MICROSTRUCTURALLY CONSTRAINED GEOCHRONOLOGY OF BADDELEYITE WITHIN SHERGOTTITES NORTHWEST AFRICA (NWA) 7257, NWA 8679 AND ZAGAMI.

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Introduction: Baddeleyite (monoclinic ZrO_2; m-ZrO_2) is a widespread accessory phase within planetary materials and an important U-Pb geochronometer within mafic lithologies [1]. Recently, *in-situ* U-Pb geochronology of baddeleyite within shergottites has confirmed late Amazonian magmatism on Mars [*e.g.* 2,3]. However, while experimental studies indicate baddeleyite retain robust U-Pb isotope systematics to ca. 57 GPa [4], up to 80 % Pb loss was recorded within baddeleyite from Northwest Africa (NWA) 5298 [2,5]. Significantly, [5] found a strong correlation between baddeleyite microstructure and the magnitude of Pb mobility, with microstructures documenting partial to complete reversion from high P-T zirconia polymorphs and, where associated with shock melt, recrystallization. As NWA 5298 experienced greater shock metamorphism than most shergottites, the integrity of U-Pb isotope systematics within more moderately shocked samples remains unclear.

At temperatures and pressures below ~1170 °C and ~3.3 GPa, respectively, m-ZrO_2 is stable [6,7]. With increasing temperatures, m-ZrO_2 undergoes martensitic transformation to tetragonal (t-ZrO_2; >1170 °C) and cubic (c-ZrO_2; >2370 °C) polymorphs, while a series of orthorhombic polymorphs (o-ZrO_2) form at pressures of ≥3.3 GPa. Zirconia polymorphs are unstable at ambient P-T conditions and so rapidly revert to m-ZrO_2, forming domains linked by systematic orientation relationships (ORs). Reversion from t-ZrO_2 or o-ZrO_2 is shown by orthogonal ORs, enabling constraints on baddeleyite phase heritage to be determined through microstructural analyses. Here, we use electron backscatter diffraction (EBSD) to elucidate the reversion history of martian baddeleyite, and determine the effects of phase transformation on measured U-Pb isotope systematics.

Samples and Methods: This study has focused on three enriched, basaltic shergottites: NWA 7257, NWA 8679 and Zagami. As is typical for many shergottites, these samples have undergone significant shock metamorphism, including extensive fracturing of pyroxene and complete transformation of plagioclase to maskelynite. Thin veinlets of shock melt within NWA 8679 and Zagami attest to micron-scale heterogeneity of shock metamorphism, with localized pockets of shock melting present in all samples. However, the pervasive shock melting and vesiculation observed within NWA

5298 is absent [5], indicating substantially lower bulk post-shock temperatures (*e.g.* Zagami ≤220 °C [10]). Baddeleyite in these samples is largely associated with late-stage magmatic crystallization products, including Si- and K-rich mesostasis, Fe-Ti oxides, and phosphates (merrillite and Cl-apatite) [8,9]. There is no strong association of baddeleyite with shock melt, testifying to the igneous crystallization of studied grains.

Baddeleyite targets were identified and imaged using a Zeiss EVO MA10 LaB_6 SEM at the University of Portsmouth. EBSD analyses were conducted on the same SEM using an Oxford Instruments Nordlys-nano detector; samples were run uncoated at 20 kV and ~2 nA, with a step size of 50 nm to 100 nm. SIMS analyses were undertaken using the Heidelberg Ion Microprobe after the method of [11]. A 0.5 nA primary O_2^- beam was focused to ~5 µm, with secondary ions extracted at 10 kV.
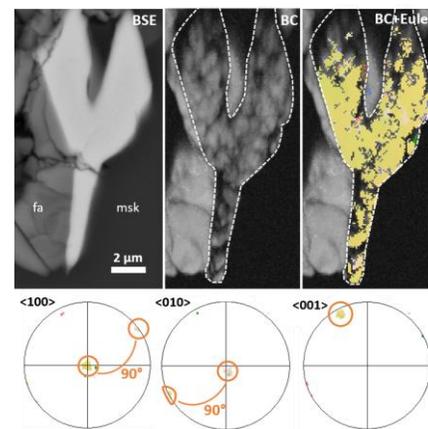

***Fig. 1:** Group 1; NWA 7257 baddeleyite_12 showing magmatic twining (180°/<001>) and minor CPD.*

Microstructure: NWA 7257, NWA 8679 and Zagami show considerable microstructural variability within each individual thin section. We document widespread reversion from t-ZrO_2 or o-ZrO_2, attesting to zirconia phase heritage that is not detectable using techniques such as Raman spectroscopy. Based upon microstructural variations in EBSD data, we here define four groupings of baddeleyite; baddeleyite show a continuum of microstructures, and so groupings should not be considered absolute. Rarely, baddeleyite possess

strong diffraction, minor crystal-plastic deformation (CPD; <12 °) and orientations indicative of magmatic twin relationships (Fig. 1). Baddeleyite with such microstructural characteristics define Group 1, and have not undergone reversion from high P-T zirconia polymorphs. Increased microstructural response to shock metamorphism is shown by baddeleyite within Group 2. Within this grouping, baddeleyite retain a dominant orientation (CPD; ≤20 °) that hosts numerous subgrains related by orthogonal ORs. Group 2 baddeleyites underwent partial transformation to t-ZrO_2 or o-ZrO_2 at sufficient post-shock temperatures to nucleate micron-scale m-ZrO_2 subgrains.

Group 3 baddeleyites yield a marked decrease in crystallinity, as shown by darker band contrast (BC); localized areas of indexing yielding simple or orthogonal ORs (Fig. 2). Comparable microstructures have previously been reported [5,6], and document quasi-amorphous m-ZrO_2 at length-scales lower than EBSD interaction volumes (a few tens of nm for our analyses). Group 3 baddeleyite therefore indicate partial (>50 %) to complete reversion from high P-T polymorphs, but at low post-shock temperatures that inhibit nucleation of reverted m-ZrO_2 [5]. This grouping is the most abundant within NWA 7257 and Zagami, testifying to low bulk post-shock temperatures within these samples [10]. Finally, two baddeleyite within NWA 8679 diffract strongly, but are composed of granular subgrains with orthogonal ORs separated by areas of poorer diffraction. These baddeleyites form Group 4; this grouping denotes complete reversion from t-ZrO_2 or o-ZrO_2 at post-shock temperatures sufficient to allow the nucleation of >micron-scale m-ZrO_2.
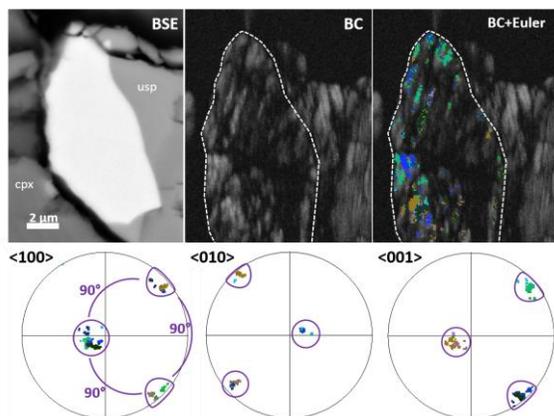

Fig. 2: *Group 3; NWA 7257 baddeleyite_5. Slight shift during EBSD run. Distinct loss of crystallinity with localized areas of indexing yielding orthogonal ORs.*

U-Pb geochronology: Thirty-two *in-situ* U-Pb SIMS measurements of baddeleyite were undertaken within NWA 7257 (n = 17), NWA 8679 (n = 10) and Zagami (n = 5), with microstructural groupings 1-3 represented. Uncorrected U-Pb isotopic ratios form well defined discordia on Tera-Wasserburg plots. As baddeleyite within each sample are cogenetic, the discordia denotes mixing between unradiogenic (e.g. common Pb; $^{238}U/^{206}Pb$ = 0) and radiogenic reservoirs. Thus, regression of this array to upper and lower intercepts define the common $^{207}Pb/^{206}Pb$ isotopic composition and the crystallization age of the sample, respectively. We therefore present two new *in-situ* U-Pb baddeleyite ages from discordia lower intercepts: 195 ± 15 Ma (95 % confidence; MSWD 5.6) for NWA 7257 and 220 ± 23 Ma (95 % confidence; MSWD 2.2) for NWA 8679. Critically, we observe no link between baddeleyite microstructural groupings and U-Pb isotope systematics. Instead, U-Pb isotopic compositions are controlled by grain size and subsequent overlap with surrounding phases. Reversion of zirconia polymorphs is therefore shown induce no resolvable Pb mobility in these samples, providing further evidence that elevated post-shock temperatures are required to induce U-Pb open system behavior within shocked baddeleyite [5, 6].

Conclusions: Within this study, we have shown that where baddeleyite microstructures and independent physiochemical constraints indicate low post-shock temperatures, baddeleyite U-Pb isotopic compositions record the crystallization age of shergottites. Previously derived baddeleyite ages within moderately shocked shergottites [*e.g.* 3] record magmatic processes, not shock resetting events, and are unequivocal proof of young shergottite crystallization ages. We note that careful microstructural analysis of baddeleyite remains necessary to assess the integrity of U-Pb measurements; the robustness of our Group 4 grains remains unknown and an ongoing investigation. However, we show that where careful microstructural analysis is undertaken, the magmatic and impact history of shergottites may be discerned from a single thin section. *In-situ* U-Pb baddeleyite geochronology is therefore applicable in a range of planetary materials, enabling high resolution temporal constraints on the magmatic and impact evolution of extraterrestrial samples.

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