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Further Characterisation of the 91500 Zircon Crystal

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This paper reports the results from a second characterisation of the 91500 zircon, including data from electron probe microanalysis, laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS), secondary ion mass spectrometry (SIMS) and laser fluorination analyses. The focus of this initiative was to establish the suitability of this large single zircon crystal for calibrating *in situ* analyses of the rare earth elements and oxygen isotopes, as well as to provide working values for key geochemical systems. In addition to extensive testing of the chemical and structural homogeneity of this sample, the occurrence of banding in 91500 Cet article présente les résultats d'une nouvelle caractérisation du zircon 91500, dont des données de microanalyse par sonde électronique, d'analyse par ablation laser en couplage à un ICP-MS, d'analyse par sonde ionique (SIMS) et d'analyse par fluorination laser. Le but de cette étude était de démontrer que ce large monocristal de zircon pouvait être utilisé pour la calibration d'analyses in situ de Terres Rares et des isotopes de l'Oxygène, et en même temps de fournir des valeurs "de travail" pour un certain nombre de systèmes géochimiques cruciaux. En complément des tests systématiques d'homogénéité de l'échantillon, tant chimiquement



in both backscattered electron and cathodoluminescence images is described in detail. Blind intercomparison data reported by both LA-ICP-MS and SIMS laboratories indicate that only small systematic differences exist between the data sets provided by these two techniques. Furthermore, the use of NIST SRM 610 glass as the calibrant for SIMS analyses was found to introduce little or no systematic error into the results for zircon. Based on both laser fluorination and SIMS data, zircon 91500 seems to be very well suited for calibrating *in situ* oxygen isotopic analyses.

Keywords: zircon 91500, reference material, technique intercomparison, working values.

que structurellement, l'existence, dans le zircon 91500, de zonages visibles en électrons rétro diffusés et en cathodoluminescence, est décrite en détail. Une comparaison en aveugle des résultats obtenus par LA-ICP-MS et par SIMS, dans des laboratoires différents, montre que les différences systématiques entre les ensembles de données obtenues par ces deux techniques sont très faibles. De plus, l'utilisation du verre NIST SRM 610 comme calibrant lors de l'analyse par SIMS n'introduit qu'une erreur systématique très faible si ce n'est inexistante sur les résultats du zircon. Sur la base des analyses par fluorination laser et par SIMS, le zircon 91500 semble être parfaitement adapté à son utilisation pour la calibration d'analyses isotopiques in situ d'oxygène.

Mots-clés : zircon 91500, matériau de référence, intercomparaison entre techniques, valeurs de travail.

The 91500 zircon specimen originally consisted of a single crystal which entered the mineralogical collection of Harvard University in 1931 as part of a specimen exchange with the Royal Ontario Museum (Canada). The original collection site of the sample is recorded as Kuehl Lake in Ontario, Canada. The U-Pb systematics of this sample have been described in detail by Wiedenbeck *et al.* (1995) who published the following description of this crystal:

"This sample consists of one crystal with an original mass of 238 g which was provided by the Harvard Mineralogical Museum in Cambridge, USA. This grain has a single, well developed pyramidal termination, on the other end it is broken with many protruding fragments. The interior of the grain contains many fractures which tend to be roughly parallel and which are spaced at 1 to 5 mm. No staining or inclusions are visible on the fracture faces. The crystal's faces are flat with well defined edges, implying that this sample was found in situ. Also present on the pyramidal terminations of this sample is a single vug of approximately 5 mm size (this portion has been returned to the Harvard Museum). This sample is dark red in colour and is clear and transparent with no visible inclusions under transmitted light".

This earlier characterisation reported a near concordant U-Pb age of 1065 Ma for this crystal. The rock type from which this sample was collected is not known; however the locality is dominated by porphyroblastic syenite gneiss which is cross-cut by sheets or sills of syenite pegmatite (Wiedenbeck *et al.* 1995). Further information about the local and regional geology and metamorphic history of this locality have been published elsewhere (Hewitt 1953, Mezger *et al.* 1993, Cosca *et al.* 1995).

As part of this earlier study, the grain was cut into two portions, the smaller of which (85 g) along with additional large fragments (totalling 44 g) were returned to Harvard for storage. From the remaining portion a total of 128 splits with grain sizes 200 μ m < Φ < 2 mm were produced and these were subsequently made available to the broader geochemical community for calibrating *in situ* zircon isotopic studies. Wiedenbeck *et al.* (1995) also reported data on the REE abundances in 91500 using INAA, SIMS and isotope dilution TIMS. Unfortunately, the compiled data set failed to show acceptable consistency between the various analytical techniques.

The second characterisation

In order to overcome the lack of a widely available zircon reference sample for geochemical analyses, it was decided to conduct a second characterisation of this large and apparently homogeneous, inclusionpoor sample (see also scanning electron imaging section, below). This new round of analyses was based on a blind, interlaboratory comparison and targeted



Table	1.		
List of	institutions	that reported	data

EPMA	LA-ICP-MS	SIMS	Laser fluorination
Geol. Survey, Tsukuba	Geol. Survey, Trondheim	Geol. Survey, Tsukuba *	Geol. Survey, Orléans
GFZ-Potsdam	Memorial Univ., St. John's	GFZ-Potsdam	Geol. Survey, Tsukuba
Open University	Univ. Tasmania	Hiroshima University	Open University
Univ. Göttingen	Univ. Saskatchewan	NORDSIMS, Stockholm	Univ. Lausanne
Univ. Mainz	Univ. Utrecht	Univ. Edinburgh	Univ. Tübingen
Univ. Maryland			Univ. Wisconsin, Madiso USTC Heifei

The sequence of laboratories in this list does not correspond to the laboratory designations given in the data tables, as this study was designed so that the origin of data sets remained confidential. * REE, trace element and oxygen isotope data reported.

both the major elements (Si, Zr and Hf) as well as the REEs and other important trace elements. In addition to concentration determinations, an interlaboratory comparison of the oxygen isotopic composition of this sample was conducted. All data reported here are based on four random fragments (totalling 6 g of material) which were provided by the Harvard Museum. As such, the sample material used in this second study, though not part of the original 128 aliquots generated by the early work of Wiedenbeck et al. (1995), may be assumed to be representative of the original crystal as originally collected in 1930. Prior to distribution, these 6 g of material were crushed, thoroughly mixed and sieved to a size fraction of 200 μ m < Φ < 2 mm. The resulting fragments were cleaned ultrasonically in high purity acetone (two times, five minutes each), followed by high purity ethanol (two times, five minutes each), followed by double distilled water (two times, five minutes each). The sample was dried at 75 °C prior to generating the random splits which were distributed to participating laboratories in mid-2001.

Participation in this interlaboratory comparison/characterisation study was limited to four analytical techniques: EPMA, ICP-MS, SIMS and laser fluorination. A total of thirty-five institutions agreed to participate in this project, each of which was sent circa 100 mg in a plastic vial; many laboratories offered to provide data sets from multiple techniques. Each institute worked on independent sample material and no exchange of material between laboratories took place. Ultimately, data were reported only by the nineteen institutions listed in Table 1. At the time of sample distribution the participants also received instructions concerning data acquisition in order to make the results more directly comparable. When reporting their data the laboratories were also required to submit a brief description of their analytical procedure and an estimate of their external precision. Furthermore, it was requested that each laboratory that

conducted *in situ* analyses should, if possible, submit backscattered electron and cathodoluminescence images of the fragments that were analysed. Many of the laboratories conformed closely to these instructions, though in a number of cases the analytical method and data reporting diverged significantly from the given instructions, resulting in additional uncertainties when comparing data. All data reporting was done electronically.

Sample homogeneity testing

Light elements by SIMS

In addition to the blind interlaboratory comparison, we also conducted extensive homogeneity testing on random fragments from 91500. This work focused on light elements and employed the Cameca ims 6f ion microprobe at the GFZ Potsdam. Because no matrixmatched reference sample exists for the elements selected, it was not possible to determine the absolute concentrations by this approach. Nonetheless, these data provide constraints on the homogeneity of the sample and also suggest whether 91500 might prove a useful material to develop as a reference material for new geochemical systems. The sample used for this series of measurements consisted of four fragments of 91500. Prior to analysis, the polished sample mount was cleaned ultrasonically in high purity ethanol and was coated with 35 nm of high purity gold.

Li, Be and B: The $^{7}Li^{+}/^{30}Si^{+}$, $^{9}Be^{+}/^{30}Si^{+}$ and $^{11}B^{+}/^{30}Si^{+}$ ratios were determined for thirteen locations distributed quasi-randomly over three fragments of the 91500 zircon. Additionally, seven analyses on a single tablet of the NIST SRM 610 glass were conducted in order to assess the external reproducibility of the analytical procedure. These measurements employed a 20 nA, ^{16}O - primary beam which was focused to a ~ 25 μ m diameter spot. Each analysis area was subjected



Table 2.Results from SIMS light element homogenity testing

Fragment	⁷ Li+/ ³⁰ Si+	Li/Si 1s (%)	⁹ Be+/ ³⁰ Si ⁺	Be/Si 1s (%)	¹¹ B +/ ³⁰ Si +	B/Si 1 <i>s</i> (%)
91500-1	1.93E-03	2.8	3.01E-05	14.9	1.19E-04	6.0
91500-1	1.92E-03	3.9	3.17E-05	13.6	1.06E-04	7.8
91500-1	3.42E-03	2.3	3.65E-05	9.9	9.96E-05	4.6
91500-1	1.95E-03	3.3	5.47E-05	11.9	1.07E-04	6.5
91500-1	1.60E-03	6.0	4.00E-05	18.2	1.18E-04	10.1
91500-1	1.59E-03	3.3	2.85E-05	14.9	1.12E-04	6.7
91500-2	1.35E-03	3.2	3.58E-05	12.6	9.69E-05	6.5
91500-2	1.27E-03	4.7	4.46E-05	9.6	9.31E-05	7.1
91500-2	1.42E-03	4.2	4.12E-05	9.4	9.64E-05	8.4
91500-2	1.32E-03	4.0	6.38E-05	16.3	9.14E-05	6.5
91500-2	1.41F-03	3.2	4.62F-0.5	6.9	9.59E-0.5	70
91500-3	2.24E-03	3.1	4.46E-05	9.4	1.03E-04	7.6
91500-3	2.29F-03	3.5	3.76E-0.5	11.0	1.12F-04	74
91500-3	2.06F-03	2.8	4 10F-05	9.5	121E-04	79
mean (n = 13)	1.72F-03	3.7	4.15E-0.5	12.2	1.05F-04	73
ls obs	3.617E-04	-	9.831F-06	-	1.034F-05	-
ls ext	21.0%	_	23.7%	-	9.8%	_
	21.070		20.770		7.676	
NIST SRM 610	2.27E-01	0.43	1.15E-01	0.32	3.12E-02	0.30
NIST SRM 610	2.28E-01	0.47	1.14E-01	0.46	3.12E-02	0.22
NIST SRM 610	2.32E-01	0.27	1.12E-01	0.50	3.07E-02	0.22
NIST SRM 610	2.32E-01	0.25	1.12E-01	0.41	3.08E-02	0.20
NIST SRM 610	2.17E-01	0.86	1.12E-01	0.31	3.10E-02	0.51
NIST SRM 610	2.26E-01	0.32	1.12E-01	0.50	3.06E-02	0.27
mean (n = 6)	2.27E-01	0.43	1.13E-01	0.42	3.09E-02	0.29
1s obs	5.490E-03	-	1.359E-03	-	2.656E-04	-
ls ext	2.4%	-	1.2%	-	0.9%	-
Fragment	¹⁹ F-/ ²⁸ Si-	F/Si 1s (%)	³⁵ Cl-/28Si-	Cl/Si 1s (%)		
91500-3	8.41E-04	0.6	5.94E-05	0.9		
91500-3	7.75E-04	0.8	4.24E-05	2.2		
91500-3	7.02E-04	0.6	3.00E-05	1.7		
91500-3	6.87E-04	0.6	2.75E-05	1.8		
91500-3	6.45E-04	0.7	2.43E-05	1.7		
91500-4	6.23E-04	0.7	2.25E-05	2.3		
91500-4	6.15E-04	0.5	2.27E-05	2.1		
91500-4	6.17E-04	0.8	2.71E-05	2.0		
91500-4	5.49E-04	0.7	2.30E-05	2.1		
91500-4	9.32E-04	1.7	-	-		
91500-2	5.82E-04	0.7	2.40E-05	1.7		
91500-2	6.59E-04	2.9	2.67E-05	2.3		
91500-2	1.95F-03	40	3.80F-0.5	3.9		
91500-2	1.47E-03	0.9	3.70E-05	2.0		
91500-2	1.26E-03	0.6	3.70E-05	2.1		
mean $(n = 15)$	8.60F-04	11	3.15E-0.5	2.1		
ls obs	3.98E-04	-	1.04E-05	-		
ls ext	46.2%	-	32.9%	-		
NIST SRM 610	2.25E-02	1.7	6.44E-03	1.0		
NIST SRM 610	1.95E-02	1.5	5.02E-03	1.4		
NIST SRM 610	3.42E-02	1.0	7.18E-03	1.4		
NIST SRM 610	4.15E-02	2.0	5.54E-03	1.8		
NIST SRM 610	3.75E-02	2.2	5.82E-03	1.7		
NIST SRM 610	4.84E-02	1.8	5.34E-03	1.5		
mean (n = 6)	3.39E-02	1.7	5.89E-03	1.5		
1s obs	1.11E-02	-	7.95E-04	-		
ls ext	32.8%	-	13.5%	-		

to a three minute unrastered preburn prior to initiating data collection. The mass spectrometer was operated at a mass resolving power of $M/\Delta M \approx 1360$. A single cycle of the peak stepping sequence consisted of: 6.6 bkg (background 0.1 seconds integration), ⁷Li (2 s), ⁹Be (8 s), ¹¹B (8 s) and ³⁰Si (2 s). A single analysis, including both the preburn and the forty cycles of the peak stepping sequence, required 20 minutes.

The measurements on the zircon fragments gave relatively poor external reproducibilities of 21%, 24% and 10% for Li, Be and B, respectively (Table 2). In the cases of Li and Be these precision values are significantly worse than those found for NIST SRM 610, suggesting that genuine variability for these elements is present in 91500. The measured ratios suggest that a genuine systematic difference may exist between the individual zircon fragments for Li. In the case of B the difference between the mean internal precision (1s =7.3%) and the overall observed external precision (1s = 9.8%) is not large enough to assert that genuine boron heterogeneity does exist in 91500. However, the reported data pattern (Table 2) indicated that fragment 2 had on average a ~ 15% systematically lower B concentration as compared to fragments 1 and 3, so we can conclude that the boron content also shows real variations.

F and Cl: The 19F728Si and 35Cl728Si ratios were measured at five quasi-random locations on each of three fragments of the 91500 crystal. Additionally, six locations were measured on a single tablet of NIST SRM 610 glass in order to assess whether the external scatter between the measurements on the zircon was substantially larger than that of a presumed homogeneous sample. These measurements employed an 8 nA, mass filtered ¹³³Cs⁺ primary beam that was focused to a \sim 15 μ m diameter beam. In order to suppress any possible surface contamination of the halogens, the beam was rastered over a 50 x 50 μ m area for 10 minutes prior to beginning data acquisition. Despite such pre-rastering, surface contamination remained a problem for these measurements; tests showed that conducting the actual measurements employing a rastered beam was beneficial. Hence, data collection employed a 50 x 50 μ m raster in conjunction with a 400 μ m diameter field stop, equivalent to a 30 μ m field of view. The mass spectrometer was operated at an elevated mass resolving power of $M/\Delta M \approx 2550$ and electron flooding was used for charge compensation. A single cycle of the peak stepping sequence included 18.8 bkg (0.1 s), ¹⁹F (8 s), ²⁸Si (2 s) and ³⁵Cl



(15 s). A single analysis, including both the preburn and the forty cycles of the peak stepping sequence, required 28 minutes.

The resulting data (Table 2) show a large scatter in the observed ratios with the fifteen measurements yielding 1s external precisions of 46% and 33% for fluorine and chlorine, respectively. Despite the relatively low concentrations of both of these elements in 91500, this level of scatter seems to suggest that real variation in the concentrations of these two elements might be present. The data failed to show any systematic differences between the individual fragments, but rather showed as much variation within fragments as between them. The six measurements on NIST SRM 610 also showed a high degree of scatter between analyses, but this was somewhat less than that seen for the zircon sample. This poor external reproducibility for the sample and NIST SRM 610 may be, in part, related to the use of a rastered primary beam during the analysis, which was meant to suppress the background contamination. Further work using an approach which provides better external reproducibility will be necessary in order to demonstrate conclusively whether or not these elements are heterogeneously distributed in the 91500 crystal.

Scanning electron imaging

The homogeneity of zircon 91500 was further assessed by a systematic study conducted using cathodoluminescence (CL) and backscattered electron (BSE) imaging at Göttingen and Mainz Universities. Images from twelve random chips of 91500 were obtained in both modes using a JEOL 8900 electron microprobe. The CL total signal intensity was found to vary between the chips; many chips revealed comparably little internal zoning which could only be observed after fine-tuning signal intensity and brightness. Such fragments that were either unzoned or weakly zoned in CL generally appeared homogeneous in BSE. In contrast, three of the twelve chips showed strong, localised banding, which could readily be detected by both CL and BSE detectors. The most dramatic example was found along the right-hand margin of grain 10 (Figure 1) where a dark CL emission zone correlates with a light zone in BSE. Lighter CL banding elsewhere in the same fragment was not detected by BSE imaging. With the exception of one image that indicated the presence of an apparent inclusion, all variations found by both CL and BSE were consistent with primary zoning; no patchiness suggestive of post-crystallisation alteration was found.





Figure 1. Images obtained from Göttingen chip number 10. (A) CL image of entire fragment showing location of CL dark band on the right. In order to make the weak CL band visible, the epoxy, which would normally be dark in CL, has been inverted to white. (B) BSE image of the same fragment also with the epoxy inverted to white. (C) Higher magnification image of the strongly zoned right-hand margin of this same fragment showing the locations of EPMA (light spots surrounded by solid circles) and SIMS analyses (larger dotted circles depicting approximate crater size). Here the adjacent epoxy has not been inverted to a white colour. See Table 3 for data.

This most extreme image of heterogeneity was used to target a series of EPMA (measured in Göttingen), SIMS (Potsdam) and laser-Raman microprobe (Mainz, see below) analyses in order to establish the degree of variation that could be attributed to this sample. The location of these analyses are shown in Figure 1C and the corresponding chemical data are given in Table 3. The EPMA results indicated that the CL dark band possesses a significant enrichment in U above the bulk U content of the fragment. This observation was confirmed by the SIMS data which showed a factor of \sim 3 higher U content in the CL dark zones as compared to the volumetrically dominant middle of the fragment. SIMS data also indicated a higher U concentration for the CL bright zone relative to the bulk of the crystal. Yttrium and the REEs concentrations also seemed to differ between the CL dark zone and the bulk of the crystal (Table 3). Hence, it would seem that such atypical domains should be avoided and that monitoring the U concentration when analysing 91500 will provide an indication of whether such a domain has inadvertently been encountered. Although this imaging study does not provide any quantitative information about the fraction of this sample which could be assigned to such extreme banding, the Göttingen and Mainz images along with other images acquired as part of this study suggest that such banding represents a modest volume fraction of the crystal as a whole. Finally, it should be noted that some of the domains that appeared to give homogeneous CL and BSE intensities may, in fact, represent regions where the polished sample surface is nearly parallel to the zoning in the crystal. Techniques that penetrate deeply into the sample in the course of an analysis (e.g., LA-ICP-MS) might traverse such bands during a single analysis.

Raman analyses

The Jobin Yvon LabRam HR 800 system at the University of Mainz was used to estimate quantitatively the structural state of the unzoned to weakly zoned domains and the areas that show clear banding in CL. Confocal measurements were done using the 632.816 nm emission of a He-Ne laser (3 mW at the sample). For experimental details and data reduction procedures see Nasdala *et al.* (2001, 2002).

GEO DARDS and GEOANALYTICAL RESEARCH

Table 3. EPMA and SIMS results from Göttingen grain 10

			E	PMA date	* r				
Analysis number/location	ZrO ₂	SiO ₂	HfO ₂	P ₂ O ₅	Y ₂ O ₃	UO ₂	total (%)		
E121 / CL medium	66.83	32.61	0.633	0.007	0.016	0.006	100.10		
E122 / CL medium	66.97	32.49	0.640	0.001	0.009	0.005	100.11		
E123 / CL medium	67.23	32.65	0.627	0.014	0.003	0.006	100.53		
E124 / CL medium	66.99	32.68	0.636	0.012	0.032	0.001	100.35		
E125 / CL medium	66.97	32.61	0.615	0.007	0.023	0.004	100.23		
E126 / CL medium	66.90	32.65	0.626	0.009	0.009	0.006	100.20		
E127 / CL medium	67.05	32.61	0.617	0.007	0.011	0.007	100.30		
mean (n=6)	66.99	32.61	0.628	0.008	0.015	0.005	-		
Is absolute	0.13	0.06	0.009	0.004	0.010	0.002	-		
E128 / CL dark	66.85	32.89	0.647	0.011	0.047	0.023	100.47		
E141 / CL bright	66.98	32.68	0.583	0.005	0.012	0.003	100.26		
				S	IMS data	**			
Analysis number/location	89Y/30Si	¹³⁸ Ba/ ³⁰ Si	¹³⁹ La/ ³⁰ Si	¹⁴⁰ Ce/ ³⁰ Si	¹⁴¹ Pr /30 Si	¹⁴⁶ Nd/ ³⁰ Si	¹⁴⁷ Sm/ ³⁰ Si	¹⁵³ Eu/ ³⁰ Si	¹⁵⁷ Gd/ ³⁰ Si
S1 / CL dark	5.3E-02	6.7E-05	5.6E-06	4.6E-04	6.1E-06	1.5E-05	1.7E-05	2.5E-05	7.4E-05
S2 / CL bright	2.7E-02	3.0E-05	2.1E-06	2.6E-04	2.1E-06	7.4E-06	8.5E-06	1.2E-05	3.5E-05
S3 / CL medium	1.8E-02	2.8E-05	1.7E-06	1.7E-04	1.2E-06	4.5E-06	4.0E-06	7.0E-06	2.0E-05
S4 / CL medium	2.2E-02	3.1E-05	2.1E-06	1.9E-04	1.2E-06	4.6E-06	5.5E-06	8.3E-06	2.5E-05
S5 / CL medium	2.3E-02	2.6E-05	2.0E-06	1.9E-04	8.7E-07	4.6E-06	5.0E-06	7.3E-06	2.6E-05
S6 / CL medium	2.6E-02	3.2E-05	3.2E-06	2.2E-04	2.0E-06	6.3E-06	6.3E-06	1.0E-05	3.0E-05
other grain / CL dark	4.6E-02	3.0E-05	3.1E-06	3.8E-04	3.3E-06	1.1E-05	1.3E-05	2.0E-05	6.0E-05
other grain / CL bright	6.1E-02	3.6E-05	4.4E-06	5.4E-04	5.6E-06	1.7E-05	1.9E-05	2.9E-05	8.8E-05
other grain / CL banded	3.0E-02	3.0E-05	2.2E-06	2.6E-04	1.6E-06	6.6E-06	7.8E-06	1.2E-05	3.9E-05
other grain / CL banded	3.7E-02	2.8E-05	2.2E-06	3.1E-04	2.6E-06	8.2E-06	1.0E-05	1.6E-05	4.6E-05
other grain / CL banded	3.9E-02	3.2E-05	2.4E-06	3.2E-04	2.0E-06	8.6E-06	1.1E-05	1.7E-05	5.2E-05
random spot other grain	3.0E-02	-	2.6E-06	2.5E-04	2.1E-06	7.8E-06	9.0E-06	1.2E-05	3.8E-05
random spot other grain	3.4E-02	-	2.9E-06	2.6E-04	2.2E-06	9.2E-06	1.0E-05	1.3E-05	4.1E-05
random spot other grain	2.9E-02	4.4E-05	3.3E-06	2.4E-04	1.8E-06	7.7E-06	8.7E-06	1.1E-05	3.9E-05
random spot other grain	3.1E-02	4.4E-05	3.0E-06	2.6E-04	1.8E-06	7.7E-06	7.6E-06	1.2E-05	3.8E-05
random spot other grain	3.0E-02	4.3E-05	3.3E-06	2.6E-04	2.4E-06	8.3E-06	8.0E-06	1.4E-05	4.3E-05
random spot other grain	2.8E-02	4.3E-05	2.8E-06	2.4E-04	1.4E-06	7.7E-06	8.0E-06	1.3E-05	3.5E-05
random spot other grain	2.8E-02	3.0E-05	3.5E-06	2.3E-04	1.9E-06	6.2E-06	5.6E-06	1.1E-05	3.3E-05
random spot other grain	2.8E-02	3.4E-05	2.5E-06	2.2E-04	1.6E-06	6.5E-06	6.7E-06	1.0E-05	3.3E-05
random spot other grain	2.8E-02	2.6E-05	2.4E-06	2.2E-04	2.0E-06	6.8E-06	6.5E-06	1.1E-05	3.5E-05
random spot other grain	3.2E-02	3.4E-05	2.5E-06	2.7E-04	3.2E-06	7.3E-06	7.8E-06	1.3E-05	3.9E-05
random spot other grain	2.4E-02	4.3E-05	2.0E-06	2.1E-04	1.1E-06	6.4E-06	7.1E-06	7.6E-06	2.9E-05
random spot other grain	2.6E-02	4.3E-05	2.3E-06	2.3E-04	1./E-06	6./E-06	6.6E-06	8.0E-06	3.1E-05
random spot other grain	3.0E-02	4.2E-05	2.4E-06	2.5E-04	1.4E-06	7.7E-06	7.6E-06	1.0E-05	3.4E-05
ls absolute	2.9E-02 2.5E-03	3.9E-05 6.4E-06	2.7E-06 4.4E-07	2.4E-04 1.7E-05	1.9E-06 5.3E-07	7.4E-06 8.5E-07	7.6E-06 1.2E-06	1.1E-05 1.9E-06	3.6E-05 4.0E-06
Analysis number/location	¹⁶¹ Dv / ³⁰ Si	¹⁶⁵ Ho/ ³⁰ Si	166 Er /30 Si	172 Yb 30 Si	175Lu/30Si	178 Hf /30 Si	²³² Th/ ³⁰ Si	238U/30 Si	
	405.04	0.05.0.4	1.55.00	0.05.00	105.00	0.75.00	0.75.00	0.05.00	
S1 / CL dark	4.0E-04	8.3E-04	1.5E-03 73E 04	2.0E-03	1.9E-03	9.7E-02	3./E-U3	9.3E-03	
S3 / CL medium	1.3E-04	2 7F-04	5.0F-04	77F-04	7.7 L=04	9.2E-02	6.9F-04	2.3E-03	
S4 / CL medium	1.5E-04	3.3E-04	6 1 F-04	9.0F-04	9.0E-04	9.2E-02	8 0F-04	2.5E-03	
S5 / CL medium	1.5E-04	3.4F-04	6.3E-04	9.4F-04	9.0F-04	9.1F-02	8.2F-04	2.7E-03	
S6 / CL medium	1.8E-04	3.9E-04	7.2E-04	1.0E-03	9.9E-04	9.6E-02	9.4E-04	2.8E-03	
other grain / CL dark	3.5E-04	/.3E-04	1.3E-03	1.8E-03	1.7E-03	I.1E-01	2.9E-03	/./E-03	
other grain / CL bright	4./E-04	1.0E-03	1.8E-03	2.3E-03	2.2E-03	1.0E-01	5.6E-03	1.2E-02	
other grain / CL banded	2.1E-U4	4.0E-U4	0.2E-U4	1.2E-U3	1.1E-U3		1.3E-U3	3.7E-U3	
other grain / CL banded	2.7 E-U4	5.7 E-04	1.UE-U3	1.4E-U3	1.4E-U3		2.UE-U3	5.0E-U3	
onier grunn / CE bunded	L.7L-04	0.21-04	1.11-03	1.JL-03	1.31-03	1.0L-01	L.ZL-UJ	0.51-03	



Table 3 (continued). EPMA and SIMS results from Göttingen grain 10

			S	MS data	**			
Analysis number/location	¹⁶¹ Dy/ ³⁰ Si	¹⁶⁵ Ho/ ³⁰ Si	¹⁶⁶ Er/ ³⁰ Si	¹⁷² Yb ³⁰ Si	¹⁷⁵ Lu/ ³⁰ Si	¹⁷⁸ Hf/30 Si	²³² Th/ ³⁰ Si	238U/30 Si
random spot other grain	2.1E-04	4.6E-04	8.3E-04	1.2E-03	1.1E-03	9.2E-02	1.2E-03	3.6E-03
random spot other grain	2.4E-04	5.1E-04	9.5E-04	1.3E-03	1.3E-03	9.4E-02	1.2E-03	3.6E-03
random spot other grain	2.1E-04	4.6E-04	8.2E-04	1.2E-03	1.1E-03	9.1E-02	1.2E-03	3.5E-03
random spot other grain	2.3E-04	4.8E-04	8.8E-04	1.3E-03	1.2E-03	9.0E-02	1.3E-03	3.7E-03
random spot other grain	2.2E-04	4.6E-04	9.0E-04	1.2E-03	1.2E-03	9.3E-02	1.2E-03	3.6E-03
random spot other grain	2.1E-04	4.5E-04	7.9E-04	1.1E-03	1.1E-03	9.6E-02	1.2E-03	3.4E-03
random spot other grain	2.0E-04	4.2E-04	7.5E-04	1.1E-03	1.0E-03	9.2E-02	1.0E-03	2.9E-03
random spot other grain	1.9E-04	4.2E-04	7.7E-04	1.1E-03	1.0E-03	9.4E-02	1.0E-03	2.9E-03
random spot other grain	1.9E-04	4.1E-04	7.5E-04	1.1E-03	1.0E-03	9.2E-02	1.0E-03	2.9E-03
random spot other grain	2.3E-04	5.0E-04	9.1E-04	1.3E-03	1.2E-03	9.1E-02	1.4E-03	3.9E-03
random spot other grain	1.7E-04	3.1E-04	6.6E-04	1.0E-03	9.7E-04	9.3E-02	8.4E-04	2.7E-03
random spot other grain	1.8E-04	3.2E-04	7.4E-04	1.0E-03	1.0E-03	9.5E-02	9.6E-04	2.5E-03
random spot other grain	2.0E-04	4.5E-04	8.4E-04	1.3E-03	1.3E-03	9.9E-02	1.2E-03	3.8E-03
mean for random spots (n=13)	2.1E-04	4.3E-04	8.1E-04	1.2E-03	1.1E-03	9.3E-02	1.1E-03	3.3E-03
1s absolute	2.1E-05	6.1E-05	8.1E-05	1.1E-04	1.1E-04	2.4E-03	1.5E-04	4.6E-04

Note: see Figure 1 for location of analyses. * EPMA absolute concentrations obtained in Göttingen. Values in % m/m. ** SIMS measured ratios determined with the Potsdam Cameca ims 6f. Analytical conditions: 40 nA ¹⁶O⁻ primary, ~ 30 μm diameter spot, 50 V energy window, 125 V energy offset, M/ΔM ~ 350, 12 cycles per analysis.

In order to document Raman spectra and their variations in zircon 91500, Figure 2A shows the spectra from three distinct domains shown in Figure 1. Clearly, variations in the degree of radiation damage exist within the sample. An overview of 91500 is given in Figure 2B which plots parameters for the most intense Raman band at *ca.* 1000 cm⁻¹ $[v_3(SiO_4)]$ internal vibration]. This plot comprises the results of twenty-five random Raman measurements representing multiple fragments, including data from the CL dark band visible in Figure 1. The plot illustrates the internal heterogeneity of the short range order within 91500 as well as the structural divergence of zircon 91500 from completely crystalline zircon, as represented by the spectrum obtained from synthetic ZrSiO₄ (Dawson et al. 1971, Nasdala et al. 2002). The $v_3(SiO_4)$ band of crystalline zircon (Raman shift ~ 1008 cm⁻¹) was characterised by a small FWHM (full width at half band maximum) of less than 2 cm⁻¹ (Nasdala et al. 2002). Strongly metamict but not yet fully amorphous zircon typically shows broadened and shifted Raman bands of the remnant crystalline zircon, with FWHMs exceeding 30 cm⁻¹ (Nasdala *et al.* 2001). Based on the observed $v_3(SiO_4)$ FWHMs in the range 2.7-7.3 cm⁻¹ (Figure 2B) zircon 91500 can in general be characterised as very little to (at the most) moderately radiation-damaged.

Seen as a whole, 91500 is clearly not as structurally homogeneous as would be necessary for an ideal Raman reference sample. Radiation damage revealed

by increasing Raman band broadening was found to correlate with the BSE intensity and anti-correlated with the total CL intensity. This is a typical feature of primarily zoned zircon that has not experienced structural alteration such as recrystallisation or annealing during a chemical overprinting process, and it is explained by the finding that the CL of zircon is most strongly controlled by the degree of its radiation damage (Nasdala et al. 2002). Note that, by contrast, positively correlated or different BSE and CL patterns would be indicative of secondary processes (e.g., Kempe et al. 2000). Even though the susceptibility of zircon to the secondary loss of radiogenic Pb is enhanced in radiation-damaged micro-areas (Nasdala et al. 1998), the observed internal variations in the degree of radiation damage do not intrinsically affect the suitability of zircon 91500 as a U-Pb age or trace element reference sample. This is because radiation damage does not cause, but just enhances the susceptibility of zircon to the secondary loss of radiogenic Pb. No indication of alteration or other secondary processes, which might be connected with partial Pb-loss, were observed.

SIMS oxygen isotope measurements

The final component of the overall homogeneity testing phase involved the *in situ* measurement of the oxygen isotope ratio of fifteen random spots distributed over three fragments of 91500. These fragments were selected at random from the vial of sample material



Figure 2. (A) Three Raman spectra in the SiO₄ stretching range obtained from the zircon shown in Figure 1: narrowest, medium and broadest peaks correspond to the CL bright, CL medium and CL dark bands, respectively. (B) Raman band frequencies plotted versus FWHMs (band broadening: full width at half band maximum) of the anti-symmetric stretching vibration: a = mean values for twenty five individual CL domains observed on 91500; b = synthetic pure ZrSiO₄. The point at the lowest right represents the CL dark band of Göttingen chip number 10.

that was provided to the Geological Survey of Japan. The Cameca ims 1270 in Tsukuba was used in Faraday Cup multi-collector mode to determine the δ^{18} O value on ~ 40 μ m diameter spots using a 1.8 nA $^{133}Cs^+$ beam. The instrument was operated at M/ Δ M

≈ 1800 and the area analysed was restricted by a rectangular field aperture to give a field of view of 20 μ m x 20 μ m. A 50 V energy bandpass was used, to which no offset voltage was applied, and normal incidence electron flooding was used for charge compensation. A single measurement consisted of forty 10 second integrations employing two Faraday Cups in static multi-collection mode. Absolute δ^{18} O values were calibrated using the Z8 in-house zircon calibrant (δ^{18} O composition determined by laser fluorination, HfO₂ ≈ 0.8% m/m). Further details are published elsewhere about this technique for the analysis of oxygen isotopes by SIMS (Morishita *et al.* 1998) and the use of Faraday Cup multi-collection (Morishita *et al.* 2000).

The SIMS δ^{18} O data (Table 4) showed no clustering in values as a function of measurement location; no systematic differences were observed between the three individual test fragments of 91500. The determined mean external reproducibility of ± 0.3‰ (1*s*) was close to the reported internal precision of the method. These data are fully consistent with the three random fragments being homogeneous for their oxygen isotopic composition at the 20 µm sampling scale. BSE imaging of the three fragments revealed no internal structure and CL images showed either a very subdued banding (fragment 1 on Table 4) to no structure (fragments 2 and 3). We therefore conclude that the material analysed by SIMS during the oxygen isotope

Table 4. Results from SIMS oxygen isotope homogenity test

Frag. / spot	δ ¹⁸ Ο *	
1/1	10.1 ± 0.3	
1 / 2	10.3 ± 0.2	
1/3	9.6 ± 0.3	
1 / 4	10.0 ± 0.3	
1/5	9.7 ± 0.3	
2 / 1	9.9 ± 0.3	
2 / 2	10.3 ± 0.3	
2/3	9.4 ± 0.2	
2 / 4	10.4 ± 0.3	
2/5	9.6 ± 0.3	
3 / 1	10.1 ± 0.3	
3 / 2	10.0 ± 0.2	
3/3	9.5 ± 0.2	
3 / 4	10.0 ± 0.2	
3 / 5	9.7 ± 0.2	
mean	9.9	
1 <i>s</i> external	0.3	

 * Quoted precisions are ± 1 s internal for the individual measurements. Absolute values were calibrated using the Z8 in-house zircon reference sample, which gave an external precision of ~ 0.2 ‰ (n = 6).





Figure 3. Cathodoluminescence image of the three fragments investigated by ICP-MS Laboratory 1, see Table 9 for data. (A) Fragment 1 and (C) fragment 3 are typical for the bulk of the sample, whereas (B) fragment 2 shows an example of the extreme CL banding which is found in occasional fragments from zircon 91500.

homogeneity test was representative of the volume majority of the crystal and did not include any of the strongly banded "exotic" domains (see Figure 3 and its discussion below).

EPMA intercomparison

An important application of sample 91500 is as a primary (or secondary) reference material for the assessment of the precision and accuracy of EPMA determinations of Zr, Si and Hf in unknown zircon samples. Due to the low abundances of other trace elements in the sample under study (Wiedenbeck *et al.* 1995), the relatively large uncertainties for other elements makes 91500 poorly suited for an EPMA reference standard for other elements. In the absence of synthetic zircon and hafnon (HfSiO₄) crystals for Zr, Si, and Hf, a well characterised homogeneous natural zircon is a good alternative for an EPMA reference sample. Also, the Hf content of zircon is commonly used as an internal standard for LA-ICP-MS analyses of natural zircon will be helpful for establishing the accuracy of SIMS and LA-ICP-MS analyses.

Comments on earlier published results

In the earlier study by Wiedenbeck et al. (1995), EPMA wavelength dispersive spectrometry (WDS) analyses (n = 99) from five fragments of the 91500 zircon produced the following mean concentrations values: $SiO_2 = 32.27 \pm 2\%$ m/m; $ZrO_2 = 62.87 \pm 8$; $HfO_2 =$ 0.659 ± 5 (Hf = 5590 ± 42 µg g⁻¹); P₂O₅ = 0.045 ± 1; $Y_2O_3 = 0.289 \pm 10$; and a total of 96.14 ± 10 (1s mean). The low total elicits questions concerning the overall quality of these analyses. One source of error could be the use of Hf metal as the Hf calibration sample because of the significant matrix mismatch between a metal and orthosilicate. It seems improbable, however, that a matrix mismatch problem for Hf alone could have been responsible for the low mean total. More importantly, the ZrO₂ content reported by Wiedenbeck et al. (1995) deviated significantly from the stoichiometric concentration of ZrO_2 in pure zircon (e.g., 67.22% m/m ZrO₂). Even by taking into account Hf substituting for Zr in the Zr site, the sum of ZrO_2 plus HfO₂ falls short of ideal zircon stoichiometry. This suggests that the main problem with the reported EPMA analyses is in the Zr determination, possibly indicative of a problem with the Zr calibrant used (natural zircon) or to other, subordinate factors such as sample polish, carbon coat or the stability of the EPMA during the course of data acquisition. SiO₂ is close to stoichiometric zircon composition, but slightly lower than the ideal concentration for SiO₂ (e.g., 32.78% m/m SiO₂), again most likely due to the natural zircon standard used for those analyses. By further taking into account the fact that P most likely substitutes for Si in the Si site in the zircon structure, the ideal concentration is even better approximated.

In a subsequent study by Nesbitt *et al.* (1997) a LA-ICP-MS Hf value for 91500 of 5960 μ g g⁻¹ (HfO₂ = 0.703% m/m) (with no error estimate cited) was

reported as their preferred value for Hf for this sample. This is a relative difference of 6.21% from the EPMA Hf value presented in Wiedenbeck *et al.* (1995), which is well outside of the analytical precision that can be achieved by EPMA for a minor (to major) element such as Hf where an internal precision of better than 1% is often reported. In the study by Nesbitt *et al.* (1997) no EPMA values (or totals) for Zr or Si were reported and hence it is difficult to access the quality of the reported value for Hf or to know what element was used as an internal standard for the LA-ICP-MS analyses.

Also reported in Wiedenbeck *et al.* (1995) were four bulk sample Lu-Hf isotope dilution data for 91500 with a simple mean value for Hf of 5895 μ g g⁻¹ (HfO₂ = 0.695% m/m), which is in good agreement with the LA-ICP-MS Hf value reported by Nesbitt *et al.* (1997). The ID-TIMS values for Hf and Lu reported by Wiedenbeck *et al.* (1995) are estimated to be accurate to within 5%, corresponding to *circa* ± 300 μ g g⁻¹, reflecting mainly the uncertainty in the weights of the aliquots and of the spike used for the concentration determinations. Proton probe data (n = 18) reported by Wiedenbeck *et al.* (1995) for Hf has a summed value of 0.693 ± 5% m/m HfO₂ (Hf = 5876 ± 42 μ g g⁻¹), which is also in very good agreement with the isotope dilution Hf results.

Instructions to participating laboratories

The six laboratories participating in the EPMA intercomparison (Table 1) were instructed to mount two random, mm-sized fragments that should have been polished to a roughness of 0.3 µm or better (using alumina or diamond paste). Prior to analysis the sample was to be cleaned in de-ionised water using an ultrasonic bath, rinsed in ethanol, and then carbon coated. Each participating EPMA laboratory was requested to provide for each fragment ten, randomly spaced determinations of Zr, Si, Hf, P, Y, and U. It was recommended that determinations be done using an accelerating voltage of 20 kV, an analysis beam current of 150 nA (the selection of the optimal current was left to the best judgement of the analyst), and a beam diameter of 1 µm. If dead time for Si proved to be a problem, then the Si K_{β} peak was to be used instead of the usual Si K_{α} . It was recommended that peaks were to be counted for 240 seconds, and background positions on either side of the peak were to be counted for 120 seconds (except for Zr, Si where the two background positions were to be counted long enough to achieve an internal analytical precision of



0.1 to 0.2%, relative, and Hf which was to be counted long enough to achieve an internal precision of between 0.1 and 1.0%, relative).

Data for the 91500 zircon were submitted by six electron microprobe laboratories (Tables 5, 6 and 7); these are discussed in the following section. As seen in Tables 5 and 6, although specific recommendations were given for data acquisition and reporting, there were some deviations from this. As such, the submitted analyses have been accepted at their face value. In addition to a range of analytical conditions, a range of calibration samples were also used in this study. A primary objective of the present study was to better understand the nature of inherent heterogeneities in the 91500 zircon and to ascertain if apparent heterogeneities are real, or due to analytical problems, or the result of using differing primary calibration materials.

Variations within and between fragments

Participating EPMA laboratories were asked to analyse two fragments, ten analyses each, of the 91500 zircon. Some laboratories did more analyses than required, and some analysed more than two fragments. In this discussion, however, only two results - the mean of ten analyses with the respective observed 1*s* uncertainties - from each laboratory are discussed (Table 7). The submitted analyses with at least ten analyses per fragment and totals between 99.5% m/m and 100.5% m/m (where possible) were incorporated into the discussion.

In general, for a given laboratory there is very good internal consistency for all elements analysed with relatively small standard deviations of the sample populations based on ten random analyses per fragment. Likewise, it is encouraging that for each laboratory the data for both fragments fell within error, indicating that the Si and Zr concentrations were homogeneous at the micrometre-scale at the precision levels provided by EPMA. As there appears to have been no significant between-laboratory variation in the Si and Zr results, the mean values for these two elements have been calculated (Table 7); these are our preferred values for 91500.

Variations between EPMA laboratories

Of more concern, however, are the differences in Hf between the different EPMA laboratories. If the assumption is made that the 91500 zircon is homogenous at



Table 5.Basic instrument parameters used by participating EPMA laboratories

Lab number	1	2	3	4	5	6
Brand and	JEOL JXA	JEOL JXA	JEOL JXA	Cameca	Cameca	JEOL JXA
model of EPMA	8900	8900	8800	SX-50	SX- 100	8900
Data acq. software	JEOL	JEOL	JEOL	Cameca	Cameca	JEOL
Quantitative	CITZAF	CITZAF	ZAF	PAP	PAP	CITZAF
Analytical software	Armstrong (1995)	Armstrong (1995)	-	-	-	Armstrong (1995)
Acc. voltage (kV)	20	25	20	20	20	20
Beam current (nA)	150	80	30	40	20	150
Beam diameter (mm)	2	1	2	2	10	1

Some of the analytical conditions used deviated from the original instructions.

Table 6.Measurement conditions used by participating EPMA laboratories

Element	Primary calibrant material	X-ray line	Peak time (seconds)	Bkg time (sec. x 2)	Spectrometer crystal
Lab 1					
Zr	ZrSiO₄	La	240	240	TAP
Si	ZrSiO ₄	κ̈́α	240	240	TAP
Hf	Hf metal	Ma	240	240	TAP
Р	Apatite	Ka	240	240	PET
Y	Y ₃ Al ₅ O ₁₂ (synthetic)	La	240	240	PETH
U	U metal	Mß	1350	480	PET
Lab 2		F			
Zr	ZrSiO₄ (USNM 117288-3)	La	30	30	PET
Si	ZrSiO ⁴ (USNM 117288-3)	K	15	10	TAP
Hf	HfSiO₄ (synthetic)	M	300	300	TAP
Р	Apatite	Ka	300	300	PET
Y	$Y_3AI_5O_{12}$ (synthetic)	La	300	300	PET
U	U metal	M	300	300	PETHS
Lab 3		ŭ			
Zr	ZrSiO₄	La	40	40	PET
Si	ZrSiO₄	К	40	40	PET
Hf	$(Zr, Hf)O_2$ (synthetic)	L	240	240	LIF
Р	KTiOPO ₄ (synthetic)	К	240	240	PET
Y	$Y_3AI_5O_{12}$ (synthetic)	La	240	240	PET
U	n/a	n/a	n/a	n/a	n/a
Lab 4					
Zr	ZrSiO₄	L	30	30	TAP
Si	ZrSiO₄	K	30	30	TAP
Hf	HfO ₂ (synthetic)	Lß	50	50	LIF
Р	PrPO ₄ (synthetic)	K	30	30	PET
Y	YPO ₄ (synthetic)	L	30	30	PET
U	U metal	M _B	50	50	PET
Lab 5		Р			
Zr	ZrO_2 (synthetic)	La	80	80	PET
Si	K feldspar	κ̈́α	20	20	TAP
Hf	Hf metal	L	50	50	LIF
Р	Apatite	К	60	60	PET
Y	YPO_{4} (synthetic)	L	60	60	PET
U	UO_2 (synthetic)	M _B	50	50	PET
Lab 6	2 . ,	Р			
Zr	ZrSiO₄ (synthetic)	La	80	80	PET
Si	ZrSiO₄ (synthetic)	Кa	20	20	TAP
Hf	HfSiO₄ (synthetic)	L	50	50	LIF
Р	YPO₄ (synthetic)	К̈́́́́́	60	60	PET
Y	YPO₄ (synthetic)	L	60	60	PET
U	UO ₂ (synthetic)	M _β	50	50	PET

Unless otherwise noted in this table, natural minerals and metals were used as primary calibrants.

n/a Indicates not applicable, as this element was not analysed.

Lab. / frag. number	Ν	SiO ₂	ZrO ₂	HfO ₂	P ₂ O ₅	Y ₂ O ₃	UO ₂	Total
1/1	10	33.05 ± 16	65.49 ± 21	0.577 ± 4	0.005 ± 5	0.019 ± 2	0.003 ± 4	99.15 ± 25
1 / 2	10	33.19 ± 14	65.04 ± 34	0.580 ± 12	n.d	0.019 ± 2	0.009 ± 6	98.83 ± 33
2 / 1	10	32.72 ± 11	66.54 ± 20	0.595 ± 19	0.011 ± 3	0.027 ± 8	0.007 ± 2	99.90 ± 15
2 / 2	10	32.69 ± 9	66.60 ± 15	0.598 ± 10	0.009 ± 3	0.026 ± 7	0.006 ± 2	99.94 ± 18
3 / 1	10	32.82 ± 13	66.14 ± 23	0.809 ± 22	0.008 ± 3	0.005 ± 5	-	99.78 ± 16
3 / 2	10	32.70 ± 41	66.53 ± 28	0.766 ± 10	0.010 ± 5	0.010 ± 7	-	100.01 ± 26
4 / 1	10	32.45 ± 11	66.67 ± 26	0.789 ± 82	n.d.	n.d.	0.019 ± 17	99.93 ± 29
4 / 2	10	32.45 ± 8	66.47 ± 32	0.823 ± 78	n.d.	n.d.	0.018 ± 16	99.76 ± 34
5 / 1	10	32.33 ± 9	65.68 ± 19	0.820 ± 28	0.03 ± 1	0.01 ± 2	n.d.	98.90 ± 21
5 / 2	10	32.13 ± 9	65.83 ± 17	0.790 ± 22	0.04 ±1	n.d.	0.02 ± 2	98.81 ± 23
6 / 1	10	32.93 ± 9	66.40 ± 24	0.616 ± 13	n.d.	0.012 ± 3	0.006 ± 3	99.97 ± 23
6 / 2	10	32.81 ± 31	66.72 ± 44	0.625 ± 9	n.d.	0.012 ± 3	0.005 ± 3	100.17 ± 30
Simple mean	120	32.69 ± 30	66.17 ± 54	-	-	-	-	-

Table 7. Results from WDS electron microprobe analyses

Values given in % m/m. Reported uncertainties are the observed 1s absolute of the mean of the population and refer to the final digits of the the quoted value. N Denotes the number of analyses done on a fragment. n.d. Denotes below the minimum detection limit for the conditions used for analyses. Laboratory 3 did not measure the U content of the sample, and this is denoted by a dash. Data are presented with the number of significant figures provided by the analyst. No mean for the Hf data has been calculated due to the large scatter seen between the data from the reporting laboratories.

the EPMA precision level, as noted above, then the observed differences must be due to either problems with the analytical methods and/or the calibrants used (see also discussion section, below).

Using the isotope dilution value for Hf as a benchmark, EPMA laboratories 1 and 2 show the greatest deviation. This is interesting because laboratory 1 used Hf metal as the primary Hf calibrant, whereas laboratory 2 used pure synthetic hafnon, which is very close in matrix to zircon and would therefore minimise any matrix corrections. Laboratory 6 is the closest in Hf content to the isotope dilution value, although it is still significantly lower than the ID value; laboratory 6 also used synthetic pure hafnon as the primary Hf calibrant. Laboratories 3, 4 and 5 all used widely different primary Hf calibration samples (Table 5), yet the results for these three laboratories were relatively close though distinctly high compared to the isotope dilution value. Clearly, many factors affect the accuracy of EPMA analyses at these levels of scrutiny.

Regarding other elements analysed by EPMA in the 91500 zircon, P, Y, and U are present only in low concentrations, resulting in large uncertainties, yet appear to be in generally good agreement both between fragments and between laboratories. Exceptions include the Y data from laboratory 2, which were higher than the other reported data, and the U data from by laboratory 4, which also seems anomalously high relative to the other analyses in Table 7. The mean U isotope dilution concentration reported in Wiedenbeck et al. (1995) is 81.2 μ g g⁻¹. The average EPMA U concentration in Table 3 for "Göttingen grain 10" is $44 \pm 18 \mu g$ g⁻¹, and one determination from a dark CL domain produced a U content of 203 μ g g⁻¹ (no uncertainty reported). The U concentrations in Table 7 were generally lower than the isotope dilution value, and as with the Hf results discussed above, the scatter in the data from a given laboratory was less than the variations found between the different laboratories. The U concentrations for EPMA laboratories 4 and 5 were the closest to the isotope dilution value. One would expect that laboratories that used U metal as the uranium calibrant would have had a greater problem with accuracy, however, the data from laboratory 4 (U metal calibrant) and laboratory 5 (synthetic UO₂ calibrant) were within error of each other and within error of the isotope dilution value reported in Wiedenbeck et al. (1995).

Comparison with Hf isotope dilution results

In that isotope dilution is a primary analytical method for determining trace element concentrations in materials, we consider the isotope dilution data for



91500 for Hf (Wiedenbeck et al. 1995) to provide an accurate approximation of the bulk composition of the sample against which the EPMA analyses in this current study may be evaluated. The results presented in Table 7 reveal that none of the 91500 HfO_2 EPMA data were within 10%, relative, of the isotope dilution results of $HfO_2 = 0.695\%$ m/m; three laboratories were too high and three too low. However, all of the determinations were within 20%, relative. In light of this, if any of these EPMA results are used for an internal standard for SIMS or LA-ICP-MS, the introduction of this potential systematic error, and the extent to which it will affect future analyses, must be kept in mind. The fact that none of the six EPMA data sets, despite having analysed independent and random fragments, were consistent with the earlier isotope dilution data suggests that significant bias may still plague this approach.

Recommendation for EPMA data acquisition

In order to obtain the highest quality EPMA analyses, one clearly must have both good primary calibrants and carefully defined analytical protocols based on experience. In addition to accounting for obvious issues like dead time from Si K_{α} (if this X-ray line is used), using an appropriate accelerating voltage, beam current and beam diameter, a thorough understanding of the data reduction method used and the implications of the different options (e.g., ZAF vs. CIT-ZAF phi-rho-z), one must also seriously address the issue of primary and secondary reference samples.

For EPMA an ideal primary reference material is a synthetic version of the natural mineral of interest. This

minimises matrix corrections, and the electron beamsolid interactions between the calibrant and the unknown will be similar. A pure synthetic calibrant also allows the peak and background positions to be checked for the X-ray lines of interest, and to test if all possible inferences have been adequately addressed. For example, after interference corrections have been made, the interfering element should produce neither positive bias (indicating that insufficient correction has been made) nor negative bias (indicating an overcorrection has been made) for the pure synthetic material. Alternatively, using a suite containing both synthetic and natural materials have that been well characterised is the ideal route as this will permit an assessment of systematic calibration errors. What is clear from the data set presented here is that achieving the highest quality of data from the electron probe requires both an extensive set of calibration materials and great attention to analytical detail. Only when these criteria have been met is it possible to have real confidence in the absolute concentration values that are obtained and only under these circumstances can independent EPMA data sets really be compared.

ICP-MS intercomparison

Five laboratories (Table 1) reported data collected with instruments and procedures summarised in Table 8. Four laboratories used a quadrupole ICP-MS and one used a single collector magnetic sector ICP-MS. Four laboratories employed a 266 nm Nd:YAG laser and one a 193 nm excimer laser. NIST glass samples were used as calibrant by three laboratories, whereas one laboratory used BR266 (a Sri Lankan gem zircon; Stern 2001) and the fifth laboratory used USGS TB-1

Table 8. Laser ablation ICP-MS data collection parameters

	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
ICP-MS	Magnetic sector	Quadrupole	Quadrupole	Quadrupole	Quadrupole
Carrier gas(es)	Ar + He	Ar	Ar+He	Ar+He	Ar+He
Laser wavelength (nm)	266 (Nd:YAG)	266 (Nd:YAG)	266 (Nd:YAG)	193 (ArF excimer)	266 (Nd:YAG)
Beam diameter (μm)	30	50	50	80	50
Raster size (µm or n/a)	400x150	n/a	n/a	n/a	n/a
Laser pulse rate (Hz)	20	10	10	10	4
Laser pulse width (ns)	3	4	7	25	3 - 5
Calibration reference sample	NIST glasses *	BR266 zircon	NIST 612 Glass	NIST 612 Glass	TB-1 Basalt Glass
Internal standard isotope	²⁹ Si	178Hf	177,179 Hf	178Hf	178Hf
Concentration (µg g-1) - Ref. Sample	variable	8200	34.77	34.77	5.84
Concentration (µg g-1) - 91500 Zircon	149578	5935	5649, 5911, 5340	7000	5900

* This laboratory used a regression line derived from NIST SRM 610, 612, 614 and 616 reference samples. The Si concentration varies between these reference samples.



synthetic basaltic glass. All laboratories employed Hf as the internal standard element except laboratory 1, which used silicon. Each laboratory measured five spots in each of three fragments of 91500 except laboratory 5, which measured four spots on each of four fragments. Three laboratories collected data on a 50 μ m diameter spot but laboratory 4 used an 80 μ m spot and laboratory 1 performed a raster analysis over a 400 x 150 μ m area with a 30 μ m diameter beam.

Instructions to participating laboratories

It was requested that those participating ICP-MS laboratories which had the capacity to provide laser ablation and solution analyses should submit data for both techniques. Unfortunately, due to the extreme chemical inertness of this sample, reliable data were only possible using laser sampling. Concentration data in $\mu g g^{-1}$ were requested for the following elements ranked in importance:

Essential: All REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu).

Highly desirable: Y, Ba, Pb, Th, U plus, if not used as an internal standard for laser measurements, Hf.

If possible: Ca, Cr, Sr, Nb.

At the time of data submission, the participating laboratories were to submit details about their analytical approach including: instrument type (quadrupole or magnetic sector), laser type and wavelength (Nd:YAG or excimer, with makes and models included) and operating conditions for both the ICP-MS and the laser. It was recommended that laboratories should use the preferred values of Pearce et al. (1997) for the NIST SRM 612 glass for external calibration; however other calibration standards (other zircons of known composition, NIST SRM 610, BCR2-G, simultaneouslyaspirated solutions) were considered acceptable as long as the calibration values were included in the data reporting file. Participants were recommended to use internal standards (in order of decreasing preference) and the assumed concentrations in zircon 91500 of: Hf (~ 0.7% m/m oxide), Si (~ 32% m/m oxide), Zr (~ 63% m/m oxide). Five randomly located analyses from each of three different sample chips were requested, giving a total of fifteen analyses to report.

Variations within and between fragments

The ICP-MS data received from the five laboratories are given in Table 9. For the high abundance heavy REEs (Gd to Lu), Ce, Y, Pb, Th and U, spot-to-spot homogeneity within individual 91500 fragments was generally better than 10% in twelve of the sixteen fragments. Fragment 2 of laboratory 1, fragment 2 of laboratory 2 and fragment 3 of laboratory 5 showed more variability, typically 10 to 20% relative, in abundances of heavy REEs, Ce, Y, Pb, Th and U. Fragment 1 of laboratory 2 exhibited heavy REE variations of 23 to 46%. With the exception of Ce, the measured concentrations for the light REE (La to Eu) were more variable, typically 10 to 50%, than the heavy REEs. This is, at least in part, due to the light REEs having concentrations that are \sim 10 to 100 times lower than the heavy REEs, which inevitably results in lower analytical precisions for the lighter elements.

Variability between fragments of 91500 is illustrated by the relative standard deviation of the grand mean of the individual means for each fragment analysed. For most elements analysed by laboratories 1 to 4, the % RSD of the grand mean tends to be greater than the % RSD for elements measured in each fragment (Table 9). This suggests that the trace element heterogeneity in 91500 is greater on the larger scale between most grains than the smaller scale within most grains. However, the bulk of the betweenfragment variability is the result of a few fragments of 91500 with anomalous elemental concentrations, in particular fragment 2 of laboratory 1, and all 3 fragments of laboratory 2. Thus, a large majority (twelve of sixteen or 75%) of the fragments exhibited comparable degrees of intra- and inter-grain heterogeneity. In the case of fragment 2 of laboratory 1 subsequent CL imaging clearly documents that this entire fragment is affected by a strong and highly regular banding (Figure 3). In the case of the other seemingly anomalous fragments we do not possess the scanning electron images necessary in order to establish the presence or absence of such banding.

Variations between laboratories

An interlaboratory comparison of the mean ICP-MS data is shown in Table 10. Mean chondrite-normalised REE patterns for 91500 are plotted for each laboratory in Figure 4. The mean trace element concentrations from the five laboratories were remarkably consistent, in particular varying by 10% or less for the high-



Lab 1 Element	Fragment 1 (mean (µg g ⁻¹)	n = 5) % RSD	Fragment 2 mean (μg g ⁻¹)	(n = 5) % RSD	Fragment 3 (mean (μg g ⁻¹)	n = 5) % RSD	All Frag. (n mean (µg g ⁻¹)	= 3) % RSD
La	< 0.1	-	< 0.1	-	< 0.1	-	-	-
Ce	2.53	5	3.29	13	2.77	2	2.86	14
Pr	< 0.04	-	٥.04 ‹ 0	-	٥.04 <	-	-	-
Nd	0.18	12	0.33	24	0.25	10	0.26	29
Sm	0.40	4	0.67	22	0.49	9	0.52	26
Eu	0.20	9	0.32	19	0.25	6	0.26	25
Gd	1.91	7	3.18	20	2.46	4	2.52	25
Tb	0.70	5	1.10	18	0.90	3	0.90	23
Dy	9.86	8	14.9	17	12.4	4	12.4	20
Ho	4.19	8	6.17	17	5.20	3	5.19	19
Er	22.2	9	32.7	16	27.7	4	27.5	19
Tm	6.05	8	8.26	14	7.24	2	7.18	15
Yb	69.3	4	87.2	12	78.0	3	78.2	11
Lu	12.1	8	17.5	13	15.3	4	14.9	18
Υ	126	9	193	19	158	3	159	21
Ba	< 10	-	< 10	-	< 10	-	-	-
²⁰⁶ Pb	11.8	2.9	16.6	21.1	11.9	3.2	13.4	20
²⁰⁷ Pb	1.01	3.8	1.31	20.8	1.09	4.7	1.14	14
²⁰⁸ Pb	1.52	4.2	1.95	23.4	1.74	9.1	1.74	12
Th	23.6	8	44.9	27	29.7	3	32.7	34
U	72.1	3	113.4	21	74.3	4	86.6	27
Hf	5340	8	6445	3	6411	1	6065	10
Cr	-	-	-	-	-	-	-	-
Sr	-	-	-	-	-	-	-	-
Nb	-	-	-	-	-	-	-	-
Lab 2 Element	Fragment 1 (mean (µg g-1)	n = 5) % RSD	Fragment 2 mean (µg g-1)	(n = 5) % RSD	Fragment 3 (mean (µg g-1)	n = 5) % RSD	All Frag. (n mean (μg g-1)	= 3) % RSD
Lab 2 Element	Fragment 1 (mean (μg g ⁻¹) 0.008	n = 5) % RSD	Fragment 2 mean (μg g-1) 0.015	(n = 5) % RSD	Fragment 3 (mean (μg g ⁻¹) 0.008	n = 5) % RSD 78	All Frag. (n mean (μg g-1) 0.010	= 3) % RSD 38
Lab 2 Element La Ce	Fragment 1 (mean (μg g-1) 0.008 2.27	n = 5) % RSD 14 30	Fragment 2 mean (μg g ⁻¹) 0.015 1.41	(n = 5) % RSD 51 10	Fragment 3 (mean (μg g-1) 0.008 0.92	n = 5) % RSD 78 9	All Frag. (n mean (μg g-1) 0.010 1.53	38 38
Lab 2 Element La Ce Pr	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041	n = 5) % RSD 14 30 44	Fragment 2 mean (μg g ⁻¹) 0.015 1.41 0.043	(n = 5) % RSD 51 10 67	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038	n = 5) % RSD 78 9 17	All Frag. (n mean (μg g-1) 0.010 1.53 0.041	38 38 44 6
Lab 2 Element La Ce Pr Nd	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35	n = 5) % RSD 14 30 44 47	Fragment 2 mean (μg g ⁻¹) 0.015 1.41 0.043 0.23	(n = 5) % RSD 51 10 67 49	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30	n = 5) % RSD 78 9 17 42	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29	38 38 44 6 21
Lab 2 Element La Ce Pr Nd Sm	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74	n = 5) % RSD 14 30 44 47 36	Fragment 2 mean (µg g-1) 0.015 1.41 0.043 0.23 0.62	(n = 5) % RSD 51 10 67 49 32	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47	n = 5) % RSD 78 9 17 42 85	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61	38 44 6 21 22
Lab 2 Element La Ce Pr Nd Sm Eu	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36	n = 5) % RSD 14 30 44 47 36 71	Fragment 2 mean (µg g-1) 0.015 1.41 0.043 0.23 0.62 0.27	(n = 5) % RSD 51 10 67 49 32 26	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18	n = 5) % RSD 78 9 17 42 85 79	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27	38 44 6 21 22 33
Lab 2 Element La Ce Pr Nd Sm Eu Gd	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14	n = 5) % RSD 14 30 44 47 36 71 23	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69	(n = 5) % RSD 51 10 67 49 32 26 47	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83	n = 5) % RSD 78 9 17 42 85 79 37	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89	38 38 44 6 21 22 33 12
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62	n = 5) % RSD 14 30 44 47 36 71 23 26	Fragment 2 mean (μg g ⁻¹) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37	(n = 5) % RSD 51 10 67 49 32 26 47 12	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35	n = 5) % RSD 78 9 17 42 85 79 37 9	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45	38 38 44 6 21 22 33 12 33
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6	n = 5) % RSD 14 30 44 47 36 71 23 26 35	Fragment 2 mean (μg g ⁻¹) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03	(n = 5) % RSD 51 10 67 49 32 26 47 12 18	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10	n = 5) % RSD 78 9 17 42 85 79 37 9 6	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25	38 38 44 6 21 22 33 12 33 68
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35	Fragment 2 mean (μg g ⁻¹) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71	38 38 44 6 21 22 33 12 33 68 68 68
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 35 34	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 1.83 1.9	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8	38 38 44 6 21 22 33 12 33 68 68 68 65
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 35 34 46	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 11.9 3.20	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6 8 6 8	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80	38 38 44 6 21 22 33 12 33 68 68 65 78
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9 125.1	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 34 46 34	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32 60.5	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13 5	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 11.9 3.20 42.7	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6 8 6 8 10	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80 76.1	38 38 44 6 21 22 33 12 33 68 68 65 78 57
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9 125.1 21.7	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 34 46 34 33	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32 60.5 9.28	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13 5 22	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 11.9 3.20 42.7 6.75	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6 8 6 8 10 4	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80 76.1 12.6	38 38 44 6 21 22 33 12 33 68 68 65 78 57 64
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9 125.1 21.7 172	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 35 34 46 34 33 26	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32 60.5 9.28 133	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13 5 22 3	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 11.9 3.20 42.7 6.75 124	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6 8 10 4 1	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80 76.1 12.6 143	38 38 44 6 21 22 33 12 33 68 68 65 78 57 64 18
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y Ba	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9 125.1 21.7 172 0.048	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 35 34 46 34 33 26 39	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32 60.5 9.28 133 0.026	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13 5 22 3 33	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 11.9 3.20 42.7 6.75 124 0.058	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6 8 10 4 1 74	All Frag. (n mean (µg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80 76.1 12.6 143 0.044	38 38 44 6 21 22 33 12 33 68 68 65 78 57 64 18 38
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tb Dy Ho Er Tm Yb Lu Y Ba 200Pb	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9 125.1 21.7 172 0.048	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 35 34 46 34 33 26 39 -	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32 60.5 9.28 133 0.026	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13 5 22 3 33 33	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 11.9 3.20 42.7 6.75 124 0.058	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6 8 6 8 10 4 1 74 -	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80 76.1 12.6 143 0.044	38 38 44 6 21 22 33 12 33 68 68 68 65 78 57 64 18 38 -
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y Ba 200Pb 207Pb	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9 125.1 21.7 172 0.048 -	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 34 46 34 33 26 39 - -	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32 60.5 9.28 133 0.026 -	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13 5 22 3 33 33 -	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 11.9 3.20 42.7 6.75 124 0.058 -	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6 8 6 8 10 4 1 74 - -	All Frag. (n mean (µg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80 76.1 12.6 143 0.044 -	38 38 44 6 21 22 33 12 33 68 68 65 78 57 64 18 38 - -
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y Ba 206Pb 207Pb 208Pb	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9 125.1 21.7 172 0.048 -	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 34 46 34 33 26 39 - - -	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32 60.5 9.28 133 0.026 - -	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13 5 22 3 33 - - -	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 11.9 3.20 42.7 6.75 124 0.058 - - -	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6 8 6 8 10 4 1 74 - -	All Frag. (n mean (µg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80 76.1 12.6 143 0.044 - -	38 38 44 6 21 22 33 12 33 68 68 65 78 57 64 18 38 - -
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y Ba 200Pb 200Pb 200Pb 200Pb	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9 125.1 21.7 172 0.048 - - 21.4	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 34 46 34 33 26 39 - - - 10	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32 60.5 9.28 133 0.026 - 18.5	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13 5 22 3 33 - - - 14	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 11.9 3.20 42.7 6.75 124 0.058 - .12.7	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6 8 6 8 10 4 1 74 1 74 - - 6	All Frag. (n mean (µg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80 76.1 12.6 143 0.044 - - - 1.5	38 44 6 21 22 33 12 33 68 68 65 78 57 64 18 38 - - 25
Lab 2 Element	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9 125.1 21.7 172 0.048 - - 21.4 42.8	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 34 46 34 33 26 39 - - - 10 9	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32 60.5 9.28 133 0.026 - 18.5 80.8	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13 5 22 3 33 - - - 14 15	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 11.9 3.20 42.7 6.75 124 0.058 - 12.7 79.7	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6 8 10 4 1 74 - - 6 17	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80 76.1 12.6 143 0.044 - - - 17.5 67.7	38 38 44 6 21 22 33 12 33 68 68 65 78 57 64 18 38 - - 25 32
Lab 2 Element	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9 125.1 21.7 172 0.048 - 21.4 42.8 5935	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 34 46 35 35 34 46 34 33 26 39 - - - 10 9 -	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32 60.5 9.28 133 0.026 - 18.5 80.8 5935	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13 5 22 3 33 - - - 14 15 - - 14	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 0.35 4.10 1.83 0.35 4.10 1.83 11.9 3.20 42.7 6.75 124 0.058 - - 12.7 79.7 5935	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6 8 10 4 1 74 - - 6 17 -	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80 76.1 12.6 143 0.044 - - 17.5 67.7 -	38 44 6 21 22 33 12 33 68 68 65 78 57 64 18 38 - - 25 32 -
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y Ba 200Pb 200Pb 200Pb 200Pb 200Pb 200Pb 200Pb 200Pb Th U Hf * Cr	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9 125.1 21.7 172 0.048 - - 21.4 42.8 5935 1.34	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 34 46 35 35 34 46 34 33 26 39 - - 10 9 - 10	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32 60.5 9.28 133 0.026 - 18.5 80.8 5935 1.16	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13 5 22 3 33 - - - 14 15 - 14 15 - 9	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 0.35 4.10 1.83 11.9 3.20 42.7 6.75 124 0.058 - 12.7 79.7 5935 1.14	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 8 10 4 1 74 - - 6 17 - 8	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80 76.1 12.6 143 0.044 - - 17.5 67.7 - 1.75	38 38 44 6 21 22 33 12 33 68 68 65 78 57 64 18 38 - - 25 32 - 9
Lab 2 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y Ba 206Pb 207Pb 208Pb Th U Hf * Cr Sr	Fragment 1 (mean (μg g-1) 0.008 2.27 0.041 0.35 0.74 0.36 2.14 0.62 14.6 6.56 38.1 12.9 125.1 21.7 172 0.048 - - 21.4 42.8 5935 1.34 0.060 -	n = 5) % RSD 14 30 44 47 36 71 23 26 35 35 34 46 34 33 26 39 - - 10 9 - 10 31	Fragment 2 mean (μg g-1) 0.015 1.41 0.043 0.23 0.62 0.27 1.69 0.37 6.03 2.73 15.6 4.32 60.5 9.28 133 0.026 - 18.5 80.8 5935 1.16 0.061	(n = 5) % RSD 51 10 67 49 32 26 47 12 18 15 16 13 5 22 3 33 - - - 14 15 - 9 32	Fragment 3 (mean (μg g-1) 0.008 0.92 0.038 0.30 0.47 0.18 1.83 0.35 4.10 1.83 0.35 4.10 1.83 11.9 3.20 42.7 6.75 124 0.058 - 12.7 79.7 5935 1.14	n = 5) % RSD 78 9 17 42 85 79 37 9 6 8 6 8 10 4 1 74 - - 6 17 - 8 52	All Frag. (n mean (μg g-1) 0.010 1.53 0.041 0.29 0.61 0.27 1.89 0.45 8.25 3.71 21.8 6.80 76.1 12.6 143 0.044 - - - 17.5 67.7 - 1.21 0.057	38 38 44 6 21 22 33 12 33 68 68 68 65 78 57 64 18 38 - - 25 32 - 9 10

Table 9.Reported trace element results from laser ablation ICP-MS analyses

Lab 3 Element	Fragment 1 (mean (µg g ⁻¹)	n = 5) % RSD	Fragment 2 mean (µg g ⁻¹)	(n = 5) % RSD	Fragment 3 (mean (μg g ⁻¹)	n = 5) % RSD	All Frag. (n = mean (μg g-1)	= 3) % RSD
La	0.004	117	0.014		0.005	20	0.008	72
Ce	2.34	3	2.32	5	2.52	3	2.39	5
Pr	0.014	6	0.014	29	0.008	76	0.012	27
Nd	0.14	42	0.21	39	0.25	64	0.20	27
Sm	0.41	23	0.35	39	0.45	19	0.41	12
Eu	0.21	13	0.17	42	0.20	29	0.20	10
Gd	2.28	16	1.69	7	2.09	11	2.02	15
Tb	0.85	6	0.67	6	0.81	8	0.78	12
Dy	11.8	2	10.2	6	11.4	2	11.1	8
Но	4.71	2	3.92	4	4.56	4	4.40	10
Er	25.0	3	21.5	3	24.0	3	23.5	8
Tm	6.79	3	5.90	3	6.63	5	6.44	7
Yb	73.7	2	63.3	4	70.2	4	69.1	8
Lu	12.7	3	11.4	2	12.6	3	12.2	6
Y	133	12	114	13	131	6	126	8
Ва	0.041	44	0.069	10	0.137	29	0.082	60
²⁰⁸ Pb	3.27	14	2.95	5	3.59	5	3.27	10
Th	28.9	4	24.7	8	29.1	4	27.6	9
U	74.6	12	71.1	7	83.9	4	76.5	9
Hf *	5649	-	5911	-	5340	-	5633	5
Sr	0.051	44	0.127	78	0.097	50	0.092	42
Nb	0.73	16	0.75	36	0.77	12	0.75	3
Lab 4 Element	Fragment 1 (mean (µg g-1)	n = 5) % RSD	Fragment 2 mean (μg g ⁻¹)	(n = 5) % RSD	Fragment 3 (mean (µg g-1)	n = 5) % RSD	All Frag. (n = mean (µg g-1)	= 3) % RSD
Lab 4 Element	Fragment 1 (mean (μg g ⁻¹) 0.0023	n = 5) % RSD	Fragment 2 mean (μg g ⁻¹) 0.0024	(n = 5) % RSD	Fragment 3 (mean (μg g ⁻¹) 0.0023	n = 5) % RSD	All Frag. (n = mean (μg g ⁻¹) 0.0023	= 3) % RSD
Lab 4 Element La Ce	Fragment 1 (mean (μg g ⁻¹) 0.0023 3.12	n = 5) % RSD 6 4	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84	(n = 5) % RSD 26 7	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58	n = 5) % RSD 15 5	All Frag. (n = mean (μg g-1) 0.0023 3.51	3) % RSD 3
Lab 4 Element La Ce Pr	Fragment 1 (mean (μg g ⁻¹) 0.0023 3.12 0.032	n = 5) % RSD 6 4 7	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033	(n = 5) % RSD 26 7 13	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033	n = 5) % RSD 15 5 17	All Frag. (n = mean (μg g-1) 0.0023 3.51 0.032	3 3 10 2
Lab 4 Element La Ce Pr Nd	Fragment 1 (mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44	n = 5) % RSD 6 4 7 9	Fragment 2 mean (µg g ⁻¹) 0.0024 3.84 0.033 0.49	(n = 5) % RSD 26 7 13 8	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49	n = 5) % RSD 15 5 17 13	All Frag. (n = mean (µg g-1) 0.0023 3.51 0.032 0.47	3 10 2 6
Lab 4 Element La Ce Pr Nd Sm	Fragment 1 (mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43	n = 5) % RSD 6 4 7 9 8	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57	(n = 5) % RSD 26 7 13 8 8 8	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54	n = 5) % RSD 15 5 17 13 10	All Frag. (n = mean (μg g-1) 0.0023 3.51 0.032 0.47 0.51	3 3 10 2 6 15
Lab 4 Element La Ce Pr Nd Sm Eu	Fragment 1 (mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19	n = 5) % RSD 6 4 7 9 8 12	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28	(n = 5) % RSD 26 7 13 8 8 8 9	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25	n = 5) % RSD 15 5 17 13 10 8	All Frag. (n = mean (μg g-1) 0.0023 3.51 0.032 0.47 0.51 0.24	3 3 10 2 6 15 18
Lab 4 Element La Ce Pr Nd Sm Eu Gd	Fragment 1 (mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00	n = 5) % RSD 6 4 7 9 8 12 5	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66	(n = 5) % RSD 26 7 13 8 8 9 5	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36	n = 5) % RSD 15 5 17 13 10 8 3	All Frag. (n = mean (μg g ⁻¹) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34	3 3 10 2 6 15 18 14
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb	Fragment 1 (mean (μg g ⁻¹) (0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77	n = 5) % RSD 6 4 7 9 8 12 5 4	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01	(n = 5) % RSD 26 7 13 8 8 8 9 5 7	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91	n = 5) % RSD 15 5 17 13 10 8 3 3 3	All Frag. (n = mean (μg g-1) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90	3 3 10 2 6 15 18 14 14
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy	Fragment 1 (mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8	n = 5) % RSD 6 4 7 9 8 12 5 4 3	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0	(n = 5) % RSD 26 7 13 8 8 8 9 5 7 4	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7	n = 5) % RSD 15 5 17 13 10 8 3 3 2	All Frag. (n = mean (μg g ⁻¹) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5	3 3 10 2 6 15 18 14 14 13
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho	Fragment 1 (mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8 4.34	n = 5) % RSD 6 4 7 9 8 12 5 4 3 3 3	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0 5.60	(n = 5) % RSD 26 7 13 8 8 8 9 5 7 4 4 4	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7 5.24	n = 5) % RSD 15 5 17 13 10 8 3 3 2 2	All Frag. (n ² mean (μg g ⁻¹) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5 5.06	3 3 10 2 6 15 18 14 14 13 13
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er	Fragment 1 (mean (μg g ⁻¹) (0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8 4.34 22.9	n = 5) % RSD 6 4 7 9 8 12 5 4 3 3 3 2	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0 5.60 29.6	(n = 5) % RSD 26 7 13 8 8 8 9 5 7 4 4 4 4	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7 5.24 2.73	n = 5) % RSD 15 5 17 13 10 8 3 3 2 2 2 1	All Frag. (n = mean (μg g-1) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5 5.06 26.6	3 3 10 2 6 15 18 14 14 13 13 13
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm	Fragment 1 (mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8 4.34 22.9 6.14	n = 5) % RSD 6 4 7 9 8 12 5 4 3 3 2 2 2	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0 5.60 29.6 7.96	(n = 5) % RSD 26 7 13 8 8 8 9 5 7 4 4 4 4 5	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7 5.24 27.3 7.36	n = 5) % RSD 15 5 17 13 10 8 3 3 2 2 2 1 3	All Frag. (n = mean (μg g ⁻¹) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5 5.06 26.6 7.15	3 3 10 2 6 15 18 14 14 13 13 13 13
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb	Fragment 1 (mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8 4.34 22.9 6.14 65.0	n = 5) % RSD 6 4 7 9 8 12 5 4 3 3 2 2 2 3	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0 5.60 29.6 7.96 82.8	(n = 5) % RSD 26 7 13 8 8 9 5 7 4 4 4 4 5 4	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7 5.24 27.3 7.36 76.4	n = 5) % RSD 15 5 17 13 10 8 3 3 2 2 1 3 3 3	All Frag. (n ² mean (μg g ⁻¹) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5 5.06 26.6 7.15 74.7	3 3 10 2 6 15 18 14 14 13 13 13 13 12
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu	Fragment 1 mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8 4.34 22.9 6.14 65.0 11.5	n = 5) % RSD 6 4 7 9 8 12 5 4 3 3 2 2 3 2 2 3 2	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0 5.60 29.6 7.96 82.8 14.8	(n = 5) % RSD 26 7 13 8 8 9 5 7 4 4 4 4 5 4 3	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7 5.24 27.3 7.36 76.4 13.7	n = 5) % RSD 15 5 17 13 10 8 3 2 2 2 1 3 3 3 1	All Frag. (n ² mean (μg g ⁻¹) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5 5.06 26.6 7.15 74.7 13.3	3 3 10 2 6 15 18 14 14 13 13 13 13 13 12 13
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y	Fragment 1 mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8 4.34 22.9 6.14 65.0 11.5 129	n = 5) % RSD 6 4 7 9 8 12 5 4 3 3 2 2 2 3 2 2 2 2	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0 5.60 29.6 7.96 82.8 14.8 161	(n = 5) % RSD 26 7 13 8 8 8 9 5 7 4 4 4 4 5 4 3 3 3	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7 5.24 27.3 7.36 76.4 13.7 148	n = 5) % RSD 15 5 17 13 10 8 3 3 2 2 1 3 3 1 3 1 1	All Frag. (n = mean (μg g ⁻¹) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5 5.06 26.6 7.15 74.7 13.3 146	3 3 10 2 6 15 18 14 14 13 13 13 13 12 13 11
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y Ba	Fragment 1 mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8 4.34 22.9 6.14 65.0 11.5 129 -	n = 5) % RSD 6 4 7 9 8 12 5 4 3 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 2 3 2 3 3 2 3	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0 5.60 29.6 7.96 82.8 14.8 161	(n = 5) % RSD 26 7 13 8 8 9 5 7 4 4 4 4 5 4 3 3 0	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7 5.24 27.3 7.36 76.4 13.7 148	n = 5) % RSD 15 5 17 13 10 8 3 3 2 2 1 3 3 1 1 1 1 -	All Frag. (n ² mean (μg g ⁻¹) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5 5.06 26.6 7.15 74.7 13.3 146 -	3 3 10 2 6 15 18 14 14 13 13 13 13 13 12 13 11 -
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y Ba 208Pb	Fragment 1 mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8 4.34 22.9 6.14 65.0 11.5 129 - 2.16	n = 5) % RSD 6 4 7 9 8 12 5 4 3 3 2 2 3 2 2 3 2 2 2 2 2 2 2 2 2 2 2	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0 5.60 29.6 7.96 82.8 14.8 161 - 2.48	(n = 5) % RSD 26 7 13 8 8 9 5 7 4 4 4 4 5 4 3 3 0 8	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7 5.24 27.3 7.36 76.4 13.7 148 - 2.32	n = 5) % RSD 15 5 17 13 10 8 3 10 8 3 2 2 1 3 3 2 2 1 3 3 1 1 1 7	All Frag. (n ² mean (μg g ⁻¹) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5 5.06 26.6 7.15 74.7 13.3 146 - 2.32	3 3 10 2 6 15 18 14 14 13 13 13 13 13 13 13 13 13 13
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y Ba 208Pb Th	Fragment 1 mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8 4.34 22.9 6.14 65.0 11.5 129 - 2.16 24.9	n = 5) % RSD 6 4 7 9 8 12 5 4 3 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 3 2 2 3 3 2 2 3 3 2 2 3 3 2 2 3 3 2 3 3 2 3 3 2 3 3 2 3	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0 5.60 29.6 7.96 82.8 14.8 161 - 2.48 34.0	(n = 5) % RSD 26 7 13 8 8 9 5 7 4 4 4 4 5 4 3 3 0 8 4 4	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7 5.24 27.3 7.36 76.4 13.7 148 - 2.32 30.7	n = 5) % RSD 15 5 17 13 10 8 3 3 2 2 1 3 3 2 2 1 3 3 1 1 1 - 7 3	All Frag. (n * mean (μg g-1) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5 5.06 26.6 7.15 74.7 13.3 146 - 2.32 29.9	3 3 10 2 6 15 18 14 14 13 13 13 13 13 13 13 13 13 13
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y Ba 208Pb Th U	Fragment 1 mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8 4.34 22.9 6.14 65.0 11.5 129 - 2.16 24.9 68.3	n = 5) % RSD 6 4 7 9 8 12 5 4 3 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 3 2 2 3 3 3 3	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0 5.60 29.6 7.96 82.8 14.8 161 - 2.48 34.0 92.4	(n = 5) % RSD 26 7 13 8 8 9 5 7 4 4 4 4 5 4 3 3 0 8 4 6	Fragment 3 (mean (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7 5.24 27.3 7.36 76.4 13.7 148 - 2.32 30.7 83.7	n = 5) % RSD 15 5 17 13 10 8 3 3 2 2 1 3 3 2 2 1 3 3 1 1 - 7 3 3 3	All Frag. (n ² mean (μg g ⁻¹) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5 5.06 26.6 7.15 74.7 13.3 146 - 2.32 29.9 81.5	3 3 10 2 6 15 18 14 14 13 13 13 13 13 13 13 13 13 13
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y Ba 208Pb Th U Hf *	Fragment 1 mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8 4.34 22.9 6.14 65.0 11.5 129 - 2.16 24.9 68.3 7000	n = 5) % RSD 6 4 7 9 8 12 5 4 3 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 3 2 2 3	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0 5.60 29.6 7.96 82.8 14.8 161 - 2.48 34.0 92.4 7000	(n = 5) % RSD 26 7 13 8 8 9 5 7 4 4 4 4 5 4 3 3 0 8 4 6 0	Fragment 3 (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7 5.24 27.3 7.36 76.4 13.7 148 - 2.32 30.7 83.7 7000	n = 5) % RSD 15 5 17 13 10 8 3 10 8 3 2 2 1 3 3 2 2 1 3 3 1 1 1 - 7 3 3 3 -	All Frag. (n ² mean (μg g ⁻¹) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5 5.06 26.6 7.15 74.7 13.3 146 - 2.32 29.9 81.5 -	3 3 10 2 6 15 18 14 14 13 13 13 13 13 13 13 13 13 13
Lab 4 Element La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Th U Y Ba 208Pb Th U Hf * Sr	Fragment 1 mean (μg g ⁻¹) 0.0023 3.12 0.032 0.44 0.43 0.19 2.00 0.77 10.8 4.34 22.9 6.14 65.0 11.5 129 - 2.16 24.9 68.3 7000 0.048	n = 5) % RSD 6 4 7 9 8 12 5 4 3 3 2 2 3 2 2 3 2 2 3 2 2 3 2 2 3 3 2 2 3 3 2 2 3 3 2 2 3 3 3 3 3 1 2 1 2	Fragment 2 mean (μg g ⁻¹) 0.0024 3.84 0.033 0.49 0.57 0.28 2.66 1.01 14.0 5.60 29.6 7.96 82.8 14.8 161 - 2.48 34.0 92.4 7000 0.051	(n = 5) % RSD 26 7 13 8 8 9 5 7 4 4 4 4 5 7 4 4 4 5 7 4 3 3 0 8 4 6 0 2	Fragment 3 (μg g ⁻¹) 0.0023 3.58 0.033 0.49 0.54 0.25 2.36 0.91 12.7 5.24 27.3 7.36 76.4 13.7 148 - 2.32 30.7 83.7 7000 0.051	n = 5) % RSD 15 5 17 13 10 8 3 10 8 3 2 2 1 3 3 2 2 1 3 3 1 1 - 7 3 3 5 1 1 1 - 7 3 3 5 1 1 1 5 17 13 10 8 3 12 15 17 13 10 8 3 12 15 17 13 10 10 8 10 10 10 10 10 10 10 10 10 10 10 10 10	All Frag. (n * mean (μg g-1) 0.0023 3.51 0.032 0.47 0.51 0.24 2.34 0.90 12.5 5.06 26.6 7.15 74.7 13.3 146 - 2.32 29.9 81.5 - -	3 % RSD 3 10 2 6 15 18 14 14 13 13 13 13 13 13 13 13 13 13

Table 9 (continued). Reported trace element results from laser ablation ICP-MS analyses



Table 9 (continued).Reported trace element results from laser ablation ICP-MS analyses

Lab 5 Element	Fragment 1 (mean (µg g-1)	n = 4) % RSD	Fragment 2 (mean (µg g ⁻¹)	n = 4) % RSD	Fragment 3 mean (µg g ⁻¹)	(n = 4) % RSD	Fragment 4 (mean (µg g-1)	n = 4) % RSD	All Frag. (n mean (µg g ⁻¹)	= 4) % RSD
La	< 0.039	-	< 0.056	-	< 0.058	-	0.005	-	0.005	-
Ce	2.59	6	2.28	6	2.61	16	2.27	10	2.43	8
Pr	0.012	12	0.011	13	0.009	16	0.010	7	0.010	13
Nd	0.22	4	0.24	23	0.25	46	0.20	19	0.23	10
Sm	0.44	20	0.47	15	0.49	23	0.41	10	0.45	8
Eυ	0.26	13	0.20	12	0.22	22	0.22	8	0.22	11
Gd	2.44	9	2.11	6	2.42	29	2.17	10	2.28	7
Tb	-	-	-	-	-	-	-	-	-	-
Dy	11.6	9	10.8	7	11.1	21	10.7	9	11.0	4
Ho	5.08	6	4.50	4	4.78	22	4.56	5	4.73	6
Er	24.7	7	22.8	3	24.0	19	23.1	8	23.6	4
Tm	-	-	-	-	-	-	-	-	-	-
Yb	77.0	12	67.3	4	72.9	20	68.2	8	71.4	6
Lu	13.0	5	12.1	6	13.0	20	12.4	3	12.6	4
Y	139	7	119	8	128	24	119	10	126	8
Ba	٥.08 ،	-	< 0.13	-	< 0.11	-	< 0.04	-	-	-
²⁰⁴ Pb	0.11	-	< 0.18	-	× 0.13	-	< 0.07	-	-	-
²⁰⁶ Pb	16.4	2	16.2	5	17.4	5	15.2	4	16.3	6
²⁰⁷ Pb	1.27	9	1.15	3	1.35	9	1.21	3	1.25	7
²⁰⁸ Pb	-	-	1.62	2	2.04	4	1.73	1	1.79	12
Th	29.7	3	28.0	4	31.1	19	29.2	5	29.5	4
U	92.4	13	81.3	13	94.6	17	82.5	8	87.7	8
Hf *	5900	-	5900	-	5900	-	5900	-	-	-
Sr	0.08	71	0.02	7	0.08	133	0.02	16	0.05	68
Nb	0.94	10	0.81	10	0.85	18	0.74	14	0.84	10
Ta	0.63	8	0.55	9	0.55	9	0.55	6	0.57	7
V	< 0.03	0	< 0.04	-	< 0.05	-	٥.03 ‹ 0	-	-	-
Co	< 0.04	0	٥.05 ‹ 0	-	٥.03 ‹ 0	-	< 0.03	-	-	-
Ni	0.07	52	٥.08 ›	-	0.08	-	< 0.07	-	0.07	3
Cu	0.19		< 0.17	-	٥.18 ،	-	< 0.13	-	0.19	-
Zn	1.2	6	1.1	17	2.1	106	2.1	29	1.6	34
Rb	0.06 ›	-	٥.06 ،	-	٥.08 ،	-	٥.06 ›	-	-	-

The quoted uncertainties for individual fragments (expressed in % RSD) reflect the observed scatter between the individual analyses. The quoted uncertainties for the individual laboratories reflects the observed scatter between the fragment means. * Hf concentrations assumed for internal calibration.



Figure 4. Chondrite-normalised plot for the LA-ICP-MS intercomparison data (chondrite values from Anders and Grevesse 1989). Element spacing is based on ionic radii.



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Element	La (µg g ⁻¹)	b 1 (% RSD)	La (µg g-1)	b 2 (% RSD)	Lal (µg g-1)	b 3 (% RSD)	Lak (µg g-1)	o 4 (% RSD)	Lab (μg g ⁻¹)	5 (% RSD)	Working (μg g ⁻¹)	g values (% RSD)
La	< 0.1	-	0.010	38	0.008	72	0.0023	3	0.005	-	0.006	54
Ce	2.86	14	1.53 *	44	2.39	5	3.51 *	10	2.43	8	2.56	10
Pr	٥.04 ،	-	0.041	6	0.012	27	0.032	2	0.010	13	0.024	63
Nd	0.26	29	0.29	21	0.20	27	0.47 *	6	0.23	10	0.24	16
Sm	0.52	26	0.61	22	0.41	12	0.51	15	0.45	8	0.50	15
Eu	0.26	25	0.27	33	0.20	10	0.24	18	0.22	11	0.24	12
Gd	2.52	25	1.89	12	2.02	15	2.34	14	2.28	7	2.21	11
Tb	0.90	23	0.45 *	33	0.78	12	0.90	14	-	-	0.86	8
Dy	12.4	20	8.25 *	68	11.1	8	12.5	13	11.0	4	11.8	7
Ho	5.19	19	3.71 *	68	4.40	10	5.06	13	4.73	6	4.84	7
Er	27.5	19	21.8	65	23.5	8	26.6	13	23.6	4	24.6	10
Tm	7.18	15	6.80	78	6.44	7	7.15	13			6.89	5
Yb	78.2	11	76.1	57	69.1	8	74.7	12	71.4	6	73.9	5
Lu	14.9	18	12.6	64	12.2	6	13.3	13	12.6	4	13.1	8
Y	159	21	143	18	126	8	146	11	126	8	140	10
Ва	-	-	0.044	38	0.082	60	-	-	-	-	0.06	43
²⁰⁶ Pb	13.4	20	-	-	-	-	-	-	16.3	6	14.9	14
²⁰⁷ Pb	1.14	14	-	-	-	-	-	-	1.25	7	1.19	7
²⁰⁸ Pb	1.74	12	-	-	3.27 *	10	2.32 *	7	1.79	12	1.76	2
Th	32.7	34	17.5 *	25	27.6	9	29.9	15	29.5	4	29.9	7
U	86.6	27	67.7	32	76.5	9	81.5	15	87.7	8	80.0	10
Sr	-	-	0.057	10	0.092 *	42	0.050	2	0.049	68	0.052	8
Nb	-	-	2.24 *	6	0.75	3	6.22 *	9	0.84	10	0.79	8

Table 10. Laboratory means and working values from laser ablation ICP-MS analyses

The working values reported here and their accompanying external precisions should be interpreted with caution when used for microanalytical applications due to the fact that some fragments/domains provided anomalous data. The quoted uncertainty for the working values reflect the observed scatter between the individual laboratories. See Table 9 for the results from the individual sample fragments. Working values for the REEs are plotted in Figure 7. Omitted from calculated mean for preferred values.

abundance elements. This is rather surprising given (1) the apparently anomalous fragments analysed by laboratories 1 and 2; (2) the within-fragment variability of up to ~ 10% found for the heavy REEs, Ce, Y, Pb, Th and U in most of the other grains; (3) the grain-tograin variability in the concentration of the internal standard element Hf observed by the EPMA intercomparison; and (4) the variety of calibration strategies employed. The consistency of results between laboratories suggests that as few as about fifteen laser spot analyses on three to four fragments of 91500 are able to average out the natural heterogeneities within and between individual fragments to < 10% for the highabundance elements. In this sense, 91500 would be a very good bulk reference sample for the highabundance trace elements in that only three or four fragments would need to be sampled in total in order to achieve consistent results. The use of 91500 as a microbeam reference sample for trace elements is more problematic, however, in that roughly one out of four fragments are significantly more heterogeneous than others and a similar proportion have anomalous concentrations of trace elements. By pre-screening the fragments to avoid material possessing strong CL banding (such as illustrated in fragment 2 of Figure 3), it may be possible to avoid the more "chemically anomalous" domains.

Working values and procedures for data acquisition

The working values for the REEs and other trace elements contents in 91500 as determined by laser ablation ICP-MS are given in Table 10 and are shown in Figure 4. These values have been calculated by pooling the mean concentration values for each of sixteen fragments of 91500 which were investigated by ICP-MS; some outlier values were excluded. The working values given here for the heavy REE, Th and U tend to be greater than previous laser ablation ICP-MS results reported for 91500 by Garbe-Schönberg and Arpe (1997). Our results are, however, within 10% of the values for 91500 given by Nesbitt et al. (1997) for all REEs except La, Ce and Pr, which tend to be higher here. The working values reported in Table 10 for Lu (13.1 μg g⁻¹), Th (29.9 μg g⁻¹) and U (80.0 μg g⁻¹) are in very good agreement with the isotope dilution values of Wiedenbeck et al. (1995) for these elements



(Lu = 12 μ g g⁻¹, Th = 28.6 μ g g⁻¹, U = 81.2 μ g g⁻¹). With regards to the LA-ICP-MS determined Pb concentration of the 91500 crystal, data were submitted by four of the five participating laboratories. Laboratories 1 and 5 provided measurements of all three radiogenic Pb isotopes and all laboratories calibrated their procedures using reference samples (either NIST SRM 610-614 or TB-1 basalt) containing Pb with a different isotopic composition than that in 91500. Laboratory 1 corrected for the difference in isotopic compositions by assuming values for the isotopic composition of the Pb in the calibrant and unknown. Using an alternative approach, laboratory 5 summed the counts for all of the Pb isotopes in the calibrant, then calculated a sensitivity factor for the total radiogenic Pb, and finally applied this factor to the count rates measured for each radiogenic isotope in 91500. These two approaches vielded similar results (Table 10), though the data reported by the two laboratories for ²⁰⁶Pb do diverge somewhat more from values seen for other elements at similar concentration levels.

The consistency of results generated by the various laser ablation ICP-MS procedures employed by the five participating laboratories indicates that there are several calibration and data acquisition protocols that are entirely suitable for analysis of the 91500 zircon. The choice of which analytical procedure is "best" for a particular ICP-MS-laser hardware combination is most appropriately made by the analyst familiar with the performance of the particular equipment. The greatest uncertainty in the use of 91500 zircon as a microbeam calibration material for trace elements is in knowing, a priori, the composition and degree of homogeneity of the particular fragment to be analysed. In view of the variations observed both by ICP-MS and by scanning electron imaging (Figure 1), it would seem prudent that any fragment of 91500 that is to be used for quality assurance purposes or for verifying microanalytical procedures should first be investigated using CL and BSE imaging. In view of the now detected micro-scale heterogeneities in 91500, using this sample for calibrating absolute concentration measurements may be unwise, unless a large number of domains are analysed in order to average out the variations in the sample.

SIMS trace element intercomparison

Five SIMS laboratories participated in the 91500 intercomparison programme (Table 1). A summary of the instrument parameters and analytical routines used by each laboratory is presented in Table 11. Laboratories 1, 2 and 4 used large geometry SIMS instruments operating at a variety of mass resolving powers. Laboratory 4 used extremely high mass resolution (M/ Δ M \approx 9300 at 1% valley) for all species with no energy offset being applied. Laboratories 1 and 2 used high mass resolution (M/ Δ M \approx 4000 at 10% valley) combined with moderate energy offsets. This mass resolution was sufficient to resolve La, Ce and Pr from the interfering matrix Zr-Si-O species while the energy offset was used to eliminate molecular interferences such as light REE oxides on middle/heavy REE that cannot be resolved at $M/\Delta M \approx 4000$. Laboratory 2 also used a hybrid multi-collector measurement at $M/\Delta M \approx 4000$ for the light REE (La, Ce, Pr, Nd, Sm, Eu) with a lower resolution (ca. 1300) energy-filtered mono-collection routine for the rest of the REE. Laboratories 3 and 5 used small geometry SIMS instruments operating at low mass resolution with large energy offsets to deal with molecular interferences. Four of the laboratories (laboratories 1, 2, 3 and 5) used NIST SRM 610 as the calibration reference as requested in the instructions to participating laboratories, while laboratory 4 used its own in-house zircon reference calibrant.

Instructions to participating laboratories

Participating SIMS laboratories were asked to provide a full set of concentration data for REEs (La - Lu) as well as Y and Hf. In order to make the data from different laboratories directly comparable, all measurements were to be calibrated against the NIST SRM 610 glass using the recommended values of Pearce et al. (1997). The data were to be collected using the "normal" analytical parameter of the individual laboratory (i.e., offset, counting times, number of cycles) and these values were to be stated in the data report. In addition to the REEs, laboratories were requested to submit data for any other trace element that they might be able to measure (e.g., P, Sc), although this was of secondary importance to this study. For each class of analysis (e.g., if the laboratory was running the REEs + Y + Hf separate from other trace elements) the analyst were asked to make five, randomly located spot analyses on a single chip and to repeat these measurements on a total of three different sample chips.

Variations between fragments

Table 12 presents analytical data from each of the laboratories as averages of the analysed chips along with grand averages of the complete data sets. For

	•													
Lab	number		-			2			3		4		5	
Prime specie currer spot s	ary beam es nt (nA) size (µm)		160 ⁻ 6 25			16O ₂ 6 30			160 ⁻ 40 35		1602 ⁻ 15 43		160 ⁻ 10 25	
Secoi mass energ callib cycles	ndary beam resolution (M/∆M) jy window (eV) rant material	2	3500 50 4IST SRM 610 10		۲ SI Z	4200/ 1300 [⊲] 30 5T SRM 610 6		Ĺ	350 50 4IST SRM 610 10		9300b wide open zircon 7	Ż	600 40 57 SRM 610 5	
Anal) La	ytical parameters	lsotope ^c 139	offset (V) -60	count (s) 10	lsotope ^c 139	offset (V) -45	count (s) 60	lsotope 139	offset (V) -125	count (s) 30	Isotope	Isotope^c 139 (ZrSiO)	offset (V) -120	count (s) 10 - 15
P Ce		140 141	09- 09-	4 0	140 141	-45 -45	60 60	140 141	-125 -125	20 30	140 141	140 (ZrSiO) 141 (ZrSiO)	-120 -120	2 - 5 10 - 15
РЧ		145	-60	10	144 (Sm)	-45	09	146	-125	30	145/146	143 (ZrSiO)	-120	5 - 8
Sm E.		147 15-2	09-	0	152 153	-45	09	147 151 / 152	-125	20	147/149 147/149	149	-120	5 - 8
2 PO		157 (PrO)	09-	5 4	160 (Dy)	-85	20	157	-125	20/20	155/157	157 (PrO)	- 120	2 - -
Ъ ^р		159	-60	4	159	-65	15	159	-125	20	159	159 (NdO)	-120	5
6		163 17 E	-60	2 0	161 17. E	-85	15	161/163 125	-125	20/20	161/163	161 (NdO)	-120	3 - 5 - 5
е т		col 167	09-	7 7	co1	co- 29-	5	col 991	-125	10	col 166/167	col 167	-120 -120	ω - 4 4 - 4
ш		169	-60	2	169	-65	8	169	-125	10	169	169	-120	2 - 4
ď		172	-60	2	172	-65	4	172/173	-125	10/10	171/172	171	- 120	2 - 3
Ŀ		175	-60	2	175	-65	9	175	-125	10	175	175	-120	2 - 3
≻		89	-60	-	89	-65	4	·	ı	,		89 (178Hf2+)	-120	5
Ŧ		178	-60	-	180	-85	30	178	-125	2		177	-120	c
σ_	Laboratory 2 utilized	a hybrid multi	i- and mono-c	ollection meth	od with higher	mass resoluti	on used in th	e multi-collecti	on sub-group	of La, Ce, Pr, h	Ad, Sm and Eu.			
م	Laboratory 4 defined	mass resolutio	on using a 1%	valley; other	laboratories us	ied a 10% val	ley definition	-						
	Species in parenthesu	s in the isotop.	e column indic	ate tor which	intertering spe-	cies peak-strip	ping was pe	rtormed.						

Table 11. Basic instrument parameters used by participating SIMS laboratories for trace element analysis

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Lab 1 Element	Fragment 1 (mean (µg g ⁻¹)	n = 5) % RSD	Fragment 2 mean (μg g ⁻¹)	(n = 5) % RSD	Fragment 3 (mean (µg g ⁻¹)	n = 5) % RSD	All fragments (mean (µg g ⁻¹)	(n = 3) % RSD			
La	0.017	61	0.023	34	0.042	66	0.027	48			
Ce	2.72	6	2.38	0.4	2.57	5	2.56	7			
Pr	0.022	43	0.024	31	0.033	31	0.026	22			
Nd	0.23	43	0.17	24	0.26	9	0.22	19			
Sm	0.38	12	0.35	15	0.41	7	0.38	8			
Eu	0.20	13	0.17	7	0.21	3	0.19	12			
Gd	1.84	16	1.34	6	1.60	16	1.59	16			
Tb	0.81	7	0.69	3	0.84	7	0.78	10			
Dy	10.4	4	9.1	5	10.2	5	9.9	7			
Ho	4.45	5	3.92	4	4.41	6	4.26	7			
Er	22.8	4	19.3	3	22.2	3	21.4	9			
Tm	6.04	5	5.13	4	5.84	5	5.67	8			
Yb	59.1	5	51.0	2	57.3	1	55.8	8			
Lu	13.4	9	11.5	2	12.9	4	12.6	8			
Υ	145	3	126	2	141	1	137	7			
Hf	5691	4	5602	2	5603	2	5632	1			
Lab 2 Element	Fragment 1 (mean (µg g-1)	n = 5) % RSD	Fragment 2 mean (μg g ⁻¹)	(n = 5) % RSD	Fragment 3 (mean (µg g-1)	n = 3) % RSD	All fragments (mean (µg g-1)	(n = 3) % RSD			
La	0.0017	61	0.0022	133	0.0011	41	0.0016	35			
Ce	2.15	11	2.24	9	2.93	4	2.44	18			
Pr	0.011	13	0.012	19	0.015	2	0.013	16			
Nd	0.23	11	0.23	9	0.22	17	0.23	5			
Sm	0.40	11	0.41	8	0.44	5	0.41	5			
Eu	0.20	13	0.20	9	0.21	6	0.20	4			
Gd	2.07	7	1.76	11	1.90	6	1.91	8			
Tb	0.88	3	0.88	5	0.84	5	0.87	3			
Dy	11.2	4	11.0	5	11.2	3	11.2	1			
Ho	4.94	4	4.75	9	4.91	2	4.87	2			
Er	26.0	2	26.1	2	26.3	1	26.1	0.5			
Tm	6.76	2	6.57	2	6.65	2	6.66	1			
Yb	70.8	5	74.4	2	64.6	4	69.9	7			
Lu	16.8	3	17.3	5	15.6	3	16.5	5			
Y	164	3	155	2	167	4	162	4			
Hf	6895	6	7353	4	6975	5	7074	3			
Lab 3 Element	Fragment 1 (mean (µg g-1)	n = 5) % RSD	Fragment 2 mean (μg g-1)	(n = 5) % RSD	Fragment 3 (mean (µg g-1)	n = 5) % RSD	All fragments (mean (µg g-1)	(n = 3) % RSD			
La	0.021	70	0.017	33	0.015	23	0.018	17			
Ce	2.47	5	2.29	6	2.42	6	2.39	4			
Pr	0.016	30	0.017	47	0.016	29	0.016	4			
Nd	0.23	20	0.21	17	0.24	5	0.23	6			
Sm	0.37	8	0.30	14	0.34	19	0.34	10			
Eu	0.17	12	0.15	11	0.19	11	0.17	11			
Gd	1.41	6	1.19	4	1.39	7	1.33	9			
Tb	0.77	4	0.67	5	0.78	4	0.74	8			
Dy	9.9	6	8.9	4	9.6	5	9.5	5			
Ho	4.27	4	3.89	2	4.24	4	4.13	5			
Er	22.7	5	20.6	2	22.5	4	21.9	5			
Tm	5.66	4	5.25	2	5.63	4	5.51	4			
Yb	53.2	3	49.3	3	52.8	6	51.8	4			
Lu	12.9	4	11.9	3	13.0	6	12.6	5			
Y	-	-	-	-	-	-	-	-			
Hf	6059	2	6416	1	6287	1	6254	3			

Table 12.Reported trace element concentrations from SIMS intercomparison

Lab 4 Element	Fragment 1 (mean (μg g ⁻¹)	(n = 5) % RSD	Fragment 2 mean (µg g ⁻¹)	(n = 4) % RSD	Fragment 3 mean (µg g ⁻¹)	(n = 5) % RSD	All fragments (mean (μg g-1)	n = 3) % RSD
La	0.0035	28	0.0027	31	0.0021	30	0.0028	26
Ce	6.93	21	7.91	8	4.93	16	6.59	23
Pr	0.04	13	0.022	21	0.011	16	0.025	59
Nd	0.43	11	0.37	23	0.21	18	0.34	33
Sm	0.22	5	0.22	14	0.14	11	0.19	25
Eυ	0.20	10	0.21	9	0.11	16	0.18	30
Gd	1.34	12	1.29	5	0.94	9	1.19	18
Tb	0.69	8	0.66	5	0.48	8	0.61	19
Dy	10.7	8	10.6	3	7.7	6	9.7	18
Ho	3.92	9	3.83	3	2.85	6	3.54	17
Er	24.7	8	24.4	4	17.6	7	22.2	18
Tm	5.68	8	5.66	4	4.10	6	5.15	18
Yb	60.4	7	60.8	4	43.9	7	55.0	18
Lu	14.2	20	15.6	5	11.4	7	13.7	15
Y	-	-	-	-	-	-	-	-
Hf	-	-	-	-	-	-	-	-
Lab 5 Element	Fragment 1 (mean (μg g ⁻¹)	(n = 4) % RSD	Fragment 2 mean (µg g-1)	(n = 3) % RSD	Fragment 3 mean (µg g-1)	(n = 3) % RSD	All fragments (mean (μg g-1)	n = 3) % RSD
La	0.012	13	0.012	83	0.016	66	0.013	15
Ce	2.84	3	2.92	4	2.82	5	2.86	2
Pr	0.019	18	0.017	67	0.026	70	0.021	24
Nd	0.25	45	0.19	23	0.32	49	0.25	26
Sm	0.33	35	0.40	7	0.40	39	0.38	10
Eυ	0.23	11	0.22	13	0.23	25	0.22	3
Gd	2.05	10	2.23	3	2.35	16	2.21	7
Tb	0.96	12	0.88	2	0.91	3	0.91	4
Dy	11.0	3	11.6	3	11.4	10	11.3	3
Ho	5.06	2	5.27	1	5.07	7	5.13	2
Er	26.6	3	26.5	6	27.7	8	26.9	2
Tm	6.77	2	6.90	2	6.57	4	6.75	2
Yb	69.3	4	68.2	4	66.9	7	68.1	2
Lu	14.9	5	15.5	1	15.0	4	15.1	2
Y	162	3	155	1	161	5	159	3
Hf	5875	2	6254	1	5523	2	5884	6
Th	32.8	5	31.1	1	32.0	8	31.9	3
U	101	4	97	2	96	6	98	3

Table 12 (continued).Reported trace element concentrations from SIMS intercomparison

comparative purposes, the REE data are plotted on a chondrite-normalised diagram (Figure 5). Most of the SIMS laboratories taking part in this study detected only modest inter-grain variations in trace-element concentrations (Table 12 and Figure 5). With regard to the more abundant elements, the observed relative standard deviations closely matched the relative standard deviation of the individual fragment means (in both cases, generally 5-10%), although in some cases the observed differences between fragments do somewhat exceed the quoted precisions (e.g., low Yb value for fragment 3 of laboratory 2). The only major exception to this consistency were the data from laboratory 4 fragment 3, which showed systematically lower concentrations across the entire REE as compared to the other two fragments analysed by the same laboratory. In the absence of CL images of the analysed fragments, it is not possible to distinguish between real heterogeneity at the fragment scale and a potential analytical problem. The increased dispersion in data for the least abundant LREE (especially La and Pr) is reflected by much higher uncertainties on the means of the individual fragments. However, as with the more abundant elements, there appears to be little support in these data for gross heterogeneities at the SIMS sampling scale.





Figure 5. Chondrite-normalised plots for the SIMS intercomparison data. The light grey lines indicate the individual measurements. The lower right panel provides a summary of the mean results for each of the five participating laboratories.

Variations between laboratories

The overall mean of the REE analyses from each of the laboratories are also presented in Table 13 and Figure 5. Although each laboratory has been able to produce internally coherent data from the analysed chips of 91500, it is clear that considerable interlaboratory bias exists. These variations are more clearly illustrated in Figure 6 where the data from four of the participating SIMS laboratories have been normalised to that from laboratory 2 which produced the lowest light REE concentrations. In general, all laboratories generated sub-parallel patterns over the middle to heavy REE (Sm - Lu), though the data from laboratory 4 showed more scatter and did not reproduce the small negative Eu anomaly visible in the other data sets.

. .	, Lal	6 1 (2, 252)	, Lak	2 2	, Lab		, Lak	5 4 (0, 200)	, Lak	5	Working ve	alues SIMS	LA-ICP-	MS S	Simple
Element	(1-6 6ri)	(W KSU)	(6 6 n)	(% KSU)	(1-6 6n)	(UCX %)	(1-6 6n)	(UCX %)	(1-6 6n)	(UCX %)	(1-6 6nl)	(WS KSU)) (1-6 6n)	(UCX %	mean ∓
La	0.027	48	0.002	35	0.018	17	0.003	26	0.013	15	0.013	85	0.006	54	0.009
Ce	2.56	7	2.44	18	2.39	4	6.59 *	23	2.86	2	2.56	ω	2.56	10	2.56
Pr	0.026	22	0.013	16	0.016	4	0.025	59	0.021	24	0.020	28	0.024	63	0.022
PN	0.22	19	0.23	5	0.23	9	0.34	33	0.25	26	0.25	19	0.24	16	0.25
Sm	0.38	8	0.41	5	0.34	Q	0.19 *	25	0.38	10	0.38	8	0.50	15	0.44
Eu	0.19	12	0.20	4	0.17	Ξ	0.18	30	0.22	ю	0.19	11	0.24	12	0.22
Gd	1.59	16	1.91	8	1.33	6	1.19 *	18	2.21	7	1.76	22	2.21	Ξ	1.99
Tb	0.78	10	0.87	e	0.74	8	0.61	19	0.91	4	0.78	15	0.86	8	0.82
Dy	06.6	7	11.2	-	9.46	5	9.65	18	11.3	с	10.3	6	11.8	7	1.11
Но	4.26	7	4.87	2	4.13	5	3.54 *	17	5.13	2	4.60	10	4.84	7	4.72
Er	21.4	6	26.1	0	21.9	5	22.2	18	26.9	2	23.7	1	24.6	10	24.2
Tm	5.67	8	6.66	-	5.51	4	5.15	18	6.75	2	5.95	12	6.89	5	6.42
Yb	55.8	8	6.69	7	51.8	4	55.0	18	68.1	2	60.1	14	73.9	5	67.0
Lu	12.6	ø	16.5	5	12.6	5	13.7	15	15.1	2	14.1	12	13.1	8	13.6
×	137	7	162	4	'	ı	,		159	e	153	6	140	10	147
Ξ	5632	-	7074 *	S	6254	ю	,	,	5884	9	5923	5		,	,
						

Laboratory means and working values from SIMS analyses

Table 13.

The working values reported here and their accompanying external precisions should be interpreted with caution when used for microanalytical applications due to the fact that some fragmants/domains provided anomalous data. See Table 12 for the results from the individual sample fragments. Working values are plotted in Figure 7. The quoted uncertainty for the working values reflects the observed scatter between the individual laboratories. Laboratory 3 did not measure Y, and laboratory 4 did not measure Y or Hf, and are thus denoted by dashes in the above table.

Outlier values omitted from calculated working value.

*

Working values from LA-ICP-MS data set copied from Table 10.
Simple mean of SIMS and LA-ICP-MS working values (in µg g⁻¹)

Simple mean of SIMS and LA-ICP-MS working values (in µg g-1). No attempt has been made to assign uncertainties to these values.



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Figure 6. Comparison of the REE results from the five participating SIMS laboratories. The ordinate axis gives the mean measured concentration by the individual laboratories divided by the value obtained by laboratory 2.

Laboratories 2 and 5 reported similar concentrations of mid- to heavy REE that were *ca.* 30% higher than the other three laboratories and also reported similarly higher levels of Y (Table 12). The source of these differences is unclear at this time.

With regard to the light REE (La - Nd), there was considerably more variation between laboratories with reported La concentrations ranging over more than an order of magnitude (Figures 5 and 6). Two factors can be considered that might result in systematically high light REE determinations, particular for La and Pr, which are very depleted in zircon. The first possibility, a contribution of the matrix species Zr-Si-O to La, Ce and Pr, applies only to laboratories 3 and 5, which used small geometry SIMS instruments and therefore relied solely on energy filtering and (laboratory 5) on peak stripping of Zr-Si-O species. Underestimation of this interference potentially could result in erroneously high concentrations. Laboratories 1, 2 and 4 utilised high mass resolution, that should adequately resolve this matrix peak interference. A second possibility common to all participating laboratories concerns the detection limit of digital ion counting systems. Typically, La and Pr signals are less than a few tens of counts per minute in 91500 and may be adversely affected by high background levels on the electron multiplier. For example, assuming an intensity of 30 Si of ~ 10^5 cps with moderate energy filtering, a background level of 0.01 cps corresponds to ca. 0.002 µg g⁻¹ (0.009 x chondrite) La and 0.003 μ g g⁻¹ (0.03 x chondrite) Pr, and so it is clearly essential to obtain low background levels to avoid a systematic over-estimate for these low abundance elements.

The results for the light REE concentrations indicate that analytical factors are more influential than crystal heterogeneity. As such, 91500 has more utility as a quality control sample for SIMS analytical methodology than as an actual primary calibrant. A zircon for the latter purpose ideally should be at least an order of magnitude more enriched in the light REEs. As such, 91500 is only well suited for assessing the presence of significant isobaric interferences or detector dark noise on the light REEs.

Comparison between ICP-MS and SIMS

It is also worthwhile to compare the ICP-MS and the SIMS working values (Table 13 and Figure 7). With the exception of only La, which has a high percent relative standard deviation in both data sets due to its low abundance, all of the REEs as well as Y from the two data sets are within 25%. Taking the quoted precisions for both sets of working values into account reveals that for all of the REEs, including La and also Y, the determined concentration values for the two methods are identical to within 1.5s. In other words, the two data sets are remarkably similar. The only apparent difference between the laser ablation and the SIMS results is that SIMS seems to give consistently lower concentration values across the entire mid-REE spectrum (Figure 7 bottom). Whether this is a systematic difference inherent between the two analytical approaches is difficult to say due to the relatively small number of laboratories that contributed to this study. In any event, it appears that any differences between techniques are no more severe than the differences that one might expect between independent laboratories





Figure 7. Chondrite-normalised diagram of both the LA-ICP-MS and SIMS working values (upper panel) and plot of the ratio between the two sets of working values as a function of REE (lower panel). See Tables 10 and 13 for data.

using the same analytical technique. This is an important result for SIMS, as it demonstrates that no significant matrix-induced differences in the ion yields exist between zircon and the NIST SRM 610 reference sample used by most of the SIMS laboratories. The simple mean of the SIMS and LA-ICP-MS data sets for the fourteen REEs and Y are also given in Table 13, and we recommend that these concentration values should be used for future technique development work or when this sample is used as a secondary reference sample for quality assurance purposes.

Oxygen isotope intercomparison

Seven laboratories participated in the laser fluorination analysis of the oxygen isotope ratio in 91500 (Table 1). Details of the analytical methods vary, but are similar to those discussed by Sharp (1992) and Valley *et al.* (1995). All laboratories used IR lasers ($\lambda = 10.6 \mu m$) for heating during fluorination and extraction of oxygen. The laser powers ranged from 16 to 52 watts. Six laboratories used BrF₅ as the fluorinating reagent and one used F₂. Four laboratories analysed the oxygen isotope ratio as O₂, while the other three converted O₂ to CO₂.

Instructions to participating laboratories

Participating laser fluorination laboratories were asked to determine both the δ^{18} O of zircon 91500 as well as the fractionation between the zircon and

UWG-2, a homogeneous garnet reference sample that has been analysed extensively (Valley et al. 1995). Each participant in this part of the study received ca. 100 mg of zircon 91500 and ~ 125 mg of UWG-2 for analysis. The recommended value for UWG-2 is $\delta^{18}\text{O}$ = +5.8‰ SMOW (Valley et al. 1995). Each laboratory was requested to analyse between four and ten ~ 2 mg aliquots of zircon 91500 as well as UWG-2 during a single analysis session, along with the internal standards commonly analysed by the specific laboratory. Data reporting was to indicate which reference samples were run, the weight of the mineral separate analysed and the number of micromoles of CO_2 or O_2 evolved from each sample. We suggested that a modestly defocused beam (~ 1 mm diameter) should be used during lasing of UWG-2 and 91500, beginning at low power and increasing power during lasing. Participants were asked to analyse these materials at the grain size provided (i.e., that the laboratories should not regrind the samples). To help compare interlaboratory results, laboratories were asked to report the approximate spot size and wattage of their laser, the percentage of total power used during the laser fluorination and the wavelength of the laser used.

Oxygen isotope data acquisition and reporting

Fifty-two aliquots of 91500 were analysed with forty-eight aliquots of the garnet reference sample



Table 14. Determined $\delta^{18}\text{O}$ values for garnet UWG-2 and zircon 91500

Lab Number	Day	Reagent	Mass Spec.	Gas	δ ¹⁸ O * UWG-2	Ν	δ ¹⁸ O * 91500	Ν	δ ¹⁸ Ο (91500-UWG-2)	δ ¹⁸ O ** 91500 _(UWG-2)
1	1	BrF ₅	251	CO ₂	5.56 ± 0.02	3	9.74 ± 0.06	7	4.18	9.98
	2			-	5.55 ± 0.11	3	9.78	1	4.23	10.03
2	1	BrF ₅	252 & Ds	CO ₂	5.80 ± 0.09	2	9.78 ± 0.13	3	3.98	9.78
	2			_	5.80 ± 0.04	2	9.89 ± 0.10	3	4.09	9.89
	3				5.80 ± 0.04	2	10.03 ± 0.04	2	4.23	10.03
3	1	BrF ₅	D+	0 ₂	5.83 ± 0.10	10	10.00 ± 0.11	10	4.17	9.97
4	1	BrF ₅	Prism 3	02	5.79	1	9.76	1	3.97	9.77
	2			_	5.60 ± 0.01	2	9.74 ± 0.10	3	4.14	9.94
	3				5.61 ± 0.16	4	9.80 ± 0.02	3	4.19	9.99
5	1	F ₂	252	0 ₂	5.72 ± 0.09	6	9.92 ± 0.04	5	4.20	10.00
	2	-		-	5.88 ± 0.01	2	9.88 ± 0.01	2	4.00	9.80
6	1	BrF ₅	251	0 ₂	5.67 ± 0.02	5	9.80 ± 0.07	5	4.13	9.93
7	1	BrF ₅	251	CO ₂	5.80 ± 0.02	6	10.07 ± 0.03	7	4.27	10.07
			simple mean (n	= 13)	5.72		9.86		4.14	9.94
			1 s absolute		0.11		0.11		0.10	0.10

Mass spectrometers: 251, 252, D+, Ds and Prosm 3 indicate Finnigan MAT/251, MAT/252, Delta plus, Delta-s and Micromass Prism III, respectively. All uncertainties are 1s.

* Values referenced to SMOW $\delta^{18}O = 0\%$.

** δ^{18} O of zircon 91500 based on the assigned values for UWG-2 of δ^{18} O = +5.80‰.

UWG-2 (Valley et al. 1995) on a total of 13 days by the seven laboratories. The megacryst zircon 91500 and UWG-2 both behaved similarly during laser fluorination. Neither "jumped" excessively during heating, so the fractionation between 91500 and UWG-2 should not be biased by differences in lasing technique between analysts in different laboratories. Quartz is more difficult to analyse by laser fluorination and is more sensitive to the power of the laser used than garnet (see Spicuzza et al. 1998), so NBS-28 was not used in this study. UWG-2 is well-characterised with respect to homogeneity and isotope ratio, and has been distributed to sixty-six laboratories world-wide as an oxygen isotope standard. Sample masses for 91500 and UWG-2 ranged from ~ 1.0 to 2.5 mg, and were typically ~ 1.5 mg. These data indicated no systematic variations in measured oxygen isotope ratio and no correlation was seen with differences in laser, reagent, sample size, analysis gas, or mass spectrometer model.

Table 14 reports the measured δ^{18} O values for 91500 and UWG-2. Because of between-laboratory differences in normalisation procedures, UWG-2 was used as a common reference. For the seven laboratories, the fractionation between 91500 and UWG-2, denoted as Δ (91500 - UWG-2), covered a total range of 0.3%. Averaging the fractionation from each of the laboratories (n = 7) yields Δ (91500 - UWG-2) = 4.15 \pm 0.07‰ (1*s*). Note that some laboratories analysed 91500 and UWG-2 on more than one day, and these different analysis days can also be treated separately. Averaging the fractionation between 91500 and UWG-2 over the 13 analysis-days in Table 14 yields Δ (91500 - UWG-2) = 4.14 ± 0.10‰ (1*s*). The fact that the 1*s* value for the SMOW calibrated absolute δ ¹⁸O values of both UWG-2 and 91500 are equivalent to the 1*s* observed for the population of Δ (91500 - UWG-2) implies that systematic bias existed between laboratories, though any such bias was clearly small in magnitude.

Oxygen isotope discussion

The degree of agreement between the UWG-2 and 91500 results was excellent given the differences in techniques between different analysts in different laboratories. Taken in the light of the reported precisions, no evidence for δ^{18} O heterogeneity at the mg sampling size has been found in 91500. No subset of laboratories dominated this average; a weighted average of Δ (91500 - UWG-2) based on the number of samples analysed in each session yields Δ (91500 -UWG-2) = 4.17‰. If the daily average in UWG-2 is compared to the fifty-two analyses of 91500 individually, then an average value of Δ (91500 - UWG-2) = 4.15‰ is obtained. The only systematic variability detected between laboratories is that the measurements of reproducibility in analysis of 91500 correlate



weakly with Δ (91500 - UWG-2), with more precise measurements showing a very slight tendency towards larger differences between the two samples (Table 14). A single laboratory (laboratory 1) reported values for both UWG-2 and 91500 that were at the low end of the data sets for both samples. However, because of the small size of this data set as a whole, it cannot be concluded that laboratory 1 showed a systematic bias in its results.

Small differences in gas chemistry, mass spectrometry and standardisation procedures could potentially cloud the direct comparison of the oxygen isotope ratios reported by the seven laboratories. The reported data, however, demonstrate that any such bias must have been small; the mean value for UWG-2 differed from the assigned value (Valley et al. 1995) by only -0.08‰, which is well within statistical uncertainty. Using the isotopic values for UWG-2 measured during the same analytical session to correct the measurements of 91500 results in no better clustering of the data (Table 14): the standard deviation of the data population is essentially the same with or without this correction. However, the one laboratory that tended towards low values for both the garnet and the zircon falls closer to the midpoint of the population after the correction is applied.

Preferred $\delta^{18}O$ value

The laser fluorination data thus provide two δ^{18} O values for 91500, either the mean 9.86 ± 0.11‰ based on the directly reported isotopic values or 9.94 ± 0.10‰ based on correcting the data for the assigned value of the UWG-2 garnet reference sample. The difference between these two values is small; based on their assigned uncertainties, they are identical. Because the first of these values is not linked to the NBS-28 quartz sample, the value of δ^{18} O = +9.86 ± 0.11‰ (1*s*) SMOW is assigned to the 91500 zircon. This result is in excellent agreement with the independently determined, but less precise SIMS result reported earlier (Table 4).

No evidence of sample heterogeneity was found at the ~ 1 mg sampling scale. Likewise, the fifteen SIMS oxygen isotope analyses reported earlier (Table 4) show no significant variation at the 20 μ m x 20 μ m sampling size distributed over 400 μ m² large regions on three random fragments. Existing oxygen data thus indicate that this sample is homogeneous at both the micro- and mesoscopic scales. However, it would be prudent for future users of this sample for microanalytical applications to remain wary of the banding which has been observed in CL images (Figures 1 and 3) as we have not been able to address whether such features affect the δ^{18} O systematics of this sample. One final note of caution for researchers who wish to use 91500 for calibrating SIMS oxygen isotope analyses, namely that the HfO₂ \approx 0.7% m/m of 91500 may make this sample less than ideal for calibrating analyses on Hf rich samples due to the slight dependence of oxygen instrumental mass fractionation on the Hf content of a sample (Peck *et al.* 2001).

Discussion: Hf concentration

At this point it is appropriate to discuss briefly the hafnium concentration data which are available for zircon 91500. Both EPMA and SIMS data from single laboratories indicate that there is some genuine heterogeneity in the Hf content of 91500 at the microanalytical scale (e.g., Table 3). However, this observed variability does not seem to justify the systematic interlaboratory variations seen by both of these techniques. Despite the typically high concentration of this element in zircon, it appears that the true accuracy of the analytical results from an individual laboratory may not be reflected by the reported precision values. This observation is particularly relevant to ICP-MS operators who traditionally use one of the Hf isotopes as an internal calibrant. Use of either EPMA or SIMS to determine the Hf content of a domain, be it in 91500 or in any other zircon, prior to laser ablation analysis will entail the propagation of any systematic errors in the Hf value into all results which have used this element as an internal calibrant for ICP-MS.

Based on all of the data now available for 91500, our best estimate for the hafnium content of this single crystal remains the isotope dilution "bulk" value of 5895 μ g g⁻¹ (Wiedenbeck *et al.* 1995). By avoiding the zones which show strong zoning in cathodoluminescence images, we believe that this bulk value can, with a prudent level of caution, be used for the purpose of quality assurance by conducting a sufficiently large number of random analyses on multiple sample fragments. Nonetheless, it must be acknowledged that a more homogeneous material will be necessary in order to fully address the analytical challenges presented by this element.

Conclusions

The data reported here in conjunction with the earlier study by Wiedenbeck *et al.* (1995) make 91500



by far the most well characterised zircon sample currently available. Due to the wide distribution now achieved for this sample, it may be expected that 91500 will continue to play an important analytical role over the coming years. The much more detailed homogeneity testing that was undertaken as part of this second characterisation and, in particular, the extensive scanning electron imaging, have identified previously undocumented zoning in this sample. All future users must remain alert to the presence of such features and the chemical variations that they may reflect. Although the 91500 may currently be the "best available" zircon reference sample, it is clearly not the ideal material for use as a primary calibrant for trace element work. Rather, we would recommend that its use as a trace element reference sample is limited to technique development work and as a "secondary standard" for quality assurance purposes. Equally clear is that any future "international" zircon reference samples will need to be documented and reported at the level of detail presented here. Only with this much detail can the broader microanalytical community gain maximum value from the development and characterisation of such materials.

Despite the now identified presence of banding, 91500 remains a valuable reference material. Many of the most important geochemical ratios (e.g., ¹⁸O/¹⁶O, U/Pb, ²⁰⁷Pb/²⁰⁶Pb) apparently are unaffected by this feature. (We note that an unpublished compilation of > 7500 U-Pb analyses of 91500 conducted at the NORDSIM facility has failed to identify any clearly discordant domains.) As this banding (Figures 1 and 3) is easily identified and can be readily avoided, the challenges that it presents regarding the absolute concentration of the various elements can be addressed. The Raman data which were produced as part of this study indicate that the level of radiation damage in 91500, including that observed in the most extreme CL dark bands, is at most modest. Despite intensive effort, no evidence of alteration or other secondary processes has been found.

Beyond providing a more detailed characterisation of this valuable specimen, this work clearly documents that significant zircon calibration issues are yet to be adequately addressed by the analytical geochemist. Even the seemingly straight-forward determination of the minor element Hf by EPMA can present pitfalls. The results of this study clearly indicate that the intralaboratory reproducibilities reported in the EPMA, LA-ICP-MS and SIMS data sets do not adequately reflect the interlaboratory variabilities. It is likewise clear that, given the current state of the art of analysing zircons as portrayed here, comparing independent data sets based on quoted precisions is a risky activity. Nonetheless, in the case of trace element analyses, the comparison between laboratory data sets and between analytical methods failed to detect gross discrepancies and, in general, the consistency of the data was good. Only in the case of the mg-sampling scales provided by laser heating analysis for oxygen isotope determinations does the quoted precision of the individual laboratories closely reflect the observed interlaboratory reproducibility.

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