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Determination of Trace Element Mass Fractions in Ultramafic Rocks by HR-ICP-MS: A Combined Approach Using a Direct Digestion/Dilution Method and Pre-concentration by Co-precipitation

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A procedure is described for the determination of thirty-seven minor and trace elements (LILE, REE, HFSE, U, Th, Pb, transition elements and Ga) in ultramafic rocks. After Tm addition and acid sample digestion, compositions were determined both following a direct digestion/dilution method (without element separation) and after a pre-concentration procedure using a double co-precipitation process. Four ultramafic reference materials were investigated to test and validate our procedure (UB-N, MGL-GAS [GeoPT12], JP-1 and DTS-2B). Results obtained following the pre-concentration procedure are in good agreement with previously published work on REE, HFSE, U, Th, Pb and some of the transition elements (Sc, Ti, V). This procedure has two major advantages: (1) it avoids any matrix effect resulting from the high Mg content of peridotite, and (2) it allows the pre-concentration of a larger trace elements set than with previous methods. Other elements (LILE, other transition elements Cr, Mn, Co, Ni, Cu, Zn, as well as Ga) were not fully co-precipitated with the pre-concentration method and could only be accurately determined through the direct digestion/dilution method.

Keywords: trace elements, ultramafic rocks, reference materials, thulium spike, co-precipitation, HR-ICP-MS.

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Ultramafic rocks are an important component of the Earth, constituting more than 80% of its volume. Exposed in response to tectonic processes (ophiolites, orogenic massifs or abyssal peridotites) or as xenoliths in lavas, mantle peridotites are viewed as residues of partial melting. Undoubtedly linked to the petrogenesis of basaltic magmas, to their transfer as well as to their chemical signature, peridotites have, up to the present, been mostly investigated through the chemistry of their pyroxenes, either after mineral separation or with *in situ* measurement techniques (i.e., SIMS and LA-ICP-MS). In contrast with the wealth of data acquired for pyroxene, olivine remains poorly studied for its trace element contents, despite making up more than half of the modal content of peridotites. In fact, olivine reveals significant differences in mass fractions that can reach ten orders of magnitude between major Mg and Fe cations (approx. MgO ~ 50 g/100 g and FeO ~ 10 g/100 g) and trace elements such as REE or HFSE (sub ng g⁻¹) (e.g., Rampone *et al.* 2016, Stead *et al.* 2016). Attempts to investigate the chemical content of olivine and/or bulk olivine-rich lithologies (dunites, orthopyroxene-poor harzburgites) commonly used ICP-MS after dissolution followed by simple dilution. In rock analysis by ICP-MS, the high mass fraction of major elements in the rock solution can lead to a reduction of trace element signal intensities or to a partial blockage of the ICP-MS orifice (Beauchemin *et al.* 1987, Kawaguchi *et al.* 1987, Makishima and Nakamura, 1997). Consequently the dilution factor is critical in order to investigate trace element mass fractions in peridotites: when the dilution factor is *high*, most of the trace elements occur below the detection limit; when *low*, matrix effects become a critical issue (Makishima and Nakamura 1997, 2006).

To overcome the matrix effects caused by high major element contents and to minimise the dilution factor, separating trace elements from the matrix and pre-concentrating them may be performed either by extraction chromatography or by co-precipitation process. The co-precipitation method was first applied to seawater and soil analyses (e.g., Goldberg *et al.* 1963, Akagi *et al.* 1985, Greaves *et al.* 1989, Taicheng *et al.* 2002, Shaw *et al.* 2003, Jeandel *et al.* 2011). It consists of co-precipitating trace elements with an induced precipitation of iron, magnesium, titanium or gallium hydroxides after Fe, Mg, Ti or Ga addition. This method was later adapted to ultramafic rocks to investigate their elemental and isotopic chemistry, using the sample's natural Mg and Fe contents, and does not therefore need addition of other cations (e.g., Sharma *et al.* 1995, Sharma and Wasserburg 1996, Bizzarro *et al.* 2003, Qi *et al.* 2005, Bayon *et al.* 2009). A pH higher than 10 triggers the precipitation of Mg(OH)₂, co-precipitating the trace elements and leaving iron in solution; however, a pH of

ca. 9 leads to the precipitation of Fe(OH)₃ and leaves the magnesium in the supernatant (Sharma and Wasserburg, 1996, Qi *et al.* 2005). Recently, the Tm addition method (Barrat *et al.* 1996) was introduced in co-precipitation procedures allowing (1) the calculation of the trace element compositions using the Tm positive anomaly in the REE pattern and (2) correction for any loss of analyte during preparation (Bayon *et al.* 2009, Freslon *et al.* 2011).

During our experiments, the aim was to combine and extend previous methods in order to measure the mass fractions of a large set of trace elements that may potentially give information on the magmatic history of ultra-depleted residual peridotites, such as harzburgite or dunite. Following the Tm addition (Barrat *et al.* 1996, Bayon *et al.* 2009), we associated the sample digestion/dilution method from Yokoyama *et al.* (1999) with an adapted pre-concentration procedure combining specific aspects of different co-precipitation methods (Bizzarro *et al.* 2003, Qi *et al.* 2005). The procedure of Qi *et al.* (2005) is a way to avoid any potential matrix effect caused by the high Mg content in peridotites, using two successive Mg(OH)₂ and Fe(OH)₃ co-precipitations for the determination of REE + Y. In their study Bizzarro *et al.* (2003) showed the efficiency of the co-precipitation method to determine the mass fraction of other HFSE such as Zr and Hf. Our approach, combining the direct method after sample digestion and dilution and an adapted co-precipitation method, allowed us to determine thirty-seven minor and trace elements including Li, LILE (Rb, Sr, Cs, Ba), HFSE (Y, Zr, Nb, REE, Hf, Ta, Th, U), Pb, other transition elements (Sc, Ti, V, Cr, Mn, Co, Ni, Zn) and Ga in four ultramafic reference materials ranging for example from 10⁻² to two times the chondritic values in REE (DTS-2B, JP-1, MGL-GAS, UB-N).

Experimental procedure

Reagents and reference materials

During all experiments we used de-ionised water (18.2 MΩ cm) purified with a Milli-Q system (Millipore®), hydrochloric (~ 37 g/100 g, Fisher Scientific®, Loughborough, England) and nitric (68 g/100 g, GPR RECTAPUR®, VWR International S.A.S., Fontenay-sous-Bois, France; VWR BDH Prolabo®) acids cleaned by sub-boiling distillation, 49 g/100 g hydrofluoric acid for ultra trace analysis (*TraceSELECT*® Ultra, Fluka® analytical, SIGMA-ALDRICH®, St. Louis, USA) and 69–72 g/100 g certified ACS reagent grade perchloric acid (Fluka® analytical, SIGMA-ALDRICH®, St. Louis, USA) without further purification, and a high purity thulium solution (custom grade, 62N-1, AccuStandard®).

To trigger co-precipitation during the pre-concentration procedure, 25 g/100 g ammonia (Suprapur[®], Merck KGaA, Darmstadt, Germany) and 7.5 mol l⁻¹ sodium hydroxide solutions were used. This latter was prepared by dissolving about 300 g of anhydrous NaOH pellets (purity > 99%, AnalR NORMAPUR[®], VWR International BVBA, Leuven, Belgium; VWR BDH Prolabo[®]) in one litre of high purity water.

To test and to validate the measurement precision of our procedure we investigated four ultramafic reference materials (RMs) including the serpentinite UB-N (ANRT), the peridotite JP-1 (Geological Survey of Japan, GSJ), the serpentinite MGL-GAS (GeoPT12; International Association of Geoanalysts, IAG) and the dunite DTS-2B (United States Geological Survey, USGS). BHVO-2 (USGS) was analysed as the calibrator during our measurement sessions.

Sample preparation

Our experimental procedure combined further aspects of previous studies: (1) the Tm addition of Barrat *et al.* (1996), later adapted by Bayon *et al.* (2009); (2) the sample digestion presented by Yokoyama *et al.* (1999); (3) a pre-concentration of trace elements in ultramafic samples especially following the double Mg(OH)₂-Fe(OH)₃ co-precipitation method developed by Qi *et al.* (2005).

About 0.200 g of sample powder were accurately weighed and transferred to 22 ml Savillex[®] PFA beakers. From about 1.5 to 15 ng of Tm (in solution) were added to each sample – except to the blank and to the reference material BHVO-2 – depending on the expected bulk-rock trace element content: about 1.5, 3, 6 and 15 ng for DTS-2B, JP-1, MGL-GAS and UB-N respectively.

Our sample digestion procedure largely followed method C of Yokoyama *et al.* (1999), following three distinctive stages. The first stage consisted to add 1 ml 72 g/100 g HClO₄ + 1 ml 49 g/100 g HF to each sample; then capped beakers were placed on a hot plate at 130 °C for 24 h. After cooling acids were evaporated following three dryness steps: 8 h at 130 °C, 12 h at 165 °C and 1–2 h at 195 °C. Due to the high evaporation temperature of perchloric acid, these steps allowed us to remove silica without forming fluorides which are known to co-precipitate trace elements and to be insoluble (Langmyhr and Sveen 1965, Croudace 1980, Boer *et al.* 1993, Yokoyama *et al.* 1999). The second stage comprised 1 ml 72 g/100 g HClO₄,

a heating step of 10–12 h at 140 °C, and a replication of the three previous dryness steps. Because the complete dissolution of spinel in ultramafic rocks is particularly difficult to achieve (Jain *et al.* 2000, Nakamura and Chang 2007), this second stage required repeated heating and treatments in ultrasonic bath steps for DTS-2B, which contains a higher amount of spinel than the three other investigated RMs. For the same reason, the duration of the heating step needed to be extended to 24 h for DTS-2B. The third and last stage consisted of the addition of 1 ml HCl (6 mol l⁻¹) and evaporation to dryness at 110 °C. The 6 mol l⁻¹ HCl was previously prepared from our in-house produced doubly distilled HCl.

The solid residue was dissolved in 1 ml HNO₃ (15 mol l⁻¹) and diluted with 4 ml of high purity water. The solution was transferred to a 50 ml centrifuge tube and the volume adjusted to 40 ml with high purity water to reach a solution concentration of 0.37 mol l⁻¹ HNO₃. At this stage a fraction of 0.8 ml was collected from this “mother solution”, transferred to a 50 ml centrifuge tube and adjusted to 40 ml with 0.37 mol l⁻¹ HNO₃ to give a dilution factor of 10000. This final solution was dedicated to the direct measurement of trace element content, i.e., without pre-concentration, and is referenced for the following as the fraction being analysed through the *direct method*. BHVO-2 and blanks were analysed only following this procedure with dilution factors of 6000 and 1000 respectively.

The remnant mother solution was retained in order to be processed through a double co-precipitation reaction, mainly adapted from Qi *et al.* (2005). First, 400 µl of a 7.5 mol l⁻¹ sodium hydroxide solution were added to raise pH above 12, leading to Mg(OH)₂ precipitation from the sample’s natural Mg content, while the main iron content remained in solution; a white to yellowish precipitate containing a small amount of iron was formed at this stage. After centrifugation for 5 min at 3600 rpm, the supernatant was discarded. Two successive rinses were made, adding 40 ml high purity water followed by further centrifugation and supernatant separation steps. Following this first Mg co-precipitation stage, the precipitates were dissolved with three drops of concentrated bi-distilled HNO₃ (15 mol l⁻¹) and diluted again in 40 ml of high purity water. Following Sharma *et al.* (1995) and Bizzarro *et al.* (2003), we added 1 ml 25 g/100 g ammonia solution leading to the formation of iron hydroxides from the small Fe amount trapped with previous Mg(OH)₂, which gave a rusty coloured precipitate. With a pH of about 9 (ammonia solution) most of the magnesium remains in solution (Sharma and Wasserburg 1996, Qi *et al.* 2005). The supernatant containing magnesium was removed by re-applying the centrifugation and the two rinse steps.

The solid precipitate was then dissolved in 0.5 ml HNO_3 (15 mol l^{-1}) and adjusted to 20 ml with high purity water. At this stage 1 ml was collected and adjusted to 9.8 ml with 0.37 mol l^{-1} HNO_3 to obtain a final solution with a dilution factor of 1000. The procedure that allowed to the determination of trace element mass fractions following co-precipitation is referred to as the *co-precipitated method*.

Instrumentation and data acquisition

An ELEMENT XRTM (Thermo ScientificTM) HR-ICP-MS at the Géosciences Environnement Toulouse laboratory, Université Paul Sabatier Toulouse III (Observatoire Midi-Pyrénées, Toulouse) was used for trace element determinations. The operating conditions are summarised in Table 1. Sample solutions (0.37 mol l^{-1} HNO_3) were introduced with a peristaltic pump through the nebuliser and transported *via* Ar gas to the quartz plasma torch and to the interface made of Ni sampling and skimmer cones. The nebuliser and the cones were dedicated to the analysis of ultra-depleted samples as those reported here, and were used only during our measurement sessions to avoid contamination.

Oxide or hydroxide recombination in the Ar plasma may generate interferences on measured intensity of a given element, especially barium oxide on europium and LREE oxides on HREE (e.g., Ionov *et al.* 1992). Daily analytical conditions showed low element recombination with oxide rates (BaO^+/Ba^+ , CeO^+/Ce^+) mainly below 1%. In Table 1 oxide rate and doubly charged for Ba are given as information values applicable to the operating conditions before the start of a measurement session. To monitor interference effects, we measured calibration solutions of high purity water, Sm + Eu + Gd + Tb, Pr + Nd and Ba + Ce at the beginning of each measurement session to estimate the oxide and hydroxide contribution on REE measurements (Ionov *et al.* 1992, Barrat *et al.* 1996), and to correct the interferences that may occur on ^{169}Tm in particular.

Measurement sequences consisted of the analysis of a 0.37 mol l^{-1} HNO_3 blank, a sample procedural blank corresponding to the sample digestion procedure, BHVO-2 as a calibrator, and test portions of the selected reference materials. Thanks to its precisely known composition (<http://georem.mpch-mainz.gwdg.de>; Barrat *et al.* 2012), BHVO-2 was measured both as a calibrator to calculate the trace element content of samples and to correct measurements for instrumental drift. As part of this protocol four reference materials were analysed between two of the calibrator BHVO-2. We also measured blanks for the NH_3

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ultrapur reagent as well as for the NaOH solution used to perform the double-co-precipitation process. They were prepared following the same procedure applied to co-precipitate trace elements including the successive dilution/evaporation steps. As explained below the RMs were corrected from the total co-precipitation blank contribution following two steps, first raw data obtained on the procedural blank ($0.37 \text{ mol l}^{-1} \text{ HNO}_3$ blank + contribution following the sample digestion) is subtracted from the samples measurements (i.e., taking into account the different dilution factor between the samples and the blanks), and then the calculated content in added NaOH and NH_3 fractions is subtracted after the samples concentrations calculation. Samples prepared following the direct method were thus corrected from the *procedural blank* only (related to the samples digestion and dilution), while co-precipitated ones were corrected from the *total co-precipitation blank* (i.e., including the blank contribution following the NaOH and NH_3 solutions using). Because sodium highly affects the stability of the plasma during acquisition by ICP-MS, we decided to analyse only one Tm-spiked NaOH fraction at the beginning of our experiment rather than measure it at each measurement session. In this way we determined a blank for our NaOH base solution, as well as for NH_3 to facilitate the correction from the both buffer/basic solution blanks contribution. Each measurement performed on pre-concentrated samples was corrected from this blank's contribution assuming that this contribution was constant from an added fraction to the other.

Data reduction

First, the raw data were corrected for instrumental drift, then for the procedural blank contribution and finally for the oxide/hydroxide interferences. The drift of the signal intensity through time was constrained by bracketing using BHVO-2. We analysed four reference materials between two BHVO-2. To calculate the mass fraction of a given element X in each RM, we used an interpolation of the BHVO-2 signal intensity (counts per second or cps), assuming that the instrumental drift was linear between two BHVO-2 analyses. Raw data obtained following both the direct and pre-concentration methods were corrected for the procedural blank (i.e., contribution from the $0.37 \text{ mol l}^{-1} \text{ HNO}_3$ and from the sample digestion) by subtracting blank signal intensities. Measured intensities were then corrected for oxide/hydroxide interferences following the method of Barrat *et al.* (1996). The blank and oxide/hydroxide corrections were made both for BHVO-2 and for the reference materials.

The following variables are used in the equations:

- $X_{\text{sample solution}}$: cps for the element X in the sample solution after blank subtraction, and REE corrected for oxide/hydroxide interferences.
- $X_{\text{BHVO-2}}$: cps for the element X in the BHVO-2 solution after blank subtraction, and REE corrected for oxide/hydroxide interferences.
- $[X]_{\text{BHVO-2}}$: reference mass fraction for the element X ($\mu\text{g g}^{-1}$) in BHVO-2 following Barrat *et al.* (2012) (see also GeoRem values).
- $[X]_{\text{sample solution}}$: mass fraction of the element X ($\mu\text{g g}^{-1}$) in the sample solution.
- $[\text{Tm}^*]$: Tm mass fraction in the sample solution with no spike contribution, interpolated from $[\text{Er}]_{\text{sample solution}}$ and $[\text{Yb}]_{\text{sample solution}}$ ($\mu\text{g g}^{-1}$).
- $[\text{Tm}]_{\text{spike}}$: Tm mass fraction in the spike solution ($\mu\text{g g}^{-1}$).
- M_{sample} : sample mass (g).
- $M_{\text{Tm spike}}$: spike mass (g).
- $[X]_{\text{sample}}$: mass fraction of the element X in the sample ($\mu\text{g g}^{-1}$).

The trace element content of BHVO-2 (GeoRem; Barrat *et al.* 2012) was used to estimate all [X] mass fractions in the sample solution following:

$$[X]_{\text{sample solution}} = \frac{(X_{\text{sample solution}} \times [X]_{\text{BHVO-2}})}{X_{\text{BHVO-2}}} \quad (1)$$

This mass fraction is an approximation, uncorrected from the Tm spike/sample ratio. The sample mass fraction was calculated using this ratio following the description of Barrat *et al.* (1996). The measured Tm signal comprises both the signal brought by the spike and the one due to the natural Tm mass fraction in the sample. The sample $[\text{Tm}^*]$ is calculated using the sample solution [Er] and [Yb] mass fractions, following:

$$[\text{Tm}^*] = 0.02561 \times \left(\frac{[\text{Er}]_{\text{sample solution}}}{0.166} \times \frac{[\text{Yb}]_{\text{sample solution}}}{0.1651} \right)^{1/2} \quad (2)$$

Equation (3) gives the mass fraction of each element X ($[X]_{\text{sample}}$) in the sample, knowing the mass fraction X and Tm in the sample solution ($[X]_{\text{sample solution}}$ and $[\text{Tm}]_{\text{sample solution}}$) calculated from (1), $[\text{Tm}^*]$ calculated from (2), and M_{sample} , $M_{\text{Tm spike}}$ and $[\text{Tm}]_{\text{Tm spike}}$:

$$[X]_{\text{sample}} = [X]_{\text{sample solution}} \times \left(\frac{M_{\text{Tm spike}} \times [\text{Tm}]_{\text{spike}}}{M_{\text{sample}} \times ([\text{Tm}]_{\text{sample solution}} - [\text{Tm}^*])} \right) \quad (3)$$

Following (3), the final mass fractions for co-precipitated fractions are obtained after NH₃ and NaOH blank subtractions.

Results and discussion

Detection limits and total procedural blanks

The procedural blank (Table 2) includes the 0.37 mol l⁻¹ HNO₃ blank in which samples were diluted and the sample blank prepared using the digestion method. Its intensity (cps) was subtracted from the data for the direct method and is given here as concentration (ng g⁻¹). The total co-precipitation blank combines the procedural blank and blanks measured for NaOH and NH₃ solutions, and was therefore subtracted from all samples processed through the pre-concentration method (see Table 3 for details).

In several cases the NaOH has to be purified (e.g., Qi *et al.* 2005). A NaOH purification was tested adding a little amount of an ultrapure Mg solution to NaOH, in order to co-precipitate trace elements together with Mg(OH)₂. This led to the purification of some trace elements by a factor of 20 to 50% but also increased Y, LREE, MREE and Hf contents in the NaOH solution. Furthermore the total co-precipitation blank, which included blanks of unpurified NaOH and NH₃, was about one to two times the procedural blank only, especially in Y, Nb, La, Ce, Pr, Tb, Ho and Th. This highlights that the NaOH and NH₃ blank contributions were low enough to hardly affect the results, and that these reagents could be used without any purification.

The total blank contribution was, with few exceptions, within the 1% of the RMs trace element mass fraction. The exceptions concern elements in very low mass fraction including Nb and Ta. The blank contribution on Nb signal intensity was about 4.7% and 4.4 % for UB-N and MGL-GAS and 6.7 and 7.9% for DTS-2B and JP-1 respectively. Concerning Ta, the blank contribution was low for UB-N (2.7%) and reached 14.4% in JP-1. Total blanks in REE were below 1% of the UB-N and MGL-GAS content, below 4% and 5% in JP-1 and DTS-2B respectively. Exceptions were the blank contributions on Eu in JP-1 (5.5%) and on MREE in DTS-2B (Eu: 10.7%, Gd: 4.3%, Tb: 8%).

Direct method *versus* co-precipitation method

In their paper Qi *et al.* (2005) show that the Mg-Fe double-co-precipitation allows the determination of REE and Y mass fractions in ultramafic rock samples with low measurement uncertainties. To investigate which additional trace elements may be determined using this method, we focussed on UB-N, a widely studied rock reference material (serpentinite) for which the literature offers mass fractions for a large set of elements.

Figure 1 shows our averaged results obtained on five replicates of UB-N following both the direct method and our adapted co-precipitation procedure. In regard to working values proposed by previous authors, we can see that REE and Y have co-precipitated as expected while mobile elements (Li, Rb, Sr, Cs, Ba) remained in the supernatant. The pre-concentration method also co-precipitated a much larger set of elements – Sc, Cr, Mn, Co, Zr, Ta, Pb, Th and U – for which determined concentrations are very similar to (1) the results following the direct method and (2) the recommended or proposed values. Some differences may further be noticed between both methods. Ti, V, Nb and Hf are systematically lower following the co-precipitation method but are nearly similar to compiled literature data, leading us to conclude that the direct method overestimates the mass fraction of these four elements. On the contrary, Ni, Cu, Zn and Ga, display lower values in the pre-concentration batch, therefore appearing to be not fully co-precipitated. The mass fraction calculated for the five co-precipitated replicates shows a huge variability for these elements, which implies that the bias is not systematic. Following these observations the co-precipitation procedure appears to be an efficient method to catch a larger set of trace elements than previously investigated (Qi *et al.* 2005, Bayon *et al.* 2009) including REE and Y, HFSE, U, Th, Pb and some of the transition elements (Sc, Ti, V, Cr, Mn, Co). On the contrary, LILE and other transition elements (Ni, Cu, Zn) and Ga seem to be well determinable only following the simpler direct digestion/dissolution method.

Measurement precision

The mass fraction of each element in the four investigated RMs is given in Table 3 following the method that displays the best accuracy. The associated standard deviation s ($\mu\text{g g}^{-1}$) and relative standard deviation (RSD in %) are given as reflecting the intermediate precision of the averaged composition. Note that our results obtained for the RM DTS-2B are compared with both DTS-2 and DTS-2B due to the lack of data concerning DTS-2B excepting the large set proposed by Robin-Popieul *et al.* (2012).

The REE mass fractions are determined following the co-precipitation procedure and display an intermediate precision expressed as RSD lower than 5% for UB-N and lower than 10% for MGL-GAS (GeoPT12), JP-1 and DTS-2B (excepting Gd in MGL-GAS ~ 11%) (Table 3). In comparison the direct method allows to a slightly lower intermediate precision on HREE (10 < RSD < 15% for MGL-GAS (GeoPT12) and DTS-2B) and the precision is particularly worse for MREE (Sm, Eu and Gd) with RSDs between 10 and 35%. Measured mass fractions are in good agreement with previously proposed values and REE patterns are particularly smoothed (Figure 2). JP-1 and MGL-GAS exhibit a well-defined negative Eu anomaly in agreement with Bayon *et al.* (2009) and Qi *et al.* (2005) respectively. On the contrary, the direct method leads to an overestimation of MREE and especially of Eu that displays a strong positive anomaly in patterns for the most depleted ultramafic RMs JP-1 and DTS-2B. This may be attributed to an under-estimation of the Ba oxide interferences during the direct method procedure leading to an overestimation of the Eu mass fraction. This is supported by the fact that the most affected reference materials are those with the highest barium mass fraction relative to middle rare earth elements (i.e., Ba/Sm = 1000–4000 in JP-1 and DTS-2B, less than 300 in UB-N and MGL-GAS). On the contrary, Ba is lost during the co-precipitation procedure and therefore barium oxide interferences are drastically lowered. The pre-concentrated samples expose a Eu mass fraction similar to working values; accordingly, the co-precipitation method is well adapted for the determination of REE, and especially of MREE, in ultra depleted ultramafic rocks.

Other (ultra-)trace elements (Y, Zr, Nb, Hf, Ta, Pb, Th and U) were measured using the two procedures. The intermediate precision after the direct method is systematically worse than after the pre-concentration process and is not specifically discussed here. Following the co-precipitation procedure the intermediate precision for Y, Pb, Th and U is, with few exceptions, better than 10%, being slightly higher for the most depleted RM DTS-2B (U: 12.3%) (Table 3). Measured mass fractions are in good agreement with published results on UB-N, MGL-GAS and JP-1. For DTS-2B, Y, Pb and U mass fractions are in good agreement with the values proposed by Robin-Popieul *et al.* (2012) while the Th content is slightly higher (Table 3).

With regard to other HFSE (Zr, Nb, Hf, Ta), measured mass fractions are close to available published data for UB-N. The measurement results for Zr and Nb in UB-N display a intermediate precision slightly higher (< 12%) than recent precise results from Godard *et al.* (2008) and Chauvel *et al.* (2011) (Table 3). Results for Zr and Hf in JP-1 show a good

precision (< 3%) while Nb (14.2%) and Ta (28.8%) show a much lower intermediate precision, which we attribute to their very low contents (30 and 3 ng g⁻¹ respectively). Results for Hf, Nb and Ta are in good agreement with working values and compiled values from GeoReM (<http://georem.mpch-mainz.gwdg.de>) while determined concentration for Zr is slightly higher (Table 3). The intermediate precision of Zr and Nb in DTS-2B remains below 20% but reaches 38.3% for Hf, and is therefore indicated as an information value only (Table 3). The values we present are higher in each Zr, Nb and Hf than previously proposed (Robin-Popieul *et al.* 2012), but they are calculated from ten replicate analyses, on the contrary to those proposed by Robin-Popieul *et al.* (2012). Similarly to JP-1, measurements on MGL-GAS display a good precision for Zr and Hf (< 6%), being much variable for Nb (17%). The result for Hf is in good agreement with the value proposed by Potts *et al.* (2003). Because they were never proposed we present new values for Zr and Nb in MGL-GAS but not for Ta, owing to its poor precision (Table 3).

Scandium, Ti, V, Cr, Mn and Co are fully co-precipitated, as shown in Figure 1. Results obtained for Sc, Ti and V are similar between direct and pre-concentration methods. The intermediate precision is better after co-precipitation in particular for Ti. RSD values for these elements were systematically lower than 10.9%. On the contrary, the intermediate precision for Cr, Mn and Co is better following the direct method, especially for UB-N and DTS-2B (< 8.3%). Mass fractions are generally in good agreement with previous studies. Titanium and V contents are slightly higher for MGL-GAS and JP-1 than values proposed by Potts *et al.* (2003) (MGL-GAS) and Makishima and Nakamura (2006) and Barrat *et al.* (2008) (JP-1) but the values for UB-N and DTS-2B are very similar to compiled values (Figure 3). Other transition elements (Ni, Cu, Zn) and Ga were not fully co-precipitated through the pre-concentration procedure (Figure 1) and were only accurately determined by the direct method. With the exception of Zn in UB-N (10.6%), the RSD values for Ni, Cu, Zn, Ga for UB-N and MGL-GAS were systematically lower than 7.5%. For JP-1 and DTS-2B, the RSD values of Ni, Cu, Zn, Ga were slightly higher, but, with the exception of Zn in both materials and Cu in JP-1, they remain below 9%. Despite the variability, our results are close to the published values (Figure 3 and Table 3).

Lithium and LILE (Rb, Sr, Cs, Ba) were totally discarded during the pre-concentration procedure and thus were determined following the direct method. The intermediate precision is lower than 6% for UB-N and MGL-GAS (excepting Cs in UB-N with a RSD = 9.5%) and

lower than 9% for JP-1. The precision was more variable for DTS-2B. RSD values were lower than 5.2% for Sr and Ba, but worse for Li (11.3%), Rb (13.2%) and particularly for Cs (21.8%). In the case of Cs this can be linked to the high blank contribution in regard to its very low mass fraction in DTS-2B (1.8 ng g⁻¹).

Conclusions

To investigate trace element contents in natural peridotite samples, the simple direct digestion/dilution method enables the measurement of a large set of elements and to determine trace element mass fractions as low as 0.1 µg g⁻¹. A pre-concentration method is however needed to determine with a good intermediate precision elements in lower mass fraction. Pre-concentration methods using co-precipitation are efficient to separate REE from major elements, avoiding matrix effect and displaying a intermediate precision generally better than 10% (e.g., Qi *et al.* 2005, Bayon *et al.* 2009). Adapting the double Mg(OH)₂ and Fe(OH)₃ co-precipitation procedure from Qi *et al.* (2005), we show that other trace elements such as HFSE and transition elements can be determined following this method. Combined with the Tm addition of Barrat *et al.* (1996), we show reproducible results for UB-N, JP-1, MGL-GAS and DTS-2B, similar to proposed values in the literature, and with good precision. Concerning DTS-2B for which trace element compositions were rarely proposed due to their very low content, we propose HFSE values that slightly differ with the ones published by Robin-Popieul *et al.* (2012). Due to the good intermediate precision obtained on other ultra depleted elements such as MREE, we propose to better refer about our new proposed values. We also provide new HFSE data for MGL-GAS. Considering the extremely depleted character of olivine and the difficulty in reaching mass fractions as low as 0.5–1 ng g⁻¹, we envision that this procedure can be applied to determine trace element contents in separated olivine or olivine-rich peridotite lithologies and to facilitate pre-concentration in the perspective of isotope studies.

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Figure captions

Figure 1. Chondrite-normalised (Barrat *et al.* 2012) minor and trace elements pattern for an average of five replicates of UB-N. To focus on the selectivity of the elements co-precipitated during the pre-concentration procedure, no distinction is made between the patterns from the literature. A more detailed comparison is shown in Figure 3. Compositions are taken from Govindaraju (1995), Carignan *et al.* (2001), Godard *et al.* (2008), Bayon *et al.* (2009), Chauvel *et al.* (2011) and Robin-Popieul *et al.* (2012). Chondrite values are from Barrat *et al.* (2012). For ease of readability, the normalised compositions of Ni on the one hand and of Li, Cs and Ba in the other are divided by 1000 and 10 respectively. The grey shaded area highlights the elements that were efficiently co-precipitated following our procedure adapted from Qi *et al.* (2005).

Figure 2. Chondrite-normalised (Barrat *et al.* 2012) REE patterns obtained for UB-N, MGL-GAS, JP-1 and DTS-2B following both the direct and co-precipitation procedures. Results are

compared with literature values from Govindaraju (1995), Raczek *et al.* (2001), Carignan *et al.* (2001), Potts *et al.* (2003), Qi *et al.* (2005), Makishima and Nakamura (2006), Nakamura and Chang (2007), Godard *et al.* (2008), Barrat *et al.* (2008), Bayon *et al.* (2009), Chauvel *et al.* (2011), Ulrich *et al.* (2012), and Sun *et al.* (2013).

Figure 3. Chondrite-normalised (Barrat *et al.* 2012) trace element patterns obtained for UB-N, MGL-GAS, JP-1 and DTS-2B compared with previous work. Mass fractions were compiled following the direct method (regular font) and the co-precipitation method (bold) (Table 3).

Results are compared with literature values from Govindaraju (1995) together with the SARM certificate for UB-N, Raczek *et al.* (2001), Carignan *et al.* (2001), Potts *et al.* (2003), Qi *et al.* (2005), Makishima and Nakamura (2006), Nakamura and Chang (2007), Godard *et al.* (2008), Barrat *et al.* (2008), Bayon *et al.* (2009), Chauvel *et al.* (2011), Gao and Casey (2012), Ulrich *et al.* (2012), Zeng *et al.* (2012), Sun *et al.* (2013) and from the USGS certificate for DTS-2B.

Table 1.
Instrumental operating conditions

Instrument	HR-ICP-MS ELEMENT XR
Plasma RF power	1200 W
Torch	Quartz glass torch with 2.2 mm quartz injector
Plasma Ar gas flow rate	15 l min ⁻¹
Auxiliary Ar gas flow rate	1 l min ⁻¹
Nebuliser Ar gas flow rate	1.17 l min ⁻¹
Nebuliser type	Quartz MicroMist™ 100 µl
Spray chamber	Dual cyclone-Scott quartz glass spray chamber
Sampler/skimmer cones	Nickel (H)
Low resolution (LR)	⁷ Li, ⁸⁵ Rb, ⁸⁸ Sr, ⁸⁹ Y, ⁹⁰ Zr, ⁹³ Nb, ¹³³ Cs, ¹³⁵ Ba, ¹³⁹ La, ¹⁴⁰ Ce, ¹⁴¹ Pr,
Medium resolution mode (MR)	^{143,146} Nd, ^{147,149} Sm, ¹⁵¹ Eu, ¹⁵⁷ Gd, ¹⁵⁹ Tb, ¹⁶³ Dy, ¹⁶⁵ Ho, ¹⁶⁷ Er, ⁴⁵ Sc, ⁴⁷ Ti, ⁵¹ V, ⁵² Cr, ⁵⁵ Mn, ⁵⁹ Co, ⁶⁰ Ni, ⁶³ Cu, ⁶⁶ Zn, ^{69,71} Ga
Acquisition mode	E-scan
Detection mode	Triple
Run	6 (LR) - 6 (MR)
Oxide BaO/Ba	0.4%
Doubly charged Ba ²⁺ /Ba	3.2%
Sample time	10 ms per mass (LR) - 40 ms per mass (MR)
Sample per peak	30 (LR) - 20 (MR)
Sample uptake rate	100 µl min ⁻¹
Total data acquisition time	148 s
Wash time	120 s (2% v/v HNO ₃)
Internal standard element	¹⁶⁹ Tm

Table 2.
Instrumental detection limits, analytical and total procedural blanks

	Instrumental detection limit	Procedural blank	Total co- precipitation
	<i>pg g⁻¹</i>	<i>ng g⁻¹</i>	<i>ng g⁻¹</i>
Li	nd	20.6	48.6
Sc	nd	1.05	1.24
Ti	0.969	630	642
V	0.278	19.6	20.2
Cr	1.56	1249	1252
Mn	2.90	76.0	82.0
Co	0.113	17.5	18.0
Ni	22.2	199	214
Cu	2.02	17.7	18.7
Zn	74.5	281	301
Ga	0.216	1.06	1.11
Rb	0.433	3.89	6.28
Sr	5.32	4.28	7.41
Y	nd	0.093	0.171
Zr	1.38	4.61	5.38
Nb	1.71	1.83	2.37
Cs	0.100	1.13	1.28
Ba	20.1	7.84	8.35
La	0.121	0.115	0.307
Ce	0.151	0.289	0.606
Pr	0.040	0.022	0.070
Nd	0.084	0.077	0.100
Sm	0.078	0.061	0.065
Eu	0.065	0.081	0.090
Gd	0.259	0.123	0.134
Tb	nd	0.018	0.047
Dy	0.079	0.041	0.045
Ho	0.025	0.008	0.018
Er	0.033	0.070	0.073
Yb	0.051	0.022	0.029
Lu	0.013	0.014	0.021
Hf	1.21	0.225	0.240
Ta	0.701	0.313	0.413
Pb	0.245	7.05	7.97
Th	0.247	0.035	0.073
U	0.036	0.064	0.076

Table 3.
Trace element mass fractions ($\mu\text{g g}^{-1}$) for UB-N, JP-1, GAS (GeoPT12) and DTS-2B

	BHVO-2			UB-N						
	Barrat <i>et al.</i> (2012)	This study			Govindaraju (1995)	Carignan <i>et al.</i> (2001)	Godard <i>et al.</i> (2008)	Bayon <i>et al.</i> (2009)	Chauvel <i>et al.</i> (2011)	Robin- Poitieu <i>et al.</i>
		Mean ($n = 5$)	<i>s</i>	% RSD						
$\mu\text{g g}^{-1}$										
Li	4.7	28.4	0.893	3.1	27	26.2		28.4	31.6	
Sc	32.3	11.8	0.523	4.4	13	10.7	14.7	12.0	13.7	
Ti	16364	706	77.0	10.9		677		542	606	
V	317	75.8	7.80	10.3	75	67		59.4	67.2	
Cr	280	2107	154	7.3	2300			2090	2280	
Mn	1290	902	48.0	5.3						
Co	45	95.9	4.00	4.2	100	102	106	95.8	102	
Ni	121	1880	122	6.5	2000	1901		1740	1930	
Cu	123	22.0	1.33	6.1	28	26.5	27	21.8	25.1	
Zn	101	73.8	7.80	10.6	85	88		79.4	90.3	
Ga	20.6	2.35	0.172	7.3	3	2.94				
Rb	9.08	3.30	0.102	3.1	4	3.5	3.49	2.54	2.83	
Sr	396	7.61	0.201	2.6	9	8	8.48	7.47	8.01	
Y	27.6	2.66	0.122	4.6	2.5	2.56	2.57	2.5	2.69	
Zr	164.9	3.58	0.351	9.8	4	4.7	4.06	3.65	3.96	
Nb	16.82	0.0509	0.00522	10.3	0.05	0.087	0.0676	0.0463	0.0516	
Cs	0.096	10.5	0.995	9.5	10	12	11.3	11.3	11.9	
Ba	131	26.3	1.10	4.2	27	24	26.4	26.4	28.4	
La	15.2	0.307	0.0106	3.5	0.35	0.351	0.321	0.29	0.34	
Ce	37.5	0.778	0.0343	4.4	0.8	0.86	0.814	0.77	0.846	
Pr	5.31	0.112	0.00517	4.6	0.12	0.12	0.119	0.118	0.126	
Nd	24.5	0.582	0.0192	3.3	0.6	0.62	0.629	0.613	0.636	
Sm	6.07	0.208	0.00621	3	0.2	0.22	0.223	0.222	0.234	
Eu	2.07	0.0792	0.00247	3.1	0.08	0.083	0.0843	0.087	0.0863	
Gd	6.24	0.302	0.00572	1.9	0.3	0.309	0.338	0.32	0.345	
Tb	0.94	0.0571	0.000506	0.9	0.06	0.055	0.0628	0.063	0.0635	
Dy	5.31	0.416	0.00653	1.6	0.38	0.38	0.462	0.434	0.455	
Ho	1	0.0948	0.00177	1.9	0.09	0.088	0.103	0.099	0.0941	
Er	2.54	0.288	0.00549	1.9	0.28	0.25	0.306	0.299	0.308	
Yb	2	0.291	0.00592	2	0.28	0.282	0.305	0.299	0.317	
Lu	0.27	0.0450	0.00142	3.2	0.045	0.046	0.052	0.047	0.0491	
Hf	4.474	0.145	0.0173	11.9	0.1	0.141	0.139	0.15	0.141	
Ta	1.1	0.0151	0.000796	5.3	0.02	0.02	0.019	0.019	0.0137	
Pb	1.51	12.8	0.859	6.7	13	12.9	13.4		15.3	
Th	1.21	0.0724	0.00792	10.9	0.07	0.09	0.074	0.063	0.0799	
U	0.41	0.0576	0.00349	6.1	0.07	0.06	0.0578		0.0638	

	This study			JP-1			
	mean (n = 5)	s	% RSD	Qi et al. (2005)	Makishima and	Barrat et al. (2008)	Bayon et al. (2009)
$\mu\text{g g}^{-1}$							
Li	1.68	0.138	8.2		1.75		
Sc	7.08	0.206	2.9		7.34	7.25	9
Ti	47.8	2.90	6.1			19.9	
V	40.0	4.25	10.6		24.9	21.65	
Cr	2959	212	7.2				
Mn	919	52.7	5.7			860	
Co	113	6.71	5.9		121	104	
Ni	2443	138	5.7		2501	2211	
Cu	3.84	0.518	13.5		4.25	3.63	
Zn	45.1	4.57	10.1		46.7	37.66	
Ga	0.518	0.0444	8.6		0.467	0.47	
Rb	0.348	0.0309	8.9		0.288		
Sr	0.675	0.0605	9		0.546	0.527	
Y	0.100	0.00280	2.8	0.0882	0.0823	0.1	0.098
Zr	8.83	0.242	2.7			5.39	5.7
Nb	0.0298	0.00424	14.2			0.04	
Cs	0.0370	0.00216	5.8		0.036		
Ba	8.98	0.502	5.6		9.5	10.04	8.8
La	0.0264	0.00144	5.5	0.0308	0.0268	0.0271	0.0278
Ce	0.0576	0.00201	3.5	0.0536	0.0597	0.0597	0.062
Pr	0.00719	0.000244	3.4	0.00765	0.0074	0.00716	0.0081
Nd	0.0296	0.00164	5.5	0.0297	0.0318	0.0298	0.031
Sm	0.00739	0.000477	6.4	0.00769	0.0084	0.00726	0.0079
Eu	0.00162	0.000134	8.2	0.00109	0.0024	0.00385	0.0016
Gd	0.00827	0.000948	11.5	0.00644	0.0097	0.0085	0.0101
Tb	0.00164	0.000105	6.4	0.00174	0.0019	0.00166	0.00195
Dy	0.0132	0.000737	5.6	0.013	0.0146	0.0135	0.0135
Ho	0.00329	0.000209	6.4	0.00312	0.0036	0.00316	0.0034
Er	0.0115	0.000502	4.4	0.0111	0.0123	0.0116	0.012
Yb	0.0198	0.000559	2.8	0.0188	0.0209	0.0194	0.0206
Lu	0.00371	0.000144	3.9	0.00338	0.0042	0.00352	0.004
Hf	0.193	0.00581	3			0.113	0.112
Ta	0.00345	0.000997	28.8				
Pb	0.0987	0.00633	6.4		0.0765		
Th	0.0108	0.000869	8		0.013	0.0122	0.009
U	0.0106	0.000386	3.6		0.0123		

	MGL-GAS [GeoPT12]					
	This study			Potts <i>et al.</i>	Qi <i>et al.</i>	Sun <i>et al.</i>
	mean (n = 5)	s	% RSD	(2003)	(2005)	(2013)
$\mu\text{g g}^{-1}$						
Li	2.25	0.126	5.6	2.28		
Sc	6.78	0.119	1.8	6.77		
Ti	134	2.79	2.1			
V	53.4	2.29	4.3	32.91		
Cr	2880	147	5.1	2788		
Mn	647	22.9	3.5			
Co	106	4.23	4	106.4		
Ni	2398	88.3	3.7	2240		
Cu	6.84	0.506	7.4			
Zn	39.0	1.83	4.7	38.84		
Ga	0.869	0.0607	7			
Rb	0.253	0.00949	3.8			
Sr	7.00	0.298	4.3	7.65		
Y	0.384	0.00561	1.5	0.4	0.403	0.389
Zr	0.987	0.0281	2.8			
Nb	0.0535	0.00910	17			
Cs	0.0273	0.00148	5.4	0.03		
Ba	7.29	0.320	4.4	9.22		
La	0.133	0.0117	8.9	0.15	0.157	0.145
Ce	0.254	0.0238	9.4	0.279	0.291	0.275
Pr	0.0309	0.00215	7	0.0308	0.0326	0.0305
Nd	0.126	0.00827	6.6	0.136	0.134	0.13
Sm	0.0307	0.00168	5.5	0.037	0.0322	0.0313
Eu	0.00664	0.000343	5.2	0.0095	0.00638	0.0106
Gd	0.0393	0.00165	4.2	0.042	0.0286	0.0441
Tb	0.00723	0.000248	3.4	0.01	0.00692	0.00831
Dy	0.0513	0.00256	5	0.057	0.0539	0.0513
Ho	0.0127	0.000265	2.1	0.012	0.0127	0.0127
Er	0.0403	0.00136	3.4	0.0421	0.0392	0.0394
Yb	0.0521	0.00171	3.3	0.05	0.0495	0.0502
Lu	0.00820	0.000263	3.2	0.0092	0.00876	0.00926
Hf	0.0215	0.00127	5.9	0.02		
Ta						
Pb	2.54	0.132	5.2			
Th	0.028	0.00170	6.1	0.03		0.0318
U	0.785	0.0178	2.3	0.464		

	DTS-2B						DTS-2					
	This study			Peng <i>et al.</i> (2011)	Robin-Popieul <i>et al.</i>	Certificate USGS	Bologne and Duchesne	Raczek <i>et al.</i> (2001)	Nakamura and Chang	Ulrich <i>et al.</i> (2009)	Gao and Casev (2012)	
	mean (n = 11)	s	% RSD									
Li	1.67	0.188	11.3		1.91						1.81	
Sc	2.99	0.385	12.9	2.72	3.04	3						
Ti	55.8	4.37	7.8		46.7							
V	25.0	1.75	7	17.6	21.5	22	31					
Cr	16659	1376	8.3	13004	14300	15500	8046					
Mn	752	61.0	8.1			830						
Co	124	9.17	7.4	115	130	120	128					
Ni	3480	298	8.6	3923	3240	3780	4152					
Cu	2.29	0.185	8.1	2.91	3.33	3						
Zn	44.3	4.78	10.8	40	50.2	45	47					
Ga	0.94	0.0597	6.4									
Pb	0.123	0.0162	13.2	1.53	0.0379	2		0.0123				
Sr	0.538	0.0277	5.1		0.538			0.534				
Y	0.0384	0.00301	7.8		0.0353							
Zr	0.471	0.0846	18		0.15							
Nb	0.0353	0.00671	19		0.019							
Cs	0.00180	0.000393	21.8		0.000948							
Ba	11.0	0.502	4.6		11.2	16		11.9				
La	0.0130	0.00104	8		0.0112			0.0127	0.0132	0.0124		
Ce	0.0264	0.00219	8.3		0.0237			0.0254	0.0263	0.0252		
Pr	0.00316	0.000264	8.4		0.00314			0.0032	0.00326	0.003		
Nd	0.0131	0.00118	9		0.0153			0.0131	0.0136	0.0132		
Sm	0.00281	0.000160	5.7		0.00253			0.00302	0.00332	0.0027		
Eu	0.000843	0.0000486	5.8		0.00113			0.00087	0.00088	0.0008		
Gd	0.00309	0.000166	5.4		0.00472			0.00304	0.0038	0.0037		
Tb	0.000596	0.0000213	3.6		0.00112			0.00063	0.00063	0.0006		
Dy	0.00421	0.000165	3.9		0.00547			0.00419	0.00469	0.0044		
Ho	0.00121	0.0000797	6.6		0.00115			0.0013	0.0013	0.0012		
Er	0.00494	0.000425	8.6		0.0046			0.00465	0.00553	0.0051		
Yb	0.0101	0.000708	7		0.00856			0.00963	0.0107	0.01		
Lu	0.00199	0.000112	5.6		0.00201			0.002	0.00237	0.0021		
Hf	0.00839	0.00322	38.3		0.00555							
Ta					0.00107							
Pb	3.53	0.354	10		4.04	4						
Th	0.00412	0.000451	11		0.00287							
U	0.00192	0.000236	12.3		0.0017							



