

Atom probe tomography of martian zircon and baddeleyite reveals a 4.4 billion year record of cool, stable and hydrothermally altered crust

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Zircon and related U-Pb dating minerals have proven to be invaluable proxies for the geochemical evolution of the Earth and its hydrosphere, as have their microstructures for reconstructing planetary bombardment histories. The integration of electron diffraction (EBSD) and atom probe tomography (APT) techniques is now revealing novel nanoscale proxies of high temperature metamorphic and strain events that have affected such micrograins and their host crust. Here we extend these relatively non-destructive techniques to a rare suite of 4.4 billion year old, microscopic martian zircon and baddeleyite grains from meteorite NWA 7475. The subhedral igneous grains were re-deposited on Mars at ~1.5 Ga to form a polymict breccia later launched to Earth during a low-pressure shock event. EBSD analysis of the population reveals the expected pervasive cracking of all minerals due to the low-pressure launch. Pre-launch shock metamorphic features are absent with the exception of one grain that shows planar features parallel to the c-axis. A subset of grains is metamict due to prolonged residence in the upper crust at temperatures less than ~150°C. APT analysis of representative zircon and baddeleyite grains did not detect any of the trace element nanoclusters observed in terrestrial zircon exposed to high-temperature metamorphism. Curvilinear chains of nanoclusters with varying proportions of Fe, Mg, Al, and Ca in one grain are interpreted as residual fluid-altered nanofractures that were annealed during breccia deposition. Post-deposition mobilization of Si created micron-scale reaction rims of zircon after baddeleyite without appreciable Pb-loss. U-rich zircon domains that attained their metamict state since the 1.5 Ga annealing event have seen additional martian fluid interaction as evidenced by Cl, Al, K and P in a metamict core. This nano-geochronological data for fragments of the oldest known martian crust are consistent with a cool, crustal lid that was stable over 4.4 billion years, and subject to episodes of fluid activity. The survival of this 'cool' crystal record places a 4.4 Ga minimum age on the global melting and bombardment episodes that created Borealis basin and the martian hemispheric dichotomy.