Determination of the REE in Geological Reference Materials DTS-1 (Dunite) and PCC-1 (Peridotite) by Ultrasonic and Microconcentric Desolvating Nebulisation ICP-MS

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Inductively coupled plasma-mass spectrometry is well suited for the precise, accurate and rapid determination of rare earth elements in most geological samples. However, determination of rare earth elements in certain mantle-derived materials, without applying preconcentration techniques, remains problematical due to low natural concentrations (generally ‹ 1 ng g^{-1}). Consequently, USGS reference materials DTS-1 (a dunite) and PCC-1 (a partially serpentinized harzburgite) have only suggested rather than recommended values for the rare earth elements in reference material compilations. We compared results obtained using two ICP-MS instruments: a U-5000AT ultrasonic nebuliser coupled to a PQ2+ quadrupole ICP-MS and an ELEMENT sector field ICP-MS equipped with a MCN-6000 microconcentric desolvating nebuliser, with the suggested literature values for these two reference materials. Precision and accuracy of analytical methods employed by both instruments were demonstrated by excellent relative standard deviations (‹ ± 2%) and inter-laboratory agreement (‹ ± 5%) for numerous analyses of BHVO-1 and BIR-1, which are well established with rare earth elements contents at the µg g^{-1} level. Repeat analyses of DTS-1 and PCC-1 at each laboratory indicate that each method is generally precise to better than ± 5% at sub-µg g^{-1} levels. Furthermore, values from both instruments generally agree to within ± 10%. Our DTS-1 and PCC-1 values agree reasonably well with selected data reported in the literature (except for Ce and Sm in DTS-1) but exhibit poorer agreement with reported compilation values. With the demonstrated level of precision and accuracy, we contend that these new values for DTS-1 and PCC-1, generated by two different instruments, are the best estimates

La spectrométrie de masse couplée à une source à plasma induit est très bien adaptée à la détermination rapide, précise et exacte des Terres Rares dans la plupart des échantillons géologiques. Néanmoins, la détermination des Terres Rares sans techniques de préconcentration dans certains matériaux dérivés du manteau, reste problématique en raison des faibles abondances naturelles (en général inférieures à 1 ng g^{-1}). En conséquence, les matériaux de référence de l'USGS, DTS-1 (dunite) et PCC-1 (harzburgite partiellement serpentinisée) ont des valeurs suggérées plutôt que recommandées dans les compilations de teneurs en Terres Rares des matériaux de référence. Nous avons comparé les résultats d'une part obtenus avec deux ICP-MS différents: un ICP-MS à quadrupôle (modèle PQ2) couplé à un nébuliseur ultrasonique U-5000AT et un ICP-MS à secteur magnétique (ELEMENT) équipé d'un nébuliseur microconcentrique MCN-6000 avec système de désolvatation, et d'autre part provenant des données suggérées de la littérature pour ces matériaux de référence. La justesse et la précision des méthodes employées avec les deux instruments sont mises en évidence par les faibles déviations standards relatives (‹ ± 2%) et par les bons accords inter-laboratoire (‹ ± 5%) sur de nombreuses analyses de BHVO-1 et BIR-1, dont les teneurs en Terres Rares sont bien établies au niveau du µg g^{-1}. Les analyses répétées de DTS-1 et PCC-1 dans chaque laboratoire montrent que chaque méthode est en général précise à plus de ± 5% pour des teneurs de l'ordre du µg g^{-1}. De plus, les valeurs provenant de ces deux instruments sont en accord à ± 10%. Nos valeurs de DTS-1 et PCC-1 sont en bon accord avec des données selectionnées provenant de la littérature, (sauf pour Ce et Sm dans DTS-1) mais montrent un moins bon accord avec les données

of the true whole-rock composition of these samples reported to date.

Keywords: rare earth elements, inductively coupled plasma-mass spectrometry, reference materials, DTS-1, PCC-1.

compilées. Avec cette démonstration du niveau de précision et justesse, nous estimons que ces nouvelles valeurs pour DTS-1 et PCC-1, acquises sur deux instruments différents, sont les meilleures estimations actuelles de la véritable teneur roche-totale de ces échantillons.

Mots-clés : Terres Rares, spectrométrie de masse couplée à une source à plasma induit, matériaux de référence, DTS-1, PCC-1.

The rare-earth elements (REE) comprise a coherent series of elements with a valence of 3+ with the exception of Ce (which can form 4+ species under oxidizing conditions) and Eu (which can form 2+ species under reducing conditions). The ionic radius of REE gradually decreases with increasing atomic number, a phenomenon known as the lanthanide contraction (*cf.* Burt 1989). This produces a unique chemical behaviour with the REE behaving as a coherent group, which in turn has proved to be extremely useful when applied to the Earth sciences (e.g. Lipin and McKay 1989). Furthermore, technological applications require accurate determination of the lanthanides in high-purity metals, semi-conductors and glasses, where they play an important role in influencing electrical, magnetic and optical properties (Kawabata *et al.* 1991). As a result, accurate determination of REE at low ng g⁻¹ levels or less is becoming increasingly important in many areas of basic and applied research and development.

Due to spectral simplicity, multi-element capability, wide dynamic range, high sample throughput and the low achievable detection limits, inductively coupled plasma-mass spectrometry (ICP-MS) has become the preferred technique for the analysis of all naturally occurring REE (Longerich *et al.* 1987, Lichte *et al.* 1987, Jenner *et al.* 1990, Jarvis *et al.* 1992, Fedorowich *et al.* 1993, Field and Sherrell 1998). However, determination of low level (ng g⁻¹) REE concentrations in certain rock types, without applying time consuming and error-inducing preconcentration techniques, is still a challenging goal. For example, REE concentrations (ng g⁻¹ level) in depleted Cretaceous spinel peridotites (collected from the Tinaquillo peridotite complex in north-central Venezuela) are at or below the detection limits of conventional ICP-MS methods (McMahon and Neal, unpublished data); REE concentrations in reference materials (RMs) DTS-1 and PCC-1 are in a similar range and are, therefore, appropriate reference materials for these rock types. At present, he REE values for DTS-1 and PCC-1 are only suggested (Govindaraju 1994) and there are discrepancies between the suggested and other available literature values. Consequently, additional REE data for DTS-1 and PCC-1 are needed for certification purposes. Here we report the results of new analyses for both DTS-1 and PCC-1, utilizing two different ICP-MS instruments, one equipped with a ultrasonic nebuliser (USN), the other with a microconcentric nebuliser (MCN).

Material and methods

Samples

DTS-1: This RM was described by Flanagan (1967) as a dunite collected from the Twin Sisters area of Hamilton, Washington. The rock is primarily composed of olivine (99%) with orthopyroxene, clinopyroxene, disseminated chromite and a trace of amphibole comprising the remainder. Serpentine occurs as an alteration product of olivine.

PCC-1: This RM was described by Flanagan (1967) as a "peridotite" collected as stream boulders from the Cazadero ultramafic massif, Sonoma County, California. Petrology reveals that the sample is composed of fresh olivine (58%), orthopyroxene (9%) and mesh-structured serpentine (32%) that is an alteration product of the primary phases. Minor phases include primary disseminated chromite, secondary magnetite, and traces of secondary talc and carbonate. It is likely that the primary rock type was a harzburgite.

Sample digestion

All digestions were conducted at the University of Notre Dame and splits of the final solutions were sent to Rutgers University, thus allowing the results to be directly comparable and not subject to errors from different dissolution procedures. In this experimental design, therefore, differences between data sets from the two laboratories will reflect instrumental bias

arising from spectrum interference effects, for example. To ensure that the reliability of the sample preparation procedure was adequately assessed, sample preparation was undertaken on replicate test portions. Three separate digestions of PCC-1 and six digestions of DTS-1 were performed (two splits of DTS-1 were obtained and three test portions from each were individually digested). Approximately 50 mg of sample powder were digested in a screw-capped Teflon™ PFA bomb (Savillex®) at 100 °C using 2 ml of concentrated (12 mol l^{-1}) HNO_3 and 1 ml of 60% v/v HF. The relatively high HNO_3/HF ratio was used in order to dissolve the small chromite grains present in the RMs. All acids were purchased at the reagent grade and then double distilled in-house using sub-boiling distillation units. Blanks were below 50 pg g^{-1} for all the REE.

PCC-1 and DTS-1 contain low abundances of the REE (cf. Govindaraju 1994). The finely disseminated chromite present in both RMs (at < 1 modal %) is renowned for being difficult to dissolve. While complete dissolution of each sample aliquot is essential for accurate and precise determination of the whole-rock REE abundances in PCC-1 and DTS-1, the REE are highly incompatible in chromite ($D_{REE} \ll 1$, e.g. Green 1994). This, coupled with the low modal abundance, indicates that chromite is not the primary REE carrier in the RMs.

Fusion of the RMs using a flux (e.g. lithium metaborate) was not used because it would have resulted in a level of total dissolved solids too high for analysis of the samples using quadrupole ICP-MS (see below). Furthermore, fusion does not guarantee chromite dissolution (see Sulcek and Povondra 1989, and references therein). For chromite ores, phosphoric acid can be used either exclusively or mixed with sulfuric or perchloric acids (Sulcek and Povondra 1989). It is our experience, after repeated experiments, that if chromite is present as a trace mineral, as it is in PPC-1 and DTS-1, excess nitric acid with HF at ~175 °C and atmospheric pressure is sufficient to dissolve it and the silicate minerals.

The HF/HNO_3 mixture was then evaporated to dryness and the residue taken into solution in 2 ml of concentrated HNO_3. The solution was dried and redissolved a second time in 2 ml of concentrated HNO_3 and dried again. The two nitric acid treatments were performed to ensure conversion of fluorides to nitrates. Finally, the residue was taken up in 2 ml of concentrated HNO_3, transferred to a 125 ml bottle and diluted with water to 100 ml to give a final stock solution

having total dissolved solids (TDS) of 0.05% m/v. This stock solution was further diluted when aliquots were placed in test tubes for analysis. The entire procedure was carried out in clean laboratory (class 1000) conditions. After the dissolution procedure was complete, no black specks were observed in the final solution, which was clear and free of particulates. Therefore, it is unlikely that any material remained undissolved.

Instrumentation and experimental procedures

A quadrupole inductively coupled plasma-mass spectrometer (a "PlasmaQuad" PQ2+ STE, VG Instruments, Beverly, MA, USA) was used for the data acquisition at the University of Notre Dame (see Table 1 for operating parameters). In standard nebulisation mode (sensitivity 20,000 cps/ng g^{-1} at In), the analyte counts for REE in DTS-1 and PCC-1 were comparable to the background levels and the barium oxide interferences on Eu were significant enough (> 30%) to render results inaccurate. To achieve a desired instrument sensitivity (> 500,000 cps/ng g^{-1} In) and to reduce relative oxide interferences to insignificant levels (counts at the BaO mass were ~ 0.005% of those at Ba), the PQ2+ quadrupole ICP-MS was interfaced with a U-5000AT Ultrasonic Nebuliser (CETAC, Omaha, NB) [hereafter, this quadrupole ICP-MS technique will be referred to as USN-QP-ICP-MS]. In addition, a 2 mm spacer was placed behind the skimmer cone. The effects of the USN and this spacer on sensitivity are shown in Figure 1. Oxide interferences were reduced to a level where corrections were found to be unnecessary; full details of the operating conditions are presented by Ely et al. (1999). Samples were introduced using a peristaltic pump (Gilson, Middleton, WI, USA) in conjunction with an autosampler (Gilson, Sample Changer Model 221-222). The wash cycle between each analysis contained three sequential 90 second washes containing 5% v/v HNO_3 with trace HF, 5% v/v HNO_3, and 2% v/v HNO_3, respectively. This protocol has been proved to be effective in removing any memory effects (McGinnis et al. 1997). The analysis was performed using an external calibration procedure and internal standards (In and Re) were used to correct for drift and matrix effects. The signal to background ratios for analytes were greatly improved, yielding detection limits (calculated as three times the standard deviation of background) ranging from 20 to 30 fg g^{-1} for all REEs. Background counts were measured on HNO_3 acid blanks using the same parameters as for the samples.

Table 1.
Instrument operating conditions

USN-QP-ICP-MS

Plasma RF power	1349 W
Reflected power	‹ 3 W
Outer (cooling) gas flow	15.5 l min^{-1}
Intermediate (auxiliary) gas flow	2.4 l min^{-1}
Aerosol (nebuliser) gas flow	0.976 l min^{-1}
Detector type	Channeltron
Acquisition mode	Peak jumping
Sample uptake rate	1.0 ml min^{-1}
USN temperature	140 °C
USN chiller temperature	-5 °C
Isotopes quantified	^{115}In, ^{147}Sm, ^{165}Ho, ^{137}Ba, ^{151}Eu, ^{167}Er, ^{139}La, ^{159}Tb, ^{169}Tm, ^{140}Ce, ^{157}Gd, ^{173}Yb, ^{141}Pr, ^{163}Dy, ^{175}Lu, ^{145}Nd, ^{185}Re

MCN-SF-ICP-MS

Tune parameters
ELEMENT:

Outer (cooling) gas flow	14 l min^{-1}
Intermediate (auxiliary) gas flow	1.0 l min^{-1}
Aerosol (Nebuliser) gas flow	0.93 l min^{-1}

MCN-6000:

Sweep gas flow	4.3 l min^{-1}
Sweep gas temperature	175 °C
Spray chamber temperature	75 °C
Nitrogen flow	0.014 l min^{-1}
Sample uptake rate	70 µl min^{-1}

Acquisition parameters

Mass window	5%
Samples/Peak	400
Sample time	2 ms
Segment time†	40 ms
Detection mode	Counting
Resolution	Low
Magnet settling time	100 ms
Magnet mass#	137

Evaluation parameters

Search window	100%
Integration window	100%
Integration type	Average
Runs	3
Passes	50
Magnet settling time	50 ms
Magnet mass#	158

Isotopes quantified

^{137}Ba*	^{151}Eu	^{165}Ho
^{139}La	^{153}Eu	^{166}Er
^{140}Ce	^{155}Gd	^{167}Er
^{141}Pr	^{157}Gd	^{169}Tm
^{143}Nd	^{158}Gd	^{171}Yb
^{145}Nd	^{160}Gd	^{172}Yb
^{146}Nd	^{159}Tb	^{173}Yb
^{147}Sm	^{163}Dy	^{175}Lu
^{149}Sm		

*   measured in analogue mode.

†   segment time is the total time spent on a peak per scan.

\#   magnet mass is the mass at which the magnet is set to electrostatically scan (E-scan) a number of isotopes. The mass ranges from 137-157 and 158-175 were E-scanned, with the magnet set at 137 and 158, respectively.
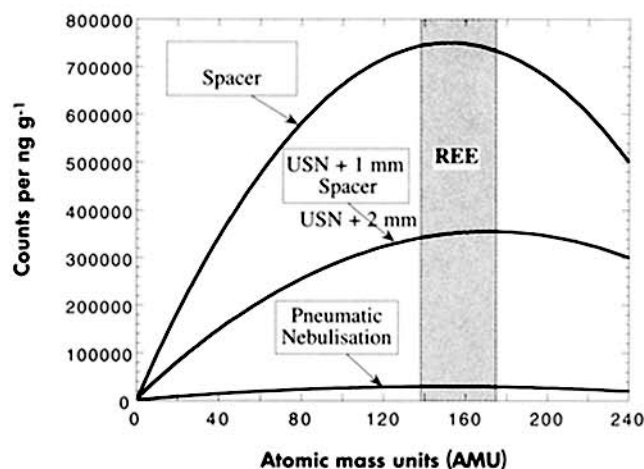

Figure 1. Sensitivity enhancement of the QP-ICP-MS using a combination of the ultrasonic nebuliser and a 2 mm spacer behind the skimmer cone. Note that the best sensitivity was achieved when both enhancements were used together.

Analyses at Rutgers University utilized the ELEMENT (Finnigan MAT, Bremen, Germany) sector field high-resolution inductively coupled plasma mass spectrometer, in conjunction with an MCN-6000 microconcentric desolvating nebuliser (CETAC, Omaha, NB) [hereafter referred to as MCN-SF-ICP-MS]. See Table 1 for operating parameters. Although the instrument has a high-resolution capability (nominal 3000 and 7500 M/ΔM), it was operated in low resolution mode (300 M/ΔM) for optimal sensitivity. The sensitivity of the ELEMENT without the MCN-6000 is ~ 200,000 cps/ng g^{-1}, which increases to ≥ 10^6 cps/ng g^{-1} when the MCN-6000 is used. Desolvation using the MCN-6000 provides a one hundred fold reduction in oxides (~ 0.0004% BaO relative to the Ba mass intensity) and a ten fold increase in sensitivity (10^6 cps/ng g^{-1} In). Full experimental details can be found in Field and Sherrell (1998). A modified isotope dilution method was used for the determination of all fourteen stable REE, providing detection limits between 2 and 40 fg g^{-1} and requiring no corrections for sensitivity drift or oxide interferences (Field and Sherrell 1998). A one minute wash using 5% v/v HNO$_3$ was employed between samples. This much shorter wash time and lower acid concentration relative to USN-QP-ICP-MS is due to the reduced surface area that the sample sees in the MCN compared to the USN and also the lower sample uptake rate (Table 1).

Results and discussion

Digestions were performed of three test portions taken from each of two splits of DTS-1 and three test

Table 2.
Average REE abundance data and standard deviations (1s) for reference materials DTS-1 and PCC-1

	DTS-1				PCC-1			
	USN-QP-ICP-MS n = 12		MCN-SF-ICP-MS n = 30		USN-QP-ICP-MS n = 6		MCN-SF-ICP-MS n = 12	
	Abundance	1s	Abundance	1s	Abundance	1s	Abundance	1s
La	25	2	25	2	33	1	29	2
Ce	55	3	51	2	60	1	56	2
Pr	6.2	0.5	6.1	0.2	7.6	0.1	7.2	0.3
Nd	24	3	23	1	26	0.7	28	2
Sm	4.5	0.3	4.2	0.2	4.9	0.4	5.1	0.1
Eu	1.1	0.4	0.7	0.1	0.9	0.1	1.00	0.03
Gd	4.4	0.8	3.8	0.2	5.3	0.5	5.93	0.07
Tb	0.7	0.2	0.65	0.02	1.0	0.1	1.12	0.01
Dy	4.2	0.5	4.8	0.2	8.5	0.5	9.41	0.03
Ho	1.1	0.2	1.21	0.02	2.3	0.1	2.69	0.01
Er	4.5	0.5	4.7	0.1	10.0	0.6	11.3	0.1
Tm	1.0	0.1	1.02	0.02	2.0	0.1	2.44	0.02
Yb	8.5	1.1	9.1	0.1	20.0	0.7	22.1	0.1
Lu	1.9	0.2	1.99	0.02	4.5	0.5	4.65	0.03

Two splits of DTS-1 and one split of PCC-1 were used, with each split having three separate digestions conducted on them. Values are in ng g^{-1}.

portions of PCC-1 (a total of nine digestions). Averages and standard deviations (1s) are presented in Table 2 and Figure 2. Each digest was analysed five times by MCN-SF-ICP-MS and twice by USN-QP-ICP-MS. Precision for values determined using MCN-SF-ICP-MS was generally better than 10% and 6% for all REE in DTS-1 and PCC-1, respectively. With the exception of Eu (36%), Gd (18%), Tb (29%) and Ho (18%), precision for REE values determined for DTS-1 and PCC-1 using USN-QP-ICP-MS, was generally better than 12%.

The better precision evident using MCN-SF-ICP-MS is a result of lower background intensities, greater stability and slightly better sensitivity. For USN-QP-ICP-MS, fewer replicates were possible because a gradual decrease in analyte signal was observed over time due to the gradual clogging of the sample cone, even though the stock solutions (see above) were diluted for analysis to < 0.02% TDS (two to four times more dilute than for MCN-SF-ICP-MS). This results in reduced counts, hence the generally lower precision in the USN-QP-ICP-MS method relative to MCN-SF-ICP-MS. However, at the low REE concentrations in DTS-1 and PCC-1 (below most previous detection limits), the precision exhibited by both methods for different digests is generally excellent.

If we compare the average data obtained by MCN-SF-ICP-MS and USN-QP-ICP-MS there is generally good agreement (Table 2 and Figure 2). Europium abundance in DTS-1 is substantially higher using the
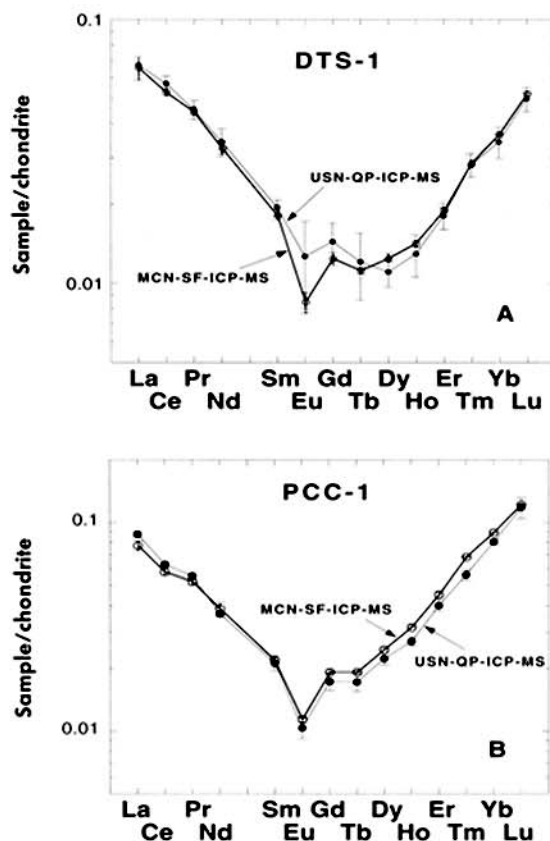

Figure 2. Chondrite-normalized REE profiles for reference materials DTS-1 (A) and PCC-1 (B) produced by USN-QP-ICP-MS at the University of Notre Dame (filled circles) and MCN-SF-ICP-MS at Rutgers University (open circles). One standard deviation error bars are also shown for each data point. Chondrite data are from Sun and McDonough (1989).

Table 3.
Comparison of REE data (this work) for reference materials
DTS-1 and PCC-1 with literature values. Values are in ng g⁻¹

	DTS-1				PCC-1					
	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)	(5)	(6)
La	25	25	24.6	29	33	29	29	52	150	-
Ce	55	51	100	72	60	56	53	100	80	-
Pr	6.2	6.1	6.3	6.3	7.6	7.2	6.8	13	-	-
Nd	24	23	23.4	29	26	28	25	42	51	-
Sm	4.5	4.2	3.1	4.6	4.9	5.1	5	6.6	7	9.6
										106
Eu	1.1	0.7	1.3	1.2	0.9	1.00	1.1	1.8	2	-
Gd	4.4	3.8	4.4	3.8	5.3	5.93	6.1	14	14	6
										54
Tb	0.7	0.65	0.7	0.8	1.0	1.12	1.2	0.8	-	-
Dy	4.2	4.8	3.8	3	8.5	9.41	8.7	10	10	-
Ho	1.1	1.21	1.4	1.3	2.3	2.69	2.7	2.5	-	-
Er	4.5	4.7	5	4	10.0	11.3	11.3	12	12	-
Tm	1.0	1.02	-	1.4	2.0	2.44	-	2.7	-	-
Yb	8.5	9.1	9	10	20.0	22.1	21.3	24	25	-
Lu	1.9	1.99	1.9	2.4	4.5	4.65	4.6	5.7	-	-

(1) USN-QP-ICP-MS, (2) MCN-SF-ICP-MS, (3) Eggins *et al.* (1997) [ICP-MS], (4) Govindaraju (1994) suggested values, (5) Hooker *et al.* (1975) [Isotope Dilution, TIMS], (6) Sands and Rosman (1997) [Isotope Dilution, TIMS].

USN-QP-ICP-MS technique (Table 2) but within error of the MCN-SF-ICP-MS datum (Figure 2). The polyatomic interference of BaO on Eu could be a possible cause for systematic bias towards higher values using USN-QP-ICP-MS (Xie *et al.* 1994). However, the suggested values for Ba in DTS-1 and PCC-1 are low (1.7 and 1.2 μg g⁻¹, respectively; Govindaraju 1994). The ten fold reduction in oxides by USN is sufficient to remove any BaO interferences as large discrepancies between values produced by the two ICP-MS techniques are not observed for Sm and Gd, which also suffer from BaO interferences. Memory effects can also be discounted, as the wash protocol used has been proved to be effective in removing any memory from the previous sample (McGinnis *et al.* 1997). In addition, PCC-1 has a similar Eu abundance to DTS-1 (Table 2) and values for this RM determined by both laboratories are in good agreement. As the same solutions were analysed in both laboratories, discrepancies in Eu and Gd concentrations in DTS-1 are probably statistical in nature, but the exact nature is enigmatic.

When the literature values are compared with our new REE data for these RMs, the suggested values (Govindaraju 1994) are not comparable generally nor do they form smooth chondrite-normalized REE profiles (Table 3 and Figure 3). In addition, data from Hooker *et al.* (1975) and Sands and Rosman (1997) for PCC-1 were collected using thermal ionisation mass spectrometry in conjunction with isotope dilution. While the
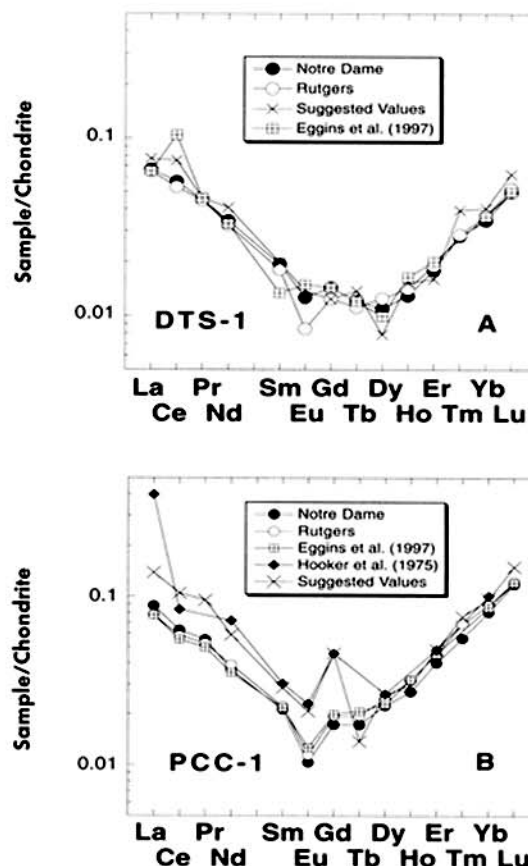

Figure 3. Comparison between the new REE data and literature values for reference materials DTS-1 (A) and PCC-1 (B) using chondrite-normalized REE profiles. Chondrite data are from Sun and McDonough (1989).

Table 4.
Average REE values calculated from this study and Eggins *et al.* (1997) for reference materials DTS-1 and PCC-1 with corresponding standard deviations (1*s*). See text for discussion. Values are in ng g^{-1}

	DTS-1	1*s*	PCC-1	1*s*
La	24.8	0.3	30.4	2.2
Ce	52.8	2.6	56.3	3.7
Pr	6.2	0.1	7.2	0.4
Nd	23.6	0.7	26.2	1.4
Sm	3.9	0.2	5.0	0.1
Eu	1.0	0.3	1.0	0.1
Gd	4.2	0.3	5.8	0.4
Tb	0.7	0.03	1.1	0.1
Dy	4.3	0.5	8.9	0.5
Ho	1.2	0.2	2.6	0.2
Er	4.7	0.3	10.9	0.7
Tm	1.0	0.01	2.2	0.3
Yb	8.9	0.3	21.1	1.1
Lu	1.9	0.05	4.6	0.1

Figure 4. Chondrite-normalized REE profiles using the average REE values calculated from this study and Eggins *et al.* (1997) for reference materials DTS-1 and PCC-1 (see text for discussion). Chondrite data are from Sun and McDonough (1989).

heavy REE data reported by Hooker *et al.* (1975) compare well with the values reported here, the abundances of the middle and light REE are much higher. Sands and Rosman (1997) reported two values for the abundance of Sm and Gd, with the lower value being comparable to our data (Table 3). The two analyses reported exhibit widely varying values. Data for DTS-1 and PCC-1 reported by Eggins *et al.* (1997) generally compare well with our new data (Table 3 and Figure 3). Therefore, we compare (Table 4) the average REE values for DTS-1 and PCC-1 reported here with those of Eggins *et al.* (1997), except for Tm, Ce and Sm in DTS-1. These latter elements are omitted because Tm was not reported by Eggins *et al.* (1997) and Ce and Sm exhibit significant positive and negative anomalies, respectively, in chondrite-normalized profiles (Figure 3a). The data reported by Eggins *et al.* (1997) for Eu and Gd are similar to those produced by the USN-QP-ICP-MS method (Table 3 and Figure 3). As the latter data have large errors associated with them that overlap the lower values produced by MCN-SF-ICP-MS, all data are used to calculate averages for DTS-1. Unlike the previously suggested values (Govindaraju 1994), these recommended REE values form smooth and coherent chondrite-normalized profiles (Figure 4).

Conclusions

It is evident from the data presented here that the REE data produced for DTS-1 and PCC-1 using two ICP-MS analytical techniques from two different laboratories are in close agreement and form smooth,
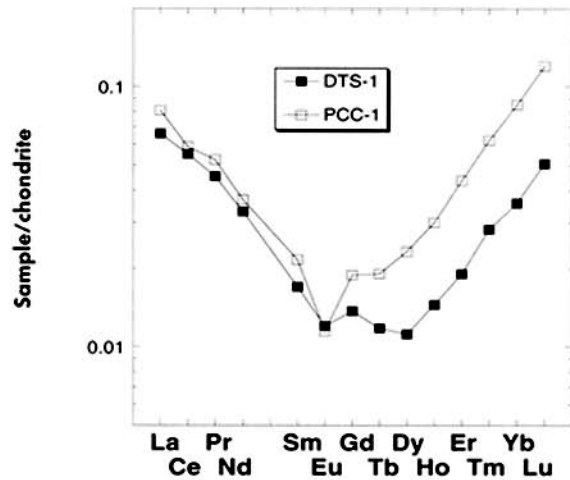
coherent chondrite-normalized REE profiles. They are generally comparable to values reported by Eggins *et al.* (1997) except for Ce and Sm in DTS-1; chondrite-normalized REE profiles reported here do not exhibit the positive Ce nor the negative Sm anomaly exhibited by the Eggins *et al.* (1997) data. Therefore, except for Ce and Sm in DTS-1 and Tm in both (not reported), we suggest that our new data be combined with those of Eggins *et al.* (1997) to derive new recommended whole-rock REE values for DTS-1 and PCC-1.

Acknowledgements

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