

Laser Ablation Inductively Coupled Plasma Mass Spectrometry for Determination of Trace Elements in Geological Glasses

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Abstract. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used as a powerful multielement analytical method for trace analysis of geological glasses which are useful as reference materials for geochemical in-situ microanalytical work. The quantification of the analytical results was carried out using the BCR-2G and NIST 612 glass standard reference material (SRM). The experimentally determined relative sensitivity coefficients (RSC) for both SRMs vary between 0.2 and 3 for most of the elements, with increasing mass an increasing of relative sensitivity coefficients was observed. The relative standard deviation (RSD) for determination of trace element concentration of most elements ($N=3$) are between 2 and 10%. The determination of trace elements in various geological glasses by LA-ICP-MS yielded a good agreement with the reference values and those results of other trace analytical methods.

Key words: Geological glasses; laser ablation inductively coupled plasma mass spectrometry; multielemental trace analysis; standard reference materials.

Laser ablation due its capability of a complete ablation of any solid material (independent from its physical and chemical properties) is the most frequent universal sample introduction technique for solid samples directly in an inductively coupled plasma of a mass spectrometer (ICP-MS) or an optical emission spectrometer (ICP-OES). Especially laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), which in contrast to non-mass spectrometric methods

allows precise isotope ratio measurements as well, is gaining increasing importance for sensitive trace analysis of solid samples in recent years [1, 2] in different application fields. The largest area of application LA-ICP-MS is the investigation of geological materials [2–10]. With growing extent this solid state analytical method is used for multielement trace analysis in environmental and biological research [11, 12], in material research of metallic, semiconducting [13] – often with high-purity – and insulating materials (such as ceramics and glasses, which are difficult to dissolve) [14–16] and for the determination of long-lived radionuclides in non-conducting materials (e.g. concrete) [17, 18]. In contrast to the other laser mass spectrometric techniques, (e.g. LIMS-laser ionization mass spectrometry) LA-ICP-MS uses the evaporation of sample material by a laser beam in an argon atmosphere under normal pressure. The ablated (evaporated) material is transported with argon in an inductively coupled argon plasma and is ionized at plasma temperatures of 6000–8000 K. In the argon plasma positively and negatively charged ions, are formed, electrons and neutrals. In general, the positively charged ions are separated according to their mass to charge ratio (and energy to charge ratio) using a double-focusing sector field, a quadrupole, a TOF mass spectrometers or in an ion trap.

A rapid survey analysis of an unknown material can be performed by LA-ICP-MS (much faster than by spark source mass spectrometry -SSMS or glow discharge mass spectrometry-GDMS) with respect to their major, minor and trace element composition (finger printing). Without any quantification procedure the unknown sample can be characterized semi-

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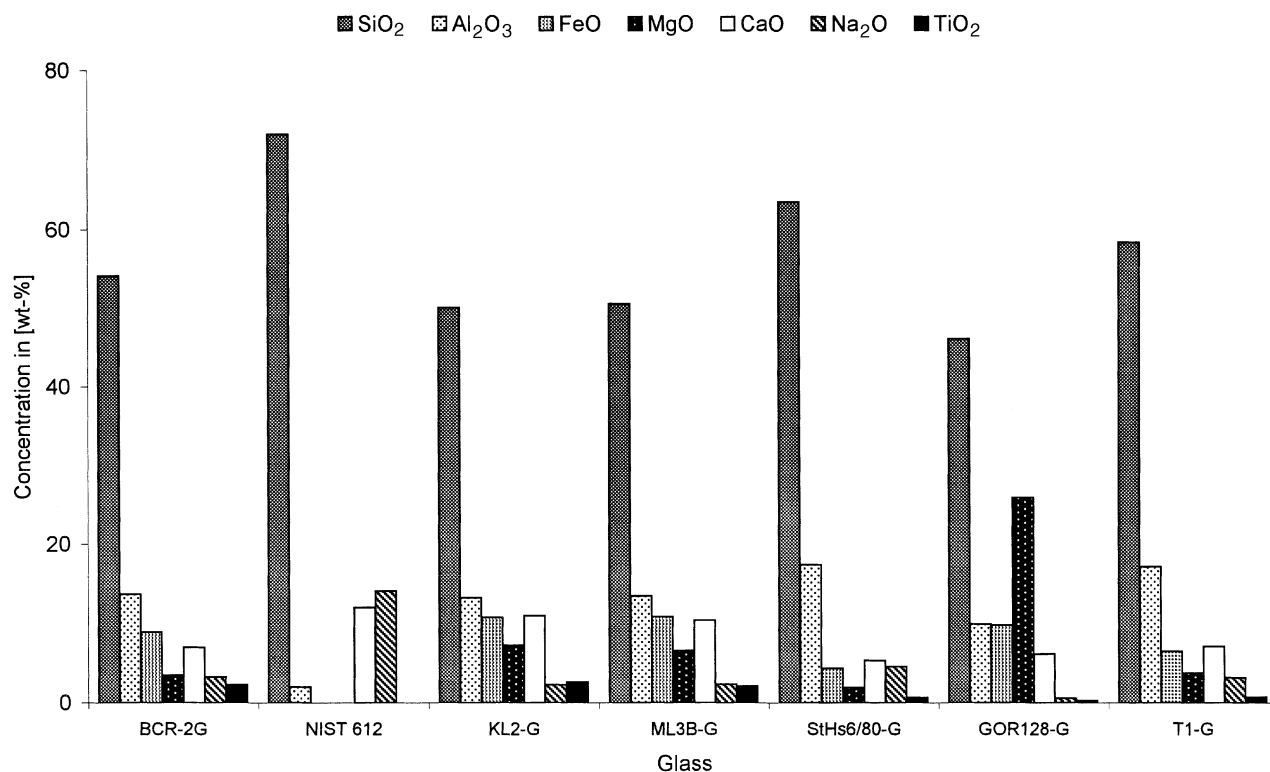


Fig. 1. Matrix composition of geological glasses and NIST SRM 612

quantitatively in respect to elemental concentration within an error factor of 2 to 3. For semiquantitative analysis one element concentration (e.g. the concentration of a matrix element which can be used as internal standard element) should be known. By analogy with other solid-state mass-spectrometric techniques (e.g., SSMS, SIMS – secondary ion mass spectrometry, GDMS) the analytical results were quantified by using solid standard reference materials with similar matrix composition. Thereby the measured analytical results of LA-ICP-MS were corrected using experimentally determined relative sensitivity coefficients (RSC of a chemical element = ratio of measured (experimental) to certified (true) element concentration in a given matrix) – under application of standard reference material (SRM). Quantification of the analytical results in LA-ICP-MS proves to be difficult if no suitable standard reference material (with the same or similar matrix composition) is available. In such case special calibration techniques using aqueous standard solutions were elaborated in different laboratories. Houk and associates [19] proposed a calibration procedure which combined the straightforward solution calibration with laser ablation for direct analysis of solids using dry aerosol particles

from both sources transported in an inductively coupled plasma. This technique using solution standards to calibrate the response of LA-ICP-MS does not require the knowledge of an internal standard element. But different evaporation rates of elements in solid sample and in solution could influence the precision and accuracy of analytes. Similar calibration procedures using the tandem introduction of dried aerosols of standard solution with laser ablated particles in inductively coupled plasma of the mass spectrometer are performed by Günther et al. [20] and Krause et al. [21]. This procedure requires an internal standard with known concentration.

Furthermore, the quantification can be performed by preparing solid synthetic (matrix-matched) standard materials [22, 23], e.g., using high-purity compounds for the syntheses of the matrix composition which were doped with trace elements in the analyzing concentration range [13, 15, 24]. Such synthetic laboratory standards are appropriate for quantification of analytical results in all solid state mass spectrometric techniques (e.g., SSMS, GDMS, SIMS, ETV-ICP-MS, LA-ICP-OES and others). Becker et al. [13] prepared for example a GaAs crystal as laboratory standard which was doped with known concentrations

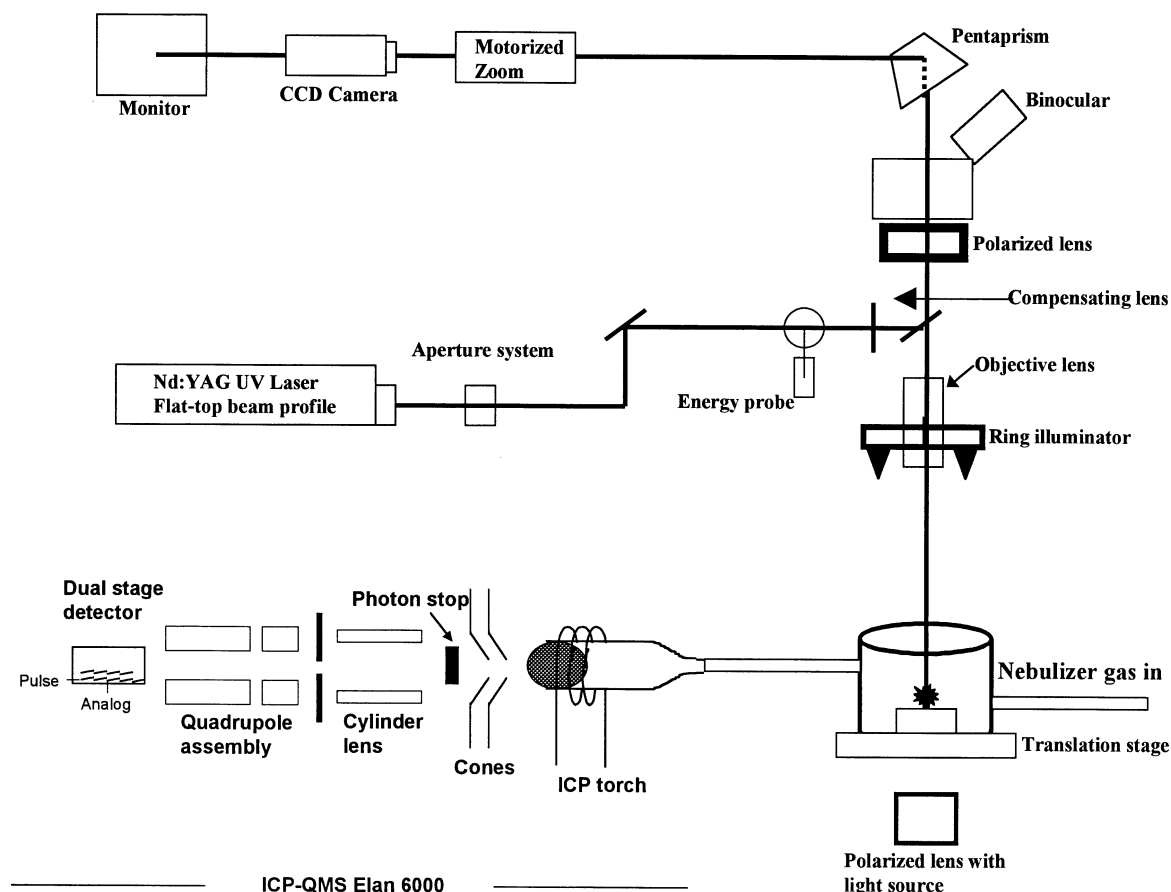


Fig. 2. Experimental arrangement of LA-ICP-MS

Table 1. Experimental parameter

| <i>Elan 6000 ICP-MS</i> | |
|------------------------------|--|
| Rf power | 1000 W |
| Coolant gas flow rate | 14 L/min |
| Auxiliary gas flow rate | 0.8 L/min |
| Carrier gas flow rate | 0.6 L/min |
| Mass resolution $m/\Delta m$ | 300 |
| Acquisition mode | peak hopping |
| Detector mode | dual |
| Auto lens | on |
| Points per peak | 1 |
| Dwell time | 10 ms |
| No. of sweeps | 10 |
| No. of readings | 1 |
| No. of replicates | 5 |
| Sampling cone | nickel with a 1.1 mm orifice |
| Skimmer cone | nickel with a 0.9 mm orifice |
| <i>Laser ablation</i> | |
| Laser ablation system | CETAC LSX-200 |
| Wavelength | 266 (4 th harmonic of Nd:YAG laser) |
| Repetition frequency | 20 Hz |
| Pulse energy | 5 mJ |
| Laser power density | $1.1 \cdot 10^9$ W/cm ² |
| Spot diameter | 340 μ m |
| Pre-ablation time | 10 s |
| Method | single line scan |

of different elements in the μ g/g range by vertical Bridgeman technique. This multielement GaAs crystal was used for determination of relative sensitivity coefficients of doping elements in the given matrix by LA-ICP-MS, SSMS, radio-frequency GDMS and SIMS. Durrant [2] concluded from the results that LA-ICP-MS competes favourably with other state-of-art solid state techniques.

Fortunately, for geological materials a lot of standard reference materials are available, but often in the literature the use of NIST glass standard reference materials [25] is described. The application of glass standard reference materials from NIST for the quantification of analytical results of geological samples is sometimes problematical due to different composition of matrix and trace elements compared to geological samples and matrix effects were observed [26]. Figure 1 compares the matrix composition of glass NIST SRM 612 with those in this work to analyze geological samples. It is demonstrated in Fig. 1 that the matrix composition of the fused BCR-2G geological glass standard better agrees with those of the geological

samples of interest. LA-ICP-MS on direct fusion whole rock glasses was proposed by Fedorowich et al. [27] as a rapid method for the determination of trace elements in homogeneous geological samples. In analogy trace elements in such homogeneous geological glasses after melting and quenching of the rock powder as standard reference materials by SSMS and LIMS were analyzed by Seufert and Jochum [28] but a relatively high amount of sample (about 100 g rock powder) for preparation of geological glasses and special melting apparatus for rocks [29] is required.

Furthermore, homogeneous laser ablation targets from inhomogeneous powdered rock sample were prepared by fusion with a lithium-borate mixture [10, 30–32] under destroying of the original crystal structure of geological material.

Jochum et al. [33] described comparative measurements on a series of fused geological glasses which should be applied as reference materials in microanalysis. In this working group SSMS has been applied for trace element determination in these homogeneous geological standard reference materials [34]. In this work SSMS with multiion counting technique (with 20 separated channeltrons of 1.8 mm width) [35] which allows the simultaneous electrical ion detection with increased sensitivity compared to SSMS with ion detection using a photoplate by factor of 20 was applied. The precision of analytical results – which are in good agreement with the reference values – ranges between 2–7%.

The aim of this work is to study the capability of the more powerful LA-ICP-MS on the determination of trace elements in five geological glass samples which are characterized by different analytical techniques.

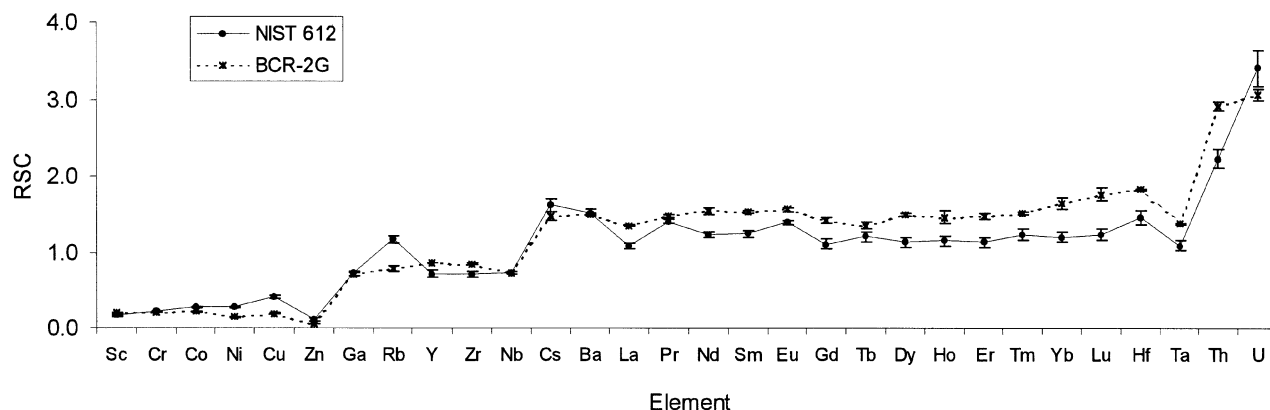


Fig. 3. Comparison of RSCs in the BCR-2G (basaltic glass prepared from BCR-2 reference material) and in NIST SRM 612 measured by LA-ICP-MS (internal standard element: Sr)

Experimental

Instrumental and Measurement Procedure

A laser ablation system (LSX 200, CETAC Technologies Inc., Omaha, USA) coupled to the inductively coupled plasma ion source of the ICP-MS (ELAN 6000, Perkin Elmer, Sciex Corp., Norwalk, CT, USA) was used in these experiments. Figure 2 shows the experimental setup of LA-ICP-MS. The UV wavelength of a Nd:YAG laser (4th harmonic, 266 nm) is used for laser ablation. The experimental parameters of laser ablation and mass spectrometric measurements are summarized in Table 1. Using the auto lens system of Elan 6000 the lens voltage was dynamically set to the optimal value for each mass. The rf power of ICP and the carrier gas flow rate are optimized using the glass NIST SRM 612 in respect to maximum ion intensity of $^{88}\text{Sr}^+$. Strontium was chosen as internal standard element. Three repetitions ($N=3$) of LA-ICP-MS measurements on three different places on the BCR-2G, glass NIST SRM 612 and the geological glasses were performed.

Samples and Sample Preparation

Reference material BCR-2G (basaltic glass prepared from BCR-2 reference material [36, 37]) and NIST glass SRM 612 were used for the determination of relative sensitivity coefficients in LA-ICP-MS. Five geological samples (basalt samples: KL2 and ML3B from the Kilauea and Mauna Loa volcanoes of Hawaii, respectively [38] the andesite StHs6/80, an ash from the St. Helens (USA) eruption, the komatiite GOR-128 from the Gorgona Island [39] and a tonalite T1 from the Italian Alps [40]) were investigated by LA-ICP-MS.

Strontium was chosen as internal standard element for the determination of RSCs in both reference materials and in the geological glasses as well. The homogeneous geological glass targets were prepared by D. Dingwell (University of Bayreuth) using a special melting technique, which is described elsewhere [29]. The homogeneity of prepared fused glass targets was checked by secondary ion mass spectrometry (SIMLAB 410, VG Scientific).

Results and Discussion

In Fig. 3 the results of determination of RSCs in the BCR-2G (basaltic glass prepared from BCR-2 refer-

Table 2. Results of LA-ICP-MS on glass geological standard in comparison to reference value [33] (concentration in µg/g; ¹ RSD < 5%; ² RSD 5–15%; ³ RSD > 15%)

| Element | Basalt KL2-G measured value | Basalt KL2-G reference value | Basalt ML3B-G measured value | Basalt ML3B-G reference value | Andesite STHs6/80-G measured value | Andesite STHs6/80-G reference value |
|---------|--------------------------------|---------------------------------|---------------------------------|----------------------------------|---------------------------------------|--|
| Cr | 286 ± 4 | 300 ²⁾ | 143 ± 6 | 160 ³⁾ | 17.0 ± 0.1 | 17 ³⁾ |
| Co | 43.0 ± 1.1 | 42 ¹⁾ | 38.2 ± 0.7 | 37 ¹⁾ | 16.8 ± 0.7 | 12 ³⁾ |
| Zn | 120 ± 27 | 111 ²⁾ | 76.7 ± 12.5 | 110 ²⁾ | (169 ± 1)* | 65 ²⁾ |
| Cu | 104 ± 5 | 86 ²⁾ | 108 ± 2 | 120 ³⁾ | 68 ± 3 | 44 ³⁾ |
| Ga | 19.4 ± 0.4 | 19 ²⁾ | 14.7 ± 0.4 | 20 ²⁾ | 29.8 ± 1.2 | 19 ²⁾ |
| Rb | 8.6 ± 0.3 | 9.42 ²⁾ | 5.1 ± 0.4 | 6.05 ²⁾ | 43 ± 2 | 31 ²⁾ |
| Y | 26.4 ± 1.0 | 26.9 ²⁾ | 24.0 ± 0.6 | 24.3 ²⁾ | 11.4 ± 0.1 | 11 ²⁾ |
| Zr | 158 ± 6 | 159 ²⁾ | 126 ± 2 | 126 ²⁾ | 119 ± 1.5 | 119 ²⁾ |
| Nb | 15.1 ± 0.6 | 16.2 ²⁾ | 8.5 ± 0.2 | 8.97 ²⁾ | 7.4 ± 0.02 | 7.7 ²⁾ |
| Sn | 1.98 ± 0.24 | 1.6 ³⁾ | 0.67 ± 0.02 | – | 0.80 ± 0.03 | 0.7 ³⁾ |
| Cs | 0.10 ± 0.02 | 0.12 ²⁾ | 0.12 ± 0.01 | 0.15 ²⁾ | 1.91 ± 0.28 | 2 ²⁾ |
| Ba | 117 ± 6 | 126 ¹⁾ | 77.4 ± 2.0 | 80 ²⁾ | 297 ± 4 | 302 ¹⁾ |
| La | 12.5 ± 0.6 | 13.2 ¹⁾ | 8.8 ± 0.1 | 9.04 ¹⁾ | 11.2 ± 0.2 | 11.9 ¹⁾ |
| Pr | 4.50 ± 0.21 | 4.62 ¹⁾ | 3.48 ± 0.05 | 3.43 ¹⁾ | 3.17 ± 0.02 | 3.17 ²⁾ |
| Nd | 2.11 ± 0.9 | 22.1 ²⁾ | 17.0 ± 0.1 | 16.8 ¹⁾ | 12.3 ± 0.3 | 12.8 ¹⁾ |
| Sm | 5.54 ± 0.30 | 5.63 ¹⁾ | 4.91 ± 0.13 | 4.78 ¹⁾ | 2.70 ± 0.07 | 2.83 ¹⁾ |
| Eu | 1.92 ± 0.11 | 1.96 ²⁾ | 1.68 ± 0.06 | 1.68 ¹⁾ | 0.97 ± 0.02 | 0.959 ¹⁾ |
| Gd | 5.91 ± 0.32 | 5.97 ¹⁾ | 5.29 ± 0.20 | 5.14 ¹⁾ | 2.33 ± 0.09 | 2.53 ²⁾ |
| Tb | 0.96 ± 0.05 | 0.96 ²⁾ | 0.87 ± 0.01 | 0.806 ¹⁾ | 0.37 ± 0.01 | 0.365 ¹⁾ |
| Dy | 5.22 ± 0.34 | 5.33 ²⁾ | 4.71 ± 0.12 | 4.78 ¹⁾ | 1.94 ± 0.05 | 2.33 ¹⁾ |
| Ho | 1.00 ± 0.08 | 0.988 ¹⁾ | 0.93 ± 0.04 | 0.908 ¹⁾ | 0.39 ± 0.01 | 0.408 ¹⁾ |
| Er | 2.44 ± 0.15 | 2.65 ¹⁾ | 2.44 ± 0.09 | 2.47 ¹⁾ | 1.04 ± 0.02 | 1.14 ²⁾ |
| Tm | 0.33 ± 0.01 | 0.33 ¹⁾ | 0.33 ± 0.01 | 0.32 ²⁾ | 0.16 ± 0.01 | 0.16 ¹⁾ |
| Yb | 2.05 ± 0.21 | 2.11 ¹⁾ | 2.00 ± 0.09 | 2.07 ¹⁾ | 1.01 ± 0.03 | 1.12 ¹⁾ |
| Lu | 0.26 ± 0.04 | 0.294 ²⁾ | 0.26 ± 0.01 | 0.289 ¹⁾ | 0.13 ± 0.01 | 0.167 ¹⁾ |
| Hf | 4.03 ± 0.37 | 4.12 ¹⁾ | 3.19 ± 0.09 | 3.35 ²⁾ | 2.57 ± 0.58 | 3.17 ²⁾ |
| Ta | 0.95 ± 0.05 | 0.955 ¹⁾ | 0.53 ± 0.05 | 0.559 ¹⁾ | 0.39 ± 0.01 | 0.955 ¹⁾ |
| Pb | 2.67 ± 0.20 | 2.23 ²⁾ | 1.56 ± 0.22 | 1.45 ¹⁾ | – | – |
| Th | 0.93 ± 0.07 | 1.08 ²⁾ | 0.49 ± 0.01 | 0.558 ¹⁾ | 1.90 ± 0.03 | 2.23 ¹⁾ |
| U | 0.54 ± 0.04 | 0.557 ²⁾ | 0.39 ± 0.01 | 0.459 ²⁾ | 1.01 ± 0.03 | 1.08 ²⁾ |

* Possible interferences.

ence material) and glass NIST SRM 612 are compared. As observed in former experiments [18, 31, 32], the experimentally determined RSCs for most elements varied in LA-ICP-MS for both reference materials between 0.2 and 3, therefore a semiquantitative determination of trace elements without a SRM is possible with an error factor in this range. In general a similar dependence for RSCs from mass for different elements compared to the former studies using a Elan 5000 [31] is found, in this work the RSCs increases with increasing masses due to increasing elemental sensitivity under optimized experimental conditions using the ICP-MS Elan 6000. LA-ICP-MS measurements (ICP-MS: Elan 6000) on fused lithium borate targets of zeolites yielded also a similar RSC distribution over mass [32].

Furthermore, by investigation of $\text{La}_{0.6}\text{Sr}_{0.35}\text{MnO}_3$ perovskite in comparison to the initial compounds (mixture of carbonates and oxides of La, Sr and Mn) we found in LA-ICP-MS in comparison to ICP-MS measurements of a multielement standard solution a similar dependence of RSCs for a number of trace elements investigated [41]. Different RSCs in LA-ICP-MS for solid material and in ICP-MS of aqueous solution with a similar matrix composition would be expected if fractionation effects during the laser ablation of ceramic material occur.

In this work the RSCs of rare earth elements (REE) in glass NIST SRM 612 were determined by LA-ICP-MS to be approximately 1, that means no fractionation effects of REE were observed in this glass matrix. In general the REE were measured in BCR-2G with higher sensitivity and following higher RSCs than 1 are

observed. This effect could be explained by different matrix composition of these two reference materials. Possible fractionation effects in LA-ICP-MS were investigated in two forthcoming papers [32, 42]. In both studies elemental fractionation was not observed using a laser power density in the range of 10^9 W/cm^2 .

The homogeneity of investigated geological glass materials as one of the most important features of reference materials was investigated for SiO_2 , La and Ba (by SIMS, EMPA – electron microprobe analysis and SR-XRF – synchrotron radiation induced X-ray fluorescence analysis [33]). Major and trace element distributions are constant with the analytical uncertainties of the analytical technique used ($\approx 1\text{--}3\%$). In our laboratory the homogeneity for some matrix elements was proofed by SIMS measurements. In these investigations a homogeneous element distribution for geological glasses was found.

In Table 2 the analytical results of trace element determination (using BCR-2G as standard reference material) by LA-ICP-MS in two basalt samples (KL2-G and ML3B-G) and in the andesite (StHs6/80-G) with the reference values (mean values of SSMS, LIMS, LA-ICP-MS, PIXE, NAA, TIMS) [33] are compared. The relative standard deviation of the determination of the concentration in geological samples on fused glass targets is mostly 2–10%. For the most elements a good agreement with the reference values was found. The accuracy was best for Zr, Ba, Pr, Sm, Eu, Gd, Ho < 5%; for Er, Cr < 10%. Problematic elements are Ga, Ni, Rb, Sn, Cs and Cu with accuracy of > 10%. The quantitative determination of some elements is disturbed by isobaric interferences with possible

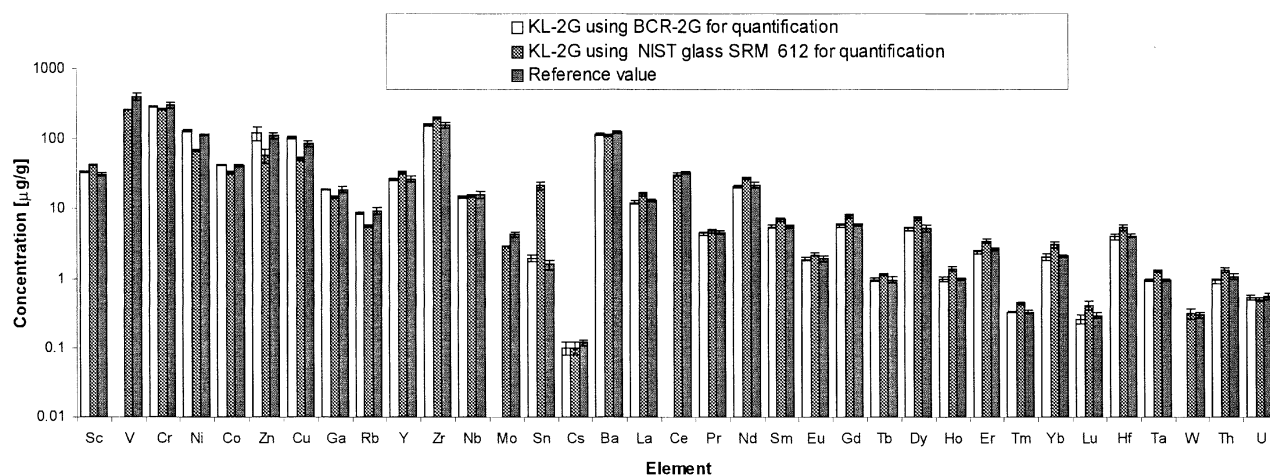


Fig. 4. Comparison of LA-ICP-MS results for trace elements in the basalt sample KL2-G [using for quantification different standard glass materials (BCR-2G and NIST SRM 612)] with reference values [33]

Table 3. Comparison of analytical results on geological glasses GOR128-G (komatiite) and T1-G (tonalite) using BCR-2G and NIST 612 for quantification (concentration in $\mu\text{g/g}$; ¹ RSD < 5%; ² RSD 5–15%; ³ RSD > 15%)

| Element | GOR128-G (measured using BCR-2G) | GOR128-G (measured using NIST 612) | GOR128-G reference value | T1-G (measured using BCR-2G) | T1-G (measured using NIST 612) | T1-G reference value |
|---------|----------------------------------|------------------------------------|--------------------------|------------------------------|--------------------------------|----------------------|
| Sc | 33.0 ± 1.0 | 39.3 ± 1.2 | 30 ¹⁾ | 27.8 ± 0.4 | 31.7 ± 0.5 | 26.6 ¹⁾ |
| Cr | 2422 ± 160 | 2315 ± 153 | 2120 ¹⁾ | 22.0 ± 1.1 | 21.0 ± 1.0 | 19 ³⁾ |
| Ni | (1627 ± 81) | 815 ± 42 | 1070 ¹⁾ | 15.9 ± 1.2 | 8.62 ± 0.65 | 14 ³⁾ |
| Co | 105 ± 7 | 84.0 ± 5.5 | 77 ²⁾ | 21.7 ± 0.7 | 18.2 ± 0.6 | 18.4 ²⁾ |
| Zn | 50.0 ± 13.1 | 25.1 ± 6.6 | 76 ²⁾ | (137 ± 4)* | 52 ± 2 | 73 ²⁾ |
| Cu | (93 ± 5) | 40.9 ± 2.3 | 40 ²⁾ | 22.9 ± 0.9 | 9.9 ± 0.4 | 38 ³⁾ |
| Ga | 9.0 ± 0.8 | 6.78 ± 0.58 | 8.7 ³⁾ | 19.6 ± 0.1 | 18.9 ± 0.1 | 18 ²⁾ |
| Rb | <0.4 | <0.4 | 0.382 ¹⁾ | 88 ± 1 | 61.7 ± 1.0 | 78.4 ²⁾ |
| Y | 11.9 ± 0.4 | 13.7 ± 0.5 | 11.1 ¹⁾ | 23.7 ± 0.5 | 26.6 ± 0.5 | 22.9 ¹⁾ |
| Zr | 10.6 ± 0.3 | 12.1 ± 0.3 | 9.84 ²⁾ | 146 ± 3 | 164 ± 3 | 146 ²⁾ |
| Nb | 0.09 ± 0.02 | 0.09 ± 0.02 | 0.11 ²⁾ | 8.5 ± 0.1 | 8.4 ± 0.03 | 10.2 ²⁾ |
| Sn | (1.06 ± 0.2) | (10.2 ± 1.8) | - | (1.15 ± 0.10) | (11.6 ± 1.0) | 4 ³⁾ |
| Sr | 0.35 ± 0.10 | 0.30 ± 0.09 | 0.27 ²⁾ | 2.11 ± 0.09 | 2.02 ± 0.09 | 3 ²⁾ |
| Ba | 1.10 ± 0.09 | 1.09 ± 0.08 | 1.1 ²⁾ | 340 ± 11 | 345 ± 11 | 387 ²⁾ |
| La | 0.11 ± 0.02 | 0.13 ± 0.02 | 0.125 ²⁾ | 58.3 ± 2.0 | 71.3 ± 2.4 | 70 ²⁾ |
| Pr | 0.10 ± 0.01 | 0.10 ± 0.01 | 0.1 ²⁾ | 10.9 ± 0.2 | 11.5 ± 0.2 | 12 ²⁾ |
| Nd | 0.76 ± 0.06 | 0.91 ± 0.08 | 0.803 ²⁾ | 35.5 ± 1.2 | 44.1 ± 1.5 | 41.5 ²⁾ |
| Sm | 0.50 ± 0.04 | 0.55 ± 0.11 | 0.574 ²⁾ | 5.76 ± 0.30 | 6.97 ± 0.36 | 6.71 ¹⁾ |
| Eu | 0.28 ± 0.01 | 0.30 ± 0.02 | 0.272 ²⁾ | 1.08 ± 0.06 | 1.20 ± 0.07 | 1.24 ²⁾ |
| Gd | 1.13 ± 0.06 | 1.37 ± 0.07 | 1.25 ²⁾ | 4.44 ± 0.2 | 5.49 ± 0.24 | 5.05 ²⁾ |
| Tb | 0.27 ± 0.02 | 0.29 ± 0.02 | 0.235 ²⁾ | 0.70 ± 0.02 | 0.76 ± 0.02 | 0.809 ²⁾ |
| Dy | 1.95 ± 0.07 | 2.40 ± 0.09 | 1.99 ²⁾ | 3.72 ± 0.17 | 4.70 ± 0.21 | 4.52 ¹⁾ |
| Ho | 0.44 ± 0.01 | 0.53 ± 0.02 | 0.436 ²⁾ | 0.74 ± 0.04 | 0.91 ± 0.05 | 0.82 ²⁾ |
| Er | 1.33 ± 0.12 | 1.65 ± 0.12 | 1.48 ²⁾ | 2.06 ± 0.1 | 2.65 ± 0.14 | 2.41 ²⁾ |
| Tm | 0.21 ± 0.02 | 0.24 ± 0.02 | 0.187 ²⁾ | 0.31 ± 0.03 | 0.37 ± 0.03 | 0.35 ²⁾ |
| Yb | 1.33 ± 0.07 | 1.76 ± 0.10 | 1.48 ²⁾ | 1.96 ± 0.05 | 2.64 ± 0.06 | 2.41 ¹⁾ |
| Lu | 0.18 ± 0.01 | 0.25 ± 0.01 | 0.22 ²⁾ | 0.28 ± 0.01 | 0.39 ± 0.01 | 0.354 ²⁾ |
| Hf | 0.34 ± 0.01 | 0.41 ± 0.02 | 0.357 ¹⁾ | 3.17 ± 0.13 | 3.84 ± 0.18 | 4.13 ¹⁾ |
| Ta | <0.02 | <0.02 | 0.02 ³⁾ | 0.38 ± 0.01 | 0.47 ± 0.01 | 0.477 ¹⁾ |
| Pb | 0.64 ± 0.05 | 0.21 ± 0.02 | 0.42 | 17.9 ± 1.0 | 6.35 ± 0.34 | 11 ²⁾ |
| Th | <0.008 | <0.008 | 0.007 ²⁾ | 23.3 ± 0.9 | 29.8 ± 1.2 | 31.3 ²⁾ |
| U | 0.014 ± 0.001 | 0.012 ± 0.001 | 0.013 ²⁾ | 1.43 ± 0.02 | 1.39 ± 0.02 | 1.69 ²⁾ |

* Possible contamination.

molecular ions (e.g., $^{52}\text{Cr}^{+40}\text{Ar}^{12}\text{C}^{+}$; $^{64}\text{Ni}^{+40}\text{Ar}^{24}\text{Mg}^{+}$ and $^{36}\text{Ar}^{28}\text{Si}^{+}$; $^{63}\text{Cu}^{+23}\text{Na}^{40}\text{Ar}^{+}$ and others) therefore other isotopes were chosen for quantification. Even an empirical correction of possible interferences which is usually applied in quadrupole based LA-ICP-MS is sometimes insufficient. An accurate determination of these elements can be performed by separation of such interferences of molecular ions and atomic ions of analyte using double-focusing sector field LA-ICP-MS at the required mass resolution [43]. Detailed discussion of the capability of different trace analytical methods which are used for characterization of reference geological glasses with respect to accuracy and uncertainty for different trace elements are given in [33]. Figure 4 compares the analytical results by LA-ICP-MS on the basalt glass (KL2-G) using the BCR-2G and NIST SRM 612 for quantification as well. For the most elements (except Zn and Sn – the reference value for Sn is not certified) a sufficient agreement of analytical results was found. But nevertheless the use of BCR-2G as reference material lead to result which are in a better agreement with the reference values. Best agreement of LA-ICP-MS values and reference values has been found for KL-2G and ML3B-G (accuracy < 5% for most of the elements). In our measurements the application of NIST SRM 612 for

quantification of geological glasses yielded in general significantly higher Sn concentrations (about one order of magnitude higher using both Sn isotopes ^{118}Sn and ^{120}Sn) compared to the application of BCR-2G as reference material.

Table 3 compares the analytical results on geological glasses GOR128-G (komatiite) and T1-G (tonalite) using BCR-2G and NIST 612 for quantification. The quantification of analytical LA-ICP-MS results using both standard reference materials leads for many elements to comparable trace element concentrations. Furthermore, the results in Table 3 demonstrate the limits of the applied analytical method also, namely by the determination of some difficult to analyse elements especially in higher concentration range [such as Cr and Ni, for the determination of such elements should chosen alternative (less sensitive) solid analytical techniques] or at lower concentration (e.g., Cu and Zn – interference with $^{26}\text{Mg}^{40}\text{Ar}^{+}$ on $^{66}\text{Zn}^{+}$). The application of glass NIST SRM 612 for Sn determination yielded – as discussed above – too high values for all geological glasses. Furthermore the use of BCR-2G as reference material gives more accurate results for all samples (except for T1-G where LA-ICP-MS results determined with NIST SRM 612 are closer to the reference values for all REEs – the reason for this is unknown yet). Therefore, for trace element determina-

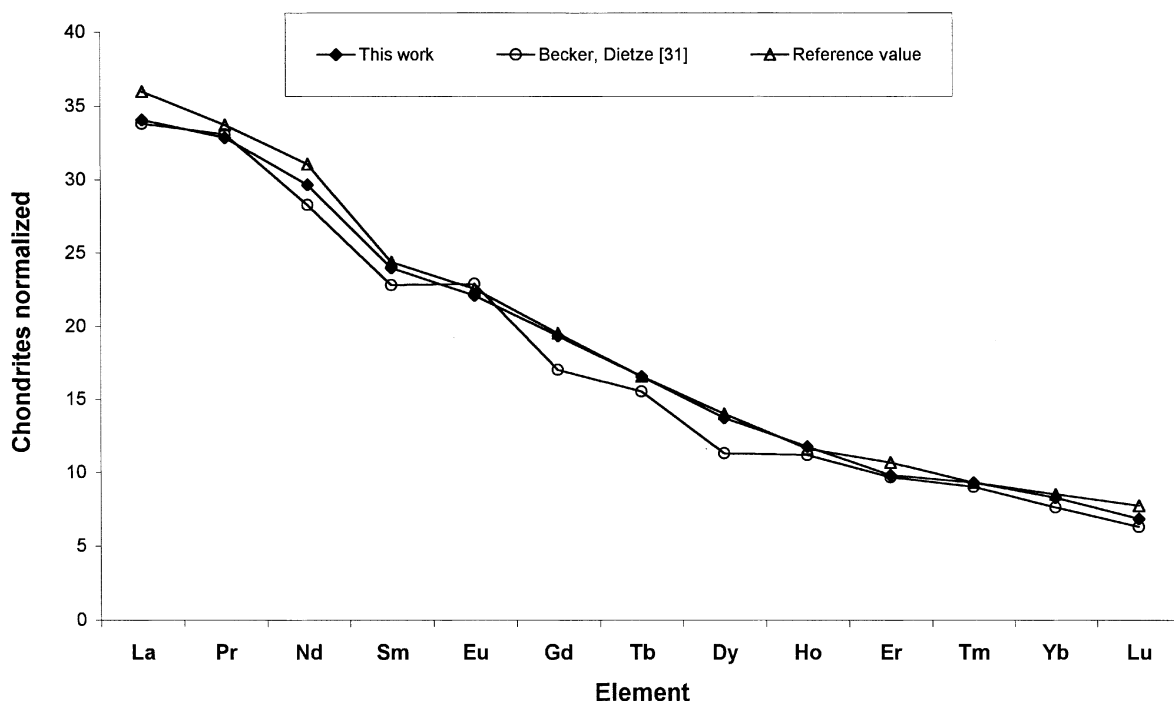


Fig. 5. Comparison of former data, new data and reference values for KL2-G normalized to chondrites

Table 4. Detection limits (in $\mu\text{g/g}$) for trace elements in geological glass samples

| Element | Detection limits | Element | Detection limits |
|---------|------------------|---------|------------------|
| Sc | 2.2 | Pr | 0.01 |
| Cr | 3.5 | Nd | 0.04 |
| Ni | 4.7 | Sm | 0.02 |
| Co | 0.12 | Eu | 0.02 |
| Zn | 45 | Gd | 0.05 |
| Cu | 3.7 | Tb | 0.01 |
| Ga | 0.9 | Dy | 0.03 |
| Rb | 0.5 | Ho | 0.01 |
| Sr | 0.29 | Er | 0.02 |
| Y | 0.9 | Tm | 0.01 |
| Zr | 0.08 | Yb | 0.04 |
| Nb | 0.03 | Lu | 0.01 |
| Sn | 0.005 | Hf | 0.01 |
| Cs | 0.05 | Ta | 0.01 |
| Ba | 0.03 | Th | 0.004 |
| La | 0.007 | U | 0.005 |

tion in geological glasses we propose to use BCR-2G as reference material.

In comparison to a former investigation on these geological glasses [31] accuracy of the method is improved in this work due to new experimental conditions as demonstrated in Fig. 5 for geological glass KL2-G.

The experimentally determined detection limits of the gas blank (due to lack of high-purity glass sample) in LA-ICP-MS using an ELAN 6000 are summarized in Table 4. The detection limits using the 3σ criteria (the limit of detection is given by $m_b + 3\sigma_b$, where m_b is the mean value of the blank measurements and σ_b the standard deviation of five independent measurements of the blank value) for the gas blank are in the lower sub $\mu\text{g/g}$ range. In general higher detection limits were measured for the light elements due to lower sensitivity, possible interferences with molecular ions, higher background or memory effects in the mass spectrometer.

The detection limits of elements can be improved significantly by application of double-focusing sector field mass spectrometer for LA-ICP-MS due a lower background and a higher elemental sensitivity [43].

Conclusions

The preparation of homogeneous glass targets for LA-ICP-MS from powdered samples is a practicable method for sample preparation for multielement bulk analysis in geological science. But this sample preparation technique of homogeneous glass targets is

expensive in comparison to other techniques, e.g., the fusion with a lithium borate mixture. The applied technique by LA-ICP-MS yielded on fused geological glasses for most trace elements concentrations with good accuracy and better precision compared to the results on fused lithium borate targets. Possible memory effects of the LA-ICP-MS due to relatively high sample input during the measurements are solved by careful cleaning of the ICP torch, sampler and skimmer cones, photon stop and ion optical lens.

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