ATOM PROBE TOMOGRAPHY OF 4.45 GA LUNAR ZIRCON FROM THE APOLLO 17 CIVET CAT NORITE CLAST

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Introduction: U/Pb geochronology of zircons is an important tool for constraining the timescales of planetary processes. Lead mobility during secondary processes has been shown to create spurious U-Pb and Pb-Pb ages [1]. Six NanoSIMS analyses of micro-zircon from the Civet Cat norite clast in Apollo 17 impact melt breccia 72255 yielded an average $^{207}Pb/^{206}Pb$ age of 4453 ± 34 Ma [2]. This is the oldest lunar zircon age dated so far but could be the result of unsupported radiogenic Pb clusters at sub-micrometer scale [2]. Here, we use atom-probe tomography (APT) to investigate the nanoscale distribution of trace elements Pb, Y, and Hf in one of the oldest zircons in 72255 to better understand the nanoscale features of this zircon and provide further constraints on the significance of the Pb-Pb age of the zircons measured by [2]. In APT, atoms are field-evaporated from the surface of a sample and analyzed by a position-sensitive time-of-flight mass spectrometer, allowing for the detection of individual isotopes, as well as the position of ions in three dimensions. The technique has previously been used to study extraterrestrial and terrestrial zircons, e.g., from other Apollo 17 samples [3], Martian meteorites [4] and the Jack Hills conglomerate from Western Australia [5].

Methods: A 1 μm by 10 μm lamella was lifted out from zircon Z14 of Apollo 17 thin section 72255,123 (Z14 pit #1 = 4457 ± 47 Ma, pit #2 = 4399 ± 46 Ma) [1], encompassing the pits left by SIMS analysis that did not overlap with metamict zones (based on CL images). Five nanotips, prepared using established APT sample preparation methods (e.g. [6]) were analyzed with the LEAP 5000XS tomograph at the NUCAPT facility of Northwestern University. Instrumental conditions were chosen to maximize sample stability as well as minimize thermal noise due to laser heating. CAMECA's IVAS software was used to reconstruct the tomographic data from each nanotip sample.

Results: Three of the five nanotips yielded data, for a total of ~50 M ions and a length of ~500 nm. These three nanotips are all sourced from the same SIMS pit #2, and are laterally separated by about 1 μm. In two of the nanotips, large thermal tails in the mass spectra resulted in a detection limit of ~1 at. %. In nanotip A, less abundant species were detected, including ^{89}Y, $^{176-180}Hf$, ^{208}Pb, and ^{232}Th. We determine the ^{208}Pb concentration to be 170 at. ppm. Isotopes ^{206}Pb and ^{207}Pb were below our detection limits with reported concentrations [2] of 28 and 16 wt. ppm, respectively, whereas Y in pit #2 was reported at 203 wt. ppm with SIMS and was detected with APT. Several different methods were used to survey for heterogeneity in the nanotips. Density isosurface analysis and nearest-neighbor distribution analysis of Pb and Y do not show any clusters, such as those presented in [4]. These elements are homogeneously distributed through the zircon and there is no difference between the spacing of Pb atoms in the nanotip and a model of Pb atoms randomly distributed.

Discussion: The ancient age of 4453 ± 34 for the Civet Cat norite zircons could either be induced by nanoscale Pb clusters or record an authentic crystallization age with normal Pb loss [2]. If radiogenic Pb clusters occurred in these grains, their intercluster distance must be larger than 500 nm. Trace element mobility in zircons has been documented on the nanoscale (e.g. [3-5, 7, 8]) in volumes that are of the same scale as what was measured in this study. Although we could not obtain $^{207}Pb/^{206}Pb$ distribution and corresponding ages, the absence of ^{208}Pb and trace-element clusters likely indicates that no significant Pb clustering occurred within Z14 pit #2. This provides evidence that the old age reported by NanoSIMS Pb-Pb dating – 4453 ± 47 Ma – is the true age of crystallization of this zircon, and the younger age of pit #2 results from normal Pb loss. Our study demonstrates how important APT analysis is to survey Pb mobility and to establish the significance of U-Pb and Pb-Pb ages obtained from ion-microprobe data.

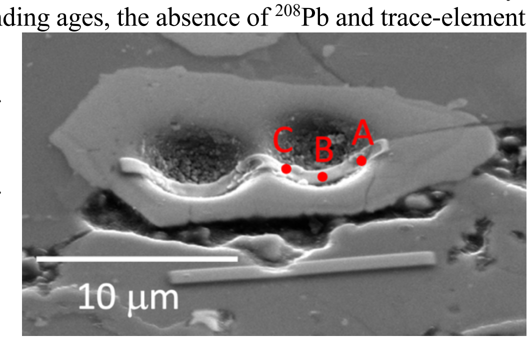

Fig. 1: SEM image (tilted 55° from the normal) showing the location of the three analyzed nanotips in pit #2 of zircon Z14 of the Civet Cat norite clast in Apollo 17 breccia 72255.

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