

# Problems Associated with the Determination of Rare Earth Elements of a "Gem" Quality Zircon by Inductively Coupled Plasma-Mass Spectrometry

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A gem quality zircon crystal from the Mud Tank Carbonatite, Australia, was carefully crushed, sieved, acid leached and hand-picked to produce three different zircon fractions: 1) clear and apparently free of inclusions; 2) with inclusions; 3) with inclusions and adhering alteration/matrix material. Each separate and the bulk sample was dissolved by 1) lithium metaborate fusion and 2) Parr bomb digestion utilizing 29 mol l<sup>-1</sup> hydrofluoric (HF) and 16 mol l<sup>-1</sup> nitric (HNO<sub>3</sub>) acids. *In situ* analyses were performed using laser ablation ICP-MS and demonstrate that, on the basis of REE, two types of inclusions are present: 1) those with a positive Ce anomaly and 2) those with no Ce anomaly. The former type of inclusion appears to be smaller than the latter. Analysis of the digested samples for the rare earth elements (REE) was then performed using a quadrupole ICP-MS. Comparison of the chondrite-normalized REE patterns for the different fractions gave apparent positive anomalies at Sm and Eu in the acid digestions but not in the fused samples. Zirconium has five isotopes (<sup>90</sup>Zr, <sup>91</sup>Zr, <sup>92</sup>Zr, <sup>94</sup>Zr and <sup>96</sup>Zr) and there is a strong tendency for Zr to combine with fluorine (<sup>19</sup>F). Based on calculations and experiments, the increased levels of Sm and Eu in the acid digested samples were due to interferences of <sup>90</sup>Zr<sup>19</sup>F<sub>3</sub> on <sup>147</sup>Sm and of <sup>94</sup>Zr<sup>19</sup>F<sub>3</sub> on <sup>151</sup>Eu. Decreasing the ratio of HF:HNO<sub>3</sub> did not remove these interferences, nor did post-treatment with perchloric acid. A mathematical method was developed to correct for these polyatomic interferences.

Keywords: zircon, polyatomic interferences, dissolution, REE, zirconium fluoride, ICP-MS.

*Un cristal-gemme de zircon provenant de la carbonatite de Mud Tank, Australie, a été soigneusement broyé, tamisé, lessivé à l'acide et trié à la main pour obtenir trois fractions de zircon: 1) limpide et sans inclusions apparentes; 2) avec inclusions; 3) avec inclusions et matrice/produits d'altération. Chaque fraction séparée et la roche totale ont été dissoutes par 1) une fusion avec métaborate de lithium et 2) une attaque acide en bombe de Parr avec HF 29 mol l<sup>-1</sup> et HNO<sub>3</sub> 16 mol l<sup>-1</sup>. Des analyses in situ ont été réalisées par ICP-MS avec ablation laser et mettent en évidence, du point de vue des Terres Rares, deux types d'inclusions: 1) avec une anomalie positive en Ce et 2) sans anomalie en Ce. Le premier type d'inclusions semble plus petit que le second. L'analyse des Terres Rares des échantillons issus de l'attaque acide a été réalisée par ICP-MS à quadrupôle. La comparaison des spectres de Terres Rares normalisés aux chondrites des différentes fractions montre des anomalies positives apparentes en Sm et Eu seulement pour les attaques acides. Le zirconium a cinq isotopes (<sup>90</sup>Zr, <sup>91</sup>Zr, <sup>92</sup>Zr, <sup>94</sup>Zr et <sup>96</sup>Zr) et une forte tendance à se combiner au fluor (<sup>19</sup>F). A partir de calculs et d'expérimentations, l'enrichissement en Sm et en Eu des échantillons issus de l'attaque acide serait dû aux interférences <sup>90</sup>Zr<sup>19</sup>F<sub>3</sub> sur <sup>147</sup>Sm et <sup>94</sup>Zr<sup>19</sup>F<sub>3</sub> sur <sup>151</sup>Eu. La diminution du rapport HF/HNO<sub>3</sub> ne supprime pas ces interférences, pas plus qu'un traitement final à l'acide perchlorique. Une méthode mathématique a été développée pour corriger ces interférences polyatomiques.*

Mots-clés : zircon, interférences polyatomiques, dissolution, Terres Rares, fluorure de zirconium, ICP-MS.

Zircon ( $ZrSiO_4$ ) is a common accessory mineral occurring in a wide variety of rock types. The zircon crystal lattice allows the preferential incorporation of the heavy rare earth elements (HREE) and Y into the matrix. Recent experimental evidence, however, indicates that REE partitioning in zircon is not simply a function of decreasing REE<sup>3+</sup> ionic radii. Structural strain by the REE, in addition to charge balancing P<sup>5+</sup> at the Zr and Si sites, exerts a significant influence on the amount of these elements that can be taken up into the zircon matrix (Hancher *et al.* 2001a, Finch *et al.* 2001).

Zircon is widely used in geochronology as it crystallizes with an extremely high U/Pb ratio and retains the daughter products of radioactive decay, thus allowing precise U-Pb ages to be measured (e.g. Meyer *et al.* 1989, Ireland *et al.* 1998). This, coupled with its durability, explains why the oldest recorded ages of minerals on Earth have come from detrital zircons (Froude *et al.* 1983, Compston and Pidgeon 1986, Maas *et al.* 1992).

While the chemical and physical stability of zircon is a useful property for geochronologists, it is problematical for geochemists, where analytical techniques require the complete dissolution of a particular sample. Zircon is only slightly attacked by hydrofluoric acid (HF) at atmospheric pressure, so incomplete dissolution of a zircon-bearing rock sample can produce spurious whole rock compositions (e.g. depletions at Zr and Hf in normalized trace element diagrams and Zr/Hf ratios that depart from chondritic [i.e. Zr/Hf  $\neq$  36-37]; see May and Rowe 1965, Sulceck and Povondra 1989). Therefore, methods of dissolution employ either a flux to fuse the mineral (e.g. Feldman 1983, Perkins *et al.* 1992) or a high ratio of HF to nitric (HNO<sub>3</sub>) acids in pressure digestion vessels (e.g. Krogh 1973, Sulceck and Povondra 1989). However, the fusion method can potentially introduce contaminants and increase the total dissolved solids of the final solution so that some elements of interest may be diluted below detection limits. Inductively coupled plasma-mass spectrometry (ICP-MS) is well suited for the precise, accurate and rapid determination of the REE in geological samples (Xie *et al.* 1994, Jain *et al.* 2000), but complete dissolution must be assured.

Use of laser ablation (LA) ICP-MS removes the need for dissolution (Fedorowich *et al.* 1993) as the laser acts as a "micro-hammer", chipping away at the solid sample as a stream of argon carries the particles

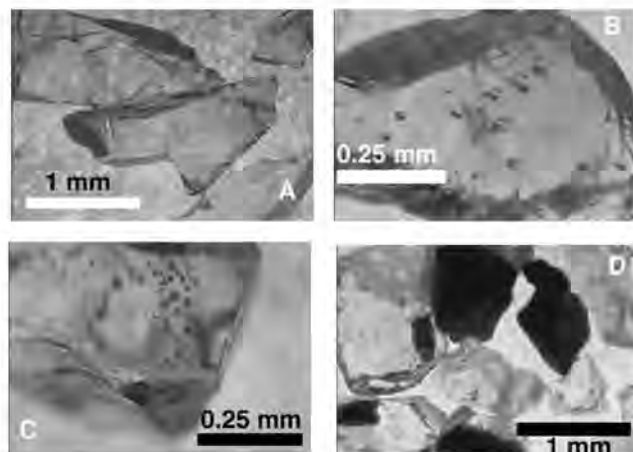
to the torch for ionisation prior to introduction into the mass spectrometer. LA-ICP-MS is ideal for mineral analyses (Feng *et al.* 1993, Hirata and Nesbitt 1995) provided that inter-element fractionation is controlled and accurate calibration is achieved. To undertake analysis via conventional solution ICP-MS requires that a specific mass of *clean* mineral be handpicked and dissolved. Ensuring mineralogical purity of such separates is a difficult and time-consuming process, as each mineral fragment has to be checked for adhering matrix material and fluid/mineral inclusions. LA-ICP-MS using time-resolved analysis can detect changes in signal due to the presence of inclusions/matrix material and these spectra can be omitted from the final integration. However, LA-ICP-MS does have limitations due to higher detection limits and poorer precision and accuracy as compared to solution data. Ion microprobe is another technique that can be used for trace element mineral analyses (e.g. Hoskin and Ireland 2000). While the spatial resolution is currently superior to LA-ICP-MS, data acquisition time is much longer.

In routine quadrupole ICP-MS trace element analyses, interferences on a specific mass can be caused by the formation of polyatomic ions. Such interferences are particularly troublesome if the elements of interest lack any interference-free isotope. For example, the oxide interferences on the REE are well defined and published methods (e.g. Jenner *et al.* 1990) have demonstrated accuracy using schemes to correct for polyatomic oxide interferences. In this paper we highlight polyatomic interferences associated with the REE analysis of zircon that has been digested using a combination of HF and HNO<sub>3</sub> acids. With zirconium having an extremely strong affinity for fluorine, we confirm that HNO<sub>3</sub> cannot dissociate the Zr-F complexes and demonstrate that aggressive perchloric acid attack is also ineffectual (see Sulceck and Povondra 1989, for review). A method based on mathematical corrections is designed to obtain interference-free results.

## Experimental

### Sample preparation

A gem quality zircon was obtained from the Mud Tank Carbonatite, Australia. The Mud Tank Carbonatite complex consists of a series of lenses that were emplaced about 732 Ma ago (Black and Gulson 1978). This complex is located northeast of Alice Springs in the



**Figure 1.** Examples of the different hand-picked mineral separates of zircon from the Mud Tank Carbonatite. **A:** Clean separate, free of inclusions and adhering material; **B and C:** Inclusion separate showing inclusions in the zircon; **D:** Dirty separate that includes zircon with inclusions and adhering matrix material.

Strangeways Range of the Northern Territory. The zircon crystals used in this study were collected from the ground surface and separated from the carbonatite residual material.

An approximately 5 g zircon crystal was carefully crushed, sieved and leached in *aqua regia* for 20 minutes to remove any adhering non-silicate material. The crushed mineral was then washed in ultrapure (18 M $\Omega$ ) water and hand picked under a binocular microscope into three distinct groups: 1) Clear and free of inclusions and adhering surface material (Figure 1a); 2) containing inclusions but no adhering surface material (Figure 1b, c); and 3) containing inclusions and adhering surface material (Figure 1d). We analysed all three separates in order to examine the contribution of the inclusions and adhering matrix material to the bulk zircon REE budget. Each separate was powdered using a clean agate mortar and pestle. A portion of the unsieved zircon was also crushed and powdered for analysis.

### Sample digestion

Approximately 0.05 g of the finely powdered sample was weighed into a clean Teflon vessel to which was added 1 ml of 16 mol l<sup>-1</sup> HNO<sub>3</sub> and 4 ml of 29 mol l<sup>-1</sup> HF. The acids used were purchased at the reagent grade and then doubly distilled in-house. Dissolution employed high-pressure Parr bombs to ensure complete sample digestion (e.g. Krogh 1973, Ely *et al.* 1999) by heating in an oven at 170 °C for 7 days. The HF/HNO<sub>3</sub> mixture was then evaporated to dryness and the residue taken into solution in 2 ml of

16 mol l<sup>-1</sup> HNO<sub>3</sub>, capped and kept on a hotplate at ~ 120 °C overnight. The solution was then dried and redissolved a second time in 2 ml of 16 mol l<sup>-1</sup> HNO<sub>3</sub> and immediately dried on a hotplate. The two HNO<sub>3</sub> treatments were used in an attempt to convert fluorides to nitrates. Finally, the residue was dissolved in 2 ml of 16 mol l<sup>-1</sup> HNO<sub>3</sub>, transferred to a 125 ml of bottle and diluted with ultrapure water to 100 g to give a final total dissolved solid content of ~ 0.05%. The entire procedure was carried out under class 1000 clean laboratory conditions. A procedural blank was also prepared and analysed together with the samples (Table 1).

### Fusion

The rationale behind fusing the samples was to test whether the method described above produced complete dissolution of the sample. The procedure to fuse the samples was slightly modified from that described by Feldman (1983) and Hall and Pelchat (1990a, b). Approximately 0.1 g of powdered sample was mixed with 0.5 g of lithium metaborate (from SPEX Certiprep, New Jersey, USA) in a weighing boat. The mixture was transferred into a clean graphite crucible and fused in a muffle furnace at 1000 °C for 30 minutes. The crucible was removed from the furnace and the molten mass was poured directly into a clean Teflon beaker containing 50 ml of 0.8 mol l<sup>-1</sup> HNO<sub>3</sub>. The contents of the beaker were accurately weighed before and after the addition of the molten sample and the mixture was transferred to a 125 ml screw-capped polypropylene bottle and made up to 100 g by the addition of 0.8 mol l<sup>-1</sup> HNO<sub>3</sub>. The bottle containing the suspension

**Table 1.**  
 Detection limits and blank levels of the Parr bomb, fusion and laser ablation analytical methods used to examine the REE contents of zircons from the Mud Tank zircons. All values are in  $\mu\text{g g}^{-1}$

	Laser ablation* detection limit	Parr bomb detection limit	LiBO <sub>2</sub> fusion detection limit	Parr bomb blank	LiBO <sub>2</sub> fusion blank
La	0.004	0.007	0.036	bdl	0.062
Ce	0.002	0.006	0.147	bdl	bdl
Pr	0.002	0.006	0.008	bdl	0.017
Nd	0.011	0.015	0.037	bdl	0.037
Sm	0.012	0.008	0.019	bdl	bdl
Eu	0.003	0.002	0.023	bdl	bdl
Gd	0.013	0.006	0.013	bdl	0.006
Tb	0.002	0.004	0.007	bdl	0.0016
Dy	0.006	0.006	0.008	bdl	0.0133
Ho	0.002	0.003	0.003	bdl	bdl
Er	0.005	0.006	0.011	bdl	0.0116
Tm	0.002	0.003	0.003	bdl	bdl
Yb	0.005	0.005	0.008	bdl	0.0115
Lu	0.001	0.004	0.018	bdl	bdl

\* Hafnium was used as the internal standard for the laser ablation analyses. Hafnium data were obtained by electron microprobe (Hanchar, unpublished data). bdl below detection limit.

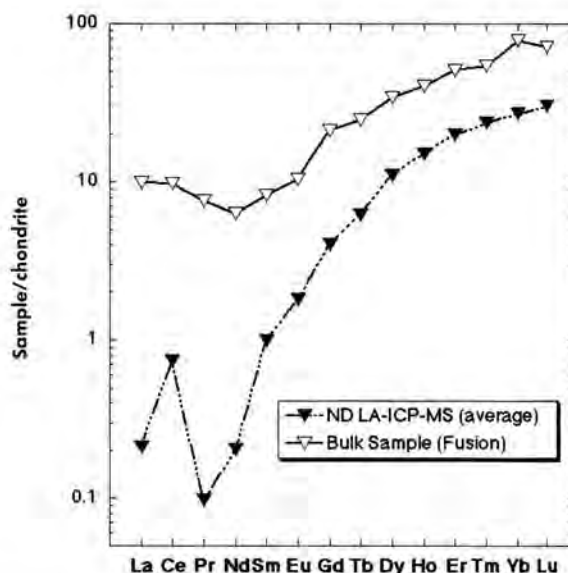
was placed in a sonic bath until all solids dissolved, resulting in a clear solution. A procedural blank was also prepared and analysed with the samples (Table 1).

### Instrumentation

A Plasma Quad model PQII (Fisons Instruments, Beverly, MA, USA) inductively coupled plasma-mass spectrometer was used for all data acquisition. The spray chamber was cooled to 5 °C by means of a mini chiller model RTE 100 (Neslab Instruments, Portsmouth, NH, USA). Samples were introduced using a peristaltic pump (Gilson, Middleton, WI, USA), at 1.0 ml min<sup>-1</sup> in conjunction with an auto-sampler (Gilson, Sample Changer Model 221-222). The data reduction procedure was adapted from Jenner *et al.* (1990) and is described in Neal (2001). The machine operating conditions and analytical procedure followed were described by McGinnis *et al.* (1997).

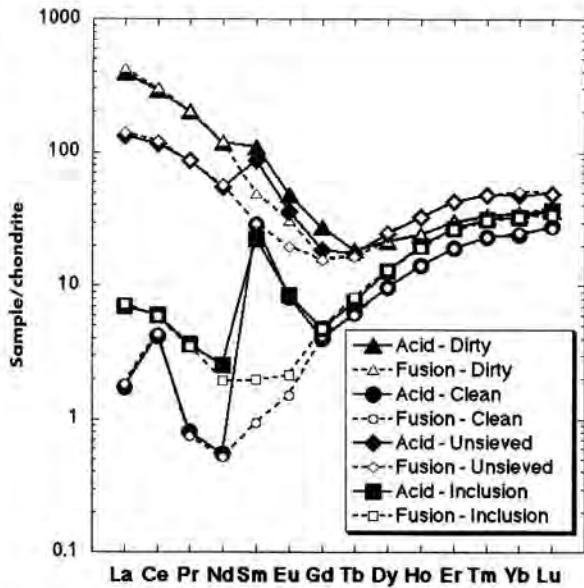
### Results and discussion

At the University of Notre Dame, we initially analysed the bulk zircon both by solution (using the fusion method) and by *in situ* LA-ICP-MS, using Hf as the internal standard (J. Hanchar, unpublished electron microprobe data) (Figure 2). The fusion analysis completely dissolved the zircon, but has elevated REE abundances compared to the average *in situ* analyses and does not contain a positive Ce anomaly.



**Figure 2.** Comparison of *in situ* and bulk REE analyses. *In situ* analyses are by LA-ICP-MS (filled symbols) and the bulk sample (open symbol) was analysed by solution ICP-MS at Notre Dame. See text for discussion. In this and subsequent REE diagrams Pm has been omitted for convenience.

Samples from each of the three groups of mineral separates (Figure 1) and the bulk sample were dissolved in a mixture of 16 mol l<sup>-1</sup> HNO<sub>3</sub> and 29 mol l<sup>-1</sup> HF (1:4) and digested using Parr bombs as described above. As with the initial study, an aliquot from each fraction and the bulk sample was fused to see if the



**Figure 3.** Comparison of REE profiles for the three mineral separates and the bulk sample, each dissolved via lithium metaborate fusion (open symbols) and HF/HNO<sub>3</sub> acid in a Parr bomb (filled symbols). Generally the acid digests and fused samples have the same profiles demonstrating total dissolution of the sample in the Parr bomb. However, the acid digested samples have positive anomalies at Sm and Eu. Bulk sample = diamonds; dirty mineral fraction = triangles; clean mineral fraction = circles; inclusion-rich mineral separate = squares. See text for discussion.

Parr bomb acid digestion method resulted in complete dissolution. The fusion and Parr bomb digested fractions produced similar results. The bulk and dirty separates were LREE-enriched due to adhering carbonatitic matrix. The inclusion-rich separate was enriched in the HREE over the LREE, but had a (La/Sm)<sub>N</sub> ratio > 1. The clean fraction contained similar HREE abundances to that of the inclusion-rich separate, but lower LREE and a positive Ce anomaly. The difference between the zircon profiles of the two preparation techniques is that the Parr bomb digested samples exhibited large apparent positive anomalies at Sm and Eu that were absent in the fused samples (Figure 3).

Why pursue the Parr bomb method when the fusion technique adequately dissolves zircon? As noted above, the fusion method can potentially introduce contaminants and increase the total dissolved solids of the final solution so that some elements of interest may be diluted below detection limits. The detection limits and blank levels of both methods are presented in

Table 1. It is evident that the blank levels for the Parr bomb digestion are far superior to those of the fusion method. With detection limits calculated as 3s above the acid blank, the Parr bomb procedure yielded blank levels that were below the detection limit (after blank subtraction) for all the REE, whereas this was not the case for the fusion method. While the blank levels are still low, they explain the reason why La abundances are slightly higher in the fusion digestion of the clean separate versus the Parr bomb digestion (Figure 3). Therefore, the contribution to the REE by the blank imparted by the lithium metaborate flux may be significant when analysing samples containing ultra-trace levels of these elements.

### Polyatomic zirconium interferences

Apart from the absence of flux in the Parr bombs, the only other difference between the two modes of dissolution was the presence of a large quantity of HF in the acid-digested sample. The positive Sm and Eu anomalies (Figure 3) are a result of the strong affinity between Zr and F (*cf.* Sulceck and Povondra 1989) and the formation of polyatomic zirconium fluoride interferences. Zirconium, a major element in zircon, has five isotopes, which are summarized in Table 2 together with zirconium fluoride-related molecular interferences on various analyte ions. It is evident that if all possible combinations of Zr and F are considered, interferences are observed not only with the determination of Sm and Eu, but also with Ag, Cd, Pd, Sn, In, Te, (Xe), Ba and Nd. However, all potential interferences can be avoided by selecting alternative isotopes for quantification. The exception is Eu. Furthermore, although Sm has three isotopes free from ZrF<sub>3</sub> polyatomic interferences (at masses 150, 152, 154), isobaric interferences are present on each of these (from <sup>150</sup>Nd and <sup>152, 154</sup>Gd).

In order to test for the presence of zirconium fluoride interferences, two drops of 29 mol l<sup>-1</sup> HF were added to a 10 ml solution containing only 100 µg g<sup>-1</sup> Zr.

**Table 2.**  
**Zirconium fluoride interferences**

Zr Isotopes	Abundance (%)	Molecular interference		
		<sup>19</sup> F	<sup>19</sup> F <sub>2</sub>	<sup>19</sup> F <sub>3</sub>
<sup>90</sup> Zr	51.46	<sup>109</sup> Ag	<sup>128</sup> Te	<sup>147</sup> Sm
<sup>91</sup> Zr	11.23	<sup>110</sup> Cd, <sup>110</sup> Pd	-	<sup>148</sup> Nd, <sup>148</sup> Sm
<sup>92</sup> Zr	17.11	<sup>111</sup> Cd	<sup>130</sup> Ba, <sup>130</sup> Te	<sup>149</sup> Sm
<sup>94</sup> Zr	17.4	<sup>113</sup> Cd	<sup>132</sup> Ba	<sup>151</sup> Eu
<sup>96</sup> Zr	2.8	<sup>115</sup> Sn, <sup>115</sup> In	<sup>134</sup> Ba	<sup>153</sup> Eu

**Table 3.**  
**Counts per second on zirconium fluoride**  
**masses measured using a 100 µg ml<sup>-1</sup> Zr**  
**solution with a trace (two drops) of 29 mol l<sup>-1</sup>**  
**HF. Values are blank-subtracted**

Measured atomic mass	Molecular species	Counts/s
<b>Mono-fluorides and oxides</b>		
107(Ag)	<sup>91</sup> Zr <sup>16</sup> O, <sup>90</sup> Zr <sup>16</sup> O <sup>1</sup> H	1,426,702
109(Ag)	<sup>90</sup> Zr <sup>19</sup> F	100,419
110(Cd, Pd)	<sup>91</sup> Zr <sup>19</sup> F, <sup>94</sup> Zr <sup>16</sup> O	1,842,916
111(Cd)	<sup>92</sup> Zr <sup>19</sup> F	95,464
112(Cd, Sn)	<sup>96</sup> Zr <sup>16</sup> O	322,696
113(Cd, In)	<sup>94</sup> Zr <sup>19</sup> F	18,573
115(In, Sn)	<sup>96</sup> Zr <sup>19</sup> F	402
<b>Di-fluorides</b>		
128(Xe, Te)	<sup>90</sup> Zr <sup>19</sup> F <sub>2</sub>	1,382
129(Xe)	<sup>91</sup> Zr <sup>19</sup> F <sub>2</sub>	406
130(Xe, Te, Ba)	<sup>92</sup> Zr <sup>19</sup> F <sub>2</sub>	874
132(Xe, Ba)	<sup>94</sup> Zr <sup>19</sup> F <sub>2</sub>	725
134(Xe, Ba)	<sup>96</sup> Zr <sup>19</sup> F <sub>2</sub>	155
<b>Tri-fluorides</b>		
147(Sm)	<sup>90</sup> Zr <sup>19</sup> F <sub>3</sub>	18,318
148(Sm, Nd)	<sup>91</sup> Zr <sup>19</sup> F <sub>3</sub>	3,721
149(Sm)	<sup>92</sup> Zr <sup>19</sup> F <sub>3</sub>	7,105
151(Eu)	<sup>94</sup> Zr <sup>19</sup> F <sub>3</sub>	8,255
153(Eu)	<sup>96</sup> Zr <sup>19</sup> F <sub>3</sub>	887

Blanks comprised 0.8 mol l<sup>-1</sup> HNO<sub>3</sub> solutions. The blank-subtracted counts demonstrate the presence of zirconium mono-, di- and tri-fluoride molecular interferences. The magnitude of the mono-fluoride interference is complicated by zirconium oxide and hydroxide (Table 3). The effect of ZrO<sup>+</sup> and ZrOH<sup>+</sup> can be seen at masses 107 (<sup>91</sup>Zr<sup>16</sup>O, <sup>90</sup>Zr<sup>16</sup>O<sup>1</sup>H) and 112 (<sup>96</sup>Zr<sup>16</sup>O), which are ZrF-free masses. While the di-fluoride interferences are the least obtrusive, they are still present, with the blank-subtracted counts on masses 128, 129, 130, 132 and 134 being in the same approximate proportions as the Zr isotopes in Table 2. Zirconium tri-fluoride interferences are more pervasive, with the blank-subtracted counts again being approximately in the same proportions as the Zr isotopes.

In the Parr bomb digests of the zircon, repeated HNO<sub>3</sub> treatment did not break down the Zr-F complexes that formed during the dissolution procedure (*cf.* Sulceck and Povondra 1989). We also treated the samples with perchloric acid after the initial HF/HNO<sub>3</sub> dissolution, but only a slight reduction in the magnitude of the interferences was observed after two perchloric acid treatments. While increasing the RF power has been shown to reduce molecular interferences (*e.g.* Longerich *et al.* 1987), this was not done as it has

been demonstrated that doing this also increases the formation of hydrides (Jain *et al.* 1992). This would cause more interferences on the REE than were present in the Parr bomb procedure with the existing machine using an RF power of 1350 W.

In an attempt to remove interferences from REE profiles for the zircon using the acid dissolution method, a method was devised to subtract out the counts produced by the polyatomic interferences. It is often possible to make corrections for the interference by subtracting the interfering peak from the desired one (Date *et al.* 1987). Therefore, we used the REE-free zirconium/HF solution to calculate the percentage interference on Sm and Eu and then applied these corrections to the zircon data. As machine operating parameters play an important role in formation of polyatomic ions, all solutions were analysed under the same instrument conditions. The interferences can be reduced during the tuning process but can not be eliminated completely (Jarvis *et al.* 1992). The instrumental parameters used in this study were chosen based on a compromise between reduced polyatomic interferences and sufficient instrumental sensitivity (see McGinnis *et al.* 1997). We included Zr in the analytical package to monitor the interferences on <sup>147</sup>Sm and <sup>151</sup>Eu. Calculations of Sm and Eu concentrations required corrections for <sup>90,94,96</sup>ZrF<sub>3</sub>. Fluoride formation under the specified instrumental conditions is approximately 0.0027% of the Zr signal on <sup>147</sup>Sm, 0.00025% on <sup>151</sup>Eu and 0.000028% on <sup>153</sup>Eu. With Zr being a major element in zircon, these interferences on the REE are significant. Applications of zirconium tri-fluoride corrections deduced in this way successfully removed the positive Sm and Eu anomalies observed in the acid digested samples (Figure 4). We also monitored mass 152, which is a significant isotope of Sm (26.7%), but also a minor isotope of Gd (0.2%); appropriate corrections were made. The corrected Sm data were identical using both isotopes and comparable to those obtained by the fusion procedure.

The interference-corrected data were further compared with the results obtained from LA-ICP-MS (Figures 2, 3 and 4). While HREE abundances are similar in both methods the LREE and MREE contents of acid digested samples were found to be higher as compared to *in situ* data. Monazite [(Ce,La,Th)PO<sub>4</sub>] crystals are common constituents of carbonatites and are known to occur in the Mud Tank Carbonatite (A.N. Mariano, pers. comm.). Monazite crystals are characterized by a pronounced enrichment of LREE relative to the HREE

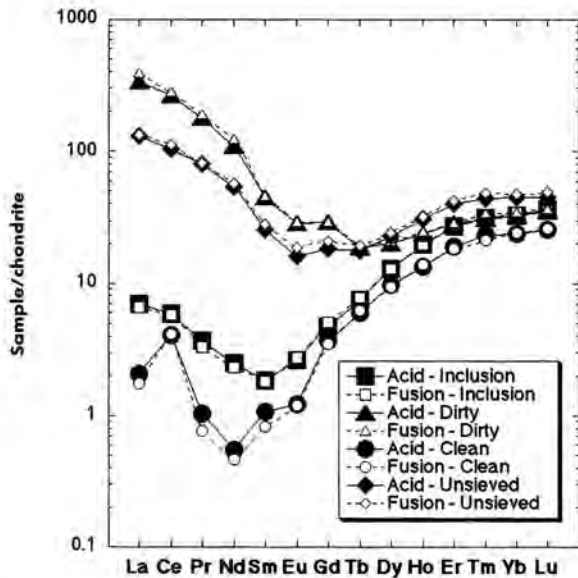


Figure 4. Comparison of fusion (open symbols) and HF/HNO<sub>3</sub> acid digested (filled symbols) REE profiles for the three mineral separates of the Mud Tank zircon and the bulk sample after the latter have been corrected for ZrF<sub>3</sub> interferences. Bulk sample = diamonds; dirty mineral fraction = triangles; clean mineral fraction = circles; inclusion-rich mineral separate = squares.

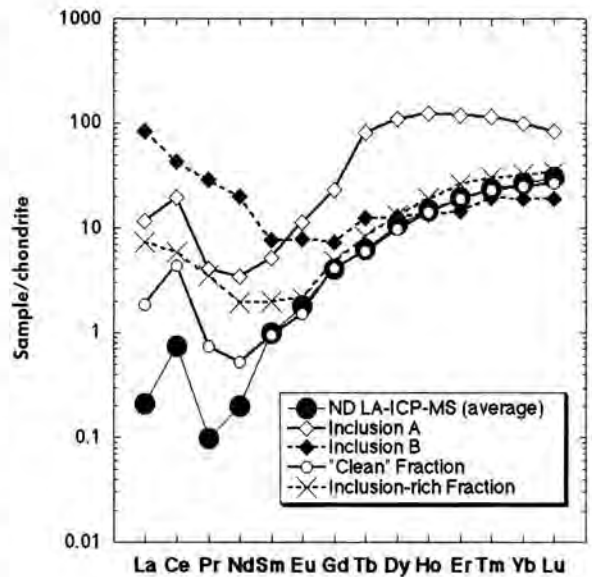


Figure 5. REE profiles of the Mud Tank zircon. The average LA-ICP-MS zircon profile (filled circle) is compared with the clean (open circle) and inclusion-rich (cross) mineral fractions. Also shown are the two types of inclusions observed - one with a positive Ce anomaly (open diamond) and one with no Ce anomaly (filled diamond).

(Deer *et al.* 1992) and in the light of their known presence in the Mud Tank rocks, we analysed the zircon mineral fractions by acid dissolution to see if there was a correlation between P and the LREE contents. While bulk samples were found to have c. 200 µg g<sup>-1</sup> P, no detectable level of P was present in either the clean or inclusion mineral fractions. This suggests that the differential REE contents of *in situ* and acid-dissolved analyses are not associated with monazite contamination. A mineral or minerals from the pyrochlore group may also form in zircon inclusions, being found in alkali igneous rocks and carbonatites. The zircon mineral separates containing inclusions have elevated Nb, Y, Th and U contents (7, 140, 4.3 and 12.4 µg g<sup>-1</sup>, respectively) relative to the "clean" separate (2, 33.5, 0.8 and 2.1 µg g<sup>-1</sup>, respectively); both fractions contain c. 1 µg g<sup>-1</sup> Ta. Pyrochlore minerals are also significant carriers of the REE [e.g. ceriopyrochlore - (Ce, Ca, Y)<sub>2</sub>(Nb,Ta)<sub>2</sub>O<sub>6</sub>(OH,F)], which accounts for the elevated LREE abundances of the inclusion separate relative to the clean separate (Figures 4 and 5).

A comparison of chondrite-normalized REE profiles for all fractions analysed demonstrates a positive Ce anomaly in the clean separate, which is in agreement

with the *in situ* results (Figure 5), although the La, Ce, Pr and Nd abundances are elevated relative to the *in situ* analyses (Figure 5). The presence of significant Nb, Y, Th and U contents in the bulk analysis of the clean separate suggests that not all of the inclusions were removed during the handpicking and the presence of pyrochlore-group minerals has preserved the positive Ce anomaly. Use of LA-ICP-MS allows the nature of the inclusions to be semi-quantified through integration of spectra reflecting inclusion material (i.e. departures from the general zircon spectra). The analyses are termed semi-quantitative because the internal standard for the zircon was used for quantifying the inclusion spectra despite a mismatch in matrices. The REE profiles of the inclusions contain elevated LREE contents relative to the zircon and some also are highly enriched in the HREE (Figure 5). The profiles can be divided into two groups on the presence/absence of a positive Ce anomaly (Figure 5). It would appear that the inclusions are dominated by the type displaying no Ce anomaly (compare the profile of the inclusion-rich separate with "Inclusion B"). Hand picking the clean separate has removed these inclusions, but not all those containing a positive Ce anomaly (compare the clean separate profile with "Inclusion A"), suggesting

these inclusions are smaller. Only a few percent of these small inclusions in the clean separate will elevate the LREE of the zircon profile while preserving the positive Ce anomaly (see Hanchar *et al.* 2002, for complete details).

## Conclusions

Complete acid dissolution of zircon requires a high ratio of HF to HNO<sub>3</sub> coupled with elevated temperatures and pressures that also produces ZrF<sub>3</sub> polyatomic interferences on Sm and Eu. These can be avoided through dissolution using a flux, but this introduces contaminants (Table 1) and increases the total dissolved solids, such that dilution may put some elements below detection levels. In order to avoid these potential problems, the positive Sm and Eu anomalies observed in the acid digested samples can be removed by subtracting the counts caused by the polyatomic interferences. The correction is calculated using a zirconium solution with traces of HF and free of the REE that is analysed with the zircon sample solutions under the same instrumental conditions. The percentage of counts contributed from ZrF<sub>3</sub> is calculated and subtracted from the counts of Sm and Eu to find the actual concentrations in the zircons.

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