

Shocked titanite records Chicxulub hydrothermal alteration and impact age

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Abstract

Hydrothermal activity is a common phenomenon in the wake of impact events, yet identifying and dating impact hydrothermal systems can be challenging. This study provides the first detailed assessment of the effects of shock microstructures and impact-related alteration on the U-Pb systematics and trace elements of titanite (CaTiSiO₅), focusing on shocked granite target rocks from the peak ring of the Chicxulub impact structure, Mexico. A > 1 mm long, shock-twinned titanite grain preserves a dense network of irregular microcracks, some of which exploit shock twin interfaces. Secondary microcrystalline anatase and pyrite are heterogeneously distributed along some microcracks. In situ laser ablation multi-collector inductively-coupled plasma mass spectrometry (LA-MC-ICPMS) analysis reveals a mixture of three end-member Pb components. The Pb components are: 1) common Pb, consistent with the Pb isotopic signature of adjacent alkali feldspar; 2) radiogenic Pb accumulated since magmatic crystallization; and 3) a secondary, younger Pb signature due to impact-related complete radiogenic Pb loss. The youngest derived ages define a regression from common Pb that intersects Concordia at 67 ± 4 Ma, in agreement with the established age of 66.04 ± 0.05 Ma for the Chicxulub impact event. Contour maps of LA-MC-ICPMS data reveal that the young ages are spatially restricted to microstructurally-complex domains that correlate with significant depletion in trace elements (REE-Y-Zr-Nb-Mo-Sn-Th) and reduction in magnitude of the Eu/Eu* anomaly. Mapping by time-of-flight secondary ion mass spectrometry (ToF-SIMS) show that patterns of localised element depletion in titanite are spatially related to microcracks, which are enriched in Al. The spatial correlation of ages and trace element abundance is consistent with localised removal of Pb and other trace elements from a pervasive network of fast fluid pathways in

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fractured domains via a fluid-mediated element transport process associated with the impact event. Here we interpret the 67 ± 4 Ma U-Pb age to represent hydrothermal Pb-loss in the Chicxulub peak ring in the wake of the impact event. These results highlight the potential of our analytical approach using titanite geochronology and geochemistry for dating post-impact hydrothermal activity in impact structures elsewhere.

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1. INTRODUCTION

Hypervelocity impact events have played a key role in the evolution of Earth's lithosphere, biosphere, and atmosphere (e.g. [Kring, 2003](#); [Marchi et al., 2016](#)), and are well known for generating craters and ejecta horizons throughout Earth's history ([Grieve and Shoemaker, 1994](#)). Impact events generate extremely high pressures (on the order of tens of GPa and greater) in target rocks over geologically instantaneous time periods (ms–s; [Melosh \(1989\)](#)). The passage of a shockwave through the target and impactor creates unique deformation and metamorphic effects, such as shatter cones, high-pressure phases, and various planar microstructures in minerals (e.g. [French and Koeberl, 2010](#)). The impact-generated melting of large volumes of target rocks and the uplift of deep-seated target rocks can induce long-lived hydrothermal circulation cells that are effective at chemical mobilization and redistribution. Hydrothermal activity that often follows terrestrial impact events (e.g. [Naumov, 2002](#); [Osinski et al., 2013](#)) can have profound geochemical and physical effects on rocks at impact sites ([Abramov and Kring, 2007](#)).

Identifying and dating impacts, especially after the topographic evidence of craters has been weathered and eroded, remains challenging. Many advances have been made in the age-dating of impact events using shocked U- and Th-bearing accessory phases such as zircon, monazite, xenotime, and baddeleyite, especially via recent studies of these minerals that combine quantitative microstructural and geochronological approaches (e.g. [Darling et al., 2016](#); [Erickson et al., 2017](#); [Kenny et al., 2017](#); [Hauser et al., 2019](#); [Erickson et al., 2020](#)). Due to shock metamorphism, U- and Th-bearing accessory phases can develop a wide variety of microstructures including fractures, twins, crystal-plastic deformation, polymorphism, dissociation, and granular textures with domains of recrystallisation known as neoblasts (e.g. [Timms et al., 2017](#)). In weakly to moderately shocked zircon, the U-Pb system is often only partially reset or not reset at all, and U-Pb data may provide important constraints on the magmatic or pre-impact metamorphic age for crystalline target rocks (e.g. [Krogh et al., 1993b](#)). A general consensus has emerged that neoblastic domains that form as a consequence of recrystallisation during high-temperature impact metamorphism result in resetting of the U-Pb system and, along with grains grown directly from impact melt (e.g. [Grange et al., 2013](#)), can be targeted to date impact events (e.g. [Cavosie et al., 2015](#); [Erickson et al., 2017](#); [Kenny et al., 2017](#); [Hauser et al., 2019](#)). Nevertheless, targeted U-Pb geochronology of neo-

blasts does not always reliably date impact events ([Kamo et al., 1996](#); [Schmieder et al., 2015](#)).

Other recrystallization processes may also be important for dating impact events. Hydrothermal systems generated by impacts ([Naumov, 2002](#); [Osinski et al., 2013](#)) are common and have been recognized at over 70 impact structures, including Chicxulub ([Ames et al., 2004](#); [Hecht et al., 2004](#); [Zürcher and Kring, 2004](#)), and may be critically important for the redistribution of radiogenic isotopes. Ideal U-Pb geochronometers rely on the presence of U (and/or Th) in the crystal lattice, and a generally low initial Pb content, with most Pb being generated by radioactive decay of U (i.e., radiogenic Pb). Radioactive decay leads to some level of radiation damage in the crystal lattice ([Meldrum et al., 1998](#)), and as a result, radiogenic Pb is relatively loosely bound in the primary crystal lattice. Hence radiogenic Pb is, in comparison to U and/or Th, relatively mobile, and is particularly susceptible to loss at the margins of the crystal and along fractures. Loss of radiogenic Pb from U-bearing crystals may be driven by metamorphism, recrystallization, and reaction with fluids. Radiogenic Pb loss within zircon has been invoked as a process that may directly date the timing of impact-induced hydrothermal systems ([Rasmussen et al., 2019](#)). However, the utility of this approach to impact dating is questionable because zircon commonly remains remarkably robust to Pb loss. Metamictization can make zircon susceptible to geochemical alteration, and U-Pb analysis of shocked radiation-damaged zircon can yield variably spurious ages due to post-impact Pb-loss from a metamict structure ([Schmieder et al., 2015](#); [Rasmussen et al., 2019](#)).

Titanite (CaTiSiO_5) is a common U-bearing accessory mineral in a wide range of lithologies, can crystallise from melt, grow as a reaction product from other phases, or recrystallise during metamorphism, and is a useful geochronometer for a wide range of geological processes (e.g. [Kylander-Clark et al., 2008](#); [Kohn and Corrie, 2011](#); [Spencer et al., 2013](#); [Bonamici et al., 2015](#); [Kohn, 2017](#); [Marsh and Smye, 2017](#); [Scibiorski et al., 2019](#)). Incorporation of a wide range of trace elements in titanite, such as Sr, Nb, Mo, Y, and rare earth elements (REE) can be linked to magma composition, crystal fractionation, and fluid composition during titanite recrystallisation, whereas Zr in titanite has been calibrated as a geothermometer (e.g. [Storey et al., 2007](#); [Hayden et al., 2008](#); [Kohn, 2017](#)). Here we document how the microstructure and trace element geochemistry of titanite grains within the crystalline basement of the Chicxulub impact structure are affected by the shock metamorphic history and subsequent impact-induced hydrothermal activity. Particular attention is given

to the response of the U–Pb system in titanite to test whether the shocked granite target rocks in the peak ring of Chicxulub have preserved an isotopic record of the impact event.

1.1. Titanite in impact metamorphic contexts

The mechanical response of titanite to impact includes the development of sub-planar and planar fractures, crystal-plastic deformation, and deformation twinning (e.g. Borg, 1970; Deutsch and Schärer, 1990; Papapavlou et al., 2018; Timms et al., 2019). Timms et al. (2019) used electron backscatter diffraction analysis to index crystal-plastic deformation bands in {130} and polysynthetic twins in $\sim\{111\}$ and less commonly {130} in titanite within granitoids shocked at $\sim 12 \pm 5$ to 17 ± 5 GPa (Rae et al., 2019), more recently refined to ~ 15 to 18 GPa (Feignon et al., 2019) pressure conditions in the peak ring of the Chicxulub impact structure, Mexico. These twin modes are crystallographically distinct from $\sim\{221\}$ lamellar deformation twins that can form under tectonic stresses (Borg and Heard, 1972). Papapavlou et al. (2018) reported neoblastic domains in shock-twinned titanite from the Sudbury and Vredefort impact structures, in Canada and southern Africa, respectively, and suggest that neoblasts can be formed in impact environments. However, these microstructures are similar in appearance to tectonically-driven recrystallisation domains (e.g. Papapavlou et al., 2017), indicating that neoblastic microstructures are not uniquely impact-related features in titanite. In target rocks from the peak ring of the Chicxulub structure, titanite has been reported to vary from apparently unaltered crystals, to grains with aggregates of small ($<5 \mu\text{m}$) crystals of TiO_2 decorating fracture surfaces and grain boundaries, to titanite entirely pseudomorphed by aggregates of microcrystalline TiO_2 (rutile), calcite, chlorite, and silica, and/or epidote (Schmieder et al., 2017; Timms et al., 2019). However, some pseudomorphed titanite preserves evidence of the high-pressure PbO_2 -structured TiO_2 polymorph (formerly TiO_2 -II, named recently as srilankite by Tschäuner et al. (2020)) as aggregates of crystals up to $\sim 70 \mu\text{m}$ across replacing rutile and/or anatase after titanite (Schmieder et al., 2017; Schmieder et al., 2019). This shock-induced transformation has been interpreted to be a product of shock metamorphism of pre-impact alteration products of titanite (Schmieder et al., 2017; Schmieder et al., 2019).

A few studies have investigated the effects of impact metamorphism on U–Pb resetting in titanite, and found variable responses for the correlation between microstructure and age. Laboratory shock deformation experiments on titanite up to 59 GPa by Deutsch and Schärer (1990) showed no significant effects on U–Pb systematics. Papapavlou et al. (2018) demonstrated that twinned titanite from Sudbury can record a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1851 ± 12 Ma, which is contemporaneous with the date of the impact event. Texturally distinct (low-U, dark in backscattered electron images) domains in the same sample yield U–Pb ages younger than the impact event that are associated with an orogeny that post-dates Sudbury. However, twinned titanite grains from Vredefort preserve predomi-

nantly pre-impact ages, with limited U–Pb isotopic disturbance localised around twins which did not yield the age of the Vredefort impact event via SIMS analysis. Titanite in impactites from Steen River impact structure, Canada, preserve partial U–Pb age resetting, with greater Pb-loss recorded by grains within impact melt and recrystallised matrix (McGregor et al., 2020). McGregor et al. (2019) analysed U–Pb in titanite grains (one LA-ICPMS analysis spot per grain) in impactites from the 8 km diameter Lac La Moine impact structure, Canada, and reported that age-resetting is related to different textural settings, with most resetting restricted to grains in contact with impact melt, which date the impact event. These studies show potential for U–Pb disturbance of titanite during impact events, but no common mechanisms or conditions for complete resetting are yet understood.

1.2. Geological setting

The ~ 66 Ma, ~ 200 km-diameter Chicxulub impact structure, on the Yucatán Peninsula and Gulf of Mexico (Fig. 1) (Hildebrand et al., 1991; Gulick et al., 2008; Renne et al., 2013), is one of the three largest known terrestrial impact structures (Grieve and Theriault, 2000). The Chicxulub impact event is widely regarded to have caused the K–Pg global mass extinction (e.g. Schulte et al., 2010). The impact event resulted in globally-distributed ejecta deposits (Claeys et al., 2002) with a distinctive iridium anomaly key to the K–Pg impact – mass-extinction hypothesis (Alvarez et al., 1980). Chicxulub has a complex crater structure with a well-defined peak-ring (Morgan et al., 2016). Drill cores from the structure, including the recently recovered International Ocean Discovery Program (IODP) – International Continental Scientific Drilling Program (ICDP) Expedition 364 Hole M0077A ($21^\circ 27.009'\text{N}$, $89^\circ 56.962'\text{W}$) indicate that the target rocks are comprised of a sequence of shallow marine platform sediments overlying granitic basement rocks of the Maya Block (Morgan et al., 2017). The granitic target rocks are coarse-grained and primarily composed of alkali feldspar, quartz, plagioclase, minor biotite, and accessory muscovite, apatite, titanite, epidote, magnetite, ilmenite, and zircon (Morgan et al., 2017; Schmieder et al., 2017). Pre-impact mafic and felsic dykes cut across the granitic rocks. The granitic rocks are also intercalated with impact breccia and impact melt rocks (Morgan et al., 2017; Riller et al., 2018).

Recently obtained U–Pb age data for zircon in the uplifted granite from the peak ring of the impact structure yielded a weighted mean U–Pb age of 326 ± 5 Ma ($n = 40$, $\text{MSWD} = 0.75$) (Zhao et al., 2020). U–Pb studies on shocked zircon crystals in K–Pg boundary ejecta deposits indicate lower intercept ages from 57 ± 4 Ma to 69 ± 1 Ma (Bohor et al., 1993; Krogh et al., 1993a; Kamo and Krogh, 1995; Keppie et al., 2010; Kamo et al., 2011), whereas $^{40}\text{Ar}/^{39}\text{Ar}$ of glass fragments ejected from the crater indicate a precise age of 66.04 ± 0.05 Ma for the impact event (Renne et al., 2013). The $^{40}\text{Ar}/^{39}\text{Ar}$ ages are consistent with a U–Pb age of 66.02 ± 0.08 Ma for the K–Pg boundary exposed in the Denver Basin, Colorado, USA (Clyde et al., 2016). Furthermore, metamict zircon from

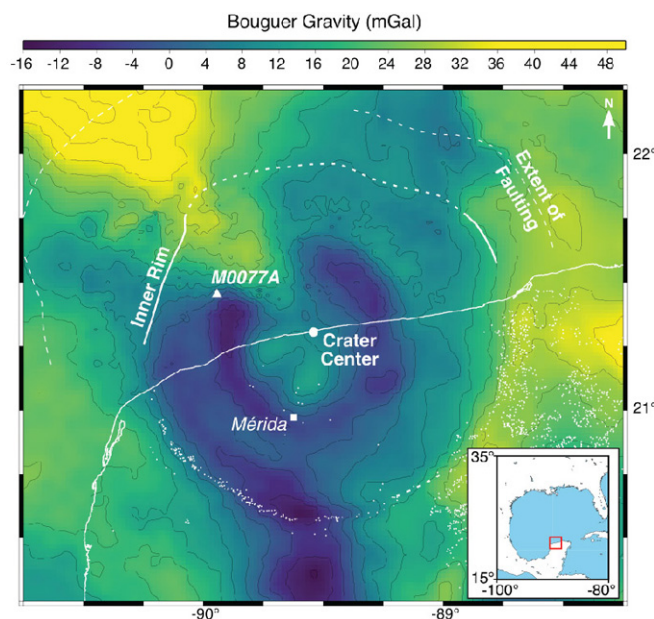


Fig. 1. Map showing the gravity anomaly expression of the Chicxulub impact structure, Mexico. Modified after [Gulick et al. \(2013\)](#), and [Timms et al. \(2019\)](#).

IODP-ICDP Expedition 364 Hole M0077A drill core yields a U–Pb age of 66.0 ± 6.2 Ma ([Rasmussen et al., 2019](#)). Based on these studies, it could be expected that any U–Th–Pb ratios may variably reflect the age of the target rocks and also the impact event as a function of the degree of impact metamorphism. However, accessory phases within the impact structure may also have experienced a prolonged period of high temperatures and fluid–rock interaction due to impact-induced shock heating, nearby impact melts, and a circulating post-impact hydrothermal system ([Ames et al., 2004](#); [Zürcher and Kring, 2004](#); [Abramov and Kring, 2007](#)). Thus, prolonged impact-related heating of the lithologies may have caused additional Pb diffusion and generated younger and/or disturbed U–Pb systematics in minerals.

Textural and mineralogical evidence of hydrothermal alteration of target rocks seen in the drill core from Yaxcopoil-1 and Hole M0077A have led to the interpretation of an early high temperature (>350 °C) stage involving Ca-, Na-, and K-alteration, dissolution of silica, and precipitation of calcite, Fe-sulphide, magnetite, titanite, muscovite, and apatite ([Zürcher and Kring, 2004](#)). Subsequent lower temperature (<300 °C) alteration minerals include epidote, chlorite, calcite, galena, TiO_2 , and various clay minerals ([Zürcher and Kring, 2004](#); [Schmieder et al., 2019](#)). Numerical simulations suggest that the impact-induced hydrothermal activity at Chicxulub may have been active for several millions of years ([Abramov and Kring, 2007](#)). However, the preservation of srilankite ($\text{TiO}_2\text{-II}$) in the peak ring requires rapid cooling to inhibit transformation to rutile, which can occur over timescales of hours (>550 °C) to weeks (>440 °C) ([Linde and DeCarli, 1969](#); [Smith et al., 2016](#); [Schmieder et al., 2019](#)).

2. MATERIALS AND APPROACH

2.1. Sample material

This study focuses on a large (>1 mm long) euhedral titanite grain in drill core from IODP-ICDP Expedition 364 Hole M0077A ([Morgan et al., 2017](#)) investigated previously by [Timms et al. \(2019\)](#). The titanite grain occurs within a polished thin section of shocked granite from 814.85 metres below sea floor (mbsf) (IODP sample ID: 364-77-A-121-R-1-75-77), hereafter referred to as sample #814.85 ([Supplementary Fig. S1](#)). The thin section comprises relatively intact domains of shocked primary magmatic quartz, alkali feldspar containing perthite lamellae, and plagioclase, with minor titanite, apatite, and zircon, typical of basement granite recovered from Hole M0077A. Intact granite domains are cut by cataclasite veins comprising locally-derived fragments of quartz and feldspar ([Supplementary Fig. S1A](#)). The rock has abundant fracture-related porosity. Precipitated calcite, and pyrite are in the section, as well as heavy saussuritization of all plagioclase grains in the sample. There is some evidence of quartz dissolution where PDFs or FFs meet the edge of the grains on fractures. The titanite grain in this study is enclosed within a large, primary igneous alkali feldspar grain within a shocked granite domain (i.e., not a cataclasite domain), and is in contact with plagioclase grains at its tips ([Supplementary Fig. S1B](#)). Alkali feldspar contains multiple sets ($n > 5$) of planar microstructures near the tips of the titanite grain ([Timms et al., 2019](#)). Surrounding quartz grains contain multiple sets of planar deformation features (PDFs), planar fractures (PFs), and feather

features (FFs), and high densities of lobate/irregular Dauphiné twins (Timms et al., 2019). Neighbouring and included zircon grains within the titanite grain do not show any shock features (Timms et al., 2019).

2.2. Optical and scanning electron microscopy

The phase distribution and deformation microstructure of the titanite grain were characterised using backscattered electron (BSE) imaging, energy-dispersive X-ray (EDX) mapping, and electron backscatter diffraction (EBSD) mapping using a Tescan MIRA3 field emission scanning electron microscope (FE-SEM) with an Oxford Instruments AZtec combined EDX-EBSD acquisition system in the John de Laeter Centre (JdLC) at Curtin University. Prior to characterisation via scanning electron microscopy (SEM), the sample was polished using 0.06- μm colloidal silica in NaOH on a Buehler Vibromet II for 4 hours, imaged using a Zeiss Axio Imager M2m auto-mosaic optical imaging system in plane polarized light (Fig. S1A), and carbon coated. BSE images were collected before and after LA-ICPMS analysis using acceleration voltage = 10 kV and working distances = 20 mm and 14 mm, respectively. EDX and EBSD data were collected prior to LA-ICPMS analysis simultaneously using both Oxford Instruments AZtec/Nordlys and Symmetry EBSD Detector and XMax 20 mm SDD EDX Detector, 20 kV acceleration voltage, $\sim 1.5\text{ nA}$ beam current, 70° stage tilt, 18.5 mm working distance, and mapping speeds of between 40 and 233 points per second. EDX mapping utilised the ‘TruMap’ tool in AZtec that utilised all X-ray peaks for each element to deconvolve unwanted X-ray counts from overlapping elemental peaks, and removal of X-ray background to display the variation of EDX intensity for each element more accurately. Colour K- α EDX intensity maps of Ti, Ca, Na, Zr, P, Fe, S, and Zr L- α were combined in Adobe Photoshop to produce a composite phase map. EBSD data were processed using Oxford Instruments Channel 5.12 to produce maps of phase and crystallographic orientation, and pole figures. Data points in EBSD maps and pole figures were coloured for cumulative misorientation angle up to 30° from a user-defined reference point in the grain, and/or for known host-twin misorientation relationships (Timms et al., 2019). Further details of the EBSD data acquisition and processing settings are documented by Timms et al. (2019).

2.3. Pb isotope analysis of alkali feldspar

Titanite typically contains variable common Pb contents, necessitating accurate correction of U-Pb data to yield meaningful U-Pb ages (Storey et al., 2006). In many cases, Pb isotope data from titanite defines mixing lines between radiogenic and common Pb components when plotted in Terra-Wasserburg space (Storey et al., 2006). Feldspar and titanite are both primary magmatic phases that crystallised within the granite. Therefore, it is reasonable to assume that titanite and feldspar shared the same initial Pb ratio during crystallization. Pb substitutes for Ca in the structure of titanite during growth (Kramers

et al., 2009), hence the isotopic signature of Pb in titanite will comprise structurally-bound common Pb and more loosely-trapped radiogenic Pb (derived from U). Importantly, previous studies indicate that titanite is not susceptible to post-growth influx of common Pb (Kirkland et al., 2018). Given that feldspar does not incorporate U, the measured feldspar Pb is taken to be the initial ratio for both phases during crystallisation.

In this study, the Pb isotopic composition of alkali feldspar surrounding titanite in sample #814.85 was quantified on the thin section using laser ablation–multi-collector inductively coupled plasma–mass spectrometry (LA-MC-ICPMS) in order to provide a robust value for the common Pb composition for correction of the titanite U-Pb data. The analyses ($n = 30$) were carried out on a Nu Plasma II (NPII) multi-collector mass spectrometer used in conjunction with a Resonetics S-155-LR 193 nm excimer laser ablation system in the GeoHistory Facility, JdLC, Curtin University. Standards and alkali feldspar were spot ablated using a 50 μm beam diameter, laser fluence (measured at sample surface) of 2 J cm^{-2} , pulse frequency of 10 Hz, 40 s of baseline collection (no ablation) before target ablation and 20 s of baseline collection after target ablation. Two cleaning pulses were applied prior to the start of analysis. The sample cell was flushed with ultrahigh purity He (350 mL min^{-1}) and N_2 (1.0 mL min^{-1}) and high purity Ar was employed as the plasma carrier gas. Spot locations were chosen to avoid any heterogeneities (alteration, cracks, inclusions) identified using BSE images (Fig. S1B). Mass stations on the NPII were set as follows: ^{200}Hg , ^{202}Hg , ^{203}Ti , ^{204}Pb and ^{204}Hg on ion counters; ^{205}Ti , ^{206}Pb , ^{207}Pb , and ^{208}Pb on Faraday cups with a 0.8 s integration time for all mass stations. The ^{204}Pb signal size for an unknown was typically seven times the baseline signal (0.00003 V) on the ion counter. In this study, Pb compositions were referenced to matrix-matched Shap feldspar (Tyrrell et al., 2006) in a block with NIST 612 glass (Kent, 2008), which were both analysed once for every 15 unknowns ($n = 15$ for all standards). Data were reduced using Iolite 3.5 using an in-house data reduction scheme that yields Pb isotopic ratios (Shap primary reference material) and an estimated Pb concentration (calculated using NIST 612 as the primary reference material). NIST 612, treated as an unknown, yielded Pb isotopic ratios within uncertainty of the recommended values. Corrected data are provided in Supplementary Table 1.

2.4. Trace element and U-Pb analysis of titanite

The titanite grain was analysed for U-Pb and trace elements using split stream laser ablation–multi-collector inductively coupled plasma–mass spectrometry (LA-MC-ICPMS). Data were collected using a Nu Plasma II (NPII) multi-collector mass spectrometer used in conjunction with a Resonetics RESolution M-50A-LR system, incorporating a COMPEX 193 nm excimer UV laser in the GeoHistory Facility, JdLC, Curtin University. Data for U, Th, and Pb isotopes and Y, Zr, Nb, Mo, Sn, rare earth elements (REE), Hf, Ta were collected from 167 30- μm -wide spots on a regular grid pattern (Fig. S1B).

Following two cleaning pulses and a 40 s period of background analysis, samples were spot ablated for 30 s at a 4 Hz repetition rate using a 30 μm beam and laser fluence at the sample surface of 2.3 J/cm^{-2} . An additional 20 s of baseline was collected after ablation. The sample cell was flushed with ultrahigh purity He (320 mL min^{-1}) and N_2 (3.1 mL min^{-1}) and high purity Ar was employed as the plasma carrier gas (2.6 mL min^{-1}). The ablated material was split between two mass spectrometers allowing simultaneous trace element and high precision U-Pb data collection. U-Pb isotopes were measured using LA-MC-ICPMS (NPII), whereas trace elements were measured using a quadrupole LA-ICPMS (Agilent 7700 s).

U and Pb isotopes were counted simultaneously in static mode, using Faraday detectors for ^{238}U and ^{232}Th and ion counters for ^{208}Pb , ^{207}Pb , ^{206}Pb , ^{204}Pb , and ^{202}Hg . Titanite mass spectra were reduced using the U_Pb_geochron4 data reduction scheme in Iolite (Paton et al., 2010; Chew et al., 2014), and in-house Excel macros as the in-house piece of the primary titanite standard (OLT1, from Otter Lake skarn, Quebec) contains negligible common Pb ($1015 \pm 2 \text{ Ma}$) (Kennedy et al., 2010). BLR (source not reported; $1047 \pm 0.4 \text{ Ma}$) (Aleinikoff et al., 2007) and TCB (from Campbell's Bay, Quebec; $1018 \pm 2 \text{ Ma}$) (Kennedy et al., 2010) were both utilized as secondary reference materials. Regressions from contemporaneous common Pb through uncorrected data for the reference materials, treated as unknowns, yields lower intercept ages of $1045 \pm 10 \text{ Ma}$ (MSWD = 0.9; $n = 21$) for BLR and $1028 \pm 10 \text{ Ma}$ (MSWD = 0.4; $n = 21$) for TCB, both within analytical uncertainty of their accepted values. All ages were calculated from isotopic ratios using Isoplot (Ludwig, 2003).

For trace element analysis, the following masses were monitored for 0.03 s each: ^{89}Y , ^{91}Zr , ^{93}Nb , ^{95}Mo , ^{118}Sn , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{178}Hf , ^{181}Ta , ^{232}Th , ^{238}U . REE data for titanite unknowns were reduced using the Trace Elements data reduction scheme in Iolite (Woodhead et al., 2007; Paton et al., 2011). Internationally-recognised glass standard NIST 610 was used as the primary standard to calculate elemental concentrations (using ^{29}Si as the internal standard element) and to correct for instrument drift. A stoichiometric value of 14.2 wt% Si was assumed for titanite unknowns. Secondary trace element standard NIST 612, treated as an unknown, reproduced recommended values to within 3% for all elements. Sample REE concentrations were normalized to chondritic REE values of Boynton (Boynton, 1984).

Titanite U-Pb corrected for alkali feldspar common Pb and trace element concentrations are provided in Supplementary Table 2.

2.5. Focussed ion beam time of flight secondary ion mass spectrometry (FIB ToF-SIMS) mapping

In order to visualise the major- and trace element compositional heterogeneity at a scale comparable to an LA-MC-ICPMS spot, regions of interest were mapped using focussed ion beam (FIB) time of flight secondary ion mass spectrometry (ToF-SIMS) on a Tescan Lyra3 FIB-SEM at

the JdLC at Curtin University (Rickard et al., 2020). This approach enables high lateral resolution SIMS analysis by utilising the Ga^+ focussed ion beam as a primary ion source. The advantages of this approach are that sub-micrometre x-y-z spatial resolution is achievable (often $< 100 \text{ nm}$) and trace sensitivity to REE such as Ce, permitting better comparison with the microstructure characterized by EBSD and BSE imaging. This technique remains semi-quantitative because results are susceptible to variations in element ionisation efficiency and mass peak interferences. Nevertheless, this approach can give useful insight into relative compositional variability over short length-scales that is otherwise homogenized in the volume of a LA-ICPMS analysis spot. This study utilised a Ga^+ ion source and a ToFwerks C-TOF ToF-SIMS detector. Data were acquired with an ion beam energy and current of 20 kV and 200–500 pA, respectively. This bias of the extractor optics was configured for positive ions and maps were collected with 1024×1024 pixels (4×4 binning) over square regions of between $16 \times 16 \mu\text{m}$ and $25 \times 25 \mu\text{m}$ for > 50 frames (complete scans of analysis area), resulting in an x-y pixel resolution of 60 to 100 nm, and total sampling depth of $\sim 100 \text{ nm}$. The data collected as the ion beam sputtered away the carbon coating (approximately the first 10 frames) was excluded from the datasets. Ion maps were constructed for the intensity of mass peaks corresponding to $^{40}\text{Ca}^+$, $^{28}\text{Si}^+$, $^{48}\text{Ti}^+$, $^{89}\text{Y}^+$, $^{140}\text{Ce}^{16}\text{O}^+$, and $^{27}\text{Al}^+$. In these analyses Th, U and Pb were below the detection limit, and some REE were affected by isobaric interferences from other elements. $^{140}\text{Ce}^{16}\text{O}^+$ had a high peak intensity and was identified as a suitable proxy for REE spatial variations in the sample.

3. RESULTS

3.1. Deformation microstructure of the studied titanite grain

A dense network of sub-planar and irregular fractures cut across the grain (Fig. 2A). Sub-planar fractures have exploited the interfaces of two sets of twins revealed by EBSD mapping, with the thickest twins oriented sub-parallel to the long axis of the grain (Fig. 2A-B). Heterogeneously-developed zones of intense irregular fractures cut across the grain, are stepwise across titanite twin boundaries, and link to significant fracture damage in the surrounding phases (Fig. 2A). Both sets of twins index with composition planes (K_1) = $\sim \{111\}$ and shear directions (η_1) = $\langle 110 \rangle$, and are symmetrically equivalent twin modes in titanite inferred to form during shock conditions (Timms et al., 2019). Shock twinning was accompanied by crystal-plasticity that has resulted in up to 30° cumulative crystallographic misorientation defining broad bands across the grain that are oblique to the twins (Fig. 2B). Rigid rotation of fractured blocks is relatively minor (Fig. 2B).

3.2. Included phases and reaction textures

The titanite grain contains several inclusions of zircon and apatite that are $< 20 \mu\text{m}$ in diameter, euhedral, similar in appearance to magmatic grains elsewhere in the sample,

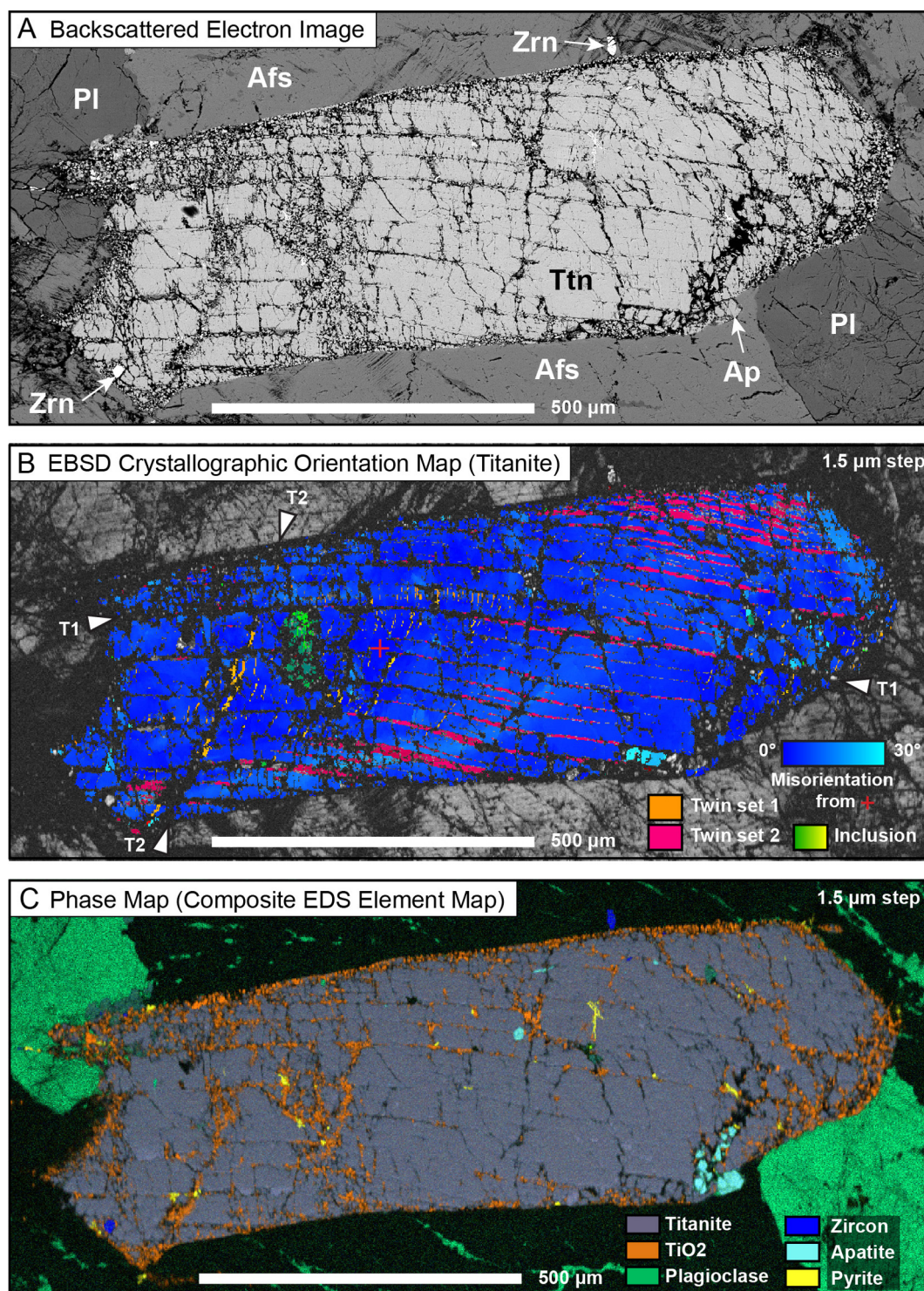


Fig. 2. The microstructure of titanite (Ttn) grain in sample #814.85. A. BSE image showing that the grain is enclosed in alkali feldspar (Afs) and plagioclase (Pl), and contains inclusion of zircon (Zrn) and apatite (Ap). B. EBSD map to show variations in crystallographic orientations within titanite. The grain preserves up to 30° of misorientation from the reference orientation (indicated by the red cross) and two sets of lamellar mechanical twins along $\sim\{111\}$ with 74°/ $\langle 102 \rangle$ disorientation from the reference orientation. Twin trace orientations are labelled T1 and T2, respectively. A primary titanite inclusion (shown in green) also preserves $\sim\{111\}$ twins. C. Composite energy-dispersive X-ray intensity map of Ti, Ca, S, P and Zr shows that the grain contains inclusions of zircon and apatite, and has microcrystalline TiO₂, and pyrite localised along fractures. A and B are modified after Timms et al. (2019). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and are cut by brittle fractures (Fig. 2A, C) (Timms et al., 2019). These inclusions are interpreted as primary magmatic grains. The rim and many fractures are lined with fine-grained (1–2 μm), idiomorphic secondary anatase crystallites, which replace primary titanite (Fig. 2C). These were not reported by Timms et al. (2019). Although anatase crystals generally have wide-ranging crystallographic orientations, localized clusters of crystals have similar crystallographic orientations. However, the orientation clusters are not consistent across the entire titanite grain (Supplementary Fig. S2). Mapping by EBSD indicates randomly-oriented crystallites of titanite also occur in these domains (Fig. 2C; grey data points in Supplementary Fig. S2C, F), which are interpreted to be pseudomorphic neoblasts produced by a back-reaction from TiO_2 plus CaCO_3 and SiO_2 . Minor Fe-sulphide (pyrite) and plagioclase also occurs along fractures within the titanite (Fig. 2C).

3.3. U-Pb and Pb-Pb isotopic signatures

3.3.1. Alkali feldspar

Thirty LA-MC-ICPMS analyses on primary magmatic alkali feldspar in the immediate area surrounding #814.85 titanite were conducted and yield a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ of 0.84896 ± 0.00029 (MSWD = 2.4). The alkali feldspar contains 30–67 ppm Pb and has a $^{206}\text{Pb}/^{204}\text{Pb}$ of 18.3–19.0 (average 18.6 ± 0.2), $^{207}\text{Pb}/^{204}\text{Pb}$ of 15.6–16.1 (average 15.7 ± 0.1) and $^{208}\text{Pb}/^{204}\text{Pb}$ of 38.0–39.4 (average 38.4 ± 0.3).

3.3.2. Titanite

The titanite U-Pb data in #814.85 defines a triangular-shaped array in Tera-Wasserburg Concordia space (Fig. 3A). Three spots out of a total of 167 analyses intersected zircon inclusions identified on BSE images and the composite EDX intensity map (Fig. 2A and C; Supplementary Fig. S1B). These analyses are shown on the Concordia plot (Fig. 3A), but are not considered further. The remaining data points are distributed from the ordinate intercept, which has a $^{207}\text{Pb}/^{206}\text{Pb}_c$ value comparable to the common Pb value determined from the alkali feldspar analyses (Fig. 3). ^{207}Pb -corrected apparent ages were calculated using the measured alkali feldspar common Pb value with multiple probability peaks from ~ 63 Ma to ~ 307 Ma (Fig. 3, inset (i)). We interpret the triangular-shaped array as a consequence of variable amounts of resetting of a common Pb-radiogenic Pb mixing array. Almost all analytical spots overlap fractures, and frequently incorporate a volumetrically minor component of TiO_2 and secondary titanite crystallites (Figs. 2, 4–6). No analyses intersected apatite inclusions identified on the polished sample surface via pre-LA-MC-ICPMS BSE images and the EDX map (Figs. 2–4). Regression of the five apparently youngest analyses (based on ^{207}Pb -corrected ages) yield a lower intercept age of 67 ± 4 Ma (MSWD = 1.05), when anchored to the feldspar common Pb composition. A free-fitted regression through the same titanite data points yields a lower intercept of 53 ± 12 Ma with an upper $^{207}\text{Pb}/^{206}\text{Pb}$ intercept of 0.79 ± 0.06 (MSWD = 0.4), within uncertainty of the

anchored regression intercepts. A contour map of interpolated ^{207}Pb -corrected ages reveals a strong spatial correlation between apparent U-Pb age and the deformation/reaction microstructure, with younger ages associated with intensely fractured zones that are decorated by TiO_2 crystallites and titanite neoblasts (Figs. 4–6). There are no discernible relationships between apparent U-Pb age and twinning or crystal-plastic microstructures. The oldest well-determined (i.e., low uncertainty) ^{207}Pb -corrected apparent age of 307 ± 10 Ma was collected at a spot (#49) that is relatively unaffected by fractures and associated reaction textures (Fig. 4). Therefore, this data point represents the best estimate of the minimum age for the titanite grain.

3.4. Trace elements

A REE spider plot shows a consistent humped pattern across all 164 analyses, with relatively elevated light REE centred on Pr and Nd and a weak negative Eu anomaly with Eu/Eu^* of ~ 0.6 to ~ 0.8 (Fig. 3B). However, absolute chondrite-normalized concentrations across the grain span three orders of magnitude, with a good correlation between REE concentration and ^{207}Pb -corrected apparent age, whereby REE depletion corresponds to younger apparent ages (Fig. 3B). The magnitude of the Eu anomaly correlates with apparent U-Pb age, with the highest Eu/Eu^* values of ~ 0.8 corresponding to the youngest ^{207}Pb -corrected apparent age domains (Fig. 3A). Concentrations of all measured trace elements are highly variable across the grain, and are strongly positively correlated with one another and ^{207}Pb -corrected apparent ages (Fig. 3B, C; Supplementary Fig. S3). Contour maps of trace element (REE-Y-Zr-Nb-Mo-Sn-Th) concentrations from LA-MC-ICPMS spots all show very similar distinctive patterns of depletion that are spatially associated with fractures and microcrystalline anatase, with the lowest concentrations in domains of high fracture intensity and reaction textures (Figs. 4–6; Supplementary Figs. S4–S6). The exception is a conspicuous trace element-poor linear zone parallel to the long axis of the grain and adjacent to a prominent twin, which preserves old apparent ages and may represent heterogeneity due to initial primary growth zoning (Figs. 4–6). Trace elements such as Y, Ce, and Nb show the most extreme variations, with maxima at several weight percent in undisturbed domains, and depletion down to a few hundred ppm in intense fracture zones. A similar pattern of depletion is revealed for Th, considered to be an immobile element, with values less than 100 ppm in microstructurally complex zones, but greater than 500 ppm in relatively unfractured domains. Excluding analyses that incorporated zircon inclusions ($n = 3$), the measured range in Zr concentration is from 26 to 1957 ppm. There does not appear to be any clear relationships between trace element concentrations and the intensity of twinning and/or crystal-plasticity sampled by the LA-MC-ICPMS pits (Figs. 4–6).

FIB-ToF-SIMS was used to study the major and trace element distribution at high magnification as the technique has sufficient spatial resolution (~ 50 nm) to identify the composition of the various domains. Sensitivity was limited

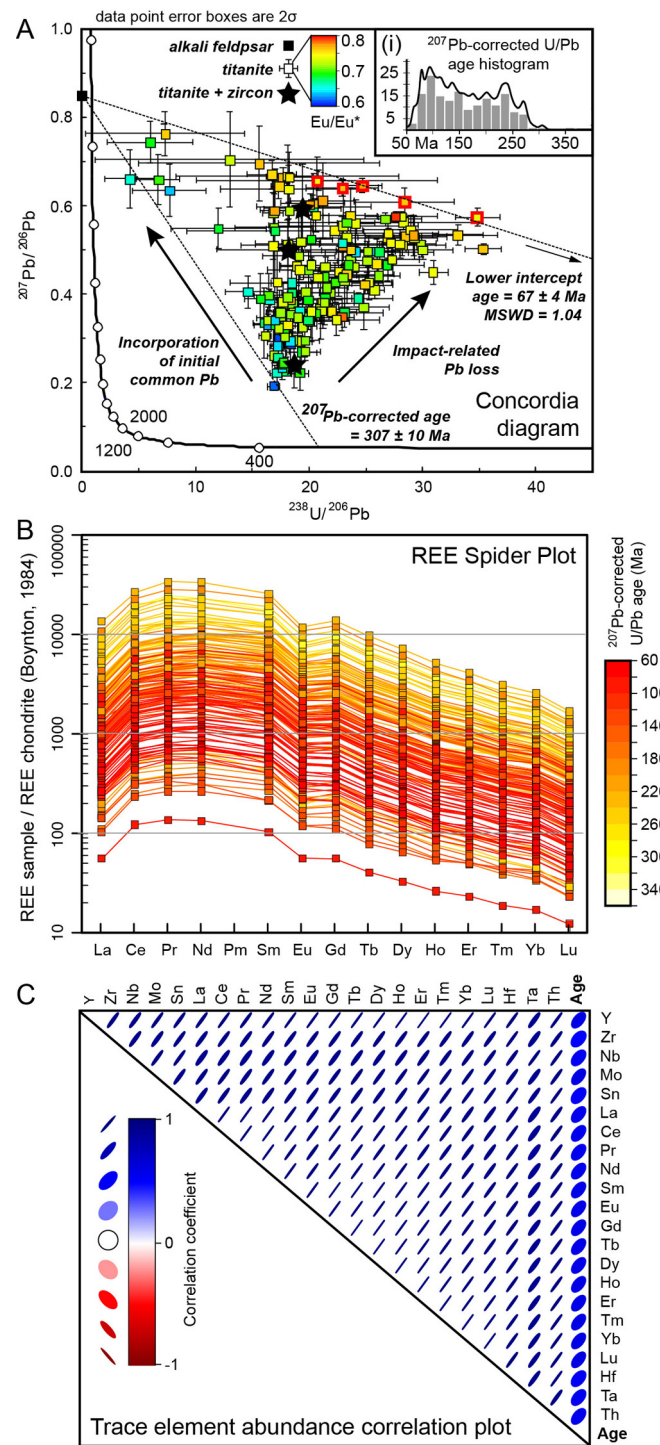


Fig. 3. A. Tera-Wasserburg plot of U-Pb data for the titanite grain ($n = 167$) and measured common Pb composition in alkali feldspar ($n = 30$) shown by the black square. Titanite data points are coloured for Eu anomaly (Eu/Eu^*). Analyses that incorporated zircon inclusions are annotated with black stars. Symbols with thick red outlines denote the five analyses with the youngest apparent ^{207}Pb -corrected U-Pb ages that are dominated by a completely reset component. Inset (i) shows a histogram of apparent ^{207}Pb -corrected U-Pb ages. B. Chondrite-normalized REE spider plot, coloured for apparent ^{207}Pb -corrected U-Pb age. $n = 164$. C. Correlation diagram for measured trace element concentrations and apparent ^{207}Pb -corrected U-Pb age (Age). Correlation coefficient between data pairs are indicated by the colour and shape of ellipses. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

for some elements (e.g., U and Th), but excellent for others (e.g., Al, which was not measured by LA-MC-ICPMS) due to variable ionization efficiency and/or peak interferences

(Rickard et al., 2020). A set of maps summarizing the relationships observed in the titanite grain are shown in Fig. 7, with a more expansive set of maps provided in the

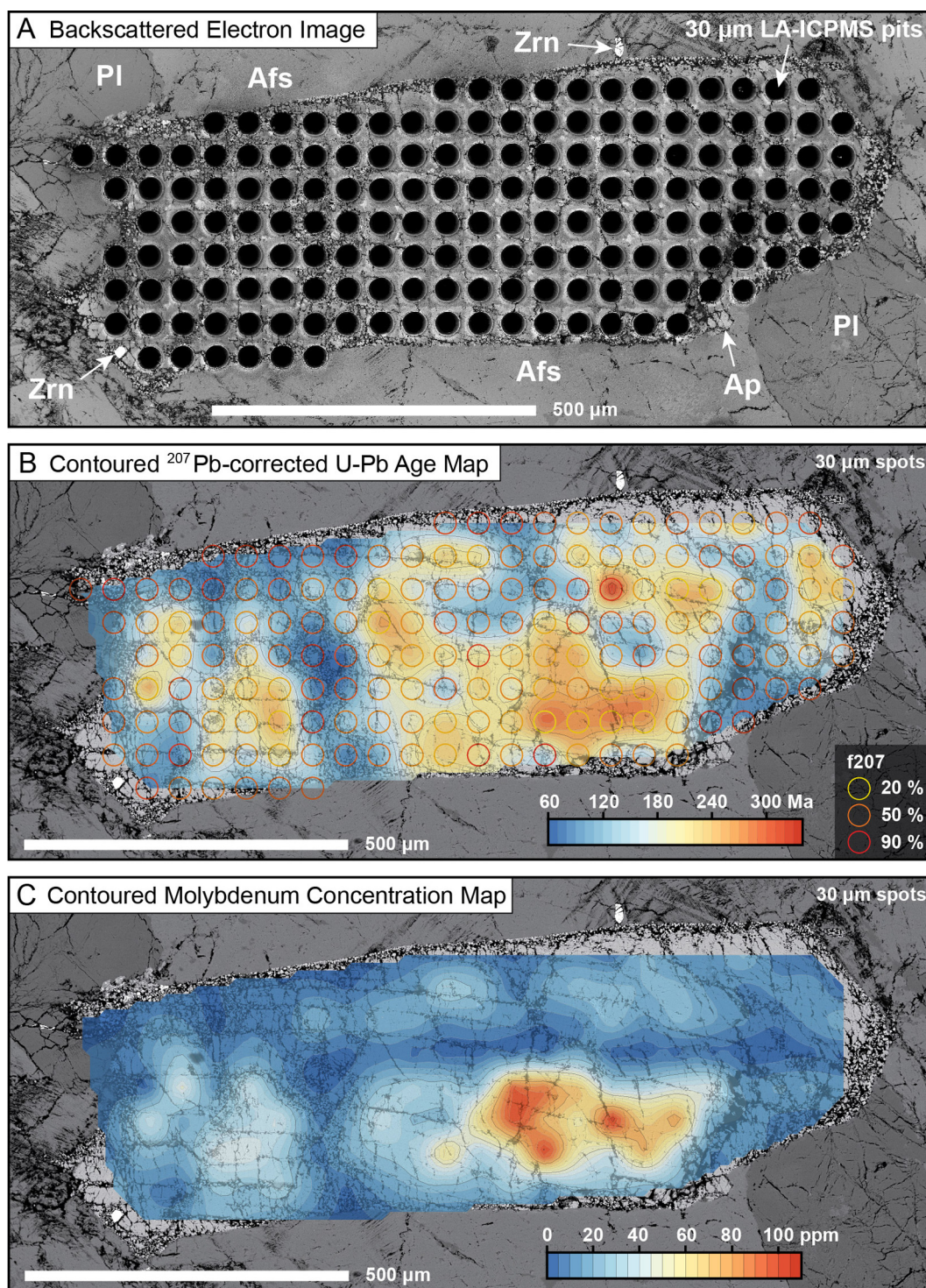


Fig. 4. A. BSE image after LA-MC-ICPMS analysis showing the location of 30 µm analysis pits. B. Map contoured for apparent ^{207}Pb -corrected U-Pb age. Line colour of open circles (analytical spots) represents $f^{207}\text{Pb}$. C. Map contoured for Mo concentration measured via LA-MC-ICPMS. Contour maps in B and C are superimposed on BSE image shown in Fig. 2A. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

[supplementary file](#) (Supplementary Figs. S7–S14). It is clear from Fig. 3c that all trace elements measured via LA-MC-ICPMS (REE-Y-Zr-Nb-Mo-Sn-Th) are correlated with one

another, and therefore maps of Ce (measured as an oxide) can be used as a proxy for these elements (with the exception of Eu). Consistently throughout the grain, titanite

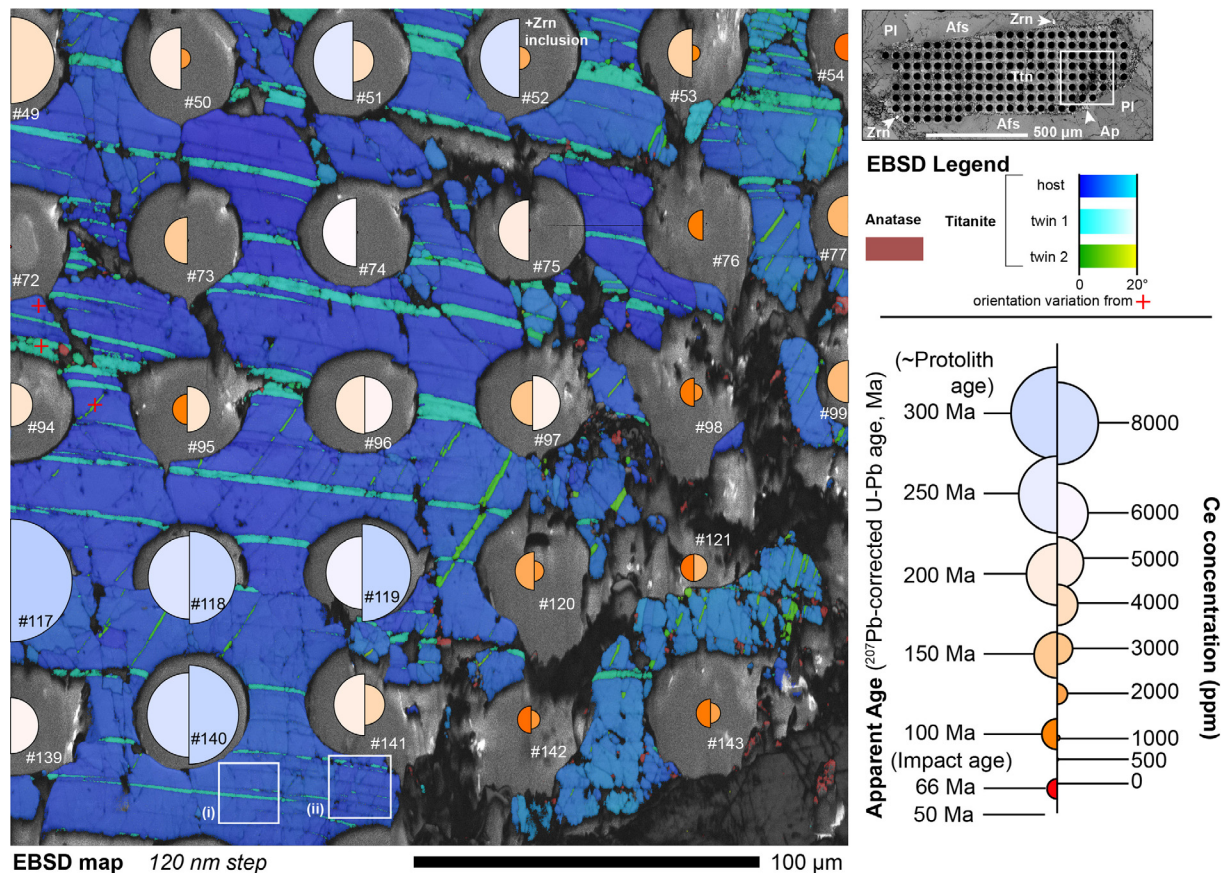


Fig. 5. EBSD map of the lower right tip of the titanite grain, collected after LA-ICPMS analysis. Coloured semi-circles depict the apparent age and measured Ce concentration (left- and right-hand side, respectively). LA-ICPMS spot IDs are indicated by #numbers. White squares labelled (i) and (ii) indicate areas of ToF-SIMS maps. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

adjacent to microcracks is depleted in Ce (and by proxy other trace elements) yet enriched in Al (Fig. 7). The Ce-depleted regions are noticeably wider (up to 3–5 μm) proximal to open fractures, especially in the vicinity of dense crack networks spatially associated with anatase crystallites (Fig. 7 iv). Anatase crystallites were determined to be largely free of trace element impurities (Fig. 7). There are no detectable element variations associated with pristine shock twins in titanite, only where brittle fractures have exploited twin interfaces (Fig. 7).

4. DISCUSSION

4.1. Establishing the microstructural history of the grain

Mechanical twinning along $\sim\{111\}$ has not been recorded in tectonically-deformed titanite, and appears to have formed concurrently with crystal-plastic strain (Timms et al., 2019). Therefore, these microstructures are interpreted to be a consequence of shock deformation during the first few seconds of the Chicxulub impact event (Timms et al., 2019) (Fig. 8). The presence of planar deformation features in quartz in core from Hole M0077A indicate a shock pressure range between ~ 15 and 18 GPa

(Feignon et al., 2019), which provides the best estimate of shock conditions experienced by the titanite grain (Timms et al., 2019). Numerical simulations of the impact event using the shock physics code iSALE indicate that shear stresses on the order of 200 MPa accompanied these shock pressures (Rae et al., 2019), which is interpreted here as the critically resolved shear stress required for $\sim\{111\}$ twinning in titanite to the first order.

Brittle fractures clearly cross-cut and displace twins and exploit twin interfaces, which provide strong evidence that the fracture network post-dates twinning, and therefore peak shock pressure conditions. Fractures formed either during decompression from shock, or more likely during post-shock stress cycling and acoustic fluidization during the evolution of the peak ring in the crater modification stage (Riller et al., 2018; Rae et al., 2019) (Fig. 8). Prior to the impact, the granite that would eventually become the peak ring was at a depth of 8 to 10 km and, thus, experienced a lithostatic pressure of ~ 200 MPa, under greenschist-facies conditions (Morgan et al., 2016). Hydrocode iSALE modelling indicates that confining pressures fluctuated from 10 to 100 MPa in this region within the first ten minutes following impact, and were accompanied by shear stresses on the order of 5 to 20 MPa (Rae et al., 2019).

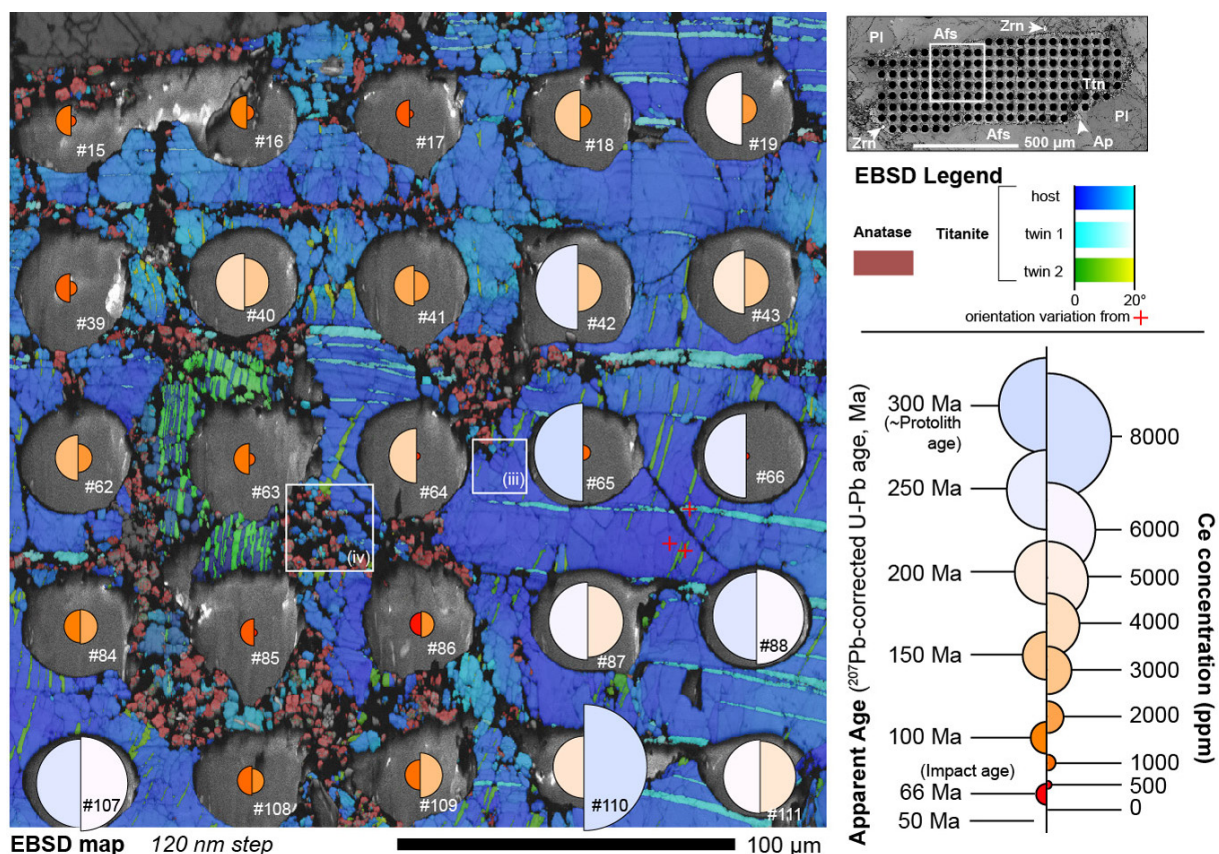


Fig. 6. EBSD map of the upper left domain of the titanite grain, collected after LA-ICPMS analysis. Coloured semi-circles depict the apparent age and measured Ce concentration (left- and right-hand side, respectively). LA-ICPMS spot IDs are indicated by #numbers. White squares labelled (iii) and (iv) indicate areas of ToF-SIMS maps. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Our results indicate that fractures became pathways for further trace element modification of titanite, reaction, dissolution, and mineral precipitation. In this grain, reaction to anatase, the low-temperature polymorph of TiO_2 , and reversion to titanite were restricted to fracture interfaces and the grain rim. This implies that for these reactions to proceed, pathways for mass transfer and/or heat were required. Nevertheless, the presence of Fe-sulphide precipitates in the fractures is clear evidence that the titanite grain was affected by hydrothermal activity, and these precipitates are interpreted to have formed during a hydrothermal stage following crater modification (Fig. 8). The replacement of titanite by anatase and minor reversion to titanite are consistent with new mineral growth in the proposed high-temperature hydrothermal environment associated with the impact event (Zürcher and Kring, 2004). Spatial links between the intensity of trace element depletion halos, titanite dissolution, and anatase precipitation appear consistent with a continuum of processes that require material transport along fracture interfaces. The duration of hydrothermal activity at Chicxulub may have lasted for as long as 1.5 to 2.3 Myr after the impact event (Abramov and Kring, 2007).

Linking titanite trace element geochemistry, U-Pb analyses, and microstructure to discern geologic processes

4.2. Interpreting the old U-Pb age preserved by the titanite grain

The titanite crystal is interpreted to be a primary magmatic grain for the following reasons: Firstly, the grain is euhedral and texturally included within magmatic alkali feldspar, plagioclase, and apatite. Additionally, the trace element geochemistry is consistent with crystallisation with co-existing apatite, producing humped (or ‘spoon-shaped’) chondrite-normalized MREE to LREE patterns and relatively depleted HREE (Henderson, 1980; Papapavlou et al., 2017). These REE patterns are distinct from metamorphic and hydrothermal titanite elsewhere, which typically have flat chondrite-normalized REE patterns or depletions in the LREE relative to the HREE (e.g. Storey et al., 2007; Smith et al., 2009; Kohn, 2017; Olierook et al., 2019). Furthermore, slow diffusivity of trace elements such as REE, Zr, Pb, Nb, Sr, and Pb in titanite indicate that, in many geological scenarios, fine-scale zoning and U-Pb ages are retained in titanite and reflect magmatic or metamorphic crystallization, not later cooling (e.g. Cherniak, 2015; Stearns et al., 2015). In this context, the age of ca. 300 Ma for the oldest component within the studied titanite grains is our best estimate of the minimum magmatic crystallization age for the sampled granite.

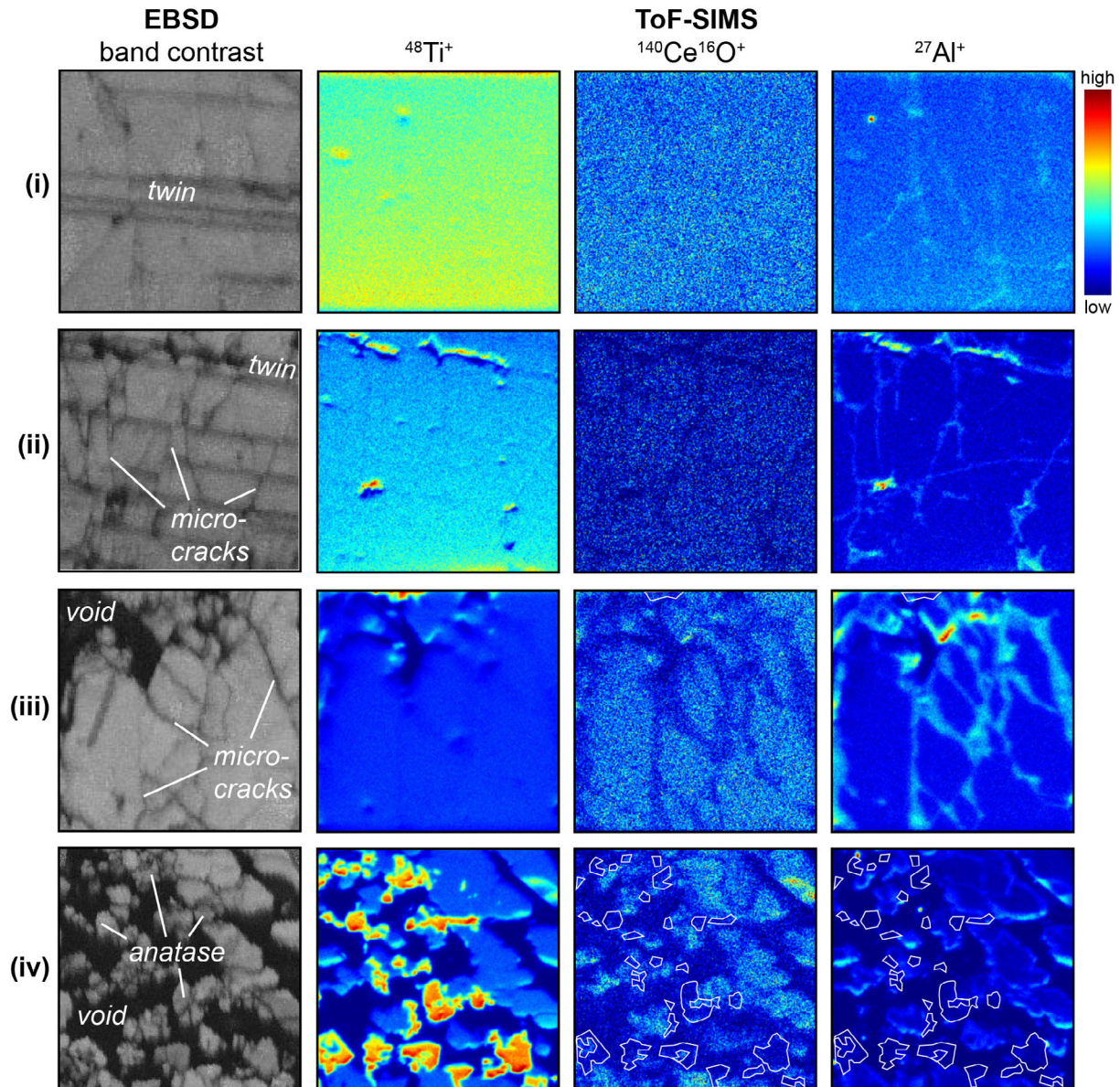


Fig. 7. FIB-based ToF-SIMS ion maps of selected regions of interest and elements to illustrate the links between geochemistry, deformation microstructures, and reaction textures in titanite. (i) Area adjacent LA-ICPMS spots that preserve old ages and high concentrations of trace elements. Very minor localised depletion of Ce (measured as an oxide) and enrichment of Al associated with microcracks, and no discernible modification along shock twins. (ii) Area with minor age resetting showing narrow domains of modification localised along a network of microcracks. (iii) Strongly age-reset domain with broad domains of depleted Ce (CeO) and enriched Al adjacent to microcracks. (iv) Area adjacent the youngest age LA-ICPMS spot showing significant trace element modification associated with a dense network of microcracks, neoblasts of microcrystalline anatase, and voids localised along fractures.

Granites with ages of *ca.* 300 Ma are rare in the currently known basement of the Yucatán Peninsula. Nonetheless, concordant U-Pb ages of zircon crystals from granitoids reported by Zhao et al. (2020) from the same drill core as investigated here are identical within analytical uncertainty to the oldest titanite components we report. Specifically, a range of samples from IODP-ICDP Expedition 364 yield concordant zircon U-Pb spot analyses of ~ 300 to ~ 370 Ma (weighted mean = 326 ± 5 Ma) that are comparable to the oldest titanite U-Pb ages in sample #814.85, 307 ± 10 Ma. Other similar crystallization ages,

potentially related to Chicxulub basement, include three grains from K-Pg boundary deposit in Saskatchewan and Colorado, ~ 360 Ma, 320 ± 31 Ma, and ~ 330 Ma old (Kamo and Krogh, 1995).

4.3. Mechanisms of Pb-loss and resetting of the U-Pb system

The lower intercept age based on the youngest dates of 67 ± 4 Ma on titanite #814.85 is clearly in agreement with the age of the Chicxulub impact event (Bohor et al., 1993; Renne et al., 2013; Clyde et al., 2016). Therefore, it appears

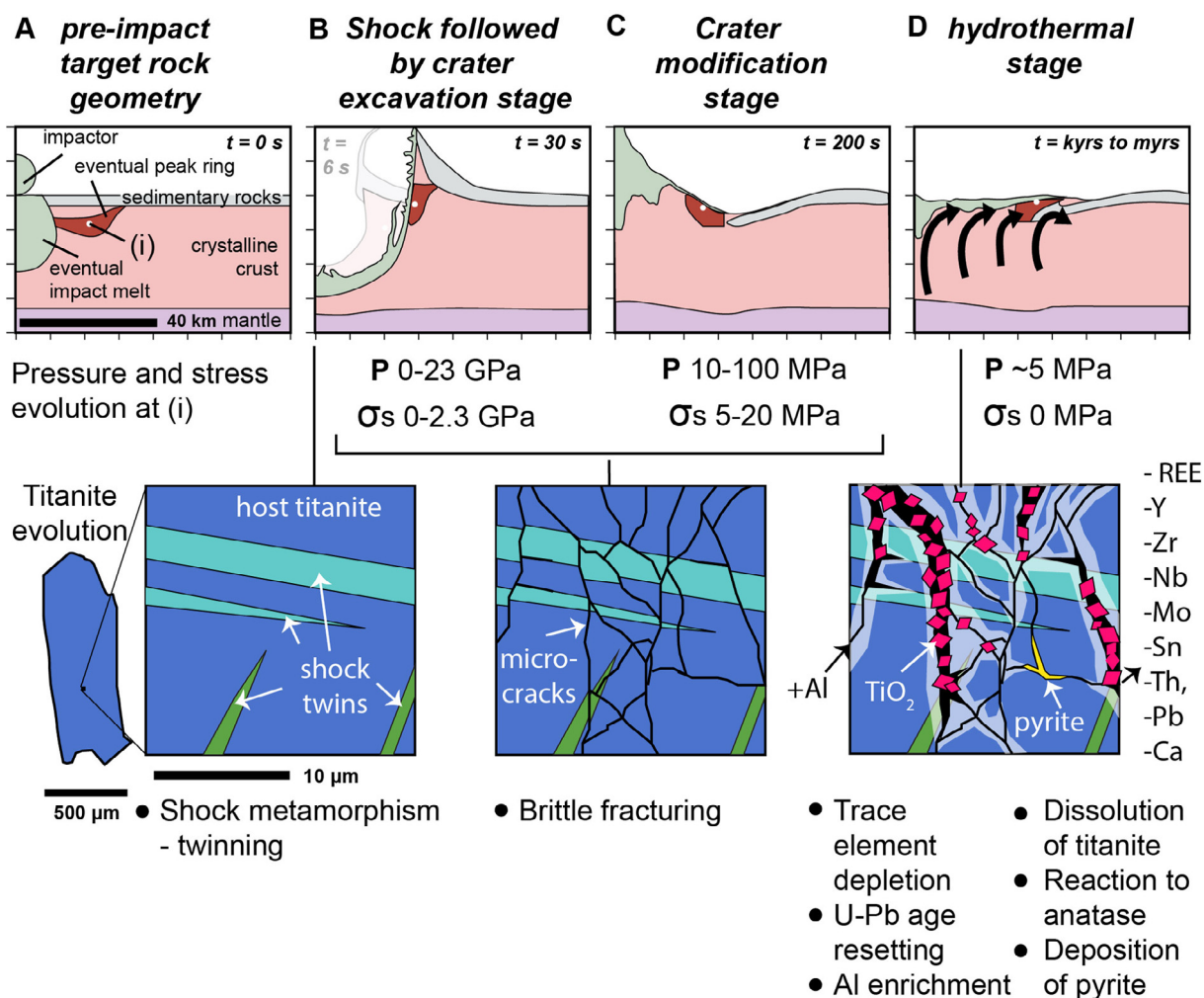


Fig. 8. Schematic diagrams to show the impact-related evolution of titanite (bottom row) and how they link to development stages of the Chicxulub impact structure (top row). Crater stages, pressure and stress evolution based on iSALE modelling of [Rae et al. \(2019\)](#).

that the grain records Pb loss associated with the Chicxulub impact event. The apparent U-Pb age variations and microstructural complexity of the titanite grain raises questions about the mechanism(s) of resetting of the U-Pb system, i.e., what process(es) is/are being dated? A widely-held assumption, rooted in the experimental data of [Cherniak \(1993\)](#), is that U-Pb dates from titanite reflect the timing of closure of the U-Pb system to volume-diffusion. Many recent studies on natural titanite confirm that the U-Pb system in titanite is actually robust at high-temperature conditions of at least 840 °C ([Kylander-Clark et al., 2008](#); [Kohn and Corrie, 2011](#); [Kohn, 2017](#); [Hartnady et al., 2019](#); [Olierook et al., 2019](#)). However, titanite is susceptible to fluid-related alteration processes ([Tilley and Eggleton, 2005](#); [Morad et al., 2009](#)). The lack of any systematic correlation between apparent age and twinning and crystal-plasticity suggest that Pb-loss is unlikely to have occurred due to fast-pathway diffusion associated with these microstructures during passing of the shock wave. The investigated titanite grain preserves individual ^{207}Pb -corrected spot ages as young as 63 ± 6 Ma. Such young

ages are spatially restricted to heavily fractured zones in the titanite crystal ([Figs. 5 and 6](#)). These young domains correlate with depletion in trace element concentrations, consistent with the removal of Pb from these volumes. The implication of this correlation is that radiogenic Pb was removed through fluid mediated processes in these structurally complex areas of the crystal, resetting the U-Pb system to varying degrees. Specifically, the fractured zones clearly represent fast fluid pathways that facilitated relatively rapid removal of Pb by reactive fluids.

Expulsion of radiogenic Pb from the system during the growth of anatase and minor recrystallisation of titanite provide viable mechanisms for U-Pb resetting. However, newly-grown anatase and recrystallised titanite domains account for a very minor proportion of the analytical volume of the LA-MC-ICPMS analyses. Even if an analytical spot incorporated a 5 μm wide domain of anatase crystallites, which is approximately equivalent to the highest abundance for any LA-MC-ICPMS pit in the grain, then anatase would only constitute ~1% of the analytical volume. Assuming that newly-grown crystals were completely reset

at the time of the impact event and any radiogenic Pb was removed from the vicinity, then the presence of these crystals in the LA-ICPMS analytical volume would not have a significant impact on the apparent ages. Therefore, an additional mechanism for local Pb-loss is required to explain the young ages and trace element depletion. Furthermore, this implies that the presence of newly-grown TiO_2 did not have a significant effect on the apparent U-Pb ages. Loss of Pb and other trace elements could have occurred by either (a) volume diffusion or (b) recrystallization via a dissolution-reprecipitation process along the fracture network, which conceivably acted as fast-pathways for element migration. However, there is no clear evidence for (b). Therefore, variable Pb-loss from primary titanite via fracture-assisted volume diffusion combined with complete Pb-loss of anatase and secondary titanite replacement assemblages are our preferred mechanisms of resetting the U-Pb system in the grain. Consequently, the 67 ± 4 Ma lower intercept age reflects the alteration of titanite associated with post-impact hydrothermal activity in the Chicxulub crater. The efficiency of this fluid-driven Pb-loss process is variable as even domains within the twinning plane are incompletely reset. The common Pb indicated by the ordinate intercept of the U-Pb data implies that both feldspar and titanite have the same common Pb source reflecting the magmatic environment of initial growth.

4.4. Implications for dating impact-related processes using altered and/or shocked titanite

Regression of a triangular U-Pb data array has been successfully applied to shocked titanite and yielded a lower intercept impact age for the Lac La Moine impact structure (McGregor et al., 2019). These authors fitted a regression line through the youngest analyses in their dataset to yield a lower intercept impact age of 444 ± 15 Ma (MSWD = 2.2), which is within analytical uncertainty of the impact age defined by U-Pb of shocked apatite (lower intercept age of 453 ± 5 Ma; MSWD = 1.2) and zircon (lower intercept age of 433 ± 21 Ma, MSWD = 2.6). In contrast, our study represents the first to apply this approach using only data from a single titanite grain, and is the first to successfully date the Chicxulub impact event using impact metamorphosed, post-impact altered titanite in shocked basement rock. Nevertheless, it is important to consider the mechanism of radiogenic-Pb loss to facilitate the application of this titanite U-Pb approach elsewhere in order to date otherwise age-unconstrained impact sites. A clear link between deformation microstructure, age, and impact process is required before any titanite U-Pb age can be interpreted as dating the impact or its related processes.

4.5. Hydrothermal alteration of titanite: Implications for trace element-based petrologic interpretations

With the exception of Al, all measured trace elements in titanite #814.85 show a distinct depletion associated with microcracks and reaction to anatase (Figs. 3B, C, 4C, 7, S7–S14). The spatial pattern of element depletion is consis-

tent with these intra-grain interfaces acting as pathways for hydrothermal fluids. Such fluid access in a post-impact environment evidently locally stripped a wide range of elements, including relatively immobile elements, such as REEs, Y, Zr, Nb, Mo, Sn, Th, and Pb, and added Al (Fig. 7). The intensity of this process is evidenced in the ~ 67 Ma titanite domains by significant reductions in concentration of elements typically considered as immobile to diffusion at temperatures less than ~ 600 °C over the time-frame available since the impact event (e.g. Cherniak, 2015). The wide-ranging measured trace element concentration values clearly puts the use of various trace elements to identify and discriminate between geological processes under scrutiny in some scenarios. This finding also raises questions about the intragrain transport mechanism, temperature conditions, nature of the fluids for trace element modification, and eventual sinks for the trace elements.

Partition coefficients for trace elements between titanite and aqueous fluids are unknown. The magnitude of modification is approximately the same among the REE (except Eu), indicating that most REE were partitioned into the fluid broadly equally. The chondrite-normalized REE pattern for altered titanite mimics that of the unaltered magmatic signature (Fig. 3b), unlike REE patterns from metamorphic titanite elsewhere (e.g. Storey et al., 2007; Lucassen et al., 2011; Olierook et al., 2019) which superficially makes the alteration difficult to discern. Nevertheless, the difference in Eu/Eu* correlates with U-Pb resetting across the grain (Fig. 3a) and may provide an insight into the redox state of the fluid that influenced the alteration geochemistry of the titanite. Eu/Eu* values are higher (i.e. closer to 1) in the altered domains. Therefore, Eu was not as mobile during alteration as Sm and Gd (and all other REE). Given that Eu valence state can be +2 whereas the other REEs are +3, the shift to higher Eu/Eu* values indicates action of a reducing fluid in which REEs are soluble yet Eu was relatively less mobile (e.g. Storey et al., 2007), as well as Zr, Y, Mo, Nb, Th, Pb, and Al.

The patterns of Al enrichment in titanite #814.85 (Fig. 7) are similar in appearance to the irregular ‘channel-and-island’ Al zoning patterns observed in polycrystalline metamorphic titanite (Lucassen et al., 2011). Similarly, sharp borders and smooth gradients between domains can be explained by solid state diffusion of elements proximal to titanite-fluid interfaces rather than a replacement reaction texture (Lucassen et al., 2011). The trend of increasing Al content with depletion of other trace elements can most likely be attributed to element partitioning between titanite and fluid, favouring incorporation of the smaller ionic radius of Al compared to other trace elements for substitution into the octahedral Ti site during alteration (e.g. Lucassen et al., 2011).

Depletion of Zr in titanite #814.85 (from 1957 ppm to ~ 26 ppm, excluding analyses that incorporated zircon inclusions) clearly has implications for Zr-in-titanite thermometry. Using the relationship provided by Hayden et al. (2008) and assuming the activities of TiO_2 and SiO_2 are both equal to 1 and pressure = 0.25 GPa, then titanite #814.85 records a wide range of apparent temperatures

from 827 °C to ~600 °C, from the least to most depleted domains, respectively. While it may be tempting to infer initial crystallisation and subsequent alteration temperatures from the maximum and minimum values, respectively, it is unlikely that any of the apparent temperatures are geologically meaningful because of: (1) the lack of reliable constraints on the activity of TiO₂ during initial crystallisation of the titanite which may affect the initial activity assumptions and results that follow; and (2) volume mixing between unaltered and altered titanite and anatase the LA-MC-ICPMS pits, as demonstrated by compositional heterogeneity visualised by ToF-SIMS mapping (Fig. 7), which results in spurious, mixed apparent temperature values. Similarly, the evidence for different degrees of volume mixing between primary and altered titanite as evidenced in ToF-SIMS mapping (Fig. 7) means that intermediate measured values of most other trace elements in titanite #814.85 (e.g., Fig. 4C) have no particular geological meaning.

Hydrothermal alteration of titanite is consistent with the presence of hydrothermal pyrite within the titanite grain (Fig. 2C), and the presence of calcite-TiO₂ veins elsewhere in titanite within target granites of the peak ring of Chicxulub (e.g. Timms et al., 2019). The source, geochemistry, and temperature history of the hydrothermal activity within the peak ring of Chicxulub is a topic of ongoing research. Nevertheless, our findings are comparable with observations from the base of the impactite sequence in the Yaxopoil-1 drill core (as well as the target rocks below), which host feldspar-sulphide (as opposed to feldspar-oxide) veins and hydrocarbons (Zürcher and Kring, 2004), also consistent with the initial fluid in the impact breccia lens near the inner rim being at least initially reducing (Ames et al., 2004), potentially sourced in the underlying limestone and evaporite target rocks or perhaps thicker impactites towards the crater's annular trough (e.g. Mayr et al., 2007). The source of the fluids in the peak ring granites is beyond the scope of this paper. Nevertheless, impact-induced circulation of fluids inside the Chicxulub crater was clearly able to rapidly hydrothermally alter peak ring titanite in susceptible domains along fast fluid pathways.

5. CONCLUSIONS

This study used EDS, EBSD, ToF-SIMS mapping, and in situ LA-MC-ICPMS spot analysis to resolve impact-related deformation and metamorphism of a single magmatic titanite grain in shocked granite target rocks in the peak ring of the Chicxulub impact structure. It is the first detailed assessment of the effects of the Chicxulub impact on the U-Pb system and trace elements of titanite, and to investigate mechanisms of age resetting and link with hydrothermal alteration. The titanite grain preserves a network of microcracks that cross-cuts and therefore post-dates $\sim\{111\}$ shock twins resolved by EBSD. Heterogeneously-developed microcrystalline anatase and pyrite along microcracks (illuminated by EBSD and EDS mapping) show that microcracks were conduits for material transport enabling fluid-mediated reactions and hydrothermal mineral precipitation. ToF-SIMS mapping shows that

titanite has been locally altered proximal to these microcrack interfaces, stripped of most trace elements and enriched in Al relative to the unaltered host grain. The spatial pattern of trace element depletion is supported by 167 LA-MC-ICPMS spot analyses across the grain. These analyses quantitatively demonstrate that correlated depletion of REEs, Y, Zr, Nb, Mo, Sn, Th, and Pb has occurred to a greater extent (commonly from a few thousand ppm down to a few tens of ppm) in domains where open microcrack density is highest. These domains also record the highest degree of radiogenic Pb-loss, defining an upper bounding isochron in a triangular mixing field of U-Pb data between two radiogenic Pb reservoirs and a common Pb source in Tera-Wasserburg space. Significantly, regression of both the upper and lower isochrons anchored by the measured Pb isotope composition of the surrounding feldspar, define lower intercept ages of 67 ± 4 Ma and 307 ± 10 Ma, respectively. The young age is within uncertainty of the Chicxulub impact event and dates impact-induced hydrothermal alteration, whereas the old age is consistent with magmatic ages determined for the target rocks within the peak ring. All other data points are intermediate apparent ages that represent a continuum of partial U-Pb resetting, volume mixing of material with two different radiogenic Pb compositions in the laser analysis, or some combination of both.

While the exact nature of the fluid and temperature conditions is not clear, the generation of a weak Eu anomaly (Eu/Eu*) in the most altered titanite domains suggests a reducing fluid in which divalent Eu was less mobile. This study shows that concentrations of petrologically significant trace elements (e.g., Zr) can be wide ranging in hydrothermally-altered titanite, potentially resulting in misleading geological interpretations (e.g., spurious apparent Zr-titanite temperatures). Nevertheless, this study demonstrates how titanite can be used to date hydrothermal alteration in impact settings.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDIX A. SUPPLEMENTARY MATERIAL

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Shocked Chicxulub titanite records hydrothermal alteration and impact age – Supplementary File

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Supplementary Figures

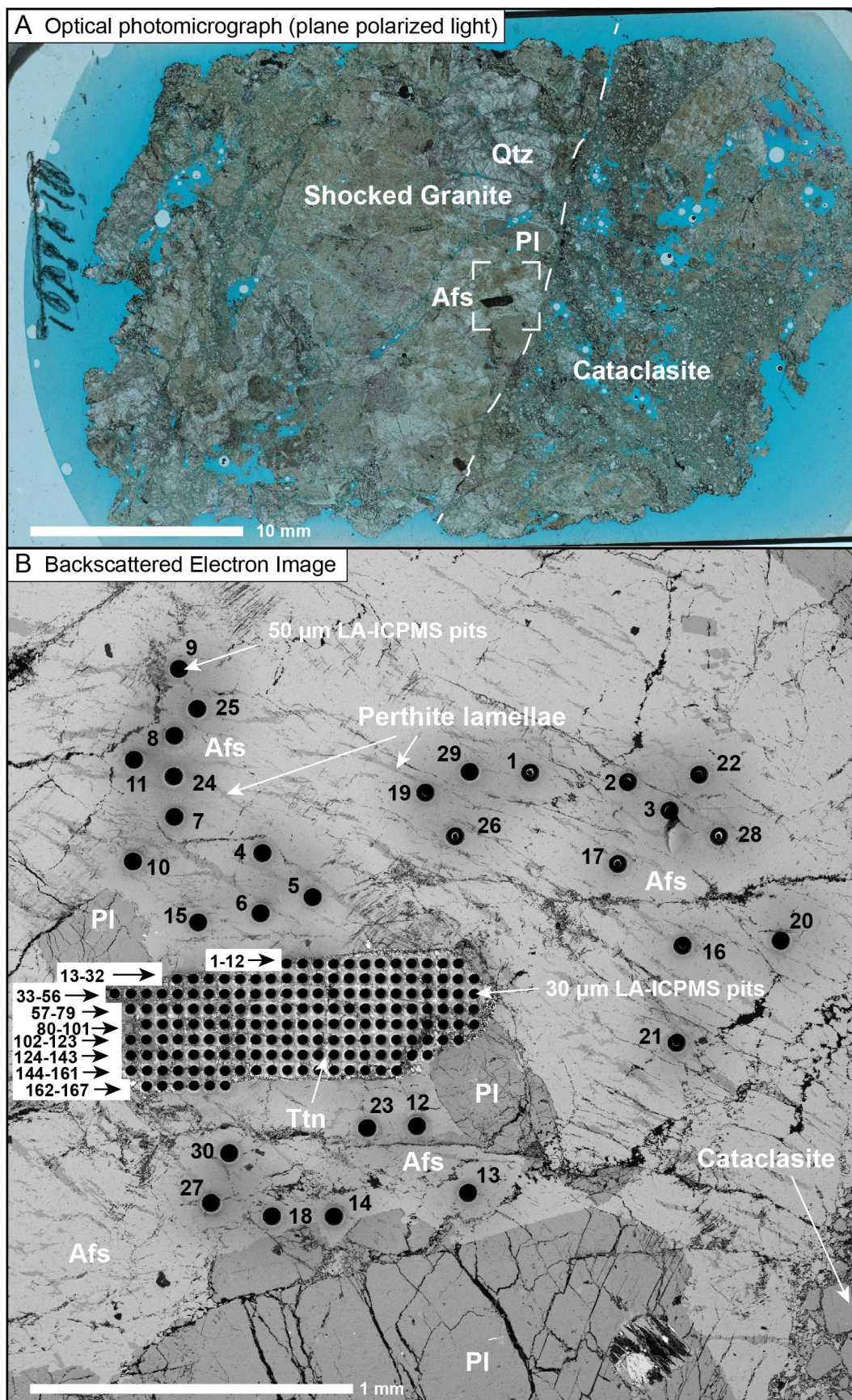


Figure S1. A. Optical photomicrograph (plane polarized light) of sample #814.85 showing the context of the titanite grain in this study. B. Backscattered electron image showing the locations of LA-ICPMS analysis spots in alkali feldspar and titanite. Numbers refer points listed in Table X. Qtz = quartz; Afs = alkali feldspar; Pl = plagioclase; Ttn = titanite.

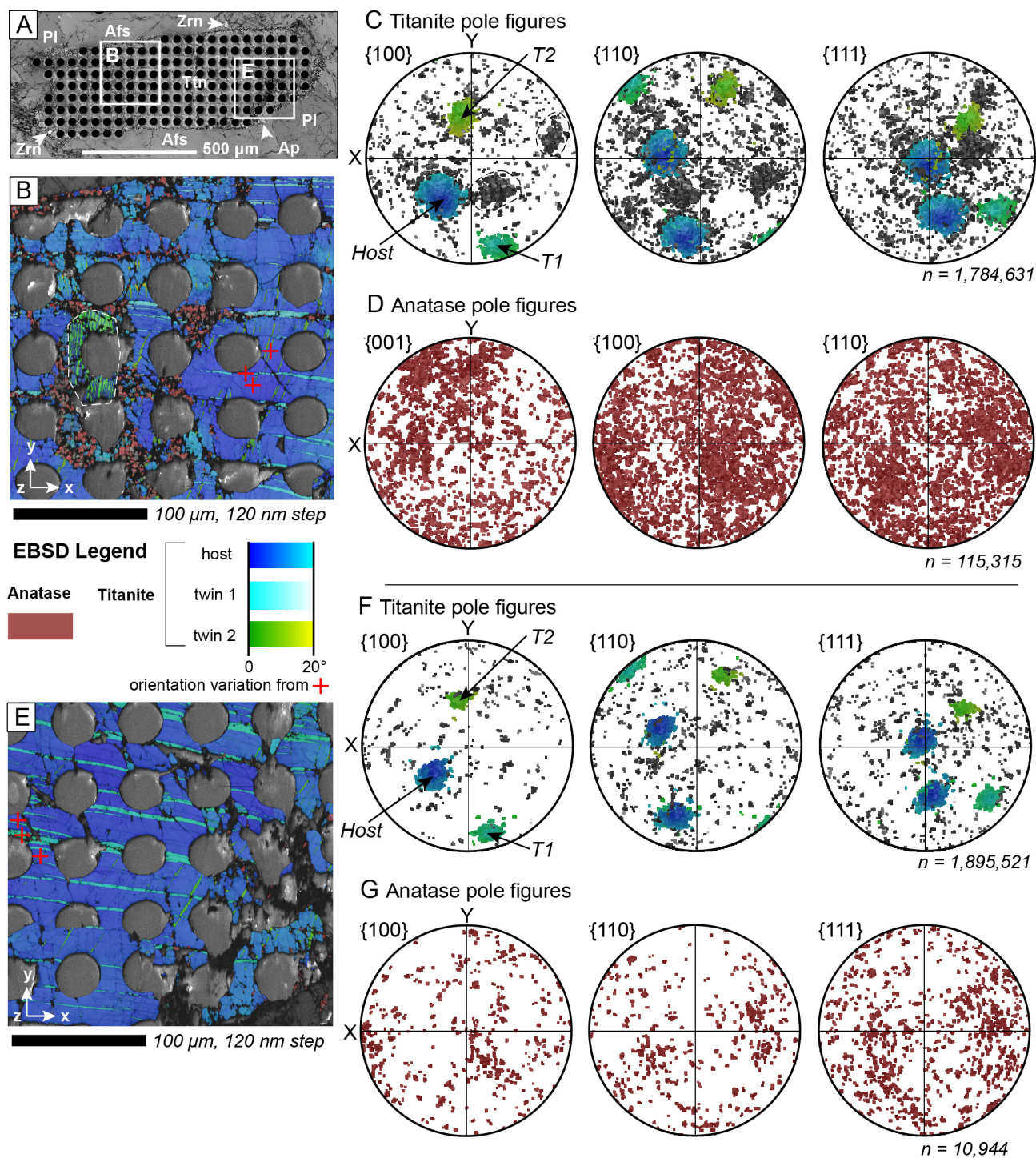


Figure S2. EBSD data for titanite and anatase from two regions of interest in sample #814.85. A. BSE image showing location of regions of interest. B. EBSD Crystallographic orientation map of upper left region of interest shown in A. Titanite coloured relative to user-defined reference orientations for the host grain, twin 1 and twin 2 orientations. Dark circles indicate LA-MC-ICPMS pits where no indexing was possible. C. Selection of pole figures for titanite shown in B. D. Selection of pole figures for anatase shown in B. E. EBSD Crystallographic orientation map of lower right region of interest shown in A. Colour scheme as for B. F. Selection of pole figures for titanite shown in E. G. Selection of pole figures for anatase shown in E. Pole figures are equal area, lower hemisphere projections in the map x-y-z reference frame. Pole figures utilise colours shown in maps B and E (see ‘EBSD Legend’).

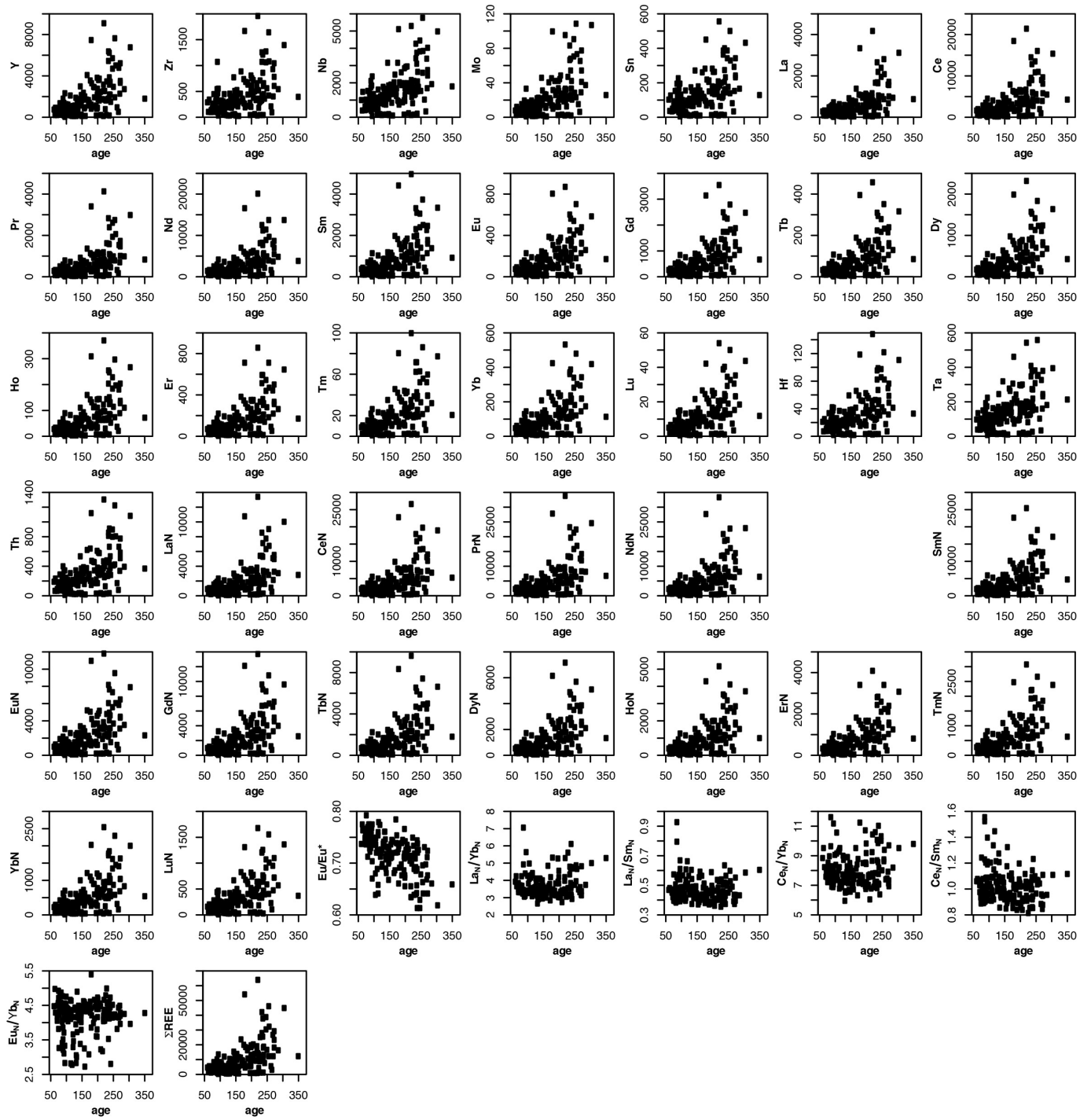


Figure S3. Plots of trace element concentration, trace element ratios, and Eu anomaly as a function of apparent ^{207}Pb -corrected U-Pb age (age). $n = 167$.

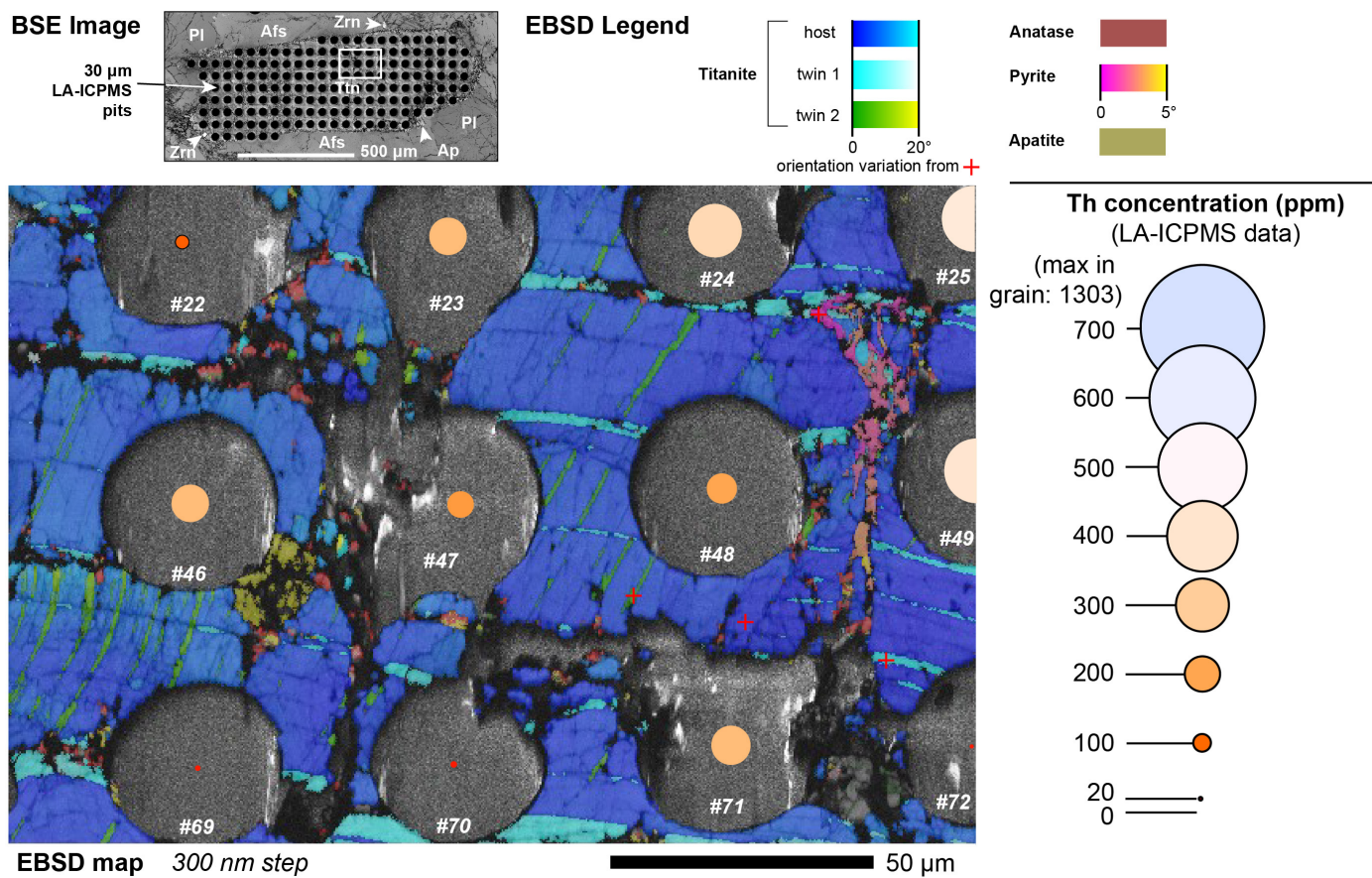


Figure S4. EBSD map of the central domain of the titanite grain, collected after LA-ICPMS analysis. Coloured circles depict measured Th concentration. LA-ICPMS spot IDs are numbered according to Table 1.

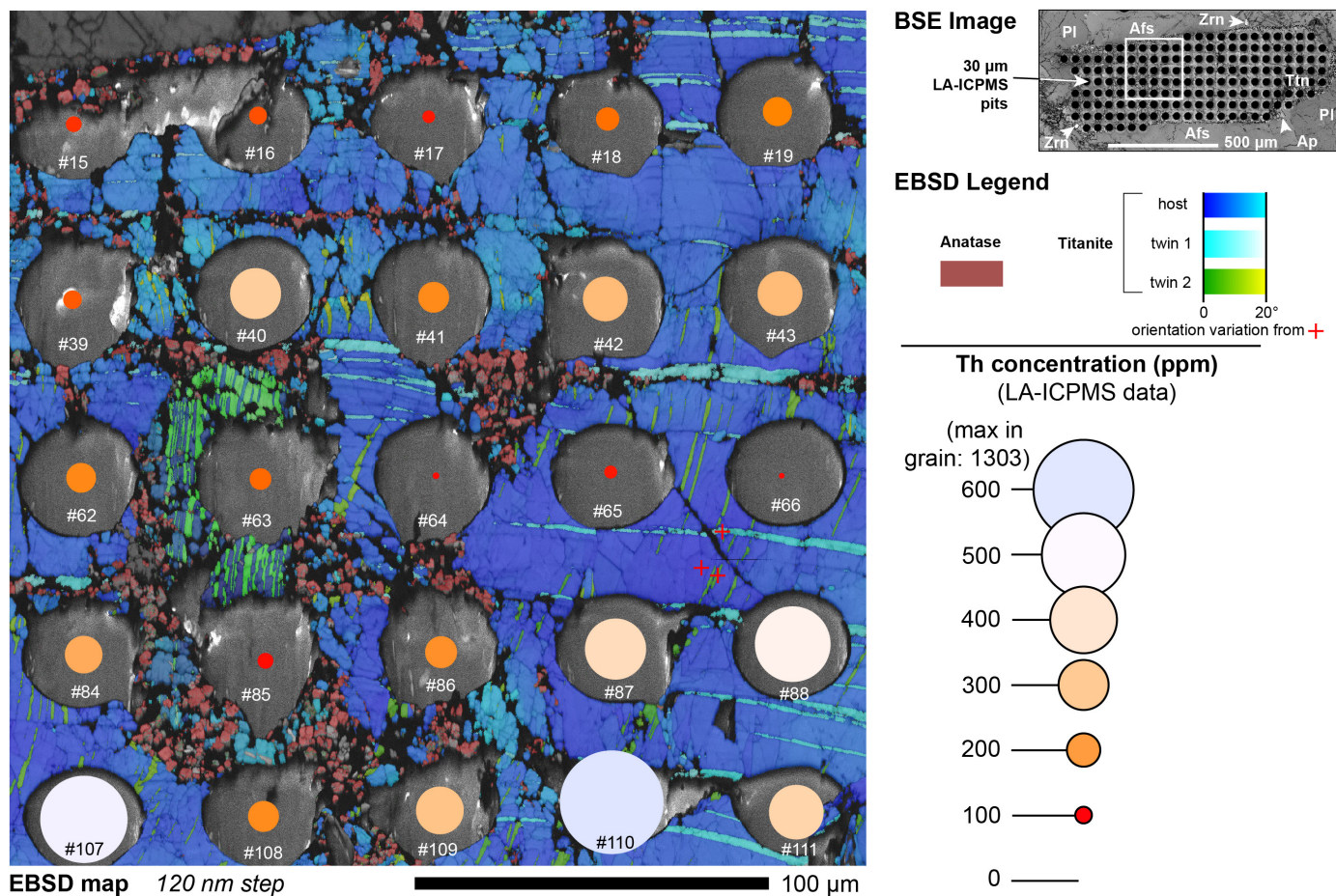


Figure S5. EBSD map of the upper left domain of the titanite grain, collected after LA-ICPMS analysis. Coloured circles depict measured Th concentration. LA-ICPMS spot IDs are numbered according to Table 1.

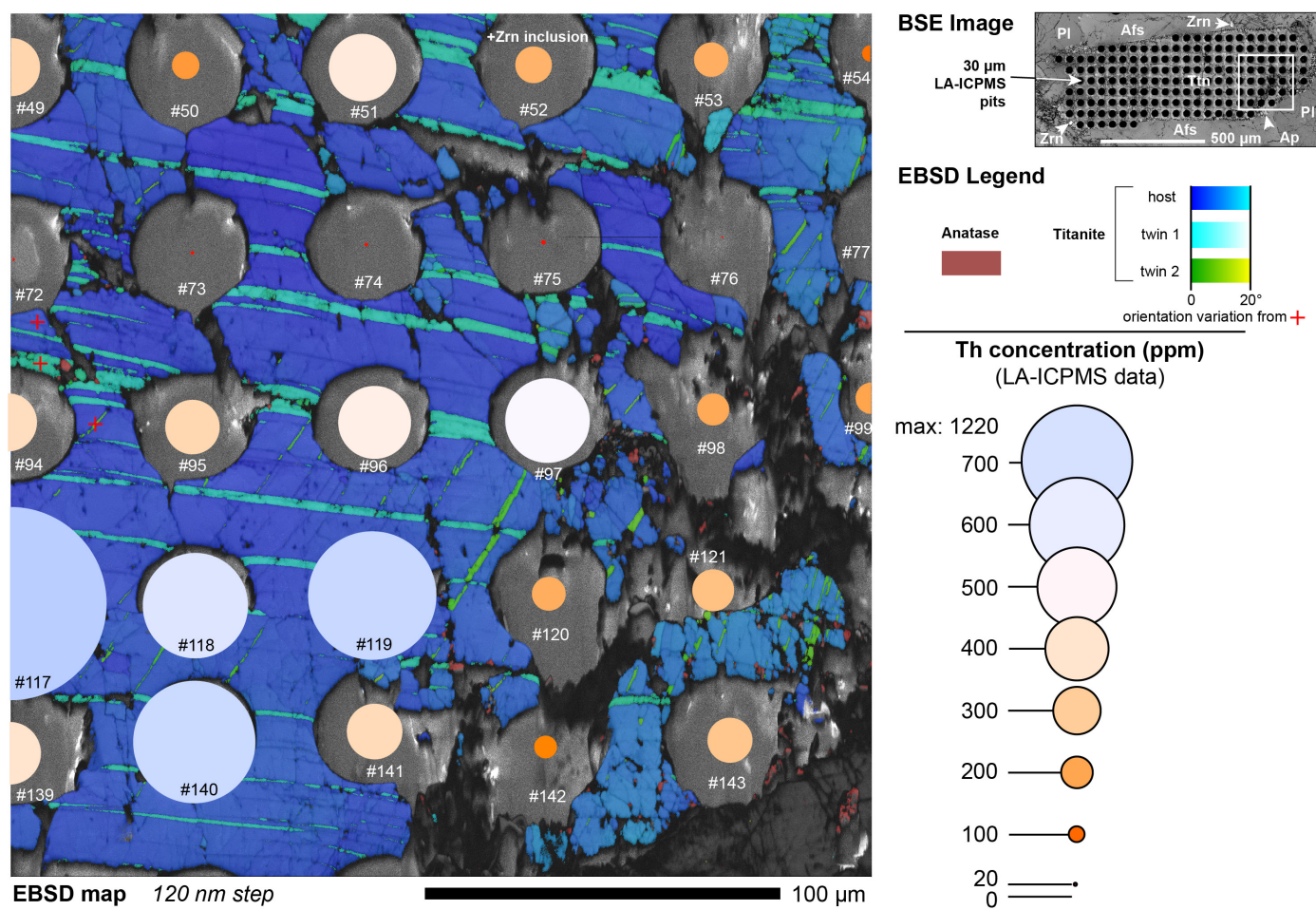


Figure S6. EBSD map of the lower right domain of the titanite grain, collected after LA-ICPMS analysis. Coloured circles depict measured Th concentration. LA-ICPMS spot IDs are numbered according to Table 1.

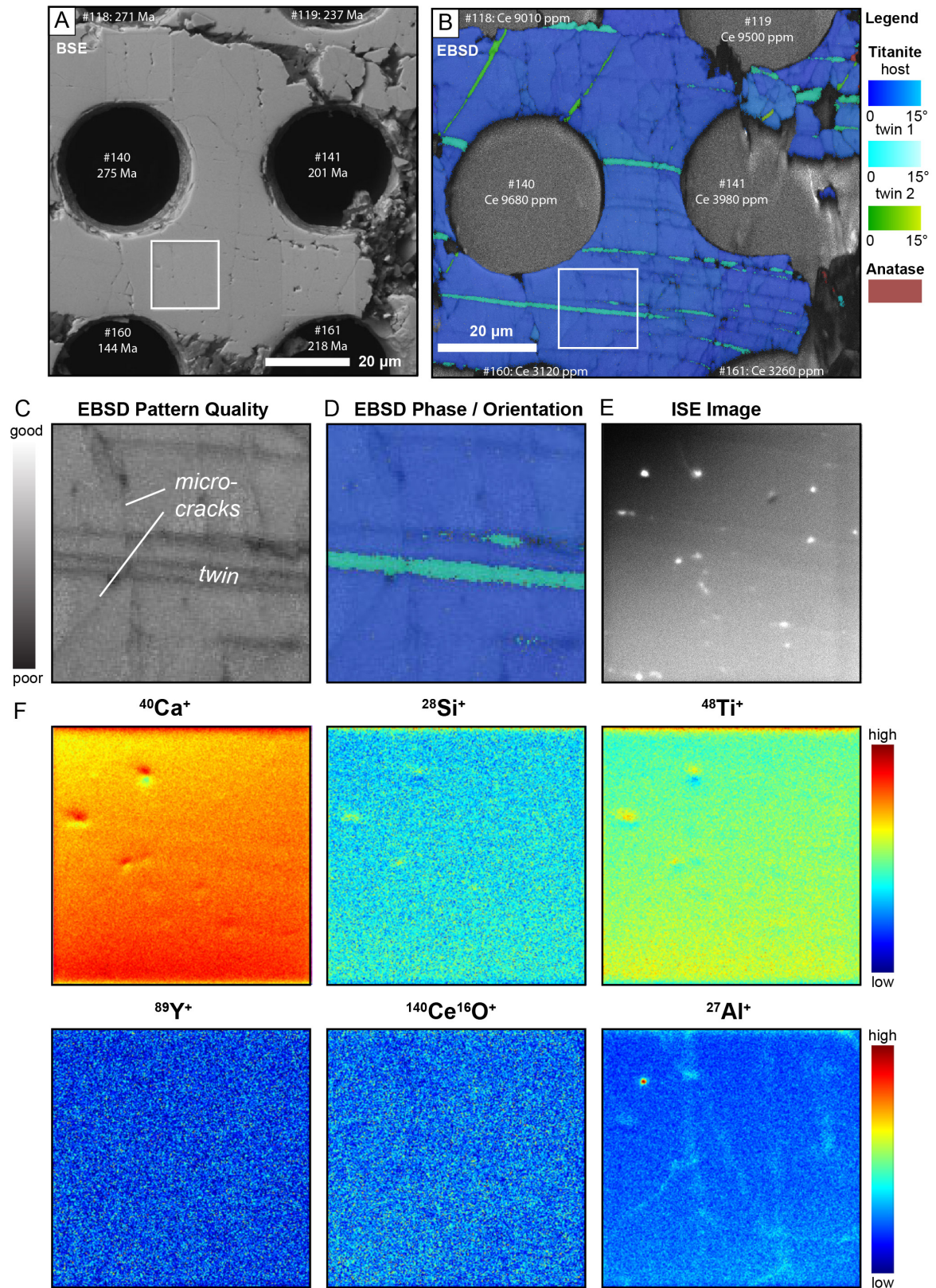


Figure S7. EBSD and ToF-SIMS maps of a region of interest in the titanite grain. A. SE image annotated for LA-MS-ICPMS spot ID and ^{207}Pb -corrected U-Pb age. White square indicates area covered by ToF-SIMS map. B. EBSD map of area shown in A, annotated for LA-MS-ICPMS spot ID and Ce concentration. Colour scheme as used in Figs S4-6. C. EBSD pattern quality (band contrast) map. D. EBSD phase and orientation map from B. E. ISE = ion secondary image. F. ToF-SIMS maps for selected ionic species.

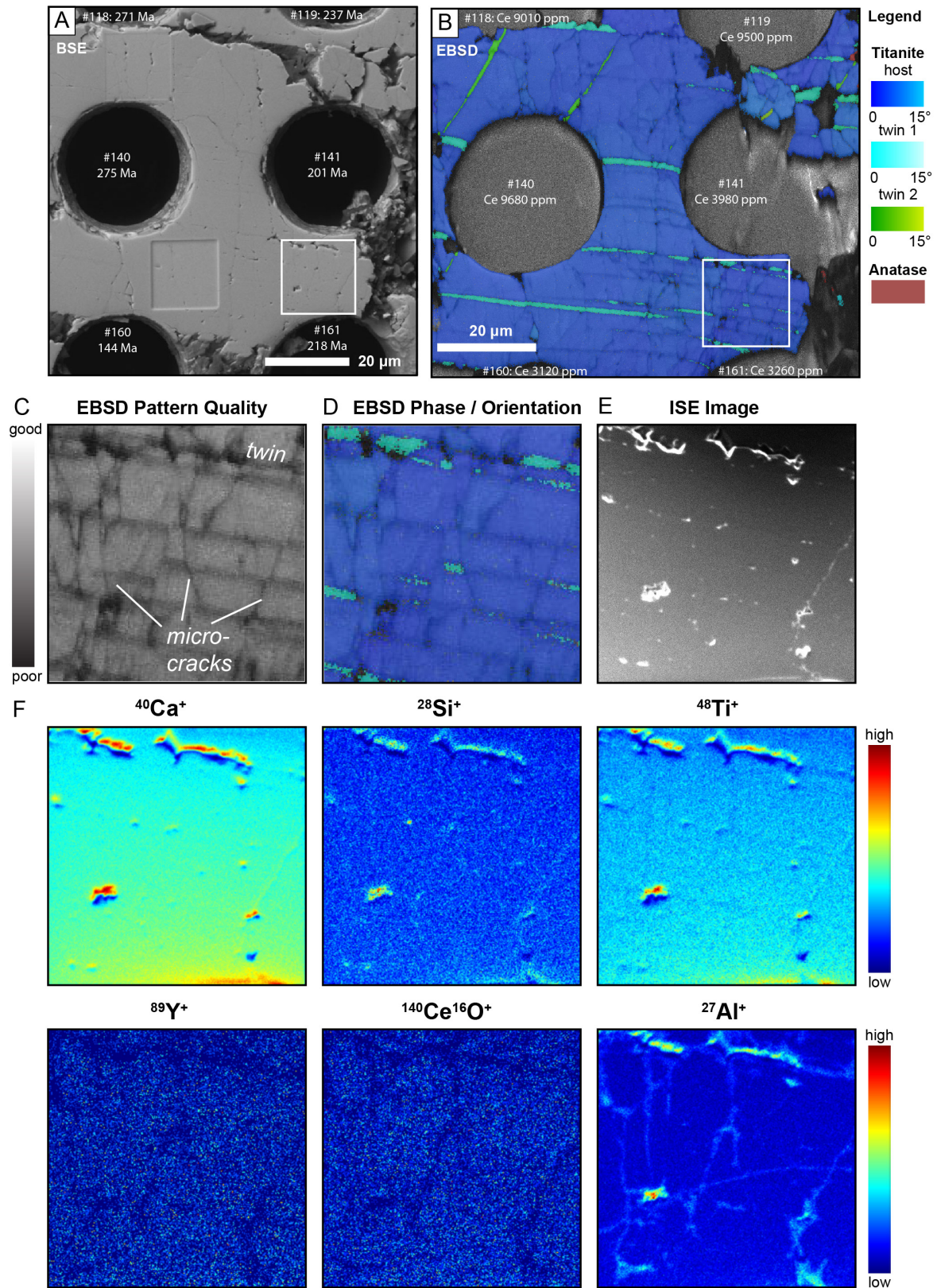


Figure S8. EBSD and ToF-SIMS maps of a region of interest in the titanite grain. A. SE image annotated for LA-MS-ICPMS spot ID and ^{207}Pb -corrected U-Pb age. White square indicates area covered by ToF-SIMS map. B. EBSD map of area shown in A, annotated for LA-MS-ICPMS spot ID and Ce concentration. Colour scheme as used in Figs S4-6. C. EBSD pattern quality (band contrast) map. D. EBSD phase and orientation map from B. E. ISE = ion secondary image. F. ToF-SIMS maps for selected ionic species.

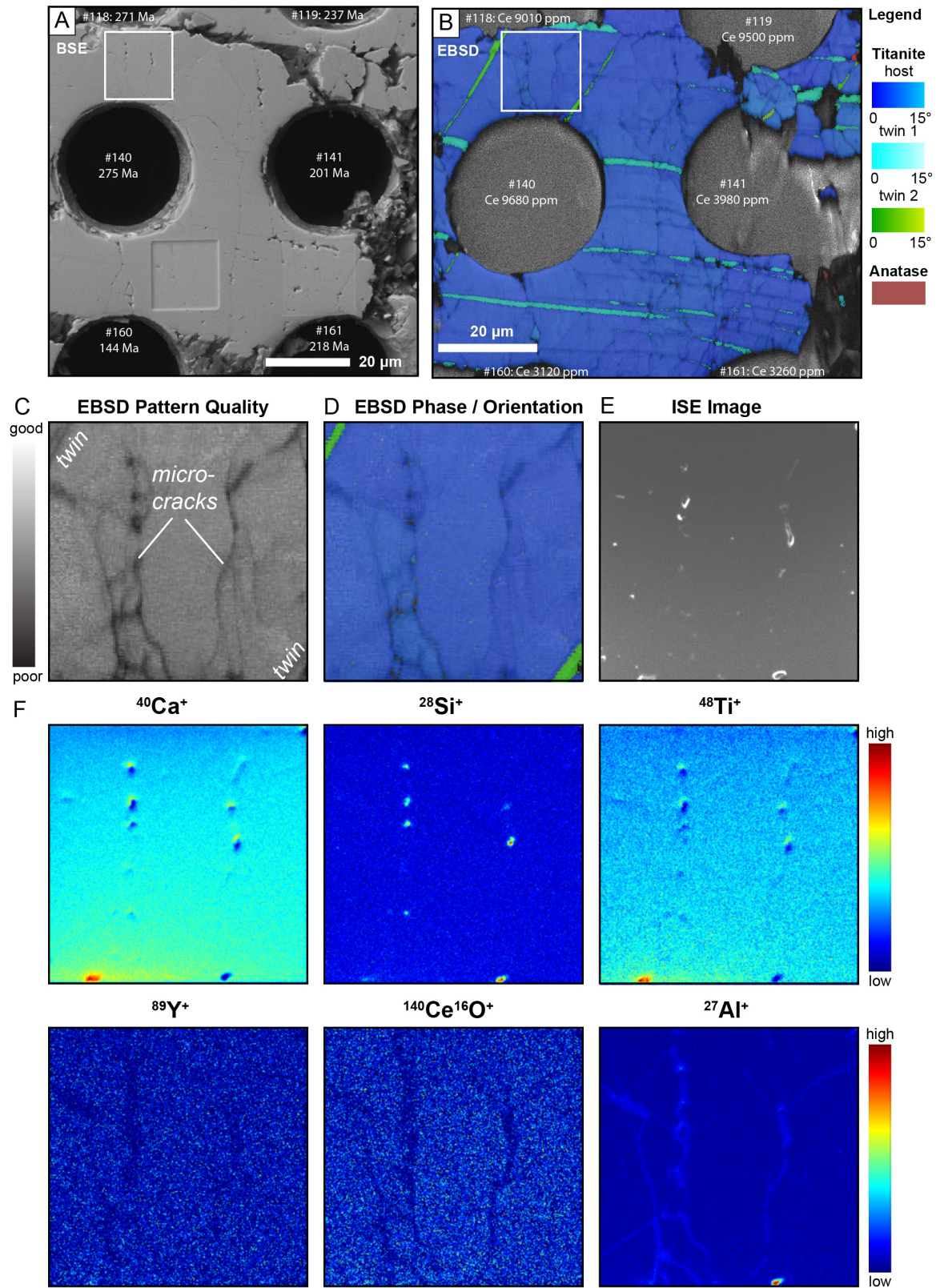


Figure S9. EBSD and ToF-SIMS maps of a region of interest in the titanite grain. A. SE image annotated for LA-MS-ICPMS spot ID and ^{207}Pb -corrected U-Pb age. White square indicates area covered by ToF-SIMS map. B. EBSD map of area shown in A, annotated for LA-MS-ICPMS spot ID and Ce concentration. Colour scheme as used in Figs S4-6. C. EBSD pattern quality (band contrast) map. D. EBSD phase and orientation map from B. E. ISE = ion secondary image. F. ToF-SIMS maps for selected ionic species.

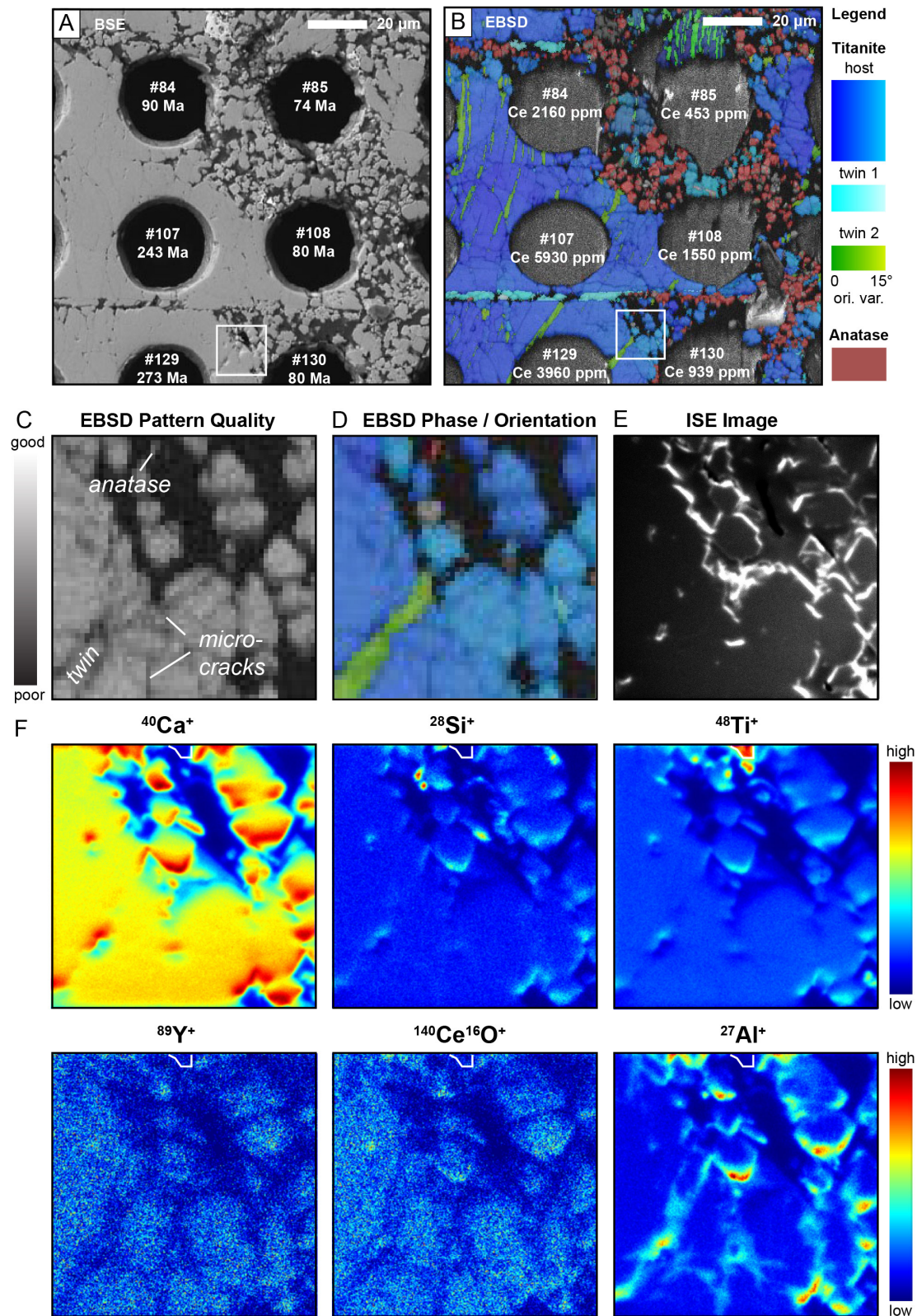


Figure S10. EBSD and ToF-SIMS maps of a region of interest in the titanite grain. A. SE image annotated for LA-MS-ICPMS spot ID and ^{207}Pb -corrected U-Pb age. White square indicates area covered by ToF-SIMS map. B. EBSD map of area shown in A, annotated for LA-MS-ICPMS spot ID and Ce concentration. Colour scheme as used in Figs S4-6. C. EBSD pattern quality (band contrast) map. D. EBSD phase and orientation map from B. E. ISE = ion secondary image. F. ToF-SIMS maps for selected ionic species.

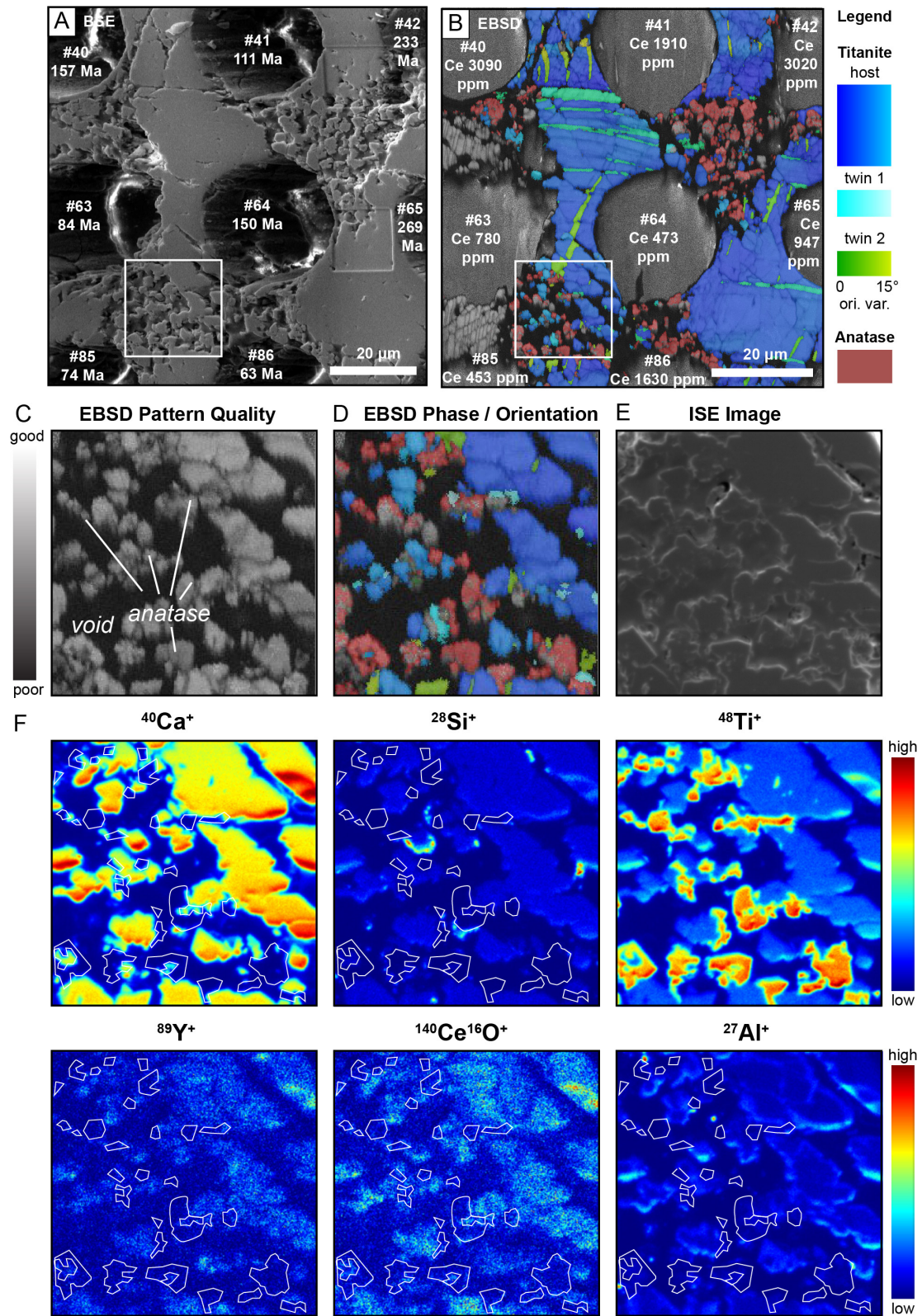


Figure S11. EBSD and ToF-SIMS maps of a region of interest in the titanite grain. A. SE image annotated for LA-MS-ICPMS spot ID and ^{207}Pb -corrected U-Pb age. White square indicates area covered by ToF-SIMS map. B. EBSD map of area shown in A, annotated for LA-MS-ICPMS spot ID and Ce concentration. Colour scheme as used in Figs S4-6. C. EBSD pattern quality (band contrast) map. D. EBSD phase and orientation map from B. E. ISE = ion secondary image. F. ToF-SIMS maps for selected ionic species.

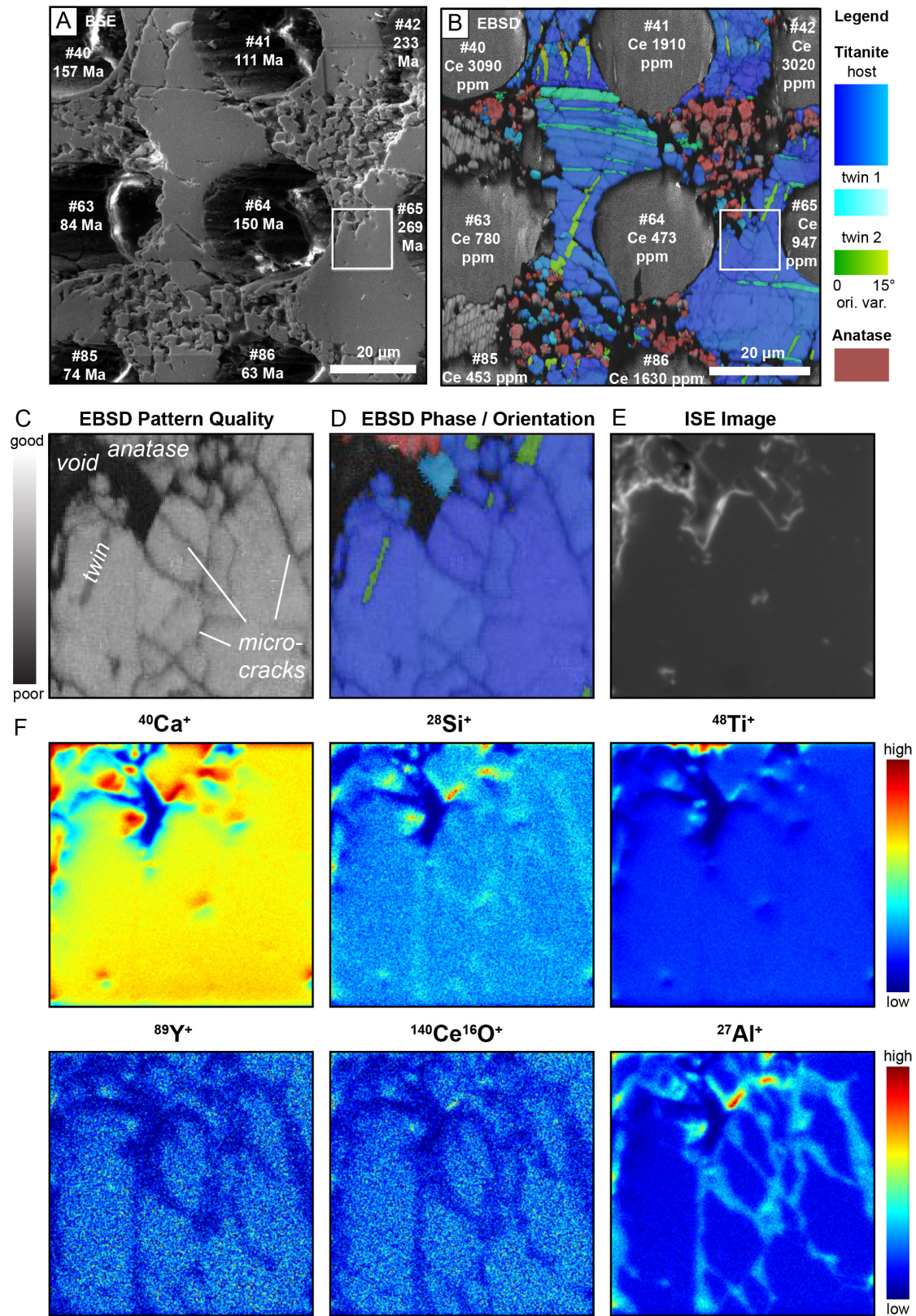


Figure S12. EBSD and ToF-SIMS maps of a region of interest in the titanite grain. A. SE image annotated for LA-MS-ICPMS spot ID and ^{207}Pb -corrected U-Pb age. White square indicates area covered by ToF-SIMS map. B. EBSD map of area shown in A, annotated for LA-MS-ICPMS spot ID and Ce concentration. Colour scheme as used in Figs S4-6. C. EBSD pattern quality (band contrast) map. D. EBSD phase and orientation map from B. E. ISE = ion secondary image. F. ToF-SIMS maps for selected ionic species.

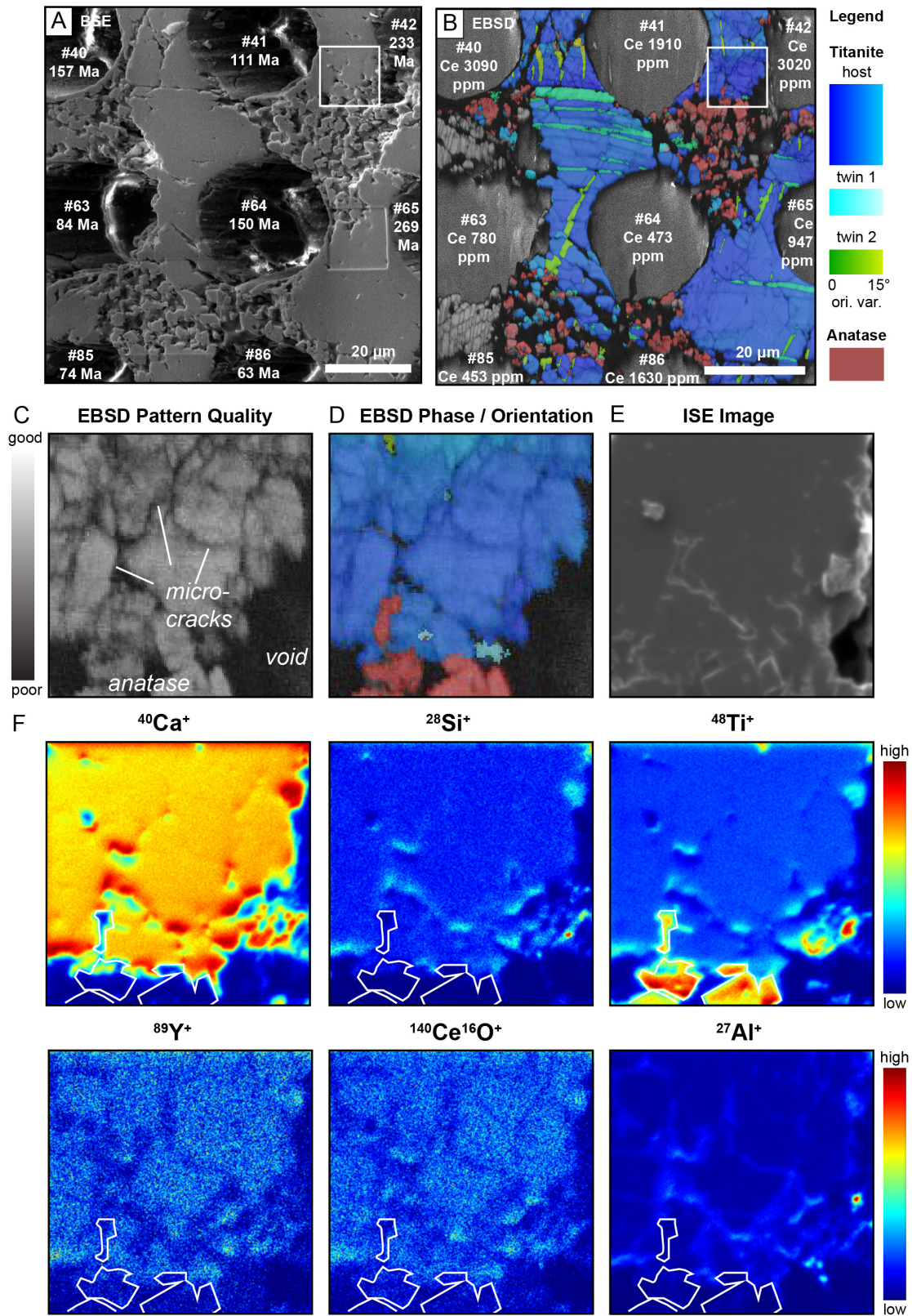


Figure S13. EBSD and ToF-SIMS maps of a region of interest in the titanite grain. A. SE image annotated for LA-MS-ICPMS spot ID and ^{207}Pb -corrected U-Pb age. White square indicates area covered by ToF-SIMS map. B. EBSD map of area shown in A, annotated for LA-MS-ICPMS spot ID and Ce concentration. Colour scheme as used in Figs S4-6. C. EBSD pattern quality (band contrast) map. D. EBSD phase and orientation map from B. E. ISE = ion secondary image. F. ToF-SIMS maps for selected ionic species.

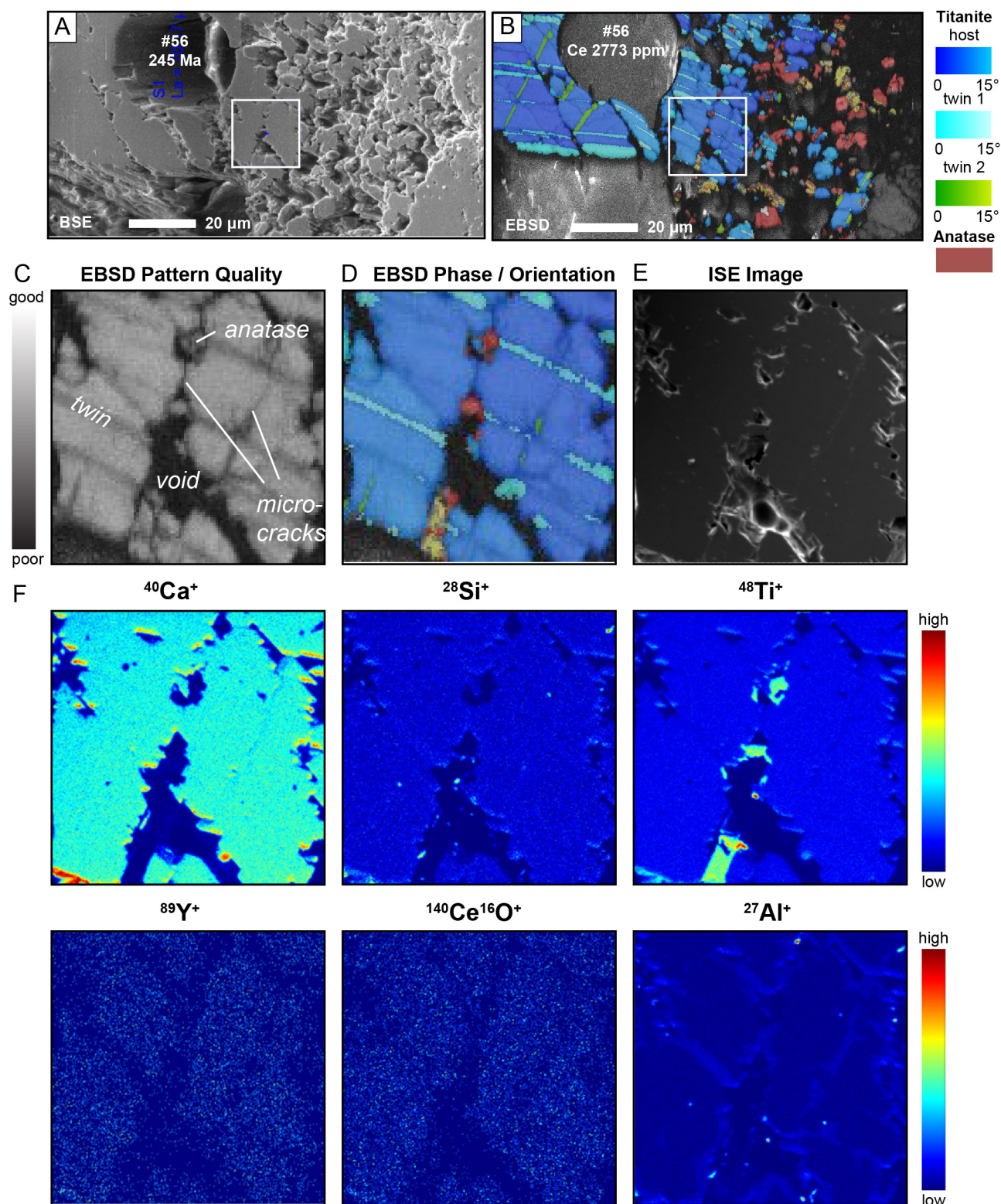


Figure S14. EBSD and ToF-SIMS maps of a region of interest in the titanite grain. A. SE image annotated for LA-MS-ICPMS spot ID and ^{207}Pb -corrected U-Pb age. White square indicates area covered by ToF-SIMS map. B. EBSD map of area shown in A, annotated for LA-MS-ICPMS spot ID and Ce concentration. Colour scheme as used in Figs S4-6. C. EBSD pattern quality (band contrast) map. D. EBSD phase and orientation map from B. E. ISE = ion secondary image. F. ToF-SIMS maps for selected ionic species.

Table 1. Lead isotope data for feldspars from the Chicxulub impact site (IODP-ICDP Expedition 364 Hole Moo77A) and reference material. Lead isotope data have been corrected for fractionation.

Sample	$^{206}\text{Pb}/^{204}\text{P}$ b	$\pm 2\sigma$	$^{207}\text{Pb}/^{204}\text{P}$ b	$\pm 2\sigma$	$^{208}\text{Pb}/^{204}\text{P}$ b	$\pm 2\sigma$	Pb (ppm)	$\pm 2\sigma$
121-1-75-77 - 1	18.670	0.160	15.850	0.140	38.700	0.330	41.0	1.2
121-1-75-77 - 2	18.680	0.110	15.870	0.085	38.690	0.220	39.7	1.1
121-1-75-77 - 3	18.494	0.093	15.709	0.080	38.320	0.200	42.2	1.6
121-1-75-77 - 4	18.580	0.210	15.760	0.180	38.460	0.440	39.2	4.0
121-1-75-77 - 5	18.530	0.150	15.740	0.120	38.380	0.290	38.6	3.1
121-1-75-77 - 6	18.570	0.230	15.760	0.180	38.440	0.440	39.2	3.7
121-1-75-77 - 7	18.680	0.170	15.850	0.140	38.680	0.340	49.1	4.7
121-1-75-77 - 8	18.540	0.210	15.770	0.180	38.440	0.420	39.0	1.6
121-1-75-77 - 9	18.730	0.110	15.855	0.085	38.730	0.210	34.4	1.6
121-1-75-77 - 10	19.030	0.250	16.130	0.200	39.360	0.490	52.7	6.0
121-1-75-77 - 11	18.760	0.160	15.930	0.150	38.880	0.340	54.0	5.0
121-1-75-77 - 12	18.632	0.073	15.815	0.058	38.590	0.160	57.7	3.7
121-1-75-77 - 13	18.700	0.130	15.860	0.100	38.700	0.240	38.8	1.8
121-1-75-77 - 14	18.390	0.210	15.620	0.180	38.110	0.440	49.9	2.5
121-1-75-77 - 15	18.369	0.081	15.592	0.068	38.030	0.170	30.5	0.5
121-1-75-77 - 16	18.400	0.140	15.630	0.110	38.130	0.270	34.5	1.3
121-1-75-77 - 17	18.471	0.092	15.696	0.069	38.280	0.180	35.1	1.4
121-1-75-77 - 18	18.400	0.110	15.620	0.100	38.080	0.240	42.2	2.6
121-1-75-77 - 19	18.471	0.078	15.689	0.070	38.270	0.160	46.3	3.1
121-1-75-77 - 20	18.640	0.170	15.820	0.140	38.610	0.330	50.6	3.4
121-1-75-77 - 21	18.640	0.110	15.820	0.110	38.610	0.230	49.5	2.1
121-1-75-77 - 22	18.710	0.120	15.886	0.096	38.780	0.220	66.9	2.2
121-1-75-77 - 23	18.780	0.230	15.920	0.200	38.860	0.480	58.6	2.5
121-1-75-77 - 24	18.420	0.130	15.643	0.094	38.180	0.240	55.0	2.7
121-1-75-77 - 25	18.360	0.120	15.600	0.110	38.050	0.240	34.9	1.7
121-1-75-77 - 26	18.310	0.110	15.570	0.100	37.960	0.240	39.6	0.9
121-1-75-77 - 27	18.450	0.160	15.640	0.110	38.220	0.290	42.0	1.8
121-1-75-77 - 28	18.334	0.055	15.569	0.042	38.010	0.110	37.9	0.9
121-1-75-77 - 29	18.380	0.130	15.610	0.110	38.110	0.270	46.0	3.2
121-1-75-77 - 30	18.380	0.170	15.600	0.150	38.090	0.350	57.5	2.4
shap - 1	18.288	0.056	15.681	0.049	38.270	0.120	54.4	2.3
shap - 2	18.220	0.140	15.610	0.110	38.130	0.280	59.2	7.8
shap - 3	18.317	0.057	15.699	0.044	38.320	0.120	55.0	2.8
shap - 4	18.202	0.043	15.612	0.035	38.114	0.087	45.8	2.1
shap - 5	18.144	0.063	15.548	0.054	37.950	0.130	45.0	1.2
shap - 6	18.304	0.042	15.687	0.034	38.309	0.088	61.0	2.9
shap - 7	18.075	0.055	15.518	0.049	37.880	0.120	48.2	1.7
shap - 8	18.152	0.076	15.559	0.068	38.000	0.160	41.8	1.6
shap - 9	18.174	0.051	15.583	0.044	38.050	0.100	48.8	1.3
shap - 10	18.429	0.049	15.729	0.040	38.476	0.099	28.7	0.7

All concentrations are relative to NIST612. The primary reference material for the unknown is shap feldspar (excluding shap; Tyrrell et al., 2006). Shap feldspar is referenced to NIST612 (Woodhead and Hergt, 2001). Sigma refers to standard error.

S. Tyrrell, J.S. Daly, T.F. Kokfelt, D. Gagnevin Common-Pb isotopic composition of detrital K-feldspar grains: validation as a provenance tool and its application to Upper Carboniferous paleodrainage, Northern England, *Journal of Sedimentary Research*, 76 (2006), pp. 324-345

J.D. Woodhead, J.M. Hergt Strontium, Neodymium and Lead isotope analyses of NIST glass certified reference materials: SRM 610, 612, 614, *Geostandards and Geoanalytical Research*, 25 (2001), pp. 261-266

<i>Spot</i>	<i>sample</i>	<i>Y</i>	<i>Zr</i>	<i>Nb</i>	<i>Mo</i>	<i>Sn</i>
1	77 - 1	391	9.30E+03	486	4.15	44.1
2	77 - 2	538	202	783	6.7	67.4
3	77 - 3	237	106.5	411	3.06	34.3
4	77 - 4	739	231.1	880	9.09	76.9
5	77 - 5	838	189.4	736	9.92	68.3
6	77 - 6	410	113.7	461	5.17	40
7	77 - 7	1760	610	1587	22.3	149.2
8	77 - 8	885	266	849	11.18	76.8
9	77 - 9	990	221	868	11.93	81
10	77 - 10	1825	376	1489	22.1	148.4
11	77 - 11	475	4.40E+03	465	6.1	36.1
12	77 - 12	273	101.6	491	3.49	43
13	77 - 13	345	151.7	567	4.6	48.8
14	77 - 14	718	1070	999	8.64	91.1
15	77 - 15	336	138.2	596	5.09	51
16	77 - 16	494	144	600	6.6	47.7
17	77 - 17	254	105.2	412	3.49	36.7
18	77 - 18	709	180	815	10.1	65
19	77 - 19	848	209.7	988	13.03	71.8
20	77 - 20	2177	450	2077	33.2	162.5
21	77 - 21	1625	292.5	1600	24.88	117.5
22	77 - 22	327	101.2	469	5.82	31.4
23	77 - 23	1138	294	1279	17.2	96.5
24	77 - 24	1673	404	1725	24.14	137.8
25	77 - 25	1700	457	2024	21.3	135.9
26	77 - 26	1392	330.8	1693	19.85	112.7
27	77 - 27	1318	310.6	1613	21.88	110.6
28	77 - 28	733	212.7	1119	12.58	72.8
29	77 - 29	600	189.4	1213	7.93	68.6
30	77 - 30	824	221.1	1652	11.14	91.4
31	77 - 31	981	209.3	1035	15.23	82.2
32	77 - 32	114.5	38.7	173.8	1.37	15.11
33	77 - 33	373	136	540	5.22	40
34	77 - 34	162.1	92.2	371	2.4	28.8
35	77 - 35	872	303	880	10.48	73.9
36	77 - 36	917	295	954	10.4	89.9
37	77 - 37	213.9	104.1	385	2.61	37.3
38	77 - 38	850	219	829	9.94	72.8
39	77 - 39	460	153.1	555	5.16	51.7
40	77 - 40	1768	400	1616	22.2	137.2
41	77 - 41	1051	256.1	936	12.36	82.3
42	77 - 42	1725	318	1280	21.3	112.2
43	77 - 43	1671	361	1234	19	118.5
44	77 - 44	908	211	741	9.84	69.9
45	77 - 45	1119	234.1	1071	15.01	88.3
46	77 - 46	1229	320	1031	13.1	94.4
47	77 - 47	533	216	1027	6.57	67.8
48	77 - 48	580	170	917	8.43	51.2

49 77 - 49	1806	395	1783	25.5	130
50 77 - 50	907	201.4	947	11.94	63.6
51 77 - 51	1919	423.7	2582	22.93	138.6
52 77 - 52	1203	1.24E+04	1163	16.8	86.2
53 77 - 53	860	212.1	1349	11.48	86.2
54 77 - 54	340	141.9	756	5.49	47.7
55 77 - 55	795	179.1	804	12.32	66.2
56 77 - 56	1508	359	1768	20.6	143.7
57 77 - 57	574	175	637	6.78	56.2
58 77 - 58	1214	267	972	13.65	97
59 77 - 59	2209	424	1633	25.7	158.7
60 77 - 60	387	108	435	5.04	38.3
61 77 - 61	1220	265	919	13.8	91.3
62 77 - 62	969	257.1	806	9.47	85.7
63 77 - 63	356	127	619	4.69	44.9
64 77 - 64	239	57.5	169	2.32	18
65 77 - 65	530	96.5	344	6.24	32.9
66 77 - 66	220.5	43.9	142.3	2.4	14.18
67 77 - 67	224	53.9	161.3	2.42	16.52
68 77 - 68	205	50.4	170.4	2.44	15.59
69 77 - 69	182.3	47.6	141.7	1.75	13.52
70 77 - 70	158.8	41.6	212	1.96	12.1
71 77 - 71	1156	281	977	17.4	83.3
72 77 - 72	117.3	31.19	120	1.68	9.52
73 77 - 73	133.7	32.26	122	1.807	9.52
74 77 - 74	139.2	31.4	118.4	1.94	10.16
75 77 - 75	178.6	39.3	161.8	2.69	13.18
76 77 - 76	51.2	34.8	74.7	0.802	5.75
77 77 - 77	111.8	30.9	149.5	1.837	11.13
78 77 - 78	207	56	233	3.2	19
79 77 - 79	214	104	335	2.87	27.1
80 77 - 80	107.8	26.2	96.7	1.196	9.45
81 77 - 81	3730	717	2940	48.5	262
82 77 - 82	682	237.8	1023	9.54	91.4
83 77 - 83	3800	804	2840	42	282
84 77 - 84	1122	333	1118	11.86	120.1
85 77 - 85	217	135.8	638	3.28	48.5
86 77 - 86	750	293	991	7.62	102
87 77 - 87	2462	497	1694	25.3	164.4
88 77 - 88	3170	602	1969	33.3	204.5
89 77 - 89	3153	654	1894	31.8	208
90 77 - 90	2544	550	1658	25.5	173.9
91 77 - 91	9090	1957	5300	95.3	556
92 77 - 92	5720	1270	4450	90.5	387
93 77 - 93	4980	1083	3850	73.1	330
94 77 - 94	2150	504	1843	31.2	155.9
95 77 - 95	2300	555	2380	33	194.6
96 77 - 96	2944	677	2592	42.3	205.6
97 77 - 97	2980	770	3170	46	272
98 77 - 98	895	304	1228	12.4	107.9
99 77 - 99	1030	396	1250	16.7	101
100 77 - 100	1150	322	1483	16.8	116.5

101 77 - 101	945	301.1	1401	13.3	117.2
102 77 - 102	1045	318	1186	11.88	114.9
103 77 - 103	3324	602	2427	40.9	231.1
104 77 - 104	1382	285	1114	16	102
105 77 - 105	1920	442	1860	25.7	151
106 77 - 106	2540	517	1909	31.9	184.5
107 77 - 107	3410	661	2635	42.3	232.5
108 77 - 108	769	261	967	9.2	91.2
109 77 - 109	1336	451	1531	15.1	153
110 77 - 110	4060	890	2486	40.7	259.6
111 77 - 111	2233	450	1292	22.2	138.6
112 77 - 112	2090	444	1610	19.5	154.9
113 77 - 113	6360	1254	3409	66.2	388
114 77 - 114	7460	1666	5110	99.3	451
115 77 - 115	4700	1059	3820	70.3	343
116 77 - 116	3870	863	3100	54.4	274
117 77 - 117	7640	1642	5780	108.3	500
118 77 - 118	4770	926	3391	65.3	292.9
119 77 - 119	5440	1069	4270	83.4	362.6
120 77 - 120	1087	277	1209	16.5	97.8
121 77 - 121	994	318	1396	14.3	195.4
122 77 - 122	508	166.3	755	7.88	60.2
123 77 - 123	346	165.3	760	5.66	63.9
124 77 - 124	692	211	858	8.4	73.8
125 77 - 125	1720	375	1620	22.8	151.4
126 77 - 126	1258	308	1331	17.1	131.9
127 77 - 127	3610	750	2930	44.1	262
128 77 - 128	3570	736	3170	45.5	281
129 77 - 129	2290	406	1673	28.9	152.5
130 77 - 130	442	154.2	590	5.9	53.9
131 77 - 131	1654	406	1457	19.5	135
132 77 - 132	2034	457	1678	26.3	155
133 77 - 133	2900	629	1975	30.2	214
134 77 - 134	6230	1210	3750	67.9	401
135 77 - 135	2753	565	1675	30.3	178.8
136 77 - 136	3474	714	2101	46.6	200.1
137 77 - 137	6760	1399	4970	106.7	433
138 77 - 138	3521	779	2724	54.4	242.3
139 77 - 139	2718	542	1912	37.4	166.9
140 77 - 140	5220	1046	4020	77.6	341
141 77 - 141	2183	484	1961	33.7	167.4
142 77 - 142	626	221	858	8.5	155
143 77 - 143	1050	384	1725	15	135.7
144 77 - 144	1318	326	1325	17.9	124.7
145 77 - 145	722	177	736	9.66	65.8
146 77 - 146	398	128	546	5.61	47.9
147 77 - 147	2170	473	1970	27.5	175
148 77 - 148	1650	385	1574	22	139.3
149 77 - 149	2520	524	2157	32.9	194
150 77 - 150	1184	291.6	1186	14.28	106.2
151 77 - 151	292	102.5	421	3.63	37.3
152 77 - 152	1065	285	1141	13.2	99

153 77 - 153	1624	373	1518	20.3	133.3
154 77 - 154	1786	328.2	1333	22.1	120.1
155 77 - 155	1720	361	1192	19.4	118.5
156 77 - 156	3290	681	2015	31.8	219
157 77 - 157	1240	319	943	13.1	98.4
158 77 - 158	2930	559	1511	28.2	176
159 77 - 159	2350	524	1890	26.6	180
160 77 - 160	1740	381	1499	21.6	134.3
161 77 - 161	1750	333	1491	18.5	153
162 77 - 162	910	338	1470	12.3	126
163 77 - 163	1076	256	1052	13.4	108.3
164 77 - 164	1890	457	1773	22.3	174.3
165 77 - 165	1799	545	2116	19.3	226
166 77 - 166	1410	466	1853	14.4	168
167 77 - 167	664	188	764	6.76	66

<i>La</i>	<i>Ce</i>	<i>Pr</i>	<i>Nd</i>	<i>Sm</i>	<i>Eu</i>	<i>Gd</i>	<i>Tb</i>
113	677	117	585	153	33.1	112	14.5
200	1140	201	1020	269	55.4	188	23.5
81.7	486	86.2	441	114	23.7	78.6	10.2
253	1485	262	1329	353	72.6	249	31.2
260	1527	271	1430	409	84.7	305	38.1
129.7	761	135.9	712	201.6	41.7	146.4	18.24
526	3130	563	3040	880	184.7	658	82.1
272	1632	288	1522	442	91	316	39.3
301	1793	315	1681	485	101.6	359	44.8
566	3301	585	3061	866	176.5	639	80.6
144	860	152	790	231	48	168	21.4
104.9	573	95.5	452	98.9	20.9	68.8	9.06
123.1	701	123.1	635	172	36.2	124	15.7
238.4	1427	253.7	1300	347	72.7	247	30.8
111.9	662	123	632	179	37.2	122	15.9
158	950	170	900	254	52.9	181	22.6
88.9	525	92	459	122.2	25.2	86.5	11.04
248	1440	250	1280	347	71.8	250	31.1
332	1874	320	1640	421	88.1	294	35.9
769	4431	777	4066	1131	231.7	815	100.5
470.5	2812	516	2791	835	171.7	613	77.2
141.2	801	136	682	176.9	36.1	121.2	15.02
412	2400	406	2091	567	111	417	53.4
662	3451	653	3215	820	159.4	604	76.9
760	3880	690	3440	849	163	631	78.7
557	3050	558	2770	685	141.4	480	61.3
496	2873	512	2508	644	137.8	448	55.7
323	1810	299	1537	379	80.1	261	31.8
215.2	1207	197	959	240	49.1	177.8	22.8
274	1505	250	1171	285	59.5	214.8	27.5
344	1910	331	1654	442	89.8	319	40.1
44.2	251.2	40.8	187.3	41.9	8.78	28.7	3.71
128.1	747	131.9	667	175	37.3	126	15.9
71.7	353	66.3	320	79	16.28	54	6.89
302	1770	305	1556	431	87.6	317	38.3
339	1939	336	1690	450	93.3	322	40.8
85.9	502	85.5	430	112.5	23.9	79	9.8
264	1530	273	1410	401	81.8	301	38
154.4	912	156.6	784	206	42	147.8	19
517	3090	560	3022	880	183.7	661	81.1
327	1910	338	1789	507	103.1	378	47.6
515	3020	533	2890	856	174.9	647	81.1
533	3095	540	2902	810	165.8	612	75.6
311	1810	309	1590	440	87.9	328	41.3
319	1850	318	1666	472	97.1	358	47.2
459	2680	474	2260	594	113.3	437	55.4
243	1346	220	1071	270	46.9	187	23.4
290	1500	267	1260	299	55.6	215	26.5

882	4240	821	3820	917	168.9	671	84.3
346	1971	346	1718	456	86.8	337.8	41.64
869	4064	784	3910	916	179.1	677	84.5
403	2230	375	1890	515	102.1	384	49.6
288.1	1591	265.3	1302	327	66.3	248.4	32.2
119	688	113.9	548	135	28.2	94.1	12.4
240.2	1403	251.5	1316	366	77.6	274.1	33.9
487	2773	458	2228	543	110.6	400	51.8
185	1103	196	1018	288	58.8	205	25.7
367	2158	381	2043	584	118.1	429	53.6
669	3885	707	3742	1093	229.4	813	102.3
119	720	130	700	195	42.3	143	17.7
404	2310	390	1990	541	111	403	52.3
310	1788	307	1564	409	82.8	303	39.1
141	780	141	670	175	35.8	123	15.6
82	473	81	418	114	22.5	85	10.7
162	947	168.4	884	259	51.3	195.1	24.6
73.8	422	75.7	385	109.7	21.18	80.6	10.24
86.5	493	85	422	112.5	21.3	81.4	10.28
77.3	451	77.1	380	99.5	19.1	72.3	9.29
70.7	402	67.4	341	89.1	16	65.4	8.23
85.2	401	76.9	379	84.6	14.43	61.2	7.55
570	3020	482	2390	609	116	439	54.6
44.4	254	43.2	220.1	58.7	11.24	41.9	5.29
46.4	267.1	45.6	239.1	65.7	12.94	48.3	6.08
47	274	46.5	241.3	65.6	13.41	50.2	6.29
55.3	324	54.2	280.5	75.2	15.3	57.4	7.39
17.2	99.1	16.7	80.4	20.1	4.14	14.4	1.93
32.1	188.1	31.98	158.5	41.5	8.77	31.49	4.09
60.9	350	60.3	305	82.6	17	61.8	7.92
75.5	434	73	342	78.4	16.4	55.6	7.21
34.4	203	36	188	52.4	10.77	37.6	4.76
1061	6420	1146	6220	1850	378	1394	173.7
218.3	1278	229.2	1187	347	73.9	252	31.7
1130	6540	1120	5890	1650	336	1240	159
371	2160	374	1910	512	103.9	378	48
82	453	83	411	112	22.7	77	9.7
277	1630	284	1410	371	75	261	33.6
767	4500	801	4150	1179	237.1	880	111.4
1047	5990	1095	5440	1543	298.1	1136	146.4
1171	6640	1183	5670	1523	281.3	1131	143.2
964	5530	990	4870	1263	223	914	115.3
4160	21450	4120	20030	4950	869	3550	456
2400	13510	2600	11370	3050	538	2240	279
2092	11000	2061	9690	2499	447	1820	233.4
813	4520	789	3840	1039	194	760	97.1
717	4470	781	4130	1148	226	841	106.9
944	5490	921	4780	1331	263.8	1004	130.4
924	5370	912	4550	1192	247	899	116.6
291	1696	286	1366	340	71.6	250.9	33.3
308	1810	314	1610	440	93.9	324	42.2
362	2090	358	1780	451	92.8	327	41.8

332	1934	318	1507	353	71.6	247	31.8
338	2020	348	1790	494	102.1	357	45.1
1008	5830	1018	5450	1602	328.4	1200	149
462	2569	435	2266	654	130.1	476	61.3
578	3400	617	3280	980	203	720	91
755	4440	788	4090	1163	236.3	882	110.7
995	5930	1055	5720	1681	340.9	1246	157.8
262	1550	273	1360	370	75.4	264	34
478	2820	505	2520	701	137.7	498	61.9
1381	7940	1362	6980	1981	384	1478	187.7
779	4500	788	3840	1057	201.7	796	100.6
639	4000	712	3660	1019	189	758	95.3
2650	14480	2830	12520	3320	601	2490	310
3340	18430	3400	16600	4420	804	3136	395
1955	10870	1931	8900	2390	409	1743	216.5
1644	9030	1586	7680	1997	362.9	1427	178.5
2809	15980	2745	13660	3724	700	2799	350.9
1574	9010	1529	7890	2269	429	1698	214.2
1680	9500	1604	8230	2300	447	1732	223.4
349	1983	327	1616	429	86.3	320	41.5
525	2680	417	1892	416	86.2	278	36
176	1047	175	861	232	48	163	21
132.1	748	131.4	614	145.1	30.8	97.3	12.52
219	1310	232	1200	337	70.2	247	31
525	3140	559	3030	886	188	645	79.8
516	2860	484	2470	666	136.2	482	59.8
1040	6160	1100	5860	1740	357	1300	163
1096	6380	1140	6070	1810	373	1320	168
671	3960	700	3730	1132	227	841	104.7
157.2	939	163.1	831	228	46.9	165	20.6
558	3280	571	2990	849	169.2	621	77.2
658	3850	683	3560	1028	206.8	752	94.2
1056	6120	1042	5330	1433	269.5	1035	131.2
2200	1.28E+04	2390	11150	3090	560	2300	293
1102	6200	1183	5830	1472	270.7	1084	136
1667	8210	1627	8150	1949	351	1448	175.4
3106	15360	2993	13720	3340	582	2479	314.9
1550	8150	1469	7000	1771	321.3	1325	162
952	5460	991	4870	1383	257.8	1029	129.8
1706	9680	1723	8640	2466	476	1877	238.1
690	3980	667	3333	912	184.5	695	91.7
427	1830	294	1317	290	57.8	203	25.7
340	2010	352	1780	493	102	359	45.2
443	2580	454	2350	659	132.6	467	59
231	1360	235	1210	341	70.7	253	31.3
133	770	141	720	208	43.8	147	18.7
695	4150	726	3840	1107	227	809	99
546	3200	559	2930	839	168	608	75.2
832	4900	834	4350	1250	247	902	112.2
402.4	2352	403.9	2089	566	116.9	422	52.5
96.4	560	99.9	516	145	30.5	104.1	13.3
355	2120	369	1910	530	108.6	383	47.4

529	3171	551	2910	825	169.3	601	74.1
538	3188	557	3009	899	181.7	683	84.4
538	3180	543	2880	843	167	633	79.1
1074	6160	1072	5560	1570	308	1181	151
484	2730	457	2290	619	120	457	58
1000	5600	983	4900	1399	269	1052	134.2
802	4650	772	4150	1168	232	855	109.7
532	3120	535	2770	795	161.5	595	76.4
601	3260	525	2620	704	139	517	66.4
330	1940	328	1660	442	92	307	37.4
350	2050	356	1810	504	102.5	370	46.3
599	3520	607	3080	845	175	623	78.4
595	3490	597	2970	778	158.2	566	71.8
483	2800	473	2310	560	115.2	402	51.9
217	1260	212	1040	252	52.2	188	23.7

<i>Dy</i>	<i>Ho</i>	<i>Er</i>	<i>Tm</i>	<i>Yb</i>	<i>Lu</i>	<i>Hf</i>
78.9	14.38	38.5	5.25	32.9	4.48	200
122	20.3	51.2	6.46	36.5	3.78	15.2
53.3	9.1	23	2.85	16.6	1.8	7.81
163.5	27.6	70	8.71	50.3	5.36	18.13
196	32.4	80.4	9.8	54.4	5.93	15.01
94	15.65	38.2	4.62	26.2	2.78	8.61
416	68.6	167.1	20.39	112.1	12.12	33.8
206.5	33.9	84.2	10.44	56.3	6.07	18
235	38.3	95.7	11.62	64.8	6.86	17.51
417	69.3	173.5	21.65	120	13.1	30.6
110	18.4	47.1	5.8	33.9	3.97	103
49.7	9.22	25.4	3.43	21	2.43	8.31
81.1	13.19	32.8	4.14	22.5	2.46	10.61
159.5	26.8	66.1	8.3	47.4	5.21	35.2
78.5	13.1	32.2	3.86	21.8	2.3	9.98
117	19.1	45.9	5.57	31.6	3.33	11.06
58.4	9.75	24.2	3.1	17.2	1.85	7.7
163	27.1	67.9	8.56	47.3	5.02	13.7
189.7	32	79.9	10.3	56.9	6.2	16.12
516	83.5	209.7	25.48	139.6	14.95	34.9
392.1	63.6	151.1	18.41	101.9	10.79	23.56
76.3	12.51	31.6	3.91	22.04	2.391	7.72
277	44.9	109.7	12.95	71.2	7.33	23.6
397	65.6	158.2	18.71	102.7	10.82	35.3
409	67.8	164	19.2	105.6	11.03	41.6
317	53.2	130.6	16.09	90	10.05	26.6
289.1	49	122.9	15.05	88.4	9.58	24.27
167.8	27.9	68.4	8.76	49.2	5.47	16.06
121.3	21.6	55.8	7.26	40.3	4.54	16.02
155.1	28.5	75.6	10.21	59.9	6.56	19.56
209.6	36.18	92.3	11.77	66.9	7.35	17.45
20.76	3.82	10.52	1.456	8.99	1.015	3.11
83.2	14.31	36	4.49	25.4	2.75	10.49
36.3	6.14	15.21	1.958	11.01	1.21	6.55
200	33.8	82.2	10	57.2	6.18	20.2
209	34.8	87	10.46	59.9	6.49	20.6
51.2	8.14	19.85	2.51	13.64	1.486	6.93
198	32.9	80.4	9.89	55	5.68	16.7
100.8	17.32	44.2	5.59	31.3	3.24	11.65
426	68.5	167.4	20	113	11.72	31
248	40.8	98.6	12.01	67.1	7.16	18.74
412	68.5	163.4	19.7	109.2	11.46	24.8
397.1	64.8	156.7	19.08	104.3	10.95	27.6
217	36	87.9	10.28	56.4	5.93	17
250	42.6	105	13.09	72.8	7.56	18.92
286	46.9	113.7	13.4	75.7	7.77	26.2
122.2	20.2	49.3	6.08	33	3.59	19.5
139	22.4	53.6	6.4	34.7	3.66	14.1

427	71.1	169.1	20.45	112.1	11.75	32.7
216.9	35.24	85.3	10.37	55.6	5.8	15.73
447	73.8	182.7	21.65	120.1	12.85	35.9
266	45.2	115	14.43	82.4	9.63	303
175	30.42	79.7	9.97	57.9	6.29	17.37
69.3	12.2	32	4.11	24.5	2.73	11.39
179.4	29.55	73.5	9.26	52.9	5.81	13.89
284.3	51.7	141.1	19.17	112.2	12.71	30.5
131	22	54.1	6.8	38.5	3.98	13.68
278	45.7	112.9	14.22	78.2	8.65	20.71
521	85.8	206.3	25.48	142.7	14.93	35.1
91	14.8	35.8	4.46	24.7	2.49	8.1
274	46.8	116	14.5	81.8	8.6	20.3
212	35.7	90.3	11.46	64.3	6.83	19.19
81	13.1	33.2	3.96	22.5	2.29	9.6
55.8	9.3	22.3	2.75	15.3	1.62	4.25
126.1	20.7	50.5	6	32.9	3.51	7.38
52.4	8.62	20.62	2.5	13.96	1.468	3.4
53.6	8.79	21.5	2.55	14.33	1.461	4.23
47.8	7.77	19.1	2.33	12.57	1.322	4.05
43.4	7.12	17	2.03	11.08	1.164	3.82
38.6	6.25	14.78	1.769	9.42	0.936	3.42
278	45.3	110.9	13.1	72.8	7.73	21.4
28.22	4.53	10.92	1.362	7.31	0.748	2.437
32.01	5.22	12.59	1.457	8.47	0.877	2.407
33.07	5.47	13.25	1.659	9.09	0.958	2.24
39.1	6.89	16.65	2.121	12.06	1.287	3.018
10.55	1.88	4.85	0.611	3.53	0.394	1.68
22.99	4.01	10.57	1.372	8.17	0.889	2.41
42.4	7.5	19.3	2.51	15	1.64	4.12
41	7.43	19.9	2.73	16.54	1.8	6.42
24.7	4.1	10.24	1.263	7.07	0.74	2.16
885	143.1	349	43.2	236	24.9	55.1
161.7	26.22	63.9	7.92	42.7	4.51	17.86
838	142	352	43.8	251	26.2	62.5
254	42.8	107.4	13.03	72.8	7.81	25.2
50	8.2	20.9	2.54	14.4	1.51	11.11
174	27.9	70.9	8.8	47.7	5.05	21.3
578	93.4	224.8	27.2	150.8	15.41	37.3
753	124.4	301	36.3	199.2	20.67	47
747	122	295.4	35.28	198.2	20.54	51.1
602	98.1	235.3	28.6	154.9	16.32	44.5
2311	370.8	858	99.8	531	53.9	148.3
1413	228	546	62.8	339	34.4	97.7
1233	196.3	471	55.7	303.3	32.6	82.4
489	82.8	197	23.3	137.3	13.98	38
551	90.1	218	26.4	145	14.9	41.3
673	111.8	280.6	34.7	187.8	20.5	51.2
635	110.3	278	35.2	208	21.6	59.3
184.9	31.8	84.3	10.85	63.5	6.97	22.36
227	38.1	98	12.3	71.7	8.04	24.5
228	40.5	109	14.2	85.7	9.47	25.5

179.4	32.1	87.7	11.91	74.6	8.46	24.16
238	39	98.7	12.54	70.9	7.53	24.5
762	128.1	310.6	39	217.3	23.28	48.4
314	52.5	129.4	15.53	89.1	9.43	22.1
466	76	181	22.2	124	13	33.3
580	96.3	239	29.4	166	18.1	40.2
801	131.8	320.1	39	217.6	23.36	52
178	29.9	72.9	9.07	50.7	5.44	19.62
320	52.8	129.7	15.49	88	9.11	33.3
973	159.9	383	45.5	252.5	26.52	65.5
526	86.6	212.3	25.7	137.9	14.5	34.6
497	82.4	194	23.4	125.9	13.24	37.1
1566	254	592	71.4	372	38.7	95.6
1983	308.9	712	80.2	424	42.2	118.5
1127	184.6	440	52.3	280.5	29.3	85.3
927	151.3	359	42.5	237	24.45	67
1828	295.9	713	86.2	479	50.1	121.7
1109	181.1	441	52.3	294.3	30.5	69.7
1205	203.4	513	62.3	360	38.9	82.5
230	39.9	104	13.14	74.6	8.3	22.4
194	34.4	92.5	12.1	71.8	8.08	23.2
110.6	18.8	48.9	6.31	36.8	4	12.99
70.1	12.35	33.5	4.4	26.8	2.91	12.49
161	26.7	65.1	8.12	45.7	4.86	15.9
414	67.7	162	19.6	109.3	11.36	29.1
296	49	117.7	14.58	81.6	8.45	23.2
850	143	340	41.5	231	23.7	58.3
861	142	348	42.1	230	24.4	59
547	88.9	217	26.2	143.8	15.35	31.5
105.4	17.23	41.9	5.21	28.5	3.01	11.27
400	65	160.4	19.72	107.3	11.19	30.9
483	79.6	190.6	23.5	129.3	13.58	34.8
683	114.9	276	33.6	186	19.2	51.3
1520	248	593	71.6	386	40.3	98.7
703	110.6	263.7	31	163	16.66	43.7
894	144.3	333.7	38.42	200.2	20.72	52.7
1637	267.3	647	77.4	418	43.7	110.7
834	136.9	333	39.4	217.4	23.06	58.5
677	109.9	263.5	32.1	172.3	18.37	41.2
1244	203.6	501	59.9	341.5	35.3	76.6
484	82.1	209.6	26.22	146	16.06	38.1
129.9	21.6	59.3	7.26	40.8	4.87	13.7
241	40.6	101	12.2	75.1	8.08	29.2
305	50.5	127.7	15.43	88.3	9.31	24.6
166	27.6	67.8	8.41	47.7	5.16	13.54
96	15.6	37.5	4.66	26.4	2.72	9.5
515	84.2	208	25.3	142	15.2	37.8
384	63.8	156	19.8	107	11.37	29.9
576	96.6	241	29.4	163.6	17.9	41.3
272	45.2	111.5	13.73	78.5	8.23	23.45
69.2	11.37	28.2	3.34	19	1.98	7.75
249	40.8	101	12.48	70.2	7.43	22

386	63.9	156	18.71	106.7	11.64	30.1
435.5	70.7	173	20.58	113.7	12.2	25.9
413	68	165	19.7	108.7	11.47	26.9
786	132	314	37.4	208	21.8	51.7
298	49.5	120	14.5	79.4	8.18	24.1
697	113.3	279	32.8	181	19	41.8
566	93.2	226	27.6	151	16.1	39
395	66.4	163.3	20.6	113	12.16	29.2
362	62.7	165	21.1	124.6	14.2	28.1
203	33.7	85	10.5	61	6.6	24.8
243	40.1	101.6	12.7	70.1	7.77	20.3
418	70.9	177.5	22.5	126	13.69	35.7
385	66.3	172.4	21.7	127.9	14.09	42.1
281	50.7	132	17.5	105.3	11.66	37.5
133	23.9	63.2	8.6	49.4	5.55	15.9

<i>Ta</i>	<i>Th</i>	<i>Eu/Eu*</i>	²³⁸ U/ ²⁰⁶ Pb	±1s	²⁰⁷ Pb/ ²⁰⁶ Pb	±1s	<i>f207%</i>
46.4	157		19.40	1.70	0.595	0.049	68.3
74.5	137	0.75	18.21	1.00	0.665	0.013	77.0
39.5	69.6	0.77	22.90	1.60	0.641	0.010	74.0
89.4	160.3	0.75	22.25	0.95	0.545	0.005	62.0
74.2	146.5	0.73	21.06	0.66	0.363	0.014	39.2
45.5	83.7	0.74	30.92	0.64	0.451	0.013	50.3
165.3	309.6	0.74	19.00	0.62	0.362	0.012	39.0
87.4	159.2	0.74	16.80	1.40	0.511	0.015	57.7
91	171.8	0.74	17.20	2.10	0.428	0.035	47.3
150.7	309.7	0.73	17.27	0.29	0.324	0.005	34.2
50.1	99		18.10	3.10	0.502	0.074	56.6
45.5	75.5	0.77	20.11	0.40	0.603	0.012	69.3
53	89.8	0.76	16.70	1.10	0.671	0.016	77.8
97.8	171.4	0.76	17.33	0.36	0.644	0.014	74.4
56.3	94.4	0.77	17.70	0.44	0.665	0.011	77.0
60	105.8	0.75	23.60	1.20	0.579	0.031	66.3
40	74.5	0.75	20.80	1.10	0.658	0.011	76.1
82.5	139	0.75	22.60	1.70	0.453	0.028	50.5
99.8	174.4	0.77	18.29	0.58	0.388	0.010	42.3
218.5	377.5	0.74	17.37	0.26	0.317	0.007	33.4
169	270.6	0.73	19.20	0.38	0.296	0.007	30.7
49	77.1	0.75	25.99	0.59	0.470	0.012	52.7
135.5	211.9	0.70	23.48	0.83	0.467	0.017	52.3
182.4	302.9	0.69	17.78	0.33	0.318	0.008	33.4
277	374	0.68	23.10	1.70	0.360	0.016	38.8
192.6	293	0.75	21.97	0.52	0.363	0.007	39.1
172.6	269.9	0.78	22.88	0.56	0.350	0.015	37.6
121.9	169.2	0.78	22.90	2.10	0.511	0.032	57.8
156.1	168.4	0.73	16.80	0.46	0.584	0.023	66.9
245	257	0.74	25.77	0.43	0.411	0.010	45.3
103.3	170.5	0.73	16.13	0.27	0.308	0.005	32.2
16.84	27.43	0.77	16.95	0.65	0.590	0.019	67.7
54.5	91	0.77	20.30	1.40	0.606	0.009	69.7
35.7	65.9	0.76	7.30	3.50	0.762	0.024	89.1
88.9	166.5	0.72	18.22	0.41	0.590	0.009	67.6
100.7	190	0.75	20.55	0.60	0.579	0.019	66.3
38.1	69.8	0.78	24.67	0.88	0.646	0.008	74.6
86.3	160	0.72	25.10	1.30	0.477	0.022	53.5
54.9	111.1	0.74	28.10	1.60	0.577	0.006	66.0
167	305	0.74	20.75	0.84	0.439	0.011	48.7
96.7	184.4	0.72	25.20	1.40	0.499	0.017	56.3
123.9	268	0.72	19.64	0.68	0.273	0.004	27.8
124.3	267.7	0.72	21.36	0.36	0.382	0.024	41.6
75.7	165	0.71	23.06	0.96	0.441	0.008	49.0
104.2	199.8	0.72	19.10	1.60	0.487	0.045	54.7
119.7	213	0.68	26.20	2.40	0.496	0.012	55.9
118.2	150.1	0.64	25.96	0.82	0.499	0.013	56.3
107	171	0.67	20.40	2.50	0.598	0.037	68.7

213.3	366	0.66	4.20	1.10	0.661	0.033	76.4
117.7	173	0.68	19.91	0.36	0.343	0.010	36.6
350.1	425.8	0.70	19.19	0.39	0.224	0.019	21.6
136.7	230.7		18.68	0.33	0.243	0.026	24.0
180.9	216.9	0.71	21.59	0.93	0.416	0.010	45.9
80.6	101.7	0.77	28.50	1.80	0.531	0.018	60.3
80.8	130.8	0.75	18.08	0.34	0.331	0.012	35.1
169.5	280.3	0.73	16.37	0.26	0.342	0.015	36.5
64.8	120	0.74	24.09	0.81	0.561	0.026	64.1
99.6	203.4	0.72	19.72	0.59	0.405	0.006	44.5
164	339.2	0.74	17.95	0.52	0.304	0.022	31.7
44.3	75	0.77	29.20	3.70	0.534	0.023	60.7
95.5	211	0.73	21.00	2.00	0.369	0.034	39.9
83.5	178.1	0.72	23.63	1.00	0.479	0.010	53.7
70.5	129	0.75	28.90	2.10	0.546	0.017	62.2
18.2	38.6	0.70	22.30	2.50	0.429	0.022	47.5
34.6	76.8	0.70	17.71	0.24	0.247	0.005	24.5
14.56	32.77	0.69	15.74	0.74	0.391	0.028	42.6
16.03	38.3	0.68	17.00	3.90	0.544	0.069	61.9
17.12	36.3	0.69	26.90	1.60	0.468	0.018	52.4
15.46	30.7	0.64	24.10	2.30	0.496	0.022	55.9
24.98	36.03	0.61	18.37	0.33	0.290	0.018	30.0
95.5	222	0.69	12.00	2.10	0.549	0.023	62.5
11.78	22.17	0.69	20.16	0.97	0.525	0.023	59.5
11.88	21.67	0.70	21.33	0.89	0.441	0.011	49.0
11.79	21.68	0.71	17.45	0.28	0.360	0.012	38.8
16.19	28.29	0.71	18.11	0.77	0.395	0.010	43.1
6.97	11.1	0.74	27.20	2.00	0.516	0.012	58.4
14.21	23.5	0.74	25.11	0.70	0.426	0.012	47.1
21.7	36.7	0.73	19.42	0.61	0.329	0.034	34.9
31.8	59	0.76	23.70	1.30	0.501	0.021	56.5
9.83	19.7	0.74	19.18	0.88	0.457	0.011	51.0
299.5	580	0.72	18.98	0.95	0.349	0.030	37.4
101.2	165.4	0.76	35.32	0.80	0.504	0.006	56.9
298	608	0.72	20.10	1.70	0.340	0.018	36.3
116.4	225	0.72	29.86	1.10	0.512	0.013	57.9
68	93.3	0.75	20.70	5.30	0.657	0.027	76.0
97.8	191	0.74	34.83	1.00	0.574	0.010	65.7
176.2	366	0.71	18.38	0.35	0.356	0.009	38.3
198.1	452	0.69	17.01	0.27	0.332	0.021	35.2
199.2	464.4	0.66	16.50	0.56	0.389	0.012	42.4
168.6	377.2	0.63	7.70	1.60	0.635	0.029	73.2
543	1303	0.63	17.42	0.30	0.360	0.025	38.8
383	900	0.63	16.40	0.64	0.332	0.013	35.2
355.2	806	0.64	17.20	0.33	0.284	0.011	29.2
181	366	0.67	24.30	1.50	0.393	0.006	43.0
223	344	0.70	23.30	3.00	0.562	0.011	64.2
243.3	460	0.70	20.53	0.52	0.358	0.008	38.5
319	534	0.73	18.10	1.40	0.515	0.026	58.3
119.5	202.5	0.75	27.00	2.20	0.538	0.006	61.2
125.4	197	0.76	23.30	2.10	0.446	0.032	49.6
138.5	232	0.74	21.20	1.40	0.382	0.029	41.6

134.8	218.5	0.74	18.92	0.74	0.465	0.022	52.0
116.3	222.3	0.74	28.18	0.90	0.513	0.012	58.1
231.7	511.5	0.72	16.87	0.26	0.263	0.008	26.5
113.6	229.2	0.71	16.90	1.70	0.552	0.057	62.9
194	341	0.74	20.20	2.00	0.362	0.033	39.1
197	396	0.71	17.47	0.57	0.351	0.011	37.6
272.3	532	0.72	17.81	0.25	0.304	0.011	31.7
94.8	184.7	0.74	28.30	3.30	0.564	0.009	64.5
148.8	286	0.71	26.70	1.60	0.570	0.007	65.2
264.5	621	0.69	21.40	1.20	0.392	0.005	42.9
135.9	327.4	0.67	19.99	0.54	0.342	0.005	36.5
162.3	305	0.66	22.95	1.00	0.516	0.008	58.4
346.5	855	0.64	16.96	0.44	0.342	0.006	36.5
461	1119	0.66	18.44	0.88	0.427	0.014	47.2
308.3	801	0.61	17.35	0.26	0.301	0.006	31.3
274.6	664	0.66	14.60	1.00	0.407	0.018	44.6
558	1220	0.66	17.26	0.29	0.287	0.007	29.5
326	665	0.67	17.25	0.24	0.258	0.004	25.9
408	811	0.68	19.35	0.67	0.271	0.018	27.6
117	212.5	0.71	26.12	0.95	0.444	0.011	49.4
129	263.5	0.78	21.20	1.40	0.612	0.042	70.4
73.3	119.5	0.75	26.90	1.30	0.529	0.023	60.1
68.3	107.3	0.79	27.62	0.76	0.575	0.006	65.9
79.8	151.9	0.74	29.28	1.00	0.527	0.024	59.8
159	290	0.76	24.90	1.20	0.423	0.010	46.7
122.5	244.7	0.74	23.00	3.30	0.556	0.039	63.4
296	581	0.73	19.40	2.00	0.349	0.021	37.4
306	637	0.74	22.40	1.90	0.344	0.017	36.8
160.7	338	0.71	17.60	0.42	0.243	0.016	24.0
55.4	109.9	0.74	18.10	4.90	0.667	0.035	77.3
147	285.3	0.71	22.99	0.71	0.440	0.007	48.9
166.1	335	0.72	21.80	1.10	0.405	0.013	44.5
204.3	455	0.68	18.45	0.43	0.404	0.010	44.3
376	912	0.64	18.31	0.98	0.295	0.004	30.6
169.3	380	0.66	19.13	0.54	0.363	0.024	39.2
189.3	477	0.64	17.76	0.28	0.332	0.006	35.2
393.7	1079	0.62	16.88	0.27	0.194	0.004	17.8
243.7	583	0.64	17.62	0.34	0.236	0.006	23.1
180.5	394.9	0.66	17.12	0.27	0.225	0.011	21.7
379.6	773	0.68	17.92	0.29	0.227	0.004	22.0
189.8	351.4	0.71	18.55	0.60	0.379	0.015	41.2
73	143.4	0.73	13.00	5.90	0.704	0.053	81.9
157.4	284	0.74	18.20	3.00	0.638	0.042	73.7
130.8	230.9	0.73	20.20	1.40	0.467	0.010	52.2
71.3	130.2	0.74	23.30	2.10	0.529	0.022	60.0
49.9	91	0.77	15.60	5.30	0.696	0.042	80.9
190	370	0.73	18.59	0.40	0.360	0.023	38.8
149.9	294	0.72	24.80	1.10	0.372	0.025	40.4
201	422	0.71	19.63	0.60	0.297	0.022	30.9
112.7	253.2	0.73	21.43	0.68	0.462	0.012	51.6
39	72.7	0.76	33.10	1.10	0.535	0.011	60.8
105.2	208	0.74	27.30	1.20	0.480	0.018	53.9

146.6	278.9	0.74	17.70	0.52	0.384	0.022	41.8
130	268.4	0.71	18.55	0.50	0.298	0.010	30.9
121.5	250	0.70	6.70	0.95	0.660	0.028	76.3
215	472	0.69	19.90	1.50	0.388	0.008	42.3
91.5	230	0.69	6.00	1.90	0.743	0.023	86.8
155.3	413	0.68	16.03	0.50	0.337	0.040	35.8
176.2	386	0.71	19.90	1.80	0.456	0.021	50.9
146	286	0.72	23.10	1.50	0.431	0.019	47.8
138.2	296	0.70	16.42	0.63	0.399	0.024	43.6
133	231	0.76	28.40	2.20	0.609	0.016	70.1
98.9	200	0.73	23.90	1.70	0.463	0.010	51.7
169.8	346	0.74	25.26	1.00	0.429	0.020	47.5
193	402	0.73	30.00	1.30	0.501	0.010	56.5
172.9	345	0.74	28.01	0.73	0.514	0.016	58.2
73	151	0.73	19.29	0.84	0.520	0.037	58.9

207 corrected age (Ma) Pb based on feldspar							comment
Feldspar							
	±1s	Pbc	error	x	y		
105	22	0.84896	0.00029	47465.207	56449.6953	zr in ablation	
81	7	0.84896	0.00029	47515.207	56449.6953	youngest grp	
73	6	0.84896	0.00029	47565.207	56449.6953		
109	5	0.84896	0.00029	47615.207	56449.6953		
183	8	0.84896	0.00029	47665.207	56449.6953		
103	4	0.84896	0.00029	47715.207	56449.6953		
204	8	0.84896	0.00029	47765.207	56449.6953		
160	15	0.84896	0.00029	47815.207	56449.6953	zr in ablation	
195	28	0.84896	0.00029	47865.207	56449.6953		
241	5	0.84896	0.00029	47915.207	56449.6953		
153	41	0.84896	0.00029	47965.207	56449.6953		
98	5	0.84896	0.00029	48015.207	56449.6953		
85	9	0.84896	0.00029	47115.207	56499.6953		youngest grp
94	7	0.84896	0.00029	47165.207	56499.6953		
83	5	0.84896	0.00029	47215.207	56499.6953		
91	11	0.84896	0.00029	47265.207	56499.6953		
74	6	0.84896	0.00029	47315.207	56499.6953		
140	14	0.84896	0.00029	47365.207	56499.6953		
200	8	0.84896	0.00029	47415.207	56499.6953		
243	5	0.84896	0.00029	47465.207	56499.6953		
229	5	0.84896	0.00029	47515.207	56499.6953		
116	5	0.84896	0.00029	47565.207	56499.6953		
130	7	0.84896	0.00029	47615.207	56499.6953	youngest grp	
237	5	0.84896	0.00029	47665.207	56499.6953		
168	13	0.84896	0.00029	47715.207	56499.6953		
176	5	0.84896	0.00029	47765.207	56499.6953		
173	7	0.84896	0.00029	47815.207	56499.6953		
118	15	0.84896	0.00029	47865.207	56499.6953		
126	11	0.84896	0.00029	47915.207	56499.6953		
135	4	0.84896	0.00029	47965.207	56499.6953		
265	5	0.84896	0.00029	48015.207	56499.6953		
122	10	0.84896	0.00029	48065.207	56499.6953		
96	7	0.84896	0.00029	46915.207	56549.6953	youngest grp	
95	52	0.84896	0.00029	46965.207	56549.6953		
113	5	0.84896	0.00029	47015.207	56549.6953		
105	8	0.84896	0.00029	47065.207	56549.6953		
66	4	0.84896	0.00029	47115.207	56549.6953		
118	9	0.84896	0.00029	47165.207	56549.6953		
78	5	0.84896	0.00029	47215.207	56549.6953		
157	8	0.84896	0.00029	47265.207	56549.6953		
111	8	0.84896	0.00029	47315.207	56549.6953		
233	8	0.84896	0.00029	47365.207	56549.6953		
174	9	0.84896	0.00029	47415.207	56549.6953		
141	6	0.84896	0.00029	47465.207	56549.6953		
151	22	0.84896	0.00029	47515.207	56549.6953		
108	10	0.84896	0.00029	47565.207	56549.6953		
108	5	0.84896	0.00029	47615.207	56549.6953		
98	19	0.84896	0.00029	47665.207	56549.6953		

353	109	0.84896	0.00029	47715.207	56549.6953	old imprecise
202	5	0.84896	0.00029	47765.207	56549.6953	
258	9	0.84896	0.00029	47815.207	56549.6953	
257	12	0.84896	0.00029	47865.207	56549.6953	zr in ablation
160	8	0.84896	0.00029	47915.207	56549.6953	
89	8	0.84896	0.00029	47965.207	56549.6953	
227	7	0.84896	0.00029	48015.207	56549.6953	
245	8	0.84896	0.00029	48065.207	56549.6953	
95	9	0.84896	0.00029	46965.207	56599.6953	
179	6	0.84896	0.00029	47015.207	56599.6953	
241	12	0.84896	0.00029	47065.207	56599.6953	
86	13	0.84896	0.00029	47115.207	56599.6953	
182	21	0.84896	0.00029	47165.207	56599.6953	
125	6	0.84896	0.00029	47215.207	56599.6953	
84	8	0.84896	0.00029	47265.207	56599.6953	
150	18	0.84896	0.00029	47315.207	56599.6953	
269	4	0.84896	0.00029	47365.207	56599.6953	
231	18	0.84896	0.00029	47415.207	56599.6953	
143	46	0.84896	0.00029	47465.207	56599.6953	
113	9	0.84896	0.00029	47515.207	56599.6953	
117	13	0.84896	0.00029	47565.207	56599.6953	
241	9	0.84896	0.00029	47615.207	56599.6953	
199	38	0.84896	0.00029	47665.207	56599.6953	
128	11	0.84896	0.00029	47715.207	56599.6953	
152	8	0.84896	0.00029	47765.207	56599.6953	
222	6	0.84896	0.00029	47815.207	56599.6953	
199	9	0.84896	0.00029	47865.207	56599.6953	
98	8	0.84896	0.00029	47915.207	56599.6953	
134	5	0.84896	0.00029	47965.207	56599.6953	
213	15	0.84896	0.00029	48015.207	56599.6953	
117	9	0.84896	0.00029	48065.207	56599.6953	
163	9	0.84896	0.00029	47015.207	56649.6953	
209	16	0.84896	0.00029	47065.207	56649.6953	
78	2	0.84896	0.00029	47115.207	56649.6953	
201	18	0.84896	0.00029	47165.207	56649.6953	
90	5	0.84896	0.00029	47215.207	56649.6953	
74	22	0.84896	0.00029	47265.207	56649.6953	youngest grp
63	3	0.84896	0.00029	47315.207	56649.6953	
213	6	0.84896	0.00029	47365.207	56649.6953	
241	10	0.84896	0.00029	47415.207	56649.6953	
221	9	0.84896	0.00029	47465.207	56649.6953	
221	54	0.84896	0.00029	47515.207	56649.6953	
223	12	0.84896	0.00029	47565.207	56649.6953	
250	11	0.84896	0.00029	47615.207	56649.6953	
260	7	0.84896	0.00029	47665.207	56649.6953	
150	9	0.84896	0.00029	47715.207	56649.6953	
98	13	0.84896	0.00029	47765.207	56649.6953	
190	6	0.84896	0.00029	47815.207	56649.6953	
147	16	0.84896	0.00029	47865.207	56649.6953	
92	8	0.84896	0.00029	47915.207	56649.6953	
138	16	0.84896	0.00029	47965.207	56649.6953	
175	16	0.84896	0.00029	48015.207	56649.6953	

162	11	0.84896	0.00029	48065.207	56649.6953
95	5	0.84896	0.00029	46965.207	56699.6953
275	6	0.84896	0.00029	47015.207	56699.6953
140	30	0.84896	0.00029	47065.207	56699.6953
192	23	0.84896	0.00029	47115.207	56699.6953
226	9	0.84896	0.00029	47165.207	56699.6953
243	6	0.84896	0.00029	47215.207	56699.6953
80	10	0.84896	0.00029	47265.207	56699.6953
83	5	0.84896	0.00029	47315.207	56699.6953
170	10	0.84896	0.00029	47365.207	56699.6953
202	6	0.84896	0.00029	47415.207	56699.6953
116	6	0.84896	0.00029	47465.207	56699.6953
237	7	0.84896	0.00029	47515.207	56699.6953
182	10	0.84896	0.00029	47565.207	56699.6953
250	5	0.84896	0.00029	47615.207	56699.6953
240	19	0.84896	0.00029	47665.207	56699.6953
258	5	0.84896	0.00029	47715.207	56699.6953
271	4	0.84896	0.00029	47765.207	56699.6953
237	11	0.84896	0.00029	47815.207	56699.6953
124	6	0.84896	0.00029	47865.207	56699.6953
89	17	0.84896	0.00029	47915.207	56699.6953
95	8	0.84896	0.00029	47965.207	56699.6953
79	3	0.84896	0.00029	48015.207	56699.6953
88	7	0.84896	0.00029	46965.207	56749.6953
137	7	0.84896	0.00029	47015.207	56749.6953
102	20	0.84896	0.00029	47065.207	56749.6953
205	23	0.84896	0.00029	47115.207	56749.6953
179	16	0.84896	0.00029	47165.207	56749.6953
273	10	0.84896	0.00029	47215.207	56749.6953
80	27	0.84896	0.00029	47265.207	56749.6953
142	5	0.84896	0.00029	47315.207	56749.6953
162	9	0.84896	0.00029	47365.207	56749.6953
192	6	0.84896	0.00029	47415.207	56749.6953
240	13	0.84896	0.00029	47465.207	56749.6953
202	11	0.84896	0.00029	47515.207	56749.6953
231	4	0.84896	0.00029	47565.207	56749.6953
307	5	0.84896	0.00029	47615.207	56749.6953
275	6	0.84896	0.00029	47665.207	56749.6953
288	7	0.84896	0.00029	47715.207	56749.6953
275	5	0.84896	0.00029	47765.207	56749.6953
201	9	0.84896	0.00029	47815.207	56749.6953
89	52	0.84896	0.00029	47865.207	56749.6953
93	24	0.84896	0.00029	47915.207	56749.6953
151	11	0.84896	0.00029	46965.207	56799.6953
110	12	0.84896	0.00029	47015.207	56799.6953
78	34	0.84896	0.00029	47065.207	56799.6953
209	11	0.84896	0.00029	47115.207	56799.6953
153	10	0.84896	0.00029	47165.207	56799.6953
223	11	0.84896	0.00029	47215.207	56799.6953
144	6	0.84896	0.00029	47265.207	56799.6953
76	4	0.84896	0.00029	47315.207	56799.6953
108	7	0.84896	0.00029	47365.207	56799.6953

209	11	0.84896	0.00029	47415.207	56799.6953	
236	7	0.84896	0.00029	47465.207	56799.6953	
224	45	0.84896	0.00029	47515.207	56799.6953	
184	14	0.84896	0.00029	47565.207	56799.6953	
141	54	0.84896	0.00029	47615.207	56799.6953	
253	21	0.84896	0.00029	47665.207	56799.6953	
157	16	0.84896	0.00029	47715.207	56799.6953	
144	11	0.84896	0.00029	47765.207	56799.6953	
218	14	0.84896	0.00029	47815.207	56799.6953	
68	7	0.84896	0.00029	47015.207	56849.6953	youngest grp
129	10	0.84896	0.00029	47065.207	56849.6953	
133	8	0.84896	0.00029	47115.207	56849.6953	
93	5	0.84896	0.00029	47165.207	56849.6953	
96	5	0.84896	0.00029	47215.207	56849.6953	
136	16	0.84896	0.00029	47265.207	56849.6953	