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

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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_{cryst}) of ~685 °C. This could possibly indicate wet minimum-melting conditions producing granitic melts, implying very different Hadean terrestrial geology from that of other rocky planets. Here we report the first comprehensive ion microprobe study of zircons from a transect through the differentiated Sudbury impact melt sheet (Ontario, Canada). The new zircon Ti results and corresponding T_{cryst} fully overlap with those of the Hadean zircon population. Previous studies that 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_{cryst} 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 as old as 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_{cryst}) 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_{cryst}, represent 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 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 δ7Li values are distinct from those of zircons crystallized from mantle-derived melts, but similar to those of Archean tonalitic granitoids, suggesting growth in “protocontinental crust”. Regarding the sensu stricto granite origin hypothesis, a number of studies have conclusively shown that the modal compositions of inclusions in zircons 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 commonly relative 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_{cryst} of Hadean zircon is not unique to felsic rocks by documenting a number of mafic rock suites with T_{cryst} identical to that of 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 (Ontario, Canada), missing all of 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).

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.
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 (QCMs). The zircons were later re-polished to remove the SIMS pits and reanalyzed for Ti simultaneously with a selection of rare earth elements (REEs) by LA-ICPMS. QCMs were analyzed during the LA-ICPMS analytical session all grains were U-Pb dated as QCMs. In a separate analytical session, all grains were U-Pb dated as QCMs. The zircons were noted to be higher than 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 QCMs analyzed during the LA-ICPMS 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 ~600–1000 °C. Outlying higher Ti values as high as >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 notables 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 as apparent in CL (Fig. DR1) and invariably enriched in light REEs (LREEs; 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 $T_{\text{zir}}$ of 768 ± 31 °C, in the stratigraphically lowest sample (14GGK107), 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 $T_{\text{zir}}$ value of 678 ± 48 °C (n = 33), while the norite has a mean of 742 ± 47 °C (n = 56).

Ti-in-Zircon Thermometry by SIMS

Both QCMs analyzed during the SIMS analytical session returned Ti contents in agreement with previously published values (see methods above). The exact geological significance of the calculated $T_{\text{zir}}$ is uncertain, given the effects of variable reduced $\alpha$TiO$_2$, or $\alpha$SiO$_2$, variable pressure, possible deviations from Henry’s Law, and subsolidus Ti exchange (Fu et al., 2008). Corrections for reduced $\alpha$TiO$_2$ or $\alpha$SiO$_2$ or for variable pressure are generally not applied to the Hadean detrital zircons due to lacking geological context (although many grains do contain quartz inclusions, buffering $\alpha$SiO$_2$, to 1 at the time of crystallization, and there are rare instances of rutile inclusions buffering $\alpha$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 $T_{\text{zir}}$) 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 $\alpha$TiO$_2$ or $\alpha$SiO$_2$ or for pressure. Thus, calculated $T_{\text{zir}}$ is not intended to accurately determine crystallization in the melt sheet but for comparison with the Hadean zircon data. However, we note that $\alpha$SiO$_2$ would be constrained to 1 in all studied samples because of consistent presence of magmatic quartz, and $\alpha$TiO$_2$ would be constrained to 1 in the quartz gabbro unit due to the presence of rutile (Fig. DR2). In all other units of the melt sheet, titane and rutile occur, constraining $\alpha$TiO$_2$ to $>$0.6, meaning that $T_{\text{zir}}$ may be underestimated by as much as ~60–70 °C.

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

RESULTS

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

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

$T_{\text{zir}}$ values vary from 13.1 ± 3.9 ppm (n = 14), corresponding to a $T_{\text{zir}}$ of 768 ± 31 °C, in the stratigraphically lowest sample (14GGK107), 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 $T_{\text{zir}}$ value of 678 ± 48 °C (n = 33), while the norite has a mean of 742 ± 47 °C (n = 56).

Figure 2. Ti-in-zircon crystallization temperature ($T_{\text{zir}}$) for Ti content measured by secondary ion mass spectrometry in Sudbury melt sheet (Ontario, Canada). Average error of 13 °C (1 standard deviation) includes uncertainty introduced when calculating $T_{\text{zir}}$ 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.

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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 QCMs 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 LREEs to heavy REEs (HREEs) 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 a result of 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 >20 ppm, corresponding to apparent T<sub>zir</sub><sup>sat</sup> 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 >20 ppm (Watson and Harrison, 2005; Fu et al., 2008), with most Ti contents >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 to be 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<sub>zir</sub><sup>sat</sup>.

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<sub>zir</sub><sup>sat</sup> 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 of 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 down-hole 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 ~250,000–500,000 yr (Ivanov and Deutsch, 1999; Davis, 2008) and differentiate, resulting in the wide range of Ti contents and T<sub>zir</sub><sup>sat</sup> observed in this study. This suggests that a hydrosphere may be necessary to produce a wide range of relatively low T<sub>zir</sub><sup>sat</sup> 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<sub>zir</sub><sup>sat</sup> obtained by ion microprobe is ~100 °C higher than the zircon saturation model temperature, T<sub>zir</sub><sup>sat</sup>~ (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<sub>zir</sub><sup>sat</sup> of ~680 °C is more than 150 °C lower than the T<sub>zir</sub><sup>sat</sup> 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<sub>zir</sub><sup>sat</sup> can be more than 150 °C lower than T<sub>zir</sub><sup>sat</sup> in the late-stage felsic melts of a differentiated impact melt sheet, despite early-cooling mafic melt following the expected trend of T<sub>zir</sub><sup>sat</sup> > T<sub>zir</sub><sup>sat</sup>.

In light of this, the assumption that T<sub>zir</sub><sup>sat</sup> = T<sub>zir</sub><sup>sat</sup> + 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<sub>zir</sub><sup>sat</sup> 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-$T_{\text{min}}$ 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 $T_{\text{min}}$, 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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