¹) proposed by NIST. Only a few reliable values for S were available. Our S reference value for NIST SRM 612–613 is much higher (377 µg g⁻¹) than the value of 5 ± 16 µg g⁻¹ proposed by Pearce et al. (1997), which was based on a single semiquantitative LIMS value (Bonham and Quattlebaum 1988).
Highly siderophile elements

There is a great need for micro-analytical reference materials containing well-known compositions of highly siderophile elements, including the noble metals Ru, Rh, Pd, Os, Ir, Pt and Au. One of the major problems is that in geological reference glasses (e.g., MPI-DING, USGS) these elements may be inhomogeneously distributed using small test portion masses (Jochum and Stoll 2008). As shown in Figure 4a–d this is also the case for Rh, Pd, Pt and Au in the NIST SRM 610–615 glasses. In particular, Pd and Pt showed relative inhomogeneities of up to 50% at very low test portion masses. Because of their very low abundances, Ru and Os concentrations have not been determined in the NIST glasses; only one Ir determination exists for NIST SRM 612. Because of the few published data the overall mean Rh, Pd, Pt and Au values in Tables 8–10 are only for information, although ID values for Pd and Pt are available (Sylvester and Eggins 1997). NIST SRM 616–617 seem to be homogeneous with respect to noble metals (Figure 4d). Even for test portion masses of 0.01 μg, RSDinhom was < 2%. This means that this sample may be useful as a calibration material for noble metals. Because of the high quality ID data of Sylvester and Eggins (1997), the overall means are confident.

Accuracy

Of particular importance is the accuracy of micro-analytical data, that is the closeness of agreement between the measured and the ‘true’ values. The reference and information values of the NIST glasses (Tables 8–11) have a high degree of confidence. Compared with former compilations (e.g., Pearce et al. 1997) the overall means were determined mainly from recent studies that used improved instrumental and analytical procedures, such as ID-TIMS and ID-MC-ICP-MS (e.g., Rocholl et al. 2000, Nebel et al. 2009), and multi-element (ID)-ICP-MS measurements (this work) to obtain high-precision and accurate data, new laser ablation systems with low wavelengths and femtosecond pulses to minimise elemental fractionation (e.g., Hom and von Blancenburg 2007), the use of dynamic reaction cells to minimise formation of metal-argide ions in the ICP-MS (e.g., Hattendorf et al. 2001), and high-resolution sector field ICP-MS to separate interferences from the mass peaks of interest (e.g., Guillong et al. 2008, Regnery et al. 2010). LA-ICP-MS data for lithophile refractory elements have been less influenced by the technological progress of lasers, because the fractionation factors of these elements are nearly identical as shown by Fryer et al. (1995). The chalcophile and siderophile elements are most prone to elemental fractionation relative to lithophile elements (e.g., Ca). As mentioned above, differences in elemental fractionation are significantly diminished using shorter wavelengths, which leads to more reliable LA-ICP-MS data. Although some of the bulk techniques (e.g., ID, solution ICP-MS) yield highly precise data, the results may be questionable for the characterisation of the core when parts of the depleted rim were used. However, as shown earlier, this affects only some elements (e.g., Ti, Se and Au; Figure 2). The ID and solution ICP-MS Ti data for NIST SRM 610 and 612 (Tables 8, 9) agree with the LA-ICP-MS data, indicating no systematic differences for this element. There is also no indication of a systematic difference for Se and Au data obtained using bulk- and micro-analytical techniques respectively.

The new reference and information values have been used to determine trace element concentrations in the synthetic certified reference glasses BAM-S005-A and BAM-S005-B (http://www.rm-certificates.bam.de). Data were obtained by LA-ICP-MS at MPI Mainz (Yang et al. 2011) and calibrated with NIST SRM 610 (Table 8), which has approximately the same major element composition as the BAM glasses. Figure 8 shows the results for BAM-S005-A. All data agreed within uncertainty limits with the BAM certified reference values. The figure also shows the LA-ICP-MS results using the Pearce et al. (1997) values for calibration. There were only small differences for Ti, Zr, V, Cr, Fe and Zn values. As mentioned earlier, the NIST certified Mn value for SRM 610 leads to a systematically higher concentration. Differences for As, Cd, Mo, Sn, Sb and especially Se and Cl are even higher; no value for sulfur in Pearce et al. (1997) exists.

The knowledge of the uncertainty of the reference values in reference materials is essential for assessment of the quality of the results of micro-analytical investigations. Unfortunately, some analysts only use the reference value and do not pay attention to its uncertainty. For example, when using NIST SRM 612–613 for calibration and the reference value has an uncertainty of 10%, the analytical result of an unknown sample cannot have measurement uncertainty better than 10%. As discussed earlier, the
uncertainty of the reference and information values (Tables 8–11) is dependent on both the uncertainty of the overall mean data and the degree of inhomogeneity at a specific test portion mass (spot size in LA-ICP-MS). Figure 7 gives an overview of the expected uncertainty, which can be obtained by using NIST SRM 610–611 and 612–613 glasses for calibration of bulk- and micro-analytical methods. It illustrates the values for the relative uncertainty at the 95% CL in percent (= 100 \cdot U>/<Overall mean>) of different elements and element groups obtained for different test portion masses. Using this figure, the minimum test portion mass (or spot size in LA-ICP-MS) can be inferred, where the uncertainty for a trace element is less than 3%, 5%, 10% and 20% in NIST SRM 610–611 and 612–613.

Conclusions

Most reference values for the NIST SRM 610–617 glasses obtained by following ISO guidelines and the IAG protocol for certification of reference materials have a high degree of confidence. This is especially the case for most lithophile elements of NIST SRM 610–611 and SRM 612–613, where many published data using quite different analytical techniques including ID were available. In addition, these elements are homogeneously distributed at the small-scale and the large-scale. Altogether we have established forty-six reference and certified values for NIST SRM 610–611, forty-three for SRM 612–613, thirty-three for SRM 614–615, and five for NIST SRM 616–617. The data of many elements could not be classified as reference values because they did not satisfy the requirements of the ISO guidelines and the IAG protocol. This was particularly the case for the depleted NIST SRM 616–617 glasses. However, many of these elements (major elements, some lithophile and chalcophile/siderophile trace elements, where concentrations were partly determined by ID) are homogeneously distributed at the small- and the large-scale, and give reliable information values with uncertainties ≤ 10% at test portion masses as low as 0.1 μg. The numbers of such information values are: 13 (SRM 610/611), 14 (SRM 612/613), 12 (SRM 614/615) and 24 (SRM 616/617). This means that the NIST glasses are suitable calibration materials for nearly all elements.

For some chalcophile and siderophile elements inhomogeneities occur, especially in the rim region (about 1–1.5 mm) of the wafers; but for most applications they are moderate in NIST SRM 610–611 and 612–613. Because of the extremely inhomogeneous distribution of Pd, Pt, Ni, Se some NIST glasses may be suitable for bulk-analytical but not for micro-analytical purposes at very low test portion masses. For F, Cl, Br and S few published data exist, which are partly inconsistent with one another; no data exist for Ru, Os, I and Hg.

In summary, we report the reference and information values of this work as a state of the art data set for inter-laboratory comparisons. Furthermore, we are confident that the data quality of micro-analytical investigations will improve by using these recommended values for calibration. However, further analyses are needed to improve the analytical data of some trace elements by reducing their uncertainties. This is especially true for elements where only information values can currently be determined.

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The following supporting information is available online:

Table S1. Used data for NIST SRM 610 and 611.

Table S2. Used data for NIST SRM 612 and 613.

Table S3. Used data for NIST SRM 614 and 615.

Table S4. Used data for NIST SRM 616 and 617.

Table S5. GeoReM numbers and references.

Table S6. Abbreviations of analytical techniques.

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