Dating shear zones with plastically deformed titanite: New insights into the orogenic evolution of the Sudbury impact structure (Ontario, Canada)

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Abstract

The Sudbury structure is a mineralized impact crater that hosts different families of ore-controlling shear zones with poorly known orogenic affinities. Discriminating whether these deformation events relate to the 1.85 Ga crater modification stage or later regional tectonism, that collapsed the impact structure, is important both for crustal and mineral exploration studies. We have combined underground mapping with isotopic and microstructural analysis of titanite and host minerals in a benchmark ore-controlling mylonitic shear zone of the mining camp, the Six Shaft Shear Zone from the Creighton Mine. Three growth stages of chemically and microstructurally-characterised titanite grains were identified related with the pre-, syn and late deformation stages. \textit{In-situ} U-Pb age dating of the syndeformational grains demonstrates that a shearing event took place at 1645 ± 54 Ma during the Mazatzalian – Labradorian orogeny (1.7 – 1.6 Ga). This event led to the plastic deformation and local-scale remobilization of primary Ni-Cu-PGE sulphides in Creighton Mine (Sudbury, South Range). The adopted novel petrochronological approach can reveal the age significance of syn-deformational processes and holds promise for the untangling of complex syn-orogenic processes in Precambrian terranes globally.

Keywords: Shear zones, Titanite, Mineralization, Sudbury impact structure, Orogeny

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1. Introduction

High-strain mylonitic shear zones control the location, geometry, and metal tenor of a range of ore-deposits in many mining camps around the world (McQueen, 1987, Phillips et al., 1987, Cook et al., 1993, Blenkinsop, 2004, Duuring et al., 2007). The world-class polymetallic Ni-Cu-PGE Sudbury mining camp (Ontario, Canada) is not an exception. The structural architecture of this camp is controlled by a crustal-scale network of greenschist to amphibolite facies shear zones, collectively termed as the South Range Shear Zone (Shanks and Schwerdtner, 1990). The timing of operation and the orogenic affinity of the structures that define this system of shear zones remains unclear (Bailey et al., 2004). Better age constraints on their operation will provide new insights on the tectono-thermal events that induced the orogenic deformation of the crater and remobilization of some of the magmatic sulphide ore bodies to satellite positions. In this regard, the concept of petrochronology has emerged as a novel means to understand the chronologic significance and constrain the rates of metamorphic and deformational processes in polyphase deformed terranes globally.

Petrochronology is the linkage of isotopic ages with microstructural, geochemical, and/or thermobarometric constraints from the same or adjacent intra-grain domains of accessory phases. Constraining the timing of deformation remains a challenging endeavour but U-Th-Pb-bearing accessory phases have revealed, in several cases, a great potential to resolve the timing of deformation and fluid flow events in mylonitic shear zones (Parrish et al., 1988, Storey et al., 2004, Clark et al., 2005, Mahan et al., 2006, Cenki-Tok., 2013). In this contribution, we focus on a uniquely exposed mylonitic shear zone from the Creighton mine (Figure 1) that is spatially related with magmatic and remobilized Ni-Cu-PGE sulphide ore bodies. The main aims of this study are to: (a) bracket the timing of operation and the orogenic affinity of the shear zone, by adopting a petrochronologic approach using the accessory phase titanite and (b) characterise in detail this ore-controlling deformation zone and the mineralization that it hosts with new field, kinematic, mineral-chemical, and quantitative microstructural data (electron backscatter diffraction; EBSD).
Figure 1. Simplified geological map of the Sudbury impact structure and composite North-South seismic cross section along the traverses 1 and 2 that are depicted with blue jagged lines (map modified from Ames et al. 2008 and cross section from Adam et al., 2000).
2. The Sudbury impact structure

2.1 Geological setting and styles of mineralization

The 1.85 Ga Sudbury impact structure is a unique example of an ore-bearing terrestrial impact crater that underwent multiple orogenic events that extensively modified its structural architecture and metallogenic potential (Krogh et al., 1982; Riller, 2005). It is located at the junction of three Precambrian orogenic provinces (Superior, Grenville and Southern provinces), and is traditionally divided into the North, East, and South Ranges (Figure 1). The three major impact-related lithostratigraphic units of the Sudbury structure are: (a) the pseudotachylitic Sudbury Breccia (Spray, 1998, Rousell et al., 2003), (b) the Sudbury igneous complex (SIC) or Main Mass (Lightfoot et al., 1997), and (c) the elliptical Sudbury Basin (Pye et al., 1984 and references therein). In the South Range, Paleoproterozoic metamorphosed volcano-sedimentary rocks of the Huronian Supergroup form the footwall of the SIC (Card et al., 1984). In the North and East Ranges, the footwall of the SIC contains the 2.71 Ga Levack Gneiss Complex which consists of amphibolite to granulite facies tonalitic gneisses (Card et al., 1990; Ames and Farrow., 2007).

Four main types of sulphide mineralization are recorded in the Sudbury mining camp (Lightfoot et al., 1997; Mukwakwami et al., 2012). The dominant type comprises contact-style Ni-Cu-PGE sulphide ore bodies that accommodate more than 50% of the Sudbury ores (Lightfoot et al., 2001). These are characterised by massive and disseminated sulphide ore bodies that settled gravitationally as immiscible liquids from a voluminous supra-liquidus silicate melt to thermally eroded embayments at the bottom of the SIC (Barnes and Lightfoot., 2005). The Offset-style deposits constitute the second major style of mineralization. These deposits are hosted within inclusion-bearing quartz diorite dykes (i.e. Offset Dykes) that exhibit pinch and swell geometry and thin away from the SIC (Lightfoot and Farrow., 2002). The third major ore-bearing environment comprises Cu-Ni-PGE footwall-style deposits that are hosted mainly within the Sudbury breccia (South Range) and the Archean gneiss complex (North Range) (Ames and Farrow., 2007). The fourth type is associated with mylonitic shear zones that host, displace and remobilize high metal tenor contact and footwall-style ore bodies and is exemplified mainly by deposits in Garson, Thayer Lindsley, Falconbridge and Creighton mines (Bailey et al., 2006; Gibson et al., 2010; Mukwakwami et al., 2012).
2.2.1 Structural and metamorphic evolution of the South Range

The main deformation system of the South Range is the South Range Shear Zone that comprises a moderately dipping array of top-to-the-north ductile and brittle-ductile structures that transect the SIC and the southern footwall of the Sudbury Structure (Shanks and Schwerdtner., 1990). Quantitative thermobarometric constraints and mineral-chemical analyses of amphiboles place the peak metamorphic conditions, and the operation of the South Range Shear Zone, within the epidote-amphibolite facies stability field ($T = 550° - 600°C$, $P = 4-5$ Kbar) (Thomson et al., 1985, Fleet et al., 1987, Mukwakwami et al., 2014). The western segment of the South Range Shear Zone comprises ENE-trending, top-to-the-NW thrusts whereas the eastern exhibits a map-scale switch in the orientation of the structural grain with development of WNW-trending structures (Figure 1). These two structural domains are characterised by distinct kinematics (Santimano and Riller, 2012). A kinematic domain dominated by thrusting in the western part of the complex and a domain of dextral transpression in the eastern part (Riller et al., 1999). Generally, the following processes have been proposed that influenced the deformation pattern of the South Range during and/or after the impact event: (a) the formation of syn-impact fractures (Siddorn and Ham., 2006), (b) the mechanical weakening of the crust by the impact event (Riller et al., 2010), (c) the orogenic buckling of the Sudbury Igneous Complex in a flexural – slip mode (Mukwakwami et al., 2012), and (d) a tri-shear fault – propagation folding of the crater units (Lenauer and Riller., 2012).

Despite recent advances on the structural characterization of the impact crater, the timing of syn and post-impact orogenic events and associated tectonic deformation is disputed. Specifically, high temporal resolution age dating (ID-TIMS) of syn-tectonic titanite grains from the #4 shear zone of the Garson mine (Figure 1), indicates operation of the shear zone at 1849 ±6 Ma (Mukwakwami et al., 2014). In contrast, titanite grains from the Thayer Lindsley shear zone, also from the south-eastern part of the complex, yielded a mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1658 ± 68 Ma (Bailey et al., 2004). At the southwestern part of the complex, K-Ar and $^{40}\text{Ar}^{39}\text{Ar}$ dates from fabric-forming biotite and muscovite grains yielded ages related to a thermal event between 1450 and 1480 Ma (Szentpeteri, 2009). Overall, the age dating of shear zones from the South Range of the Sudbury structure provides hints of three distinct thermal episodes related with the Penokean (ca. 1.9-1.8 Ga), the Mazatzalian-
Labradorian (ca. 1.7-1.6 Ga), and the Chieflakian (ca. 1.5 – 1.4 Ga) orogenies. These results indicate that the impact event temporally may overlap with the Penokean orogeny (1.9 – 1.8 Ga) but the relative importance and control of post-impact events on the structural evolution of the crater remain far from well understood.

2.3 Shear zone families in the Creighton mine (South Range)

Creighton Mine is located at the southwestern margin of the Sudbury Structure (Figure 1) and hosts one of the largest contact-style deposits in the mining camp (i.e. the Creighton Deposit with 280 Mt of mined and unmined reserves). Many smaller contact and footwall-style ore bodies are located at depth in the Creighton Mine (e.g. 125, 126, 403, 461, 649 ore bodies, Figure 2) (Farrow and Lightfoot., 2002; Dare et al., 2010). Ductile shear zones exert a strong control on the geometry and location of these ore bodies (O’Donell., 1979). The following four main families of biotite-rich mylonitic shear zones are detected in the Creighton Mine (Snelling, 2009, Snelling et al., 2013): (a) the ENE-striking, steeply dipping 118 family of shear zones, (b) the NW-striking, moderately dipping family of footwall-type shear zones, (c) the steeply dipping family of E-W striking shear zones, and (d) the family of splay shears that link the NE-striking structures. The focus of this study is a deformation zone that is not categorized within any of the existing orientation families, exhibits listric geometry, and constitutes an important mechanical link between contact and footwall-style Ni-Cu-PGE magmatic ore bodies (Figure 2, Six Shaft Shear Zone).

3. Six Shaft Shear Zone (Creighton Mine, 5400 level)

3.1 Sampling

The Six Shaft Shear Zone is exposed underground from the 5000 (1524 m depth) to the 5400 (1767 m depth) level of the Creighton Mine and is also identified by multiple drillholes (Figure 2). Twenty-four samples of biotite-rich mylonite and two samples of shear-hosted ore were collected along a transect of approximately 25m from the 5400 level drift (Figure 3). The transect cross-cuts marginal lower strain and higher strain core domains of the Six Shaft Shear Zone. Eighteen of the mylonitic samples were collected for microtectonic and kinematic analysis. These samples were oriented normal to the foliation and parallel to the stretching lineation (XZ plane of the strain ellipsoid), taking into consideration field
observations that this plane hosts highly asymmetric kinematic indicators and can be regarded as the vorticity profile plane of the shear zone.

Figure 2. Simplified cross-section of the Creighton mine (modified from Vale ltd internal report), that depicts the spatial relationship of ductile shear zones with sulphide mineralization. The exact location of the cross section is depicted in the geological map (Figure 1, traverse A-B). With black bold letters is indicated the location of the Six Shaft Shear Zone in the 5400 level. The thickness of the ore bodies in the cross section is apparent since the location of the ore bodies has been projected on the cross-section using a wide clipping technique.

3.2 Field relationships

The Six Shaft Shear Zone is a km-scale mylonitic shear zone that exhibits a NNW to ENE strike swing (Figure 3). In this study the NNW-striking domain of the shear zone was accessed (Figure 3). This domain hosts a moderately dipping, high-strain fabric, defined by aligned biotite flakes and foliation-parallel, decimetre to meter-scale mylonitic quartz veins. A well-developed stretching lineation on the foliation planes is defined by elongate
amphibole prisms and biotite flakes. The strong development of foliation and stretching lineation characterise the biotite-rich mylonites as S-L tectonites. The average stretching lineation on the foliation planes plunges moderately towards the northeast and pitches around 80° (Figure 3, pole figures).

![Figure 3](image)

**Figure 3.** Simplified structural map of the Six Shaft Shear Zone at the 5400 level of the Creighton mine. The rectangular area in the inset depicts the NNW-striking domain of the Six Shaft Shear Zone and the spatial relationship of the shear with the 401 contact-style ore body. With red and black lines are depicted the foliation trajectories in the low (foliated-metagranitoid) and high strain domains of the shear zone, respectively. The pole figures show orientation data of stretching lineations and mylonitic foliations from the biotite-rich mylonitic domain. The black circles denote the location of each sample. The samples with underscored names were chosen for U-Pb titanite geochronology.

Parasitic folds defined by quartz-rich veins have axial planes sub-parallel to the mylonitic foliation. Refolded isoclinal quartz veins are observed also locally. Massive, quartz-rich, discordant veins occur in association with the biotite-rich mylonitic core. Marginally, the main body of the mylonitic zone is bounded by a weakly foliated meta-granitoid (i.e. black porphyry in the local literature). At the contact of the meta-granitoid with the mylonite, deflected quartz veins and quartz porphyroclasts with asymmetric strain shadows show a top-to-the-SW sense of shear (Figure 4a, b). Millimetre-scale asymmetric quartz...
veins also demonstrate a south-vergent sense of movement. Hand samples oriented normal to the foliation and the stretching lineation (YZ plane of strain ellipsoid) exhibit cm-scale eye-shaped sheath folds defined by quartz veinlets (Figure 4c). Pyrrhotite-rich sulphide ore bodies with pentlandite porphyroblasts and durchbewegt-type structures are oriented sub-parallel to the mylonitic foliation at the core of the mylonitic zone (Figure 4d). These outcrop-scale ore slivers host in their pyrrhotite-rich matrix biotite, amphibole, and quartz-rich wallrock clasts that locally define a crude foliation.

Figure 4. Field photographs from the Six Shaft Shear Zone that show: (a) Quartz porphyroclast with asymmetric strain shadows that indicate top-up-to-the-SW sense of shear (looking normal to the foliation and parallel to the stretching lineation), (b) Deflected quartz vein and quartz sigmoids that indicate southward translation at the contact of the foliated meta-granitoid with the biotite-rich mylonitic core, (c) cm-scale, eye-shaped, sheath folds developed at the YZ plane of strain ellipsoid (normal to the foliation and stretching lineation). The closure of the fold hinge lines is indicated with arrows. The tip of the pencil for scale is approximately 2 cm. (d) durchbeweng-style brecciated sulphides with quartz and biotite-rich mylonitic clasts in a pyrrhotite-rich matrix. Note that the chalcopyrite grains wrap around the more competent biotite and quartz clasts while pentlandite grains define porphyroblasts in the pyrrhotite-rich matrix.
3.3 Petrography and microstructures

3.3.1 Petrographic features of the Six Shaft Shear Zone

Biotite is the most abundant mineral phase (70-80% modally) and defines the penetrative high-strain fabric. Hornblende grains aligned with the fabric are observed in textural equilibrium with the biotite flakes. Relict hornblendes with corroded boundaries locally exhibit pinch and swell microstructures. Titanite, allanite with epidote rims, and apatite grains are ubiquitous accessory phases and commonly occur in close spatial association with each other (see section 5.2.2). The titanite grains in the biotite-rich mylonitic domain have patchy zoning in reflected light and occur chiefly as fine-grained clusters that define bands parallel to the high-strain fabric. Recrystallized titanite grains that host accessory phase inclusions (i.e. apatite and epidote) are observed within mm-scale, plagioclase-rich ultramylonitic bands. Blocky, anhedral, millimetre-scale titanite grains are also observed locally. In the marginal meta-granitoid domain, biotite flakes and chalcopyrite-pyrrhotite grains wrap around feldspar and quartz-rich porphyroclasts. Titanite grains in the quartzofeldspathic lithologies of this domain occur at the rims of epidote grains or in a textural disequilibrium with the rims of plagioclase grains (Figure 5).

Reflected light microscopy of the mylonitised sulphides reveals a pyrrhotite-rich matrix with millimetre-scale pentlandite and chalcopyrite grains. The chalcopyrites are commonly located at the boundaries of pentlandite grains or they fill intragranular fractures within pentlandite grains. Isolated, detached grains of biotite and zoned calcic amphiboles occur as inclusions in pentlandites and chalcopyrites. The detailed paragenetic relationships in the studied samples are described in Table 1.

3.3.2 Microstructures

Shear sense indicators in the biotite-rich mylonitic domain have monoclinic symmetry and consistently indicate a top-to-the-SW sense of shear (Figure 6). The main indicators are asymmetric polycrystalline quartz aggregates, feldspar porphyroclasts with asymmetric wings, biotite sigmoids, and C-S/C’-S composite fabrics (Figure 6a-d). Recrystallized feldspars with a strong grain shape fabric define millimetre-scale ultramylonitic bands between coarse-grained equigranular quartz grains with granoblastic
Figure 5. Photomicrographs from the marginal foliated metagranitoid of the Six Shaft Shear Zone that depict:
(a) titanite replacing epidote in a plagioclase and K-feldspar-rich matrix, (b) titanite in textural disequilibrium at the marginal domains of a plagioclase grain, (c) titanite rimming epidote adjacent to K-feldspar that exhibits myrmekitic texture, (d) reflected light image of the photomicrograph c that shows titanite (brighter) rimming the epidote grain.

4. Analytical techniques and methodology

4.1 Electron beam imaging and microstructural analysis (SEM/EBSD)

Accessory phases were detected in thin section-scale reflected light maps and imaged using different scanning electron microscopes (SEM) at the University of Portsmouth (UK). The spectral composition and identification of different accessory phases was
determined using a silicon drift (SDD) Oxford X-max 80mm² detector attached to a Zeiss EVO MA 10 LaB6 SEM at the University of Portsmouth. Electron backscatter diffraction analysis (EBSD) of titanite grains was performed using a Hitachi SU6600 (variable pressure-field emission gun SEM) equipped with an Oxford Instruments Nordlys EBSD detector at the Zircon and Accessory Phase Laboratory (ZAPLab, University of Western Ontario). The thin sections were vibratory polished (Buehler VibroMet 2) using an 0.05 µm alumina suspension. During the EBSD analysis, specimens were tilted to 70° and analysed with a beam current of 8 nA and accelerating voltage of 20 kV. The only post-analysis noise reduction processing performed was to replace ‘wild-spikes’ (interpreted as isolated,
erroneously-indexed pixels) with a zero solution. The EBSD data were processed using the
Oxford Instruments software package Channel 5.

4.2 Mineral chemistry by electron probe microanalysis (EPMA)

Major element data from silicates were measured with a Cameca SX-100 at the
University of Bristol using the TAP, LPET, and LLIF crystal spectrometers. An electron beam
of 10μm diameter with 20 kV accelerating voltage and 20nA beam current was used in all
the analyses. Natural silicates and synthetic materials were used as standards. Counting
times for the analysed elements were from 10 to 60 seconds both at peak and background
positions. The recalculation in the mineral-chemical analyses of calcic amphiboles was
performed using the spreadsheet of Tindle and Webb (1994). The biotites were recalculated
based on 22 oxygens per formula unit (Table 1, supplementary material). The amphiboles
were recalculated based on 23 oxygens per formula unit with Fe²⁺/Fe³⁺ estimation assuming
13 cations in total (Table 2, supplementary material). The amphibole mineral-chemical data
were classified based on the method and nomenclature of Leake et al (1997).

4.3 Trace element micro-analysis by laser-ablation-inductively-coupled-mass-spectrometry.
(LA-ICP-MS)

Trace element data from titanite and apatite grains were collected using an ASI
RESOlution 193 nm ArF excimer laser coupled to an Agilent 7500cs quadrupole ICP-MS at
the University of Portsmouth. The following isotopes were analysed ²⁷Al, ²⁹Si, ³¹P, ⁴³Ca, ⁴⁵Sc,
⁴⁹Ti, ⁵¹V, ⁵³Cr, ⁵⁵Mn, ⁵⁹Co, ⁶⁰Ni, ⁶⁶Zn, ⁶⁹Ga, ⁷²Ge, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁵Mo, ¹₁⁸Sn, ¹₂³Ba, ¹³⁹La,
¹⁴⁰Ce, ¹⁴³Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁷Er, ¹⁶⁹Tm, ¹⁷³Yb, ¹⁷⁵Lu, ¹⁷⁷Hf,
²⁰⁸Pb, ²³²Th, ²³⁸U. The laser spot size used in the analyses was between 15 and 40 μm. All the
analyses were performed at frequency of 10 Hz and fluence of 4.5 J/cm². NIST 612 was used
as the primary bracketing standard (Jochum et al., 2011). MPI-DING reference glasses (i.e.
GOR128_G and T1G) Khan titanite (Heaman., 2009) and Durango apatite (Marks et al., 2012)
were included as secondary standard every four or five unknowns. The analysed elements
are within 10% in accuracy relative to published values for the MPI-DING reference glasses
and the Khan titanite (Jochum et al., 2006, Heaman, 2009, Table 3, supplementary
material). Six analyses were rejected because were positioned above ilmenite inclusions
and cracks. Representative microprobe analyses demonstrate that titanites andapatites are
stoichiometric in their CaO abundance (28.6 wt% for titanite and 55 wt% for apatite) (Table 4, supplementary material). Thus, the CaO value was used as the internal standard to normalise the intensity of the unknown analytes. The raw data were reduced using the matlab-based software package SILLS (Guillong et al., 2008).

4.4 U-Pb geochronology by laser-ablation-inductively-coupled-plasma-mass-spectrometry (LA-ICP-MS)

U-Pb isotopic analyses on titanite were performed using an ASI RESOlution 193 nm ArF excimer laser coupled to a quadrupole Agilent 7500cs ICP-MS at the University of Portsmouth. Analytical and instrumentation parameters are provided in Table 5 (supplementary material). All the analyses were performed with spot size between 15 and 30 μm. The laser fluence was approximately 3 J/cm² and the frequency 2 or 3 Hz. A sample-standard bracketing method was used to correct for mass fractionation, using Khan titanite (ID-TIMS age of 522.2 ± 2.2 Ma, Heaman., 2009) as the primary standard. Downhole U-Pb elemental fractionation was corrected using an exponential downhole correction fit to the time-resolved data for each analysis. A $^{207}$Pb based correction scheme was applied to the variably common lead-bearing primary reference material (Khan titanite) using the Visuage_Ucombine add-in for Iolite (Paton et al., 2010, Chew et al., 2014). The resulting corrections in the raw measured ratios of Khan titanite are negligible and within analytical uncertainty. Taking in consideration the recrystallization features in the unknown titanite grains, and the relatively high background signal of $^{204}$Pb due to the interference of $^{204}$Hg, a $^{204}$Pb correction scheme based on crustal lead evolution models (Stacey and Kramers., 1975) was avoided. Thus, the U-Pb data (Table 6, supplementary material) are presented uncorrected for common lead in Tera-Wasserburg space. The Bear Lake Ridge Titanite (ID-TIMS age of 1047.4 ± 1.4 Ma, Aleinikoff et al., 2007) and Fish Canyon Tuff titanite (ID-TIMS age of 28.40 ± 0.02 Ma, Schmitz and Bowring., 2001) were analysed as secondary standards every four or five unknowns. The LA-ICP-MS analyses of the secondary standards are within uncertainty of the ID-TIMS values both for BLR and FCT titanite, yielding lower intercept ages of 1044 ± 23 Ma and 23.2 ± 6.3 Ma respectively on Tera-Wasserburg plots (Table 5, supplementary material). The isochrons of secondary standards were anchored to $^{207}$Pb/$^{206}$Pb isotopic ratios of 0.912 ± 0.05 (Stacey and Kramers., 1975) and 0.84 ± 0.05 (Schmitz and Bowring., 2001), for BLR and FCT, respectively.
5. Results

5.1 Mineral chemistry of mylonitic fabrics

5.1.2 Amphiboles

The calcic amphiboles, according to their morphology and their relationship with the deformation fabrics, are classified in two micro-textural settings: (a) as relict, subhedral boudinaged grains, and (b) as pristine elongate grains that define the wings of feldspar porphyroclasts and the penetrative mylonitic fabric (Sm). The mineral-chemical analyses of these two textural populations manifest distinct differences. A core to rim zoning pattern is evident in the co-axially deformed amphiboles. The cores record an alternation of magnesio-hornblende, ferro-actinolite, and actinolitic hornblende domains (XMg = 0.49 – 0.66) (Figure 7a). The rims of the boudinaged amphiboles and the fabric-forming grains show compositional similarities and plot in the field of ferro-tschermakitic hornblende (XMg = 0.45-0.50). Comparatively, the fabric-forming grains have a marked increase in the IVAl, IVAl, (Na + K)(A) and Ti contents relative to the cores of the relictic boudinaged amphiboles.

Similar core to rim zoning patterns in calcic amphiboles are commonly attributed to amphibole growth at increasing P-T conditions along the prograde path of metamorphic terranes (Spear, 1993, Zenk and Schulz, 2004).

5.1.1 Biotite

The fabric-forming biotites of the Six Shaft Shear Zone show a progressive decrease in the XFe (Fe²⁺/Mg + Fe²⁺) from XFe = 0.62 to XFe = 0.53 (Figure 7b). This trend towards more phlogopitic compositions, along a traverse oblique to the strike of the mylonitic fabric, coincides with the exposure of foliation-parallel brecciated sulphides. The biotite grains are halogen-poor and have a slightly increasing trend in the abundance of chlorine from the marginal meta-granitoid (Cl = 0.14 wt %) to the biotite-bearing mylonitic core (Cl = 0.23 wt %).

5.2 Electron beam imaging and microstructural analysis of titanite (SEM/BSE-EBSD)

5.2.1 Electron beam imaging
Figure 7. Compositional plots from fabric forming amphiboles and biotites of the Six Shaft Shear Zone: (a) Mineral chemical data of calcic amphiboles that are plotted with different colors according to the intra-grain location of the analytical spot (core-rim) and the textural relationship of the grains with the deformation fabrics, (b) Mineral chemical data of biotites from different structural levels of the shear zone. Titanite grains were located in thin section-scale reflected light maps and imaged using backscatter electron microscopy (BSE). The majority of the imaged grains were classified based on their textural relationship with the deformation fabrics as pre-deformational relict cores (Group 1), syn-deformational (Group 2), and post/late-deformational grains (Group 3). A large population of grains though, has an ambiguous relationship with the deformation fabrics. Specifically, the Group 1 grains are expressed as darker, sector-zoned cores, within grains that show overgrowth zoning (Figure 8a). These grains commonly are decorated by a
sub-micrometer mantle zone with brighter BSE response that mimics their embayed
group. The **Group 2** grains are characterised by strong shape preferred orientation,
patchy BSE zoning, and micrometer-scale ilmenite, allanite, and apatite inclusions (**Figure 
8b**).

These patchily-zoned grains commonly show amalgamation and define larger 
polycrystalline aggregates. Grains with overgrowth zoning and dissolution-precipitation 
features, such as darker sector zoned embayed cores (**Group 1 grains**), have idioblastic rims 
in textural equilibrium with fabric-forming silicates (**Figure 8c**) and are classified in the same 
textural population with the rest of the syn-deformational grains. In this population also 
 occur locally grains with porphyroclastic texture and asymmetric wings (**Figure 8d**). The 
post/late-deformational population of titanite grains (**Group 3**) does not exhibit any 
systematic relationship with the deformation fabrics. These grains have blocky idioblastic 
habit, faint BSE zoning, and amphibole-biotite inclusions (**Figure 8e**). In addition, titanite 
grains from different textural populations are in mutual contact with allanite-cored epidotes 
and apatites indicating textural equilibrium during the growth of the three phases (**Figure 
8f**).

### 5.2.2 Microstructural features of titanite and plagioclase grains

Titanite grains from the syn and post-deformational textural populations (**Groups 2 and 3**) were selected for quantitative microstructural analysis using the technique of 
electron backscatter diffraction (EBSD). The development of intragranular high-angle grain 
boundaries (i.e. boundaries with misorientation angles above 10°) in the symdeformational, 
ribbon-shaped grains, induced the development of discrete crystallites (**Figure 9a-d**). These 
boundaries are evident also in BSE images as ovoid fractures (e.g. **Figure 8b**). Low angle 
grain boundaries (i.e. boundaries with misorientation angles between 2° and 10°) are 
observed within the crystallites of both textural populations. The cumulative misorientation, 
relative to a reference point (white cross), differs considerably between grains of the two 
populations. In grains of Group 2 are recorded misorientation values up to 100° whereas in 
the blocky grains of Group 3 up to 8° (**Figure 9e-f**). Moreover, in grains of Group 3 the. 
Figure 8. Backscatter electron images of titanite grains from the Six Shaft Shear Zone: (a) Darker sector zoned titanite grains (Group 1 grains) overgrown by titanite grains with ilmenite inclusions, (b) titanite grains with ilmenite, allanite, and apatite inclusions that show a strong shape preferred orientation and are hosted in bands of recrystallized feldspar (Group 2 grains), (c) darker embayed titanite cores (Group 1 grains) overgrown by euhedral titanite rims (Group 2 grains) with the latter in textural equilibrium with apatite and biotite grains, (d) patchily zoned titanite grain with ilmenite inclusion and porphyroclastic texture (Group 2 grains), (e) blocky anhedral titanite grains that exhibit faint zoning and host ilmenite and silicate inclusions (Group 3 grains). (f) Apatite grain in contact with a titanite grain that hosts an allanite inclusion.
gradational increase in misorientation values is accommodated only locally by low-angle grain boundaries (Figure 9f). The blocky grains of Group 3 exhibit a strong CPO (crystallographic preferred orientation) that is expressed by point maxima in the pole figures (Figure 9e). In stark contrast, in the recrystallized grains of Group 2 the poles of the {100}, {010}, and {001} crystallographic planes show girdle-shaped patterns in lower hemisphere-equal area projections (Figure 10a). The grains of Group 2, that show a strong shape preferred orientation, have maximum MUD values up to 13 whereas the blocky grains of group 3 up to 165. The Multiples of Uniform Density value (MUD) is a parameter that characterise the fabric intensity, with MUD>1 indicative for the development of a fabric (Bland et al., 2011). Plagioclase grains have a different microstructural response relative to the Group 2 titanite grains that they host (e.g. sample SSS18.4, Figure 10a-b). They show 120° triple junctions in band contrast maps and exhibit random CPO in pole figures of the {100}, {010}, and {001} crystallographic planes (Figure 10b).

5.3 Titanite and apatite trace element geochemistry

In-situ trace element analyses were performed on titanite (n = 93) and apatite grains (n = 21) from different samples of the shear zone (Table 7 and 8, supplementary material). Eight apatite and five titanite analyses were rejected after inspection of the SEM images since they were located above or close to fractures. The analytical positions overlaid, where possible, the EPMA spots. Twenty-two (n=22) analyses in titanite grains of Group 2 were located adjacent to spots that were selected for U-Pb isotopic microanalysis. A distinction between the different titanite groups can be inferred based on the uranium concentrations. Specifically, from the eighteen analyses in grains of Group 1 twelve analyses show uranium contents below 1.5 ppm, and six between 2 and 6ppm. From forty-five analyses in grains of Group 2 (patchy zoning and ilmenite inclusions), twenty-seven show uranium contents between 1.5 and 6.7 ppm. In addition, in twenty-five analyses from Group 2 grains with overgrowth zoning eleven analyses show uranium contents between 5 and 11.8 ppm of uranium (Figure 11). The main compositional feature that is observed in the majority of the
Figure 9. Misorientation maps of representative titanite grains from the Six Shaft Shear Zone that show from (a) to (d): Misorientation maps of Group 2 dynamically recrystallized titanite grains hosted within plagioclase and biotite-rich matrices. Black lines denote high-angle grain boundaries and red low angle. (e) Blocky titanite grain (Group 3 grain) with abrupt transition between misorientation domains and maximum cumulative misorientation values up to 5 degrees relative to the white cross. In the upper-right part of the map is depicted the pole figure of the {100} crystallographic plane. (f) Anhedral titanite that shows amalgamation and local crystal-plastic deformation that is expressed with the development of low-angle grain boundaries. Note that the maximum cumulative misorientation value of 8 degrees is observed in association with low angle grain boundaries at the upper right part of the grain.
Figure 10. Misorientation and phase map of a dynamically recrystallized titanite grain (Group 2) in a plagioclase-rich matrix. Both maps overlay a band contrast map. Below each map are depicted pole figures (lower hemisphere-equal area diagrams) for titanite (red) and plagioclase (blue) of the principal crystallographic axes.
grains (n=90), independently of zoning pattern and textural classification is depletion of LREE relative to HREE (La/Yb (n) = 0.001 – 0.041) (Figure 11). No or negative europium anomalies (Eu/Eu(N)=0.56 – 1) are recorded in most of the grains (n = 76). Positive europium anomalies (Eu/Eu(N) = 1.25 – 2.25) are recorded chiefly in grains from a plagioclase-rich sample (i.e. sample SSS11A, n=11). Interestingly, titanite grains from this sample show also elevated Sm/Yb ratios (0.20 – 0.46) relative to grains from the other biotite-rich samples. In the titanite grains with overgrowth zoning, a slight increase of Y+REE contents from the darker in BSE resorbed cores (Group 1 grains) to the lighter in BSE mantle and rim zones (Group 2 grains) occurs (Table 7, supplementary material). In addition, thirteen analyses (n=13) of matrix-hosted fluorapatites (Table 8, supplementary material) exhibit also LREE-depleted patterns (La/Yb (n) = 0.01 – 0.16) with most of them (n=19) having negative europium anomalies (Eu/Eu(N) = 0.46-0.92) (Figure 11, bottom).

5.4 U-Pb titanite geochronology

Fifty-six analyses were performed in thin sections from six mylonitic samples (Figure 12a). The spots for U-Pb isotopic analysis were located primarily in fabric-forming titanite grains, free of fractures, which exhibit patchy zoning in BSE images (Group 2 grains). Four analyses were performed within the idioblastic rims of overgrowth zoned titanite grains that are in textural equilibrium with biotite (Group 2 grains-overgrowth zoning). U-Pb data from the texturally older populations of Group 1 grains were not collected since for the majority of the grains the trace element microanalysis showed that the ^{238}U content was below 1.5 ppm with a spot size of 20-30 μm. Thus, in order to get potentially meaningful age data, we would have needed to increase the spot size to 35-40 μm. In this case though, we would ablate cracked and/or inclusion-bearing domains. With the same rationale, age data from group 3 grains were not collected since they show uranium contents below 0.1 ppm. The uranium contents in the analysed grains vary from ca. 1 to 11 ppm. The U-Pb isotope data were plotted in Tera-Wasserburg concordia diagram taking into consideration that the analysed grains have cogenetic textural features and spread in U/Pb ratios (Figure 12a-b). The spread in the U/Pb isotopic ratios defines a single ^{238}U/^{206}Pb – ^{207}Pb/^{206}Pb isochron in Terra-Wasserburg space denoting that the selected targets belong to a single age population within uncertainty (Figure 12). The analysed grains yield a regressed lower
...the point with the lowest
$^{207}\text{Pb}/^{206}\text{Pb}$ ratio, that has a strong
bearing on the date, yields a lower
intercept date of 1634±60 Ma (2σ)
(MSWD = 1.9). The U-Pb isotopic
data are uncorrected for common
Pb and the intersection of a
regression line through all the data
points with the y axis represents the
$^{207}\text{Pb}/^{206}\text{Pb}$ isotopic composition of
common lead ($\text{Pb}_{\text{com}}$) that is
estimated at 1.02 ± 0.02. The
$^{207}\text{Pb}/^{206}\text{Pb}$ isotopic composition of
common lead, based on crustal Pb
evolution models for this age is
estimated at 0.97 (Stacey and
Kramers., 1975). In a plagioclase-rich
sample (i.e. SSS11A), eleven trace

**Figure 11.** Plot of selected trace
elements from titanite and apatite
grains of the Six Shaft Shear Zone. From
top to bottom are depicted the
following: U versus Sm/Yb scatter plot
from the different titanite textural
populations, REE diagram from titanite
grains of Group 1 (resorbed dark cores),
REE diagram from titanite grains the
belong to the Group 2 (patchy zoning
with ilmenite inclusions), and at the
bottom REE diagram from apatite grains
hosted in a biotite-rich matrix of the
shear zone.
element analyses in grains that were used for U-Pb isotopic microanalysis consistently indicate the presence of positive Europium anomalies (Eu* = 1.25 – 2.27, Table 2, Figure 12b). The rest of the samples, that are biotite or amphibole-rich, show no or negative Eu anomalies. U-Pb analyses of two microstructurally characterised (EBSD) titanite grains are depicted with red outline in order to demonstrate the relationship of the microstructurally characterised titanite grains with the grains that define the dominant age population (Figure 12b).

**Figure 12.** Terra Wasserburg concordia diagrams that show: (a) U-Pb ellipses colored in different shades of grey for different samples and (b) the same diagram colored based on the presence of Europium anomalies. Note that in figure 12b is presented also a REE diagram from titanite grains of the plagioclase-rich sample SSS11A. With red outlines in Figure 12b are depicted the two grains in the misorientation maps of Figure 9 (9a and 9c). The X and Y axes depict the total $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{238}\text{U}/^{206}\text{Pb}$ isotopic ratios.
6. Discussion

6.1 Petrogenetic origin of the shear-hosted titanites

6.1.1 Titanite grains with ilmenite cores and patchy zoning

The presence of titanite grains with darker embayed cores (Group 2 grains), patchy zoning, and ilmenite cores or inclusions are features that are attributed as evidence of intracrystalline dissolution and fluid-mediated growth (Harlov et al., 2006; Lucassen et al. 2010; Villa and Williams., 2013). Specifically, Harlov et al., (2006) tested amphibolite-facies samples if a H2O-rich fluid phase is responsible for the removal of Fe from ilmenite and the addition of Ca for the formation of titanite. By adopting a phase equilibria approach discussed mineral reactions in the CaO-FeO/Fe2O3-TiO2-SiO2-H2O-O2 (CFTSH) and CaO-FeO/Fe2O3-Al2O3-SiO2-H2O-O2 (CFASH) systems, as function of H2O and O2 fugacity. According to these researchers, in amphibole and clinopyroxene-absent samples the two main reactions that led to titanite formation are the: (a) plagioclase + ilmenite + H2O = plagioclase + titanite + biotite and/or (b) 54 Anorthite + 6 Annite + 18 Titanite + 12 H2O = 18 ilmenite + 36 Clinozoisite + 6 K-feldspar + 18 Quartz (for epidote-bearing samples). The presence of titanite in textural disequilibrium with plagioclase and epidote/clinozoisite (e.g. sample SSS 26, Figure 5) indicates that in the felsic domains of the shear zone the fluid-mediated break down of Ca-bearing phases led to the growth of titanite.

Patchy zoning is a textural feature that indicates redistribution of the major structure-forming cations through open system recrystallization (Villa and Williams., 2013). In an experimental study, Lucassen et al., (2010) synthesized titanite in expense of rutile at run conditions of 600°C and 4Kbar (amphibolite-facies conditions) using a saline fluid phase to enhance solubility of rutile. In their results, titanite exhibits patchy compositional zoning in Ti-Al-F-OH, as a result of heterogeneities in the fluid composition. In the case of the Six Shaft Shear Zone, patchy zoning in BSE-compositional imaging is the main type of zoning and is interpreted as evidence for the existence of intragrain compositional heterogeneities. The presence of patchy zoning in grains with ilmenite inclusions possibly indicates that the fluid-induced breakdown of ilmenite and the development of irregular brighter and darker BSE domains are two interrelated processes.
6.1.2 Apatite and allanite inclusions in titanite

The nucleation of fluorapatite and allanite grains (LREE-enriched epidote) as inclusions in the LREE-depleted titanite grains is another textural line of evidence that can be related with the fluid-mediated petrogenesis of titanite in the Six Shaft Shear Zone. Similar micro-textural relationships between different REE-bearing accessory phases are attributed to the process of dissolution-reprecipitation in accessory phases from natural metasomatic settings (Pan et al., 1993, Dempster et al., 2006, Dempster and Macdonald, 2016). Experimental studies have also shown that permeating metasomatic fluids can exploit micro and nano-scale intragranular porosity paths (e.g. high-angle grain boundaries) and induce the development of analogous intragrain associations. For instance, the instantaneous growth, in geological timescales, of LREE-enriched monazite inclusions in fluorapatite (Harlov et al., 2005, Krenn et al., 2012, Harlov pers. com.).

In the case of the Six Shaft Shear Zone one scenario is that the LREE-depleted signature of both matrix-hosted apatite and titanite grains implies that pulses of fluid mobilized the LREE into other LREE-rich repositories such as allanite. Another scenario that seems more feasible in the examined shear zone, is that titanite co-crystallized with a LREE-enriched mineral, such as allanite, with the partitioning of LREE in allanite. BSE imaging provides support for the second scenario since both phases share sharp optical boundaries and are in textural equilibrium.

6.3 Chronologic significance of titanite age data

The suggested closure temperature of titanite, for typical cooling rates of most geological settings, varies from 600 to 800°C with fluid-assisted recrystallization rather than temperature-controlled thermal diffusion being also a controlling factor on the loss or exchange of radiogenic daughters (Cherniak, 1993, Verts et al., 1996, Villa, 1998, Frost et al., 2000, Rubatto and Herman, 2001, Spencer et al., 2013, Stearns et al., 2015, Kirkland et al., 2016). The syn-kinematic assemblage in the Six Shaft Shear Zone (i.e. Hbl-Pl-Ep-Qtz±Ttn±Ilm±Zr±Ap) indicates operation at epidote-amphibolite facies conditions (450 - 550°C). Further constraints are provided also by the microstructural data (EBSD) from plagioclase grains. The presence of annealing textures in band contrast maps and the absence of CPO (i.e. Figure 10b) indicate that plagioclase grains underwent crystal-plastic
deformation via a dissolution-precipitation creep mechanism (Menegon et al., 2008, Mukai et al., 2014). This deformation mechanism has been described again in deformed lithologies at epidote-amphibolite facies conditions and places the peak temperatures of shear zone operation at 600°C (Wintsch and Yi., 2002). The positive europium anomalies in titanite grains of Group 2, from the plagioclase-rich sample SSS11A, are interpreted to record the break-down of plagioclase via a dissolution-precipitation creep mechanism. This trace element signature suggests that titanite grains of Group 2 (higher U grains) grew during crystal-plastic deformation in the shear zone. These grains belong to the age population of 1645 ± 54 Ma (Figure 12b) and document the timing of crystal-plastic deformation and shear zone activity. In the case of the examined shear zone though, there is strong evidence for crystallite development and sub-grain formation in the titanite grains. These grain-scale modifications could have a strong impact on the diffusion characteristics of titanite and to the age significance of that date (i.e growth versus cooling age).

In a recent study, Kirkland et al., (2016) show through thermochronological modelling that titanite grains with length ≥ 210μm were not reset by a metamorphic event that reached 695 - 725°C demonstrating the critical role of grain size on preservation or resetting of isotopic information. Therefore, the relatively large grain size of the selected grains (i.e median length = 208μm, Table 2 supplementary material) possibly inhibited the modification of the closure temperature below the suggested range (600 - 800°C). On another note, the relatively high MSWD (Mean Square of Weighted Deviation) value (MSWD = 1.9) indicates that the titanite age data contain geologically meaningful scatter, possibly recording fluid-mediated and deformation processes throughout an orogenic cycle. The deviation in \(^{207}\text{Pb}/^{206}\text{Pb}\) common lead ratios compared to model Pb estimates indicates that in shear zone settings localized fluid flow and deformation can induce fractionation of U/Pb, Th/Pb and Th/U ratios (e.g. Cenki-Tok et al., 2013).

6.4 Implications for the orogenic evolution of the South Range

The presence of top-to-the-SW monoclinic symmetry shear sense indicators in the Six Shaft Shear Zone indicate dominantly a non-coaxial strain path. Field-based mesoscale kinematic data are sparse in Creighton Mine, but biotite-rich shear zones from the deeper levels of the Mine show an opposite top-to-the-NW sense of shear (Snelling et al., 2013). Mineral phases with different rheological behavior and strain memory paint a more complex
picture in the strain history of the examined shear zone. Paradoxically, feldspars with a
diffuse CPO host dynamically recrystallized titanites with a strong CPO. This denotes that
titanite is a robust recorder of strain increments and resilient to fluid-mediated annealing
and randomization of the CPO. The age dating of these syn-deformational titanite grains
(Group 2 grains) from the Six Shaft Shear Zone indicate operation during an important, but
under-recognised event, the Mazatzalian – Labradorian orogeny (1.7 – 1.6 Ga) (Romano et
al., 2000, Bailey et al., 2004). Structural data from the north-central United States show
that during the Mazatzalian event a thin-skinned fold and thrust belt accommodated, via
North and South-vergent structures, more than 600km of crustal shortening in 70 Myr
(Craddock and McKiernan., 2007; Czeck et al., 2007, Duebendorfer et al., 2015). The new
age data challenge the widely-held view that shear zones operated exclusively during the
Penokean orogeny (ca. 1.9 – 1.8 Ga) (Shanks and Schwerdtner., 1991; Milkereit et al., 1992;
Riller and Schwerdtner., 1997; Riller et al., 1999).

6.5 Implications for the mode and timing of sulphide remobilization in the Creighton mine

The extent of deformation-assisted remobilization of magmatic sulphides in
Creighton Mine is not well constrained relative to other mines (e.g. Thayer Lindsley and
Garson Mines, Bailey et al., 2006, Mukwakwami et al., 2014). However, the spatial
relationship of the Six Shaft Shear Zone, with contact and footwall-style ore bodies suggests
that this shear operated as a transfer pathway between contact (e.g. 125 ore body, Figure
2) and footwall-style deposits (e.g. 403 and 126 ore bodies, Figure 2) (O’Donell, 1979). The
presence of meso-scale remobilization structures (i.e. durchbewegt) in the shear-hosted
sulphides indicate a strong component of mechanical remobilization (Marshall and Gilligan.,
scale evidence does not exist though to support the hypothesis that the footwall ore system
of the Creighton Mine was emplaced entirely via mylonitic shear zones. The more probable
scenario is that ductile shear zones in the South Range, as foci of orogenic strain and fluid
flow, led to a local-scale remobilization of primary contact and footwall-style Ni-Cu-PGE
sulphide ore bodies. The texturally-controlled age dating of the Six Shaft Shear Zone
demonstrates that this remobilization event can be linked with the Mazatzalian-Labradorian orogeny (1.7 – 1.6 Ga).

7. Conclusions

The Six Shaft shear zone is a top-to-the-SW ductile thrust that was active at epidote-amphibolite-facies conditions. The age dating of dynamically recrystallized titanite grains shows that this structure operated at 1645 ± 54 Ma during the Mazatzalian-Labradorian convergent orogeny (1.7 – 1.6 Ga). Syndeformational titanite grains with positive europium anomalies (Eu* = 1.25 – 2.25) record the breakdown of plagioclase grains with diffuse CPO via a dissolution-precipitation creep mechanism. The development of mechanical remobilization structures in sulphides at the mesoscopic scale indicates that the Six Shaft shear zone accommodated the local-scale transfer of contact and footwall-style Ni-Cu-PGE sulphide ore bodies. The synergistic approach on the study of the Six Shaft Shear Zone enhances our understanding of the operation of the structures that belong to the South Range Shear Zone and place maximum age constraints (1.7 – 1.6 Ga) on the local-scale remobilization of Ni-Cu-PGE sulphides during the orogenic deformation of the Sudbury impact structure.

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