Earth and Planetary Science Letters 444 (2016) 1–12

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Variable microstructural response of baddeleyite to shock metamorphism in young basaltic shergottite NWA 5298 and improved U–Pb dating of Solar System events

James R. Darling [a,*], Desmond E. Moser [b], Ivan R. Barker [b], Kim T. Tait [c], Kevin R. Chamberlain [d], Axel K. Schmitt [e,f], Brendt C. Hyde [c]

[a] School of Earth and Environmental Sciences, University of Portsmouth, Portsmouth PO1 3QL, UK
[b] Department of Earth Sciences, University of Western Ontario, London, Ontario N6A 5B7, Canada
[c] Department of Natural History, Mineralogy, Royal Ontario Museum, Toronto, Ontario M5S 2C6, Canada
[d] Department of Geology and Geophysics, University of Wyoming, 3006, Laramie, WY 82071, USA
[e] Department of Earth and Space Sciences, UCLA, Los Angeles, CA 90095, USA
[f] Institut für Geowissenschaften, Universität Heidelberg, 69120 Heidelberg, Germany

A R T I C L E I N F O

Article history:
Received 27 October 2015
Received in revised form 11 March 2016
Accepted 14 March 2016
Available online xxxx
Editor: T.A. Mather

Keywords:
Mars
shergottite
geochronology
baddeleyite
EBSD
uranium–lead

A B S T R A C T

The accurate dating of igneous and impact events is vital for the understanding of Solar System evolution, but has been hampered by limited knowledge of how shock metamorphism affects mineral and whole-rock isotopic systems used for geochronology. Baddeleyite (monoclinic ZrO_2) is a refractory mineral chronometer of great potential to date these processes due to its widespread occurrence in achondrites and robust U–Pb isotopic systematics, but there is little understanding of shock-effects on this phase. Here we present new nano-structural measurements of baddeleyite grains in a thin-section of the highly-shocked basaltic shergottite Northwest Africa (NWA) 5298, using high-resolution electron backscattered diffraction (EBSD) and scanning transmission electron microscopy (STEM) techniques, to investigate shock-effects and their linkage with U–Pb isotopic disturbance that has previously been documented by *in-situ* U–Pb isotopic analyses.

The shock-altered state of originally igneous baddeleyite grains is highly variable across the thin-section and often within single grains. Analyzed grains range from those that preserve primary (magmatic) twinning and trace-element zonation (baddeleyite shock Group 1), to quasi-amorphous ZrO_2 (Group 2) and to recrystallized micro-granular domains of baddeleyite (Group 3). These groups correlate closely with measured U–Pb isotope compositions. Primary igneous features in Group 1 baddeleyites ($n = 5$) are retained in high shock impedance grain environments, and an average of these grains yields a revised late-Amazonian magmatic crystallization age of 175 ± 30 Ma for this shergottite. The youngest U–Pb dates occur from Group 3 recrystallized nano- to micro-granular baddeleyite grains, indicating that it is post-shock heating and new mineral growth that drives much of the isotopic disturbance, rather than just shock deformation and phase transitions.

Our data demonstrate that a systematic multi-stage microstructural evolution in baddeleyite results from a single cycle of shock-loading, heating and cooling during transit to space, and that this leads to variable disturbance of the U–Pb isotope system. Furthermore, by linking *in-situ* U–Pb isotopic measurements with detailed micro- to nano-structural analyses, it is possible to resolve the timing of both endogenic crustal processes and impact events in highly-shocked planetary materials using baddeleyite. This opens up new opportunities to refine the timing of major events across the Solar System.

1. Introduction

Achondrites provide unique insights into planetary evolution in the inner Solar System. To fully understand the record that these precious igneous meteorites provide, it is critical to distinguish the effects of extreme compression and heating that occur during impact events from the original characteristics of the sample. Such "shock metamorphism" affects all meteorites during their ejection from planetary surfaces, and can produce transformation, deformation and pathways for chemical exchange amongst their con-

* Corresponding author.
E-mail address: james.darling@port.ac.uk (J.R. Darling).

http://dx.doi.org/10.1016/j.epsl.2016.03.032

stituent mineral phases. As a result, accurate radiometric dating of events recorded by meteorites from the Moon, Mars and the asteroid belt is often highly challenging: a reflection of our inability to resolve, by geochemical methods alone, the severity of mineral age resetting by impact events.

The implications for our understanding of planetary evolution can be huge. In the case of shergottites, basaltic meteorites from Mars (e.g. Marti et al., 1995; Meyer, 2012), debate over the effects of shock metamorphism on different isotopic systems used for dating has led to interpreted crystallization ages of individual meteorites that vary by as much as 4 billion years (Gyr). The shergottites yield Rb–Sr, U–Pb, Sm–Nd and Lu–Hf isotope mineral and whole-rock isochrons with relatively young ages of between ca. 150 and 600 Ma (e.g. Shih et al., 1982; Chen and Wasserburg, 1986; Jagoutz and Wanke, 1986; Jones, 1986; Nyquist et al., 2001, 2009; Borg et al., 2002, 2003). However, Pb–Pb isotope data from a range of shergottites have been interpreted to represent mineral isochrones that yield ancient ages of 4.1–4.5 Ga (Bouvier et al., 2005, 2008, 2009). This has led to debate as to whether the younger isochron ages reflect the timing of Martian magmatism or disturbance by metamorphic events on Mars, including shock metamorphism before and during meteorite ejection. The interpretation of isotopic results based on bulk mineral separate techniques is especially challenging given the susceptibility of these data to the presence of minor phases (e.g. phosphate inclusions), terrestrial or Martian contamination or preferential leaching during acid washing.

The dating of individual uranium-bearing accessory phases using *in-situ* methods is much less susceptible to such effects, and has great potential to push forward understanding of Martian chronology. Baddeleyite, monoclinic ZrO_2, is a common accessory mineral in mafic igneous rocks and has been found in many shergottites (e.g., Niihara, 2011; Jiang and Hsu, 2012; Moser et al., 2013; Zhou et al., 2013), Lunar meteorites (e.g. Wang et al., 2012), other achondrites and chondrites (e.g. Krot et al., 1993). Similarly to zircon (tetragonal $ZrSiO_4$), the benchmark chronometer of geological time on Earth, baddeleyite takes up significant quantities of U (up to thousands of ppm), typically excludes initial common-Pb (Heaman, 2009), and is very resistant to Pb-loss during crustal and weathering processes. Recent studies have shown that baddeleyites record young ages in the Roberts Massif 04261 (ca. 200 Ma; Niihara, 2011), Grove Mountains 020090 (192 ± 10 Ma; Jiang and Hsu, 2012), Northwest Africa (NWA) 5298 (187 ± 33 Ma, Moser et al., 2013), and Zagami (187 ± 6.9 Ma; Zhou et al., 2013) shergottites, although questions persist as to whether the young dates reflect crystallization of the magmatic protolith or disturbance by multiple shock metamorphic events by processes including reversion from unquenchable high-pressure polymorphs back to the monoclinic baddeleyite structure (El Goresy et al., 2013).

Laboratory experiments predict that shock-loading up to 57 GPa and attendant heating do not cause significant Pb-loss from baddeleyite (Niihara et al., 2012). However, contrary results are presented by Moser et al. (2013), who demonstrate that baddeleyite grains in the highly-shocked meteorite NWA 5298 have been structurally altered by shock metamorphism, with degraded crystallinity in some grains, and that the shock metamorphism caused by the launch event resulted in minor to approximately 80% loss of radiogenic Pb from baddeleyite. Nowhere in that study was there any report of baddeleyite melting, as mistakenly claimed by Werner et al. (2014). Such mis-interpretation of documented observations has led to the unsupported inferences that the shergottites, the largest class of Martian meteorites, are a) older than 4 Ga in age, and b) from a single crater source in the southern highlands. There is thus a clear need to thoroughly establish the micro- to nano-structural states of shergottite baddeleyite grains and their relation to U–Pb systematics, to establish a framework for more substantive interpretation of isotopic ages.

Here we address this issue by applying powerful techniques for *in-situ* crystallographic and nano-structural measurements, including electron backscatter diffraction (EBSD) and scanning transmission electron microscopy (STEM), to shock metamorphosed baddeleyite. We present new backscattered electron (BSE) imaging, cathodoluminescence (CL) imaging, EBSD data and STEM analyses for 42 grains in a single thin-section of the highly-shocked basaltic shergottite NWA 5298. These include 15 grains with previously reported U–Pb isotope ratios (Moser et al., 2013). The principal aim is to better document the range of micro- to nano-structures caused by shock metamorphism on baddeleyite and to test the apparent correlation with U–Pb age disturbance, with the hope of better informing future geochronology of planetary materials.

2. Basaltic shergottite northwest Africa 5298

Meteorite NWA 5298 is an unbrecciated, evolved basaltic shergottite with a primary phaneritic igneous texture (Irving and Kuehner, 2008). Apart from its relatively oxidized state, being close to the QFM buffer, it is chemically similar to other basaltic shergottites including Shergotty, Zagami and Los Angeles (Hui et al., 2011). As shown in Fig. 1, the meteorite is predominantly comprised of zoned clinopyroxene (65.1%) and shocked plagioclase (30.0%), along with phosphates (merrillite and apatite; 2.1%), Fe–Ti oxides (ilmenite and titanomagnetite; 2.0%), silica (0.5%) and mesostasis (aphanitic interstitial late-stage melt at the margins of phosphate and plagioclase grains; 0.5%). Clinopyroxene crystals occur as prismatic grains up to 4 mm in length, and are irregularly zoned from pigeonite to augite compositions (Hui et al., 2011). The pyroxenes also contain domains with symplectites that are similar to some of the other basaltic shergottites: e.g. Shergotty, Zagami and Los Angeles (Aramovich et al., 2002; Warren et al., 2004). These symplectites consist of Ca-pyroxene, silica and fayalitic olivine, and are interpreted to have been formed via breakdown of ferrosilite-rich pyroxene (pyroxferroite breakdown material: PBM) at low pressure during cooling (Aramovich et al., 2002).

NWA 5298 is a highly shocked meteorite, and shock metamorphic features are pervasive throughout the studied sample. These include: (1) dark pockets of quenched, glassy impact melt up to 3 mm in diameter (Fig. 1A), which contain fragments of shocked and unmelted clinopyroxene with resorbed margins, and REE patterns that are parallel to that of phosphates in NWA 5298 (Hui et al., 2011), distinguishing them chemically from mesostasis; (2) highly fractured clinopyroxene grains exhibiting sub-parallel sets of irregularly-spaced fractures; (3) and pervasive transformation of plagioclase to an isotropic, glassy form (maskelynite).

The maskelynite grains typically have central domains of isotropic glass with smooth textures in reflected light, and margins or entire grains with spherulitic textures and melt veins within surrounding clinopyroxene, suggesting that melting of the plagioclase was widespread (e.g. Fig. 2A, B). Shock transformation of plagioclase in NWA 5298 (An40-55; Hui et al., 2011) to maskelynite suggests a shock pressure of at least 29 GPa (Stöffler et al., 1986). Furthermore, the maskelynite is commonly vesicular, with vesicles up to hundreds of microns in diameter, similar to observations from other highly shocked shergottites including NWA 4797 (Walton et al., 2009), NWA 6342 (Irving et al., 2011) and Dhofar 378 (Ikeda et al., 2006). Given that vesiculation of silicate melts is inhibited at high pressures (Chen and El Goresy, 2000), this indicates that plagioclase melting took place at relatively low pressures during or immediately following decompression. This relative timing is supported by the presence of radiating fractures within pyroxene grains that surround maskelynite, as expected from volume increase of the maskelynite. Pyroxene grains in contact with