CONSTRAINING THE SHOCK CONDITIONS EXPERIENCED BY HAUGHTON CRYSTALLINE BASEMENT ROCKS: A COMBINED RAMAN SPECTROSCOPY AND ELECTRON BACKSCATTER DIFFRACTION STUDY OF ANOMALY HILL ZIRCONS. H. A. M. Jurak[1], E. L. Walton[1], N.E. Timms[2], and G. R. Osinski[3], [1]Department of Physical Sciences, MacEwan University, 10700 104 Ave, Edmonton, AB, T5J 4S2 (waltone5@macewan.ca), [2]School of Earth and Planetary Sciences, The Institute for Geoscience Research (TIGeR), Curtain University, GPO Box U1987, Perth, WA, Australia, [3]Department of Earth Sciences / Institute for Earth and Space Exploration, University of Western Ontario, London, ON, N6A 5B7, Canada.

Introduction: Haughton is a 23 million-year-old well-preserved impact structure, situated on Devon Island, Nunavut, Canada [1]. The 23 km-diameter crater is complex and bears a subdued central uplift [2]. At the time of impact, the target stratigraphy comprised ~1880 m of Lower Paleozoic sedimentary rocks, unconformably overlying granulite-facies tonalitic and granitic gneisses of the Precambrian Canadian Shield [2]. Near the centre of the structure, is a location characterized by negative gravimetric and positive magnetic anomalies, known as “Anomaly Hill” [3]. Highly-shocked, pumice-like lithic clasts are abundant at this locale, and include gneissic and carbonate-rich clasts [4, 5]. In this study, we examined 20 zircon grains from a single crystalline clast collected at Anomaly Hill, using a combination of field emission scanning electron microscopy (FESEM), Raman spectroscopy and electron backscatter diffraction (EBSD) mapping to reveal microstructures at the micrometer to nanometer scale. Earlier work on Haughton zircons [6] did not incorporate EBSD, and so, is missing a wealth of information to facilitate the identification of key microstructures including FRIGN (former reidite in granular neoblasts) zircon, non-FRIGN granular textures, neoblasts versus sub-grain rotation formation of subdomains, and various dissociation textures, as described in [7, 8]. The goal of our study is to constrain the shock conditions experienced by crystalline basement rocks at Haughton using zircon, a mineral that is increasingly recognized as a sensitive shock indicator. Both the strengths and limitations of Raman spectroscopy versus EBSD mapping, as they relate to the identification of high-pressure phases in shocked rocks, as well as their crystallography and microtextures, are explored.

Samples and Methods: An ~8 cm x 6 cm fragment of crystalline rock was collected from Anomaly Hill in 1999 by GRO. From this hand specimen, three thin sections were prepared. The distribution of 24 elements over one entire thin section was mapped using a Bruker M4 Tornado micro-X-ray fluorescence (XRF) instrument (University of Western Brittany). The resultant XRF maps show the location and distribution of major, minor, and accessory minerals – notably, zircon, identified as zirconium (Zr) ‘hotspots’. The optical properties of 20 Zr-bearing grains were then observed using a petrographic microscope, with microtextures characterized using a ZEISS Sigma 300 FESEM in back-scattered electron (BSE) imaging mode (University of Alberta). Images were collected using an accelerating voltage of 20 kV. A Bruker X-ray energy dispersive spectrometer (EDS), fitted to the FESEM, aided in mineral identification. Zr-bearing grains were characterized by micro-Raman spectroscopy using a Bruker SENTERRA instrument, to identify Zr-bearing phases (MacEwan University). A 532 nm Ar+ laser was directed through the 100X objective lens of an optical microscope to achieve a ~1 µm spot size. The Raman signal was collected in the interval 45–1550 cm^{-1}, with a spectral resolution of 2–3 cm^{-1}. Each spectrum was collected for a total of 30 seconds as six-5 s exposures, which were then summed to achieve the final spectrum. Both peak positions and intensities in the Raman spectrum were compared to those acquired from zircon and baddeleyite standards, as well as reidite reported by [9]. Phase and orientation maps of 18 zircon grains were acquired via EBSD mapping with a Tescan MIRA3 FESEM fitted with Oxford Instruments Aztec combined EDS-EBSD system (Curtin University). EBSD/EDS data were collected using an EBSD detector and XMax 20 mm SDD EDS detector with a specimen tilt of 70°, acceleration voltage of 20 kV, and a working distance of 18.5 mm. EBSD camera parameters were optimized for an acquisition speed of 198 Hz. EBSD data were processed using Oxford Instruments Channel 5.12 by removing isolated erroneous data points via a ‘wildspike’ filter, followed by extrapolative infill of unindexed points using a minimum of seven nearest neighbours. Maps of EBSD pattern quality, phase, crystallographic orientation, and pole figures were produced in Channel 5.12.

Results and Discussion:

Mineralogy and Texture of the Clast: The hand specimen is weakly foliated and highly vesiculated, composed of major quartz and K-feldspar, minor biotite and Fe-Ti-oxides, and accessory apatite, Fe-sulfide, thorite, and zircon. The layered texture and mineralogy of the sample is evidence that the protolith was a granitic basement gneiss. This clast has been assigned to shock stage III by [10], based on shock effects described in quartz and feldspar.

Shock Effects in Zircon: BSE imaging, EBSD mapping, and Raman spot analysis of zircon grains identified in XRF thin section maps, demonstrate that zircon records a range of distinct microstructures, including: crystalline zircon with no definitive evidence of shock, but some fracturing and limited crystal-plasticity (n = 10); poor crystallinity zircon, often with irregular fractures and microvesicles (n = 3); lamellar reidite within zircon (n = 2); patchy and/or granular textured reidite (n = 3); and granular textured zircon (n = 2). No evidence of planar deformation bands, shock twins, or thermal decomposition, which could be identified in BSE images and EBSD maps of zircon, were observed.

Lamellar reidite appear in BSE images as thin (<1 μm wide), closely-spaced sets of bright (greyscale), roughly parallel lamellae that cut across the primary growth zoning of zircon. These lamellae are identified as reidite by a broad, low-intensity peak at 608 cm^{-1} in the Raman spectrum, along with a doublet at 816 and 862 cm^{-1}. Peaks are accompanied by a triplet at 192, 200, and 212 cm^{-1}, and sharp, well-defined peaks at 344, 426, 962, and 994 cm^{-1}, all of which are consistent with zircon. Reidite lamellae yield poor EBSD patterns that could not be indexed. Granular reidite occurs as sub-micrometer size individual grains in poorly crystalline zircon and is spatially associated with fractures and grain margins of highly-crystalline zircon. In contrast to lamellar reidite, reidite with this texture are indexed well by EBSD mapping. EBSD maps show that reidite typically has a distinctive epitaxial crystallographic orientation relationship with the host zircon, with one $\{110\}_{reidite}$ aligned with $(001)_{zircon}$, and the other $\{110\}_{reidite}$ aligned with $\{110\}_{zircon}$. These relationships have been described elsewhere [7, 11] and are readily explained by transformation from a single zircon orientation via multiple symmetrically equivalent pathways, resulting in broadly two orthogonal reidite orientations. Discrete, sub-micrometer granular-textured zircon domains are spatially associated with reidite, and predominantly define up to three mutually orthogonal crystallographic orientation clusters. This microstructure is attributed to neoblasts formed by back-transformation to zircon from reidite [7], a texture termed FRIGN by [8]. Raman spectra acquired from these grains show mixed spectral signatures with peaks assigned to reidite, including sharp, well-defined peaks at 316, 384, 429, and 441 cm^{-1}, and broad, low-intensity signals at 546, 812, and 862 cm^{-1}; zircon peaks include a doublet at 192 and 212 cm^{-1}, a singlet at 343 with increased intensity, and signals at 962 and 994 cm^{-1} that are broadened as a result of increasing shock-pressures [11]. Peak positions at 571, 726, and 773 cm^{-1} were collected at grain boundaries that appear bright in BSE images. These cannot be assigned to zircon, reidite, or baddeleyite.

Shock Conditions from Zircon Microstructures; Available experimental data shows that shock transformation of zircon to reidite begins at ~30 GPa and is complete by ~53 GPa [12]. Thus, it is reasoned that zircon grains preserving reidite, or evidence of its former presence (i.e., FRIGN zircon), experienced a minimum shock-pressure of ~30 GPa. Reidite is also sensitive to post-shock temperature and has been documented to revert to zircon at temperatures >1200°C [13]. Therefore the presence of FRIGN zircon could indicate that these grains reached >1200°C. However, the lack of any dissociation textures in zircon grains (e.g., coronas of baddeleyite + silica glass), imply that zircon did not reach temperatures >1673°C [7, 13]. The remaining zircons described in this study exhibit typical igneous textures, with a subset possessing highly porous growth zones and margins. These porous grains yield Raman spectra that exhibit low intensity, broad peaks at 344, 426, 962, and 994 cm^{-1}. Broadened peaks in the Raman spectrum suggest these materials are poorly crystalline, consistent with localized radiation damage of U-rich growth zones (i.e., metamict zircon). Vesicles are interpreted as a consequence of degassing from pre-existing impurity-rich metamict domains during impact-related heating.

Conclusions: Our combined FESEM, Raman and EBSD study has identified reidite exhibiting a range of microtextures in a subset of zircon grains. The presence of FRIGN zircon, identified for the first time at Haughton (this study), but lack of zircon dissociation textures, indicates that basement temperatures locally reached >1200°C but did not exceed ~1673°C. Based on the experimentally-determined stability of reidite [e.g., 13], shock pressures were >30 GPa, consistent with a shock stage III classification [12]. However, the heterogeneous distribution of shock features in zircon suggests that shock pressure and temperature conditions varied locally at the grain scale.

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