

Zircon U-Pb CA-ID-TIMS analysis

Following standard zircon separation by density and magnetic susceptibility, individual zircon grains were rinsed in 3 ml teflon beakers with distilled acetone and MQ H₂O. Single crystals were loaded into 200 µl Savillex microcapsules with 100 µl 29 M HF + 15 µl 3 N HNO₃ for a single leaching step in high-pressure Parr bombs at 195 °C for 12 h to remove crystal domains affected by Pb loss (Mattinson 2005; Mundil et al. 2004). Grains were rinsed post-leaching with 6 N HCl, MQ H₂O, and 3 N HNO₃ prior to spiking with the EARTHTIME (²⁰²Pb-²⁰⁵Pb-²³³U-²³⁵U) tracer and addition of 100 µl 29 M HF + 15 µl 3 N HNO₃. In particular, the ²⁰²Pb-containing “double spike” was used only in samples analyzed at the University of Geneva (denoted with postscript “_G” in Fig. 2 and data tables).

Zircons were then dissolved to completion in Parr bombs at 210 °C for 48 h. Dissolved zircon solutions were subsequently dried down, redissolved in 100 µl 6 N HCl and converted to chlorides in Parr bombs at 195 °C for 12 h, after which solutions were dried again and brought up in 50 µl 3 N HCl. The U-Pb and trace element aliquots were then separated by anion exchange column chromatography using 50 µl columns and AG-1 X8 resin (200-400 mesh, chloride form from Eichrom) (Krogh 1973) and dried down with a microdrop of 0.05 M H₃PO₄. The dried U and Pb aliquot was loaded in a silica gel emitter (Gerstenberger & Haase 1997) to an outgassed, zone-refined Re filament. Isotopic determinations were performed using an IsotopX Phoenix-62 TIMS at PU and a Thermo-Finigan Triton TIMS at Geneva, with Pb analyses performed in peak-hopping mode on a Daly-photomultiplier ion counting detector for the Phoenix and on a modified Masscom secondary electron multiplier (SEM) for the Triton. A correction for mass-dependent Pb fractionation was applied cycle-by-cycle, calculated from the deviation of measured ²⁰²Pb/²⁰⁵Pb from the known tracer ²⁰²Pb/²⁰⁵Pb (0.99924 ± 0.00054 (2σ)). A Daly-photomultiplier Pb dead time of 40.5 ns was used at PU, as determined by >100 measurements of NBS981 and NBS982 standards and using a least squares fit to measured data over the range of 100 kcps to 2.5 Mcps ²⁰⁸Pb; an SEM deadtime of 23.5 ns was determined at Geneva by similar procedures.

Isobaric interferences under masses 202, 204, and 205 were monitored by measuring masses ²⁰¹BaPO₄ and ²⁰³Tl which can be correlated using natural isotopic abundances to ²⁰²BaPO₄, ²⁰⁴BaPO₄, ²⁰⁵BaPO₄, and ²⁰⁵Tl, as well as by measuring masses 202 and 205 in unspiked samples. These interferences were not found to be a significant source of error and no interference correction was performed. Typical ion yields for ²⁰⁵Pb were 100-200 kcps for ~20 pg ²⁰⁵Pb, sustainable for 3-4 hours of analysis (160-220 ratios collected) and typical ²⁰⁶Pb/²⁰⁵Pb ratios were 0.1-3.0.

Uranium measurements (as UO_2^+) at both PU and Geneva were performed in static mode on Faraday cups with 10^{12} ohm resistors using an oxide composition of $^{18}\text{O}/^{16}\text{O}$ of 0.00205 (Nier 1950; Wasserburg et al. 1981). Mass fractionation of U was determined cycle-by-cycle, calculated from the deviation of measured $^{233}\text{U}/^{235}\text{U}$ from the known tracer $^{233}\text{U}/^{235}\text{U}$ (0.995062 ± 0.000108 (2σ)) and assuming a $^{238}\text{U}/^{235}\text{U}$ of 187.818 ± 0.045 (2σ) for sample U (Hiess et al. 2012). Typical U ion beams on 10^{12} ohm resistors at PU were 500-1000 mV of ^{233}U for ~ 1 ng ^{233}U at PU, resulting in measurement precision of 0.004-0.02% (2 SE) for $^{270}\text{U}/^{265}\text{U}$.

Data reduction was performed using the programs Tripoli and U-Pb_Redux (McLean & Bowring 2011; Bowring & McLean 2011) and the U decay constants of Jaffey et al. (1971). All Pb_c was attributed to laboratory blank with a mean isotopic composition determined by total procedural blank measurements, carried out separately for each analyst. Fractionation correction and tracer blank subtraction were conducted during data reduction using the ET2535 v3.0 tracer composition for double-spiked samples and ET535 v3.0 for single-spiked samples, defined as follows:

Composition	ET2535 v3.0		ET535 v3.0	
	Value	$\pm 1s$ (abs)	Value	$\pm 1s$ (abs)
$^{202}\text{Pb}/^{205}\text{Pb}$	0.99924	0.00027	N/A	N/A
$^{204}\text{Pb}/^{205}\text{Pb}$	0.000105	0.000009	0.00009	0.000009
$^{206}\text{Pb}/^{205}\text{Pb}$	0.00048	0.00017	0.00038874	0.00016886
$^{207}\text{Pb}/^{205}\text{Pb}$	0.00043	0.00014	0.00029607	0.00014014
$^{208}\text{Pb}/^{205}\text{Pb}$	0.00104	0.00033	0.00074438	0.00034704
$^{233}\text{U}/^{235}\text{U}$	0.995062	0.000054	0.99506218	0.00005384
$^{238}\text{U}/^{235}\text{U}$	0.00307993	4.00E-07	0.00307993	3.9555E-07
$[\text{}^{205}\text{Pb}]$ (mol/g)	1.03E-11	2.60E-14	1.03E-11	2.58E-14
$[\text{}^{235}\text{U}]$ (mol/g)	1.03E-09	2.60E-12	1.03E-09	2.60E-12

The effects of initial daughter product disequilibrium were corrected using the methods of McLean & Bowring (2011), using measured Turkey Creek magma Th/U ratios from du Bray and Pallister (1991). Uncertainties in reported U-Pb zircon dates are

reported at 2-sigma (the 95% confidence interval) and exclude uncertainties in tracer calibration and decay constants unless otherwise noted.

In addition to semi-weekly measurements of Pb standards NBS981 and 982 to monitor Pb fractionation and ion counter deadtime, laboratory reproducibility and inter-laboratory bias were assessed using the natural zircon standard AUS-Z2 (Kennedy et al. 2014). Data from PU measured at the time of this study are presented in (Schoene et al. 2015) and yield a statistically significant cluster in concordia space with a weighted-mean $^{206}\text{Pb}/^{238}\text{U}$ CA-ID-TIMS age of $38.905 \pm 0.013/0.017/0.045$ Ma (MSWD = 1.0, $n = 9/10$; 2σ uncertainties stated as internal/+tracer calibration/+decay constant). These values are in good agreement with the published age of $38.8963 \pm 0.0044/0.012/0.043$ Ma (MSWD = 1.0, $n = 12/12$) from Geneva (Kennedy et al. 2014). As seen in Figure 2, Turkey Creek samples analyzed at Princeton University and the University of Geneva agree well, with no obvious systematic bias.

Zircon trace element geochemistry

The trace element compositions of the same zircon fragments dated by ID-TIMS were characterized following the analytical protocol of Schoene et al. (2010) at PU. Trace element washes isolated during U-Pb column chemistry were dried down in pre-cleaned 2.0 ml polypropylene vials (CETAC #SP5540) and redissolved in 1.0 ml 1.5 M HF + 0.1 M HNO₃ + 1 ppb Ir. Measurements were performed on a Thermo Fisher ELEMENT2 sector field-inductively coupled plasma-mass spectrometer (SF-ICP-MS) with a sample introduction system consisting of a CETAC Aridus II desolvating nebulizer + ASX-100 autosampler, with an uptake rate of 100 $\mu\text{l}/\text{min}$. Measured elements included Zr, Hf, Y, Nb, Ta, REEs, Pb, U, Th and Ir, with iridium monitored as an internal standard during mass spectrometry. The instrument was tuned in low resolution mode with an optimal signal intensity of 0.5–2 Mcps on the peak height (not the integrated signal) for 1 ppb Ir.

A matrix-matched, gravimetric external calibration solution was prepared with the relative abundance of targeted elements representing that observed in natural zircon (e.g., $\text{Zr}/\text{Hf} = 50$). A dilution series was generated using this solution to cover the range of concentrations observed in unknowns (e.g., $[\text{Zr}] = 10^1\text{--}10^4$ ppb solution), which was then used to generate a concentration-intensity calibration curve for each trace element at the beginning of the analytical session. Samples and interspersed instrumental and total procedural blanks were analyzed in sets of 24 over ~ 3 h, with a line wash time of 120 s and uptake time of 90 s. Following data acquisition, solution concentrations were converted to stoichiometric concentrations in zircon by normalizing solution concentration data assuming all trace elements partition into the Zr^{4+} site in ZrSiO_4 , where $\Sigma \text{Zr} + \text{Hf} + \dots + \text{Th} = 497,646$ ppm. Since the elements that partition into the Zr^{4+} site are well-known, this normalization provides an more accurate estimate of trace element con-

centration in zircon than would be obtained using the ratio of zircon mass to column wash solution volume, which is difficult to accurately measure.

Trace element uncertainties are reported at the 95% confidence level and include subtraction of the mean and standard deviation of blank measurements. Uncertainties in ratios were calculated using standard uncertainty propagation techniques, assuming uncorrelated uncertainties in measured elemental abundances. Trace element data from eight analyses of the AUS-Z2 zircon standard measured using the same techniques (including chemical abrasion and column chemistry) are presented in Schoene et al. (2015). These single-zircon analyses show good reproducibility as well as concentrations of Zr, Hf, and the REE that agree with published laser ablation ICPMS data (Kennedy et al. 2014) well within the range of total external 2-sigma uncertainty.

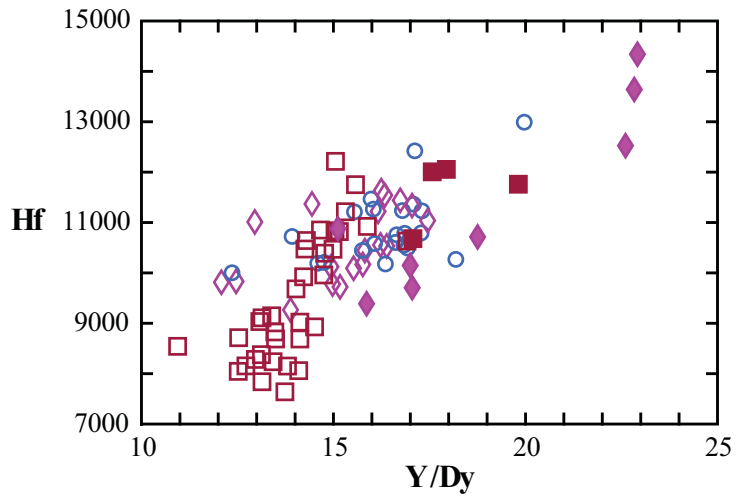
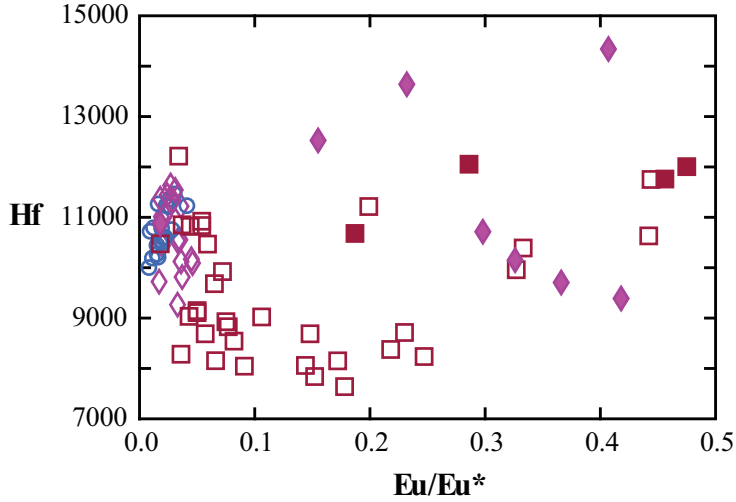
Table DR1 - Turkey Creek U-Pb isotopic data

Table DR2-Revised-TEA data

Methods References

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Supplementary Figure.

Filled symbols represent zircons from the Rhyolite Canyon Tuff considered xenocrystic because they are compositionally distinct. These grains also have a range in ages that overlap with pre-Turkey Creek caldera rocks (shown below) that are from geographically local lithologies. Open symbols that are compositionally similar to the ‘xenocrystic’ zircons did not yield usable dates (e.g. Pb loss) and are, therefore, not included in the discussion. Symbols are the same as Figure 3.

Pre-Turkey Creek Caldera rocks (⁴⁰Ar/³⁹Ar)

Halfmoon Valley granodiorite	74.6±0.06 Ma
High Lonesome Canyon rhyolite tuff	34.16±0.17 Ma
Joe Glenn Ranch rhyolite	33.81±0.08 Ma
Rucker Canyon rhyolite lava	33.32±0.07 Ma
Rucker Canyon pyroclastic rocks	33.21±0.09 Ma
Mackey Canyon granodiorite	30.62±0.15 Ma

Xenocrystic zircon Rhyolite Canyon tuff ages (CA-TIMS)

Single zircon from intracaldera unit	85.16 Ma
Range of most zircons	30.78 to 34.2 Ma

Zircon cathodoluminescence images

Samples

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TC-DPI-060813-4

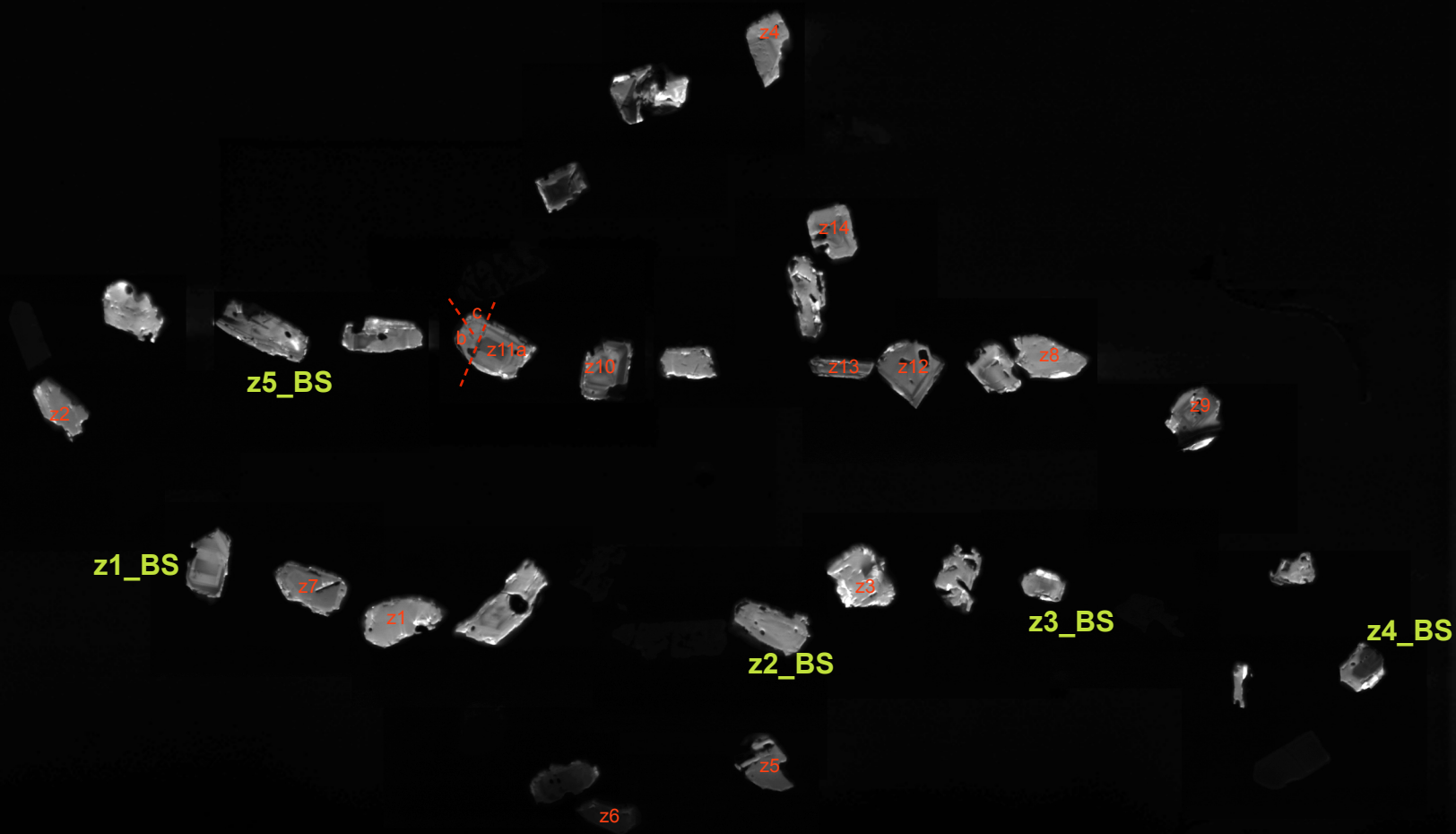
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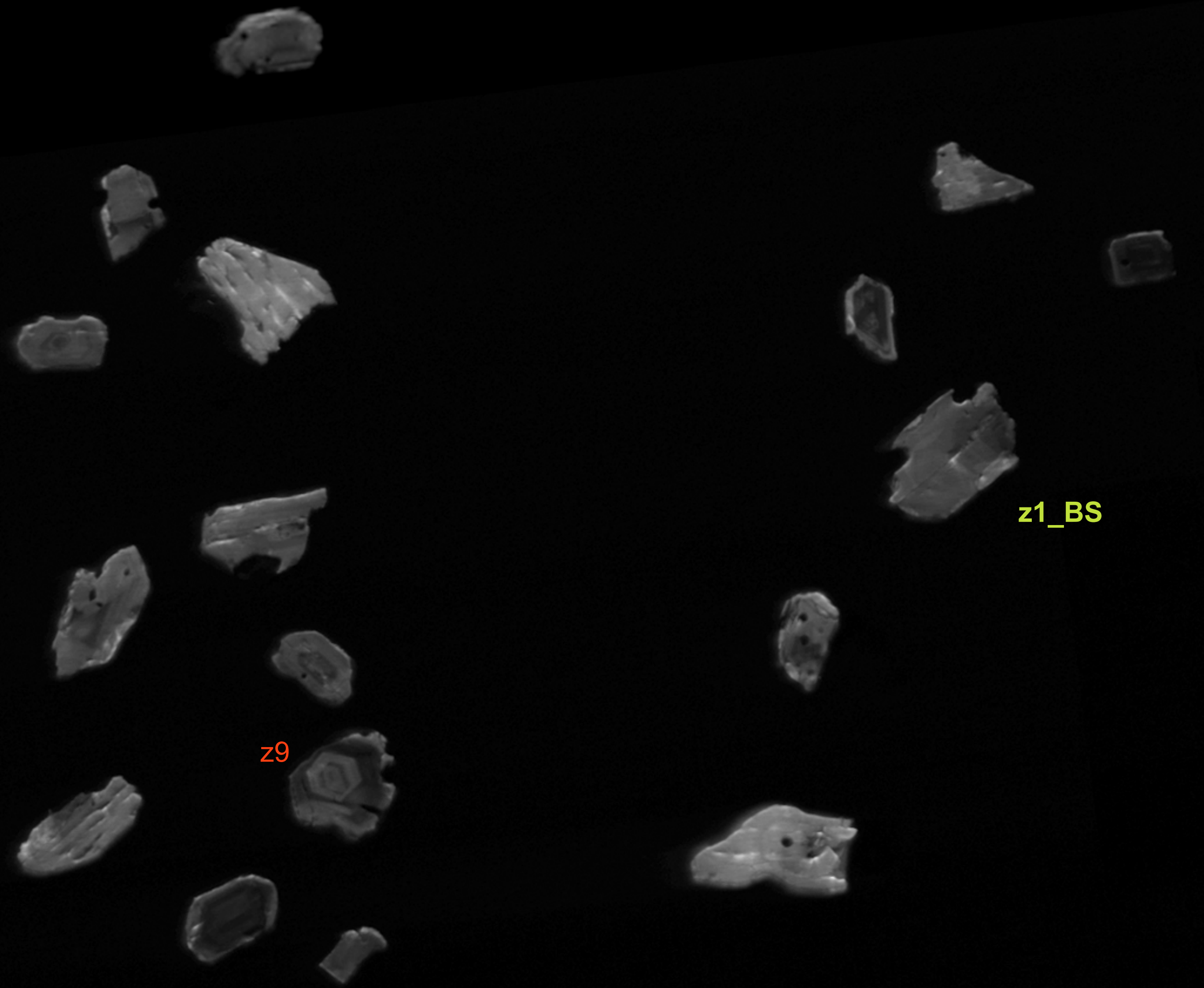
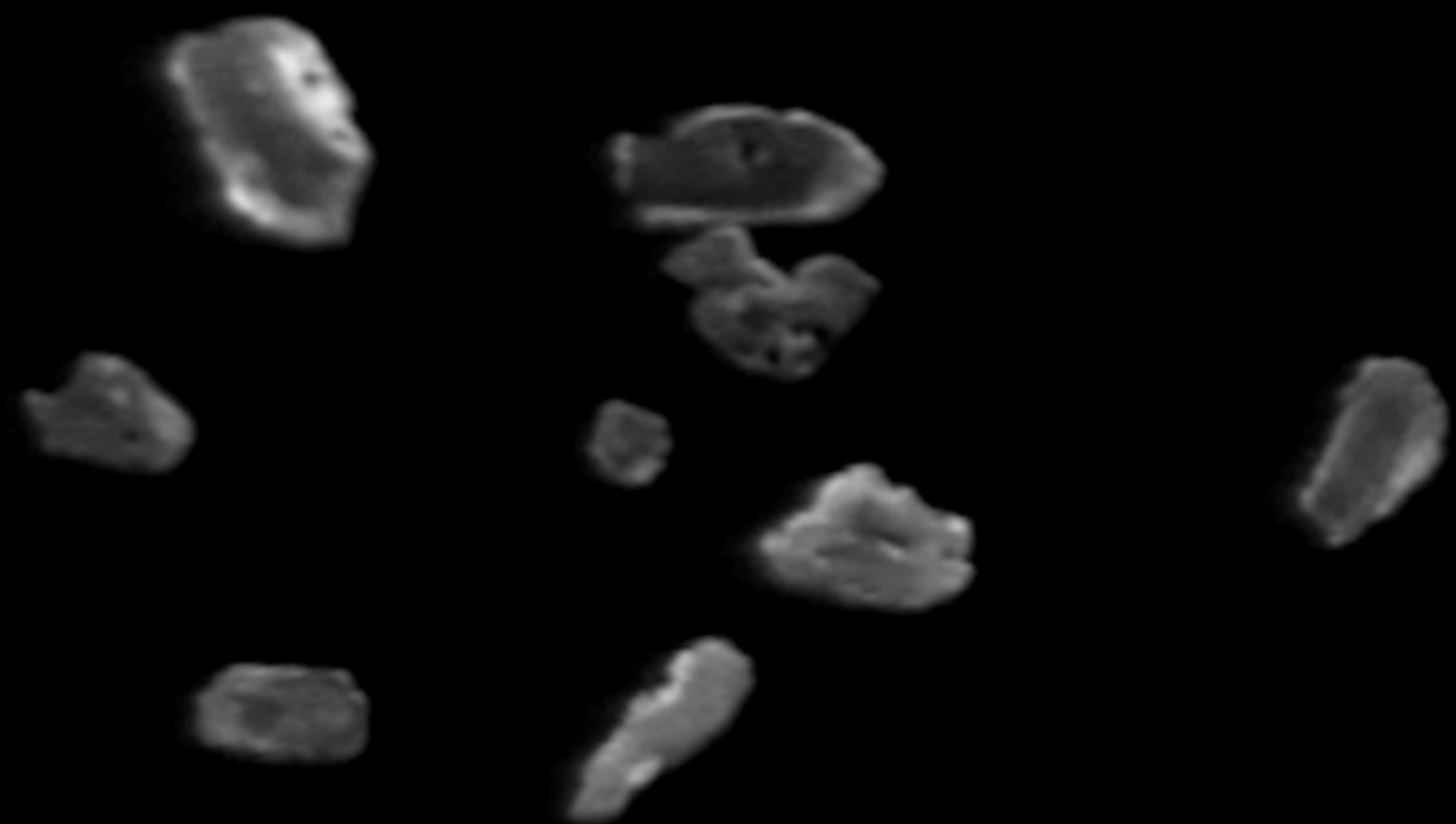
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Note: Two samples were analyzed in Geneva and do not have cathodoluminescence images.



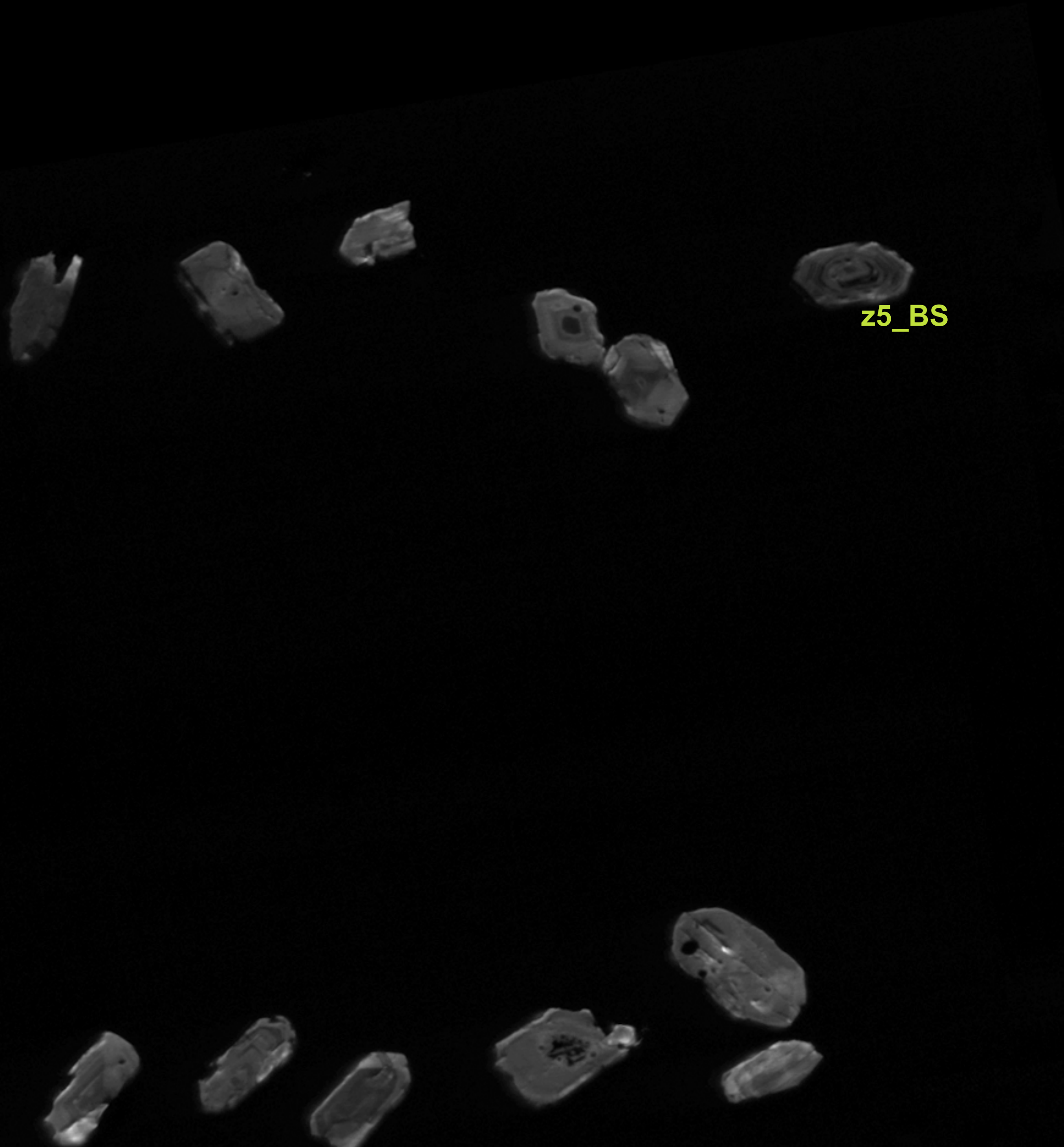
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z1_BS

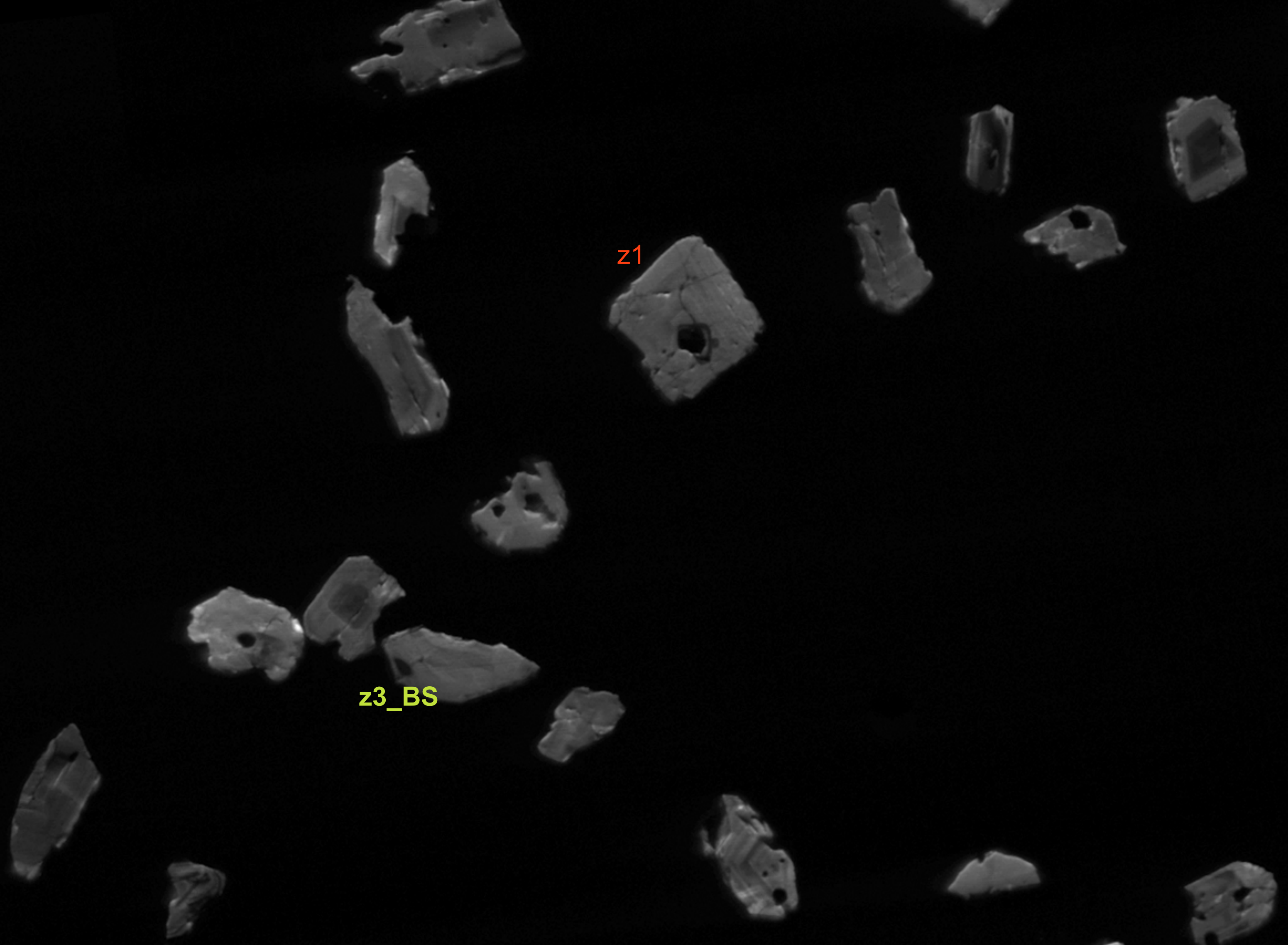
z9



z5_BS



z8



z1

z3_BS

z2

z3

z4

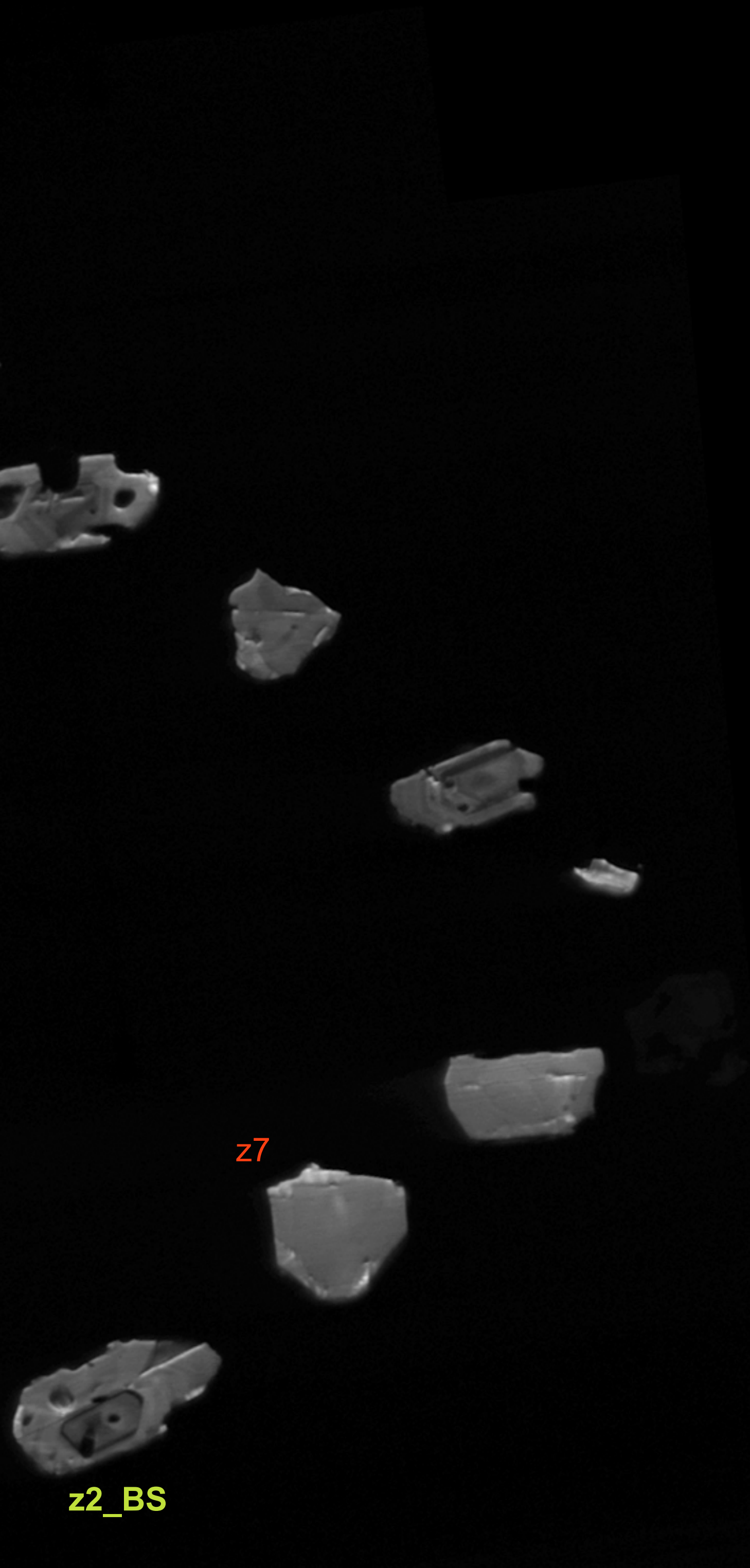
z4_BS

z5

z6

z7

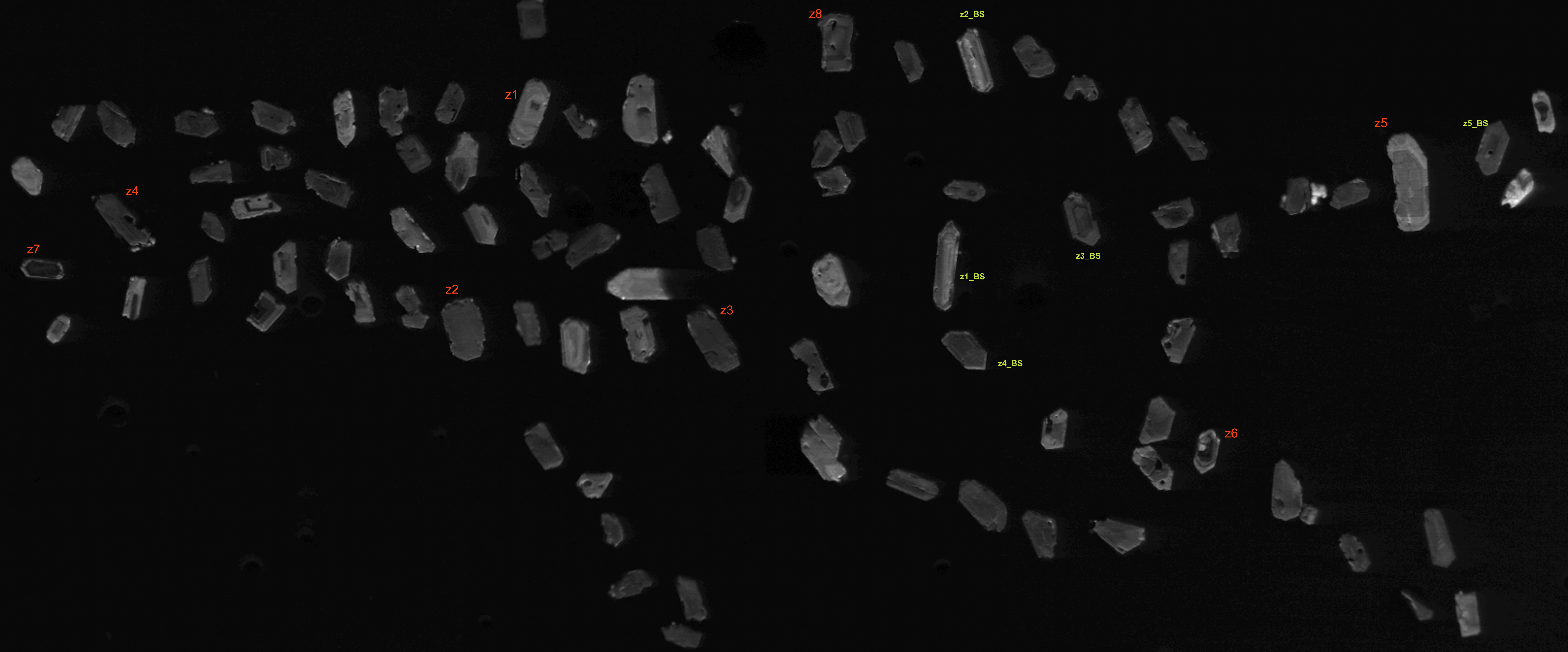
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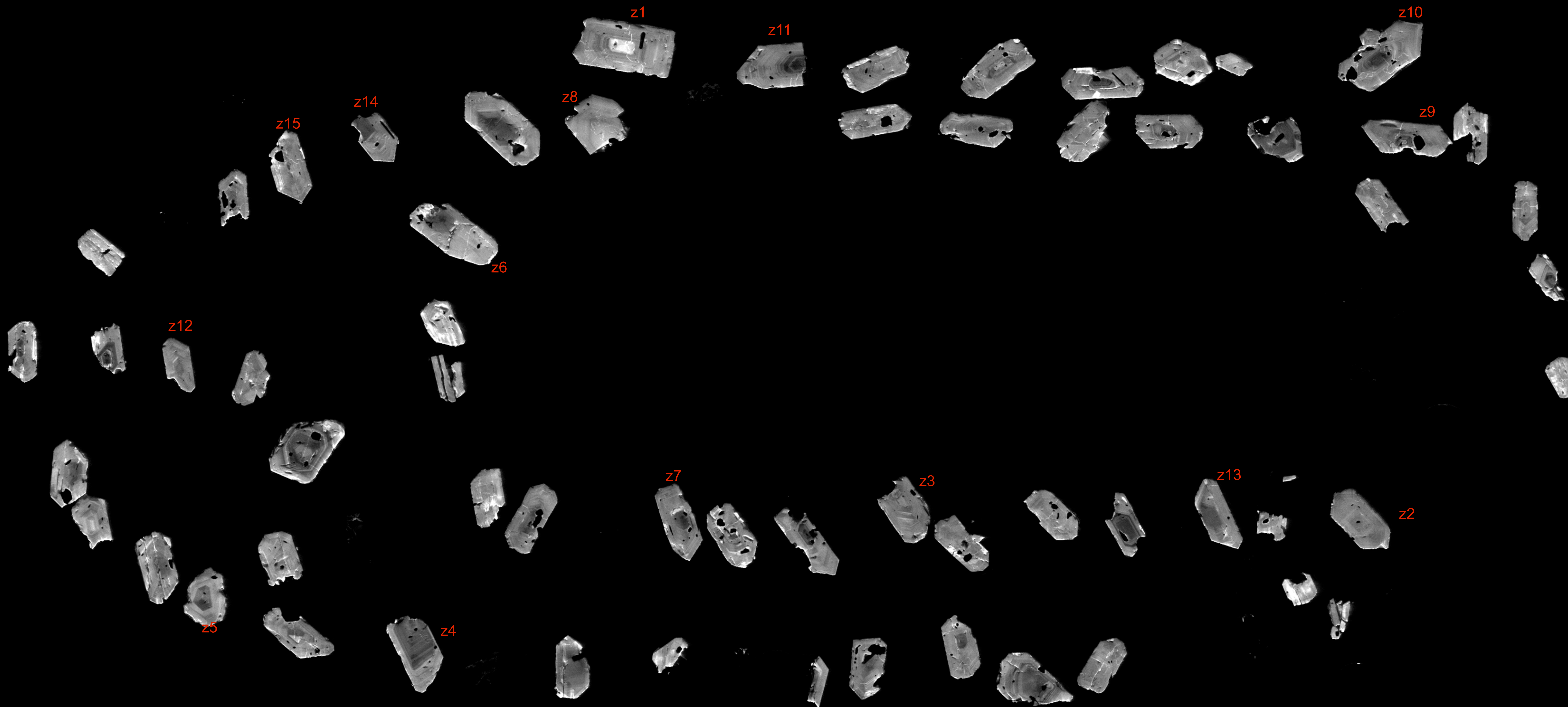


TC-0601113-1A

400 μ







TC-RCM-060913-8b