ATOM PROBE INSIGHTS INTO U-PB AGE RESETTING IN BADDELEYITE

L. F. White[1], D. Reinhard[2], D. Moser[3], J. R. Darling[1], D.Bullen[1], T. J. Prosa[2], D. Olson[2], D. J. Larson[2], P. H. Clifton[2], D. Lawrence[2] and I. Martin[2], [1]School of Earth and Environmental Sciences, University of Portsmouth, Portsmouth, PO1 3QL, UK. (lee.white@port.ac.uk). [2]CAMECA, Madison, Wi 537711, USA. [3]Department of Earth Sciences, University of Western Ontario, London, Ontario N6A 5B7, Canada.

Introduction: Baddeleyite (monoclinc-ZrO_2) is a widely occurring accessory phase reported from an array of terrestrial mafic and ultra-mafic rocks [e.g. 1] as well as within shergottites [2,3], Lunar meteorites and Apollo samples [e.g. 4,5], asteroidal achondrites [6] and ordinary chondrites [7]. As an established U-Pb geochronometer [8], baddeleyite has the potential to resolve the timing of Solar System crystallization events for a number of low-Si lithologies where zircon ($ZrSiO_4$) is absent. However, the exposure of these grains to shock metamorphism induces partial to complete loss of lead, resetting the U-Pb chronometer and complicating their interpretation. Recent work has focused on coupling isotopic analysis with microstructural observations, linking the extent of amorphisation and recrystallisation to the severity of lead-loss for the first time [i.e. 2, 9]. This approach allows for the targeting of pristine or deformed crystals in an attempt to differentiate the timings of igneous and impact events. However, given a discrepancy between the severity of lead diffusion within natural [2, 9] and experimental [10] shock conditions, our fundamental understanding of U-Pb age resetting in this potentially key planetary chronometer is poorly constrained. The application of atom probe tomography (APT) to zircon has proven exceptionally useful in distinguishing the response of Pb to both post-crystallization annealing [11] and deformation [12]. However, this approach has never been applied to heavily shock loaded material. Here we present the first insights into the atomic-scale shock response of lead cations within baddeleyite, coupling these observations with detailed EBSD analysis to produce a first order insight into the mechanisms of U-Pb age resetting in baddeleyite.

Results: By analyzing samples with a well-constrained geological history, all analyses can be placed within a defined geological context often absent from *ex-situ* meteoritic samples. Here we target the highly-shocked rocks of the Matachawan dyke swarm, Ontario, which crystallized around 2.47 Ga and underwent shock metamorphism as a result of the Sudbury impact event around 1.85 Ga [13]. EBSD analysis of a population of baddeleyite grains sampled ~500m beneath the lower contact of the melt sheet yields a variety of microstructure development, including (partial) amorphisation and shock-induced retrogressive twinning of monoclinic domains following localized transformation to a high pressure orthorhombic phase. A single atom probe pullout from this population yields a bulk U-Pb age of 2.33 Ga ($\pm$ 4.5% 2σ), younger than that reported for the crystallization of the dyke swarm (~2.47 Ga [13]). This suggests that a small amount of radiogenic lead has escaped the tip during the 1.85 Ga impact event, yielding a partially reset age between crystallization and impact. However, closer inspection of the tip reveals a planar dislocation feature decorated with clusters of Fe, Y and other incompatible cations (principally Si, Mg and Mn). Segregation of this tip yields a U-Pb age of 1.45 Ga ($\pm$ 15% 2σ), significantly younger than the impact event. By removing the influence of this planar feature, a crystallization age of 2.45 Ga ($\pm$ 4.7% 2σ) can be generated.

Conclusions: Our results suggest that age resetting in monoclinic-ZrO_2 is driven by lead diffusion along planar (and potentially curvi-planar) features that encourage pipe diffusion long past their (shock-induced) generation. The scale of these features (~5nm wide planes) is unresolvable at EBSD length scales, requiring the coupled isotopic / structural visualization aspect of atom probe tomography to accurately segregate regions of post-impact lead diffusion. Going forward, true crystallization ages may be drawn from partially reset bulk grains (such as those reported from shergottites [9]), greatly enhancing our ability to date Solar System igneous processes.

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