

Reference Values Following ISO Guidelines for Frequently Requested Rock Reference Materials

Klaus Peter **Jochum** (1, 2)*, Ulrike **Weis** (1, 2), Beate **Schwager** (1, 2), Brigitte **Stoll** (1, 2), Stephen A. **Wilson** (3), Gerald H. **Haug** (2), Meinrat O. **Andreae** (1) and Jacinta **Enzweiler** (4)

(1) Biogeochemistry Department, Max Planck Institute of Chemistry, PO Box 3060, Mainz, 55020, Germany

(2) Climate Geochemistry Department, Max Planck Institute of Chemistry, PO Box 3060, Mainz, 55020, Germany

(3) US Geological Survey, Denver Federal Center, Box 25016, MS 973, Denver, CO, 80225, USA

(4) Institute of Geosciences, University of Campinas, UNICAMP, PO Box 6152, Campinas, 13083-970, Sao Paulo, Brazil

* Corresponding author. e-mail: kjochem@mpic.de

We present new reference values for nineteen USGS, GSJ and GIT-IWG rock reference materials that belong to the most accessed samples of the GeoReM database. The determination of the reference values and their uncertainties at the 95% confidence level follows as closely as possible ISO guidelines and the Certification Protocol of the International Association of Geoanalysts. We used analytical data obtained by the state-of-the-art techniques published mainly in the last 20 years and available in GeoReM. The data are grouped into four categories of different levels of metrological confidence, starting with isotope dilution mass spectrometry as a primary method. Data quality was checked by careful investigation of analytical procedures and by the application of the Horwitz function. As a result, we assign a new and more reliable set of reference values and respective uncertainties for major, minor and a large group of trace elements of the nineteen investigated rock reference materials.

Keywords: reference material, reference value, ISO, certification protocol, rock reference materials.

Received 14 Oct 15 – Accepted 15 Dec 15

Nous présentons de nouvelles valeurs de référence pour dix-neuf matériaux de référence de roche de l'USGS, GSJ et GIT-IWG qui appartiennent aux échantillons les plus recherchés de la base de données "GeoReM". La détermination des valeurs de référence et leur incertitude au niveau de confiance de 95% suit d'aussi près que possible les directives de l'ISO et le protocole de certification de l'Association Internationale des Géoanalystes. Nous avons utilisé des données d'analyse obtenues par les techniques de l'état de l'art publiées principalement dans les 20 dernières années et disponibles dans GeoReM. Les données sont regroupées en quatre catégories de différents niveaux de confiance métrologiques, en commençant par la dilution isotopique par spectrométrie de masse comme méthode principale. La qualité des données a été vérifiée par un examen attentif des procédures d'analyse et par l'application de la fonction de Horwitz. En conséquence, nous attribuons un nouveau et plus fiable ensemble de valeurs de référence et des incertitudes respectives pour les éléments majeurs, mineurs et un grand groupe d'oligo-éléments des dix-neuf matériaux de référence de roche étudiés.

Mots-clés : matériel de référence, valeur de référence, ISO, protocole de certification, matériaux de référence de roche.

Reference materials (RMs), and certified RMs (CRM) in particular, are essential in any measurement. They find use for instrument calibration, to establish metrological traceability, to assess trueness during method validation, to assign values to other materials and in quality control (ISO Guide 33 2015). The main difference between RMs and CRMs resides in the reference values of the latter, which must have been derived by valid metrological procedures, and be accompanied by the respective uncertainties and a

statement of metrological traceability. Also, information of the degree of homogeneity, stability and minimum mass should be provided for a CRM. ISO Guide 34 (2009) outlines the scheme of the work needed to produce RMs, while ISO Guide 35 (2006) provides guidance on principles for their certification.

Several thousands of RMs have already been produced for geochemical and environmental applications;

most of them originate from raw materials that match the matrix (e.g., type of rock, mineral or environmental material) and approximate the chemical composition of unknown samples (see the detailed review by Jochum and Enzweiler 2014). The GeoReM database (Jochum *et al.* 2005; <http://georem.mpch-mainz.gwdg.de>) currently contains analytical data for 3100 RMs. It also has a list of the most accessed RMs. Although these samples are considered as being some of the most valuable RMs available for geochemical research, their reference values have – with some exceptions – not been established by the state-of-the-art metrological procedures of the International Organization for Standardization (ISO). Their reference values were obtained by the best practices available at the time and by compilation of the literature data (Govindaraju 1980, 1994, Gladney and Roelandts 1988a, b, Gladney *et al.* 1990, 1991, 1992, Itoh *et al.* 1993, Govindaraju *et al.* 1994, Terashima *et al.* 1994, Imai *et al.* 1995). This also applies to the so-called GeoReM preferred values of the GeoReM database, which were determined for the most frequently requested RMs. An exception is the basalt NIST SRM 688 (NIST 1981), but this CRM has only a small set of certified reference values.

In an effort to align the production of new geochemical RMs to international metrological practices, Kane *et al.* (2003) developed a protocol that encompasses all steps required by ISO guidelines. Some rock CRMs were already produced following these recommendations, such as slate OU-6 (Kane 2004), serpentinite MGL-GAS, alkaline granite MGL-OShBO, komatiite OKUM, harzburgite MUH-1, all certified by the IAG, and basalt BRP-1 (Cotta and Enzweiler 2008); however, these RMs do not belong to the top thirty accessed rock RMs of the GeoReM database.

Our aim was to establish new ‘quasi-certified’ reference values and their uncertainties at the 95% confidence level following ISO guidelines and the procedures that are summarised in the IAG Certification Protocol (Kane *et al.* 2003, 2007). Our procedures are performed in a way similar to that used for the determination of reference values of the NIST reference glasses (Jochum *et al.* 2011).

We did not organise a characterisation study, as proposed by ISO Guide 34 (2009), but used data sets that include technically valid approaches to assign the values. These comprise primary methods and two or more independent methods of demonstrable accuracy performed by competent laboratories. The used data currently constitute the most reliable available for the most important geochemical rock RMs. The resultant new reference values can be

used as quasi-certified ones and are therefore valuable for the future geochemical research.

Samples

The GeoReM database lists the most popular rock RMs that are used in many laboratories world-wide (Table 1). This list has been derived from the number of requested RMs in the database since 2006. Rock RMs are generally used for bulk analytical purposes in various instrumental techniques and calibration strategies. These include isotope dilution (ID) by thermal ionisation mass spectrometry (TIMS) or inductively coupled plasma-mass spectrometry (ICP-MS), matrix or standard solution ICP-MS and inductively coupled plasma-atomic emission spectrometry (ICP-AES), matrix-matched or synthetic standard X-ray fluorescence spectrometry (XRF), instrumental neutron activation analysis (INAA) and other methods. In a few applications, powdered RMs were fused into glasses making them measurable by microanalytical methods, such as laser ablation-(LA) ICP-MS or electron probe microanalysis (EPMA).

To obtain sufficient material, the powdered rock RMs are produced mostly from large amounts (> 100 kg) of raw materials, crushed and pulverised usually to a particle size of < 74 µm. The crucial next step consists of the homogenisation of the whole batch and its division into the final units, used for characterisation of the RM and also for distribution to final users. Sample preparation was conducted by internationally highly respected institutions, such as the United States Geological Survey (USGS), Geological Survey of Japan (GSJ) and others (Table 1). The USGS RMs W-1, G-1, BCR-1, BHVO-1, AGV-1 and BIR-1 are among the most valuable samples available, because they played an important role in the improvement of geochemical analysis since 1951 (Fairbairn *et al.* 1951). Because rock powders of these original RMs are no longer available, the USGS has prepared large amounts of new batches of those RMs, for example, W-2, G-2, BCR-2, BHVO-2, AGV-2, sampled at the same sites as the original RMs. In the last 10–20 years, these second-generation RMs have achieved the same or even higher (e.g., W-2, G-2) importance in geochemical analysis as the original ones. While the USGS no longer distributes samples of AGV-1, BCR-1, BHVO-1, BIR-1, G-2, DTS-1, RGM-1, W-1 and W-2, many laboratories still utilise these RMs, and therefore, the reference values provided here may be very valuable.

Other important rock RMs are those from the GSJ, for example, JB-1, JB-2; JB-3, JB-1a, JA-1, JA-2, JP-1, which have

Table 1.

Rock RMs investigated in this study from the USGS (crustal.usgs.gov/geochemical_reference_standards/), GSJ (seishin-syoji.co.jp/en/products/standard/index.html) and GIT-IWG (helium.crpq.cnrs-nancy.fr/SARM/pages/geostandards.html/#)

Rock RM	Provider	Rock type	Source	Number of data	Percentage of outliers
AGV-1	USGS	andesite	Guano Valley, Lake County, Oregon, USA	2845	3.7
AGV-2	USGS	andesite	Guano Valley, Lake County, Oregon, USA	1948	1.0
BCR-1	USGS	basalt	Columbia River Group basalt, Bridal Veil Flow Quarry, Washington, USA	2103	5.9
BCR-2	USGS	basalt	Columbia River Group basalt, Bridal Veil Flow Quarry, Washington, USA	3590	2.6
BHVO-1	USGS	basalt	Kilauea caldera, Kilauea volcano, Hawaii, USA	5052	3.3
BHVO-2	USGS	basalt	Kilauea caldera, Kilauea volcano, Hawaii, USA	5249	2.9
BIR-1	USGS	basalt	12 km east of Reykjavik, Iceland	4075	4.6
DTS-1	USGS	dunite	Twin Sister area, Hamilton (Washington), USA	573	11
G-2	USGS	granite	Westerly granite, from Sullivan quarry, Bradford, Rhode Island, USA	1348	5.1
RGM-1	USGS	rhyolite	Glass Mountain, Siskiyou County, California, USA	1287	1.6
W-2	USGS	diabase	Bull Run Quarry, Fairfax county, Virginia, USA	2014	3.2
JA-1	GSJ	andesite	Hakone volcano, Manazuru-machi, Kanagawa prefecture, Japan	743	6.9
JA-2	GSJ	andesite	Goshikidai sanukitoid, Sakaide, Kanagawa prefecture, Japan	1111	2.8
JB-1	GSJ	basalt	Kitamatsuura basalt, Sasebo, Nagasaki prefecture, Japan	582	2.6
JB-1a	GSJ	basalt	Kitamatsuura basalt, Sasebo, Nagasaki prefecture, Japan	1119	4.5
JB-2	GSJ	basalt	Oshima volcano, Oshima, Tokyo, Japan	2074	7.6
BE-N	GIT-IWG	basalt	old volcano near Nancy, France	1275	4.2
PM-S	GIT-IWG	microgabbro	Insch Gabbro outcrop, near Pitcaple, Scotland	400	3.5
WS-E	GIT-IWG	dolerite	Great Whin Sill, Crag Hill quarry, Northumberland, England	569	2.5

mainly been used in Japanese laboratories and/or by Japanese geochemists. Rock RMs from other providers are listed in Table 1.

Because powdered rock RMs contain particles of different minerals, a test of sufficient homogeneity between units (Fear and Thompson 2001), performed before characterisation, is required as evidence that the RM is fit for its purpose. The homogeneity tests of the investigated RMs (e.g., Flanagan 1986, Fear and Thompson 2001) were performed by their original producers or by contracted third parties (see review by Jochum and Enzweiler 2014). ISO Guide 34 (2009) and ISO Guide 35 (2006) give guidance on how to assess and implement the homogeneity testing of RMs, respectively. The minimum test portion mass, where a RM is homogeneous with respect to an element, depends on the rock type and the constituent of interest. Whereas, for lithophile elements in fine-grained RMs, such as basalts, the minimum test portion mass is about 50–100 mg, it is larger for coarse-grained materials, such as granite or peridotite powders, and for siderophile and chalcophile elements (> 300 mg). Because of the nugget effect, the phenomenon that trace minerals are the main bearing phases of certain trace elements, the test portion for an analysis can exceed several grams for noble metals (Meisel *et al.* 2001). Further grinding, before characterisation, of small batches to obtain very fine powders is an alternative to overcome grain size heterogeneities (Wang *et al.* 2004). Contaminations from

materials used for crushing or powdering, for example, steel mortars, can also introduce extra inhomogeneities; typical examples are Pb in BCR-1 and BHVO-1 and Mo in BCR-2 (e.g., Weis *et al.* 2006, Jochum and Nohl 2008).

A further requirement for RMs is a stability assessment and monitoring. This is usually not an important issue for most geological rock RMs, including those investigated here, because their property values do not change measurably during their shelf life of several tens of years provided that proper storage and handling conditions are met.

Determination of reference and information values

To determine reference values, we adopted ISO Guide 35 (2006): *Reference materials – General and statistical principles for certification* and the protocol of the IAG (Kane *et al.* 2003, 2007), which promotes best practice in the certification of geochemical RMs.

Certifying body

ISO Guide 34 (2009) states that the producer is responsible for the certification of reference materials using metrologically valid procedures (ISO Guide 35 2006). However, the USGS, which provides most of the RMs listed in Table 1, has historically not used an ISO-approved certification protocol.

We used the IAG-recommended strategy for recertifying to obtain reference values (Kane *et al.* 2009).

Analytical data

For the certification programme of a metrological institution, guidelines of a collaborative study have to be developed to measure the mass fraction of the elements and to demonstrate their metrological traceability (ISO Guide 35 2006). In our study, we used all analytical data from the GeoReM database mainly published between 1995 and 2015 in analytical, geochemical and geological journals. These data were obtained using the state-of-the-art techniques and newly developed analytical procedures. We are confident that we have access to a nearly a complete data set for the last 20 years.

Analytical results for elements in the different RMs are listed in Tables 3 and 4. Appendix Table S1 (online supporting information) lists all published analyses together with the references (GeoReM numbers). We also compared the data with earlier compilations (Govindaraju 1980, 1994, Gladney and Roelandts 1988a, b, Gladney *et al.* 1990, 1991, 1992, Itoh *et al.* 1993, Govindaraju *et al.* 1994, Terashima *et al.* 1994, Imai *et al.* 1995). For different reasons, such as the use of obsolete or outdated analytical techniques or changes in scientific interest, for some elements there are only few data (e.g., As, Cl). In such cases, we adopted the previous compilation values. This does not imply that some 'old' techniques provide less accurate data than modern techniques. However, most of them are more time-consuming and less user-friendly. The definitive and highly precise gravimetric and isotope dilution methods, for example, belong to this category.

A minimum number of competent laboratories are required for a certification programme (ISO Guide 35 2006). For well-established methods of measurement, as for instance primary methods, this number can be as small as two or three. Results from six to eight laboratories are required in situations of less, but still adequate, statistical and metrological control. In situations where statistically as well as technically invalid results can occur, a minimum number of laboratories of at least 10 and preferably 15 is recommended.

Another variable is the number of different methods of characterisation. If primary methods are not available, when possible three methods should have been used by six competent laboratories (ISO Guide 35 2006).

The IAG protocol (Kane *et al.* 2003, 2007) requires experienced laboratories, selected on the basis of their

performance in the Proficiency Test GeoPT regularly run by the IAG. For the present study, we were not able to judge the competence of all laboratories as it is carried out by the IAG. However, the IAG protocol also allows qualification to be based on published geochemical research reports that focus on detailed method validation or the quantification of uncertainty (Kane *et al.* 2007). This means that laboratories that regularly publish reference material data in peer-reviewed analytical and geochemical international journals are also competent to take part in a characterisation procedure.

Similar to the procedures carried out for the characterisation of the NIST reference glasses (Jochum *et al.* 2011), data quality was checked in several ways: analytical techniques used and calibration procedures were verified, and the Horwitz function (Horwitz and Albert 1995; Equation (1)) was used to identify 'outliers'.

$$H_a = \kappa * X_a^{0.8495} \quad (1)$$

In Equation (1) 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) and the factor $\kappa = 0.01$ or 0.02 refers to pure and applied geochemical laboratories, respectively. We used a factor κ of 0.02 because of the large number of laboratories involved in different research fields. X_a is the mean of the results if the data are roughly symmetrically distributed (applicable for this study) or the median value if the results are clearly skewed.

For each mass fraction X , z-scores were determined using Equation (2):

$$z = (X - X_a) / H_a \quad (2)$$

Z-score results in the range $-2 < z < 2$ are considered to be satisfactory (Kane *et al.* 2003). If the z-score is outside this range, we examined the procedures of the laboratory in question to ensure that the analytical value was not subject to unsuspected analytical bias (Figure 1).

As already mentioned, we grouped the analytical data according to the technique used into four categories (Table 2):

Data in category 1 include ID analyses using TIMS, MC-ICP-MS and ICP-MS. ID-MS can be considered a primary ratio method of an unknown to a standard of the same quantity and is described by a measurement equation (CCQM 1988). Primary methods have the highest metrological properties, whose operation can be completely described and understood and for which a complete uncertainty statement can be written down in terms of SI units (CCQM 1988).

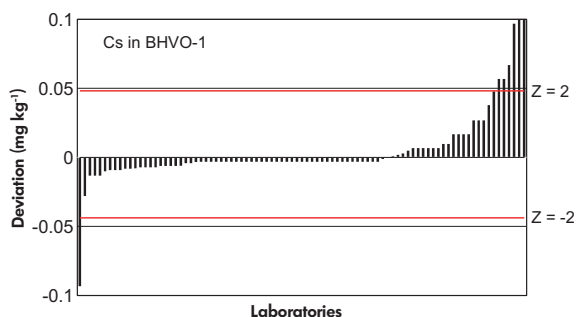


Figure 1. Data distribution chart for Cs in BHVO-1. Horizontal lines show the limits of the z-score results for $-2 < z < 2$ (Horwitz and Albert 1995). Only z-score results in this range are considered to be satisfactory. Outliers are due to obvious typographic errors or analytical problems rather than to sample inhomogeneity (see Table S1 for details).

Data in category 2 have a high level of confidence. They were obtained by solution methods (e.g., ICP-MS, ICP-AES, AAS), and either certified standard solutions or matrix-matched (C)RMs were used for calibration.

Data in category 3 also have a high level of confidence. Results were obtained using a variety of analytical techniques (e.g., XRF, INAA, SSMS) with calibration performed using mostly non-certified RMs.

Data in category 4 were obtained from microanalytical methods (e.g., LA-ICP-MS, SIMS, EPMA). Glass beads or pressed powder pellets were analysed, which had been produced from the powdered rock RMs. Because of possible inhomogeneities using small test portions and matrix effects, they have the lowest degree of confidence, although new techniques and calibration procedures have improved the reliability of trace element data considerably (e.g., Hervig *et al.* 2006, Jochum *et al.* 2014).

To test whether systematic differences exist between the analytical techniques used in the different categories, we determined the mean values of analytical data together with their standard deviations (*s*) for each category (Table S2). The tables show that within uncertainty limits, nearly all mean values agree.

Reference and information values

The reference and information values we obtained follow as closely as possible the ISO guidelines and the IAG protocol. Reference values are comparable to certified

Table 2. Categories of analytical techniques

Categories			
1	2	3	4
Primary	Standard solution-based	Reference material-based	Microanalytical
ID-TIMS	MC-ICP-MS	INAA	EPMA
ID-ICP-MS	ICP-MS	PNAA	LA-ICP-MS
ID-MC-ICP-MS	ICP-AES	PGAA	LIMS
GRAV	DCP-AES	GAMMA	PIXE
	PHOTOM	SSMS	LIBS
	AAS	MIC-SSMS	SEM
	GFAAS	XRF	SIMS
	IC	IPAA	
	HPLC	MS	
	TIT	CEA	
	FIA	MANOM	
	CZE	ISE	
	SPEC		

ID, isotope dilution; TIMS, thermal ionisation mass spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry; MC-ICP-MS, multiple collector ICP-MS; GRAV, gravimetry; ICP-AES, inductively coupled plasma-atomic emission spectrometry; DCP-AES, direct current-atomic emission spectrometry; IC, ion chromatography; PHOTOM, photometry; AAS, atomic absorption spectrometry; GFAAS, graphite furnace AAS; HPLC, high-pressure liquid chromatography; TIT, titrimetry; FIA, flow injection analysis; CZE, capillary zone electrophoresis; SPEC, spectroscopy (general); INAA, instrumental neutron activation analysis; PNAA, preconcentration neutron activation analysis; PGAA, prompt gamma ray activation analysis; GAMMA, gamma ray counting; SSMS, spark source mass spectrometry; MIC-SSMS, multiple ion counting SSMS; XRF, X-ray fluorescence; MS, mass spectrometry (general); CEA, combustion elemental analyser; MANOM, manometry; ISE, ion-selective electrode; EPMA, electron probe microanalysis; LA-ICP-MS, laser ablation ICP-MS; LIMS, laser plasma ionisation mass spectrometry; PIXE, proton-induced X-ray emission; LIBS, laser-induced breakdown spectroscopy; SEM, scanning electron microscopy; SIMS, secondary ion mass spectrometry.

values obtained in a recertification programme (Kane *et al.* 2003, 2007). Information values that do not comply with the ISO guidelines contain different levels of reliability and are provided for information purposes only. All reference values are averages of the single mean of analytical results of the different laboratories (Table S1), according to the following criteria:

- 1 For the determination of the mean values, unweighted means were calculated, because weighting procedures cannot be applied successfully to data from many laboratories (Kane *et al.* 2003).
- 2 Some data were not used for these calculations, because they were inappropriately calibrated (e.g., semi-quantitative analyses), have low precision or are due to obvious typing errors (marked by ^{††††}, Table S1), or did not fulfil the Horwitz requirement (marked by ^{†††},

Table S1). The number of these ‘outliers’, however, is small and ranges between 1 and 11% of the element data set (Table 1).

- 3 As mentioned above, 2–3 analytical data from the primary methods of measurement are sufficient to obtain a certified reference value in a metrologically valid procedure (ISO Guide 35 2006). In this study of rock powders, only ID-MS data belong to category 1 (Table 2) of primary methods. Because of our use of literature values, where in some cases we are not able to judge the competence of the laboratory, we generally used at least 5 ID data from different laboratories to derive a ‘quasi-certified’ reference value.
- 4 In cases, where less than five ID data exist, we calculated the unweighted mean of all data in categories 1–3 (Table 2). Data in category 4 (microanalytical methods) were generally not considered. We report reference values when they are derived from at least seven laboratories. The number of methods should be ideally at least two (when available). When only one method (this is the case only for ICP-MS and XRF, respectively, in this work) was used, the reference value is annotated ‘stated on one method (ICP-MS or XRF, respectively) only’.
- 5 If the number of analyses is less than 7 or the analyses are derived from only one technique or only from category 4, the mean values were assigned as information values.

Overall analytical uncertainties

The overall analytical uncertainty U at the 95% confidence level (CL) of the reference values and of most information values (Tables 3 and 4) was calculated using the IAG protocol (Kane *et al.* 2003) by

$$U = t * u \quad (3)$$

where t is the coverage factor. Student’s t -distribution was used to assign t , which is about 2 for N (the number of laboratories’ mean data) > 30 and much larger at small values of N . The uncertainty ‘ u ’ is mainly based on three components of variance which were combined in quadrature:

$$u^2 = \text{VAR}(Y_{\text{mean}}/\sqrt{N} + \text{VAR}_{\text{inhom}} + \text{VAR}_{\text{bias}}) \quad (4)$$

where the first component is the standard deviation of the mean of N laboratories’ mean data. The second and the third components account for inhomogeneities in the RMs and the between-laboratory biases. As demonstrated in many reports from the providers and publications in

international journals (see also the review by Jochum and Enzweiler 2014), the RMs listed in Table 1 are homogeneous within uncertainty limits of several per cent at test portion masses of about 0.1–1 g with respect to most, mainly lithophile, elements; this means that $\text{VAR}_{\text{inhom}} = 0$ for these elements. Exceptions are some elements that may be heterogeneously distributed because of material variability. This applies mainly to siderophile and chalcophile elements, such as noble metals, Se, elements introduced by contamination, for example, Mo in BCR-2, or elements that are present in hardly soluble minerals, such as Zr and Hf in zircon. However, because of the high number of analytical data, this heterogeneity component is already incorporated in the first component. Biases between the different analytical techniques were not observed in the data sets (Table S2).

Metrological traceability

Metrologically traceable results are the basis for comparisons in time and space. There are few recognised ways to assign metrological traceability (ISO Guide 35 2006) to measurement results. The first (category 1) is to make them traceable directly to the SI. In geochemical analysis, this can be achieved using primary methods, such as gravimetry and ID-MS (De Bièvre and Peiser 1997). Another approach (category 2) is through calibration against appropriate measurement standards such as synthetic or matrix CRMs. Part of the data used to calculate the reference values and the uncertainties of some constituents fall within category 2, but most of them do not. This is due to the fact that the geochemical community still lacks CRMs, with respect to both number of materials and matrix types represented. While we cannot improve this situation, we characterised nineteen frequently requested RMs by determining new reference values and uncertainties derived by agreement among independent measurement results.

Results and discussion

Tables 3 and 4 list the reference and information values for nineteen international rock RMs. Also provided are the overall analytical uncertainties at 95% confidence level U and the number n of values contributing to the reference value. In some cases, where no or only few data from publications between 1995 and 2015 exist, we used compilation values (Govindaraju 1980, 1994, Gladney and Roelandts 1988a, b, Gladney *et al.* 1990, 1991, 1992, Itoh *et al.* 1993, Govindaraju *et al.* 1994, Terashima *et al.* 1994, Imai *et al.* 1995) for information.

Table 3.
Reference values in bold (RV)[§], information values in plain (IV)[§] and uncertainties at 95% CL (U) of rock RMs

Analyte	Unit	AGV-1			AGV-2			BCR-1			BCR-2		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Al ₂ O ₃	g/100 g	17.11	0.13	22	17.03	0.12	3	13.56	0.08	18	13.48	0.12	20
CaO	g/100 g	4.890	0.052	23	5.15	0.10	5	6.980	0.086	17	7.114	0.075	22
Fe ₂ O ₃ (t)	g/100 g	6.755	0.079	20	6.78	0.17	4	13.43	0.15	19	13.77	0.19	20
K ₂ O	g/100 g	2.935	0.037	21	2.898	0.033	5	1.731	0.016	13	1.774	0.019	20
MgO	g/100 g	1.508	0.021	20	1.80	0.15	3	3.474	0.041	14	3.599	0.044	20
MnO	g/100 g	0.0966	0.0018	23	0.1004	0.0026	11	0.1838	0.0028	22	0.1966	0.0030	21
Na ₂ O	g/100 g	4.251	0.050	23	4.204	0.080	6	3.327	0.053	16	3.120	0.042	20
P ₂ O ₅	g/100 g	0.4927	0.0085	19	0.483	0.043	6	0.3646	0.0062	12	0.3593	0.0095	17
SiO ₂	g/100 g	59.38	0.41	16	59.14	0.58	5	54.53	0.48	14	54.00	0.20	19
TiO ₂	g/100 g	1.050	0.014	30	1.051	0.023	13	2.242	0.035	20	2.265	0.024	30

Analyte	Unit	BHVO-1			BHVO-2			BIR-1			DTS-1		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Al ₂ O ₃	g/100 g	13.69	0.05	46	13.44	0.06	24	15.51	0.07	31	0.196	0.026	4
CaO	g/100 g	11.43	0.04	48	11.40	0.06	28	13.29	0.06	38	0.17 ^a		74
Fe ₂ O ₃ (t)	g/100 g	12.32	0.04	42	12.39	0.09	25	11.40	0.05	36	8.68	0.24	8
K ₂ O	g/100 g	0.5256	0.0046	52	0.5130	0.0037	25	0.0290	0.0030	25	0.002		2
MgO	g/100 g	7.213	0.032	45	7.257	0.042	26	9.689	0.052	35	49.5 ^a		77
MnO	g/100 g	0.1689	0.0011	52	0.1690	0.0019	35	0.1731	0.0016	41	0.1163	0.010	3
Na ₂ O	g/100 g	2.313	0.022	45	2.219	0.048	27	1.832	0.022	35	0.0058	0.0016	4
P ₂ O ₅	g/100 g	0.2773	0.0024	42	0.2685	0.0050	27	0.0300	0.0043	23	0.0013		1
SiO ₂	g/100 g	49.79	0.12	43	49.60	0.14	27	47.79	0.16	33	40.4 ^a		88
TiO ₂	g/100 g	2.742	0.012	60	2.731	0.018	50	0.9587	0.0066	50	0.0037	0.0015	5

Analyte	Unit	G-2			RGM-1			W-2		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Al ₂ O ₃	g/100 g	15.31	0.17	9	13.83	0.20	9	15.38	0.09	15
CaO	g/100 g	1.910	0.037	12	1.178	0.023	10	10.91	0.03	20
Fe ₂ O ₃ (t)	g/100 g	2.644	0.048	10	1.871	0.030	11	10.80	0.05	17
K ₂ O	g/100 g	4.500	0.061	9	4.293	0.065	10	0.6242	0.0076	16
MgO	g/100 g	0.754	0.029	9	0.284	0.036	9	6.431	0.045	15
MnO	g/100 g	0.0306	0.0008	7	0.0387	0.0021	6	0.1658	0.0025	24
Na ₂ O	g/100 g	4.045	0.059	9	4.086	0.060	11	2.196	0.028	16
P ₂ O ₅	g/100 g	0.129	0.022	7	0.0491	0.0016	5	0.1362	0.0059	12
SiO ₂	g/100 g	68.74	0.47	9	73.12	0.45	9	52.57	0.32	15
TiO ₂	g/100 g	0.4799	0.0089	13	0.2654	0.0065	10	1.064	0.010	29

Analyte	Unit	JA-1			JA-2			JB-1			JB-1α		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Al ₂ O ₃	g/100 g	15.19	0.23	7	15.51	0.11	18	14.53	0.14	9	14.51	0.10	16
CaO	g/100 g	5.72	0.11	8	6.259	0.056	20	9.33	0.16	9	9.314	0.073	18
Fe ₂ O ₃ (t)	g/100 g	7.05	0.14	7	6.289	0.042	18	8.99	0.13	8	8.996	0.063	16
K ₂ O	g/100 g	0.779	0.015	8	1.779	0.015	21	1.420	0.027	10	1.407	0.015	17
MgO	g/100 g	1.540	0.063	7	7.841	0.091	15	7.807	0.088	8	7.810	0.078	16
MnO	g/100 g	0.1543	0.0043	8	0.1092	0.0021	18	0.1494	0.0058	9	0.1419	0.0073	15
Na ₂ O	g/100 g	3.91	0.14	7	3.072	0.047	15	2.749	0.066	9	2.738	0.042	16
P ₂ O ₅	g/100 g	0.1595	0.0058	9	0.1519	0.0031	16	0.2627	0.0078	10	0.2610	0.0050	13
SiO ₂	g/100 g	64.43	0.31	6	56.39	0.23	17	52.46	0.53	8	52.56	0.27	15
TiO ₂	g/100 g	0.850	0.018	12	0.6695	0.0070	23	1.299	0.021	10	1.290	0.012	18

Analyte	Unit	JB-2			BE-N			PM-S			WS-E		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Al ₂ O ₃	g/100 g	14.62	0.10	26	9.982	0.088	15	17.16	0.31	5	13.77*	0.14	8
CaO	g/100 g	9.852	0.082	27	13.99	0.11	15	12.60	0.32	7	8.996	0.080	9
Fe ₂ O ₃ (t)	g/100 g	14.28	0.12	26	12.70	0.12	17	10.12	0.08	7	13.09	0.12	9
K ₂ O	g/100 g	0.4224	0.0059	23	1.422	0.020	14	0.137	0.018	5	0.9961	0.0090	8

Table 3 (continued).

Reference values in bold (RV)[§], information values in plain (IV)[§] and uncertainties at 95% CL (*U*) of rock RMs

Analyte	Unit	JB-2			BE-N			PM-S			WS-E		
		RV, IV	<i>U</i>	<i>n</i>	RV, IV	<i>U</i>	<i>n</i>	RV, IV	<i>U</i>	<i>n</i>	RV, IV	<i>U</i>	<i>n</i>
MgO	g/100 g	4.43	0.35	23	13.06	0.15	13	9.39	0.16	5	5.630*	0.059	8
MnO	g/100 g	0.2130	0.0028	27	0.2002	0.0021	15	0.158	0.003	5	0.1701	0.0016	10
Na ₂ O	g/100 g	2.054	0.030	21	3.218	0.030	15	2.06	0.07	6	2.481	0.051	8
P ₂ O ₅	g/100 g	0.0969	0.0023	21	1.042	0.024	11	0.038	0.015	4	0.3042	0.0071	8
SiO ₂	g/100 g	53.14	0.18	23	38.22	0.28	14	47.24	0.35	5	51.07*	0.20	8
TiO ₂	g/100 g	1.167	0.009	31	2.612	0.029	19	1.10	0.02	5	2.428	0.034	11

* RV stated from one method (XRF) only. [§]Definition see page 5 ff.

n, number of values after outlier rejection contributing to the RV and IV, respectively.

[°] Gladney *et al.* (1991).

Table 4.

Reference values in bold (RV)[§], information values in plain (IV)[§] and uncertainties at 95% CL (*U*) of rock reference materials

Analyte	Unit	AGV-1			AGV-2			BCR-1			BCR-2		
		RV, IV	<i>U</i>	<i>n</i>	RV, IV	<i>U</i>	<i>n</i>	RV, IV	<i>U</i>	<i>n</i>	RV, IV	<i>U</i>	<i>n</i>
Ag	µg kg ⁻¹	78 [°]		23	90		1	27 ^b		55	90		2
As	mg kg ⁻¹	0.954	0.070	8	0.67	0.13	6	0.6 ^b		25	0.86	0.22	5
Au	µg kg ⁻¹	0.6 [°]		8				0.6 ^b		61	1.3		1
B	mg kg ⁻¹	8.1		2	6.45	0.52	3	5.1		2	4.4		2
Ba	mg kg ⁻¹	1218	7.2	66	1134	8	43	683.3	11.3	43	683.9	4.7	79
Be	mg kg ⁻¹	2.30*	0.19	13	2.209*	0.066	18	1.70	0.20	5	2.17*	0.10	25
Bi	mg kg ⁻¹	0.045	0.012	4	0.0520*	0.0079	9	0.047 ^b		40	0.050*	0.015	8
Br	mg kg ⁻¹	0.29	0.21	3	0.13		1	0.072 ^b		27	0.17		1
Cd	mg kg ⁻¹	0.075	0.022	6	0.184*	0.069	11	0.139	0.011	4	0.69*	0.29	9
Ce	mg kg ⁻¹	68.61	0.54	87	69.43	0.57	47	53.94	0.34	8(ID)	53.12	0.33	89
Cl	mg kg ⁻¹	133	82	3	68		2	59 ^b		26	96	16	3
Co	mg kg ⁻¹	15.14	0.32	41	15.46	0.50	36	37.55	0.64	27	37.33	0.37	60
Cr	mg kg ⁻¹	9.474	0.33	41	16.22	0.72	34	13.5	1.3	35	15.85	0.38	58
Cs	mg kg ⁻¹	1.252	0.022	51	1.173	0.018	36	0.964	0.021	26	1.160	0.023	62
Cu	mg kg ⁻¹	58.42	0.63	41	51.51	0.65	33	19.6	1.7	22	19.66	0.72	58
Dy	mg kg ⁻¹	3.583	0.040	68	3.549	0.031	47	6.391	0.075	8(ID)	6.424	0.055	78
Er	mg kg ⁻¹	1.825	0.019	68	1.825	0.013	47	3.658	0.056	8(ID)	3.670	0.038	78
Eu	mg kg ⁻¹	1.658	0.035	75	1.553	0.015	47	1.957	0.018	8(ID)	1.989	0.024	79
F	mg kg ⁻¹	425 [°]		35	400		2	490 ^b		40	470	40	2
Ga	mg kg ⁻¹	20.36	0.27	32	20.42	0.17	36	22.19	0.42	15	22.07	0.19	47
Gd	mg kg ⁻¹	4.862	0.069	70	4.678	0.064	47	6.725	0.054	9(ID)	6.811	0.078	78
Ge	mg kg ⁻¹	1.126	0.082	7	1.202	0.083	6	1.4		2	1.46	0.26	6
Hf	mg kg ⁻¹	5.086	0.042	62	5.137	0.057	45	4.923	0.060	41	4.972	0.034	7(ID)
Hg	mg kg ⁻¹	0.02 [°]		27				0.0079 ^b		28	0.0012		1
Ho	mg kg ⁻¹	0.680	0.010	72	0.6818	0.0081	45	1.268	0.016	49	1.313	0.011	78
I	mg kg ⁻¹	0.270 [°]		5	0.007		1	0.18		2	0.017		1
In	mg kg ⁻¹	0.042	0.007	4	0.0478	0.0059	3	0.092 ^b		43	0.7		3
Ir	µg kg ⁻¹	0.2 [°]		6				0.004 ^b		21	0.018		2
La	mg kg ⁻¹	38.19	0.27	81	38.21	0.38	48	25.46	0.65	6(ID)	25.08	0.16	79
Li	mg kg ⁻¹	10.72	0.210	26	10.80*	0.21	22	12.98	0.46	12	9.13	0.22	36
Lu	mg kg ⁻¹	0.2518	0.0042	77	0.2507	0.0033	49	0.4988	0.0048	8(ID)	0.5049	0.0078	7(ID)
Mo	mg kg ⁻¹	2.103	0.079	10	2.00*	0.11	13	1.517	0.053	10	250.6	6.7	21
Nb	mg kg ⁻¹	14.53	0.23	66	14.12	0.22	42	12.74	0.23	39	12.44	0.20	74
Nd	mg kg ⁻¹	32.07	0.31	81	30.49	0.47	7(ID)	28.68	0.10	32(ID)	28.26	0.37	23(ID)
Ni	mg kg ⁻¹	15.41	0.28	44	18.87*	0.41	36	11.68	0.84	27	12.57	0.30	59
Os	µg kg ⁻¹				0.0042		1	0.009 ^b		3	0.025	0.011	3
Pb	mg kg ⁻¹	36.35	0.44	53	13.14	0.15	42	13.44	0.23	5(ID)	10.59	0.17	74
Pd	µg kg ⁻¹	2.2 [°]		3							0.36		2
Pr	mg kg ⁻¹	8.31	0.11	69	8.165	0.084	47	6.765	0.066	50	6.827	0.044	79
Pt	µg kg ⁻¹	1.1 [°]		2				2 ^b		2	1.2		2
Rb	mg kg ⁻¹	67.80	0.64	67	67.79	0.66	43	46.61	0.62	10(ID)	46.02	0.56	11(ID)

Table 4 (continued).

 Reference values in bold (RV)^S, information values in plain (IV)^S and uncertainties at 95% CL (U) of rock reference materials

Analyte	Unit	AGV-1			AGV-2			BCR-1			BCR-2		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Re	µg kg ⁻¹	0.38 ^a		3	0.29		1	0.84 ^b		30	12.6	2.0	4
Rh	µg kg ⁻¹							0.23 ^b		2	0.2		1
Ru	µg kg ⁻¹							1.0 ^b		2	0.033		1
S	mg kg ⁻¹	26 ^a		9	24		3	410 ^b		22	318	94	6
Sb	mg kg ⁻¹	4.24	0.19	12	0.458*	0.061	14	0.632	0.050	9	0.302*	0.029	14
Sc	mg kg ⁻¹	12.43	0.22	41	13.11	0.31	39	32.41	0.55	34	33.53	0.40	68
Se	mg kg ⁻¹	0.006		1				0.088 ^b		53	0.082		1
Sm	mg kg ⁻¹	5.764	0.060	79	5.509	0.078	6(ID)	6.603	0.022	31(ID)	6.547	0.047	20(ID)
Sn	mg kg ⁻¹	4.88	0.45	10	1.83*	0.25	18	2.44	0.15	6	2.28	0.13	22
Sr	mg kg ⁻¹	661.0	3.7	72	659.5	5.7	44	334.9	3.5	9(ID)	337.4	6.7	13(ID)
Ta	mg kg ⁻¹	0.866	0.016	56	0.865	0.019	43	0.786	0.021	28	0.785	0.018	72
Tb	mg kg ⁻¹	0.673	0.011	74	0.6510	0.0073	45	1.063	0.013	49	1.077	0.026	77
Te	µg kg ⁻¹	2.2	2.5	3	2.9		1	4.9 ^b		24	4		2
Th	mg kg ⁻¹	6.351	0.059	64	6.174	0.063	47	5.79	0.11	6(ID)	5.828	0.050	15(ID)
Tl	mg kg ⁻¹	0.337*	0.031	10	0.275*	0.010	17	0.34	0.08	3	0.267*	0.018	19
Tm	mg kg ⁻¹	0.2737	0.0071	50	0.2623	0.0035	39	0.535	0.012	37	0.5341	0.0060	64
U	mg kg ⁻¹	1.903	0.020	62	1.885	0.015	46	1.678	0.019	8(ID)	1.683	0.017	16(ID)
V	mg kg ⁻¹	119.4	1.6	45	118.5*	1.2	35	404.4	5.2	39	417.6	4.5	60
W	mg kg ⁻¹	0.579	0.080	5	0.553*	0.094	10	0.43	0.12	4	0.465	0.050	13
Y	mg kg ⁻¹	19.69	0.31	69	19.14	0.84	45	36.91	0.55	49	36.07	0.37	73
Yb	mg kg ⁻¹	1.660	0.015	75	1.653	0.013	47	3.377	0.037	8(ID)	3.392	0.036	78
Zn	mg kg ⁻¹	86.8	1.2	43	86.7	1.2	34	128.5	2.9	25	129.5	1.8	60
Zr	mg kg ⁻¹	231.5	2.4	71	232.0	2.3	43	190.3	2.2	44	186.5	1.5	75

Analyte	Unit	BHVO-1			BHVO-2			BIR-1			DTS-1		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Ag	µg kg ⁻¹	71		3	89	37	5	41		2	13 ^d		18
As	mg kg ⁻¹	0.565	0.078	7	0.70*	0.11	9	0.17	0.14	6	0.05		2
Au	µg kg ⁻¹	2.2		2	2.6		1	2.5		1	0.92 ^d		22
B	mg kg ⁻¹	3.0	1.5	3	2.95	0.26	4	0.25		3	0.5 ^d		3
Ba	mg kg ⁻¹	134.4	2.5	5(ID)	130.9	1.0	125	6.75	0.13	94	0.342	0.063	10
Be	mg kg ⁻¹	0.984*	0.060	15	1.076*	0.046	33	0.102*	0.011	10	0.0022	0.0003	4
Bi	mg kg ⁻¹	0.0121*	0.0015	7	0.0148*	0.0043	12	0.0051	0.0014	4	0.0046	0.0010	5
Br	mg kg ⁻¹	0.2		1	0.3	0.1	2	0.065		1	0.110 ^d		3
Cd	mg kg ⁻¹	0.107	0.013	8	0.152	0.049	23	0.077	0.017	13	0.0082	0.0037	4
Ce	mg kg ⁻¹	38.08	0.22	141	37.53	0.19	134	1.920	0.023	113	0.0503	0.0023	14
Cl	mg kg ⁻¹	93		2	107	94	3	44		1	10.5 ^d		14
Co	mg kg ⁻¹	44.90	0.36	75	44.89	0.32	102	52.22	0.57	67	136.1	4.4	9
Cr	mg kg ⁻¹	287.6	3.9	92	287.2	3.1	93	392.9	3.9	72	4100	210	8
Cs	mg kg ⁻¹	0.1032	0.0026	77	0.0996*	0.0022	92	0.00646	0.00072	46	0.0060*	0.0008	7
Cu	mg kg ⁻¹	137.2	1.6	68	129.3	1.4	92	120.7	1.6	65	5.7	1.1	8
Dy	mg kg ⁻¹	5.272	0.034	129	5.280	0.028	130	2.544	0.028	108	0.0050	0.0006	14
Er	mg kg ⁻¹	2.501	0.021	126	2.511	0.014	128	1.680	0.015	106	0.0049	0.0003	14
Eu	mg kg ⁻¹	2.053	0.014	135	2.043	0.012	132	0.5201	0.0047	111	0.0011	0.0002	17
F	mg kg ⁻¹	385 ^c		11	396	43	3	55		1	13 ^d		9
Ga	mg kg ⁻¹	21.32	0.42	41	21.37	0.20	74	15.46	0.23	43	0.411	0.035	4
Gd	mg kg ⁻¹	6.285	0.146	5(ID)	6.207	0.038	130	1.809	0.021	109	0.0041	0.0002	13
Ge	mg kg ⁻¹	1.57	0.13	5	1.623	0.039	10	1.460	0.098	6	0.9		1
Hf	mg kg ⁻¹	4.44	0.11	8(ID)	4.470	0.025	6(ID)	0.5822	0.0088	5(ID)	0.0053	0.0010	12
Hg	mg kg ⁻¹	0.01		1	0.002		1	0.0073 ^e		1	0.007 ^d		22
Ho	mg kg ⁻¹	0.9839	0.0080	127	0.9887	0.0053	130	0.5718	0.0047	107	0.0014*	0.0002	13
I	mg kg ⁻¹				0.02		2	0.014		1	0.14		1
In	mg kg ⁻¹	0.0851	0.0081	6	0.117	0.045	7	0.0576	0.0028	5	0.0023	0.0005	4
Ir	µg kg ⁻¹	0.090	0.013	3	0.070	0.011	5(ID)	0.18	0.04	5	0.69 ^d		17
La	mg kg ⁻¹	15.44	0.10	140	15.20	0.08	132	0.627	0.012	113	0.0264	0.0033	15
Li	mg kg ⁻¹	4.68	0.090	32	4.500	0.085	66	3.203	0.069	31	1.99	0.16	5
Lu	mg kg ⁻¹	0.2775	0.0072	9(ID)	0.2754	0.0024	7(ID)	0.2484	0.0032	117	0.0021	0.0001	16
Mo	mg kg ⁻¹	1.061	0.059	20	4.07	0.16	31	0.068	0.021	12	0.057	0.019	5

Table 4 (continued).

Reference values in bold (RV)[§], information values in plain (IV)[§] and uncertainties at 95% CL (U) of rock reference materials

Analyte	Unit	BHVO-1			BHVO-2			BIR-1			DTS-1		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Nb	mg kg ⁻¹	18.53	0.23	135	18.10	0.20	121	0.553	0.014	107	0.0154	0.0037	13
Nd	mg kg ⁻¹	24.78	0.26	11(ID)	24.27	0.25	8(ID)	2.397	0.043	8(ID)	0.0232	0.0008	17
Ni	mg kg ⁻¹	120.0	1.5	86	119.8	1.2	105	168.9	1.9	77	2298	49	9
Os	µg kg ⁻¹	0.091	0.015	3	0.111	0.021	6(ID)	0.38		2	0.9 ^d		3
Pb	mg kg ⁻¹	2.037	0.067	5(ID)	1.653	0.038	100	3.037	0.049	76	8.5	1.6	13
Pd	µg kg ⁻¹	3.0	0.4	3	2.7	0.4	2	6.0	1.1	3	3 ^d		9
Pr	mg kg ⁻¹	5.419	0.038	124	5.339	0.028	126	0.3723	0.0047	102	0.0061	0.0003	14
Pt	µg kg ⁻¹	2.8	1.1	3	8.9	1.6	5(ID)	4.6	0.9	3	3.1 ^d		10
Rb	mg kg ⁻¹	9.52	0.10	127	9.261	0.096	119	0.2100	0.0081	68	0.066	0.010	10
Re	µg kg ⁻¹	0.40	0.38	3	0.543	0.029	6(ID)	0.65		2	9.5 ^d		2
Rh	µg kg ⁻¹	0.11		1	0.7		1	0.34		1	0.83 ^d		3
Ru	µg kg ⁻¹	0.24		3	0.125	0.018	5(ID)	0.37		3	2.5 ^d		1
S	mg kg ⁻¹	76	29	5	164	25	6	70		3	12 ^d		5
Sb	mg kg ⁻¹	0.155	0.012	14	0.1034*	0.0079	26	0.462	0.032	17	0.473	0.082	8
Sc	mg kg ⁻¹	31.42	0.35	77	31.83	0.34	96	43.21	0.59	71	3.35	0.25	10
Se	mg kg ⁻¹	0.090	0.018	2	0.18	0.04	3	0.019	0.012	3	0.0057 ^d		2
Sm	mg kg ⁻¹	6.165	0.079	12(ID)	6.023	0.057	9(ID)	1.113	0.018	8(ID)	0.0044	0.0004	16
Sn	mg kg ⁻¹	2.09	0.15	13	1.776*	0.059	34	0.701	0.067	14	0.60	0.28	5
Sr	mg kg ⁻¹	399.2	5.0	5(ID)	394.1	1.7	123	108.6	0.7	101	0.300	0.029	11
Ta	mg kg ⁻¹	1.174	0.018	116	1.154	0.019	114	0.0414	0.0020	76	0.0012	0.0003	10
Tb	mg kg ⁻¹	0.9455	0.0091	130	0.9392	0.0060	130	0.3623	0.0050	104	0.00071	0.00009	15
Te	µg kg ⁻¹	7.3	4.2	5	14	6	3	5.7	2.4	3	1.2		1
Th	mg kg ⁻¹	1.225	0.017	132	1.224	0.016	124	0.0328	0.0015	92	0.0098	0.0006	11
Tl	mg kg ⁻¹	0.0461	0.0039	22	0.0224	0.0015	28	0.0021*	0.0007	13	0.0024		4
Tm	mg kg ⁻¹	0.3289	0.0040	105	0.3349	0.0031	104	0.2558	0.0040	81	0.0010*	0.0001	12
U	mg kg ⁻¹	0.4182	0.0045	115	0.412	0.035	5(ID)	0.01051	0.00041	81	0.0032	0.0004	11
V	mg kg ⁻¹	313.8	3.2	68	318.2	2.3	101	320.6	2.9	68	10.0	1.5	7
W	mg kg ⁻¹	0.212	0.012	13	0.251	0.035	23	0.027	0.015	11	0.0092	0.0023	3
Y	mg kg ⁻¹	26.23	0.31	142	25.91	0.28	127	15.60	0.17	112	0.0363	0.0026	12
Yb	mg kg ⁻¹	1.987	0.015	132	1.994	0.027	132	1.631	0.015	112	0.0095	0.0004	16
Zn	mg kg ⁻¹	105.1	1.5	69	103.9	1.0	90	70.4	1.1	61	43.8	5.7	7
Zr	mg kg ⁻¹	174.6	1.3	147	171.2	1.3	121	14.80	0.22	111	0.153	0.025	11

Analyte	Unit	G-2			RGM-1			W-2		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Ag	µg kg ⁻¹	40 ^a		16	105		2	70		2
As	mg kg ⁻¹	0.258	0.056	3	3.04	0.11	8	1.07	0.16	7
Au	µg kg ⁻¹	1.03 ^a		10	0.33 ^c		2	1.2 ^e		1
B	mg kg ⁻¹	2.4 ^a		15	27.4	2.8	3	12.5	1.6	4
Ba	mg kg ⁻¹	1860	17	28	826.8	6.2	27	172.8	1.9	52
Be	mg kg ⁻¹	2.486*	0.081	8	2.5	0.23	6	0.672*	0.048	10
Bi	mg kg ⁻¹	0.0340	0.0074	4	0.27		2	0.032	0.011	4
Br	mg kg ⁻¹	0.2 ^a		7	1.7		2			
Cd	mg kg ⁻¹	0.08		5	0.078	0.019	4	0.074	0.014	8
Ce	mg kg ⁻¹	161.2	2.3	40	46.01	0.42	31	23.21	0.17	53
Cl	mg kg ⁻¹	70 ^a		24	510 ^c		20	190 ^e		9
Co	mg kg ⁻¹	4.478	0.098	22	2.043	0.049	16	44.37	0.65	40
Cr	mg kg ⁻¹	7.88	0.38	20	4.45	0.61	17	92.0	1.6	40
Cs	mg kg ⁻¹	1.357	0.021	24	10.10	0.15	21	0.915	0.016	36
Cu	mg kg ⁻¹	10.98	0.65	18	11.09	0.31	16	105.9	1.5	33
Dy	mg kg ⁻¹	2.278	0.063	38	3.667	0.085	29	3.806	0.029	49
Er	mg kg ⁻¹	0.927	0.021	36	2.293	0.061	28	2.208	0.025	50
Eu	mg kg ⁻¹	1.414	0.028	40	0.622	0.019	29	1.091	0.011	54
F	mg kg ⁻¹	1280 ^a		37	342 ^c		15	205 ^e		7
Ga	mg kg ⁻¹	23.32	0.52	20	16.06	0.27	11	17.88	0.31	31
Gd	mg kg ⁻¹	4.23	0.16	35	3.682	0.059	28	3.713	0.039	49
Ge	mg kg ⁻¹	1.09	0.10	7	1.26^c		2	1.589*	0.089	7
Hf	mg kg ⁻¹	7.78	0.22	30	6.032	0.086	27	2.444	0.041	47

Table 4 (continued).

 Reference values in bold (RV)[§], information values in plain (IV)[§] and uncertainties at 95% CL (U) of rock reference materials

Analyte	Unit	G-2			RGM-1			W-2		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Hg	mg kg ⁻¹	0.051 ^a		30	0.055		1	0.004		1
Ho	mg kg ⁻¹	0.3725	0.0098	37	0.763	0.027	27	0.7908	0.0061	51
I	mg kg ⁻¹	0.31 ^a		1	0.024		1			
In	mg kg ⁻¹	0.0272	0.0030	3	0.034		1	0.0610	0.0041	4
Ir	µg kg ⁻¹	0.04 ^a		6	0.002		1	0.08		2
La	mg kg ⁻¹	88.4	1.4	41	22.94	0.29	31	10.63	0.12	54
Li	mg kg ⁻¹	33.6	2.9	12	60.7*	2	12	9.21*	0.19	16
Lu	mg kg ⁻¹	0.1019	0.0039	40	0.397	0.011	32	0.3090	0.0034	52
Mo	mg kg ⁻¹	0.38	0.14	6	2.44	0.17	6	0.465	0.030	7
Nb	mg kg ⁻¹	12.02	0.24	31	9.13	0.14	22	7.51	0.15	51
Nd	mg kg ⁻¹	53.81	0.67	40	19.19	0.18	33	13.09	0.12	56
Ni	mg kg ⁻¹	3.46	0.57	24	3.41	0.50	16	72.0	1.0	40
Os	µg kg ⁻¹				0.0015		1	0.009		1
Pb	mg kg ⁻¹	30.00	0.66	25	23.37	0.39	19	7.83	0.19	36
Pd	µg kg ⁻¹	0.25 ^a		2	0.12		1	11		1
Pr	mg kg ⁻¹	16.88	0.30	37	5.285	0.044	26	3.018	0.033	48
Pt	µg kg ⁻¹	5.9 ^a		1	0.7		2	11		1
Rb	mg kg ⁻¹	168.5	2.9	31	149.5	1.7	29	20.23	0.27	49
Re	µg kg ⁻¹				0.044		2	0.26		1
Rh	µg kg ⁻¹				0.014		1	0.63		1
Ru	µg kg ⁻¹				0.0075		1	0.36		1
S	mg kg ⁻¹	100 ^a		17	25		2	150		2
Sb	mg kg ⁻¹	0.058	0.013	6	1.23	0.11	9	0.809	0.069	10
Sc	mg kg ⁻¹	3.66	0.12	24	4.74	0.15	19	35.86	0.38	42
Se	mg kg ⁻¹	0.07 ^a		7	0.006 ^c		3	0.09		1
Sm	mg kg ⁻¹	7.19	0.10	43	3.968	0.058	33	3.30	0.13	58
Sn	mg kg ⁻¹	1.72	0.19	8	4.34	0.61	6	1.92*	0.12	10
Sr	mg kg ⁻¹	474.9	6.1	34	104.8	1.6	28	195.4	1.6	47
Ta	mg kg ⁻¹	0.834	0.031	27	0.950	0.016	24	0.489	0.014	43
Tb	mg kg ⁻¹	0.495	0.019	39	0.597	0.016	27	0.6270	0.0082	51
Te	µg kg ⁻¹	6.7		2	8		2	2.3		2
Th	mg kg ⁻¹	24.54	0.39	33	14.56	0.16	26	2.179	0.031	53
Tl	mg kg ⁻¹	0.884*	0.026	7	0.99*	0.15	7	0.104*	0.013	8
Tm	mg kg ⁻¹	0.1232	0.0046	35	0.3620	0.0090	17	0.3315	0.0064	40
U	mg kg ⁻¹	1.964	0.067	26	5.58	0.10	25	0.5048	0.0070	50
V	mg kg ⁻¹	35.12	0.81	22	11.76	0.48	14	265.8	2.9	40
W	mg kg ⁻¹	0.121	0.049	5	1.49	0.13	4	0.29	0.05	3
Y	mg kg ⁻¹	9.88	0.17	36	23.48	0.39	23	21.82	0.33	48
Yb	mg kg ⁻¹	0.722	0.020	39	2.468	0.043	31	2.054	0.016	53
Zn	mg kg ⁻¹	83.5	1.0	19	33.2	1.3	18	77.7	1.6	38
Zr	mg kg ⁻¹	319.0	7.8	29	227.9	3.5	27	93.3	1.4	55

Analyte	Unit	JA-1			JA-2			JB-1			JB-1a		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Ag	µg kg ⁻¹	33 ^f		4	43 ^f		4	49 ^f		6	39		2
As	mg kg ⁻¹	2.8		2	0.71	0.28	6	2.5	0.5	3	2.2		2
Au	µg kg ⁻¹	0.16 ^f		7	0.26 ^f		5	0.79 ^f		5	0.71 ^f		7
B	mg kg ⁻¹	25	8	3	21.1	1.9	4	7.6	4.8	3	7.6	1.5	4
Ba	mg kg ⁻¹	304.0	6.9	20	308.4	5.1	23	501.2	7.2	13	495.1	6.9	22
Be	mg kg ⁻¹	0.53	0.24	3	2.26*	0.19	9	1.4	0.3	3	1.44 ^f		6
Bi	mg kg ⁻¹	0.0042	0.0010	3	0.0922	0.0073	6	0.03		1	0.031		3
Br	mg kg ⁻¹	7 ^f		1				0.5		1			
Cd	mg kg ⁻¹	0.097		1	0.069	0.019	3	0.11 ^f		14	0.10 ^f		5
Ce	mg kg ⁻¹	13.15	0.58	13	32.86	0.85	25	66.81	0.85	12	65.93	0.70	29
Cl	mg kg ⁻¹	42.9	5.6	3	16		3	169.7	8.1	9	163	34	3
Co	mg kg ⁻¹	11.51	0.68	13	28.33	0.97	17	37.8	2.4	7	38.53	0.78	14
Cr	mg kg ⁻¹	7.5	1.5	16	424.8	9.3	18	430	31	8	408	11	14
Cs	mg kg ⁻¹	0.627	0.016	9	4.780	0.087	19	1.35	0.11	8	1.216	0.027	15

Table 4 (continued).

Reference values in bold (RV)[§], information values in plain (IV)[§] and uncertainties at 95% CL (U) of rock reference materials

Analyte	Unit	JA-1			JA-2			JB-1			JB-1a		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Cu	mg kg ⁻¹	42.5	1.2	14	29.0	1.5	15	54.9	1.3	7	54.5	2.2	10
Dy	mg kg ⁻¹	4.75	0.11	11	2.851	0.071	22	4.09	0.13	10	4.07	0.11	24
Er	mg kg ⁻¹	2.959	0.065	12	1.676	0.031	21	2.213	0.071	10	2.232	0.053	22
Eu	mg kg ⁻¹	1.112	0.027	13	0.893	0.018	23	1.492	0.026	12	1.484	0.017	26
F	mg kg ⁻¹	160		2	230		1	385 ^f		15	357 ^f		6
Ga	mg kg ⁻¹	16.7	1.4	6	16.85	0.77	13	17.3	1.8	3	18.13	0.41	11
Gd	mg kg ⁻¹	4.15	0.12	13	3.013	0.085	24	4.84	0.10	10	4.70	0.12	27
Ge	mg kg ⁻¹	1.2		1	1.1		1	0.9 ^f		6	1		1
Hf	mg kg ⁻¹	2.510	0.079	15	2.838	0.062	23	3.408	0.075	14	3.470	0.094	21
Hg	mg kg ⁻¹	0.018		1	0.0018 ^f		1	0.0299 ^f		7	0.009		1
Ho	mg kg ⁻¹	1.032	0.036	12	0.591	0.015	21	0.798 [*]	0.034	8	0.805	0.019	22
I	mg kg ⁻¹	0.015 ^f		1	0.005 ^f		1	0.030		2	0.009		1
In	mg kg ⁻¹	0.0440	0.0025	3	0.0368	0.0037	4	0.054	0.007	3	0.054		2
Ir	µg kg ⁻¹	0.0028 ^f		2	0.016		1						
La	mg kg ⁻¹	4.88	0.13	12	15.46	0.40	23	38.40	0.85	12	37.74	0.35	28
Li	mg kg ⁻¹	10.43	0.80	10	29.18	0.56	12	11.2	0.7	3	10.8	0.7	3
Lu	mg kg ⁻¹	0.454	0.018	14	0.2549	0.0092	24	0.3102	0.0098	14	0.3147	0.0065	25
Mo	mg kg ⁻¹	1.43	0.17	10	0.581	0.035	8	31.6	2.6	3	1.57	0.14	6
Nb	mg kg ⁻¹	1.333	0.097	9	9.30	0.24	24	34.8	1.6	7	27.57	0.66	25
Nd	mg kg ⁻¹	10.69	0.29	14	14.04	0.24	27	26.21	0.87	12	26.15	0.42	29
Ni	mg kg ⁻¹	2.20	0.34	10	136.0	2.2	19	138.6	5.9	9	139.5	2.1	19
Os	µg kg ⁻¹	0.011		1	0.0114	0.0002	3	1.9 ^f		1	0.0185 ^f		1
Pb	mg kg ⁻¹	5.86	0.28	13	18.88	0.29	16	7.13	0.33	11	6.44	0.33	12
Pd	µg kg ⁻¹				0.16		1	0.7 ^f		1			
Pr	mg kg ⁻¹	2.082	0.054	12	3.691	0.079	20	7.16 [*]	0.35	8	7.10	0.14	24
Pt	µg kg ⁻¹				0.17		1						
Rb	mg kg ⁻¹	11.02	0.47	11	69.8	1.3	23	39.8	1.1	13	38.15	0.71	23
Re	µg kg ⁻¹	0.5		1	0.0461	0.0023	4	3.8		2	0.18 ^f		2
Rh	µg kg ⁻¹												
Ru	µg kg ⁻¹				0.022		1						
S	mg kg ⁻¹	23		1	6.8		1	20.9		2			
Sb	mg kg ⁻¹	0.230	0.021	7	0.150	0.030	7	0.295	0.027	5	0.29	0.11	3
Sc	mg kg ⁻¹	27.9	1.4	8	18.93	0.34	17	27.3	3.8	3	27.81	0.92	16
Se	mg kg ⁻¹	0.008		2	0.0062	0.0041	3	0.02		1	0.012		2
Sm	mg kg ⁻¹	3.396	0.077	15	3.032	0.043	27	5.08	0.10	14	5.099	0.068	29
Sn	mg kg ⁻¹	0.88	0.13	7	1.69	0.15	7	2.0		1	2.0	0.9	2
Sr	mg kg ⁻¹	259.3	5.8	22	245.8	3.0	26	440.5	5.9	13	443.4	5.4	29
Ta	mg kg ⁻¹	0.0979	0.0089	7	0.652	0.017	14	2.22	0.27	11	1.738	0.072	17
Tb	mg kg ⁻¹	0.727	0.029	13	0.4786	0.0076	21	0.710	0.036	9	0.699	0.015	25
Te	µg kg ⁻¹	1		1	1.1		3	1.8		2	1		1
Th	mg kg ⁻¹	0.761	0.026	17	4.80	0.11	22	9.14	0.40	12	8.97	0.21	23
Tl	mg kg ⁻¹	0.106	0.017	8	0.330 [*]	0.013	7	0.1		1	0.072	0.042	4
Tm	mg kg ⁻¹	0.445	0.014	8	0.2546	0.0065	16	0.320 [*]	0.010	7	0.3197	0.0064	20
U	mg kg ⁻¹	0.340	0.016	20	2.182	0.061	21	1.654 [*]	0.040	10	1.615	0.050	20
V	mg kg ⁻¹	106.2	3.4	15	119.7	2.4	17	213	13	6	200.3	6.0	13
W	mg kg ⁻¹	0.49	0.14	3	1.15	0.03	6	18		1	2.2		2
Y	mg kg ⁻¹	28.0	1.6	12	16.89	0.58	24	22.7	1.0	13	22.91	0.62	24
Yb	mg kg ⁻¹	2.949	0.085	13	1.645	0.036	23	2.108	0.052	12	2.100	0.051	26
Zn	mg kg ⁻¹	88.3	4.0	7	64.5	2.3	17	83.7	5.4	6	88.5	6.2	6
Zr	mg kg ⁻¹	83.7	3.2	13	108.5	2.6	25	137.9	4.3	13	140.1	2.9	24
Ana-lyte	Unit	JB-2			BE-N			PM-S			WS-E		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Ag	µg kg ⁻¹	64		2	40		1						
As	mg kg ⁻¹	3.00	0.66	4	1.91	0.19	9	0.2 ⁱ		8	1.3		3
Au	µg kg ⁻¹	6.1		2	2.5		2	0.9		2	1.4		1
B	mg kg ⁻¹	29.98	0.74	10	6.6		2						

Table 4 (continued).

 Reference values in bold (RV)[§], information values in plain (IV)[§] and uncertainties at 95% CL (U) of rock reference materials

Ana-lyte	Unit	JB-2			BE-N			PM-S			WS-E		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Ba	mg kg ⁻¹	218.1	2.7	55	1039	13	33	148.1	4.0	8	335	11	13
Be	mg kg ⁻¹	0.273*	0.028	9	1.9 ^{g-h}		2	0.418	0.079	4	1.10	0.14	5
Bi	mg kg ⁻¹	0.0312	0.0064	5	0.01		1						
Br	mg kg ⁻¹	0.716	0.081	3	1		3	0.24		1			
Cd	mg kg ⁻¹	0.3		2	0.2		4	0.078		1	0.12		1
Ce	mg kg ⁻¹	6.552	0.087	50	153.0	2.2	34	6.87	0.25	10	59.8	1.3	13
Cl	mg kg ⁻¹	290	12	10	180		2						
Co	mg kg ⁻¹	37.57	0.67	39	59.0	1.5	25	49.0	2.0	8	45.2	1.6	9
Cr	mg kg ⁻¹	26.65	0.69	31	353.1	8.6	24	319.0	9.4	9	97.0	4.1	9
Cs	mg kg ⁻¹	0.800	0.020	38	0.729	0.023	24	0.372	0.047	7	0.482	0.014	9
Cu	mg kg ⁻¹	222.1	3.6	30	68.8	2.3	14	57.2	1.3	6	66.2	3.0	9
Dy	mg kg ⁻¹	3.868	0.064	47	6.48	0.11	30	2.095	0.045	8	6.131	0.091	12
Er	mg kg ⁻¹	2.537	0.039	47	2.605	0.049	31	1.140	0.036	8	3.069	0.056	12
Eu	mg kg ⁻¹	0.836	0.012	47	3.679	0.065	35	1.069	0.04	9	2.206	0.057	12
F	mg kg ⁻¹	90	7	4	1100		1	100 ⁱ		6	540 ^j		7
Ga	mg kg ⁻¹	16.62	0.36	18	17.2	1.3	7	15.6	1.5	4	21.6	1.0	8
Gd	mg kg ⁻¹	3.123	0.049	47	10.09	0.26	31	2.040	0.083	8	7.24	0.20	12
Ge	mg kg ⁻¹	2		2	1.17	0.13	3	1		1	2		1
Hf	mg kg ⁻¹	1.487	0.033	43	5.72	0.11	28	1.10	0.07	6	5.20	0.21	9
Hg	mg kg ⁻¹	0.00478 ^f		6	0.012		1	0.01		1	0.011		1
Ho	mg kg ⁻¹	0.863	0.017	46	1.084	0.021	27	0.428	0.013	7	1.176	0.026	11
I	mg kg ⁻¹	0.061	0.014	3	0.02		1						
In	mg kg ⁻¹	0.070	0.008	3	0.07		1	0.048		2	0.089		2
Ir	µg kg ⁻¹							2		1			
La	mg kg ⁻¹	2.281	0.037	49	82.55	0.73	33	2.683	0.092	9	26.61	0.45	12
Li	mg kg ⁻¹	8.08	0.15	29	12.9	0.2	6	7.55	0.08	4	13.5	1.0	5
Lu	mg kg ⁻¹	0.3894	0.0058	48	0.2489	0.0052	30	0.151	0.005	8	0.357	0.014	12
Mo	mg kg ⁻¹	1.014	0.065	14	2.75	0.38	5	1.70	0.32	3	3.54	0.36	3
Nb	mg kg ⁻¹	0.565	0.034	36	113.2	2.3	27	2.44	0.23	7	17.89	0.74	10
Nd	mg kg ⁻¹	6.392	0.063	50	66.35	0.92	34	5.52	0.21	9	32.77	0.51	12
Ni	mg kg ⁻¹	14.77	0.51	35	269.7	6.8	22	117.8	3.5	10	53.7	1.9	12
Os	µg kg ⁻¹	0.0043 ^f		1									
Pb	mg kg ⁻¹	5.25	0.11	40	4.081	0.086	22	2.47	0.82	6	12.33	0.96	9
Pd	µg kg ⁻¹												
Pr	mg kg ⁻¹	1.129	0.024	46	17.39	0.22	27	1.069	0.045	7	7.74	0.16	12
Pt	µg kg ⁻¹												
Rb	mg kg ⁻¹	6.40	0.11	50	47.61	0.80	30	0.978	0.057	7	25.77	0.76	13
Re	µg kg ⁻¹	0.4 ^f		3									
Rh	µg kg ⁻¹												
Ru	µg kg ⁻¹												
S	mg kg ⁻¹	19		1	315	18	4	1040		2	584	200	3
Sb	mg kg ⁻¹	0.261	0.022	13	0.269	0.02	6	0.028		2	0.074		2
Sc	mg kg ⁻¹	54.08	0.76	33	22.55	0.60	21	34.0	1.5	8	27.6	1.1	10
Se	mg kg ⁻¹	0.146	0.018	3	0.064	0.012	5	0.15		1	0.16		1
Sm	mg kg ⁻¹	2.266	0.023	51	12.03	0.12	35	1.784	0.058	9	8.70	0.18	12
Sn	mg kg ⁻¹	0.635	0.054	12	1.68	0.32	3	3		3	15	12	3
Sr	mg kg ⁻¹	178.2	1.5	56	1392	19	29	279.2	6.2	11	407.5	8.6	14
Ta	mg kg ⁻¹	0.0396	0.0030	21	5.64	0.19	22	0.19	0.03	5	1.116	0.050	8
Tb	mg kg ⁻¹	0.5863	0.0096	44	1.303	0.037	30	0.338	0.015	8	1.082	0.024	10
Te	µg kg ⁻¹	3.5	1.4	3	1		2	4.2		2	7.3		2
Th	mg kg ⁻¹	0.2576	0.0048	7(ID)	10.58	0.14	33	0.053	0.015	6	2.992	0.086	10
Tl	mg kg ⁻¹	0.0340	0.0036	16	0.0363	0.0092	4	0.044	0.016	3	0.21		2
Tm	mg kg ⁻¹	0.393	0.012	34	0.3216	0.0057	19	0.169	0.015	5	0.422	0.010	5
U	mg kg ⁻¹	0.1528	0.0028	6(ID)	2.440	0.040	28	0.019	0.014	5	0.624	0.019	9
V	mg kg ⁻¹	572.4	8.3	34	231.9	4.7	16	186.4	7.6	7	336	12	10
W	mg kg ⁻¹	0.308	0.030	6	28		2	0.3 ⁱ		9	0.5		1
Y	mg kg ⁻¹	23.56	0.44	48	29.44	0.56	29	11.31	0.35	11	31.8	1.1	14
Yb	mg kg ⁻¹	2.529	0.034	48	1.817	0.021	35	0.997	0.022	9	2.513	0.032	12

Table 4 (continued).

Reference values in bold (RV)[§], information values in plain (IV)[§] and uncertainties at 95% CL (U) of rock reference materials

Analyte	Unit	JB-2			BE-N			PM-S			WS-E		
		RV, IV	U	n	RV, IV	U	n	RV, IV	U	n	RV, IV	U	n
Zn	mg kg ⁻¹	110.4	2.6	25	122.9	3.5	16	60.0	4.2	7	113.4	5.9	9
Zr	mg kg ⁻¹	48.25	0.88	48	272.9	3.8	33	38.2	1.7	8	203.6	5.9	13

n, number of values after outlier rejection contributing to the RV and IV, respectively. [§]Definition: see page 5 ff.

^aGladney *et al.* (1992), ^bGladney *et al.* (1990), ^cGladney and Roelandts (1988b), ^dGladney *et al.* (1991), ^eGladney and Roelandts (1988a), ^fImai *et al.* (1995), ^gGovindaraju (1980), ^hGovindaraju (1994), ⁱGovindaraju *et al.* (1994).

* stated from one method (ICP-MS) only.

In the following, the results will be discussed in detail. The relative overall analytical uncertainties U_{rel} are about 1–3% for most reference values, except for those of the very trace element-depleted sample DTS-1, where U_{rel} is about 10%. This is shown in Figure 2, where U_{rel} is plotted for BCR-1 and BCR-2 for selected elements. Exceptions are the data for elements that are heterogeneously distributed (e.g., Mo, W in BCR-2) or where only few data exist (e.g., noble metals, In, As). The new reference values for major elements, Sr, Zn and other elements agree reasonably well with the former compilation values (Govindaraju 1980, 1994, Gladney and Roelandts 1988a, b, Gladney *et al.* 1990, 1991, 1992, Itoh *et al.* 1993, Govindaraju *et al.* 1994, Terashima *et al.* 1994, Imai *et al.* 1995). However, the previous reference values are much higher for several elements, such as Nb, Th and the mono-isotopic REE Pr, Tm, especially for trace element-depleted RMs, for example, BIR-1, DTS-1 (Figure 3). The reasons for this are presumably analytical difficulties with the techniques or procedures used at the time.

The RM pairs BCR-1 and BCR-2, BHVO-1 and BHVO-2 and AGV-1 and AGV-2 are of particular interest, because they belong to the most accessed rock RMs in the GeoReM database. Most reference values were obtained from many (up to 150) published analytical data. This means that these values have a high degree of confidence. Any significant difference between analytical results for these six RMs and the reference values (Tables 3 and 4) can be related to possible matrix effects, contamination or loss of elements during sample preparation, or to other analytical problems.

As already recognised in earlier publications (e.g., Jochum and Nohl 2008), most major, minor and trace element values in these first- and second-generation RMs agree within uncertainty limits of 1–2.5% (Figure 4). However, there are some exceptions: Tl, Pb and Sn are depleted in BHVO-2 by about 15–50% compared with BHVO-1, whereas W, Bi and Mo are enriched (Table 4). BCR-2 is also depleted in Tl, Pb and Sn compared with BCR-

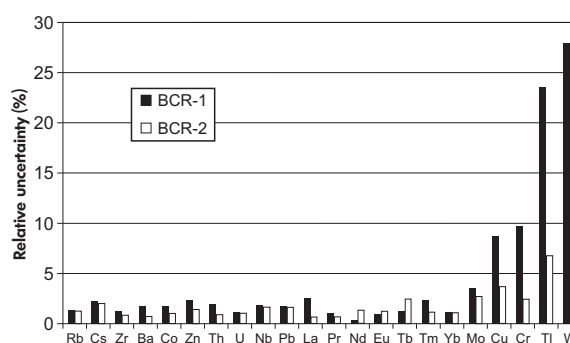


Figure 2. Relative uncertainties of the reference values for BCR-1 and BCR-2. They lie between 1 and 3% for most elements having mass fractions between about 0.5 and 700 mg kg⁻¹. Exceptions are some elements (Mo, Cu, Cr, Tl, W) with similar contents between 0.3 and 250 mg kg⁻¹ that are presumably heterogeneously distributed in the samples.

1, whereas Cd and Mo are highly enriched, attaining enrichment factors of 3.7 and 166, respectively (Table 4). Similar variabilities were also found for the pair AGV-2 and AGV-1, where the Pb value in AGV-1 is nearly three times higher than in AGV-2, and Cr abundance is 70% lower in AGV-1 compared with AGV-2. Discrepancies in element mass fractions can be due to slight differences in collected material from the same site or contamination from equipment during the RM comminution process (Baker *et al.* 2004, Weis *et al.* 2006, Jochum and Nohl 2008, Jochum and Enzweiler 2014).

The new reference values are useful not only for calibration, method validation and quality control purposes, but also for geochemical investigations. The matrix RMs of different rock types examined here currently belong to the best-characterised rock samples available. In the following, some examples are given. The reliability of analytical data may be demonstrated by means of the reference values of

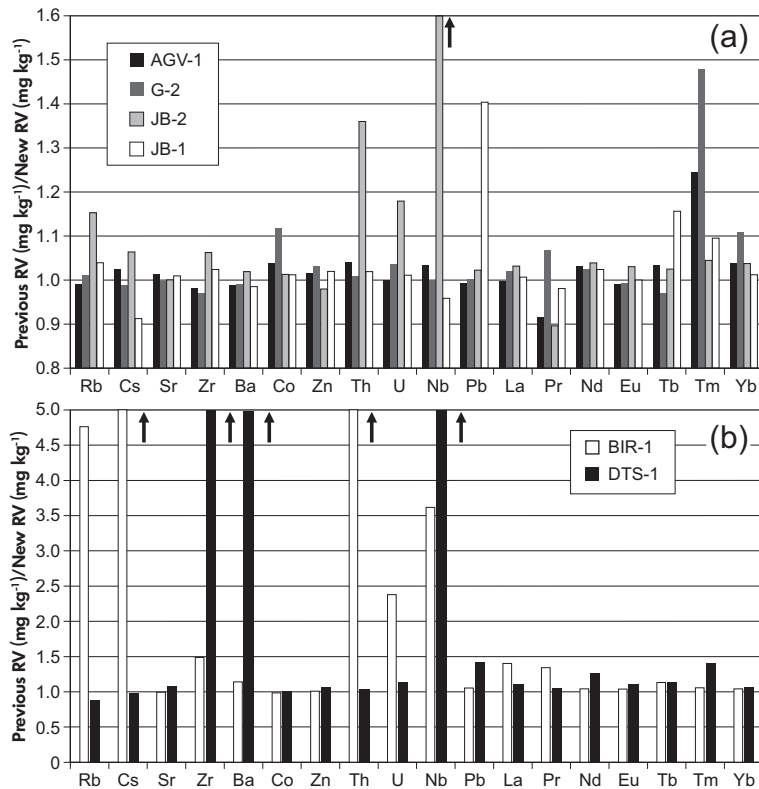


Figure 3. Comparison of the previous reference values (RV) published between 1980 and 1994 (for references see text) with the new RV (this work) for different RMs (andesite AGV-1, granite G-2, basalts JB-1, JB-2; see Table 1). The previous values for some elements (e.g., Nb, Th and Tm) are much higher (a, b), especially in the trace element poor RMs BIR-1 and DTS-1 (b), than the new ‘quasi-certified’ values, mainly because of analytical difficulties at the time.

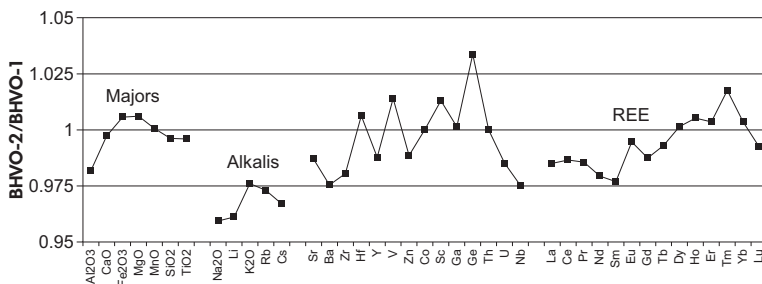


Figure 4. The reference values of the basalt BHVO-1 agree within 1 and 2.5% with the replacement sample BHVO-2 for most elements. The alkali metals seem to be depleted in BHVO-2 relative to BHVO-1.

elements that behave in a geochemically coherent manner, such as the rare earth elements (REEs). Figure 5a shows the CI chondrite-normalised (Palme *et al.* 2014) REE mass fractions of RMs of different rock types with smooth patterns. The Hawaiian RMs BHVO-1 and BHVO-2, originating from the 1919 flow of the Kilauea volcano (Flanagan 1967), are typical examples of oceanic island basalts, and their reference values currently represent the most accurate values

for such a matrix. Figure 5b shows that the normalised REE patterns of both samples are smooth and agree very well. Thulium seems to be an exception. The Tm mass fractions in BHVO-1 and BHVO-2 and also in most other RMs are ca. 5% lower than the Tm* value calculated from the linear interpolation of the logarithm of the CI-normalised abundances of the neighbouring elements Er and Yb. Dauphas and Pourmand (2015) interpreted the small negative Tm

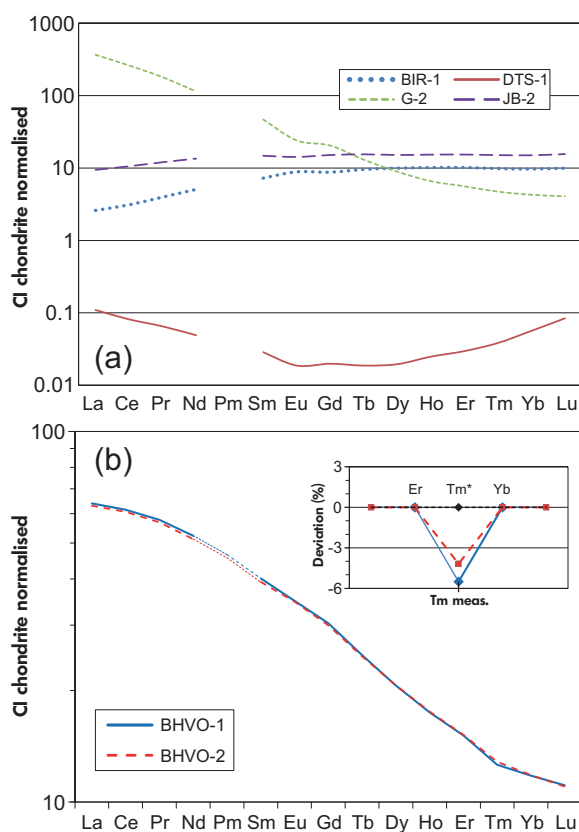


Figure 5. CI chondrite-normalised REE patterns for several rock RMs of different types (a) and BHVO-1 and BHVO-2 (b) with smooth patterns. The origin of the small negative Tm anomaly is presently unclear (see text). The inset shows the percentage deviation of Tm (measured) from the theoretically determined Tm* value, which is determined from the reference values of Er and Yb in BHVO-1 and BHVO-2, respectively.

anomaly in terrestrial rocks to be related to accretion processes during the formation of the solar system. Another explanation may be that the CI chondrite value of Tm is not well constrained, because Tm is a mono-isotopic element, which cannot be determined by the highly precise ID technique, and Tm and REE may be heterogeneously distributed in carbonaceous chondrites (Stracke *et al.* 2012).

BCR-1 and BCR-2 are appropriate control samples in studies of large igneous provinces, including continental flood basalts (Stoeppler *et al.* 2001). As shown in Table 1, G-2 is also one of the most accessed rock RMs. G-2 is a granite powder, and therefore, discrepancies of the analytical data from different laboratories using different analytical techniques can be expected when only small sample amounts were used for analysis. This is particularly valid for

Zr and Hf, major and minor elements in zircon mineral grains, which may be heterogeneously distributed in the powder. In addition, problems can arise when solution techniques have been applied, and the rock powder has not been dissolved completely because of the existence of the largely insoluble mineral zircon. Table S1 shows that the Zr and Hf mass fraction data from ICP-MS vary from 39 to 348 mg kg⁻¹ and from 0.9 to 8.4 mg kg⁻¹, respectively. However, the majority of the data has high values at about 320 mg kg⁻¹ and 7.8 mg kg⁻¹ for Zr and Hf, respectively, which agree well with data obtained by XRF and INAA, where no chemical treatment of the granite powder was performed and larger sample masses were used.

The dunite RM DTS-1 is a trace element-depleted sample, where the mass fractions of many trace elements are in the µg kg⁻¹ range. The REE shows a typical U-shaped pattern with a small negative Eu anomaly and is a factor of 10–50 lower than the chondritic values (Figure 5a). The GSJ RM JB-1 and its replacement sample JB-1 contain identical mass fractions of the REE, within uncertainty limits. Both the USGS BIR-1 and the GSJ JB-2 have flat heavy REE patterns and are depleted in light REE. A possible inhomogeneity of some elements (e.g., Zr, Hf) in BIR-1 (Jochum *et al.* 1994) was not confirmed by these investigations as shown by the new analytical data (Tables S1 and S2) and may presumably be related to former analytical problems.

Conclusions

Very few reference materials available to the geochemical community are certified according to metrological guidelines. Most of these certifications are relatively recent and result from an effort to align geochemical measurements to general metrological requirements. Ideally, more formally certified geological CRMs are needed. Unfortunately, the most requested rock RMs do not have certified values for their constituents for a variety of reasons. Therefore, we determined reference values and their uncertainties by following ISO guidelines and the IAG Certification Protocol. We used analytical data for these materials published mainly between 1995 and 2015. These data were obtained by the state-of-the-art techniques. This set of new reference values (will be given as GeoReM preferred values) is currently the most reliable one available can be used for accurate calibration, trueness evaluation and quality control in future geochemical research with rock samples.

Acknowledgements

We thank the editor Thomas Meisel, Andreas Stracke and an anonymous reviewer for their helpful comments.

References

- Baker J., Peate D., Waight T. and Meyzen C. (2004)**
Pb isotopic analysis of standards and samples using a ^{207}Pb - ^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. *Chemical Geology*, 211, 275–303.
- CCQM (1988)**
Minutes from the fifth meeting (February 1998) of the Consultative Committee on the Quantity of Material (CCQM) of the Bureau International des Poids et Mesures (BIPM). Sèvres, France.
- Cotta A.J.B. and Enzweiler J. (2008)**
Certificate of analysis of the geochemical reference material BRP-1 (Paraná Basin Basalt). *Geostandards and Geoanalytical Research*, 32, 231–235.
- Dauphas N. and Pourmand A. (2015)**
Thulium anomalies and rare earth element patterns in meteorites and Earth: Nebular fractionation and the nugget effect. *Geochimica et Cosmochimica Acta*, 163, 234–261.
- De Bièvre P. and Peiser H.S. (1997)**
Basic equations and uncertainties in isotope-dilution mass spectrometry for traceability to SI of values obtained by this primary method. *Fresenius' Journal of Analytical Chemistry*, 359, 523–525.
- Fairbairn H.W., Schlecht W.G., Stevens R.E., Dennen W.H., Ahrens L.H. and Chayes F. (1951)**
A co-operative investigation of precision and accuracy in chemical, spectrochemical and modal analysis of silicate rocks. *USGS Bulletin*, 980, US Government Printing Office (Washington, DC, USA), 77pp.
- Feam T. and Thompson M. (2001)**
A new test for 'sufficient homogeneity'. *Analyst*, 126, 1414–1417.
- Flanagan F.J. (1967)**
U.S. Geological Survey silicate rock standards. *Geochimica et Cosmochimica Acta*, 31, 289–308.
- Flanagan F.J. (1986)**
Reference samples in geology and geochemistry. *US Geological Survey Bulletin*, 1582, 1–70.
- Gladney E.S. and Roelandts I. (1988a)**
1987 compilation of elemental concentration data for USGS BIR-1, DNC-1 and W-2. *Geostandards Newsletter*, 12, 63–118.
- Gladney E.S. and Roelandts I. (1988b)**
1987 compilation of elemental concentration data for USGS BHVO-1, MAG-1, QLO-1, RGM-1, SCo-1, SDC-1, SGR-1 and STM-1. *Geostandards Newsletter*, 12, 253–362.
- Gladney E.S., Jones E.A., Nickell E.J. and Roelandts I. (1990)**
1988 compilation of elemental concentration data for USGS basalt BCR-1. *Geostandards Newsletter*, 14, 209–359.
- Gladney E.S., Jones E.A., Nickell E.J. and Roelandts I. (1991)**
1988 compilation of elemental concentration data for USGS DTS-1, G-1, PCC-1 and W-1. *Geostandards Newsletter*, 15, 199–396.
- Gladney E.S., Jones E.A., Nickell E.J. and Roelandts I. (1992)**
1988 compilation of elemental concentration data for USGS basalt AGV-1, GSP-1 and G-2. *Geostandards Newsletter*, 16, 111–300.
- Govindaraju K. (1980)**
Report (1980) on three GIT-IWG rock reference samples: Anorthosite from Greenland, AN-G; Basalte d'Essey-la-Cote, BE-N; Granite de Beauvoir, MA-N. *Geostandards Newsletter*, 4, 49–138.
- Govindaraju K. (1994)**
1994 compilation of working values and sample description for 383 geostandards. *Geostandards Newsletter*, 18 (Special issue), 158pp.
- Govindaraju K., Potts P.J., Webb P.C. and Watson J.S. (1994)**
1994 report on Whin Sill dolerite WS-E from England and Pitscurrie microgabbro PM-S from Scotland: Assessment by one hundred and four international laboratories. *Geostandards Newsletter*, 18, 211–300.
- Hervig R.L., Mazdab F.K., Williams P., Guan Y., Huss G.R. and Leshin L.A. (2006)**
Useful ion yields for Cameca IMS 3f and 6f SIMS: Limits on quantitative analysis. *Chemical Geology*, 227, 83–99.
- Horwitz W. and Albert R. (1995)**
Precision in analytical measurements: Expected values and consequences in geochemical analyses. *Fresenius' Journal of Analytical Chemistry*, 351, 507–511.
- Imai N., Terashima S., Itoh S. and Ando A. (1995)**
1994 compilation of analytical data for minor and trace elements in seventeen GSJ geochemical reference samples, "igneous rock series". *Geostandards Newsletter*, 19, 135–213.
- ISO Guide 33 (2015)**
Reference materials – good practice in using reference materials. *International Organization for Standardization (Geneva)*, 31pp.
- ISO Guide 34 (2009)**
General requirements for the competence of reference material producers. *International Organization for Standardization (Geneva)*, 34pp.
- ISO Guide 35 (2006)**
Reference materials – general and statistical principles for certification. 3, *International Organization for Standardization (Geneva)*, 64pp.
- Itoh S., Terashima S., Imai N., Kamioka H., Mita N. and Ando A. (1993)**
1992 compilation of analytical data for rare-earth elements, scandium, yttrium, zirconium and hafnium in twenty-six GSJ reference samples. *Geostandards Newsletter*, 17, 5–79.



references

Jochum K.P. and Enzweiler J. (2014)

Reference materials in geochemical and environmental research. In: Holland H.D. and Turekian K.K. (eds), *Treatise on geochemistry* (2nd edition), volume 15. Elsevier (Oxford), 43–70.

Jochum K.P. and Nohl U. (2008)

Reference materials in geochemistry and environmental research and the GeoReM database. *Chemical Geology*, 253, 50–53.

Jochum K.P., Rehkämper M. and Seufert H.M. (1994)

Trace element analysis of basalt BIR-1 by ID-SSMS, HPLC and LIMS. *Geostandards Newsletter*, 18, 43–51.

Jochum K.P., Nohl U., Herwig K., Lammel E., Stoll B. and Hofmann A.W. (2005)

GeoReM: A new geochemical database for reference materials and isotopic standards. *Geostandards and Geoanalytical Research*, 29, 333–338.

Jochum K.P., Weis U., Stoll B., Kuzmin D., Yang Q., Raczek I., Jacob D.E., Stracke A., Birbaum K., Frick D.A., Günther D. and Enzweiler J. (2011)

Determination of reference values for NIST SRM 610–617 glasses following ISO guidelines. *Geostandards and Geoanalytical Research*, 35, 397–429.

Jochum K.P., Stoll B., Weis U., Jacob D.E., Mertz-Kraus R. and Andreae M.O. (2014)

Non-matrix-matched calibration for the multi-element analysis of geological and environmental samples using 200 nm femtosecond LA-ICP-MS: A comparison with nanosecond lasers. *Geostandards and Geoanalytical Research*, 38, 265–292.

Kane J.S. (2004)

Report of the International Association of Geoanalysts on the certification of Penrhyn slate, OU-6. *Geostandards and Geoanalytical Research*, 28, 53–80.

Kane J.S., Potts P.J., Wiedenbeck M., Carignan J. and Wilson S. (2003)

International Association of Geoanalysts' protocol for the certification of geological and environmental reference materials. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 27, 227–244.

Kane J.S., Potts P.J., Meisel T. and Wiedenbeck M. (2007)

International Association of Geoanalysts' protocol for the certification of geological and environmental reference materials: A supplement. *Geostandards and Geoanalytical Research*, 31, 285–288.

Kane J.S., Batjargal B. and Erdenetsetseg D. (2009)

Report on the 2007 recertification of the certified reference materials GAS (serpentinite) and OShBO (alkaline granite). *Geostandards and Geoanalytical Research*, 33, 295–308.

Meisel T., Moser J. and Wegscheider W. (2001)

Recognizing heterogeneous distribution of platinum group elements (PGE) in geological materials by means of the Re-Os isotope system. *Fresenius' Journal of Analytical Chemistry*, 370, 566–572.

NIST (1981)

Certificate of analysis – standard reference material 688. National Institute of Standards and Technology (Washington, DC, USA), 2pp.

Palme H., Lodders K. and Jones A. (2014)

Solar system abundances of the elements. In: Holland H.D. and Turekian K.K. (eds), *Treatise on geochemistry* (2nd edition), volume 2. Elsevier (Oxford), 15–36.

Stoeppler M., Wolf W.R. and Jenks P.J. (eds) (2001)

Reference materials for chemical analysis. Wiley-VCH Verlag (Weinheim), 296pp.

Stracke A., Palme H., Gellissen M., Münker C., Kleine T., Birbaum K., Günther D., Bourdon B. and Zipfel J. (2012)

Refractory element fractionation in the Allende meteorite: Implications for solar nebula condensation and the chondritic composition of planetary bodies. *Geochimica et Cosmochimica Acta*, 85, 114–141.

Terashima S., Imai N., Itoh S., Ando A. and Mita N. (1994)

1993 compilation of analytical data for major elements in seventeen GSJ geochemical reference samples, "Igneous rock series". *Bulletin of the Geological Survey of Japan*, 45, 305–381.

Wang Y., Gao Y., Wang X., Wu S. and Gu T. (2004)

Investigations into the preparation of ultra-fine particle size geochemical reference materials. *Geostandards and Geoanalytical Research*, 28, 113–121.

Weis D., Kieffer B., Maerschalk C., Barling J., de Jong J., Williams G.A., Hanano D., Pretorius W., Mattielli N., Scoates J.S., Goolaerts A., Friedman R.M. and Mahoney J.B. (2006)

High-precision isotopic characterization of USGS reference materials by TIMS and MC-ICP-MS. *Geochemistry Geophysics Geosystems*, 7, Q08006.

Supporting information

The following supporting information may be found in the online version of this article:

Appendix Table S1. Mass fraction data of reference materials.

Appendix Table S2. Mean and standard deviations of single values of materials using analytical techniques in categories 1–4.

This material is available as part of the online article from: <http://onlinelibrary.wiley.com/doi/10.1111/j.1751-908X.2015.00392.x/abstract> (This link will take you to the article abstract).