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New application of microwave digestion – inductively coupled plasma-mass spectrometry for multi-element analysis in komatiites

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Abstract

A new method using microwave digestion combined with inductively coupled plasma-mass spectrometry (ICP-MS) was studied to analyze the elemental composition of a variety of komatiites samples. Microwave digestion consisted in two-stage heating and pressurizing acid treatments for maximum dissolution of the samples. We report here different quality control measurements (external and internal calibration, monitoring of reference materials) which involve standard deviation calculations and recovery examinations in order to test the precision and accuracy of the analytical procedure. Data for 17 elements (Na, P, K, T, V Cr, Mn, Co, Ni, Cu, Zn, Zr, Pb, Al, F, Ca and Mg) in eight komatiite samples and two USGS basalt reference samples (BCR-2 and BHVO-2) are presented. We evaluate our new digestion and instrumental procedure. The element concentration obtained for BCR-2 and BHVO-2 agreed well with the certified values, the relative standard deviations were lower than 5% and recoveries were good. Our analytical results demonstrate that it reproduces accurately the concentrations of minor and trace elements in komatiites. The ease of digestion of the samples and the

speed (less than 12 hours) to digest the komatiite material makes this technique an efficient method to be used easily and routinely for preparing and analyzing komatiites samples for multiple elements determination.

Keywords: Microwave digestion; Inductively coupled plasma-mass spectrometry (ICP-MS); Komatiites

1. Introduction

During the last decades, microwave digestion technique has been widely developed in several applications related to chemical disciplines such as organic, organometallic, inorganic synthesis, and catalysis. Particularly, in analytical chemistry, microwave digestion has promptly revealed to be really advantageous for its easy, fast and versatile use in sample treatment. And since the beginning of the use of microwave in the 70's, the sample preparation time has been hugely reduced from days or hours to minutes, replacing wet open-vessel digestion to high pressure and high temperature closed vessel systems. Moreover, nowadays, the computerized monitoring of temperatures and/or pressures in microwave allows controlling closely the digestion or extraction process, increases the repeatability and the analytical precision, and reduces the technician labour participation.

For geological materials, the most common sample treatments for analyzing trace and ultra-trace elements by inductively coupled plasma-mass spectrometry (ICP-MS) consist in digestion methods incorporating hot plate open-vessels wet acid treatment, fusion treatment including NiS fire assays, Carius tube (CT) Technique, high-pressure decomposition systems (with Teflon bombs), and more recently microwave (MW) heating [1-6].

Hot plate open-vessels wet acid treatment is widely used for the decomposition of materials containing palladium, platinum and gold, but the dissolution of minerals at low temperatures and pressures limits the determination of other elements, e.g. ruthenium, rhodium, osmium and iridium [6]. Moreover, the technique implies long reaction times (from many hours to several days) and the use of large amount of acids which increases the cost of the process, the sample contamination and the loss of volatile compounds.

Fusion treatment [7] can be very efficient in the digestion of very refractory minerals and provides the highest recovery of precious metals (with Nickel sulphide fire assay) from a large number of complex matrices (rocks, minerals, concentrates, soils, and ores). Time consumption is limited, but it requires substantial amounts of samples as well the use of large amounts of fusion reagents which increases the contamination introduced to the sample and the possible interferences in the analysis. This digestion method may then provide high procedural blanks and difficulties in the direct analysis of the obtained solution by instrumental techniques [6].

Highly efficient acid (HNO_3/HCl) digestion procedures for some rocks have been developed using a Carius tube design [1, 8]. Acid treatment is performed in sealed thick-walled PyrexTM borosilicate glass tubes at high temperature (240°C) and elevated pressure for several hours or days (12 to 72 h). High efficiency in leaching analytes and low procedural blanks are achieved, and CT method has been found to be particularly suitable for the recovery of osmium and other Platinum-group elements (PGE). However, the digestion of some geological materials requires 1) a first treatment step of desilicification of the samples with HF/HCl in separated fluorinated ethylene propylene (FEP) beakers prior to the Carius tube digestion, 2) higher pressures than the ones reached in CT method. Moreover, Carius tubes may pose thermal and chemical hazards due to the generation of permanent gas upon heating which can not escape or to exothermic reactions which create high vapor pressures that the sealed glass tube may not withstand. Such effects may generate an explosive hazard and therefore strict safety procedures should be followed when using CT.

The use of high-pressure decomposition systems with polytetrafluoroethylene (PTFE) bombs (TB) [2, 3] and microwave heating [5, 9] substantially accelerates the decomposition of complex samples like geological materials and leaching analytes. Both methods also reduce the sample contamination and loss of volatile compounds. However, high-pressure decomposition with conventional Teflon bombs may last from few (2 days) to several days (up to 1 week). Examples are as listed in Table 1. This is the first major difference and disadvantage of digestion with conventional Teflon pressure vessels compared to microwave digestion. Microwave digestion does have the advantage of greatly reducing processing time, short time is required for the decomposition (minutes) enabling start-to finish total sample preparation in few hours. The interaction of microwave radiation with sample and reagents causes both ionic migration and dipole rotation, resulting in fast heating inside the mixture with

consequent decomposition [10, 11]. Microwaves only heat the liquid phase because the vapors do not absorb microwave energy which provides a safer working environment [12]. Another important advantage of the closed pressurized microwave system upon the PTFE bomb decomposition technique are linked to the very high pressure levels reached (up to 1500 psi for microwave, 70-100 psi for PTFE bomb decomposition). Finally, microwave digestion includes the ability to strictly control heating power and the length of time that the heat is applied with the potential for complete automation of the processes with real time graphics and data acquisition of the temperature and pressure parameters [12].

It is well known that magmas extruded on a planet surface can provide clues about geological processes in the interior. They include remarkable petrologic and geochemical proxy-records which help to understand the pristine matter and hence the origin of a planet. This is mainly true for the most primitive lava, which rise to the surface with minimal change. In astrobiology research, komatiites are an important rocky component of the primitive environments in Early Earth and, as well, as a possible extraterrestrial planetary volcanic material [13]. For example, Bérczi et al. [14] have reported that planetary body comparisons indicate that diogenites which has been found in Antarctic achondritic meteorites, might have been the earliest, less changed Vestan basalts, like ancient terrestrial komatiites and therefore are analogous to Archean komatiites. Martian ALHA shergottite also belongs to this early stage group. As well, the compositions and crystallization sequences of pyroxenes in Archean and Tertiary komatiites and in lunar basalts are similar in many ways. Bouquain and Arndt [15] have compared them and concluded that basalts from Apollo 12 and 15, collected during missions in 1970 and 1971, have similar textures [15].

Under such astrobiological context, we began to investigate experimentally on komatiites and, prior to their use in laboratory simulations, our first experimental step was to determine the mineralogical and elemental composition of the collected komatiites samples. For the determination of their minor and trace element abundances, we have used our ICP-MS facility.

Analyzing komatiite rocks by ICP-MS requires digestion of the samples. In the published literature, sample digestion and ICP-MS methods for the elemental analysis in komatiite material (presented in Table 1) are principally based on the use of Carius tubes (CT) and high-pressure Teflon bombs (TB). CT technique is efficiently used to

digest PGE carriers in komatiites and to successfully achieve isotopic measurements of Os, Re, Pt [16-20], after a long procedure of sample treatment. TB applications for komatiites are related to the determination of trace element composition [21-25]. Hot plate open-vessels treatment (HP) is rarely utilized for dissolving komatiites and limited to the analysis of some very specific trace elements like rare Earth elements (REE) [26-27]. Finally, fusion treatment (FU) by NiS fire assay is employed to extract PGEs from bulk rock samples and examine isotopic compositions [18, 28]. As a first observation, all four digestion methods are each designed to analyze precise elements like PGEs and therefore can not achieve total sample dissolution for a multi-elements analysis. Secondly, they are time-consuming procedures: as referred in Table 1, the digestion times are long (couple of days for CT and HP, several days for TB), which extends all the more the total time of the sample treatment (when including evaporation, extraction, pre-concentration after the dissolution, separation).

Here, we have decided to use a simpler and more rapid method to dissolve the komatiite samples: the microwave digestion. In the absence of an available published method for the microwave digestion of komatiites, we have developed in our laboratory a new method for their total decomposition by microwave digestion and have successively used ICP-MS for their elemental analysis. We have tested the validity of the method for komatiites samples selected from different geodynamic settings and with variable age and composition.

[Table 1]

2. Analytical procedure

2.1. Samples

Eight komatiites rocks were provided from different institutions and were chosen for their distinct geological localities, assemblages inside a country location and different ages (see Table 2) which reflects as distinct mineralogy and secular variations in major, minor and trace elements geochemistry. The details of their geology and mineralogy are reported in the references listed in Table 2.

[Table 2]

2.2. Standard reference materials

To control and document the quality of our methodological procedure, analyses of two U.S Geological Survey (USGS) basalt reference samples, BCR-2 (Bridal Veil Flow Quarry, Columbia River, Oregon) and BHVO-2 (pahoehoe lava from the Halemaumau crater, Hawaiian Volcanic Observatory) were done. The choice of both rock reference samples was guided by two observations. Firstly, no komatiite certified reference material is currently available for major, minor and trace elements. In the literature only “made-in-house” komatiite standards are reported: KAL-1, WITS-1, GOR-128-G and GOR-132-G. KAL-1 [45] and WITS-1 [46] are exclusively used for high-precision PGE and noble metals data and studies. GOR-128-G and GOR-132-G [47] are komatiite fused glass standards which are only used for *in situ* microanalytical techniques (such as Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and Secondary ionisation mass spectrometry (SIMS)) in order to perform *in situ* isotope and trace element analyses of mineral and inclusions. Secondly, because of this lack of certified komatiite reference material, basalt powder standards as BCR, BHVO, and BIR are commonly used for standard calibrations of the analysis [21, 22] and to monitor the data quality [48] when analyzing the major and minor elemental composition of komatiites.

2.3. Microwave digestion procedures

Four digestion methods were developed in a chronological time and tested for their efficiency in recovering the elements of both certified reference materials. The selection of the final method used for all samples was done when achieving a complete recovery. Basically, the four methods differed in the type of acids mixtures and the acid volumes in order to optimize the digestion. We describe first in detail the method which was selected and afterwards summarize the three other methods.

Previous to any digestion method, the sample preparation consisted in cutting the komatiites samples in small-sized pieces using a diamond cutting-machine, cleaning the pieces with deionized water in an ultrasonic bath for 1h, drying them in an oven at

60°C during 1h and finally grinding them in an agate mill. Samples were finally stored in sterilized polypropylene (PP) vials with caps.

The dissolution of the samples was achieved using a closed vessel digestion system described as a programmable microwave apparatus (Milestone Ethos Touch Control) equipped with a high temperature and pressure rotor for 10 Teflon vessels of 100 ml (maximum work conditions of 1500 psi and 300°C).

100-115 mg of powdered samples were loaded into Teflon vessels used for the microwave digestion.

For the selected method, a combination of two digestion stages was carried out. The microwave temperature programs for the two-stage digestion are illustrated in Fig. 1. In the first stage, 3 mL of HNO₃, 3 mL of HF and 2mL of H₂O (or 3HNO₃:3HF:2H₂O) were added to the vessels. HNO₃ and HF were suprapure® reagent grade (Merk), H₂O was deionized water (18.2 MΩ) produced by a Milli-Q® water system (Millipore). Teflon vessels were capped, placed in the microwave system and digested in 28 min. After cooling, the digested solution was then evaporated and dried down on a hot plate (*DigiPREP Jr.* from SCP Science) at 110°C during 7 hours until getting a final residue. Afterwards, a second acid treatment with microwave was carried out during 34 min (temperature conditions in Fig. 1): the residue was dissolved in the Teflon vessels in a mixture of 2 mL HCl (Merck, suprapure® grade) plus 1 mL HNO₃ in 5 mL H₂O. The final solution was brought to a total volume of 100 mL with deionized water in a polymethylpentane (PMP) volumetric flask, ready for the ICP-MS analysis.

The three methods were carried out as following:

Method 1: it consisted in a typical procedure which we previously employed routinely for digesting by microwave hard geological material containing silicates. There was only one acid treatment for the digestion which was a mixture of 3HCl:1HNO₃:2HF:1H₂O₂. The solution was then dried on a hot plate at 100-120°C, 3ml of HNO₃ were added and then the solution was heated at 120°C until dryness. Finally 2ml of HNO₃ were appended to the residue before diluting to 100ml with MilliQ® water.

Method 2: the digestion efficiency was improved by combining two microwave digestions. 3HF:3HNO₃:2H₂O was used for the first acid decomposition in the microwave apparatus. And after drying the solution on a hot plate at 105°C, the residue

was dissolved in 5HCl:5H₂O for a second microwave digestion. The solution was then again totally evaporated on a hot plate at 105°C, 2ml of HNO₃ were added and the obtained solution was diluted to 100ml with MilliQ water.

Method 3: the same acid treatments and procedure as in method 2 were employed but the dissolution of the residue for the second microwave digestion was made in 3HCl:5H₂O. Less amounts of HCl were introduced in order to reduce interferences mainly due to the formation of chlorine polyatomic ions (ArCl⁺, ClO⁺, and ClOH⁺). After the second evaporation step, no HNO₃ was added to the solution before the dilution with deionized water.

The final selected method described earlier differed from this third method by using aqua regia in the second digestion in order to dissolve totally the final residue.

We indicate also that the individual volumes of the acids in the mixtures were depending on the total minimum volume that can be used in the Teflon vessels for the microwave digestion in order for the temperature probe to reach the solution. This volume was 8 mL.

Lab ware used for the digestion process were PP, PMP or Teflon material to avoid reacting with any acid and were decontaminated with the following cleaning procedures. PMP volumetric flasks used for making the final digestion solutions were first rinsed several times with deionized water, then cleaned with deionized water in ultrasonic bath for 10 min followed by a cleaning in a HNO₃:HCl:8H₂O solution during 48 hours. Afterwards they were rinsed with deionized water, put again in ultrasonic bath during 15min and finally dried and stored in a glass storage cabinet. Regarding Teflon vessels, they were also cleaned first with tap water, rinsed with deionized water, then put in ultrasonic bath with deionized water for 10 min followed by a cleaning in the microwave apparatus in a 3HNO₃:3HCl:4H₂O acid solution during 30 min (temperature ramp from 0 to 150°C during 10 min then kept at 150°C during 20 min). Ultimately, they were rinsed with deionized water and dried at ambient air. All lab ware were stored in a glass storage cabinet.

Finally, we mention that all samples manipulations were carried out in a protective environment, working in a fume hood with clean air laminar flow.

[Figure 1]

2.4. ICP-MS instrumentation, calibration and analysis

The measurements of major, minor and trace elements were performed on a PerkinElmer ELAN9000 ICP-MS quadrupole spectrometer. The samples were introduced into the ICP-MS via a Rytan™ cross-flow nebulizer (PerkinElmer), Scott spray chamber (PerkinElmer) and Cetac ASX-510 autosampler. The sample transport from the autosampler to the nebulizer was established by a peristaltic pump. The operating parameters of the spectrometer are summarized in Table 3.

[Table 3]

The calibration and optimization of the instrument were done using a calibration standard solution containing 10 ppb of Mg, Cu, Rh, Cd, In, Ba, Ce, Pb, U in 1% HNO₃ (ELAN 6100 Setup/Stability/Masscal Solution from PerkinElmer) in order to obtain the maximum ¹⁰³Rh intensity for optimal counting statistics (>300 000 cps), as well as oxide/double charge ion levels lower than 3%.

Quantitative ICP-MS analysis was performed using external calibration and internal standardization. The internal standard, which was ¹⁰³Rh, was added to the blank, standards reference materials and komatiite sample solutions. Multi-elements standard solutions were used for the external calibration. They consisted of a mixture of diluted solutions prepared from initial mono-element solutions of 1000 mg L⁻¹ (all from Panreac Química SA, Spain) containing the analytes. The diluted solutions ranged from 0.001 to 5 mg L⁻¹ for Na, P, K, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Zr, Pb and 0.1 to 10 mg L⁻¹ for I, Ca, Fe, Mg, generating the calibration curves. The plots of the changes of instrumental response with changing concentration of analyte (calibration curves) create linear relationship. As an example, for two analytes Cr and Mg, we obtained the following calibration equations:

$$y(\text{Cr}) = 34573x(\text{Cr}) + 758128 \quad \text{with} \quad r(\text{Cr}) = 0,9996$$

$$y(\text{Mg}) = 14769x(\text{Mg}) - 622100 \quad \text{with} \quad r(\text{Mg}) = 0,9998$$

where y is the instrument response (millions of counts per seconds) for the indicated element, x the concentration of the element (in ng g⁻¹), and r the correlation coefficient.

Both elements are selected as example because: 1- they represent different mineralogical contexts in komatiites (Cr in chromites and Mg in olivines) and 2- they are geochemically significant in this type of volcanic rock.

As our ICP-MS instrument was not equipped with a dynamic reaction cell (DRC), the only way to test how polyatomic interferences could affect the isotopes was using certified reference materials. If good recovery of the measured isotope in these reference materials is obtained, therefore we concluded that the effects of the formation of polyatomic ions are insignificant. If the elements were incompletely recovered in the samples, we changed the acid mixtures; for example, we used less quantities of HCl in order to minimize polyatomic interferences and/or choose another isotope of the element.

All the ICP-MS measurements were made within a working day according to the following analytical sequence: (1) the blank (digestion blank), (2) the multi-elements external standard solutions, (3) the eight digested komatiites sample solutions, (4) both basalt reference materials BHVO-2 and BIR-2, and (5) a quality control multi-elements standard solution with a different concentration than the previous external standards solutions.

2.5. X-ray Fluorescence (XRF) analysis

X-ray Fluorescence (XRF) analysis was performed by the Scientific technical Services (SCT) of the Oviedo University in Spain. A sequential X-ray fluorescence spectrometer (PW2404, Philips) equipped with an automatic charger (PW22540, Philips), a rhodium x-ray tube, 4 kW generator and 5 analyzing crystals (LiF 200, LiF 220, PE, Ge y PX 1) was used.

XRF analysis was done on fused glass beads. For preparing the samples into glass beads the rock samples were first milled to less than 75 μm particle size. Then, to determine the loss on ignition (LOI), 5 g of sample material was heated at 975 °C for 1 hour. Subsequently, 0.5 g of the residue was mixed with 6 g of lithium tetraborate, and the mixture was fused at 1100-1150°C for 5 min using a Perl'X 3 automatic fusion machine (Philips).

The instrumental total error for each sample was less than 1%. For the particular case of performing the XRF analysis onto glass beads, the detection was limited to ~0.1% and therefore was restricted for the examination of major elements only.

3. Results and discussion

3.1. Recovery of the internal standard and the quality control multi-elements standard solutions

Instrumental drift and matrix effect were controlled by monitoring the recovery of the internal standard added to all analyzed solutions. The initial concentration of 300 ng g⁻¹ of ¹⁰³Rh was totally recovered at 100.6% with a relative standard deviation (RSD) of 3.16% (calculated from 3 measurements).

The precision, accuracy and also memory effects of the analysis were verified evaluating the recoveries of all the analytes in the quality control multi-elements standard solutions. A summary of these results can be found in Table 4. Recovery percentages were ranging between 90-104 % and therefore validated the accuracy and reproducibility of our analysis.

The calculated RSD was lower than 3.5 % for most of the analyzed isotopes.

[Table 4]

3.2. Analysis of basalt reference materials

The accuracy of the complete methodology including the microwave digestion and the analytical procedure was assessed by comparing our results for basalt reference materials BCR-2 and BHVO-2 with the certified concentrations, i.e. by monitoring the recovery of the analytes of both reference materials. Table 5 shows the elemental recoveries obtained for BCR-2 and BHVO-2. Our analytical results agreed well with the certified values, the digested samples were efficiently recovered by 90 - 120 % with a precision comprised between 0.2 to 2.8 %. The only exception where the elemental recovery was low occurred for Cu in BCR-2. Cu was recovered only by 51%. Also for for BCR-2, the recovery of Pb was very high (164.54%). In the USGS certificate of

analysis of BCR-2, Cu and Pb concentrations were given as an information values and not recommended element which may possibly cause the discrepancy in these results.

^{103}Rh recoveries were also estimated for BCR-2 and BHVO-2 and the values were 94.5 % and 104.6 %, respectively.

Excellent agreement for the reference materials was obtained between the concentrations from the method developed in this study and the USGS recommended values for all elements (except Cu and Pb) which demonstrate the good accuracy and reproducibility of our digestion method followed by ICP-MS analysis.

The recoveries of the elements were also determined for the other three digestion methods performed previously in order to compare the sample digestion efficiency with highest accuracy and precision in the multi-elemental analysis by ICP-MS. For the method 1, Al and Mg were recovered at lower than 75% and the recoveries of Ni, Zn, Cu, Cr, Co and V were lower than 85%. In some cases, the results for Fe were also lower than 80%. For the second method, Al had recoveries lower than 50%, Ni, Zn, Cu, Cr and Co lower than 80%. And the third method gives low recoveries of Ti, Cu (about 80%) and Cr (lower than 75%) and the recoveries of Co and Mn were also lower than the selected method (lower than 88%). None of the three methods achieved a complete digestion, they were not appropriate for analyzing some specific elements (like Al, Mg) therefore appeared not enough accurate and efficient for doing multi-elements analyses.

[Table 5]

3.3. Analysis of komatiite samples

The minor and trace element concentrations (total of 13 elements: Na, P, K, Ti, V, Cr, Mn, Co, Cu, Ni, Zn, Zr, Pb) were detected above their respective limits of detection in the komatiite samples using the new method of microwave digestion followed by ICP-MS. The results are summarized in Table 6. Na concentrations ranged from 24300 to 36 $\mu\text{g g}^{-1}$, P concentrations from 215 to 8 $\mu\text{g g}^{-1}$, K from 776 to 38 $\mu\text{g g}^{-1}$, Ti from 3600 to 272 $\mu\text{g g}^{-1}$, V from 237 to 56 $\mu\text{g g}^{-1}$, Cr from 759 to 2838 $\mu\text{g g}^{-1}$, Mn from 1613 to 701 $\mu\text{g g}^{-1}$, Co from 101 to 60 $\mu\text{g g}^{-1}$, Ni from 1788 to 189 $\mu\text{g g}^{-1}$, Zn from 586 to 31 $\mu\text{g g}^{-1}$, Zr from 32 to 0.85 $\mu\text{g g}^{-1}$ and finally Pb from 664 to 0.56 $\mu\text{g g}^{-1}$.

[Table 6]

The reproducibility of the measurements was studied doing 3 replicates of the analysis and afterwards monitored by the relative standard deviations (RSD) which was for most elements and samples < 5 %.

The limits of detection (LOD) for all analyzed elements were estimated using Miller and Miller statistical calculation [49]. They define the limit of detection as the concentration of the analyte which corresponds to the instrument response (signal) of the analyte y according to the equation:

$$y - y_B = 3S_B$$

where y_B is the instrument response of the blank, and S_B the standard deviation of the blank.

The results reported in table 6 demonstrate that a wide variety of komatiitic compositions with variations in the minor and trace elements abundances can be analyzed with our method with a good precision. The control of the good efficiency, and accuracy of our new method for minor and traces elements was validated previously with the USGS certified reference materials BCR-2 and BHVO-2 (results in Table 5).

We have also measured the major element abundances in the komatiite samples with our analytical method (Table 7). Table 7 shows the results in comparison with the values obtained by XRF. The concentrations obtained by our new method were reproducible with comparable values to XRF analyses.

The accuracy of the XRF analysis was previously controlled examining elemental recovery of both reference materials BCR-2 and BHVO-2 (Table 8) for the major elements. Results gave recoveries between 98 - 133 %. A large discrepancy for MnO (133% of recovery) was observed. As indicated earlier in the analytical procedure, performing XRF analysis onto glass beads limits the detection of the elements to a concentration of ~0.1% and therefore is restricted for the examination of major elements only. MnO is present in both USGS reference materials in small amounts, 0.15% for BCR-2 and 0.129% for BHVO-2 which is very close to the limit of detection by XRF. This may cause the uncertainties on the values of MnO determined by XRF and therefore the discrepancy in its recovery.

Usually the major elements in komatiites are analyzed by XRF, Electron probe microanalysis (EPMA), Proton induced X-ray emission (PIXE) or Instrumental neutron activation analysis (INAA), while the rest of minor and trace elements by ICP-MS or to a lesser extent by other techniques like Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), Secondary ionization mass spectrometry (SIMS), Laser plasma ionization mass spectrometry (LIMS) and Thermal ionization mass spectrometry (TIMS). Our results indicate that, for komatiite samples, microwave digestion following by ICP-MS can perform an accurate and precise analysis of both major (excluding SiO₂) and minor/trace elements together, which makes the coupled technique getting even more useful.

The present study was limited to major, minor and trace elements and did not include PGE's measurements due to the limitation of the equipment actually available in our facilities. Indeed, PGE analyses involves additional specific technical procedures. It requires doing specifically isotope-dilution/ isotopic composition measurements by previously spiking the samples with a mixed tracer of enriched isotopes (e.g. ⁹⁹Ru, ¹⁰⁵Pd, ¹⁹¹Ir, ¹⁹⁸Pt) during the sample preparation, and then, after the digestion, by using the cation/anion-exchange chromatography technique [5] to separate the PGE from the rock matrix and collect Ru, Pd, Pt, Rh, Ir, Au in separate elemental fractions [19, 50].

However we want to point out that conducting experiments to test the method to determine PGE's abundances in komatiites samples would be really useful. PGE's measurements in primitive volcanic rocks like komatiites are very interesting for understanding their geochemical behaviour in the earth's mantle. The komatiite lavas provide the type of material that can be used to test models of core-mantle interaction and oceanic crust recycling by studying the variations in PGE's and highly siderophile elements (HSE) [17].

[Table 7]

[Table 8]

4. Conclusions

Experiments were conducted to optimize instrumental operating parameters for multiple elements measurement in komatiites by microwave digestion – ICP-MS. The

results show that low RSD% and good recoveries can be achieved for such measurement using our digestion and ICP-MS analytical methods.

Data for 13 trace elements in two reference materials BCR-2 and BHVO-2 and in 8 komatiites have been obtained by microwave digestion – ICP-MS using our new method. Accurate recoveries of reference material demonstrate the applicability of the microwave digestion method and ICP-MS for elemental analysis in komatiites. This method was also capable of yielding good results for major elements Mg, Fe, Al and Ca in komatiites with good precision.

The results then indicate that precise and accurate multiple element data including major (except silica), minor and trace elements can be obtained by this combined method for komatiite samples. Microwave digestion combined with ICP-MS is shown to be a good alternative method to perform easier and faster multi-element analysis in komatiites than other commonly used method. Furthermore, this method could also be applied to analyse terrestrial volcanic rocks (e.g. basalts, ultramafic rocks) and extraterrestrial material (e.g. Martian SNC meteorites and other chondritic meteorites) with similar geochemical compositions to komatiites.

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Fig.1. Temperature ramp programs (at maximum power of 1000 W) of the Ethos TC microwave set up during both digestion stages for the sample acid treatment.

Table 1

Digestion procedures combined with ICP-MS for the elemental analysis of komatiite samples

Table 2

Information of the komatiites rock samples used in this analytical work

Table 3

ICP-MS operating parameters used for trace element determination

Table 4

Elemental recovery of the quality control standard solutions (QC Std) after analysis by ICP-MS

Table 5

Elemental recovery of basalt reference materials BCR-2 and BHVO-2 by ICP-MS after microwave digestion and analysis by ICP-MS

Table 6

Minor and trace elements concentrations ($\mu\text{g g}^{-1}$) in eight komatiites rocks determined by ICP-MS after microwave digestion

Table 7

Major elements concentrations (%) in komatiites rocks determined by ICP-MS after microwave digestion compared with XRF analysis

Table 8

Major element composition (%) and elemental recovery determined for both basalt reference materials by XRF compared with the USGS certified values

Table 1

Digestion procedures combined with ICP-MS for the elemental analysis of komatiite samples

Digestion Method	Sample treatment	Determined element	Komatiite Sample*	Reference
CT	Aqua regia (HCl/HNO ₃) 270°C for 48h or 240°C for 72h 220°C for 48h	PGE, HSE	AL, PH, KO	[16,17]
		PGE Isotopic measurements	VB	[18]
CT	HCl/HNO ₃ 230°C for 36 - 48h	PGE	MO, AL, ZA	[19]
CT	Aqua regia 230°C	Os and Pt Isotopic ratios	GOR	[20]
TB	HF-HNO ₃ /HCl 220°C for 5 days	Trace elements	BGB	[21]
TB	HF/HNO ₃ 180°C for 5 days	Trace elements	BGB	[22]
TB	HNO ₃ /HF 150°C for 2 days	Trace elements	MO, BO, TI	[23]
TB	HF 245°C for 2 days	HFSE	ZA	[24]
TB	HF/HNO ₃ /HClO ₄	Hf	BGB	[25]
HP	Two digestions HClO ₄ /HF 180°C	REE	MO	[26]
HP	HF/ Aqua regia 160°C for >10h	Sc, Hf, Nb, Ta, Rb, Th, U, Pb	VB	[27]
FU	Ni and sulphur powders 1050-1100°C for 75 to 90 min	PGE Isotopic measurements	KO, VB	[18, 28]

CT = Carius tube

TB = Teflon bombs

HP = Hot plate

FU = Fusion

HFSE = High field strength elements

*Komatiite locations: AL = Alexo, Abitibi greenstone belt, Ontario Canada; BGB = Barberton greenstone belt, South Africa; BO = Boston, Abitibi greenstone belt; GOR = Gorgona Island, Colombia; KO = Kostomuksha greenstone belt, Baltic Shield; MO = Munro, Abitibi greenstone belt, Ontario Canada; PH = Pyke Hill, Abitibi greenstone belt, Ontario Canada; TI = Tisdale, Abitibi greenstone belt; VB = Vetreny belt, Baltic Shield; ZA = Belingwe greenstone belt, Zimbabwe.

Table 2

Information of the komatiites rock samples used in this analytical work

Sample name	Geological setting	Location	Age (Ga)	Reference
8-PPR-97	Central Lapland Greenstone Belt	Finland	2.06	[29, 30]
20/LaC	Kuhmo Greenstone Belt	Finland	2.75	[31, 32]
AC-2	Alexo, Abitibi Greenstone Belt	Canada	2.7 - 2.9	[33, 34]
HCOM-3	Commondale Greenstone Belt	South Africa	3.5 – 3.2	[35, 36]
K5-31-99C	Barberton Greenstone Belt	South Africa	3.6 – 3.2	[37, 38]
U-23	Ura Guba, Kola Peninsula	Russia	> 2.83	[39, 40]
ZV-58	Belingwe Greenstone Belt	Zimbabwe	2.7	[41, 42]
MCD-106	Norseman-Wiluna Greenstone Belt	Western Australia	2.7	[43, 44]

Table 3
ICP-MS operating parameters used for trace element
determination

Instrument	PerkinElmer ELAN9000
RF power	1000 W
Nebulizer gas flow	0.9 l min ⁻¹
Plasma gas flow	15 l min ⁻¹
Auxiliary gas flow	0.5 l min ⁻¹
Nebulizer	Cross flow
Spray chamber	Scott Type
Cones	Nickel
Lens voltage	8 volts
Analog stage voltage	-1850 volts
Pulse stage voltage	1100 volts
Sweep / reading	15
Reading / replicate	1
Replicate	3
Scan mode	Peak Hopping

Table 4
Elemental recovery of the quality control standard solutions
(QC Std) after analysis by ICP-MS

Element	Initial QC Std (ng g ⁻¹)	Obtained QC Std (ng g ⁻¹)	Recovery (%)	RSD (%)
²³ Na	1100	1070	97.3	1.9
³¹ P	600	587	97.9	2.7
³⁹ K	1100	1085	98.7	2.8
⁴⁷ Ti	1100	1057	96.1	1.0
⁵¹ V	600	604	100.7	1.6
⁵² Cr	600	602	100.3	3.3
⁵⁵ Mn	600	607	101.2	2.8
⁵⁹ Co	600	616	102.6	1.6
⁶⁰ Ni	600	617	102.9	2.9
⁶³ Cu	600	624	104.0	0.9
⁶⁶ Zn	600	615	102.5	1.9
⁹⁰ Zr	600	596	99.3	1.4
²⁰⁸ Pb	600	603	100.5	1.4
²⁷ Al	1100	1096	99.7	1.3
⁵⁴ Fe	1100	1140	103.7	1.1
⁴⁴ Ca	1100	996	90.6	2.2
²⁴ Mg	1100	1078	98.05	1.1

RSD = Relative standard deviation (precision) estimated from
3 replicates of the ICP-MS analysis for the same
digested solution, done on the same day.

Table 5

Elemental recovery of basalt reference materials BCR-2 and BHVO-2 by ICP-MS after microwave digestion and analysis by ICP-MS

Element	BCR-2				BHVO-2			
	This work ICP-MS ($\mu\text{g g}^{-1}$)	USGS certified ($\mu\text{g g}^{-1}$)	Recovery (%)	RSD (%)	This work ICP-MS ($\mu\text{g g}^{-1}$)	USGS certified ($\mu\text{g g}^{-1}$)	Recovery (%)	RSD (%)
²³ Na	21730	23400±800	93	2.0	15262	16400±600	93	1.6
³¹ P	1803	1500±100	120	2.0	1333	1200±100	111	0.6
³⁹ K	14447	14900±400	97	1.8	4283	4300±100	100	1.7
⁴⁷ Ti	12972	13500±300	96	0.9	15930	16300±200	98	2.3
⁵¹ V	463	416±14	111	1.2	370	317±11	117	1.6
⁵² Cr	19	18±2	107	0.9	294	280±19	105	1.1
⁵⁵ Mn	1567	1520±60	103	0.3	1397	1290±40	108	1.9
⁵⁹ Co	39	37±3	107	1.8	41	45±3	91	0.2
⁶⁰ Ni	6.9	NC	N/A	0.4	110	119±7	92	1.2
⁶³ Cu	9.7	19±2 (IC)	51	2.0	114	127±7	89	1.4
⁶⁶ Zn	148	127±9	116	1.5	114	103±6	111	1.2
⁹⁰ Zr	187	188±16	99	0.4	173	172±11	101	0.6
²⁰⁸ Pb	18.1	11±2 (IC)	164	0.4	9.97	NC	N/A	0.2
²⁷ Al	70016	71400±1000	98	2.8	70062	71600±800	98	2.2
⁵⁴ Fe	93327	96500±1500	97	2.4	83865	86300±1400	97	1.0
⁴⁴ Ca	49185	50900±800	97	0.9	78087	81700±1200	96	1.1
²⁴ Mg	20980	21600±300	97	1.7	38853	43600±700	89	0.9

Note:

NC means that the concentration for the element was not given for the reference material in the USGS certificate of analysis.

IC = Information value given by the USGS certificate.

RSD = Relative standard deviation (precision) estimated from 3 replicates of the ICP-MS analysis for the same digested solution, done on the same day.

N/A = Not applicable

Table 6

Minor and trace elements concentrations ($\mu\text{g g}^{-1}$) in eight komatiites rocks determined by ICP-MS after microwave digestion

Element	Concentration ($\mu\text{g g}^{-1}$)							
	8-PPR-97	RSD (%)	20/LaC	RSD (%)	AC-2	RSD (%)	HCOM-3	RSD (%)
Na	439	1.3	24332	2.4	2211	4.4	564	3.0
P	176	1.9	138	4.0	96	7.3	8.3	18.7
K	250	1.4	720	3.4	776	2.9	50	5.4
Ti	3632	2.9	3237	2.6	1925	1.9	272	0.6
V	198	3.6	237	3.2	137	1.9	56	0.9
Cr	2049	0.6	759	2.0	2374	2.3	2003	1.2
Mn	1205	1.5	1613	1.2	1164	2.4	701	1.3
Co	96	1.2	60	1.9	82	2.5	87	1.8
Cu	31	0.8	31	1.1	44	2.5	BLOD	N/A
Ni	1294	1.1	189	0.2	1261	0.7	1788	0.4
Zn	586	1.0	58	2.2	63	2.6	31	1.9
Zr	32	11.4	17	12.9	14	2.2	0.85	1.5
Pb	3.2	1.5	5.9	1.8	664	0.5	BLOD	N/A

Concentration ($\mu\text{g g}^{-1}$)									
	K5-31-99C	RSD (%)	U-23	RSD (%)	ZV-58	RSD (%)	MCD-106	RSD (%)	LOD (ng g^{-1})
Na	679	2.4	36	4.0	5727	2.1	148	1.2	1.7
P	215	1.2	68	1.3	196	4.5	80	1.7	2.9
K	346	1.1	38	2.8	720	4.4	58	4.3	4.8
Ti	2186	3.0	3001	3.6	1646	0.9	1837	2.1	0.3
V	109	3.9	166	2.9	110	1.4	145	2.0	2.2
Cr	2197	1.7	2838	1.6	1236	1.7	1810	0.7	0.7
Mn	1474	1.2	1012	2.7	1297	1.8	1213	0.5	0.4
Co	89	0.5	101	0.9	94	0.7	98	2.3	0.4
Cu	87	1.2	79	3.2	50	0.7	98	2.7	3.6
Ni	1090	0.2	1403	2.5	1420	1.9	1665	1.7	1.0
Zn	66	1.2	63	0.7	64	3.4	59	1.4	5.7
Zr	16	1.0	2.4	1.3	12	1.1	8.5	11.4	0.5
Pb	0.56	2.4	BLOD	N/A	BLOD	N/A	8.2	0.2	0.4

RSD = Relative standard deviation (precision) estimated from 3 replicates of the ICP-MS analysis for the same digested solution, done on the same day.

LOD = Limit of detection

BLOD = Below the limit of detection

N/A = Not applicable

Table 7

Major elements concentrations (%) in komatiites rocks determined by ICP-MS after microwave digestion compared with XRF analysis

Element	Concentration (%)											
	8-PPR-97			20/LaC			AC-2			HCOM-3		
	ICP-MS	RSD (%)	XRF	ICP-MS	RSD (%)	XRF	ICP-MS	RSD (%)	XRF	ICP-MS	RSD (%)	XRF
MgO	21.1	1.2	22.1	11.8	3.1	12.8	25.6	0.8	27.6	42.2	2.1	38.0
Fe ₂ O ₃	11.6	1.1	11.5	12.1	1.3	12.4	10.2	0.9	10.1	6.6	1.2	6.6
Al ₂ O ₃	7.8	3.2	7.0	12.1	1.6	11.2	6.6	1.2	6.1	3.4	2.0	3.0
CaO	7.9	1.5	8.5	8.6	0.5	8.5	5.6	1.4	5.3	1.3	0.9	1.4

	Concentration (%)												
	K5-31-99C			U-23			ZV-58			MCD-106			LOD
	ICP-MS	RSD (%)	XRF	ICP-MS	RSD (%)	XRF	ICP-MS	RSD (%)	XRF	ICP-MS	RSD (%)	XRF	ICP-MS (ng g ⁻¹)
MgO	25.6	0.8	25.8	30.4	1.2	28.1	30.0	1.5	28.9	29.7	3.1	30.2	3.8
Fe ₂ O ₃	11.8	1.1	12.2	12.7	0.4	12.3	10.7	1.0	10.8	9.2	0.2	10.0	2.7
Al ₂ O ₃	3.2	0.7	3.3	6.6	1.7	6.5	6.0	1.7	5.3	4.4	2.5	4.3	0.5
CaO	7.3	0.7	7.2	2.6	1.7	3.1	5.5	0.9	5.2	4.8	0.5	5.2	0.8

RSD = Relative standard deviation (precision) estimated from 3 replicates of the ICP-MS analysis for the same digested solution, done on the same day.

Table 8

Major element composition (%) and elemental recovery determined for both basalt reference materials by XRF compared with the USGS certified values

Element	BCR-2			BHVO-2		
	XRF	USGS	Recovery (%)	XRF	USGS	Recovery (%)
SiO ₂	53.27	54.1	98	48.92	49.9	98
Fe ₂ O ₃	14.16	13.8	103	12.48	12.3	101
Al ₂ O ₃	13.20	13.5	98	13.23	13.5	98
CaO	7.15	7.12	100	11.45	11.40	100
MgO	3.71	3.59	103	7.42	7.23	103
Na ₂ O	3.13	3.16	99	2.18	2.22	98
TiO ₂	2.33	2.26	103	2.74	2.73	100
MnO	0.20	0.15	133	0.17	0.129	132
P ₂ O ₅	0.35	0.35	100	0.27	0.27	100