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

Kenny et al.

2016143_Table DR1 Ti and REE data.xlsx
Full analytical methods.

Following CL imaging, Ti concentrations in zircon were determined by secondary ion mass spectrometry (SIMS) on the CAMECA IMS1280 large geometry ion microprobe at the Swedish Museum of Natural History. Ti was measured on the $^{49}\text{Ti}$ peak due to $\text{Zr}^{2+}$ interferences on $^{46}\text{Ti}$, $^{47}\text{Ti}$ and $^{48}\text{Ti}$ and possible interferences of $^{50}\text{Cr}$ and $^{50}\text{V}$ on $^{50}\text{Ti}$, although these are probably minimal (Coogan and Hinton, 2006). An O$_2^-$ primary beam of c. 4.5 nA was used to sample a c. 15 µm spot. Sputtered secondary ions were admitted to the mass spectrometer via high transmission transfer ion optics and measured in peak-hopping mode in either a Faraday detector ($^{28}\text{Si}$) or low-noise, ion-counting electron multiplier ($^{30}\text{Si}$ and $^{49}\text{Ti}$) at a mass resolution $(M/\Delta M)$ of 3000. The $^{28}\text{Si}$ signal was used only for beam centering at the start of the analysis, following a pre-sputter to remove the Au coating. NIST610 glass (434 ± 14.7 ppm Ti; 1 standard deviation [SD]; (Pearce et al., 1997)) was used as the calibration reference material (RM) with 91500 (5.2 ± 1.5 ppm Ti; 1SD; n=15; (Fu et al., 2008)) and Temora-2 (10.2 ± 3.6 ppm Ti; 1SD; n=16; (Fu et al., 2008)) analyzed as quality control materials (QCM). In order to account for matrix differences between NIST standard glass, used as the RM, and zircon previous workers have applied correction factors to their zircon results – e.g. Fu et al. (2008) applied a correction factor of 1.16 to all of their zircon Ti measurements, based on their observation of a 16 % difference in “relative sensitivity factor” (RSF) between NIST and zircon. In contrast, by energy filtering the $^{30}\text{Si}$ and $^{49}\text{Ti}$ species (at -90 eV using a 30 eV bandpass), we here obtained perfectly accurate results for the zircon QCM 91500 and Temora-2 which are indistinguishable from previously published values, including the final, corrected, values of Fu et al. (2008), without the need for any post-analysis correction. Following SIMS analysis, the zircons were then polished down approximately 3-4 µm to remove the SIMS analysis pits. Ti was then measured simultaneously with a selection of rare earth elements (REE) were then measured by LA-ICPMS using a Photon Machines Analyte Excite 193 nm ArF laser coupled to a Thermo Scientific iCAP Qc at Trinity College Dublin. NIST610 was again used as the RM and fresh chips of 91500 and Temora-2 were analyzed as QCM. Zr was used as an internal standard. In a separate analytical session all grains were U-Pb age dated by LA-ICPMS to confirm they date to the established 1.85 Ga age of the impact melt sheet (Davis, 2008) and are not inherited. A 24 µm-diameter circular spot was used for all LA-ICPMS analyses.

Additional references

Figure DR1. Example CL images of zircon from the Sudbury melt sheet. A: A CL-dark zircon from the norite. B: A zircon from the granophyre displaying fine igneous growth zoning. C: A zircon from the granophyre displaying subtle igneous growth zoning close to its perimeter. D: An extremely altered zircon from close to the top of the melt sheet. All scale bars 50 μm.
A: An example of Ti-bearing titanite with its distinctive pyramidal form in the Granophyre unit. Image taken in plane polarized light.

B: An example of rutile found in mineral separates from the Quartz Gabbro.

C: Scanning Electron Microscopy image of location selected for qualitative energy-dispersive X-ray analysis (EDS) on grain shown in B.

D: EDS energy spectrum for analysis location shown in C. Ti and O peaks confirm the presence of a Ti-oxide in the Sudbury melt sheet. The C peak is due to carbon coating of the sample to prevent electron charging. All scale bars 50 µm.
Figure DR3. Chondrite-normalized abundances of REE in Sudbury melt sheet zircons. Normalization uses the chondrite values of Anders and Grevesse (1989). Elements are spaced according to their effective ionic radii in eightfold coordination (Shannon, 1976), indicated in picometres on the upper x-axis. Blue: norite; green: quartz gabbro; red: granophyre.


Figure DR4. Downhole variation in Ti/Zr ratio during laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) analyses of Ti in zircon. Traces represent the five period moving average of the geometric mean of background-corrected signal ratios. Note that the Y-axis represents ablation time and cannot be strictly equated with depth, as ablation progresses more effectively in zircon of lower crystallinity. A: Quality control material (QCM) standard zircons 91500 (mean of n=24 analyses) and Temora-2 (n=26) show no appreciable Ti/Zr fractionation with ablation progress. This is consistent with the accurate measurement of Ti in these natural standards by LA-ICPMS, yielding results indistinguishable from SIMS. B: Comparative down-hole evolution of Ti/Zr in three sample zircons shows two contrasting types of behavior. First, unknown zircons in which Ti measured by LA-ICPMS was distinguishably higher (at 1 SD analytical uncertainty) than Ti measured by SIMS consistently show consistent trends of increasing Ti/Zr ratios down-hole. This is illustrated with samples 14GGK110 (n=12) and GSM073 (n=17). In the sample 14GGK110, for example, all apparent Ti concentrations by LA-ICPMS were distinguishably higher than the corresponding SIMS analysis. Second, for the samples in which Ti concentrations by LA-ICPMS and SIMS are generally in better agreement, there is no clear down-hole Ti/Zr increase. This is shown for sample 14GGK118 (n=12; excluding one outlier).
The inspection of down-hole Ti/Zr signals suggests that the over-estimation of Ti content in some sample zircons analyzed in this study is related to more efficient transport and ionization of Ti with increasing pit depth compared to the calibration and quality control zircons. This contrasts with the proposal of Wielicki et al. (2011) who attributed the offset between SIMS and LA-ICPMS to the larger sampling volume of LA-ICPMS, thereby enhancing the probability of encountering discrete zones of extraneously high Ti.

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

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

Additional references