**Supplementary A—Methodology**

A1. LA-ICP-MS U-Pb analysis

A2. LA-ICP-MS geochemical analysis and PCA

A3. EPMA

**A1. LA-ICP-MS U-Pb analysis**

All reported LA-ICP-MS data was obtained from grains within one-inch-diameter polished blocks. Data was collected at Adelaide Microscopy, The University of Adelaide, using a RESOlution-LR excimer laser microprobe (Australian Scientific Instruments) coupled to an Agilent 7900x Quadrupole ICP-MS. This combination of laser and ICP-MS offers good spatial resolution (~29 µm) coupled with sub-ppm sensitivity for most trace elements. The laser has a large format S155 two-volume ablation cell designed by Laurin Technic Pty. Laser ablation was performed in an atmosphere of UHP He (0.38 l/min). The aerosol was mixed with Ar carrier gas (1.05 l/min) immediately above the ablation site before being transported to the ICP-MS via a ‘squid’ pulse-homogenizing device (Laurin Technic Pty). Uranium-Pb zircon analyses were undertaken using a spot diameter of 29 μm, resulting in crater depths generally between 10-15 μm over the 30 s ablation time. The ICP-MS was optimized daily using NIST612 reference glass to maximize sensitivity on isotopes of the mass range of interest, while keeping production of molecular oxide species (i.e., 232Th16O/232Th) and doubly charged ion species (i.e., 140Ce2+/140Ce+) as low as possible, and generally at <0.2 %. The plasma conditions were tuned for a robust plasma with U/Th ratio of 1.00-1.05. The GJ-1 zircon (Jackson et al., 2004) was used as the primary reference material, while 91500 (Wiedenbeck et al., 1995) and Plešovice (Sláma et al., 2008) were analysed as secondary reference materials. Reference material and unknows were analyzed using a pulse repetition rate of 5 Hz and a constant fluence of 2.5 J/cm2 within a single analytical session. Data collection consisted of a 30 second gas blank followed by 30 seconds of data acquisition with the laser firing. Isotopes measured were 204Pb, 206Pb, 207Pb, 208Pb, 232Th, and 238U with dwell times of 20, 50, 50, 10, 10, and 50 ms, respectively; 235U was calculated using the 238U/235U ratio of 137.88 (Steiger and Jäger, 1977). Mass 204Pb was measured as a monitor for Pbc content, but due to the unresolvable isobaric interference of 204Hg on 204Pb, Pbc corrections were not considered or conducted using 204Pb. Data reduction was performed and presented using Iolite™ and GLITTER in combination with Isoplot 3.75 (Ludwig, 2012).

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**A2. LA-ICP-MS geochemical analysis and PCA**

LA-ICP-MS spot analysis

LA-ICP-MS spot analysis of zircon was conducted using the same instrument and configurations as previously indicated in A1. A laser spot size diameter of 19 µm was employed to target areas of interest within zircon, using pulse repetition rates of 5 Hz and fluence of 3.5 J/cm2. Prior to each spot analysis, the targeted areas were pre-ablated to avoid surface contamination. Acquisition time comprised a 30 s measurement of the background and 30 s acquisition of the signal while the laser ablates. Analytical standards were run before and after each individual set of ~25 zircon unknowns using NIST-610 as the primary standard, and GSD-1G as the secondary standard. In addition, Plesovice was also analyzed between batches for quality control.

Data reduction was performed in Glitter using stoichiometric concentrations of Si in zircon as the internal standard element. Minimum detection limits (mdl) indicated by Glitter are individually calculated for each element in each spot analysis. A suite of 33 elements, including three Pb isotopes, was measured. Depending on the required mdl, different dwell times were employed, using (i) 0.005 s for: 27Al, 29Si, 31P and 91Zr; (ii) 0.01 s for 43Ca and 89Y; and (iii) 0.02 s for: 45Sc, 49Ti, 55Mn, 57Fe, 89Y, 93Nb, 118Sn, 139La, 140Ce, 141Pr, 146Nd, 147Sm, 153Eu, 157Gd, 159Tb, 163Dy, 165Ho, 166Er, 169Tm, 172Yb, 175Lu, 178Hf, 181Ta, 206Pb, 207Pb, 208Pb, 232Th and 238U. Two polyatomic interferences (17O28Si, 16O29Si) on 45Sc preclude its quantification at low concentrations and is therefore used qualitatively for monitoring elevated Sc contents.

LA-ICP-MS isotope mapping

Isotope mapping was conducted using the same instrumentation as described for spot analysis. Data acquisition involved ablating sets of parallel line rasters in a rectangular grid across the area of interest using a beam size of 7 µm (square profile) and a scan speed of 7 µm/s. Line spacing was kept at a constant 7 µm to match the size of the laser beam used. The effect of redeposition during mapping was minimized by pre-ablating each line immediately prior to its analysis. A laser repetition rate of 10 Hz was used with a fluence of ~3.5/Jcm-2. Such conditions meant the depth of ablation during mapping was around <5 µm. Isotopes measured were 206Pb, 208Pb, 232Th, 238U and the REE’S Y, Ce, Gd, Dy, Er, Yb, with dwell times of 30 ms for U, Th and Pb isotopes and 5 ms for REE’s. A 30 s background was acquired at the start of every raster, and a delay of 15 s was applied after each line to allow for sample washout.

Images were compiled and processed using Iolite™. The presented map in figure 2 ran over a ~4-hour session, in which significant instrument drift could occur. To correct for this, the average background was subtracted from its corresponding signal from the ablated area for each raster and element. NIST610 was analyzed immediately before and after the run to assess drift, and if present, was corrected for by applying a linear fit between the two sets of reference materials. The rasters were then compiled into a 2-D image displaying combined background-subtracted and drift corrected intensities for each element.

*Principal component analysis*

PCA was undertaken using singular value decomposition of centred logratio (clr) transformed data. Such transformation was required to respect its simplicial geometry. The above-mentioned procedures were performed in the R package ‘compositions’.

**A3. EPMA**

**Spot Analysis Methodology**

*Operating conditions and Processing*

Quantitative compositions of zircon were determined using a Cameca SX-Five electron probe microanalyzer (EPMA), equipped with 5 tuneable wavelength-dispersive spectrometers, located at Adelaide Microscopy. The instrument is running PeakSite v6.2 software for microscope operation, and Probe for EPMA software (distributed by Probe Software Inc.) for all data acquisition and processing. Combined operating conditions were utilized in which for each individual spot, major and mobile elements were analysed first at 17 kV/20 nA, then the beam subsequently changed to 17 kV/100 nA for the remaining analysis of low-level elements. Due to the need for spatial resolution, all analyses were done with a focused beam.

The full list of elements analysed along with primary and interference standards are presented in Tables 1 and 2.Oxygen was calculated by stoichiometry, assuming that all Fe was Fe3+. Matrix corrections of Armstrong-Love/Scott φ(ρz) (Armstrong, 1988) and Henke MACs were used for data reduction.

All elements were acquired using a traditional 2-point linear, excluding F Kα which was acquired using a multipoint fit. Following traditional 2-point background analysis, the “shared” background fit option in Probe for EPMA was used across the list of elements. For Nb, a traditional 2-point linear fit was used. Other elements, including those with more complex regions of the spectrum such as in the case some of the REE, multipoint or “shared” fits were used to accurately model the background continuum and/or avoid off peak interferences (Goemann et al., 2016, Goemann et al., 2017, Goemann and Donovan, 2017).

Due to the need for a focused beam, beam damage and alkali element migration (e.g., Na, F, Cl) in zircon analyses were monitored and minimized via analysis of these elements first on the detector, plus application of the Time Dependent Intensity (TDI) correction feature of Probe for EPMA (e.g., Donovan and Rowe, 2005). Using this method, the decay of x-ray counts over time is measured and modelled to return a *t*=0 intercept, and from this a concentration is calculated.

**Mapping Methodology**

*Operating conditions and processing*

Zircon grains were both qualitatively and quantitatively X-ray mapped utilising the same instrument at the University of Adelaide. Beam conditions were set at an accelerating voltage of 15 kV and 200 nA, utilising a focussed beam. Mapped area dimensions ranged from 100-200 µm in both x and y axes, at a pixel resolution of 1 µm. Pixel dwell time in all maps was set to 2000 ms, and ranged in acquisition time from ~2-24 hours depending on grain size. Calibration and quantitative data reduction of maps was carried out in Probe for EPMA, distributed by Probe Software Inc. Colour images of the maps were processed in Surfer 10® distributed by Golden Software. Calibration was performed on certified natural and synthetic standards from Astimex Ltd.

Zircon grains from LCD13, and LCD17 were quantitatively mapped via measurement of Cl Kα on four separate spectrometers (3 LPET and 1 PET crystal), and Fe Kα measured on a single LLIF crystal.

Map quantification was conducted in CalcImage, a module of Probe for EPMA. Background subtraction on the maps was performed via the Mean Atomic Number (MAN) background correction (Donovan and Tingle, 1996; Donovan et al., 2016), omitting the need for a second pass “off-peak” map acquisition. Following this each pixel goes through full φ(ρz) corrected quantification identical to traditional spot analysis. Major/minor elements were not acquired in the maps, and thus for accurate ZAF correction and quantification, specified concentrations as acquired from spot analysis were entered into the map quantification procedure for elements such as Zr, Si, Hf etc.

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**Table S1. EPMA setup for spot analysis of zircon**

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Element and Line** | **Diffracting Crystal (Sp#)** | **Background type/fit** | **kV/nA/spot size(µm)** | **Peak Count Time** | **Bkgd Count Times** | | **# bkgd points acquired (Lo/Hi)** | **Standards\*** | | **Overlapping element and order/interference correction standard** | | | |
| **Lo** | **Hi** | **Primary Standard** | **Interference Standards** | **Interfering line** | **Int. std** | **Interfering line** | **Int. std** |
| Zr Lα | LPET (1) | Shared | 17/20/0 | 15 | 10 | 10 | 1/1 | 728 |  |  |  |  |  |
| Ca Kα | LPET (1) | Shared | 17/20/0 | 20 | 20 | 20 | 1/1 | 535 |  |  |  |  |  |
| K Kα | LPET (1) | Shared | 17/100/0 | 40 | 20 | 20 | 1/1 | 541 |  |  |  |  |  |
| P Kα | LPET (1) | Shared | 17/100/0 | 40 | 20 | 20 | 1/1 | 504 |  |  |  |  |  |
| Y Lα | LPET (1) | Shared | 17/100/0 | 120 | 60 | 60 | 1/1 | 1214 |  |  |  |  |  |
| U Mβ | LPET (1) | Shared | 17/100/0 | 200 | 100 | 100 | 1/1 | 631 |  |  |  |  |  |
| Ce Lα | LPET (1) | Shared | 17/100/0 | 100 | 50 | 50 | 1/1 | 1201 |  |  |  |  |  |
| Ti Kα | LPET (1) | Shared | 17/100/0 | 100 | 50 | 50 | 1/1 | 540 |  |  |  |  |  |
| F Kα | PC0 (2) | Multipoint | 17/20/0 | 20 | 10 | 10 | 2/2 | 505 | 502,723 | Fe Lα (I) | 502 | Zr Lα1 (III) | 723 |
| Fe Kα | LLIF (3) | Shared | 17/20/0 | 40 | 20 | 20 | 1/1 | 502 |  |  |  |  |  |
| Hf Lα | LLIF (3) | Shared | 17/20/0 | 20 | 10 | 10 | 1/1 | 723 |  |  |  |  |  |
| Sc Kα | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 1/1 | 619 |  |  |  |  |  |
| Mn Kα | LLIF (3) | Shared | 15/20/0 | 40 | 20 | 20 | 1/1 | 539 |  |  |  |  |  |
| Lu Lα | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 1/1 | 1213 |  |  |  |  |  |
| Yb Lα | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 1/1 | 1212 |  |  |  |  |  |
| Er Lα | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 3/2 | 1210 |  |  |  |  |  |
| Gd Lβ | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 1/1 | 1206 |  |  |  |  |  |
| Dy Lα | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 1/2 | 1208 |  |  |  |  |  |
| Tb Lα | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 1/1 | 1207 |  |  |  |  |  |
| Sm Lβ | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 1/1 | 1204 |  |  |  |  |  |
| Eu Lα | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 1/1 | 1205 |  |  |  |  |  |
| Nd Lβ | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 1/1 | 1203 |  |  |  |  |  |
| Pr Lβ | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 1/1 | 1202 |  |  |  |  |  |
| Tm Lα | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 1/2 | 1211 |  |  |  |  |  |
| Ho Lβ | LLIF (3) | Shared | 17/100/0 | 40 | 20 | 20 | 1/1 | 1209 |  |  |  |  |  |
| Na Kα | TAP (4) | Shared | 17/20/0 | 20 | 20 | 20 | 7/0 | 501 |  |  |  |  |  |
| Si Kα | TAP (4) | Shared | 17/20/0 | 15 | 10 | 10 | 1/1 | 728 |  |  |  |  |  |
| Αl Kα | TAP (4) | Shared | 15/20/0 | 20 | 20 | 20 | 1/1 | 501 |  |  |  |  |  |
| Mg Kα | TAP (4) | Shared | 15/20/0 | 30 | 20 | 20 | 1/1 | 502 |  |  |  |  |  |
| Cl Kα | LPET (5) | Shared | 17/20/0 | 60 | 30 | 30 | 1/1 | 545 |  |  |  |  |  |
| La Lα | LPET (5) | Shared | 17/100/0 | 100 | 50 | 50 | 1/1 | 1200 |  |  |  |  |  |
| Th Mα | LPET (5) | Shared | 17/100/0 | 150 | 75 | 75 | 1/1 | 629 |  |  |  |  |  |
| Pb Mβ | LPET (5) | Shared | 17/100/0 | 200 | 100 | 100 | 3/1 | 627 |  |  |  |  |  |
| Nb Lα | LPET (5) | 2-pt | 17/100/0 | 100 | 50 | 50 | 1/1 | 616 | 723 | Zr Lβ4 (I) | 723 |  |  |
| \* Standard # refers to internal database. Full list of standards in Table 2 | | | | |  |  |  |  |  |  |  |  |  |

**Table S2. Standard information**

|  |  |  |  |
| --- | --- | --- | --- |
| **Reference #** | **Mineral composition** | **Natural/Synthetic** | **Manufacturer** |
| 501 | Albite | Natural | Astimex |
| 502 | Almandine garnet | Natural | Astimex |
| 504 | Apatite | Natural | Astimex |
| 535 | Plagioclase | Natural | Astimex |
| 539 | Rhodonite | Natural | Astimex |
| 540 | Rutile | Natural | Astimex |
| 541 | Sanidine | Natural | Astimex |
| 545 | Tugtupite | Natural | Astimex |
| 616 | Niobium | Synthetic | Astimex |
| 619 | Scandium | Natural | P&H and Associates |
| 627 | K227 (Pb silicate) | Synthetic | NIST |
| 629 | Huttonite | Natural | DAS |
| 631 | UO2 | Synthetic | DAS |
| 723 | Zircon | Natural | GJ Zircon standard |
| 728 | Zircon | Natural | 91500 zircon standard |
| 1200 | LaPO4 | Synthetic | Cherniak phosphate |
| 1201 | CePO4 | Synthetic | Cherniak phosphate |
| 1202 | PrPO4 | Synthetic | Cherniak phosphate |
| 1203 | NdPO4 | Synthetic | Cherniak phosphate |
| 1204 | SmPO4 | Synthetic | Cherniak phosphate |
| 1205 | EuPO4 | Synthetic | Cherniak phosphate |
| 1206 | GdPO4 | Synthetic | Cherniak phosphate |
| 1207 | TbPO4 | Synthetic | Cherniak phosphate |
| 1208 | DyPO4 | Synthetic | Cherniak phosphate |
| 1209 | HoPO4 | Synthetic | Cherniak phosphate |
| 1210 | ErPO4 | Synthetic | Cherniak phosphate |
| 1211 | TmPO4 | Synthetic | Cherniak phosphate |
| 1212 | YbPO4 | Synthetic | Cherniak phosphate |
| 1213 | LuPO4 | Synthetic | Cherniak phosphate |
| 1214 | YPO4 | Synthetic | Cherniak phosphate |

**Minor element substitution in zircon and formula calculation routine**

*Background*

Aside from direct, charge-balanced substitution of Hf4+, U4+, Th4+ for Zr4+, the most common minor elements in zircon are Y and HREE, which can readily substitute for Zr due to the similarity in ionic size between (Y3+,HREE3+) and Zr4+. Typically, this substitution correlates with incorporation of P into the Si site (so-called ‘xenotime substitution’; [(Y,REE)3+ + P5+ ↔ Zr4+ +Si4+]) to maintain charge balance (Hoskin and Schaltegger, 2003). Empirical observation suggests, however, that more complex substitutions may also operate (see below). Pentavalent Nb and Ta are considered to preferentially substitute into the Zr site (Akhtar and Waseem, 2001).

Although most researchers have reached a consensus on the main mechanisms of substitution and the likely sites for each substituent, there exists some lack of equivocality, notably with respect to the potential role of interstitial sites, and even the charge of some substituted ions, e.g., Fe (Pérez-Soba et al., 2007). The routines used here are adapted from those used for hydrogarnet and are based on a logical, sequential approach but inevitably, also several of assumptions.

Volatile content in zircon is often invoked from low EPMA totals, either as substituted OH- or molecular H2O within amorphous domains within the zircon structure. A theoretical background and empirical evidence for OH- substitution into zircon is well documented (Frondel, 1953; Caruba et al., 1985; Nasdala et al., 2009; Trail et al., 2011; de Hoog et al., 2014). Experimental evidence shows that [(OH,F)4]4- can occupy more than half the [SiO4]4- positions in zircon (Caruba et al., 1985). Unequivocal evidence for halogen substitution in natural samples remains less well documented, even if low levels of substitution are reported (e.g., Zeng et al., 2017).

*Formula calculation routine*

The zircon formulae, in terms of atoms-per-formula-unit (apfu), was calculated based on full occupancy of the tetrahedral IV*B, with* ∑*B*≥1, and variable occupancy of the dodecahedral VIII*A* site, with *A*+*B*=2. Rarely, ∑(Si, P, Ti) can exceed 1 apfu in the *B*-site, which is therefore compensated by <1 apfu in the *A*-site, and distribution of Al over both sites. The allocation of Fe exclusively into the *A*-site bears on the amount of water (as OH-) incorporated by the hydrogarnet-type substitution. Based on average oxide totals (dry; no F or Cl included) across the dataset of ~99.2 wt%, the correction procedure considering hydrogarnet-type substitution and REY+Sc incorporation, as explained below, is considered to best represent our data, even if some assumptions are inevitably involved. Considering these substitutions, the corrected totals, including water moderately increase, approaching 100% (average totals of ~99.6 wt%).

Limited, monovalent cation incorporation (Me+: Na, K) is considered within interstitial positions (*i*) in distorted octahedral coordination, or within a 4-fold coordinated site (Finch and Hanchar, 2003). Cations were assigned following the general formula *iAB*O4, although also permitting vacancies in oxygen sites and incorporation of halogens (F, Cl) or OH--groups, with:

*i*: Na+, K+ (and potentially also Li+);

*A*: Mg2+, Al3+\*, Ca2+, Sc3+, Mn2+, Fe3+, Y3+, Zr4+, Nb5+, REE3+, Hf4+, Pb2+, Th4+ and U4+;

*B*: Al3+[[1]](#footnote-1)\*, Si4+, P5+, Ti4+, Si\*, with Si\* representing missing Si due to hydrogarnet-type substitution: (see Frondel and Collette, 1957; Botis et al., 2013).

Molecular proportions of metals were obtained by dividing the measured oxides by their molecular weights and multiplying by the number of cations per oxide molecule; molecular proportions of halogens (F, Cl) were obtained by dividing the measured concentrations by their respective atomic weights.

Titanium has been experimentally shown to substitute Si in the *B*-site (Tailby et al., 2011). Simulation modelling has indicated that Al may be preferentially present in the *B*-site (Akhtar and Waseem, 2001). The amount of Si missing by the hydrogarnet substitution is calculated from the difference between cations allocated in the *A*- and *B*-sites excluding Al; if ∑B>∑A then Al is assigned to the *A*-site so that ∑B=∑A. However, after this step, if ∑B+Al is still lower than ∑A, the difference between ∑B+Al and ∑A is considered to represent substituted Si by the hydrogarnet substitution (Si\*). Following this step, a normalization factor is calculated: *f*n=2/(∑*A*+∑*B*) and applied, after which the normalized cations, in apfu, are distributed between the different sites, as indicated above.

Calculated OH- by the hydrogarnet substitution scheme must be corrected for already-incorporated F and/or Cl, if measured, which are subtracted.

Zircon favours (H)REE-incorporation, proposed to occur by charge-balance, coupled substitution involving P, which forms isostructural compounds with REE, Y and Sc, including xenotime (YPO4) and pretulite (ScPO4) (Finch and Hanchar, 2003 and references therein): . In several cases, the presence of P alone cannot, however, support the observed REE concentrations, a phenomenon reflected by ∑(REEs,Y,Sc)/P ratios that deviate from unity. This is interpreted in terms of more complex substitution mechanisms:

(1) , with Me3+ as a REY+Sc;

(2) , with Me+ as Li, Na and/or K;

(3) , with Me5+ as Nb for example.

Uncompensated substitution of REY+Sc, is balanced by incorporation H+ within interstitial sites. Other incorporated Me2+ and Me3+ in the *A*-site, are compensated by O-vacancies.

In theory, other trivalent cations might be present in dodecahedral sites, incorporated by the same type of substitution: Zr4+ + O2- ↔ Me3+ + (F, Cl, OH)-. Incorporation of, e.g., Fe and Al, in this way is, however, poorly supported in the literature.

Experimental support for Fe incorporation in zircon has been given by several authors, albeit with subtly different results and interpretations. Váczi (2009) reports the doping of zircon with Fe (0.01-0.39 wt.%). Iron, both as dominant Fe3+ and subordinate Fe2+, was found to be “predominantly located on the six-coordinated interstitial site”. Important for the present work, incorporated Fe was present within oscillatory-zoned bands within the zoned crystals. Carreto Cortés et al. (2004) have demonstrated limited solid solution, up to about 2.5 mol% Fe, may be hosted within the zircon structure, with excess Fe3+ forming α-Fe2O3 particles that become trapped in the zircon matrix. Based on synthesis at 1100-1600 °C and refinement of X-ray diffraction patterns, Herrera-Pérez (2015) proposes that Fe3+ is distributed into tetrahedral sites, replacing Si4+.

*Lanthanide concentrations*

The lower abundance of lanthanides with odd atomic numbers, commonly below minimum detection limits (mdl) of the EPMA method needs to be considered for accurate assessment of zircon stoichiometry and estimation of water contents. The abundance of HREE, with odd atomic numbers, where <mdl, has been estimated from the adjacent, even atomic number HREE considering the consistent behaviour of HREE fractionation in zircon. This approach is corroborated by the LA-ICP-MS data on the same zircons. So, if Tm2O3 is <mdl, and Er2O3 = 0.071 wt% and Yb2O3 = 0.255 wt%, Tm2O3\* was obtained by dividing the measured concentrations of Er2O3 and Yb2O3 by their respective molecular oxide masses and multiplied by the elemental mass of the respective REE to obtain their elemental concentration. Following this step, both elements are divided by their chondrite abundance to obtain their normalized values, from which the concentration of Tm can be interpolated. The geometric means of these two values are then multiplied by the chondrite value for Tm, and then multiplied by the oxide molecular weight of Tm2O3 and finally multiplied by the elemental mass of Tm, yielding Tm2O3\*= 0.021 wt%.

*Modified calculation routine for Charleston zircon*

EPMA analysis of zircon from the Charleston Granite sample was undertaken simultaneously with the other samples, however recalculation of formula using the above routine does not give reasonable results in terms of A:B stoichiometry.

The main difference with the previous calculation is that substitution of Fe into the *B*-site is also considered, following a similar approach as described above. If after allocation of Al in the *B*-site, ∑*A*>∑*B* (without considering Fe), then Fe is assigned to the *B*-site so that ∑B=∑A. However, if after this step ∑B+Fe is lower than ∑A, the difference between ∑B+Fe and ∑A is considered to represent missing Si by the hydrogarnet substitution. In general, this approach produces lower estimates for the incorporation of OH.

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1. \* In this model, Al will be distributed between the A and B site, so that B is always >=1, and if there is excess Al, this will be incorporated in the A site. [↑](#footnote-ref-1)