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Accurate whole-rock geochemistry analysis by combined ICP-OES and LA-ICP-MS instruments

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Short Note

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ABSTRACT

ICP-OES and LA-ICP-MS instruments routinely used to assess the geochemical properties of the various natural and synthetic materials. In this contribution, the analytical routines and method development procedures of the ICP-OES and LA-ICP-MS facilities installed at the İstanbul University-Cerrahpaşa Geological Engineering Department, Geochronology and Geochemistry Laboratory have been evaluated using well-known international rock standards. Sample preparation techniques, method development, experimental setup and measurement conditions for the both ICP-OES and LA-ICP-MS instruments were discussed and specific analyze results of NIST SRM 614, BCR-2, AGV-2, BCR-2G and AGV-2G were evaluated. Flux-free USGS glass standards were produced by in-house techniques and flux-bearing glasses were produced by fusion of sample with the mixture of ultra-pure lithium-tetraborate, lithium metaborate and lithiumbromide were evaluated and compared with the well-known reference values in the literature. Relative standard deviation (RSD) values for the major oxide measurements for standards given range of 0.0 wt. % to 1.5 wt. %. RSD values for the trace and rare-earth-elements values were mainly lower than 10 wt. %. The results confirm that the both flux-bearing and flux-free glasses reasonably match with the worldwide inter-laboratory values for international standards samples. The combination of these two instruments can be used to conduct geochemistry of various solid earth materials.

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1. Introduction

Whole-rock geochemical data is the benchmark of the petrological studies and different aspects of the geological research. From the beginning of the 1970s large compilation and datasets from the various parts of the world have been created for igneous, metamorphic and sedimentary petrology studies by using whole-rock geochemistry (Pearce et al.,

1984). Majority of these data have been determined successively by instruments of X-ray Fluorescence (XRF, Potts and Webb, 1992), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Jenner et al., 1990), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES; Dahlquist and Knoll, 1978) and many different techniques outlined in Jochum et al., (2011).

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Together with the XRF techniques, ICP-OES also frequently used to assess the whole-rock geochemical or specific element contents of the desired samples (Jarvis and Jarvis, 1992; Navarro et al., 2002; Alomary and Belhadj, 2007). ICP-OES is a spectrometric technique to assess the elemental content of the aqueous solutions. Sample preparation techniques, dilution factors, element infiltration and interpretation of the output data significantly affect the results of the ICP-OES instrumentation. However, ICP-OES routinely used to analyze for the major oxide elements and high concentration (>100 ppm) element ratios (Elburg et al., 2012; Shao et al., 2017).

By the development of the combined analysis of Laser Ablation (LA) and ICP-MS, these combined instruments became also a powerful and routine tool to detect the whole rock geochemistry of the geological samples (Longerich et al., 1996; Norman et al., 1996; Günther et al., 2001; Petrelli et al., 2008; Tamura et al., 2015). Apart from the spot analysis of the actual samples such as minerals, glass or rock powder pellets; sample preparation techniques such as powdering (Imai, 1990), flux-free fusion (Fedorowich et al., 1993; Norman et al., 1996), Pt-crucible flux-free fusion (Chen et al., 2000), Pt-capsule flux-free fusion (Kurosawa et al., 2006) and lithium borate ($\text{Li}_2\text{B}_4\text{O}_7$) fusion (Günther et al., 2001; Eggins, 2003) are frequently used to create samples that are suitable for LA-ICP-MS measurements.

In this contribution, we will explore the analytical capabilities of the ICP-OES and LA-ICP-MS instruments installed at the Geochronology and Geochemistry Laboratory of İstanbul University-Cerrahpaşa, Faculty of Engineering, Department of Geological Engineering. Developed methods to measure the whole rock geochemistry of the natural rock associations for combined ICP-OES and LA-ICP-MS and evaluated experimental scheme of the analysis will be checked by measuring the international reference samples of BCR-2 (and BCR-2G- flux free), AGV-2 (and AGV-2G flux free) by USGS (United States Geological Survey) and SRM NIST 614. In the following chapter, we first give the general outlines of the experimental setup of the ICP-OES and LA-ICP-MS for the whole rock geochemistry analysis; we will explain the samples preparation techniques, then we

further discuss the data acquisition, data interpretation and subsequent results.

2. Instrumentation

We use Perkin Elmer AVIO 200 ICP-OES together with Perkin Elmer NexION 2000 ICP-MS combined with ESI NWR213 solid state laser for the whole rock analytical measurements. First we present the general configuration, sample preparation and experimental conditions of the ICP-OES instrument, and then we will evaluate the general characteristics of the LA-ICP-MS configuration.

2.1. Sample Dissolution Procedures and Experimental Conditions for ICP-OES

Rock powders of the BCR-2 and AGV-2 used for the whole rock measurements. We mainly measure the major oxide elements (analytes) to deduce the desired content of the studied samples with ICP-OES. 0.2 gram of rock powder was fused with 1 gram of ultra-pure lithium-tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), lithium metaborate (LiBO_2) and lithiumbromide (LiBr) (We mention this technique as lithium tetraborate fusion or fusion for the remainder of the text). Mixed powders were poured in the platinum-gold (95 wt. %) Pt + 5 wt. % Au crucibles and heated at 1050 °C for 20 minutes. Fused rock powders dissolved in 5 wt. % trace metal grade (63.012 %) HNO_3 solution on hot plates with magnetic mixer. The solutions were transferred to falcon tubes of known weight and additional 5 wt. % HNO_3 added up to 50 g total mass of the final solution. Depending on the type of the sample, they were diluted by 1/1000 or 1/2000 dilution factors. Apart from the three different USGS standards, Geological Survey of Japan (GSJ; JR-1, JG1-A), additional USGS standards (BHVO-1; GSP-2; and reagent blanks) were also prepared for calibration and internal standardization.

Perkin Elmer AVIO 200 ICP-OES has very low argon consumption rate (8 L/min) and generates matrix-tolerant plasma during the measurement stage. Attenuated radial, attenuated axial, radial and axial modes of plasma views using for the specific elements. All the tables for the manuscript stored in Mendeley Database. Plasma operating conditions for ICP-OES given in Mendeley Database, 2021. More common major oxides were mainly measured with radial modes while the scarcer elements have been measured

by axial modes. Sample measurement takes place 100 seconds and sample washout cleaning sessions between samples also taken as 60 seconds. Limit of detection with spectral wavelengths for the major oxide analytes are given in Mendeley Database, 2021. Coefficient of correlation for the ICP-OES analysis always calibrated for greater values than 0.9995 ($>r$).

2.2. Sample Dissolution Procedures and Experimental Conditions for ICP-OES

Perkin Elmer NexION 2000 ICP-MS combined with ESI NWR213 laser system have been used to measure the specific analyte content of the desired samples. We use BCR-2, AGV-2, BCR-2G and AGV-2G USGS glass standards and NIST 614 standard to show to how accurate the geochemistry analysis done by LA-ICP-MS measurements. Besides, during analysis, a reagent blank glass that only contain 1 gram of ultra-pure $\text{Li}_2\text{B}_4\text{O}_7$, LiBO_2 and LiBr added to the analyze section to allow correction during data interpretation.

BCR-2 and AGV-2 glass discs were created by using lithium tetraborate fusion procedure that were explained in the section above. Contrary to dissolving processes that we have conducted before the ICP-OES analysis, the fused glass discs were left in the crucibles and cooled. The cooled discs were ripped-off from the crucibles. These fused glass discs were embedded in the epoxy then polished it acquire a flat surface for analysis. We also produced flux-free BCR-2 and AVG-2 glass discs (without adding a lithium-

tetraborate) by the scheme given in Wilson (2017). We also embedded these flux-free glasses of BCR-2G and AGV-2G in epoxy and polished the embedded surface (Figure 1).

The surface of the different samples were cleaned with methanol, 2 wt. % HNO_3 trace metal grade nitric acid and 18 M Ω ultrapure water before the analysis. We use NIST glasses 610 and 612 for initial instrument calibration and within session measurements. Helium was used as a carrier gas for ablated aerosol. LA-ICP-MS operating conditions were outlined in the Mendeley Database, 2021.

LA-ICP-MS measurements were carried out using time resolved analysis operating in a peak jumping mode. The laser repetition rate and the laser energy density are fixed to 10 Hz and $\sim 7 \text{ J/cm}^2$, respectively (Mendeley Database, 2021). Data were collected by runs that consists three standard measurements at the beginning (each on 610 and 612), nine spot measurement three standard measuring on the closing of the measurements with session. The selected measuring scheme were implemented from Petrelli et al., (2008). Internal standards were selected as ^{29}Si or ^{42}Ca which were given by the measurements in ICP-OES for BCR-2 and AGV-2. The internal standard values for NIST 614 were from the GEOREM database. All samples (standards, samples and blanks) were in the same sample holder.

Limits of detections (LODs) values have been evaluated according to outline given in Longerich et al., (1996). In the Figure 2, we plotted the general

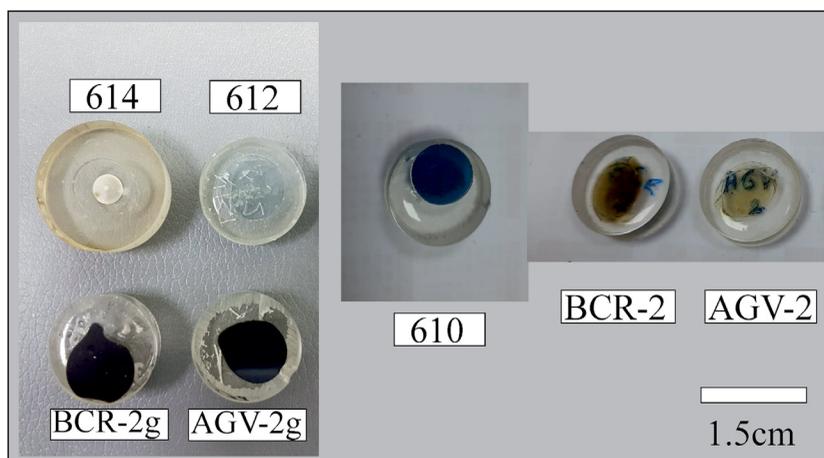


Figure 1- Embedded glass discs prepared for LA-ICP-MS measurements.

LODs values for standard reference material 610. LODs values were dispersed along 4.7 to 0.01 ug/g for 40 μm spot size. Differences in the LODs values were extremely sensitive to spot size, instrument counting power, accuracy, behaviour of the elements and background gas values in the measurement system (Günther et al., 2001). If all other parameters except spot size were fixed, range of the LODs mainly were controlled by increase or decrease of the spot size. If we pick a lower value of spot size such as 20 μm , range of LODs reduced but the sampling area by laser might represent a lower fraction of the glass disc and therefore poor representation of the measured samples. Thus, in our attempts, we experienced the most reliable results achieved by using 40 μm even the LODs slightly large range comparing the other spot values.

3. Data Reduction for ICP-OES and LA-ICP-MS

The data reduction of ICP-OES analysis were done by Perkin Elmer SYNGISTIX data reduction software. The measured intensities were directly calculated as weight percent by the algorithms written in the software. For the natural samples, pre-calculated loss of ignition values were added during the calculation. The iron content of the samples were given as total FeO in the results.

Trace element analysis of the selected samples have been conducted by LA-ICP-MS and data

reduction was done by the SILLS (Guillong et al., 2008); ICPMSDatCAL (Liu et al, 2010) softwares. SILLS (Guillong et al., 2008); ICPMSDatCAL (Liu et al, 2010) softwares (Figure 3 and 3b).

4. Discussion

In this section, first we will present and discuss the results of ICP-OES measurements on the two USGS standards that were dissolved by nitric acid techniques. Afterwards, we presented the results of the measurements conducted by LA-ICP-MS system and discussed the accuracy and homogeneity of the produced flux-bearing and flux-free glasses of the standard materials.

4.1. Discussion of the ICP-OES Measurements

The results of the major oxide compositions of the BCR-2 and AGV-2 were situated in the reasonable range with the standards values given in the literature for these two well-known samples (Govindaraju, 1994; Jochum et al., 2016). The measured values were compared with the large-scale data set of the Jochum et al., (2016) that contain measurement for BCR-2 and measurement for AGV-2 that were compiled from various techniques. The measured values from our results were compared to the compilation values fits well (Mendeley Database, 2021). The biggest RSD values belong to P_2O_5 and MnO measurements but they remain below 1.5. Accuracy (here expressed

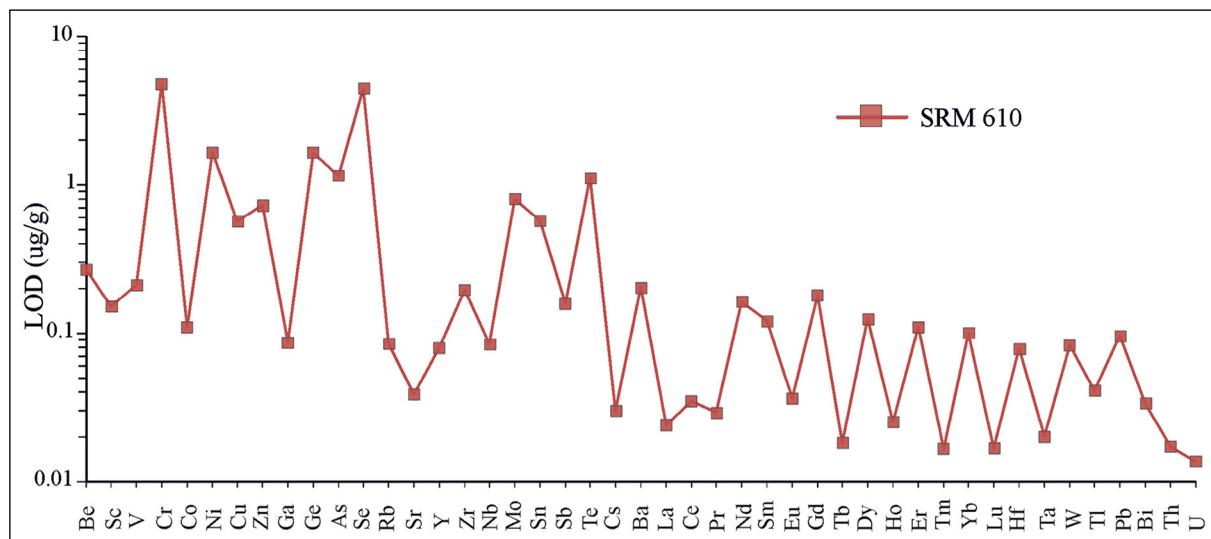


Figure 2- Limits of detection for 40 μm laser spot size on SRM 610.

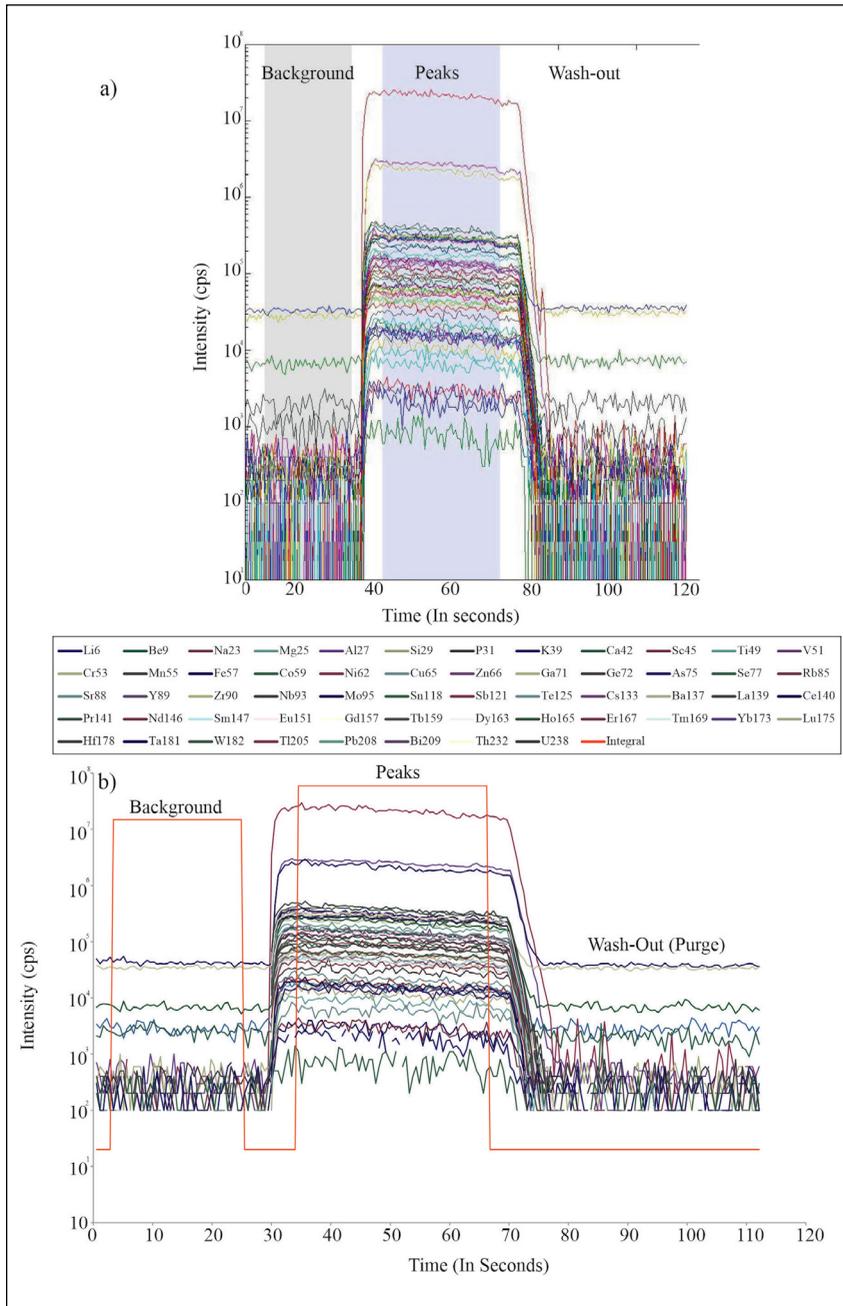


Figure 3- a) Signal selection window of the SILLS software, b) data reduction and signal selection window of the ICPMSDataCal.

as relative deviation from the standard reference material) is 2.5 % better than all the measurements. Thus the measured USGS glasses give accurate results and they can be used to constrain the internal standards for the various natural and synthetic rock and mineral samples that evaluated at the LA-ICP-MS system.

4.2. Discussion of the LA-ICP-MS Measurements

Even though there are many different problems can effect and alter the measurement on LA-ICP-MS systems as outlined in the previous sections, the glass producing techniques and glass homogeneity also significantly affect the measurements (Liu et al., 2013). The contribution of the Jochum et al. (2011)

clearly was indicated core and rim variations of the different elements along the whole scale measurements on NIST SRM 610 to 617. To tackle this problem, we also mainly measure the core regions of the both our in-house produced glass discs with or without-fusion processes.

Results of the measured standards have been given in Mendeleev Database. In all measurements, the standards were reasonably matched well with the measurements that have been conducted in different laboratories. Error values were displayed as two sigma (σ) and reasonably low for the majority of the trace element values.

The lithium tetraborate fusion mainly sustains robust sample digestion and creates nearly homogeneous and intact samples that can be easily stored and re-measured after long periods of time (Eggins, 2003). However, in house generation of the flux-free glasses can posses problems since the absence of the fluxing agent and possible case of incomplete homogenization throughout the sample (Petrelli et al., 2008, Jochum et al., 2016). We plot the results of our samples and compare their relative deviation from a standard value (Figure 4). Majority of the plotted samples created by the lithium tetraborate fusion (BCR-2 and AGV-2) display more minor relative deviation than flux-free

glasses (BCR-2g and AGV-2g). The most prominent spikes come from Tb and Lu measurements on flux-free glass samples. Thus it can be postulated that the flux-bearing glasses are more reasonable agents to understand the general trace element chemistry of the desired samples.

Since the rare earth elements are one of the most common geochemical discriminator in the geochemical studies (e.g. Pearce et al., 1984) we specifically show their RSD values in weight percent to show the reliability of our measurement in Figure 5. In these RSD values are mainly calculated lower than the 10 % percent relative to standard reference values for the fused discs, while the flux-free glasses display much higher relative standard distributions as outlined above. Besides, SRM 614 values also display values always lower better than 10 % relative distribution values. Surprisingly, in both AGV-2g and BCR-2g samples, Tb values display high relative deviations. The reason of this defect related with the possible incomplete homogenization during fusion processes. But even so, the case majority of the sample was situated within the reasonable range.

Thus, the results show the good precision levels of both in-house produced flux-free glass standards and flux-bearing fused glass discs during the ICP-OES and LA-ICP-MS measurements.

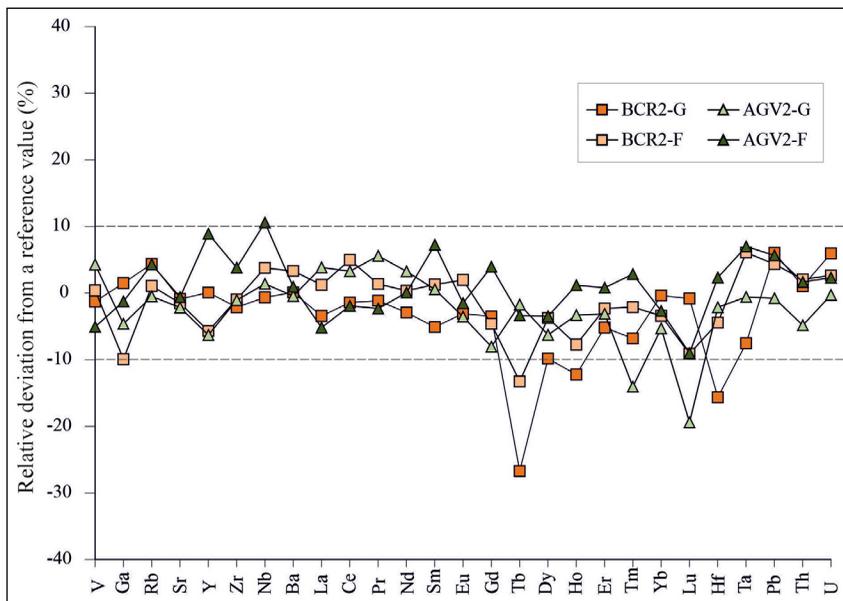


Figure 4- Relative standard deviation from a reference value of the measurements conducted in this study. The reference values taken from Jochum et al. (2016) (BCR-2F and AGV2-F represent samples generated by lithium tetraborate fusion).

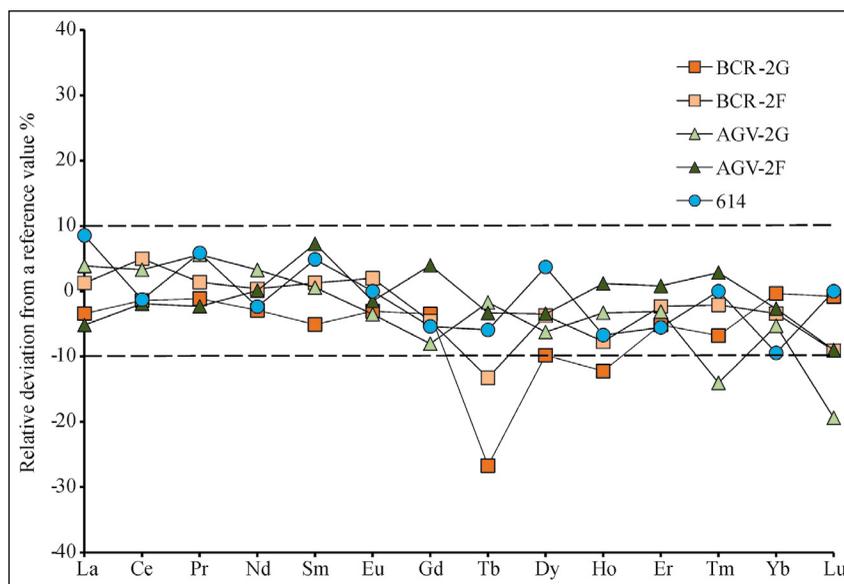


Figure 5- Relative deviation from a reference value for specifically for REE values of the measured samples. Values for SRM 614 taken from Jochum et al. (2011) other values taken from Jochum et al. (2016) (BCR-2F and AGV2-F represent samples generated by lithium tetraborate fusion).

5. Results

ICP-OES and LA-ICP-MS measurements, which are installed at İstanbul University-Cerrahpaşa Geological Engineering Department Geochronology and Geochemistry Laboratory display accurate analysis capabilities have been conducted in international known standard reference materials. ICP-OES analysis of major oxide elements reasonably match with the international standards. Mainly, majority of the samples display better relative deviation values than 10%. The flux-free glasses of BCR-2g and AGV-2g often display much higher relative deviation comparing to standard values as high as 25%. Thus, the lithium tetraborate fusion displays more homogeneous glasses for the LA-ICP-MS measurements. The reason of this situation can be related with the incomplete homogenization of the desired sample. Anyhow, samples reasonably display close values with the international standard values.

Therefore, the combined measurement systems confirm the well resolved capabilities and application potential of this laboratory on various areas of petrology, geochemistry, analysis of natural and synthetic minerals, metals, environmental samples and archaeological - archaeometry samples.

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