Differentiated impact melt sheets may be a potential source of Hadean detrital zircon

Gavin G. Kenny¹, Martin J. Whitehouse², and Balz S. Kamber¹

¹Department of Geology, School of Natural Sciences, Trinity College Dublin, Dublin 2, Ireland

²Department of Geosciences, Swedish Museum of Natural History, 104 05 Stockholm, Sweden

ABSTRACT

Constraining the origin and history of very ancient detrital zircons has unique potential for furthering our knowledge of Earth's very early crust and Hadean geodynamics. Previous applications of the Ti-in-zircon thermometer to >4 Ga zircons have identified a population with relatively low crystallization temperatures ($T_{\text{zir}}^{\text{xtln}}$) of ~685 °C. This could possibly indicate wet minimum-melting conditions producing granitic melts, implying very different Hadean terrestrial geology from other rocky planets. Here we report the first comprehensive ion microprobe study of zircons from a transect through the differentiated Sudbury impact melt sheet. The new zircon Ti contents and corresponding $T_{\text{zir}}^{\text{xtln}}$ fully overlap with those of the Hadean zircon population. Previous studies, which measured Ti in impact melt sheet zircons did not find this wide range because they analyzed samples only from a restricted portion of the melt sheet and because they used laser ablation analyses that can overestimate true Ti content. It is important to note that internal differentiation of the impact melt is likely a prerequisite for the observed low $T_{\text{zir}}^{\text{xtln}}$ in zircons from the most evolved rocks. On Earth, melt sheet

differentiation is strongest in subaqueous impact basins. Thus, not all Hadean detrital zircon with low Ti necessarily formed during melting at plate boundaries but at least some could also have crystallized in melt sheets caused by intense meteorite bombardment of the early, hydrosphere-covered protocrust.

INTRODUCTION

In the absence of widespread rocks older than 4 Ga, Hadean detrital zircons up to ca. 4.4 Ga (Valley et al., 2014a), found in Archean metasedimentary rocks, constitute the only direct evidence of geodynamics on early Earth. The first application of the newly discovered thermometer based on the titanium (Ti) content in zircon was thus to this early detrital zircon population. Watson and Harrison (2005) found that the >4.0 Ga population displays a sharp peak in Ti contents of ~5 ppm, corresponding to a Ti-in-zircon crystallization temperature ($T_{\text{zir}}^{\text{xtln}}$) of ~685 °C. Further Ti-in-zircon analyses of Hadean zircons (e.g., Harrison and Schmitt, 2007; Trail et al., 2007; Fu et al., 2008) and recalibration of the thermometer (Ferry and Watson, 2007) have not greatly affected this distribution. Watson and Harrison (2005) argued that the sharp peak in Ti contents, and corresponding $T_{\text{zir}}^{\text{xtln}}$, represents a regulated melting mechanism reoccurring throughout the Hadean and that together with apparently ‘felsic’ mineral inclusion assemblages (Maas et al., 1992; Cavosie et al., 2004; Hopkins et al., 2008; Bell et al., 2015) this suggests zircon crystallization in granitic melts *sensu stricto* (s.s.) of crustal anatectic origin. This was further argued to imply extremely early plate tectonic interactions similar to those in operation today. Alternatively, unrelated to zircon Ti contents and inclusion assemblages, others have argued for a granite *sensu lato* origin for the Hadean zircons. Bouvier et al. (2012) noted that early zircon Li contents and $\delta^7\text{Li}$ values are

distinct from those of zircons crystallized from mantle-derived melts, but similar to those of Archean tonalitic granitoids, suggesting growth in “proto-continental crust”.

Regarding the *s.s.* granite origin hypothesis, a number of studies have conclusively shown that the modal compositions of inclusions in zircon are not representative of those in the whole rock (e.g., Nutman and Hiess, 2009; Jennings et al., 2011). Most notably, Darling et al. (2009) showed that zircons which crystallized in mafic melts may display ‘felsic’ inclusion assemblages containing quartz, biotite and alkali feldspar due to the often relatively late crystallization of the mineral in residual liquids. While the relatively high abundance of muscovite in Hadean zircons (Hopkins et al., 2008; Bell et al., 2015) deserves further research, this has never been shown as indicative of a granitic host rock. In their comprehensive study of the Ti-in-zircon thermometer, Fu et al. (2008) showed that the $T_{\text{zir}}^{\text{xtln}}$ of Hadean zircon is not unique to felsic rocks by documenting a number of mafic rock suites with $T_{\text{zir}}^{\text{xtln}}$ identical to the Hadean grains.

In light of these findings and the clear importance of meteorite bombardment on early Earth, two studies (Darling et al., 2009; Wielicki et al., 2012) have attempted to test whether Hadean zircons could have crystallized in impact melt sheets by using younger impact analogues and modeling. These studies have the limitations that Darling et al. (2009) measured Ti content not by ion microprobe but by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICPMS); and that Wielicki et al. (2012) sampled a restricted portion of the Sudbury melt sheet, missing all the more evolved rock types. Here, we present a new, more comprehensive ion microprobe investigation of zircon covering the full stratigraphy of the differentiated Sudbury impact melt sheet in an

attempt to more thoroughly test the hypothesis that differentiated impact melt sheets may have been a major source of the Hadean detrital zircon population.

SAMPLES

The 2.5–3.0-km-thick impact melt sheet at Sudbury cooled over ~250,000–500,000 yr (Ivanov and Deutsch, 1999; Davis, 2008), allowing the complex to differentiate into a mafic base (norite), intermediate middle layer (quartz gabbro) and more felsic top (granophyre).

Zircons were separated from 12 samples (five norite, one quartz gabbro and six granophyre) from the southern limb of the impact melt sheet, collected along the transect previously studied by Lightfoot and Zotov (2005) and Darling et al. (2009), and one sample (norite) from the northern limb for comparison (Fig. 1). The zircons are generally euhedral and quite equant with long axes <250 μm , and vary from entirely cathodoluminescence (CL)-dark to displaying simple oscillatory zoning, consistent with previous observations (Fig. DR1 in GSA Data Repository¹) (Darling et al., 2009; Wielicki et al., 2012).

ANALYTICAL METHODS

Titanium concentrations in zircon were determined by secondary ion mass spectrometry (SIMS) on the CAMECA IMS1280 ion microprobe at the Swedish Museum of Natural History, Stockholm. NIST610 glass (434 ppm Ti) was used as the calibration reference material (RM) with 91500 (5.2 ± 1.5 ppm Ti; 1 standard deviation [SD]; $n = 15$; Fu et al., 2008) and Temora-2 (10.2 ± 3.6 ppm Ti; 1 SD; $n = 16$; Fu et al., 2008) analyzed as zircon quality control materials (QCM). The zircons were later re-polished to remove the SIMS pits and re-analyzed for Ti simultaneously with a selection of rare earth

elements (REE) by LA-ICPMS at Trinity College Dublin. NIST610 was again used as the RM and fresh chips of 91500 and Temora-2 were analyzed as QCM. In a separate analytical session all grains were U-Pb age dated by LA-ICPMS to confirm that they date to the established 1.85 Ga age of the impact melt sheet (Davis, 2008). Full analytical methods can be found in the Data Repository.

RESULTS

$T_{\text{zir}}^{\text{xtln}}$ was calculated from measured Ti contents using the calibration of Ferry and Watson (2007):

$$\log(\text{ppm Ti}) = (5.711 \pm 0.072) - \frac{4800 \pm 86}{T(\text{K})} - \log(a\text{SiO}_2) + \log(a\text{TiO}_2). \quad (1)$$

The exact geological significance of the calculated $T_{\text{zir}}^{\text{xtln}}$ is uncertain, given the effects of variably reduced $a\text{TiO}_2$ or $a\text{SiO}_2$, variable pressure, possible deviations from Henry's Law, and subsolidus Ti exchange (Fu et al., 2008). Corrections for reduced $a\text{TiO}_2$ or $a\text{SiO}_2$, and variable pressure are generally not applied to the Hadean detrital zircons due to lacking geological context (although many grains do contain quartz inclusions, buffering $a\text{SiO}_2$ to 1 at the time of crystallization, and there are rare instances of rutile inclusions buffering $a\text{TiO}_2$ to 1; Bell et al., 2015). Consequently, because the ultimate goal of our study was to compare our measured Ti contents (and corresponding $T_{\text{zir}}^{\text{xtln}}$) in melt sheet zircons with those of the Hadean zircons, we applied the same assumptions to our grains and did not attempt to correct for reduced $a\text{TiO}_2$ or $a\text{SiO}_2$, and pressure. Thus, calculated $T_{\text{zir}}^{\text{xtln}}$ are not intended to accurately determine crystallization in the melt sheet but for comparison with the Hadean zircon data. However, we note that $a\text{SiO}_2$ would be constrained to 1 in all studied samples because of consistent presence of magmatic quartz, and $a\text{TiO}_2$ would be constrained to 1 in the quartz gabbro unit due to

the presence of rutile (Fig. DR2). In the remainder of the melt sheet titanite and ilmenite occur, constraining $a\text{TiO}_2$ to $> \sim 0.6$ meaning that $T_{\text{zir}}^{\text{xtln}}$ may be underestimated by up to $\sim 60\text{--}70$ °C.

Ti-in-Zircon Thermometry by SIMS

Both QCM analyzed during the SIMS analytical session returned Ti contents in agreement with previously published values (see methods above). Ti concentrations in 91500 were 5.0 ± 0.2 ppm ($n = 14$; all standard deviations are reported at 1 SD) while Temora-2 yielded 10.7 ± 2.0 ppm ($n = 9$). Most new SIMS measurements of zircon from the impact melt sheet fall within the range of 1–90 ppm, corresponding to crystallization temperatures of $\sim 600\text{--}1000$ °C. Outlying higher Ti values up to >6000 ppm are generally associated with Ti-rich mineral inclusions, visible in CL. Individual samples display much tighter ranges of values and the mean Ti concentration measured in each sample generally decreases with increasing stratigraphic height (Fig. 2), as previously noted by Darling et al. (2009) in their LA-ICPMS data set. The notable exceptions are the two stratigraphically highest samples (14GGK131 and 14GGK132) which display anomalously high Ti values (42.0 ± 16.8 ppm [$n = 12$] and 50.7 ± 16.7 ppm [$n = 5$], respectively). Given the fact that these grains are extremely altered in CL (Fig. DR1) and invariably enriched in light REE (LREE; Fig. DR3) we confidently attribute their anomalous Ti concentrations to post-crystallization alteration. Excluding these samples, mean Ti contents vary from 13.1 ± 3.9 ppm ($n = 14$), corresponding to a $T_{\text{zir}}^{\text{xtln}}$ of 768 ± 31 °C, in the stratigraphically lowest sample (14GGK107) through to 2.0 ± 0.6 ppm ($n = 9$), corresponding to 612 ± 21 °C, in the highest remaining sample (14GGK129). The single sample analyzed from the North Range of the Sudbury crater (GSM104) has a

mean Ti concentration of 6.2 ± 2.9 ppm ($n = 13$), corresponding to 697 ± 32 °C. The granophyre has a mean value of 678 ± 48 °C ($n = 53$) while the norite has a mean of 742 ± 47 °C ($n = 56$).

Ti-in-Zircon Thermometry by LA-ICPMS

After the ion microprobe analyses, Ti was also measured by LA-ICPMS to provide a comparison with the published data of Darling et al. (2009), which were noted to be higher than the new ion microprobe data and previous such data (Wielicki et al., 2012). Both QCM analyzed during the LA-ICPMS analytical session returned Ti contents in agreement with previously published values: 91500 yielded 5.2 ± 0.7 ppm ($n = 24$) while Temora-2 yielded 10.8 ± 2.0 ppm ($n = 26$). However, 78% of LA-ICPMS measurements of Ti in the unknown zircons from the Sudbury transect produced Ti values that were distinguishably higher (at 1 SD analytical uncertainty) than the corresponding SIMS result.

Rare Earth Element Compositions

Most analyzed zircons from the melt sheet display REE patterns typical of igneous crustal zircon, with a smooth trend of increasing abundance from LREE to heavy REE (HREE) apart from Ce and Eu anomalies (Hoskin and Schaltegger, 2003). However, all analyzed grains from the two stratigraphically highest samples (14GGK131 and 14GGK132) consistently show extreme LREE-enrichment, here interpreted as pervasive alteration. Consequently the relatively elevated Ti contents of these grains (Fig. 2) are not considered representative of the original magmatic Ti composition and are not considered further.

DISCUSSION

Our new ion microprobe data show that differentiation of a large body of impact melt can produce zircons with magmatic Ti contents fully overlapping the range observed in the Hadean detrital zircon population. The impact melt sheet at Sudbury displays Ti contents in unaltered zircon ranging from 1.2 ± 0.1 ppm to *c.* 20 ppm, corresponding to apparent $T_{\text{zir}}^{\text{xtln}}$ values of 578 ± 17 °C to ~ 815 °C, compared to the Hadean detrital zircon population which has reported Ti contents varying from 1.3 ppm (Trail et al., 2007) to over 20 ppm (Watson and Harrison, 2005; Fu et al., 2008), with most Ti contents greater than ~ 20 ppm associated with cracks or other crystal imperfections (Harrison and Schmitt, 2007).

Two previous studies of impact melt sheet zircons did not find the same Ti contents and thus reached the opposite conclusion to our study: namely that impact melt sheets were unlikely major sources of Hadean zircon on the basis of Ti contents. This apparent contradiction has two main reasons. Firstly, we sampled much higher into the differentiated melt sheet than the earlier ion microprobe study by Wielicki et al. (2012). These authors reported average Ti contents of 10.0 ± 3.7 and 11.7 ± 7.2 ppm for two samples of the lowermost norite unit. While our new data for this unit agree, Wielicki et al. (2012) did not discover the clear trend of upward decrease in zircon Ti content and lower apparent $T_{\text{zir}}^{\text{xtln}}$.

The second reason is that Darling et al. (2009), who studied ten samples spanning a much greater range of stratigraphy than Wielicki et al. (2012), used LA-ICPMS for their analysis. The LA-ICPMS technique yielded apparent Ti contents of no less than 6.5 ppm, corresponding to $T_{\text{zir}}^{\text{xtln}}$ of ~ 700 °C, in contrast to our SIMS values as low as 1.2

ppm (~ 580 °C). The empirical mismatch between LA-ICPMS and ion microprobe Ti content in unknown zircons at Sudbury is also seen in our new comparative data and demands an explanation. Wielicki et al. (2012) hypothesized that the much larger volume of material sampled by LA-ICPMS might increase the likelihood of encountering extraneous Ti hosted in cracks or inclusions. However, this proposal does not adequately explain all observations of LA-ICPMS data sets, including Ti changing with stratigraphic height or with growth zoning within single crystals. It also does not fully explain why LA-ICPMS yields accurate data for QCM 91500 and Temora-2.

In an effort to offer a more consistent explanation for the elevated Ti content by LA-ICPMS, we investigated all the Ti signals of our LA-ICPMS analyses. When plotted as the Ti/Zr intensity ratio, a consistent picture emerged. In RM zircon there is no resolvable downhole fractionation (Fig. DR4). Relatively constant down-hole Ti/Zr traces also characterize sample zircons for which ion microprobe and LA-ICPMS Ti data agree. By contrast, sample zircons for which LA-ICPMS yielded higher apparent Ti contents than ion microprobe all showed a down-hole increase in Ti/Zr intensity ratio. This suggests that the higher Ti values might be artifacts of down-hole elemental fractionation in less-crystalline unknown zircons but a full physical explanation for the observed pattern is beyond the scope of this contribution. We stress that the study of Darling et al. (2009) was undertaken with entirely different LA-ICPMS instrumentation and protocol and we cannot speculate whether down-hole fractionation also affected their analyses. Regardless, until this issue is resolved, terrestrial analogue studies for Hadean zircon need to use ion microprobe Ti data.

The crystallized Sudbury impact melt sheet is not a perfect analogue for Hadean impact melt bodies because it has a dioritic bulk composition, whereas planetary protocrusts are envisaged to be more mafic. However, petrological modeling suggests that significant volumes of intermediate-felsic melt can form from initially basaltic impact melt (Grieve et al., 2006), thus producing a wide range of zircon crystallization temperatures and Ti contents. Importantly, at Sudbury the impact melt is overlain by a 1.5-km-thick complex series of breccias and tuffs, produced by repeated explosive interaction of impact melt with water (Grieve et al., 2010). This deposit provided the melt sheet with sufficient insulation to cool slowly over *c.* 250,000–500,000 yr (Ivanov and Deutsch, 1999; Davis, 2008) and differentiate, resulting in the wide range of Ti contents and $T_{\text{zir}}^{\text{xtln}}$ observed in this study. This suggests that a hydrosphere may be necessary to produce a wide range of relatively low $T_{\text{zir}}^{\text{xtln}}$ in impact melt sheets. This is consistent with other evidence for the early existence of the terrestrial hydrosphere (e.g., Valley et al., 2002) as well as the lack of magmatic differentiation in large lunar impact melt sheets (e.g., the Orientale basin; Spudis et al., 2014) and thus higher Ti contents in lunar zircons (Valley et al., 2014b).

In the norite unit at Sudbury, $T_{\text{zir}}^{\text{xtln}}$ obtained by ion microprobe is ~ 100 °C higher than the zircon saturation model temperature, $T_{\text{zir}}^{\text{xtln}}$, (Watson and Harrison, 1983) at ~ 650 °C (Lightfoot and Zotov, 2005; Darling et al., 2009). This is typical of the offset observed in many rocks (Harrison et al., 2007). However, in the granophyre unit the calculated $T_{\text{zir}}^{\text{xtln}}$ of ~ 680 °C is over 150 °C lower than the $T_{\text{zir}}^{\text{xtln}}$ of ~ 850 °C (Lightfoot and Zotov, 2005; Darling et al., 2009). Darling et al. (2009) first noticed this offset and suggested that the composition of the granophyre could be outside the experimentally calibrated

range of Zr saturation studies (Watson and Harrison, 1983). Further work is clearly needed to explain the empirical finding that $T_{\text{zir}}^{\text{xtln}}$ can be over 150 °C lower than $T_{\text{zir}}^{\text{sat}}$ in the late stage felsic melts of a differentiated impact melt sheet, despite early-cooling mafic melt following the expected trend of $T_{\text{zir}}^{\text{xtln}} > T_{\text{zir}}^{\text{sat}}$. In light of this, the assumption that $T_{\text{zir}}^{\text{xtln}} = T_{\text{zir}}^{\text{sat}} + 50$ °C in the models of Wielicki et al. (2012), and Wielicki and Harrison (2015), may not be justified and their findings of relatively high model $T_{\text{zir}}^{\text{xtln}}$ for impact melts derived from Archean crust (~783 °C) may be based on unsubstantiated assumptions.

Our study shows that impact melt sheets cannot be ruled out as a possible source of the Hadean zircon population on the basis of their Ti contents (Fig. 3). Given the detrital nature of the Hadean zircon population, it is almost certainly not representative of the true distribution of zircons in the Hadean crust (Nebel et al., 2014). The dominant low- $T_{\text{zir}}^{\text{xtln}}$ population may be a result of preferential selection of certain grains during sedimentary transport or preferential sourcing from a limited provenance area. Our findings are consistent with the latest bombardment model of the Hadean Earth (Marchi et al., 2014) in which the age distribution of Hadean zircons matches the modeled production of impact-generated melt on early Earth.

Titanium contents, and corresponding $T_{\text{zir}}^{\text{xtln}}$, in the Hadean zircon population may not uniquely require wet, minimum-melting conditions on the early Earth and the implied plate tectonic interactions, but may also have been produced in melt sheets caused by the intense meteorite bombardment of an early, hydrosphere-covered protocrust.

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FIGURES

Figure 1. Map of sampling locations in the Sudbury impact melt sheet (Canada). Location of sample GSM104 from the North Range is shown in inset map. Lakes are shown in white. Maps modified from Ames et al. (2005).

Figure 2. Ti-in-zircon crystallization temperature ($T_{\text{zir}}^{\text{xtln}}$) for Ti content measured by secondary ion mass spectrometry. Average error of 13 °C (1 SD) includes uncertainty introduced when calculating Ti-in-zircon crystallization temperature from Ti content. Outliers, shown in gray, were excluded when calculating sample means, which are shown by open symbols. Elevated Ti contents of uppermost two samples are related to alteration (see text). Nor.—norite; Q.G—quartz gabbro; Gran—granophyre; alt. —altered.

Figure 3. Comparison of Ti (and Ti-in-zircon crystallization temperature, T_{zir}^{xtln}) distribution in the Hadean zircon population with that of melt sheet zircons at Sudbury. Curves represent all analyses and not grain averages. Analyses with Ti >100 ppm have been excluded. The following numbers refer to: number of analyses/number of grains analyzed/number of samples. Hadean data compiled from Fu et al. (2008), Harrison and Schmitt (2007), Trail et al. (2007), and Watson and Harrison (2005): 286/134/34; Sudbury transect (this study) 124/124/10; Sudbury granophyre only (this study) 54/54/4; Sudbury samples (Wielicki et al., 2012) 26/26/2; Sudbury transect (Darling et al., 2009) 144/120/10. All data obtained by ion microprobe except Darling et al. (2009) which is LA-ICPMS data. Kernel density estimates (KDE) were produced in MATLAB using the free software package of Botev et al. (2010) which implements an automatic bandwidth selection method.

¹GSA Data Repository item 2016143, full analytical methods, Figure DR1 (CL images of melt sheet zircons), Figure DR2 (images of Ti-bearing phases), Figure DR3 (zircon REE diagrams), Figure DR4 (variation in Ti/Zr during LA-ICPMS analyses), and Table DR1 (Ti and REE data), is available online at www.geosociety.org/pubs/ft2016.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

Text DR2. Full analytical methods.

Following CL imaging, Ti concentrations in zircon were determined by secondary ion mass spectrometry (SIMS) on the CAMECA IMS1280 large geometry ion microprobe at the Swedish Museum of Natural History. Ti was measured on the ^{49}Ti peak due to Zr^{2+} interferences on ^{46}Ti , ^{47}Ti and ^{48}Ti and possible interferences of ^{50}Cr and ^{50}V on ^{50}Ti , although these are probably minimal (Coogan and Hinton, 2006). An O_2^- primary beam of *c.* 4.5 nA was used to sample a *c.* 15 μm spot. Sputtered secondary ions were admitted to the mass spectrometer via high transmission transfer ion optics and measured in peak-hopping mode in either a Faraday detector (^{28}Si) or low-noise, ion-counting electron multiplier (^{30}Si and ^{49}Ti) at a mass resolution ($M/\Delta M$) of 3000. The ^{28}Si signal was used only for beam centering at the start of the analysis, following a pre-sputter to remove the Au coating. NIST610 glass (434 ± 14.7 ppm Ti; 1 standard deviation [SD]; (Pearce et al., 1997)) was used as the calibration reference material (RM) with 91500 (5.2 ± 1.5 ppm Ti; 1SD; $n=15$; (Fu et al., 2008)) and Temora-2 (10.2 ± 3.6 ppm Ti; 1SD; $n=16$; (Fu et al., 2008)) analyzed as quality control materials (QCM). In order to account for matrix differences between NIST standard glass, used as the RM, and zircon previous workers have applied correction factors to their zircon results – e.g. Fu et al. (2008) applied a correction factor of 1.16 to all of their zircon Ti measurements, based on their observation of a 16 % difference in “relative sensitivity factor” (RSF) between NIST and zircon. In contrast, by energy filtering the ^{30}Si and ^{49}Ti species (at -90 eV using a 30 eV bandpass), we here obtained perfectly accurate results for the zircon QCM 91500 and Temora-2 which are indistinguishable from previously published values, including the final, corrected, values of Fu et al. (2008), without the need for any post-analysis correction. Following SIMS analysis, the zircons were then polished down approximately 3-4 μm to remove the SIMS analysis pits. Ti was then measured simultaneously with a selection of rare earth elements (REE) were then measured by LA-ICPMS using a Photon Machines Analyte Excite 193 nm ArF laser coupled to a Thermo Scientific iCAP Qc at Trinity College Dublin. NIST610 was again used as the RM and fresh chips of 91500 and Temora-2 were analyzed as QCM. Zr was used as an internal standard. In a separate analytical session all grains were U-Pb age dated by LA-ICPMS to confirm they date to the established 1.85 Ga age of the impact melt sheet (Davis, 2008) and are not inherited. A 24 μm -diameter circular spot was used for all LA-ICPMS analyses.

Additional references

Pearce, N. J. G., Perkins, W. T., Westgate, J. A., Gorton, M. P., Jackson, S. E., Neal, C. R., and Chenery, S. P., 1997, A Compilation of New and Published Major and Trace Element Data for NIST SRM 610 and NIST SRM 612 Glass Reference Materials: *Geostandards Newsletter*, v. 21, no. 1, p. 115-144.

Figure DR1. Example CL images of zircon from the Sudbury melt sheet. A: A CL-dark zircon from the norite. **B:** A zircon from the granophyre displaying fine igneous growth zoning. **C:** A zircon from the granophyre displaying subtle igneous growth zoning close to its perimeter. **D:** An extremely altered zircon from close to the top of the melt sheet. All scale bars 50 μm.

Figure DR2. Examples of Ti-bearing phases observed in the Sudbury melt sheet.
A: An example of Ti-bearing titanite with its distinctive pyramidal form in the Granophyre unit. Image taken in plane polarized light. **B:** An example of rutile found in mineral separates from the Quartz Gabbro. **C:** Scanning Electron Microscopy image of location selected for qualitative energy-dispersive X-ray analysis (EDS) on grain shown in B. **D.** EDS energy spectrum for analysis location shown in C. Ti and O peaks confirm the presence of a Ti-oxide in the Sudbury melt sheet. The C peak is due to carbon coating of the sample to prevent electron charging. All scale bars 50 μm .

Figure DR3. Chondrite-normalized abundances of REE in Sudbury melt sheet zircons. Normalization uses the chondrite values of Anders and Grevesse (1989).

Elements are spaced according to their effective ionic radii in eightfold coordination (Shannon, 1976), indicated in picometres on the upper x-axis. Blue: norite; green: quartz gabbro; red: granophyre.

Anders, E., and Grevesse, N., 1989, Abundances of the elements: Meteoritic and solar: *Geochimica et Cosmochimica Acta*, v. 53, no. 1, p. 197-214.

Shannon, R. D., 1976, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides: *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography*, v. 32, p. 751-767.

Figure DR4. Downhole variation in Ti/Zr ratio during laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) analyses of Ti in zircon. Traces represent the five period moving average of the geometric mean of background-corrected signal ratios. Note that the Y-axis represents ablation time and cannot be strictly equated with depth, as ablation progresses more effectively in zircon of lower crystallinity. **A:** Quality control material (QCM) standard zircons 91500 (mean of $n=24$ analyses) and Temora-2 ($n=26$) show no appreciable Ti/Zr fractionation with ablation progress. This is consistent with the accurate measurement of Ti in these natural standards by LA-ICPMS, yielding results indistinguishable from SIMS. **B:** Comparative down-hole evolution of Ti/Zr in three sample zircons shows two contrasting types of behavior. First, unknown zircons in which Ti measured by LA-ICPMS was distinguishably higher (at 1 SD analytical uncertainty) than Ti measured by SIMS consistently show consistent trends of increasing Ti/Zr ratios down-hole. This is illustrated with samples 14GGK110 ($n=12$) and GSM073 ($n=17$). In the sample 14GGK110, for example, all apparent Ti concentrations by LA-ICPMS were distinguishably higher than the corresponding SIMS analysis. Second, for the samples in which Ti concentrations by LA-ICPMS and SIMS are generally in better agreement, there is no clear down-hole Ti/Zr increase. This is shown for sample 14GGK118 ($n=12$; excluding one outlier).

The inspection of down-hole Ti/Zr signals suggests that the over-estimation of Ti content in some sample zircons analyzed in this study is related to more efficient transport and ionization of Ti with increasing pit depth compared to the calibration and quality control zircons. This contrasts with the proposal of Wielicki et al. (2011) who attributed the offset between SIMS and LA-ICPMS to the larger sampling volume of LA-ICPMS, thereby enhancing the probability of encountering discrete zones of extraneously high Ti.

Down-hole elemental fractionation is widely recognized as one of the most significant difficulties associated with LA-ICPMS of zircon, particularly in U/Pb dating (e.g. Allen and Campbell, 2012; Marillo-Sialer et al., 2014). A factor that contributes to this problem and distinguishes zircon from many other silicates, is the alpha-dose-induced lattice damage, which in many sample zircons is much higher than in standard zircons. As a result of these “matrix effects”, different zircons ablate at different rates, resulting in different pit depths and concomitant different elemental behavior over the course of the ablation. It remains to be addressed to which extent the apparent down-hole inter-element fractionation is related to the difficulty of transporting aerosols from the pit to the plasma and/or to the particle size distribution of ablated zircon, and/or the efficiency with which different elements are ionized from particles produced from zircon of different crystallinity.

Regardless, in the present dataset, it is clear that the over-estimation of Ti concentration in some LA-ICPMS analyses can be attributed to the uncorrected for down-hole increase in Ti/Zr ratio. This is consistent with a number of observations, including: 1) LA-ICPMS analyses of Ti in QCM standard zircons (such as 91500 and Temora-2) return values in agreement with published ion microprobe data (as standard zircons have accumulated relatively low alpha-dose-induced lattice damage, resulting in predictable ablation and no fractionation between Ti and Zr); 2) multiple analyses on single unknown zircons by LA-ICPMS may still show systematic variation from core to rim (this would not be expected if higher Ti values were a result of encountering extraneous Ti); 3) LA-ICPMS studies are likely to still pick up real stratigraphic variation in zircon Ti content, despite potentially being offset to higher values than would be measured by SIMS. This final point is significant as it is one of the reasons that LA-ICPMS studies of Ti in zircon should not be dismissed as inherently problematic. However, caution should clearly be applied when comparing LA-ICPMS and SIMS data for Ti concentrations in zircon.

Additional references

- Allen, C. M., and Campbell, I. H., 2012, Identification and elimination of a matrix-induced systematic error in LA-ICP-MS $^{206}\text{Pb}/^{238}\text{U}$ dating of zircon: *Chemical Geology*, v. 332–333, p. 157-165.
- Marillo-Sialer, E., Woodhead, J., Hergt, J., Greig, A., Guillong, M., Gleadow, A., Evans, N., and Paton, C., 2014, The zircon 'matrix effect': evidence for an ablation rate control on the accuracy of U-Pb age determinations by LA-ICP-MS: *Journal of Analytical Atomic Spectrometry*, v. 29, no. 6, p. 981-989.

2016143 Table DRL1 Ti and REE data

Sample/ Spot	unit	Easting* *NAD83 UTM zone 17N	Northing* Ti (ppm)	SIMS ± 1 SD	F-W 2007 Temp (degC) ± 1 SD	LA-ICPMS Ti (ppm) ± 1 SD	F-W 2007 Temp (degC) ± 1 SD	Normalized (Anders and Greesse 1989)												
								La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Er	Yb			
484184	Norite	5147468	12.80	0.35	769	13	7.20	0.70	716	14	5.20	158	8	13	47	27	202	1030	4110	11015
484184	Norite	5147468	1764.52	31.36	1675	34	2780.00	265.00	1844	55	108.65	275	138	210	426	209	696	1351	2876	4985
484184	Norite	5147468	6.70	0.45	710	13	21.40	2.25	823	18	234.34	403	246	334	462	677	570	2366	4474	
484184	Norite	5147468	180.51	4.95	1116	20	332.00	13.50	1232	23	275.24	565	618	913	1557	2766	1775	1430	2253	4406
484165	Quartz Gabbro	5148518	29.96	0.88	860	14	18.00	2.15	804	18	45.16	220	59	82	247	80	789	2320	6010	12000
484165	Quartz Gabbro	5148518	6.06	0.18	701	12	7.30	0.85	717	15	16.83	75	29	48	180	51	662	1768	3883	5483
484165	Quartz Gabbro	5148518	45.41	0.91	911	15	20.80	1.45	820	15	16.83	224	19	42	222	31	878	2892	6614	10492
484165	Quartz Gabbro	5148518	12.66	0.35	768	13	74.20	3.50	977	18	5496.38	3282	3221	2608	1475	879	1043	1508	3109	4837
484165	Quartz Gabbro	5148518	9.77	0.27	744	12	13.20	0.65	773	13	2.55	24	10	27	109	30	358	861	1919	2935
484165	Quartz Gabbro	5148518	6.79	0.21	711	12	19.30	2.55	811	19	323.82	288	186	228	355	104	987	2505	5444	8123
484165	Quartz Gabbro	5148518	7.30	0.20	717	12	18.60	2.80	808	21	6.60	7	3	7	5	31	111	319	680	1035
484165	Quartz Gabbro	5148518	8.84	0.44	734	13	6.80	0.65	711	14	3.20	110	8	14	71	10	311	1084	2763	4548
484165	Quartz Gabbro	5148518	2.64	0.11	634	11	5.90	1.10	698	19	21.69	91	49	66	80	64	149	353	829	1532
484165	Quartz Gabbro	5148518	25.21	1.78	841	16	14.20	1.25	780	15	64.34	183	135	128	199	105	215	470	1171	2609
484165	Quartz Gabbro	5148518	4.12	0.14	669	11	68.00	11.50	964	28	11.29	109	27	41	132	93	412	1265	2889	5108
484265	Granophyre	5149033	6.56	0.19	708	12	9.60	0.55	742	13	0.13	24	3	11	59	10	203	548	1347	2222
484265	Granophyre	5149033	7.06	0.20	714	12	7.90	0.70	724	14	3.20	32	8	24	101	21	342	911	1970	3138
484265	Granophyre	5149033	8.47	0.24	730	12	9.50	0.55	741	13	0.29	24	8	27	114	26	374	914	2014	3065
484265	Granophyre	5149033	8.39	0.22	729	12	8.90	0.80	735	14	1.31	25	9	28	120	25	371	887	2020	2948
484265	Granophyre	5149033	10.48	0.48	750	13	11.70	0.70	761	14	26.84	48	30	44	115	26	346	873	1951	3028
484265	Granophyre	5149033	8.80	0.23	734	12	9.40	0.65	740	14	15.76	40	23	40	122	26	393	968	2115	3243
484265	Granophyre	5149033	10.02	0.25	746	12	36.40	2.60	884	17	80.95	90	56	55	90	20	269	661	1485	2388
484265	Granophyre	5149033	7.93	0.21	724	12	11.70	0.70	761	14	289.73	333	266	252	244	48	409	871	1938	2966
484265	Granophyre	5149033	9.10	0.23	737	12	11.50	0.75	759	14	3.66	30	9	20	89	21	312	754	1705	2665
484265	Granophyre	5149033	6378.24	104.91	2245	53	603.00	42.00	1365	30	28.63	31	24	28	63	19	185	515	1095	1822
484265	Granophyre	5149033	7.73	0.24	722	12	14.60	2.00	783	13	0.06	21	3	11	65	13	229	595	1388	2222
484265	Granophyre	5149033	8.24	0.22	728	12	10.40	0.70	749	14	4.39	33	34	32	120	26	397	1022	2234	3471
484265	Granophyre	5149033	8.55	0.23	731	12	9.80	0.55	744	13	0.23	24	7	23	99	22	327	869	1901	3009
484265	Granophyre	5149033	12.08	0.33	764	13	14.70	1.00	783	14	22.16	55	40	50	133	43	338	890	1894	2775
484367	Granophyre	5149463	4.08	0.14	668	11	4.10	0.55	668	15	0.62	171	17	57	366	23	1531	4433	9748	14425
484367	Granophyre	5149463	5.10	0.22	686	12	5.90	0.65	698	15	2.56	75	11	30	165	13	604	1623	3593	5569
484367	Granophyre	5149463	3.84	0.13	663	11	4.70	0.65	679	16	4.94	88	19	43	229	25	870	2410	5286	8074
484367	Granophyre	5149463	5.62	0.34	694	12	49.70	2.50	922	16	89.05	184	116	133	318	78	880	2394	5362	8615
484367	Granophyre	5149463	10.59	0.26	751	12	11.70	0.80	761	14	1.33	137	35	67	412	46	1531	3815	7930	11858
484367	Granophyre	5149463	8.39	0.22	730	12	9.40	1.25	740	17	6.05	176	35	79	385	61	1490	4026	8716	12862
484367	Granophyre	5149463	6.46	0.18	706	12	10.00	0.85	746	14	1.63	78	19	48	273	33	1017	2592	5840	8652
484367	Granophyre	5149463	3.67	0.14	660	11	5.40	0.55	691	14	0.37	87	10	35	222	16	915	2522	5765	8425
484367	Granophyre	5149463	5.92	0.17	699	12	12.50	1.30	767	16	11.50	133	45	84	394	82	1434	3626	8055	11631
484367	Granophyre	5149463	5.23	0.16	688	11	7.40	0.75	718	15	11.67	68	31	49	197	35	661	1784	4053	6105
484367	Granophyre	5149463	83.36	2.01	993	17	6.10	1.50	701	24	66.89	250	131	162	358	148	860	2588	5890	9662
484367	Granophyre	5149463	3.89	0.13	664	11	5.80	0.55	697	14	0.60	104	13	47	263	20	1077	2897	6432	9778
484367	Granophyre	5149463	5.59	0.18	694	11	6.60	0.60	708	14	0.46	49	10	33	175	20	634	1656	3537	5538
484367	Granophyre	5149463	6.45	0.18	706	12	19.90	1.75	815	16	48.15	274	84	107	291	73	763	1904	4229	6191
484367	Granophyre	5149463	5.79	0.18	697	11	16.30	1.90	794	18	43.89	312	155	212	721	314	2060	5233	10636	16554
484367	Granophyre	5149463	4.66	0.15	679	11	6.70	0.75	709	15	0.56	117	16	48	284	21	1139	3169	6916	10394
484367	Granophyre	5149463	6.88	0.20	712	12	12.50	1.30	767	16	1.52	272	41	60	286	33	1190	3160	6822	10055
484454	Granophyre	5149961	6.88	0.74	712	15	5.80	0.70	697	15	0.42	63	4	13	93	6	422	1434	3531	5292
484454	Granophyre	5149961	3.08	0.14	646	11	9.40	1.10	740	16	9.80	55	7	11	56	5	218	828	2190	3717
484454	Granophyre	5149961	3.84	0.13	663	11	4.80	0.60	681	15	0.54	18	1	13	2	65	251	736	1446	2176
484454	Granophyre	5149961	2.88	0.11	641	11	5.50	0.65	693	15	0.03	26	1	3	26	2	113	400	1196	2086
484454	Granophyre	5149961	3.48	0.16	655	11	4.80	0.70	681	16	2.73	91	12	24	139	15	570	1693	4292	6382
484454	Granophyre	5149961	3.13	0.16	647	11	4.28	0.44	672	14	0.03	23	1	3	25	2	103	375	1032	1858
484454	Granophyre	5149961	3.03	0.16	645	11	3.40	0.75	654	20	0.26	115	9	34	239	13	1048	3164	7577	11102
484454	Granophyre	5149961	3.79	0.16	662	11	5.40	0.60	691	15	1.01	14	1	7	1	39	174	524	1121	1121
484454	Granophyre	5149961	3.15	0.12	648	11	19.20	2.55	811	19	12.44	32	10	8	23	5	85	310	887	1551
484454	Granophyre	5149961	4.09	0.14	654	11	4.20	0.60	670											