

Mineralogy of zirconium in iron-oxides: a micron- to nanoscale study of hematite ore from Peculiar Knob, South Australia

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Supplementary Material A: Details of analytical methodology and supporting Figure S1

Whole-rock geochemistry

A whole-rock assay for the studied sample was performed by Intertek Genalysis (Adelaide). Sample preparation for whole-rock assays involved sample crushing to approximately 2 mm size, from which a 3 kg homogeneous portion of the sample was extracted for pulverising. This ensured that the homogeneous sub-sample was representative of the material submitted for testing. The resulting powder was then either treated by four-acid digestion or lithium borate fusion.

The four-acid digest involved digesting the sample in a mixture of four acids: Hydrochloric acid (HCl), nitric acid (HNO₃), hydrofluoric acid (HF) and perchloric acid (HClO₄). The resulting solution from the four-acid digestion was then analysed using either Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), depending on the target elements.

Lithium borate fusion involved mixing the solid sample with a solid strong base in a platinum crucible and heating it for 1–2 min. Distilled water was added gently to the sample mixture to initiate oxidation of the sample and the base. The fusion is then carried out at approximately 1000 °C within an automatic fusion fluxer. The molten mixture was then poured into dilute mineral acid and stirred until the flux dissolves. The resulting solution was then analysed using either ICP-OES or ICP-MS, depending on the target elements (Table S1).

Table 1. Methodology, analysed elements, and detection limits for whole-rock analyses.

Element	Ag	Al	As	Ba	Be	Bi	C	Ca	Cd	Ce	Co
Method	4AB/MS	FB6/OE	4AB/MS	FB6/MS	FB6/MS	4AB/MS	CSA	FB6/OE	4AB/MS	FB6/MS	4AB/MS
	ppm	%	ppm	ppm	ppm	ppm	%	%	ppm	ppm	ppm
ldl	0.01	0.01	1.0	1.0	0.50	0.05	0.01	0.01	0.05	0.50	0.10
upl	500	50.0	2000	50000	20000	500	40.0	70.0	500	300000	2000
Element	Cr	Cs	Cu	Dy	Er	Eu	Fe	Ga	Gd	Ge	Hf
Method	FB6/OE	FB6/MS	4AB/OE	FB6/MS	FB6/MS	FB6/MS	FB6/OE	FB6/MS	FB6/MS	4AB/MS	FB6/MS
Element	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm
ldl	20.0	0.05	1.0	0.05	0.05	0.05	0.01	0.10	0.05	0.10	0.10
udl	50000	10000	20000	50000	50000	50000	70.0	50000	50000	2000	50000
Element	Ho	In	K	La	Li	Lu	Mg	Mn	Mo	Na	Nb
Method	FB6/MS	4AB/MS	FB6/OE	FB6/MS	4AB/MS	FB6/MS	FB6/OE	FB6/OE	FB6/MS	FB6/OE	FB6/MS
	ppm	ppm	%	ppm	ppm	ppm	%	%	ppm	%	ppm
ldl	0.02	0.05	0.01	0.20	0.10	0.02	0.01	0.01	1.0	0.01	0.10
upl	20000	2000	80.0	200000	1000	10000	60.0	75.0	10000	75.0	50000
Element	Nd	Ni	P	Pb	Pr	Rb	Re	S	Sb	Sc	Se

Method	FB6/ MS	4AB/OE	FB6/OE	4AB/OE	FB6/MS	FB6/MS	4AB/MS	CSA	FB6/MS	FB6/OE	4AB/MS
	ppm	ppm	%	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm
ldl	0.10	1.0	0.01	5.0	0.05	0.10	0.05	0.01	0.50	2.0	1.0
upl	2000 00	20000	40.0	10000	100000	50000	2000	50.0	10000	50000	2000
Element	Si	Sm	Sn	Sr	Ta	Tb	Te	Th	Ti	Tl	Tm
Method	FB6/ OE	FB6/MS	FB6/MS	FB6/MS	FB6/MS	FB6/MS	4AB/MS	FB6/MS	FB6/OE	4AB/MS	FB6/MS
	%	ppm	%	ppm	ppm						
ldl	0.01	0.05	1.0	0.50	0.10	0.02	0.10	0.05	0.005	0.02	0.05
upl	45.0	100000	50000	200000	50000	20000	2000	20000	60.0	500	10000
Element	U3O 8	V	W	Y	Yb	Zn	Zr	LOI-1000			
Method	FB6/ MS	FB6/OE	FB6/MS	FB6/MS	FB6/MS	4AB/OE	FB6/MS	LOI/GR			
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%			
ldl	0.50	10.0	1.0	0.50	0.05	1.0	1.0	0.01			
upl	1000 0	50000	50000	500000	50000	20000	500000	100			
CSA	Induction Furnace Analyzed by Infrared Spectrometry										
4AB/MS	Multi-acid digest including Hydrofluoric, Nitric, Perchloric and Hydrochloric acids in Teflon Beakers. Analyzed by Inductively Coupled Plasma Mass Spectrometry.										
4AB/OE	Multi-acid digest including Hydrofluoric, Nitric, Perchloric and Hydrochloric acids in Teflon Beakers. Analyzed by Inductively Coupled Plasma Optical (Atomic) Emission										
FB6/MS	Lithium metaborate/tetraborate fusion Analyzed by Inductively Coupled Plasma Mass Spectrometry.										
FB6/OE	Lithium metaborate/tetraborate fusion Analyzed by Inductively Coupled Plasma Optical (Atomic) Emission										
LOI/GR	Loss on Ignition. Gravimetric Determination.										
ldl / upl	Lower detection limit / Upper detection limit										

Laser-ablation inductively-coupled mass spectrometry (LA-ICP-MS)

LA-ICP-MS equipment housed at Adelaide Microscopy, The University of Adelaide was used to analyse trace elements in minerals prepared in one-inch polished blocks. The laser ablation system used was a RESOLUTION-LR (Applied Spectra Inc., Fremont, SA, USA) with a S-155 large format, two-volume ablation cell designed by Laurin Technic Pty. Ablation was performed in an atmosphere of UHP He (0.38 L/min). Upon exiting the cell, the aerosol was mixed with Ar (1.05 L/min) and passed through a pulse-homogenizing device prior to injection into the torch. The ICP-MS system was optimized daily to maximize sensitivity of isotopes in the mass range of interest, while keeping the production of oxide and doubly-charged species as low as possible (usually <0.2%).

The following isotopes were monitored for trace element analyses: ²⁴Mg, ²⁷Al, ²⁸Si, ³¹P, ⁴³Ca, ⁴⁵Sc, ⁴⁹Ti, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁶⁹Ga, ⁷⁵As, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ⁹⁵Mo, ¹¹⁸Sn, ¹²¹Sb, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸¹Ta, ¹⁸²W, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th and ²³⁸U. The spot diameter range, frequency and average fluence used for trace element analysis were 60 µm, 10 Hz and 3.5 J/cm², respectively. Analysis time for each spot was 60-s, comprising a 30-s measurement of background (laser-off), and 30-s analysis of the unknown (laser-on). Detection limits were calculated for each element in each spot analysis.

During trace element analysis, the primary standard GSD-1G [33] and secondary standard NIST-610 [34] were run before and after the batch of 20 unknowns. For quantification of iron-oxides, ^{57}Fe was used as the internal standard element assuming ideal stoichiometry. All data reduction was performed using 'GLITTER' software with reference values from the GeoREM database (<http://georem.mpch-mainz.gwdg.de>). Average minimum detection limits are given in Table S2.

Table S2: Average minimum detection limits (mdl) for LA-ICP-MS analysis of iron-oxides.

Element	mdl (ppm)	Element	mdl (ppm)	Element	mdl (ppm)	Element	mdl (ppm)
Mg	0.086	Ni	0.059	Ba	0.031	Tm	0.002
Al	0.113	Cu	0.046	La	0.002	Yb	0.008
Si	28.60	Zn	0.148	Ce	0.002	Lu	0.002
P	4.094	Ga	0.013	Pr	0.002	Hf	0.008
Ca	24.40	As	0.144	Nd	0.011	Ta	0.002
Sc	0.028	Sr	0.005	Sm	0.011	W	0.010
Ti	0.295	Y	0.003	Eu	0.003	^{206}Pb	0.009
V	0.012	Zr	0.007	Gd	0.013	^{207}Pb	0.011
Cr	0.236	Nb	0.003	Tb	0.002	^{208}Pb	0.005
Mn	0.086	Mo	0.023	Dy	0.007	Th	0.002
Fe	2.505	Sn	0.048	Ho	0.002	U	0.002
Co	0.009	Sb	0.020	Er	0.006		

Element maps were created by ablating sets of parallel line rasters in a grid across hematite grains. A beam size of 7 μm and scan speed of 7 $\mu\text{m/s}$ were chosen in order to acquire adequate sensitivity and spatial resolution. Pre-ablation was used on each line prior to main data collection to minimize the effect of redeposition. A laser repetition rate of 10 Hz was used with an energy density of $\sim 3 \text{ J/cm}^2$. To allow for cell wash-out, a 20-second delay was used before acquisition of the 20 second gas background for each line analysis. Two 51 μm spots were ablated on reference material GSD-1G [33] and BHVO-2G at the beginning and end of each map.

SHRIMP U-Pb zircon geochronology

All isotopic measurements were reduced by off-line computer programs using standard techniques (SQUID) [55]. During zircon analysis, data were collected during six cycles through nine or ten magnetic-field values. The resultant data set for all peaks over all cycles is used to calculate count rates integrated over time from the first peak of the first cycle to the last peak of the last cycle. These count rates are used to calculate isotopic ratios for the analysis. Decay constants used are those recommended by IUGS and ^{235}U was calculated using the decay constant of Steiger and Jäger (1977) [56]. A 20–30 μm -diameter spot was used, with a mass-filtered O_2^- primary beam of 2–3 nA. Data for each spot are collected in sets of 6 or 7 scans through the mass range of $^{196}\text{Zr}_2\text{O}^+$, $^{204}\text{Pb}^+$, background, $^{206}\text{Pb}^+$, $^{207}\text{Pb}^+$, $^{208}\text{Pb}^+$, $^{238}\text{U}^+$, $^{248}\text{ThO}^+$, and $^{254}\text{UO}^+$. Concentrations of U, Th and Pb are calculated using a similar approach with the unknown referenced to the standard with known U, Th and Pb abundances [38,39,57]

Electron probe microanalyzer

Quantitative compositions of zircon were determined using a Cameca SX-Five electron probe microanalyzer (EPMA), equipped with 5 tuneable wavelength-dispersive spectrometers, located at the University of Adelaide. The instrument is running PeakSite v6.2 software for microscope operation, and Probe

for EPMA software (distributed by Probe Software Inc.) for all data acquisition and processing. Combined operating conditions were utilized in which for each individual spot, major and mobile elements were analysed first at 17 kV/20 nA, then the beam subsequently changed to 17 kV/100 nA for the remaining analysis of low-level elements. Due to the need for spatial resolution, all analyses were done with a focused beam.

The full list of elements analysed along with primary and interference standards are presented in Tables S3 and S4. Oxygen was calculated by stoichiometry, assuming that all Fe was Fe³⁺. Matrix corrections of Armstrong-Love/Scott $\varphi(\rho z)$ [58] and Henke MACs were used for data reduction.

All elements were acquired using a traditional 2-point linear, excluding F K α which was acquired using a multipoint fit. Following traditional 2-point background analysis, the “shared” background fit option in Probe for EPMA was used across the list of elements. For Nb, a traditional 2-point linear fit was used. Other elements, including those with more complex regions of the spectrum such as in the case some of the REE, multipoint or “shared” fits were used to accurately model the background continuum and/or avoid off peak interferences [59–61].

Due to the need for a focused beam, beam damage and alkali element migration (e.g., Na, F, Cl) in zircon analyses were monitored and minimized via analysis of these elements first on the detector, plus application of the Time Dependent Intensity (TDI) correction feature of Probe for EPMA [62]. Using this method, the decay of x-ray counts over time is measured and modelled to return a $t=0$ intercept, and from this a concentration is calculated.

Zircon grains were both qualitatively and quantitatively X-ray mapped utilising the same instrument at the University of Adelaide. Beam conditions were set at an accelerating voltage of 15 kV and 200 nA, utilising a focussed beam. Mapped area dimensions ranged from 100-200 μm in both x and y axes, at a pixel resolution of 1 μm . Pixel dwell time in all maps was set to 2000 ms, and ranged in acquisition time from ~2-24 hours depending on grain size. Calibration and quantitative data reduction of maps was carried out in Probe for EPMA, distributed by Probe Software Inc. Colour images of the maps were processed in Surfer 10® distributed by Golden Software. Calibration was performed on certified natural and synthetic standards from Astimex Ltd.

Zircon grains were quantitatively mapped via measurement of Cl K α on four separate spectrometers (3 LPET and 1 PET crystal), and Fe K α measured on a single LLIF crystal.

Map quantification was conducted in CalcImage, a module of Probe for EPMA. Background subtraction on the maps was performed via the Mean Atomic Number (MAN) background correction [63,64], omitting the need for a second pass “off-peak” map acquisition. Following this each pixel goes through full $\varphi(\rho z)$ corrected quantification identical to traditional spot analysis. Major/minor elements were not acquired in the maps, and thus for accurate ZAF correction and quantification, specified concentrations as acquired from spot analysis were entered into the map quantification procedure for elements such as Zr, Si, Hf etc.

Table S3: EPMA setup for spot analysis of zircon.

Element and Line	Diffracting Crystal (Sp#)	Background type/fit	kV/nA/spot size(μm)	Peak Count Time	Bkgd Count Times		# bkgd points acquired (Lo/Hi)	Standards*		Overlapping element and order/interference correction standard			
					Lo	Hi		Primary Standard	Interference Standards	Interfering line	Int. std	Interfering line	Int. std
Zr Lα	LPET (1)	Shared	17/20/0	15	10	10	1/1	728					
Ca Kα	LPET (1)	Shared	17/20/0	20	20	20	1/1	535					
K Kα	LPET (1)	Shared	17/100/0	40	20	20	1/1	541					
P Kα	LPET (1)	Shared	17/100/0	40	20	20	1/1	504					
Y Lα	LPET (1)	Shared	17/100/0	120	60	60	1/1	1214					
U Mβ	LPET (1)	Shared	17/100/0	200	100	100	1/1	631					
Ce Lα	LPET (1)	Shared	17/100/0	100	50	50	1/1	1201					
Ti Kα	LPET (1)	Shared	17/100/0	100	50	50	1/1	540					
F Kα	PC0 (2)	Multipoint	17/20/0	20	10	10	2/2	505	502,723	Fe Lα (I)	502	Zr Lα1 (III)	723
Fe Kα	LLIF (3)	Shared	17/20/0	40	20	20	1/1	502					
Hf Lα	LLIF (3)	Shared	17/20/0	20	10	10	1/1	723					
Sc Kα	LLIF (3)	Shared	17/100/0	40	20	20	1/1	619					
Mn Kα	LLIF (3)	Shared	15/20/0	40	20	20	1/1	539					
Lu Lα	LLIF (3)	Shared	17/100/0	40	20	20	1/1	1213					
Yb Lα	LLIF (3)	Shared	17/100/0	40	20	20	1/1	1212					
Er Lα	LLIF (3)	Shared	17/100/0	40	20	20	3/2	1210					
Gd Lβ	LLIF (3)	Shared	17/100/0	40	20	20	1/1	1206					
Dy Lα	LLIF (3)	Shared	17/100/0	40	20	20	1/2	1208					
Tb Lα	LLIF (3)	Shared	17/100/0	40	20	20	1/1	1207					
Sm Lβ	LLIF (3)	Shared	17/100/0	40	20	20	1/1	1204					
Eu Lα	LLIF (3)	Shared	17/100/0	40	20	20	1/1	1205					
Nd Lβ	LLIF (3)	Shared	17/100/0	40	20	20	1/1	1203					
Pr Lβ	LLIF (3)	Shared	17/100/0	40	20	20	1/1	1202					
Tm Lα	LLIF (3)	Shared	17/100/0	40	20	20	1/2	1211					
Ho Lβ	LLIF (3)	Shared	17/100/0	40	20	20	1/1	1209					
Na Kα	TAP (4)	Shared	17/20/0	20	20	20	7/0	501					
Si Kα	TAP (4)	Shared	17/20/0	15	10	10	1/1	728					
Al Kα	TAP (4)	Shared	15/20/0	20	20	20	1/1	501					
Mg Kα	TAP (4)	Shared	15/20/0	30	20	20	1/1	502					
Cl Kα	LPET (5)	Shared	17/20/0	60	30	30	1/1	545					
La Lα	LPET (5)	Shared	17/100/0	100	50	50	1/1	1200					
Th Mα	LPET (5)	Shared	17/100/0	150	75	75	1/1	629					
Pb Mβ	LPET (5)	Shared	17/100/0	200	100	100	3/1	627					
Nb Lα	LPET (5)	2-pt	17/100/0	100	50	50	1/1	616	723	Zr Lβ4 (I)	723		

* Standard # refers to internal database. Full list of standards in Table S4

Table S4: Details of EPMA standards used

Reference #	Mineral composition	Natural/Synthetic	Manufacturer
501	Albite	Natural	Astimex
502	Almandine garnet	Natural	Astimex
504	Apatite	Natural	Astimex
535	Plagioclase	Natural	Astimex
539	Rhodonite	Natural	Astimex
540	Rutile	Natural	Astimex
541	Sanidine	Natural	Astimex
545	Tugtupite	Natural	Astimex
616	Niobium	Synthetic	Astimex
619	Scandium	Natural	P&H and Associates
627	K227 (Pb silicate)	Synthetic	NIST
629	Huttonite	Natural	DAS
631	UO ₂	Synthetic	DAS
723	Zircon	Natural	GJ Zircon standard
728	Zircon	Natural	91500 zircon standard
1200	LaPO ₄	Synthetic	Cherniak phosphate
1201	CePO ₄	Synthetic	Cherniak phosphate
1202	PrPO ₄	Synthetic	Cherniak phosphate
1203	NdPO ₄	Synthetic	Cherniak phosphate
1204	SmPO ₄	Synthetic	Cherniak phosphate
1205	EuPO ₄	Synthetic	Cherniak phosphate
1206	GdPO ₄	Synthetic	Cherniak phosphate
1207	TbPO ₄	Synthetic	Cherniak phosphate
1208	DyPO ₄	Synthetic	Cherniak phosphate
1209	HoPO ₄	Synthetic	Cherniak phosphate
1210	ErPO ₄	Synthetic	Cherniak phosphate
1211	TmPO ₄	Synthetic	Cherniak phosphate
1212	YbPO ₄	Synthetic	Cherniak phosphate
1213	LuPO ₄	Synthetic	Cherniak phosphate
1214	YPO ₄	Synthetic	Cherniak phosphate

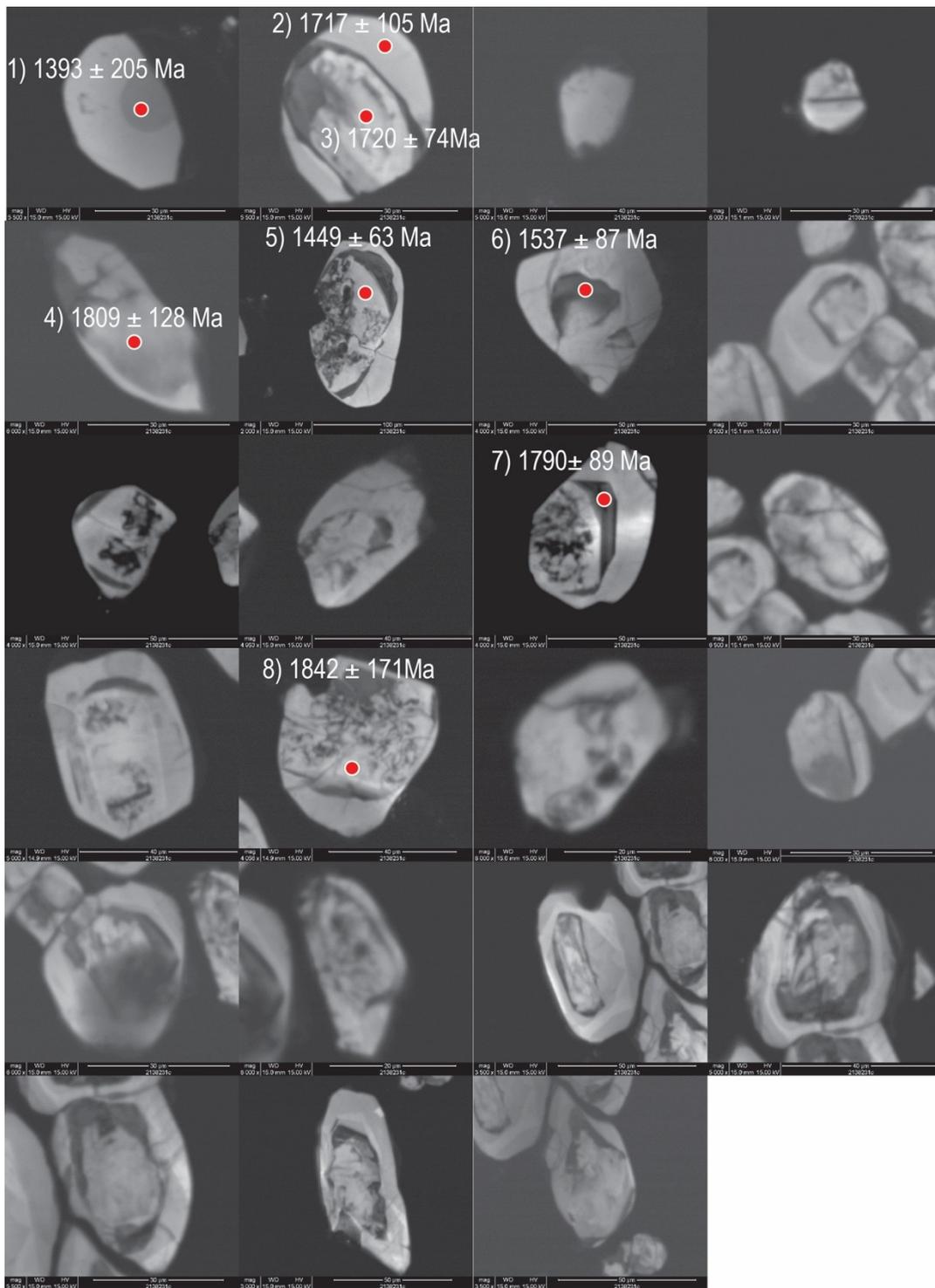


Figure S1: Cathodoluminescence (CL) images of the various textures of zircon from within the PK1 sample with the respective $^{206}\text{Pb}/^{238}\text{U}$ ages ($\pm 1\sigma$) of analyzed grains.