

Supplementary Materials for “Half a million years of magmatic history recorded in a K-feldspar megacryst of the Tuolumne Intrusive Complex, California”

Sample Selection and Zircon Separation

A single K-feldspar megacryst (LFO-74: 37.81042°, -119.32002°; NAD27 projection) was separated from the host rock by using a hammer to knock loose a partially weathered out megacryst. Any remaining host rock on the megacryst was shaved off, and then the K-feldspar was cut perpendicular to the b-axis using a trim saw. Both halves were cut into core, mantle, and rim sections (Fig. 2). The core was defined by abundant mafic mineral inclusions, while the rim was ~1 cm of the outer edge of the megacryst. The mantle, represented by the part of the megacryst between the core and rim, was excluded from analyses. Zircons were separated by traditional density and magnetic techniques after crushing the relevant K-spar sections. Additional zircons were separated from the groundmass material by cutting slabs of groundmass and removing megacrystic K-feldspars using a trim saw. After crushing, traditional density and magnetic separation techniques using heavy liquid and a Frantz magnetic separator were used.

CA-ID-TIMS Zircon Geochronology

Eleven to thirteen zircons were selected from each sample (K-spar core, K-spar rim, and matrix) for U-Pb chemical abrasion-isotope dilution-thermal ionization mass spectrometry (CA-ID-TIMS; Mattinson, 2005) geochronology. The grains were first annealed for 60 hours at 900°C and then individually leached in 29 M HF at 215°C in a Parr acid digestion vessel. Subsequently, the leachate was discarded and the zircons were repeatedly rinsed in 29M HF, H₂O, and 6N HCl. After rinsing, ~0.006 g of EARTHTIME ²⁰²Pb-²⁰⁵Pb-²³³U-²³⁵U isotopic tracer (McLean et al., 2015; Condon et al., 2015) and 75-100 µl of 29M HF were added to each zircon-bearing microcapsule. The microcapsules were then re-loaded into Parr dissolution vessels and the zircons were completely digested at 215°C for 48-60 hours. The resulting solutions were then dried down and dissolved in 6N HCl at 180°C for ~12 hours to convert the samples to chloride. Uranium and Pb were purified from the dissolved sample with AG-1 X8 200-400 mesh anion exchange resin using methods modified from (Krogh, 1973). Samples were first loaded onto 50 µl anion exchange columns in 50-75 µl of 3N HCl and rinsed drop-wise to remove trace elements. Pb and U were then eluted using 200 µl of 6N HCl and 250 µl of H₂O, respectively. Samples were dried down with a micro-drop of 0.05N H₃PO₄ prior to analysis via TIMS.

All of the isotopic data was collected on the Isotopx Phoenix TIMS at Princeton University. Lead was run as a metal and measured by peak hopping on a Daly photomultiplier. Uranium was analyzed as UO₂ and was measured statically on a series of faraday cups. Measured UO₂ ratios were corrected assuming an ¹⁸O/¹⁶O of 0.00205 ± 0.00004 (2σ), corresponding to the modern atmospheric value (Nier, 1950). Corrections for mass dependent fractionation were done using the known ratios of ²⁰²Pb/²⁰⁵Pb and ²³³U/²³⁵U in the ET2535 isotopic tracer and assuming a ²³⁸U/²³⁵U of 137.818 ± 0.045 (2σ), which represents the mean value of ²³⁸U/²³⁵U measured in natural zircon (Hiess et al., 2012). Corrections for Pb fractionation were done cycle-by-cycle. However, the correction for U fractionation was done using the mean ²³³U/²³⁵U for the analysis. Daly photomultiplier dead time for Pb was monitored by running the NBS981 and NBS982 Pb isotopic standards over the range 1000 cps to 2.5 Mcps.

A well-known problem in the measurement of small amounts of Pb by TIMS is the effect of isobaric interferences. Known isobaric interferences include BaPO₄ and Tl. These interferences were corrected by measuring masses 201 and 203, assuming that they represent ²⁰¹BaPO₄ and ²⁰³Tl, and using the natural abundances of ²⁰²BaPO₄, ²⁰⁴BaPO₄, ²⁰⁵BaPO₄, and ²⁰⁵Tl to correct the measurements of masses 202, 204, and 205. These corrections were minor and have no effect on our data interpretations.

A correction for common Pb (Pb_c) was done by assuming that all Pb_c is from laboratory contamination and using the measured ^{204}Pb and a laboratory Pb_c isotopic composition to subtract the appropriate mass of Pb_c from each analysis. We consider the assumption that all measured Pb_c is from laboratory contamination to be robust, because the typical Pb_c seen in zircon analyses (< 1 pg) is comparable to the mass of Pb_c seen in procedural blanks. These procedural blanks are also used to quantify the Pb_c isotopic composition at Princeton University. The resulting composition is $^{206}Pb/^{204}Pb = 18.6 \pm 0.6$ (2σ), $^{207}Pb/^{204}Pb = 15.8 \pm 0.4$ (2σ), $^{208}Pb/^{204}Pb = 38.5 \pm 0.8$ (2σ) for 31 measurements made from January 2017 through the course of our study.

A correction for initial secular disequilibrium in the ^{238}U - ^{206}Pb system due to the exclusion of Th during zircon crystallization (e.g., Schärer, 1984) was made for each analysis using a ratio of zircon/melt partition coefficients (f_{ThU}) of 0.119. This empirically determined value is taken from coexisting high- SiO_2 glass and zircon rims/surfaces in dacite from Mt. St. Helens (Claiborne et al., 2018). We view this as the best analogue available for silicic, hydrous, arc magmatism. Nevertheless, we have applied a generous uncertainty of ± 1 (2σ) for the calculated $[Th/U]_{Magma}$.

All data reduction was done with the Tripoli and ET_Redux software packages (Bowring, 2011) using the algorithms presented in McLean (2011). The U decay constants are from Jaffey (1971). Isotopic data is presented in Table S1. All uncertainties are presented as 2-sigma or 95% confidence intervals (CI). Since all of the data used in our interpretations was determined using the same isotopic tracer (ET2535) and isotopic system (U-Pb), we only report analytical uncertainties in Figure 2 and Table S1.

To check the reproducibility and external reproducibility of U-Pb age determinations produced in the Princeton Geochronology Laboratory, we analyzed a synthetic solution (ET100) designed to have a $^{206}Pb/^{238}U$ ratio equivalent to a zircon that is 100 Ma. During the course of this study, we analyzed 18 aliquots of this solution and obtained a $^{206}Pb/^{238}U$ date of 100.168 ± 0.011 Ma (2σ , analytical uncertainties only) with an MSWD of 0.75. The MSWD of 0.75 gives us confidence that systematic uncertainties are appropriately constrained at Princeton University. The data for these standard solutions was collected coeval with the data presented in this study, as well as the data presented in Schoene et al. (2019) and was previously published as part of the supplementary material for Schoene et al. (2019).

Zircon Trace Element Analyses

The trace element composition of the analyzed zircons was analyzed using the TIMS-TEA method of Schoene et al. (2010). It utilizes the wash solutions obtained during anion exchange column chemistry during U-Pb separations. This solution contains all of the trace elements from the dissolved volume of zircon, except U and Pb, and can be analyzed by solution inductively coupled plasma-mass spectrometry (ICP-MS). To accomplish this, the trace element aliquots were dried down and then re-dissolved in 3% HNO_3 + 0.2% HF + 1 ppb In. The resulting solution was analyzed on a Thermo-Fisher iCAP quadrupole ICP-MS using a Teledyne-Cetac ASX-100 autosampler. Uptake time was 20s and 60s was used to wash the line with 3% HNO_3 + 0.2% HF between each analysis. Measured elements include Y, Zr, Hf, REE, Th and In (used as an internal standard). A dilution series of a synthetic zircon solution was used to generate a concentration-intensity calibration curve over the range of concentrations observed in most zircon TIMS-TEA analyses. Reproducibility was assessed using a homogeneous solution of Plešovice zircon (Sláma et al., 2008) in addition to a solution with a known Zr/Hf ratio of 50. Measurements of procedural blanks were monitored for laboratory trace element contamination. Sets of 4 unknowns were bracketed by measurements of the Zr/Hf and Plešovice standard, and a new calibration curve was made for every 20 unknowns. Measurement of these unknowns was done concurrently with several other datasets, and the total number of standards run during these sessions is reported. Solution measurements were converted to zircon concentrations by assuming that all of the measured trace elements substitute for Zr^{4+} , such that $\Sigma = Zr + Hf + Sc + Y + Nb + Ta + REE = 497,646$ ppm. The results from the analyses are presented in Table S2. Procedural blanks show no significant laboratory trace element contamination for the elements of interest. Repeat analyses of the Zr/Hf ratio in our Zr/Hf standard solution give a weighted mean value of 50.53 ± 0.29 (2σ , MSWD = 0.30), within $\sim 1\%$ of the reference value of 50. Consequently, we consider our long-term reproducibility to be within $\sim 1\%$. Repeat runs of the Plešovice zircon solution are highly reproducible for REE heavier than Nd (Fig. S1 in GSA

Data Repository), with one outlier analysis, and provide confidence in our reproducibility of natural zircon trace element concentrations.

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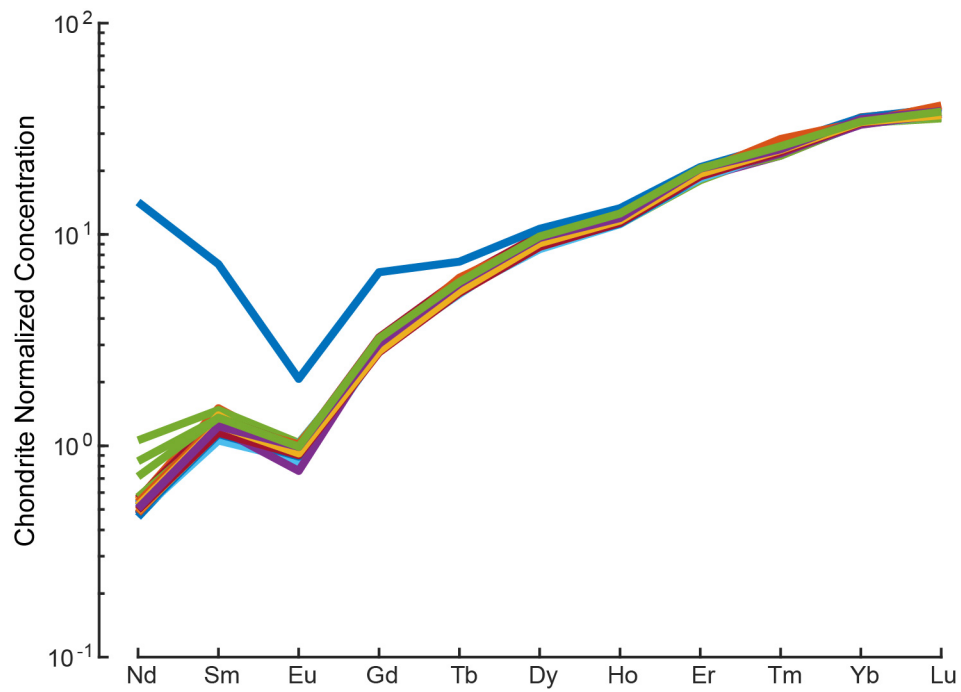


Figure DR1. Repeat runs of the Plešovice zircon solution with one analysis forming an outlier. Reproducibility is within 1% for REE heavier than Nd and provide confidence in our reproducibility of natural zircon trace element concentrations.

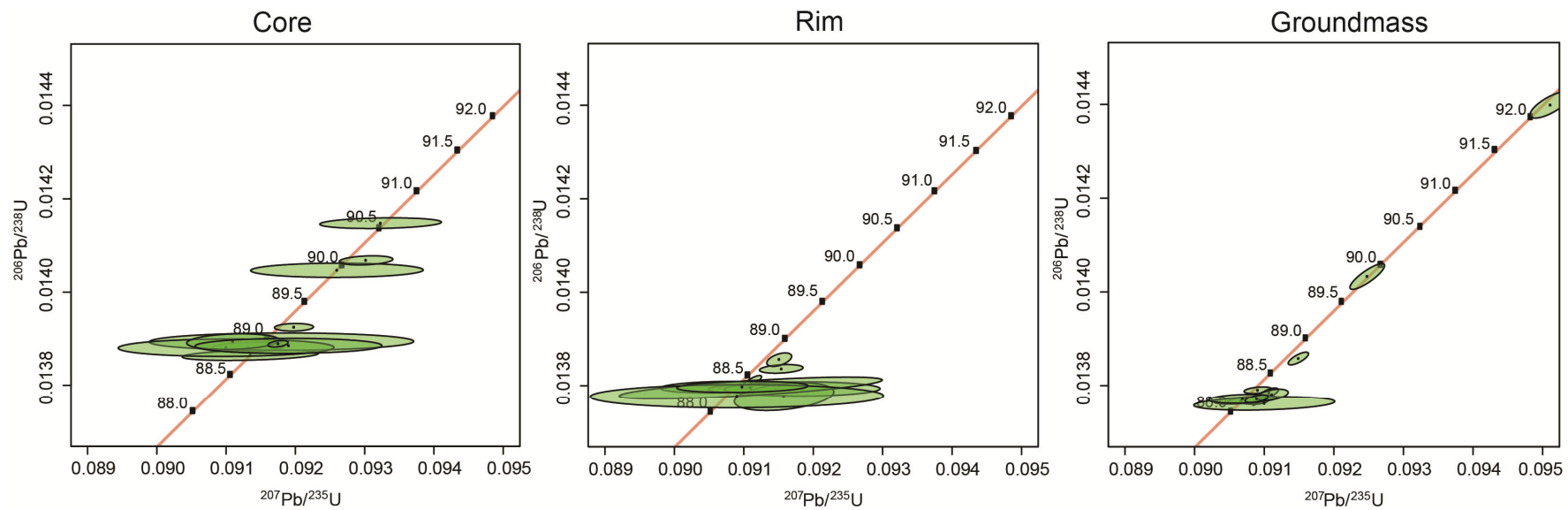


Figure DR2. Concordia plots for zircons separated from the core and rim of megacryst LFO-74 and its surrounding groundmass.

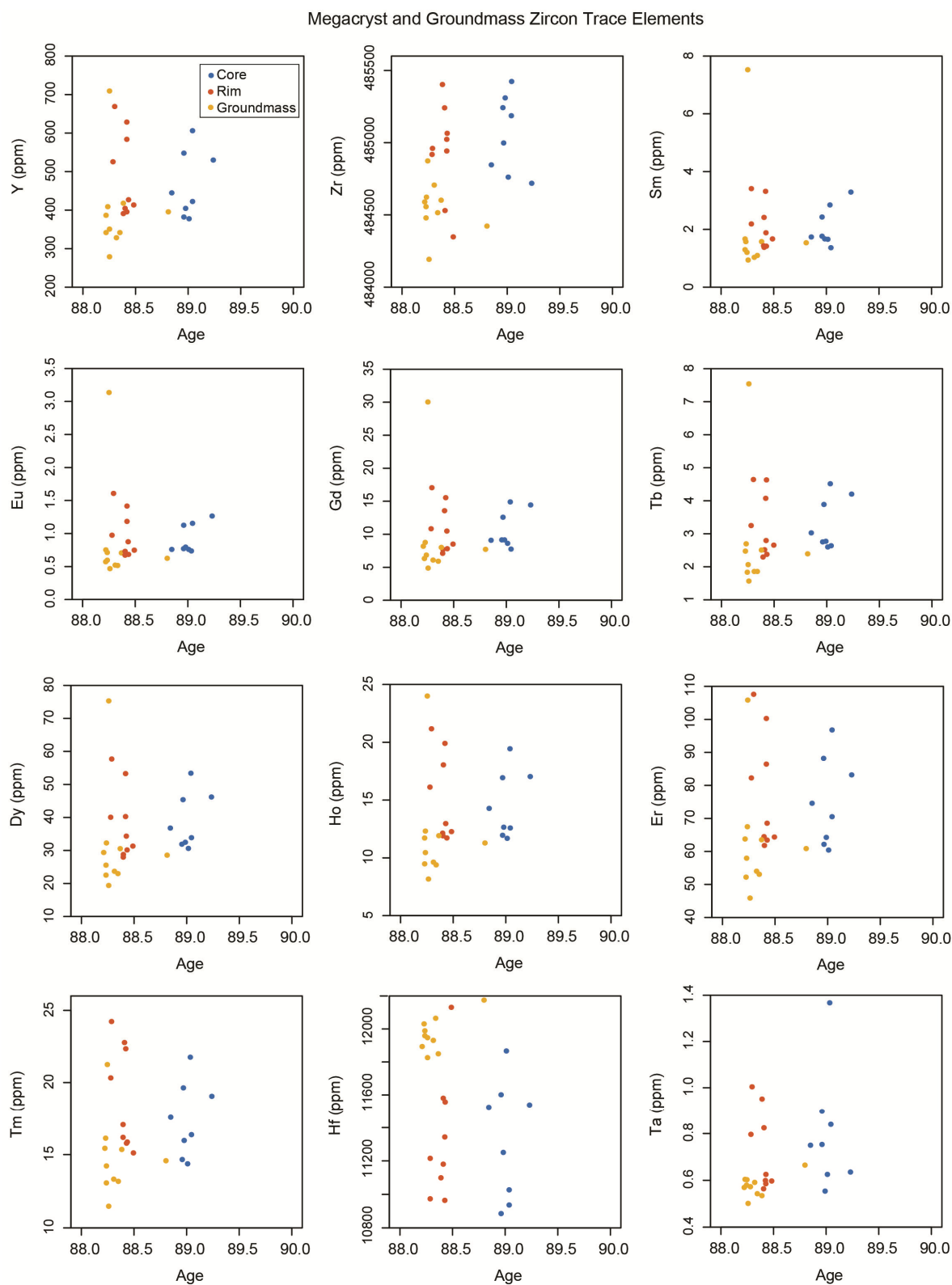
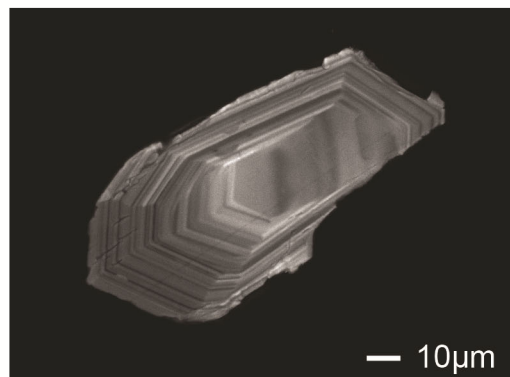
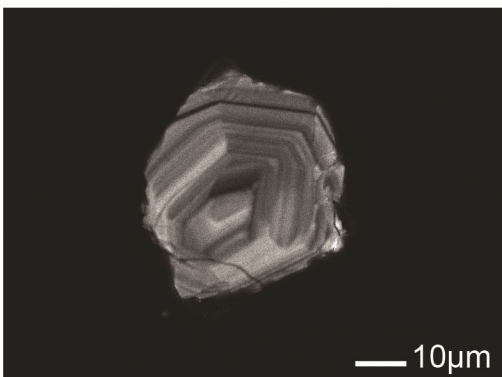
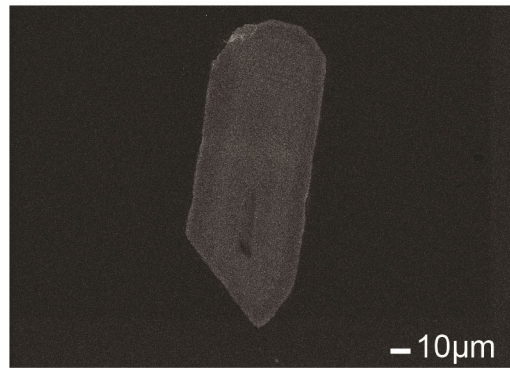
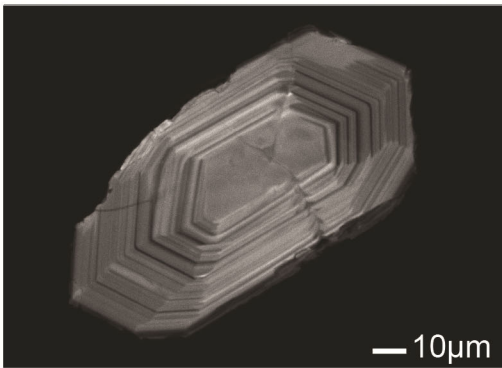
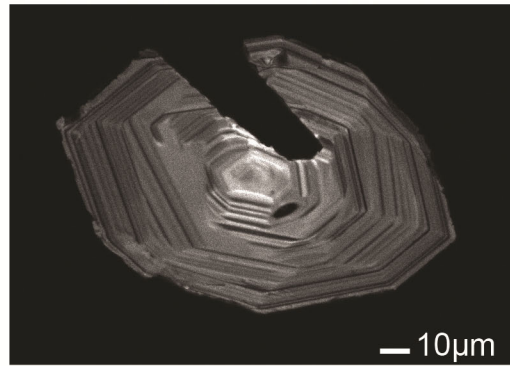
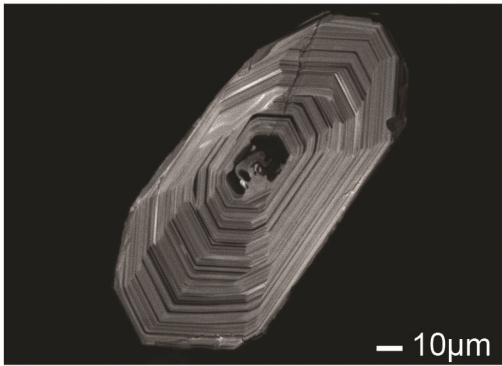
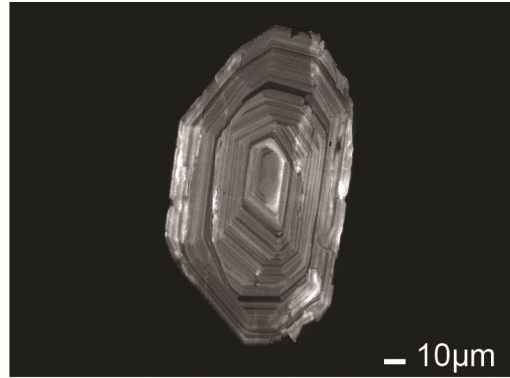
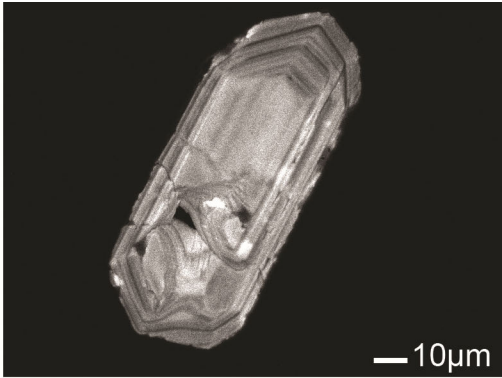


Figure DR3. Additional elements analyzed from the core, rim, and groundmass zircons of LFO-74 showing overlapping concentrations for core and rim, while groundmass values remain separate.



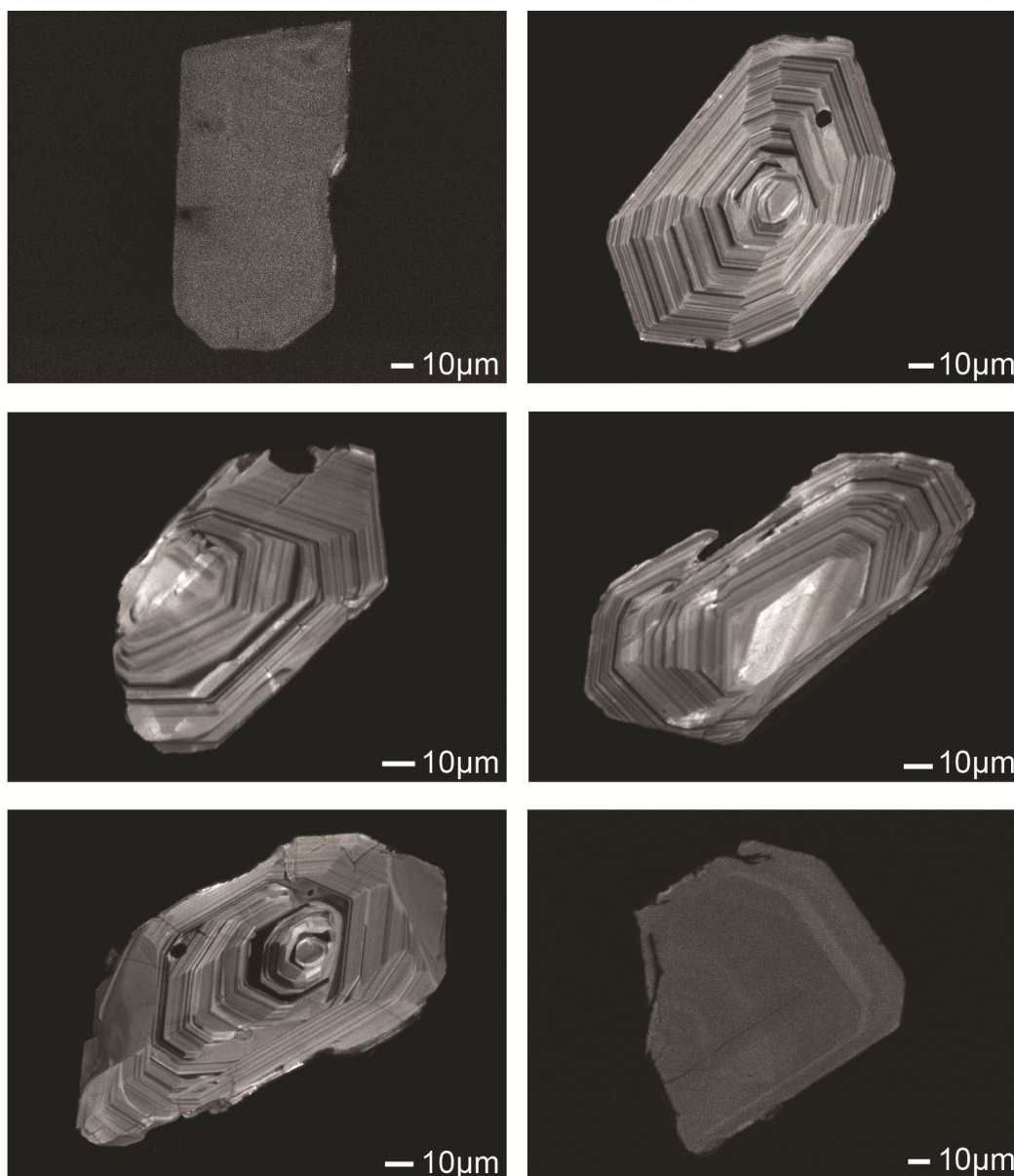


Figure DR4. Cathodoluminescence images of oscillatory zoned zircon inclusions from the core and rim of megacryst LFO-74. These images are representative of each zircon fraction.