Transformations to granular zircon revealed: Twinning, reidite, and \( \text{ZrO}_2 \) in shocked zircon from Meteor Crater (Arizona, USA)

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ABSTRACT

Granular zircon in impact environments has long been recognized but remains poorly understood due to lack of experimental data to identify mechanisms involved in its genesis. Meteor Crater in Arizona (USA) contains abundant evidence of shock metamorphism, including shocked quartz, the high-pressure polymorphs coesite and stishovite, diaplectic SiO\textsubscript{2} glass, and lechatelierite (fused SiO\textsubscript{2}). Here we report the presence of granular zircon, a new shocked-mineral discovery at Meteor Crater, that preserve critical orientation evidence of specific transformations that occurred during formation at extreme impact conditions. The zircon grains occur as aggregates of sub-micrometer neoblasts in highly shocked Coconino Sandstone (CS) comprised of lechatelierite. Electron backscatter diffraction shows that each grain consists of multiple domains, some with boundaries disoriented by 65° around \langle110\rangle, a known \{112\} shock-twin orientation. Other domains have \{001\} in alignment with \{110\} of neighboring domains, consistent with the former presence of the high-pressure ZrSiO\textsubscript{4} polymorph reidite. Additionally, nearly all zircon preserve \text{ZrO}_2 + \text{SiO}_2, providing evidence of partial dissociation. The genesis of CS granular zircon started with detrital zircon that experienced shock twinning and reidite formation at pressures from 20 to 30 GPa, ultimately yielding a phase that retained crystallographic memory; this phase subsequently recrystallized to systematically oriented zircon neoblasts, and in some areas partially dissociated to \text{ZrO}_2. The lechatelierite matrix, experimentally constrained to form at >2000 °C, provided the ultrahigh-temperature environment for zircon dissociation (~1670 °C) and neoblast formation. The capacity of granular zircon to preserve a cumulative pressure-temperature record has not been recognized previously, and provides a new method for investigating histories of impact-related mineral transformations in the crust at conditions far beyond those at which most rocks melt.

GRANULAR ZIRCON

Granular zircon is of interest to studies of shock metamorphism as it is considered to represent the highest-shock-intensity morphotype of zircon, resulting from recrystallization of diaplectic ZrSiO\textsubscript{4} glass into newly grown domains (neoblasts) at conditions in excess of 50 GPa (Wittmann et al., 2006). However, its formation conditions remain poorly constrained as it has not been produced by experiment. The Meteor Crater (Arizona, USA) granular zircon described here consist of aggregates of sub-micrometer neoblasts and are similar to those found in other impact environments, including distal ejecta (Bohor et al., 1993), impact melt (Kamo et al., 1996), tektites (Deloule et al., 2001), lunar breccia (Grange et al., 2013), and meteorites (Zhang et al., 2011). The examples cited above are readily distinguished from grains consisting of neoblasts up to 100 \( \mu \)m across that have only been reported from the Vredefort impact structure (South Africa) (Moser, 1997; Cavosie et al., 2015a).

SHOCK METAMORPHISM AT METEOR CRATER

Meteor Crater (also known as Barringer Crater) is a 1.2-km-diameter simple crater (Fig. 1A) that formed ~49 k.y. ago in northern Arizona (Shoemaker, 1963; Kring, 2007). The impact punctured Permian and Triassic sedimentary rocks, however the CS has received the most study for effects of shock metamorphism, as most other lithologies at Meteor Crater are carbonates. The CS is a Permian oolite that is widespread across the Colorado Plateau; it is a mature, white, fine-grained quartz arenite (~97 wt% SiO\textsubscript{2}) that contains few minerals besides detrital quartz (Kring, 2007). Reports of shock metamorphism of CS include the first discoveries of both coesite (Chao et al., 1960) and stishovite (Chao et al., 1962) in nature. Five classes of CS have been recognized based on increasing shock intensity of SiO\textsubscript{2} phases (Kieffer, 1971; Kieffer et al., 1976). Class 1 includes fractured detrital quartz grains (<1 GPa), classes 2 and 3 feature collapsed pores and microcrystalline coesite (5–13 GPa) as well as stishovite and coesite (25–30 GPa), class 4 includes diaplectic...
glass and vesicular lechatelierite, and class 5 consists entirely of lechatelierite (≥30 GPa and >1000 °C). In addition to SiO₂ phases, impact melts also occur at SiO₂ phases, impact melts also occur at SiO₂ phases (see the GSA Data Repository1, Item DR1). In white and powdery with no visible crystals and were documented in one thin section, each in (additional sample images), Item DR2 (location and contact with vesicular lechatelierite (Fig. 1B; Item DR1), 12 of which were analyzed by EBSD (Table DR2). The grains range from 5 to 37 µm in length, and many appear to retain their original shape; their small size and generally round shape are consistent with detrital zircon. On the polished surface, single grains expose between 111 and 2329 neoblasts each (Figs. 2A and 2B), which range from 0.26 to 0.42 µm in mean diameter.

Systematic Orientation Relationships

Neoblasts in all of the granular zircon grains are crystallographically contiguously and may have different orientations relative to each other, whereby domains comprise groups of adjacent neoblasts in similar orientation (Item DR3). Grain 13 (Figs. 2A and 2B) is an example of a granular zircon composed of three distinctly different orientation domains that each contain from 48 to 134 similarly oriented neoblasts on the polished surface (Fig. 2C, labeled I–III). The orientation of individual neoblasts within each domain show minor, non-systematic dispersion relative to each other that do not overlap in orientation with adjacent domains [compare locations of poles to (001) in Figs. 2D and 2E]. Domain boundaries are irregular at the neoblast scale but are otherwise approximately straight. The boundary between domains I and II (Fig. 2C) is defined by a 65° disorientation relationship about <110>, which results in alignment of both a {110} and a {112} (Fig. 2D). The unique disorientation of 65° about <110> in zircon is a hallmark of {112} twinning, which has only been reported in shocked zircon (e.g., Moser et al., 2011; Timms et al., 2012; Erickson et al., 2013a, 2013b; Thomson et al., 2014; Cavosie et al., 2015b). In contrast, neoblasts in domains II and III (Fig. 2C) have a different orientation relationship; poles to (001) for each domain are aligned with a <110> direction in the other domain (Fig. 2E). This results in further alignment of the second <110> for each domain, as well as alignment of a {100} with {112} of the other domain (Fig. 2E). The crystallographic relations described above for domains II and III are the same orientation relations previously described between zircon and the high-pressure ZrSiO₄ polymorph reidite, where (001)zircon is parallel to {110} Reidite, there is alignment of a {110} between the two phases, and {112}zircon is aligned with {100}reidite (Leroux et al., 1999; Cavosie et al., 2015b; Reddy et al., 2015). Given that domains I and II in grain 13 define a {112} twin relation, it follows that the orientation relation between domains II and III was established by transformation of domain III to reidite (Figs. 2C–2E). While reidite was not identified (indexed) during analysis of Meteor Crater zircon, orientation relationships consistent with the former presence of reidite were found in eight of 12 grains analyzed by EBSD, and [112] twin orientations were found in seven of the 12 grains (Item DR3; Table DR2).

Zirconia and Silica Oxides

Two morphologically distinct types of ZrO₂ were found in BSE images for 11 of 14 grains (Figs. 3A and 3B). Rounded ~250-nm-sized grains were indexed as baddeleyite (monoclinic ZrO₂) by EBSD in 10 of 12 grains; the other type occurs as ~50-nm-sized ZrO₂ grains that form vermicular intergrowths with SiO₂ and did.

Figure 2. Granular zircon (grain 13) with twin and reidite orientations. A: Backscattered electron image showing granular zircon in lechatelierite matrix. B: Band contrast image showing neoblasts. C: Orientation map color coded for Euler coordinate projection, showing three domains with distinct orientations (labeled I–III). D: Pole figures of domains I and II, showing twin relationships. E: Pole figures of domains II and III, showing reidite relationships.
not yield EBSD patterns, indicating that they are either amorphous or composed of grains too small to yield unique diffraction patterns by EBSD (Figs. 3B and 3C). The occurrence of ZrO$_2$ phases is primarily along boundaries between zircon neoblasts, rather than occurring within neoblast interiors (Schmieder et al., 2015). In some grains ZrO$_2$ was found only along the outer margin, whereas in others it occurs throughout the interior of the grain.

**DISCUSSION**

**Genesis of Granular Zircon**

**Shock Twinning, Reidite, and Disordered ZrSiO$_4$**

The Meteor Crater results allow new constraints to be placed on granular zircon genesis based on preserved microstructures. Systematic crystallographic orientations of neoblast domains in the granular zircon described here indicate that their pressure-temperature path involved both shock twinning and formation of reidite prior to recrystallization. The preservation and identification of former twin domains in grains that have pervasively recrystallized has not been reported in zircon previously. However, EBSD has been used to identify inherited twin orientations in recrystallized carbonate from non-impact environments (Pearce et al., 2013). Zircon {112} twins have been produced in static experiments at 20 GPa (Morozova, 2015), and reidite forms from 30 to 40 GPa in shock experiments (Kusaba et al., 1985; Leroux et al., 1999). Thus, the {112} twins and evidence of reidite record minimum shock pressure of at least ~30 GPa, which is consistent for a porous rock composed entirely of lechatelierite (Kieffer et al., 1976; Stöffler and Langenhorst, 1994).

Peak pressure experienced by the granular zircon described here is difficult to constrain, as there is no indication of what state the granular zircon existed in above 30 GPa (e.g., a ZrSiO$_4$ polymorph, or constituent oxides). However, the systematically oriented neoblasts indicate that the phase was unlikely to have been amorphous. A moderately disordered phase would provide an energetically favorable medium for neoblast nucleation, given impact conditions favoring high nucleation and rapid crystal growth rates.

Evidence for the former presence of reidite in Meteor Crater zircon is indirect and based on preserved systematic crystallographic relations among zircon neoblasts that are not known to form by any process other than shock deformation. Transformation of zircon to reidite occurs via the specific systematic orientation relationships described above; reversion back to zircon could occur via several possible symmetrically equivalent relationships, resulting in neo-formed zircon with the observed crystallographic orientation of domain III relative to the original orientation (domain II) (Figs. 2C and 2E). While this observation is new in studies of shock-deformed zircon, the former existence of high-pressure phases has been demonstrated in a baddeleyite megacryst in a kimberlite from twin relationships that could have only have arisen through transformation from cubic and tetragonal ZrO$_2$ (Kerschhofer et al., 2000).

**High-Temperature Dissociation and Neoblast Formation**

Zircon dissociation is experimentally well constrained to occur at 1673 °C at 1 atm (Kaiser et al., 2008) and has also been documented in high-pressure shock experiments from 53 to 94 GPa, where temperatures reach “several thousand degrees” in porous targets (Kusaba et al., 1985, p. 436). In the CS, jetting of molten material into pore spaces has been cited as a process that created extreme temperatures, resulting in the formation of lechatelierite (Kieffer et al., 1976), which recent experiments have confirmed forms at >2000 °C in tektites (Macris et al., 2014). Given that the granular zircon in shock-melted CS are entirely surrounded by lechatelierite and vesicles (Fig. 1B; Item DR1), they must have experienced heating to ~2000 °C during lechatelierite formation. The extremely high temperatures required for both lechatelierite formation and zircon dissociation only occur in crustal rocks as a consequence of hypervelocity impact; considered in this context, the presence of baddeleyite in CS granular zircon is unambiguously attributed to high-temperature dissociation of zircon, and is thus a product of the impact event. Natural occurrences of ZrO$_2$ in impact-dissociated shocked zircon have long been recognized (El Goresy, 1965). The striking similarity in texture of the vermicular ZrO$_2$-SiO$_2$ intergrowths found in both Meteor Crater zircon (Fig. 3) and in experimentally calcinated zircon powders (Kaiser et al., 2008) provides further microstructural support for an origin by high-temperature dissociation. We note further that the baddeleyite documented here may have reverted from a higher-symmetry polymorph of ZrO$_2$ produced during dissociation, as baddeleyite is not stable above 1200 °C (Kusaba et al., 1985; Kaiser et al., 2008). While the effects of high-pressure conditions in the formation of granular zircon remain unconstrained, these results clearly identify the role of ultrahigh temperature in its formation.

**Newly Identified Shocked Minerals at Meteor Crater**

The granular zircon from shocked CS described here constitute the first new shocked mineral reported at Meteor Crater since stishovite in 1962 (Chao et al., 1962) and expand the current repertoire of shocked minerals beyond the known SiO$_2$ phases. Baddeleyite is not uniquely a shocked mineral, but its occurrence in CS is here shown to be a consequence of the Meteor Crater impact. Reidite was not encountered during this study, but the data presented here provide compelling evidence for its former presence based on preservation of systematic orientation relationships among neoblasts in granular zircon. More broadly, the recognition that granular zircon can preserve evidence of its transformation history, as well as survive in fused rocks, provides new opportunities for investigating the extreme formation conditions of impact melts, tektites, meteorites, and other highly shocked materials from Earth and other planetary bodies.
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