CRYSTALLOGRAPHIC AND CHRONOLOGICAL EVIDENCE FOR A LARGE BASIN-FORMING LUNAR IMPACT AT ~4.33 Ga. White, L. F.[1,2*], Černok, A.[1,2,3], Darling, J. R.[4], Whitehouse, M.[5], Joy, K. H.[6], Cayron, C.[7], Dunlop, J.[4], Tait, K. T.[1,2] & Anand, M.[3,8]. [1]Centre of Applied Planetary Mineralogy, Department of Natural History, Royal Ontario Museum, Toronto, Ontario, M5S 2C6, Canada. [2]Department of Earth Sciences, University of Toronto, Toronto, Ontario, M5S 3B1, Canada. (*Email: lwhite@rom.on.ca). [3]School of Physical Sciences, The Open University, Milton Keynes, MK7 6AA, UK. [4]School of Earth and Environmental Sciences, Burnaby Building, Burnaby Road, University of Portsmouth, Portsmouth, PO1 3QL, UK. [5]Swedish Museum of Natural History, Frescativägen 40, Stockholm, Sweden. [6]School of Earth and Environmental Science, University of Manchester, Oxford Road, Manchester, M13 9PL, UK [7]Laboratory of ThermoMechanical Metallurgy (LMTM), École Polytechnique Fédérale de Lausanne (EPFL), Rue de la Maladière 71b, 2000 Neuchâtel, Switzerland.. [8]Department of Earth Sciences, The Natural History Museum, Cromwell Road, London, SW7 5BD, UK.

Introduction: Insights into the formation, differentiation and bombardment of planetary bodies have been provided through geodynamic modelling, remote sensing observations, and isotopic analysis of planetary meteorites. The resulting models are hindered by the paucity of mineralogical evidence that can place direct constraints on these very high temperature processes. Although many mineral thermobarometers can record geological temperatures ranging up to a max of ~1500 °C, empirical mineralogical and geochemical evidence of higher temperatures is often lost due to extensive melting (and melt loss) at such conditions [1]. Recently, microstructural analysis of the accessory mineral baddeleyite has revealed new insights into the pressure temperature time (P-T-t) history of shock-melted and mantle-derived rocks [2, 3], with grains preserving microstructural evidence of high temperature and pressure ZrO_2 polymorphs, despite reversion to the stable monoclinic structure at ambient conditions. For example, tracing the phase heritage of baddeleyite to the cubic-ZrO_2 structure constrains peak temperature conditions to > 2370 °C at ambient surface pressures [4, 5], far in excess of that attainable with traditional mineral geothermometers. Here, we analyse an exceptional baddeleyite grain in an Apollo troctolite (76535) to reveal the diagnostic crystallographic relationships indicative of cubic-ZrO_2 phase heritage. This observation places new constraints on the driving mechanism of lunar crustal formation, and represents the first mineralogical evidence for a large, super-heated impact melt sheet on the near-side of the Moon at ~4.33 Ga.

Methods: All work was conducted *in situ* within a thin-section that was vibratory polished with 0.05 micron alumina. The target baddeleyite grain was located in section 76535,51 using traditional microscopy techniques, and backscatter electron (BSE) images were collected using a Zeiss EVO MA10 LaB_6 scanning electron microscope (SEM) housed at the University of Portsmouth. Micro- to nano-scale structural analysis was conducted by electron backscatter diffraction (EBSD) using an Oxford Instruments Nordlys EBSD detector mounted on the same SEM instrument following previously described techniques [3]. Electron probe micro analysis (EPMA) of mineral chemistry was conducted at the Open University. Pb-Pb isotopic measurements were performed using CAMECA 1280 ion microprobe at the NordSIMS facility, located at the Swedish Museum of Natural History (Stockholm), following previously reported protocols for Ca-phosphate analyses [6]. In total, four $^{207}Pb/^{206}Pb$ ages were measured from the grain, subsampling different microstructural domains.

Results: Within the analysed section a large (80 × 250 μm) subhedral baddeleyite crystal displays several distinctive crystallographic domains (each 2 to 50 μm in width), clearly observable at the resolution of optical microscopy. Detailed analysis of the grain using electron backscatter diffraction (EBSD) techniques facilitated the quantification of these variant orientations, revealing a range of unique disorientation relationships between the domains, predominately 90°/<001>, 180°/<001>, and 180°/<9,0,10>. Reduction of the entire EBSD dataset using the ARPGE [7] software package highlights peaks in disorientation analysis at 90°, 120° and 180° which, along with the presence of three unique crystallographic axes in the <010> (*b*-axis) direction along three <100> cubic directions, cannot be explained by reversion from the tetragonal or orthorhombic systems alone [5]. As such, the phase heritage of the grain can be confidently associated with reversion from a single cubic-ZrO_2 precursor. No amorphous or crystalline SiO_2 was observed in direct contact with the analysed baddeleyite grain, suggesting the phase does not represent high temperature dissociation from a zircon precursor [2] and instead remained pure ZrO_2 throughout its formation and evolution. EPMA of the grain reveals 1.26 wt% TiO_2 and 1.4 wt% HfO_2, though other impurities (Mg, Ca, Fe, Al, and Si) fall below 0.08 wt%. Dating of the grain using secondary ion mass spectrometry (SIMS) reveals a spread of $^{206}Pb/^{207}Pb$ ages between 4311.3 ± 6.7 Ma (2σ uncertainty) and

4334.5 ± 4.6 Ma, yielding high scatter on the calculated weighted average age of 4326 ± 16 Ma (2 standard deviation uncertainty, MSWD = 13). The grain is between 40 and 63 Myr older than previously reported ages from smaller baddeleyite grains within the same rock (4271 ± 29 Ma [8]), while the youngest analysis is concordant with Sm-Nd ages (4301 ± 11 Ma; [9]).

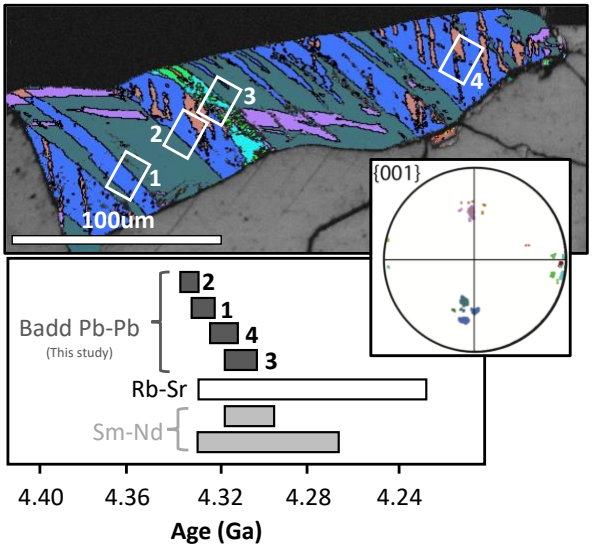

Figure 1: *Raw EBSD data (all euler coloring with highlighted high angle (>10°) boundaries) for large baddeleyite in Apollo troctolite 76535. SIMS Pb-Pb analysis spots are overlain, revealing the microstructurally constrained age resetting of the crystal between 4334 and 4311 Ma. The youngest age is concordant with previously analysed Sm-Nd results, while the oldest is older than Rb-Sr ages [9] inferring partial resetting of the grain during cooling.*

Discussion and conclusions: Formative temperatures for cubic-ZrO_2 vary based on the major element composition of the grain. Although the influence of TiO_2 and HfO_2 on the P-T-t conditions required to induce high symmetry ZrO_2 polymorphs is unconstrained, oxide impurities typically have to occur in concentrations on the order of 5 to 10 mol% to substantially influence phase transformation temperatures within the ZrO_2 system [10]. The temperature required to induce the cubic-ZrO_2 phase also varies based on the confining pressure of the annealed sample [10], while the influence of oxygen fugacity on the transition is currently unknown. However, at ~30 km depth an estimated ~0.2 GPa of confining pressure would allow formation of cubic-ZrO_2 at ~2300 °C. Models for the thermal history of the Moon cannot reconcile these required temperatures through endogenic processes alone [11], although impact-induced melting of the lunar crust has been modelled to generate sufficient temperatures (~2300 °C) as to facilitate cubic-ZrO_2 formation [4]. Importantly, recent studies into the formation of the South Pole-Aitken basin suggest the impact generated a 50 km deep melt pool [12]. An event of this magnitude would be more than sufficient to produce the deep, super-heated impact melt sheet required to produce both a coarse-grained assortment of differentiated mafic rocks and the high temperature cubic-ZrO_2 polymorph. Given that disturbance of the U-Th-Pb isotope system within the baddeleyite grain likely occurred during both phase transition [13] and subsequent annealing (with a closure temperature to Pb diffusion of ~900 °C, comparable to zircon [14]) it is assumed that the Pb-Pb isotope systematics of the grain record the age of reversion from the high temperature cubic-ZrO_2 structure. The 23 Ma spread of Pb-Pb ages (4311.3 ± 6.7 to 4334.5 ± 4.6 Ma) supports this observation, hinting at partial to complete resetting of the U-Th-Pb systematics during incorporation into the impact melt sheet. Though a differentiated impact-melt sheet origin was previously proposed for the Mg-suite troctolites in the early 1990's [15], this model has been generally disregarded by more recent studies. However, our new temperature and temporal constraints strongly suggest that at least one key sample from the Mg-suite (troctolite 76535) records empirical evidence for a large basin forming event. On a larger scale, our findings provide evidence for large-scale bombardment events in the early history of the Moon (≥ 4.33 Ga), suggesting that the evolution of evolved planetary crusts around this time is intrinsically linked to impact events. Such evidence has previously remained concealed in the lunar rock record.

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