Diachroneity of the Clearwater West and Clearwater East impact structures indicated by the (U-Th)/He dating method

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Abstract

The (U-Th)/He method has been applied to constrain the formation ages of the Clearwater West and East impact structures of Quebec, Canada. Zircons were separated from impact melt samples derived from a surface exposure at Clearwater West (32 km diameter), and from a drill core at Clearwater East (26 km diameter). The (U-Th)/He results yield ages of 280 ± 27 Ma (2σ , $n = 7$) for Clearwater West, and 450 ± 56 Ma (2σ , $n = 8$) for Clearwater East. Our (U-Th)/He age for Clearwater West concurs with those of previous Rb-Sr (266 ± 15 Ma; 2σ) and $^{40}\text{Ar}/^{39}\text{Ar}$ (280 ± 4 Ma and 283.8 ± 2.2 Ma, 2σ) impact melt studies. Our (U-Th)/He age for Clearwater East also overlaps with previously published $^{40}\text{Ar}/^{39}\text{Ar}$ dating results, which yielded U-shaped spectra, with ‘maximum’ and ‘best-estimate’ dates of ~ 460 - 470 Ma. Our results support the contention, previously based solely on $^{40}\text{Ar}/^{39}\text{Ar}$ data, that the Clearwater West and East impact structures do not comprise an impact doublet that formed coevally from a binary asteroid pair.

1. Introduction

Impact crater doublets have been observed on the Moon, Venus, and Mars (Bottke and Melosh, 1996), and impacts of binary asteroids are widely accepted as the most plausible formation mechanism for crater doublets (e.g., Bottke and Melosh, 1996). Binary asteroids consist of two bodies that orbit one another and share a common center-of-mass (Melosh and Stansberry, 1991), and they may comprise ~15-16% of the Near Earth Asteroid (NEA) population. Six potential crater doublets have been proposed on Earth (Melosh and Stansberry, 1991; Miljković et al., 2013). One of these terrestrial impact doublets, the adjacent Clearwater East and West impact craters in Quebec, Canada (Fig. 1), have long been thought to have formed by coeval impacts at ~280-290 Ma (Dence et al., 1965; Palme et al., 1978; Reimold et al., 1981; Melosh and Stansberry, 1991; Miljković et al., 2013). However, geochronological data from the eastern crater imply that its age is much older (~460-470 Ma; Bottomley et al., 1990; Schmieder et al., 2015) than that of the western crater (~270-310 Ma; Wanless et al., 1965; Reimold et al., 1981; Bottomley et al., 1990; Schmieder et al., 2015). In an effort to further explore the two competing models, we obtained (U-Th)/He thermochronologic data from zircons found in impactites associated with the two craters.

Although the (U-Th)/He technique is not yet as widely applied to dating impact structures as the U-Pb, Rb-Sr, K-Ar, or $^{40}\text{Ar}/^{39}\text{Ar}$ methods, it is proving to be a viable technique, both when neoblastic U-Th phases like zircon form from impact melts and, especially, when impact heating was sufficiently limited so that the resetting of higher-temperature chronometers was incomplete (e.g., van Soest et al., 2011; Wartho et al., 2012).

The (U-Th)/He isotope system was the first dating method to be used as a geochronometer in the early 1900s. It is based on the α decay of ^{238}U , ^{235}U , ^{232}Th , ^{147}Sm (and

their intermediate daughter isotopes) to ^4He . Early results associated with this geochronometer were perceived as “nonsensical”, due to ^4He daughter concentrations reflecting both production and diffusive loss, but these initial drawbacks were later understood to be scientifically tractable when the method was used as a thermochronometer that could determine low-temperature thermal histories recorded in Earth’s upper crust (Farley, 2002 and references therein).

The primary analytical issue affecting the reliability of (U-Th)/He dates is α -ejection, which occurs when radiogenic α -particles (^4He nuclei) are propelled out of the crystal structure due to the energy released by decay (Farley et al., 1996; Hourigan et al., 2005). This causes the outermost margins of the crystal to be depleted in ^4He and may result in anomalously young dates. Methods for calculating and applying α -ejection corrections can result in accurate ages with total 2σ analytical errors typically in the range of 6-10%, but sometimes larger errors (up to 30%) are obtained (Hourigan et al., 2005). Properly corrected (U-Th)/He ages are consistent with results obtained using other geochronological systems (e.g., U-Pb and $^{40}\text{Ar}/^{39}\text{Ar}$) on rapidly cooled samples (e.g., Farley, 2002). (U-Th)/He dating has been successfully deployed on a wide variety of minerals (e.g., zircon, apatite, monazite, titanite, garnet, magnetite, hematite, and merrillite) over a wide range of ages (e.g., ka to Ga; Min et al., 2013 and references therein). This thermochronological method offers a reliable and powerful tool for constraining the thermal histories of the upper crust of the Earth and Mars (e.g., Farley, 2002; Min et al., 2013), as well as the shock metamorphism history of meteorites (e.g., Min et al., 2013 and references therein). Here we apply the technique to date a renowned pair of impact craters on Earth.

2. Geologic background

The ~32 km diameter Clearwater West impact structure is located approximately 110 km east of Hudson Bay (56°13'N; 74°30'W) in northern Quebec, Canada, where it lies adjacent to the smaller ~26 km diameter Clearwater East impact structure (56°05' N and 74°07' W). Approximately 30 km separates the centers of the two craters (Fig. 1, Dence et al., 1977; Bottke and Melosh, 1996). The Clearwater East and West structures are now fully and partially submerged, respectively, by Clearwater Lake/Lac à l'Eau Claire.

The Clearwater East and West structures were first linked to probable meteorite impacts by Beals et al. (1956), and their impact origin was later confirmed by petrographic, geochemical and structural studies (McIntyre, 1962; Dence et al., 1965; Grieve, 1978; Simonds et al., 1978). Both structures are classified as complex craters with central uplifts (Dence et al., 1977; Grieve, 1978; Simonds et al., 1978).

The target rocks for both impact structures are predominantly late Archean (~2694-2711 Ma) granitic gneisses, and metamorphosed granodiorite, diorite, and tonalite, with subordinate occurrences of more mafic lithologies, all belonging to the Superior Province of the Canadian Shield (Rosa and Martin, 2010 and references therein). Metamorphic assemblages in these Archean rocks indicate amphibolite to granulite facies conditions. Various down-faulted blocks of limestone reflect the impact-induced disruption of the Ordovician (~485-443 Ma) sedimentary cover at Clearwater West (Reimold et al., 1981; Rosa and Martin, 2010). Rock outcrops in the Clearwater West crater are primarily limited to the prominent 16-20 km diameter island ring and the central cluster of four small islands where basement rocks are exposed, while the Clearwater East structure is almost completely submerged.

Three distinct impact-related rock types are observed on the central ring of islands of Clearwater West. The basal unit is a 20 m thick red, friable impact-melt-bearing breccia consisting of moderately shocked (12-15 GPa) Archean basement, overlain by an 18 m-thick red, well-jointed, fine-grained, clast-rich impact melt unit, and an 85 m-thick coarser-grained, poorly-jointed, clast-poor impact melt sheet (Reimold et al., 1981; Rosa and Martin, 2010). Overall, the melt rocks exposed on the islands have a minimum combined thickness of ~120 m (Simonds et al., 1978). Much of what is known about both structures comes from the study of numerous drill cores obtained by the Dominion Observatory of Canada (Ottawa) during the early 1960s. Impactites known from Clearwater East (drill hole 2-63) include an impact breccia enclosed in a crystalline melt matrix that grades from a dark-green fine-grained layer starting at ~245 m depth, into a gray-colored highly-vesicular coarser-grained section, before transitioning into a darker, non-vesicular coarse-grained phase where drilling was stopped at a depth of ~300 m (grain size of the melt matrix at this depth suggests drilling was stopped near the middle of the breccia lens, Dence et al., 1965).

3. Previous geochronological dating of Clearwater East and West

The Clearwater impact craters have been dated previously using a variety of geochronological techniques (Wanless et al., 1965; Reimold et al., 1981; Bottomley et al., 1990; Schmieder et al., 2015), although most work has focused on the better-exposed Clearwater West structure. For the sake of clarity, we only refer to K-Ar, $^{40}\text{Ar}/^{39}\text{Ar}$ and Rb-Sr ages using the decay constants of Steiger and Jäger (1977) in the text. However, recalculated K-Ar, $^{40}\text{Ar}/^{39}\text{Ar}$ and Rb-Sr ages using more recent decay constants (e.g., Renne et al., 2011 and references therein; Rotenburg et al. 2012) are shown in Table 1.

3.1. Clearwater West

K-Ar whole rock dating of Clearwater West impactites yielded ages of 291 ± 30 and 306 ± 30 (2 σ ; Wanless et al., 1965; recalculated using the decay constants of Steiger and Jäger, 1977). Impact melt glasses yielded very young fission track ages of ~ 34 Ma (Fleischer et al., 1969), but Rb-Sr whole-rock analyses of impact melt rocks indicated a 266 ± 15 Ma age (2 σ ; Wooden & Simonds, pers. comm., in Reimold et al., 1981). A $^{40}\text{Ar}/^{39}\text{Ar}$ study of a clast-bearing impact melt yielded a plateau age of 280 ± 4 Ma (2 σ ; Bottomley et al., 1990). More recently, the detailed study of Schmieder et al. (2015) obtained a combined $^{40}\text{Ar}/^{39}\text{Ar}$ impact melt age of 283.8 ± 2.2 Ma (2 σ) for Clearwater West by integrating results from optically fresh impact melt fragments.

3.2. Clearwater East

Reimold et al. (1981) used Rb-Sr data for whole rock and mineral separates from one impact melt drill core sample (9A, obtained at a depth of 306.5 m) to yield a mineral isochron age of 287 ± 26 Ma (2 σ , $n = 4$). However, the other 8 whole rock impact melt samples failed to yield a Rb-Sr isochron age. Bottomley et al. (1990) dated two clast-bearing impact melt core samples by the $^{40}\text{Ar}/^{39}\text{Ar}$ method and obtained U-shaped age spectra, which they interpreted to represent either the presence of excess ^{40}Ar or contamination from older inherited material. The lowest temperature step of a step-heating experiment on sample CWE1090 produced a small fraction of gas (1% of the total ^{39}Ar in the sample) with a date of 1075 Ma, falling to a minimum apparent age of 465 Ma, before rising again to 640 Ma in the final high-temperature step. A second sample (CWE1070) displayed a much broader U-shaped age spectrum with a low-

temperature step date of ~590 Ma, a plateau consisting of 4 mid-temperature steps (representing 80% of the total ^{39}Ar) yielding dates of ~460 Ma, before rising again to give final high-temperature step date of 1150 Ma (Bottomley et al., 1990). Bottomley et al. (1990) concluded that it was not possible to infer a reliable $^{40}\text{Ar}/^{39}\text{Ar}$ impact age from their Clearwater East samples, but suggested a ~460 Ma maximum age for the impact structure.

More recently, Schmieder et al. (2015) performed $^{40}\text{Ar}/^{39}\text{Ar}$ step heating analysis on two chloritized impact melt samples, but they too, were unable to obtain statistically defined $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages due to problems with excess ^{40}Ar . Given the difficult-to-interpret dating results, Schmieder et al. (2015) combined their dates with those of Bottomley et al. (1990) to offer a “best-estimate” impact age range of ~460-470 Ma for Clearwater East, and used this result to argue for diachroneity of the two impact structures.

4. Samples and analytical methods

Our Clearwater West sample material consisted of 2.5 kg of a dark red, fine-grained, slightly altered and oxidized, clast-bearing impact melt (primarily of granodioritic to quartz-monzonitic in composition along with lesser amounts of mafic gneiss, gabbro, and diabase; Grieve, 1978) collected from Atkinson island. Our Clearwater East impact melt rock sample material consisted of ~1 kg of a black, coarse-grained impact melt rock (primarily a mixture of granodiorite and quartz-monzonite; Grieve, 1978), that was obtained from drill core 2-63, at a drill core depth of 335-341 m (Fig. 1). Both impact melt samples were crushed and sieved, and heavy minerals were separated using standard density and magnetic techniques. A Leica *MZI6* binocular microscope was used to select and accurately measure the dimensions of eighteen

zircon grains (9 from each sample) for dating using the (U-Th)/He method (Online Supplement Table 1).

Individually measured zircon crystals were loaded into Nb tubes for analysis. An Australian Scientific Instruments *Alphachron Mk I* helium extraction line and quadrupole mass spectrometer was used for this study. ^4He was released from the Nb-encapsulated zircon crystals by heating *in vacuo* using an infrared (980 nm) diode laser. The evolved gasses were purified using an *NP10* getter kept at $\sim 350^\circ\text{C}$ in the extraction line. A ^3He spike was added to enable He analysis by isotope dilution via a Balzers *QMS 200* quadrupole mass spectrometer.

After He extraction and measurement, the encapsulated zircon crystals were spiked with a solution of $^{230}\text{Th}/^{235}\text{U}$ in HNO_3 , and then dissolved in concentrated acids (a sequential step using 1:3 HNO_3/HF , followed by HCl) using Parr digestion vessels heated to 225°C . After a final dry down, samples were made up into a 6% $\text{HNO}_3/0.8\%$ HF solution and analyzed with a Thermo Scientific *iCap Qc* quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Both the *Alphachron* and *iCap Qc* systems used are located at the Group 18 Laboratories, at Arizona State University (ASU). The (U-Th)/He dates were calculated iteratively from blank-corrected ^4He , ^{232}Th , and ^{238}U concentrations, and the raw calculated dates were corrected for α -ejection based on optical dimension measurements of the crystals prior to analysis, following the protocols developed for zircon α -ejection correction by Hourigan et al. (2005). Each (U-Th)/He dataset was evaluated with the Hampel identifier method (Pearson, 2011 and references therein) to aid in testing for the presence of statistical outliers. Additional details of the ASU (U-Th)/He analytical procedures can be found in van Soest et al. (2011).

Secondary electron (SE) and backscattered electron (BSE) imaging and energy dispersive X-ray spectrometry (EDS) were performed on eight small ($n = 2$) or broken ($n = 6$) zircons using

a JEOL JXA-8530F electron Microprobe housed at the John M. Cowley Center for High Resolution Electron Microscopy, ASU. These grains and grain fragments were not dated with the (U-Th)/He method because they were too small or broken, plus the carbon coating required for SE/BSE/EDS analysis would cause a hydrocarbon contamination problem when measuring He on the quadrupole mass spectrometer. However, their SE, BSE, and EDS characteristics are considered representative of the population of (U-Th)/He dated zircons. Microprobe operating conditions were 10 kV acceleration voltage, ~250 pA beam current, and a working distance of ~11 mm. The EDS analyses were performed using a silicon drift diode detector (SDD). Acquisition times were typically ~25 seconds and EDS analyses were ZAF matrix-corrected and calibrated using an instrument-specific mineral standard database.

5. (U-Th)/He results

5.1. Clearwater West

Binocular microscope inspection of zircons extracted from the Clearwater West impact melt rock sample revealed the presence of two distinct populations (Fig. 2). One population displayed characteristics that resemble zircons inherited from rocks affected by meteorite impact (Figs. 2a-e), including fairly euhedral shapes (Figs. 2a-b), with occasional rounded grain edges, typically associated with metamorphic or detrital zircons (Corfu et al., 2003; Figs. 2c-e), and a turbid or milky appearance (Figs. 2c-d). We term these “relict” crystals. Some of these semi-opaque grains (Figs. 2a-b) contained an internal array of microfractures (Corfu et al., 2003).

The second distinct zircon population we observed was composed of clear and sharply-defined euhedral crystals (Figs. 2f-i), without the rounding commonly observed in the relict zircon population. The majority of this second population contained pervasive fractures,

206 resulting in an abundance of crystal shards within the mineral separate, and a scarcity of
207 complete euhedral grains. Based on our experience with similarly distinct zircons from the
208 Manicouagan impact melt sheet (van Soest et al., 2011), we interpret the second population of
209 zircons to be likely/probably neocrystalline (i.e., crystallized from the impact melt), rather than
210 relic grains inherited from the target rocks.

211 Light microscope, SE and BSE imaging of the 8 small non-dated grains ($n = 2$) and
212 fragments ($n = 6$), all confirmed as zircon by EDS, revealed a variety of textures, and the details
213 of 4 grains/fragments are shown in Figs. 3a-f. Some grains were broken or split (most likely
214 during the crushing process), but their remaining interiors and exteriors are relatively smooth
215 with no evidence of fracturing (e.g., SEM-Z01 in Fig. 3a). One broken grain (SEM-Z02)
216 exhibited a smooth, but fractured exterior (Fig. 3b). Another grain exhibited a granular-textured
217 surface (i.e., SEM-Z03 in Fig. 3c). A fourth zircon fragment (SEM-Z04 in Figs. 3g-i) exhibited
218 an exterior similar to SEM-Z02, but it contained a micro-vesiculated interior. Previous studies
219 have reported granular surface textures on naturally shocked zircons and interpreted them as the
220 shock-induced transformation of pre-impact zircons into polycrystalline aggregates of zircon
221 crystallites in a glassy ZrSiO_4 matrix, a transient phase that, after time, reverts back to zircon
222 (Wittmann et al., 2006 and references therein). The exact range of pressures associated with this
223 transition remains poorly constrained because shock experiments up to ~ 80 GPa have failed to
224 consistently produce similar textures (Wittmann et al., 2006). Previous workers have also
225 observed the presence of microvesicles in shocked zircon and have suggested that they may form
226 during degassing of a ZrSiO_4 melt, at or near the melting point of zircon (i.e., $\sim 1680^\circ\text{C}$,
227 Wittmann et al., 2006). However, the impact melt temperature at the Clearwater West crater
228 appears to be insufficiently consistent to melt and assimilate all of the observed relic zircons.

A total of nine zircon grains were selected for analysis, five from the first inherited/relict population, and four from the second neocrystalline population. The Th/U ratios of the individual grains support the existence of the two populations that were observed optically. Th/U ratios for the four neocrystalline crystals range from 3.87 ± 0.08 to 4.82 ± 0.90 (2σ), whereas the Th/U ratios of the five inherited/relict crystals are lower and show a range of 0.38 ± 0.01 to 1.25 ± 0.08 (2σ). These Th/U ratio ranges are distinctive given that the 2σ errors are on the order of $\sim 2\%$ (Fig. 2 and Online Supplement Table 1).

The individual zircon (U-Th)/He dates from Clearwater West range from 233.5 ± 6.1 to 323.8 ± 9.5 Ma (2σ , Online Supplement Table 1, Figs. 2 and 4). All nine analyses yielded an inverse variance-weighted mean age of 275.0 ± 2.6 Ma (2 standard error (SE); probability (P) = 0.0), with a large Mean Square Weighted Deviation (MSWD) of 46.6. This large MSWD value implies that the data show much more dispersion than what might be expected from analytical imprecision alone (York et al., 2004). However, the distribution of dates suggests that the highest and lowest may be outliers given the substantially better clustering of the remaining analyses (Fig. 4). This was confirmed by application of the Hampel identifier method (using an outlier indicator value of >4) as applied to the chi-squared values for each date (Pearson, 2011 and references therein). The inverse-variance weighted mean of the remaining seven analyses is 280.3 ± 3.0 Ma ($2SE$; $P = 0.0$), with a MSWD of 11.4, but it still indicates substantial over-dispersion within the dataset. A commonly used method to constrain the external uncertainties associated with dating analyses, involves multiplying the calculated mean age error by the square root of the MSWD (York et al., 2004), which in this case, yields an age of 280.3 ± 10.2 Ma ($2SE$, $n = 7$). However, the MSWD of 11.4 is still far outside the error bounds predicted by Wendt and Carl (1991; for an ideal MSWD of 1.0) so we choose to apply a more conservative

expanded uncertainty estimate of twice the standard deviation of the subpopulation of dates (e.g., Heckert and Filliben, 2003), with two outliers removed, to yield our preferred age of 280 ± 27 Ma (2σ , $n = 7$), which we interpret as the (U-Th)/He zircon age of the Clearwater West impact structure (Fig. 4).

We also determined the (U-Th/He) inverse variance-weighted mean and expanded 2σ error ages of the two relict and neocrystalline zircon populations yielding values of 298 ± 30 Ma (MSWD = 11.1, $n = 5$) and 259 ± 40 Ma (MSWD = 35.2, $n = 4$), respectively, which overlap within 2σ errors. As the MSWD values of these two populations of zircons was either similar to, or much higher than, the MSWD (i.e., 11.4) of the combined zircon dataset, and owing to the small number of zircon grains analyzed, we prefer to use the combined dataset to determine the (U-Th)/He age of the Clearwater West impact structure. One plausible explanation for the relict grain mean age being so much older than the likely neocrystalline group could be the incomplete degassing of the relict grains despite their residence time within the impact melt sheet.

5.2. Clearwater East

The nine zircon grains selected from the Clearwater East (CWE) drill core sample revealed moderate variability in crystal size, habit, and clarity (Fig. 5). The majority of the grains showed significant rounding of the crystal edges (Figs. 5a-h) suggesting that they may be relict metamorphic grains (Corfu et al., 2003). One grain appears opaque, which may suggest it was shock-metamorphosed (Fig. 5h), and one grain is clear and euhedral, which may indicate a neocrystalline nature (Fig. 5i). However, most of the zircon grains contained few features that could be clearly identified as impact related (Corfu et al., 2003). (U-Th)/He analyses of nine single zircon crystals from Clearwater East yielded dates ranging from 132.1 ± 4.0 to 490 ± 14

Ma (2σ , Online Supplement Table 1, Figs. 4-5). The Hampel identifier method, applied as above, suggests that the youngest 132.1 ± 4.0 Ma date is a clear outlier (Fig. 4), and the inverse variance-weighted mean age of the eight remaining dates is 447.1 ± 4.6 Ma (2SE; $P = 0.0$) with a MSWD of 18.3. Expanding the uncertainty by multiplying the weighted mean by the square root of the MSWD, yields an age of 447.1 ± 19.8 Ma (2SE, $n = 8$; York et al., 2004), but again the large MSWD indicates over-dispersion, therefore we applied an expanded uncertainty estimate of twice the standard deviation of the subpopulation of dates (e.g., Heckert and Filliben, 2003), with one outlier removed, to yield our preferred (U-Th)/He zircon age of 450 ± 56 Ma (2σ) for the Clearwater East impact crater (Fig. 4).

6. Discussion

6.1 Robustness of the (U-Th)/He dating technique

Having applied the (U-Th)/He dating technique to the Clearwater doublet, and compared our results to previous geochronological studies, we now assess its robustness. Analytical uncertainties associated with the individual Clearwater East and West (U-Th)/He zircon dates (2.6-3.9% at 2σ , Online Supplement Table 1) and with our mean ages (9.6% for Clearwater West and 12.4% for Clearwater East) are comparable to the results of many published (U-Th)/He dating studies (e.g., Hourigan et al., 2005). However, our datasets are overdispersed with regards to their analytical uncertainties and causes for this overdispersion could be related to a non-uniform disturbance of the (U-Th)/He zircon system (e.g., due to locally variable degrees of shock metamorphism that affected the individual zircon grains, causing differential resetting), variations in He diffusion kinetics related to radiation damage that might affect resetting

susceptibility during impact, post-impact He loss, or chemical zoning that might invalidate the basic assumption of U-Th homogeneity used for the α -ejection corrections.

There is no evidence for major re-heating events since the time of impacts in the Clearwater Lake region (e.g., Ciesielski, 1991), although it is possible that a portion of Clearwater East may have experienced a transient thermal pulse during the formation of Clearwater West. Minor Mesozoic thermal perturbations of the Clearwater East and West impact melt samples are not impossible via kimberlitic intrusive activity documented to the west, south, and southeast of Clearwater (Zurevinski et al., 2011 and references therein). However, these kimberlite locations are situated ~600 to 1200 km away from the Clearwater structures, so thermal effects associated with them are unlikely to have had an effect on the (U-Th)/He zircon systematics. To show this, we will discuss our (U-Th)/He zircon data using a theoretical minor heating event to demonstrate that there is little evidence to support post-impact ^4He loss in the zircons.

Partial radiogenic ^4He loss due to a later heating event (e.g., post-impact burial or thermal effects of a nearby igneous intrusion etc.) would preferentially affect 1) smaller zircon crystals (Farley, 2002 and references therein), 2) crystals with greater amounts of radiation damage (Guenther et al., 2013 and references therein) and 3) shock-induced damage (Schmieder et al., 2015, and references therein), much more than larger crystals and/or those with lesser radiation damage. However, a plot of the average zircon crystal half-widths versus individual (U-Th)/He dates (Fig. 6a) does not provide evidence for a relationship of increasing (U-Th)/He dates with crystal size for either of these two impact craters. For Clearwater West, it actually shows the exact opposite (Fig. 6a).

The effects of radiation damage on He diffusion in zircon crystals are complex, with Guenther et al. (2013) showing that He diffusion is greatly enhanced in zircons that have experienced high (i.e., $>2 \times 10^{18} \alpha/\text{g}$) alpha particle doses, compared to α particle doses in the lower range of 5×10^{16} to $2 \times 10^{18} \alpha/\text{g}$. The significant increase in He diffusion with higher α particle doses is linked to increasing amounts of structural metamictization within the zircon crystal lattice. For example, the He closure temperature for metamict zircons is $<100^\circ\text{C}$ (Guenther et al., 2013), whereas the He closure temperature of normal (non-metamict) zircons is much higher at 180°C (Reiners et al., 2004, for grain radii of $60 \mu\text{m}$, using a spherical diffusion geometry, and a cooling rate of $10^\circ\text{C}/\text{Ma}$).

We chose a common approach, to plot eU versus (U-Th)/He date, to evaluate the potential of radiation damage effects on our comparatively old zircons (grains that are assumed to have undergone the same thermal history). eU is the effective uranium concentration in a zircon, which is a measure of the combined α particle production from the ^{235}U , ^{238}U and ^{232}Th parent isotopes in the crystal (Flowers et al., 2007), and is often used as a proxy for α particle radiation damage. Fig. 6b shows eU concentrations vs. (U-Th)/He dates from the Clearwater East and West impact craters. There is a slight negative correlation (trend slope of -0.14) observed in our Clearwater East results, suggesting that radiation damage may have reduced the He retentivity in some of our analyzed zircons (Fig. 6b). In contrast, the data plotted for the Clearwater West relict and neocrystalline populations show little to no correlation (e.g., trend slopes of -0.04 and 0.01, respectively) between eU and (U-Th)/He dates. While eU - age relationships are often used to evaluate the effects of helium diffusion changes related to radiation damage of the crystal lattice, it does not actually represent a real measure of how much radiation damage is retained in a particular crystal. Another way to evaluate He diffusion kinetics

in zircons is to calculate α particle doses that grains may retain, using their U-Th/He ages as a proxy for their radiation damage retention age (following arguments presented in Guenthner et al., 2013).

α particle doses of individual analyzed zircons were calculated using their eU values and our determined Clearwater East and West impact ages (~ 450 and ~ 280 Ma, respectively), to further evaluate the potential of radiation damage effects on our results. The calculations yield α particle doses ranging from 9.6×10^{17} to 1.9×10^{18} α/g for the neocrystalline zircon population from Clearwater West, 5.7×10^{16} to 4.7×10^{17} α/g for the relict population from Clearwater West, and 4.1×10^{17} to 1.1×10^{18} α/g for the relict zircons from Clearwater East (Fig. 6c). These calculated values are all lower than the $\sim 2 \times 10^{18}$ α/g alpha particle dose suggested by Guenthner et al. (2013) as the lower cutoff value for enhanced He diffusion in metamict zircons, and therefore suggest that minor post-impact heating events are unlikely to have been the cause for the dispersion observed in our (U-Th)/He zircon data.

The above scenario assumes that the impact events that reset the He systematics of the crystals also annealed the radiation damage these crystals had retained (following the arguments by Guenthner et al. (2013) that alpha particle damage anneals at the same or close to the same temperature range that He systematics are reset). However, not much is known about the actual α radiation damage annealing kinetics so it is possible that the relict grains may retain radiation damage from their history prior to the impact. To calculate the maximum α particle doses that the relict zircon crystal populations in both craters may have received, we assumed that their pre-impact formation ages are ~ 2.7 Ga based on 2.4-3.1 Ga ages quoted for basement rocks of the Superior Province (e.g., Reimold et al., 1981). The calculations yield maximum α particle doses ranging from 7.3×10^{17} to 8.3×10^{18} α/g (Fig. 6c) for relict zircon grains in both impact craters

(with the exception of one zircon crystal), all higher than the 2×10^{18} α /g metamict zircon dose of Guenthner et al., (2013) (Fig. 6c). If the relict grains retained this much radiation damage we would expect a much stronger correlation between the eU concentrations and (U-Th)/He zircon dates compared with those observed in Fig. 6b, in response to a minor post-impact heating event.

Based on these calculations it is unlikely that radiation damage is a major cause for the age overdispersion observed in our (U-Th)/He data, and there is no evidence of post-impact heating events that affected the He systematics of the zircons. It is plausible that radiation damage could explain the young date of relict grain CWE Z01 (132 ± 4 Ma, 2σ , Online Supplement Table 1), but it is unclear how this one grain's thermal and radiation damage histories could be so different from the other grains analyzed.

In our opinion, the most likely cause for overdispersion is U and Th zoning in the analyzed zircons, which can result in anomalously old and young (U-Th)/He dates. Natural zircons are well documented to generally be highly zoned in U and Th (e.g., Corfu et al., 2003). If a zircon grain rim is enriched in U and Th relative to the grain core, the (U-Th)/He α -ejection corrected date would be too young (Reiners et al., 2004; Hourigan et al., 2005). Conversely, if this one grain's rim is depleted in U and Th compared to the core, the α -ejection corrected (U-Th)/He date would be too old (Hourigan et al., 2005 and references therein). Extreme cases of U and Th zoning in zircons can lead to deviations from the actual (U-Th)/He age of up to 30%, and in some cases even higher (Hourigan et al., 2005), which easily covers the spread in helium ages observed in our dataset.

Schmieder et al. (2014) questioned the validity of using the (U-Th)/He method to date the formation ages of terrestrial impact structures, and suggested that the accuracy of the method must be tested on well-dated, impact melt-hosted mineral specimens before it

could be applied to the dating of impact structures with poorly constrained ages. We agree that such tests are valuable, and they have already been undertaken. For example, zircons from the crystalline impact melt of the Manicouagan impact structure in Quebec, Canada have been successfully dated by both the U-Pb technique (214 ± 1 Ma; 2σ ; Hodych and Dunning, 1992) and the (U-Th)/He method (213.2 ± 5.4 Ma, 2SE; van Soest et al., 2011). Inevitably, the (U-Th)/He method is less precise than the U-Pb method, but studies have shown that the U-Pb systematics of relict target rock zircons are commonly not fully reset during impact crater formation events, even for very large impacts (e.g., Moser et al., 2011), and instead neocrystalline zircon grains are required for reliable U-Pb dating of impact events (e.g., Hodych and Dunning, 1992). The $^{40}\text{Ar}/^{39}\text{Ar}$ technique offers more promise than the U-Pb method for shock metamorphism chronology, but this system is also not without issues; especially complications associated with (1) extraneous ^{40}Ar contamination as encountered by Bottomley et al. (1990) and Schmieder et al. (2015) on studies of Clearwater East, and (2) ^{39}Ar and ^{37}Ar recoil during fast neutron irradiation, resulting in complex ages (e.g., Bottomley et al., 1978). However, Schmieder et al. (2015) produced isochron plots and data tables to determine the possible influence of extraneous argon on the sampled melt rock, and to assess the validity and accuracy of their own Clearwater East results and those of Bottomley et al. (1990).

We would argue that no single geochronological technique can be used in all cases to successfully date impact structures. With knowledge of the availability and condition of suitable impactite material, the most accurate ages will be obtained by employing multiple geochronological techniques, especially when dealing with complex datasets from impact structures that have experienced post-impact heating and/or alteration. In addition, careful

petrological, chemical and isotopic analyses can also be undertaken to fully characterize samples, giving greater confidence in the quality of the ages (e.g., Mark et al., 2014).

6.2. Geochronological dating of Clearwater East and West impact craters and evidence of their diachronous nature

Our 280 ± 27 Ma (U-Th)/He weighted mean zircon age for Clearwater West (2σ ; Fig. 7a) overlaps with previous K-Ar and Rb-Sr ages of 291 ± 30 and 306 ± 30 Ma (2σ ; Wanless et al., 1965) and 266 ± 15 Ma (2σ ; Wooden and Simonds, quoted in Reimold et al., 1981), respectively (Fig. 7a). Our (U-Th)/He age is also statistically indistinguishable from the more precise $^{40}\text{Ar}/^{39}\text{Ar}$ impact melt ages of 280 ± 4 Ma (2σ ; Bottomley et al., 1990) and 283.8 ± 2.2 Ma (2σ ; Schmieder et al., 2015).

As Fig. 7b shows, our Clearwater East (U-Th)/He age of 450 ± 56 Ma overlaps with both the maximum ~ 460 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ age estimate reported by Bottomley et al. (1990), and the ~ 460 -470 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ “best-estimate” age range given by Schmieder et al. (2015). The Clearwater East $^{40}\text{Ar}/^{39}\text{Ar}$ age estimates and (U-Th)/He ages are not in agreement with the Rb-Sr whole-rock and mineral isochron age of 287 ± 26 Ma (2σ , $n = 4$; Reimold et al., 1981). The Reimold et al. (1981) Rb-Sr isochron age was obtained from one whole rock sample and 3 mineral separates (sample 9A), but 8 other analyzed whole rock impact melt samples failed to yield a Rb-Sr isochron age. Replotting the Reimold et al. (1981) Rb-Sr data using Isoplot v. 4.15 (Ludwig, 2011) yields a Rb-Sr whole rock and mineral isochron age of 287 ± 110 Ma (95% confidence, initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.7221 \pm 0.0020$, MSWD = 44, $P = 0.00$, $n = 4$) for an Isoplot Model 3 data fit, which assumes any excess scatter is the result of a uniform error in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, but also takes data point errors into consideration. This recalculated Rb-Sr isochron age of

287 ± 110 Ma (95% conf.) and its larger uncertainty, brings it within 4 Ma of our (U-Th)/He zircon age of 447 ± 56 Ma (2σ), but it still does not quite overlap.

Our new (U-Th)/He geochronological results lend credence to the interpretation of Schmieder et al. (2015) that the Clearwater East and West impact structures were formed by two different impact events separated in time by ~170 Ma, with the first projectile (forming the Clearwater East impact crater) striking during the Ordovician (Figs. 4 & 7b) and the second, later impact structure event (forming Clearwater West) occurring during the Cisuralian (i.e., Early Permian, Figs. 4 & 7a). It is worth noting that the later Permian impact of Clearwater West, appears to have had minimal thermal overprinting effect on both the (U-Th)/He and ⁴⁰Ar/³⁹Ar K-feldspar ages of Clearwater East, perhaps limiting the shock metamorphism and subsequent hydrothermal temperatures in our Clearwater East samples to temperatures of <230°C (i.e., a calculated helium closure temperature for 100 μm diameter zircon grain with a rapid (1000°C/Ma) cooling rate, using the helium diffusion parameters of Reiners et al. (2004)). Our Clearwater East sample was obtained from drill hole 2-63 at a depth of ~ 340 m, and this drill hole is situated ca. 40 km away from the center of the 32 km diameter Clearwater West impact crater (i.e., beyond the outer rim of the western crater).

There is additional corroborating evidence in support of the diachronic nature of Clearwater East and West. Firstly, the paleomagnetic study of Scott et al. (1997) showed that the Clearwater West and East impact structures have recorded different natural remnant magnetizations, an unexpected observation if they were formed at the same time. A second important observation has been the presence of Ordovician carbonate clasts detected within impact breccias sampled from the Permian Clearwater West structure, while Ordovician carbonates have not been detected in drill core samples from the older Clearwater East crater

(Schmieder et al., 2015 and references therein). A third inconsistency is that no meteoritic signature has been detected in Clearwater West impact melt samples, while Clearwater East impact melt shows a significant (~7%) chondritic signature (Palme et al., 1978).

6.3. Timing of the Clearwater East and West impact events

The Permian impact age for Clearwater West does not correlate with any well-known extinction or bio-diversification event. However, within uncertainties, the Ordovician age of Clearwater East overlaps with: 1) both pulses (~445 Ma and ~439 Ma) of the Ordovician-Silurian mass extinction event (Darroch and Wagner, 2015); 2) the Great Ordovician biodiversification event; and 3) the 470 ± 6 Ma breakup of the L-chondrite parent body (Fig. 8; Schmitz et al., 2008 and references therein). Fig. 8 shows that a comparatively large number of impact structures, mainly in Northern America and Baltoscandia, were produced on Earth during the Ordovician period.

7. Conclusions

Our (U-Th)/He zircon ages of 280 ± 27 Ma for Clearwater West and 450 ± 56 Ma for Clearwater East are here interpreted as accurate crater formation ages, supporting the hypothesis that the impact ages of these structures are diachronous (Schmieder et al., 2015). The two craters do not appear to be a crater doublet caused by the impact of a binary asteroid.

The results of this study demonstrate that the (U-Th)/He dating technique is a powerful tool for dating terrestrial impact structures. Our study has yielded reliable and informative ages from modest sample yields (9 datable zircon grains from each crater), which may offer an advantage where the sample size is limited (e.g., drill core samples), there is limited sampling

availability due to location remoteness, or if impact melt rocks have been eroded or are highly altered, and in cases where only lithic impact breccias (i.e., impactites without an impact melt portion) are available for dating.

The dispersion in our Clearwater East and West (U-Th)/He individual zircon dates serves to remind us that impact melt samples are composed of extremely complex material that incorporate: (1) existing target rocks that are shock metamorphosed and heated to varying degrees, (2) neocrystallites and, in some cases (3) a component of the extraterrestrial bolide. As Deutsch and Schärer (1994) pointed out, approximately 90% of target rocks and minerals are not completely reset during impact formation events, making geochronological dating of these structures extremely challenging.

With this in mind, we suggest that future (U-Th)/He terrestrial impact dating studies could benefit from the application of the ultraviolet (UV) laser ablation technique (e.g., Tripathy-Lang et al., 2013). UV laser microprobes have very high spatial resolution (nominally 100-250 μm) that can be used to ablate and analyze the cores of suitable U- and Th-bearing minerals. This method enables the (U-Th)/He dating of many crystals that are unsuitable for conventional (U-Th)/He work due to their crystal shapes and inclusions. This approach would improve the amount of data that can be obtained from small impactite samples. Moreover, the method eliminates the need for α -ejection correction of the resulting (U-Th)/He dates, unlike the conventional non-abraded whole grain dating technique. However, the applicability of the UV laser (U-Th)/He dating method is dependent upon the availability of grains of sufficiently large size ($\geq 100\text{-}150\text{ }\mu\text{m}$), the age of the impact structure, and the U and Th contents of the minerals being dated.

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Fig. 1. Simplified geological map for the Clearwater West (CWW) and East (CWE) impact structures. Geology modified after Simard et al. (2004), with additional compilation by L.M. Thompson. The black circles indicate impact melt sample locations from Clearwater West (Atkinson Island), and drill hole #2-63 from Clearwater East. Cpx = clinopyroxene, and opx = orthopyroxene.

Fig. 2. Light microscope photomicrographs of Clearwater West zircon grains dated in this (U-Th)/He study (with 2σ errors), showing length and width dimensions, and Th/U ratios (with 2σ errors). (a) West Z03 is a slightly rounded opaque grain. (b) The oldest zircon West Z07 is opaque and subhedral. (c) West Z04 is a semi-translucent rounded grain. (d) West Z05 is a semi-translucent rounded grain. (e) West Z09 is a clear well-rounded zircon grain. (f) The youngest grain West Z01 is semi-translucent and has an asymmetric termination. (g) West Z02 is a clear euhedral crystal. (h) Zircon West Z06 shares similarities with West Z01, Z02, and Z08 including general appearance, clarity, color, habit, and Th/U ratio. (i) Zircon West Z08 has a slight champagne-colored tint, but is relatively clear and exhibits well-defined terminations.

Fig. 3. Light microscope (color images in Figs. 3a-c and Fig. 3g) and SEM SE (grayscale images in Figs. 3d-f and Figs. 3h-i) photomicrographs of non-dated zircon grains and fragments from the Clearwater West impact melt sheet. (a) SEM-Z01 is a clear broken zircon grain fragment with a well-defined crystal outline. The lower SE image (Fig. 3d) of SEM-Z01 shows a split zircon grain fragment that lacks obvious fractures (Field of view (FOV) = 235μm). (b) SEM-Z02 is a translucent broken zircon grain with a rounded termination. The lower SE image (Fig. 3e) of SEM-Z02 shows sinuous fractures on the surface (FOV = 235μm). (c) SEM-Z03 is a subhedral opaque zircon fragment. A white rectangle marks the FOV shown in the lower photomicrograph (Fig. 3f). The lower SE image (Fig. 3f) of SEM-Z03 shows a grain fragment that displays a granular texture on its exterior (FOV= 128μm). (g) SEM-Z04 is a cloudy broken zircon grain that exhibits fractures on its exterior (see Figs. 3h-i). (h) the fractured exterior of SEM-Z04 is readily apparent in this SE image (FOV= 258μm). A white rectangle marks the FOV shown in Fig. 3i. (i) A close-up SE image of the microvesicles observed in zircon fragment SEM-Z04 (FOV = 10.6μm).

Fig. 4. Relative probability density plot of the (U-Th)/He zircon dates analyzed for the Clearwater West (blue) and Clearwater East (red) impact structures. The error-weighted (U-Th)/He mean age and expanded 2σ errors for the western structure is $280 \pm 27 \text{ Ma}$ ($n = 7$, with two outliers omitted), and the age for the eastern structure is $450 \pm 56 \text{ Ma}$ ($n = 8$, with one outlier omitted).

Fig. 5. Light microscope photomicrographs of Clearwater East zircon grains dated in this (U-Th)/He study (with 2σ errors), showing (U-Th)/He date, length and width dimensions, and Th/U ratios. (a) East Z02 is a translucent subhedral crystal. (b) East Z03 is a clear subhedral grain. (c) East Z05 is a rounded translucent grain. (d) The oldest grain East Z06 is clear and subhedral. (e) East Z07 is translucent and subhedral. (f) The East Z08 zircon is subhedral and clear with a reddish tint. (g) East Z09 is a reddish, clear subhedral zircon. (h) East Z04 is opaque and rounded, which may represent a relict grain that has been shock metamorphosed. (i) The youngest grain East Z01, is a clear euhedral zircon.

Fig. 6a. Average crystal half-width versus (U-Th)/He date (2σ error bars) plot for the Clearwater West zircons (white triangles = 5 relict grains, and white squares = 4 neocrystalline grains), and Clearwater East zircons (8 black circles).

Fig. 6b. Effective uranium (eU) versus (U-Th)/He date (2σ error bars) plot for the Clearwater West zircons (white triangles = 5 relict grains, and white squares = 4 neocrystalline grains), and Clearwater East zircons (9 black circles).

Fig. 6c. Plot of calculated alpha dose versus (U-Th)/He date (2σ error bars) for the Clearwater East and West zircons. The black and white triangles = 5 relict Clearwater West grains, the black and white squares = 4 neocrystalline Clearwater West grains, and the black and white circles = 8 oldest Clearwater East zircons. Two different periods of accumulation were used in calculating the α doses for CWE (447 Ma and 2.7 Ga) and CWW (275 Ma and 2.7 Ga) relict grains. The dotted vertical line indicates the $>2 \times 10^{18}$ α/g alpha particle dose of Guenthner et al. (2013), where we would expect enhanced He diffusive loss and lower He closure temperatures in the resulting metamict zircons.

Fig. 7a. Comparison of our Clearwater West (U-Th)/He zircon age (black circle) with previous ages (white circles) published for both the Clearwater West and East (Reimold et al., 1981) impact structures, Quebec. The stratigraphic boundary ages (shown in parentheses) are taken from the International Chronostratigraphic Chart (Cohen et al., 2015). Note that the ages of Wanless et al., (1965); i.e., 285 and 300 ± 30 Ma, and Schmieder et al. (2015; 286.2 ± 2.2 Ma) have been recalculated using the decay constants of Steiger and Jäger (1977).

Fig. 7b. Comparison of our Clearwater East (U-Th)/He zircon age (black circle with truncated error bars at upper and lower limits), with the previously determined Clearwater East $^{40}\text{Ar}/^{39}\text{Ar}$ maximum age of Bottomley et al. (1990) and the “best-estimate” $^{40}\text{Ar}/^{39}\text{Ar}$ age range of Schmieder et al. (2015). The stratigraphic boundary ages (shown in parentheses) are taken from the International Chronostratigraphic Chart (Cohen et al., 2015). See Figure 7a for the previously determined Rb-Sr Clearwater East age of $287 \pm 30 \text{ Ma}$ (Reimold et al., 1981).

Fig. 8. Timeline comparing our Clearwater East (U-Th)/He impact age with various Ordovician impacts on Earth, and the L-Chondrite parent body break-up event (figure modified from Ormö et al., 2014).

Table 1. K-Ar, $^{40}\text{Ar}/^{39}\text{Ar}$, and Rb-Sr ages recalculated using different decay constants.

Clearwater East references		Age (Ma)	Decay constants reference	Age (Ma)	Decay constants reference
Rb-Sr melt rock (Reimold et al., 1981)		287 ± 26	Steiger and Jäger (1977)	292 ± 26	Rotenburg et al. (2012)
*Rb-Sr melt rock (from Reimold et al., 1981)		287 ± 110	Steiger and Jäger (1977)	291 ± 120	Rotenburg et al. (2012)
$^{40}\text{Ar}/^{39}\text{Ar}$ melt rock (Bottomley et al., 1990)		~460	Steiger and Jäger (1977)	~464	Renne et al. (2011)
$^{40}\text{Ar}/^{39}\text{Ar}$ melt rock (Schmieder et al., 2015)		~456-466	Steiger and Jäger (1977)	~460-470	Renne et al. (2011)

Clearwater West references		Age (Ma)	Decay constants reference	Age (Ma)	Decay constants reference
K-Ar melt rock (Wanless et al., 1965)		291 ± 30	Steiger and Jäger (1977)	294 ± 30	Renne et al. (2011)
K-Ar melt rock (Wanless et al., 1965)		306 ± 30	Steiger and Jäger (1977)	309 ± 30	Renne et al. (2011)
**Rb-Sr melt rock (Wooden & Simonds)		266 ± 15	Steiger and Jäger (1977)	270 ± 15	Rotenburg et al. (2012)
$^{40}\text{Ar}/^{39}\text{Ar}$ melt rock (Bottomley et al., 1990)		280 ± 4	Steiger and Jäger (1977)	282 ± 4	Renne et al. (2011)
$^{40}\text{Ar}/^{39}\text{Ar}$ melt rock (Schmieder et al., 2015)		283.8 ± 2.2	Steiger and Jäger (1977)	286.2 ± 2.2	Renne et al. (2011)

Errors are quoted at 95% confidence or 2σ (see text).

* Recalculated in our study using the original date of Reimold et al. (1981) with Isoplot v. 4.15 (Ludwig, 2011).

** Age quoted in Reimold et al. (1981).

Single zircon crystal (U-Th)/He measurements and calculated dates for Clearwater West and Clearwater East impact structures, Quebec.

Sample	^{238}U ^a	Error ^b	^{232}Th ^a	Error ^b	^{4}He ^a	Error ^b	Th/U	Error ^b	eU	Age _{raw} ^c	Error ^b	R1 ^d	R2 ^d	L ^e	T1 ^f	T2 ^f	β	F _T ^h	Age _{corr.} ⁱ	Error ^b
Grain	pmole	1 σ	pmole	1 σ	pmole	1 σ		1 σ	ppm	Ma	1 σ	μm	μm	μm	μm	μm	1/ μm	Mean	Ma	2 σ
West Z01*	27.49	0.24	131.54	0.59	14.13	0.17	4.82	0.05	1403	188.2	2.4	65.5	51.3	226.7	48.4	57.0	0.044	0.806	233.5	6.1
West Z02*	12.95	0.11	49.72	0.24	6.28	0.07	3.87	0.04	1049	198.0	2.6	45.6	35.4	235.6	31.0	46.5	0.058	0.750	263.9	6.9
West Z03	9.12	0.08	9.31	0.04	3.41	0.04	1.03	0.01	362	231.2	3.2	48.9	46.1	259.0	57.4	66.3	0.051	0.787	293.6	8.2
West Z04	2.49	0.02	1.64	0.01	0.70	0.01	0.66	0.01	387	187.7	2.8	30.6	24.5	179.9	37.2	43.3	0.086	0.657	285.9	8.4
West Z05	4.46	0.04	5.38	0.02	1.52	0.02	1.21	0.01	513	204.9	3.0	33.9	32.9	172.9	33.7	34.7	0.072	0.707	289.9	8.4
West Z06*	20.03	0.17	79.76	0.37	10.14	0.12	4.01	0.04	2060	203.0	2.7	46.3	39.8	195.8	49.8	50.2	0.058	0.749	270.8	7.1
West Z07	3.96	0.03	1.51	0.01	1.29	0.02	0.38	0.00	329	228.4	3.4	34.7	27.9	215.4	30.5	33.5	0.073	0.705	323.8	9.5
West Z08*	13.48	0.12	56.78	0.28	7.26	0.09	4.24	0.04	1328	210.1	2.8	42.7	57.6	146.4	38.6	25.3	0.056	0.761	276.1	7.3
West Z09	0.41	0.01	0.50	0.01	0.14	0.00	1.25	0.04	63	212.5	4.0	34.6	33.7	127.9	30.5	24.9	0.075	0.694	306	12
East Z01	3.56	0.03	1.79	0.01	0.46	0.01	0.51	0.01	408	89.3	1.4	23.1	35.9	189.5	30.8	28.2	0.081	0.676	132.1	4.0
East Z02	2.92	0.03	2.74	0.02	1.52	0.02	0.94	0.01	378	325.4	4.9	34.2	34.1	145.6	31.1	32.7	0.073	0.703	463	14
East Z03	2.87	0.03	2.62	0.02	1.43	0.02	0.92	0.01	407	312.2	4.7	37.4	30.1	133.7	27.3	28.2	0.075	0.695	450	14
East Z04	6.58	0.06	4.76	0.03	2.92	0.04	0.73	0.01	704	289.1	4.3	32.9	36.5	146.3	22.4	22.8	0.071	0.712	406	12
East Z05	3.14	0.03	2.16	0.01	1.41	0.02	0.69	0.01	438	294.9	4.3	30.7	33.9	132.1	21.8	23.1	0.077	0.690	427	12
East Z06	3.17	0.03	3.46	0.03	1.80	0.02	1.10	0.01	396	344.4	5.0	30.6	38.2	140.8	23.1	23.7	0.073	0.703	490	14
East Z07	2.18	0.02	3.49	0.02	1.14	0.01	1.61	0.02	381	291.4	4.1	40.6	26.9	124.1	24.4	25.0	0.078	0.680	428	12
East Z08	2.58	0.02	2.45	0.02	1.41	0.02	0.96	0.01	271	339.3	5.0	37.0	41.2	139.2	32.1	30.5	0.067	0.727	467	14
East Z09	1.80	0.02	2.11	0.01	0.96	0.01	1.18	0.01	308	318.7	4.6	38.6	26.9	126.6	29.7	23.1	0.080	0.678	470	13

Online Supplement Table 1 legend:

^a Absolute concentrations measured for ^{238}U , ^{232}Th and ^{232}Th are used to calculate a 'raw age' that does not reflect ^4He loss due to α -ejection.^b The propagated analytical uncertainty.^c The 'raw age' was calculated with an iterative approach to solving the age equation.^d R1 and R2 are the zircon half-width dimensions.^e L represents the total crystal length.^f T1 and T2 represent the length of each pyramidal termination.^g β represents the surface-area-to-volume ratio for the crystal.^h The mean F_T was calculated assuming a bi-pyramidal prism geometry (Hourigan et al., 2005).ⁱ A F_T correction was applied to the 'raw age' following the procedures of Farley et al. (1996).

* Th/U ratio suggests 2 distinct West zircon populations (i.e., West Z01, Z02, Z06, and Z08 mean = 4.2, and West Z03-Z05, Z07 and Z09 mean = 0.9).