

**BADDELEYITE MICROSTRUCTURES IN VARIABLY SHOCKED MARTIAN METEORITES: AN OPPORTUNITY TO LINK SHOCK BAROMETRY AND ROBUST GEOCHRONOLOGY.** L. G. Staddon<sup>1\*</sup>,

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**Introduction:** Baddeleyite (monoclinic  $ZrO_2$ ;  $m$ - $ZrO_2$ ) has recently been shown to be capable of providing robust crystallisation ages for shergottites via *in-situ* U-Pb isotopic analyses [1,2]. However, in contrast to experimental work [3], these studies also highlight that U-Pb isotope systematics of baddeleyite can be strongly modified by shock metamorphism. Up to ~80% radiogenic Pb loss was recorded within North-west Africa (NWA) 5298 [1], with close correspondence of U-Pb isotopic ratios and baddeleyite microstructures [4]. Combined microstructural analysis and U-Pb geochronology of baddeleyite therefore offers tremendous potential to provide robust constraints on crystallisation and impact ages for martian meteorites.

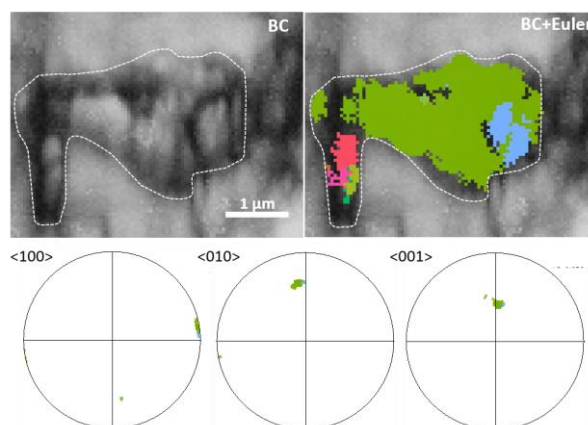
Baddeleyite ( $m$ - $ZrO_2$ ) is stable at pressures of <5 GPa and temperatures of <1200 °C, and is commonly twinned along {100} and {110}. However, at more extreme P-T conditions,  $m$ - $ZrO_2$  undergoes a series of transformations to metastable polymorphs. These include orthorhombic ( $o$ - $ZrO_2$ ) structures at >5 GPa and tetragonal ( $t$ - $ZrO_2$ ) or cubic ( $c$ - $ZrO_2$ ) structures at >1200 °C or >2400 °C, respectively. These polymorphs are unstable at ambient conditions and rapidly revert to  $m$ - $ZrO_2$ , but their former presence may be inferred from distinct orientation relationships (ORs) using electron backscatter diffraction (EBSD) [4,5].

In this study, we document the microstructural variability of baddeleyite grains within shergottites that have experienced a wide-range of shock conditions, broadly equivalent to shock classifications S1-S6 of [6]. We demonstrate that baddeleyite microstructures show significant intra- and inter- sample variability that is linked to progressive bulk shock metamorphism of the host martian meteorite.

**Samples and Methods:** Five shergottite samples have been studied. NWA 4480 is an isotopically and petrologically unique shergottite, with the retention of birefringent, twinned plagioclase indicating anomalously low levels of shock metamorphism, equivalent to shock classification S1 [6,7]. NWA 12241 is a recently discovered orthocumulate preserved at relatively low shock conditions (S2). Despite a previously reported absence of maskelynite [8], our thin section yields localised areas of shock melting and partial transformation of plagioclase to maskelynite, indicating bulk shock conditions more akin to shock classification S3

[6]. Shergottites in which plagioclase has undergone complete transformation to maskelynite (S4), suggesting shock pressures of at least ~29 GPa [6], are represented by enriched shergottites NWA 8679 and NWA 7257. Both samples are similarly evolved lithologies, abundant in late stage phases such as Fe-Ti oxides, Cl-apatite and Si- and K- rich mesostasis, though NWA 7257 is doleritic [9,10]. Enriched basaltic shergottite NWA 5298 represents the most heavily shocked martian meteorite studied here (S6), containing both maskelynite and vesicular plagioclase melt [4].

Baddeleyite grains >2  $\mu$ m in length were located via a combination of automated backscattered electron (BSE) and energy-dispersive X-Ray spectroscopy (EDS), using a Zeiss EVO MA10 LaB<sub>6</sub> SEM at the University of Portsmouth with Oxford Instruments Aztec Feature software. EBSD analysis was undertaken using an Oxford Instruments Nordlys-nano detector: sections were analysed uncoated using a 20kV 1.5-2.5 nA electron beam. To achieve the resolution required, step sizes of between 50 nm and 120 nm were used.

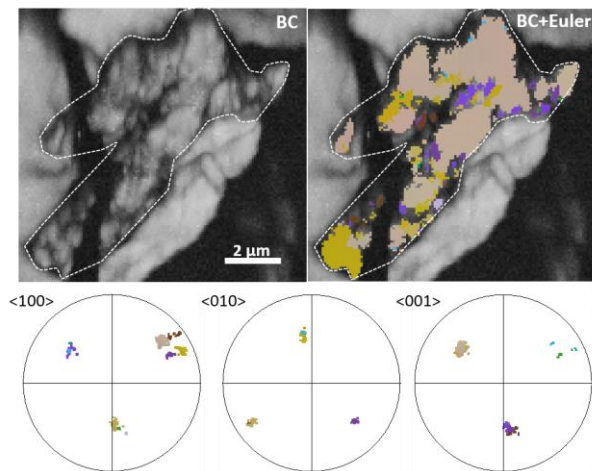


**Figure 1:** EBSD Band contrast (BC) and Euler maps of baddeleyite within lowest shock NWA 4480. Pole figures show baddeleyite hosts simple, magmatic twinning.

**NWA 4480 (S1):** Given its low shock history, baddeleyite within NWA 4480 reveals a surprising array of baddeleyite microstructures. Most baddeleyites display simple, igneous twinning (Figure 1), but some grains contain distinct subgrains that yield orthogonal ORs. This is indicative of reversion from  $o$ -

ZrO<sub>2</sub> or *t*-ZrO<sub>2</sub> and therefore P-T conditions of >5 GPa or >1200 °C. Such characteristics are identical to baddeleyites that have experienced <10 GPa shock pressures within the Sudbury impact structure [5], indicating shock pressures of NWA 4480 of 5-10 GPa.

**NWA 12241 (S2-S3):** Baddeleyite grains within NWA 12241 diffract poorly, despite forward scattered electron (FSE) imaging revealing a high-quality surface polish. Poor diffraction has previously been observed within shocked terrestrial and martian baddeleyite [4,5], where it is related to complex nanoscale structure at lengthscales less than EBSD interaction volumes (<100 nm) that result in quasi-amorphous microstructure. A single baddeleyite reveals broadly magmatic ORs, indicating that while shock conditions were heterogeneous, baddeleyites likely robust for U-Pb dating are present.



**Figure 2:** EBSD BC and Euler maps of baddeleyite in NWA 8679, showing a deformed dominant orientation and distinct subgrains with orthogonal ORs, indicative of partial reversion from *t*-ZrO<sub>2</sub> or *o*-ZrO<sub>2</sub>.

**NWA 8679 and NWA 7257 (S4):** Baddeleyite is ubiquitous in both NWA 8679 and NWA 7257, and NWA 8679 yield baddeleyite with particularly variable microstructures. While many grains yield orthogonal ORs, indicative of reversion from higher P-T polymorphs, a number of grains retain a single, though plastically deformed (<10° misorientation), magmatic orientation (Figure 2). This suggests partial conversion to *t*-ZrO<sub>2</sub> or *o*-ZrO<sub>2</sub>, similar to baddeleyite in the Sudbury impact structure from samples with bulk shock pressures of 10-20 GPa [5]. Poorly diffracting domains with complex nanostructure (quasi-amorphous) are only locally present within NWA 8679, but are abundant in NWA 7257. Where indexing occurs within such grains, these domains largely yield orthogonal ORs. Baddeleyite composed of granular crystallites

with orthogonal ORs are abundant in both samples, marking complete reversion of the some baddeleyites from *t*-ZrO<sub>2</sub> or *o*-ZrO<sub>2</sub>.

**NWA 5298 (S6):** Baddeleyite grains within NWA 5298 were divided into three groups by [4]: magmatic grains, quasi-amorphous ZrO<sub>2</sub>, and recrystallised, micro-crystalline baddeleyite with no discernable preferred orientation or ORs. In contrast to other shergottites studied here, NWA 5298 baddeleyite commonly hosts crystalline zircon rims [1,4]. This, coupled with the prevalence of vesicular plagioclase melt, indicates NWA 5298 was subjected to higher sustained temperatures during post-shock decompression.

**Conclusions:** Baddeleyite within five variably shocked martian meteorites display a wide-range of microstructures. The lowest shock samples (NWA 4480 and NWA 12241, equivalent to S1-S3 [6]) contains many grains with microstructures typical of magmatic baddeleyite. However, evidence of reversion from *t*-ZrO<sub>2</sub> or *o*-ZrO<sub>2</sub> within some grains suggests that even ‘pristine’ martian meteorites have experienced >5 GPa of shock. With increasing degree of shock metamorphism (S4-S6 [6]), the proportion of magmatic baddeleyite decreases, and more complex microstructures with orthogonal ORs are increasingly abundant. Only NWA 5298 yields zircon rims, indicative of higher temperature conditions in comparison to the four more moderately shocked studied meteorites.

These findings are important for shergottite chronology and shock-barometry. All of the studied samples possess baddeleyite with shock-microstructural complexities that may result in disturbance of U-Pb systematics, but also yield some grains or subgrain domains with preserved magmatic microstructures. The variability of baddeleyite, even within low shock samples, therefore highlights the requirement for careful microstructural characterisation of martian baddeleyite prior to interpretation of U-Pb isotope systematics, and also provides new insights into the shock-history of martian meteorites.

**References:** [1] Zhou Q. et al. (2013) *EPSL*, 374, 156-163. [2] Moser D. E. et al. (2013) *Nature*, 499, 454-457. [3] Niihara T. et al. (2012) *EPSL*, 341-344, 195-210. [4] Darling J. R. et al. (2016) *EPSL*, 444, 1-12. [5] White L. F. et al. (2018) *Geology*, 46(8), 719-722. [6] Stöffler D. et al. (2018) *MAPS*, 53(1), 5-49. [7] Irving A. J. et al. (2016) *LPSC XLVII*, Abstract #2330. [8] NWA 12241, Meteoritical Bulletin (Meteoritical Society) [9] Irving, A. J. et al. (2012) *Ann. Met. Soc. Meet. LXXV*, Abstract #5367. [10] Tait K. T. et al. (2015) *LPSC XLVI*, Abstract #2709.