

Determination of Rare Earth Elements and Y in Ultramafic Rocks by ICP-MS After Preconcentration Using $\text{Fe}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ Coprecipitation

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A simple and reliable method to separate rare earth elements (REE) from Mg, Fe, K, Na, Ca and Ba in ultramafic rocks has been developed, thereby concentrating their abundances. The sample (0.3 g) was digested with HF and HNO_3 in a PTFE bomb, placed in a stainless steel container and, after drying, the insoluble residue was dissolved in 6 ml of 10% v/v HNO_3 . Following the addition of 50% triethanolamine and 30% m/v NaOH solution, the REE were precipitated along with $\text{Mg}(\text{OH})_2$, such that the majority of Fe, K and Na in the solution could be separated by centrifuging. The precipitate was dissolved in 1 ml HNO_3 and a buffer solution of $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ at pH = 9.0 was added to precipitate the REE along with any remaining Fe as $\text{Fe}(\text{OH})_3$, and so achieve separation from Mg, Ca and Ba, which remained in the solution. In this way, REE could be separated from major elements and were concentrated by a factor of about 60. The recovery of REE was more than 95% using this method. Four ultramafic rock reference materials, PCC-1 (USGS), JP-1 (GSJ), DZE-1, DZE-2 (IGGE) and one new proficiency testing sample GeoPT12 (GAS Serpentinite) were analysed by ICP-MS using indium as an internal standard. The quantitation limits were about 0.02-0.2 ng g⁻¹. Smooth chondrite-normalised REE patterns were obtained with a precision for REE determination of about 2-9%.

Keywords: rare earth elements, ultramafic rock, ICP-MS, preconcentration, separation.

Une méthode simple et fiable de séparation des terres rares de Mg, Fe, K, Na, Ca et Ba dans les roches ultrabasiques a été développée, qui permet ainsi de les concentrer. L'échantillon (0.3 g) est attaqué par HF et HNO_3 dans une bombe en PTFE, placée dans un conteneur et, après évaporation, le résidu insoluble est repris par 6 ml de HNO_3 10% en volume. Après l'addition d'une solution de triéthanolamine à 50% et de NaOH à 30% (m/v) les terres rares sont co-précipitées avec $\text{Mg}(\text{OH})_2$ permettant à la majorité de Fe, K et Na d'être éliminée par centrifugation. Le précipité est dissout dans 1ml HNO_3 et une solution tampon de $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ à pH=9.0 est ajoutée afin de faire précipiter les terres rares, ainsi que Fe restant sous forme de $\text{Fe}(\text{OH})_3$ et de finir la séparation d'avec Mg, Ca et Ba encore présents dans la solution. Ainsi, les terres rares peuvent être séparées des éléments majeurs et être concentrées par ce biais d'un facteur 60 environ. La récupération des terres rares est supérieure à 95% par cette méthode. Quatre matériaux de référence de composition ultrabasique PCC-1 (USGS), JP-1 (GSJ), DZE-1, DZE-2 (IGGE) et un échantillon analysé lors d'un test de compétence GeoPT12 (GAS Serpentinite) ont été analysés par ICP-MS en utilisant l'indium comme standard interne. Les limites de quantification étaient de l'ordre de 0.02-0.2 ng g⁻¹. Après normalisation aux chondrites, des spectres de terres rares très réguliers ont été obtenus, avec une précision sur la détermination des terres rares de l'ordre de 2 à 9 %.

Mots-clés : éléments du groupe des terres rares, roche ultrabasique, ICP-MS, préconcentration, séparation.

The rare earth elements (REE), are a group of elements that behave coherently in most geochemical processes, and thus yield smooth chondrite-normalised patterns that can be interpreted to provide critical constraints on the petrogenetic history of geological samples (Henderson 1984, Rollinson 1993, Ionov *et al.* 1995, 1997, Glaser *et al.* 1999). Therefore, their accurate determination has been an important task for analytical laboratories for many years (Ionov *et al.* 1992, Makishima and Nakamura 1997, Pin and Joannon 1997, Robinson *et al.* 1999, Jain *et al.* 2000). Due to the simple spectra, wide dynamic range, multi-element capability and low detection limit, inductively coupled plasma-mass spectrometry (ICP-MS) has proved to be a most suitable technique for the determination of REE in geological materials (Yoshida *et al.* 1996, Liang *et al.* 2000, Liang and Grégoire 2000). However, mantle-derived ultramafic rocks have very low REE concentrations (ΣREE 0.1-1 $\mu\text{g g}^{-1}$) with some middle and heavy REE (MREE and HREE) nearly at the detection limit of ICP-MS, using a standard dilution factor of 1000. Thus, preconcentration of REE in such samples is required in order to obtain reliable data. The concentrations of MREE and HREE, especially Eu, Ho, Tm and Lu in analyte solutions (dilution factor 1000) are about 1-5 pg ml^{-1} for ultramafic samples, only 2-10 times higher than the detection limits of ICP-MS for these elements (about 0.2-0.5 pg ml^{-1} , Robinson *et al.* 1999). Even these detection limits are difficult to maintain, because of variations in the cleanliness of the sample introduction system including the cone, nebuliser, chamber and torch, and fluctuations in background noise levels. Thus, it is very difficult to obtain reliable results without either improving the sensitivity of the ICP-MS or preconcentrating the REE before the analysis. It is notable that for ultramafic reference materials, only suggested values are available rather than recommended values (Govindaraju 1994, Jain *et al.* 2000).

Jain *et al.* (2000) used an ultrasonic nebuliser and microconcentric desolvating nebuliser to increase the sensitivity of ICP-MS measurements, and produced smooth chondrite-normalised REE patterns for two ultramafic reference materials, USGS PCC-1 and DTS-1. Other workers have also reported the determination of REE in these ultramafic reference materials using HR-ICP-MS (Robinson *et al.* 1999), "special measure" (Ionov *et al.* 1992) and flow injection (Makishima and Nakamura 1997). Extraction chromatography and ion exchange techniques have been used previously to preconcentrate REE (Pin and Joannon 1997, Hongchun

et al. 2000, Christian and Sylviane 2002), but these techniques require many complicated steps and are very time consuming.

Because ultramafic rocks, such as harzburgite and dunite, have relatively simple matrix compositions (mainly SiO_2 , Fe_2O_3 and MgO), separation and removal of these major oxides will allow sample solutions to be analysed with a smaller dilution factor and thus effectively preconcentrate REE. Silica can be removed from REE using normal HF-HNO_3 digestion as volatile SiF_4 . In the procedure described below, we separated most of the iron from REE using triethanolamine as a complexing agent at $\text{pH} > 12$, causing coprecipitation of REE and Mg(OH)_2 . After dissolution of the precipitate with HNO_3 , Mg was then separated from the REE by adding a buffer solution of $\text{NH}_4\text{Cl/NH}_4\text{OH}$ at a pH of 9.0, which resulted in coprecipitation of the REE and any remaining iron in the form of Fe(OH)_3 . This paper reports the results of analysis for four ultramafic reference materials (PCC-1, JP-1, DZE-1 and DZE-2) and a new proficiency testing sample (GeoPT12 GAS Serpentinite) using this newly established technique and demonstrates the validity of the method.

Experimental

Instrumentation

The VG Plasma-Quad Excell ICP-MS installed at the University of Hong Kong was utilised for this study. All the solution introduction parts, such as the nebuliser, spray chamber, torch and the cones were carefully cleaned before use. Sample solutions were introduced using a peristaltic pump in conjunction with a CETAC autosampler. A Meinhard nebuliser and a spray chamber with an impact bead cooled to 3 °C were used in this study.

Throughout this study, the uptake time was 70 s, with an uptake rate of 1 ml per minute. The number of sweeps was set at 30 and channels per mass at 5 for a 31 s acquisition time. The sensitivity of the instrument was normally adjusted to about 50000 counts per second (cps) for 1 ng ml^{-1} ^{115}In in order to achieve the desired detection limits. Relative standard deviations were typically less than 3% for the raw data. The instrument settings are summarised in Table 1. Washing time between samples was 2 minutes using 5% v/v HNO_3 . Background counts of 2% v/v HNO_3 solution were routinely < 50 cps for LREE, < 20 cps for MREE and HREE.

Table 1.
Instrumental operating parameters

Parameter	Value
Instrument	VG PQ Excell
Forward power	1350 W
Reflected power	< 2 W
Cooling gas	13 l min ⁻¹
Auxiliary gas	0.63 l min ⁻¹
Nebuliser gas	0.75 l min ⁻¹
Extraction	- 470 mV
Lens 1	3.7 mV
Lens 2	- 89.4 mV
Lens 3	- 126.7 mV
Focus	19.5 mV
Sampling cone	1 mm
Skimmer cone	0.7 mm
Detection mode	Peak jump

Reagents

Trace metal-grade HF and HNO₃ were purified by sub-boiling distillation. Water (18 MΩ cm grade) from a Millipore purification system was used.

NaOH (30% m/v): NaOH (AR) was purified by the addition of FeCl₃ to remove REE. After dissolving 150 g NaOH in 500 ml 0.05% m/v FeCl₃ (AR) solution, the solution was stirred periodically with a Teflon bar, then cooled and allowed to stand for about 5 hours before being centrifuged to separate Fe(OH)₃ precipitate, which collected most of the REE originally in the solution.

NH₄Cl/NH₄OH (PH = 9.0) buffer solution: NH₄Cl (AR) (35 g) was dissolved in 100 ml water, and 200 mg of FeCl₃ (10 ml 20 mg ml⁻¹ FeCl₃ solution) and 24 ml of NH₄OH (30% v/v AR) were added and the solution diluted to 500 ml with water. The procedure described above was also used to purify this solution from REE.

Triethanolamine solution (50%): 500 mg MgCl₂ (10 ml 50 mg ml⁻¹ MgCl₂, AR) were added to a mixture of 250 ml triethanolamine solution (AR) and 250 ml 10% m/v NaOH solution. The procedure described above was also used to purify this solution from REE.

The ICP multi-element standard solution containing 100 μg ml⁻¹ of all the REE from AccuStandard Inc. (USA) was used to prepare a variety of calibration solutions (3% v/v HNO₃) with REE concentrations ranging from 1 to 20 ng ml⁻¹.

Laboratory ware

Acid digestions were performed in 10 ml screw-top PTFE bombs placed in stainless steel containers. The PTFE bombs were cleaned using 20% v/v HNO₃ heated to 110 °C for 3 hours in an electric oven and then rinsed with water.

Sample preparation

About 0.3 g of sample powder were weighed accurately and transferred to a PTFE bomb, along with 2 ml of HF (48% v/v) and 1 ml of HNO₃ (68% v/v). The bomb was then placed on a hot plate at 150 °C, and the solution evaporated to dryness to remove silica. An additional 1 ml of HF and 1 ml of HNO₃ were then added, the bomb was sealed, placed in an oven and heated to 190 °C for more than 24 hours. After cooling, the bomb was placed on a hot plate and the solution again evaporated to dryness. Nitric acid (0.5 ml) was then added and evaporated to dryness and this procedure (addition and evaporation of 0.5 ml of HNO₃) was repeated a second time. At this point, an additional 0.5 ml HNO₃ and 5 ml H₂O were added, together with 200 ng indium (in solution), which was used as an internal standard. The sealed bombs were then placed in the oven again and heated to 140 °C for 4 hours to dissolve any solid residue. The solution was transferred to a 50 ml centrifuge tube and the volume adjusted to 25 ml with water. Triethanolamine solution (2 ml 50% v/v) was then added to form a complex with iron, together with 6 ml 30% m/v NaOH to adjust the pH to > 12, such that a precipitate of Mg(OH)₂ was formed. At this stage, the majority of iron remained in the solution with only a small quantity (2-3 mg) included in the precipitate, whereas the REE were co-precipitated with Mg(OH)₂. The tubes were centrifuged at a rate of 3200 rpm (Hettich ROTIXA/AP) for 3 minutes. The liquid was discarded and the precipitate was dissolved in 1 ml HNO₃. All of the precipitate, including any fluoride residue from the digestion, was readily dissolved because elements were then in hydroxide form. After adding 10 ml of water, 50% v/v NH₄OH was used to adjust the pH, such that Fe(OH)₃ just began to precipitate. After making up the volume to about 25 ml with water, 10 ml of NH₄Cl/NH₄OH buffer solution (pH = 9) were added, causing the REE to co-precipitate with Fe(OH)₃. The tubes were centrifuged at 3200 rpm for 3 minutes and the liquid discarded. The precipitate was mixed thoroughly with 35 ml of water and 0.5 ml NH₄OH, the solution centrifuged again and the liquid

again discarded. The precipitate was dissolved in 1 ml HNO₃, and diluted to 20 ml with water for measurement by ICP-MS. Blank solutions were prepared in a similar manner to the sample using 15 mg high purity grade Fe₂O₃ (99.99%) and 100 mg MgO (99.99%), which contained almost the same matrix with sample.

Data reduction and calibration strategy

General calibration

The working standard solutions were prepared from the stock standard solution as follows: (1) 50 ng of REE and 500 ng indium in 50 ml; (2) 250 ng of REE and 500 ng indium in 50 ml; and (3) 1000 ng of REE and 500 ng indium in 50 ml. The concentrations of REE in unknown samples were calculated using a normal external calibration procedure except that the concentration unit of REE and indium in calibrants and samples was given in ng instead of ng ml⁻¹. There are two methods to calculate the concentration. The first method uses the concentration unit of ng ml⁻¹ for calibration, for which an accurate measure of the volume of the final solution is required. The second method uses the concentration unit of ng instead of ng ml⁻¹ for the calculation, because the intensity ratio of an element and internal standard is linear to its concentration, which is given in ng. This is very convenient because the results are then unaffected by the volume of the final solution.

The concentration can be calculated by means of the following formula:

$$C = \frac{I_{Sa} C_{St} I_{St} C_{Sal}}{W I_{St} I_{Sal} C_{St}} \quad (1)$$

where C is the analyte concentration (ng g⁻¹); I_{Sa} is an element signal intensity of the sample solution; C_{St} is the mass of an element in the calibrant solution (ng); I_{St} is the internal standard (indium) signal intensity in the calibrant solution; C_{Sal} is the mass of internal standard in the sample solution (ng); I_S is an element signal intensity of the calibrant solution; I_{Sal} is the internal standard signal intensity in the sample solution; C_{St} is the mass of the internal standard in the calibrant solution (ng) and W is the sample mass (g).

Interferences

It is well known that the Ba oxides interfere with Eu and the LREE oxides interfere with the HREE during

ICP-MS analysis. However, with careful optimisation of the instrument, these interferences can be minimised. With the instrument settings shown in Table 1, the rate of oxide formation in this study was about 0.11% for BaO⁺/Ba⁺. Because ultramafic samples have a very low concentration of Ba (often < 20 μg g⁻¹), and because most of the Ba was removed during the pre-concentration procedure, the interference was minimised. However, we still measured a 1000 ng ml⁻¹ Ba solution to correct any interference of BaO on Eu. The correction method is similar to that described in Parent *et al.* (1997). Because of the low rate of REE oxide formation during this study (0.3% for PrO⁺/Pr⁺), even the serious interference of PrO⁺ on ¹⁵⁷Gd only caused about 3% bias (if uncorrected) for the determination of ultramafic samples (in this work, ¹⁵⁸Gd was selected), whereas, other interferences were < 2%. Therefore, it was not considered necessary to correct the interferences of LREE oxides with the determination of HREE.

Procedural blanks and detection limits

The calculated detection limits for a given mass or isotope were based on the slope of a line generated by two points, a blank and a standard solution of known concentration (e.g., 10 ng ml⁻¹). The instrumental detection limit of the REE in this study was calculated as three times the standard deviation of the ion counts obtained from a 3% v/v HNO₃ solution measured five times, divided by the sensitivity determined using the 10 ng ml⁻¹ REE standard solution. Because detection limits varied from day to day due to variations in instrument sensitivity and background noise levels, the reproducibility of such low detection limits is poor. The quantitation limit was calculated as ten times the standard deviation of the ion counts obtained from the five individual procedural reagent blanks (20 ml, prepared as described above). Following purification of the solutions as outlined above, the concentration of the LREE (La, Ce, Pr and Nd) in the reagent blank ranged from 0.0022 ng ml⁻¹ (Pr) to 0.014 ng ml⁻¹ (Ce), i.e., slightly higher than the concentrations of the MREE and HREE in the blanks. The higher LREE concentrations may have been due to the fact that reagents are typically more easily contaminated with the LREE. However, even the lowest concentrations of LREE in the ultramafic samples (sample size 0.3 g) were ten times more than the concentration in the blanks (for PCC-1, 60-130 times higher). The ion counts of MREE and HREE were almost the same as the 3% v/v HNO₃ solution. Therefore, the concentrations of MREE in ultramafic samples (sample size 0.3 g) were ten times more than

Table 2.
Analytical masses, detection limits, quantitation limits and blank level

Analytical mass	Instrumental detection limit (3s)	Quantitation limit (10s)	Procedure blank level
⁸⁹ Y	0.0007	0.42	0.0004
¹³⁹ La	0.0010	1.87	0.0115
¹⁴⁰ Ce	0.0009	2.02	0.0140
¹⁴¹ Pr	0.0004	0.55	0.0022
¹⁴⁶ Nd	0.0012	1.35	0.0037
¹⁵² Sm	0.0008	0.25	0.0006
¹⁵³ Eu	0.0003	0.07	0.0005
¹⁵⁸ Gd	0.0003	0.22	0.0005
¹⁵⁹ Tb	0.0004	0.09	0.0001
¹⁶³ Dy	0.0005	0.47	0.0014
¹⁶⁵ Ho	0.0003	0.05	0.0003
¹⁶⁶ Er	0.0007	0.13	0.0007
¹⁶⁹ Tm	0.0002	0.02	0.0002
¹⁷⁴ Yb	0.0002	0.31	0.0015
¹⁷⁵ Lu	0.0001	0.09	0.0003

Values for instrumental detection limit and procedure blank level are in ng ml⁻¹ (solution values), quantitation limits are in ng g⁻¹ (sample detection limit).

the blank, and the HREE concentrations were a hundred times more than those of the blanks. The instrumental detection limit, quantitation limit and blank level are shown in Table 2.

Matrix effects

Matrix effects were examined by analysing the major elements in a solution of the reference material DZE-1. The residual concentrations of the major elements in the resultant solution (using the procedure described above for preconcentration) were about 4.5 mg Fe, 2 mg Mg, 0.5 mg Al, 2 mg Cr, and < 0.1 mg for other elements including Na, Ca, Ti and Mn. The total concentration of the matrix elements in the resultant solution was therefore below 11 mg. The concentrations of major elements in the solution of DZE-1 are shown in Table 3 and equate to a matrix concentration equal to the 1000 dilution factor for normal trace elemental analysis. No specific matrix effect was observed (monitoring the changes in intensity of the internal standard) in the ICP-MS determination.

Recoveries of REE

A sufficient recovery of the REE during the preconcentration procedure is important for the final determination of REE. To monitor the recovery, three 0.3 g replicates were prepared using DZE-1; one was prepared as a blank without the addition of REE, and 200 and 400 ng REE were added to the other two replicates. The three replicates were digested and their

Table 3.
Major element concentrations (% m/m) in the final solution (matrix) of reference material DZE-1

Elements	DZE-1 ^A	DZE-1 ^B	DZE-1 ^C
Na ₂ O	0.01	0.03	0.04
MgO	41.03	2.49	3.76
Al ₂ O ₃	0.67	0.49	0.45
CaO	0.10	0.02	0.04
TiO ₂	0.008	0.01	0.01
Cr	1.07	1.72	2.11
MnO	0.068	0.06	0.06
Fe ₂ O ₃ T	6.90	4.48	4.33
Total	-	9.30	10.79

^A is the concentration of major oxides in DZE-1 (Govindaraju 1994). ^B and ^C are the concentrations of major elements in the resulting solutions (20 ml) of DZE-1 obtained by using two separate preparation procedures (0.3 g).

REE were preconcentrated following the procedure described above. The results of two samples (to which 200 ng and 400 ng REE were added) were calculated following the calibration method described above, on the basis of deducting the concentrations in the "blank" (DZE-1 solution) to which no REE had been added. The recoveries of REE were all greater than 95%, as shown in Table 4.

Internal standard

It is necessary for ICP-MS analysis to use an internal standard to correct matrix effects and instrumental drift. An element that is likely to have a very low concentration in samples, with a mass and ionisation

Table 4.
Recovery (R %) of REE after preconcentration

	Added	Measured	R %	Added	Measured	R %
Y	200	198.4	99.2	400	386.8	96.7
La	200	192.6	96.3	400	397.1	99.3
Ce	200	190.2	95.1	400	385.8	96.5
Pr	200	194.6	97.3	400	404.6	101.2
Nd	200	196.6	98.3	400	390.8	97.7
Sm	200	191.2	95.6	400	381.2	95.3
Eu	200	194.4	97.2	400	386.8	96.7
Gd	200	195.3	97.6	400	367.3	98.8
Tb	200	202.6	101.3	400	401.5	100.4
Dy	200	197.0	98.5	400	389.2	97.3
Ho	200	202.6	101.3	400	388.2	97.1
Er	200	196.0	98.0	400	391.5	97.9
Tm	200	198.3	99.2	400	382.9	95.7
Yb	200	195.8	97.9	400	388.7	97.2
Lu	200	196.2	98.1	400	389.1	97.3

Added and measured values in ng.

energy similar to the elements being analysed, is often selected. Although, as pointed out by Robinson *et al.* (1999) and according to our previous experience, one internal standard is sufficient for the determination of REE, we examined two elements, Rh and In, as potential internal standards. Because Rh does not precipitate with REE in the preconcentration procedure, this element was added to the analyte solution at the last stage. Using this method, the recoveries of REE were about 90%. Because of its extremely low concentration in ultramafic rocks, indium behaves like the REEs in the preconcentration procedure. Indium can, therefore, be added at an early stage in the preconcentration procedure and used as the internal standard. Our experiments showed that indium has almost the same recovery as REE and can be added before preconcentration to adjust the recovery of REE (Table 4).

Precision

With the VG PQ Excell instrument, instrumental relative standard deviation (% RSD) of 0.5-3% were obtained using the REE preconcentration method described here. With the sensitivity of ^{115}In set at about 50000 cps per ng ml⁻¹, about 4000 cps were obtained for Lu in PCC-1. Good instrumental precisions were obtained with this intensity for the determination of REE in the analyte solutions. The method precision (% RSD) of REE determination for ultramafic rocks using our procedure was estimated after six separate determinations of REE concentration for PCC-1, which gave values of 2-9% (1s).

Analytical results for reference materials

Although a number of REE determinations have been carried out on the well known USGS peridotite reference material PCC-1, discrepancies still exist among the published data, especially the LREE (Table 5). Jain *et al.* (2000) used an ultrasonic nebuliser (USN) and a microconcentric desolvating nebuliser (MCN) to determine the REE in this sample by ICP-MS and obtained data that agreed well with Eggins *et al.* (1997), but differed from other reports (Ionov *et al.* 1992, Makishima and Nakamura 1997, Robinson *et al.* 1999). Our values for the LREE, including La, Ce, Pr, Nd and Sm, are slightly higher than those of Eggins *et al.* (1997) and Jain *et al.* (2000), but agree well with Olive *et al.* (2001), whereas our values for the other elements are in good agreement with results in all these papers. The value of Tm in PCC-1 was not reported by Eggins *et al.* (1997). The chondrite-normalised REE for PCC-1 obtained from this study are compared with reported literature values in Figure 1. Similar U-shaped REE patterns are observed for all the available data and our data compare well with those of Jain *et al.* (2000), Eggins *et al.* (1997) and Robinson *et al.* (1999). Other values from the literature (Ionov *et al.* 1992, Makishima and Nakamura 1997, Eggins *et al.* 1997) are generally comparable with our new REE data (Table 5 and Figure 1).

JP-1 is a peridotite reference material from the Geological Survey of Japan (GSJ). Data for Y, Ho, Tm and Lu are not available yet for this reference material

Table 5.
Comparison of REE data of this work (n = 6) with literature values for PCC-1

	This work $\pm s$	% RSD	1	2	3	4	5	6	7
Y	78.4 \pm 1.9	2.4	-	-	-	87	79	-	79
La	50.1 \pm 1.1	2.2	48	33	29	29	46	39	34
Ce	82.2 \pm 3.7	4.5	71	60	56	53	52.8	57	61
Pr	8.83 \pm 0.21	2.4	9.8	7.6	7.2	6.8	7.6	8.5	9.1
Nd	32.1 \pm 2.9	9.0	32	26	28	25	26	30	35
Sm	5.96 \pm 0.29	4.9	7	4.9	5.1	5	7	8	9.5
Eu	1.04 \pm 0.06	5.8	2	0.9	1.00	1.1	0.9	1.8	2.4
Gd	5.29 \pm 0.31	5.9	7.6	5.3	5.93	6.1	5.9	8	13
Tb	1.11 \pm 0.09	8.1	1.6	1.0	1.12	1.2	1.1	1.5	1.4
Dy	9.57 \pm 0.42	4.4	12	8.5	9.41	8.7	11	13	16
Ho	2.76 \pm 0.22	8.0	3.1	2.3	2.69	2.7	3	3.8	3.4
Er	11.1 \pm 0.8	7.2	12	10.0	11.3	11.3	11.7	12.3	16
Tm	2.43 \pm 0.13	5.3	2.7	2.0	2.44		2.8	2.5	3.2
Yb	21.7 \pm 1.1	5.1	23	20.0	22.1	21.3	22.7	21.5	28
Lu	4.42 \pm 0.19	4.3	5.0	4.5	4.65	4.6	4.7	4.9	5.4

Values are in ng g⁻¹. s standard deviation. (1) Olive *et al.* (2001). (2) and (3) Jain *et al.* (2000). (4) Eggins *et al.* (1997). (5) Robinson *et al.* (1999). (6) Ionov *et al.* (1992). (7) Makishima and Nakamura (1997).

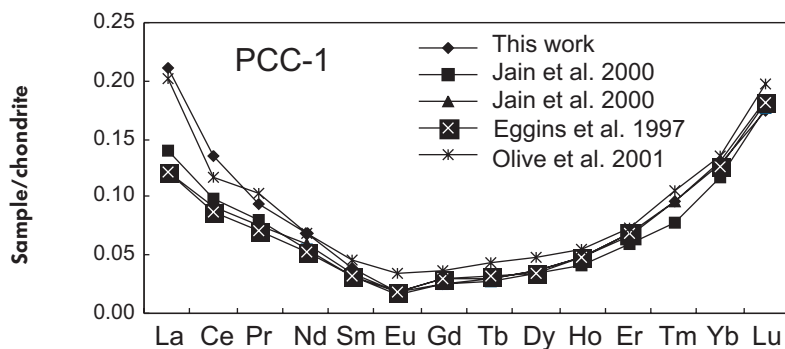
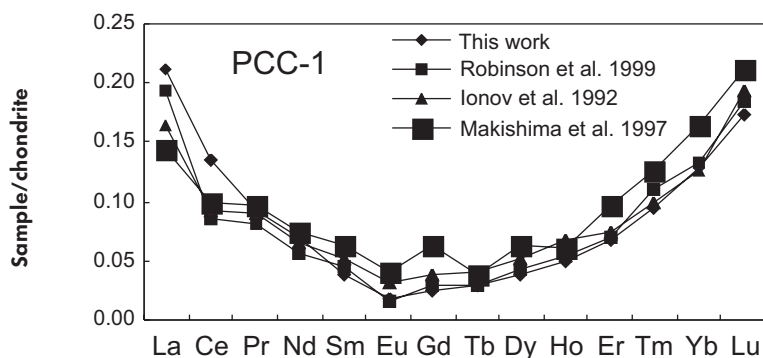


Figure 1. Comparison between the REE data of this work and literature values of Olive *et al.* (2001), Jain *et al.* (2000), Eggins *et al.* (1997), Robinson *et al.* (1999), Ionov *et al.* (1992) and Makishima and Nakamura (1997) in PCC-1 using chondrite-normalised (Sun and McDonough 1989) REE profiles.



(Ionov *et al.* 1992, Imai *et al.* 1995, Makshima and Nakamura 1997). All of our REE values for JP-1 are significantly lower than the proposed values (Table 6). Thus, our results determined by ICP-MS, which give a smooth chondrite-normalised REE pattern for this material (Figure 2) and the agreement between results obtained using a normal dilution factor of 1000 and

the preconcentration procedure described in this paper (Table 7), suggest that our results may be more accurate.

Two Chinese ultramafic rock reference materials DZE-1 and DZE-2 were prepared by XIGMR (Xian Institute of Geological and Mineral Resources, Chinese

Table 6.
Analytical results for reference materials

Elements	DZE-1		DZE-2		JP-1		GeoPT12	
	Information values*	Mean ± s	Information values*	Mean ± s	Proposed*	Mean ± s	Assigned**	Mean ± s
Y	-	n = 5 121 ± 8	-	n = 4 105 ± 6	-	n = 5 88.2 ± 5.5	400	n = 6 403 ± 14
La	190	205 ± 12	210	197 ± 15	100	30.8 ± 2.5	150	157 ± 9
Ce	360	367 ± 18	400	359 ± 26	200	53.6 ± 3.3	279	291 ± 17
Pr	-	37.1 ± 2.2	-	37.3 ± 3.6	20	7.65 ± 0.49	30.8	32.6 ± 1.5
Nd	150	119 ± 6	220	131 ± 11	70	29.7 ± 1.5	136	134 ± 8
Sm	20	19.9 ± 1.8	30	23.2 ± 1.4	20	7.69 ± 0.20	37	32.2 ± 1.3
Eu	4	3.79 ± 0.15	6	4.82 ± 0.29	3	1.09 ± 0.14	9.5	6.38 ± 0.50
Gd	24	16.9 ± 1.2	33	19.0 ± 1.5	20	6.44 ± 0.24	42	28.6 ± 1.2
Tb	2	2.63 ± 0.13	3	2.96 ± 0.17	3	1.74 ± 0.16	10	6.92 ± 0.21
Dy	-	15.2 ± 0.8	-	16.3 ± 1.1	20	13.0 ± 0.6	57	53.9 ± 2.6
Ho	5	3.6 ± 0.22	6	3.17 ± 0.18	-	3.12 ± 0.18	12	12.7 ± 0.7
Er	-	13.2 ± 0.9	-	9.89 ± 0.53	20	11.1 ± 0.46	42	39.2 ± 0.9
Tm	3	2.5 ± 0.10	2	1.51 ± 0.08	-	2.12 ± 0.17	7.5	6.89 ± 0.31
Yb	20	21.1 ± 1.0	12	11.3 ± 0.5	20	18.8 ± 1.4	50	49.5 ± 1.8
Lu	4	4.2 ± 0.2	3	2.12 ± 0.05	-	3.38 ± 0.14	9.2	8.76 ± 0.50

Values are in ng g⁻¹.

s standard deviation.

* Govindaraju K. (1994).

** Potts *et al.* (2003).

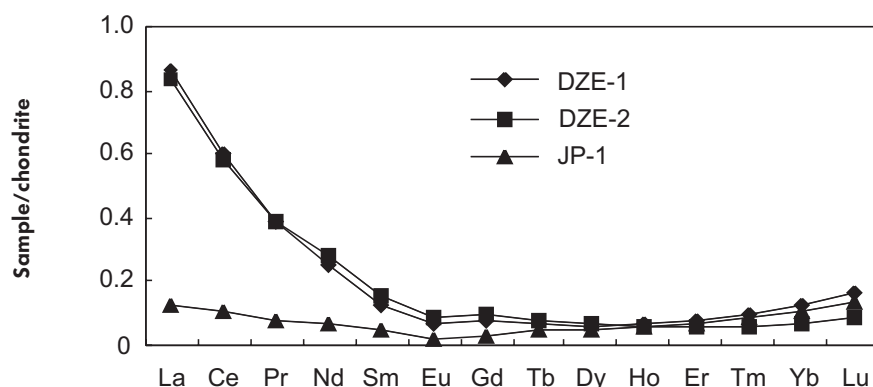


Figure 2. Chondrite-normalised patterns of REE in DZE-1, DZE-2 and JP-1. Data were obtained in this work.

Academy of Geological Science). Values of Y, Pr, Dy and Er for these materials are not yet available (Govindaraju 1994). Our results for Sm, Eu, Yb and Lu in DZE-1 and Tb and Yb in DZE-2 agree well with the information values and our results for La and Ce in both samples are close to the information values. Our results for other REEs in these samples are lower than the information values (Table 6). In order to judge the accuracy of our determinations, we normalised our results to chondrite REE values and obtained very smooth patterns for both DZE-1 and DZE-2 (Figure 2).

A new proficiency testing sample, GeoPT12 (GAS Serpentine), was recently prepared for the International Association of Geoanalysts (IAG). This material formed the basis of the twelfth international proficiency test of

analytical geochemistry laboratories and the results were reported by Potts *et al.* (2003). Our data show excellent agreement with the assigned values for LREE and HREE (Table 6 and Figure 3). Our data for the MREE, such as Eu, Gd and Tb, differ somewhat from the assigned values but produce smoother chondrite-normalised REE patterns (Figure 3). Because of the relatively high concentrations of LREE in this material, these elements can be determined directly by standard ICP-MS techniques. We have therefore measured the LREE using the method of Liang and Grégoire (2000), based on the use of HF and HNO₃ in PTFE-lined stainless steel high pressure bombs at 200 °C for 12 hours. Analytical results were compared with those obtained by the preconcentration procedure described in this paper. The two sets of data show excellent agreement for La, Ce, Pr and Nd (Table 7).

Table 7.
Analytical results for some REE in reference materials after normal dilution and preconcentration

Elements	DZE-1		DZE-2		JP-1	
	A Mean \pm s n = 4	B Mean \pm s n = 5	A Mean \pm s n = 4	B Mean \pm s n = 5	A Mean \pm s n = 4	B Mean \pm s n = 5
La	176 \pm 10	205 \pm 12	187 \pm 11	197 \pm 15	31.6 \pm 2.9	30.8 \pm 2.5
Ce	301 \pm 24	367 \pm 18	343 \pm 21	359 \pm 26	63.3 \pm 3.4	53.6 \pm 3.3
Pr	32.1 \pm 2.6	37.1 \pm 2.2	40.5 \pm 2.8	37.3 \pm 3.6	8.19 \pm 0.52	7.65 \pm 0.49
Nd	110 \pm 10	119 \pm 6	146 \pm 9	131 \pm 11	29.0 \pm 2.1	29.7 \pm 1.5
Elements	PCC-1		GeoPT12			
	A Mean \pm s n = 4	B Mean \pm s n = 6	A Mean \pm s n = 4	B Mean \pm s n = 5		
La	52.1 \pm 3.6	50.1 \pm 1.1	149 \pm 6	157 \pm 9		
Ce	74.5 \pm 7.4	82.2 \pm 3.7	246 \pm 12	291 \pm 17		
Pr	9.19 \pm 0.58	8.83 \pm 0.21	32.6 \pm 1.5	32.6 \pm 1.5		
Nd	32.8 \pm 2.7	32.1 \pm 2.9	129 \pm 11	134 \pm 8		

Values are in ng g⁻¹. s standard deviation. A determined using a normal dilution factor of 1000.
B determined after preconcentration with a dilution factor of about 60.

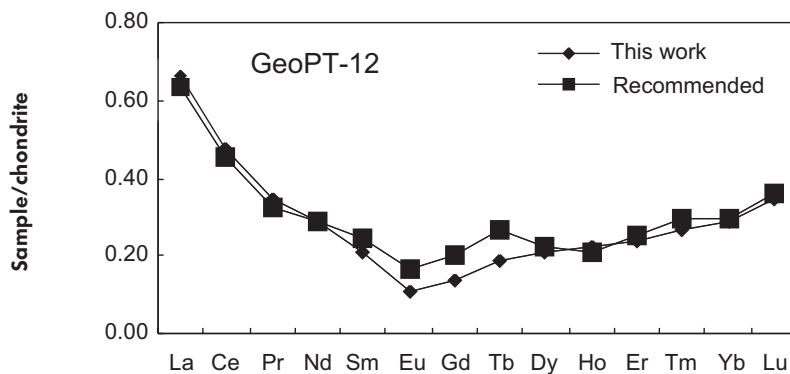


Figure 3. Comparison between the REE data of this work and the assigned values (Potts *et al.* 2003) in GeoPT12 using chondrite-normalised REE patterns.

Discussion

Alkali fusion is a quick and effective means of dissolving ultramafic samples, especially those that contain chromite (Totland *et al.* 1992). However, contamination from fusion reagents is a problem, and causes the quantitation limits of REE determined by fusion to be ten times higher than acid (Totland *et al.* 1992), especially since the fusion reagents LiBO₂ and NaOH are difficult to purify before it is used. Thus, we offer the HF-HNO₃ decomposition method using screw-top PTFE bombs in stainless steel containers to digest samples as described by Liang *et al.* (2000). Using this method, we have obtained excellent results for other trace elements especially Cr (our values are 3074, 2922, 2976 μ g g⁻¹ vs. information values of 2870, 2788, 2970 μ g g⁻¹ for DZE-2, GeoPT12 and JP-1), demonstrating the effectiveness of the method for dissolving refractory minerals in ultramafic rocks. All the

reagents used in this method can be purified from REE before the usage so that very low detection limits can be achieved.

Taicheng *et al.* (2002) used Ti(OH)₄ and Fe(OH)₃ to coprecipitate REE and some other trace elements from the major elements in soil and sediment, but for these samples, REE and trace elements can be determined directly by ICP-MS techniques. Our procedure is the first to use Fe(OH)₃ and Mg(OH)₂ coprecipitation to separate REE from Mg and Fe in ultramafic rocks. During this process other elements such as K, Na, Ca and Ba were also separated from REE. The method described in this paper for analysing REE in ultramafic samples is a significant improvement over previous analytical techniques.

The size of the test portion used here was 0.3 g and the dilution factor was about 60, so it is possible

to obtain reliable REE results for ultramafic samples using a conventional nebuliser instead of an ultrasonic nebuliser or microconcentric desolvating nebuliser, both of which require additional cost in instrumentation. All the reagents used in this work were purified by sub-boiling or coprecipitation before usage, thus achieving low reagent blanks and REE-free reagents. Indium can be quantitatively precipitated with REE and has almost the same recovery as REE, so it can be added at the beginning of the procedure and the correction to account for recovery of REE can be improved.

The procedure described in this study is suitable for REE determination in ultramafic samples that contain relatively simple compositions (mainly SiO₂, Fe₂O₃ and MgO). To account for the different matrix composition of other types of sample, for example, pure carbonate, pyrite and chalcopyrite, which also contain very low concentrations of REE, different methods should be developed.

With this new technique, fifty samples can be prepared in about 3 days. The technique involving coprecipitation is relatively simple and fast for preconcentration of REE in ultramafic samples compared to ion exchange chromatography.

Conclusions

Using Fe(OH)₃ and Mg(OH)₂ coprecipitation, REE can be separated from the major elements, including Mg, Fe, K, Na, Ca and Ba in ultramafic rocks and thus can be concentrated before determination by ICP-MS. The analytical results of the GeoPT12 sample demonstrate that the proposed method provides a reliable means of determining trace amounts of REE in ultramafic samples. The analytical data for reference material PCC-1 in this work are in close agreement with those of Eggins *et al.* (1997), Jain *et al.* (2000) and Olive *et al.* (2001) and in general agreement with other literature values. We also provide new REE data for DZE-1, DZE-2 and JP-1.

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