THE POTENTIAL APPLICATION OF BADDELEYITE (MONOCLINIC ZrO$_2$) AS A SHOCK INDICATOR. L. F. White$^1$, J.R. Darling$^1$, D. Moser$^2$, I. Barker$^3$ and D. Bullen$^1$. $^1$University of Portsmouth, UK (lee.white@port.ac.uk), $^2$University of Western Ontario, Canada

Introduction: A common uranium-bearing mineral phase in both terrestrial and extra-terrestrial mafic lithologies, baddeleyite (monoclinic ZrO$_2$ [1]) is a powerful geochronometer of increasing recognition within the Earth science community. When investigating ex-situ meteoritic samples, however, the high pressure and temperature conditions experienced by the crystal structure during ejection from planetary surfaces acts to complicate our interpretation of U-Pb dates [2]. Experimentally, pure zirconia is known to undergo a series of crystallographic phase shifts during such extreme shock loading and annealing sequences, altering the atomic structure and orientation of the material [3-6]. However, the atomic-scale crystal lattice response of naturally occurring baddeleyite to impact-derived shockwave propagation is unknown.

Here we show that the orthorhombic (high-$P$) and tetragonal (high-$T$) structure shifts of the zirconia lattice are responsible for the development of predictable internal micro-structures, which may encourage lead loss during later-stage annealing. These shifts occur in nature specifically as a result of shock-loading, with the required P-T conditions unobtainable as a result of endogenic processes. As a result, the micro-structure generated by the impact can act as a diagnostic indicator of shock deformation in settings where other evidence (i.e. planar fabrics in quartz) may have been recrystallized during post-shock metamorphism. These findings demonstrate for the first time how naturally occurring monoclinic zirconia (baddeleyite) reacts to impact-derived shock conditions on a micro- to atomic-scale, allowing us to better contextualise the crystallographic shock-response of this key extra-terrestrial (and terrestrial) U-Pb geochronometer. Zirconia Overview: The crystal lattice structure of baddeleyite (monoclinic ZrO$_2$) is a point of intrigue within both the material and Earth science communities: Initially observed to be a distortion of fluorite, the structure has since been refined to reflect the stable monoclinic crystal shape we observe most commonly in natural samples [1]. When exposed to high temperature conditions, distortion of this monoclinic structure occurs through a succession of martensitic phase shifts to the tetragonal and cubic structures [7]. High pressure conditions likewise encourage a reconfiguration of the ZrO$_2$, shifting through a series of orthorhombic structures with increasing pressure [8]. All of these shifts result from the re-coordination of the zircon-oxygen covalent bond which favours the seven-fold symmetry of the monoclinic form [9] and are unquenchable in nature (with the exception of orthorhombic I [8]).

This presents problems when examining the in-situ micro-structure of crystalline baddeleyite as any polymorphs generated by geological activity will have reverted to their stable monoclinic coordination [7,10]. Although a great deal of work has been conducted on crystallographic structures and twin planes generated in artificially quenched high temperature zirconia [11], the phase response of baddeleyite in natural lithologies has never been examined.

Methodology: Here we present our initial analyses of the atomic-scale structure of shocked crystalline zirconia, incorporating the recently developed technique of electron backscatter diffraction (EBSD) of baddeleyite crystals within the naturally shocked (~20 GPa) lithologies surrounding the 1.85 Ga Sudbury Igneous Complex [12]. Of principal interest are rocks of the ZrO$_2$-bearing Matachewan Dyke Swarm (2.45 Ga [13]), emplaced within the underlying lithologies of the Levack Gneiss Complex and Cartier Batholith of the northern range, which have been sampled proximally (800m) and distally (~20km) relative to the impact-melt sheet. In addition, an ongoing collaboration with the University of Kent (UK) provides a tremendous opportunity to experimentally shock ZrO$_2$-bearing samples with a two stage light gas gun [14]. Reproducible shots, whereby 1mm stainless steel projectiles are impacted onto 50mm x 100mm rock cores, ensure that any heterogeneities in the shock-state of grains are purely a function of depth within the core and the refractive or reflective nature of the sample mineralogy. Additionally, the ability to conduct a ‘hot shot’ (impacting the sample following attendant heating to <1000°C) allows for the simulation of shock propagation at crustal depths, where deformation would occur in a more plastic fashion than in brittle surface rocks. Baddeleyite occurs as small (<20μm) euhedral grains within both naturally and experimentally shocked samples, allowing for the calibration of micro-structure formation across a varied degree of shock conditions (~2 - >20 GPa).

Results: EBSD analysis of a range of baddeleyite within both the experimentally and naturally shocked sample sets highlight the robust response of the baddeleyite crystal lattice to shock. Unshocked, naturally occurring baddeleyite have (within this study) all dis-
played a simple twin orientated through the elongate length of the crystal. Conversely, all naturally shocked grains have lost this twin plane, instead developing a mosaic of interlocking sub-grains orientated approximately 70-75° to the master crystal. Experimentally shocked samples display a minor (<5°) ‘crumpling’ of the crystal structure orientated towards the crater, though retain the simple twin plane. Analysed EBSD patterns in all observed grains were categorized as monoclinic, suggesting that high pressure, unquenchable phases (i.e. Orthorombic I and II) have reverted to the stable monoclinic structure in ambient terrestrial conditions.

These preliminary results indicate that the development of this interlocking monoclinic microtexture can only occur within shock loaded environments, where the combination of either extreme temperature (i.e. 1600°C) and/or pressure (>3 GPa) conditions facilitate a phase change until now only observed in industry toughening of metallic alloys [3,5]. Going forward, as we develop an increasing abundance of EBSD and TEM data on shocked and unshocked baddeleyite crystals we can begin to associate structural development with certain P/T conditions, whereby the zirconia and oxygen lattice deforms in a predictable way thus facilitating a quantifiable peak shock state.

**References:**