Determination of Rare Earth Elements, Sc, Y, Zr, Ba, Hf and Th in Geological Samples by ICP-MS after Tm Addition and Alkaline Fusion

Germain Bayon, Jean-Alix J-A Barrat, Joël Etoubleau, Mathieu Benoit, Claire Bollinger, Sidonie Révillon

Geostandards and Geoanalytical Research
March 2009, Volume 33, Issue 1, Pages 51 - 62

Determination of Rare Earth Elements, Sc, Y, Zr, Ba, Hf and Th in Geological Samples by ICP-MS after Tm Addition and Alkaline Fusion

Germain Bayon[1, *], Jean Alix Barrat[2, 3], Joël Etoubleau[1], Mathieu Benoit[2, 3], Claire Bollinger[2, 3] & Sidonie Révillon[1, 2, 3]

1 Département Géosciences Marines, IFREMER, 29280 Plouzané, France
2 Université Européenne de Bretagne, Brest, France
3 Université de Brest, IUEM, CNRS UMR6538, 29280 Plouzané, France

* Corresponding author : G. Bayon, gbayon@ifremer.fr

Abstract:
We present a revised method for the determination of concentrations of rare earth (REE) and other trace elements (Y, Sc, Zr, Ba, Hf, Th) in geological samples. Our analytical procedure involves sample digestion using alkaline fusion ($NaOH$-Na_2O_2) after addition of a Tm spike, co-precipitation on iron hydroxides, and measurement by sector field-inductively coupled plasma-mass spectrometry (SF-ICPMS).
The procedure was tested successfully for various rock types (i.e., basalt, ultramafic rock, sediment, soil, granite), including rocks with low trace element abundances (sub ng g^{-1}). Results obtained for a series of nine geological reference materials (BIR-1, BCR-2, UB-N, JP-1, AC-E, MA-N, MAG-1, GSMS-2, GSS-4) are in reasonable agreement with published working values.

Résumé:
Nous présentons une méthode révisée pour la détermination des teneurs en Terres Rares et autres éléments traces (Y, Sc, Zr, Ba, Hf, Th) dans les échantillons géologiques. Notre procédure analytique implique la digestion des échantillons par fusion alcaline ($NaOH$-Na_2O_2) après ajout d'un spike de Tm, la co-précipitation avec des oxydes de Fer, et la mesure par spectrométrie de masse à secteur magnétique couplée à une source à plasma induit (SF-ICP-MS). La procédure a été testée avec succès pour plusieurs types de roches (basalte, roche ultramafique, sédiment, sol, granite), y compris des roches caractérisées par de faibles teneurs en éléments traces (sub ng g^{-1}). Les résultats obtenus pour une série de neuf matériaux de références géologiques (BIR-1, BCR-2, UB-N, JP-1, AC-E, MAN,
MAG-1, GSMS-2, GSS-4) sont en accord avec les valeurs de travail publiées dans la littérature.

Keywords: rare earth elements ; geological samples ; reference materials ; ICP-MS ; Tm spike ; sample digestion

Mots-clés: éléments du groupe des Terres Rares ; échantillons géologiques ; matériaux de référence ; ICP-MS ; spike de Tm ; digestion des échantillons

Introduction

Trace element geochemistry provides unique information on geological and environmental processes on Earth (e.g. igneous processes, sedimentary processes, past ocean chemistry). One of the methods of choice for analysing and quantifying trace elements in geological samples is inductively coupled mass spectrometry (ICPMS).

A prerequisite to determine precise and accurate trace element abundances by ICP-MS is a complete sample digestion. Incomplete dissolution of highly resistant minerals in e.g. sediments, soils, granitoid and ultramafic rocks, may cause biased results for a number of trace elements, such as for Ba (barite), Zr and Hf (zircon), and rare earth elements (e.g. garnet, zircon). Total digestion of rocks bearing refractory minerals is achieved commonly using HF-acid mixtures in highpressure sealed Teflon bombs at high temperatures (>160°C) for several days (Yu et al., 2001). An alternative method to acid digestion is the use of fusion techniques (e.g. $LiBO_2$, KHF_2, $K_2B_4O_7$, K_2CO_3, Na_2CO_3, Na_2O_2, NaOH), which ensure rapid and complete digestion of all rock-forming minerals, including those highly resistant minerals (Hall et al., 1990; Rivoldini and Fadda, 1994; Jin and Zhu, 2000; Yu et al., 2001; Meisel et al., 2002; Duan et al., 2002; Panteeva et al., 2003). Until recently, fusion techniques coupled to ICP-MS analysis have remained neglected mainly because: 1) contamination problems from impure reagents and metal crucibles (e.g. Pt); 2) the yield of high total dissolved solids, which requires large sample dilution or analyte separation before analysis (e.g. Jin and Zhu, 2000), and 3) possible loss of sample during analytical procedure. A procedure was developed

recently, which involves alkaline fusion ($NaOH$-Na_2O_2) and pre-concentration using $Fe(OH)_3$-$Ti(OH)_4$ co-precipitation prior to analysis by ICP-MS (Duan et al., 2002). This method was applied successfully to soil and sediment samples for a number of trace elements (REE, Cd, In, Tl, Th, Nb, Ta, Zr and Hf).

In this study, we investigated whether the procedure developed by Duan et al. (2002) for soils and sediments could be equally applied to other rock types, with particular emphasis on rocks bearing highly resistant minerals and highly-depleted rocks. Our aim was to simplify the overall procedure by combining alkaline fusion with the addition of Tm (Barrat et al., 1996). This approach allows calculation of trace element concentrations by adding a small amount of Tm to the sample to produce a positive Tm anomaly in the resulting REE pattern. More importantly, it allows quantification of trace element abundances even if there is sample loss during the procedure.

Experimental

Reagents and materials

During the course of our experiments, the following reagents were used: analytical pure grade (puriss. pro analysis) sodium peroxide (Na_2O_2 small beads, Fluka) and sodium hydroxide (NaOH pellets, Riedel-de-Haën), Ti (~ 10,000 μg ml^{-1}, Johnson Matthey and Co, Ltd) and Fe (~ 50,000 μg ml^{-1}, cleaned by solvent extraction with isopropyl ether) standard solutions, Tm standard solution (Custom-Grade Standard, Inorganic Ventures inc., CGTM1-1), nitric acid (Merck, commercial) purified by sub-boiling distillation, high-quality deionised (18.2 MΩ) Millipore® water. Glassy carbon crucibles made of Sigradur® (CEP Ind.) were used for fusion.

Nine certified reference materials were analysed to validate our procedure. Those included two basalts: BCR-2 (United States Geological Survey, USGS) and BIR-1 (USGS); two ultramafic rock (peridotites): UB-N (Centre de Recherches Pétrographiques et Géochimiques, CRPG) and JP-1 (Geological Survey of Japan, GSJ); two granites : AC-E (CRPG) and MA-N (CRPG); two marine sediments: MAG-1 (USGS) and GSMS-2 (Chinese Academy of

Geological Sciences, CAGS); and one soil: GSS-4 (CAGS). Another rock standard (basalt BHVO-2, USGS) was also analysed to correct for instrumental drift and calibration purpose.

Procedure

Our experimental procedure largely followed that described by Duan et al. (2002). Several separate digestions of our nine geochemical reference standards were processed. Duan et al. (2002) recommended addition of 2 mg of both TiO_2 and Fe_2O_3 to samples before fusion to ensure complete co-precipitation of REE, Nb, Ta, Zr and Hf. In this study, we considered that the rock types investigated (i.e. peridotite, basalt, granite, sediment, soil) contained sufficient amounts of Fe (from ~ 2.5 to 14 wt% Fe_2O_3) to initiate Fe-oxyhydroxide co-precipitation and, hence, did not require addition of any extra Fe. Additional Fe (2 mg) was added to one rock standard only (MA-N), because it exhibits very low Fe contents (~ 0.4 wt% Fe_2O_3). The effect of Ti addition on trace element co-precipitation was investigated further by spiking with Ti (2 mg) a few of our series of rock standards.

About 80 ng of Tm (in solution) were added to a crucible, weighed accurately, and evaporated to dryness on a hotplate. About 100 mg of sample powder were weighed carefully, then placed in the crucible with 1.2g Na_2O_2, 0.6g NaOH and fused in a muffle furnace at 650°C for 15 minutes. After cooling the crucible (~ 3 min), the melt was dissolved and iron hydroxides were precipitated by adding 10 ml of ultra-pure water, then transferred into a PTFE beaker. The crucible was rinsed with an additional 20 ml of ultra-pure water. Complete co-precipitation was achieved by heating the PTFE beaker at 130°C on a hotplate for two hours. The solution was then rinsed into a pre-cleaned centrifuge tube and centrifuged for 3 min at 3000 rpm. The clear supernatant was decanted and the centrifuge tube was filled with 15 ml of ultra-pure water, stirred, and then centrifuged again. The same procedure was repeated twice more in order to completely wash the Fe-(Ti) hydroxides. The Fe-(Ti) hydroxides were then dissolved in 6M HCl, transferred into acid-cleaned HDPE bottles, and stored as 'mother' solution (~ 20 ml). Finally, a few hours before measurement, an aliquot of the 'mother' solution was dried down, taken up in 200 µl concentrated HNO_3 acid, and diluted with 10 ml ultra-pure water.

Instrumentation and analysis

The instrument used was a ELEMENT 2 (Thermo Electron, Bremen, Germany) sector field inductively coupled plasma mass spectrometry (SF-ICP-MS), equipped with an ASX 100

autosampler (CETAC Technologies, Omaha, NE, USA). This instrument can be operated in low (LRM, m/Δm approx. 300), medium (MRM, m/Δm=4500) and high resolution mode (HRM, m/Δm=9200), depending on the required sensitivity and potential interferences for each element. Details of instrumental operating conditions and measuring parameters are given in Table 1. The REE were analysed with the low resolution mode to enhance sensitivity, but were corrected for oxide and hydroxide interferences by analysing solutions of ultra-pure water, Ba + Ce, Pr + Nd and Sm + Eu + Gd + Tb at the beginning of the measurement cycle, following the procedure of Barrat et al. (1996).

Drift correction

In each of our batches, one reference sample (BHVO-2), unspiked (no added Tm), was processed along with the other rock standards. Samples were analyzed in sequences containing acid blanks (2% HNO_3), procedural blank, BHVO-2 reference solution, and samples. The BHVO-2 reference solution was run after every three samples, for the correction of instrumental drift.

Quantification using Tm addition

The principles of the calculation of trace element abundances in any sample spiked with Tm were described previously by Barrat et al. (1996). The accuracy of the method has been illustrated for various types of samples such as volcanics, carbonates, phosphates, waters, and a variety of extraterrestrial samples (e.g., Barrat and Nesbitt, 1996; Barrat et al., 2000a,2000b, 2007; Picard et al., 2002). The calculations are briefly summarized here.

Raw data are first corrected for drift, procedural blank and interferences. Then, raw elemental concentrations in sample solutions are calculated using the corrected data for the BHVO-2 and sample solutions. At this stage, it is important to note that these calculated raw concentrations are not absolute concentrations. [X], the abundance in a sample of the element X (in μg g^{-1}) can be obtained using M, the mass of sample spiked with Tm (in g), the amount of Tm added (M_{Tm} in μg), and C_X, C_{Er} and C_{Yb}, the raw concentrations for X, Er and Yb (in μg g^{-1}) in the sample solution, respectively:

$$[X] = (M_{Tm} \cdot C_X)/((M \cdot (C_{Tm} - C_{Tm^*}))$$

Where C_{Tm^*} is the calculated Tm concentration in the sample solution with no spike contribution. C_{Tm^*} is easily obtained using the chondritic abundances (e.g., Evensen et al. 1978):

$$C_{Tm^*} = 0.02561 ((C_{Er}/0.166).(C_{Yb}/0.1651))^{1/2}$$

Of course, such a calculation is valid only if the HREE abundances of the sample are normal, i.e. in other words, only if its REE pattern does not exhibit a Yb anomaly, a feature that has been observed in rare extraterrestrial minerals, but never in terrestrial rocks. An important requirement in our procedure is that the BHVO-2 standard used for quantifying trace element abundances must be processed in the very same way as all other samples analysed, i.e. digested using alkaline fusion. In doing so, even if Tm does not behave the same way as other elements during the co-precipitation of Fe-oxides (i.e. if the effectiveness of its recovery during $Fe(OH)_3$ co-precipitation slightly differs from that of other elements), this effect is cancelled out by using BHVO-2 for quantification.

Results and discussion

Total procedural blanks

Total procedural blanks were prepared using the same method as for rock samples, with addition of Fe (2 mg) and (or without) Ti (2 mg), to initiate trace element co-precipitation (Table 2). Reagent blanks for Fe and Ti solutions were run and subtracted to the total procedural blanks. Instrumental detection limits for each element measured, calculated as three times the standard deviation on a series of ten duplicates of a 2% HNO_3 solution, are also listed in Table 2 as ng g^{-1} equivalent in rock sample. Procedural blanks are similar for most elements with or without Ti addition, with the exception of Zr, Hf and Th, which are much higher (~700%, 500% and 200%, respectively) with Ti addition. For the elements listed in Table 2, blank contributions to total signal intensities are typically below 0.1% for MAG-1, GSS-4, GSMS-2, AC-E and BCR-2, and below 1% for BIR-1. Blanks are the same throughout but, for the most depleted rocks i.e. MA-N, UB-N and JP-1, they can represent a higher proportion of the total concentration. For MA-N and UB-N, averaged blank contributions in undoped samples (without Ti addition) are below 5% for all elements, with the exception of Ba (up to 15%) and La (up to 20%). For JP-1, total blanks in undoped samples are below 5% for Y, Sc, Zr, Hf, mid REE (Gd, Tb, Dy, Ho) and heavy REE (Er, Tm,

Yb, Lu), but are higher for Ba and Eu (~20%), La and Ce (~25%), Pr (~10%), Sm (~15%) and Th (~30%).

Oxide formation rates

Oxide formation rates during the course of this study were generally ~0.1% for BaO+/Ba+, <0.1% for CeOH+/Ce+ and ~3% for PrO+/Pr+. Barium oxide interference on the ^{151}Eu signal was negligible for most studied rocks, with the exception of MA-N (~10%) and JP-1 (~40%), due to the high Ba/Eu ratios (~2000 and ~5000, respectively) in those rocks. Cerium hydroxide and Pr oxide interferences on the ^{157}Gd signal were significant, ranging from 3% for BIR-1 to 30% for GSS-4. Oxide and hydroxide interference corrections for all other REE were negligible.

Ti-doped versus undoped samples

Results for Sc, Y, Zr, Ba, Hf, Th and the REE are given in Table 3, both for Ti-doped and undoped samples. For the elements listed in Table 3, measured concentrations in Ti-doped samples are very similar to those obtained for undoped samples. Duan et al. (2002) added extra Ti to their samples before fusion to ensure complete co-precipitation of those elements (e.g. Zr, Hf) sharing similar properties with Ti. In this study, addition of Ti during the fusion procedure has not led to significantly higher concentrations for Zr and Hf. The only notable exception is for UB-N (+20% and +10% in Ti-doped vs. undoped samples for Zr and Hf, respectively), but the higher concentrations in this sample after Ti addition could be possibly due to a high blank contribution (see above). Our results suggest therefore that quantitative measurement of Zr and Hf concentrations after alkaline fusion can be achieved without the need for Ti addition, even in the case of those Ti-poor rocks, such as MA-N (TiO_2 ~ 0.01 wt%), UB-N and AC-E (~ 0.1 %), and JP-1 (~ 0.006 %).

Precision and accuracy

The precision of the measurements is given in Table 3 as the relative standard deviation (RSD), evaluated from both Ti-doped and undoped analytical series. Precision is better than 10% for most elements and typically below 5% for the REE. For BIR-1, RSDs are significantly worse for Ba (24.9%) and Th (37.9%). For GSMS-2, Zr, Ba and Th exhibit RSDs slightly higher than 10% (11.9%, 11.7% and 12.6%, respectively). Despite of their low elemental abundances, the two ultramafic rocks analysed in this study exhibit reasonably good precision for most studied elements (<10%). Exceptions are for Sc (12.6% for JP-1), Zr

(19% for UB-N), Ba (11.4% for UB-N), La (14% for UB-N), Hf (17.4% for UB-N) and Th (14.8% and 22.9% for UB-N and JP-1, respectively). Relative standard deviations are however higher for MA-N (Y: 16.5%, La: 18.4%, Eu: 13.6%, up to 24% for the heavy REE). Such high RSDs most probably reflect low element abundances (for BIR-1, UB-N, JP-1 and MA-N), but could also reflect sample heterogeneity (for MA-N). In the case of coarse-grained granitoid rocks such as MA-N, it is possible that sample sizes on the order of 100 mg are slightly heterogeneous. This may introduce a bias resulting in less reproducible elemental concentrations.

The accuracy of our procedure was assessed by comparing our results to recommended (or suggested) values (i.e. Govindaraju, 1994, 1995; Jochum, 2005) and recently published high quality reference values when available (Table 3). Chondrite-normalized (Evensen et al., 1978) REE patterns for the nine geological reference materials analysed are shown in Fig. 1. With few exceptions, our data are in agreement with those found for the reference materials BIR-1, BCR-2, MAG-1, GSS-4, GSMS-2 and AC-E. In particular, the concentrations obtained for the well-characterized basaltic standards BCR-2 and BIR-1 agree well with values obtained in our laboratory for samples digested using conventional HF-acid digestion. Exceptions are for Sc, Y and Zr in most rocks. Our Sc, Y and Zr values are on average 8%, 7% and 12% higher than published values. The cause for those systematically higher concentrations for Sc, Y and Zr is uncertain, but it is possible that the use of slightly biased reference values for BHVO-2 may propagate errors on calculated concentrations for some elements. Barium is about 11% higher in BIR-1 and GSMS-2 and 14% higher in AC-E. Hafnium is about 14% lower in AC-E. For BIR-1, BCR-2, MAG-1, GSS-4, GSMS-2 and AC-E, average accuracy values are mostly below 5% for the REE. The most notable exceptions are Sm and Nd (approximately 14% higher) in GSMS-2; Gd (17% higher) in MAG-1 and Lu (11%, 9% and 13% lower) in MAG-1, GSS-4 and AC-E, respectively. Note that our data for GSMS-2 are on average 7% higher than published values, but there are only two full sets of reference data available for this sediment standard.

Results for low level reference materials MA-N, UB-N and JP-1 are also in general agreement with published values, although MA-N and JP-1 are so low that there is little reliable data published. Smooth REE patterns were obtained for all reference materials analysed, including UB-N, MA-N and JP-1 (Fig. 1). Note that there are large discrepancies in the published Eu data for JP-1 (Fig. 1). This clearly reflects the difficulty in correcting BaO

interference on the Eu signal in this rock characterized by a high Ba/Eu ratio (Nakamura and Chang, 2007).

Other elements

In addition to those elements listed in Table 2, U, Sr, Pb, Mn, Co, Ni, Cu, Nb and Ta were also investigated (see Table 1), but failed to provide reliable results (data not shown). Several elements (Mn, Co, Ni, Cu) yielded relatively accurate results, but often with poor reproducibility. For Nb, Ta and U, accuracies were in most cases worse than 20%, both for Ti-doped and undoped series. The poor accuracy and/or precision for these elements were most likely due to a high blank contribution (e.g. > 5% for Ni and Cu) and/or variable co-precipitation efficiency (e.g. Mn, Co, Nb, Ta, U). Further studies would be required to assess whether these elements could be measured accurately and precisely by ICP-MS after sample digestion by alkaline fusion.

Conclusions

The Na_2O_2-NaOH fusion is suitable for the determination of several trace elements i.e. REE, Y, Sc, Zr, Ba, Hf and Th by ICP-MS in various geological samples, including depleted rocks such as peridotites. Our revisited protocol involves the addition of a Tm spike to samples prior to fusion, which allows precise determination of trace element abundances even when there is sample loss during fusion or handling. Results obtained in this study for a series of nine geological reference materials are in agreement with literature data. Compared to conventional HF-acid digestion methods, this procedure is rapid and particularly well suited for the determination of trace element abundances in those rocks bearing highly-resistant minerals, such as sediments, soils, granites and ultramafic rocks.

Acknowledgement

This study was funded by IFREMER through the program ‘Mineral and Energetic Resources, Sedimentary processes and Impact on Ecosystems’. Two anonymous reviewers are acknowledged for providing thoughtful and constructive reviews, which improve significantly our manuscript.

References

Baranov B.V., Werner R., Hoernle K.A., Tsoy I.B., Van den Bogaard P. and Tararin I.A. (2002)
Evidence for compressionally induced high subsidence rates in the Kurile Basin (Okhotsk Sea). Tectonophysics, 350, 63-97.

Barrat J.A. and Nesbitt R.W. (1996)
Geochemistry of the Tertiary volcanism of Northern Ireland. **Chemical Geology**, 129, 15-38.

Barrat J.A., Keller F., Amossé J., Taylor R.N., Nesbitt R.W. and Hirata T. (1996)
Determination of rare earth element in sixteen silicate reference samples by ICP-MS after Tm addition and ion exchange separation. **Geostandards Newsletter**, 20, 133-139.

Barrat J.A., Blichert-Toft J., Gillet Ph. and Keller F. (2000a)
The differentiation of eucrites: the role of in-situ crystallization. **Meteoritics and Planetary Science**, 35, 1087-1100.

Barrat J.A., Boulègue J., Tiercelin J.J. and Lesourd M. (2000b)
Strontium isotopes and rare earth element geochemistry of hydrothermal carbonate deposits from the Tanganyika Lake, East Africa. **Geochimica Cosmochimica Acta**, 64, 287-298.

Barrat J.A., Yamaguchi A., Greenwood R.C., Bohn M., Cotten J., Benoit M. and Franchi I.A. (2007)
The Stannern trend eucrites: Contamination of main group eucritic magmas by crustal partial melts. **Geochimica Cosmochimica Acta**, 71, 4108-4124.

Downes H., Kostoula T., Jones A.P., Beard A.D., Thirlwall M.F. and Bodinier J.L. (2002)
Geochemistry and Sr-Nd isotopic compositions of mantle xenoliths from the Monte Vulture carbonatite-melilitite volcano, central southern Italy. **Contributions to Mineralogy and Petrology**, 144, 78-92.

Dulski P. (2001)
Reference materials for geochemical studies: New analytical data by ICP-MS and critical discussion of reference values. **Geostandards Newsletter: The Journal of Geostandards and Geoanalysis**, 25, 87-125.

Evensen N.M., Hamilton P.J. and Onions R.K. (1978)
Rare earth abundances in chondritic meteorites. **Geochimica Cosmochimica Acta**, 42, 1199-1212.

Garrido C.J., Sánchez-Vizcaino V.L., Gómez-Pugnaire M.T., Trommsdorff V., Alard O., Bodinier J.L. and Godard M. (2005)
Enrichment of HFSE in chlorite-harzburgite produced by high-pressure dehydration of antigorite-serpentinite: Implications for subduction magmatism. **Geochemistry Geophysics Geosystems**, 6, Q01J15, doi:10.1029/2004GC000791.

Govindaraju K. (1994)
Compilation of working values and sample description for 383 geostandards. **Geostandards Newsletter**, 18, 1-158.

Govindaraju K. (1995)
1995 working values with confidence limits for twenty-six CRPG, ANRT and IWG-GIT geostandards. **Geostandards Newsletter**, 19, Special Issue, 1-32.

Hall G.M., Jain J.C. and Loop J. (1990)
Determination of zirconium, niobium, hafnium and tantalum at low levels in geological materials by inductively coupled plasma mass spectrometry. **Journal of Analytical Atomic Spectrometry**, 5, 339.

Ionov D.A., Ashchepkov I. and Jagoutz E. (2005)
The provenance of fertile off-craton lithospheric mantle: Sr–Nd isotope and chemical composition of garnet and spinel peridotite xenoliths from Vitim, Siberia. **Chemical Geology**, 217, 41-75.

Jin X. and Zhu H. (2000)
Determination of platinum group elements and gold in geological samples with ICP-MS using a sodium peroxide fusion and tellurium co-precipitation. **Journal of Analytical Atomic Spectrometry**., 15, 747-751.

Lenoir X., Garrido C.J., Bodinier J.L., Dautria J.-M. (2000)
Contrasting lithospheric mantle domains beneath the Massif Central (France) revealed by geochemistry of peridotite xenoliths. **Earth Planetary Science Letters**, 181, 359-375.

Liang Q.and Grégoire D.C. (2000)
Determination of trace elements in twenty six Chinese geochemistry reference materials by inductively coupled plasma mass spectrometry. **Geostandards Newsletter: The Journal of Geostandards and Geoanalysis**, 24, 51-63.

Makishima A. and Nakamura E. (2006)
Determination of major, minor and trace elements in silicate samples by ICP-QMS and ICP-SFMS applying isotope dilution-internal standardisation (ID-IS) and multi-stage internal standardization. **Geostandards and Geoanalytical Research**, 30, 245-271.

Meisel T., Schöner N., Paliulionyte V. and Kahr E. (2002)
Determination of Rare Earth Elements, Y, Th, Zr, Hf, Nb and Ta in geological reference materials G-2, G-3, SCo-1 and WGB-1 by sodium peroxide sintering and inductively coupled plasma-mass spectrometry. **Geostandards Newsletter: The Journal of Geostandards and Geoanalysis**, 26, 53-61.

Nakamura K. and Chang Q. (2007)
Precise determination of ultra-low (sub-ng/g) level rare earth elements in ultramafic rocks by quadrupole ICP-MS. **Geostandards and Geoanalytical Research**, 31, 185-197.

Panteeva S.V., Gladkochoub D.P., Donskaya T.V., Markova V.V. and Sandimirova G.P. (2003)
Determination of 24 trace elements in felsic rocks by inductively coupled plasma mass spectrometry after lithium metaborate fusion. **Spectrochimica Acta Part B**, 58, 341-350.

Paulick H., Bach W., Godard M., De Hoog J.C.M., Suhr G. and Harvey J (2006)|
Geochemistry of abyssal peridotites (Mid-Atlantic Ridge, 15°20´N, ODP Leg 209): Implications for fluid/rock interaction in slow spreading environments. **Chemical Geology**, 234, 179-210.

Picard S., Lécuyer C., Barrat J.A., Garcia J.P., Dromart G. and Sheppard S.M.F. (2002)
Rare Earth Element chemistry of Jurassic seawater inferred from fish and reptile apatite. **Chemical Geology**, 186, 1-16.

Plumlee G. (1998)
http://minerals.cr.usgs.gov/geo_chem_stand/, USGS.

Rivoldini A. and Fadda S. (1994)
Inductively coupled plasma mass spectrometric determination of low-level rare earth elements in rocks using potassium-based fluxes for sample decomposition. **Journal of Analytical Atomic Spectrometry**, 9, 519-524.

Robinson P., Townsend A.T., Yu Z. and Münker C. (1999)
Determination of scandium, yttrium and rare earth elements in rocks by high resolution Inductively Coupled Plasma-Mass Spectrometry. **Geostandards Newsletter: The Journal of Geostandards and Geoanalysis**, 23, 31-46.

Duan D., Hangting C. and Xianjin Z. (2002)
Determination of rare and rare earth elements in soils and sediments by ICP-MS using $Ti(OH)_4$-$Fe(OH)_3$ co-precipitation preconcentration. **Journal of Analytical Atomic Spectrometry**, 17, 410-413.

Wang Y., Luo D., Gao Y., Song H., Li J., Chen W., Teng Y. and Zhou S. (1998)
A preliminary study on the preparation of four Pacific Ocean polymetallic nodule and sediment reference materials: GSPN-2, GSPN-3, GSMS-2 and GSMS-3. **Geostandards Newsletter: The Journal of Geostandards and Geoanalysis**, 22, 247-255.

Yu Z., Robinson P. and McGoldrick P. (2001)

An evaluation of methods for the chemical decomposition of geological materials for trace element determination using ICP-MS. **Geostandards Newsletter: The Journal of Geostandards and Geoanalysis**, 25, 199-217.

Figure caption

Figure 1. Chondrite-normalized (Evensen et al., 1978) REE patterns of the nine geological reference materials studied.

Table 1 .
ICP-MS operating conditions and measurement parameters

RF power	1250 W
Sample uptake rate	1 ml/min
Coolant argon flow rates	16.11 l/min
Auxiliary argon flow rates	0.61 l/min
Nebulizer argon flow rates	0.88 l/min
Torch	quartz thermo fisher
Nebulizer	Teflon® 100 µl
Spray chamber	ESI PC3 quartz
Cones	Nickel
Low resolution mode (LRM)	^{89}Y, $^{90,91}Zr$, ^{93}Nb, ^{135}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, $^{143,146}Nd$, $^{147,149}Sm$, ^{151}Eu ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{174}Yb, ^{175}Lu, $^{177,178}Hf$, ^{181}Ta, ^{232}Th, ^{238}U
Medium resolution mode (MRM)	^{45}Sc, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{88}Sr, ^{208}Pb
Acquisition mode	E-scan
No. of scans	4 (LRM) + 4 (MRM)
Ion lens settings	Adjusted daily to obtain maximum signal intensity
Wash time	3 min (5% v/v HNO_3)

Table 2.

Instrumental detection limits, total procedural blanks and concentration values of BHVO-2 used in this study

Element	Detection limits in rock sample (ng g^{-1})	Total blank (ng) without Ti addition	Total blank (ng) with Ti addition	BHVO-2 (µg g^{-1}) (Barrat et al., 2008) best estimate
Sc	nd	0.3	0.5	32.3
Y	0.010	0.3	0.7	28
Zr	1.7	3	26	178
Ba	2.5	214	273	131
La	0.015	0.9	0.5	15.2
Ce	0.008	1.6	2.7	37.5
Pr	0.010	0.08	0.08	5.31
Nd	0.045	0.4	0.6	24.5
Sm	0.021	0.13	0.05	6.07
Eu	0.025	0.03	0.004	2.07
Gd	0.086	0.03	0.07	6.24
Tb	0.008	0.006	0.007	0.94
Dy	0.018	0.05	0.07	5.31
Ho	0.003	0.01	0.01	0.97
Er	0.012	0.02	0.01	2.54
Tm	0.008	0.03	0.01	0.35
Yb	0.010	0.03	0.04	2
Lu	0.005	0.004	0.002	0.27
Hf	0.12	0.1	0.4	4.28
Th	0.24	0.1	0.4	1.21

Table 3.
Trace element concentrations (µg g-1) for BIR-1, BCR-2 , MAG-1, GSS-4, GSMS-2, AC-E, MA-N, UB-N and JP-1.

Sample	BIR-1											BCR-2								
Reference	Bayon et al. (This work)									Jochum et al. (2006)	Barrat et al. (2001)	Bayon et al. (This work)							Jochum et al. (2006)	Barrat et al. (2007)
Element	1 (Ti)	2 (Ti)	3 (Ti)	4 (Ti)	5	6	Mean	s	RSD			1 (Ti)	2 (Ti)	3	4	Mean	s	RSD		
Sc	44	49	44	45	48	44	46	2	5.0	43	38	35	38	37	34	36	2	4.9	33	32
Y	16.3	17.6	16.5	16.5	17.6	17.3	17.0	0.6	3.6	15.6	16.16	39.7	41.4	40.2	39.2	40.1	0.9	2.4	37	37.33
Zr	16.2	15.6	15.1	14.4	15.7	16.0	15.5	0.7	4.2	14	15.29	219	209	202	199	208	9	4.2	184	198
Ba	6.7	10.3	6.3	5.6	9.4	9.6	8.0	2.0	24.9	7.14	6.3	719	729	690	709	712	17	2.3	677	696
La	0.58	0.63	0.61	0.60	0.62	0.55	0.60	0.03	5.0	0.615	0.594	26.0	27.0	25.8	25.2	26.0	0.7	2.7	24.9	25.19
Ce	1.82	2.00	1.91	1.86	1.94	1.94	1.91	0.06	3.2	1.92	1.91	54.8	57.1	55.4	54.4	55.4	1.2	2.2	52.9	53.23
Pr	0.366	0.377	0.371	0.366	0.379	0.376	0.372	0.006	1.5	0.37	0.377	7.06	7.09	7.10	7.01	7.07	0.04	0.6	6.7	6.9
Nd	2.36	2.42	2.4	2.4	2.44	2.41	2.40	0.03	1.2	2.38	2.34	29.78	29.75	29.54	29.61	29.67	0.12	0.4	28.7	29.19
Sm	1.116	1.096	1.105	1.097	1.102	1.098	1.102	0.007	0.7	1.12	1.07	7.02	6.60	6.68	6.72	6.76	0.18	2.7	6.58	6.59
Eu	0.536	0.528	0.528	0.524	0.539	0.527	0.530	0.006	1.1	0.53	0.518	2.00	1.93	2.04	2.07	2.01	0.06	2.9	1.96	1.92
Gd	1.77	1.83	1.81	1.82	1.84	1.82	1.81	0.02	1.3	1.87	1.71	7.09	7.02	7.10	7.06	7.07	0.04	0.5	6.75	6.69
Tb	0.364	0.371	0.362	0.361	0.371	0.367	0.366	0.005	1.2	0.36	0.359	1.11	1.08	1.09	1.09	1.09	0.01	1.0	1.07	1.05
Dy	2.57	2.62	2.60	2.56	2.62	2.59	2.59	0.02	1.0	2.51	2.51	6.63	6.63	6.53	6.54	6.58	0.05	0.8	6.41	6.44
Ho	0.589	0.588	0.590	0.580	0.601	0.596	0.591	0.007	1.3	0.56	0.572	1.38	1.33	1.36	1.34	1.35	0.02	1.5	1.28	1.35
Er	1.76	1.76	1.73	1.71	1.75	1.70	1.74	0.03	1.5	1.66	1.68	3.81	3.77	3.72	3.76	3.77	0.04	1.0	3.66	3.67
Yb	1.65	1.63	1.66	1.63	1.64	1.57	1.63	0.03	1.8	1.65	1.62	3.45	3.30	3.44	3.41	3.40	0.07	2.0	3.38	3.35
Lu	0.252	0.240	0.24	0.24	0.240	0.237	0.243	0.005	2.2	0.25	0.25	0.52	0.49	0.49	0.49	0.50	0.02	3.2	0.503	0.48
Hf	0.65	0.55	0.56	0.56	0.58	0.60	0.58	0.04	6.5	0.582	0.57	5.40	4.77	4.81	4.90	4.97	0.29	5.9	4.9	4.79
Th	-	0.059	0.029	0.027	0.032	0.030	0.035	0.013	37.9	0.032	0.029	7.04	6.06	5.93	5.99	6.26	0.52	8.4	5.7	5.63

Table 3 (continued).

Sample	MAG-1										GSS-4									
Reference	Bayon et al. (This work)							Govindaraju (1994)	Dulski et al. (2001)	Baranov et al. (2002)	Bayon et al. (This work)							Govindaraju (1994)	Liang and Gregoire (2002)	Duan et al. (2002)
Element	1 (Ti)	2 (Ti)	3	4	Mean	s	RSD				1 (Ti)	2 (Ti)	3	4	Mean	s	RSD			
Sc	18.1	18.8	19.6	19.5	19.0	0.7	3.7	17.2	nd	nd	21.1	21.7	19.9	23.1	21.5	1.3	6.2	20.2	22.2	nd
Y	28.6	29.1	29.1	30.7	29.4	0.9	3.1	28	25.6	28.9	47	51	47	50	49	2	3.6	39	41.5	41
Zr	140	136	134	143	138	4	2.9	126	128	127	637	580	557	624	599	37	6.2	500	487	507
Ba	483	505	488	522	500	17	3.5	479	473	489	216	214	207	228	216	9	4.0	213	223	nd
La	42.3	42.4	43.9	45.7	43.5	1.6	3.6	43	40.7	44.2	53	54	51	56	53	2	3.6	53	54.2	54
Ce	88.2	90.5	90.3	94.8	90.9	2.8	3.0	88	84	88	143	145	141	150	145	4	2.7	136	143	nd
Pr	10.2	10.4	10.6	11.0	10.6	0.3	3.1	9.3	10.3	10.5	8.0	8.2	8.1	8.6	8.2	0.3	3.4	8.4	8.45	9.1
Nd	38.8	39.6	40.2	41.2	39.9	1.0	2.5	38	36.9	38.6	25.4	25.7	25.8	27.3	26.1	0.8	3.1	27	27.5	26
Sm	7.3	7.5	7.7	7.8	7.6	0.2	2.7	7.5	7	7.32	4.02	4.15	4.19	4.34	4.17	0.13	3.2	4.4	4.34	4.3
Eu	1.51	1.51	1.58	1.52	1.53	0.03	2.1	1.55	1.43	1.59	0.82	0.84	0.87	0.87	0.85	0.03	3.0	0.85	0.87	0.82
Gd	6.4	6.9	6.9	6.7	6.7	0.2	3.4	5.8	6.2	5.59	4.5	4.9	4.9	4.7	4.8	0.2	4.2	4.7	4.82	5
Tb	0.93	0.95	0.95	0.97	0.95	0.02	1.8	0.96	0.89	1.00	0.90	0.97	0.92	0.96	0.94	0.03	3.6	0.94	0.96	0.85
Dy	5.33	5.32	5.33	5.36	5.33	0.01	0.3	5.2	5.07	5.51	6.5	7.1	6.6	6.8	6.7	0.3	3.7	6.6	6.9	6.6
Ho	1.05	1.04	1.05	1.09	1.06	0.02	2.1	1.02	0.97	1.08	1.46	1.56	1.52	1.54	1.52	0.04	2.9	1.46	1.52	1.5
Er	2.91	2.86	2.83	2.90	2.87	0.04	1.3	3	2.73	3.1	4.60	4.85	4.64	4.72	4.70	0.11	2.3	4.5	4.88	4.5
Yb	2.64	2.64	2.64	2.75	2.67	0.05	2.0	2.6	2.53	2.86	4.6	4.9	4.9	5.1	4.9	0.2	3.6	4.8	5.12	4.3
Lu	0.371	0.379	0.371	0.356	0.369	0.010	2.6	0.4	0.381	0.41	0.68	0.74	0.71	0.71	0.71	0.03	3.5	0.75	0.77	0.67
Hf	3.9	3.6	3.6	3.9	3.7	0.2	4.3	3.7	3.7	3.6	14.7	13.7	13.6	14.8	14.2	0.6	4.5	14	14.3	14
Th	14.2	12.4	12.6	13.2	13.1	0.8	6.1	11.9	11.9	10.8	31.1	27.8	27.7	29.7	29.1	1.6	5.6	27.3	28.3	27.2

Table 3 (continued).

Sample	GSMS-2								
Reference	Bayon et al. (This work)							Wang et al. (1998)	Dulski et al. (2001)
Element	1 (Ti)	2 (Ti)	3	4	Mean	s	RSD		
Sc	29.1	24.2	24.3	28.6	26.6	2.7	10.0	23	nd
Y	129	116	111	135	123	11	9.2	98	106.5
Zr	190	153	151	183	170	20	11.9	140	155
Ba	3765	3276	3061	3942	3511	412	11.7	3100	3118
La	71	62	63	73	67	6	8.6	62	62.6
Ce	93	82	80	98	88	9	9.8	82	83.2
Pr	19.7	17.9	17.6	20.6	19.0	1.4	7.6	17	18
Nd	83.4	76.4	75.3	88.8	81.0	6.3	7.8	75	69.7
Sm	19.66	17.82	17.61	20.42	18.88	1.38	7.3	18	16.3
Eu	4.49	4.46	4.49	4.93	4.59	0.22	4.9	4.5	4.5
Gd	21.1	19.1	18.8	21.6	20.2	1.4	6.9	18	19.4
Tb	3.35	2.93	2.89	3.52	3.17	0.31	9.9	3.1	2.98
Dy	19.3	17.8	17.4	20.2	18.7	1.3	7.0	17	18.1
Ho	4.07	3.62	3.58	4.06	3.84	0.27	7.0	3.6	3.62
Er	11.22	10.13	9.95	11.68	10.74	0.84	7.8	9.8	10.3
Yb	10.2	9.2	9.1	10.6	9.8	0.8	7.7	8.9	9.24
Lu	1.46	1.37	1.32	1.47	1.41	0.07	5.1	1.3	1.41
Hf	4.3	3.7	3.7	4.2	4.0	0.3	8.2	3.6	3.76
Th	14.8	11.6	11.5	13.5	12.9	1.6	12.6	11	12.07

Table 3 (continued).

Sample	AC-E										MA-N								
Reference	Bayon et al. (This work)							Govindaraju (1995)	Yu et al. (2001)	Dulski et al. (2001)	Bayon et al. (This work)							Govindaraju (1995)	Dulski et al. (2001)
Element	1	2	3	4	Mean	s	RSD				1	2	3	4	Mean	s	RSD		
Sc	1.0	0.9	0.8	0.9	0.9	0.1	10.0	0.11	0.916	0.9215	0.23	0.21	0.24	0.22	0.22	0.01	5.6	0.2	nd
Y	192	182	173	176	181	9	4.7	184	161	175	0.34	0.46	0.39	0.49	0.42	0.07	16.5	0.4	0.29
Zr	885	776	761	797	805	56	6.9	780	803	835	28	35	28	33	31	3	11.1	25	25
Ba	52	49	46	47	49	2	5.1	55	55.1	53.2	42.2	41.6	40.5	42.4	41.7	0.9	2.1	42	40
La	60	56	54	55	56	3	4.9	59	56.6	58	0.42	0.40	0.50	0.32	0.41	0.08	18.4	0.5	0.5
Ce	155	150	143	146	148	5	3.7	154	150	153	0.83	0.74	0.96	0.78	0.83	0.09	11.3	0.9	0.9
Pr	21.5	19.9	19.7	20.3	20.4	0.8	4.0	22.2	21.3	22	0.100	0.090	0.113	0.092	0.099	0.011	10.7	0.1	0.11
Nd	92	85	84	85	86	4	4.1	92	87.2	92	0.37	0.34	0.42	0.35	0.37	0.04	9.9	0.4	0.4
Sm	24.3	22.0	22.2	22.6	22.8	1.1	4.6	24.2	23.7	25	0.078	0.072	0.087	0.078	0.079	0.006	7.9	0.09	0.08
Eu	1.9	1.6	1.7	1.7	1.7	0.1	5.5	2	1.87	2	0.016	0.021	0.022	0.022	0.020	0.003	13.6	0.02	0.015
Gd	26.2	23.6	23.4	23.7	24.2	1.3	5.5	26	25.2	27.1	0.068	0.071	0.079	0.080	0.074	0.006	7.9	0.08	0.06
Tb	4.6	4.4	4.3	4.4	4.4	0.2	3.7	4.8	4.5	4.9	0.010	0.012	0.011	0.012	0.011	0.001	8.5	0.01	0.01
Dy	29.5	28.0	27.4	27.8	28.2	0.9	3.3	29	28.7	30	0.059	0.074	0.065	0.080	0.069	0.009	13.5	0.07	0.056
Ho	6.2	5.7	5.7	5.8	5.9	0.3	4.3	6.5	5.98	6.3	0.010	0.014	0.012	0.015	0.013	0.002	17.8	0.017	0.01
Er	18.0	16.3	16.0	16.3	16.7	0.9	5.5	17.7	17.4	19	0.027	0.042	0.032	0.042	0.036	0.008	21.1	0.04	0.026
Yb	16.6	15.1	15.1	15.5	15.6	0.7	4.4	17.4	16.5	17.9	0.047	0.065	0.052	0.064	0.057	0.009	15.6	0.04	0.033
Lu	2.19	2.03	2.04	2.01	2.07	0.08	3.9	2.45	2.34	2.5	0.004	0.006	0.005	0.006	0.005	0.001	23.9	0.005	0.004
Hf	26	22	23	24	24	2	8.2	27.9	27.1	28.6	4.4	4.8	4.1	4.8	4.5	0.4	7.8	4.5	3.3
Th	19.9	16.3	16.0	16.6	17.2	1.8	10.6	18.5	17.5	18.5	2.0	1.6	1.9	1.6	1.7	0.2	11.4	1.4	1.3

Table 3 (continued).
Trace element concentrations (µg g-1) for UB-N and JP-1

Sample	UB-N											JP-1									
Reference	Bayon et al. (This work)									Govindaraju (1995)	Ionov et al. (2005)	Bayon et al. (This work)								Dulski et al. (2001)	Barrat et al. (2008)
Element	1 (Ti)	2 (Ti)	3 (Ti)	4 (Ti)	5	6	Mean	s	RSD			1 (Ti)	2 (Ti)	3	4	5	Mean	s	RSD		
Sc	14.7	14.0	15.9	16.2	14.5	13.2	14.7	1.1	7.6	13	14	8.3	10.4	9.9	7.7	8.8	9.0	1.1	12.6	nd	7.25
Y	2.76	2.79	2.79	2.83	2.75	2.66	2.76	0.06	2.1	2.5	2.54	0.099	0.096	0.097	0.097	0.102	0.098	0.002	2.3	0.097	0.1
Zr	6.3	4.2	4.8	4.9	3.8	4.1	4.7	0.9	19.0	4	3.3	5.4	6.1	6.1	4.9	5.7	5.7	0.5	8.7	5.5	5.39
Ba	26	27	23	22	27	30	26	3	11.4	27	26	8.7	9.0	9.3	8.4	8.8	8.8	0.3	3.7	9.2	10.04
La	0.28	0.32	0.32	0.31	0.31	0.21	0.29	0.04	14.0	0.35	0.33	0.0276	0.0279	0.0280	0.0269	0.0287	0.0278	0.0007	2.4	0.034	0.0271
Ce	0.73	0.81	0.80	0.78	0.76	0.76	0.77	0.03	3.7	0.8	0.8	0.070	0.055	0.059	0.067	0.059	0.062	0.007	10.6	0.063	0.0597
Pr	0.116	0.118	0.120	0.119	0.116	0.117	0.118	0.002	1.3	0.12	0.123	0.0083	0.0080	0.0076	0.0077	0.0089	0.0081	0.0005	6.4	0.0089	0.00716
Nd	0.602	0.608	0.634	0.614	0.612	0.607	0.613	0.011	1.8	0.6	0.61	0.030	0.031	0.028	0.029	0.034	0.031	0.002	7.2	0.033	0.0298
Sm	0.223	0.222	0.223	0.220	0.225	0.220	0.222	0.002	0.8	0.2	0.216	0.0077	0.0078	0.0086	0.0069	0.0087	0.0079	0.0007	9.4	0.009	0.00726
Eu	0.083	0.089	0.084	0.085	0.089	0.091	0.087	0.003	3.7	0.08	0.081	0.0018	0.0016	0.0017	0.0016	0.0015	0.0016	0.0001	7.2	0.0021	0.00385
Gd	0.32	0.31	0.34	0.34	0.31	0.30	0.32	0.02	5.0	0.3	0.32	0.0099	0.0101	0.0101	0.0092	0.0112	0.0101	0.0007	6.9	0.0092	0.0085
Tb	0.064	0.060	0.066	0.064	0.062	0.061	0.063	0.002	3.3	0.06	0.06	0.00193	0.00193	0.00199	0.00193	0.00196	0.00195	0.00003	1.4	0.0016	0.00166
Dy	0.434	0.426	0.450	0.447	0.428	0.417	0.434	0.013	2.9	0.38	0.42	0.0139	0.0135	0.0136	0.0132	0.0135	0.0135	0.0003	1.9	0.0132	0.0135
Ho	0.100	0.097	0.100	0.102	0.098	0.095	0.099	0.002	2.5	0.09	0.097	0.0034	0.0033	0.0034	0.0033	0.0035	0.0034	0.0001	3.2	0.003	0.00316
Er	0.311	0.294	0.302	0.304	0.293	0.291	0.299	0.008	2.6	0.28	0.282	0.0120	0.0116	0.0117	0.0121	0.0127	0.0120	0.0005	3.7	0.0112	0.0116
Yb	0.308	0.296	0.301	0.297	0.296	0.298	0.299	0.005	1.6	0.28	0.283	0.0198	0.0202	0.0202	0.0206	0.0223	0.0206	0.0010	4.8	0.0209	0.0194
Lu	0.048	0.045	0.047	0.046	0.047	0.047	0.047	0.001	2.0	0.045	0.046	0.0038	0.0042	0.0041	0.0038	0.0043	0.0040	0.0002	5.1	0.004	0.00352
Hf	0.20	0.14	0.14	0.14	0.13	0.14	0.15	0.03	17.4	0.1	0.122	0.104	0.118	0.118	0.101	0.119	0.112	0.009	7.8	0.127	0.113
Th		0.054	0.058	0.057	0.075	0.070	0.063	0.009	14.8	0.07	0.063	0.012	0.007	0.009	0.007	0.010	0.009	0.002	22.9	0.012	0.0122

Fig1

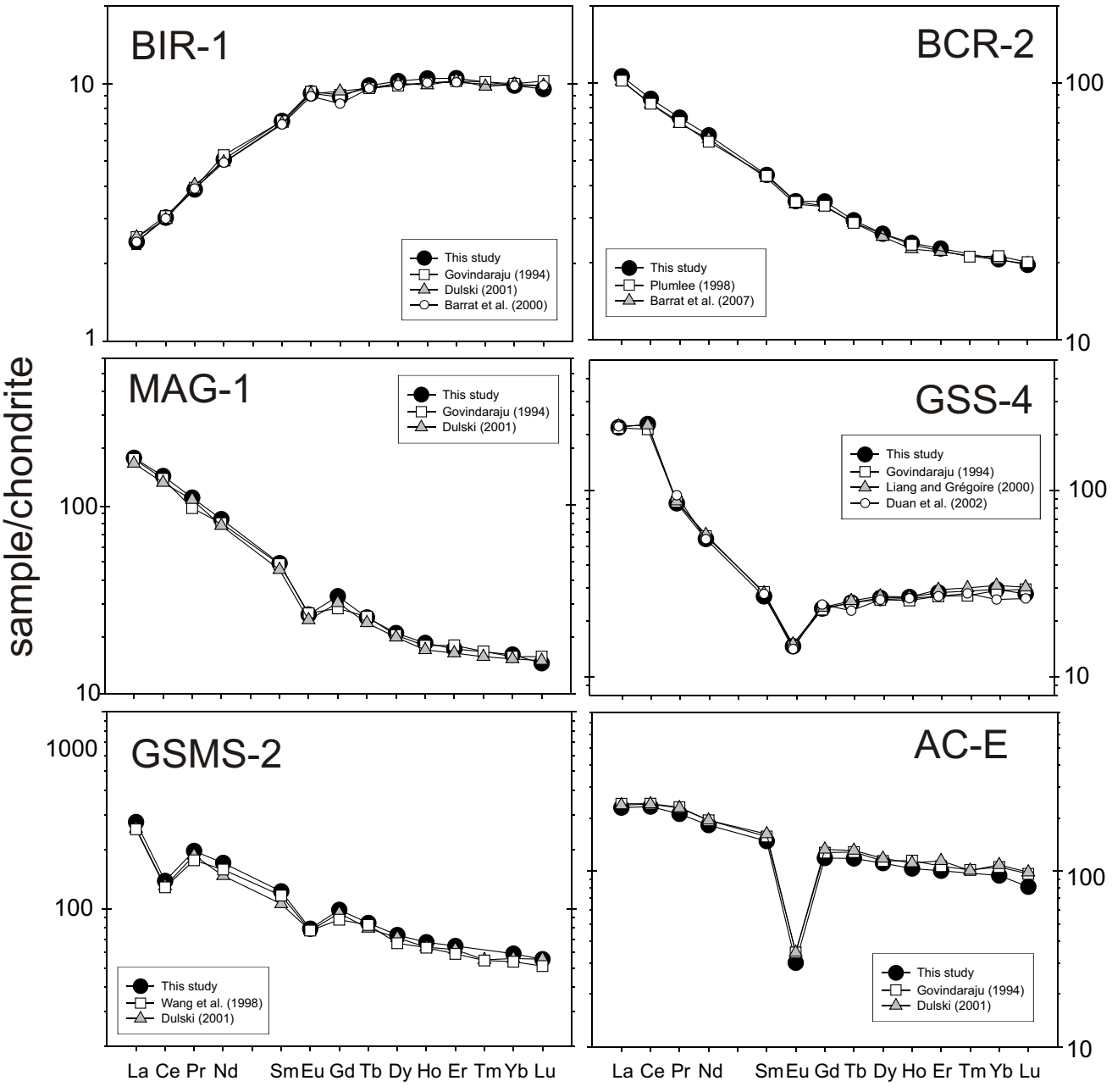
BIR-1
This study
Govindaraju (1994)
Dulski (2001)
Barrat et al. (2000)
BCR-2
This study
Plumlee (1998)
Barrat et al. (2007)
MAG-1
This study
Govindaraju (1994)
Dulski (2001)
GSS-4
This study
Govindaraju (1994)
Liang and Grégoire (2000)
Duan et al. (2002)
GSMS-2
This study
Wang et al. (1998)
Dulski (2001)
AC-E
This study
Govindaraju (1994)
Dulski (2001)
sample/chondrite
10
1
100
1000
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Fig1 - continued