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

Konstantinos Papapavlou^{a*}, James R. Darling^a, Craig D. Storey^a, Peter C. Lightfoot^b, Desmond E. Moser^c, and Stephanie Lasalle^a

^aSchool of Earth and Environmental Sciences, University of Portsmouth, Portsmouth PO1 3QL, UK

^bHarquail School of Earth Sciences, Laurentian University, Sudbury, Ontario, P3E 2C6, Canada

^cDepartment of Earth Sciences, University of Western Ontario, London N6A 5B7, Ontario, Canada

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. *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

*corresponding author (konstantinos.papapavlou@port.ac.uk)

29 1. Introduction

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

44 Petrochronology is the linkage of isotopic ages with microstructural, geochemical,
45 and/or thermobarometric constraints from the same or adjacent intra-grain domains of
46 accessory phases. Constraining the timing of deformation remains a challenging endeavour
47 but U-Th-Pb-bearing accessory phases have revealed, in several cases, a great potential to
48 resolve the timing of deformation and fluid flow events in mylonitic shear zones (Parrish et
49 al., 1988, Storey et al., 2004, Clark et al., 2005, Mahan et al., 2006, Cenko-Tok., 2013). In this
50 contribution, we focus on a uniquely exposed mylonitic shear zone from the Creighton mine
51 (**Figure 1**) that is spatially related with magmatic and remobilized Ni-Cu-PGE sulphide ore
52 bodies. The main aims of this study are to: (a) bracket the timing of operation and the
53 orogenic affinity of the shear zone, by adopting a petrochronologic approach using the
54 accessory phase titanite and (b) characterise in detail this ore-controlling deformation zone
55 and the mineralization that it hosts with new field, kinematic, mineral-chemical, and
56 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 ($T = 550^{\circ} - 600^{\circ}\text{C}$, $P = 4\text{-}5\text{ Kbar}$) (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 $1849 \pm 6\text{ Ma}$ (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 $1658 \pm 68\text{ Ma}$ (Bailey et al., 2004). At the southwestern part of the complex, K-Ar and $^{40}\text{Ar}\text{-}^{39}\text{Ar}$ 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. 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) durchbewegung-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

texture. Undulose extinction and development of polycrystalline quartz aggregates with ribbon-shaped geometry are ubiquitous features in the quartz-rich domains.

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

Figure 6. Shear sense indicators from the Six Shaft Shear Zone: (a) polycrystalline quartz aggregate with stair stepping geometry and asymmetric tails that indicate top-to-the-SW sense of shear, (b) C'-S composite fabrics that indicate top-to-the-SW sense of shear, (c) biotite sigmoids with top-to-the SW sense of shear, (d) feldspar porphyroclast with asymmetric wings that are defined by hornblende and titanite grains that show top-to-the-SW sense of shear, (e) rhomboidal biotite fish that indicates top-to-the-SW sense of shear. All the shear sense indicators were recognized in thin sections oriented normal to the foliation and parallel to the stretching lineation (XZ plane of strain ellipsoid).

(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 $\text{Fe}^{+2}/\text{Fe}^{+3}$ 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 ^{27}Al , ^{29}Si , ^{31}P , ^{43}Ca , ^{45}Sc , ^{49}Ti , ^{51}V , ^{53}Cr , ^{55}Mn , ^{59}Co , ^{60}Ni , ^{66}Zn , ^{69}Ga , ^{72}Ge , ^{85}Rb , ^{88}Sr , ^{89}Y , ^{95}Mo , ^{118}Sn , ^{121}Sb , ^{137}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{173}Yb , ^{175}Lu , ^{177}Hf , ^{208}Pb , ^{232}Th , ^{238}U . 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 and apatites 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 ²⁰⁷Pb based correction scheme was applied to the variably common lead-bearing primary reference material (Khan titanite) using the Visuage_Ucompbine add-in for Lolite (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 ²⁰⁴Pb due to the interference of ²⁰⁴Hg, a ²⁰⁴Pb 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 ²⁰⁷Pb/²⁰⁶Pb 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 (S_m). 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 ($X_{Mg} = 0.49 - 0.66$) (**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 ($X_{Mg} = 0.45-0.50$). Comparatively, the fabric-forming grains have a marked increase in the ^{vi}Al , ^{iv}Al , $(Na + K)_{(A)}$ 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 X_{Fe} ($Fe^{+2}/Mg + Fe^{+2}$) from $X_{Fe} = 0.62$ to $X_{Fe} = 0.53$ (**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 geometry. 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 syndeformational, 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 (Group2 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 ($\text{La/Yb}_{(N)} = 0.001 - 0.041$) (**Figure 11**). No or negative europium anomalies ($\text{Eu/Eu}_{(N)} = 0.56 - 1$) are recorded in most of the grains (n = 76). Positive europium anomalies ($\text{Eu/Eu}_{(N)} = 1.25 - 2.25$) 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 ($\text{La/Yb}_{(N)} = 0.01 - 0.16$) with most of them (n=19) having negative europium anomalies ($\text{Eu/Eu}_{(N)} = 0.46-0.92$) (**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 $^{238}\text{U}/^{206}\text{Pb} - ^{207}\text{Pb}/^{206}\text{Pb}$ 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

462 intercept date of 1645 ± 54 Ma (2σ) (MSWD = 1.9) (**Figure 12a-b**). Excluding from the
 463 analyses the point with the lowest
 464 $^{207}\text{Pb}/^{206}\text{Pb}$ ratio, that has a strong
 465 bearing on the date, yields a lower
 466 intercept date of 1634 ± 60 Ma (2σ)
 467 (MSWD = 1.9). The U-Pb isotopic
 468 data are uncorrected for common
 469 Pb and the intersection of a
 470 regression line through all the data
 471 points with the y axis represents the
 472 $^{207}\text{Pb}/^{206}\text{Pb}$ isotopic composition of
 473 common lead (Pb_{com}) that is
 474 estimated at 1.02 ± 0.02 . The
 475 $^{207}\text{Pb}/^{206}\text{Pb}$ isotopic composition of
 476 common lead, based on crustal Pb
 477 evolution models for this age is
 478 estimated at 0.97 (Stacey and
 479 Kramers., 1975). In a plagioclase-rich
 480 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.

481 element analyses in grains that were used for U-Pb isotopic microanalysis consistently
 482 indicate the presence of positive Europium anomalies ($Eu^* = 1.25 - 2.27$, Table 2, **Figure**
 483 **12b**). The rest of the samples, that are biotite or amphibole-rich, show no or negative Eu
 484 anomalies. U-Pb analyses of two microstructurally characterised (EBSD) titanite grains are
 485 depicted with red outline in order to demonstrate the relationship of the microstructurally
 486 characterised titanite grains with the grains that define the dominant age population (**Figure**
 487 **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 in 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 $\geq 210\mu\text{m}$ 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 = $208\mu\text{m}$, **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'Donnell, 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., 1989, Marshall and Gilligan., 1993, Marshall et al., 1998). Unambiguous micro and meso-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.

Acknowledgements

K.P. acknowledges a university of Portsmouth research studentship. Vale Ltd is gratefully acknowledged for access to underground facilities and drillcore material. Vale geologists Lisa Gibson, Rob Pelkey and Collin Mecke are thanked for the provided unpublished material, samples and feedback. Dr. Stuart Kearns (University of Bristol) is also thanked for the assistance during the collection of electron microprobe data. J.D acknowledges Higher Education Innovation Fund and Researcher Development Fund grant from the University of Portsmouth. ZAPLab support from an NSERC Discovery Grant to D.M. is gratefully acknowledged, as is assistance from I. Barker (UWO) with SEM-EBSD analyses.

References

Aleinikoff, J. N., Wintsch, R. P., Tollo, R. P., Unruh, D. M., Fanning, C. M., & Schmitz, M. D. (2007). Ages and origins of rocks of the Killingworth dome, south-central Connecticut:

642 Implications for the tectonic evolution of southern New England. *American Journal of*
643 *Science*, 307(1), 63–118. doi:10.2475/01.2007.04

644 Ames, D.E. and Farrow, C.E.G. (2007). Metallogeny of the Sudbury mining camp, Ontario, in
645 Goodfellow W.D., ed., Mineral deposits of Canada: A synthesis of major deposit-types,
646 district metallogeny, the evolution of geological provinces, and exploration methods:
647 Geological Association of Canada, Mineral Deposits Division, Special Publication no. 5, p.
648 329–350

649 Ames, D. E., Davidson, A., & Wodicka, N. (2008). Geology of the giant Sudbury polymetallic
650 mining camp, Ontario, Canda. *Economic Geology*, 103(5), 1057–1077.
651 <http://doi.org/10.2113/gsecongeo.103.5.1057>

652 Bailey, J., Lafrance, B., McDonald, A. M., Fedorowich, J. S., Kamo, S., & W.J. Davis., D. A. A.
653 (2004). Mazatzal–Labradorian-age (1.7–1.6 Ga) ductile deformation of the South Range
654 Sudbury impact structure at the Thayer Lindsley mine, Ontario. *Canadian Journal of Earth*
655 *Sciences* , 41 (12), 1491–1505. doi:10.1139/e04-098

656 Bailey, J., McDonald, A. M., Lafrance, B., & Fedorowich, J. S. (2006). Variations in Ni content
657 in sheared magmatic sulfide ore at the Thayer Lindsley Mine, Sudbury, Ontario. *Canadian*
658 *Mineralogist*, 44(5), 1063–1077. doi:10.2113/gscanmin.44.5.1063

659 Barnes, S.-J., & Lightfoot, P. C. (2005). Formation of magmatic nickel-sulfide ore deposits
660 and processes affecting their copper and platinum-group element contents. *Economic*
661 *Geology*, 179–213.

662 Bland, P. a., Howard, L. E., Prior, D. J., Wheeler, J., Hough, R. M., & Dyl, K. a. (2011). Earliest
663 rock fabric formed in the Solar System preserved in a chondrule rim. *Nature Geoscience*,
664 4(4), 244–247. <http://doi.org/10.1038/ngeo1120>

665 Blenkinsop, T. G. (2004). Orebody geometry in lode gold deposits from Zimbabwe:
666 Implications for fluid flow, deformation and mineralization. *Journal of Structural Geology*,
667 26(6-7), 1293–1301. doi:10.1016/j.jsg.2003.11.010

668 Card K. D., Gupta P. H., McGrath P. H., and Gant F. S. (1984). The Sudbury structure: its
669 regional geological and geophysical setting. In *The geology and ore deposits of the Sudbury*

670 structure, edited by Pye E. G., Naldrett A. J., and Giblin P. E. Special Publication 1. Toronto:
671 Ontario Geological Survey. pp. 25–43.

672 Card, K. D. (1990). A review of the Superior Province of the Canadian Shield, a product of
673 Archean accretion. *Precambrian Research*, 48(1-2), 99–156. doi:10.1016/0301-
674 9268(90)90059-Y

675 Cenki-Tok, B., Darling, J. R., Rolland, Y., Dhuime, B., & Storey, C. D. (2014). Direct dating of
676 mid-crustal shear zones with synkinematic allanite: new in situ U-Th-Pb geochronological
677 approaches applied to the Mont Blanc massif. *Terra Nova*, 26(1), 29–37.
678 doi:10.1111/ter.12066

679 Cherniak, D. J. (1993). Lead diffusion in titanite and preliminary results on the effects of
680 radiation damage on Pb transport. *Chemical Geology*, 110(1–3), 177–194.
681 [http://doi.org/10.1016/0009-2541\(93\)90253-F](http://doi.org/10.1016/0009-2541(93)90253-F)

682 Chew, D. M., Petrus, J. A., & Kamber, B. S. (2014). U-Pb LA-ICPMS dating using accessory
683 mineral standards with variable common Pb. *Chemical Geology*, 363, 185–199.
684 doi:10.1016/j.chemgeo.2013.11.006

685 Clark, C., Schmidt Mumm, A., & Faure, K. (2005). Timing and nature of fluid flow and
686 alteration during Mesoproterozoic shear zone formation, Olary domain, South Australia.
687 *Journal of Metamorphic Geology*, 23(3), 147–164. doi:10.1111/j.1525-1314.2005.00568.x

688 Craddock, J. P., & McKiernan, A. W. (2007). Tectonic implications of finite strain variations in
689 Baraboo-interval quartzites (ca. 1700 Ma), Mazatzal orogen, Wisconsin and Minnesota, USA.
690 *Precambrian Research*, 156(3-4), 175–194. doi:10.1016/j.precamres.2006.03.010

691 Cook, N.J., Halls, C., Boyle, A.P. (1993): Deformation and metamorphism of massive
692 sulphides at Sulitjelma, Norway. *Mineralogical Magazine*, 57, 67-81.

693 Czeck, D. M., & Ormand, C. J. (2007). Geometry and folding history of the Baraboo Syncline:
694 Implications for the Mazatzal Orogeny in the north-central U.S. *Precambrian Research*,
695 157(1-4), 203–213. doi:10.1016/j.precamres.2007.02.017

696 Dempster, T. J., Campanile, D., & Holness, M. B. (2006). Imprinted textures on apatite: A
 697 guide to paleoporosity and metamorphic recrystallization. *Geology*, 34(11), 897–900.
 698 <http://doi.org/10.1130/G22299A.1>

699 Dempster, T. J., & Macdonald, F. (2016). Controls on fluid movement in crustal lithologies:
 700 evidence from zircon in metaconglomerates from Shetland. *Geofluids*, 16(3), 507–517.
 701 <http://doi.org/10.1111/gfl.12172>

702 Duebendorfer, E. M., Williams, M. L., & Chamberlain, K. R. (2015). Case for a temporally and
 703 spatially expanded Mazatzal orogeny. *Lithosphere*, 7(6), L412.1. doi:10.1130/L412.1

704 Duuring, P., Bleeker, W., & Beresford, S. W. (2007). Structural modification of the komatiite-
 705 associated Harmony nickel sulfide deposit, Leinster, Western Australia. *Economic Geology*,
 706 102(2), 277–297. doi:10.2113/gsecongeo.102.2.277

707 Farrow CEG, Lightfoot PC (2002) Sudbury PGE Revisited: Toward an Integrated Model.
 708 Canadian Institute of Mining and Metallurgy Special Volume 54: 273- 297

709 Fleet, M. E., Barnett, R. L., & Morris, W. A. (1987). Prograde Metamorphism of the Sudbury
 710 Igneous Complex. *Canadian Mineralogist*, 25, 499–514.

711 Gibson, A.M., Lightfoot, P.C., Evans, T.C., (2010). Contrasting styles of Low Sulphide High
 712 Precious Metal Mineralization in the 148 and 109 FW zones: North and South Ranges of the
 713 Sudbury Igneous Complex, Ontario, Canada. In Jugo, P.J., Leshner, C.M., and Mungall, J.E.
 714 (Eds): Abstracts, 11th International Platinum Symposium, Sudbury, Ontario, Canada. OGS
 715 Miscellaneous Release Data 269.

716 Guillong, M., Meier, D.L., Allan, M.M., Heinrich, C.A., Yardley, B.W.D., (2008). Sills: a Matlab-
 717 based program for the reduction of laser ablation ICP-MS data of homogeneous materials
 718 and inclusions. *Laser Ablation-ICP-MS in the Earth Sciences: Current Practices and*
 719 *Outstanding Issues*, 328–333

720 Harlov, D. E., Wirth, R., & Förster, H. J. (2005). An experimental study of dissolution-
 721 reprecipitation in fluorapatite: Fluid infiltration and the formation of monazite.
 722 *Contributions to Mineralogy and Petrology*, 150(3), 268–286. doi:10.1007/s00410-005-0017-
 723 8

724 Harlov, D., Tropper, P., Seifert, W., Nijland, T., & Förster, H. J. (2006). Formation of Al-rich
 725 titanite (CaTiSiO₄O-CaAlSiO₄OH) reaction rims on ilmenite in metamorphic rocks as a
 726 function of fH₂O and fO₂. *Lithos*, 88(1-4), 72–84. doi:10.1016/j.lithos.2005.08.005

727 Heaman, L. M. (2009). The application of U-Pb geochronology to mafic, ultramafic and
 728 alkaline rocks: An evaluation of three mineral standards. *Chemical Geology*, 261(1-2), 42–51.
 729 doi:10.1016/j.chemgeo.2008.10.021

730 Jochum, K. P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Enzweiler, J. (2011).
 731 Determination of reference values for NIST SRM 610-617 glasses following ISO guidelines.
 732 *Geostandards and Geoanalytical Research*, 35(4), 397–429. doi:10.1111/j.1751-
 733 908X.2011.00120.x

734 Kirkland, C. L., Spaggiari, C. V., Johnson, T. E., Smithies, R. H., Danišík, M., Evans, N., ...
 735 McDonald, B. J. (2016). Grain size matters: Implications for element and isotopic mobility in
 736 titanite. *Precambrian Research*, 278, 283–302.
 737 <http://doi.org/10.1016/j.precamres.2016.03.002>

738 Krenn, E., Harlov, D. E., Finger, F., & Wunder, B. (2012). LREE-redistribution among
 739 fluorapatite, monazite, and allanite at high pressures and temperatures. *American*
 740 *Mineralogist*, 97(11-12), 1881–1890. doi:10.2138/am.2012.4005

741 Krogh, T.E., McNutt, R.H., and Davis, G.L. 1982. Two high precision U-Pb Zircon ages for the
 742 Sudbury Nickel Irruptive. *Canadian Journal of Earth Sciences*, 19, 723 – 728

743 Kylander-Clark, A. R. C., Hacker, B. R., & Cottle, J. M. (2013). Laser-ablation split-stream ICP
 744 petrochronology. *Chemical Geology*, 345, 99–112. doi:10.1016/j.chemgeo.2013.02.019

745 Leake, B. E., Woolley, A. R., Arps, C. E. S., Birch, W. D., Gilbert, C. M., Grice, J. D., ... Youzhi, G.
 746 (1997). Nomenclature of Amphiboles: Report of the Subcommittee of the International
 747 Commission on New Minerals and Mineral Names. *The Canadian Mineralogist*, 35, 219–246.

748 Lightfoot, P. G., Keays, R. R., Morrison, G. G., Bite, A., & Farrell, K. P. (1997). Geochemical
 749 relationships in the sudbury igneous complex: Origin of the main mass and offset dikes.
 750 *Economic Geology*, 92(3), 289–307. doi:10.2113/gsecongeo.92.3.289

751 Lightfoot, P. C., & Doherty, W. (2001). Chemical evolution and origin of nickel sulfide
752 mineralization in the sudbury igneous complex, Ontario, Canada. *Economic Geology*, 96(8),
753 1855–1875. doi:10.2113/gsecongeo.96.8.1855

754 Lightfoot, P. C., & Farrow, C. E. G. (2002). Geology, Geochemistry, and Mineralogy of the
755 Worthington Offset Dike: A Genetic Model for Offset Dike Mineralization in the Sudbury
756 Igneous Complex. *Economic Geology*, 97(7), 1419–1446. doi:10.2113/gsecongeo.97.7.1419

757 Lenauer, I., & Riller, U. (2012). Geometric consequences of ductile fabric development from
758 brittle shear faults in mafic melt sheets: Evidence from the Sudbury Igneous Complex,
759 Canada. *Journal of Structural Geology*, 35, 40–50. doi:10.1016/j.jsg.2011.11.012

760 Lucassen, F., Franz, G., Rhede, D., & Wirth, R. (2010). Ti-Al zoning of experimentally grown
761 titanite in the system CaO-Al₂O₃-TiO₂-SiO₂- NaCl-H₂O-(F): Evidence for small-scale fluid
762 heterogeneity. *American Mineralogist*, 95(10), 1365–1378. doi:10.2138/am.2010.3518

763 Marks, M. A. W., Wenzel, T., Whitehouse, M. J., Loose, M., Zack, T., Barth, M., ... Markl, G.
764 (2012). The volatile inventory (F, Cl, Br, S, C) of magmatic apatite: An integrated analytical
765 approach. *Chemical Geology*, 291, 241–255. doi:10.1016/j.chemgeo.2011.10.026

766 Marshall, B., & Gilligan, L. B. (1989). Durchbewegung structure, piercement cusps, and
767 piercement veins in massive sulfide deposits; formation and interpretation. *Economic*
768 *Geology*, 84(8), 2311–2319. doi:10.2113/gsecongeo.84.8.2311

769 Marshall, B., & Gilligan, L. B. (1993). Remobilization, syn-tectonic processes and massive
770 sulphide deposits. *Ore Geology Reviews*, 8(1), 39–64. [http://doi.org/10.1016/0169-](http://doi.org/10.1016/0169-1368(93)90027-V)
771 [1368\(93\)90027-V](http://doi.org/10.1016/0169-1368(93)90027-V)

772 Marshall, B., Vokes, F.M. & Larocque, A.C.L. 2000. Regional metamorphic remobilization:
773 upgrading and formation of ore deposits. In: SPRY, P.G., MARSHALL, B. & VOKES, F.M. (eds)
774 Metamorphosed and Metamorphogenic Ore Deposits. SEG Reviews in Economic Geology,
775 11, 19-38.

776 Mahan, K. H., Goncalves, P., Williams, M. L., & Jercinovic, M. J. (2006). Dating metamorphic
777 reactions and fluid flow: Application to exhumation of high-P granulites in a crustal-scale

778 shear zone, western Canadian Shield. *Journal of Metamorphic Geology*, 24(3), 193–217.
779 doi:10.1111/j.1525-1314.2006.00633.x

780 McQueen, K. G. (1987). Deformation and remobilization in some Western Australian nickel
781 ores. *Ore Geology Reviews*, 2(1-3), 269–286. doi:10.1016/0169-1368(87)90032-1

782 Menegon, L., Pennacchioni, G., & Spiess, R. (2008). Dissolution-precipitation creep of K-
783 feldspar in mid-crustal granite mylonites. *Journal of Structural Geology*, 30(5), 565–579.
784 <http://doi.org/10.1016/j.jsg.2008.02.001>

785 Mukai, H., Austrheim, H., Putnis, C. V., & Putnis, A. (2014). Textural evolution of plagioclase
786 feldspar across a shear zone: Implications for deformation mechanism and rock strength.
787 *Journal of Petrology*, 55(8), 1457–1477. <http://doi.org/10.1093/petrology/egu030>

788 Mukwakwami, J., Lafrance, B., & Leshner, C. M. (2012). Back-thrusting and overturning of the
789 southern margin of the 1.85Ga Sudbury Igneous Complex at the Garson mine, Sudbury,
790 Ontario. *Precambrian Research*, 196-197, 81–105. doi:10.1016/j.precamres.2011.10.020

791 Mukwakwami, J., Lafrance, B., Leshner, C. M., Tinkham, D., Rayner, N., & Ames, D. (2014).
792 Deformation, metamorphism, and mobilization of Ni–Cu–PGE sulfide ores at Garson Mine,
793 Sudbury. *Mineralium Deposita*, 49(2), 175–198. doi:10.1007/s00126-013-0479-y

794 Milkereit, B., & Green, A. (1992). Deep geometry of the Sudbury structure from seismic
795 reflection profiling. *Geology*, 20(9), 807–811. doi:10.1130/0091-7613(1992)020

796 O'Donnell, D., (1979). Creighton Mine orebody characteristics, Unpublished internal report to
797 INCO, 88P.

798 Parrish, R. R., Carr, S. D., & Parkinson, D. L. (1988). Eocene extensional tectonics and
799 geochronology of the Southern Omineca Belt, British Columbia and Washington. *Tectonics*,
800 7(2), 181–212. doi:10.1029/TC007i002p00181

801 Pan, Y., Fleet, M. E., & MacRae, N. D. (1993). Late alteration in titanite (CaTiSiO₅):
802 Redistribution and remobilization of rare earth elements and implications for U/Pb and
803 Th/Pb geochronology and nuclear waste disposal. *Geochimica et Cosmochimica Acta*, 57(2),
804 355–367. doi:10.1016/0016-7037(93)90437-

805 Paton, C., Hellstrom, J., Paul, B., Woodhead, J., & Hergt, J. (2011). Lolite: Freeware for the
806 visualisation and processing of mass spectrometric data. *Journal of Analytical Atomic*
807 *Spectrometry*, 26, 2508. doi:10.1039/c1ja10172b

808 Phillips, G. N., Groves, D. I., & Brown, I. J. (1987). Source requirements for the Golden Mile,
809 Kalgoorlie: significance to the metamorphic replacement model for Archean gold deposits.
810 *Canadian Journal of Earth Sciences*, 24(8), 1643–1651. doi:10.1139/e87-158

811 Pye E. G., Naldrett A. J., and Giblin P. E., editors. (1984). The geology and ore deposits of the
812 Sudbury structure. Special Publication 1. Toronto: Ontario Geological Survey. 603 p

813 Riller, U. (2005). Structural characteristics of the Sudbury impact structure, Canada: Impact-
814 induced versus orogenic deformation-A review. *Meteoritics & Planetary Science*, 40, 1723–
815 1740. doi:10.1111/j.1945-5100.2005.tb00140.x

816 Riller, U., Boutelier, D., Schrank, C., & Cruden, A. R. (2010). Role of kilometer-scale weak
817 circular heterogeneities on upper crustal deformation patterns: Evidence from scaled
818 analogue modeling and the Sudbury Basin, Canada. *Earth and Planetary Science Letters*,
819 297(3-4), 587–597. doi:10.1016/j.epsl.2010.07.009

820 Riller, U., Schwerdtner, W. M., Halls, H. C., & Card, K. D. (1999). Transpressive tectonism in
821 the eastern Penokean orogen, Canada consequences for Proterozoic crustal kinematics and
822 continental fragmentation. *Precambrian Research*, 93(1), 51–70. doi:10.1016/S0301-
823 9268(98)00097-7

824 Rousell, D. H., Fedorowich, J. S., & Dressler, B. O. (2003). Sudbury Breccia (Canada): A
825 product of the 1850 Ma Sudbury Event and host to footwall Cu-Ni-PGE deposits. *Earth-*
826 *Science Reviews*, 60(3-4), 147–174. doi:10.1016/S0012-8252(02)00091-0

827 Riller, U., & Schwerdtner, W. M. (1997). Mid-crustal deformation at the southern flank of
828 the Sudbury Basin, central Ontario, Canada. *Bulletin of the Geological Society of America*,
829 109(7), 841–854. doi:10.1130/0016-7606(1997)109<0841:MCDATS>2.3.CO;2

830 Romano, D., Holm, D. K., & Foland, K. A. (2000). Determining the extent and nature of
831 Mazatzal-related overprinting of the Penokean orogenic belt in the southern Lake Superior

832 region, north-central USA. *Precambrian Research*, 104(1-2), 25–46. doi:10.1016/S0301-
833 9268(00)00085-1

834 Rubatto, D., & Hermann, J. (2001). Exhumation as fast as subduction? *Geology*, 29(1), 3–6.
835 [http://doi.org/10.1130/0091-7613\(2001\)?029<0003:EAFAS>?2.0.CO](http://doi.org/10.1130/0091-7613(2001)?029<0003:EAFAS>?2.0.CO)

836 Santimano, T., & Riller, U. (2012). Revisiting thrusting, reverse faulting and transpression in
837 the southern Sudbury Basin, Ontario. *Precambrian Research*, 200-203, 74–81.
838 doi:10.1016/j.precamres.2012.01.012

839 Shanks, W. S., & Schwerdtner, W. M. (1991). Structural analysis of the central and
840 southwestern Sudbury Structure, Southern Province, Canadian Shield. *Canadian Journal of*
841 *Earth Sciences*, 28(3), 411–430. doi:10.1139/e91-037

842 Siddorn, J.P., and Hamm A., (2006). Review of Garson Mine phase 3 exploration program.
843 Unpublished SRK report for Vale, 53p.

844 Snelling, P.E., (2009). The influences of stress and structure on mining-induced seismicity in
845 Creighton Mine, Sudbury, Canada. MSc thesis. Queens university, Canada, 225p.

846 Snelling, P. E., Godin, L., & McKinnon, S. D. (2013). The role of geologic structure and stress
847 in triggering remote seismicity in Creighton Mine, Sudbury, Canada. *International Journal of*
848 *Rock Mechanics and Mining Sciences*, 58, 166–179. doi:10.1016/j.ijrmms.2012.10.005

849 Spear, F.S., (1993). Metamorphic phase equilibria and Pressure-Temperature-Time Paths.
850 Mineralogical Society of America Monograph, Washington

851 Spray, J. G. (1998). Localized shock- and friction-induced melting in response to
852 hypervelocity impact. *Geological Society, London, Special Publications*, 140(1), 195–204.
853 doi:10.1144/GSL.SP.1998.140.01.14

854 Spencer, K. J., Hacker, B. R., Kylander-Clark, A. R. C., Andersen, T. B., Cottle, J. M., Stearns,
855 M. A., Seward, G. G. E. (2013). Campaign-style titanite U-Pb dating by laser-ablation ICP:
856 Implications for crustal flow, phase transformations and titanite closure. *Chemical Geology*,
857 341, 84–101. doi:10.1016/j.chemgeo.2012.11.012

858 Stacey, J. S., & Kramers, J. D. (1975). Approximation of terrestrial lead isotope evolution by a
859 two-stage model. *Earth and Planetary Science Letters*, 26(2), 207–221. doi:10.1016/0012-
860 821X(75)90088-6

861 Stearns, M. A., Hacker, B. R., Ratschbacher, L., Lee, J., Cottle, J. M., & Kylander-Clark, A.
862 (2013). Synchronous oligocene-miocene metamorphism of the pamir and the north
863 himalaya driven by plate-scale dynamics. *Geology*, 41(10), 1071–1074.
864 doi:10.1130/G34451.1

865 Stearns, M. A., Hacker, B. R., Ratschbacher, L., Rutte, D., & Kylander-Clark, A. R. C. (2015).
866 Titanite petrochronology of the Pamir gneiss domes: Implications for middle to deep crust
867 exhumation and titanite closure to Pb and Zr diffusion. *Tectonics*, 34(4), 784–802.
868 doi:10.1002/2014TC003774

869 Storey, C. D., Brewer, T. S., & Parrish, R. R. (2004). Late-Proterozoic tectonics in northwest
870 Scotland: One contractional orogeny or several? *Precambrian Research*, 134(3-4), 227–247.
871 doi:10.1016/j.precamres.2004.06.004

872 Szentpeteri, K., 2009. Geology and mineralization of the proximal Worthington offset area in
873 the Sudbury igneous complex. Unpublished PhD thesis. Eotvos Lorand University, Hungary,
874 145p.

875 Tindle, A. G., & Webb, P. C. (1994). Probe-AMPH—A spreadsheet program to classify
876 microprobe-derived amphibole analyses. *Computers & Geosciences*, 20(7-8), 1201–1228.
877 doi:10.1016/0098-3004(94)90071-X

878 Thomson, M. L., Barnett, R. L., Fleet, M. E., & Kerrich, R. (1985). Metamorphic assemblages
879 in the South-Range norite and footwall mafic rocks near the Kirkwood mine, Sudbury,
880 Ontario. *Canadian Mineralogist*.

881 Verts, L. A., Chamberlain, K. R., & Frost, C. D. (1996). U-Pb sphene dating of metamorphism:
882 the importance of sphene growth in the contact aureole of the Red Mountain pluton,
883 Laramie Mountains, Wyoming. *Contributions to Mineralogy and Petrology*, 125(2–3), 186–
884 199. <http://doi.org/10.1007/s004100050215>

- 885 Villa, I. M. (1998). Isotopic closure. *Terra Nova*, 10(1), 42–47. <http://doi.org/10.1046/j.1365->
886 3121.1998.00156.x
- 887 Villa, I.M., & Williams, M.L. (2013). Geochronology of Metasomatic Events. In : Harlov, D. E.,
888 & Austrheim, H (Eds), *Metasomatism and the Chemical Transformation of Rock*. Berlin,
889 Heidelberg: Springer Berlin Heidelberg. doi:10.1007/978-3-642-28394-9
- 890 Wintsch, R. P., & Yi, K. (2002). Dissolution and replacement creep: A significant deformation
891 mechanism in mid-crustal rocks. *Journal of Structural Geology*, 24(6–7), 1179–1193.
892 [http://doi.org/10.1016/S0191-8141\(01\)00100-6](http://doi.org/10.1016/S0191-8141(01)00100-6)
- 893 Zenk, M., & Schulz, B. (2004). Zoned Ca-amphiboles and related P-T evolution in metabasites
894 from the classical Barrovian metamorphic zones in Scotland. *Mineralogical Magazine*,
895 68(October), 769–786. doi:10.1180/0026461046850218