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LLNL-TR-678713

Testing for Uranium Deuteride Initiation in Liquid Deuterium

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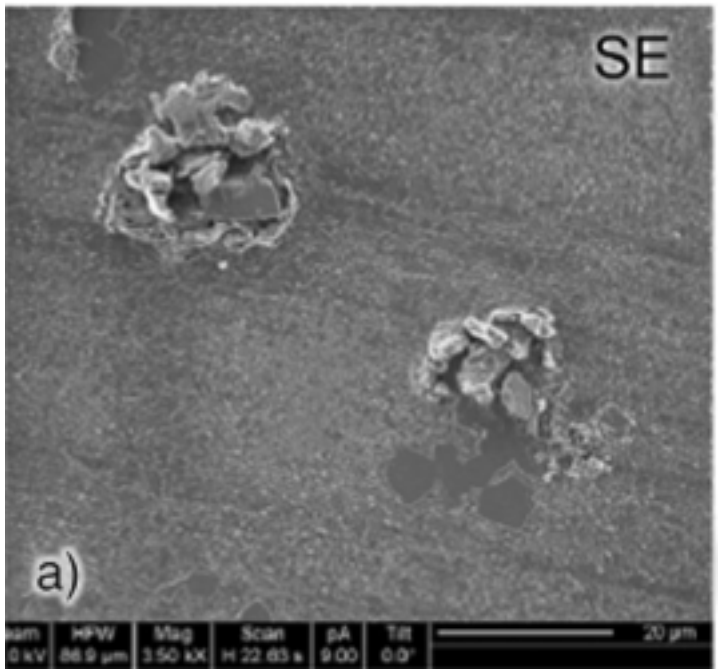
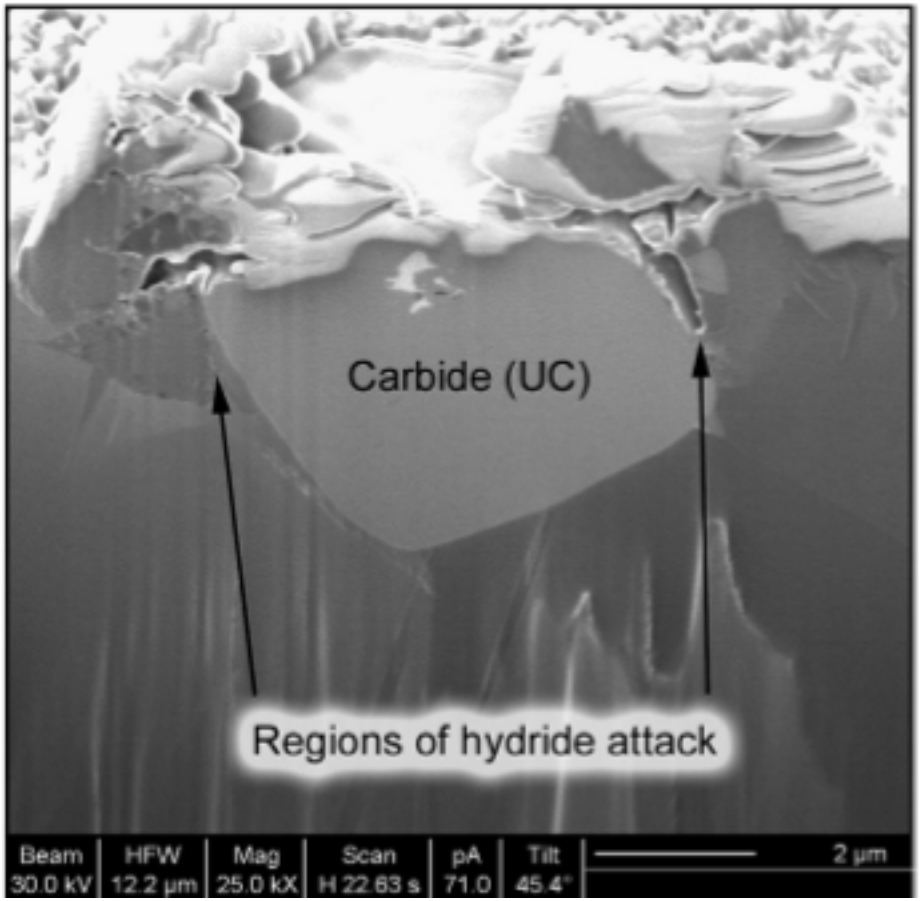
Uranium Hydriding, Introduction

- Uranium hydriding occurs 'almost exclusively at carbide inclusions'[1]





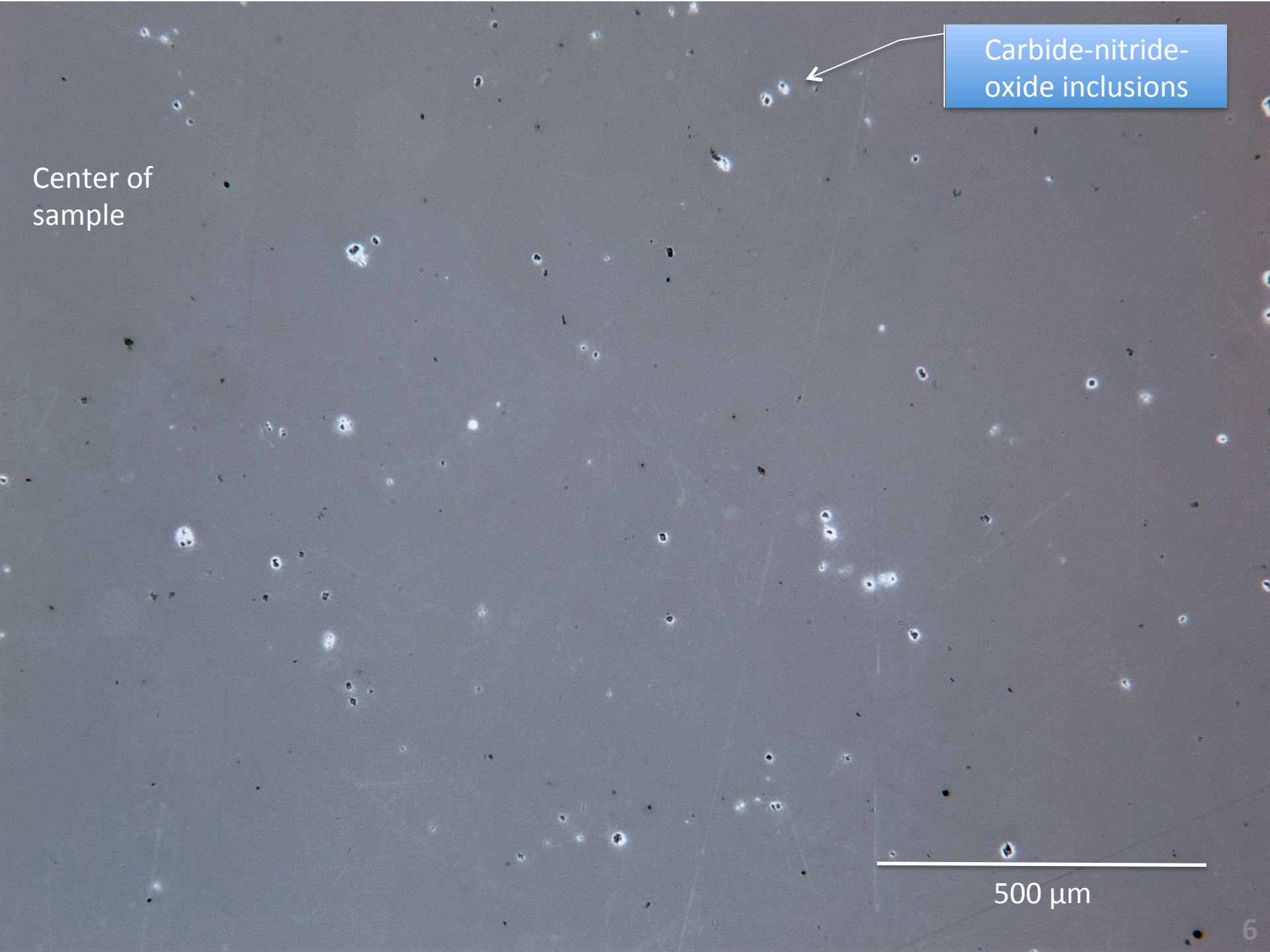
- Hence our analysis focused on carbide inclusions

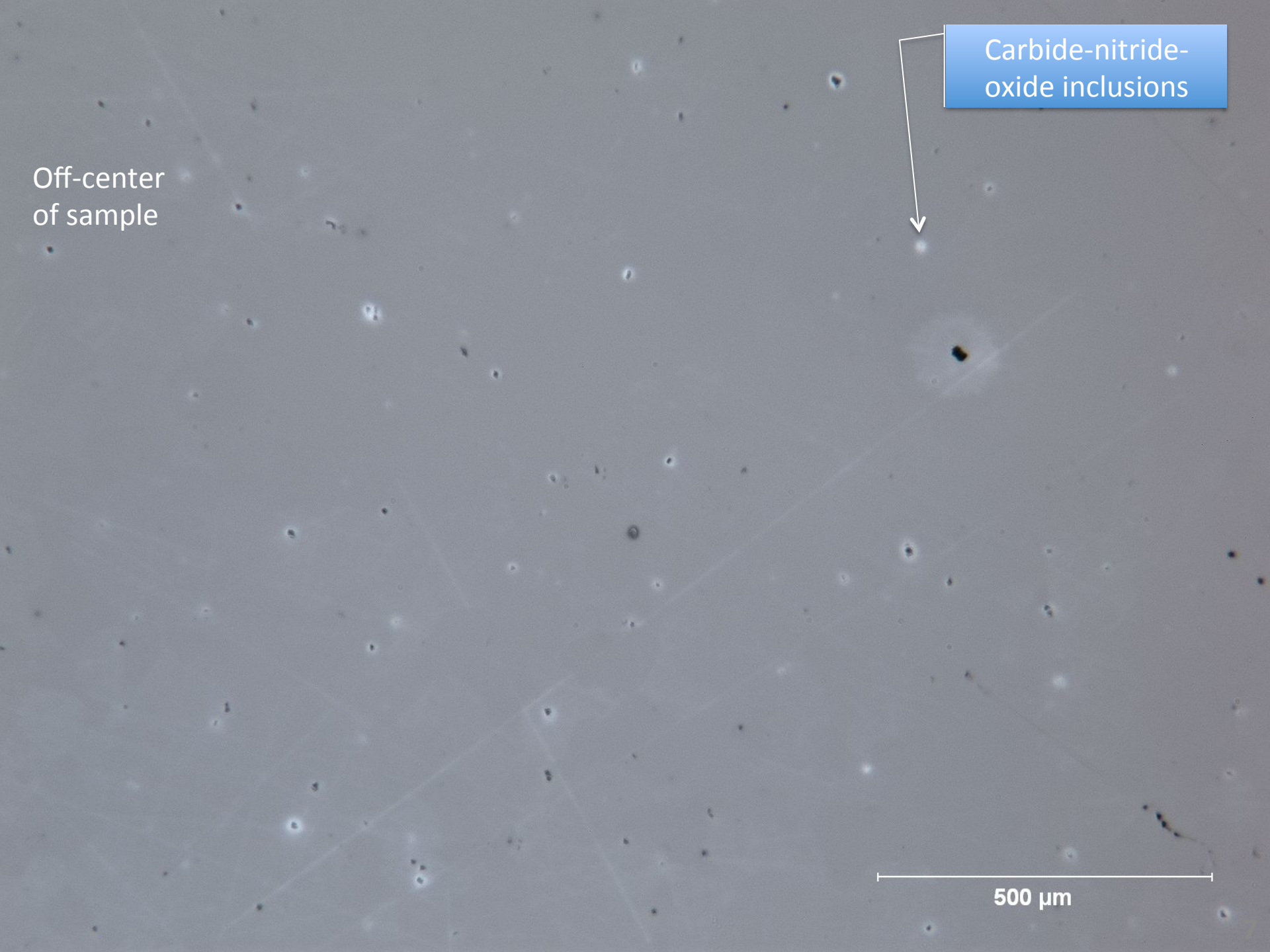
[1] N.J. Harker, T.B. Scott, C.P. Jones, J.R. Petherbridge, J. Glascott, Altering the hydriding behaviour of uranium metal by induced oxide penetration around carbo-nitride inclusions, Solid State Ionics, 241 (2013) 46-52.

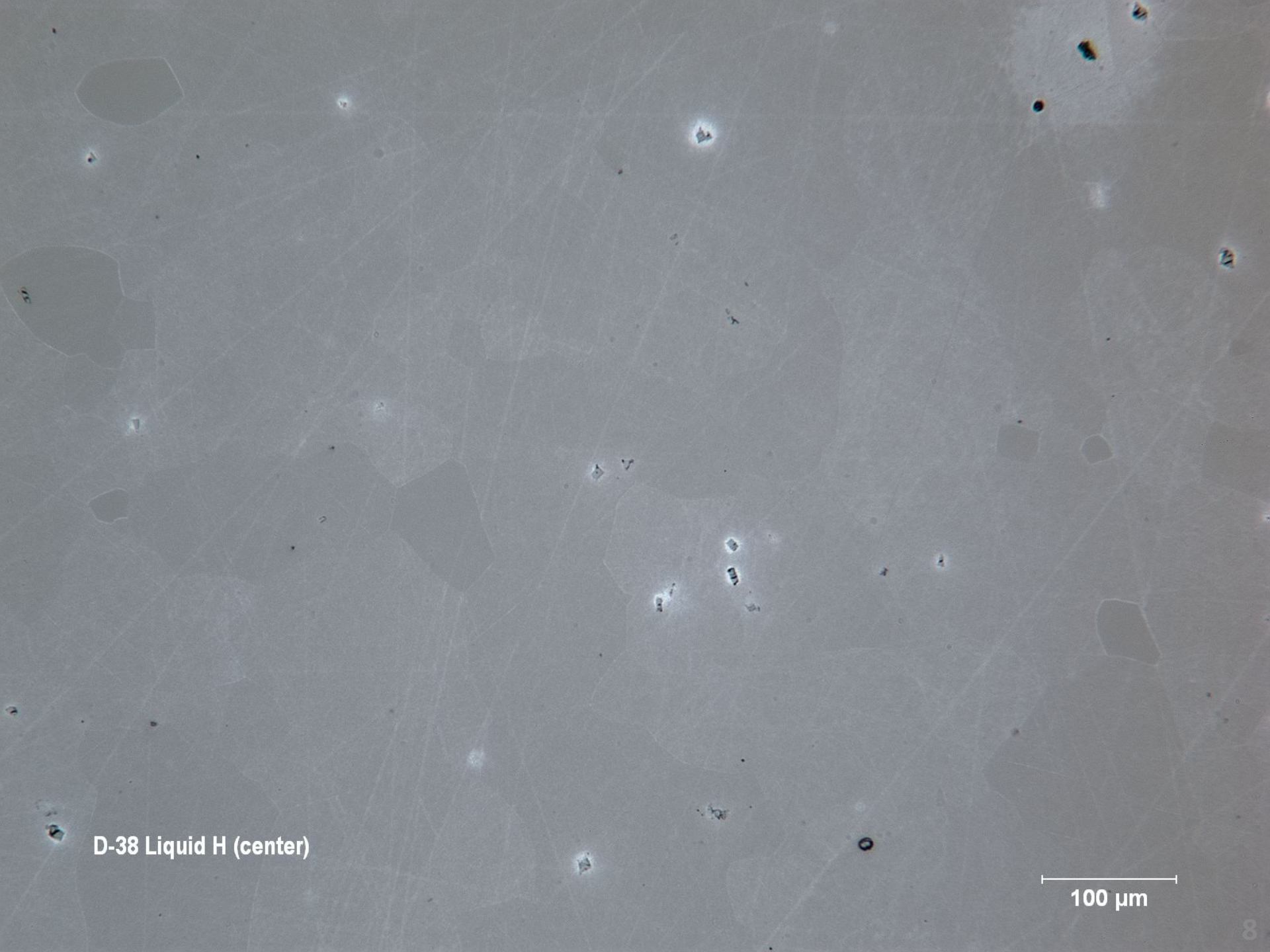
Summary

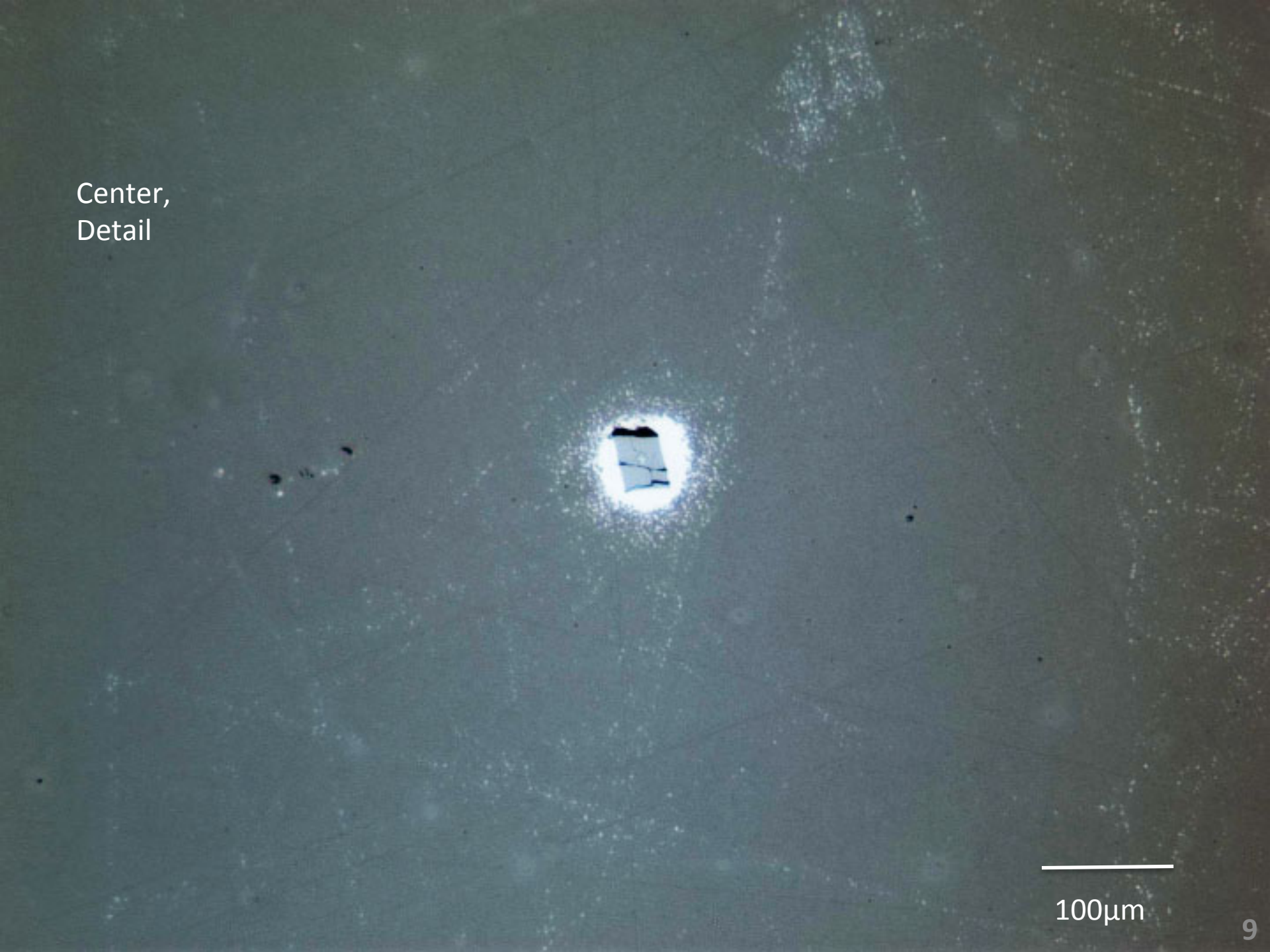
- Uranium foil (‘rolled’ at Y12, circular diameter ~0.625 inch, ~ 2 mm thick,)
  - was polished to a mirror finish on one side, while the other side was left with a thick oxide layer
    - Imaged optically and by SEM (on the polished side, with particular focus on carbo-nitride-oxide inclusions, where hydride initiation in known to preferentially occur)
  - exposed to liquid deuterium at ~ 24 K for approximately 6 days
    - Imaged again by SEM, mostly at the SAME inclusions
- NO hydride initiation was detectable by high resolution SEM
- Consistent with extrapolating Wicke&Otto’s results at ≥ 170°K to 25 °K

Optical Images of the uranium sample before exposure to deuterium

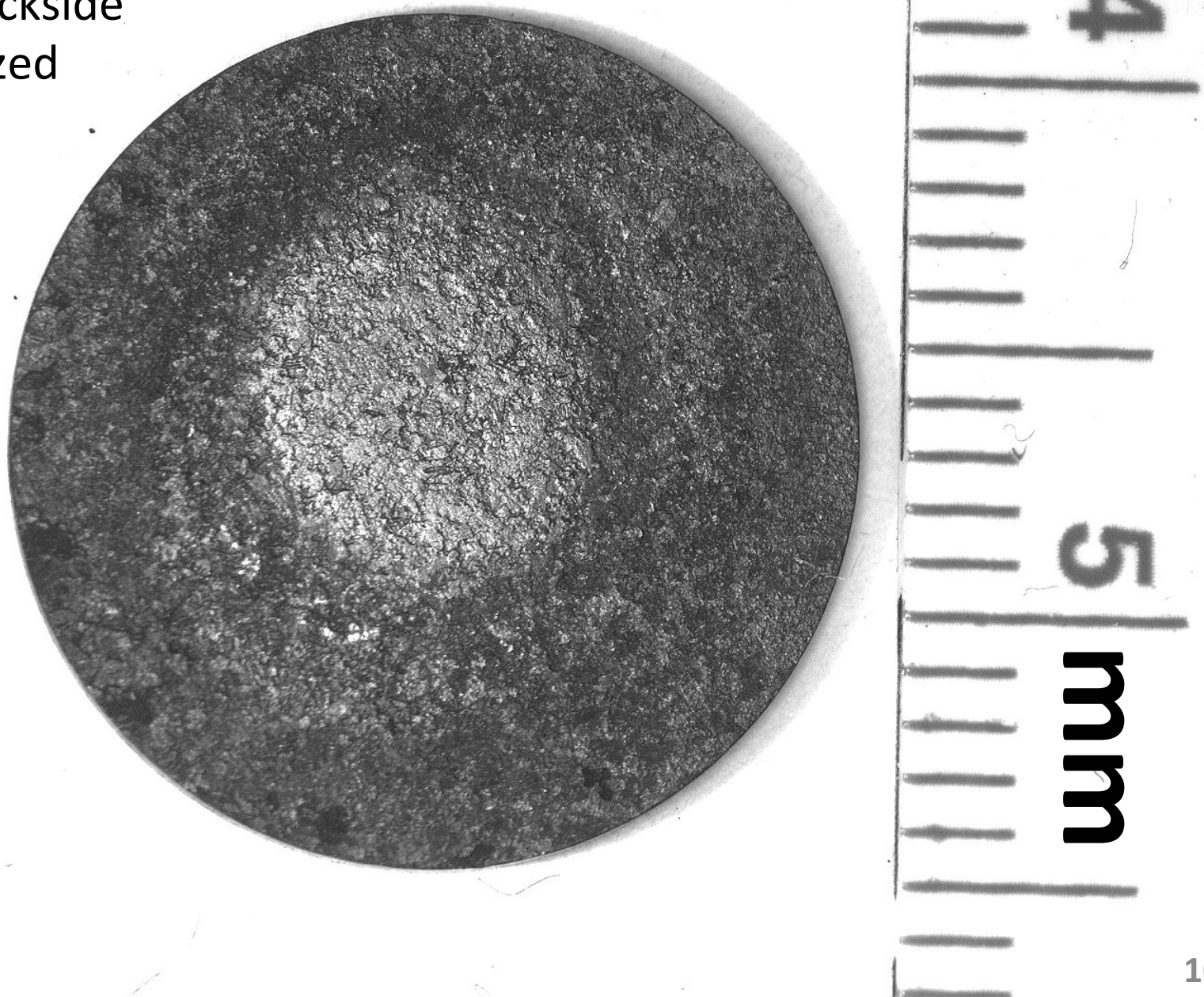

Carbide-nitride-oxide inclusions
Center of sample
500 µm


Carbide-nitride-oxide inclusions
Off-center of sample
500 µm


D-38 Liquid H (center)
100 µm


Center,
Detail
100µm

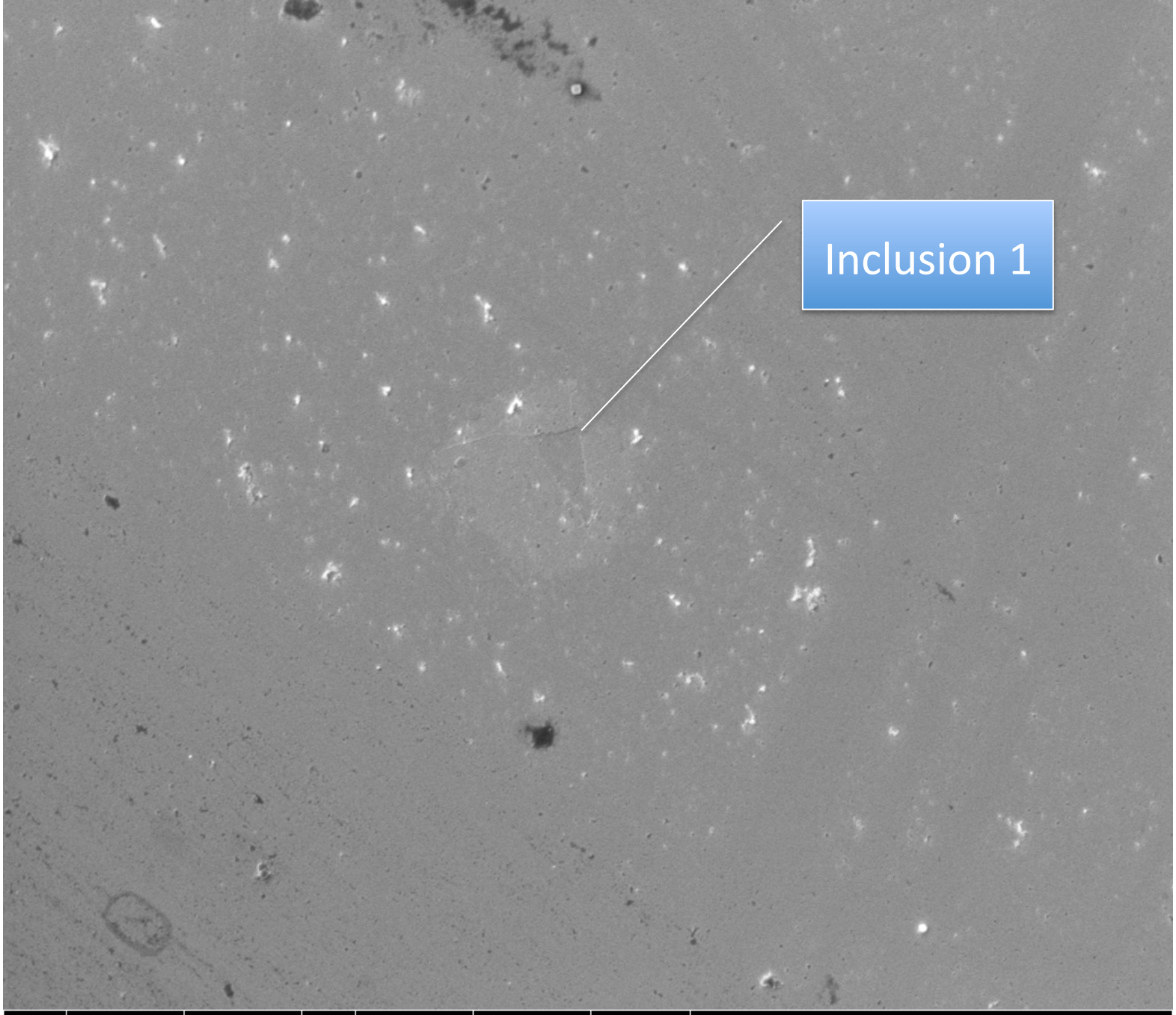
Sample's Backside
Highly oxidized

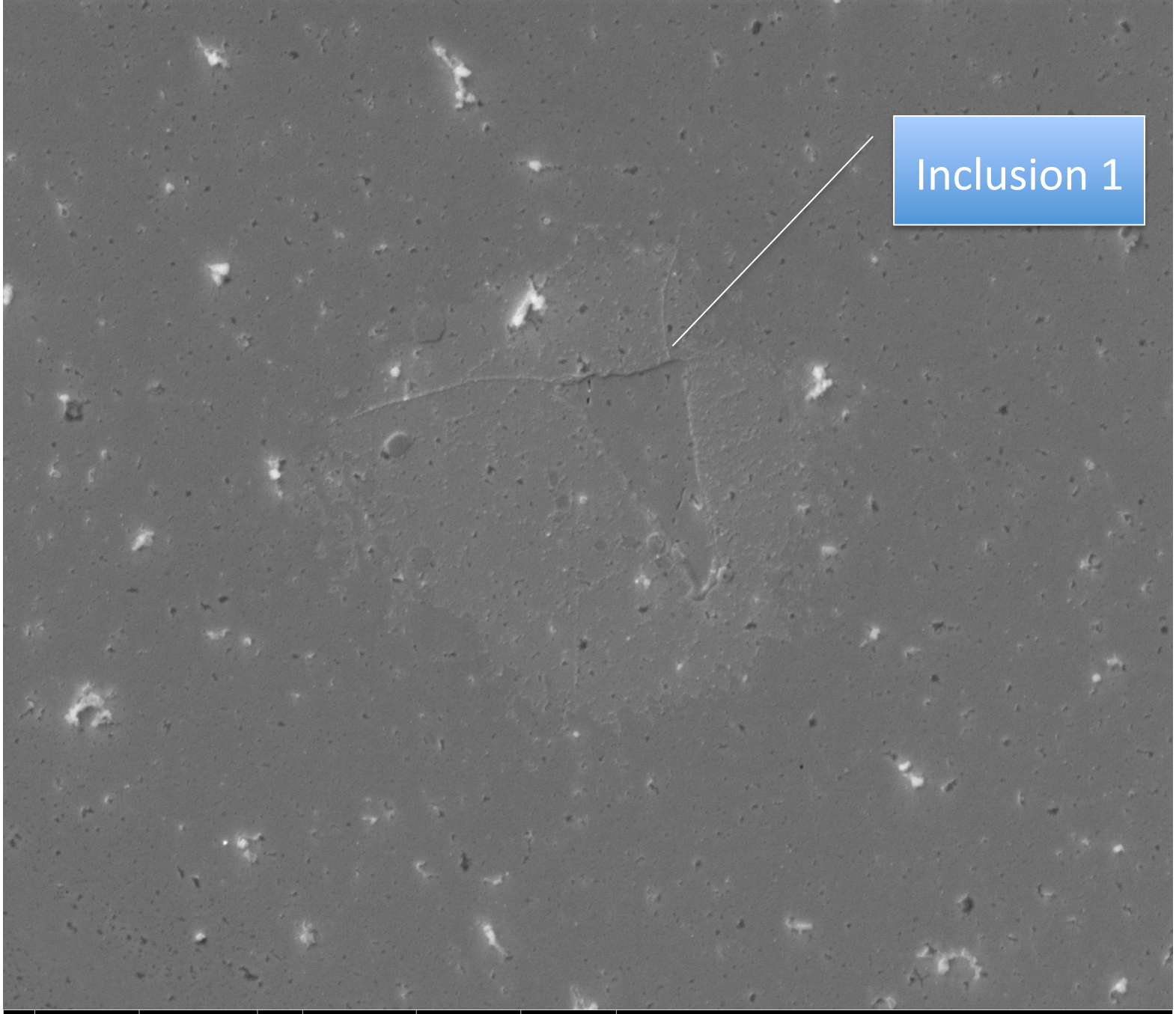


D-38

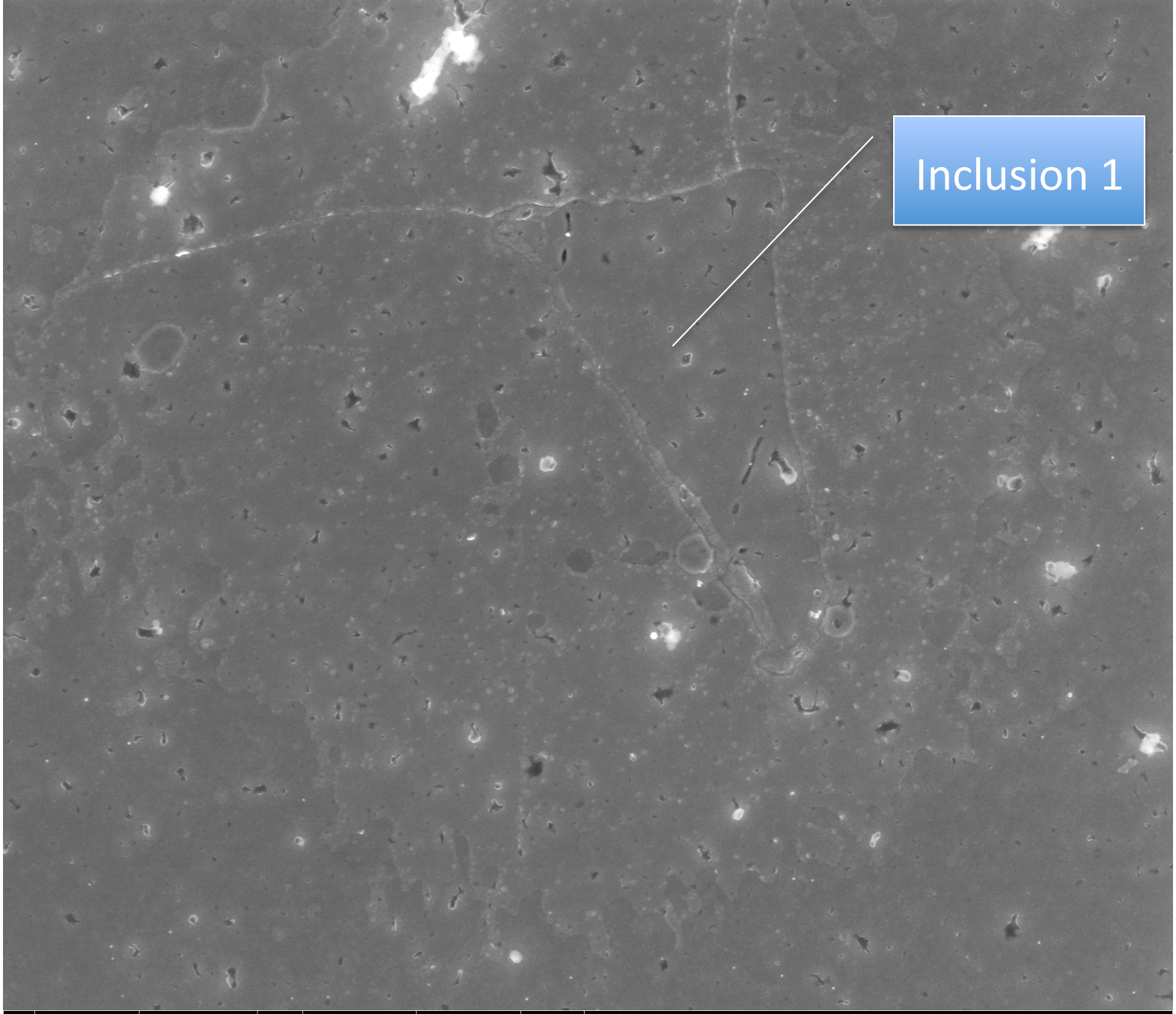
SEM images before exposure to liquid deuterium

- U-hydriding occurs preferentially at inclusions
- Therefore, a number of inclusions were imaged
  - Their location-coordinates were noted,
  - So that the SAME sites could be looked at AFTER EXPOSURE to deuterium

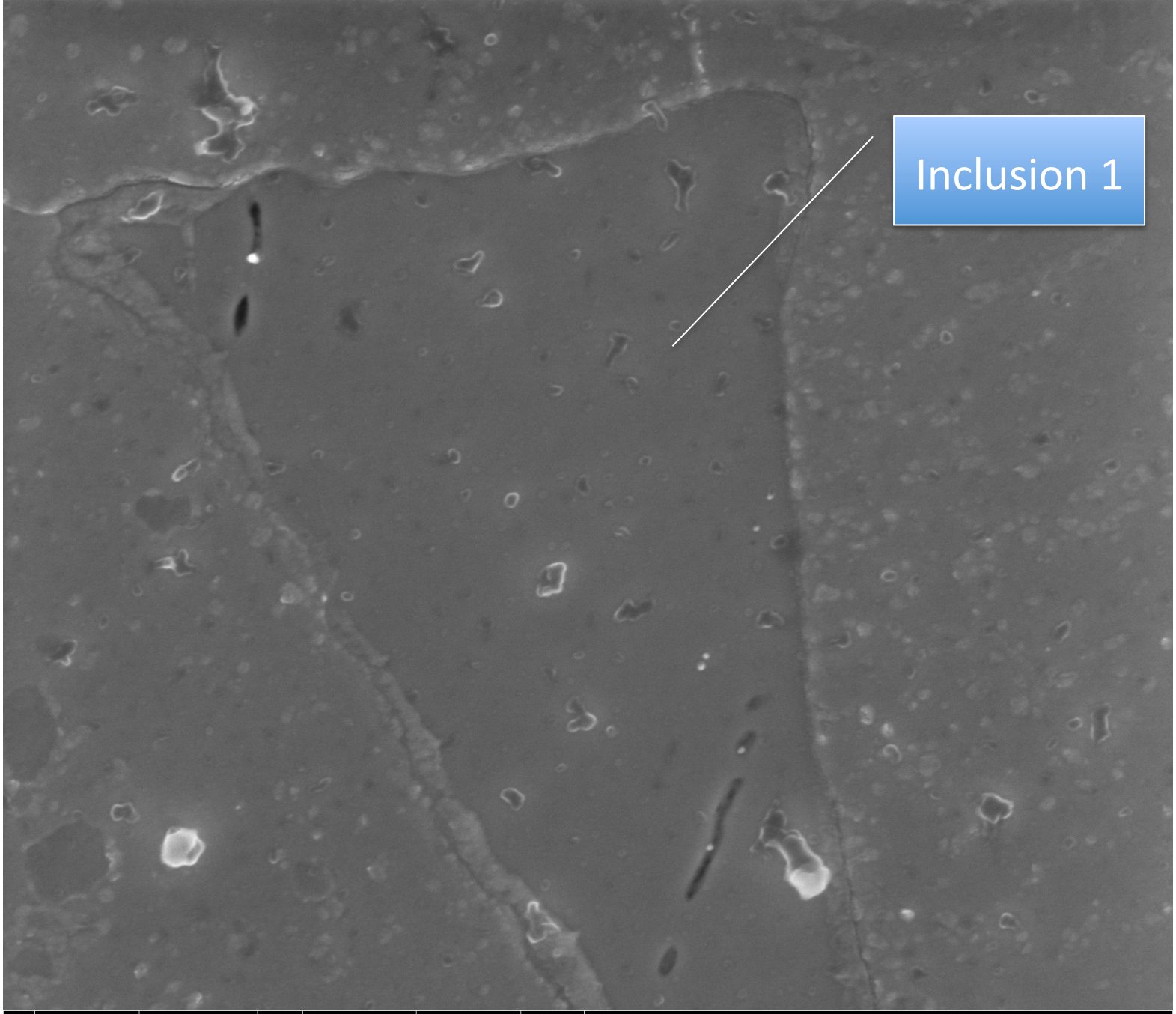

Inclusion 1
HV
5.00 kV
mag
4 997 x
tilt
0 °
HFW
60.2 µm
WD
5.1 mm
det
CDEM
20 µm
D238-polished_LQDH-baseline



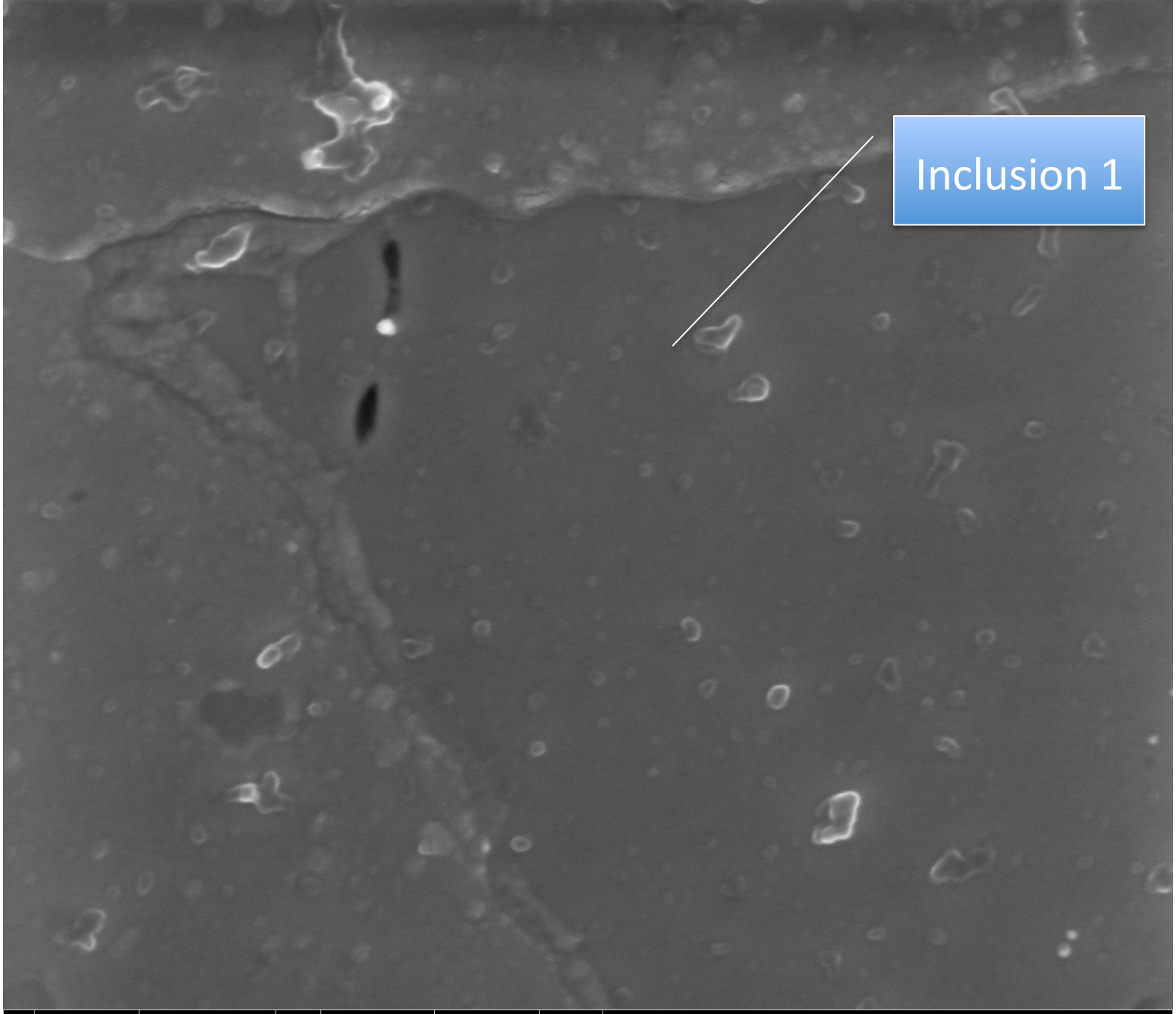
HV	mag	tilt	HFW	WD	det	10 µm
5.00 kV	12 007 x	0 °	25.1 µm	5.0 mm	CDEM	D238-polished_ LQDH-baseline



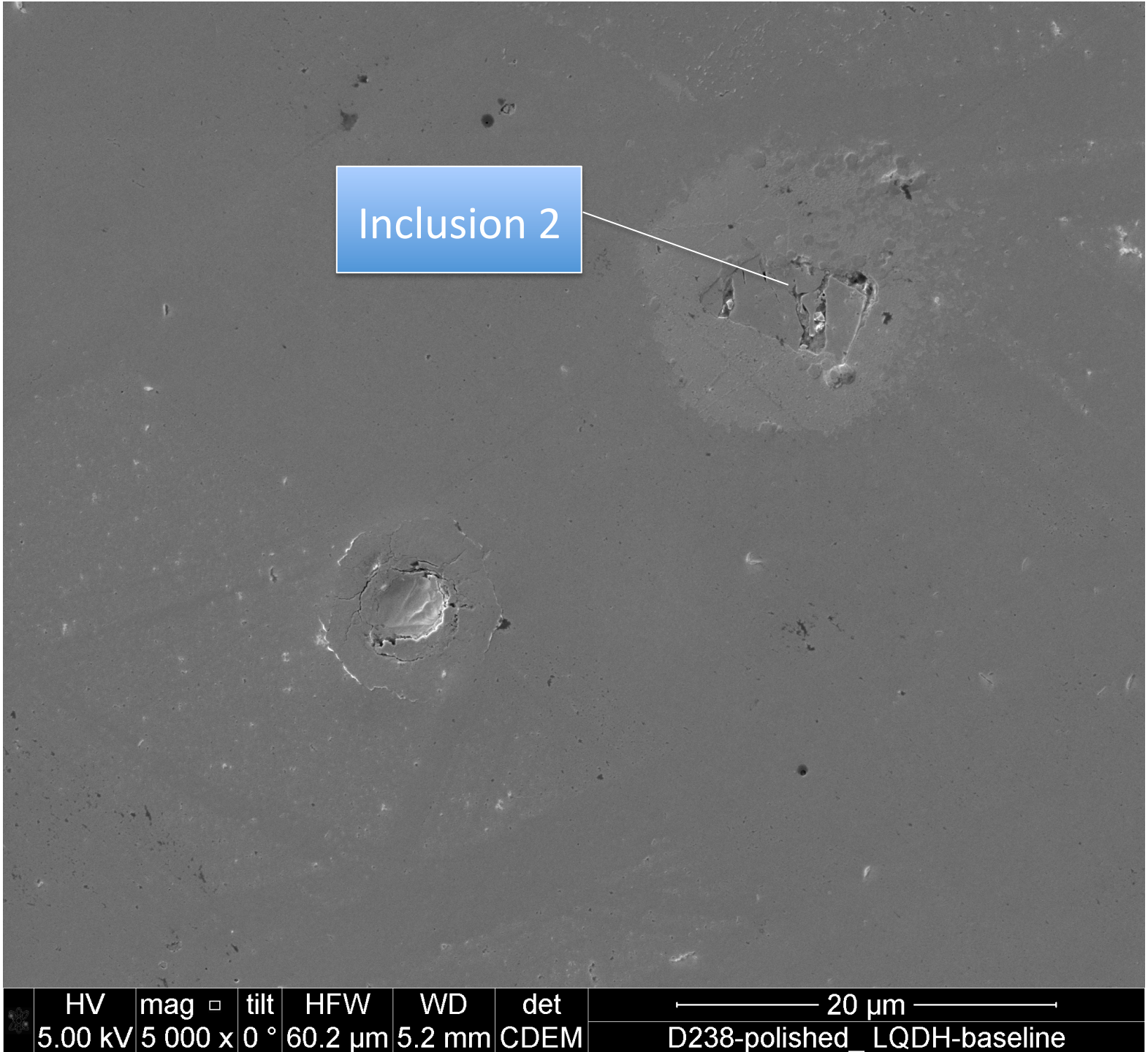
HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	24 989 x	0 °	12.0 µm	5.0 mm	TLD	D238-polished_ LQDH-baseline

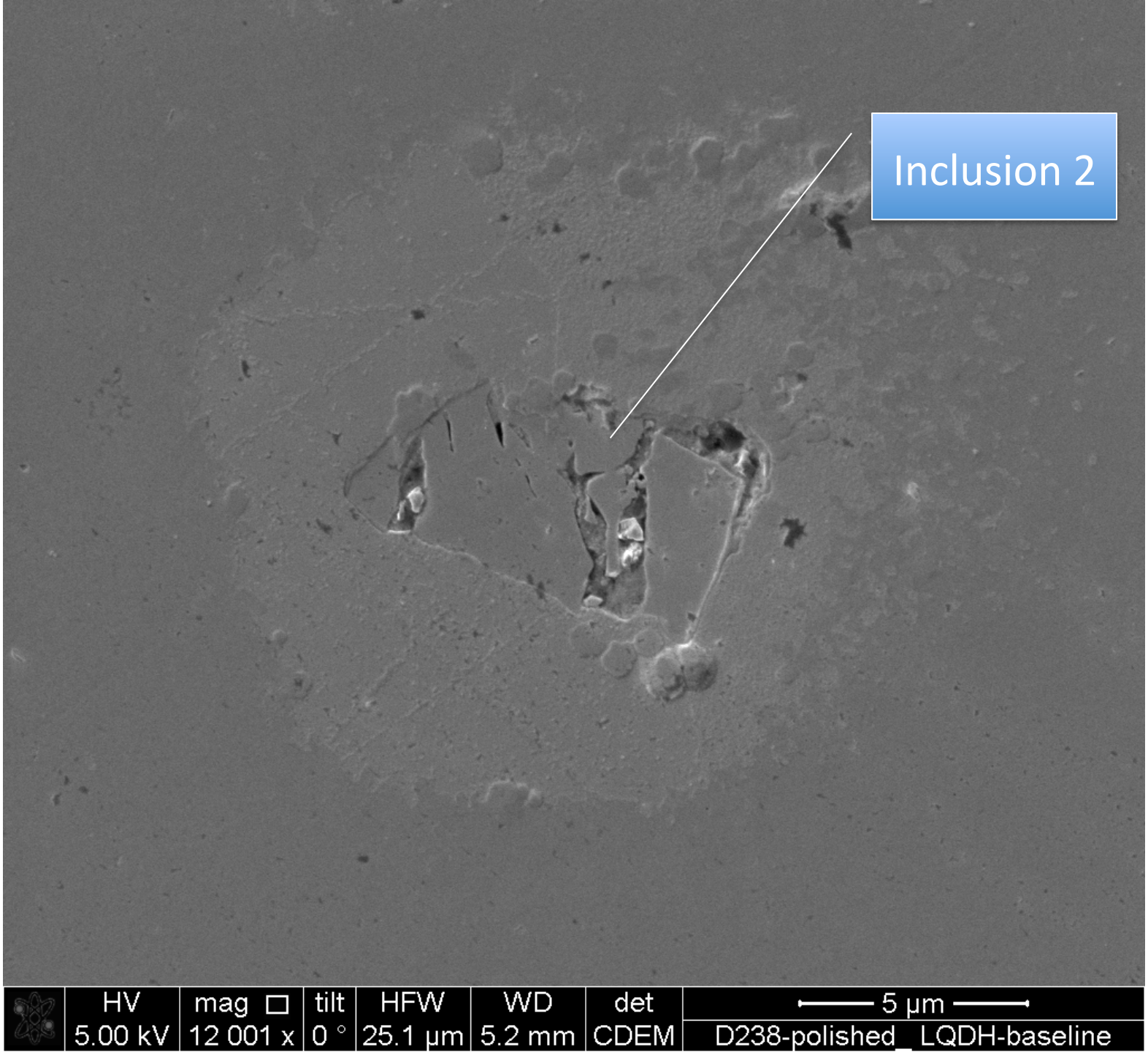


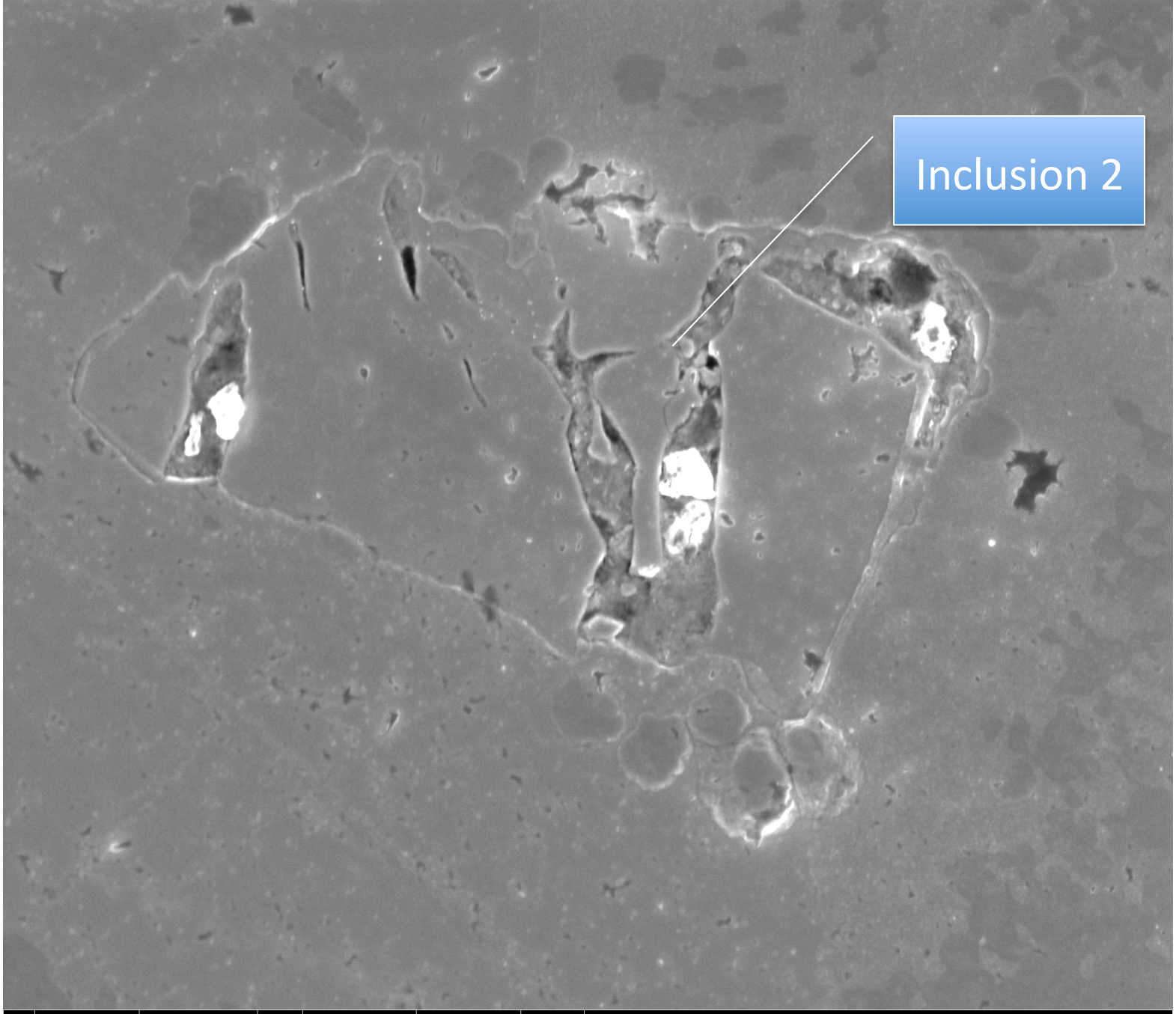
HV	mag	tilt	HFW	WD	det	2 µm
5.00 kV	64 996 x	0 °	4.63 µm	5.0 mm	TLD	D238-polished_ LQDH-baseline



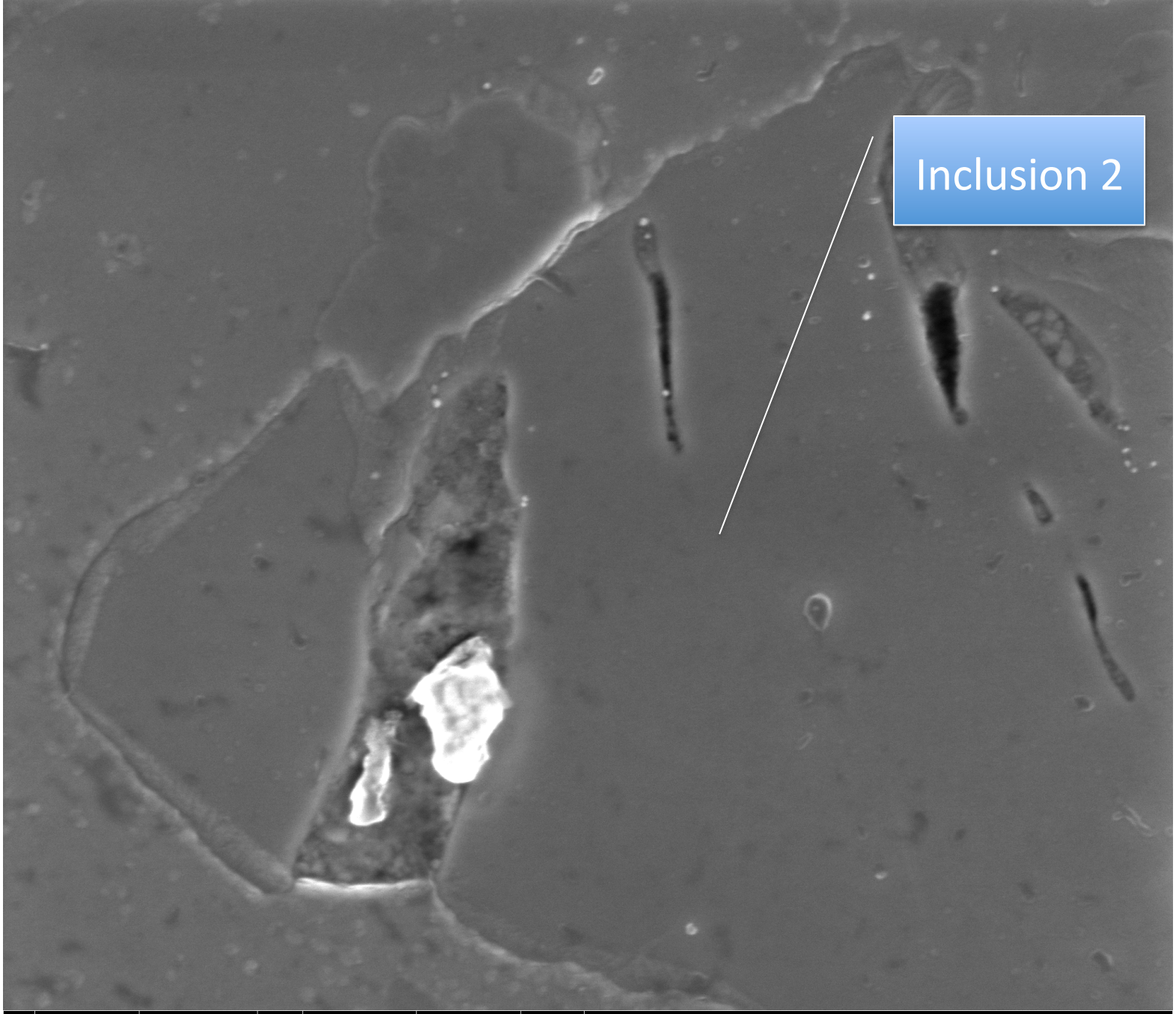
HV	mag	tilt	HFW	WD	det	1 µm
5.00 kV	100 000 x	0 °	3.01 µm	5.0 mm	TLD	D238-polished_ LQDH-baseline


Inclusion 2
HV
5.00 kV
mag
5 000 x
tilt
0 °
HFW
60.2 µm
WD
5.2 mm
det
CDEM
20 µm
D238-polished_ LQDH-baseline

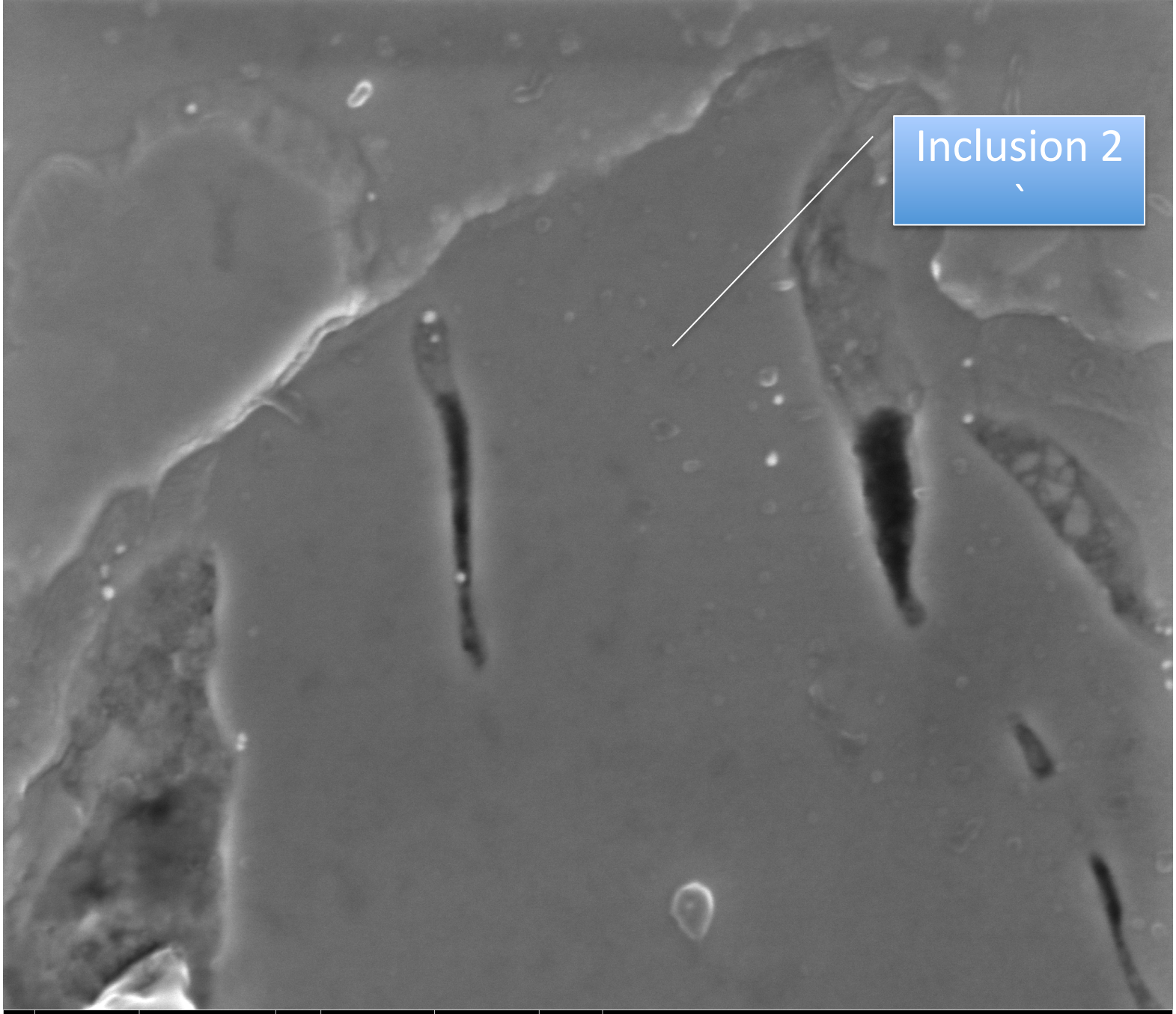

Inclusion 2
HV
5.00 kV
mag
12 001 x
tilt
0 °
HFW
25.1 µm
WD
5.2 mm
det
CDEM
5 µm
D238-polished_LQDH-baseline



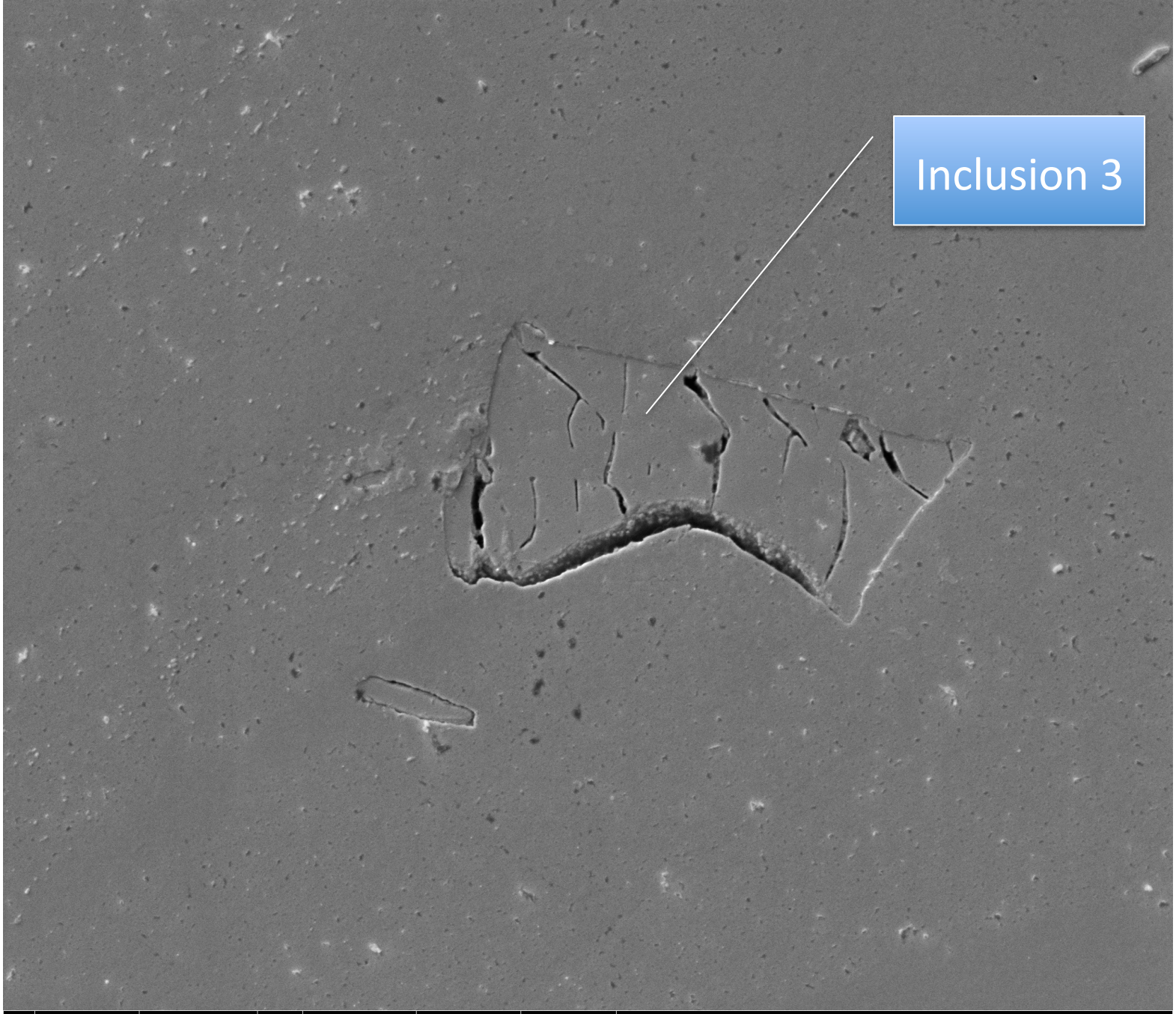
HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	25 000 x	0 °	12.0 µm	5.0 mm	TLD	D238-polished_ LQDH-baseline



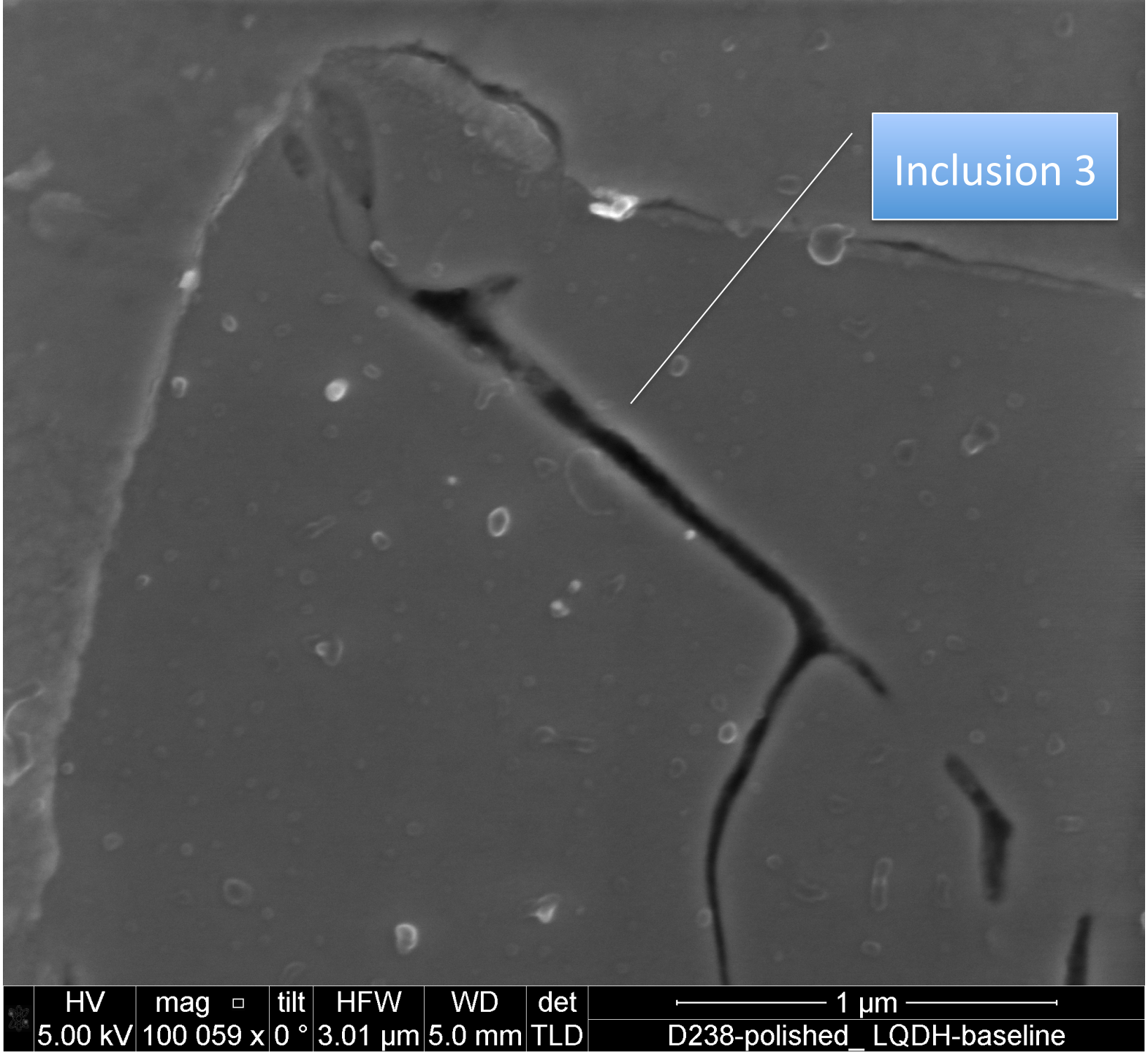
HV	mag	tilt	HFW	WD	det	2 µm
5.00 kV	65 000 x	0 °	4.63 µm	5.0 mm	TLD	D238-polished_ LQDH-baseline

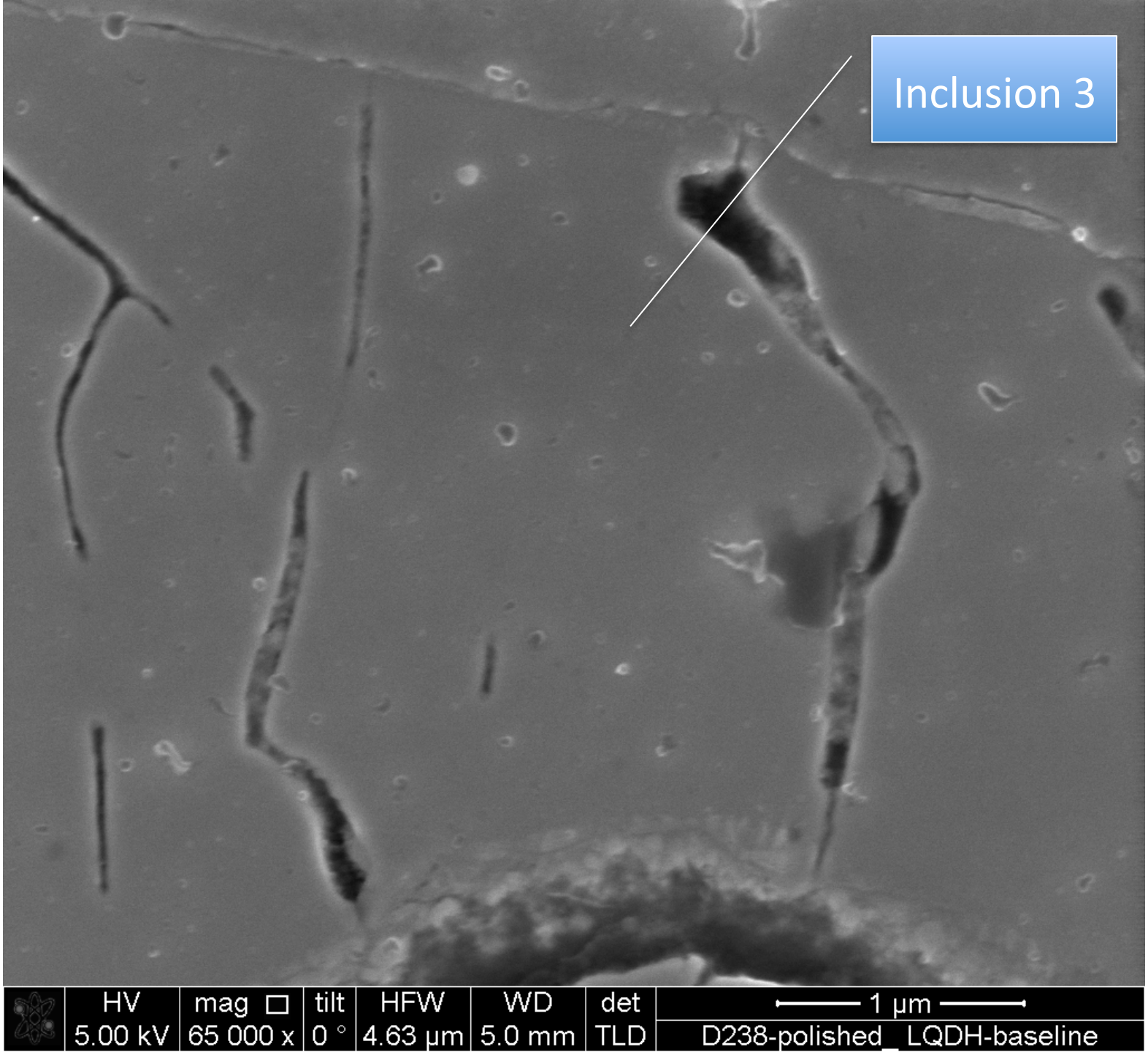


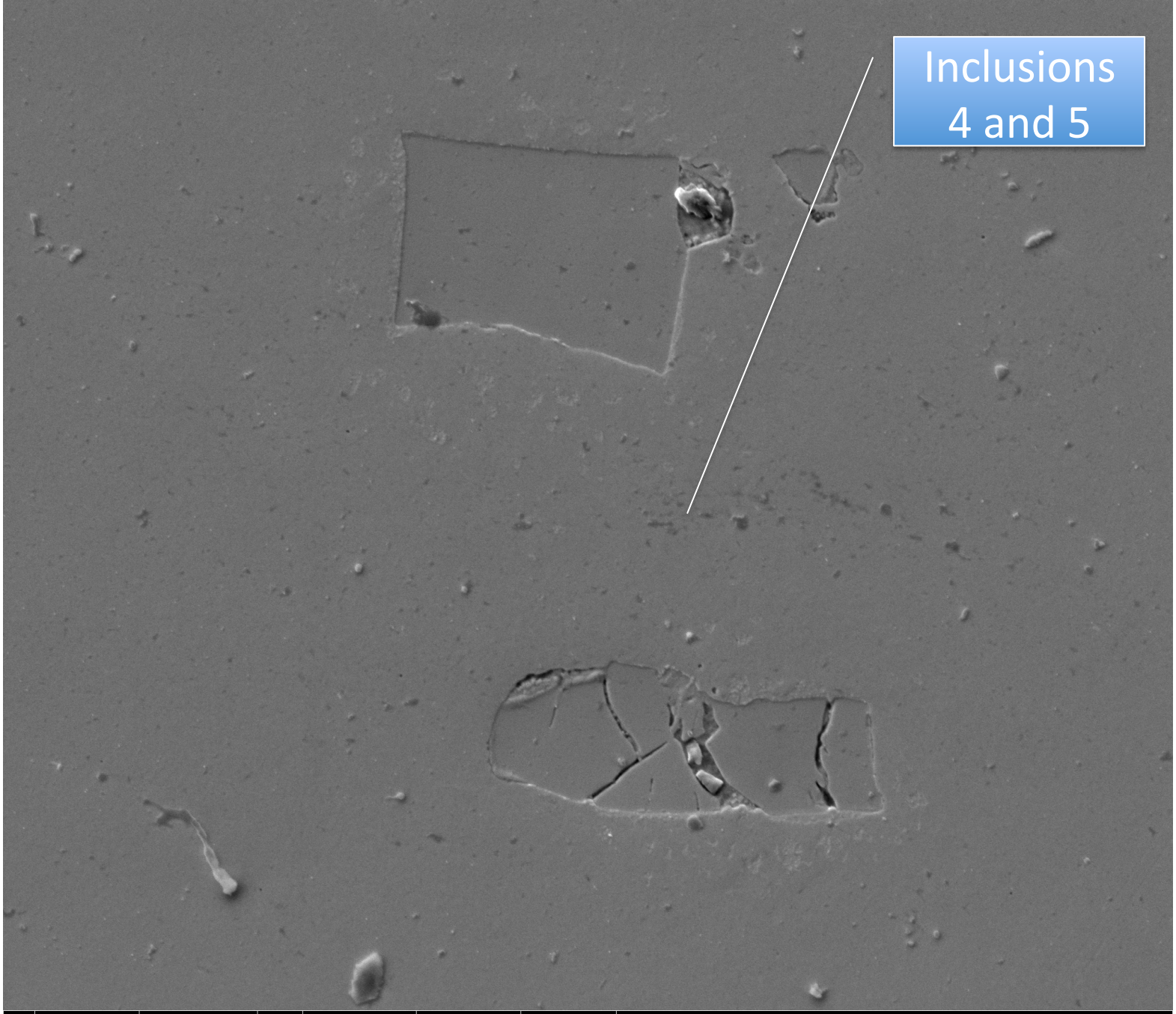
HV	mag	tilt	HFW	WD	det	1 µm
5.00 kV	100 000 x	0 °	3.01 µm	5.0 mm	TLD	D238-polished_ LQDH-baseline



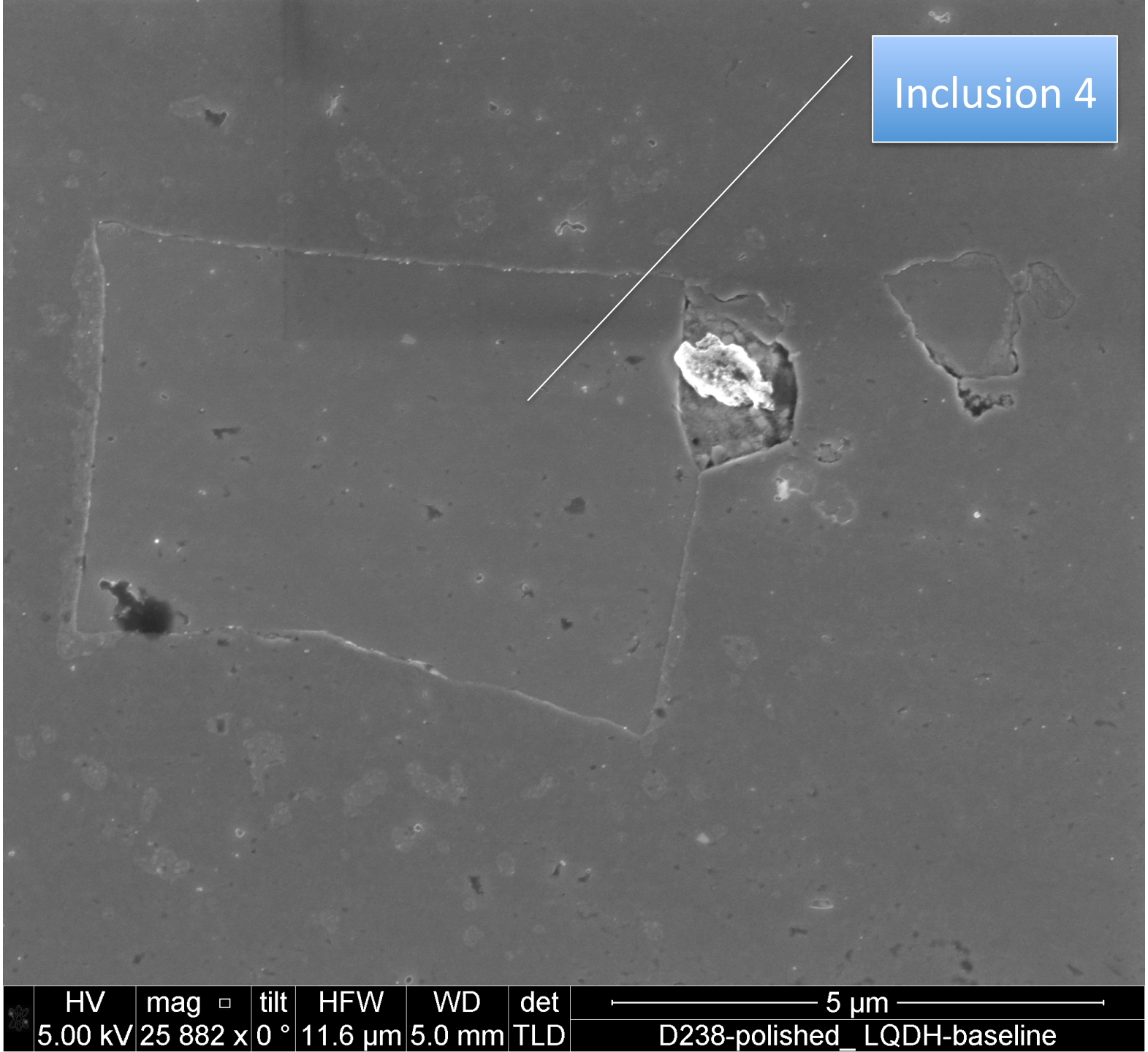
HV	mag	tilt	HFW	WD	det	10 µm
5.00 kV	12 000 x	0 °	25.1 µm	5.2 mm	CDEM	D238-polished_ LQDH-baseline

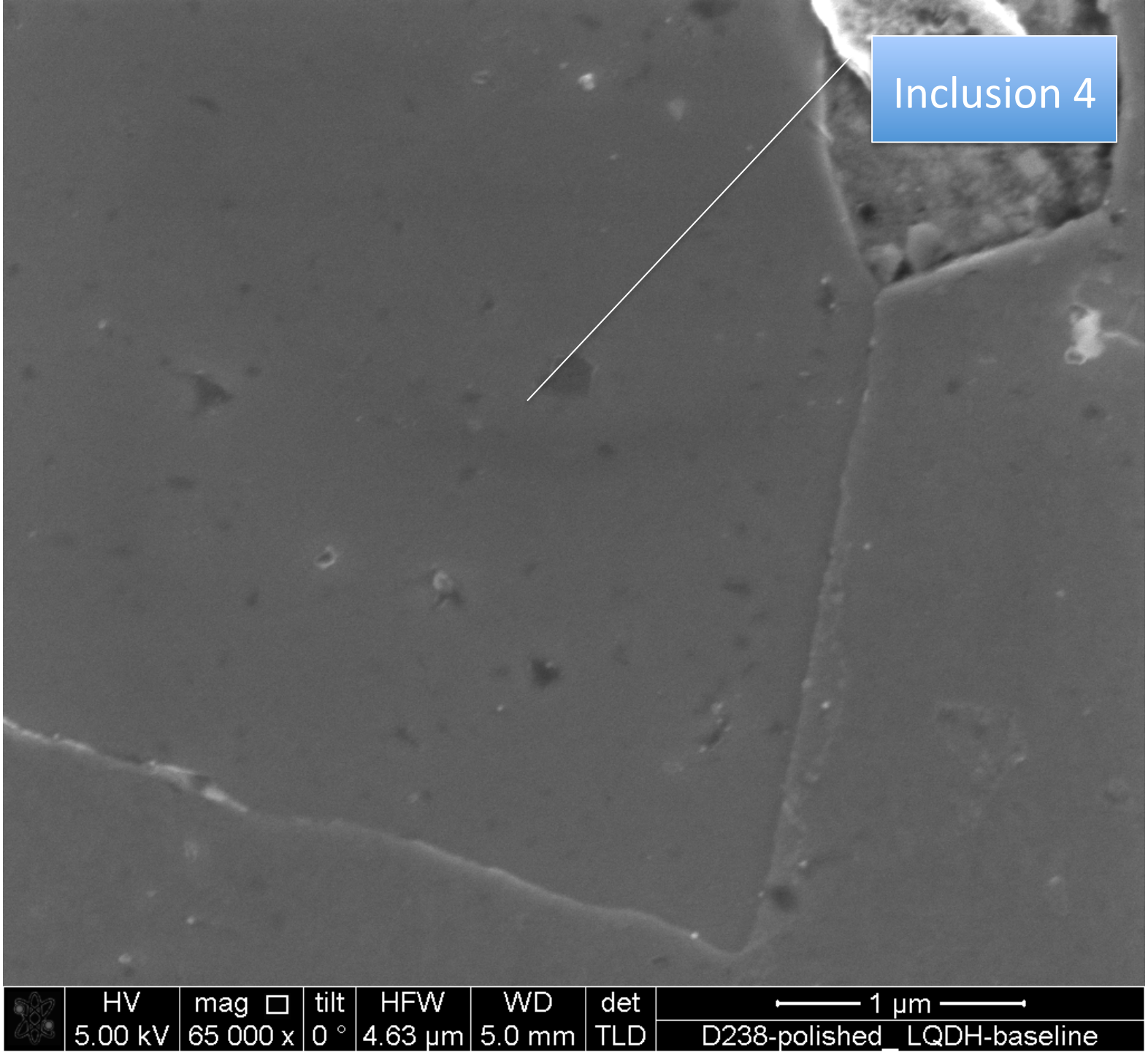

Inclusion 3
HV
5.00 kV
mag
100 059 x
tilt
0 °
HFW
3.01 µm
WD
5.0 mm
det
TLD
1 µm
D238-polished_ LQDH-baseline

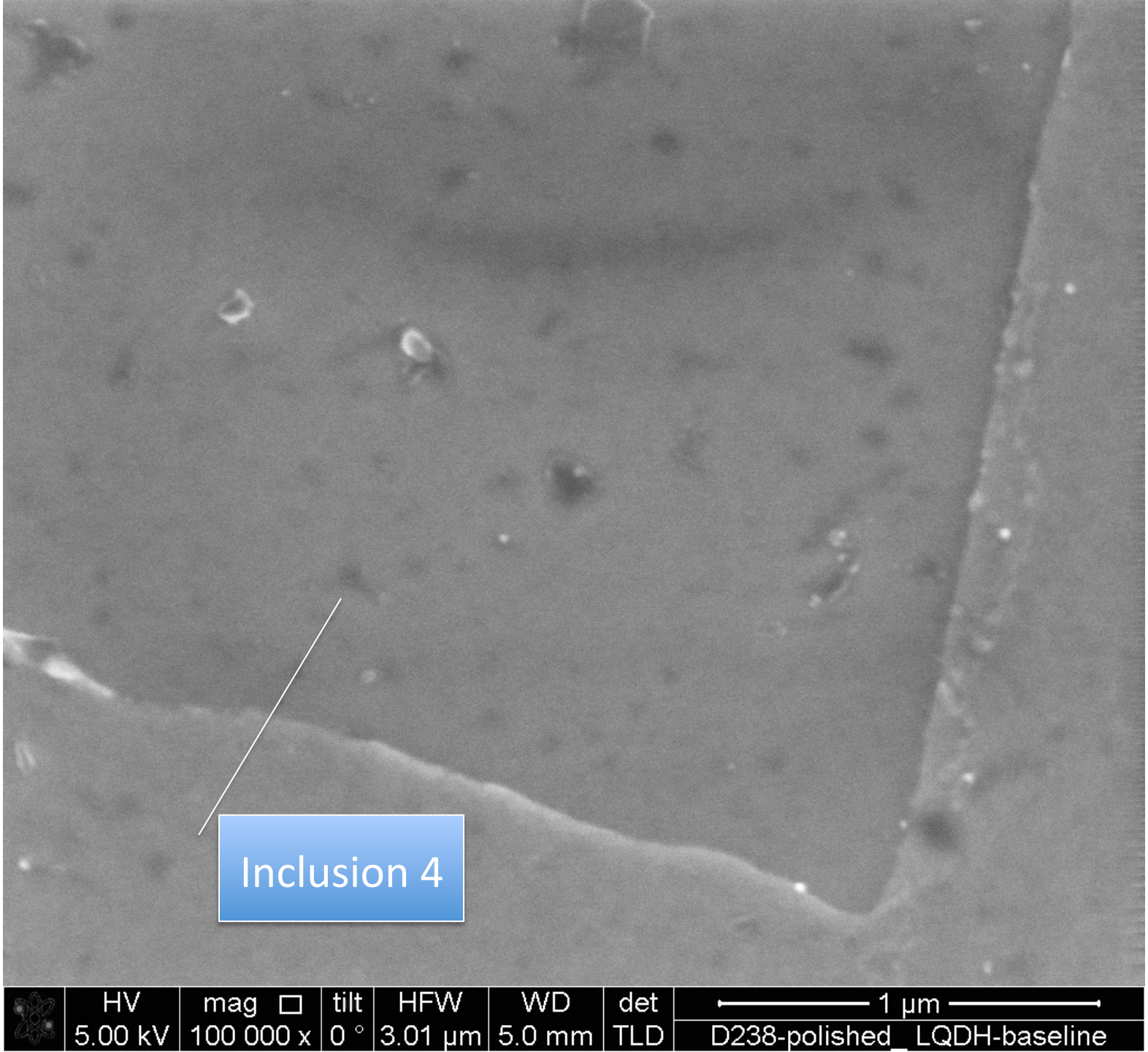

Inclusion 3
HV
5.00 kV
mag
65 000 x
tilt
0 °
HFW
4.63 µm
WD
5.0 mm
det
TLD
1 µm
D238-polished_LQDH-baseline

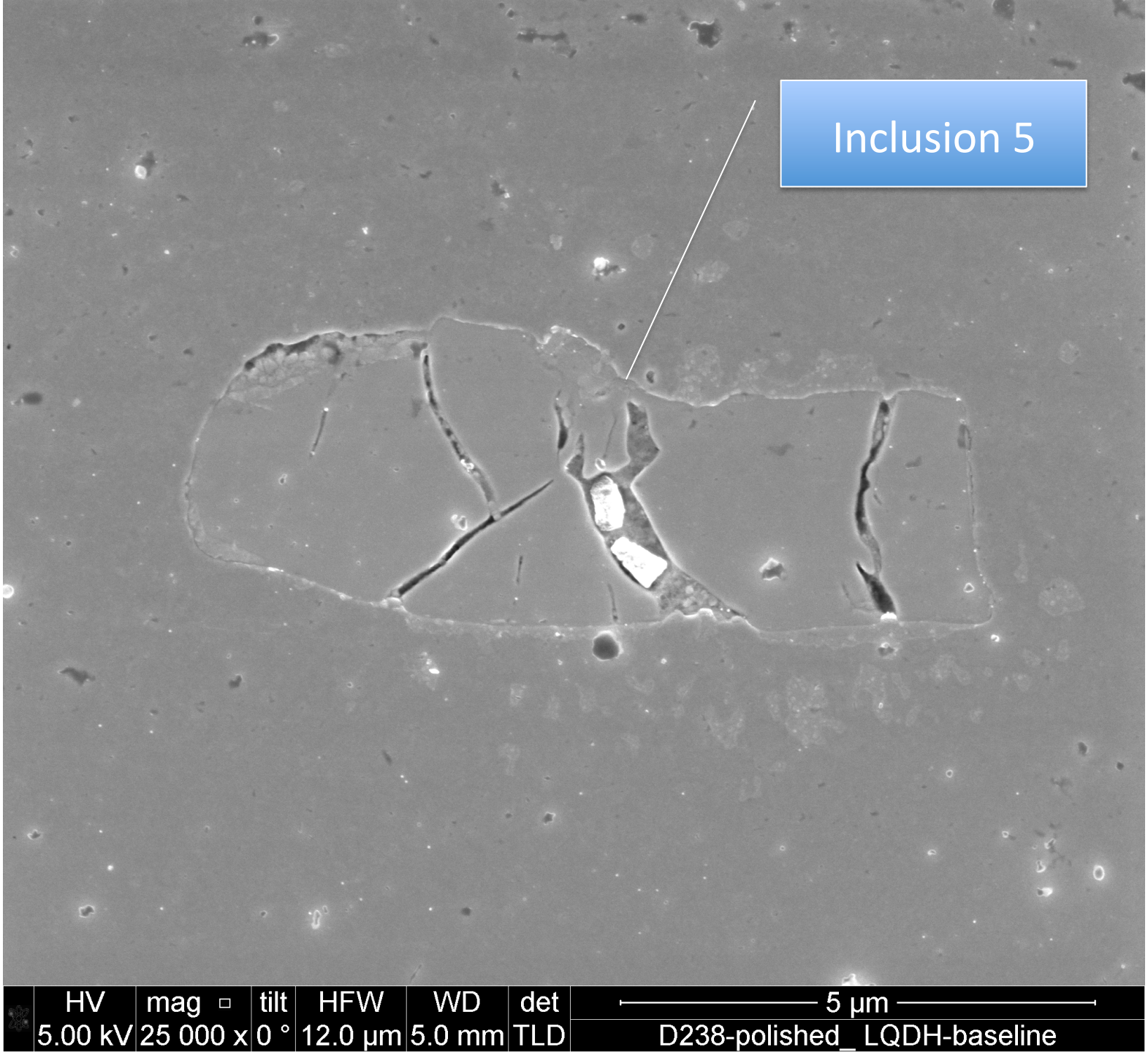


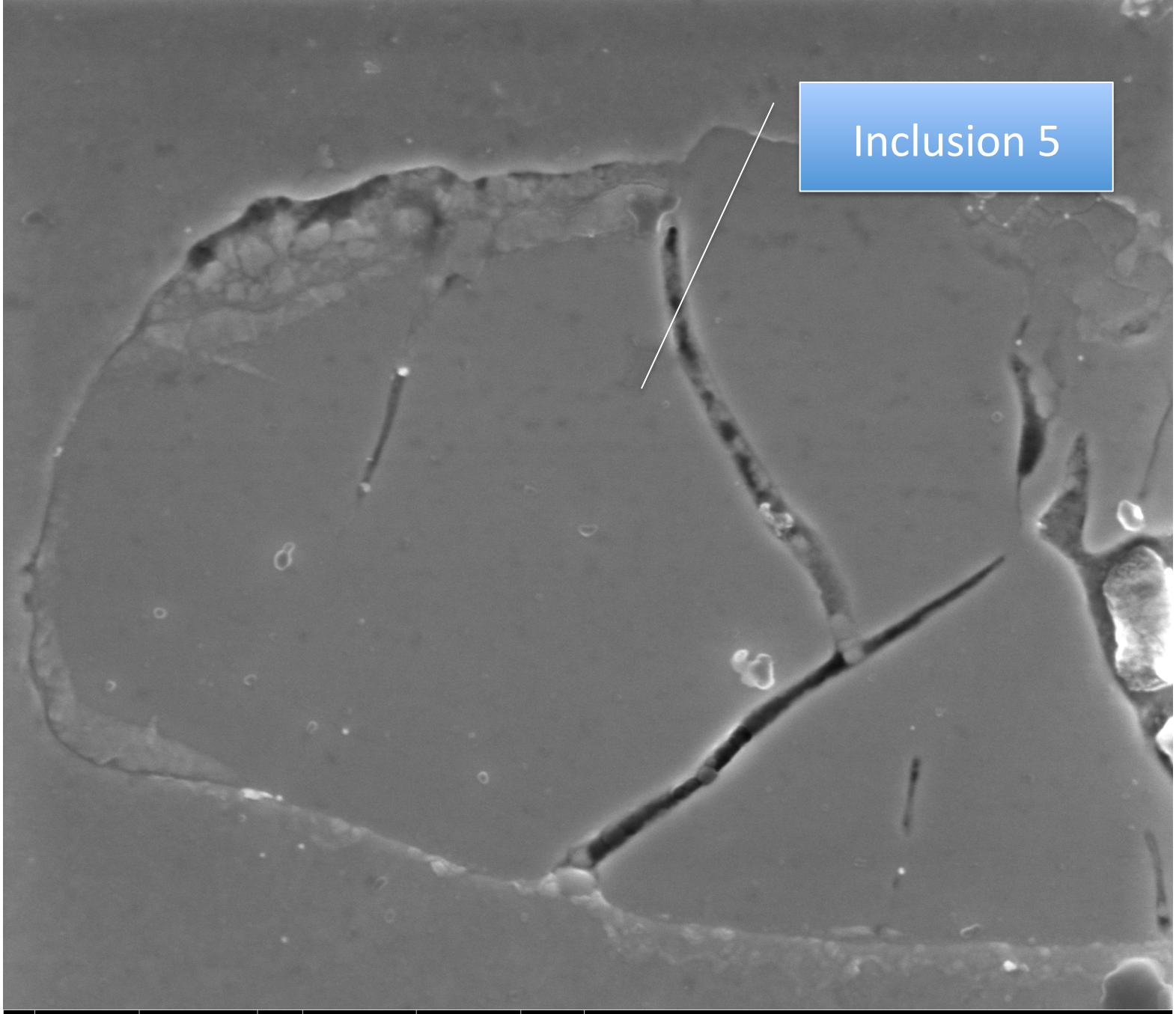
HV	mag	tilt	HFW	WD	det	10 µm
5.00 kV	12 001 x	0 °	25.1 µm	5.2 mm	CDEM	D238-polished_ LQDH-baseline


Inclusion 4
HV
5.00 kV
mag
25 882 x
tilt
0 °
HFW
11.6 µm
WD
5.0 mm
det
TLD
5 µm
D238-polished_ LQDH-baseline

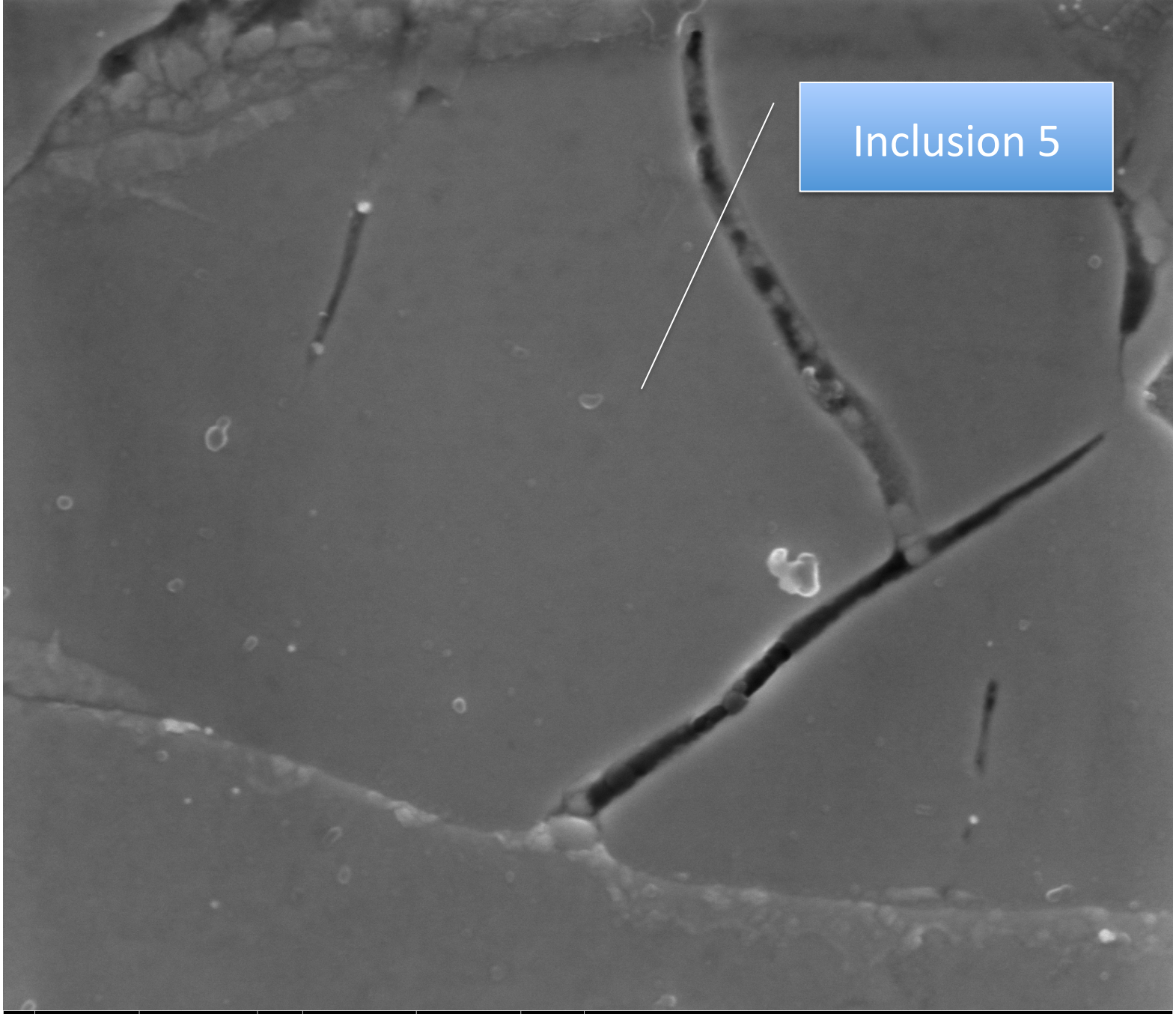

Inclusion 4
HV
5.00 kV
mag
65 000 x
tilt
0 °
HFW
4.63 µm
WD
5.0 mm
det
TLD
1 µm
D238-polished_LQDH-baseline


Inclusion 4
HV
5.00 kV
mag
100 000 x
tilt
0 °
HFW
3.01 µm
WD
5.0 mm
det
TLD
1 µm
D238-polished_LQDH-baseline

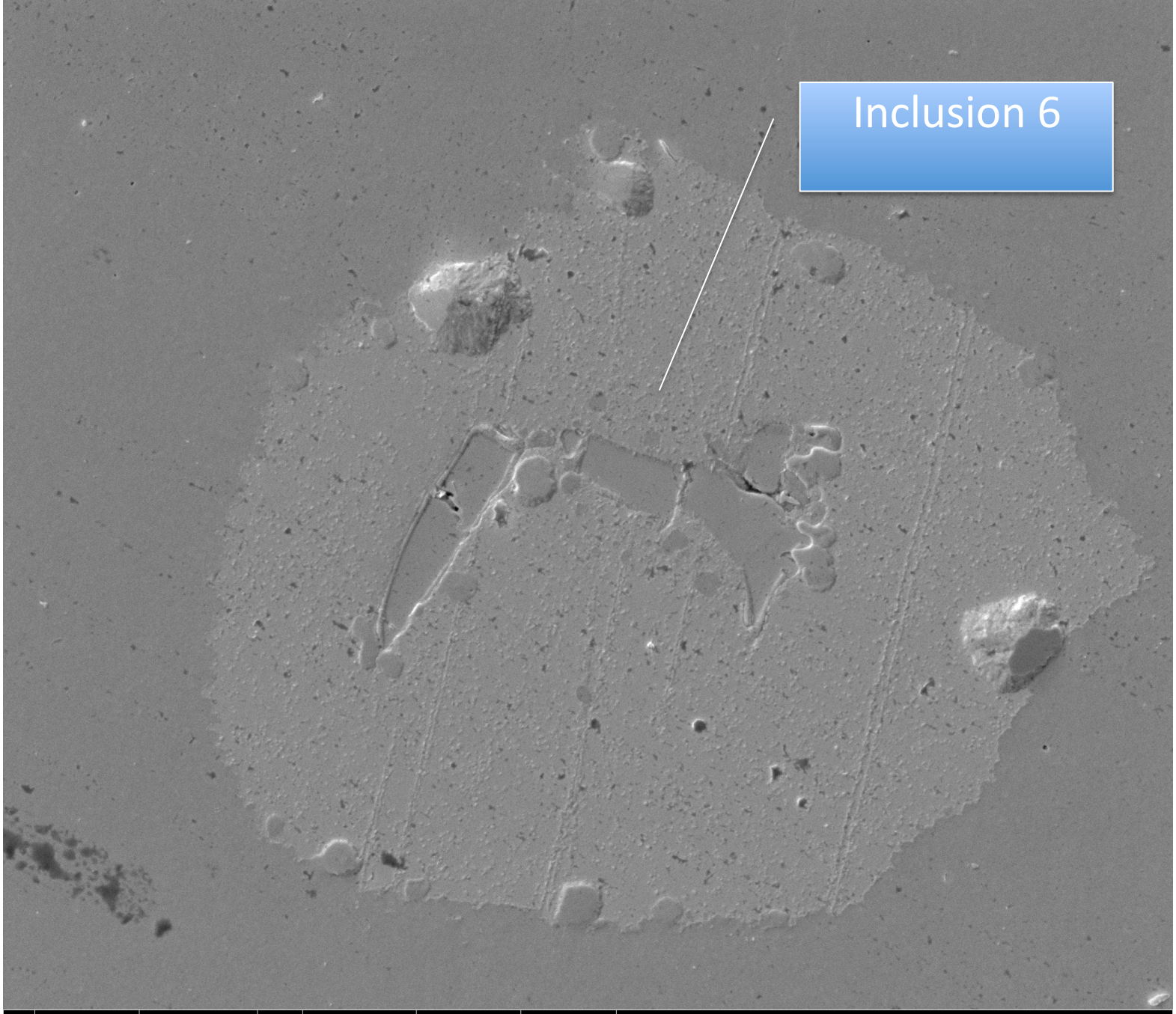

Inclusion 5
HV
5.00 kV
mag
25 000 x
tilt
0 °
HFW
12.0 µm
WD
5.0 mm
det
TLD
5 µm
D238-polished_ LQDH-baseline

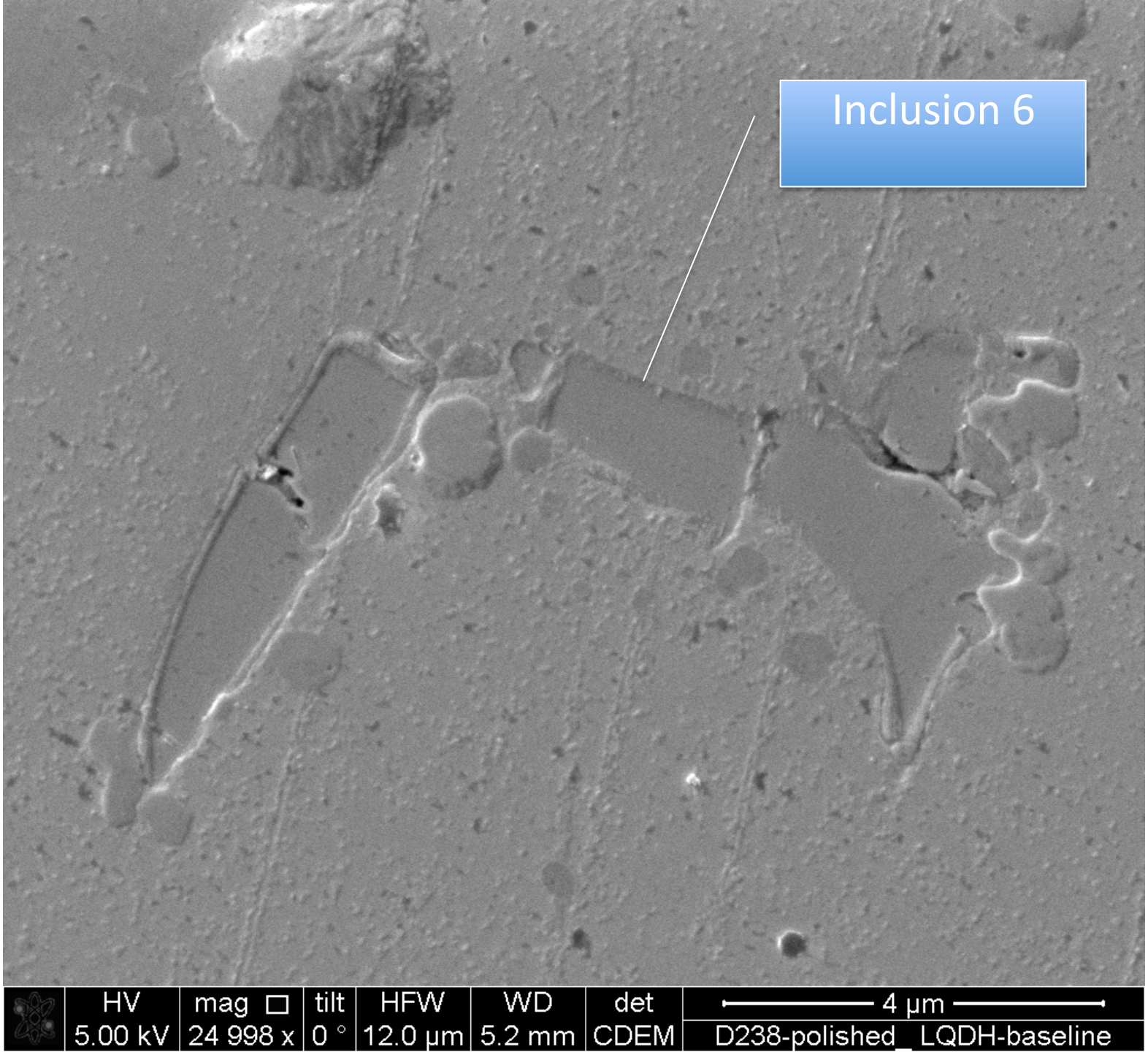


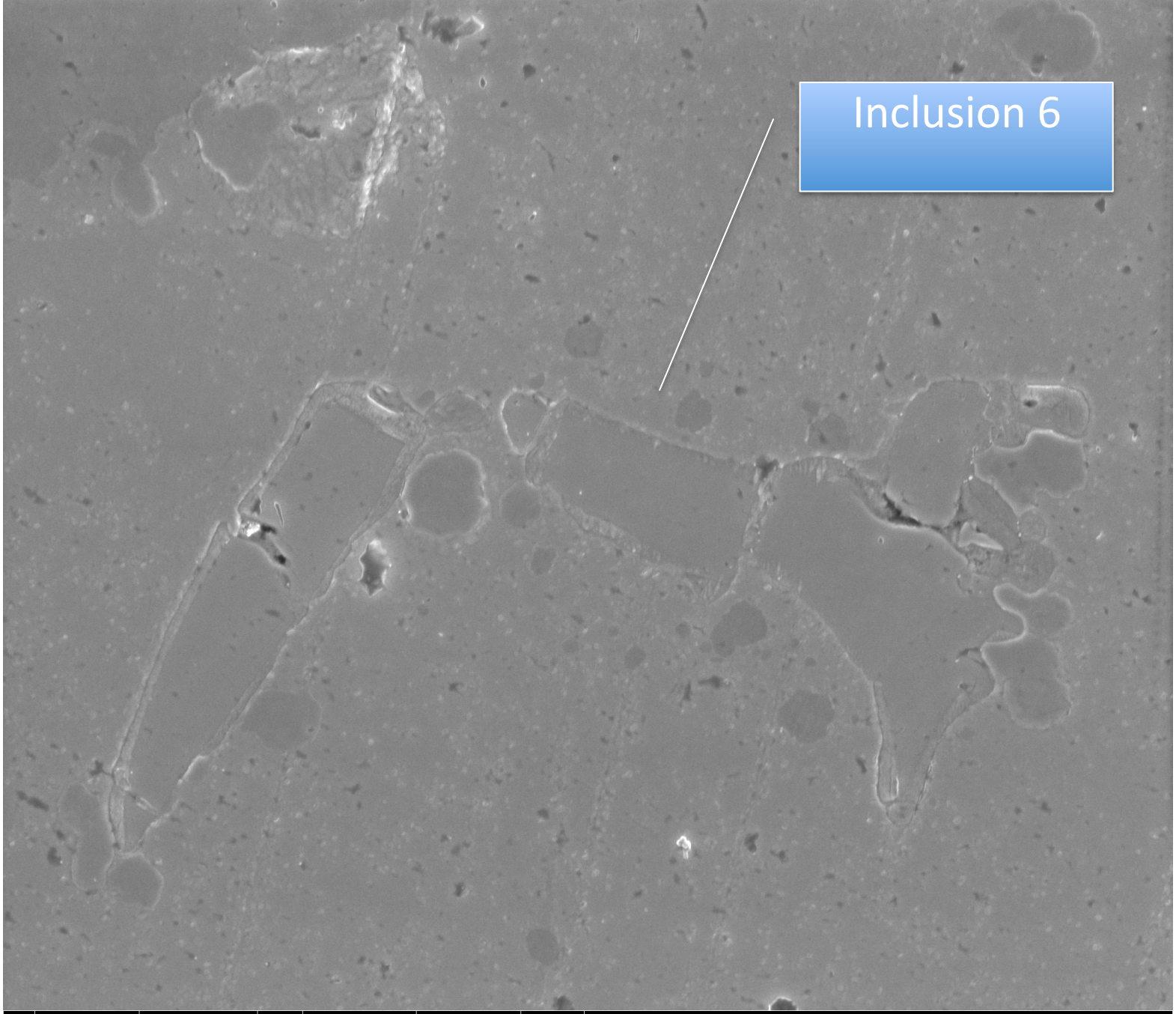
HV	mag	tilt	HFW	WD	det	2 µm
5.00 kV	65 000 x	0 °	4.63 µm	5.0 mm	TLD	D238-polished_ LQDH-baseline



HV	mag	tilt	HFW	WD	det	1 µm
5.00 kV	80 000 x	0 °	3.76 µm	5.0 mm	TLD	D238-polished_ LQDH-baseline


Inclusion 6
HV
5.00 kV
mag
12 001 x
tilt
0 °
HFW
25.1 µm
WD
5.2 mm
det
CDEM
10 µm
D238-polished_ LQDH-baseline

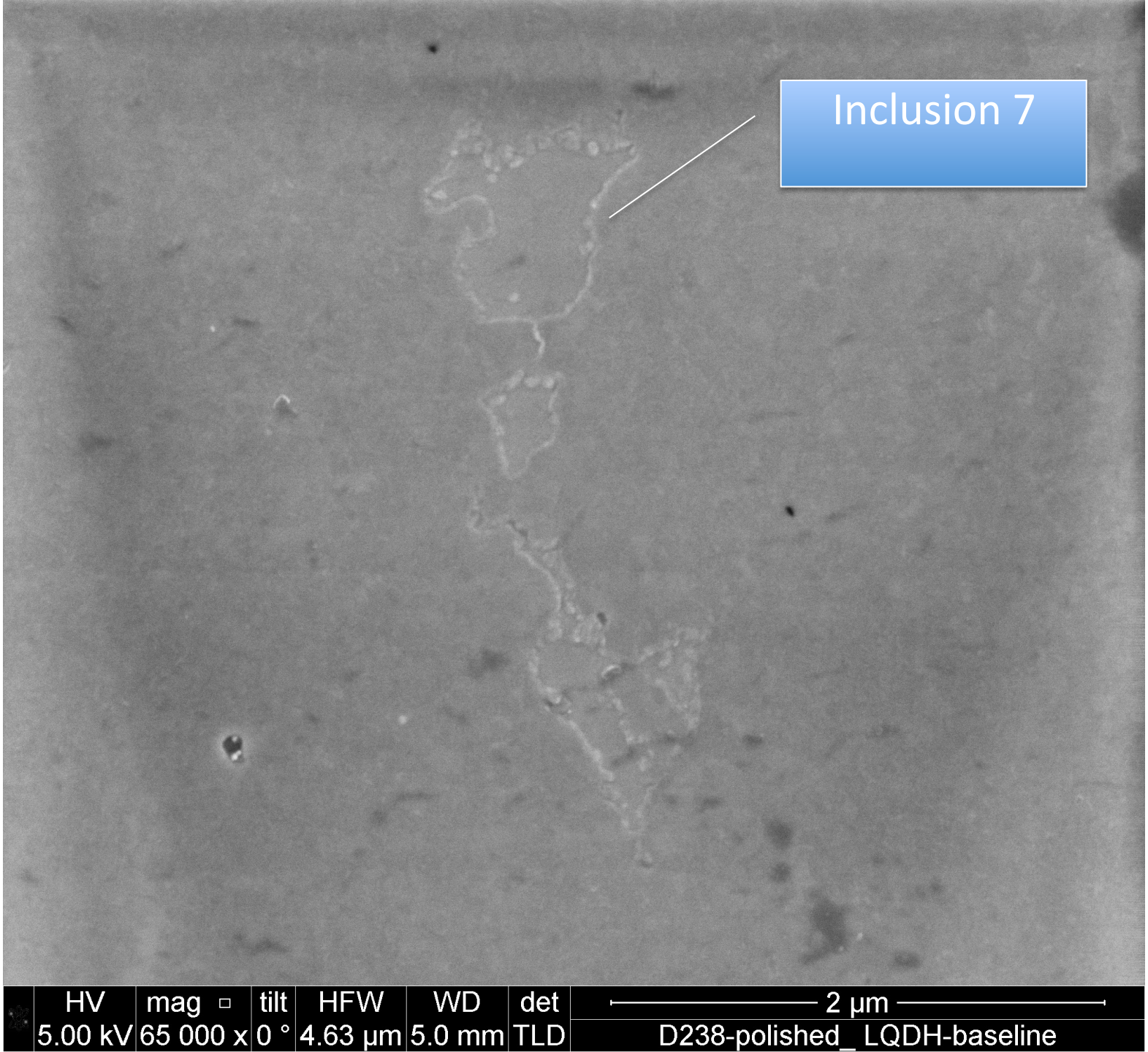

Inclusion 6
HV
5.00 kV
mag
24 998 x
tilt
0 °
HFW
12.0 µm
WD
5.2 mm
det
CDEM
4 µm
D238-polished_LQDH-baseline

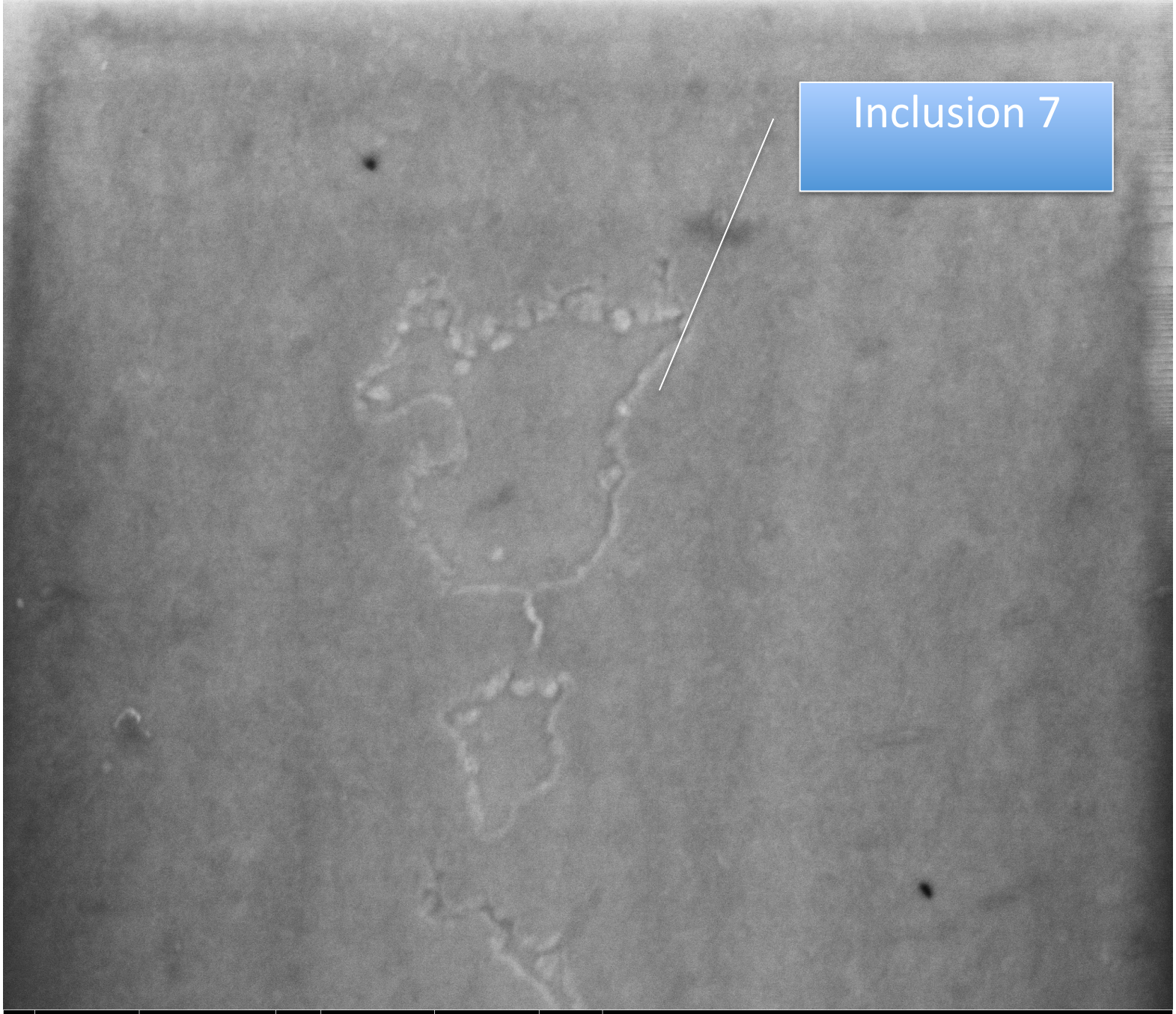


HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	25 000 x	0 °	12.0 µm	5.0 mm	TLD	D238-polished_ LQDH-baseline

Inclusion 6
HV
5.00 kV
mag
65 000 x
tilt
0 °
HFW
4.63 µm
WD
5.0 mm
det
TLD
2 µm
D238-polished_ LQDH-baseline

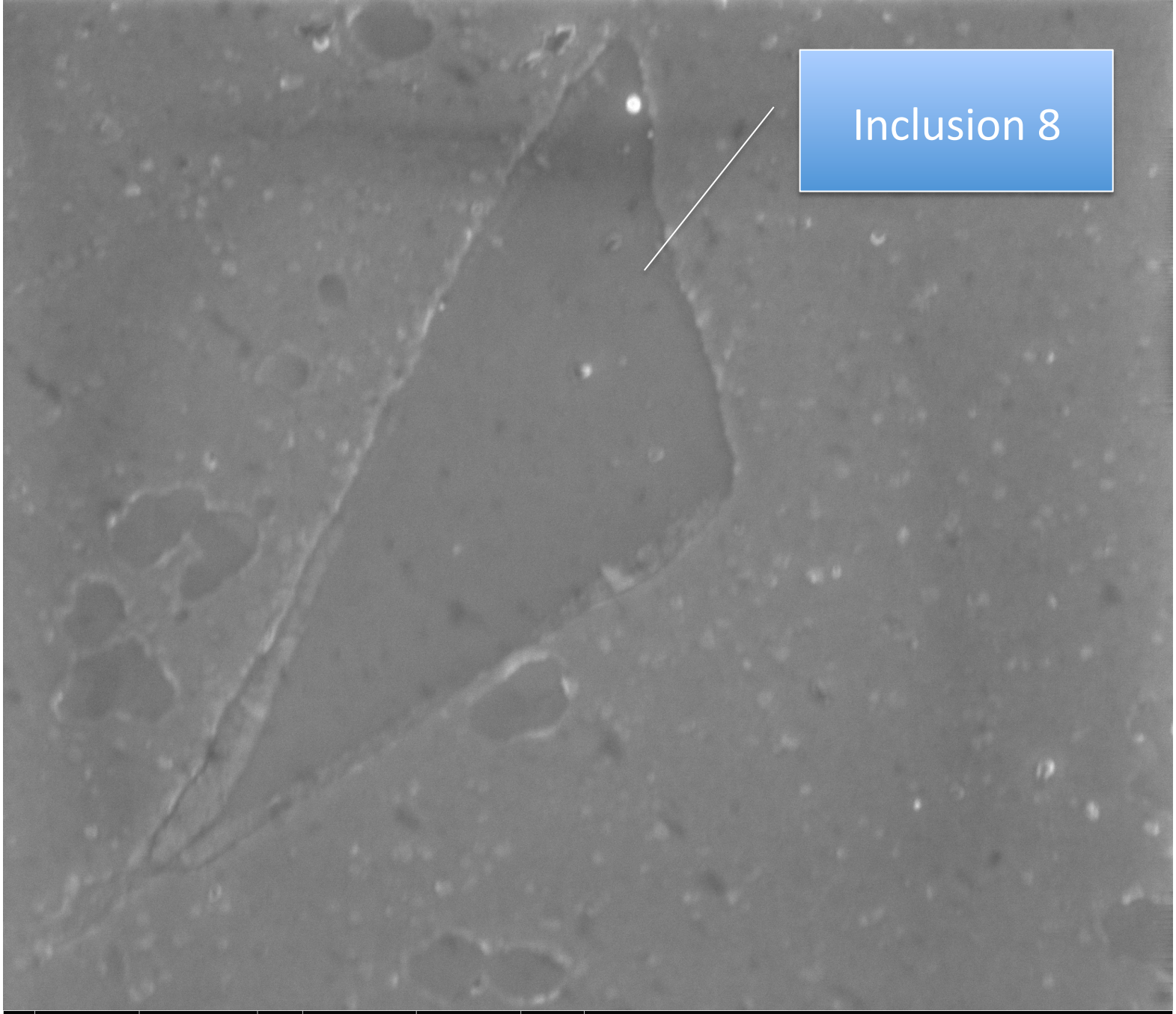
HV	mag	tilt	HFW	WD	det	1 µm
5.00 kV	100 000 x	0 °	3.01 µm	5.0 mm	TLD	D238-polished_LQDH-baseline


Inclusion 7
HV
5.00 kV
mag
65 000 x
tilt
0 °
HFW
4.63 µm
WD
5.0 mm
det
TLD
2 µm
D238-polished_ LQDH-baseline



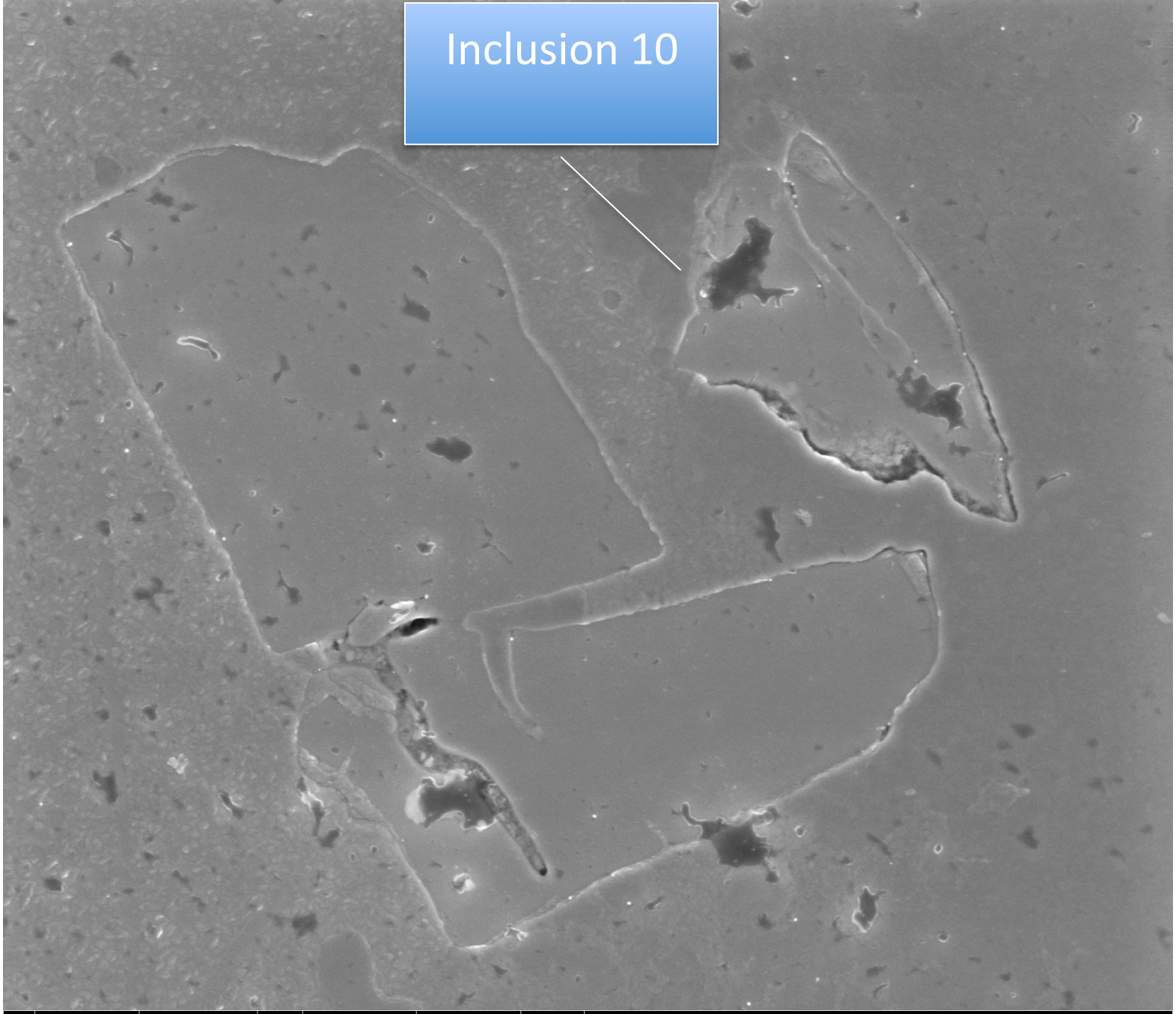
HV	mag	tilt	HFW	WD	det	1 µm
5.00 kV	100 000 x	0 °	3.01 µm	5.0 mm	TLD	D238-polished_ LQDH-baseline

HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	12 000 x	0 °	25.1 µm	5.3 mm	CDEM	D238-polished_LQDH-baseline

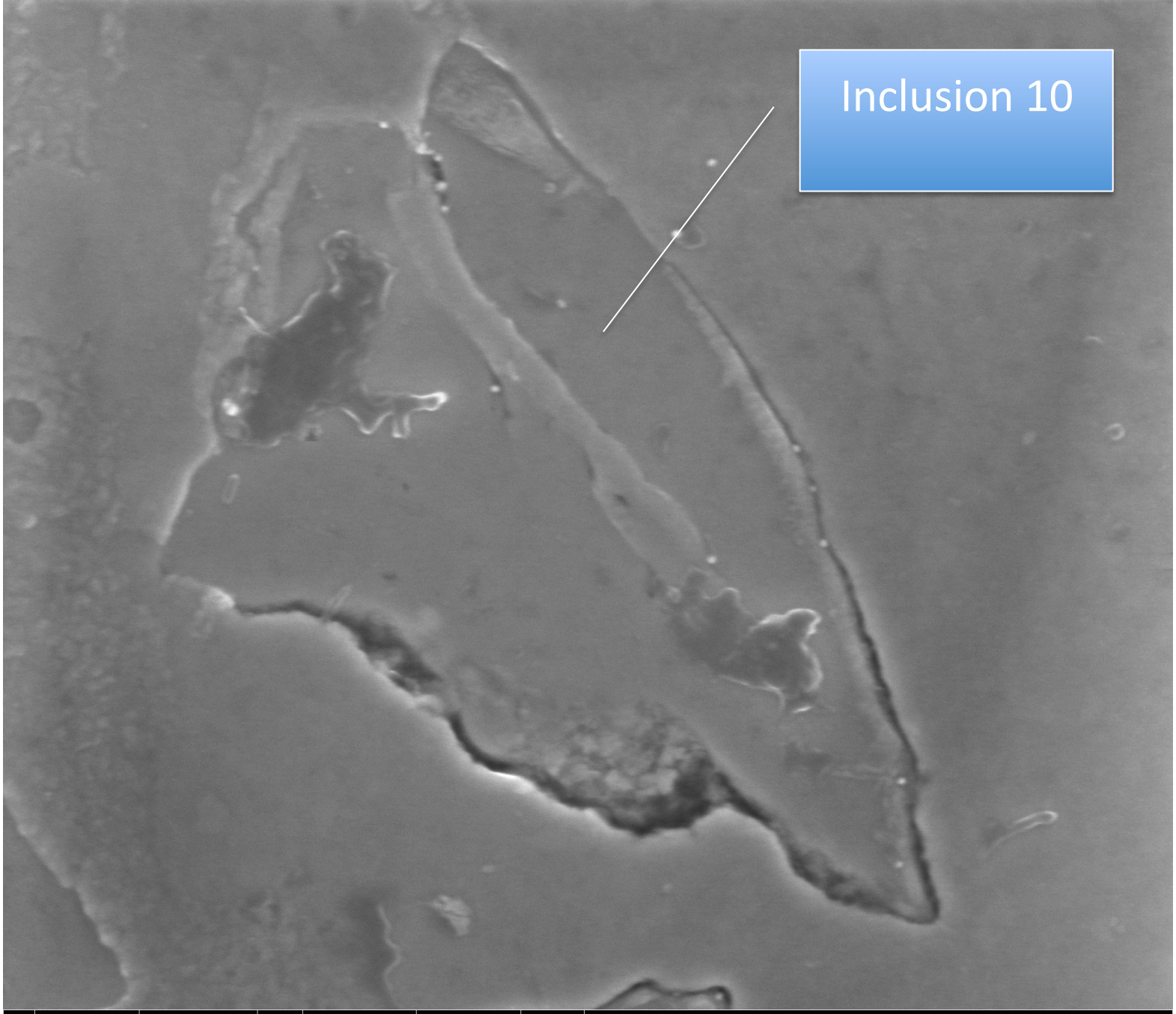

Inclusion 8
HV
5.00 kV
mag
65 000 x
tilt
0 °
HFW
4.63 µm
WD
5.0 mm
det
TLD
2 µm
D238-polished_ LQDH-baseline

HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	15 000 x	0 °	20.1 µm	5.1 mm	CDEM	D238-polished_ LQDH-baseline

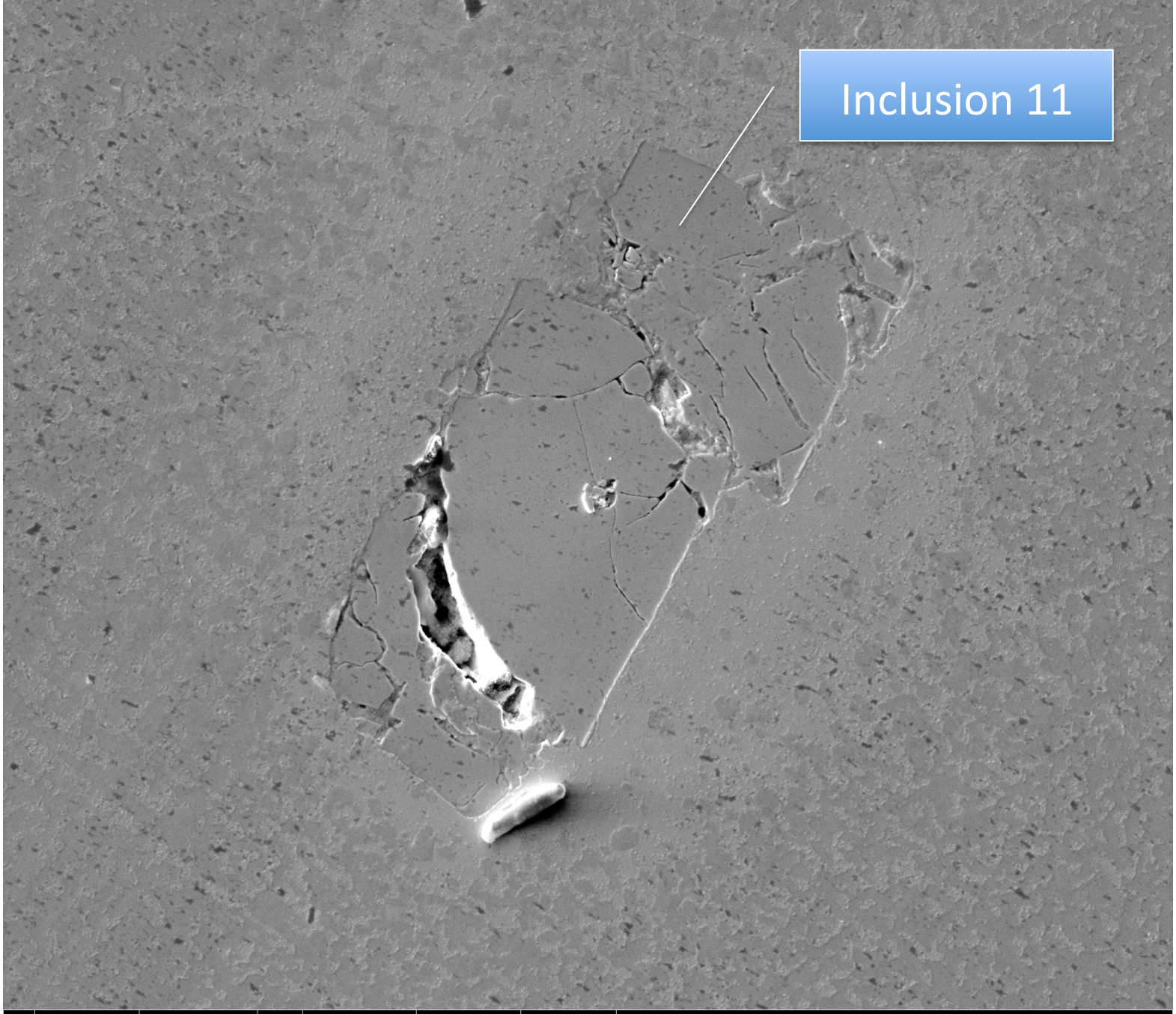
HV	mag	tilt	HFW	WD	det	4 µm
5.00 kV	34 987 x	0 °	8.60 µm	5.1 mm	TLD	D238-polished_ LQDH-baseline



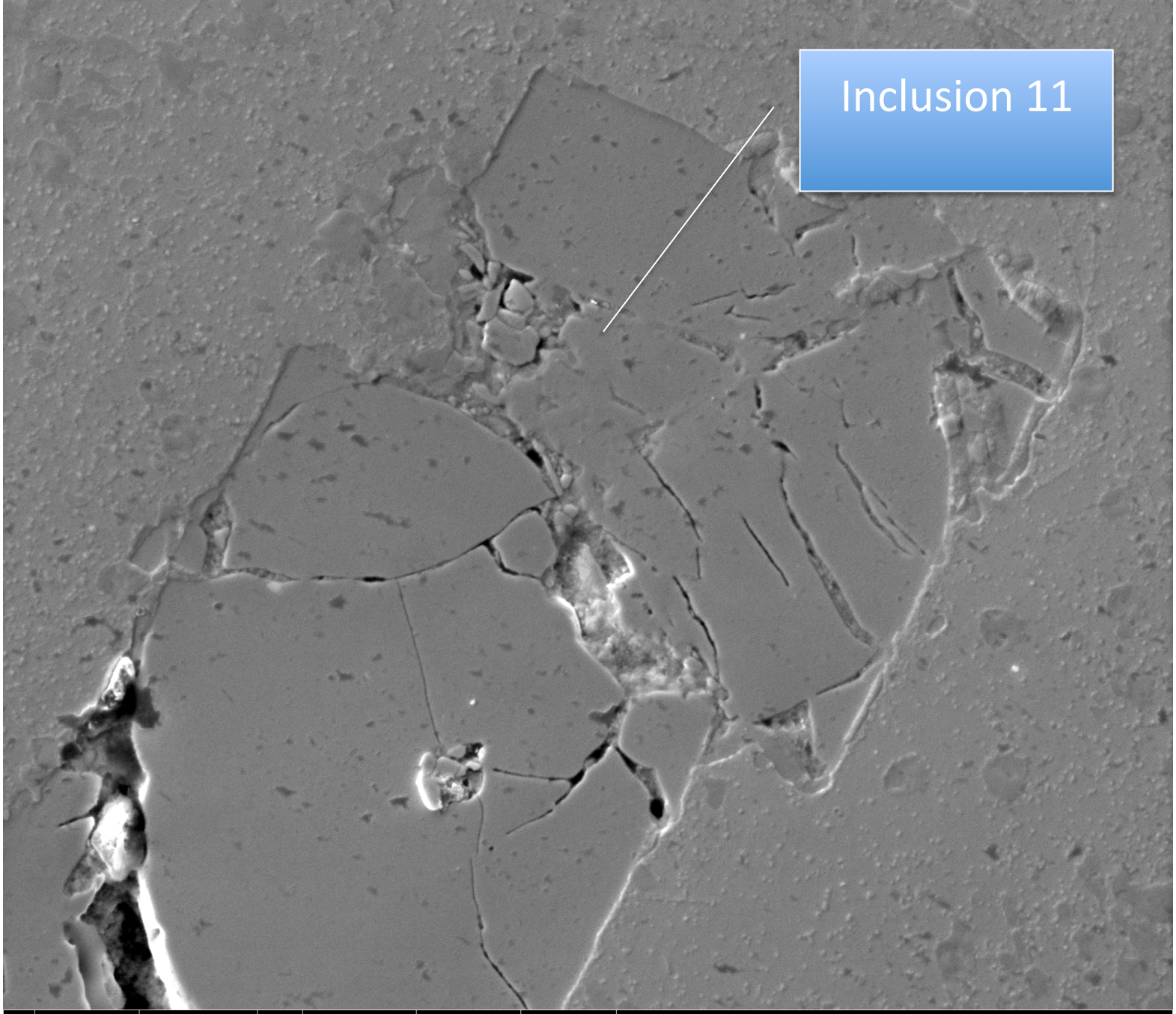
HV	mag	tilt	HFW	WD	det	4 µm
5.00 kV	35 000 x	0 °	8.59 µm	5.1 mm	TLD	D238-polished_ LQDH-baseline

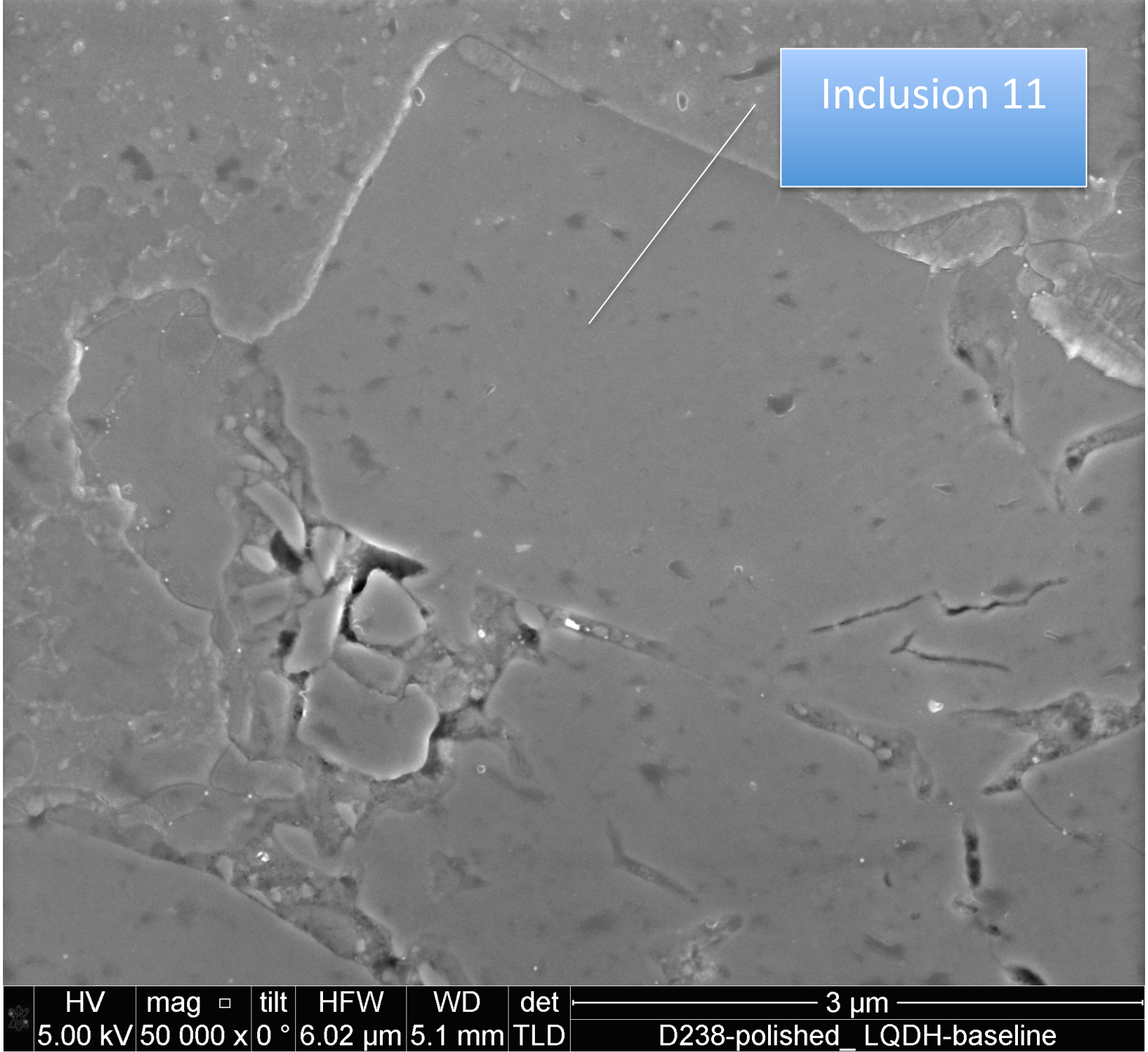


HV	mag	tilt	HFW	WD	det	1 µm
5.00 kV	79 989 x	0 °	3.76 µm	5.1 mm	TLD	D238-polished_ LQDH-baseline



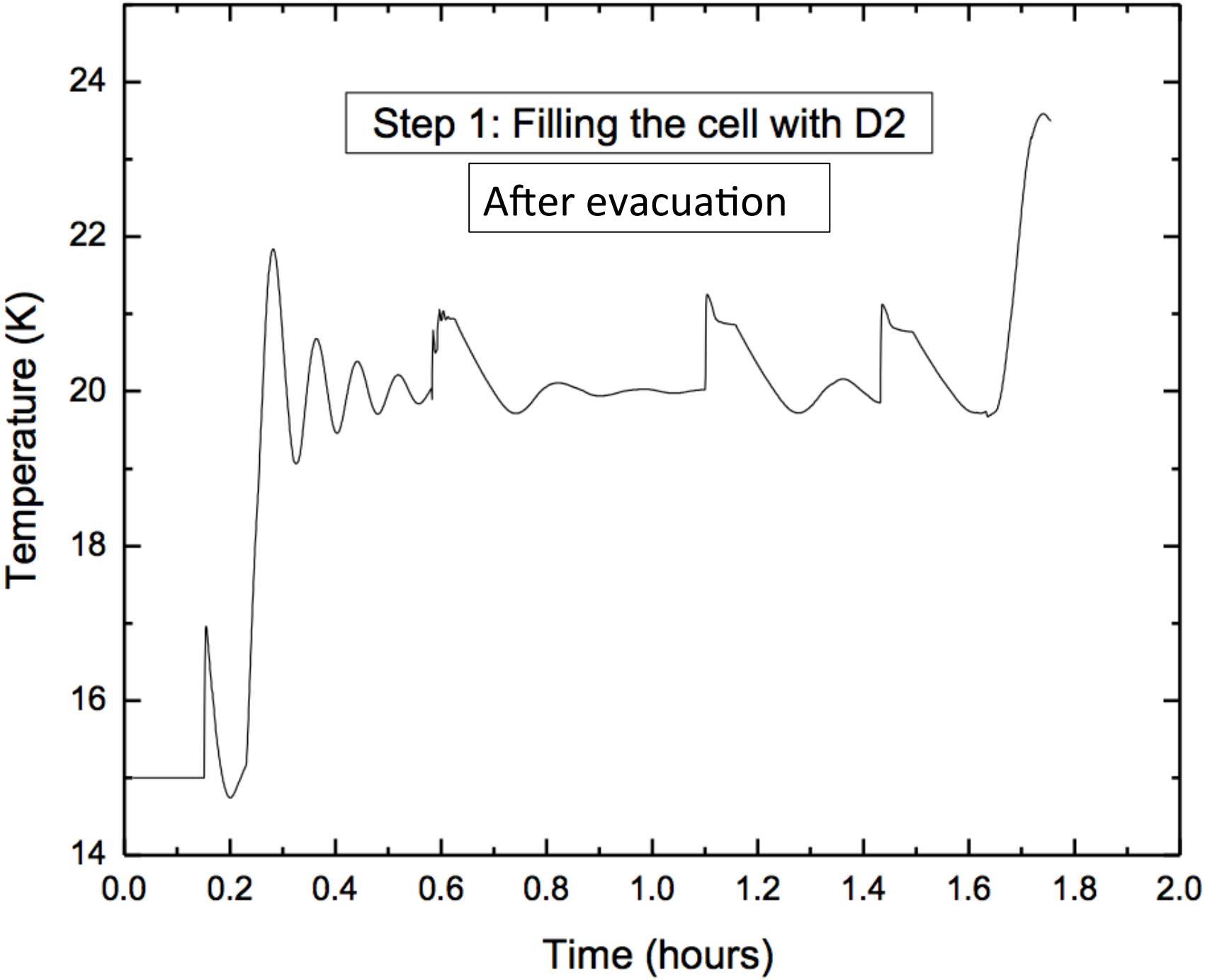
HV	mag	tilt	HFW	WD	det	10 µm
5.00 kV	10 000 x	0 °	30.1 µm	5.2 mm	CDEM	D238-polished_ LQDH-baseline

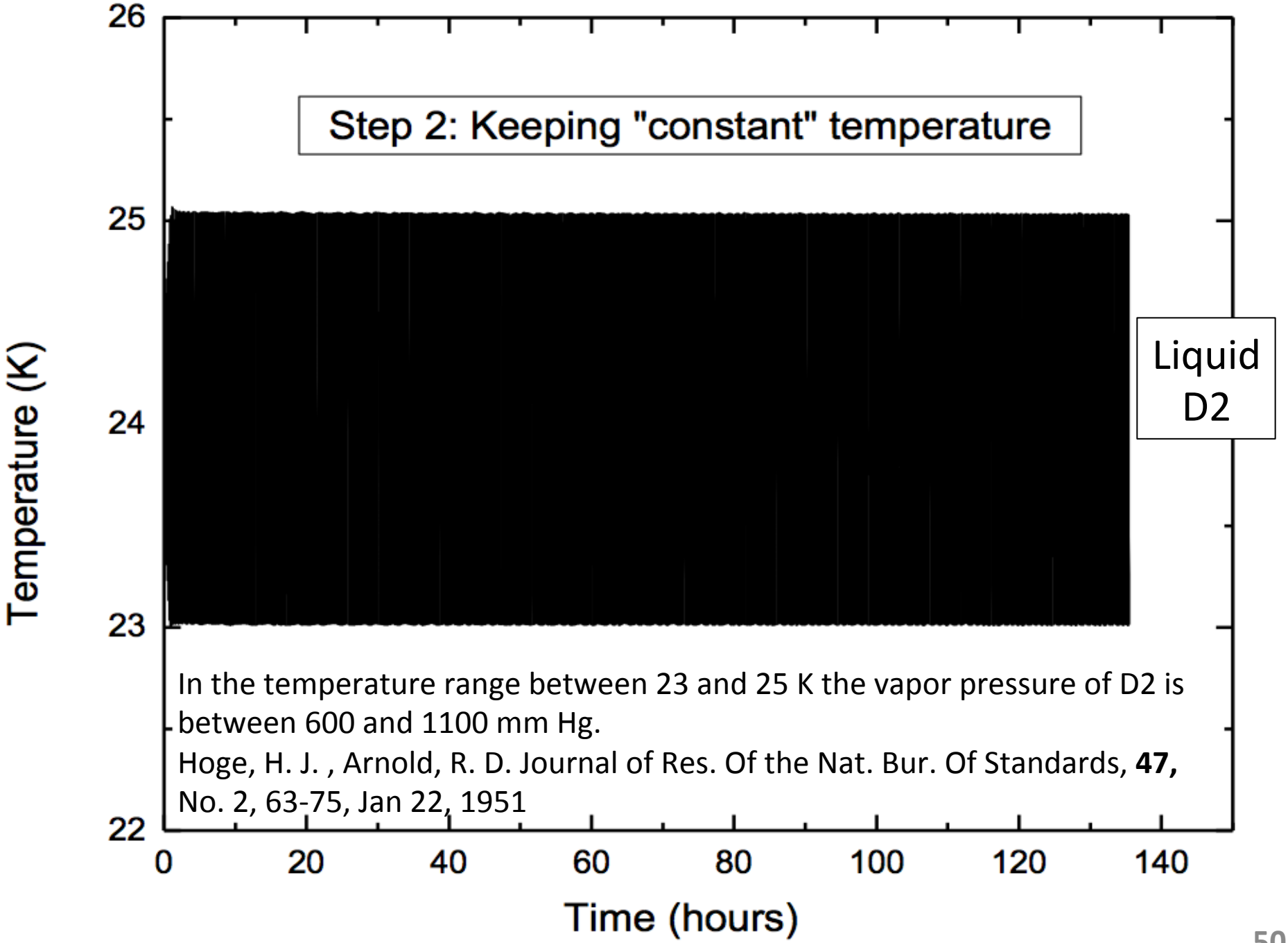

Inclusion 11
HV
5.00 kV
mag
20 000 x
tilt
0 °
HFW
15.0 µm
WD
5.2 mm
det
CDEM
5 µm
D238-polished_ LQDH-baseline


Inclusion 11
HV
5.00 kV
mag
50 000 x
tilt
0 °
HFW
6.02 µm
WD
5.1 mm
det
TLD
3 µm
D238-polished_ LQDH-baseline

D2 exposure, Sergei Kuchejev

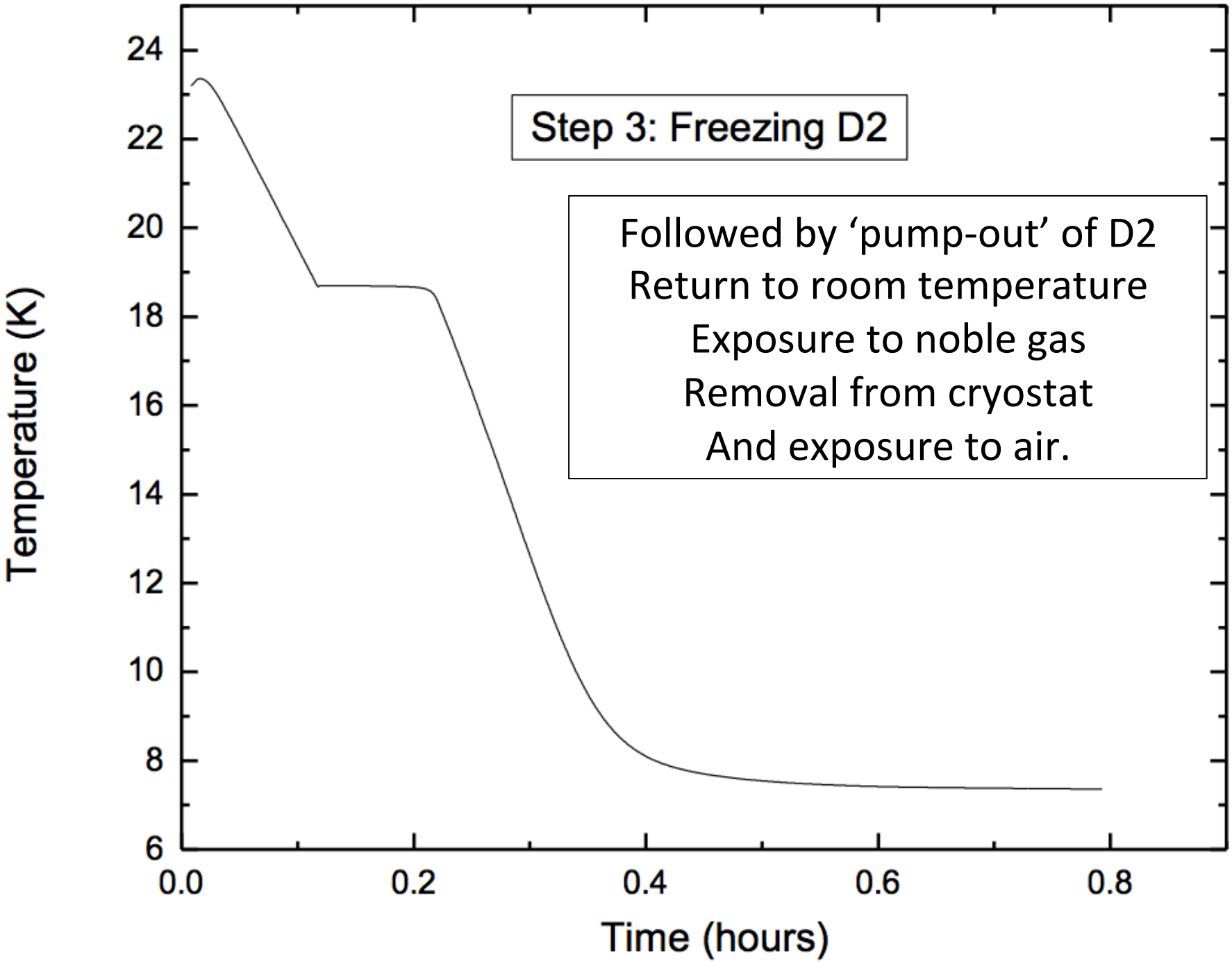
- The uranium sample was put into a cryostat enclosed in a small chamber
  - Whose temperature was monitored
  - That was evacuated,
  - Then filled with liquid D_2 and held at liquid D_2 for ~135 hr (~ 6.7 days)
  - Cooled to solid D_2 temperature
    - and evacuated to removed D2
- Re-exposed to air and removed from the small chamber


Step 1: Filling the cell with D2
After evacuation
Temperature (K)
Time (hours)
24
22
20
18
16
14
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0



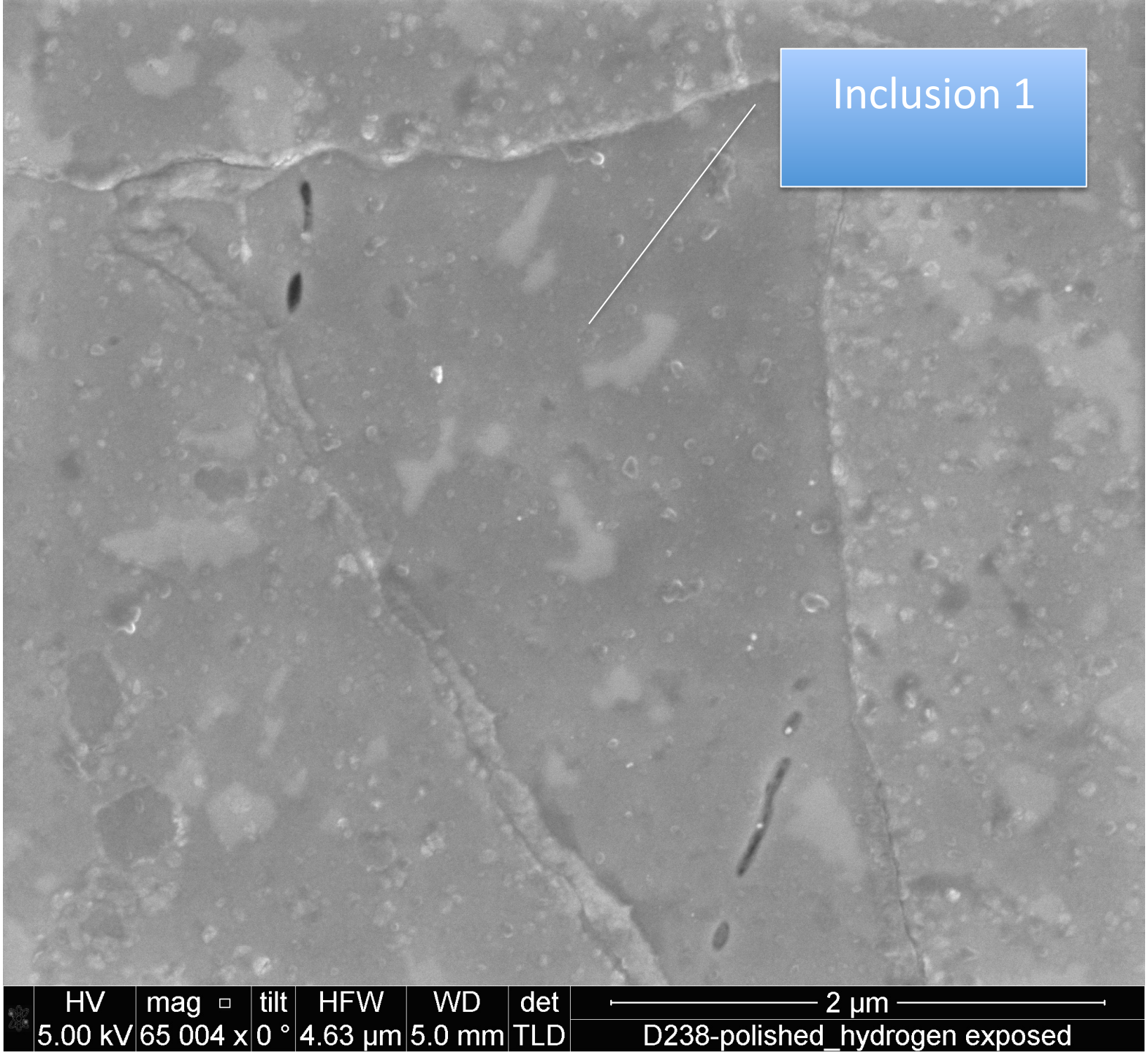
In the temperature range between 23 and 25 K the vapor pressure of D2 is between 600 and 1100 mm Hg.

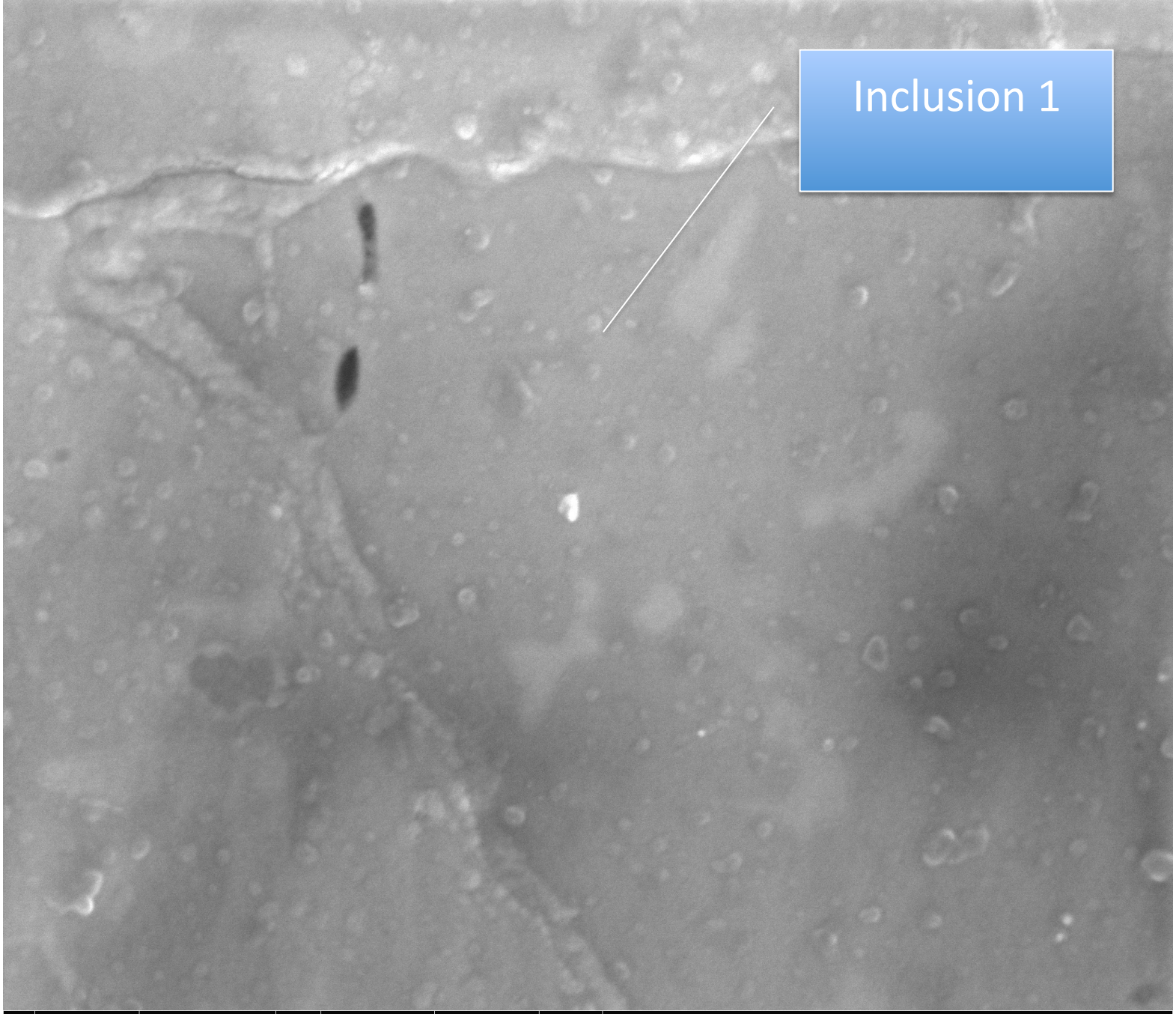
Hoge, H. J. , Arnold, R. D. Journal of Res. Of the Nat. Bur. Of Standards, **47,** No. 2, 63-75, Jan 22, 1951


Step 3: Freezing D2
Followed by 'pump-out' of D2
Return to room temperature
Exposure to noble gas
Removal from cryostat
And exposure to air.
Temperature (K)
Time (hours)
24
22
20
18
16
14
12
10
8
6
0.0
0.2
0.4
0.6
0.8

SEM images AFTER exposure

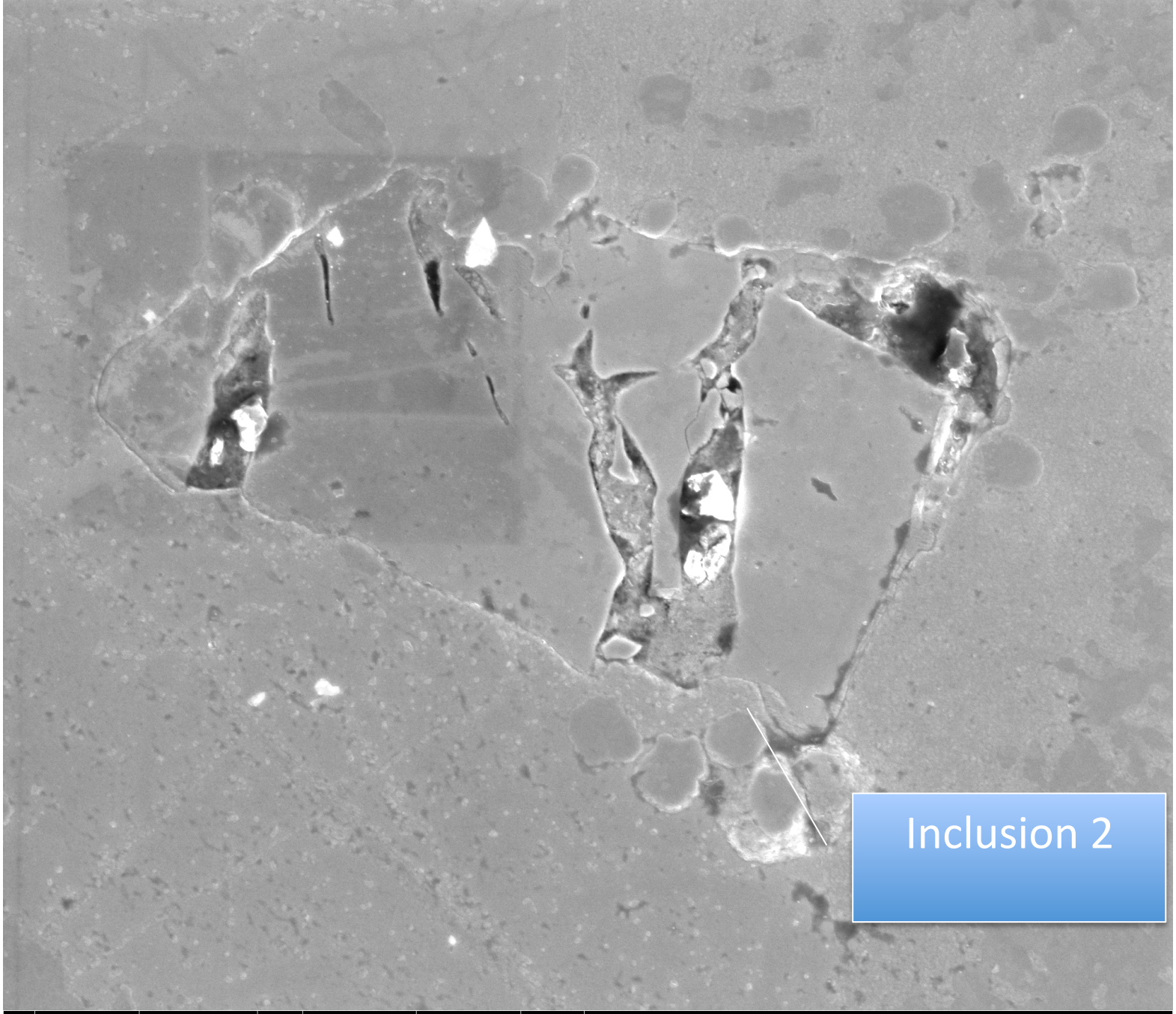
- U-hydriding occurs preferentially at inclusions
- A number of inclusions imaged before excosure were again imaged
- HOWEVER, NOT all locations could be re-located after exposure
  - Some others were imaged


Inclusion 1
HV
5.00 kV
mag
65 004 x
tilt
0 °
HFW
4.63 µm
WD
5.0 mm
det
TLD
2 µm
D238-polished_hydrogen exposed

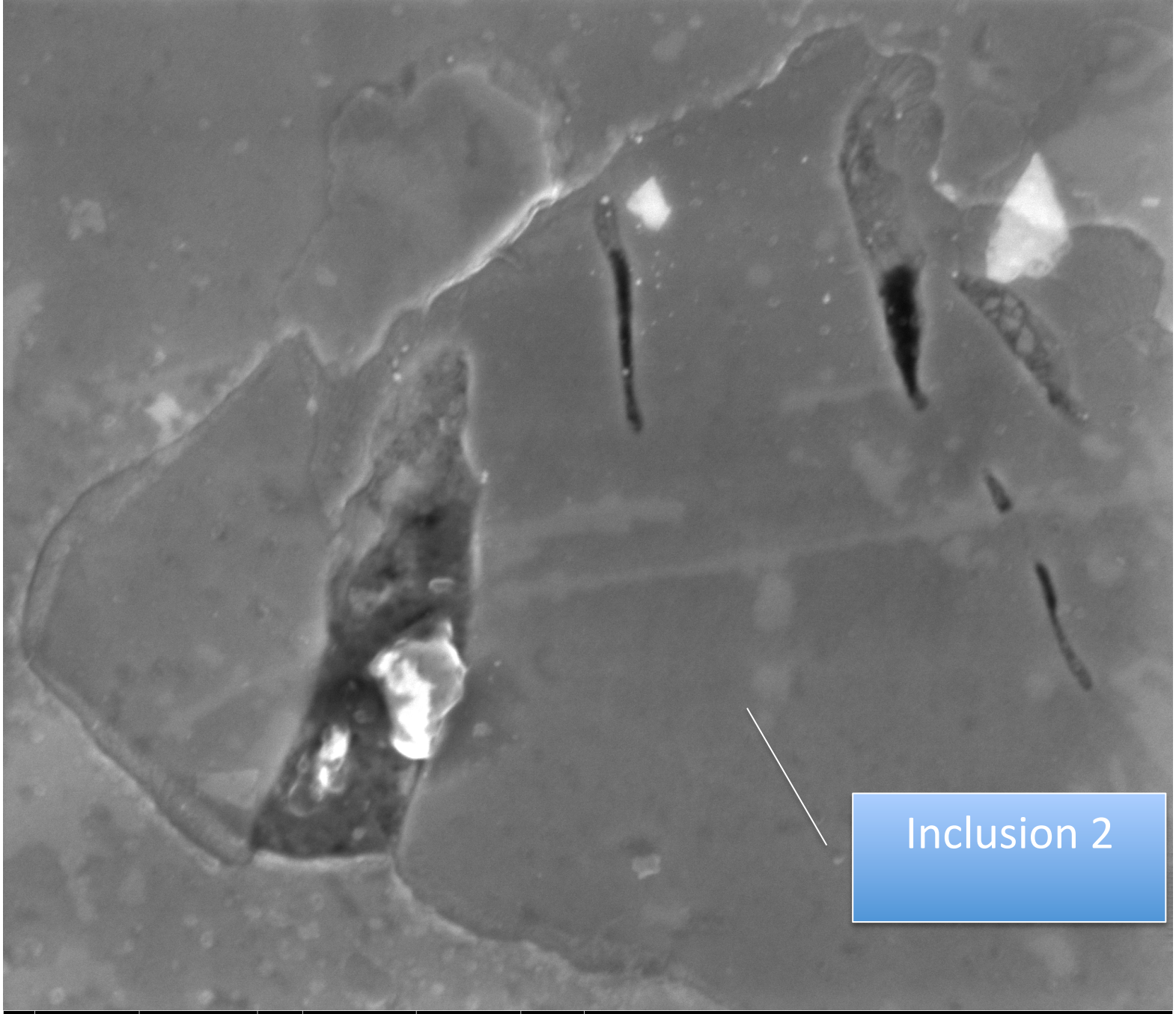


HV	mag	tilt	HFW	WD	det	1 µm
5.00 kV	100 000 x	0 °	3.01 µm	5.0 mm	TLD	D238-polished_hydrogen exposed

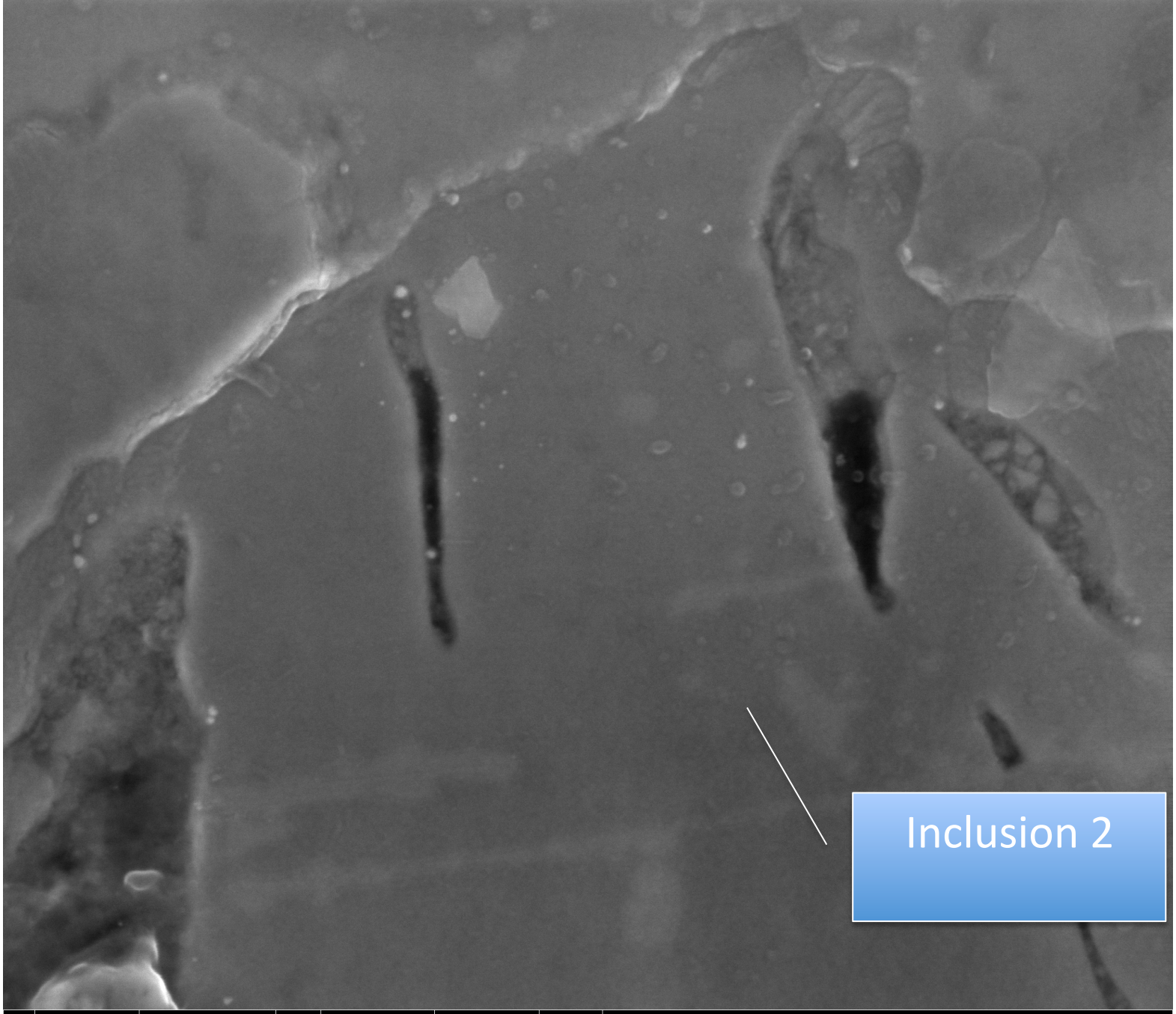
HV	mag	tilt	HFW	WD	det	10 µm
5.00 kV	12 002 x	0 °	25.1 µm	5.2 mm	CDEM	D238-polished_hydrogen exposed



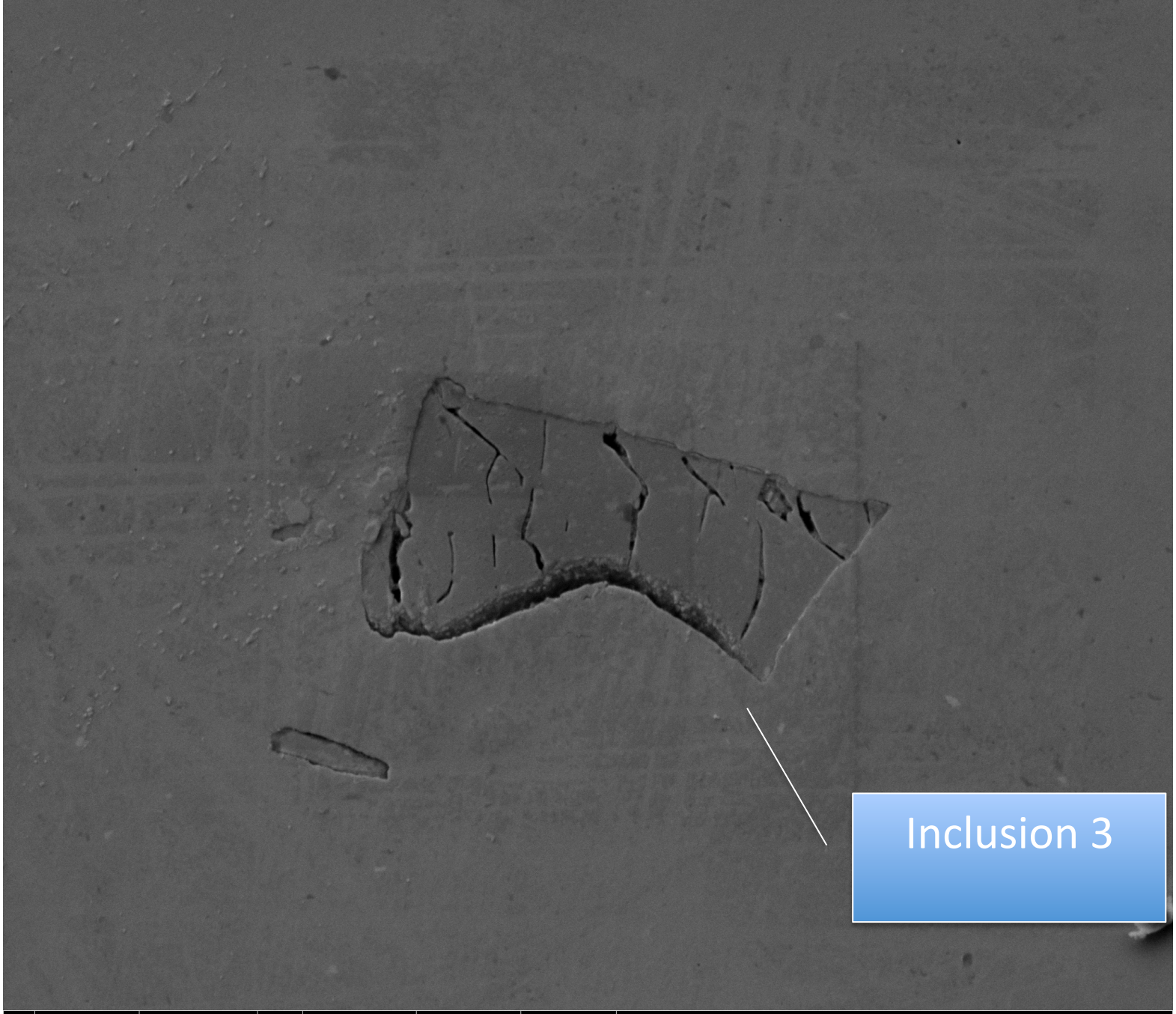
HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	25 000 x	0 °	12.0 µm	5.0 mm	TLD	D238-polished_hydrogen exposed



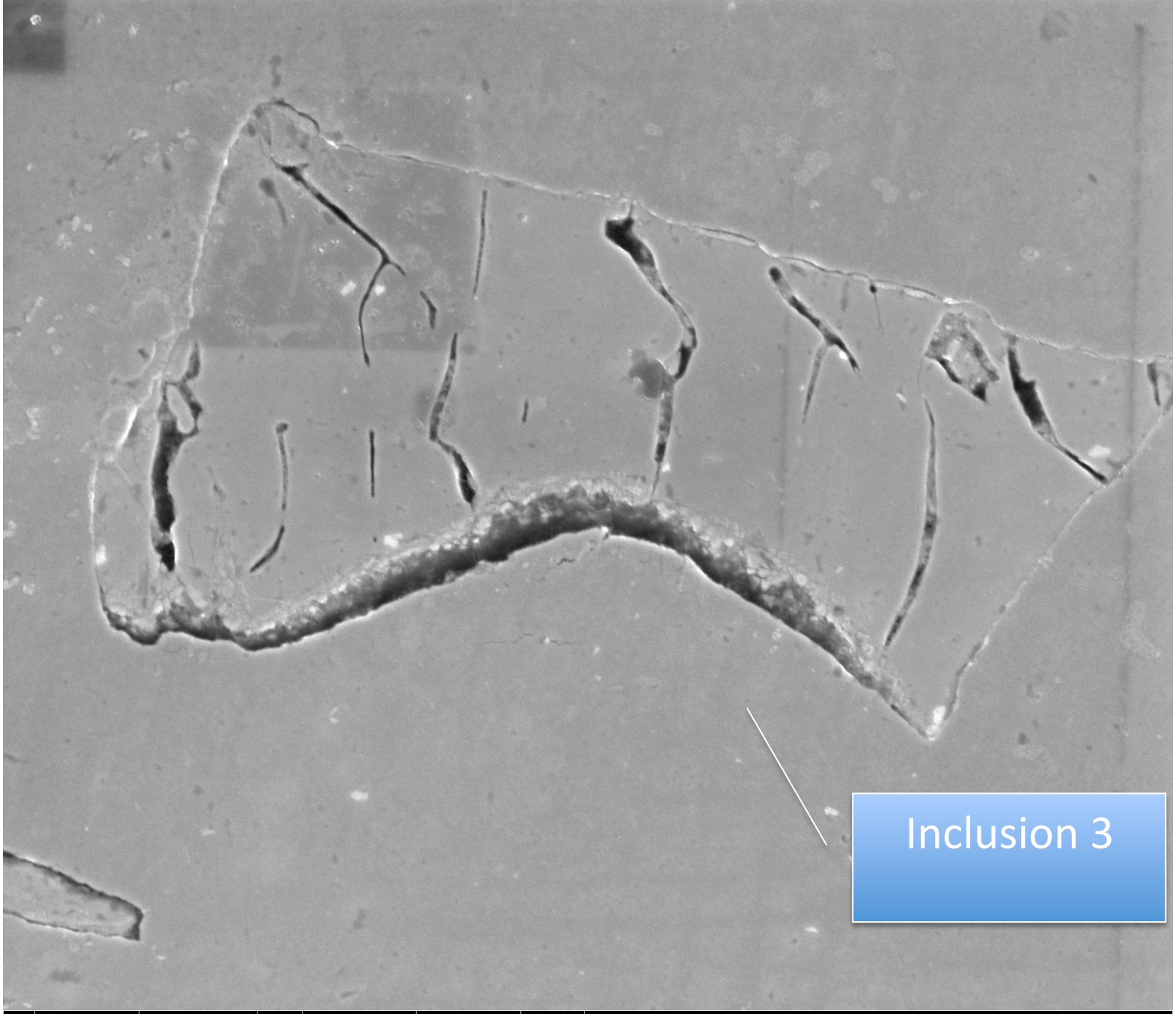
HV	mag	tilt	HFW	WD	det	2 µm
5.00 kV	64 976 x	0 °	4.63 µm	5.0 mm	TLD	D238-polished_hydrogen exposed



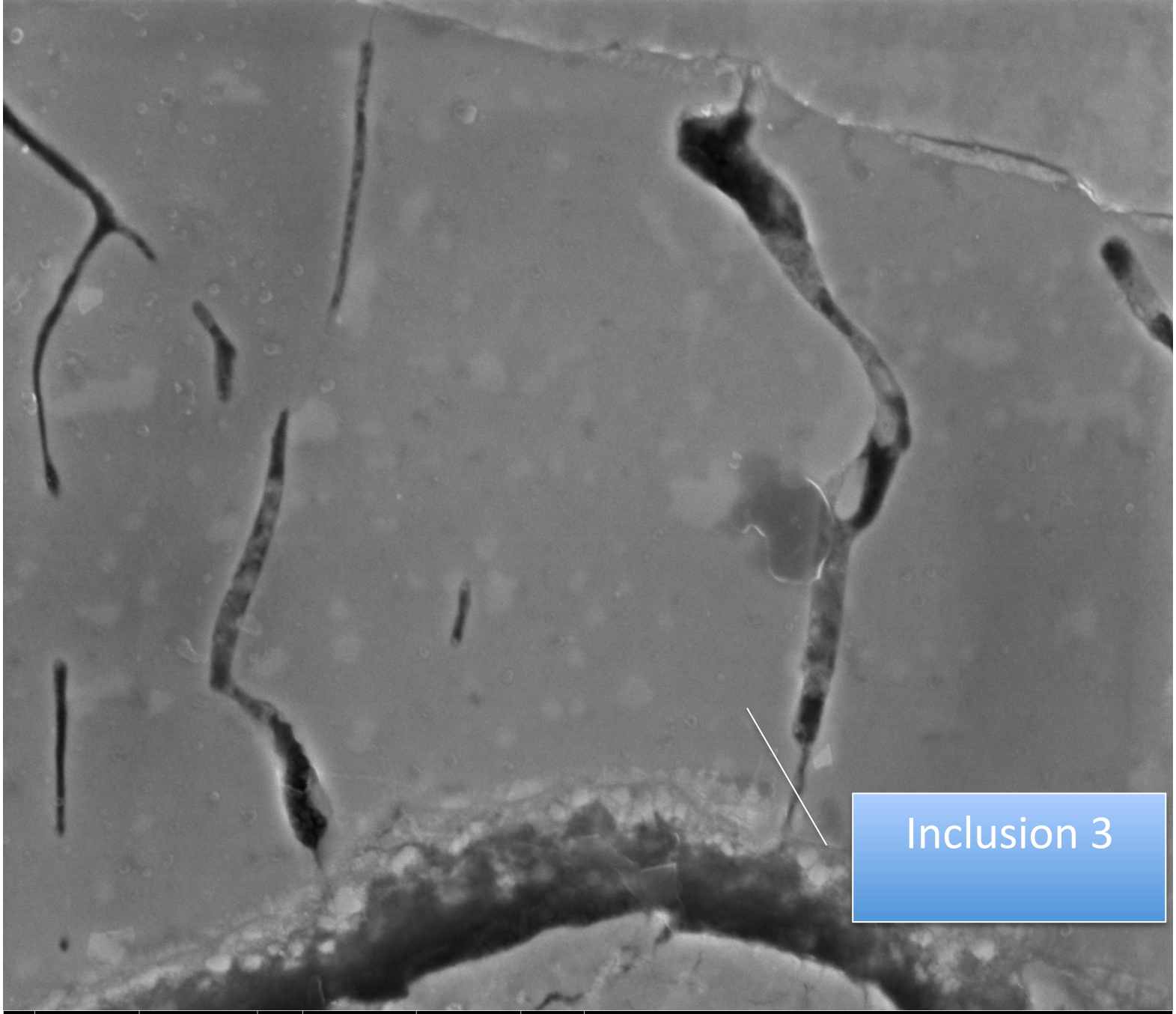
HV	mag	tilt	HFW	WD	det	1 µm
5.00 kV	100 000 x	0 °	3.01 µm	5.0 mm	TLD	D238-polished_hydrogen exposed



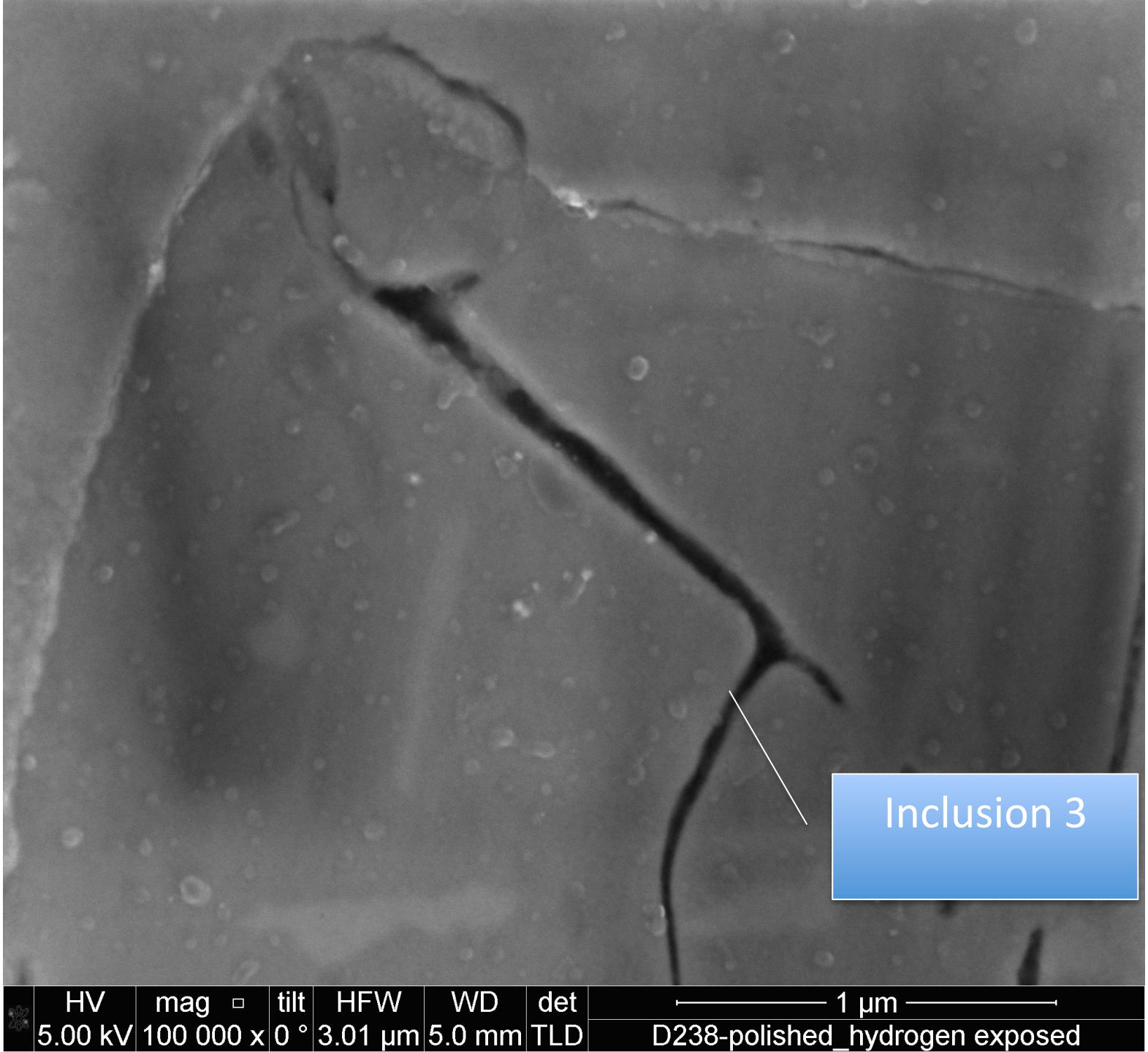
HV	mag	tilt	HFW	WD	det	10 µm
5.00 kV	11 997 x	0 °	25.1 µm	5.2 mm	CDEM	D238-polished_hydrogen exposed



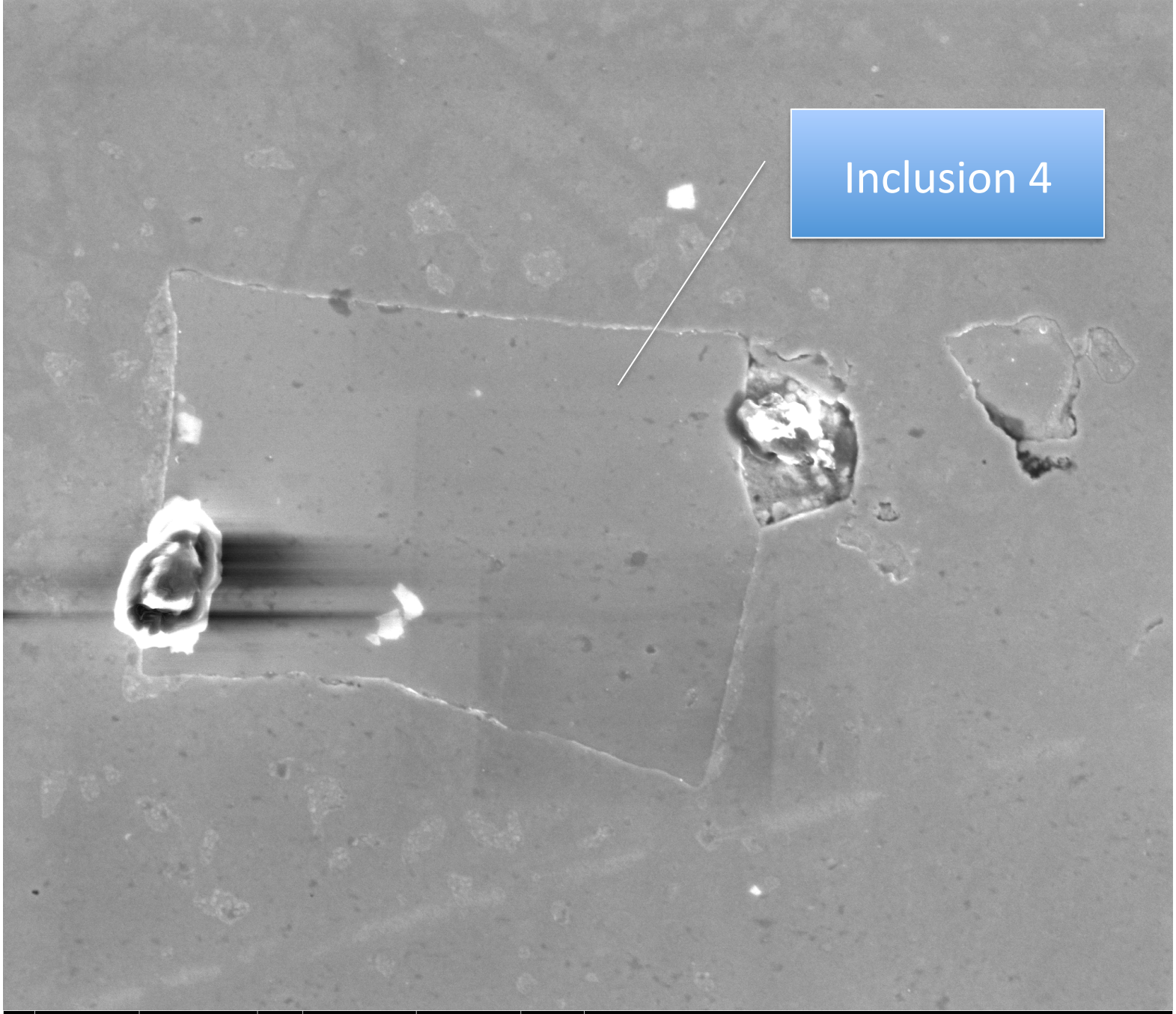
HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	25 000 x	0 °	12.0 µm	5.0 mm	TLD	D238-polished_hydrogen exposed



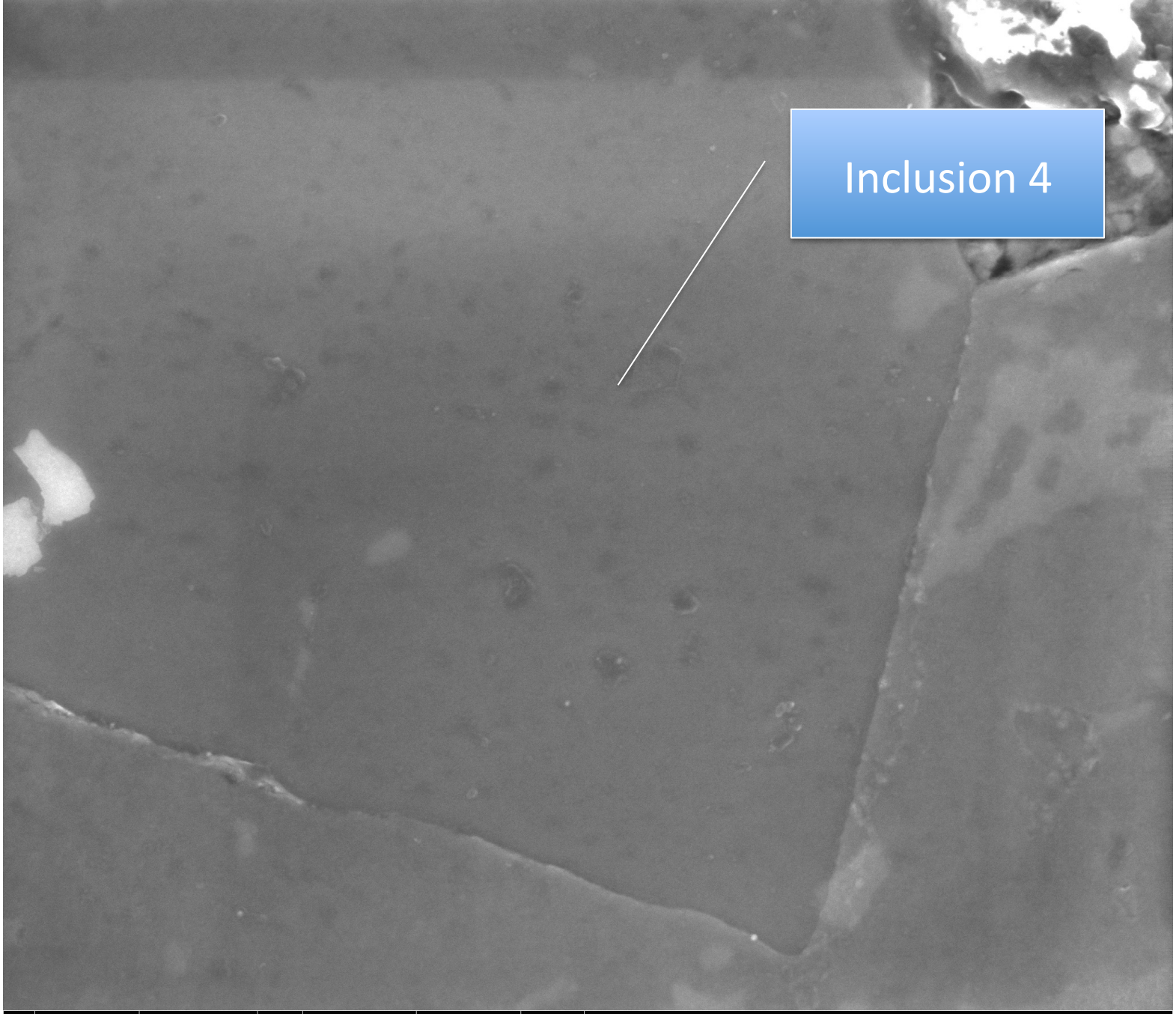
HV	mag	tilt	HFW	WD	det	2 µm
5.00 kV	65 000 x	0 °	4.63 µm	5.0 mm	TLD	D238-polished_hydrogen exposed


Inclusion 3
HV
5.00 kV
mag
100 000 x
tilt
0 °
HFW
3.01 µm
WD
5.0 mm
det
TLD
1 µm
D238-polished_hydrogen exposed

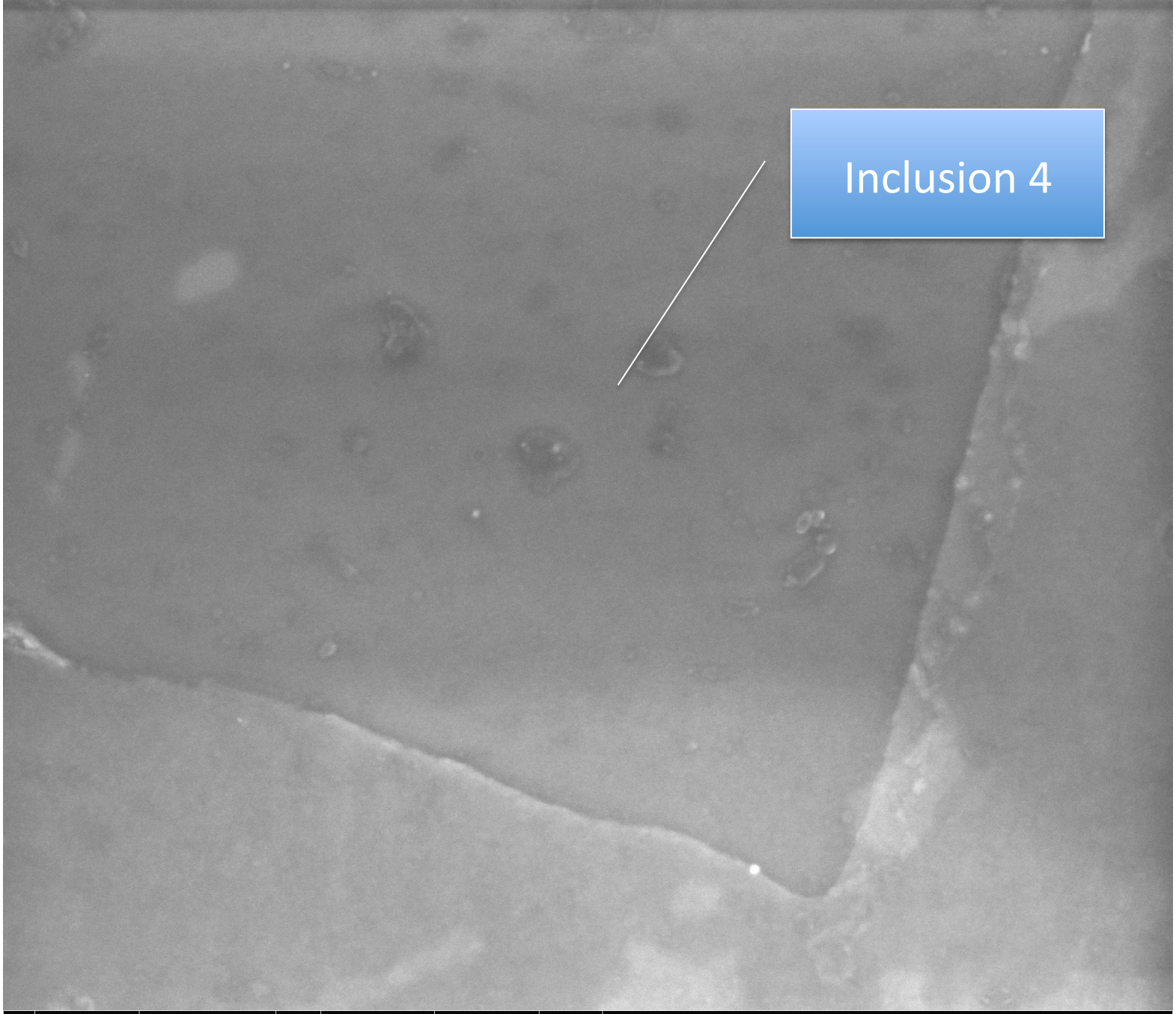
HV	mag	tilt	HFW	WD	det	10 µm
5.00 kV	12 003 x	0 °	25.1 µm	5.2 mm	CDEM	D238-polished_hydrogen exposed



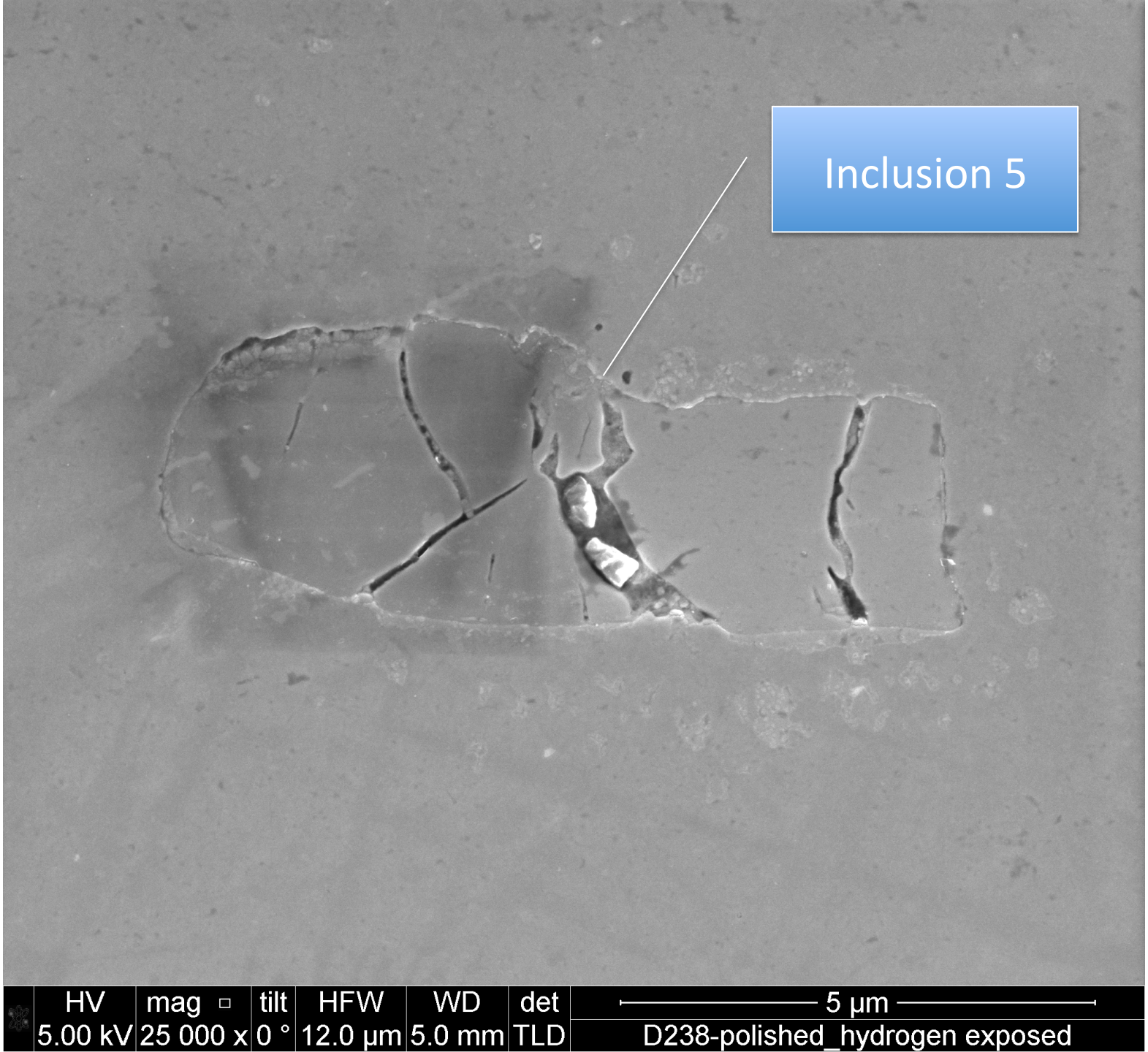
HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	25 000 x	0 °	12.0 µm	5.0 mm	TLD	D238-polished_hydrogen exposed

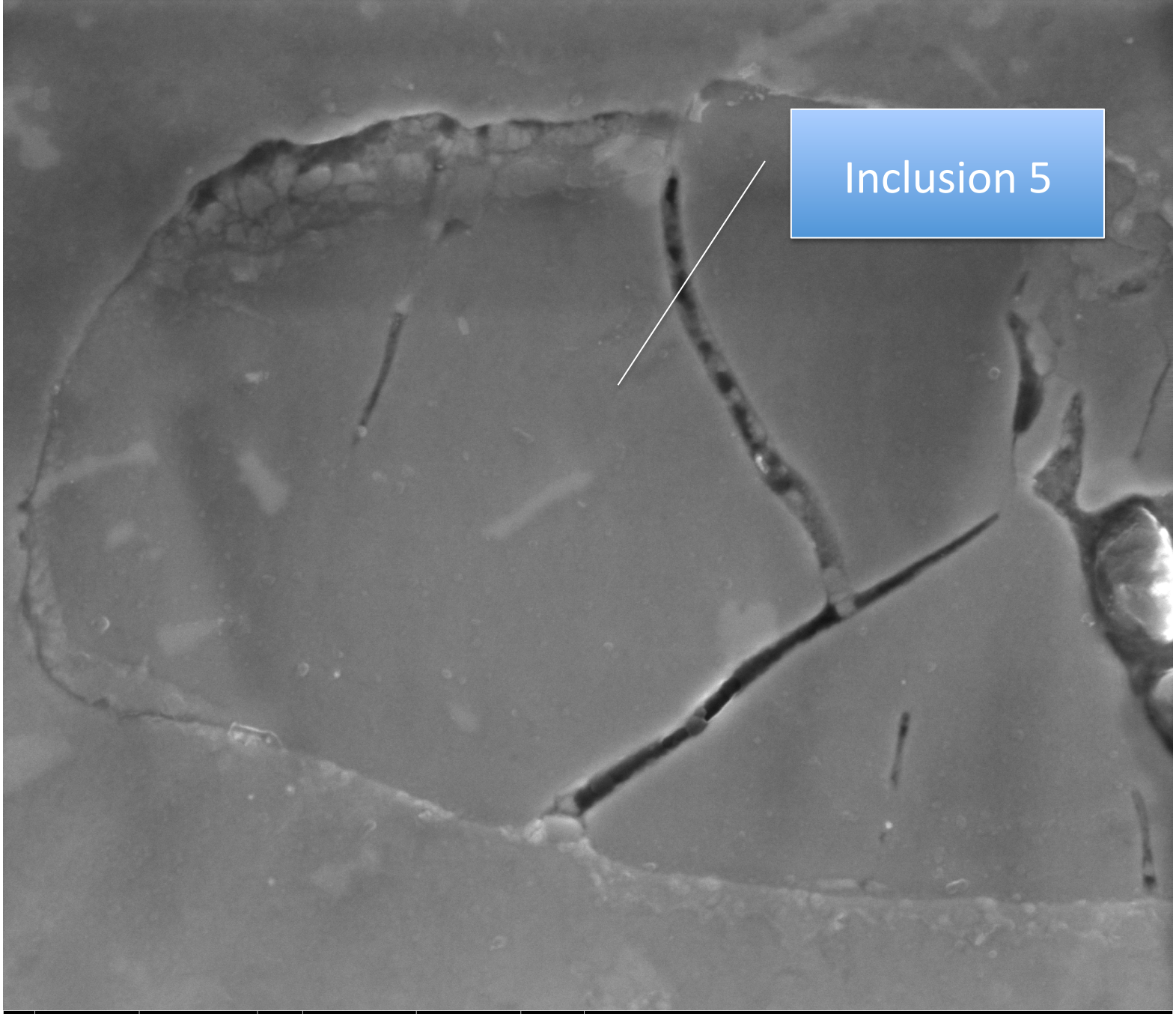


HV	mag	tilt	HFW	WD	det	2 µm
5.00 kV	65 000 x	0 °	4.63 µm	5.0 mm	TLD	D238-polished_hydrogen exposed

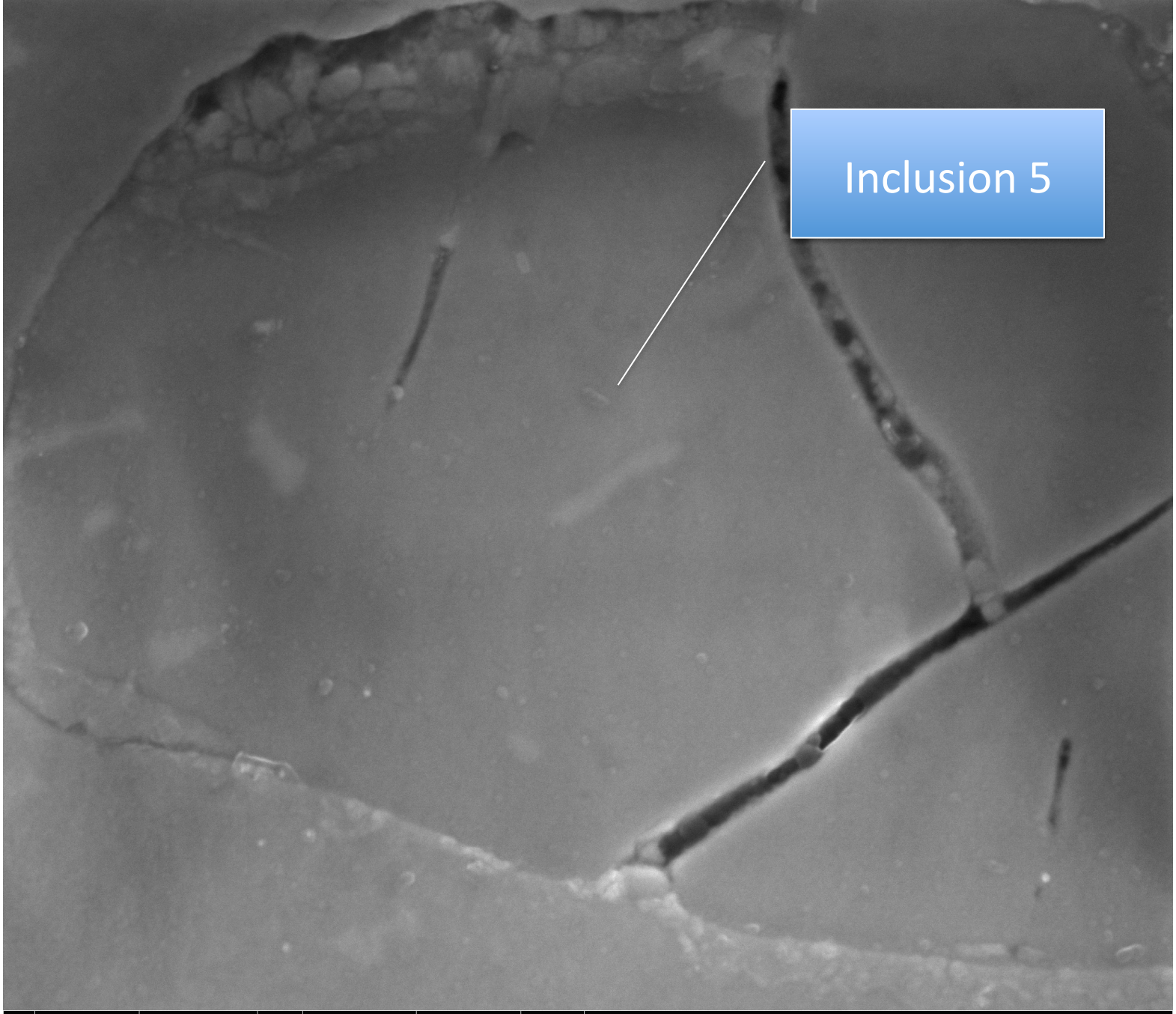


HV	mag	tilt	HFW	WD	det	1 µm
5.00 kV	100 000 x	0 °	3.01 µm	5.0 mm	TLD	D238-polished_hydrogen exposed


Inclusion 5
HV
5.00 kV
mag
25 000 x
tilt
0 °
HFW
12.0 µm
WD
5.0 mm
det
TLD
5 µm
D238-polished_hydrogen exposed



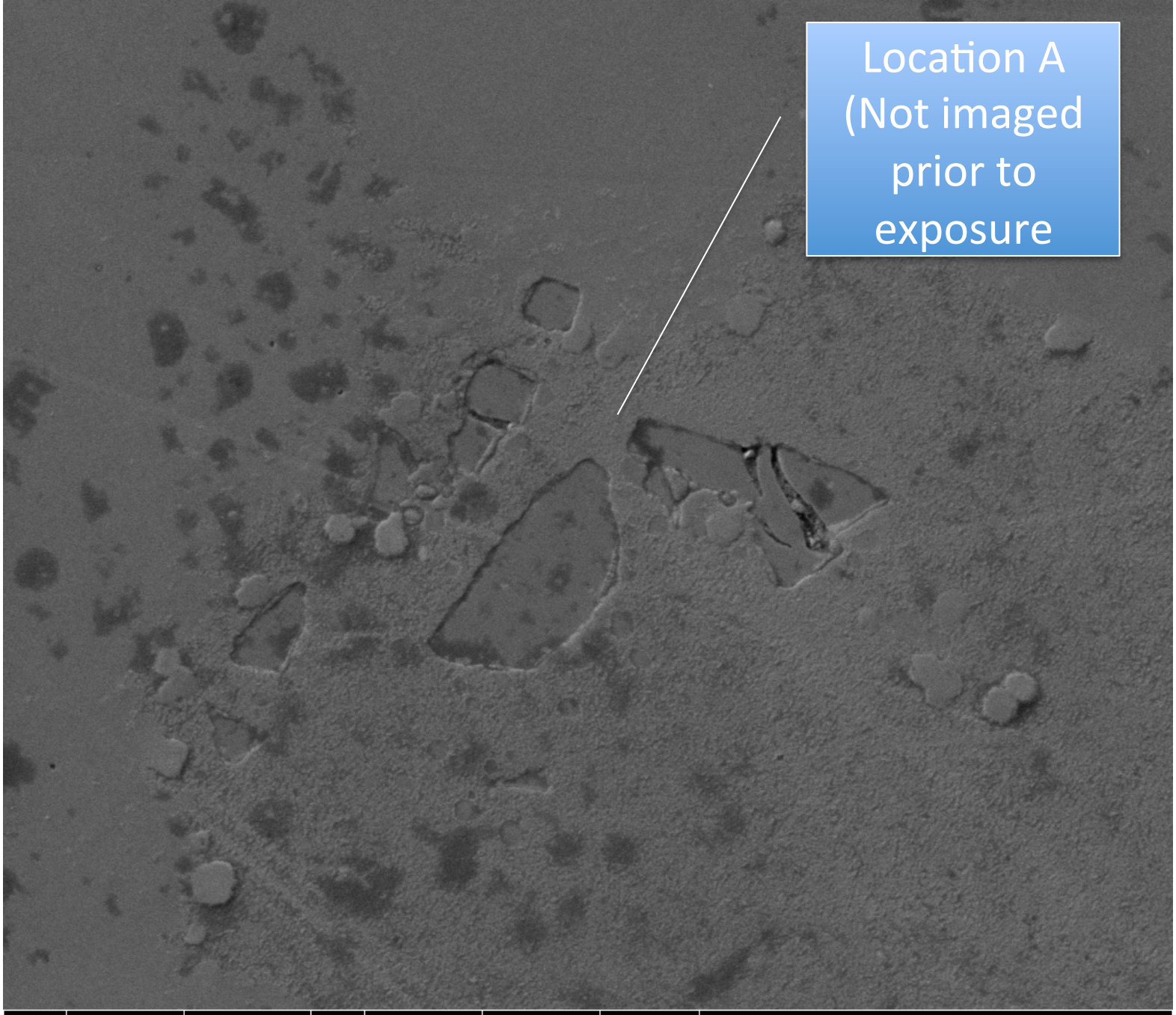
HV	mag	tilt	HFW	WD	det	2 µm
5.00 kV	65 000 x	0 °	4.63 µm	5.0 mm	TLD	D238-polished_hydrogen exposed



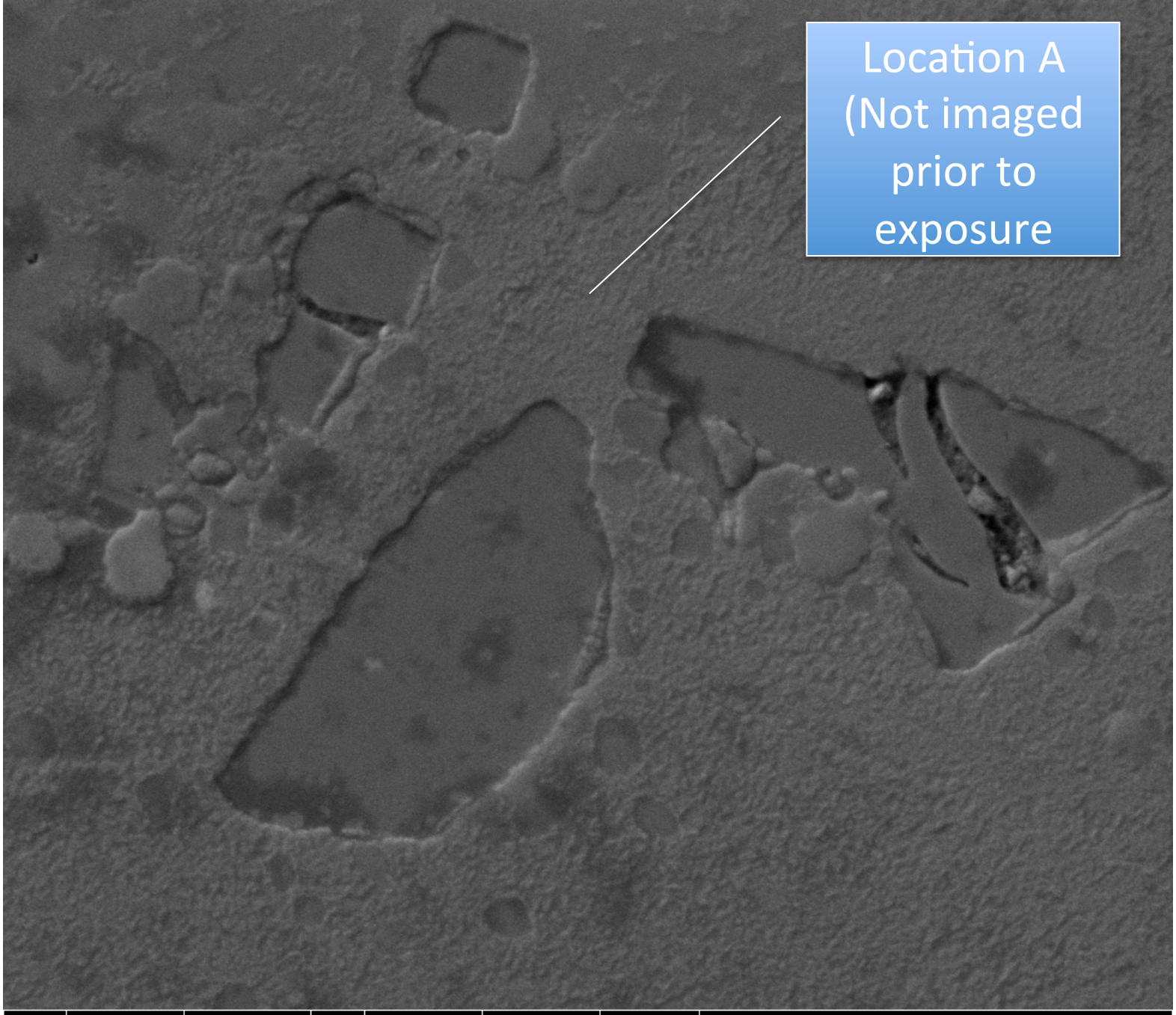
HV	mag	tilt	HFW	WD	det	1 µm
5.00 kV	80 000 x	0 °	3.76 µm	5.0 mm	TLD	D238-polished_hydrogen exposed

Additional Inclusions,

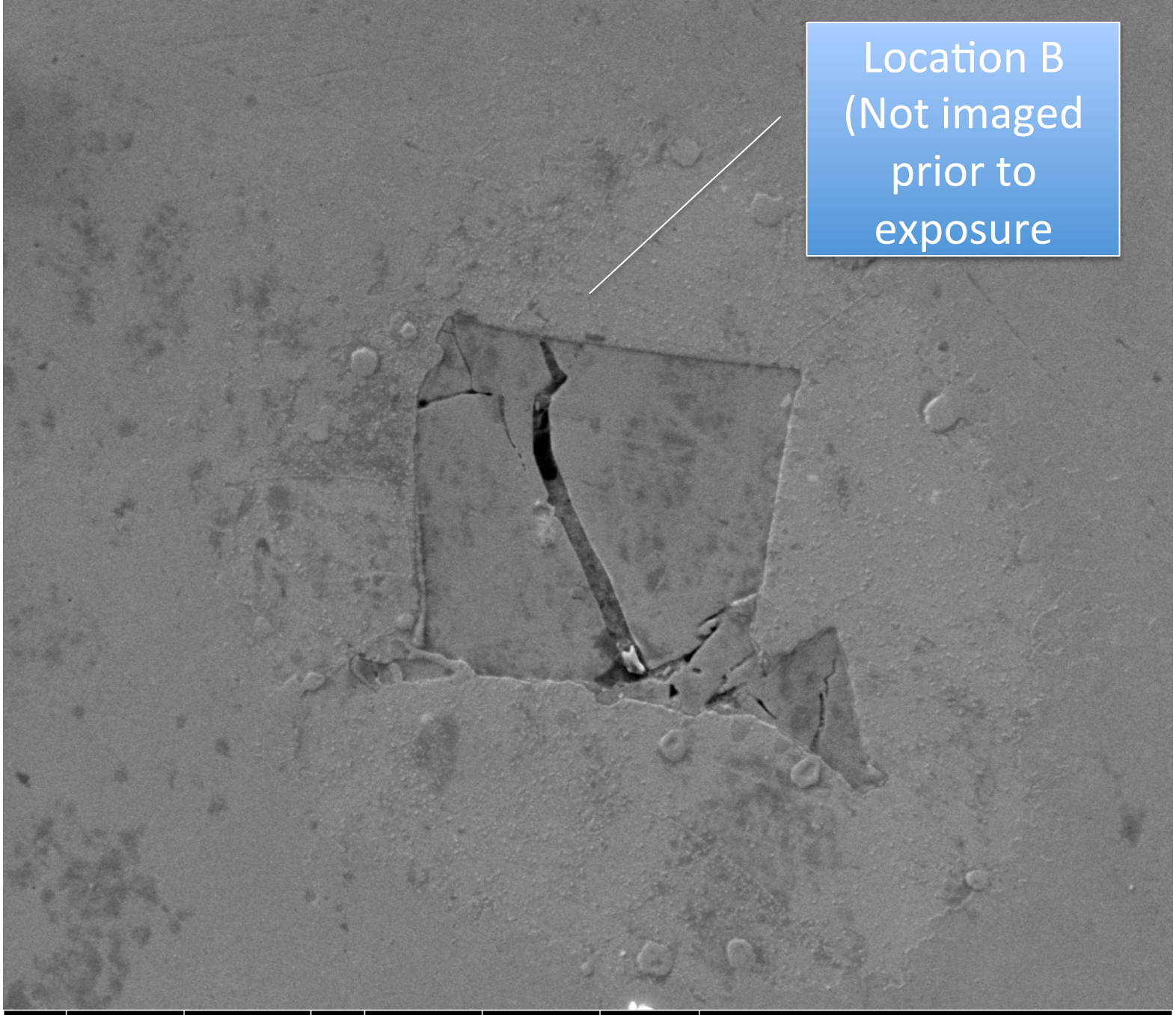
NOT imaged before exposure.

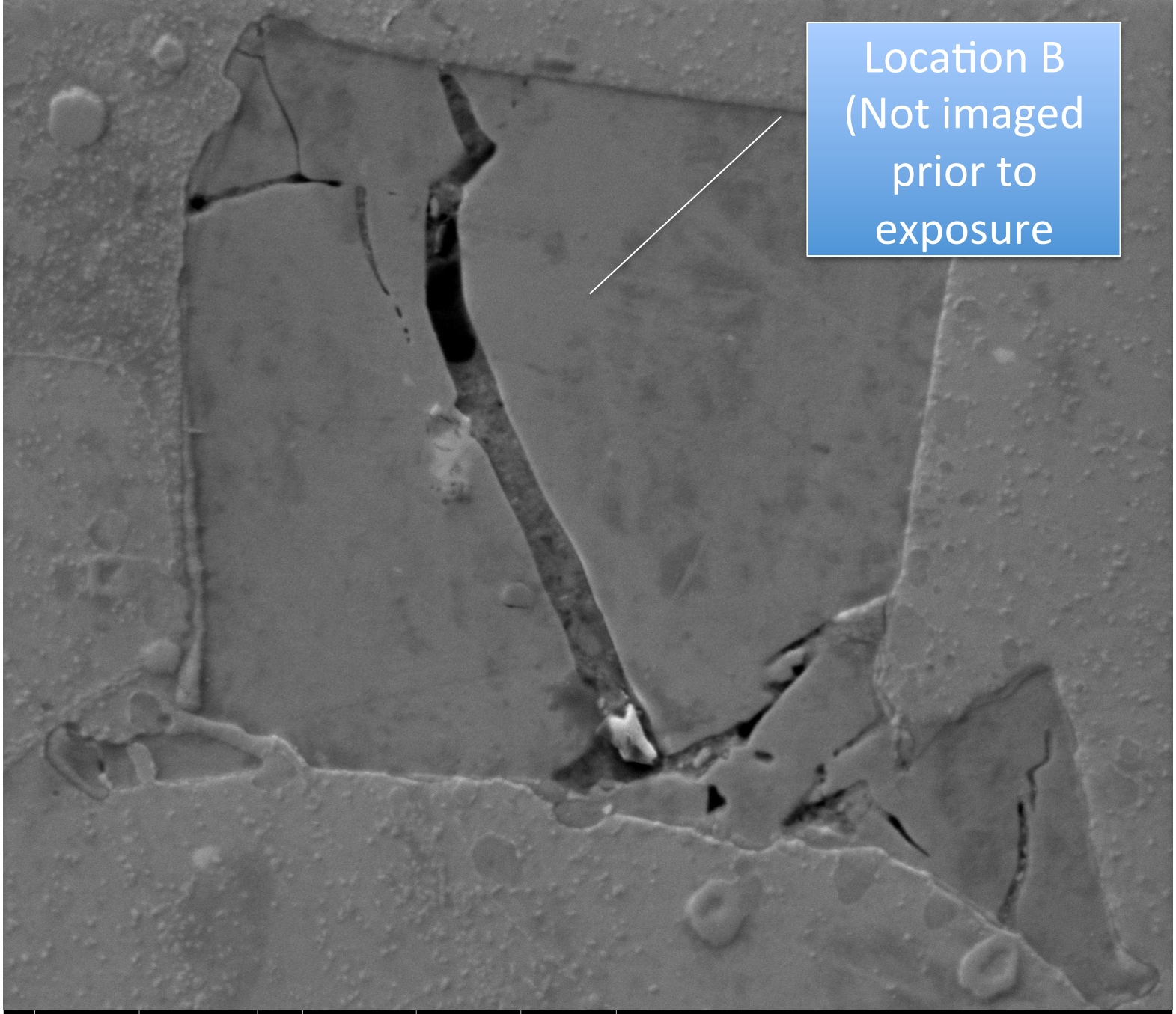


HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	12 000 x	0 °	25.1 µm	5.2 mm	CDEM	D238-polished_hydrogen exposed

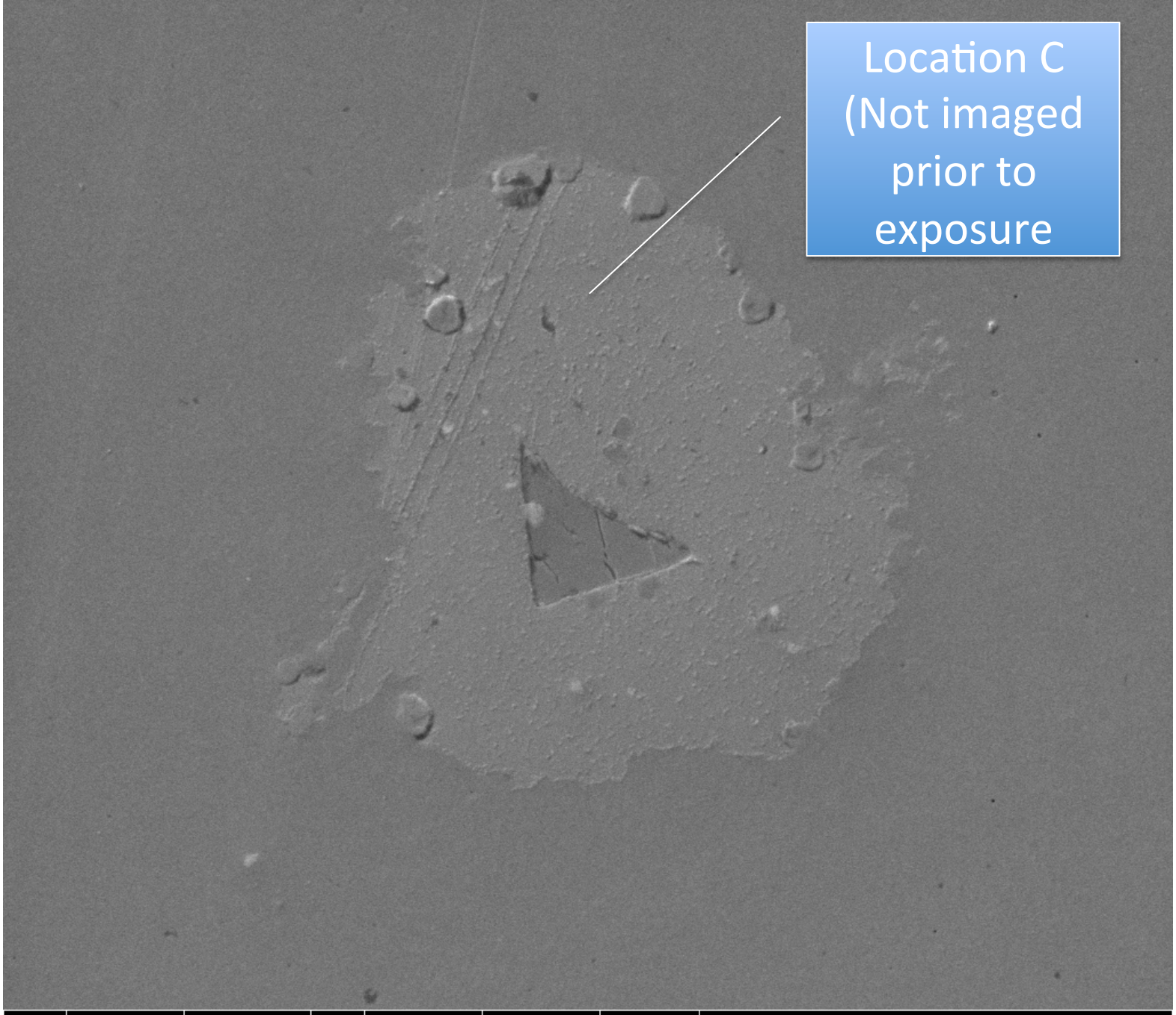


HV	mag	tilt	HFW	WD	det	4 µm
5.00 kV	25 000 x	0 °	12.0 µm	5.2 mm	CDEM	D238-polished_hydrogen exposed

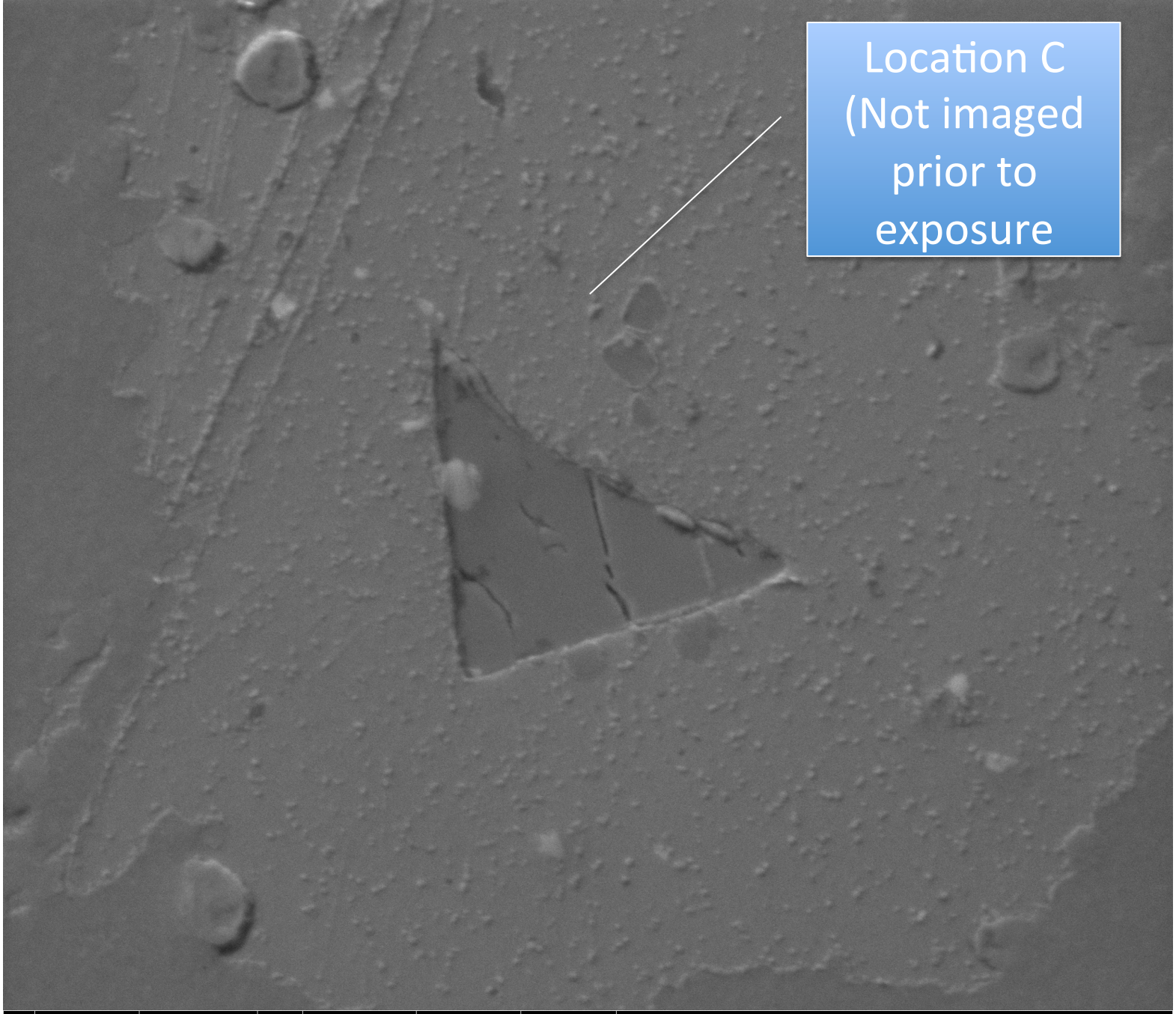

Location B
(Not imaged
prior to
exposure
HV
5.00 kV
mag
12 000 x
tilt
0 °
HFW
25.1 µm
WD
5.2 mm
det
CDEM
5 µm
D238-polished_hydrogen exposed



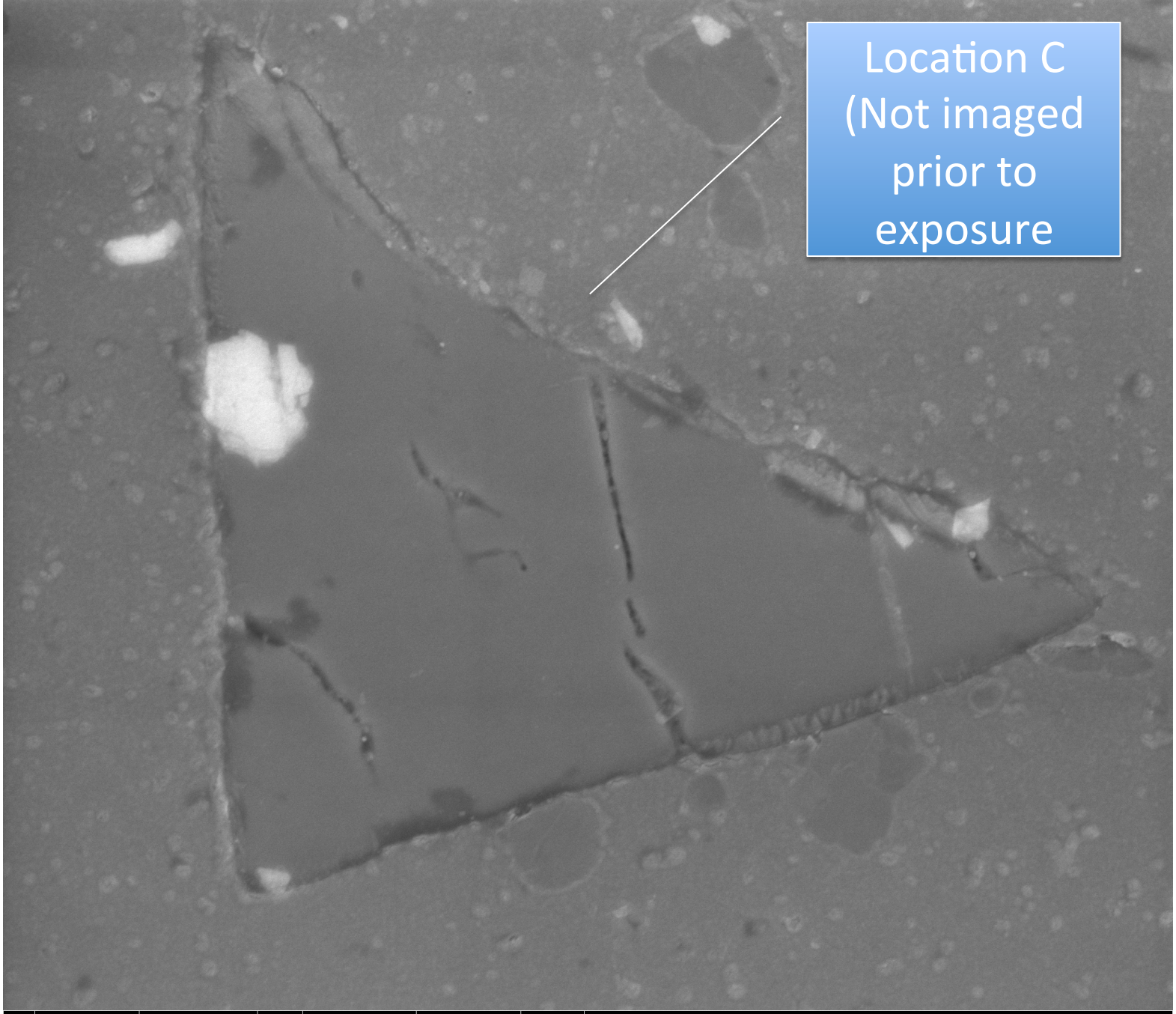
HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	25 000 x	0 °	12.0 µm	5.2 mm	CDEM	D238-polished_hydrogen exposed



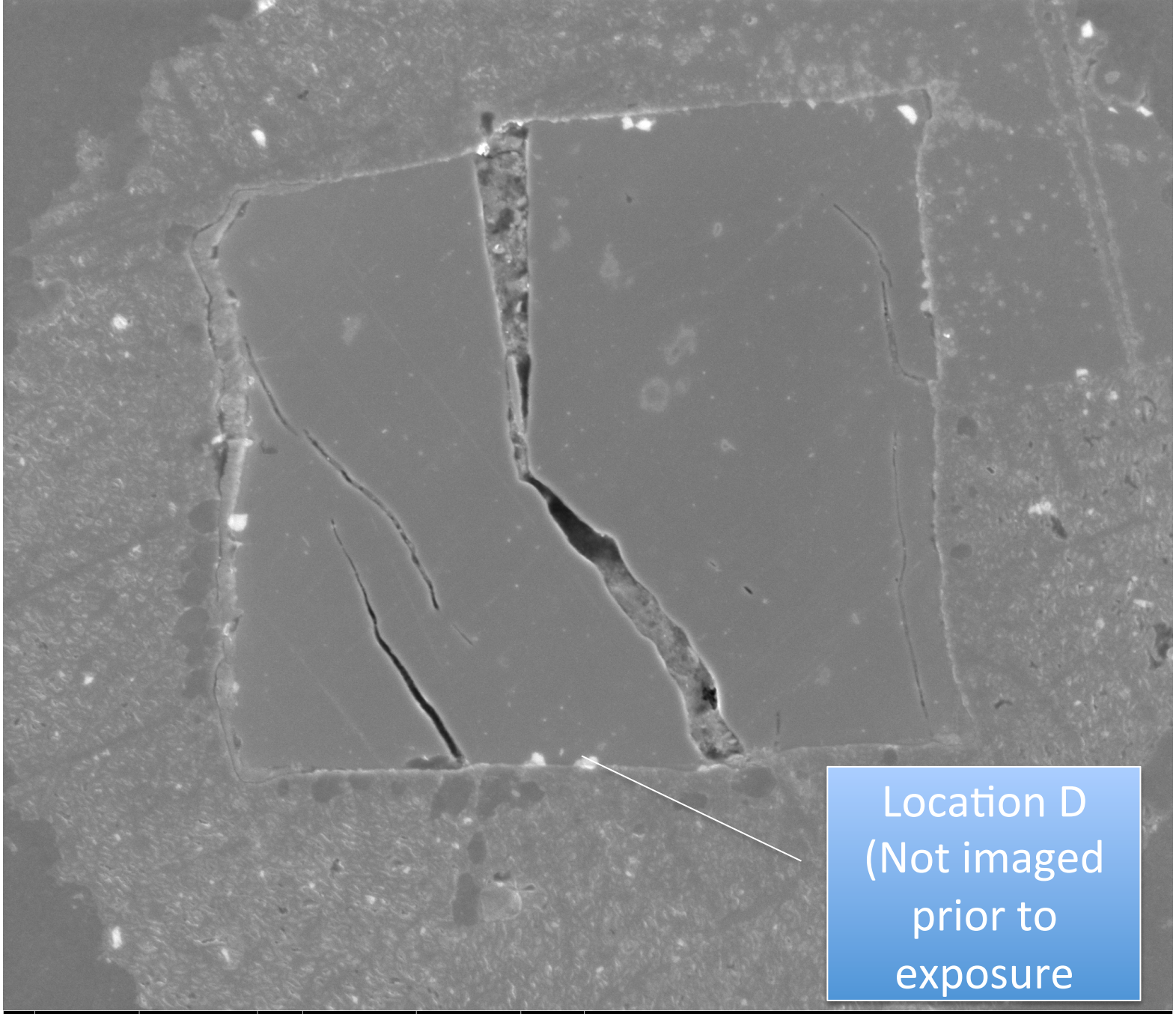
HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	12 000 x	0 °	25.1 µm	5.2 mm	CDEM	D238-polished_hydrogen exposed



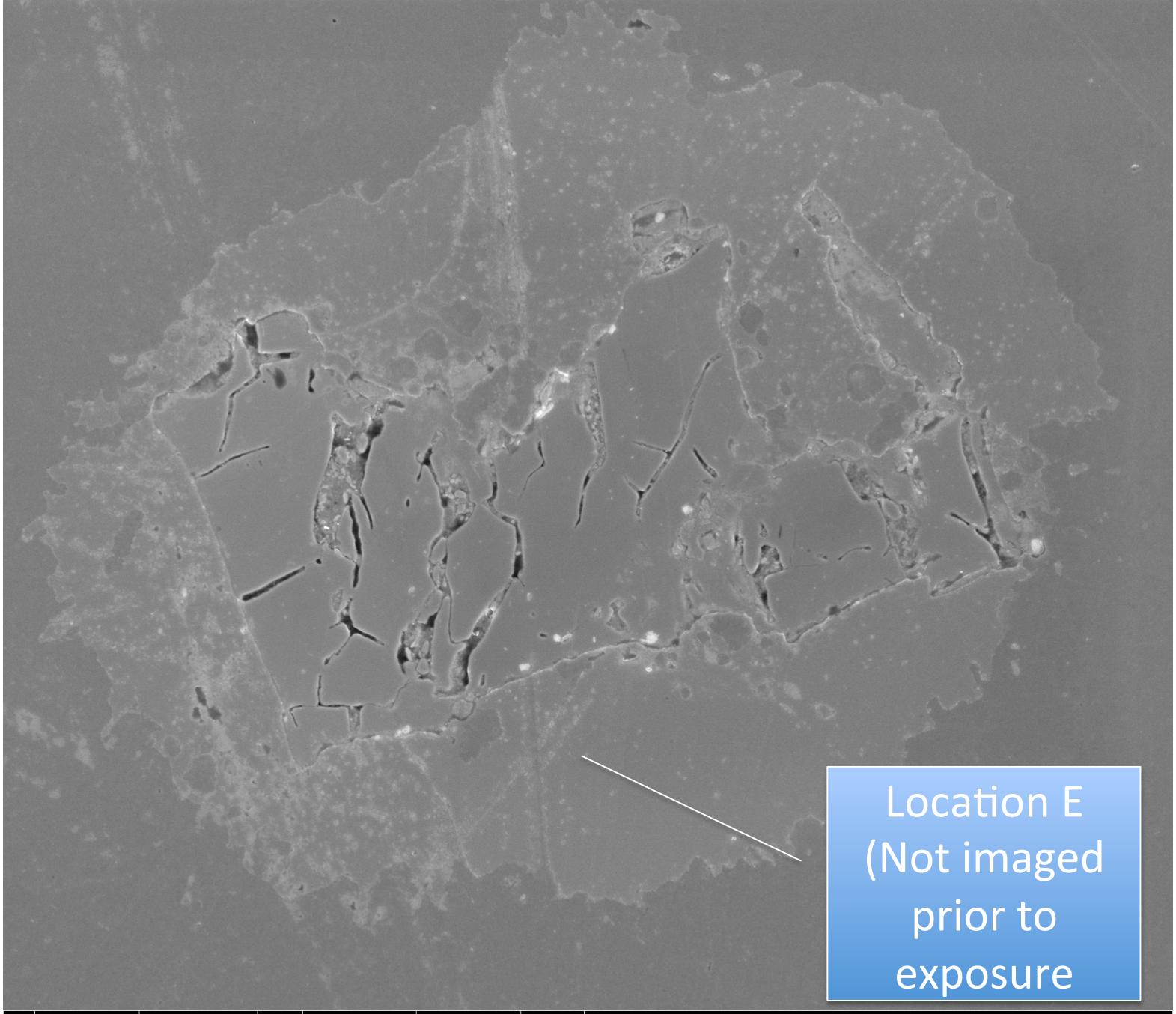
HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	25 000 x	0 °	12.0 µm	5.2 mm	CDEM	D238-polished_hydrogen exposed

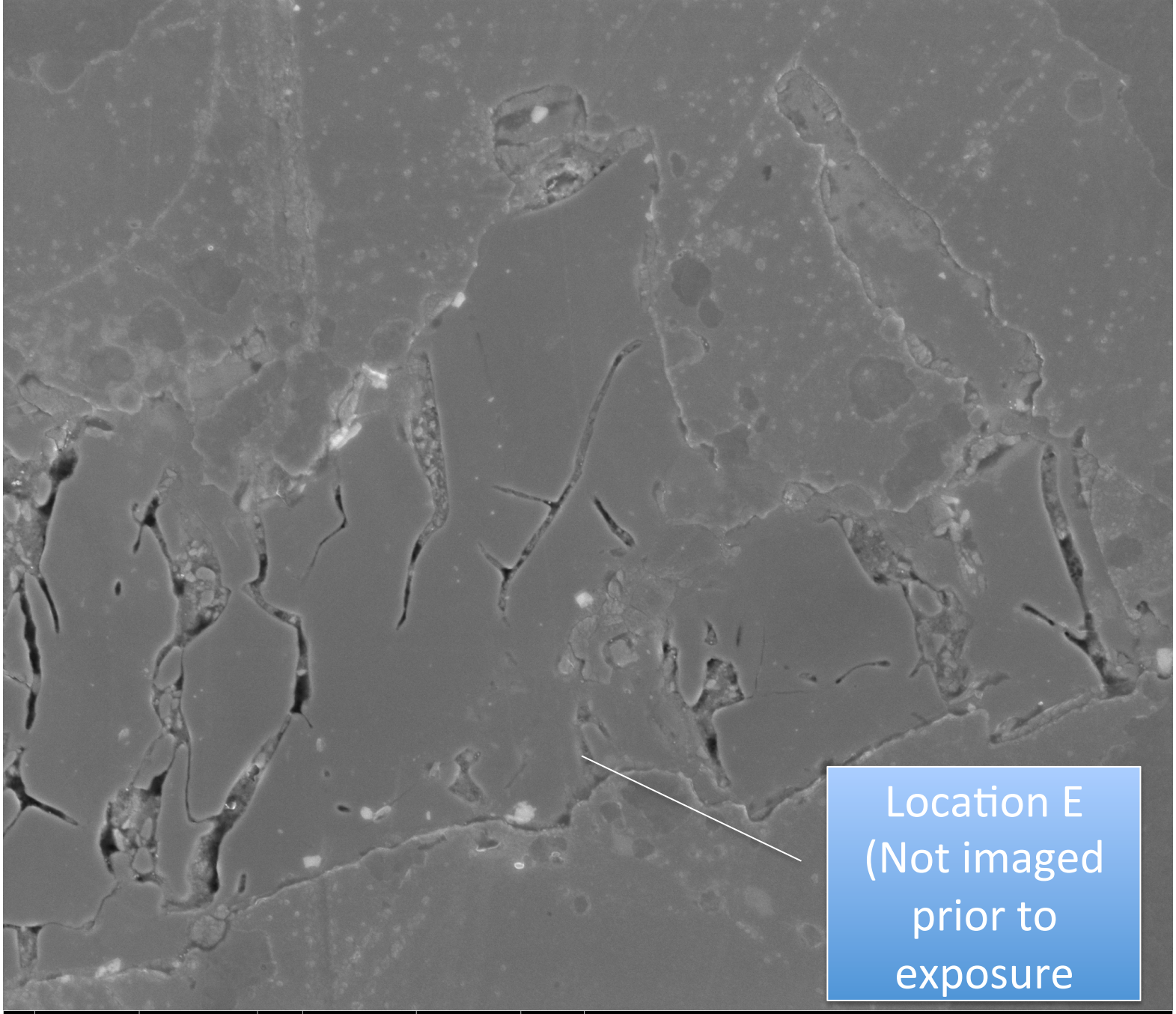


HV	mag	tilt	HFW	WD	det	2 µm
5.00 kV	65 000 x	0 °	4.63 µm	5.1 mm	TLD	D238-polished_hydrogen exposed



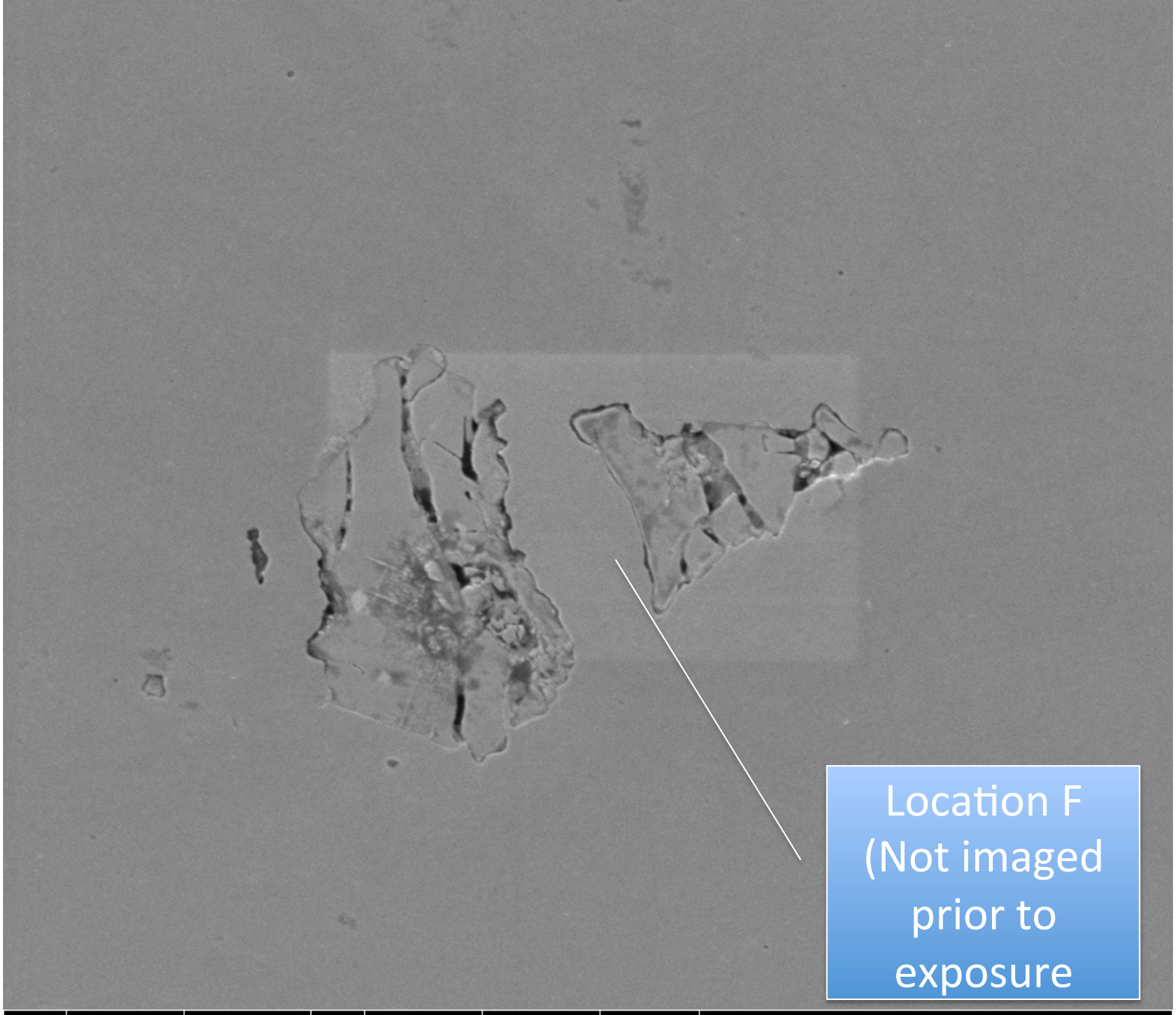
HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	25 000 x	0 °	12.0 µm	5.1 mm	TLD	D238-polished_hydrogen exposed

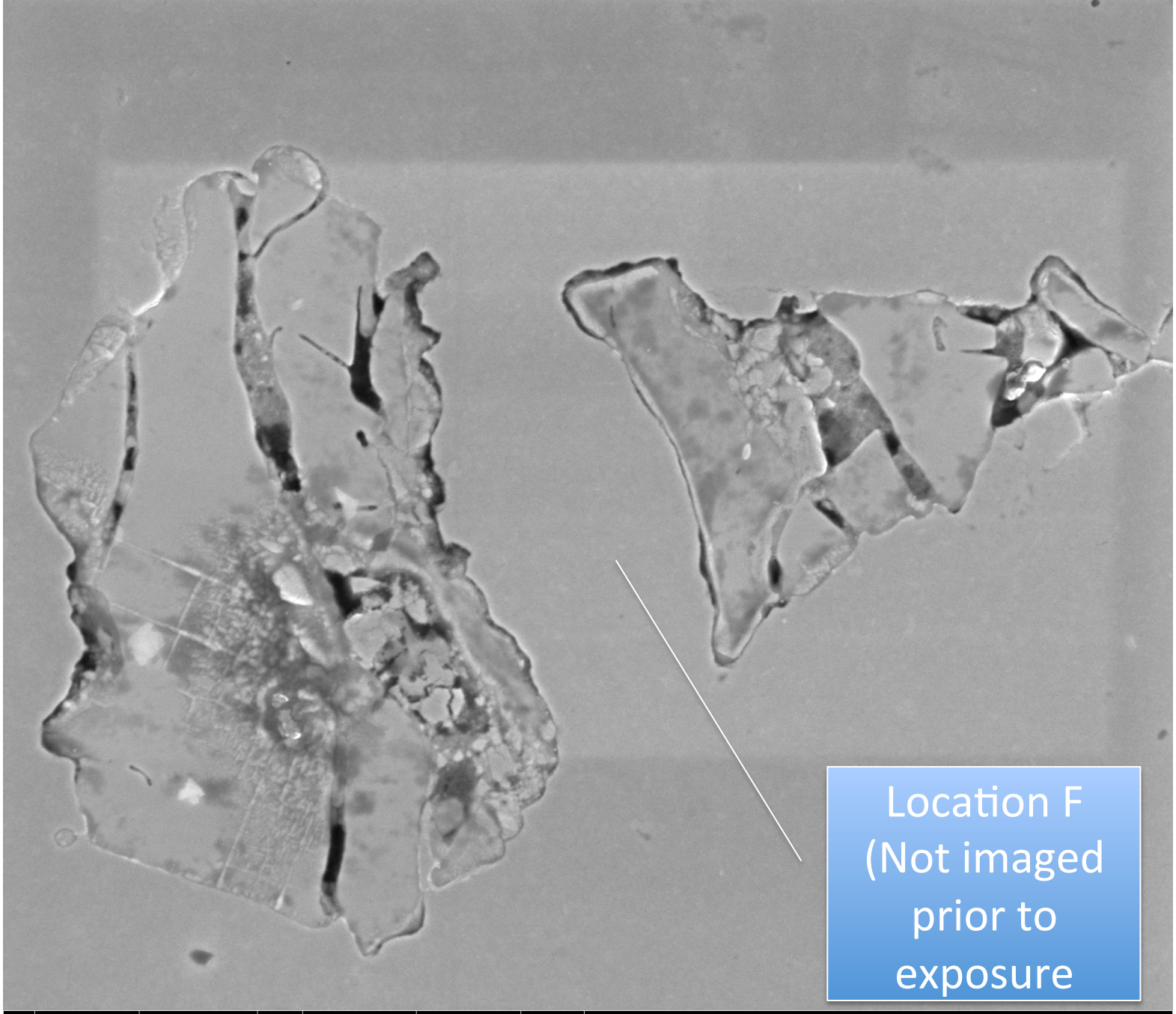

Location E
(Not imaged
prior to
exposure
HV
5.00 kV
mag
15 000 x
tilt
0 °
HFW
20.1 µm
WD
5.1 mm
det
TLD
10 µm
D238-polished_hydrogen exposed



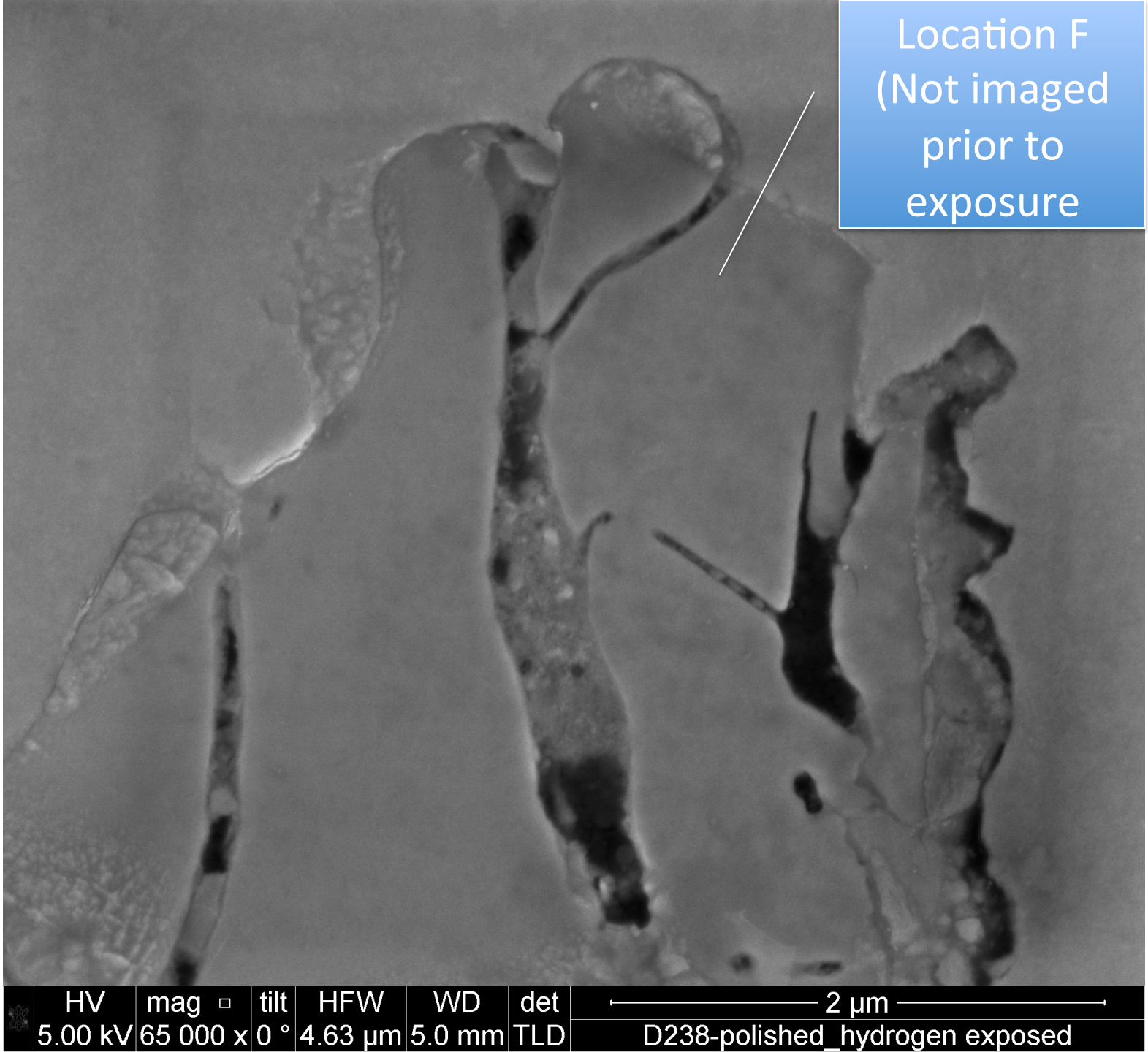
HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	25 000 x	0 °	12.0 µm	5.1 mm	TLD	D238-polished_hydrogen exposed

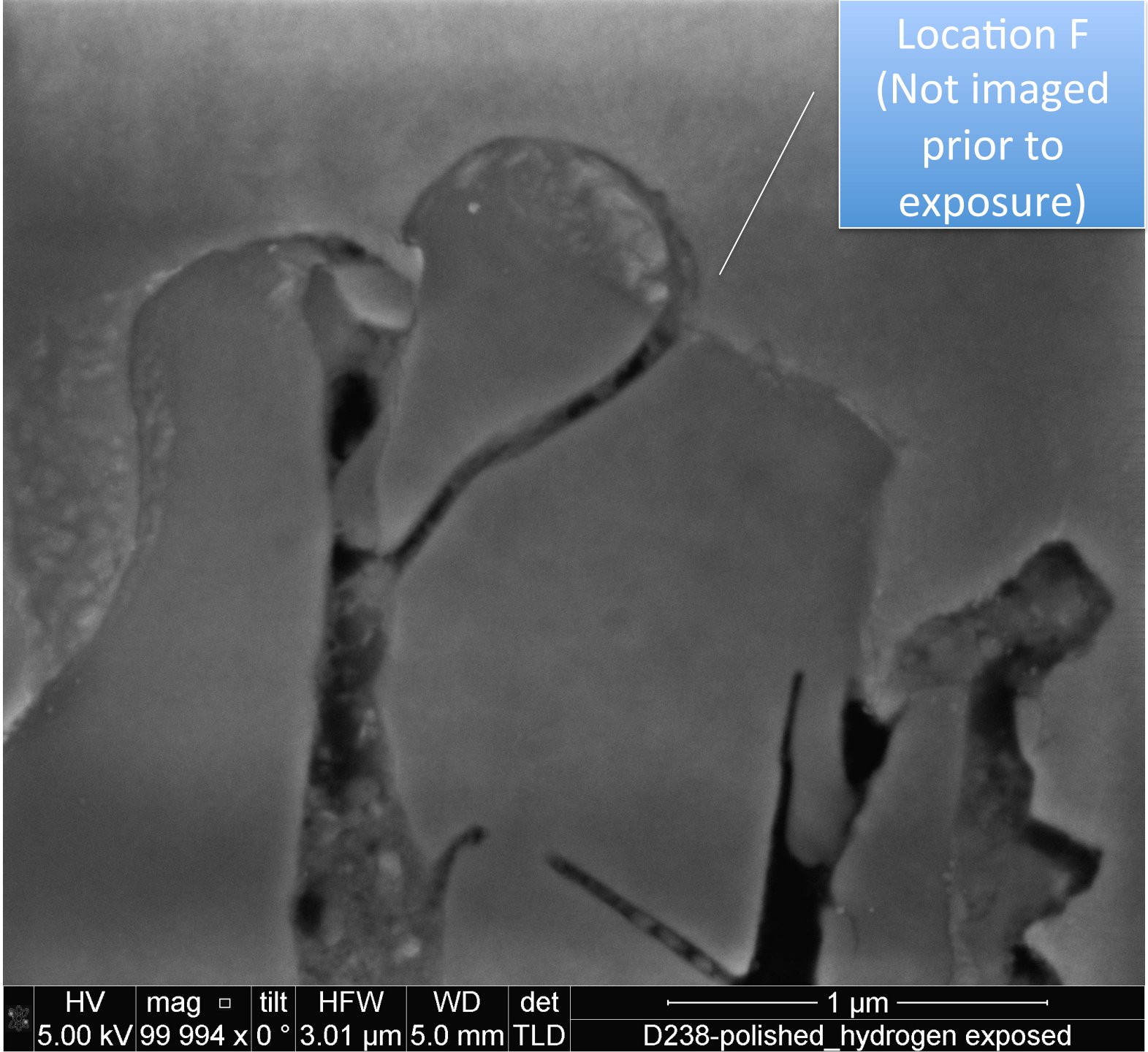
HV	mag	tilt	HFW	WD	det	20 µm
5.00 kV	5 001 x	0 °	60.1 µm	5.0 mm	CDEM	D238-polished_hydrogen exposed


Location F
(Not imaged
prior to
exposure
HV
5.00 kV
mag
12 998 x
tilt
0 °
HFW
23.1 µm
WD
5.0 mm
det
CDEM
5 µm
D238-polished_hydrogen exposed



HV	mag	tilt	HFW	WD	det	5 µm
5.00 kV	25 002 x	0 °	12.0 µm	5.0 mm	TLD	D238-polished_hydrogen exposed


Location F
(Not imaged
prior to
exposure
HV
5.00 kV
mag
65 000 x
tilt
0 °
HFW
4.63 µm
WD
5.0 mm
det
TLD
2 µm
D238-polished_hydrogen exposed


Location F
(Not imaged
prior to
exposure)
HV
5.00 kV
mag
99 994 x
tilt
0 °
HFW
3.01 µm
WD
5.0 mm
det
TLD
1 µm
D238-polished_hydrogen exposed

Discussion

- The kinetics of the hydriding reaction has not been studied at temperatures below -100°C
- In the range between -80 and + 100°C and pressures between 1 and 760 Torr the rate of deuterium gas conversion to ND_3 pro cm^2 of uranium surface is (Wicke&Otto)

$$dn_{D2}/dt = a*b*\sqrt{p}/(b+a\sqrt{p}) \ \ cm^3 \ D2 \ NTP/cm^2 \ s$$

With $a(T) = 6.3*\exp(-6000/RT)/\sqrt{2}$

$$b(T) = 3.0*10^4*\exp(-9700/RT)/\sqrt{2}$$

- Applying these equations to D_2 at 25K and 1100 Torr and exposure time of $4.86*10^5$ s (see slide 48) yields

$$dn_{D2} = 1.65*10^{-75} \ cm^3 \ NTP/cm^2$$

- The lack of ANY observable hydride formation is thus consistent with Wicke's results at higher temperature

E. Wicke, K. Otto, Ueber das System Uran-Wasserstoff und die Kinetik der Uranbildung, Zeitschrift Fuer Physikalische Chemie, 31 (1962) 222-248.

Summary

- Uranium foil (‘rolled’ at Y12, circular diameter ~0.625 inch, ~ 2 mm thick,)
  - was polished to a mirror finish on one side, while the other side was left with a thick oxide layer
    - Imaged optically and by SEM (on the polished side, with particular focus on carbo-nitride-oxide inclusions, where hydride initiation in known to preferentially occur)
  - exposed to liquid deuterium at ~ 25 K, 1100 Torr for approximately 6 days
    - Imaged again by SEM, mostly at the SAME inclusions
- NO hydride initiation was detectable by high resolution SEM
- Consistent with extrapolating Wicke&Otto’s results at ≥ 190°K to 25 °K