Empirical constraints on shock features in monazite using shocked zircon inclusions

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ABSTRACT

Shock deformation microstructures in monazite have been systematically characterized for the first time in grains from the Vredefort impact structure in South Africa. Electron backscatter diffraction mapping has identified 12 unique orientations of monazite deformation twins, including 7 orientations that have not previously been described in experiments or nature. Other shock features include planar deformation bands and strain-free neoblasts, which have been shown to date deformation. Shock-twinned zircon inclusions within the deformed monazite require pressures of 20 GPa, thus providing critical empirical constraints on formation conditions, confirming a hypervelocity impact origin of the monazite microstructures. The Vredefort monazite grains described here represent the first case of using shocked mineral inclusions to empirically calibrate shock microstructures formed in the host mineral. These results conclusively establish monazite as a recorder of shock deformation, and highlight its use in identifying and dating impact structures.

INTRODUCTION

Impact cratering is a ubiquitous geologic process in the solar system, and shocked minerals are a diagnostic criteria used to confirm an impact event (French and Koeberl, 2010). Monazite, (La, Ce, Tb)PO4, monoclinic space group P21/n, is an important accessory phase and geochronometer, and has been reported as a shocked mineral at several impact structures, including Haughton (Canada; Schärer and Deutsch, 1990), Araguaína (Brazil; Silva et al., 2016; Tohver et al., 2012), the Vredefort Dome (South Africa; Flowers et al., 2003; Hart et al., 1999; Moser, 1997), and in alluvium derived from Vredefort (Cavosie et al., 2010; Erickson et al., 2013a). However, the nature of the microstructural deformation in reportedly shocked monazite, including planar features and neoblasts, and the conditions under which they form, remain unconstrained; none of the observed features documented in natural samples have been experimentally calibrated.

Deformation twins in monazite have been produced experimentally and analyzed using transmission electron microscopy. Indentation experiments performed at room-temperature conditions with unconstrained pressures produced four orientations (composition planes) of monazite deformation twins, including [100], [001], [120], and [122] (Hay, 2004; Hay and Marshall, 2003). Electron backscatter diffraction (EBSD) analysis of tectonically deformed monazite in granulite facies rocks has identified three of the twin orientations produced experimentally, including [100], [001], and [122]; the same grains also preserve intracrystalline plastic deformation with lattice misorientation about <010> and <010> (Erickson et al., 2015). Neoblastic monazite, formed by dynamic recrystallization, has been documented in tectonic and impact environments, and has been used to date both regional (Erickson et al., 2015) and impact deformation (Moser, 1997).

Here we use EBSD mapping of deformed monazite grains and their mineral inclusions to constrain formation conditions of shock microstructures in monazite. The monazite grains in this study all have inclusions of zircon that contain diagnostic shock microstructures. Shock features develop in zircon by 20 GPa (Leroux et al., 1999), and include mechanical twins in [112] (Cavosie et al., 2015a; Erickson et al., 2013a, 2013b; Moser et al., 2011; Timms et al., 2012), the high-pressure polymorph reidite (Cavosie et al., 2015b; Leroux et al., 1999; Reddy et al., 2015; Wittmann et al., 2006), and granular texture (Bohor et al., 1993; Wittmann et al., 2006). Documenting shock microstructures of the zircon inclusions constrains the pressures undergone by the monazite, as the host grain must have experienced the conditions recorded within coexisting mineral inclusions.

GEOLOGICAL BACKGROUND AND SAMPLES

The Vredefort Dome is the erosional remnant of the central uplift of a 2020 Ma complex impact structure on the Kaapvaal Craton in South Africa (Gibson et al., 1997; Kamo et al., 1996; Moser, 1997). The 90 km circular structure comprises a 40-km-diameter inner core made up of metamorphosed Archean granitoids and deep crustal rocks, and an outer 20–25 km collar of overturned Archean and Paleoproterozoic metamorphosed sedimentary and volcanic units (Bischoff, 2000). The upper 8–11 km of the impact structure are estimated to have been removed by erosion (Gibson et al., 1998). Shocked monazite has been identified in the core of the Vredefort Dome (Flowers et al., 2003; Hart et al., 1999; Moser, 1997), which is composed of 3.42–3.0 Ga granitoids, charnockitic gneiss, and supracrustal rocks that underwent granulite facies metamorphism in the Archean, and subsequent pyroxene-hornfels facies metamorphism during impact (Gibson, 2002).

Detrital monazite with distinct planar features, interpreted to represent shock deformation, has been identified in sediment from the Vaal River and its tributaries within the Vredefort Dome (Cavosie et al., 2010), and as far as 759 km downriver (Erickson et al., 2013a). Detrital monazite grains preserve ages between 3044 ± 19 Ma to 2157 ± 94 Ma (Erickson et al., 2013a), consistent with derivation from Vredefort bedrock (Flowers et al., 2003; Hart et al., 1999).

A suite of eight detrital monazite grains in modern alluvium from the Vaal River basin described in Cavosie et al. (2010), Erickson (2012), and Erickson et al. (2013a) is the focus of this study. Three of the monazite grains (07VD07–39, 07VD07–67, and 09VD58–166) are from the Rietvlei, a tributary of the Vaal River that drains the core of the Vredefort Dome (Fig. 1). Monazite 07VD08–4 is from the channel of the Vaal River ~39 km downriver from the center of the Vredefort Dome. Three additional monazite grains (09VD16–50, 09VD16–65, 09VD16–68) are from a sample collected 103 km downriver from the Vredefort Dome, and the final monazite (09V53–26) was collected 469 km downriver.

The detrital monazite grains are anhedral, rounded, dark yellow to orange, and range in diameter from 200 to 650 µm (mean = 397 µm; Table DR2 in the GSA Data Repository1). The

1GSA Data Repository item 2016205. Items DR1 and DR2, is available online at www.geosociety.org/pubs/ft2016.htm, or on request from editing@geosociety.org.
grains are crosscut by planar microstructures visible on grain surfaces in as many as four orientations (e.g., Grain 07VD08–4, Item DR2 in the Data Repository). In addition, zircon inclusions exposed on grain surfaces display planar microstructures in orientations consistent with shock deformation (Item DR2; Erickson et al., 2013a). The scanning electron microscopy (SEM) and EBSD analytical conditions used, along with a Matlab script to convert EBSD misorientation data (reported as minimum misorientation angle/axis pairs herein) into twin relationships, are summarized in the Data Repository.

MICROSTRUCTURAL RESULTS

The detrital monazite grains preserve a variety of complex textures on polished interior surfaces. Analysis of the 8 grains by EBSD mapping reveals 12 distinct orientations of monazite deformation twins, in addition to low-angle boundaries, planar deformation bands (PDBs), and discrete strain-free subdomains (Fig. 2). Individual grains contain between 3 and 10 sets of deformation twins, the most common of which have systematic misorientation relationships of 180°/<100>, 180°/<001>, 180°/<101>, and 95°/<201>. Additional deformation twins were also found with misorientations of 180°/<201>, 110°/<111>, 107°/<110>, 147°/<100>, 55°/<001>, 85°/<401>, and 91°/<104> (Fig. 2; Items DR1 and DR2). Sets of planar low-angle grain boundaries in as many as two orientations were found in all grains (e.g., grain 07VD07–67, DR2). The low-angle boundaries are most commonly misoriented about <001>, <100>, and <110>, and record up to 17° of misorientation from the host.

In 3 grains (09VD16–68, 09VD53–26, and 09VD58–166), domains ranging from 0.5 to 11.1 µm diameter are randomly misoriented relative to the host monazite, and are uniquely located in regions with high dislocation densities (see Item DR2 for local misorientation EBSD maps). The monazite host and twins preserve large amounts of plastic strain, whereas the discrete subdomains are nearly strain free (e.g., grain 09VD58–166; Item DR2).

Individual monazite grains contain between 1 and 8 zircon inclusions that range in length between 17 and 91 µm (mean = 35 µm). The majority of the zircon inclusions (16 of 18) show oscillatory zoning, and some have planar microstructures (9 of 18). EBSD mapping confirms that planar features in zircon from 7 of the 8 monazite grains are [112] shock deformation twins that show systematic misorientation of 65° about <110> zircon (Item DR2). The eighth monazite (09VD53–26) contains a zircon inclusion with two sets of [100] PDBs. The PDBs are misoriented about <001> and accommodate as much as 13.5° of misorientation from the mean orientation of the grain.

SHOCK TWIN ORIENTATIONS IN MONAZITE

The most common microstructures in the monazite population are deformation twins, which occur in 12 orientations, including up to 10 orientations within individual grains. The misorientation relationship between each twin and the host lattice was used to calculate the compositional plane (K) and/or shear direction (τ) for each twin (for a description of the procedure, see the Data Repository). Analysis of the monazite population yields the following deformation twins: (001), (100), (101), two (122) planes, (110), (102), (212), (120) and two irrational planes (Table 1; Item DR3). Although two of the twin orientations are irrational, they are...
type 2 twin planes, and contain the rational \( \eta \) directions, \([01\bar{1}T]\) and \([\bar{T}0\bar{0}]\), respectively. Lamellae systematically misoriented 107°/41° are not traditional deformation twinning (Christian and Mahajan, 1995). The common most twins identified here include \([001]\), \([100]\) and \([\bar{1}2\bar{2}]\), which have been found in both experimentally and tectonically deformed monazite (Hay and Marshall, 2003; Erickson et al., 2015). No previous studies of deformed monazite have reported twins in conjugate \([\bar{1}2\bar{2}]\) orientations or in \([10\bar{1}]\), both of which are common here. The \([\bar{T}2\bar{0}]\) twins, found in one grain here, were also found in experimentally deformed monazite (Hay; 2003; Hay and Marshall, 2003), but not in tectonically deformed monazite. Furthermore, twins in \([\bar{T}1\bar{0}]\), \([10\bar{2}]\), \([21\bar{2}]\), and irrational planes containing \([01\bar{1}T]\) and \([\bar{T}0\bar{0}]\) shear directions have not been previously reported.

Zircon inclusions with \([11\bar{2}]\) twins provide diagnostic evidence that the monazite host grains underwent high-pressure shock deformation. Mechanical twins in natural zircon have only been documented in impact environments (Cavosie et al., 2015a, 2015b; Erickson et al., 2013a, 2013b; Moser et al., 2011; Timms et al., 2012), and have also been produced in diamond anvil cell experiments at 20 GPa (Morozova, 2015). The \([100]\) PDBs found in the zircon inclusion within monazite 09VD53-26 are consistent with a <100>/[010] glide system (Kovaleva et al., 2015). While PDBs in zircon have been reported in endogenic pseudotachylite (Kovaleva et al., 2015) and shock environments (Erickson et al., 2013b; Grange et al., 2013; Timms et al., 2012), the prevalence of shock twins in the zircon inclusion population suggest a shock origin for these PDBs as well.

The previously unreported monazite twin relationships described here, coupled with coexisting shocked zircon inclusions, suggest that the new twin orientations represent monazite microstructures unique to hypervelocity deformation. We propose that monazite deformation twins forming along \([10\bar{1}]\), \([\bar{T}1\bar{0}]\), \([10\bar{2}]\), \([21\bar{2}]\), \([\bar{T}2\bar{0}]\) and irrational planes containing \([01\bar{1}T]\) and \([\bar{T}0\bar{0}]\) uniquely result from hypervelocity impact conditions, and are therefore indicative of shock deformation. In tectonically deformed monazite, three twin sets are known; however, they have only been found in two orientations within individual grains (Erickson et al., 2015). In contrast, all of the grains reported here contain between three and eight orientations of twins. The number of monazite twins may thus be analogous to shocked quartz, where greater numbers of orientations of planar deformation features in a given grain indicate higher levels of shock deformation (Stöffler and Langenhorst, 1994). We propose that monazite containing three or more sets of twin lamellae is therefore unique to shock deformation, and represents diagnostic evidence of impact cratering. Additional work to constrain formation conditions of monazite deformation twins is ongoing and includes refining the twinning mode and shear stresses required for nucleation of different twin sets, which may further refine application of monazite as a shock barometer.

### OTHER SHOCK MICROSTRUCTURES IN MONAZITE

In addition to deformation twins, all of the shocked monazite grains contain PDBs, which have not previously been reported in monazite. The PDBs are composed of planar lamellae up to tens to hundreds of micrometers long and tens of micrometers wide, misoriented from the host domain, generally about \([100]\), \([001]\), and \([101]\) axes. PDBs misoriented about \([001]\) and \([001]\) are typically parallel to twin planes in \([001]\) and \([100]\), respectively, and therefore likely result from the \([100]\)/[010] and \([010]\)/[001] slip systems (Hay, 2008).

In addition, three of the shocked monazite grains were found to contain strain-free subdomains within regions of high dislocation density. These subdomains are micrometers to tens of micrometers across and are interpreted as a result of localized recrystallization, or neoblasts, similar in appearance to those identified in tectonically deformed monazite (Erickson et al., 2015). Neoblasts in deformed monazite nucleate within high-strain domains of the host crystal structure and grow by grain boundary migration (Erickson et al., 2015). In this process, neoblasts grow at the expense of the host and do not incorporate preexisting Pb; the grains described here could thus potentially be used to date the impact (e.g., Moser, 1997).

### POTENTIAL APPLICATIONS OF SHOCKED MONAZITE IN IMPACT STUDIES

Monazite twin sets indicative of shock deformation identified in this study include \([10\bar{1}]\), \([\bar{T}1\bar{0}]\), \([10\bar{2}]\), \([21\bar{2}]\), \([\bar{T}2\bar{0}]\), and the irrational twins with \([01\bar{1}T]\) and \([\bar{T}0\bar{0}]\), which have here been constrained to form in grains that likely underwent pressures of 20 GPa, based on the shock-twinned zircon inclusions (Leroux et al., 1999; Morozova, 2015). Confirmation of monazite as a recorder of hypervelocity bombardment provides a new diagnostic tool (French and Koeberl, 2010) that can be used to both identify and confirm evidence of impact processes. In addition, monazite is an excellent U-Pb geochronometer that occurs in a wide range of rock types and sedimentary systems, and can provide important age constraints for shocked lithologies. Monazite has been reported from three impact sites, including the Haughton (Schäfer and Deutsch, 1990), Vredefort Dome (Flowers et al., 2003; Hart et al., 1999; Moser, 1997), and Araguainha (Silva et al., 2016; Tohver et al., 2012) structures, but it is presumably present at many other craters in continental settings. Previously reported shocked monazites mostly display planar microstructures (e.g., Cavosie et al., 2010; Erickson et al., 2013a; Flowers et al., 2003; Silva et al., 2016), which, based on the results of this EBSD study, are likely to be a combination of shock twins and planar deformation bands. Monazite shocked to 59 GPa in laboratory experiments developed intense mosaicism and subparallel fractures, but did not result in U-Pb age resetting (Deutsch and Schäfer, 1990). Likewise, natural samples of shocked monazite with planar features have been shown to retain pre-impact bedrock ages rather than the impact age (Erickson et al., 2013a; Flowers et al., 2003; Tohver et al., 2012). In contrast, monazite neoblasts, formed by dynamic recrystallization, have been shown.

### TABLE 1. DEFORMATION TWINS IN SHOCKED MONAZITE

<table>
<thead>
<tr>
<th>EBSD orientation</th>
<th>Twin type</th>
<th>Twin plane ((K_i))</th>
<th>Shear direction ((\eta_j))</th>
<th>Experimental*</th>
<th>Tectonic†</th>
<th>Shock§</th>
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<tbody>
<tr>
<td>[100] 180</td>
<td>compound</td>
<td>(001)</td>
<td>[100]</td>
<td>Yes</td>
<td>Yes</td>
<td>8</td>
</tr>
<tr>
<td>[001] 180</td>
<td>compound</td>
<td>(100)</td>
<td>[001]</td>
<td>Yes</td>
<td>Yes</td>
<td>7</td>
</tr>
<tr>
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<td>compound</td>
<td>((\bar{T}0\bar{1}))</td>
<td>[101]</td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>[201]** 95</td>
<td>1</td>
<td>([12\bar{2}])</td>
<td>Yes</td>
<td>Yes</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>[201]** 95</td>
<td>1</td>
<td>([\bar{2}12])</td>
<td>Yes</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[001] 94</td>
<td>1</td>
<td>([110])</td>
<td></td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[201] 180</td>
<td>compound</td>
<td>(1(\bar{0})2)</td>
<td>[201]</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[10\bar{1}] 147</td>
<td>1</td>
<td>(21\bar{2})</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[001] 55</td>
<td>1</td>
<td>([\bar{T}2\bar{0}])</td>
<td>Yes</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[401] 85</td>
<td>2</td>
<td>([01\bar{1}T])</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[104] 91</td>
<td>2</td>
<td>([21\bar{2}])</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(&lt;41\bar{1}T&gt;)</td>
<td>107</td>
<td>(\bar{\eta})</td>
<td>(\bar{\eta})</td>
<td>(\bar{\eta})</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Note: EBSD—electron backscattered diffraction.

† Erickson et al. (2015).
§ This study.

*\(K_i\) and/or \(\eta_j\) could not be calculated for \(<41\bar{1}T>\); see text for details.
to date deformation (Erickson et al., 2015) and yield impact ages (Moser, 1997; Tohver et al., 2012). Furthermore, shocked monazite is resilient, and survives distal fluvial transport in sedimentary systems (Erickson et al., 2013b). Shocked monazite that contains both shock twins and neoblasts, such as described in this study, provides a unique opportunity to retrieve both the age of the source terrane and the impact age (Moser, 1997), whether in bedrock or in detrital grains in the sedimentary record that are far removed from the source crater.

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REFERENCES CITED
Morozov, I., 2015, Strength study of zircon under high pressure [M.S. thesis]: Ontario, Canada, University of Western Ontario, 112 p.
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