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Decline of giant impacts on Mars by 4.48 billion years ago and an early opportunity for habitability

D. E. Moser^{1*}, G. A. Arcuri¹, D. A. Reinhard², L. F. White³, J. R. Darling⁴, I. R. Barker¹,
D. J. Larson², A. J. Irving⁵, F. M. McCubbin⁶, K. T. Tait³, J. Roszjar⁷, A. Wittmann⁸ and C. Davis¹

¹Department of Earth Sciences, University of Western Ontario, London, Ontario, Canada. ²CAMECA Instruments Inc., Madison, WI, USA. ³Department of Natural History, Royal Ontario Museum, Toronto, Ontario, Canada. ⁴School of Earth and Environmental Sciences, University of Portsmouth, Portsmouth, UK. ⁵Department of Earth and Space Sciences, University of Washington, Seattle, WA, USA. ⁶NASA Johnson Space Center, Houston, TX, USA.

⁷Department of Mineralogy and Petrography, Natural History Museum Vienna, Vienna, Austria. ⁸Eyring Materials Center, Arizona State University, Tempe, AZ, USA. *e-mail: desmond.moser@uwo.ca

Supplementary Information for

**DECLINE OF GIANT IMPACTS ON MARS BY 4.48 BILLION YEARS AGO AND AN
EARLY OPPORTUNITY FOR HABITABILITY**

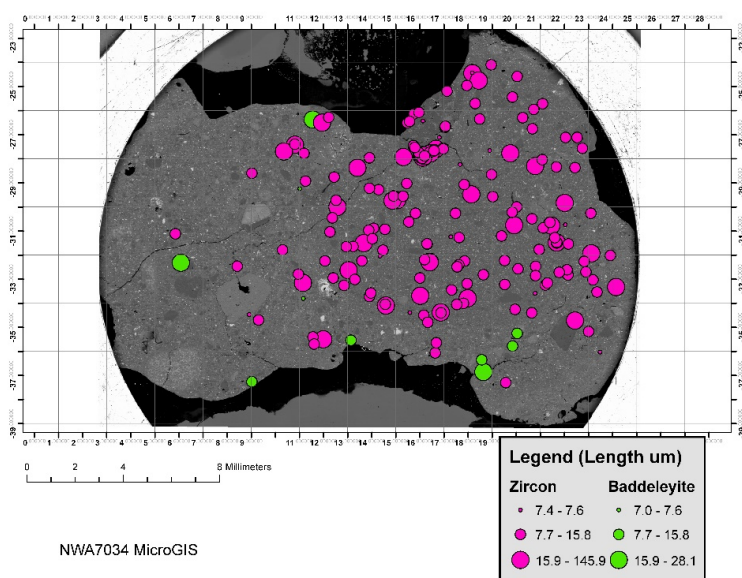
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Correspondence to: desmond.moser@uwo.ca

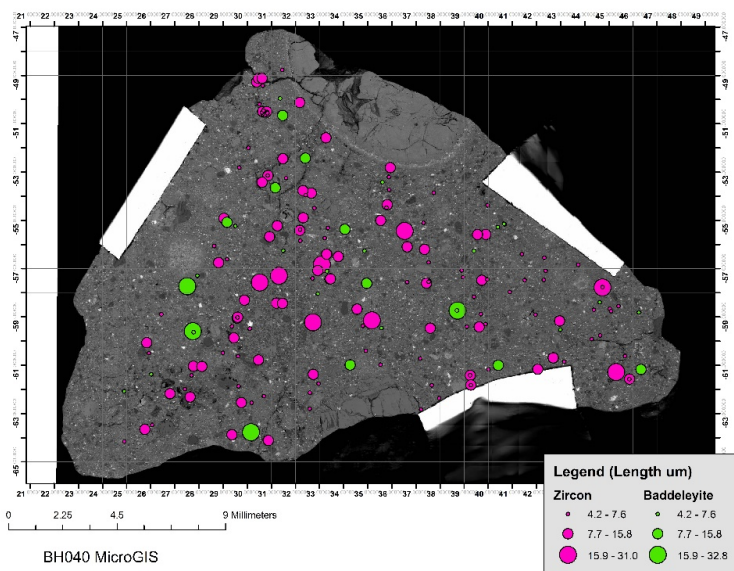
This PDF file includes:

Figs. S1 to S14

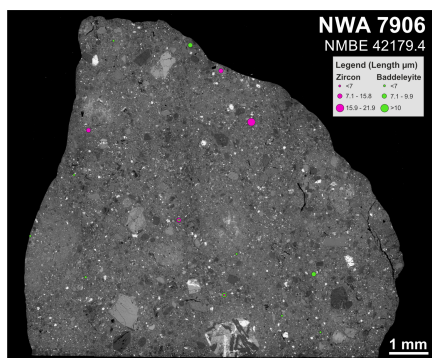
Tables S1 to S4



NWA 7034

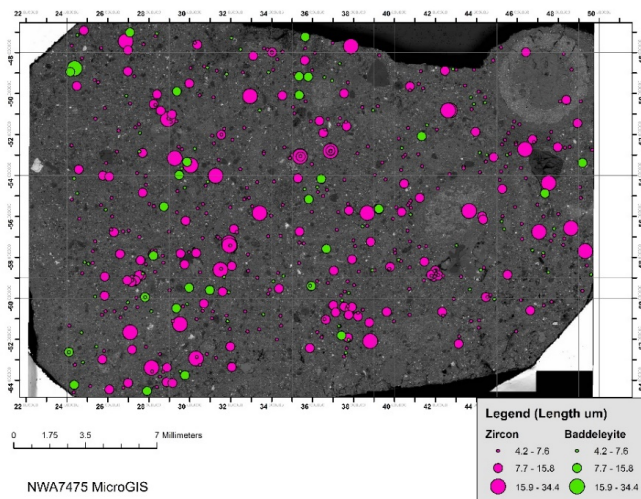


Rabt Sbayta 003

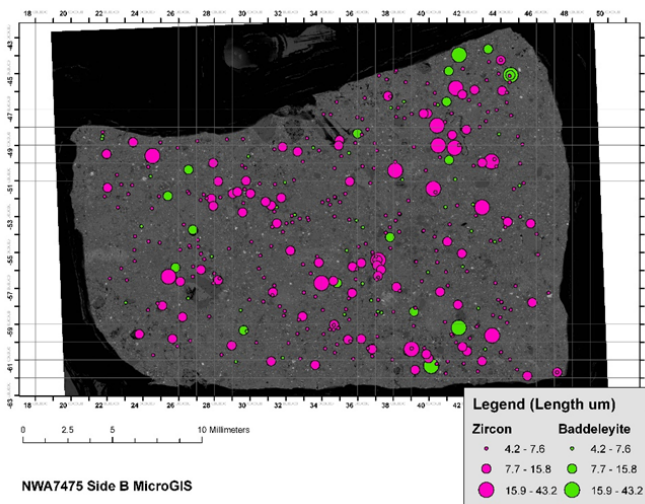


NWA 7906

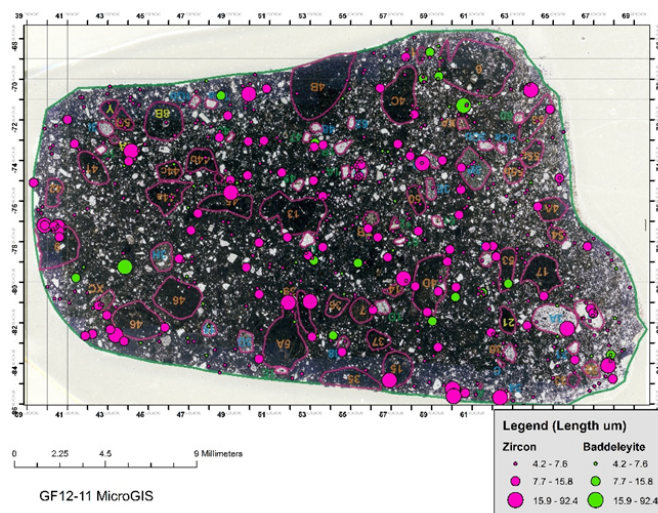
Fig. S1. Location and size distribution of zircon and baddeleyite in NWA 7034, Rabt Sbayta 003 and NWA 7906 polished surfaces.



NWA 7475a

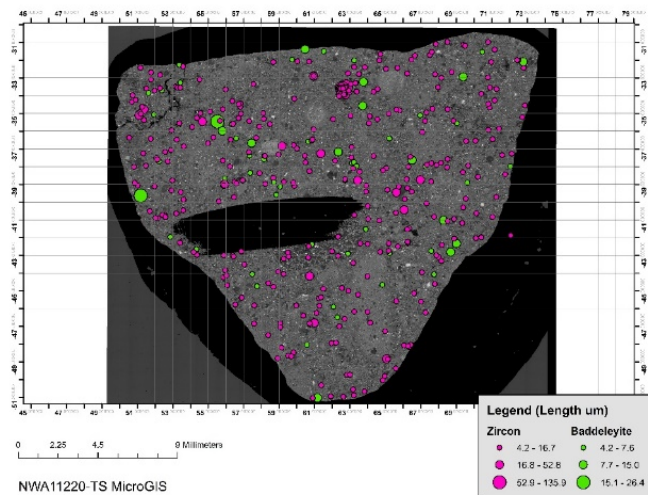


NWA 7475b

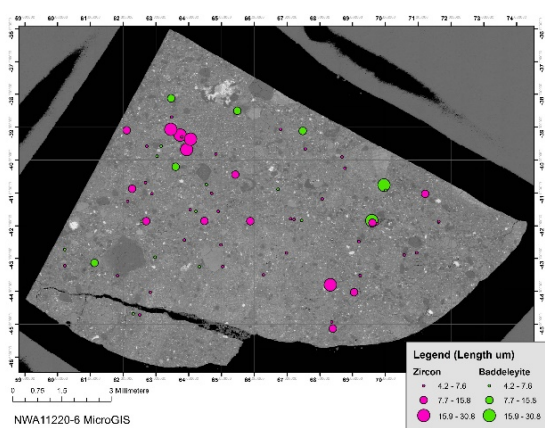


NWA 7475
(GF12-11)

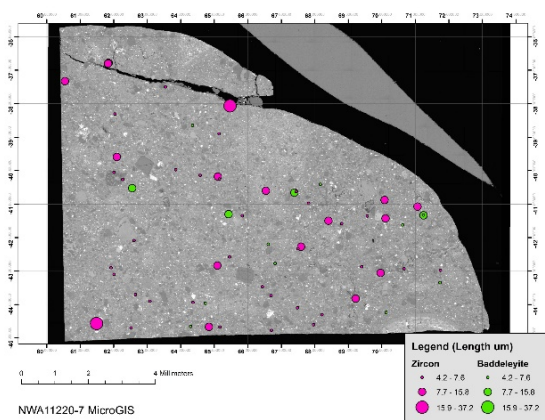
Fig. S2. Location and size distribution of zircon and baddeleyite in NWA 7475 polished surfaces.



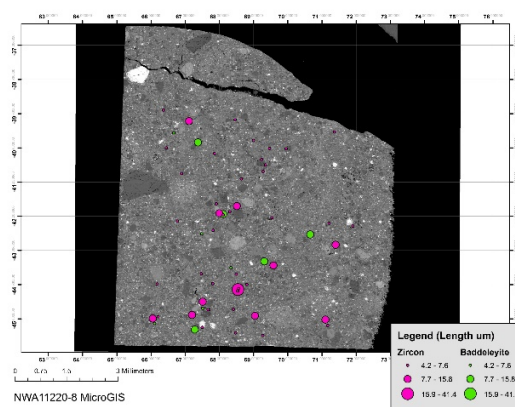
NWA 11220 -TS



NWA 11220 -6



NWA 11220 -7



NWA 11220 -8

Fig. S3. Location and size distribution of zircon and baddeleyite in NWA 11220 polished surfaces.

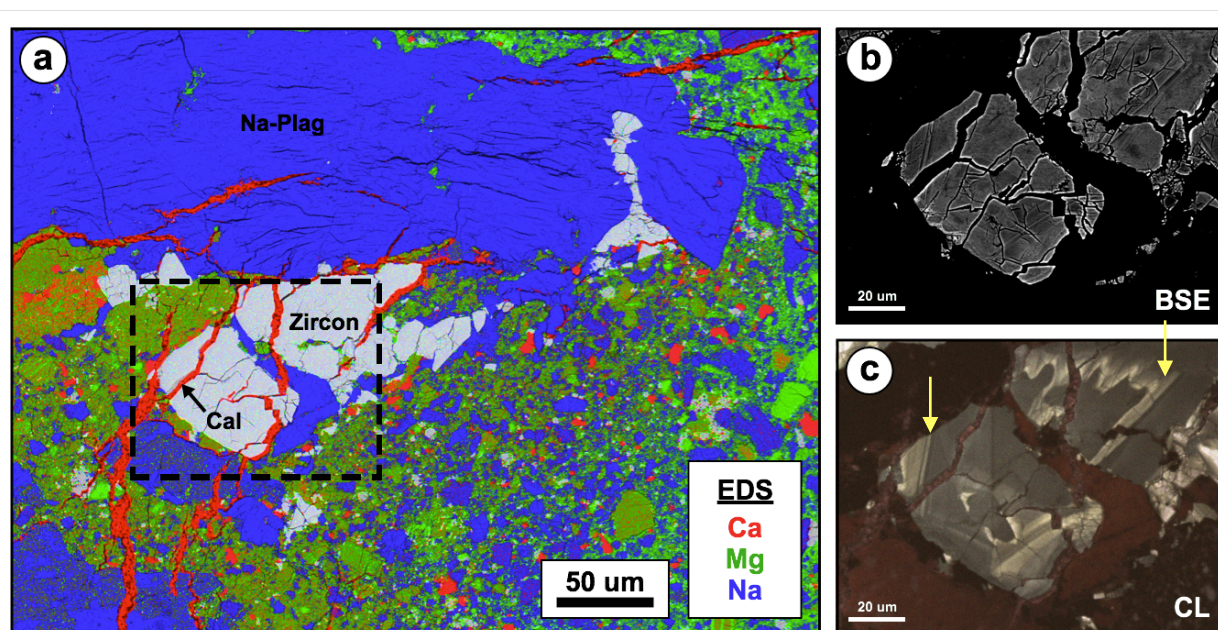


Fig. S4. Context and texture data for NWA 11220;

- (a) Context EDS element map (Green=Mg, Red=Ca, Blue=Na) of zircon F24191 intergrown with plagioclase in a lithic clast in martian meteorite NWA 11220. Note launch fractures partly filled by terrestrial Calcite (“Cal”) (red),
- (b) Higher magnification BSE image (black box in (a)) of zircon and fractures,
- (c) CL image of (b) showing the range in internal zoning patterns, from planar, concentric growth banding to more irregularly-shaped growth bands due to orientation of section (yellow arrows).

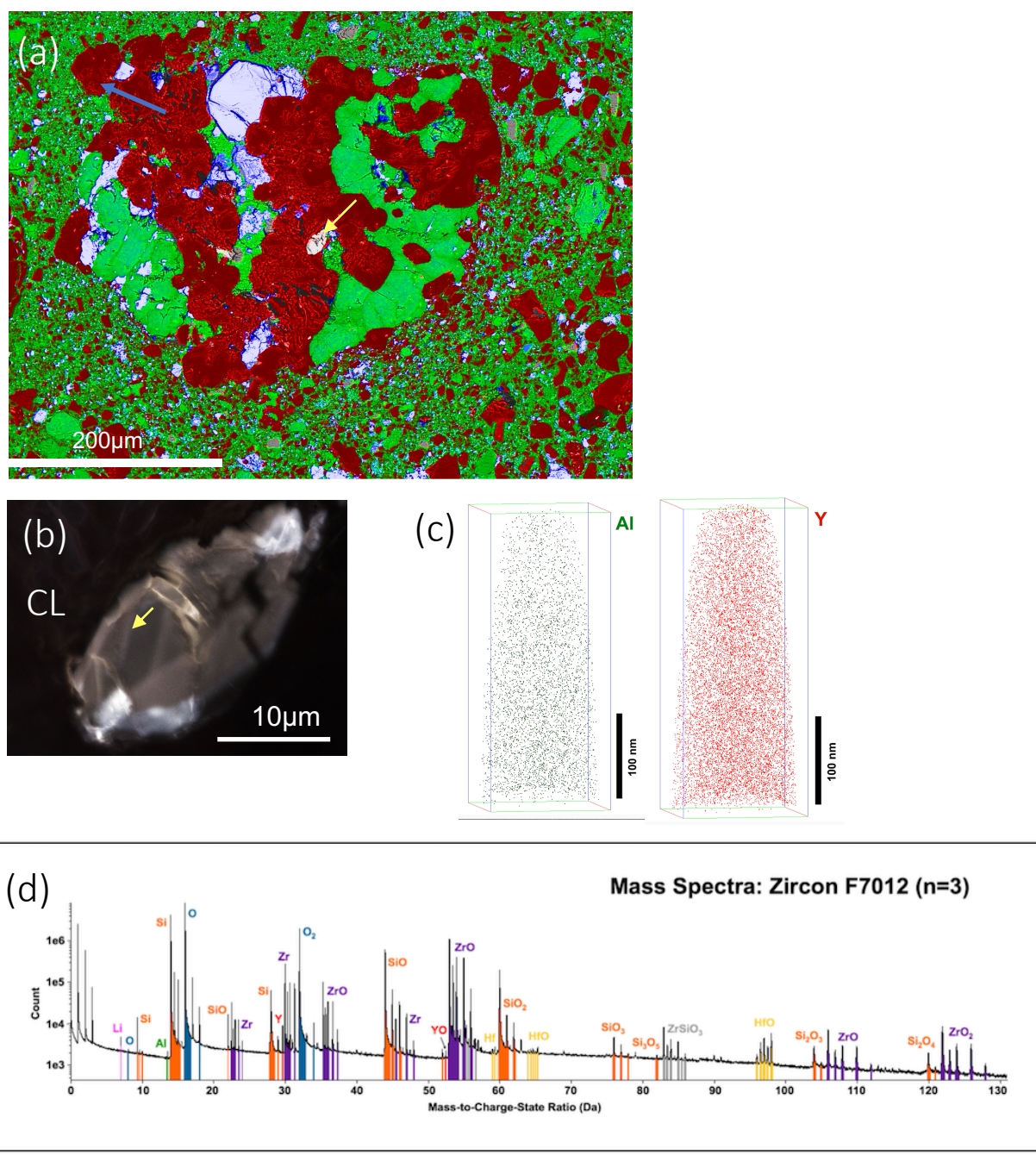


Fig. S5. Data for NWA 7475, zircon grain F7012;
 (a) Context EDS element map (Green =Mg, Red =Na, Blue=Fe) of lithic clast showing fractured but otherwise undeformed zircon grain F7012 (yellow arrow). Note clast minerals breaking at margins into matrix (blue arrow),
 (b) CL image of F7012 showing planar growth banding and location of atom probe micro-sample (yellow arrow),
 (c) APT atom maps showing homogeneous distribution of Al and Y, there is no clustering of these trace elements as exhibited by zircon exposed to temperatures $>800^\circ\text{C}$ ¹³,
 (d) APT mass spectrum corresponding to atom map (matches Earth reference zircon³⁵).

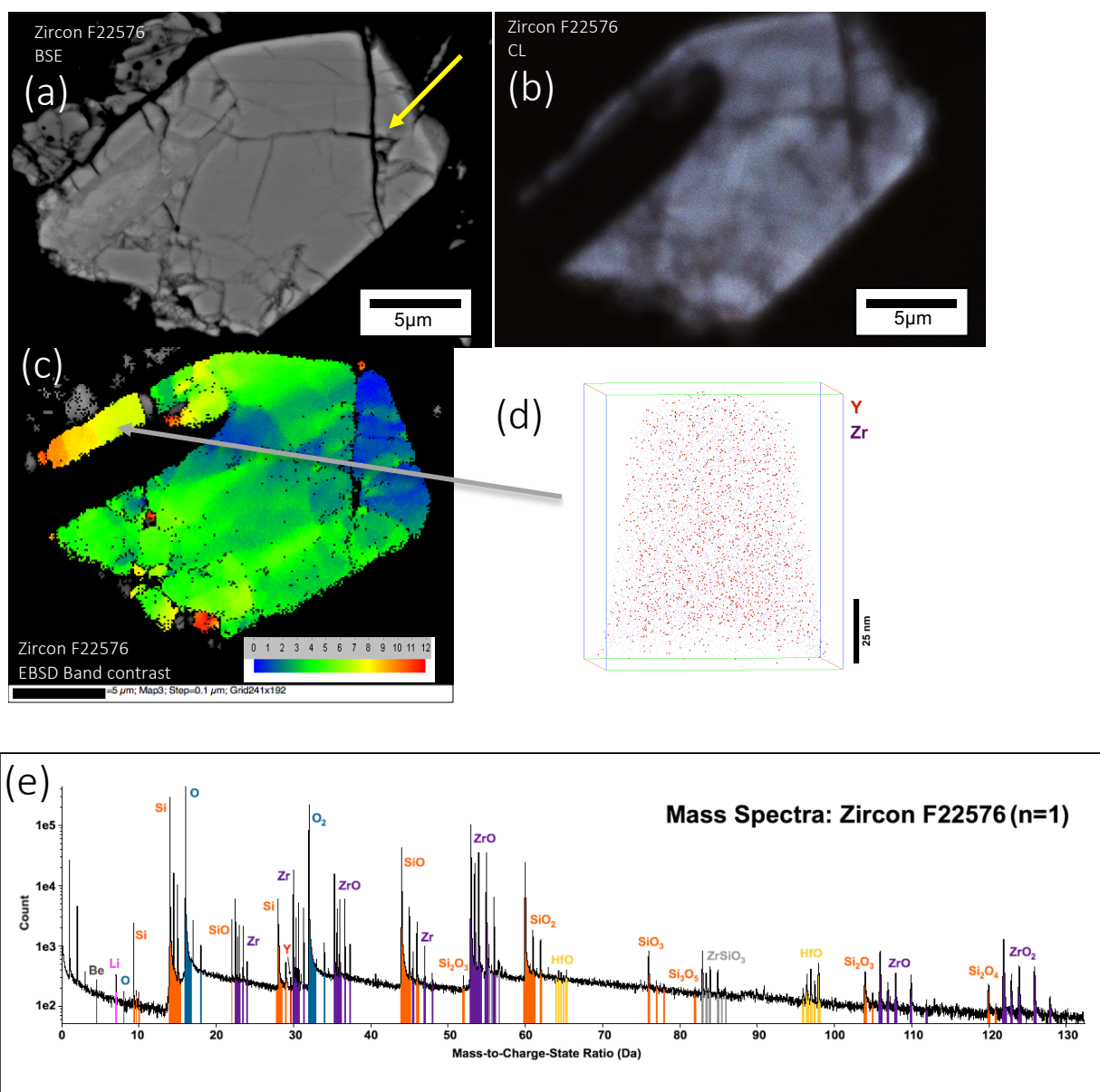


Fig. S6. Microstructural and APT data for NWA 7475, zircon grain F22576;

- BSE image showing subhedral, igneous crystal form,
- CL image showing concentric zoning and U-rich (dark) core,
- EBSD texture map coloured according to relative lattice misorientation (referenced to blue zone, east end of grain). Lattice orientation changes mostly across open, launch-related fractures. Between fractures the zircon exhibits low magnitudes (several degrees) of crystal plastic deformation due to low-grade shock metamorphism on Mars,
- APT atom map from zircon edge showing homogeneous distribution of trace element Y,
- APT mass spectrum corresponding to atom map (matches Earth reference zircon³⁵).

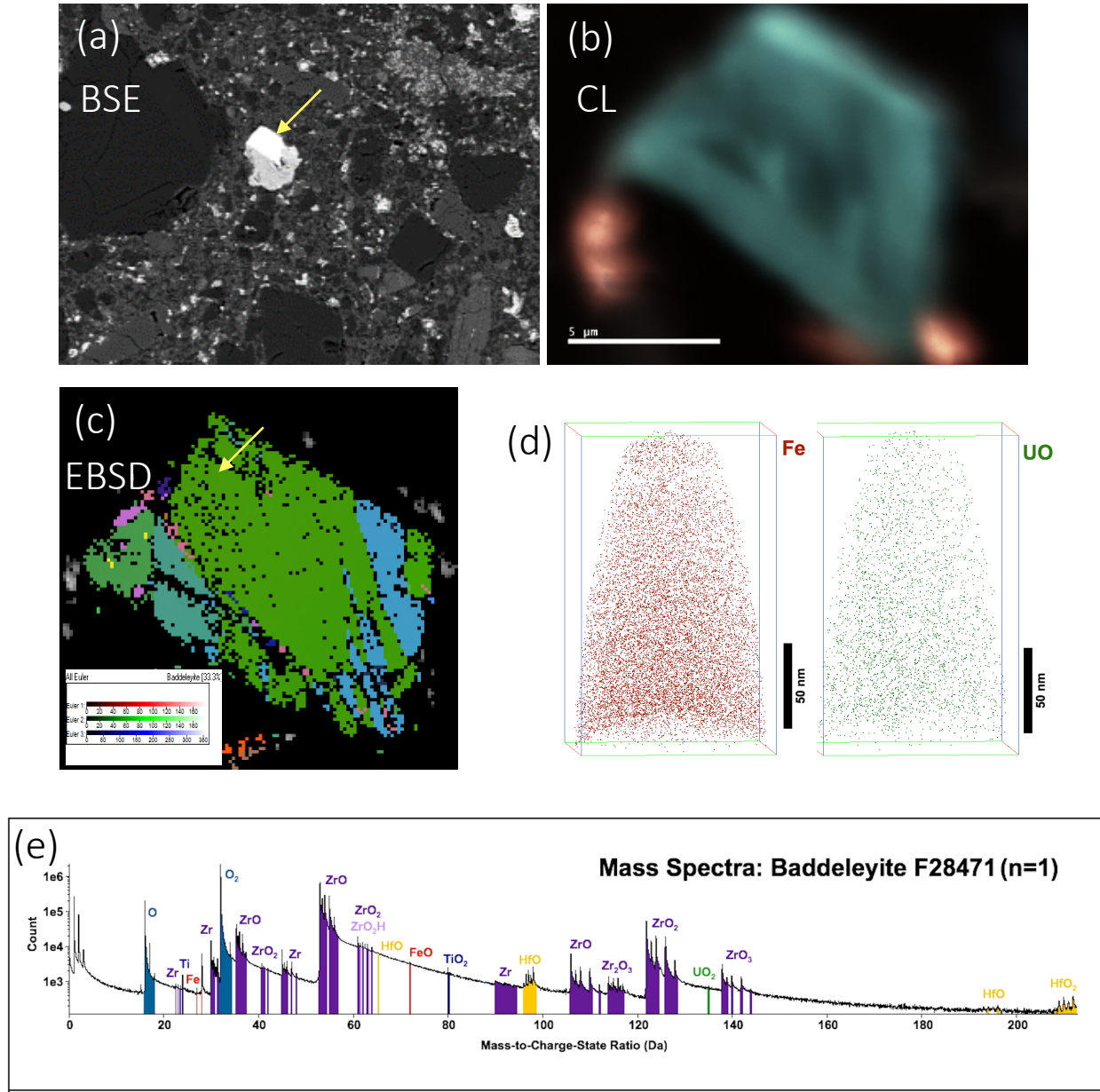


Fig. S7. Bi-mineralic clast of euhedral baddeleyite grain F28471 with ilmenite showing;
a) Low magnification BSE image,
b) CL showing concentric and planar zoning,
c) EBSD euler map showing twinning (see Fig. S8 for detail) and location of atom probe micro-sample (yellow arrow),
d) Atom maps of trace elements Fe and UO showing homogeneous distribution,
e) APT mass spectrum for this grain, identical to Earth baddeleyite³⁵. Like the zircon, the baddeleyite does not show micro- or nano-scale features characteristic of exposure to impact crater environments²¹.

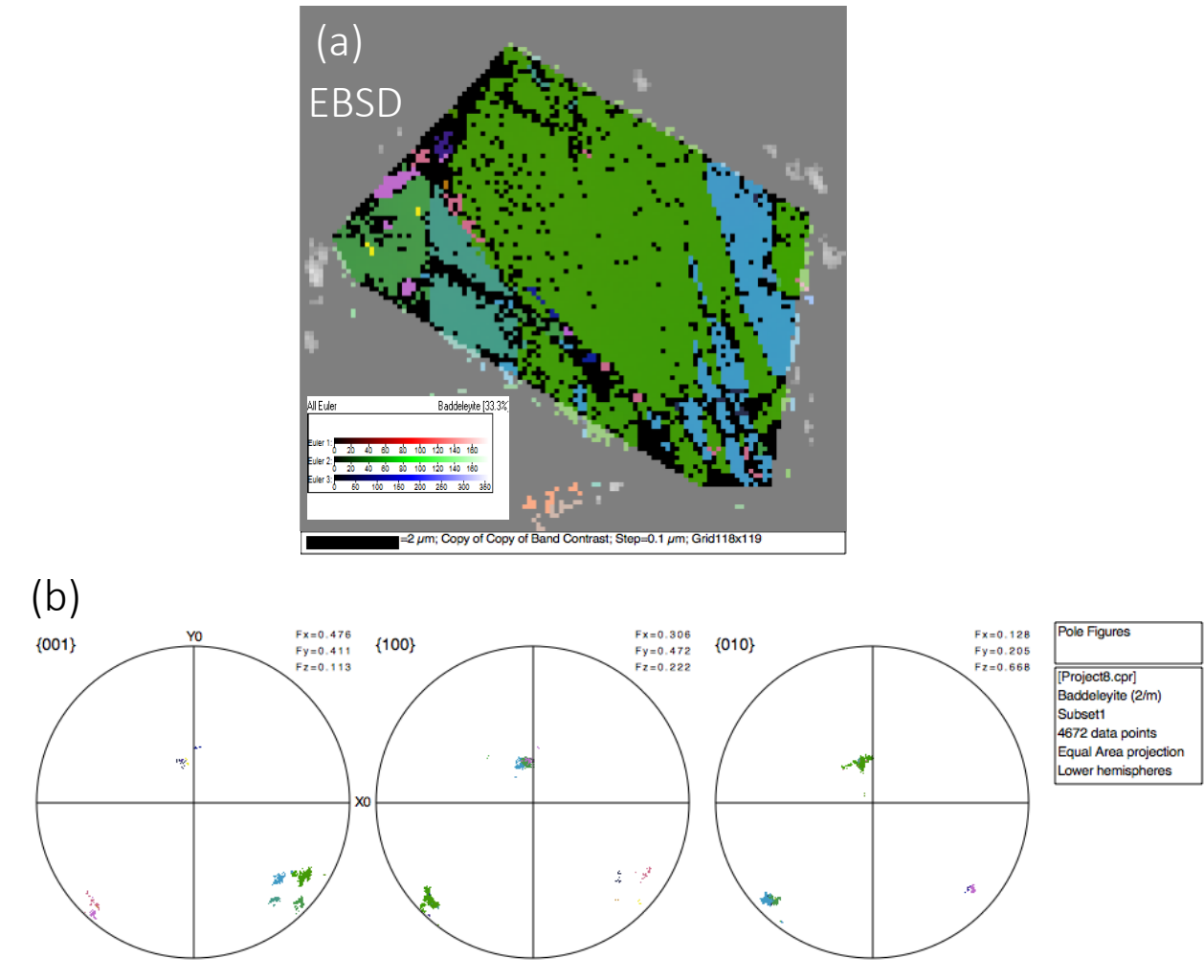


Fig. S8. EBSD data for NWA 7475, baddeleyite grain F28471;
a) EBSD map of Euler angles of baddeleyite lattice orientation relative to stage coordinates showing twinning,
b) Colour correlative inverse pole figures showing orthogonally related reversion twinning typical of low-grade (<20 GPa) shock metamorphism.

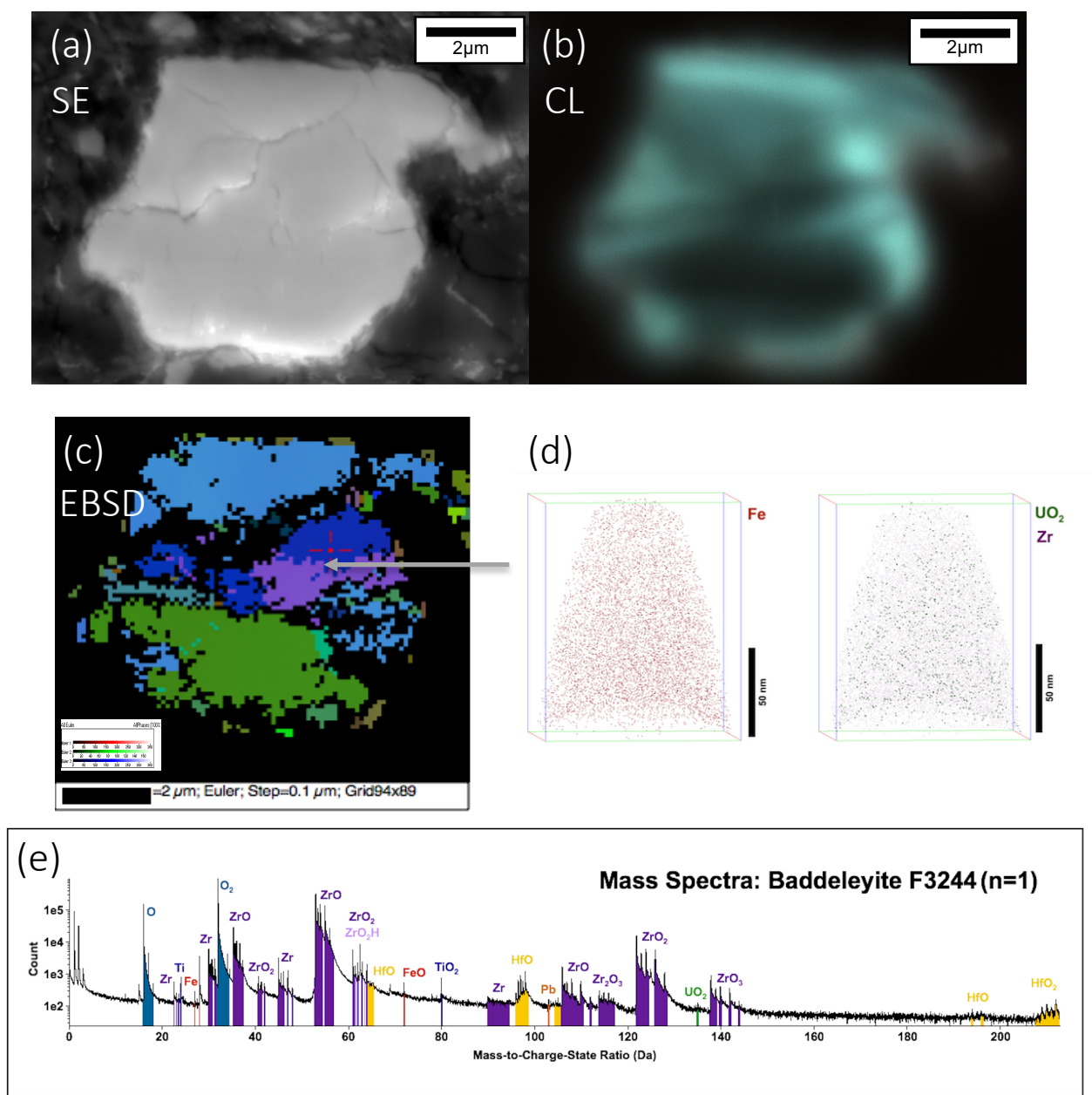


Fig. S9. Microstructural and APT data for NWA 7475 baddeleyite crystal clast F3244;
a) SE image showing open fractures,
b) CL showing concentric zoning,
c) EBSD euler map showing complex twinning (see Fig. S10 for detail) and location of atom probe micro-sample (arrow).
d) Atom maps of trace elements Fe and U (as UO_2) showing homogeneous distribution,
e) APT mass spectrum for this grain, identical to Earth baddeleyite³⁵ but unlike moderate to highly shock metamorphosed baddeleyite²¹.

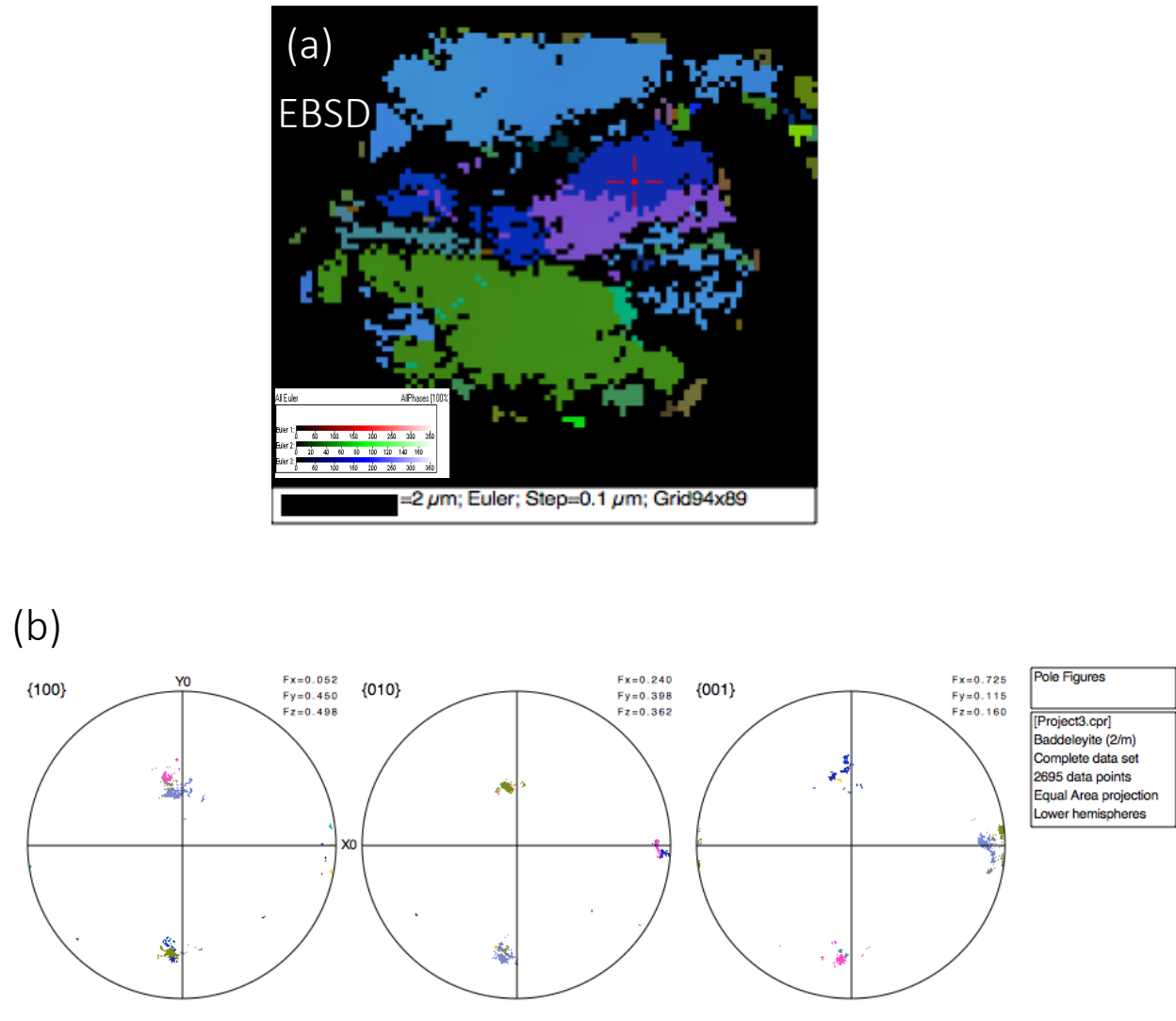


Fig. S10. NWA 7475; F3244 baddeleyite grain EBSD data;
a) EBSD map of Euler angles of baddeleyite lattice orientation relative to stage coordinates showing twinning,
b) colour correlative inverse pole figures showing orthogonally related reversion twinning typical of low-grade (<20 GPa) shock metamorphism.

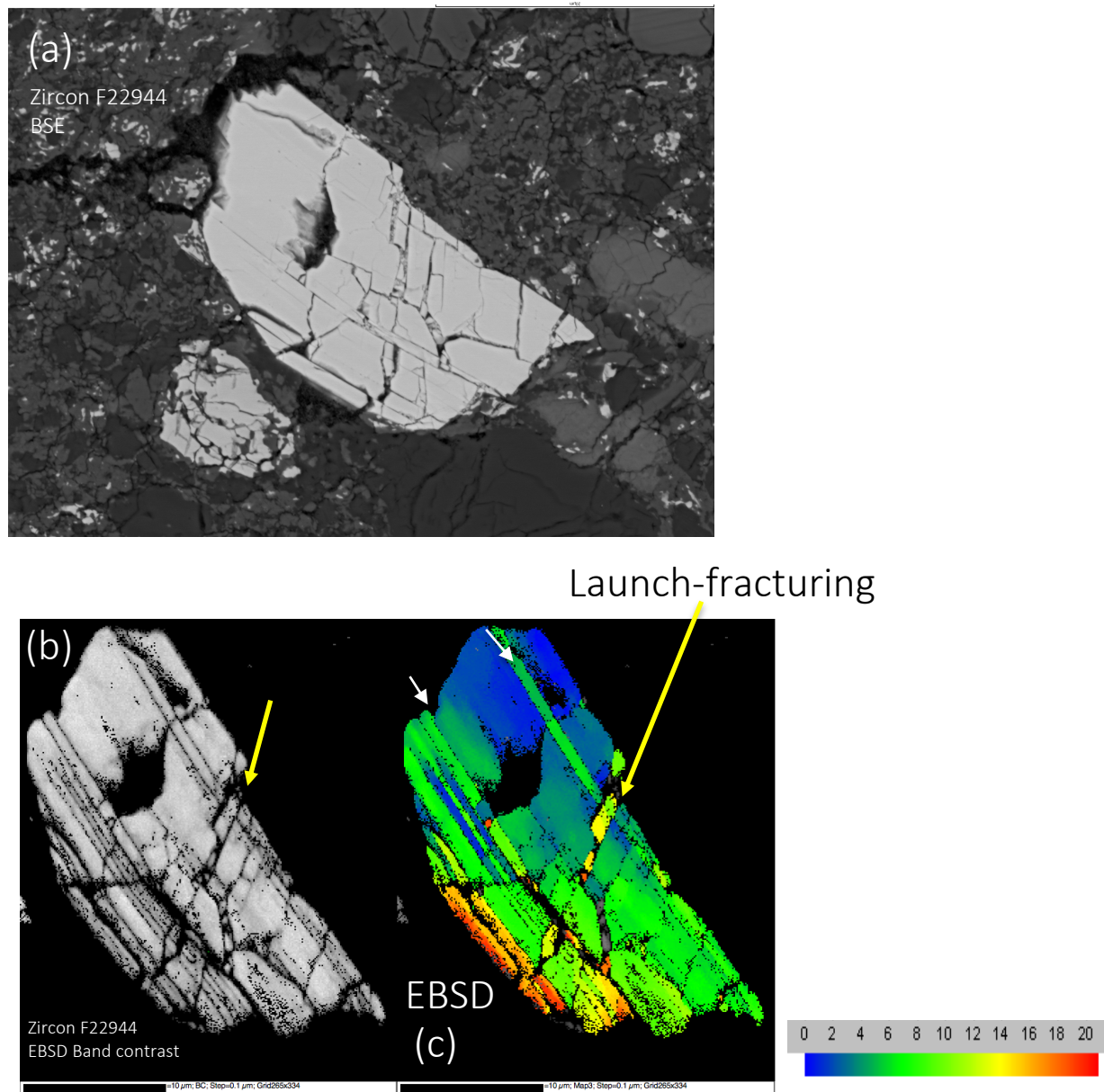


Fig. S11. NWA 7475, shocked zircon grain F22944;

- BSE image showing anhedronal crystal form, fragmented margins, and through-going open fractures,
- Band contrast (intensity of zircon electron diffraction patterns) EBSD map showing conjugate fractures attributed to ejection event off-setting planar features of reduced diffraction signal (dark) (black scale bar = 10 micrometres),
- Map of relative lattice misorientation showing crystallographically-controlled planar features (white arrows) due to moderate (~20 GPa) shock metamorphism. Abrupt orientation changes occur across open (launch) fractures, however discrete changes of severe degrees also occur across the planar deformation bands. This is the only evidence of pre-launch shock metamorphism observed in the zircon population.

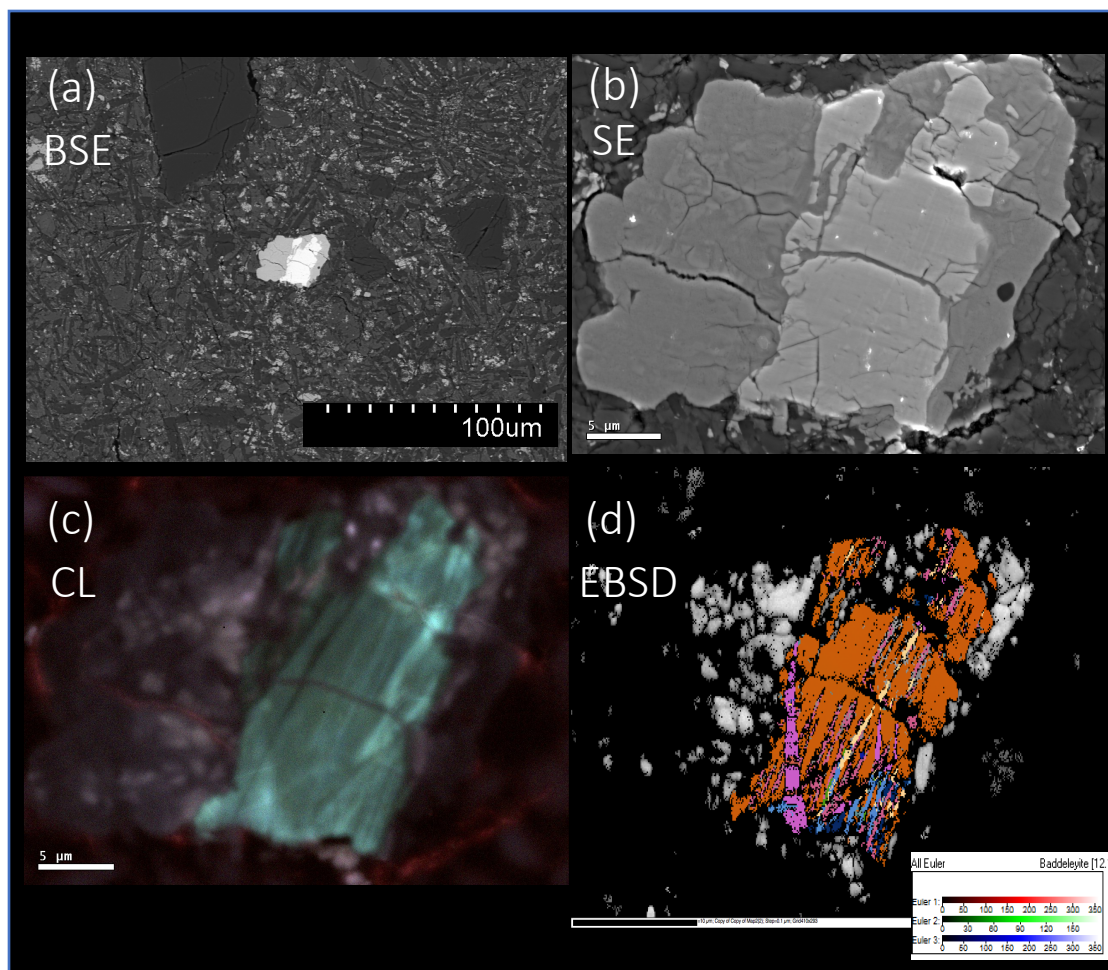


Fig. S12. NWA 7475 shocked baddeleyite grain partially replaced with zircon;

- BSE image showing relict baddeleyite within quenched, fine-grained random plagioclase (dark laths) and pyroxene melt matrix,
- SE image showing baddeleyite (light grey) partially replaced and cross-cut by zircon (medium grey) prior to fracturing (open fractures),
- CL image showing baddeleyite internal zoning (green) being replaced and cross-cut by reaction zircon (mauve),
- Map of Euler angles of baddeleyite lattice, revealing multiple twin lamellae in different orientations.

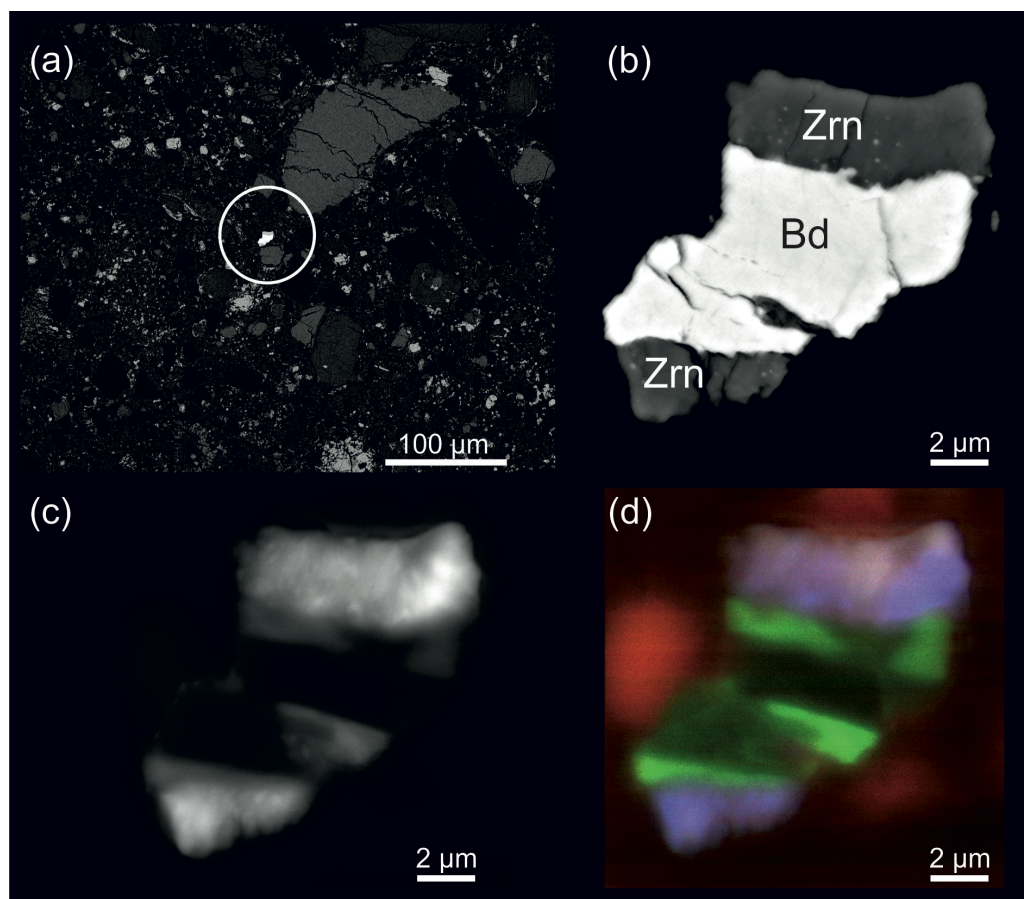


Fig. S13. NWA 7906; baddeleyite crystal clast partially replaced by zircon;

- a) BSE context image showing crystal clast in matrix,
- b) Higher magnification BSE image of (a) showing reaction texture interrupted at fractured margin of grain during deposition in breccia, indicating that reaction texture was a pre-breccia event,
- c) Panchromatic (grey-scale) CL intensity image,
- d) Composite RGB CL image showing baddeleyite planar growth zoning (green and black) cross-cut by reaction zircon (purple).

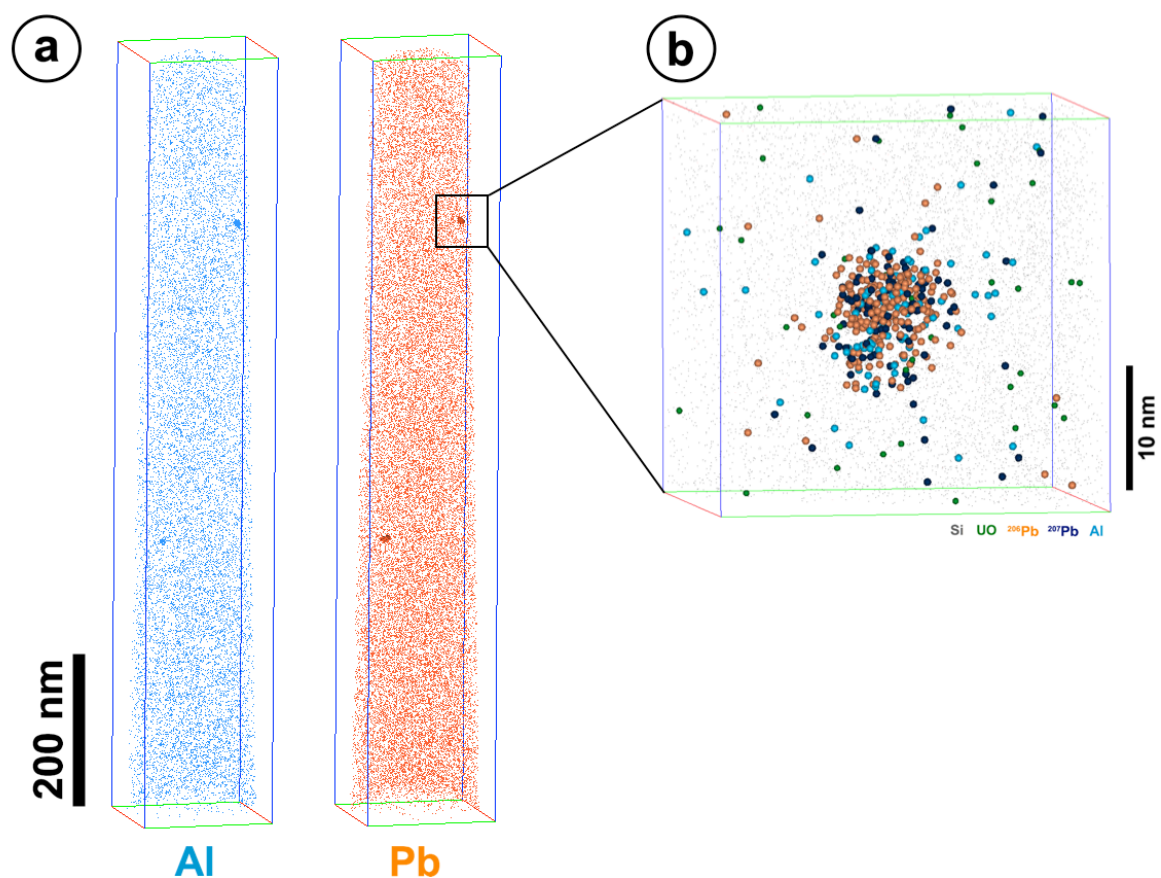


Fig. S14. Atom probe tomography results for a shock metamorphosed Archean zircon sampled from the central uplift of the Vredefort impact structure;

(a) Atom maps for a single microtip specimen showing nanoscale distribution of Al and Pb ions.

(b) APT sub-volume reconstruction of an isolated Pb-rich cluster defined using a 0.2 atoms/nm³ Pb density isosurface. Here, the high concentrations of radiogenic Pb (²⁰⁶Pb and ²⁰⁷Pb) within clusters is not supported by parent isotopes of U, which suggests that these nanoscale phenomena do not represent primary features.

Table S1. Summary of number of zircon and baddeleyite grains from NWA 7034 group meteorites, and their size and setting for each polished surface of a given meteorite (n.a.= not applicable).

Meteorite and surface identifier	Total Number Found ZIRCON	Number >10µm Examined	Average Length (µm)	Average Minimum Length (µm)	Average Maximum Length (µm)	Crystal Clast (CC) or Lithic	pre-launch Shock features
<i>NWA 7906</i>	n.a.	5	n.a.	n.a.	n.a.	n.a.	0
<i>NWA 7034</i>	195	10	51.4	30.9	145.9	<i>CC# = 7 Lithic# = 3</i>	0
<i>Rabt Sbayta 003</i>	154	5	23.5	19.4	31.0	<i>CC# = 2 Lithic# = 3</i>	0
<i>NWA 7475a</i>	469	10	26.1	20.0	30.4	<i>CC# = 8 Lithic# = 2</i>	Yes (F22944)
<i>NWA 7475b</i>	353	10	31.6	18.1	55.6	<i>CC# = 9 Lithic# = 1</i>	0
<i>NWA 7475 (GF12-11)</i>	337	10	25.3	19.6	33.1	<i>CC# = 4 Lithic# = 6</i>	0
<i>NWA 11220 - 6</i>	51	10	16.2	9.6	30.8	<i>CC# = 9 Lithic# = 1</i>	No
<i>NWA 11220 - 7</i>	49	10	15.3	10.4	37.2	<i>CC# = 4 Lithic# = 6</i>	No
<i>NWA 11220 - 8</i>	49	10	14.0	8.9	41.4	<i>CC# = 5 Lithic# = 5</i>	No
<i>NWA 11220-TS</i>	370	15	46.0	22.5	135.9	<i>CC# = 5 Lithic# = 5</i>	No
						<i>CC=58 Lithic=36</i>	
						<i>Tot. =94 Lithic=38 %</i>	

Table S1 continued. Summary of number of zircon and baddeleyite grains from NWA 7034 group meteorites, and their size and setting for each polished surface of a given meteorite (n.a.= not applicable).

Meteorite and surface identifier	Total Number Found BADDEL-EYITE	Number >10µm Examined	Average Length (µm)	Average Minimum Length (µm)	Average Maximum Length (µm)	Crystal Clast (CC) or Lithic	pre-launch Shock features
<i>NWA 7906</i>	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Possible (1)
<i>NWA 7034</i>	10	4	18.6	11.0	28.1	CC# = 4	No
<i>Rabt Sbayta 003</i>	32	5	20.8	10.8	32.8	CC# = 3 Lithic# = 2	No
<i>NWA 7475a</i>	103	9	14.3	10.4	24.2	CC# = 9	No
<i>NWA 7475b</i>	67	10	15.5	9.6	39.1	CC# = 2 Lithic# = 8	Possible (F14987)
<i>NWA 7475 (GF12-11)</i>	69	5	14.3	12.6	15.9	CC# = 1 Lithic# = 4	No
<i>NWA 11220 - 6</i>	19	5	16.5	12.2	21.0	CC# = 2 Lithic# = 3	No
<i>NWA 11220 - 7</i>	16	3	9.7	8.9	11.0	CC# = 1 Lithic# = 2	No
<i>NWA 11220 - 8</i>	10	3	9.9	9.6	10.2	CC# = 2 Lithic# = 1	No
<i>NWA 11220-TS</i>	63	8	16.1	11.0	26.4	Lithic# = 8	No
						CC=24 Lithic=28	
						Tot. =52 Lithic=54%	

Table S2. Summary of analytical techniques applied to zircon and baddeleyite grains from NWA 7034 group meteorites (Table S1) for each polished surface of a given meteorite (n.d.= not determined).

Meteorite and surface identifier	Number Examined	BSE	EBSD	SE and CL	EDS	APT	U-Pb age
	ZIRCON						
<i>NWA 7906</i>	5	n.d.	5	3	n.d.	n.d.	n.d.
<i>NWA 7034</i>	10	10	6	0	0	0	3
<i>Rabt Sbayta 003</i>	5	5	4	5	3	0	0
<i>NWA 7475a</i>	10	10	10	8	7	2	0
<i>NWA 7475b</i>	10	10	10	10	4	0	0
<i>NWA 7475 (GF12-11)</i>	10	10	7	6	0	0	0
<i>NWA 11220 - 6</i>	10	10	7	10	0	0	0
<i>NWA 11220 - 7</i>	10	10	7	10	0	0	0
<i>NWA 11220 - 8</i>	10	10	9	10	0	0	0
<i>NWA 11220-TS</i>	15	13	4	11	5	0	0
<i>Total</i>			69				

Table S2 continued. Summary of analytical techniques applied to zircon and baddeleyite grains from NWA 7034 group meteorites (Table S1) for each polished surface of a given meteorite.

Meteorite and surface identifier	Number Examined BADDELEYITE	BSE	EBSD	SE and CL	EDS	APT	U-Pb age
<i>NWA 7034</i>	4	4	1	0	0	0	1
<i>Rabt Sbayta 003</i>	5	5	2	2	1	0	0
<i>NWA 7475a</i>	9	9	9	9	0	2	0
<i>NWA 7475b</i>	10	10	9	10	1	0	0
<i>NWA 7475 (GF12-11)</i>	5	5	3	0	0	0	0
<i>NWA 11220 - 6</i>	5	5	1	1	0	0	0
<i>NWA 11220 - 7</i>	3	3	3	3	0	0	0
<i>NWA 11220 - 8</i>	3	3	2	3	0	0	0
<i>NWA 11220-TS</i>	8	8	0	0	3	0	0
<i>Total</i>			29				

Table S3. Acquisition and reconstruction parameters for atom probe data following the recommend reporting protocol⁵⁹.

Grain ID	Zircon				Baddeleyite	
	F7012 (n=3)			F22576 (n=1)	F28471 (n=1)	F3244 (n=1)
Specimen/Data Set	R52_127654	R52_128916	R52_128939	R60_147509	R60_147213	R60_147255
Instrument Model	LEAP 4000X HR	LEAP 4000X HR	LEAP 4000X HR	LEAP 4000X HR	LEAP 4000X HR	LEAP 4000X HR
Instrument setting						
Nominal flight path (mm)	382	382	382	382	382	382
Laser wavelength (nm)	355	355	355	355	355	355
Laser Pulse Energy (pJ)	400	400	400	100	200	100
Pulse Frequency (kHz)	200	200	200	238	189	186
Detection rate (%)	0.5	0.5	0.5	0.5	0.5	0.5
Sample temperature (K)	54.8	54.8	59.1	54.0	53.8	53.7
Chamber pressure (Torr)	1.1×10^{-10}	5.5×10^{-11}	7.2×10^{-11}	2.9×10^{-11}	2.8×10^{-11}	2.7×10^{-11}
Data summary						
Total Ions:	61356089	3848909	7025990	61417	136560	61722
Single (%)	81.1	74.3	76.5	53.2	93.5	91.6
Multiple (%)	18.5	25.3	23.2	46.8	6.5	8.4
Partial (%)	0.4	0.3	0.3	0.0	0.0	0.0
(M/ ΔM) †	1034	1037	1067	1127	1114	1101
Time independent background (ppm/ns)	31.8	26.2	30.3	52.1	16.6	18.0
Reconstruction						
Radius evolution model	Voltage	Voltage	Voltage	Voltage	Voltage	Voltage
Field factor (k)	1.65	1.65	1.65	1.65	1.65	1.65
Image compression factor	3.30	3.30	3.30	3.30	3.30	3.30
Assumed E-field (V/nm)	28	28	28	28	28	28
V _{Initial} (V)	4942	4019	4522	8640	3871	5657

† ΔM is at full width half maximum

Table S4. Summary of geochronology for Rabt Sbayta polymict breccia.

Sample	Average U-Pb Age (Ma)	Source
Zircon		
NWA 7034	4431±27 Ma (2 σ)	McCubbin et al 2016 ²⁹
	1502±98 Ma (2 σ)	McCubbin et al 2016 ²⁹
	4439±17 Ma (2 σ)	Yin et al 2014 (LPSC) ⁶⁰
	4350±13 Ma (2 σ)	Yin et al 2014 (LPSC) ⁶⁰
	1410±56 Ma (2 σ)	Yin et al 2014 (LPSC) ⁶⁰
	4367±65 Ma (2 σ)	Tartèse et al 2014 (LPSC) ⁶¹
	1574±32 Ma (2 σ)	Tartèse et al 2014 (LPSC) ⁶¹
NWA 7533	4428±25 Ma (2 σ)	Humayun et al 2013 ²⁴
	1712±85 Ma (2 σ)	Humayun et al 2013 ²⁴
Baddeleyite		
NWA 7034	4411±23 Ma (2 σ)	Tartèse et al 2014 (LPSC) ⁶¹
	4311±52 Ma (2 σ)	Tartèse et al 2014 (LPSC) ⁶¹
Phosphate		
NWA 7034	1495±88 Ma (2 σ)	McCubbin et al 2016 ²⁹
	1345±47 Ma (2 σ)	Yin et al 2014 (LPSC) ⁶⁰
NWA 7533	1357±81 Ma (2 σ)	Bellucci et al 2015 ⁶²
Sample	²⁰⁷ Pb/ ²⁰⁶ Pb Age (Ma)	Source
Zircon		
NWA 7034	4476±0.9 Ma (2 σ)	Bouvier et al 2018 ²⁸
	4429±1.0 Ma (2 σ)	Bouvier et al 2018 ²⁸
Baddeleyite		
NWA 7034	4382±60 Ma (2 σ)	McCubbin et al 2016 ²⁹
Sample	¹⁴⁷ Sm/ ¹⁴³ Nd Age (Ma)	Source
Whole rock and mineral separates		
NWA 7034	4420±70 Ma (2 σ)	Nyquist et al 2016 ⁶³
Sample	⁴⁰ Ar/ ³⁹ Ar Age (Ma)	Source
Whole Rock		
NWA 11552	1391±16 Ma (2 σ)	Cassata et al 2018 ⁹
Sample	U-Pu/Xe Age (Ma)	Source
Whole Rock		
NWA 7034	4319±46 Ma (2 σ)	Cassata et al 2018 ⁹
Sample	U-Th-Sm/He Ages (Ma)	Source
Whole Rock		
NWA 7034	135±6 Ma (2 σ)	Cassata et al 2018 ⁹

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61. Tartèse, R., Anand, M., Mccubbin, F. M., Santos, A. R. & Delhaye, T. Zircons in Northwest Africa 7034: records of crustal evolution on Mars. *Lunar Planet. Sci. Conf.* **45**, abstr. #2020 (2014).
62. Bellucci, J. J. *et al.* Pb-isotopic evidence for an early , enriched crust on Mars. *Earth Planet. Sci. Lett.* **410**, 34–41 (2015).
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