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UNICAMP - BRP-1, Basalt

Veranstalter: UNICAMP, Instituto de Geosciencas, Campinas, Brasilien
Ringversuchsmaterial: BRP-1, Basalt
RV geschlossen: 2007 – 11
Literatur: Certificate of Analysis of the Reference Material BRP-1 (Basalt Ribeirao Preto)

Hauptelemente [MA%]

	CRB	RV	1sRV	Z-Score
Na_2O	2,71	2,71	0,04	
MgO	3,9	3,94	0,05	
Al_2O_3	12,34	12,4	0,14	
SiO_2	50,26	50,39	0,76	
P_2O5	0,623	0,63	0,02	
K_2O	1,50	1,52	0,02	
CaO	7,91	7,95	0,11	
TiO_2	3,94	3,81	0,06	
Fe_2O_3 tot	15,64	15,59	0,16	
MnO	0,204	0,21	0,006	
L.O.I.	0,49			

Spurenelemente [µg/g]

	CRB	RV	1sRV	Z-Score
Ba	578	555	14,6	
Ce	68	93,3	2,3	
Co	32	37,5	1,8	
Cr	15	12,4	0,8	
Cu	177	160	5	
Ga	22	24,8	1	
Hf	6	8	0,3	
La	34	42,6	1,1	
Nb	25	29,1	1,6	
Nd	48	51,9	1,3	
Ni	29	23,4	1,8	
Pb	5	5,5	0,4	
Rb	34	35,5	1,5	
Sr	461	492	11,8	
V	378	391	10	
Y	41	42,6	2,2	
Zn	139	142,2	3,1	
Zr	309	310,4	6,3	

Legende

CRB: Ergebnisse CRB – **RV:** Ergebnisse Ringversuch -- **1s-RV:** Standardabweichung Ringversuch
Z-Score: Differenz des Messwertes vom Mittelwert des Ringversuchs -- *** Wert nicht zertifiziert

Certificate of Analysis of the Reference Material BRP-1 (Basalt Ribeirão Preto)

BRP-1 is a geological reference material appropriate for use in the calibration of analytical instruments, method validation and in quality evaluation of silicate matrix analysis. Each unit of BRP-1 contains 55 g of powdered material.

The material was prepared in the laboratories of USGS (United States Geological Survey). The characterization and certification followed the recommendations of IAG (International Association of Geoanalysts) protocol (Kane et al. 2003) and of ISO Guide 35 (2006).

Seventeen laboratories which regularly participate of the Proficiency Test GeoPT, organized by IAG, were responsible for the production of most data used in the certification of BRP-1. Additionally, eight other international and national laboratories also participated of the characterization.

The majority of the laboratories used analytical methods with test portions ≥ 100 mg, which is indicated for the reproduction of the reference values.

The reference values, uncertainties and standard deviations of characterization of ten major and minor oxides and of thirty four trace elements are given in Tables 1 and 2, respectively. Each value was established with results of at least of ten laboratories, obtained from results by two or more analytical methods and with proved traceability. Additionally, in Table 3 informative values are given for other twelve analytes and loss on ignition.

Sampling and preparation of BRP-1

The material is a basalt of the Paraná Magmatic Province (~130 Ma), sampled from a quarry at Ribeirão Preto – SP, Brazil (21°15'S 47° 47' W). The rock is massive, dark grey, aphiric and hypocrystalline. Rock thin sections showed predominance of plagioclase (labradorite and bitownite) and pyroxene (augite) crystallites dispersed in a vitreous mass. The rock contains small amount of serpentine, magnetite, ilmenite, apatite as well as rare grains of pyrite. The coarsely crushed sample (~160 kg), was sent to the USGS (Denver, USA), were it was comminuted (99.5 % has particle size < 75 µm), homogenized and distributed into 1920 bottles.

Table 1. Major and minor oxide certified reference values (RV), uncertainties (U), standard deviation (s_{LM}) for characterization and pooled standard deviation (s_w). Values in % m/m.

Constituent	RV	U	s_{LM}	s_w	Constituent	RV	U	s_{LM}	s_w
SiO_2	50.39	0.15	0.27	0.14	MgO	3.94	0.03	0.05	0.03
TiO_2	3.81	0.03	0.06	0.02	CaO	7.95	0.05	0.11	0.04
Al_2O_3	12.40	0.07	0.14	0.05	Na_2O	2.71	0.03	0.04	0.04
$Fe_2O_{3\,T}$	15.59	0.09	0.16	0.09	K_2O	1.52	0.01	0.02	0.01
MnO	0.214	0.003	0.006	0.004	P_2O_5	0.63	0.01	0.02	0.01

Table 2. Trace elements certified reference values (RV), uncertainties (U), standard deviation (s_{LM}) for characterization and pooled standard deviation (s_w). Values in mg/kg.

Constituent	RV	U	s_{LM}	s_w	Constituent	RV	U	s_{LM}	s_w
Ba	555	7	14.6	8	Ni	23.4	0.9	1.8	1.0
Ce	93.3	1.2	2.3	1.4	Pb	5.5	0.3	0.4	0.3
Co	37.5	1.4	1.8	1.1	Pr	12.3	0.2	0.3	0.2
Cr	12.4	1.0	0.8	1.4	Rb	35.4	1.0	1.5	1.2
Cs	0.37	0.02	0.02	0.02	Sc	28.5	0.8	1.2	0.8
Cu	160	3	5	3	Sm	11.2	0.2	0.4	0.3
Dy	8.5	0.3	0.4	0.2	Sr	492	6	11.8	6
Er	4.2	0.1	0.2	0.1	Ta	1.96	0.08	0.14	0.07
Eu	3.42	0.08	0.11	0.10	Tb	1.52	0.05	0.07	0.06
Ga	24.8	0.6	1.0	0.8	Th	3.97	0.10	0.17	0.12
Gd	10.4	0.3	0.6	0.2	Tm	0.57	0.02	0.03	0.02
Hf	8.0	0.2	0.3	0.2	U	0.82	0.03	0.03	0.02
Ho	1.62	0.06	0.09	0.06	V	391	7	10	9
La	42.6	1.0	1.1	1.3	Y	42.0	1.0	2.2	1.0
Lu	0.50	0.02	0.02	0.02	Yb	3.48	0.09	0.13	0.05
Nb	29.1	0.9	1.6	0.6	Zn	142.2	1.8	3.1	3
Nd	51.9	0.9	1.3	1.1	Zr	310.4	4.7	9.0	4

Table 3. Informative values and (s_{LM}) for characterization

Constituent	% m/m	s_{LM}	Constituent	mg/kg	s_{LM}
FeO	10.4	0.2	In	0.13	0.01
PF	0.50	0.1	Li	7.1	0.3
	mg/kg		Mo	1.5	0.1
Be	1.8	0.1	S	387	12
Cd	0.2	0.1	Sb	0.06	0.01
F	715	16	Sn	2.5	0.4
Ge	1.7	0.3	Tl	0.13	0.01

Table 1. Major and minor oxide certified reference values (RV), uncertainties (U), standard deviation (s_{LM}) for characterization and pooled standard deviation (s_w). Values in % m/m.

Constituent	RV	U	s_{LM}	s_w	Constituent	RV	U	s_{LM}	s_w
SiO_2	50.39	0.15	0.27	0.14	MgO	3.94	0.03	0.05	0.03
TiO_2	3.81	0.03	0.06	0.02	CaO	7.95	0.05	0.11	0.04
Al_2O_3	12.40	0.07	0.14	0.05	Na_2O	2.71	0.03	0.04	0.04
$Fe_2O_{3\,T}$	15.59	0.09	0.16	0.09	K_2O	1.52	0.01	0.02	0.01
MnO	0.214	0.003	0.006	0.004	P_2O_5	0.63	0.01	0.02	0.01

Table 2. Trace elements certified reference values (RV), uncertainties (U), standard deviation (s_{LM}) for characterization and pooled standard deviation (s_w). Values in mg/kg.

Constituent	RV	U	s_{LM}	s_w	Constituent	RV	U	s_{LM}	s_w
Ba	555	7	14.6	8	Ni	23.4	0.9	1.8	1.0
Ce	93.3	1.2	2.3	1.4	Pb	5.5	0.3	0.4	0.3
Co	37.5	1.4	1.8	1.1	Pr	12.3	0.2	0.3	0.2
Cr	12.4	1.0	0.8	1.4	Rb	35.4	1.0	1.5	1.2
Cs	0.37	0.02	0.02	0.02	Sc	28.5	0.8	1.2	0.8
Cu	160	3	5	3	Sm	11.2	0.2	0.4	0.3
Dy	8.5	0.3	0.4	0.2	Sr	492	6	11.8	6
Er	4.2	0.1	0.2	0.1	Ta	1.96	0.08	0.14	0.07
Eu	3.42	0.08	0.11	0.10	Tb	1.52	0.05	0.07	0.06
Ga	24.8	0.6	1.0	0.8	Th	3.97	0.10	0.17	0.12
Gd	10.4	0.3	0.6	0.2	Tm	0.57	0.02	0.03	0.02
Hf	8.0	0.2	0.3	0.2	U	0.82	0.03	0.03	0.02
Ho	1.62	0.06	0.09	0.06	V	391	7	10	9
La	42.6	1.0	1.1	1.3	Y	42.0	1.0	2.2	1.0
Lu	0.50	0.02	0.02	0.02	Yb	3.48	0.09	0.13	0.05
Nb	29.1	0.9	1.6	0.6	Zn	142.2	1.8	3.1	3
Nd	51.9	0.9	1.3	1.1	Zr	310.4	4.7	9.0	4

Table 3. Informative values and (s_{LM}) for characterization

Constituent	% m/m	s_{LM}	Constituent	mg/kg	s_{LM}
FeO	10.4	0.2	In	0.13	0.01
PF	0.50	0.1	Li	7.1	0.3
	mg/kg		Mo	1.5	0.1
Be	1.8	0.1	S	387	12
Cd	0.2	0.1	Sb	0.06	0.01
F	715	16	Sn	2.5	0.4
Ge	1.7	0.3	Tl	0.13	0.01

Homogeneity Tests

The uniform distribution of BRP-1 constituents between and within bottles was confirmed in three different tests. In the first, among bottles homogeneity of major, minor and fourteen trace elements was evaluated by XRF. In the second, Cotta et al. (2007), tested the within bottle homogeneity by X-ray micro fluorescence with synchrotron source (SXRF) and showed that portions smaller than 20 milligrams of BRP-1 are representative of all material, with relative differences smaller than 3%. Finally, the characterization data were also used to confirm the between bottles homogeneity of the elements with indicated reference values.

Characterization and establishment of values

Each participating laboratory received two bottles of BRP-1 and was asked to report analytical results in triplicate for each one. Some laboratories contributed with data obtained by more than one method. Each laboratory analyzed one aliquot of the reference material used for quality control (BCR-2, Basalt Columbia River), just identified as QC. The reported data for BRP-1 were scrutinized and only used in calculations if 1) the result of the QC sample was within the recommended value ± two standard deviation and 2) the results of BRP-1 were within the range defined by the mean of all data ± twice the Horwitz function value for research labs (GeoPT™ 2002). This last condition was imposed both because not all laboratories had been pre-qualified and because it approximates a requirement of the IAG protocol. Histograms and the Shapiro-Wilk normality test, at significance level of 0.05, were used to verify the data distribution. After exclusion of anomalous values, the mean of the laboratory means was taken as reference value.

The combined uncertainty (u) was calculated as described in ISO Guide 35 (2006), based on analysis of variance, and contains a between-laboratory contribution from the characterization ($u_{characterization} = s_L/\sqrt{n}$, where n is the number of laboratories contributing data) and a contribution from material variance between bottles, even though that variance was not statistically significant:

$$u = (u^2_{characterzaiton} + u^2_{heterogeneity})^{½}$$

The combined uncertainty was expanded using coverage factor k=2 (U=2u), so that it approximates the 95% confidence level. The standard deviation between means used to obtain the reference value is reported (s_{LM}), as is the pooled within-laboratory standard deviation for the contributing laboratories (s_w). These values help users of BRP-1 to evaluate their laboratory uncertainties following ISO Guide 33 (2000). The analytical techniques and participating laboratories are listed in Tables 4 and 5, respectively.

Recommendations for use

The storage and handling of the material must foresee the maintenance of its properties. Before use, it is recommended to homogenize the material, by inversion and rolling of the bottle. Despite the high homogeneity of the material, repeatability tests are advisable when test portions smaller than 100 mg are used.

The reference values represent the whole oxide or elemental concentrations on dry basis. For analysis, the material should be dried at 105 ± 5 °C for two hours.

The preparation of BRP-1 was coordinated by Jacinta Enzweiler (Institute of Geosciences, State University of Campinas) and had the participation of Aloísio J.B. Cotta (Institute of Geosciences, State University of Campinas); Antonio J. R. Nardy (IGCE, UNESP); João H. Larizzatti (CPRM) and Stephen A. Wilson (USGS).

Temporarily the material can be acquired by e-mail: jacinta@ige.unicamp.br.

Acknowledgements

We thank Stephen Wilson's invitation to use the USGS facilities and to Phil J. Potts (IAG) for inviting GeoPT international laboratories to participate of the characterization. and his enthusiastic help during the preparation step. We are especially grateful to all analysts work and contributed data. We also deeply thank Jean S. Kane (IAG) for her support to this project and her worthy suggestions to improve the content of this certificate. This project was funded by National Council for Scientific and Technological Development (CNPq) (Proc. 47353/2004-4).

References

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Table 4. Analytes, techniques and number of laboratories used for certification

SiO_2	XRF (17), ICP-OES (3)	Ho	ICP-MS (11), ICP-OES (1), LA-ICP-MS (1)
TiO_2	XRF (17), ICP-OES (4)	La	ICP-MS (12), XRF (5), ICP-OES (1), INAA (1), LA-ICP-MS (1)
Al_2O_3	XRF (17), ICP-OES (3)	Lu	ICP-MS (11), INAA (1), LA-ICP-MS (1)
$Fe_2O_{3\,T}$	XRF (16), ICP-OES (4)	Nb	ICP-MS (8) , XRF (10), LA-ICP-MS (1)
MnO	XRF (17), ICP-OES (5), ICP-MS (1)	Nd	ICP-MS (11), XRF (1), ICP-OES (1), LA-ICP-MS (1)
MgO	XRF (16), ICP-OES (3)	Ni	ICP-MS (8), XRF (6), LA-ICP-MS (1)
CaO	XRF (14), ICP-OES (5)	Pb	ICP-MS (11), XRF (3), LA-ICP-MS (1)
Na_2O	XRF (13), ICP-OES (4), AAS (1)	Pr	ICP-MS (11), LA-ICP-MS (1)
K_2O	XRF (16), ICP-OES (4)	Rb	ICP-MS (12), XRF (10), LA-ICP-MS (1)
P_2O_5	XRF (17), ICP-OES (4)	Sc	ICP-MS (7), XRF (5), ICP-OES (2), INAA (1)
Ba	ICP-MS (11), XRF (7), ICP-OES (3), INAA (1), LA-ICP-MS (1)	Sm	ICP-MS (12), XRF (1), INAA (1), LA-ICP-MS (1)
Ce	ICP-MS (12), XRF (2), INAA (1), LA-ICP-MS (1)	Sr	ICP-MS (10), XRF (11), ICP-OES (2), LA-ICP-MS (1)
Co	ICP-MS (9), XRF (3), AAS (1), INAA (1), LA-ICP-MS (1)	Ta	ICP-MS (10), INAA (1), LA-ICP-MS (1)
Cr	ICP-MS (6), XRF (4), INAA (1)	Tb	ICP-MS (11), ICP-OES (1), INAA (1), LA-ICP-MS (1)
Cs	ICP-MS (12), LA-ICP-MS (1)	Th	ICP-MS (12), ICP-OES (1), INAA (1), LA-ICP-MS (1)
Cu	XRF (7), ICP-OES (4), ICP-MS (5), LA-ICP-MS (1), AAS (1)	Tm	ICP-MS (11), LA-ICP-MS (1)
Dy	ICP-MS (10) , LA-ICP-MS (1)	U	ICP-MS (12), LA-ICP-MS (1)
Er	ICP-MS (10) , LA-ICP-MS (1)	V	ICP-MS (6), XRF (10), ICP-OES (2)
Eu	ICP-MS (11), INAA (1), LA-ICP-MS (1)	Y	ICP-MS (11), XRF (9), ICP-OES (2), LA-ICP-MS (1)
Ga	ICP-MS (9), XRF (8), LA-ICP-MS (1)	Yb	ICP-MS (11), LA-ICP-MS (1)
Gd	ICP-MS (11), ICP-OES (1) , LA-ICP-MS (1)	Zn	XRF (9), ICP-OES (2), ICP-MS (4), INAA (1), AAS (1)
Hf	ICP-MS (10), ICP-OES (1), INAA (1), LA-ICP-MS (1)	Zr	ICP-MS (10), XRF (8), ICP-OES (1), LA-ICP-MS (1)

Table 5. Laboratories which contributed with analytical data

Genalysis Laboratory Services Pty Ltd	Maddington, Austrália
University of Leoben	Leoben, Austria
Instituto de Geociências, USP	São Paulo, Brazil
Instituto de Pesquisas Energética e Nucleares	São Paulo, Brazil
Instituto de Geociências, UNICAMP	Campinas, Brazil
LAMIN, CPRM	Rio de Janeiro, Brazil
Instituto de Geociências, UFRGS	Porto Alegre, Brazil
Instituto de Geociências, UFRJ	Rio de Janeiro, Brazil
Departamento de Geologia, UFPE	Recife, Brazil
Departamento de Geologia, UFOP	Ouro Preto, Brazil
Geoscience Laboratories	Sudbury, Canadá
Northwest University	Xi'an, China
Geological Survey of Denmark and Greenland	Copenhagen, Denmark
Tallinn University of Technology	Tallinn, Estonia
CRPG (SARM)	Vandoeuvre-lès-Nancy Cedex, France
Max-Planck-Institut fuer Chemie	Mainz, Germany
CRB Analyse Service GmbH	Hardegsen, Germany
Università di Pisa	Pisa, Italy
Geological Survey of Norway	Trondheim, Norway
State Geological Institute of Dionyz Stur	Spisska Nova Ves, Eslováquia
University of Mexico	Mexico, México
British Geological Survey	Keyworth, United Kingdom
Department of Earth Sciences, Open University	Milton Keynes, United Kingdom
Washington State University, USA	Pullman, USA
USGS	Denver, USA