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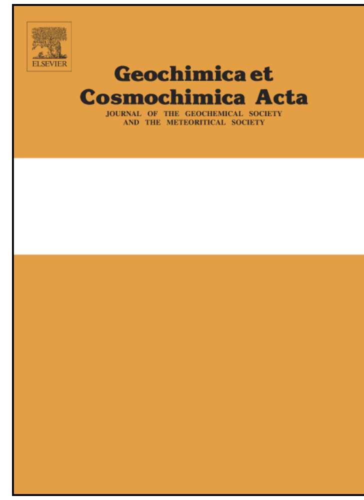

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Mechanisms of deformation-induced trace element migration in zircon resolved by atom probe and correlative microscopy

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Abstract

The widespread use of zircon in geochemical and geochronological studies of crustal rocks is underpinned by an understanding of the processes that may modify its composition. Deformation during tectonic and impact related strain is known to modify zircon trace element compositions, but the mechanisms by which this occurs remain unresolved. Here we combine electron backscatter diffraction, transmission Kikuchi diffraction and atom probe microscopy to investigate trace element migration associated with a ~20 nm wide, 2° low-angle subgrain boundary formed in zircon during a single, high-strain rate, deformation associated with a bolide impact. The low-angle boundary shows elevated concentrations of both substitutional (Y) and interstitial (Al, Mg & Be) ions. The observed compositional variations reflect a dynamic process associated with the recovery of shock-induced vacancies and dislocations into lower energy low-angle boundaries. Y segregation is linked to the migration and localization of oxygen vacancies, whilst the interstitial ions migrate in association with dislocations. These data represent the direct nanoscale observation of geologically-instantaneous, trace element migration associated with crystal plasticity of zircon and provide a framework for further understanding mass transfer processes in zircon.

1. Introduction

Zircon ($ZrSiO_4$) is a common accessory mineral that occurs in most crustal rocks. The low diffusivity of most trace elements through the zircon lattice, inferred from trace element zonation (Vavra, 1990; Hoskin, 2000) and diffusion experiments (Cherniak et al., 1997; Cherniak and Watson, 2003; Cherniak and Watson, 2007), make zircon a robust geochemical repository. Hence, the trace and rare earth elements (REE) incorporated into the zircon are commonly used to place valuable constraints on petrogenetic processes (Hoskin and Schaltegger, 2003). For example, the trace element geochemistry of zircon yields source rock type and crystallization conditions of igneous rocks (Belousova et al., 2002; Ferry and Watson, 2007; Hanchar and van Westrenen, 2007; Grimes et al., 2009; Claiborne et al., 2010) and can place constraints on recrystallization mechanisms, hydrothermal alteration and the histories of metamorphic rocks (Hoskin and Black, 2000; Hoskin, 2005; Harley et al., 2007; Marsh and Stockli, 2015). The trace element composition of zircon also has economic importance, for example being used to assess the prospectivity of granites for mineralisation (Ballard et al., 2002; Dilles et al., 2015).

The incorporation of trace amounts of uranium, and its subsequent radioactive decay to lead, enables the U-Pb dating of zircon to place temporal constraints of numerous crustal processes (Harley and Kelly, 2007; Corfu, 2013). When combined with Lu-Hf and oxygen isotopic data, zircon can be used to constrain crustal evolution over a range of timescales (Hawkesworth and Kemp, 2006; Parman, 2015; Payne et al., 2016). In addition, the ability of zircon to withstand weathering, erosion, sedimentary transport and diagenesis, make zircon a common target for sedimentary provenance analysis

(Fedo et al., 2003; Gehrels, 2014) and the geochemistry and geochronology of ancient detrital zircon grains is the principal means of understanding petrogenetic processes and environmental conditions in the earliest stages of Earth history (Maas et al., 1992; Wilde et al., 2001; Hoskin, 2005; Watson and Harrison, 2005; Harrison and Schmitt, 2007; Ushikubo et al., 2008; Harrison, 2009). Complementing the terrestrial studies of Hadean zircon are analyses from lunar and meteoritic zircon samples, that provide fundamental constraints on the early solar system and planetary evolution (Nemchin et al., 2010; Humayun et al., 2013; Iizuka et al., 2015). However, despite this broad application of zircon in geochemical and geochronological studies, it is widely recognised that a number of different processes may modify the trace element compositions of zircon.

Radiation damage within zircon can facilitate trace element redistribution and the incorporation of non-formula elements (Ewing et al., 2003; Palenik et al., 2003; Horie et al., 2006) even under low temperature hydrothermal conditions (Geisler et al., 2002; Pidgeon, 2014). Trace element modification associated with radiation damage reflects a complex interaction of the self-irradiation process, enhanced diffusion along radiation-induced defects, and reactions associated with fluid ingress by radiation-enhanced fractures and recrystallization (Geisler et al., 2007; Nasdala et al., 2010).

Detailed microstructural characterization has demonstrated that crystal plastic deformation of zircon may take place in Earth's crust due to tectonic processes (Reddy et al., 2007; Reddy et al., 2009; Piazolo et al., 2012) and meteorite impact events (Moser et al., 2011; Cavosie et al., 2015). Geochemical analyses of deformed zircon indicate that trace element compositions may be modified in the vicinity of intracrystalline defects, particularly in the regions of low-angle boundaries (Reddy et al., 2006; Timms et al., 2006; Moser et al., 2009; Nemchin et al., 2009; Moser et al., 2011; Timms et al., 2011; Piazolo et al., 2016). A number of models have been proposed to explain the observed relationship between microstructure and trace element migration including enhanced diffusion along dislocation pipes and low-angle boundaries (Reddy et al., 2006; Moser et al., 2011; Timms et al., 2011; Piazolo et al., 2016), incorporation of trace elements within migrating dislocations (Reddy et al., 2006; Reddy et al., 2007; Piazolo et al., 2016) and creep cavitation (Timms et al., 2012a). However, crystal defects may also trap trace elements; for example, Pb has been shown to segregate into dislocation loops during metamorphism (Peterman et al 2016).

Constraining the processes that are responsible for deformation-related compositional modification of zircon has remained elusive because the volume of material typically needed to characterize compositional heterogeneities (100s of μm^3) is considerably larger than the sub-micron scale microstructures in which these heterogeneities occur. Direct comparison with compositional data has required averaging of quantitative microstructural data over similar volumes to those measured by quantitative analytical techniques (Timms et al., 2006; Timms et al., 2011). Higher spatial resolution analytical methods, for example hyperspectral cathodoluminescence (CL) data, indicate variations in the concentrations of trivalent REEs at the micrometre scale, but these are not quantitative (Reddy et al., 2006; Timms and Reddy, 2009; Timms et al., 2011). As a result, the spatial relationships between deformation microstructures and compositional variations, as well as the processes responsible for trace element mobility in deformed or defect-enriched zircon, have proved difficult to resolve.

The recent applications of atom probe microscopy to zircon have highlighted the potential for this analytical technique to quantify nanoscale compositional variations and establish the controls and processes associated with trace element modification (Valley et al., 2014; Valley et al., 2015; Peterman et al., 2016; Piazolo et al., 2016). Here we combine electron backscatter diffraction (EBSD), transmission Kikuchi diffraction (TKD) and atom probe microscopy to investigate the nanoscale relationships between microstructure and trace element composition in a zircon grain that records a single shock deformation event associated with a meteorite impact.

2. Sample and Analytical Procedures

2.1 Sample Description

The Stac Fada Member of the Stoer Group of sedimentary rocks in NW Scotland represents an ejecta deposit associated with a meteorite impact ~1.18 billion years ago (Amor et al., 2008; Parnell et al., 2011; Reddy et al., 2015). The unit extends some 50 km along strike and has a variable thickness that in places exceeds 20 m (Fig. 1). It comprises three main facies types attributed to deposition from a single decelerating granular density current (Branney and Brown, 2011). The analysed sample (14-SF-01) was collected from the basal layer of the Stac Fada Member (UK Grid Reference NC 03348 28515 equivalent to Latitude 58.2014, Longitude -5.3482 in WGS84) (Fig. 1) and is a matrix-supported, poorly-sorted breccia comprising centimetre size clasts of lithic and devitrified melt fragments. The sample shows no evidence of deformation or metamorphism at the hand specimen scale. This is consistent with previous reports that the Stac Fada Member underwent diagenesis immediately after deposition (Parnell et al., 2011) and has only undergone low-grade (prehnite-pumpellyite facies) regional metamorphism and negligible post-impact deformation (Simms, 2015).

2.2 Methodologies

Details of the zircon separation, concentration and mounting methodologies have been described in detail elsewhere (Reddy et al., 2015) and only a brief summary is provided here.

Approximately 2 kg of sample 14-SF-01 was disaggregated using SelFrag high-voltage pulse power fragmentation at the Department of Applied Geology, Curtin University. Short pulses of high-voltage electrical fields were applied with a frequency of 2 Hz over a decreasing range of voltages and electrode gaps. As the sample was progressively disaggregated, grains and fragments smaller than 410 µm fell through an integrated mesh and into a collection vessel, which is isolated from further electrical pulses. Previous studies indicate that SelFrag does not lead to significant increases in the temperature or pressure of the separated phases and has no noticeable effect on zircon grains (Giese et al., 2010).

The disaggregated sample was sieved using a 355 µm disposable mesh and sodium polytungstate (NaPT) solution (specific gravity =2.85) was used to concentrate zircon grains in the <355 µm fraction. A hand magnet was used to remove the magnetic fraction and the remaining grains were passed through a Franz magnetic separator with the magnetic fractions being drawn off in increments of 0.2 to 0.5 amps over a range of current settings from 0.1 to 1.7A. The non-magnetic (>1.7A) fraction was then hand-picked for zircon. Approximately 200 separated zircon grains were investigated (Reddy et al., 2015) but data from only one of these (grain 86) are reported here.

EBSD and CL imaging of grain 86 was conducted on a Tescan MIRA3 Field Emission SEM with Oxford Instruments AZtec EBSD system, housed in the Microscopy & Microanalysis Facility (John de Laeter Centre) at Curtin University. CL imaging was undertaken using a Tescan panchromatic CL detector with 185-850 nm spectral range at 10 kV accelerating voltage and a working distance of 16mm. EBSD data were acquired using the automatic mapping capability of Oxford Instruments AZtec 2.3 software. Match units used for indexing were derived from published crystallographic data for zircon (Hazen and Finger, 1979) and reidite (Farnan et al., 2003). For grain 86, a 200 nm grid was used to systematically collect ~530,000 electron backscatter patterns. The EBSD data were post-processed using Oxford Instruments Channel 5.12 software to remove 'wildspikes' and interpolate non-indexed points using a 6 or 7 nearest neighbor filter following standard procedures for zircon EBSD analysis (Reddy et al., 2007). The post-processed data files were then used to generate EBSD maps.

Atom probe microscopy is a technique that allows the sub-nanometre scale, 3D imaging of atoms across the whole periodic table (Kelly and Larson, 2012; Larson et al., 2013b). The technique involves time-controlled field evaporation of atoms by applying a high-voltage electric field to a needle-shaped sample whose tip is then heated by a pulsing UV laser. Ideally, the instrument is set up such that a single atom is field evaporated every ~100 laser pulses. On evaporation, the atom is immediately ionized and accelerated by the field toward a position-sensitive detector. The x-y coordinates of the detector impact, combined with the order in which the ions hit the detector, allows reconstruction of the original position of the atoms in the sample (Gault et al., 2009; Larson et al., 2013a). The time-of-flight between the laser pulse and the detector impact is a function of the mass-to-charge ratio (m/z) of the emitted ion, and is used to identify the atom species emitted from the tip. The charge of the emitted ion does not represent the original charge of the species in the analysed sample, but is induced by the electric field immediately after evaporation (Kingham, 1982). This charge is therefore largely a function of experimental run conditions and sample morphology (Larson et al., 2013b).

The mass spectrometry data is reported in the form of a histogram (mass spectrum), in which the number of counts is plotted against intervals in m/z. Peaks in the mass spectrum that sit above the background noise level are identified and delineated manually, a process referred to as 'ranging'. The ions that form the ranged peaks are then used, with their x, y and z positions, to reconstruct the chemical identities and original 3D locations of the analysed atoms. Typical data sets comprise millions to tens of millions of atoms.

In contrast to most zircon analytical approaches, atom probe microscopy does not use a standard in the same manner as in ion- and electron-probe techniques. The APM technique does not lend itself to correction using standards as the analysis conditions cannot be reliably replicated between the standard and the specimen of interest. In general, the voltage applied to the specimen, the heating from the laser pulse and the shape of the specimen tip cannot be held constant between two acquisitions, and it is not clear that a discrepancy in the result from the standard analysis can be carried over and applied directly to the data of interest. However, past experience with other materials, and more recent APM studies of zircon (Valley et al., 2014; Valley et al., 2015; Peterman et al., 2016; Piazolo et al., 2016) provide a basis for confidence in the measured concentrations of trace elements reported here.

Atom probe specimens were prepared by focussed ion beam milling at CAMECA Instruments Inc., Madison, Wisconsin, USA. A region of interest, identified from the EBSD data, was targeted for site-specific atom probe sample preparation. A FEI Helios Nanolab 660 dual beam FIB-SEM was used to fabricate atom probe specimens on a microtip coupon (Thompson et al., 2007b). Tip sharpening was undertaken using several annular milling steps, each with progressively smaller inner radii and reduced beam currents. A final cleaning at 5kV was undertaken to remove most of the ion-milling induced gallium and surface contamination.

During the sharpening process, TKD analysis of the atom probe needles was carried out on a FEI Nova NanoLab 600 dual beam FIB-SEM equipped with an EBSD system from EDAX. TKD is capable of providing high spatial resolution orientation mapping for atom probe specimens (Babinsky et al., 2014) and was conducted with a 20 kV electron beam with a step size of ~10 nm. TKD data acquired using the EDAX system were exported as .ang files and post-processed using Oxford Instruments Channel 5.12 software.

Atom probe results were acquired using the CAMECA LEAP 5000 XR in laser pulsing mode with initial and final voltages of 3.2 kV and 4.6 kV respectively. Data acquisition utilised a 355 nm laser with pulse energy of ~250 pJ, focussed to a spot-size less than 0.5 μm at the specimen apex, and operating at a frequency ~180 kHz. The specimens were kept at a temperature of 30 K to inhibit thermally induced ion migration on the tip surface during field ionisation, and the ion detection rate was set to 0.01 ions per pulse (Larson et al., 2013b).

Atom probe data were acquired using LAS Root version 15.41.351, reconstructed with CAMECAROOT version 15.43.393e, and analysed with version 3.6.10 of Cameca's Interactive Visualisation and Analysis Software (IVAS). m/z values from 0-300 Da were recorded, and the background throughout the experiment was around 20 ppm/nsec, as reported by CAMECAROOT. The mass resolving power for the time-of-flight spectrum (M/ΔM) was measured at ~1150 for the $^{16}O_2^+$ peak. For peak ranging, mass peaks were compared to the local background and only those regions above twice the background level were ranged. The reconstruction stage used an initial tip radius of 25nm, and a constant shank angle of 5°. Features observed by SE imaging and TKD were adopted to validate the parameters used in 3D reconstruction.

Trace element chemical analysis was performed using a combination of iso-concentration surfaces (iso-surfaces) and proximity histograms (proxigrams). An iso-surface is a 2-dimensional contour of constant chemical concentration, with regions above a threshold level of concentration on one side of the boundary and lower concentrations on the other. Proxigrams are 1-dimensional concentration profiles that are plotted against the perpendicular distance from a particular iso-surface. Iso-surfaces are generally curved, and the proxigram analysis conducted by IVAS uses a sophisticated algorithm to calculate distances from the reference surface (Hellman et al., 2000).

3. Results

Cathodoluminescence imaging of grain 86 shows a complicated microstructure comprising a dark CL-poor core surrounded by intermediate region and a bright CL rim (Fig. 2a). A band contrast map of the zircon grain, which reflects the quality of EBSD patterns in different parts of the grain, shows additional complexity in the dark CL core. A series of ~2 μm wide, parallel lamellae, seen in both CL and band contrast maps, cut across the brighter CL zones, but do not penetrate into the dark CL core. These bands are shown by the EBSD data to be reidite, the high-pressure $ZrSiO_4$ polymorph (Fig. 2c). This reidite, the focus of a previous study (Reddy et al., 2015), along with the host zircon, record variations in lattice orientation expressed by the presence of discrete low-angle orientation boundaries that each accommodate 0.5–2° of misorientation and together accommodate a total of ~16° lattice variation across the whole grain (Fig. 2c). The distribution of low-angle boundaries in the zircon is complicated but broadly follows the spatial distribution of the reidite (Fig. 2c,d). One of these low-angle boundaries is captured in the atom probe specimen (Fig. 3). This boundary coincides with a ~2° change in orientation recorded by the TKD data (blue-green contact in Fig. 3). In addition, the TKD data indicate that the atom probe specimen comprises only zircon, with no evidence for reidite along the identified orientation boundary (Fig. 3).

Atom probe analysis of the zircon specimen shows a complex mass spectrum, which reflects the evaporation of single ions and molecular species at the +1 to +4 charge states (Fig. 4). Most peaks represent the major elements found in zircon with only a few trace element peaks being detected. The chemical sensitivity of the atom probe is often around 10 ppma, but the exact detection limit depends on the location and number of the expected peaks. Many of the REEs are likely to appear in the mass spectrum as doubly or triply charged ions, as well as possibly doubly and triply charged oxides. This means that REE peaks may be divided between a large number of mass peaks within the spectrum, significantly diluting the signal strength at any specific m/z value. Minimizing this dilution effect, by optimizing atom probe acquisition parameters for specific trace elements, is an area of future research.

Reconstruction of the data reveals a ~20 nm wide zone of trace element enrichment associated with the orientation boundary (Fig. 5). The zone shows increased concentrations in Y (0.735 at.%), Al (0.543 at.%), Be (0.055 at.%) and Mg (0.029 at.%) associated with a decrease in Zr (Table 1). These trace element concentrations represent significant increases from those measured in the host zircon (Fig. 5). Proximity histograms for the upper and lower boundaries of the enriched zone show that trace element concentrations are not constant across the low-angle boundary, with Y showing narrow maxima ~3 nm just inside both of the two boundary interfaces, and Al, Be and Mg exhibiting broader maxima around 4–5 nm inside the interfaces (Fig. 6). The concentration of Mg also shows a slight maximum outside the lower interface; a feature that is missing from the upper interface (Fig 5, 6).

Rare earth element, actinide and Pb distributions within the sample are below the detection sensitivity (50-100 appm, 50 appm, and 50 appm respectively) - as determined by the background noise local to these positions within the mass spectrum (Figure 4). Similarly, there is no observable phosphorus peak (~100 appm detection sensitivity) in the atom probe mass spectrum. This absence of P limits the extent of xenotime (YPO_4) substitution in the zircon lattice. The detection limits are relatively high due to the tails on the mass peaks between 14 and ~100 Da. These elevate the local background noise by up to 10 times its intrinsic value, and make the detection of trace elements in this part of the spectrum more difficult. Several factors may influence the shape of the mass peaks and their tails (Larson et al., 2013b), but the most likely cause in this case is poor thermal conductivity in the atom probe specimen, leading to an extended period of ion evaporation while the tip is cooling after the laser pulse.

4. Discussion

4.1 Zircon Microstructure

Cathodoluminescence data from a zircon grain from the Stac Fada impactite shows the presence of three CL-distinct zones (Fig. 2a); a dark CL core, a bright CL rim and an intermediate zone between them. Such CL variations in zircon are normally attributed to compositional zoning of trace elements associated with growth (Corfu et al., 2003). In this case, the zones identified in CL are interpreted to represent a complex igneous and metamorphic evolution prior to the reidite-forming impact event. Based on provenance analysis of the Stac Fada zircon population (Rainbird et al., 2001), this evolution is interpreted to reflect the complex tectonic and metamorphic history of the Lewisian target rocks.

Reidite is the high pressure polymorph of $ZrSiO_4$ (Glass et al., 2002) and its presence in the rims of grain 86 demonstrates that the zircon underwent shock deformation of >30 GPa associated with an impact event at ~1.18 Ga (Reddy et al., 2015). Reidite in the grain is limited to the outermost two compositional zones and stops abruptly at the CL dark core. The low CL emission from the core is consistent with radiation-damage associated with the presence of U and Th. Hence, the absence of reidite from the core of the zircon indicates that the formation of reidite is intimately linked to the crystallinity of the host zircon and that partial metamictization is likely to inhibit the development of reidite in shock environments. This is consistent with previous observations (Wittmann et al., 2006). Furthermore, the observation that low-angle boundaries are preferentially located within the areas of reidite development may indicate that radiation damage of zircon inhibits the formation and/or migration of dislocations.

A bolide impact event would produce an immense number of defects (vacancies and dislocations) within the shocked grain. However, the microstructure of both zircon and reidite is characterized by the presence of discrete low–angle boundaries that each accommodate <2° lattice distortion (Fig. 2c,d). The presence of low-angle boundaries in deformed zircon has previously been interpreted to represent the migration of dislocations into lower energy configurations. Such an interpretation is based on the geometry of the boundary with respect to the crystal lattice (Reddy et al., 2007). The low-angle boundary captured within the atom probe sample, and imaged by TKD analysis, shows no evidence of reidite and accommodates ~2° of misorientation. However, analysis of orientation differences and the low-angle boundary geometry (not presented) are not associated with any previously reported rational zircon slip system (summarized by Timms et al., 2012b). Previous estimates of the dislocation density of 10^{14} m^{-2} in 2° low-angle boundaries associated with tectonic-induced <001>{100} slip (Reddy et al., 2007) are similar to those derived from studies of unrecovered, reidite-bearing, experimentally shock-deformed zircon (Leroux et al., 1999). Thus, we interpret the low-angle boundary in the atom probe specimen to have formed by the migration and complex interaction of a large number of multiple defect types (vacancies and dislocations) that formed almost instantaneously by shock-deformation of zircon.

The recovery of minerals by the migration of defects into boundaries may take place in thermal or deformation events that significantly postdate the deformation event that caused them. However, the absence of any significant thermal or deformation events following the deposition of the Stac Fada Member precludes this. The observation that the formation of the low-angle boundaries post-dates the formation of reidite (Reddy et al., 2015), places further temporal constraints on recovery, and indicates that the observed recovery must be related to the latter stages of the impact process. This is consistent with predictions of the evolution of impact-related zircon microstructure based on shock deformation mechanism maps for $ZrSiO_4$ (Timms et al., 2012b). Thus, low-angle boundaries within the zircon are interpreted to reflect immediate post-impact recovery of defects formed during bolide impact.

4.2. Trace Element Compositions in the Zircon Host

In undeformed zircon the substitution of trivalent REEs and Y^{3+} for Zr^{4+} requires additional trace element substitutions to maintain charge balance and several different mechanisms have been postulated (Cherniak, 2010). In this study, P is below background noise levels, the ratio of Y to P is therefore high, and there is a spatial correlation between Y and the interstitial elements Al, Mg and Be both in the host zircon and the low-angle boundary. These three interstitial elements are not commonly analysed in zircon. However, when such analyses are undertaken then these elements have been reported to be incorporated into zircon at trace levels during growth (Speer, 1980; Hinton and Upton, 1991; Hoskin et al., 2000; Wiedenbeck et al., 2004). Charge compensation substitutions based on the ratio of (REE, Y) to P indicate that the important substitutions within the pre-shocked zircon were probably $(Mg, Be)^{2+}_{(int)} + 3Y^{3+} + P^{5+} = 3Zr^{4+} + Si$ and $Al^{3+}_{(int)} + 4Y^{3+} + P^{5+} = 4Zr^{4+} + Si$ (Hoskin et al., 2000). Since P in zircon tends to increase with magmatic differentiation, the high, pre-shock, Y/P ratio (>3) of the zircon points to derivation from a mafic source (Hoskin et al., 2000). The presence of hydrated mafic and ultramafic rocks in the impact target zone (Johnson et al., 2012) may explain the presence of spherules of basaltic composition within the Stac Fada Member, a feature that some find difficult to reconcile with a non-volcanic origin for the unit (Goodenough and Krabbendam, 2011).

4.3 Trace Element Variations and Microstructure

A model to explain the variations in Y, Al, Mg and Be within the atom probe specimen must account for the spatial coincidence of trace element enrichment and low-angle boundary formation (Figs. 3, 5), and the similar behaviour of both substitutional Y and interstitial Al, Mg and Be ions. The close spatial and temporal relationship between trace element segregation and the low-angle boundary indicates that the two features developed concurrently and are intimately linked. Such an interpretation is consistent with the general observation that increasing lattice misorientations, and therefore increasing dislocation density, are associated with increasing trace element segregation in metals and alloys (Watanabe, 1985).

The short-range segregation of solute atoms at interfaces is well established in the materials science literature and is recognized as a complex process that is controlled by a range of extrinsic (pressure, temperature) and intrinsic (elastic and electrostatic interactions between solute and host atoms) variables (Sutton and Balluffi, 2006). Although there is very little detailed analysis of such processes in minerals, it is clear that the segregation of trace elements into the low-angle boundary must be energetically favourable compared to maintaining the trace elements in the host zircon. However, the mechanisms responsible for segregation remain enigmatic and a number of factors may contribute to the driving force for trace element migration.

Principal amongst the drivers for substitutional ion migration is elastic strain energy associated with differences in ionic sizes between the trace element and host. Molecular dynamic and *ab-initio* modelling of point defect formation in zircon indicate that the production and migration of oxygen vacancies is likely to be energetically favourable over other defect sites (Meis and Gale, 1998; Crocombette and Ghaleb, 2001; Park et al., 2001) and the exchange of Y^{3+} on the Zr^{4+} site is likely to be intimately linked to oxygen vacancies for charge compensation (Akhtar and Waseem, 2001). The close relationship between oxygen vacancies and trace element migration may provide an explanation for the observed Y increase within the zircon low-angle boundary with initial segregation of Y due to elastic interactions being charge balanced by subsequent vacancy migration (Sun et al., 2015). However, although such a model explains the observed Y enrichment in the low-angle boundary, it fails to account for the heterogeneous distribution of Y close to the interfaces of the low-angle boundary (Fig. 6).

Hybrid Monte Carlo – molecular dynamic simulations of Y-stabilised zirconia (ZrO_2) predict the migration of oxygen vacancies into lattice orientation boundaries, due to lower vacancy energies at these microstructural locations, rather than being driven by elastic strain associated with ion size differences (Lee et al., 2013). In ZrO_2, it is energetically favourable for these oxygen vacancies to be associated with yttrium ions (Yoshiya and Oyama, 2011; Lee et al., 2013) and segregation reduces lattice strains in the boundary (Yoshiya and Oyama, 2011). Although such models cannot be quantitatively applied to $ZrSiO_4$, the qualitative distribution of Y^{3+} for Zr^{4+} associated with lattice orientation boundaries in ZrO_2 (Lee et al., 2013) are similar to the peaks of Y distribution recorded by the atom probe data for $ZrSiO_4$ in this study (Fig. 6). Based on the atom probe data presented here, this model seems to be a more likely mechanism than diffusion of Y driven solely by elastic strain.

In addition to substitutional Y ions, the low-angle boundary is also enriched in the interstitial trace elements Al, Mg and Be. The relationship between interstitial trace elements and dislocations is well known. Modelling of the elastic field around a dislocation predicts that interstitial atoms will concentrate around stationary dislocations (Cottrell and Bilby, 1949); a feature referred to as a "Cottrell atmosphere". Migrating dislocations may capture interstitial elements and continue to move. However, increasing concentrations of interstitial elements around an individual dislocation may halt its migration. Hence, the interstitial nature of Al, Mg and Be ions in the low-angle boundary is consistent with a two–stage process of interstitial migration into Cottrell atmospheres around shock–induced dislocations and the subsequent migration of both the dislocations and interstitial Cottrell atmospheres into low-angle boundaries during post-impact recovery. The additional complication of the asymmetric distribution of Mg immediately outside the lower interface of our sample may reflect asymmetric energy distributions outside the dislocation plane as modelled by kinetic Monte Carlo simulations of dislocation planes in silicon (Portavoce and Tréglia, 2014).

In contrast to non-geological materials where Cottrell atmospheres have been imaged (Blavette et al., 1999; Thompson et al., 2007a), there has been very little evidence for formation of Cottrell atmospheres in deforming minerals. Ando et al (2001) suggested a Cottrell atmosphere model for Fe–Mg variations associated with low-angle boundaries in olivine. A similar model has been inferred to explain Y mobility in tectonically deformed zircon (Piazolo et al., 2016). However, since Fe–Mg and Y–Zr exchange in these minerals is substitutional in nature, these observations cannot be explained by a Cottrell atmosphere model. A similar point has been made (Portavoce and Tréglia, 2014) regarding interpretations of Cottrell atmospheres from atom probe studies of semiconductors (Thompson et al., 2007a; Duguay et al., 2010). In contrast, the data presented here provides compelling evidence for formation of Cottrell atmospheres associated with interstitial trace elements in zircon.

4.4 A model for trace element mobility in shocked zircon

We interpret the enrichment of trace elements in the low-angle boundary to represent a combination of a) the migration of shock-induced oxygen vacancies into low-energy configurations at the low-angle boundary interface, coupled with segregation of Y into low energy sites, and b) interstitial migration of Al, Mg and Be as Cottrell atmospheres associated with dislocations that are migrating into low-angle boundary walls. The result is a charge compensated region of lattice distortion comprising both the enhanced substitutional and interstitial trace elements, as measured by the atom probe.

The nanoscale data presented here provide constraints on the processes by which trace element migration may occur in shock-deformed zircon. The data point to the important role of defect mobility, both vacancies and dislocations, in controlling the respective migration of both substitutional and interstitial ions. The high-strain rate nature of the impact, plus the extremely limited time for subsequent thermal modification of the zircon microstructure, indicate that the measured element migration is an extremely rapid and dynamic process, likely to be operating at the scale of seconds, linked to defect formation and mobility.

Similar relationships between microstructures and trace elements have been reported for tectonically-deformed zircon (Reddy et al., 2006; Timms et al., 2006; Timms and Reddy, 2009; Timms et al., 2011). These examples showed that defect mobility may also be the driver of the compositional modification of zircon during tectonic deformation. The observed relationships between low-angle boundary and trace element enrichment in zircon has often been considered to reflect fast diffusion of ions along the damaged core of a low-angle boundary (Reddy et al., 2006). However, such a long-range model does not explain variations in trace element compositions within the boundary zone and is not consistent with the short timescale available for the impact event. Although, fast diffusion along the low-angle boundary cannot be ruled out (Piazolo et al., 2016), the observations from the Stac Fada zircon are consistent with short-range mechanisms of low-angle boundary enrichment.

5. Conclusions

This research presents detailed quantitative microstructural analysis and compositional information at the nanoscale to yield unique insights into the relationships between deformation and the migration of chemical species in zircon during a single, high strain-rate, impact event. The data show that there is a clear spatial relationship between trace element compositions and low-angle boundaries formed by the recovery of defects in the later stages of the impact process. Migration of substitutional ions (Y) is associated with the migration of impact-induced oxygen vacancies to the lower energy sites associated with low-angle boundaries rather than elastic strain energies in the lattice. Interstitial ions (Al, Mg, Be) are inferred to migrate by the formation and migration of Cottrell atmospheres around impact-induced dislocations. The analysis of nanoscale compositional variations in zircon by atom probe microscopy provides a framework for understanding the processes controlling the migration and modification of trace element compositions in deforming zircon.

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Figure Captions

Figure 1. Geological map showing the location of the Stac Fada Member and the sample site. Grid coordinates refer to the Ordnance Survey National Grid coordinate system.

Figure 2. Microstructural maps of the analysed zircon grain. a & b are after Reddy et al., (2015). a) Panchromatic CL image showing dark CL core surrounded by an intermediate region and a bright CL rim. Planar black features in the CL emitting zircon are reidite lamellae. Less systematic black lines correspond to healed fractures shown in b. b) Band contrast (pattern quality) EBSD map. Brighter greyscale indicates higher pattern quality. c) EBSD texture component map of zircon (in red) overlain on the band contrast map shown in b. Lattice orientation variations are shown up to 8° from the white cross and total misorientation across the grain is 16°. Yellow lines show the locations of low-angle boundaries (0.6°-2.0°) within the zircon. Tourquoise lamellae represent reidite. The white square shows the location of map d. d) Close up of area in c. The white circle corresponds to the position of the analysed atom probe specimen.

Figure 3. a) Orientation map of the studied atom probe needle constructed from transmission Kikuchi diffraction data. The change from blue to green corresponds to a small-angle lattice misorientation accommodated by a 2° low-angle boundary. White box shows the area analysed by the atom probe following further focussed ion beam milling of the sample. Area below the green area, which has not indexed, reflects low pattern quality due to poor electron transmission through the thicker part of the specimen.

Figure 4. Atom probe mass spectrum obtained from the region of interest shown in Fig. 3. The major m/z peaks are identified, including trace elements that were only present at detectable levels within the boundary region.

Figure 5. Reconstruction of atom probe data showing trace element variations for Y, Al, Be and Mg. The coloured spheres represent the positions of the illustrated elements but are not drawn to scale. Grey points defining the shape of the atom probe data set represent the positions of 10% of measured Zr atoms. The band showing increased concentration of trace elements corresponds to the position of the low-angle boundary in the region of interest in Fig. 3.

Figure 6. Proximity histograms showing composition variation in Y, Al, Be and Mg as a function of distance from the upper and lower boundary interfaces. The upper and lower interfaces are defined by concentration contours at 0.2% Y.

Tables

Table 1. Compositional data from host zircon matrix and low-angle boundary region derived from the atom probe data.

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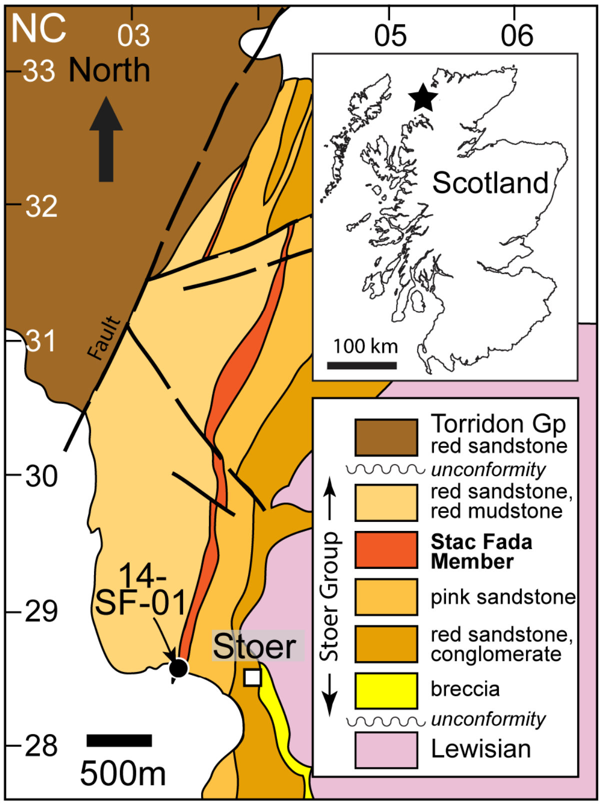
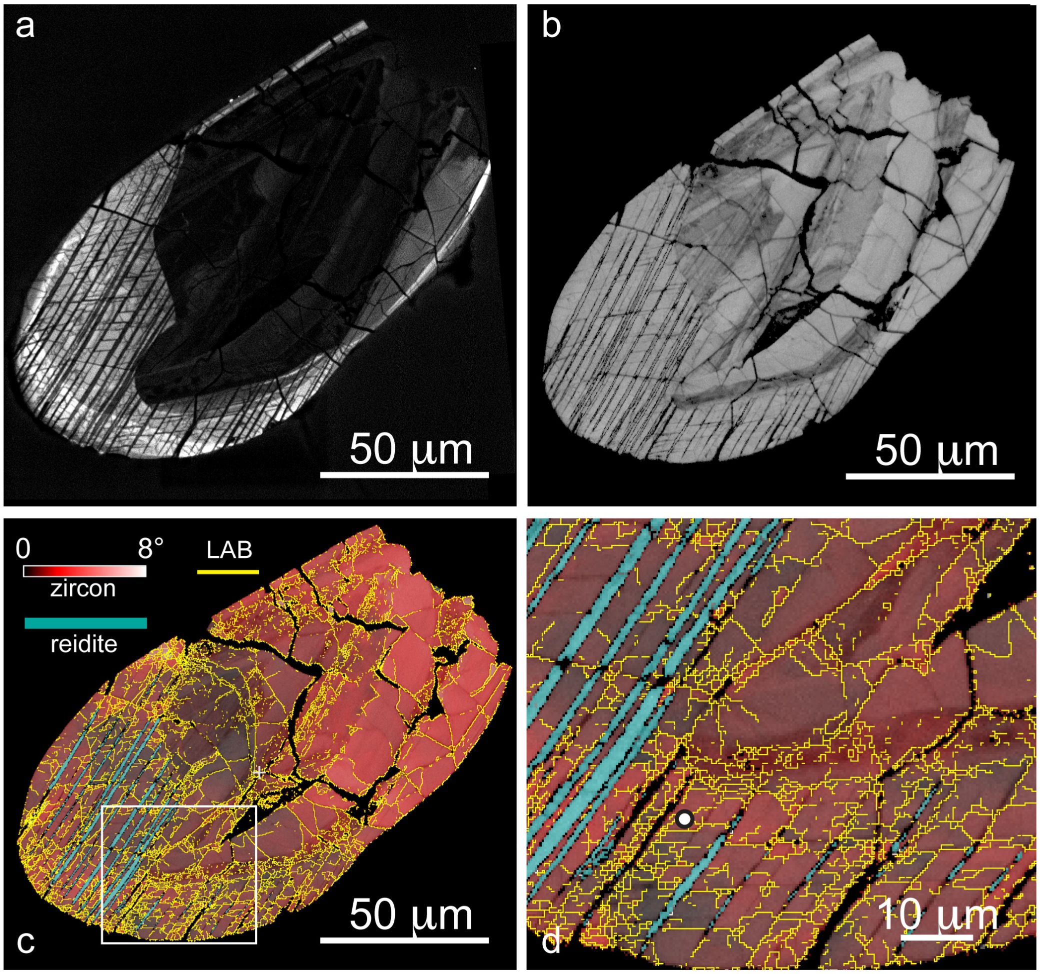
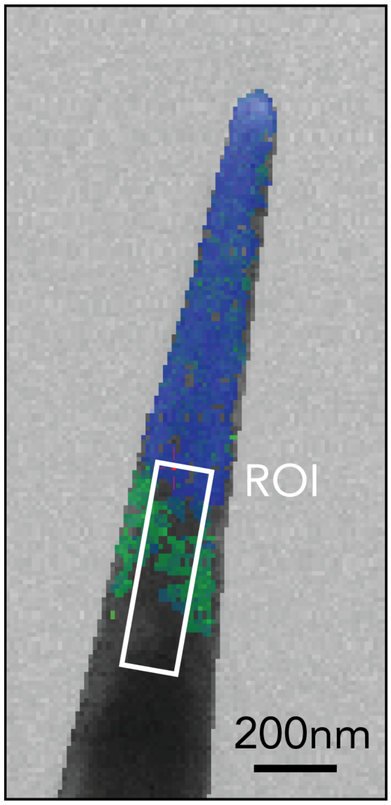
Reddy et al: Figure 1



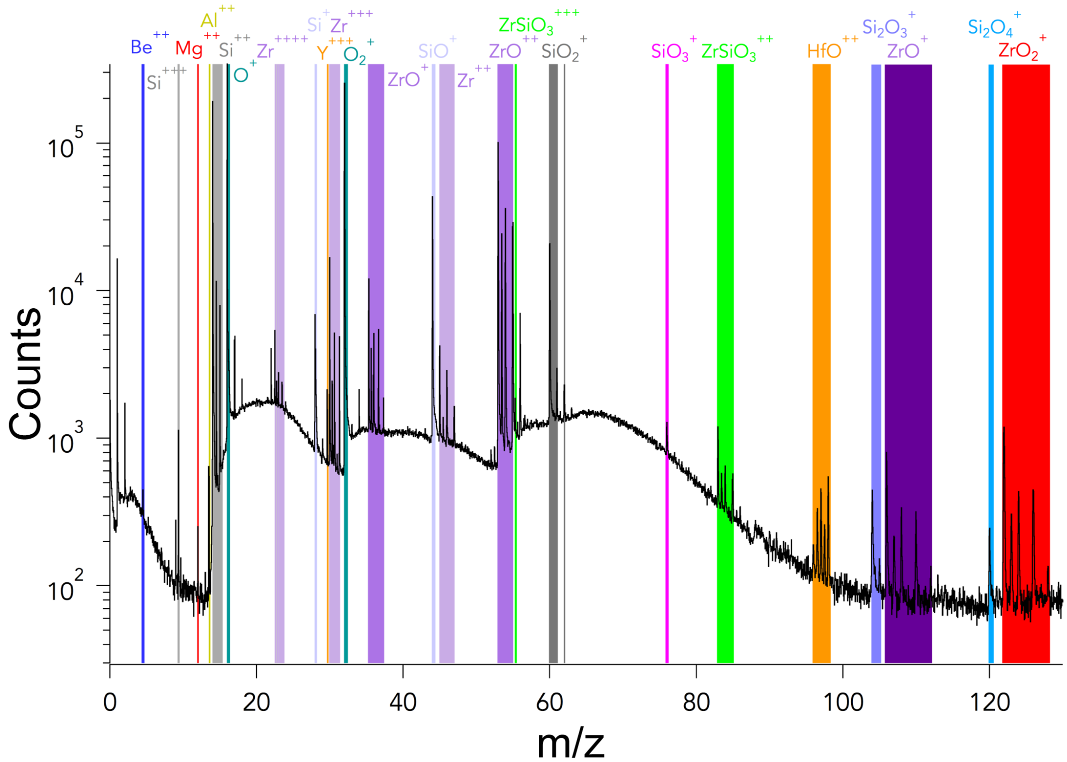
Reddy et al - Fig. 2



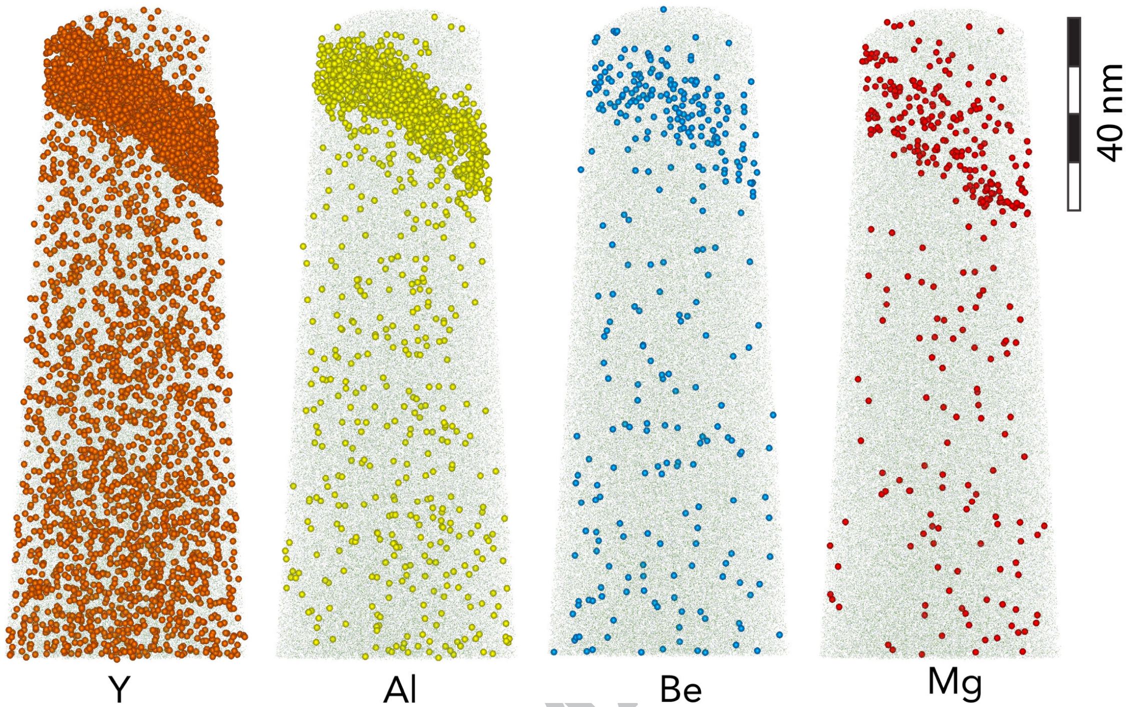
Reddy et al Fig. 3



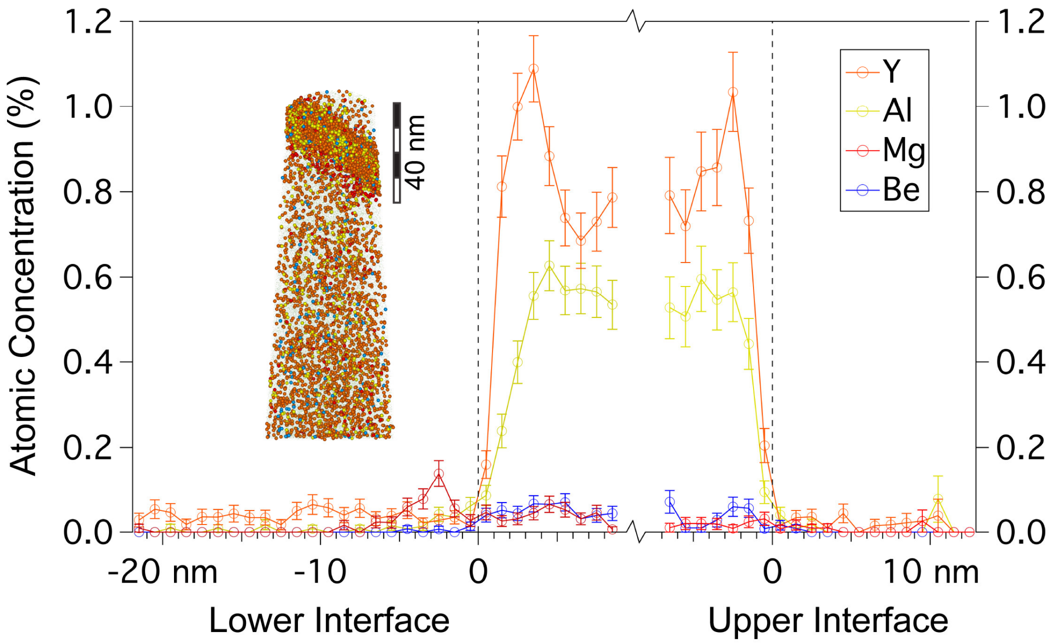
Reddy et al - Fig04



Reddy et al. Fig 5



Reddy et al Fig. 6



860

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863

	Matrix		Low-angle boundary	
Element	Concentration	+/- (1σ)	Concentration	+/- (1σ)
Zr	17.71%	0.03%	16.03%	0.09%
Si	15.61%	0.03%	15.88%	0.09%
O	66.51%	0.07%	66.54%	0.23%
Hf	0.141%	0.002%	0.106%	0.007%
Y	0.013%	0.001%	0.735%	0.019%
Al	0.0041%	0.0004%	0.543%	0.016%
Be	0.0044%	0.0004%	0.055%	0.005%
Mg	-	-	0.029%	0.004%

Table 1