PLANETARY SCIENCE

Impact and habitability scenarios for early Mars revisited based on a 4.45-Ga shocked zircon in regolith breccia

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After formation of a primordial crust, early impacts influenced when habitable conditions may have occurred on Mars. Martian meteorite Northwest Africa (NWA) 7034 is a regolith breccia that contains remnants of the earliest Martian crust. The paucity of shock deformation in NWA 7034 was previously cited as recording a decline in giant impacts by 4.48 billion years and evidence for habitable Mars by 4.2 billion years ago. We present new evidence of high-pressure shock effects in a 4.45–billion year–old zircon from the matrix of NWA 7034. The zircon contains {112} shock twins formed in the central uplift of a complex impact structure after 4.45 billion years and records impact pressures of 20 to 30 gigapascals. The zircon represents the highest shock level reported in NWA 7034 and paired rocks and provides direct physical evidence of large impacts, some potentially life-affecting, that persisted on Mars after 4.48 billion years.

INTRODUCTION

The evolution of life requires liquid water, and thus, identification of evidence for water within the Solar System remains a central focus of study [e.g., (*1*)]. Landforms on Mars suggest that liquid water flowed on the surface from ~3.8 billion years (Ga) and that an early thick atmosphere may have facilitated habitable conditions [e.g., (*2*, *3*)]. Evidence for liquid water at the Martian surface is nearly absent after 3.5 Ga, during the Amazonian period (3.4 Ga to present) (*4*, *5*), and may be coupled with a substantial thinning of the Martian atmosphere. The existence of conditions capable of supporting life after this time is debated, given the cold temperatures, higher proportion of damaging ultraviolet radiation, and lack of sustainable liquid water at the surface (*2*, *3*, *6*).

Geological samples from Mars provide a means to study the impact and volcanic-related activity and therefore place constraints on Martian surface conditions, including impact bombardment. Previous studies have shown an absence of shock microstructures in the mineral zircon within the Martian meteorite suite of breccias known as Northwest Africa (NWA) 7034 or "Black Beauty" [NWA 7034 and ~20 paired stones; e.g., (*7*)]. This finding has been interpreted as recording a decline of impacts on Mars by 4.48 Ga ago (*8*). This age constraint, in turn, led to interpretations that habitable conditions on early Mars could have developed as early as 4.2 Ga ago (*8*). Here, we describe new evidence of high-pressure shock deformation within zircon from Martian meteorite NWA 7034, which necessitates revisiting early impact scenarios for Mars and reconsideration of when habitable conditions may have developed. The presence of high-pressure shock deformation provides some of the oldest direct physical evidence of complex impact crater formation on Mars after 4.48 Ga. An intense and prolonged bombardment of Mars had the potential to sterilize the planet through vaporization of liquid water and atmosphere blow off [e.g., (*9*)]. The previously proposed 4.2-Ga habitability window based on study of Martian zircon (*8*) thus may have been punctuated by impact events or, alternatively, may have occurred later.

NWA 7034 and pairs

Components within meteorite NWA 7034 (Fig. 1) are made up of igneous clasts, sedimentary clasts (termed as "protobreccia"), melt clasts, and minerals [e.g., (*10*)]. The major minerals in these components have been shown to have experienced low shock pressures [mostly 5 to 10 GPa; e.g., (*11*–*13*)], conditions attributed to the process of ejection from Mars. Previous studies on zircon grains within NWA 7034 detected only minor evidence of deformation, such as planar deformation bands (*8*), but these features are known to form in tectonically deformed rocks on Earth [e.g., (*14*)] and therefore are not diagnostic of impact processes.

Zircon and baddeleyite from both lithic clasts and the matrix of NWA 7034 yield bimodal ages from 4485 to 4331 million years (Ma) (ancient population) and 1548 to 299 Ma (younger population) [e.g., (*10*, *15*)]. Nearly 70% of dated zircon grains in the NWA 7034 suite are older than ~4 Ga [e.g., (*10*, *16*, *17*)], indicating that a high abundance of ancient Martian crustal components are present within the breccia. The ancient grains have thus experienced up to 4.4 Ga of Martian surface and midcrustal processes. Bulk rock Sm-Nd analysis of matrix material also indicates an ancient age of ~4.4 Ga (*18*). Apatite and metamict zircon from NWA 7034 yield younger U/Pb ages of ~1.5 Ga, suggesting that a thermal resetting and/or annealing event occurred at this time (*7*, *10*, *17*, *19*).

RESULTS

A total of 66 zircon grains from three meteorites in the NWA 7034 suite [NWA 7034 (n = 26), NWA 11522 (n = 7), and NWA 11220 (n = 33)] were surveyed using backscattered electron (BSE) and cathodoluminescence (CL) imaging (Fig. 1). Grains were analyzed for crystallographic orientation in situ within polished sections of

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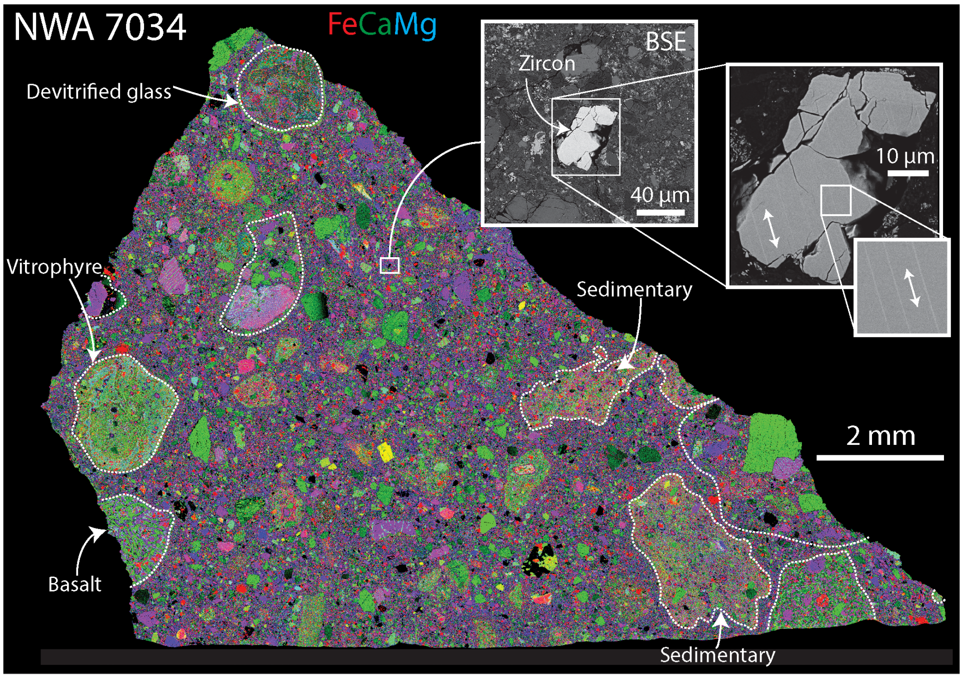

Fig. 1. Combined element map of the rock chip from Martian meteorite NWA 7034 analyzed in this study. Red, Fe; green, Ca; blue, Mg. Dashed lines outline representative clasts greater than ~1 mm. Inset shows the BSE map of matrix with the location of the shock-deformed zircon grain; double-headed arrows in inset indicate orientations of features shown to be {112} shock twins.

the meteorites with electron backscatter diffraction (EBSD) mapping (e.g., Fig. 2 and figs. S1 to S4). Zircon grains occur throughout the matrix and within clasts and range in sizes from <5 to 50 µm. The BSE and EBSD images reveal a wide variety of microstructures in the studied grains, including planar deformation bands and brittle deformation microstructures (figs. S1 to S4).

Within the matrix of NWA 7034, a 50-µm angular zircon grain was identified (Fig. 2). It is a fragment broken off from a larger grain and preserves igneous oscillatory growth zoning (fig. S1). Orientation analysis of the grain reveals a set of {112} shock deformation twin lamellae in a single crystallographic orientation that are misoriented from the host zircon by 65°/<110> (Fig. 2). The lamellar twins crosscut the grain and are ~300 to 500 nm in apparent width on the polished surface. The host grain is otherwise relatively undeformed, exhibiting <3° of cumulative crystal-plastic deformation. Four U/Pb age determinations by secondary ion mass spectrometry were made on the shock-twinned zircon grain (Fig. 3 and fig. S1). The four-spot analyses define a well-defined discordia regression, with an upper concordia intercept age of 4452 ± 8.7 Ma (1σ, mean square weighted deviation = 0.39, $n = 4$) and lower intercept age of 721 ± 270 Ma (Fig. 3 and table S6). The two most concordant spots (1 and 2) are located away from cracks, whereas the two discordant spots (3 and 4) are located on cracks. The Th/U ratios within the concordant spots are 0.85 and 0.68, values typical of igneous zircon.

DISCUSSION

Shock-twinned zircon

Lamellar {112} twins in zircon are a known impact-induced deformation microstructure that characteristically forms in rocks from the central uplifts of complex impact structures. Shock twins in zircon form between the contact/compression and excavation stages during central uplift formation (*20*–*22*) and are not known to form outside of impact environments (*23*). Shock-twinned zircon has been reported in crystalline rocks from multiple terrestrial impact structures [e.g., Vredefort Dome (*20*) and Woodleigh (*21*)] and in lunar regolith samples [e.g., (*24*, *25*)] but has not previously been described from Mars. Formation conditions of {112} shock twins in zircon have been empirically calibrated to occur in rocks that experience shock pressures of >20 GPa (*20*); however, they have also been described in reidite-bearing crystalline target rocks from multiple sites that experienced shock pressures of >30 GPa (*21*, *22*, *26*). Formation conditions of twins in zircon from crystalline target rocks thus range from 20 to 30 GPa or higher. The zircon twins in NWA 7034 are well developed and are nearly identical in appearance to those reported from the three largest impact structures on Earth, including Vredefort Dome [~300 km; e.g., (*20*)], Sudbury [~250 km; e.g., (*27*)], and Chicxulub [~180 km; e.g., (*22*)]. The shock-twinned zircon in NWA 7034 is thus best interpreted as a remnant of shocked bedrock that originated within the central uplift (or peak ring) of a complex crater on Mars and is the most intensely shocked mineral identified thus far within the NWA 7034 meteorite suite (*11*, *13*).

The origin and history of the shocked zircon grain before incorporation within material that ultimately lithified to become the NWA 7034 breccia are not known. While it most likely originated in shocked bedrock from the central uplift of a complex impact crater (Fig. 4A), it could also have been deposited as ejecta (proximal or distal) during the initial impact (Fig. 4B). It could then have remained in place or been mobilized by erosion and sedimentary transport by eolian and/or fluvial processes and deposited elsewhere on the Martian surface (Fig. 4C). In either scenario, the grain could also have been remobilized or buried by subsequent impact and/or sedimentary processes (Fig. 4D).

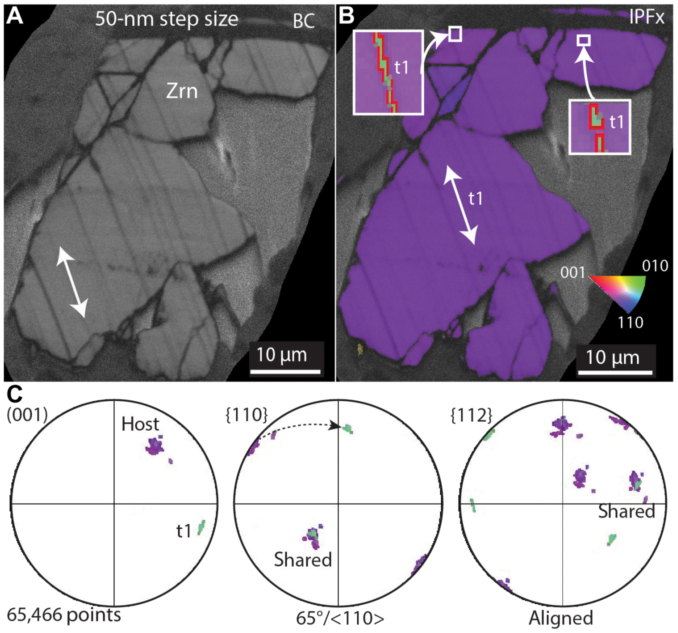

Fig. 2. Scanning electron microscope images of a shock-deformed zircon grain from NWA 7034. (**A**) Band contrast (BC) map of zircon (Zrn) grain showing planar microstructures. (**B**) Inverse pole figure (IPFx) showing one orientation of {112} twins. (**C**) Stereo plot showing the orientation relationship of the host grain and {112} shock deformation twins. Stereonets are equal area, lower hemisphere projections in the sample reference frame. t1, zircon twin.

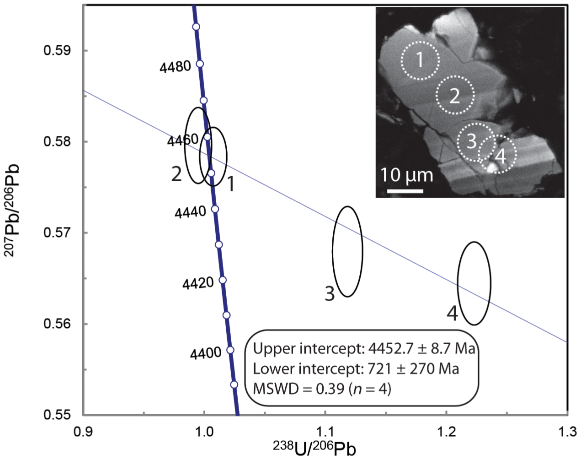

Fig. 3. U/Pb concordia diagram for the shock-deformed zircon grain in NWA 7034. The discordia regression is defined only by the four analyses; it is not anchored by an axis intercept. The inset CL image shows location and number of the four analyses; igneous growth zoning is also visible. Uncertainty cited is 1σ.

Chronology of NWA 7034

Previous studies have cited Re-Os data to suggest that the ancient terrain represented by the NWA 7034 meteorite suite was subjected to impact processes early in the formation of Mars (*28*). Components in NWA 7034 have been suggested to record multiple impact events on the Martian surface. The first event, proposed at ~4.4 Ga, formed a "melt sheet," from which the oldest zircons were either crystallized or inherited (*11*). The ancient components in NWA 7034 were subsequently protected from impacts and volcanism from ~4.3 to ~1.7 Ga based on the absence of identifiable thermal or pressure effects within isotopic systems of minerals [e.g., (*29*)]. The K-Ar and U/Pb systems of younger apatite and zircon grains within the rock, as well as whole rock ^{40}Ar/^{39}Ar, indicate that some of the ancient source material experienced protracted metamorphism from ~1500 to 1200 Ma [e.g., (*10*, *29*, *30*)].

The Hf isotopic signatures of young zircons (~299 Ma) within NWA 7034 indicate crystallization from plume magmatism, potentially originating from the Elysium and Tharsis volcanic provinces (*15*). On the basis of chondrite-like Hf isotopic composition of younger grains, it was further interpreted that Mars may have been in a stagnant-lid tectonic regime for most of its history, which may further explain how early shocked zircon grains, such as that described here, may have survived recycling/destruction by later tectonic and/or impact processes. NWA 7034 is thought to have been brecciated and lithified no earlier than 225 Ma, as indicated by (U-Th)/He and ^{40}Ar/^{39}Ar ages [e.g., (*29*, *31*)].

The NWA 7034 suite of breccias was impact-ejected from the Martian surface at ~5 Ma or possibly earlier [e.g., (*29*)]. Microstructures identified within shocked pyroxene and plagioclase grains throughout the sample indicate shock pressures mostly from 5 to <10 GPa, which have been suggested to represent conditions during impact ejection from the Martian surface (*11*, *13*). The similarity of shock microstructures in plagioclase and (100) twining in pyroxene grains throughout the matrix and clasts provides further evidence that the breccia was lithified before ejection from Mars (*13*). In contrast, formation of the {112} shock twins in zircon described here record much higher shock pressures (20 to 30 GPa or higher) than those attributed to ejection [e.g., (*23*)]. The observation that only 1 of 66 zircon grains from three NWA 7034 pairs [or 1 of 187 grains of six NWA 7034 pairs (*8*)] contains {112} shock twins further demonstrates that the shock deformation of zircon described in this study is not recorded throughout the zircon population and thus predated the launch ejection impact event.

Implications for the timing of habitability on Mars

Previous studies have proposed a decline in large-scale impact events on Mars by 4.48 Ga based on the lack of diagnostic evidence of high-pressure shock deformation, particularly in the mineral zircon (*8*). From the suggested decline in impacts by 4.48 Ga, it was further proposed that the surface of Mars had established habitable conditions by ~4.2 Ga, based on modeled rates of crustal thermal decay after postaccretion bombardment and formation of the crustal dichotomy (*8*). Multiple impact basins and complex impact structures on the Martian surface have been shown to have formed after ~4.0 Ga, including the ~2000-km-diameter Hellas basin (4.13 to ~4.05 Ga), the ~1300-km-diameter Argyre basin (4.07 to >4.0 Ga), the ~1400-km-diameter Isidis basin (~3.92 Ga), and the ~154-km-diameter Gale crater (3.8 to ~3.6 Ga), among others [e.g., (*32*–*34*)]. Large-scale impacts clearly occurred on Mars after ~4.48 Ga based on crater chronology [e.g., (*32*–*34*)] and the identification of a 4.45-Ga shocked zircon grain (Fig. 5).

On Earth, large impact events known to have produced shock twins in zircon, similar to those reported here, have resulted in global climate changes marked enough to have triggered mass extinction [e.g., Chicxulub (*22*, *35*)]. The ~65-Ma-old Chicxulub impactor created a ~180-km-diameter crater that wiped out ~75% of life on Earth [e.g., (*36*)]. Studies have suggested that life on early

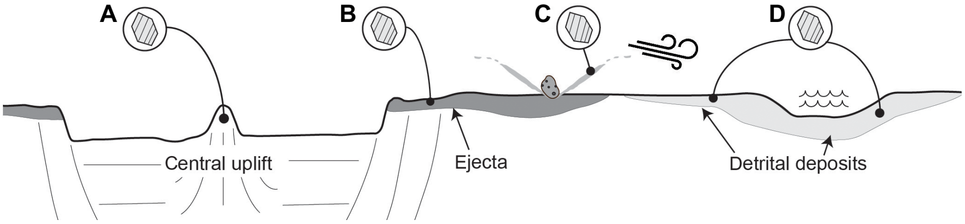

Fig. 4. Schematic diagram showing locations where the shock-twinned zircon may have originated before incorporation within and lithification of NWA 7034 breccia. (**A**) Zircon in shocked bedrock from the central uplift of a complex impact crater. (**B**) Shocked zircon deposited as ejecta (proximal or distal) during impact. (**C**) Shocked zircon remobilized or buried by subsequent impact processes. (**D**) Shocked zircon mobilized by erosion and sedimentary transport through eolian and/or fluvial processes.

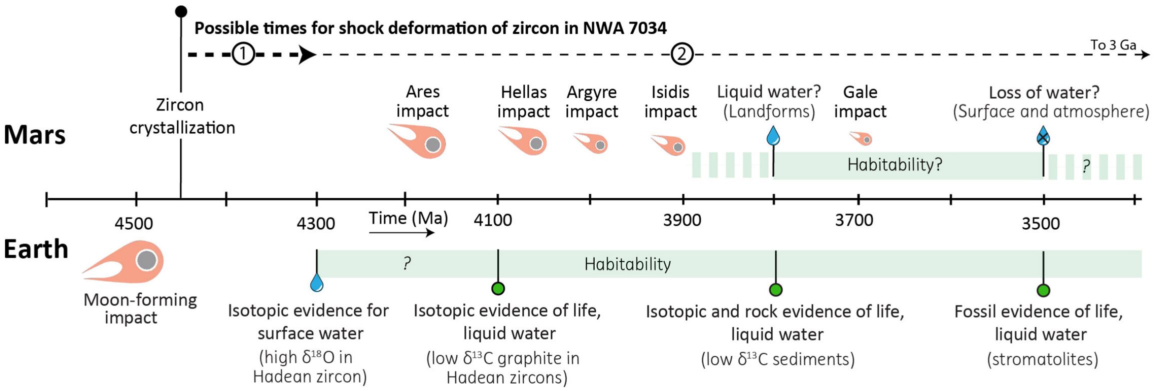

Fig. 5. Schematic timeline showing the impact history and evolution of habitability on Earth and Mars. Timeline of geological events and habitability markers on early Mars (above) and Earth (below). Selected Martian cratering events shown represent large impacts, many formed after ~4.0 Ga; fireball size indicates relatively larger or smaller impact events/craters [e.g., (*32*–*34*)]. The presence of shock-deformed zircon confirms that ancient Martian material was altered by impact deformation from complex impacts (>20 GPa). The most likely times for the zircon shock deformation event are indicated at the top of the figure and include (**A**) >4.3 Ga before a prolonged period of thermal and impact quiescence recorded in NWA 7034 (*29*) and (**B**) before the exponential decay of the global impact flux after 3 Ga (*42*). References for other features shown: geological landforms on Mars, evidence of water at the surface, and subsequent loss of habitability on Mars [e.g., (*2*, *3*, *9*, *43*)]; liquid water on Earth (*44*–*46*); graphite in zircon (*47*); low δ^{13}C sediments (*48*); and early stromatolites (*49*).

Earth may have evolved during the Hadean eon but was subsequently extinguished by the high frequency of impacts and therefore had to reevolve later (Fig. 5) in the Archean eon (*37*). Impactors that formed large craters may have produced higher extinction rates on planets such as Mars during early periods, due to the hostile, primitive conditions of the surface and crust, but would not necessarily have extinguished all life if water was present [e.g., (*9*, *38*)]. Similar to Earth, development of life from ~3.9 Ga may have occurred on Mars due to presence of water (Fig. 5) (*2*, *3*, *9*). Habitable conditions on Mars would have degraded by ~3.5 Ga due to the ending of the dynamo (*39*) and subsequent effects on the thinning of the early atmosphere and removal of liquid water from the Martian surface (Fig. 5) [e.g., (*2*, *3*)].

During evolution of early Mars, an impact that shock-deformed zircon, if sufficiently large, may have similarly affected environmental conditions critical for the rise or maintenance of life. The host rock terrain of NWA 7034 experienced minimum shock pressures of >20 GPa and possibly much higher; microorganisms on Mars would have been vulnerable to resulting perturbations in the environment and high pressures/temperatures caused by these large impact events during a habitable period. Experimental studies show that the surviving fraction of bacteria at ~3 GPa is on the magnitude of $\sim 10^{-4}$ (N/N_0) (where N = surviving bacteria and N_0 = initial bacteria), while at ~10 GPa, it is on the magnitude of 10^{-6} (N/N_0); the survival rate of bacteria is thus markedly reduced with increased pressure and temperature [e.g., (*40*)]. Therefore, the timing and duration during which life may have been present on Mars could have been markedly affected by these large-scale impact events.

Although the timing of the impact event which shock-deformed the zircon in NWA 7034 is not known, the event clearly occurred after igneous crystallization at 4452.7 ± 8.7 Ma (Fig. 3). Previous identification of a nearly ~3-Ga period of impact and thermal quiescence recorded in NWA 7034 components from 4.3 to 1.7 Ga (*29*) further constrains the timing for shock deformation of zircon. On the basis of the modeled impact rates (*31*), Mars was affected by more than 130,000 impactors forming complex craters [>6 km; (*41*)] over the past 4 Ga. The number of complex craters accumulated on the Martian surface over the past 3, 2, and 1 Ga is ~5000, ~3400, and 1600, respectively (*42*). From a purely statistical point of view, the shock deformation of zircon occurred either before 4.3 Ga [e.g., (*29*)] or before the end of the exponential decay of impact flux at ~3 Ga [e.g., (*42*)].

Our study describes the first sample of a shocked mineral interpreted to have originated from the central uplift of a complex impact structure on Mars. Identification of shocked zircon provides direct mineral evidence of large impacts on Mars after 4.45 Ga and is, to date, the highest shock pressure constraint identified within the NWA 7034 meteorite suite. Arguments for habitability of early Mars by 4.2 Ga that are crafted around a decline of impacts at 4.48 Ga (*8*) must be reconciled with these findings, as extinction-level impact events would clearly have modified habitability conditions and hindered development of putative life. Available constraints allow for the high-pressure shock event to have occurred at either >4.3 or before ~3 Ga. The former constraint is broadly consistent with existing habitability scenarios (*8*), whereas the latter favors delayed habitability conditions due to impact frustration; evidence for water on Mars by ~3.9 Ga supports habitable conditions by this time (Fig. 5).

MATERIALS AND METHODS

Three rock chips of NWA 7034, NWA 11522, and NWA 11220 were mounted in epoxy and polished (Fig. 1). For additional details on samples and methods, see text S1. The samples were analyzed using a TESCAN MIRA3 field emission scanning electron microscope at Curtin University to collect BSE and phase maps of the rock chips. A total of 66 zircon grains [NWA 7034 (n = 26), NWA 11522 (n = 7), and NWA 11220 (n = 33)] were surveyed using BSE and CL imaging and analyzed for orientation with EBSD mapping at Curtin University. Zircon grains were mapped by EBSD at step sizes from 40 to 100 nm. The U/Pb analysis of the shock-twinned zircon grain was performed using a CAMECA IMS 1280 ion microprobe at the University of Western Australia (text S1 and table S6).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.abl7497

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