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# Geochemical signatures and magmatic stability of terrestrial impact produced zircon

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## ABSTRACT

Understanding the role of impacts on early Earth has major implications to near surface conditions, but the apparent lack of preserved terrestrial craters > 2 Ga does not allow a direct sampling of such events. Ion microprobe U–Pb ages, REE abundances and Ti-in-zircon thermometry for impact produced zircon are reported here. These results from terrestrial impactites, ranging in age from ~35 Ma to ~2 Ga, are compared with the detrital Hadean zircon population from Western Australia. Such comparisons may provide the only terrestrial constraints on the role of impacts during the Hadean and early Archean, a time predicted to have a high bolide flux. Ti-in-zircon thermometry indicates an average of 773 °C for impact-produced zircon, ~100 °C higher than the average for Hadean zircon crystals. The agreement between whole-rock based zircon saturation temperatures for impactites and Ti-in-zircon thermometry (at  $a_{TiO2} = 1$ ) implies that Ti-in-zircon thermometry record actual crystallization temperatures for impact melts. Zircon saturation modeling of Archean crustal rock compositions undergoing thermal excursions associated with the Late Heavy Bombardment predicts equally high zircon crystallization temperatures. The lack of such thermal signatures in the Hadean zircon record implies that impacts were not a dominant mechanism of producing the preserved Hadean detrital zircon record.

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#### 1. Introduction

Extraterrestrial impacts are thought to have led to lunar formation (ca. 4.5 Ga; Canup and Asphaug, 2001), substantially resurfaced inner solar system bodies at ca. 3.85–3.95 Ga (i.e., the Late Heavy Bombardment 'LHB'; Tera et al., 1974), and profoundly influenced the habitability of early Earth (e.g., Grieve et al., 2006). However, their role in early Earth petrogenesis remains poorly understood. Although rare on Earth, due to constant resurfacing, impact craters preserved on other terrestrial planets (Mercury, Mars) and the Moon yield crater size–frequency distributions suggesting similar early impact histories in the inner solar system (the Venusian impact record is partially obscured by recent volcanism; Neukum et al., 2001). Because of the much greater gravitational cross-section of the Earth relative to the Moon, it is expected to receive ca. 20 times higher impact flux (e.g., Grieve et al., 2006).

The search for ancient terrestrial impacts has largely focused on shock features in minerals or impact melt spherules (e.g., Cavosie et al., 2010; Lowe et al., 2003). We are, however, unaware of any report of such features in Hadean or Archean detritus. Although low energy impacts do not produce thick melt sheets, those that result in widespread decompression melting of the middle crust (Grieve et al., 2006) should persist over time-scales sufficient for crystallization of zircon, provided target rock composition and Zr-content are conducive to zircon formation, with dimensions of >10 µm (Harrison and Watson, 1983; Watson, 1996) permitting geochemical and geochronological analysis. Many well-preserved terrestrial impact sites have now been dated using U–Pb geochronology of impact produced zircon (e.g., Hart et al., 1997; Kamo et al., 1996; Krogh et al., 1984; Moser, 1997), but using zircon to constrain the thermal (Ferry and Watson, 2007; Gibson et al., 1997; Watson and Harrison, 2005) or compositional (Grimes et al., 2007; Maas and McCulloch, 1991) evolution of impact melt sheet magmas is in its infancy. Such information could provide a baseline for understanding conditions on early Earth and permit comparison with the Hadean zircon record (see review in Harrison, 2009) to assess the hypothesis that Hadean detrital zircon formed in impact environments.

#### 2. Background

The long-standing, popular conception that the near-surface Hadean Earth was an uninhabitable, hellish world (Kaula, 1979; Solomon, 1980; Wetherill, 1980) has been challenged by the discovery (Compston and Pidgeon, 1986; Froude et al., 1983) and geochemical characterization (see review in Harrison, 2009) of >4 Ga zircon grains from Mt. Narryer and Jack Hills, Western Australia. Hadean zircon crystals may preserve environmental information regarding their formation and thus provide a rare window into conditions on early Earth. Isotopic and

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petrologic analyses of these ancient grains have been interpreted to suggest that early Earth was more habitable than previously envisioned, with water oceans, continental crust, and possibly even plate tectonics (Harrison, 2009; Hopkins et al., 2010).

Alternatively, diamonds apparently included in these ancient zircon grains have been suggested as evidence of their formation under ultra-high pressure conditions (Menneken et al., 2007; Williams, 2007). Diamonds (usually sub-µm) have been found within rocks associated with terrestrial impact events (Masaitis, 1998) and the assumed high bolide flux during the Hadean (Koeberl, 2006) might warrant investigation into the possibility of an impact origin for the Hadean zircon population if the existence of diamond inclusions can be substantiated.

In this paper, we present U–Pb zircon geochronology, Ti-in-zircon thermometry, and trace-element geochemistry from four of the bestpreserved terrestrial impactites to assess the role of impacts in the formation of the Hadean detrital zircon. These data reveal a limited range of formation conditions that strongly contrast with that documented for Hadean detrital zircon. To further generalize these empirical results which are necessarily limited by the scarcity of preserved impactites, we developed a thermochemical model to obtain a first order estimate of the abundance and temperature spectrum of impact produced zircon that could be expected from a detrital zircon population following an LHB-era impact episode on different crustal compositions (Archean vs. modern crust).

#### 3. Methods

Analysis of zircon was accomplished both in thin section and as separated grains. For all hand samples thin-sections were obtained and examined via electron imaging using a LEO 1430 VP scanning electron microscope (SEM) to assess zircon crystal size and abundance. Mineral separates were obtained from bulk rock samples by standard heavy liquid separation procedures. Separated zircon crystals were handpicked and mounted in 1 in. diameter epoxy mounts together with AS3 zircon standard (Paces and Miller, 1993).

Ion microprobe analyses were conducted with a CAMECA ims1270 using an  $\sim$ 8–12 nA mass-filtered <sup>16</sup>O<sup>-</sup> beam focused to spots between ~20 and 35 µm. We initially screened zircon grains for U-Pb dating to discriminate between inherited zircon (i.e., those older than the accepted impact age) and those formed within the impact melt. Zircon crystals with U-Pb ages similar to those of previously published impact dates (i.e., impact produced zircon) were then reanalyzed for trace elements (all rare earth elements REE, Ti, and Hf) within the same area as the U-Pb analysis, ensuring that the data acquired is from the same crystal domain. The trace element protocol also included mass/charge stations at <sup>26</sup>Mg, <sup>55</sup>Mn, and <sup>57</sup>Fe permitting monitoring of beam overlap onto inclusions in zircon that could overwhelm the low abundances of some critical trace elements in zircon (e.g., Ti). Conditions for trace element analyses were broadly similar to those of U–Pb dating, with a ~10–15 nA mass-filtered  $^{16}O^{-1}$ beam focused to a ~25–35 µm spot. Analysis yielding high Ti and Fe were re-imaged by SEM to make sure no visible cracks were within the spot. When cracks were identified grains were re-analyzed on fresh clean surfaces to avoid contamination of Ti associated with crystal defects (Harrison and Schmitt, 2007). NIST 610 glass was used as a primary REE standard (Pearce et al., 1997), checked against 91500 zircon (Harrison and Schmitt, 2007; Wiedenbeck et al., 2004). We used SL13 ( $6.32 \pm 0.3$  ppm Ti) and AS3 ( $21.6 \pm 1.6$  ppm Ti) as titanium standards (Aikman, 2007). For reconnaissance analysis, we also used a rapid analysis protocol for <sup>48</sup>Ti<sup>+</sup> and SiO<sup>+</sup> (excluding other trace elements) by multi-collection with dual electron multipliers which yield equivalent results. The U-Th-Pb, Ti, and REE data are individually tabulated in the Supplementary online materials.

#### 4. Zircon from preserved terrestrial impactites

#### 4.1. Vredefort, South Africa

The Vredefort impact structure in South Africa is the largest known terrestrial impact site (Earth Impact Database, 2011) and represents the deeply eroded remnant of an originally ~300 km wide crater (Reimold and Gibson, 1996). Although the melt sheet has been eroded due to post-impact uplift, pseudotachylite breccia and granophyre veins remain. U–Pb dating (isotope dilution thermal ionization mass spectrometry ID-TIMS) of zircon isolated from a 45 cm pseudotachylite breccia vein at ~140 m depth within a borehole near the center of the remnant crater yield an impact age of  $2023 \pm 4$  Ma (Kamo et al., 1996). Similar analysis of zircon extracted from a syn- to post-impact norite dike also yield an age of  $2019 \pm 2$  Ma (Moser, 1997). The target rocks of the Vredefort impact were the 2.7–3.6 Ga Kaapvaal craton granite–greenstone terrane (Schmitz et al., 2004) and sediments and volcanic rocks of the Witwatersrand basin.

We obtained zircon and whole rock samples of Vredefort impactite from three different sources: (1) pseudotachylite breccia collected near the quarry at Leeukop, just west of Parys was used for mineral separation (VD\_PB) as well as in-situ thin section analysis (VD\_PB\_1A and VD\_PB\_1B; Fig. 1); (2) granophyre (VD\_G; Fig. 1) from the Kommandonek Nature Preserve (provided by Roger Gibson, University of Witwatersrand); and (3) zircon from the INL borehole (VD\_INL; Fig. 1) collected just south of the geographical center of the Vredefort Dome (provided by Sandra Kamo, University of Toronto).

Pseudotachylite breccia sample VD\_PB consists of 1–3 cm clasts of Archean granite to granodioritic gneiss target material within a fine grained crystalline matrix (Reimold and Gibson, 2006). The separated zircon crystals (~35 grains isolated) range in length from 20 to 100 µm and exhibit igneous textures (i.e., elongate faceted faces, high axial ratio, pyramidal terminations; Corfu et al., 2003) and show no planar deformation features. Thin sections (VD\_PB\_1A and VD\_PB\_1B) were also imaged via SEM to identify zircon (~8 grains) within the melt fraction in-situ and avoid inherited grains associated with target rock clasts.

Granophyre sample VD\_G consists of fine-grained crystalline quartz, plagioclase and alkali feldspar with long laths of hypersthene and small grains of magnetite (Reimold and Gibson, 2006). Zircon grains (~20 grains isolated) average ~100  $\mu$ m and are fractured. Crystals lack igneous oscillatory zoning and are generally intimately intergrown with a Mg-rich pyroxene phase identified by energy dispersive X-ray analysis.

INL borehole (VD\_INL) sample was taken at 139.10 m depth, a few cm below the top contact of a ~45 cm wide intersection of pseudotachylitic breccia (Kamo et al., 1996). We obtained a zircon mineral separate of two optically distinct populations of zircon crystals (13 grains total): larger, dark, sub-rounded grains which appear to have younger overgrowths on old shocked grains, and smaller, clear, multi-faceted grains that appear to represent new impact produced zircon.

#### 4.2. Sudbury impact, Canada

The Sudbury Igneous Complex (SIC; ~250 km; Earth Impact Database, 2011) is a 2.5–3.0 km thick, elliptical igneous body with four major subunits from surface to base: granophyre, quartz gabbro, norite, contact sublayer (Therriault et al., 2002). U–Pb dating of zircon from the norite member yield an impact age of  $1849.5 \pm 0.2$  Ma (TIMS; Davis, 2008). Target rocks are a mix of Archean granite–greenstone terrains (~2.7 Ga; Krogh et al., 1996) with a small component of supracrustal Huronian rocks (Grieve, 1991).

Zircon mineral separates (provided by Don Davis) were obtained from both the mafic (SUD\_ M) and felsic norite (SUD\_ F) members (Fig. 1) along a transect of the southern exposed limb of the melt



**Fig. 1.** Sample location for preserved terrestrial impactites. (A) Vredefort Impact, South Africa (after Gibson and Reimold, 2008) showing locations of pseudotachylite breccia and granophyre hand sample (VD\_PB, VD\_G) as well as drill core INL (VD\_INL). (B) Map of Sudbury Impact, Canada and cross-section of the Sudbury Igneous Complex showing norite layer (Sud\_F and Sud\_M; after Zieg and Marsh, 2005). (C) Morokweng Impact, South Africa (after Jourdan et al., 2010) showing location and cross section of drill core M3 (MK\_157 and MK\_399). (D) Manicouagan Impact, Canada showing location of main melt sheet sample (MC\_MM; after O'Connel-Cooper and Spray, 2011).

sheet (Lightfoot and Zotov, 2005). The mafic and felsic norites are sheets at the bottom of the 2.5–3.0 km thick SIC, directly above brecciated target rocks (Therriault et al., 2002) and consist of hypersthene and augite (~2:1), plagioclase, quartz, biotite, and Fe–Ti oxides (Darling et al., 2009). Separated zircon grains range from ~20 to >100  $\mu$ m in length and show igneous textures, with those from the felsic norite being more euhedral. Some grains isolated from the mafic norite contain dark domains in SEM imaging that are characterized by high alkali and Fe contents and may reflect post-crystallization alteration and were avoided during analysis.

#### 4.3. Morokweng impact, South Africa

Morokweng, South Africa is a ~70 to 130-km-sized crater (Andreoli et al., 2008; Earth Impact Database, 2011). Zircon and biotite from the quartz norite melt sheet yield a concordant age of  $145 \pm 0.8$  Ma (U–Pb TIMS zircon age,  ${}^{40}$ Ar/ ${}^{39}$ Ar biotite age; Hart et al., 1997), which is

the accepted impact age. Basement target rocks for the Morokweng impact structure are primarily Archean granitoids (~2.9–3.0 Ga; Poujol et al., 2002) and meta-volcanics (ca. 2.7 Ga Ventersdorp Lava; Koberl and Reimold, 2003).

Drill core splits and crushed samples (provided by Marco Andreoli) were obtained from the M3 borehole drilled into the center of the aeromagnetic anomaly (Fig. 1; Jourdan et al., 2010). This drill hole intersects ~870 m of impact melt sheet consisting of differentiated granophyric to noritic rocks which overlay brecciated and shocked basement gneisses (Hart et al., 2002). Core splits from 155, 400, and 1069 m as well as crushed samples associated with the drilling processes from 156.5 to 157.98, 341.79–343.29, and 399.20 m were provided for this study. Zircon grains were separated from both the 156.5–157.98 and the 399.20 m crushed samples as well as the 1069 m target rock core split (MK\_157; MK\_399; MK\_1069). Separated zircon crystals from both crushed samples (~35 grains from each of the 156.5–157.98 and 399.20 m) range in length from 20

to 80  $\mu$ m while those separated from the 1069 m target rock core split tend to be larger, ranging from 50 to 120  $\mu$ m, with both populations exhibiting igneous textures (Corfu et al., 2003).

#### 4.4. Manicouagan impact, Canada

The Manicouagan impact, Quebec, is a ~100 km impact crater (Earth Impact Database, 2011). Post-impact uplift resulted in exposure of a ~55-km-long island surrounded by an annular, ~5-km-wide lake. Zircon isolated from the upper portions of the melt sheet near the center of the uplift yield an age of  $214 \pm 1$  Ma (TIMS; Hodych and Dunning, 1992). The target rocks for the Manicouagan impact consist predominately of the Grenville province of the Canadian Shield ranging in age from 1.0 to 1.7 Ga (Cox et al., 1998).

Hand samples of Manicouagan from the main impact melt sheet (MC\_MM) and a cross cutting dike from near the base of the melt sheet on the west side of Memory Bay (provided by John Spray) are homogenous, medium-grained quartz monzodiorite showing only minor variations in major elements (O'Connel-Cooper and Spray, 2011) (Fig. 1). Zircon crystals isolated (~40 grains) from the main melt sheet (to avoid inherited and altered grains possibly associated with cross cutting dikes) are 40–120 µm in length with prismatic elongations and pyramidal terminations indicative of an igneous origin (Corfu et al., 2003).

#### 4.5. Popigai impact, Russia

The Popigai impact, Siberia, Russia, has an estimated crater diameter of ~100 km (Earth Impact Database, 2011). An <sup>40</sup>Ar–<sup>39</sup>Ar age of tagamite (i.e. impact melt rock) suggests an impact age to  $35.7 \pm 0.2$  Ma (Bottomley et al., 1997) however no zircon grains have been reported with this age. Zircon separated from two hand samples of main melt and shocked gneiss (PG\_RR~30 grains, PG\_SG~70 grains) were subrounded, ovoid to multifaceted grains and range in size from 50 to 100 µm.

#### 5. Results and discussion

#### 5.1. U-Pb geochronology

#### 5.1.1. Vredefort, South Africa

Separated zircon crystals from the pseudotachylite breccia sample (VD\_PB) yield  ${}^{207}$ Pb/ ${}^{206}$ Pb ages of ~2.9–3.0 Ga (n = 31), with several grains (n=6) showing significant Pb-loss, presumably representing the Archean target rocks and not neo-crystalline zircon from the impact itself (Reimold and Gibson, 2006; Fig. 2). Eight zircon grains were analyzed in-situ (VD\_1A and VD\_1B; Fig. 2) within the finegrained melt matrix associated with the pseudotachylite breccia to avoid grains from target rock clasts. However, all grains also vield <sup>207</sup>Pb/<sup>206</sup>Pb ages of ~2.8–3.0 Ga, indicative of target rock ages. This result is consistent with the presumably short cooling duration of such thin (cm to m) veins of pseudotachylite breccia, which are insufficient for resorption of inherited zircon and hence never reach zircon saturation. Similarly zircon crystals isolated from the granophyre hand sample (VD\_G) yield <sup>207</sup>Pb/<sup>206</sup>Pb ages ranging from ~2.6 to 3.1 Ga (n = 17; Fig. 2) with less evidence for significant Pb-loss, however still representative of the target material and not impact produced zircon. Although no grains analyzed from the Vredefort samples provide equivalent ages to those published for the impact, two zircon grains isolated from the borehole INL yield concordant <sup>207</sup>Pb/<sup>206</sup>Pb ages  $(1978 \pm 17 \text{ Ma}, 2\sigma, \text{MSWD} = 0.3, n = 2)$ , about 2% lower than TIMS U–Pb zircon ages of  $2020 \pm 3$  Ma and  $2019 \pm 2$  (Kamo et al., 1996; Moser, 1997). We provisionally ascribe this difference to minor Pb loss. Only these two grains were selected for further analysis within this study.

#### 5.1.2. Sudbury, Canada

Ion microprobe analysis of zircon separates from the felsic and mafic norite members of the SIC yield concordant U–Pb ages of  $1848 \pm 6$  Ma ( $2\sigma$ , MSWD=1.7, n=10; Fig. 2), in close agreement with the published  $^{207}$ Pb/ $^{206}$ Pb age of  $1849.5 \pm 0.2$  Ma (Davis, 2008). Only one grain shows evidence for Pb-loss whereby post-analysis SEM imaging revealed likely post-crystalline alteration associated with high alkali and Fe contents for this crystal. There is no evidence within the melt sheet of zircon associated with the Archean granitic gneisses which comprise the target lithologies, and the uniform age distribution suggests that the impact energy associated with the Sudbury event was sufficient to fully resorb all inherited zircon. Consequently, we selected all grains for further analysis.

#### 5.1.3. Morokweng, South Africa

Zircon grains separated from both the 156.5–157.98 m and the 399.20 m crushed samples yield concordant U–Pb ages of  $150 \pm 2$  Ma (2 $\sigma$ , MSWD = 2.9, n = 56; Fig. 2) slightly older than previously reported ages of  $145 \pm 0.8$  Ma and  $144 \pm 4$  Ma ( $^{207}$ Pb/ $^{206}$ Pb ID-TIMS zircon age and  $^{40}$ Ar/ $^{39}$ Ar biotite age respectively; Hart et al., 1997). We note that previous U–Pb analysis was performed on zircon from a recrystallized portion of the quartz norite melt sheet. U–Pb analysis from zircon separated from the 1069 m target rock core split yield concordant ages ranging from ~2.8 to 3.3 Ga, similar to but slightly older than those estimated for the target rocks (~2.7–3.0 Ga; Koberl and Reimold, 2003; Poujol et al., 2002), with half of these grains showing evidence for Pb-loss possibly associated with impact shock. Only zircon grains extracted from the 156.5–157.98 m and the 399.20 m depth intervals were selected for further analysis within this study.

#### 5.1.4. Manicouagan, Canada

U–Pb analysis of zircon crystals separated from the main melt sheet of the Manicouagan impact yield concordant U–Pb ages of  $214\pm 2$  Ma ( $2\sigma$ , MSWD=1.7, n=32; Fig. 2) in close agreement with previous studies ( $214\pm 1$  Ma,  $^{207}$ Pb/ $^{206}$ Pb TIMS zircon age; Hodych and Dunning, 1992). Zircon crystals show no evidence of Pb loss and inherited grains were absent, suggesting similar conditions to that of Sudbury where the impact melt had sufficient time and heat to fully dissolve all relic zircon. All the grains isolated were selected for further analysis.

#### 5.1.5. Popigai, Russia

Zircon separated from both the main melt sheet and the shocked gneiss and from the Popigai impact mostly yield Proterozoic concordant U–Pb ages (~1.8–2.0 Ga) with one grain yielding an Archean age of ~2.5 Ga (Fig. 2). The majority of zircon ages (~80%) are concordant, with a minor population (~20%) of discordant ages. None of the ~120 crystals analyzed correspond to the  $35.7 \pm 0.2$  Ma age associated with the impact event ( $^{40}$ Ar/ $^{39}$ Ar Tagamite age; Bottomley et al., 1997).

#### 5.2. Ti-in-zircon thermometry

Although calculation of accurate magmatic zircon crystallization temperatures ( $T_{ztr}^{xtln}$ ) require knowledge of  $a_{TiO2}$  and  $a_{SiO2}$  activities (Ferry and Watson, 2007), we instead ultimately wish to compare calculated temperatures to detrital Hadean zircon, a population for which these parameters are in most cases unknown (Watson and Harrison, 2005). Although  $a_{TiO2}$  and  $a_{SiO2}$  activities are largely subunity for the samples at hand, equal sub-unity values are directly compensatory and magmatic activities of either being  $\leq 0.5$  are relatively rare (Ferry and Watson, 2007) and would result in 50–80 °C increases in calculated temperatures. Where bulk rock compositions are known,  $T_{ztr}^{xtln}$  can be compared to zircon saturation model temperatures ( $T_{ztr}^{sut}$ ; Harrison et al., 2007; Watson and Harrison, 1983).



**Fig. 2.** Concordia diagrams of zircon extracted from preserved terrestrial impactites calibrated against AS3 zircon standard (Paces and Miller, 1993). (A) Nearly all grains extracted from Vredefort are inherited from the target with exception of two grains from the INL borehole (denoted in red) which yield ages similar to the published impact age (-2020 Ma;  $^{207}\text{Pb}/^{206}\text{Pb}$  TIMS zircon age; Kamo et al., 1996; Moser, 1997). (B) Zircon from the mafic norite of the Sudbury Igneous Complex yield ages in agreement with the published impact age ( $1849.5 \pm 0.2 \text{ Ma}$ ;  $^{207}\text{Pb}/^{206}\text{Pb}$  TE-TIMS zircon age; Davis, 2008) with no signs of inheritance from the target rock. (C) Grains from the Moreowerg borehole M3 yield ages similar to, however slightly older than, the published impact age ( $145 \pm 0.8 \text{ Ma}$ ;  $^{207}\text{Pb}/^{206}\text{Pb}$  TIMS zircon age; Hart et al., 1997) with no sign of inheritance. (D) Zircon from the Manicouagan impact yield ages identical to those from previous studies ( $214 \pm 1 \text{ Ma}$ ;  $^{207}\text{Pb}/^{206}\text{Pb}$  TIMS zircon age; Hodych and Dunning, 1992) and show no inheritance also. (E) No impact produced zircon has been extracted from the Popigai samples provided for this study with all grains reflecting target rock ages.

#### 5.2.1. Vredefort, South Africa

Of the over than 60 grains analyzed from three separate samples of Vredefort, only two grains isolated from the INL drill core provided ages suitable (i.e. within 10% of the published impact age) for further analysis. Ti concentrations results for these two grains are  $11 \pm 0.7$  and  $20 \pm 1.1$  ppm which corresponds to  $T_{zir}^{xtln}$  of  $750 \pm 15$  and  $810 \pm 15$  °C, respectively (Watson and Harrison, 2005). All other grains dated from Vredefort samples are presumed to be associated with



**Fig. 3.** Titanium concentrations and Ti-in-zircon crystallization temperature, assuming  $\alpha_{TiO2} = 1$  (Watson and Harrison, 2005), of impact produced zircon. Saturation temperature underestimates crystallization temperature for differentiated impact melts (i.e. Sudbury and Morokweng; Watson and Harrison, 2005) (A) Sudbury impact produced zircon  $T_{zir}^{xtln} = 748 \pm 60$  °C, bulk norite  $T_{zir}^{soft} = 650$  °C (calculated from Lightfoot and Zotov, 2005). (B) Morokweng impact produced zircon  $T_{zir}^{xtln} = 797 \pm 70$  °C, bulk melt sheet  $T_{zir}^{soft} = 730$  °C (calculated from Andreoli et al., 1999). (C) Manicouagan impact produced zircon  $T_{zir}^{xtln} = 747 \pm 35$  °C, bulk melt sheet  $T_{zir}^{soft} = 752$  °C (calculated from Floran et al., 1978).

target rock zircon and do not fit the criteria for an impact produced zircon. Although these results agree well with the bulk zircon saturation temperature of 772 °C calculated from Reimold (1991) for the pseudotachylite breccia, more impact formed zircon grains are needed to verify this result. This result  $(T_{zir}^{xtln} \sim T_{zir}^{sat})$  is also consistent with the lack of differentiation expected within such small veins of melt.

#### 5.2.2. Sudbury, Canada

Zircon separated from the felsic (n = 12) and mafic norite (n = 13)members of the SIC yield overlapping average Ti concentrations of  $10 \pm 4$  and  $12 \pm 7$  ppm, corresponding to  $T_{zir}^{xtln}$  of ~740 and ~760 °C, respectively (Fig. 3a). There is relatively little within sample variation with > 75% of the data plotting within 700-780 °C. This temperature is slightly lower than that given in an earlier study of Sudbury (~800 °C for zircon grains isolated from the norite member and analyzed LA-ICPMS; Darling et al., 2009). This relatively small difference could potentially be due to Ti hosted in cracks (Harrison and Schmitt, 2007) which are more likely to be encountered in the larger analysis volume required by laser ablation as opposed to ion sputtering. Txtln agrees well with the calculated  $T_{zir}^{sat}$  of ~650 °C for bulk norite compositions (Lightfoot and Zotov, 2005) in that such temperatures are typically ~50-100 °C lower than that expected for the onset of zircon crystallization in a fractionating magma (Harrison et al., 2007), due to the much lower M, where  $M = (2Ca + Na + K)/(Al \cdot Si)$ , present in the melt during zircon crystallization as opposed to that calculated from the bulk rock composition. Darling et al. (2009) reported elevated REE contents within lower temperature zircon, also suggesting a fractional crystallization process causing REE enrichment within the residual melt; however an anti-correlation between Ti abundance and REE is absent in our data, possibly due to the restriction of our sample to the basal norite layer.

#### 5.2.3. Morokweng, South Africa

Average Ti concentrations of zircon crystals separated from 157 to 399 m within borehole M3 are  $25 \pm 19$  and  $15 \pm 9$  ppm respectively (n=31 for 157 m sample; n=19 for 399 m sample). This corresponds to a  $T_{zir}^{xtln}$  of ~830 °C for the 157 m sample and ~780 °C for the 399 m sample and an overall average of 797  $\pm$  70 °C (Fig. 3b). Relatively little variation in  $T_{zir}^{xtln}$  is observed from the 399 m sample, although significant variations exist within the 155 m sample with  $T_{zir}^{xtln}$  ranging from 720 to 990 °C. High sensitivity ion imaging (Harrison and Schmitt, 2007) may be helpful in ruling out contamination as a cause of the high apparent temperatures (although no cracks are apparent in SEM images). Morokweng is a differentiated impact melt sheet (Hart et al., 2002) and thus the zircon saturation of ~730 °C (Andreoli et al., 1999) underestimates the onset of zircon crystallization by ~50-100 °C (Harrison et al., 2007). The M3 borehole extends through nearly 870 m of impact melt sheet (Hart et al., 2002) and only samples from the upper half (157 and 399 m) are used within this study. Impact melt sheets tend to cool via the inward propagation of solidification fronts from both the surface and the basal layer (Zieg and Marsh, 2005).

#### 5.2.4. Manicouagan, Canada

Zircon separated from the main melt sheet of Manicouagan yield an average Ti concentration of  $\sim 12 \pm 6$  ppm, corresponding to a  $T_{ztln}^{xtln}$  of  $747 \pm 35$  °C (n = 32; Fig. 3c). Crystals analyzed in replicate using single- and multi-collection techniques yield similar values, with the exception of four crystals where single-collection Ti data are higher relative to the same grains analyzed in multi-collection (possibly due to beam overlap onto cracks). Averages for each method agree well (Ti average concentration = 11.4 ppm in multi-collection; Ti average concentration = 12.2 ppm in single-collection).

The Ti-in-zircon temperatures agree well with zircon saturation temperatures calculated from averaged bulk rock analyses (Floran et al., 1978) which predict  $T_{zir}^{sot} \sim 752$  °C. This agreement is consistent with Manicouagan being an undifferentiated impact melt. Whereas recent studies suggest possible pockets of differentiation throughout the melt (O'Connel-Cooper and Spray, 2011), we did not observe this in the sampled zircon population. In those cases where Hf is reported but Zr is not (e.g., Simonds et al., 1978), Zr content is estimated using an average Zr/Hf = 37 (Rudnick and Gao, 2003).

#### 5.3. Trace elements

Results from REE analysis of all impactite-produced zircon are, as expected, similar to terrestrial igneous zircon from a broad range of ages (Quaternary to Hadean; Grimes et al., 2007; Peck et al., 2001; Fig. 4). They are characterized by a relatively steep slope from LREE to HREE, and display positive Ce- and negative Eu-anomalies. The positive Ce-anomaly is commonly interpreted as evidence for oxidized magmas in which partitioning of Ce<sup>4+</sup> dominates over Ce<sup>3+</sup> (Hoskin and Schaltegger, 2003). The negative Eu-anomaly almost certainly reflects plagioclase fractionation of the parent magma as Eu easily substitutes for Ca within plagioclase (Hoskin and Schaltegger, 2003), and plagioclase is ubiquitously present in large impact target rocks. Differences in REE contents of differing impact sites likely reflect local concentration variations. While they are consistent within target populations, we emphasize that REE signatures of zircon cannot be used to clearly identify zircon provenance.

The trace element compositions of impact-produced zircon from Sudbury, Morokweng and Manicouagan (Fig. 5) fall generally within the fields (in U vs. Yb, U/Yb vs. Hf or Y space) defined by zircon crystallized from continental crust as do detrital Hadean zircon from the Jack Hills region (Grimes et al., 2007). Trace elements may also be useful in discriminating between neoformed and reset zircon (Abramov et al., 2011). For example, if elements that diffuse slower than Pb (e.g., Ti and REE; Cherniak and Watson, 2003; Cherniak et al., 1997) are distinctly different between melt sheet zircon and those from the target rock, it would appear likely that the zircon crystals are neoformed. REE patterns in zircon analyzed from the Morokweng M3 drill core target rock material (1069 m) show a clear distinction (primarily in the lack of a HREE enrichment) from those isolated from the melt sheet, reflecting the different geochemical conditions during crystallization of impact produced zircon and target rock zircon.

#### 5.4. Zircon saturation

The crystallization temperature spectrum of impact produced zircon from four terrestrial impacts (average  $T_{zir}^{xtln} = 773 \pm 87$  °C) is remarkably consistent with the average zircon saturation temperature  $(T_{zir}^{sat})$  of ca. 780 °C calculated by Watson and Harrison (2005) from a large (~19,000) database of whole rock samples across Australasia. Estimates of bulk continental crust composition yield similar T<sup>sat</sup><sub>zir</sub> values (ca. 780 °C, Rudnick and Gao, 2003; ca. 760 °C, Gao et al., 1998). Since it is broadly assumed that impact melts largely reflect decompression melting of the middle crust (Melosh, 1989), we also note that estimates of the composition of modern middle crust yield *T*<sup>sat</sup><sub>zir</sub> of ca. 740 °C (Rudnick and Fountain, 1995; Rudnick and Gao, 2003). Although the observed apparent crystallization temperatures  $(T_{zir}^{xtln})$  for impact produced zircon are consistent with  $T_{zir}^{sat}$  for present crustal compositions, they appear to be distinctly higher than that for detrital Hadean zircon population (i.e., ~680 °C; Watson and Harrison, 2006). On the assumption that the Hadean crust was compositionally closer to Archean than modern crust, we determined T<sub>zir</sub><sup>sat</sup> for Archean rocks in the GEOROC database with sufficient compositional data to permit calculation (n = 10,059). The resulting  $T_{zir}^{sat}$  distribution is bimodal with peaks at ca. 600 °C and 775 °C with an average value of 690 °C.

Although this average  $T_{zir}^{sat}$  is close to the Hadean value, several interpretive complexities warrant discussion when comparing  $T_{zir}^{stin}$ 



Fig. 4. Chondrite-normalized rare earth element abundances in impact produced zircon from ion microprobe measurements. REE patterns are indistinguishable from igneous zircon of all ages (Quaternary to Hadean; Hoskin and Schaltegger, 2003; Peck et al., 2001; Grimes et al., 2007), characterized by a relatively steep slope from LREE to HREE and displaying a positive Ce-anomaly and a negative Eu-anomaly.

and  $T_{zir}^{sat}$  spectra. We first note that  $T_{zir}^{stln}$  are sensitive to the activities of silica and rutile during zircon crystallization (i.e., an apparent subminimum melting temperatures could reflect either sub-unity activities or sub-solidus growth). Second, the expected  $T_{zir}^{stln}$  for zircon crystallizing from fractionating magmas are expected to be 50– 100 °C higher than that predicted from zircon saturation calculations (Harrison et al., 2007). These complications notwithstanding, the correspondence between average crustal  $T_{zir}^{sat}$  and the impact melt formed zircon reported here suggests that the small population of preserved terrestrial impact melts may be representative of a global average.

The impact-melt formed zircon temperature distribution partially overlaps the Gaussian-form Hadean temperature distribution but the overall misfit does not support an impact origin for the Hadean zircon grains. A Kolmogorov–Smirnov test yields p = 0.002, indicating that the two distributions are distinct populations at a high level of confidence (Fig. 6).

### 5.5. Modeling T<sup>xtln</sup><sub>zir</sub> of impact melt formed zircon

The LHB is generally interpreted as a relatively brief spike in impact flux (Gomes et al., 2005), although it remains possible that it instead reflects the terminal phase of a protracted cataclysm (Hartmann, 1975). In either interpretation, the terrestrial impact flux between ca. 4.0 and 3.8 Ga would be broadly similar. Thus given an estimate of that flux, we should be able to estimate the resulting  $T_{zir}^{xtln}$  spectrum and approximate the fraction of Zr in the continental crust that was processed through impact melting. We can then use these calculations to estimate the fraction of detrital zircon from a post-LHB terrane that would bear the thermal signature of an impact origin and to compare with the Hadean  $T_{zir}^{xtln}$  distribution as a partial test of whether they could reflect an impact origin.

To calculate the expected abundance of impact produced zircon within a detrital LHB-era zircon population we have used results of the thermal model of Abramov and Mojzsis (2009). They constructed a numerical framework to assess the amount of crustal heating resulting from an LHB impact history. Although their goal was to assess variations in the scale of the subsurface micro-biosphere due to the LHB, we can use their data to estimate crustal temperature changes that would lead to melting and re-precipitation of zircon.

Using the LHB impact flux inferred from the lunar cratering record and asteroid belt size distribution, Abramov and Mojzsis (2009) found that less than 10% of the lithosphere would have experienced temperature increases ( $\Delta T$ ) of  $\geq$  500 °C. However, under an elevated Archean geotherm, this could permit a significant fraction of the crust to achieve anatexis. Assuming a surface temperature of 0 °C and Archean geothermal structure that reaches 800 °C at 40 km (e.g., Condie, 1984), we coupled the thermal anomaly data of Abramov and Mojzsis (2009) with those samples from the Archean GEOROC database containing sufficient data to calculate zircon saturation temperatures to create a stochastic model of zircon formation temperatures during the LHB. In our model we ignored the limited potential of oceanic crust to preserve impact formed zircon, implicitly assume that the Archean GEOROC database is representative of continental crust between 4.0 and 3.8 Ga, and limit the upper temperature in the  $\Delta T$  distribution to 1200 °C. The latter assumption is justified on the basis that this exceeds all predicted solidus temperatures  $(T_{sol})$  in the database and only 1% of the lithosphere is predicted to have reached  $\geq$  1200 °C (Abramov and Mojzsis, 2009).

Zircon solubility in crustal melts is a simple function of zirconium content [Zr], temperature, and rock chemistry (i.e.,  $M = (2Ca + Na + K)/(Al \cdot Si)$ ; Harrison and Watson, 1983; Watson and Harrison, 1983). Thus knowledge of M, [Zr], T' (i.e., ambient temperature plus the  $\Delta T$  associated with impacts), and the relationship between M and melting



**Fig. 5.** Trace element plots of impact produced zircon from Morokweng, Sudbury and Manicouagan to discriminate between continental and oceanic target rock compositions. All grains are corrected for uranium decay. Continental field from Grimes et al. (2007) with lower boundary denoted by a solid line on each diagram, indicating the upper most limit of unambiguously oceanic zircon. End points for lines: U vs. Yb (25, 1), (20,000, 10,000); U/Yb vs. Hf (5000, 0.05), (35,000, 5); U/Yb vs. Y (200, 0.01), (100,000, 5). Nearly all impact produced zircon suggest continental target lithologies however Manicouagan plots nearly in the oceanic field possibly due to a slightly more mafic target.

conditions permits any random association of analyzed Archean rock and possible T' to be evaluated for the potential to produce impact zircon.



**Fig. 6.** Probability density function for Ti-in-zircon crystallization temperatures of Hadean zircon from Western Australia (n = 69; Harrison, 2009), mafic zircon (n = 304; Fu et al., 2008), impact produced zircon (n = 111; this study) and modeled impact produced zircon temperatures (n = 80; this study). The significant temperature contrast between impact produced zircon, modeled impact produced zircon (on an Archean target composition) and that observed for Hadean zircon grains suggests that impacts were not a major contributor to the Hadean population.

To obtain a relationship between M and melting conditions, we first note that the GEOROC database of analyzed Archean rocks (restricted to SiO<sub>2</sub> values between 35 and 85% to preclude sampling of non-silicates and quartzites) plots in a coherent fashion with a negative slope on a M vs. SiO<sub>2</sub> diagram (Fig. 7). We take this as evidence that this parameter appropriately characterizes petrogenic variation in this broad suite of rocks. Also shown in Fig. 7 is the regression of M vs. SiO<sub>2</sub> of the felsic, intermediate and mafic rocks utilized in the classic melting studies of Wyllie (1977) which essentially reproduce the Archean database trend. Using either the 5 kbar  $T_{sol}$  or 5% H<sub>2</sub>O (i.e., the average water content of Archean GEOROC samples is ~3%) liquidus temperatures ( $T_{liq}$ ) from Wyllie (1977) permits us to translate M into a melting or crystallization temperature (note that the calculations are not sensitive to assumed *P*).

To obtain impact-associated temperatures, we randomly coupled an ambient temperature (between 0° and 800 °C) with a  $\Delta T$  value scaled to the distribution given in Fig. 3 of Abramov and Mojzsis (2009) (e.g., a  $\Delta T$  of 50 °C was encountered 40 times more often than 1000 °C). We then arrayed the 10,059 samples in the database and randomly linked each synthetic impact temperature with an analyzed rock. Thus each rock is associated with an M and [Zr], a calculated solidus ( $T_{sol}$ ) and liquidus ( $T_{liq}$ ) temperature (i.e., via the M vs. *T* relationships), and a value of *T'*. Note that M will be much lower than the bulk rock value for low melt fractions. This will be particularly pronounced for mafic compositions thus requiring parameterization of M with melt fraction (described below based on synthetic experiments using MELTS; Ghiorso and Sack, 1995). The following logical statements were then applied to each of the collective data sets in the sequence:

- 1) Did the rock melt due to impact (i.e., is  $T' > T_{sol}$ )? If not, the event does not produce magmatic zircon. If true, T' is recorded and the calculation continues.
- 2) Is  $T_{zir}^{sat} < T_{sol}$ ? If true, the whole rock composition will not saturate zircon and the calculation terminates unless  $T' > T_{liq}$ , in which case we assume the melt differentiates and thus produces zircon with  $T_{zir}^{stin} = T_{sir}^{sat} + 50$  °C if  $> T_{sol}$  (i.e., we account for the high-temperature onset of zircon saturation in crystallizing intermediate to mafic melts by adding the conservative lower limit of the observed 50–100 °C difference between  $T_{zir}^{stin}$  and  $T_{zir}^{sat}$  (see



**Fig. 7.** GEOROC Archean database (n = 10,058) plotted as M vs SiO<sub>2</sub>. Top axes are experimental results from Wyllie (1977) at 5 kbar, whereby the upper and lower axes represent liquidus temperatures at 5 wt% H<sub>2</sub>O and water-undersaturated solidus temperatures, respectively. Wyllie (1977) dashed line is a fit of M vs. SiO<sub>2</sub> for melting experiments using felsic, intermediate and mafic compositions. This fit coincides with the regression of M vs. SiO<sub>2</sub> for bulk composition of impactites from this study, which underscores the validity of using experimental melting relations to model impactite formation.

Harrison et al., 2007)). If  $T_{zir}^{sat} > T_{sol}$  and  $T_{sol} \le T' \le T_{zir}^{sat}$ , then T' is taken to be  $T_{zir}^{stin}$ .

3) In cases where  $T_{sol} < T' < T_{liq}$ , we scaled M according to the relationships M' = 0.4 M if  $T_{sol} < T' < (T_{liq} - T_{sol}) \cdot 0.5 + T_{sol}$ , or M' = 0.8 M if  $T_{sol} < T' < (T_{liq} - T_{sol}) \cdot 0.5 + T_{sol}$  (these relationships approximate the compositional response of the Wyllie (1977) rock analyses to melting using the MELTS algorithm).

Only about 8% within each run batch resulted in conditions permitting zircon formation. Thus in order to attain a robust result, we executed the algorithm 1000 times. The average  $T_{zir}^{xtln}$  resulting from this calculation is ~783 °C - essentially identical to our observed value. The modeled  $T_{zir}^{xtln}$  spectrum is shown in Fig. 6. A surprising result to us was that the average M value of the zircon forming events is only 1.1 with no value exceeding 2 (i.e., felsic sources dominate). This indicates that, although mafic samples (which dominate the database) can contain substantial [Zr], their high melting temperatures and solidi restrict their ability to contribute significantly to impact produced zircon in the crust. Also of note is that the average  $T_{zir}^{xtln}$  of 780 °C is significantly higher than the average  $T_{zir}^{sat}$  of 690 °C. As a test of robustness, we also ran the model using the same large database from which Watson and Harrison (2005) reported an average  $T_{zir}^{sat}$  of 780 °C and obtained an average  $T_{zir}^{stln}$  of 810 °C. Despite model simplifications, the consistency and relative order of results from the two databases (i.e.,  $T_{zir}^{xtln} > T_{zir}^{sat}$ ) suggests that the model is at the least internally consistent and likely predicts an accurate temperature spectra. Thus we infer that the zircon crystallization temperature spectra of our necessarily limited empirical results is broadly representative of that produced globally in crustal impact melts.

An implication of this model is that the relative absence of mafic targets contributing to the zircon temperature distribution could lead to incorrect inferences regarding the nature of the crust drawn from the chemistry and inclusion assemblages in detrital zircon. For example, Harrison (2009) emphasized that the low  $T_{zir}^{xin}$  distribution

and felsic inclusion assemblage (i.e., quartz + muscovite) that characterizes the vast majority of the detrital Hadean zircon population is indicative of their origin at near water saturated granitoids. Given our model result, caution should be exercised when drawing inferences regarding whole-rock mineralogy from inclusion assemblages. Indeed, Darling et al. (2009) found rare muscovite inclusions in impact produced Sudbury zircon crystals. Nonetheless, the high  $T_{zir}^{xtln}$ found by both us and Darling et al. (2009) are distinctively higher than the detrital Hadean zircon population to effectively rule out an impact source as a significant contributor to their origin.

#### 6. Conclusions

Impacts investigated in this study contain neo-formed (Sudbury, Morokweng, Manicouagan, Vredefort) or entirely inherited zircon (Popigai), with no obviously relationship between crater diameter and zircon occurrence. Inherited grains yield ages consistent with local target rocks and their survivability reflects either low target rock [Zr] (i.e., never allowing zircon saturation), rapidly cooling melt sheets (i.e., a kinetic barrier to dissolution), or low energy impacts that never completely melted the middle crust. We note that although Vredefort is currently the largest known terrestrial impact site, erosion and resurgence of the central dome have removed much of the presumably large melt sheet that once existed (Therriault et al., 1997) explaining the rarity of impact produced zircon in the samples studied.

U–Pb geochronology of zircon from the Sudbury and Manicouagan impact melts agree well with published ages, however those for Vredefort and Morokweng do not (no impact produced zircon was observed within the Popigai samples). An impact age of ~1980 Ma for Vredefort is younger than the previously published age of ~2020 Ma, probably reflecting minor Pb loss. Morokweng U–Pb zircon ages (~150 Ma) are slightly older than previously published TIMS U–Pb age of ~145 Ma. No relic zircon grains were discovered associated with the target rocks ruling out the possibility of inheritance and leaving open the possibility that the published ages reflect postimpact effects.

Impact-produced zircon is indistinguishable from that of igneous or Hadean grains in REE, however plots of U vs. Yb and U/Yb vs. Hf or Y suggest that some inference can be made to the target rock composition (continental vs. oceanic crust). Trace element geochemistry can be used to distinguish between grains that have had their ages reset to that of the impact and those that crystallized from the impact melt, assuming that magmatic conditions within the melt sheet are different than those of the target rocks.

Crystallization temperatures ( $T_{zir}^{xtln}$ ) of 111 zircon crystals separated from Sudbury, Vredefort, Morokweng, and Manicouagan impacts indicate an average crystallization temperature of  $773 \pm 87$  °C. Based on the Ti-in-zircon thermometry results, we conclude that zircon derived from impactites do not represent a dominant source for the Hadean grains thus far documented from Western Australia.

As expected, impact produced zircon  $T_{zir}^{xln}$  values are consistent with that calculated from bulk rock zircon saturation systematic for the one presumably undifferentiated melts (Manicouagan). Zircon  $T_{zir}^{xln}$  values for Sudbury and Morokweng – both differentiated bodies – are 50–100 °C higher than  $T_{zir}^{sqt}$ , consistent with previous observations. A Monte Carlo model relating impact thermal anomalies associated with the LHB with Archean rock chemistry supports our  $T_{zir}^{xln}$  estimate – despite its limited size – as being globally representative. The significant temperature contrast between modeled impact formed zircon on Archean crust and that observed for Hadean zircon grains effectively rules out an impact source as a significant contribution to the Hadean population. The model developed in this study can also be applied to lunar compositions to predict the crystallization spectrum associated with an LHB event on the lunar surface and compared to results from lunar zircon (e.g., Taylor et al., 2009). Supplementary materials related to this article can be found online at doi:10.1016/j.epsl.2012.01.009.

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