

**ACCESSORY MINERAL CHRONOLOGY OF EUCRITES REVEALS NEW INSIGHTS INTO THE FORMATION, EVOLUTION, AND BOMBARDMENT OF VESTA.** L. F. White<sup>1,2,3,4</sup>, D. E. Moser<sup>5</sup>, J. R. Darling<sup>3</sup>, B. Rider-Stokes<sup>3,4</sup>, B. Hyde<sup>1,5,6</sup>, K. T. Tait<sup>1,2</sup>, K. Chamberlain<sup>7</sup>, A. K. Schmitt<sup>8,9</sup>, M. Anand<sup>4</sup>, and J. Dunlop<sup>3</sup>. <sup>1</sup>Royal Ontario Museum, Canada. <sup>2</sup>University of Toronto, Canada. <sup>3</sup>University of Portsmouth, UK. <sup>4</sup>Open University, UK. <sup>5</sup>Western University, Canada. <sup>6</sup>Queen's University, Canada. <sup>7</sup>University of Wyoming, USA. <sup>8</sup>University of California, Los Angeles, USA. <sup>9</sup> Universitat Heidelberg, Germany. (email: lee.white@open.ac.uk)

**Introduction:** The Howardite-Eucrite-Diogenite (HED) clan of achondritic meteorites are believed to represent the asteroid 4-Vesta, with the eucrites sampling the basaltic crust of the differentiated planetesimal. Measured <sup>40</sup>Ar/<sup>39</sup>Ar systematics of eucrites record a preponderance of ages between 3.4 and 4.1 Ga, which have been linked to an increase in impact rate and intensity associated with a period of late heavy bombardment of the inner solar system [1]. This theory builds upon a prevalence of 3.9 Ga ages which have been reported in the <sup>40</sup>Ar/<sup>39</sup>Ar systematics of samples returned by the Apollo missions, as well as lunar meteorites [2]. However, recent work examining the U-Pb systematics and microstructure of accessory minerals such as baddeleyite and apatite have revealed an absence of shock-reset ages which can be attributed to this cataclysmic event [3]. In addition, the evolution of <sup>40</sup>Ar/<sup>39</sup>Ar systematics coupled with a gradual decrease in impact events linked to late accretion could also yield the distribution of Ar ages observed in Apollo samples, weakening support for late heavy bombardment [4]. Here, we conduct U-Pb dating of structurally characterised accessory mineral phases in six eucrites to provide new constraints on the impact and thermal history of the asteroid 4-Vesta.

**Samples and Methodology:** In total, six eucrites were analyzed in this study: Northwest Africa (NWA) 1000, NWA 2202, NWA 11747, NWA 11748, NWA 12866 and NWA 12867. Of these, NWA 1000 is most unique as a Stannern-trend eucrite, though all samples are either monomict (NWA 11747 & 11748) or polymict (NWA 1000, 2202, 12866 & 12867) breccias with varying major element compositions. All samples display shock features attributed to a low pressure regime (< 20 GPa) with only NWA 1000 containing maskelynite (diaplectic feldspar glass) indicative of higher shock pressures.

Scanning electron microscopy (SEM) work was conducted on single thin sections of all six eucrites, utilizing Energy-Dispersive X-Ray Spectroscopy (EDS) to identify chemical regions of interest (P, Zr) for higher resolution imaging. Zircon was located in all sections, though apatite was located in five of the six samples (being absent only in NWA 2202), with baddeleyite present in four sections (absent in NWA 11747 and 11748). Electron backscatter diffraction (EBSD) analysis was conducted to quantify the internal microstructure of individual grains prior to dating.

For baddeleyite and zircon, secondary ionization mass spectrometry (SIMS) was utilized to measure U-Pb systematics, while laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used to date individual apatites.

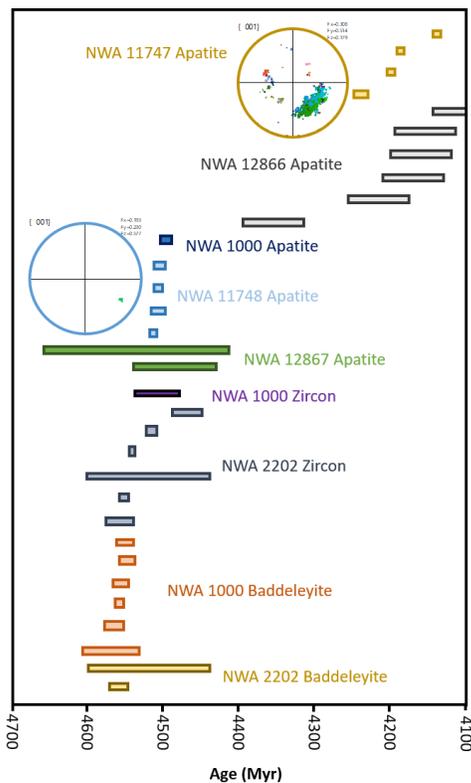
**Results:** EBSD analysis of baddeleyite within the six eucrites reveals orthogonal relationships between complex twin domains, diagnostic of reversion from a high-symmetry zirconia polymorph (such as high temperature cubic and tetragonal, or high pressure orthorhombic ZrO<sub>2</sub> [5]). Zircon grains in all samples are microstructurally simple, displaying < 2° of total misorientation and no evidence of {112} microtwins or granoblastic formation indicative of high pressure or temperature metamorphism [6]. Apatite reveals a range of structures across the five samples analyzed (Figure 1), including widespread evidence for plastic deformation; three eucrites (NWA 1000, 11748 and 12867) display < 10° cumulative misorientation, while two (NWA 11747 and 12866) contain apatite with > 40° of cumulative misorientation and evidence for recrystallization.

SIMS analysis of baddeleyite reveals ancient U-Th-Pb ages, with NWA 1000 yielding an average age of 4559 ± 9 Ma (2sd; n=6) and NWA 2202 a single age of 4559 ± 12 Ma. A single zircon grain in NWA 1000 records a U-Pb age of 4510 ± 12 Ma, while zircon in NWA 2202 preserves a spread of ages between 4559 ± 19 Ma and 4471 ± 19 Ma.

LA-ICP-MS analysis of apatite within five eucrites reveals distinct age populations, with NWA 1000, 11748 and 12867 recording ages of 4499 ± 6 Ma, 4509 ± 3 Ma (n=4), and 4511 ± 3 Ma (n=4), respectively. NWA 11747 records a spread of apatite ages between 4240 ± 5 Ma and 4138 ± 6 Ma, while NWA 12866 displays ages between 4356 Ma and 4106 Ma.

**Discussion:** Structurally-complex baddeleyite grains, which contain evidence for reversion twinning indicative of high temperature (> 1300 °C) or pressure (> 5 GPa) conditions [5], preserve the oldest measured U-Pb ages within the samples (~4559 Ma), supportive of eucrite formation within the first few million years of solar system history [7]. Zircon, despite containing no evidence for shock annealing or deformation, records a spread of ages between baddeleyite crystallization (4559 Ma) and 4471 Ma. Though comparable

young ages in eucritic zircon (e.g. 4530 Ma) have previously been attributed to impact resetting [7], the absence of microstructural features associated with impact induced Pb loss (such as {112} microtwin lamella or granoblastic textures) suggests an endogenic origin for the grains. The spread of ages preserved within the clasts and matrix of brecciated eucrite NWA 2202 are thus attributed to either thermal or hydrothermal alteration on 4-Vesta until at least 4471 Ma. This interpretation is further supported by LA-ICP-MS analysis of minimally deformed apatite grains in NWA 1000, NWA 11748 and NWA 12867, which all preserve ages around ~4500 Ma that are likely attributed to cooling of the parent body.



**Figure 1:**  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of zircon and baddeleyite, and  $^{206}\text{Pb}/^{238}\text{U}$  ages of apatite within six unique eucrites (NWA 1000, 2202, 11747, 11748, 12866 and 12867). For reference, {001} pole figures for apatite in NWA 11748 and NWA 11747 are shown to highlight the contrast between minimally and intensively plastically deformed apatite.

Extensively deformed and recrystallized apatite grains within NWA 11747 and NWA 12866 record  $^{238}\text{U}$ - $^{206}\text{Pb}$  ages of between 4356 and 4106 Ma. Correlating microstructure (EBSD) and age dating (LA-ICP-MS) of apatite grains is highly suggestive of impact-induced Pb loss and age resetting, revealing at least one significant impact event on the asteroid 4-Vesta

around 4100 Ma. Given the sensitivity of apatite to age resetting, whereby grains start to lose Pb through solid state diffusion at  $< 500\text{ }^\circ\text{C}$  (significantly lower than baddeleyite and zircon ( $900\text{ }^\circ\text{C}$ )), it is significant that the highly deformed grains within our analysed population still preserve U-Pb ages older than 4.1 Ga [e.g. 8]. Assuming the inner solar system was exposed to both more frequent and more severe impact event during a period of late heavy bombardment around 3.9 Ga, it is expected that at least some of the accessory minerals analysed within these six eucrites would preserve isotopic or structural evidence of the event. For example, it has previously been shown that the boundary domains in reversion twinned baddeleyite are highly sensitive to Pb loss during low temperature metamorphic events [9]. However, despite showing comparable microstructures, the grain population analysed here displays no evidence for Pb loss at any point following crystallization c. 4559 Ma ago.

In total, 32 unique U-Th-Pb analyses of baddeleyite, zircon, and apatite reveal a range of new insights into the formation and evolution of the eucrite parent body. Ages of reversion twinned baddeleyite support formation of the parent body around 4559 Ma, in close agreement with previous studies (e.g. 4560 Ma baddeleyite in Juvinas [10]). Structurally simple zircon grains record ages between crustal formation and 4471 Ma, which likely records a significant metamorphic event on Vesta. The six eucrites analyzed contain no geochronological evidence for a hypothesized period of late heavy bombardment (Figure 1), making our results consistent with those from accessory minerals on the Moon [3] and Mars [11]. This conclusion is supported by the microstructural state of the analysed minerals, which fail to record indicative evidence of shock deformation beyond crystal plastic deformation within  $> 4.1$  Ga apatite. This study also highlights the potential of apatite as a shock chronometer, whereby the correlated analysis of microstructure and U-Pb isotopes facilitates significantly enhanced interpretation of generated age data, here placing new constraints on the evolution of the asteroid 4-Vesta.

**References:** [1] Marchi et al., 2013. *Nat. Geosci.*, 6(4), 303-307. [2] Kring & Cohen, 2002. *Journ. Geophys. Res.*, 107(E2), 5009. [3] Crow et al., 2017. *GCA*, 202, 264-284. [4] Boehnke & Harrison, 2016. *PNAS*, 1-5. [5] White et al., 2020. *Nat. Astro.*, 4, 974-978. [6] Moser et al., 2011. *Can. Journ. Earth Sci.*, 48(2), 117-139. [7] Hopkins et al., 2015. *Icarus*, 245, 367-378. [8] Nemchin et al., 2010. *MAPS*, 44(11), 1717-1734. [9] White et al., 2017. *Nat. Comms.*, 8(1). [10] Bukovanska, M., Ireland, T. R., & Janicke, J. 1997. *Journ. Geosci.* 42(3),20. [11] Moser et al., 2019. *Nat. Geosci.* 12, 522-527.