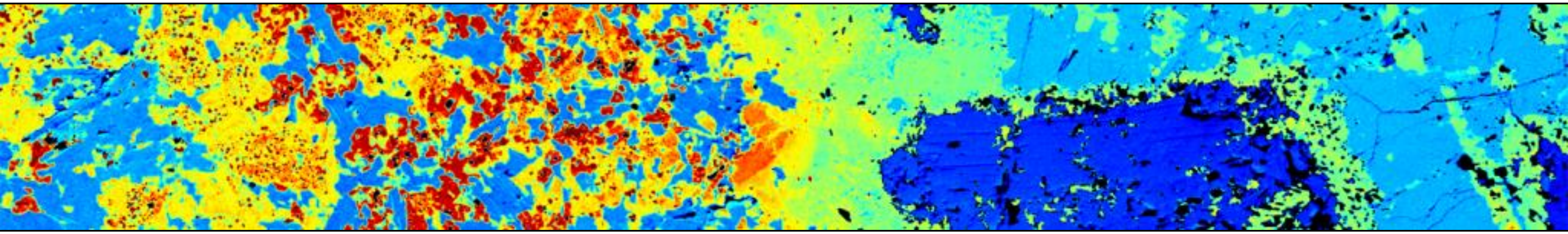


Lecture 7

Trace element mapping by LA-ICP-MS: Data collection, processing and image creation strategies

Tom Raimondo

University of South Australia – tom.raimondo@unisa.edu.au

- Data workflow from Iolite to XMapTools
- Optimizing image display
- Introduction of features specific to LA-ICP-MS datasets

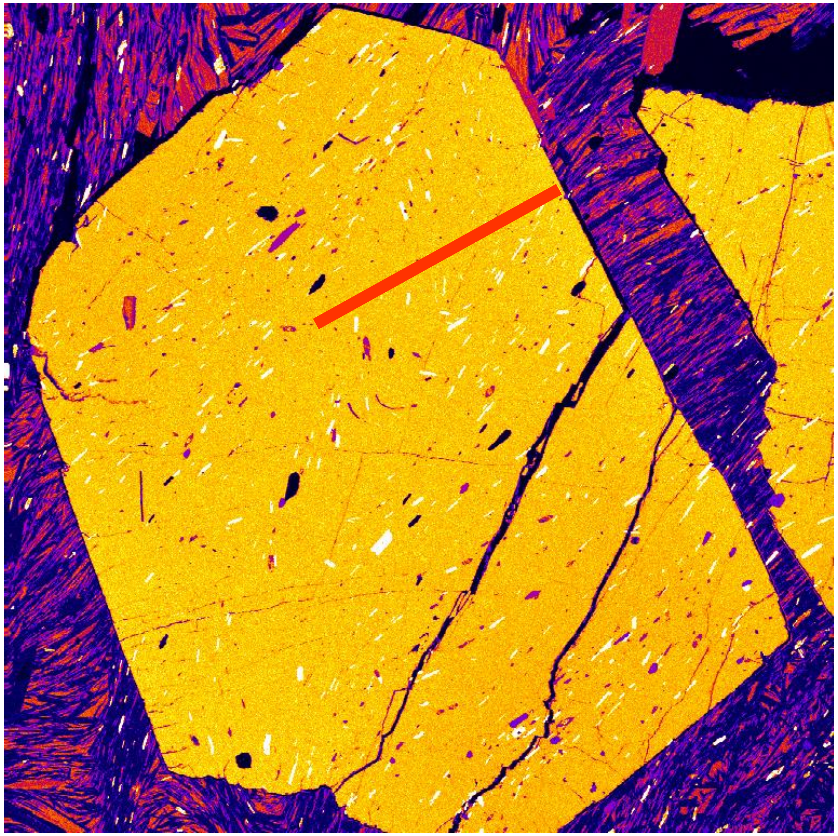
@ROKmondo

Boston (USA) - August, 11th, 12th 2018

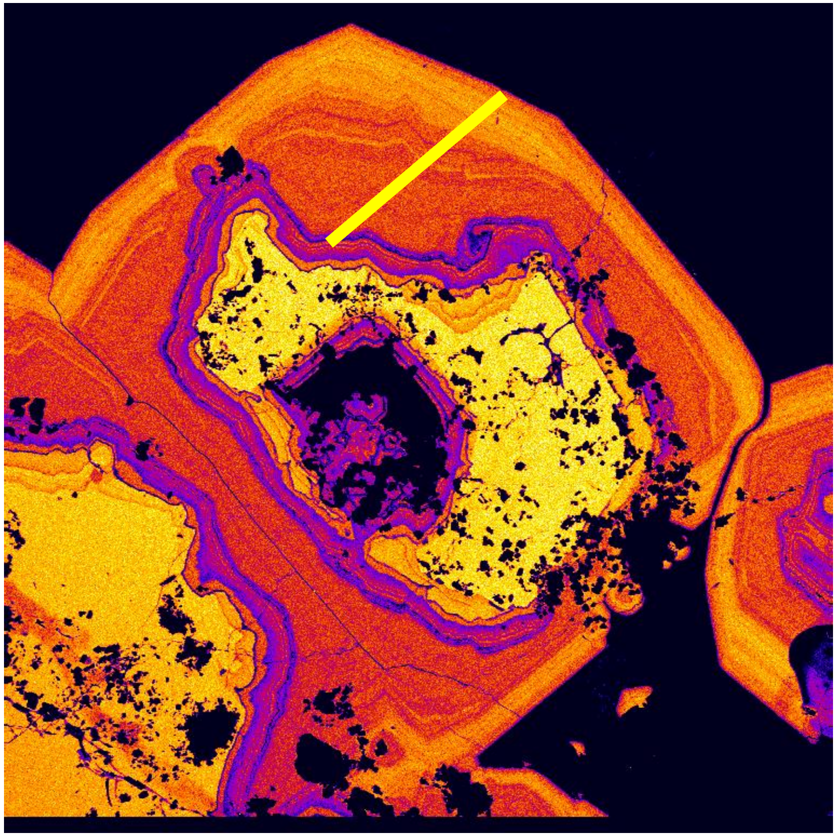
Organization: Pierre Lanari; Tom Raimondo; Laura Airaghi; Mahyra Tedeschi
Funding: University of Bern

Why map?

- Can't we just do some simple 1D transects?



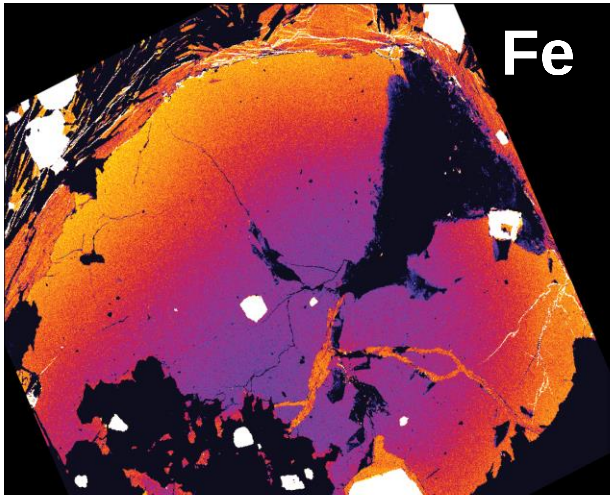
Garnet (Fe Kα X-Ray Map)

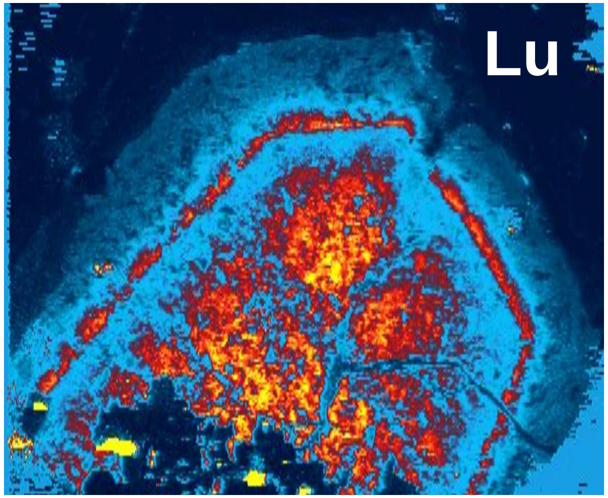


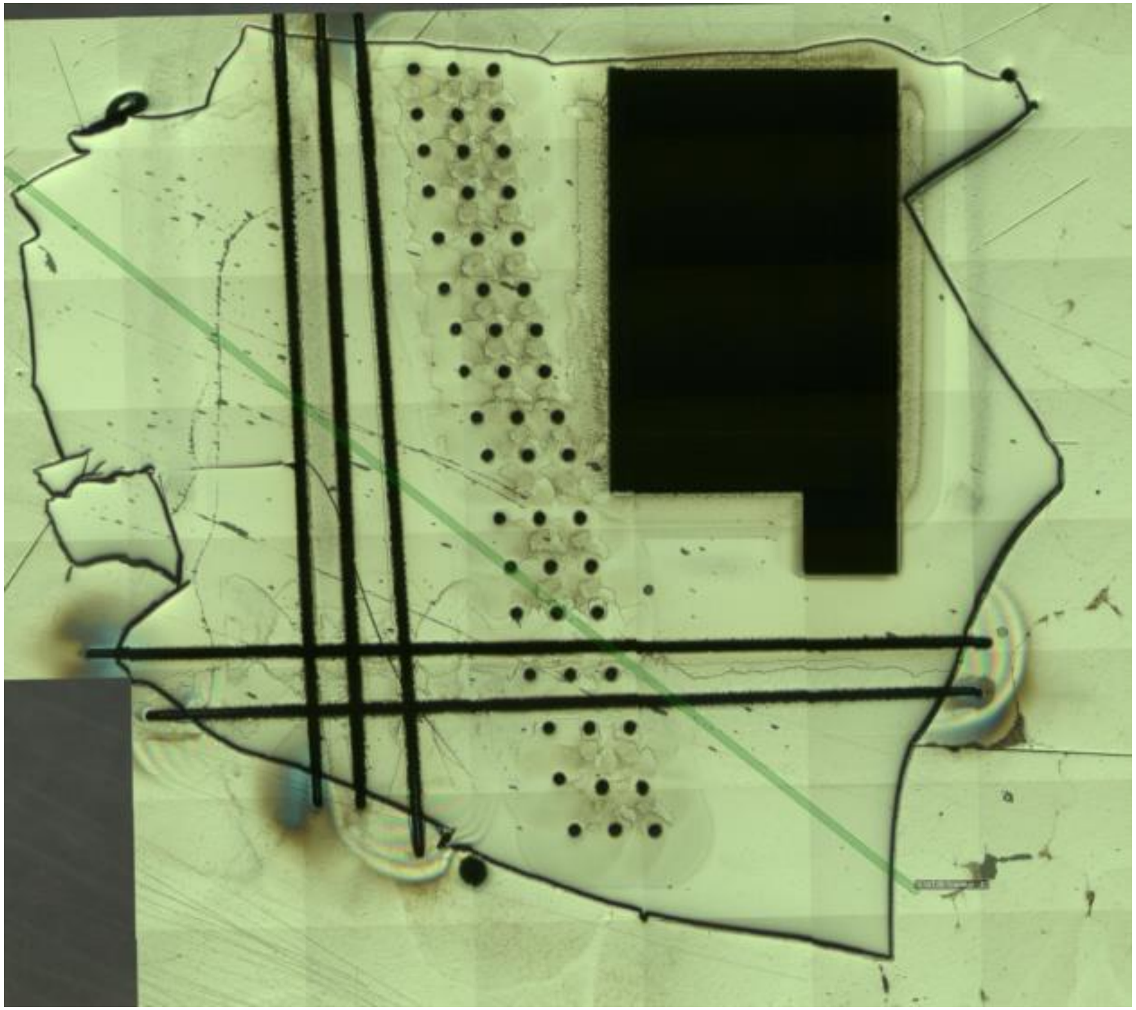
Garnet (Fe Kα X-Ray Map)

Why map?

- Spot or line transects may falsely represent the spatial distribution of trace elements – quantified maps are a powerful way to visualise and better interpret zoning patterns

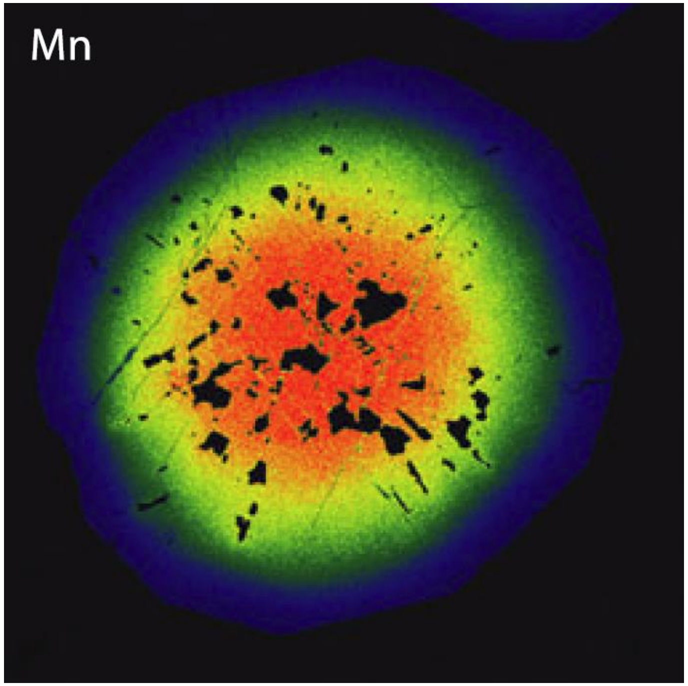




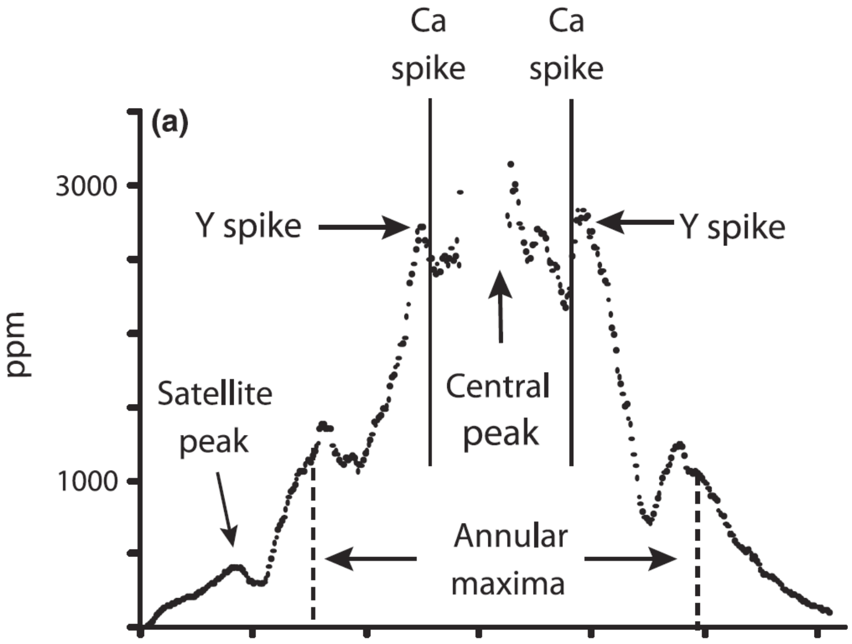


Why trace elements?

- Consideration of major elements alone ignores the wealth of information preserved by trace elements…but they are in many cases not analysed
- Generally less vulnerable to diffusive resetting – **prograde evolution**
- Sensitive to a broader spectrum of geochemical interactions involving the entire mineral assemblage, including accessory phases – **geochronology**



Major element zoning (Mn)



Trace element zoning (Y)

Moore, S. J., Carlson, W. D., & Hesse, M. A. (2013). Origins of yttrium and rare earth element distributions in metamorphic garnet. *Journal of Metamorphic Geology*, *31*(6), 663-689.

Trace element mapping by LA-ICP-MS

Contrib Mineral Petrol (2017) 172:17
DOI 10.1007/s00410-017-1339-z

ORIGINAL PAPER

Trace element mapping by LA-ICP-MS: assessing geochemical mobility in garnet

Tom Raimondo[1] · Justin Payne[1] · Benjamin Wade[2] · Pierre Lanari[3] · Chris Clark[4] · Martin Hand[5]

Received: 17 October 2016 / Accepted: 22 February 2017

Abstract A persistent problem in the study of garnet geochemistry is that the consideration of major elements alone excludes a wealth of information preserved by trace elements, particularly the rare-earth elements (REEs). This is despite the fact that trace elements are generally in garnet, which are argued to be largely dependent on the interplay between element fractionation, mineral reactions and partitioning, and the length scales of intergranular transport. Samples from the Peaked Hill shear zone, Reynolds Range, central Australia, exhibit contrasting trace ele-

Raimondo, T., Payne, J., Wade, B., Lanari, P., Clark, C. & Hand, M., 2017. Trace element mapping by LA-ICP-MS: assessing geochemical mobility in garnet. *Contributions to Mineralogy and Petrology*, 172(4), 17.

Why LA-ICP-MS?

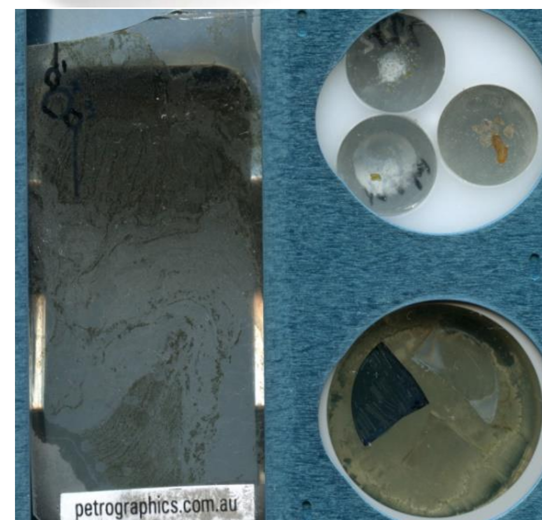
PROS

- Minimum sample preparation and no vacuum required
- Excellent detection limits (ppm-ppb)
- Isotopic mapping over wide elemental range (^{7}Li to ^{238}U)
- Relative ease of mapping elements with major overlap problems in X-Ray mapping (e.g. REE)
- Relatively cheap compared to time on SIMS, synchrotron etc.

CONS

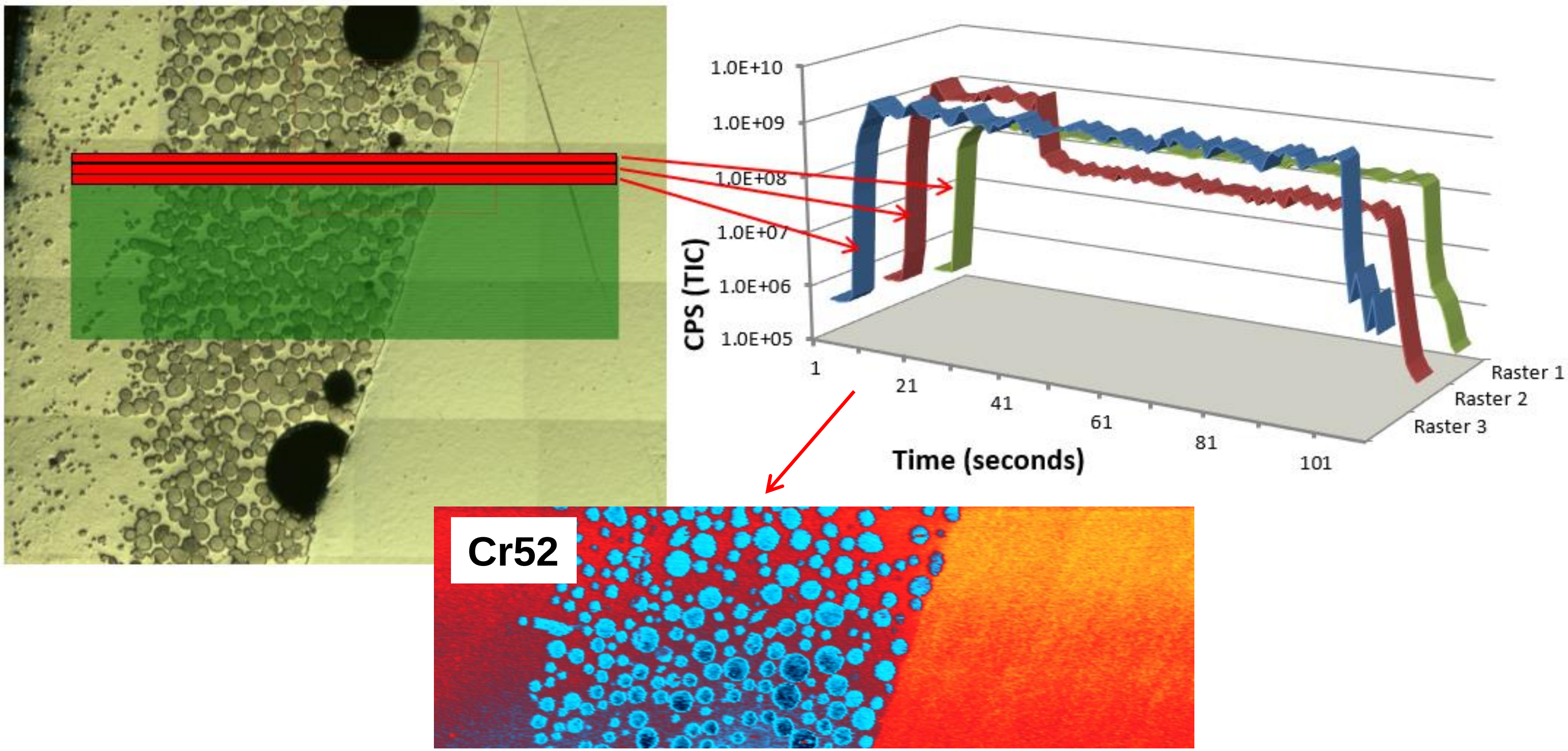
- Spatial resolution poorer than that attainable on e^- or ion beam instruments
- Destructive technique with large analytical volume
- Quantification difficult due to small range of trace element standards
- Instrument drift
- Still has some interference problems

Analytical procedure

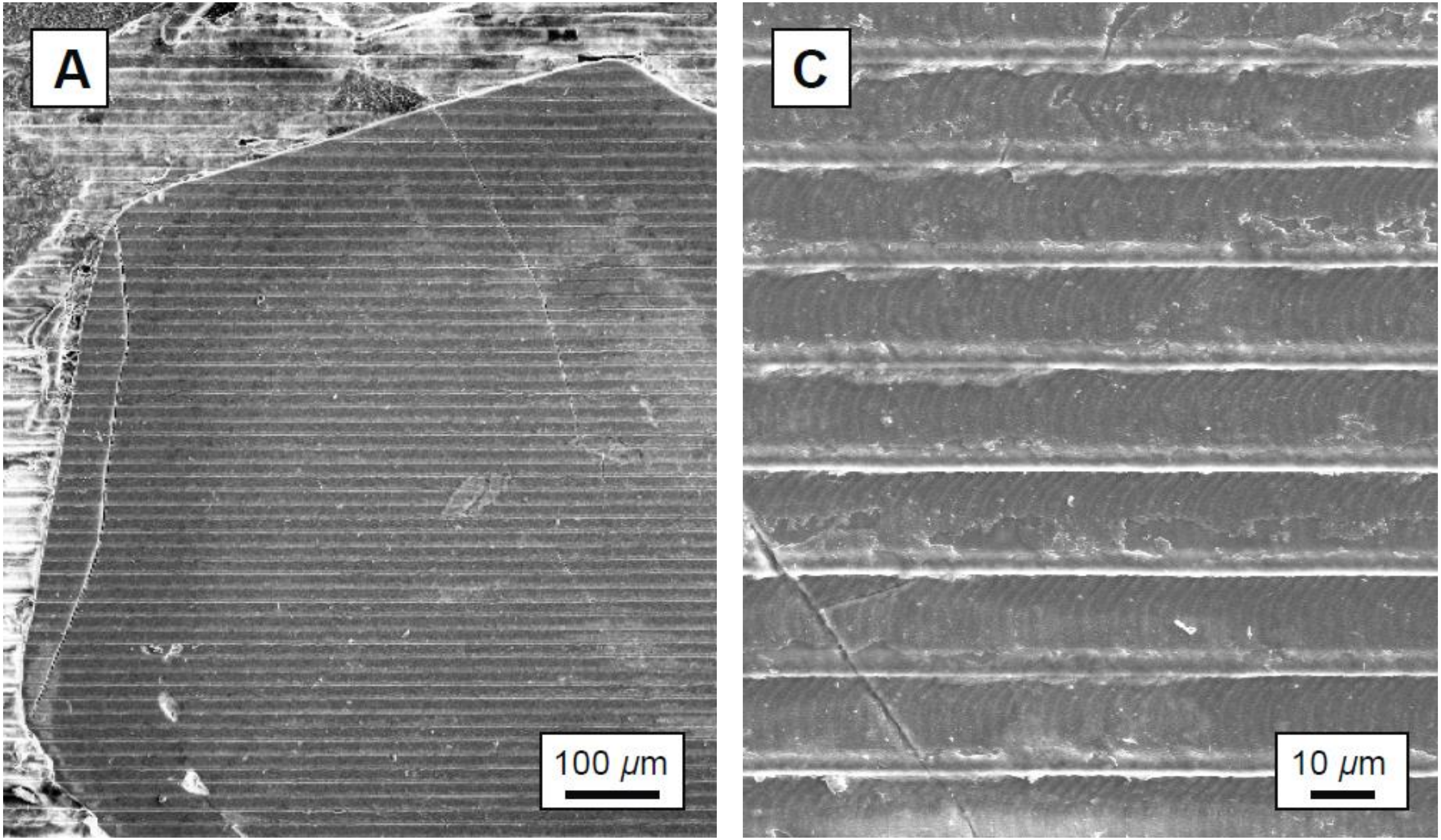


Analytical procedure

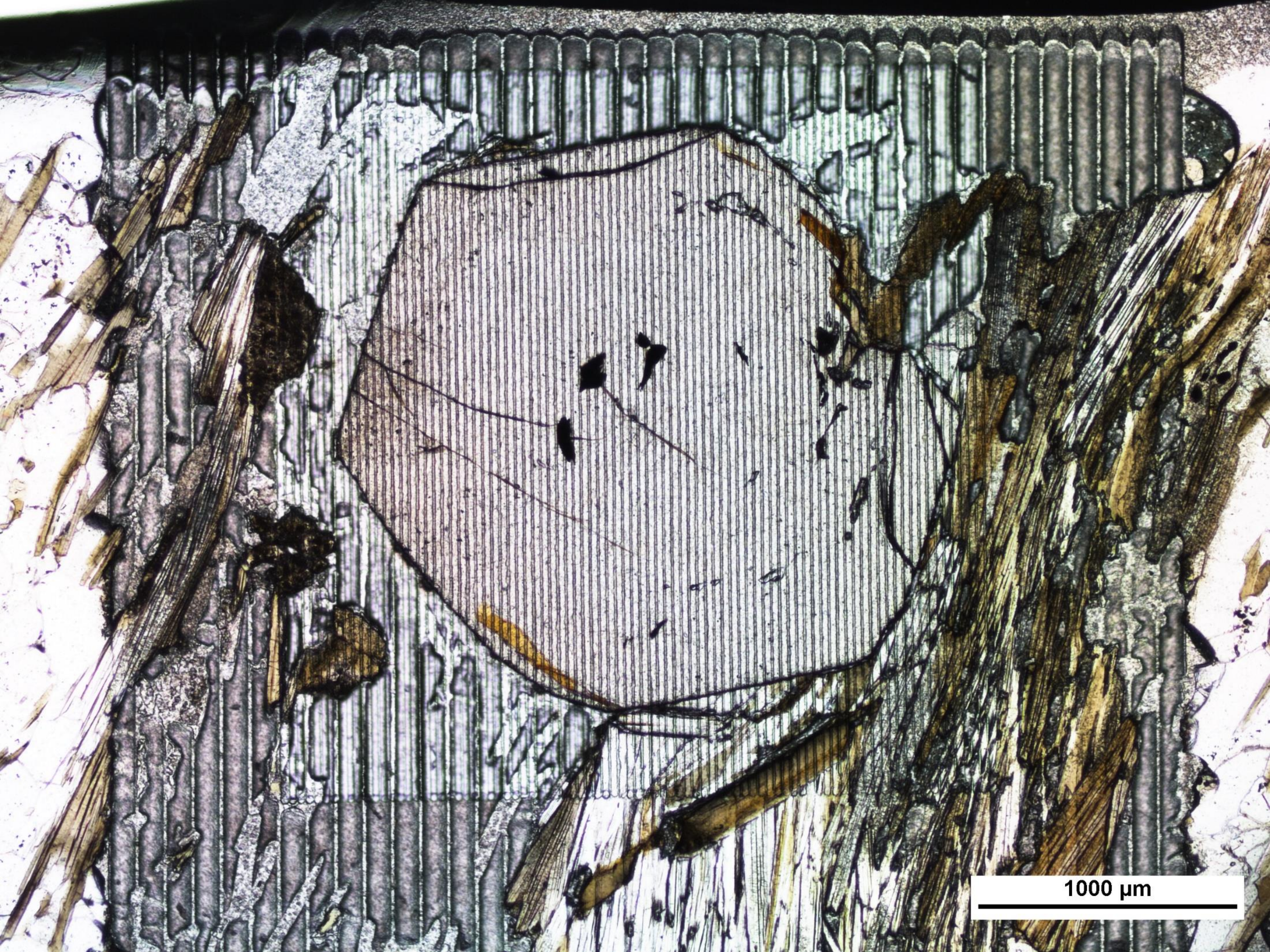
- Sampling area is chosen and infilled with parallel rasters
- Time-resolved intensity data (CPS) is recorded for each raster
- Quantification performed using major elements as an internal standard (e.g. Si for garnet, Fe for pyrite, etc), and all rasters then stitched together to form an image of background- and drift-corrected ppm values for each element



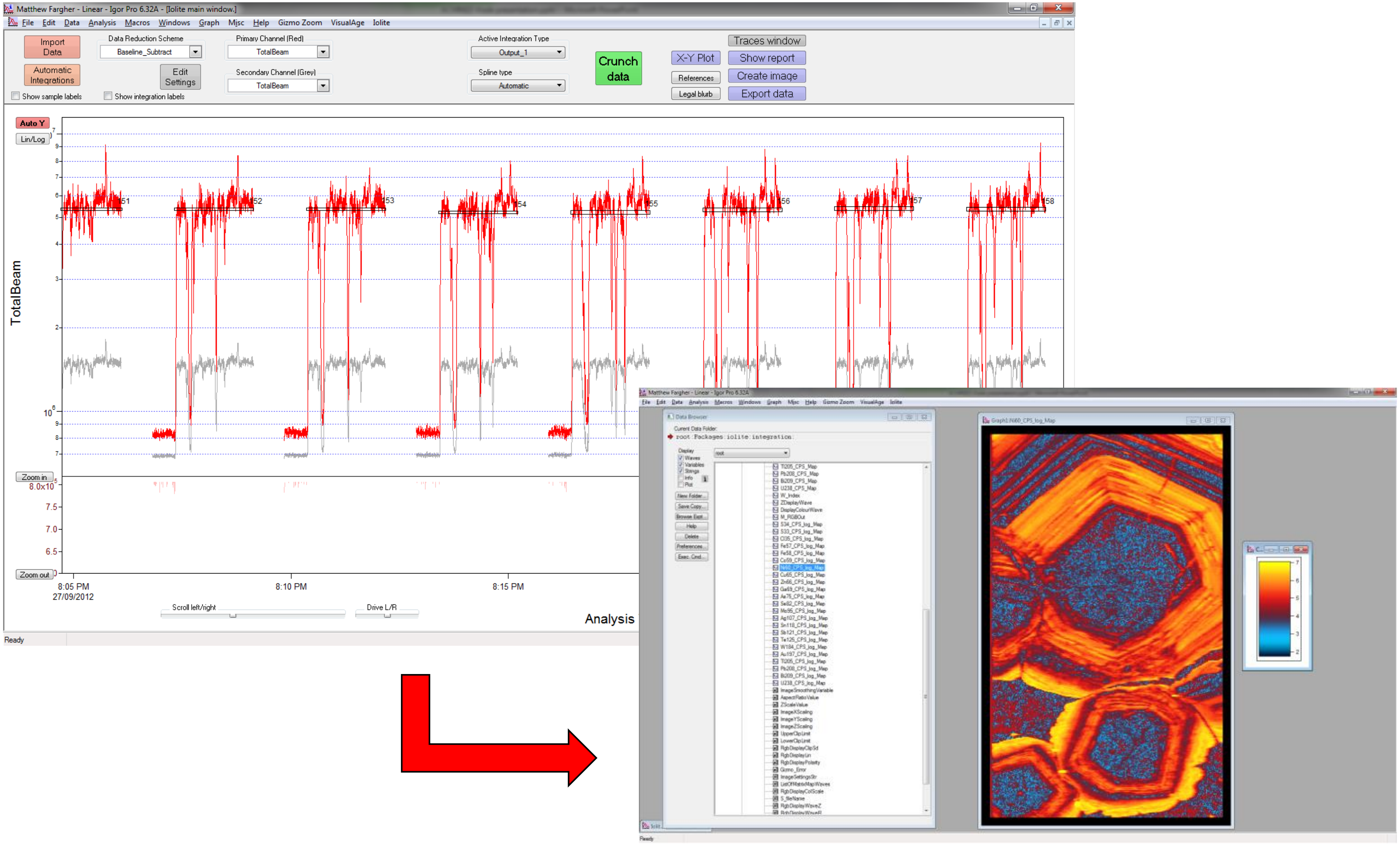
Laser ablation rasters



Direction of laser travel


1000 µm

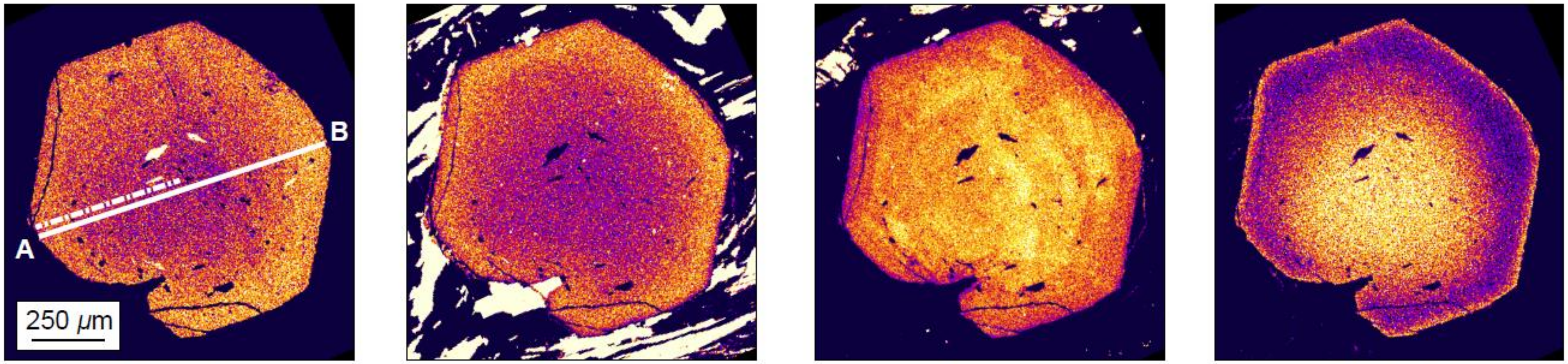
Data processing – *Iolite*



Paton, C., Hellstrom, J., Paul, B., Woodhead, J. & Hergt, J. (2011). Iolite: Freeware for the visualisation and processing of mass spectrometric data. *Journal of Analytical Atomic Spectrometry, 26(12),* 2508-2518.

Why map?

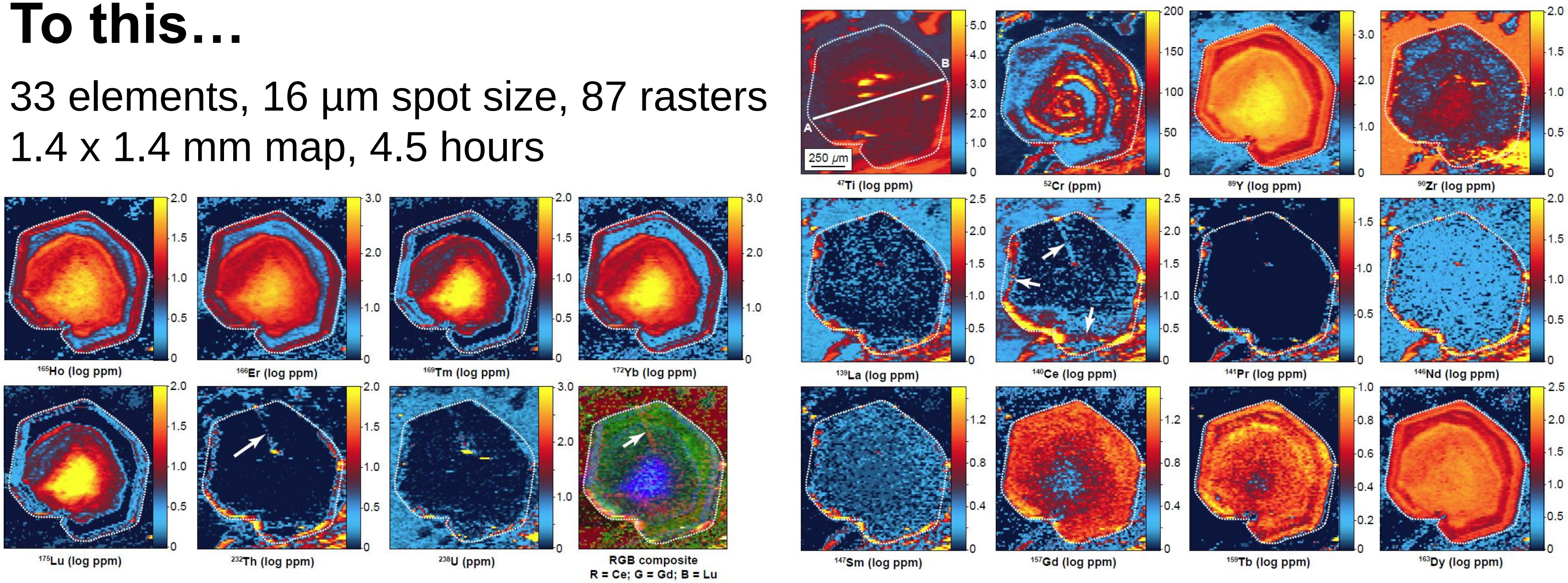
From this...



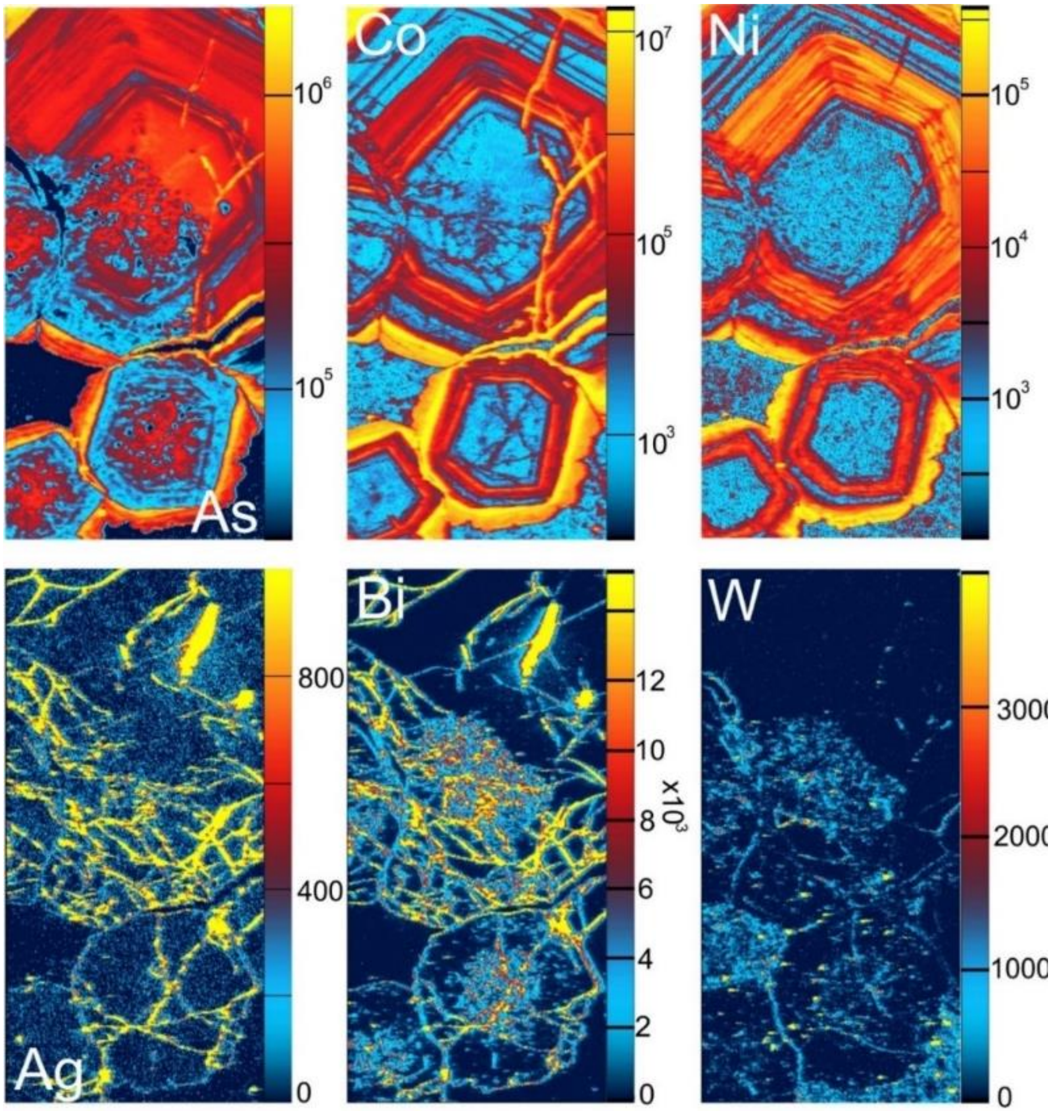
Fe (cps) | Mg (cps) | Ca (cps) | Mn (cps)

To this…

33 elements, 16 µm spot size, 87 rasters
1.4 x 1.4 mm map, 4.5 hours

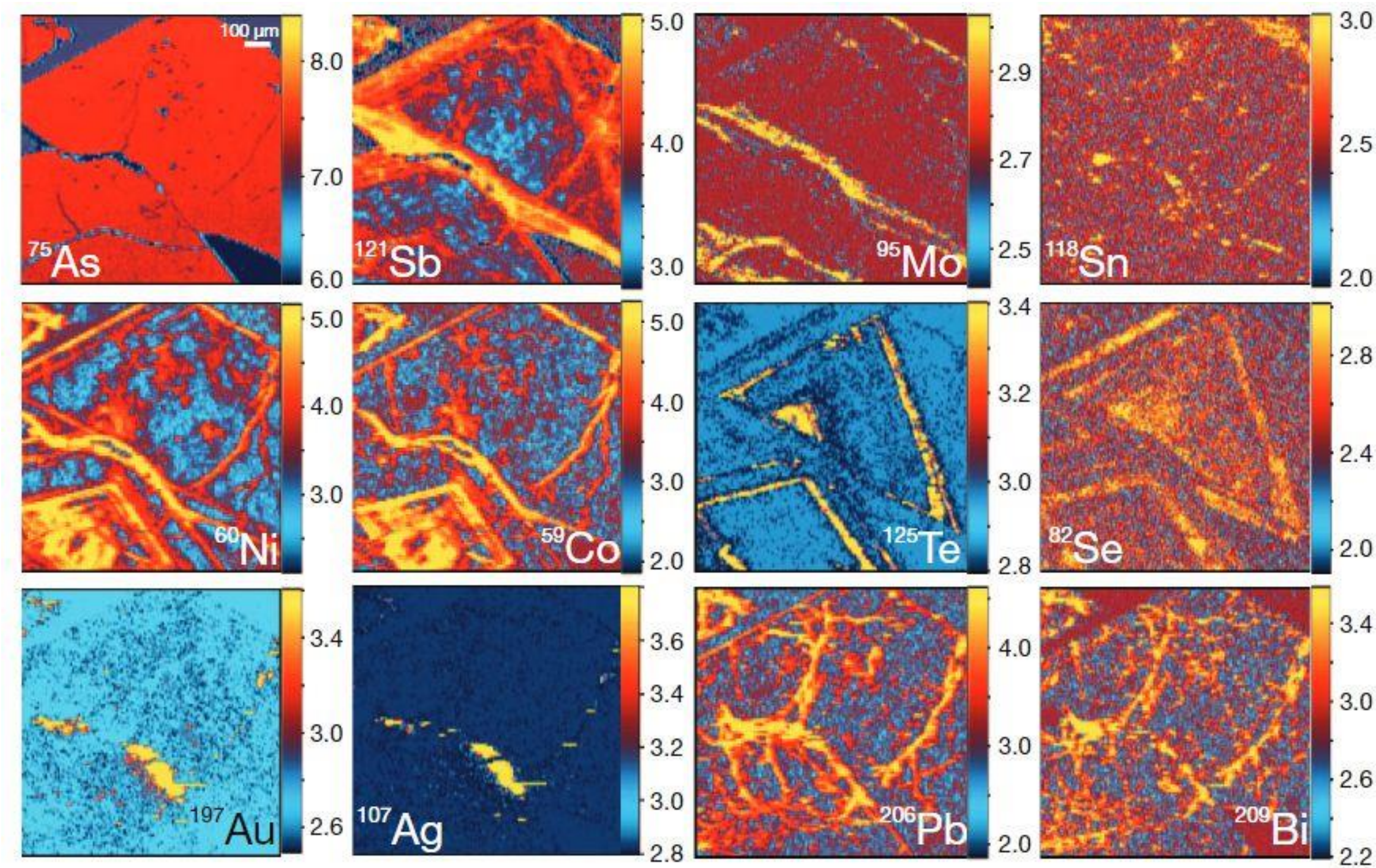


Pyrite



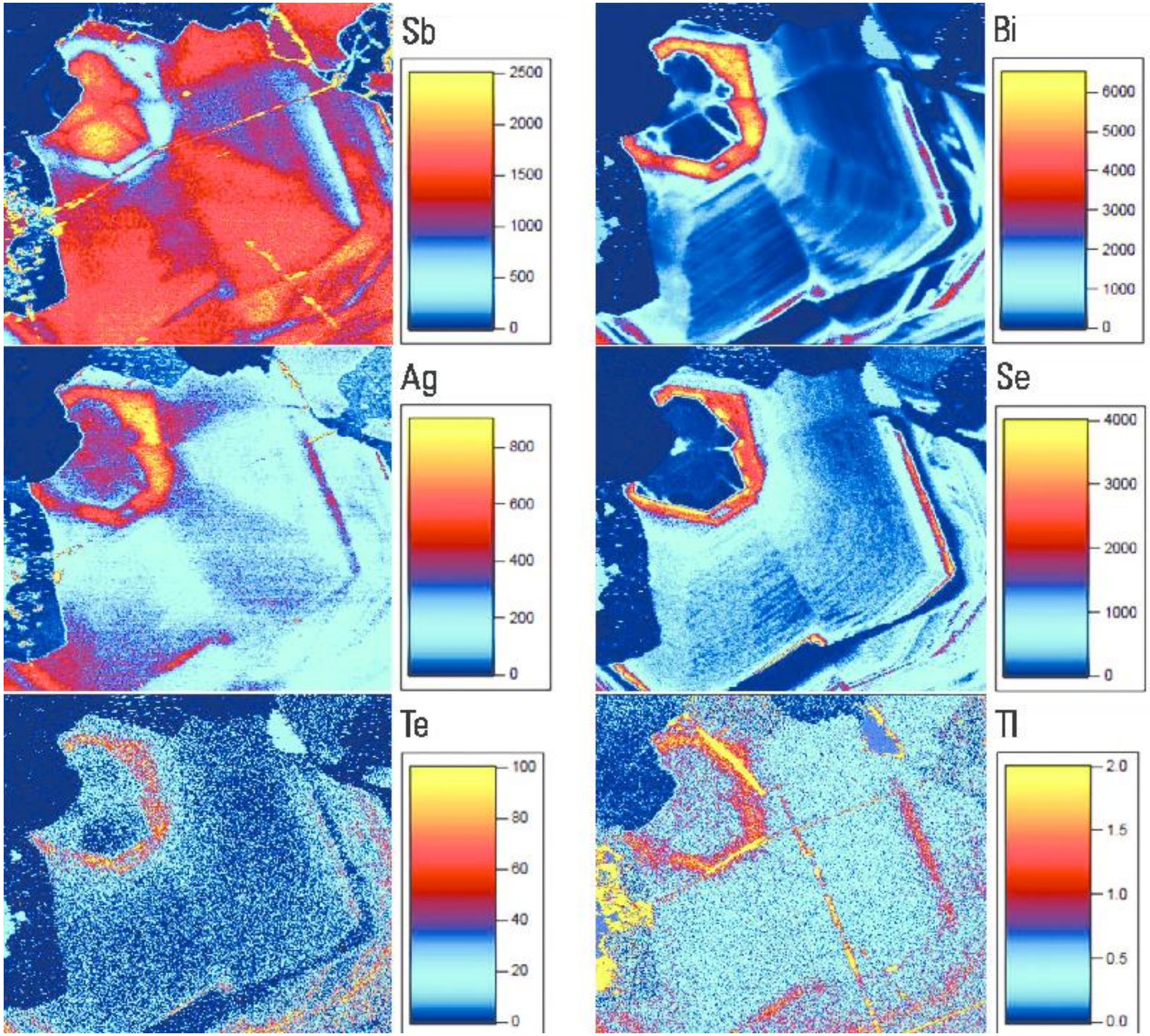
Cook, N., Ciobanu, C.L., George, L., Zhu, Z-Y., Wade, B. & Ehrig, K. (2016). Trace element analysis of minerals in magmatic-hydrothermal ores by laser ablation inductively-coupled plasma mass spectrometry: approaches and opportunities. *Minerals*, in press.

Arsenopyrite



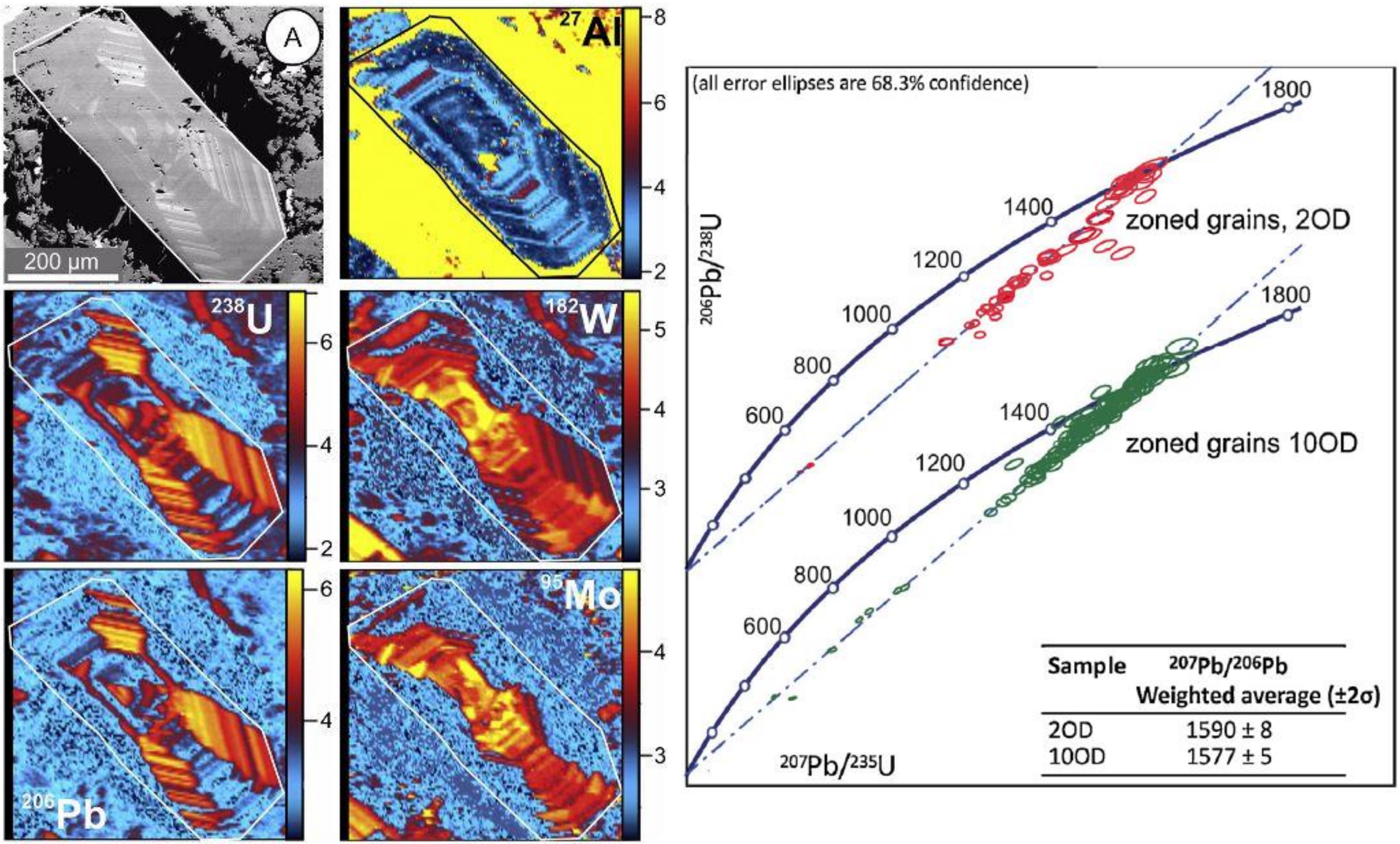
Cook, N. J., Ciobanu, C. L., Meria, D., Silcock, D., & Wade, B. (2013). Arsenopyrite-pyrite association in an orogenic gold ore: tracing mineralization history from textures and trace elements. *Economic Geology*, *108*(6), 1273-1283.

Galena



George, L., Cook, N. J., Cristiana, L., & Wade, B. P. (2015). Trace and minor elements in galena: A reconnaissance LA-ICP-MS study. *American Mineralogist*, *100*(2-3), 548-569.

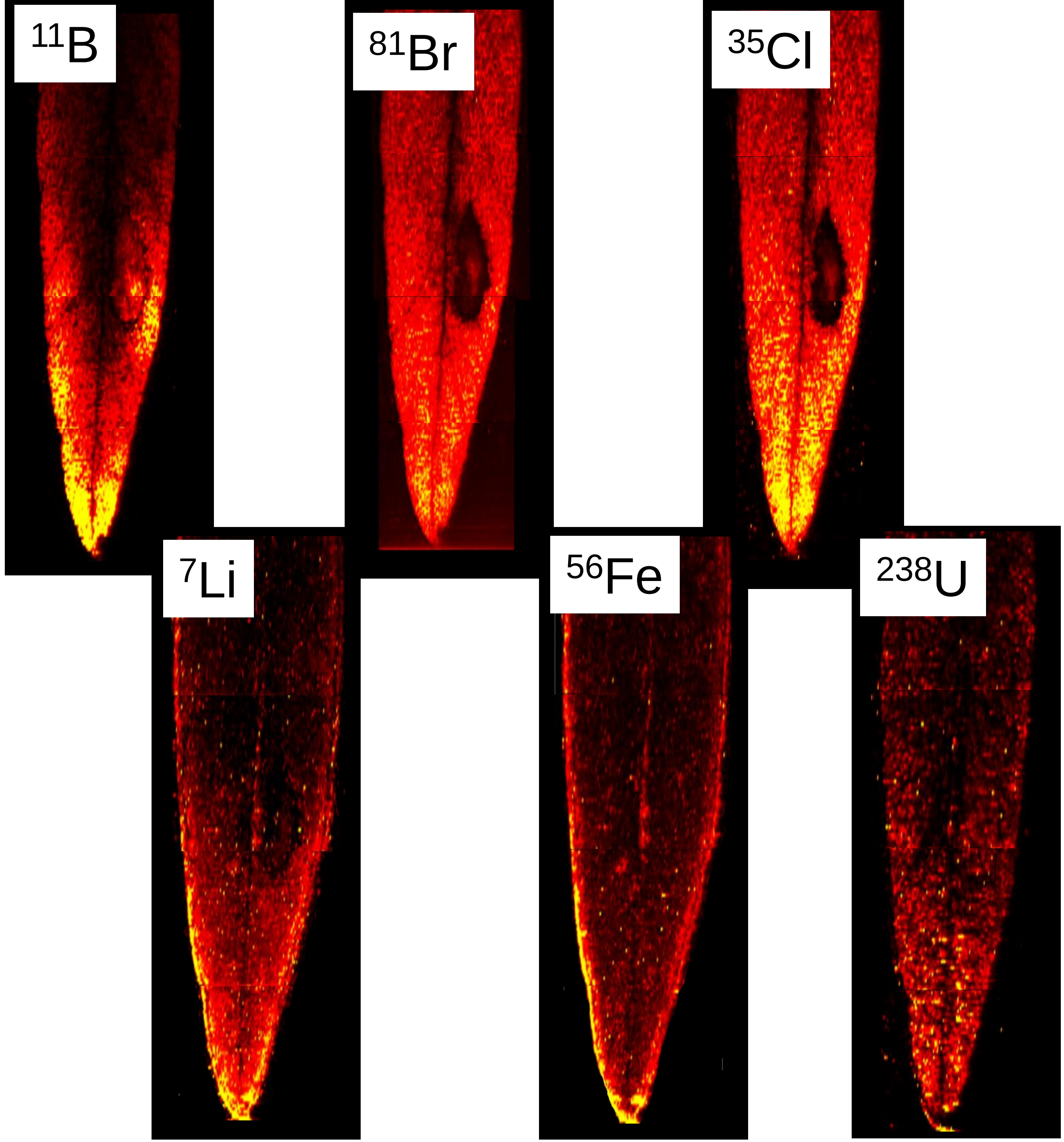
Hematite



Ciobanu, C. L., Wade, B. P., Cook, N. J., Mumm, A. S., & Giles, D. (2013). Uranium-bearing hematite from the Olympic Dam Cu–U–Au deposit, South Australia: a geochemical tracer and reconnaissance Pb–Pb geochronometer. *Precambrian Research*, *238*, 129-147.

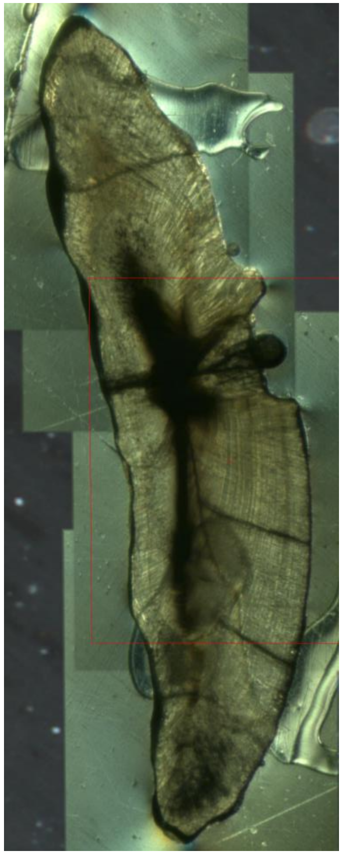
Eucalypt leaf

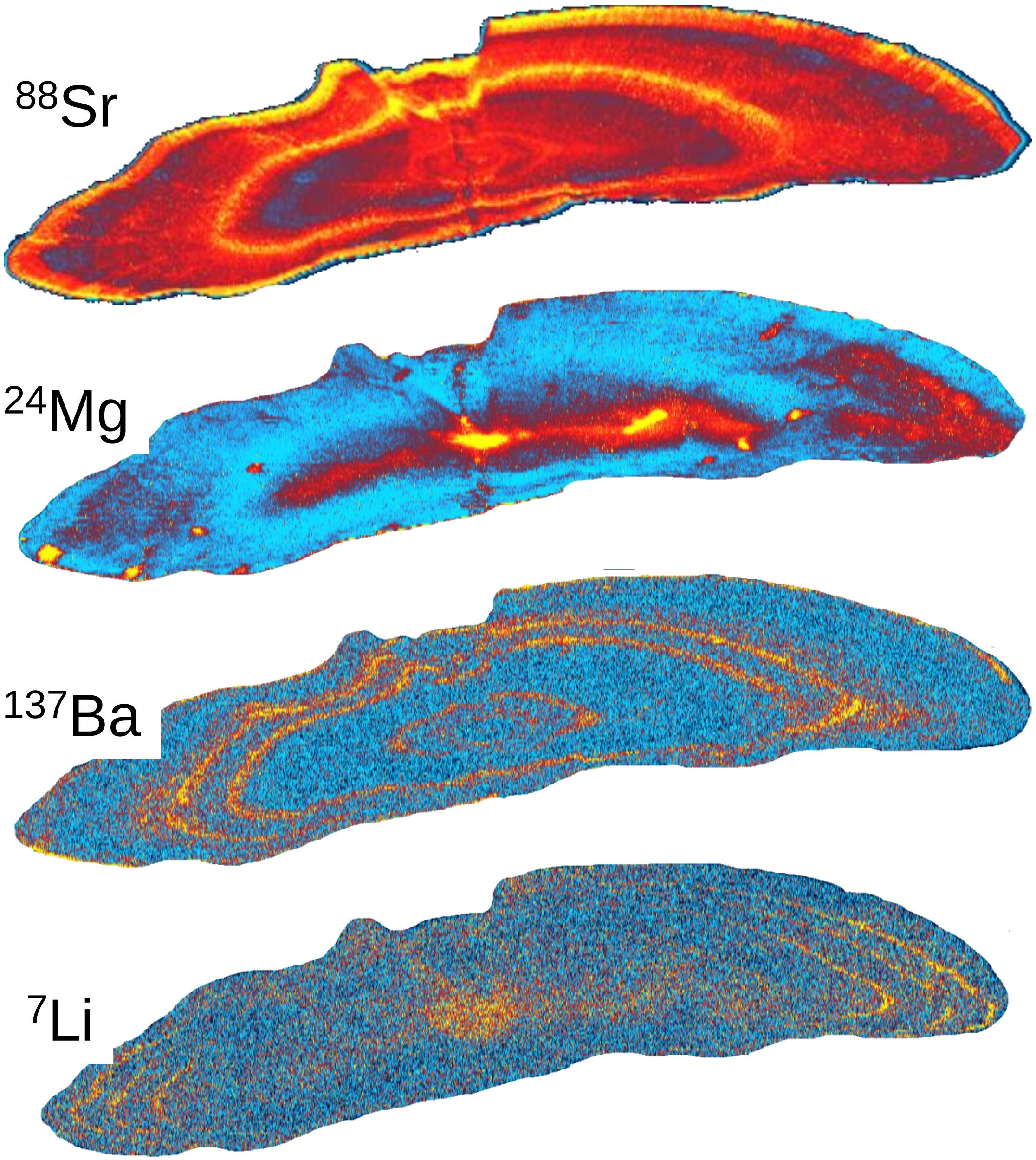
250 rasters
200 um spot size
200 um/s scan speed
~10 mm x 50 mm
~22 hours



Fish otolith

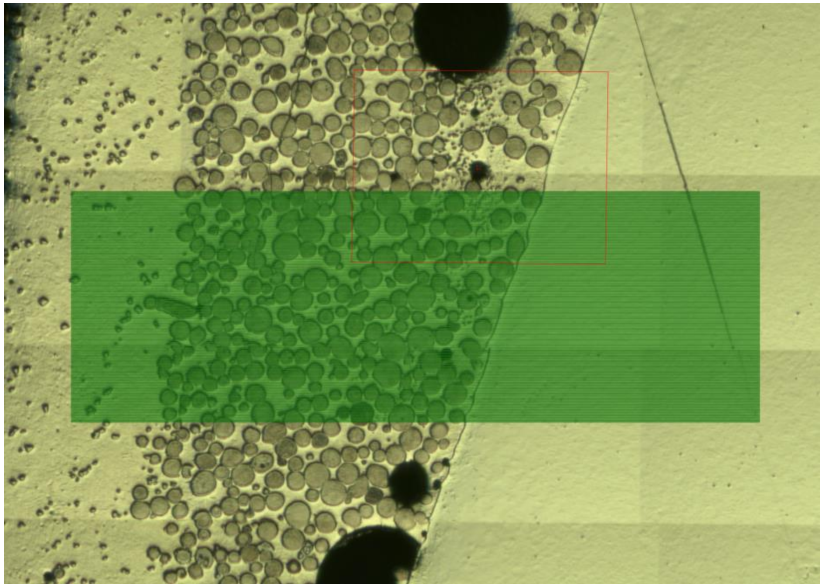
257 rasters
19 um spot size
30 um/s scan speed
~2.5 mm x 3.5mm
~11 hours

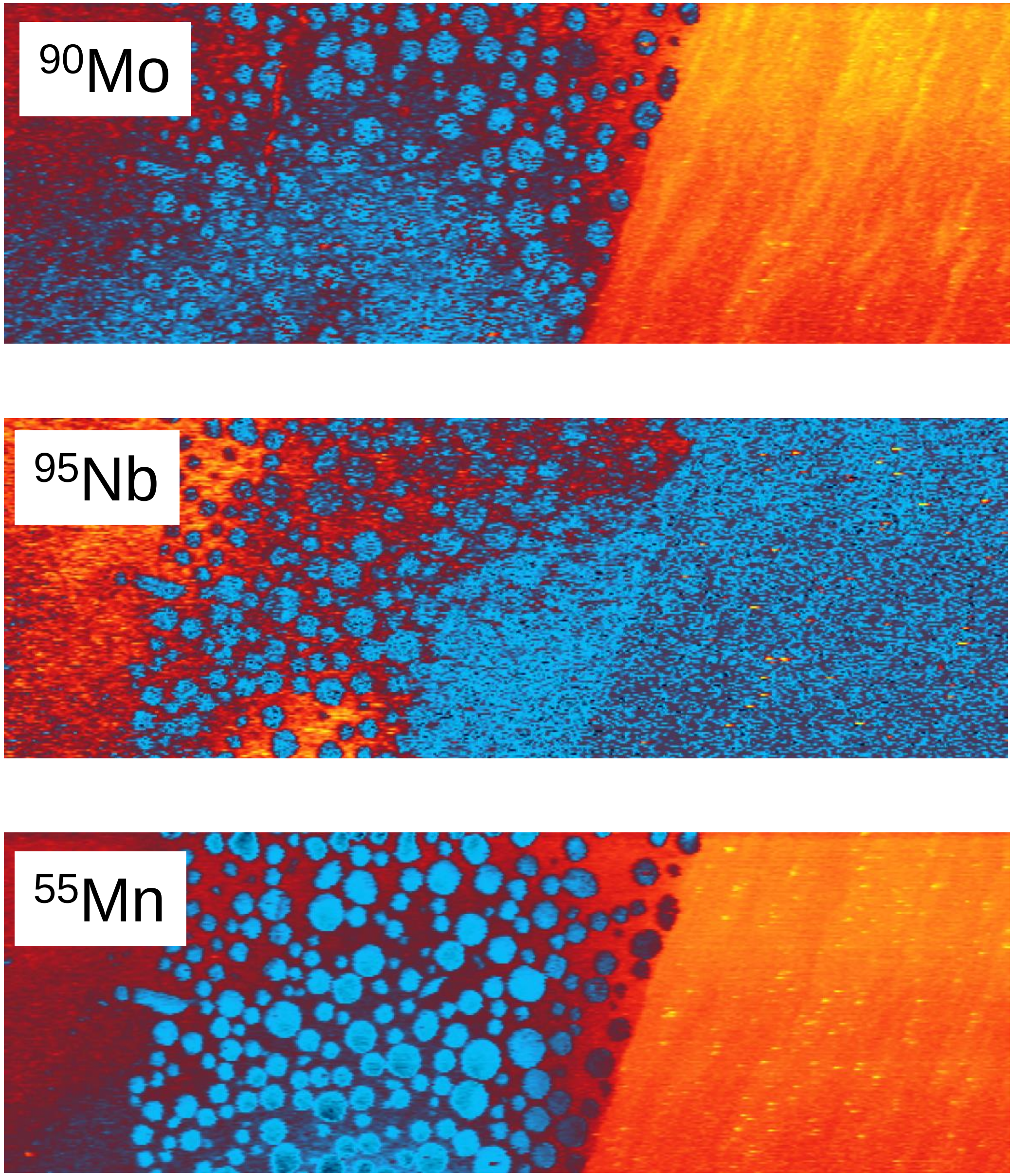




Steel casing

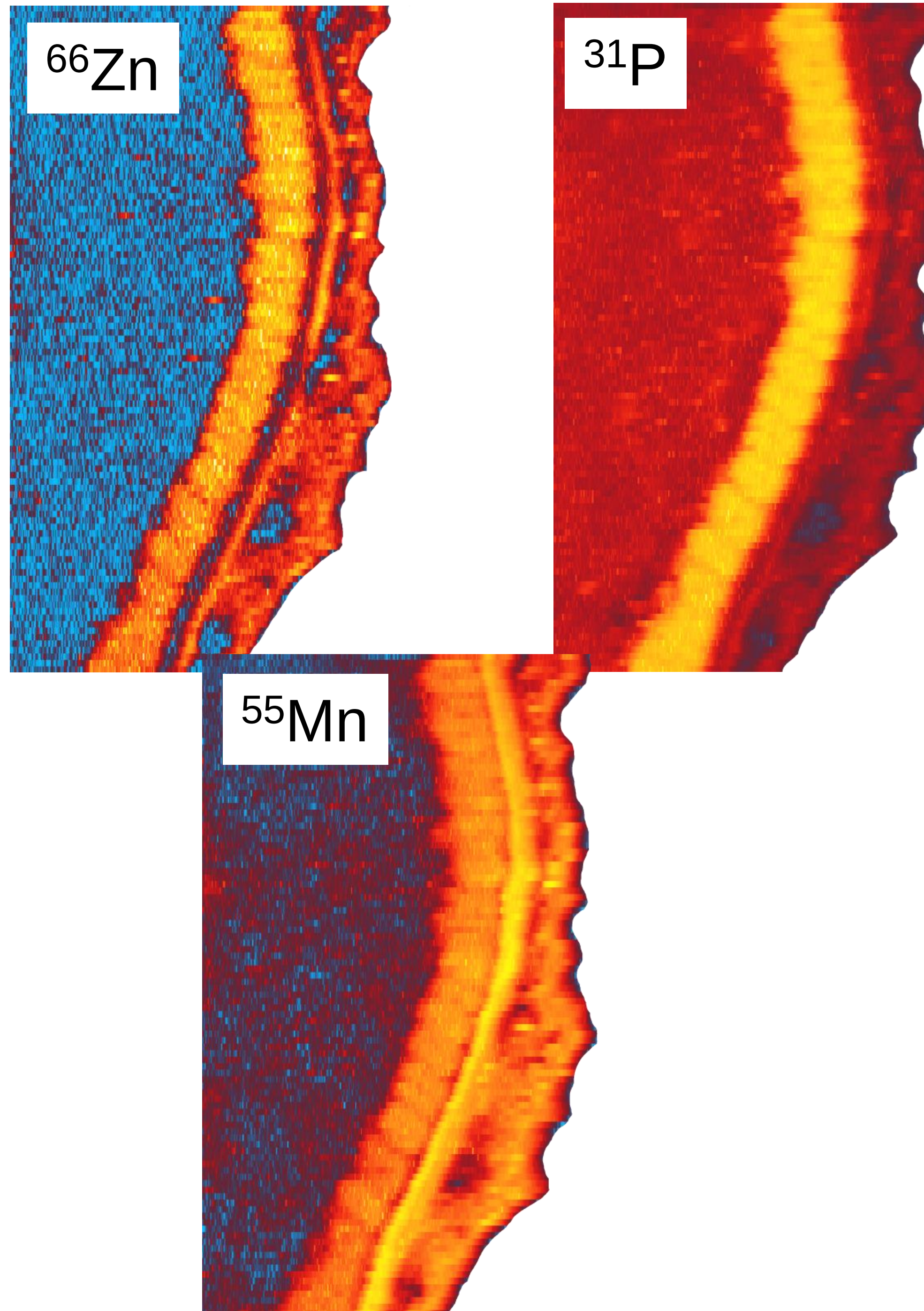
180 rasters
10 um spot size
15 um/s scan speed
~1 mm x 3.5mm
~18 hours

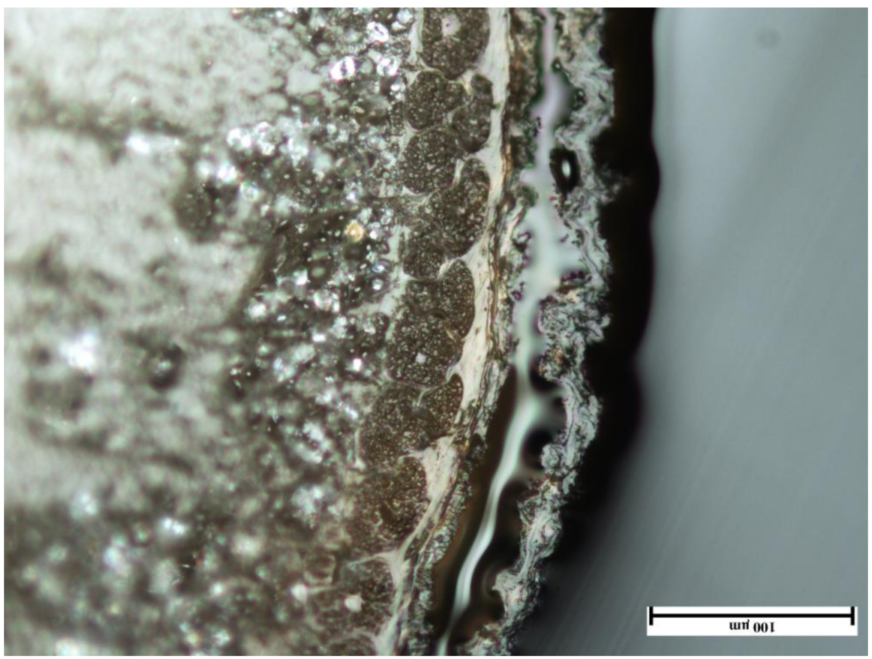




Wheat grain cell wall

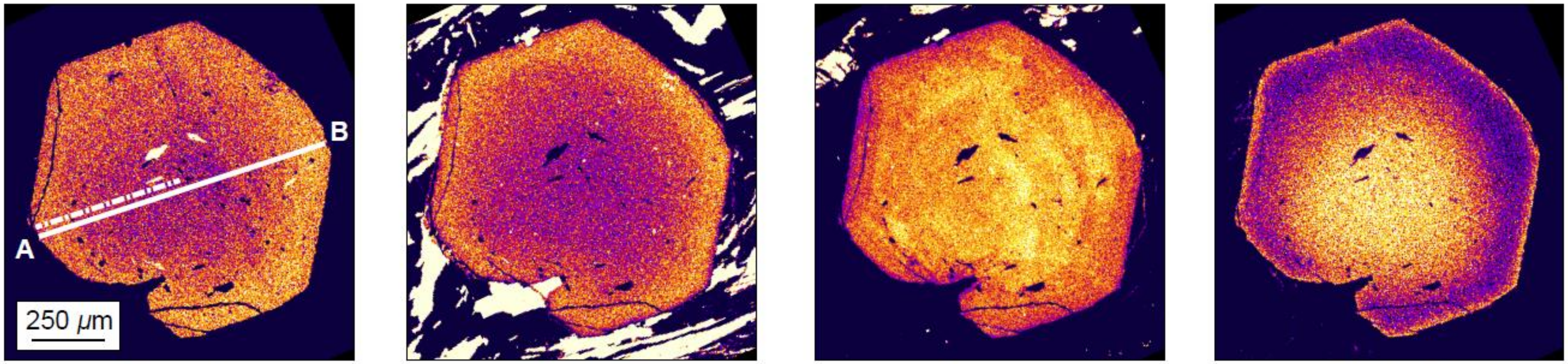
80 rasters
8 um spot size
5 um/s scan speed
0.3 mm x 0.3 mm
~4 hours





Application – major vs trace elements in garnet

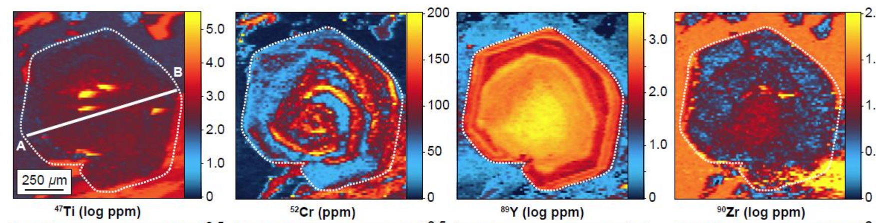
From this...

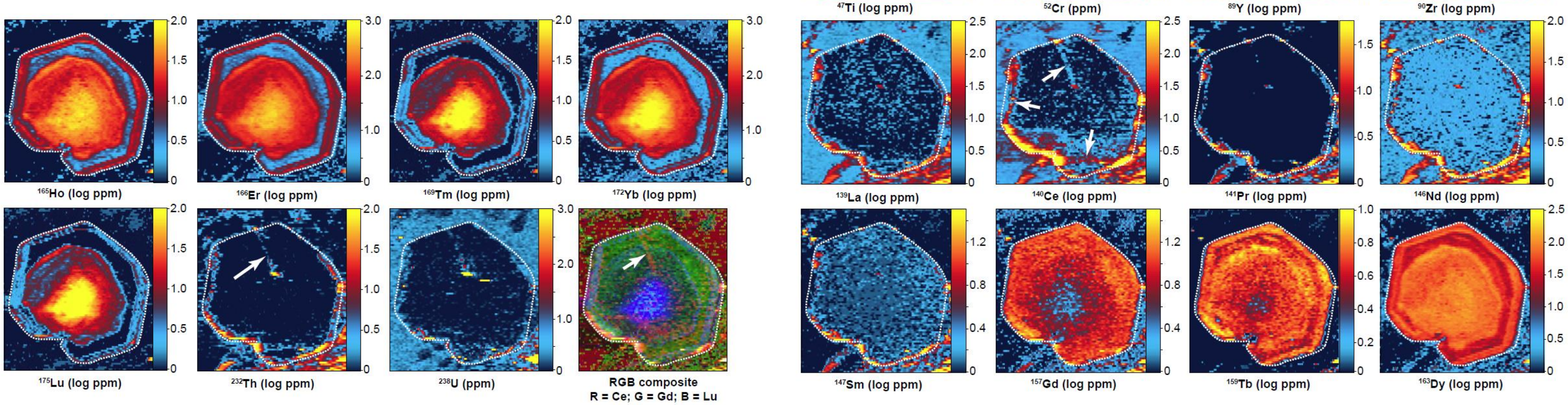


Fe (cps) | Mg (cps) | Ca (cps) | Mn (cps)

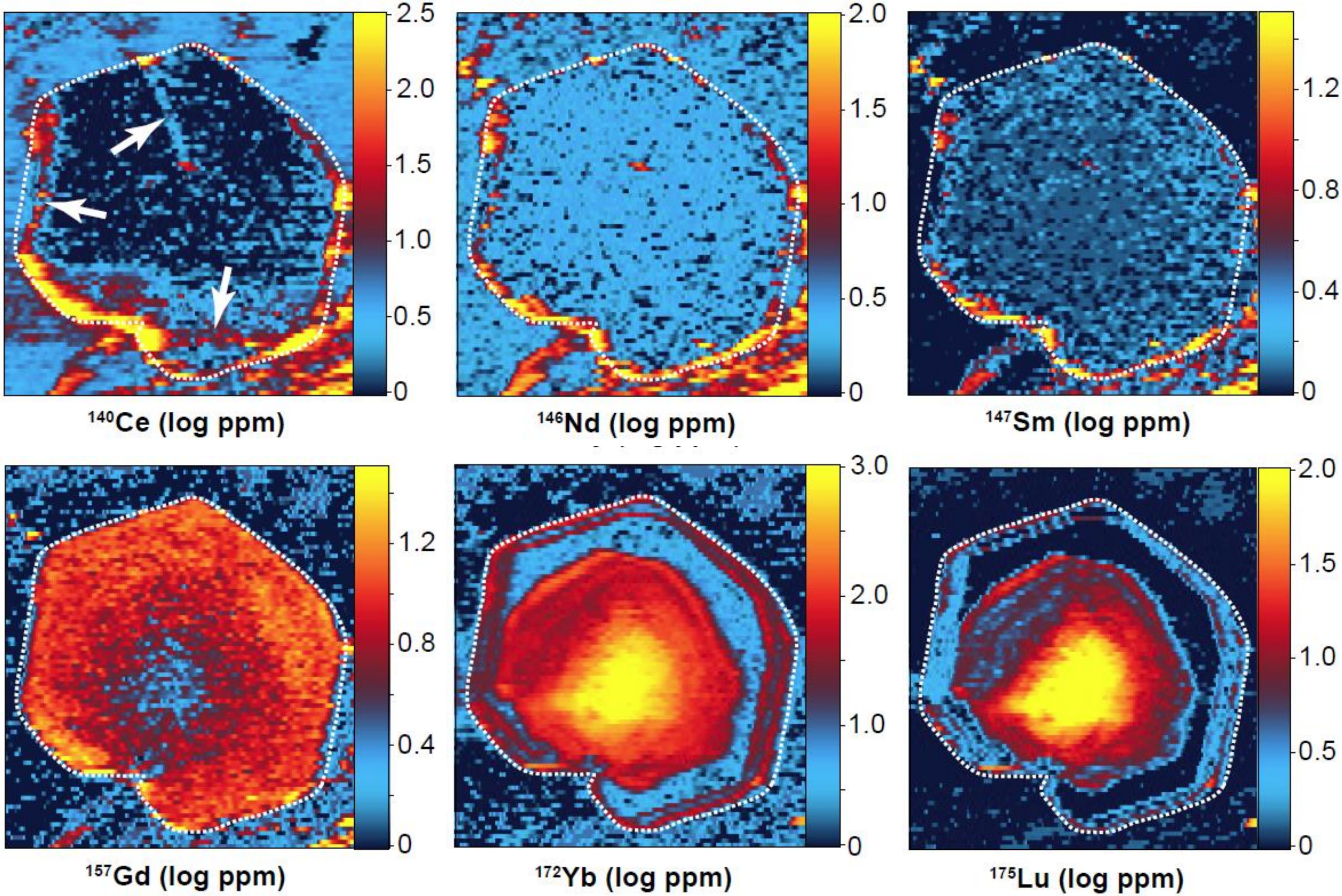
To this…

33 elements, 16 µm spot size, 87 rasters
1.4 x 1.4 mm map, 4.5 hours



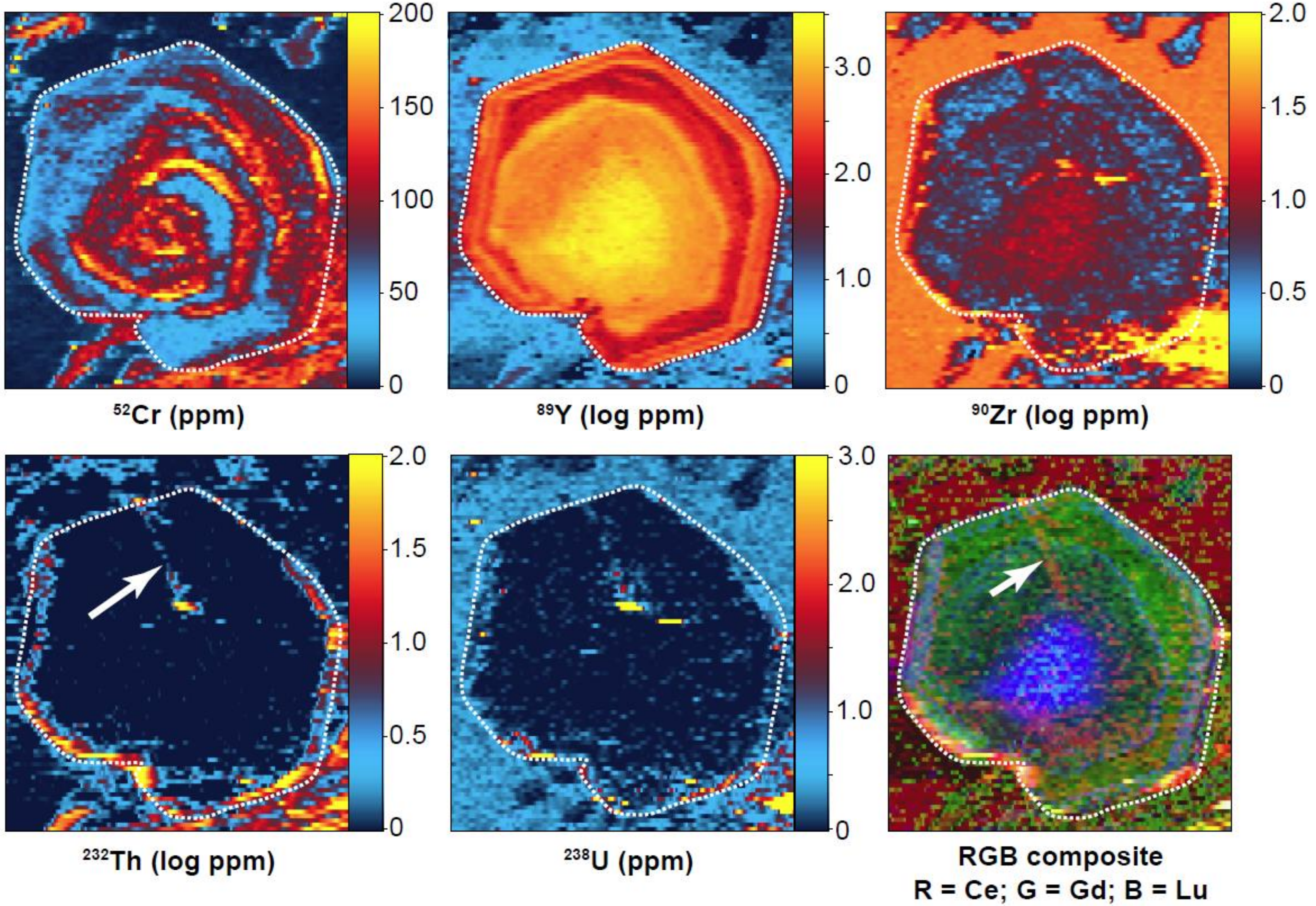


Application – major vs trace elements in garnet

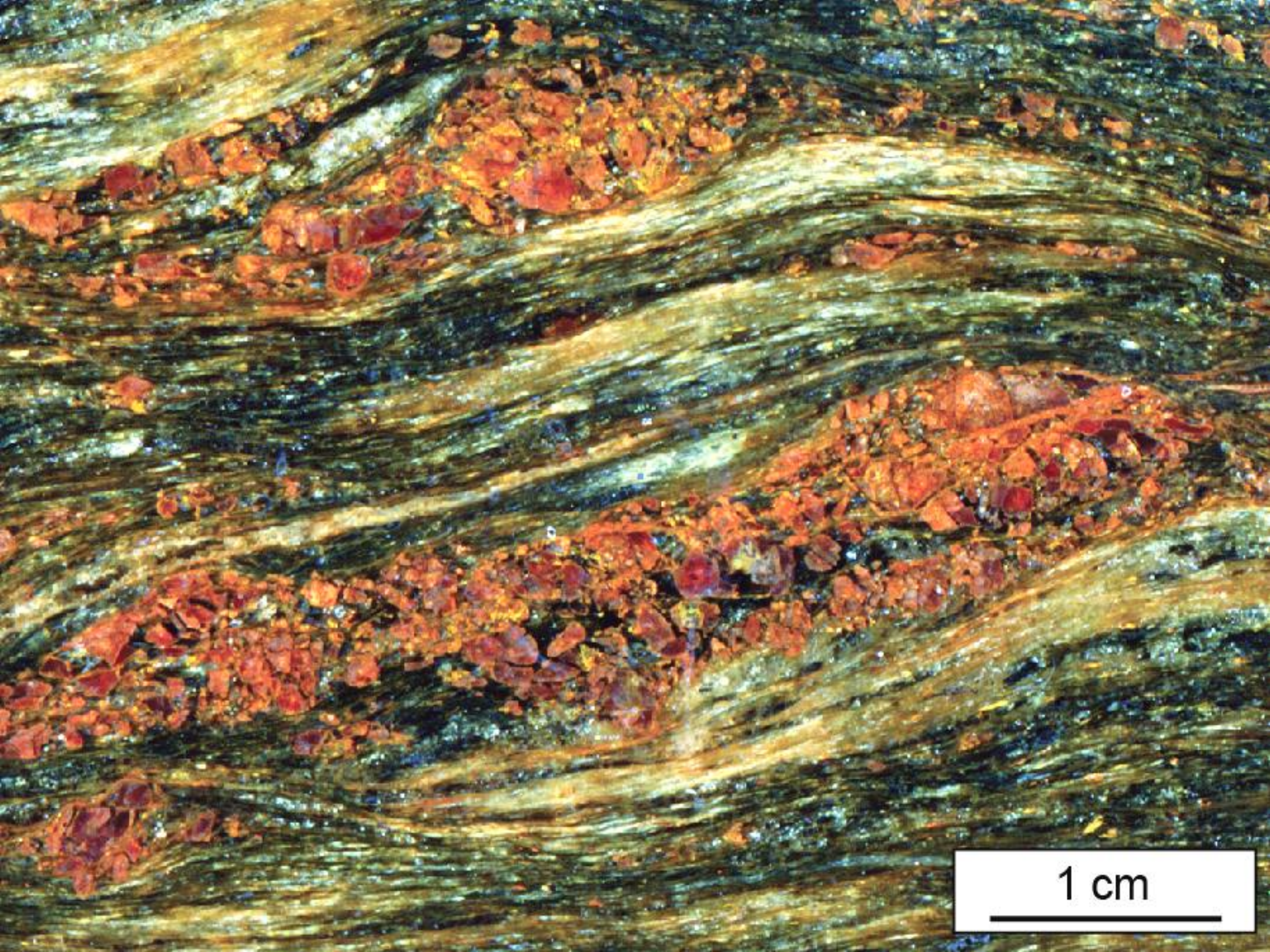


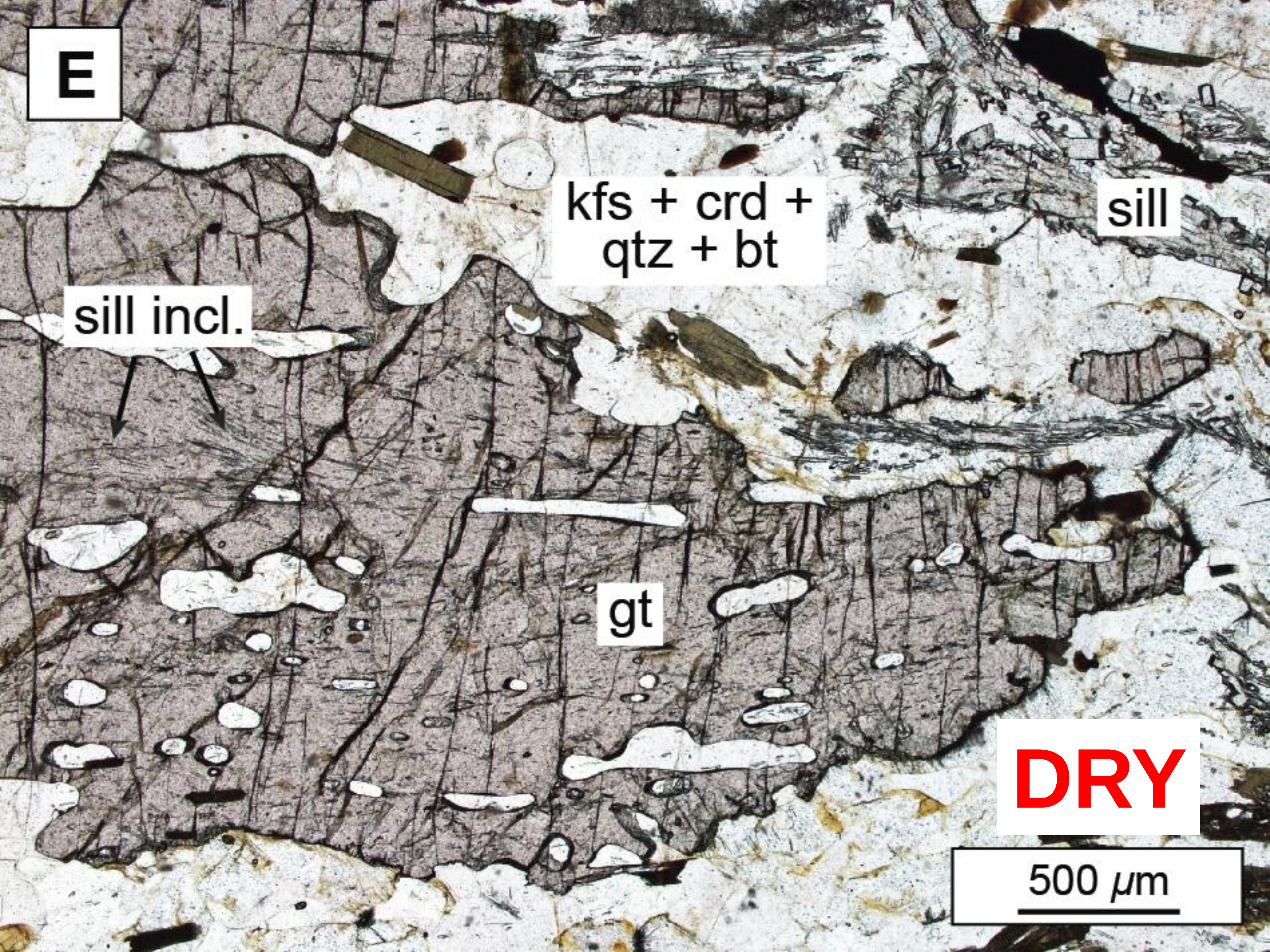
Raimondo, T., Payne, J., Wade, B., Lanari, P., Clark, C. & Hand, M. (2017). Trace element mapping by LA-ICP-MS: assessing geochemical mobility in garnet. *Contributions to Mineralogy and Petrology,* 172(4), 17.

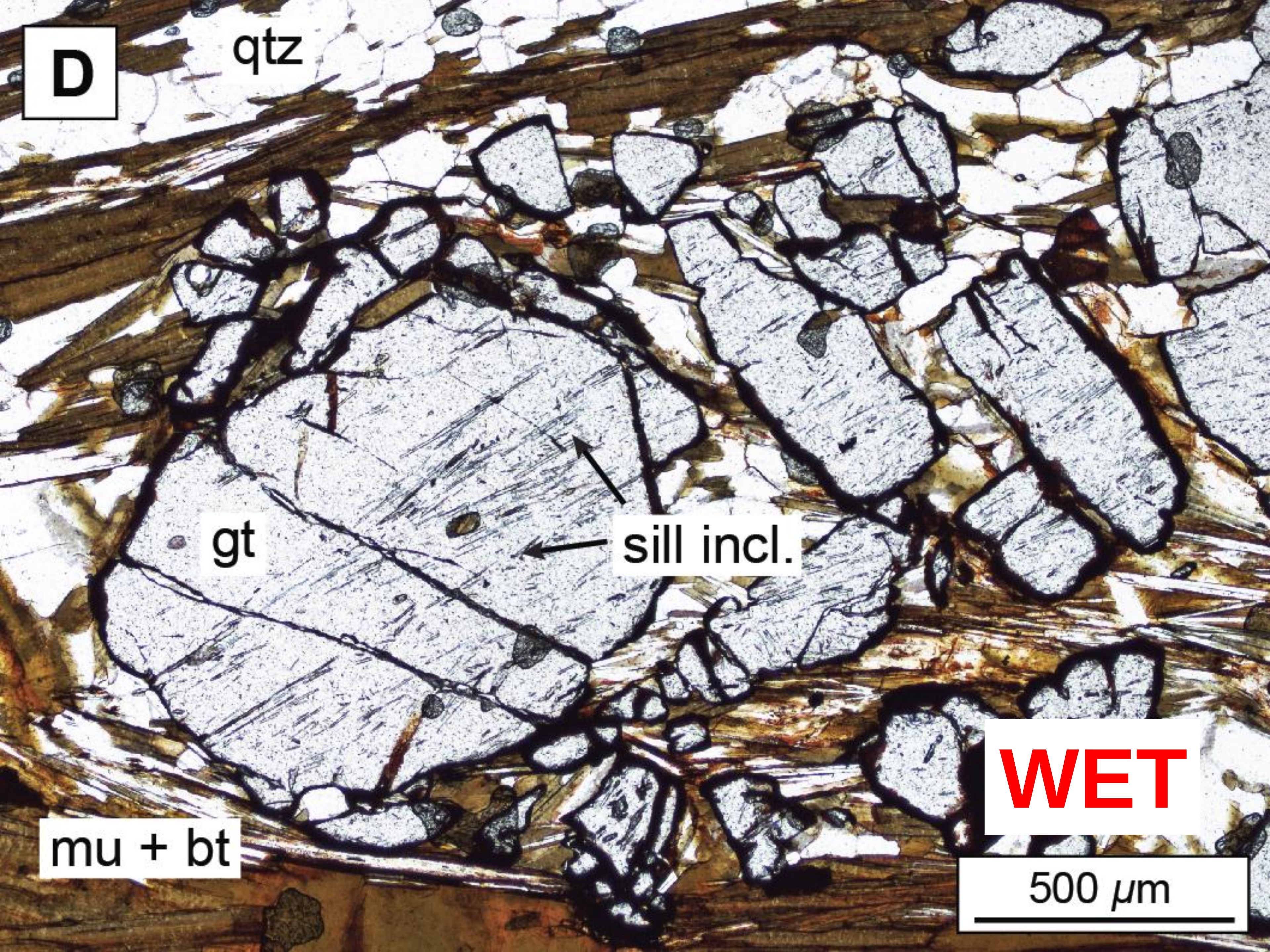
Application – major vs trace elements in garnet



Raimondo, T., Payne, J., Wade, B., Lanari, P., Clark, C. & Hand, M. (2017). Trace element mapping by LA-ICP-MS: assessing geochemical mobility in garnet. *Contributions to Mineralogy and Petrology,* 172(4), 17.

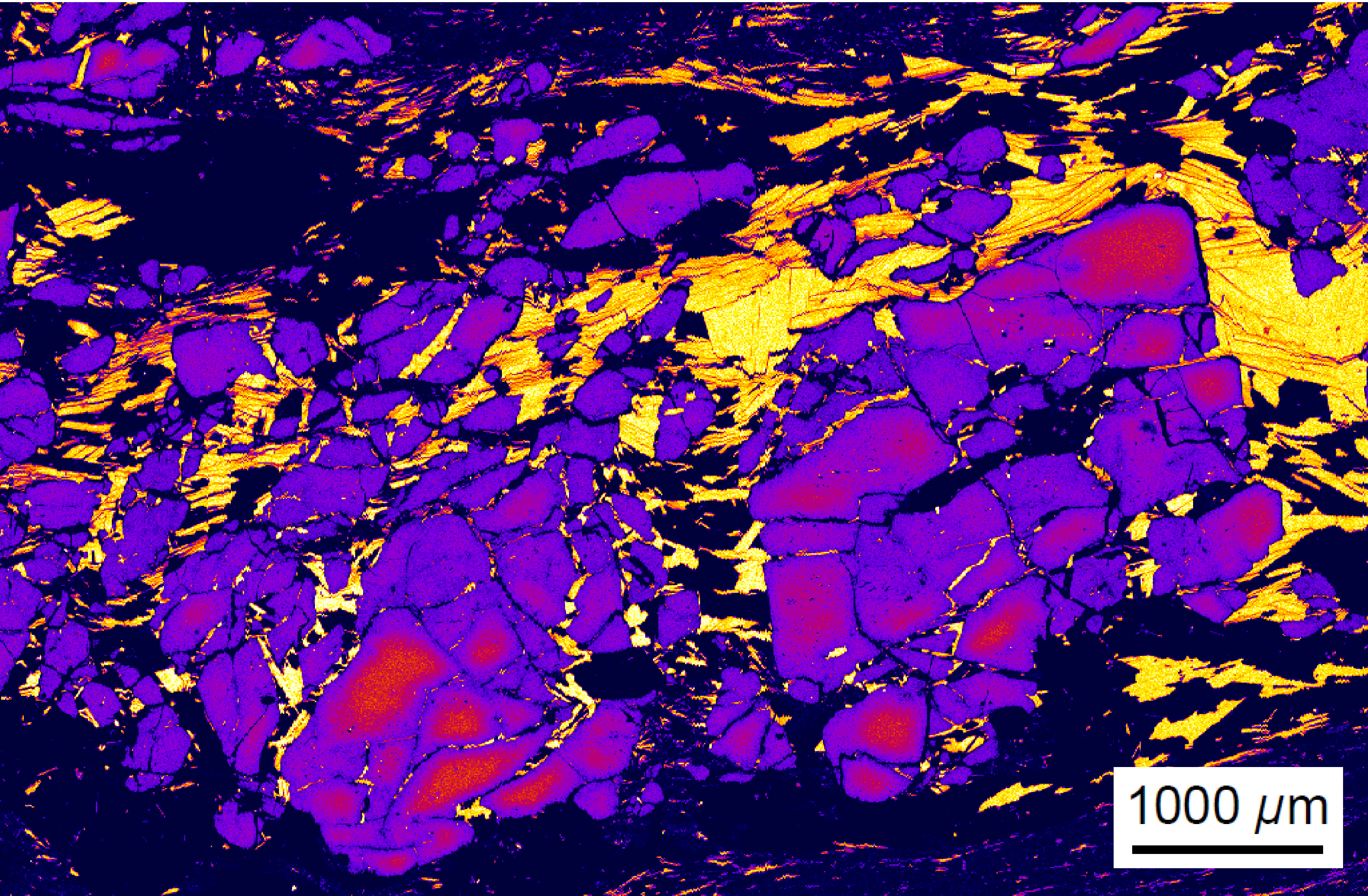

1 cm


E
kfs + crd +
qtz + bt
sill
sill incl.
gt
DRY
500 μm

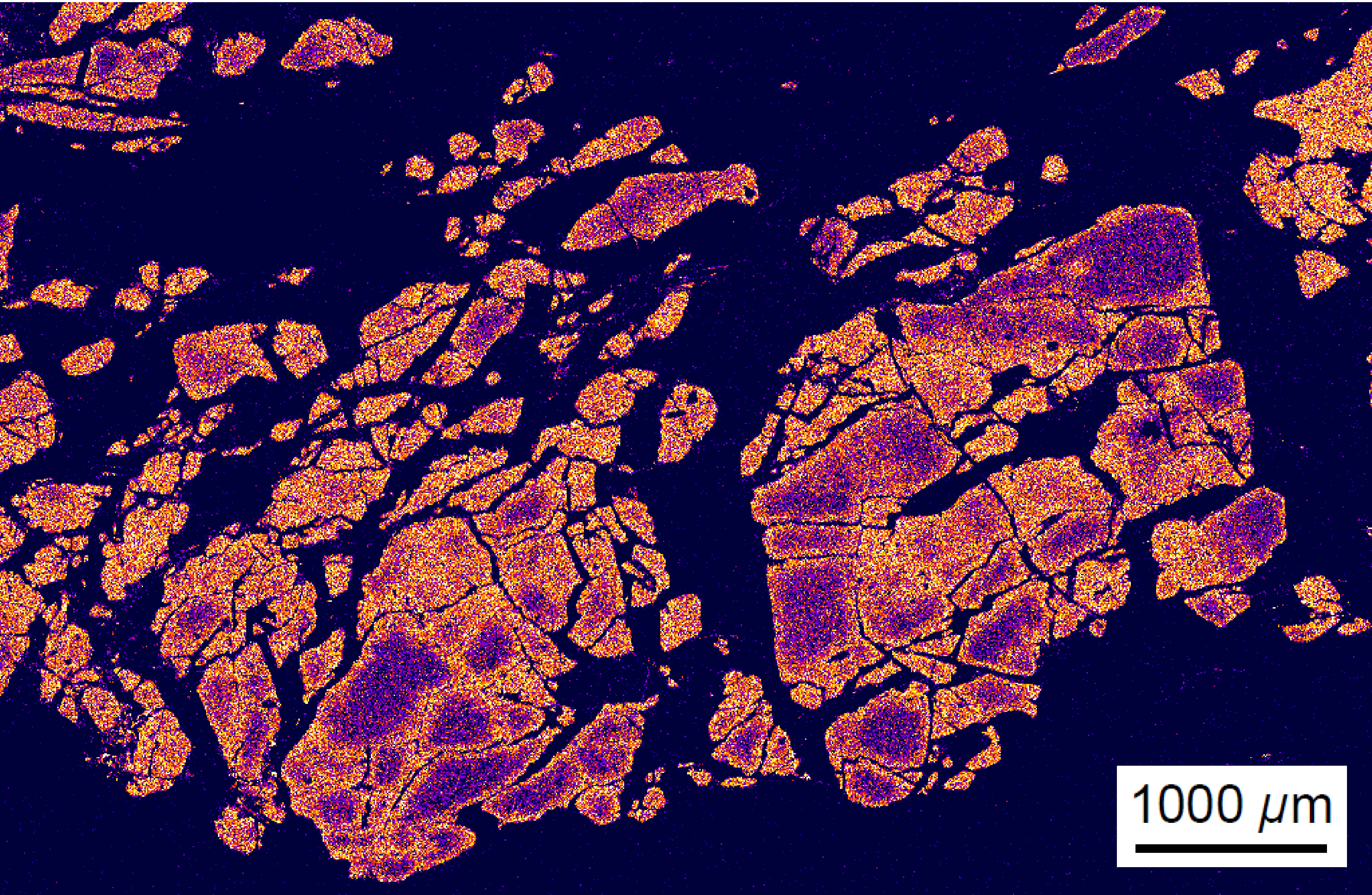


D
qtz
gt
sill incl.
mu + bt
WET
500 μm

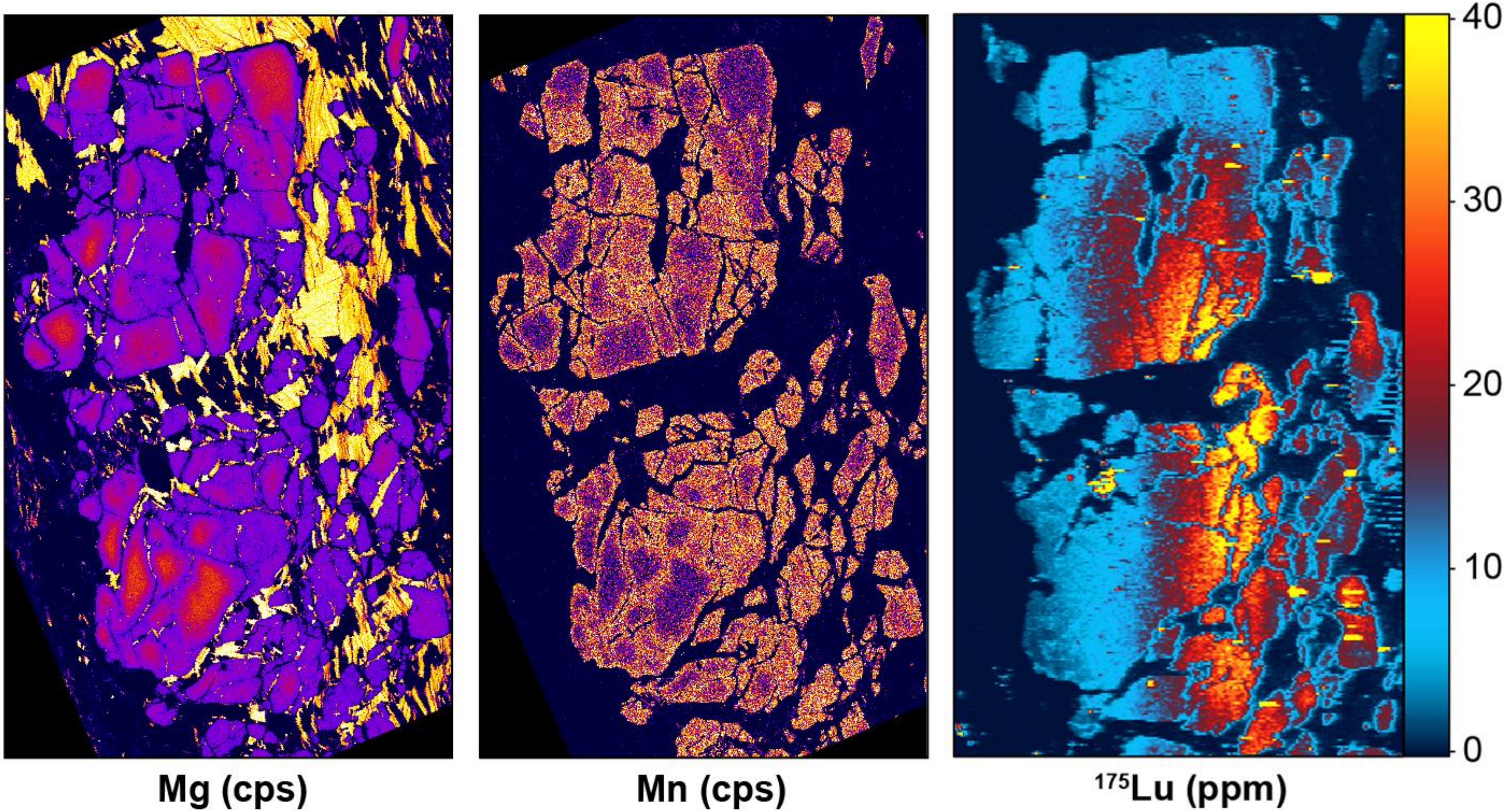
EPMA X-ray map – Mg



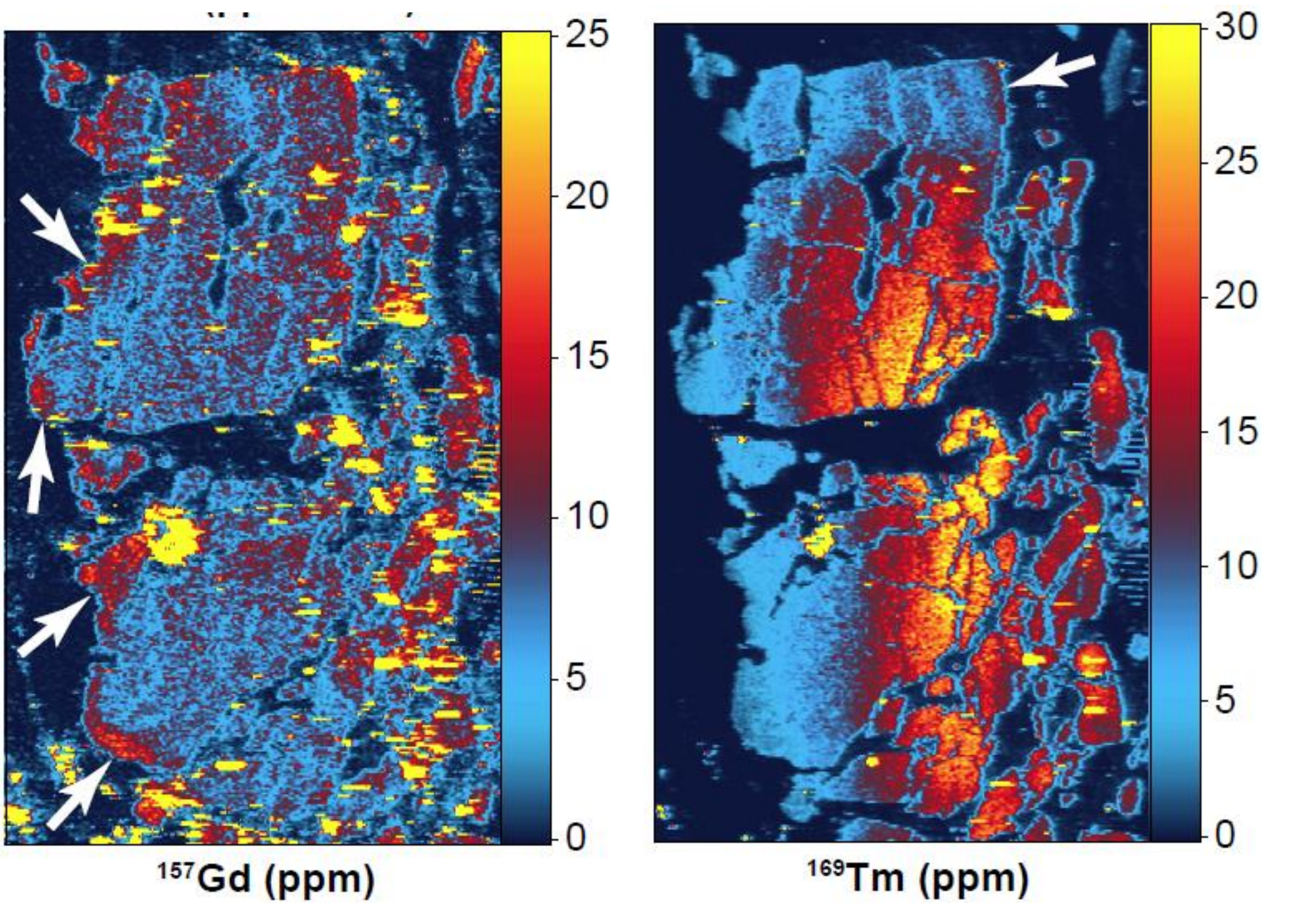
EPMA X-ray map – Mn



Comparison to REE distributions



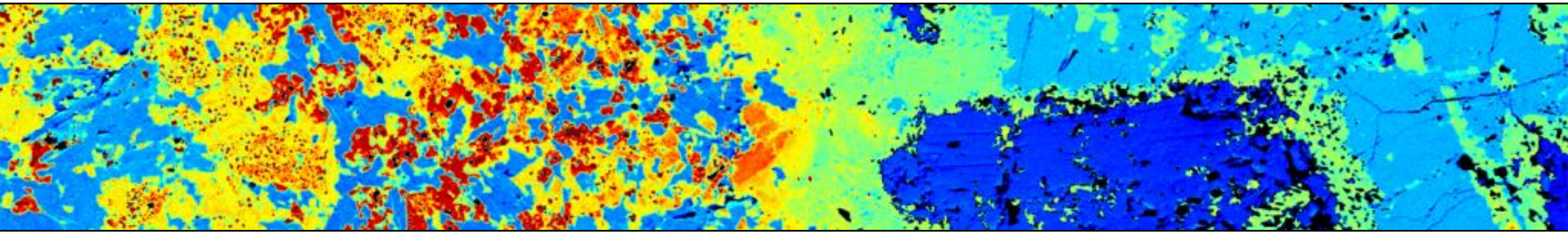
Comparison to REE distributions



Practical demonstration

Trace element mapping by LA-ICP-MS: Data collection, processing and image creation strategies

- DATA WORKFLOW FROM IOLITE TO XMAPTOOLS
- OPTIMIZING IMAGE DISPLAY
- INTRODUCTION OF FEATURES SPECIFIC TO LA-ICP-MS DATASETS



Lecture 8

Trace element mapping by LA-ICP-MS: Advanced image processing modules

Tom Raimondo

University of South Australia – tom.raimondo@unisa.edu.au

- APPLICATION OF CUSTOM LA-ICP-MS MODULES IN PETROLOGY AND PETROCHRONOLOGY
- IMAGE MASKING
- BINARY & TRIPLOT3D MODULES
- RGB IMAGES
- SPIDER DIAGRAMS AND IMAGE RATIOS

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University of South Australia

GOLDSCHMIDT®
BOSTON 2018 | AUGUST 12-17

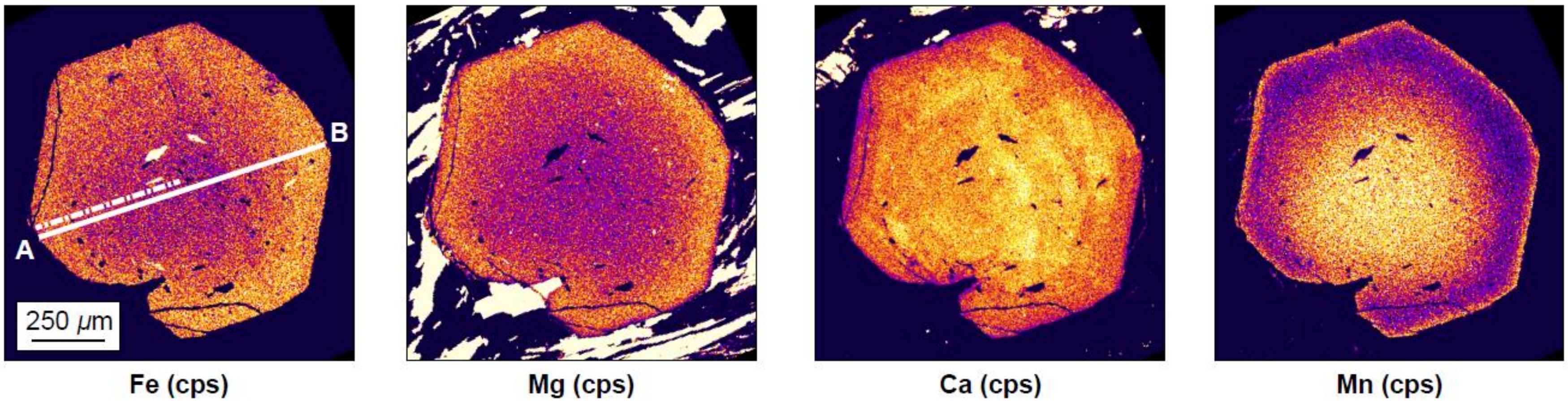
UNIVERSITÄT BERN

Boston (USA) - August, 11th, 12th 2018

Organization: Pierre Lanari; Tom Raimondo; Laura Airaghi; Mahyra Tedeschi
Funding: University of Bern

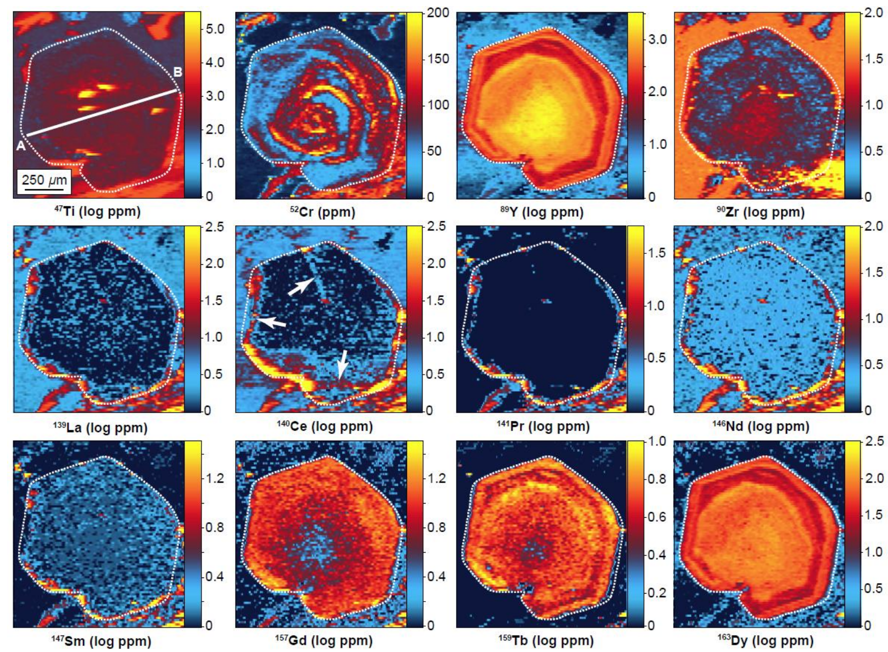
Why map?

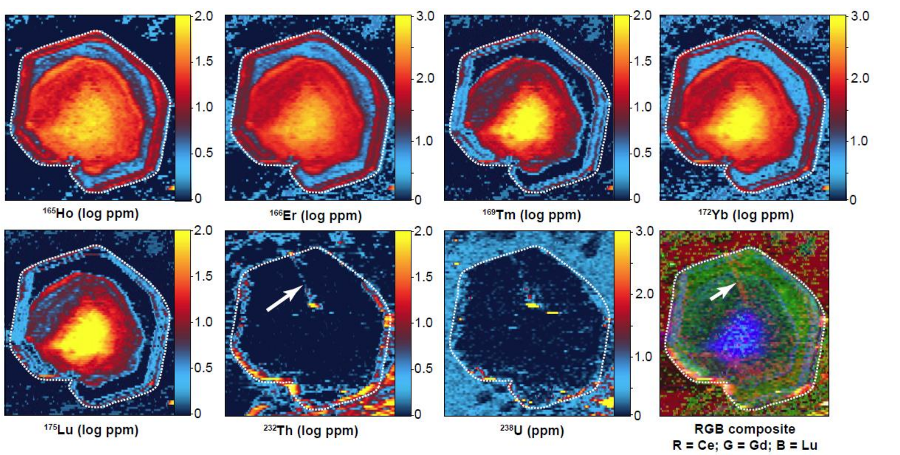
From this...



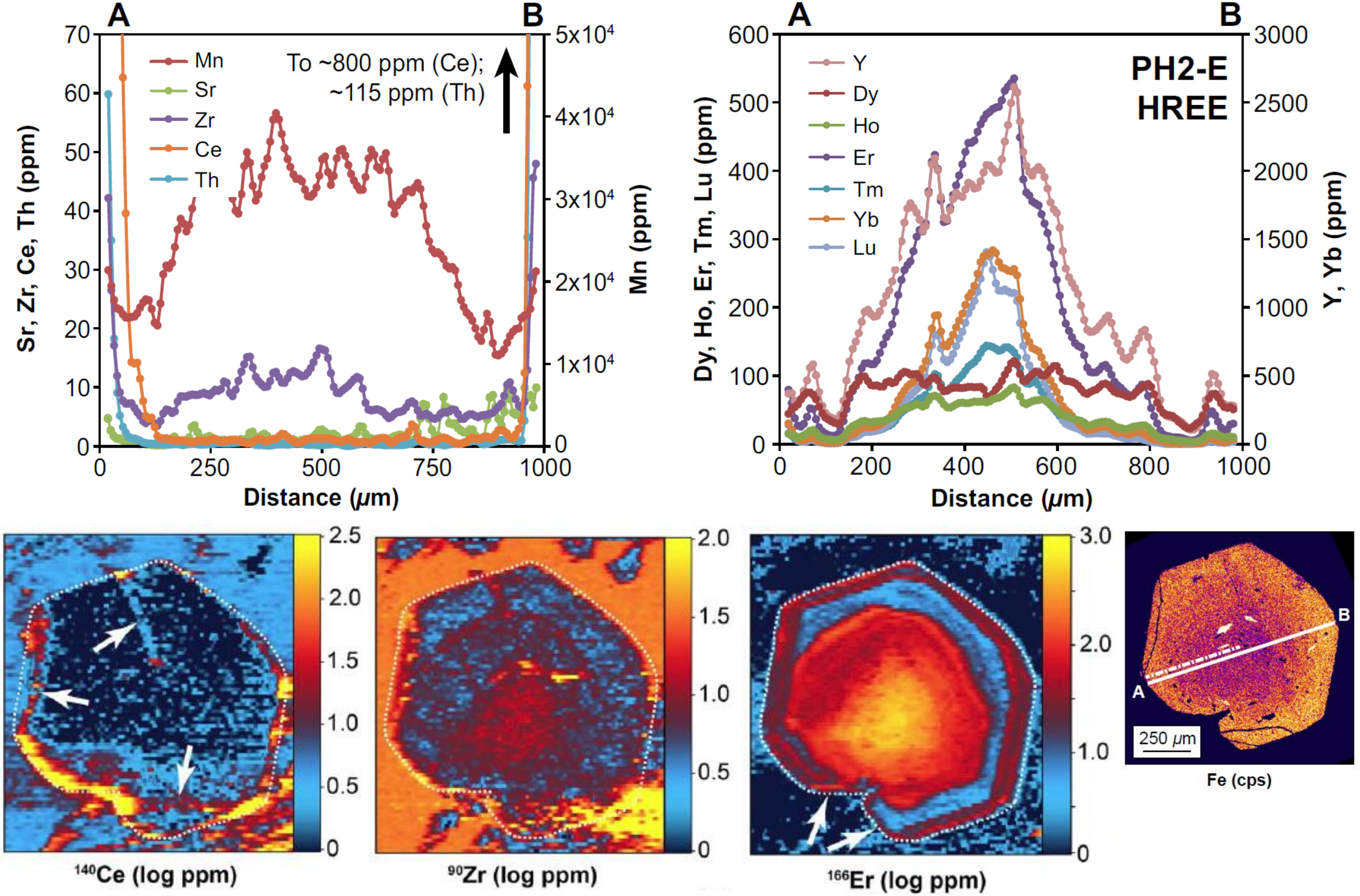
To this…

33 elements, 16 µm spot size, 87 rasters
1.4 x 1.4 mm map, 4.5 hours

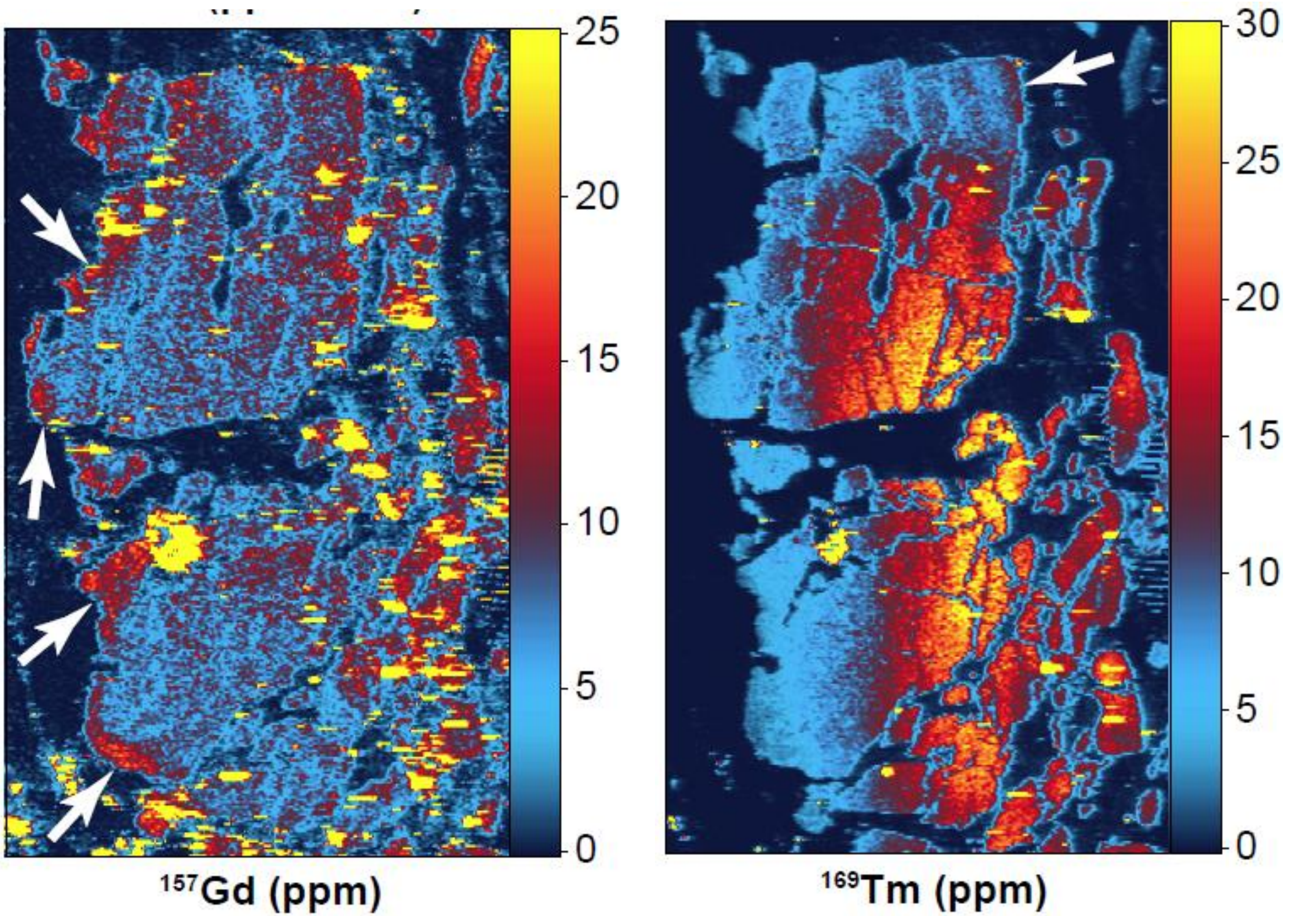




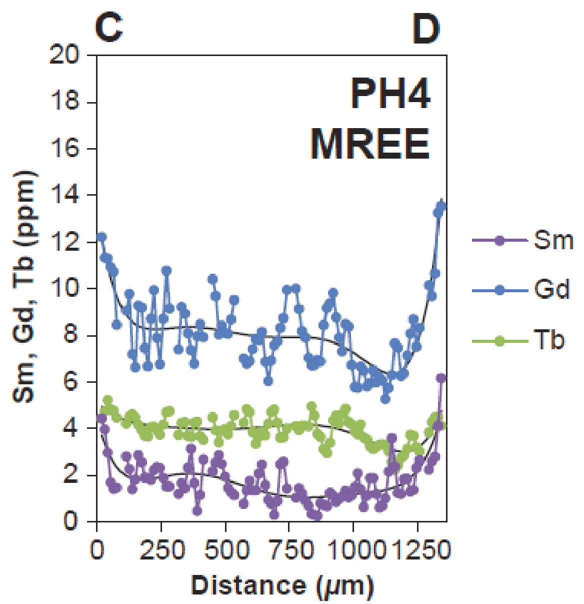
Trace element distributions – linear profiles

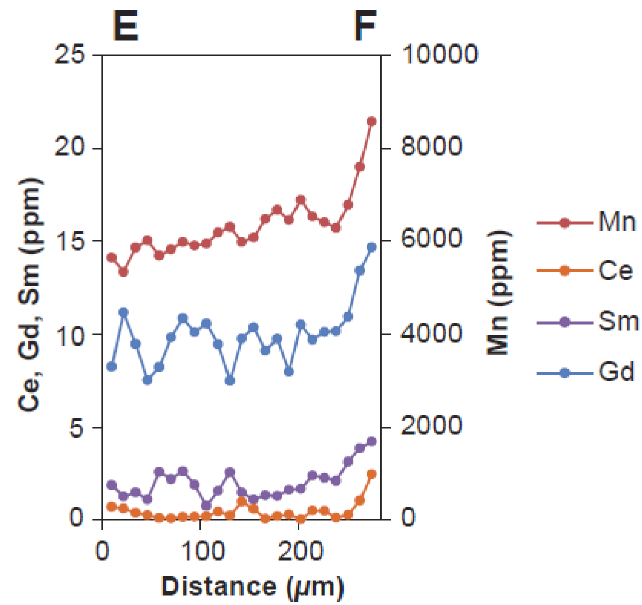


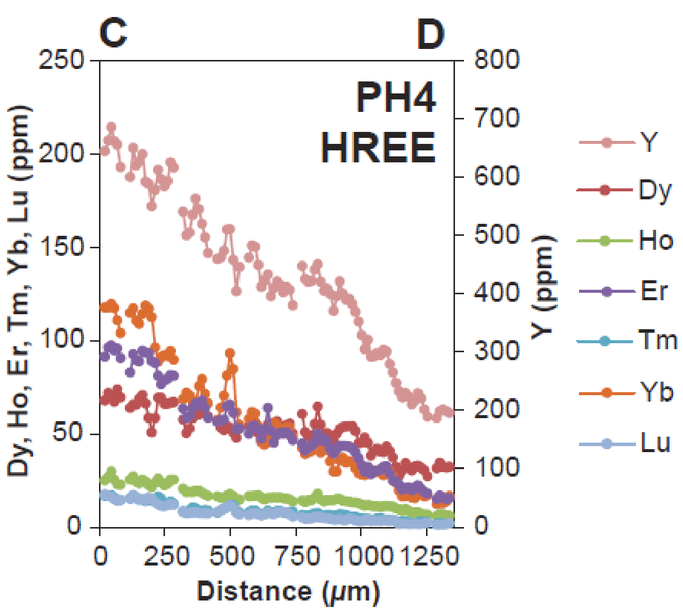
Trace element distributions – linear profiles

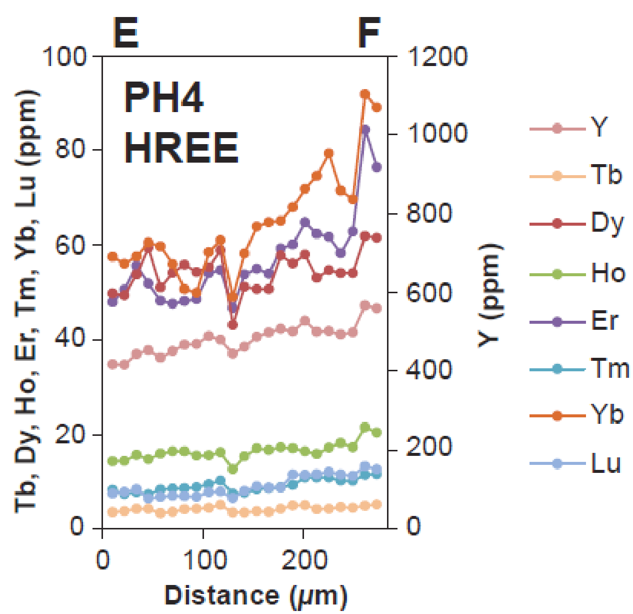


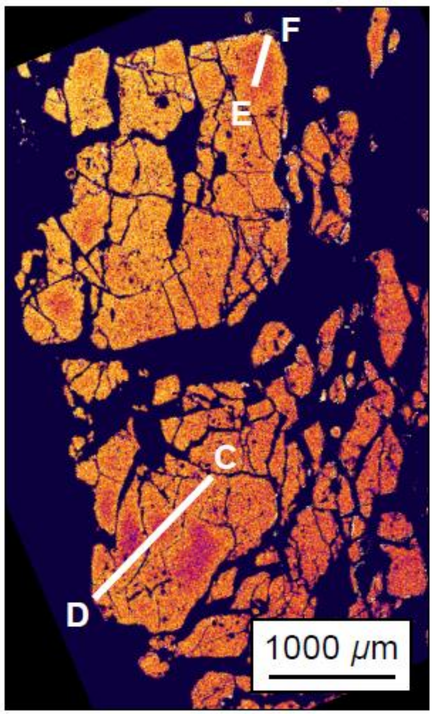
Trace element distributions – linear profiles





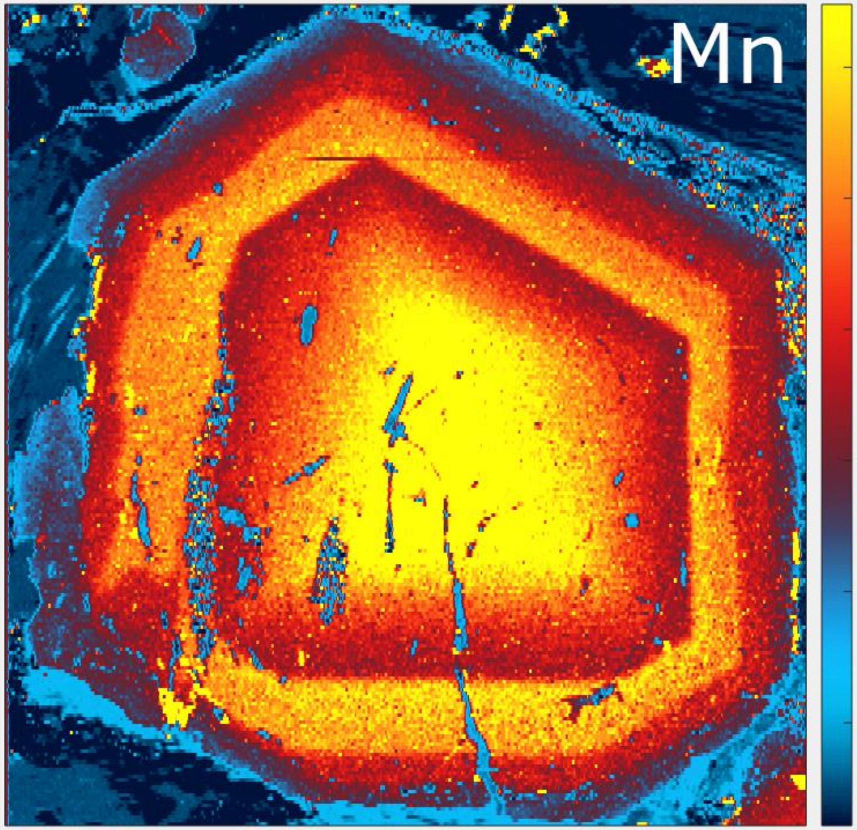




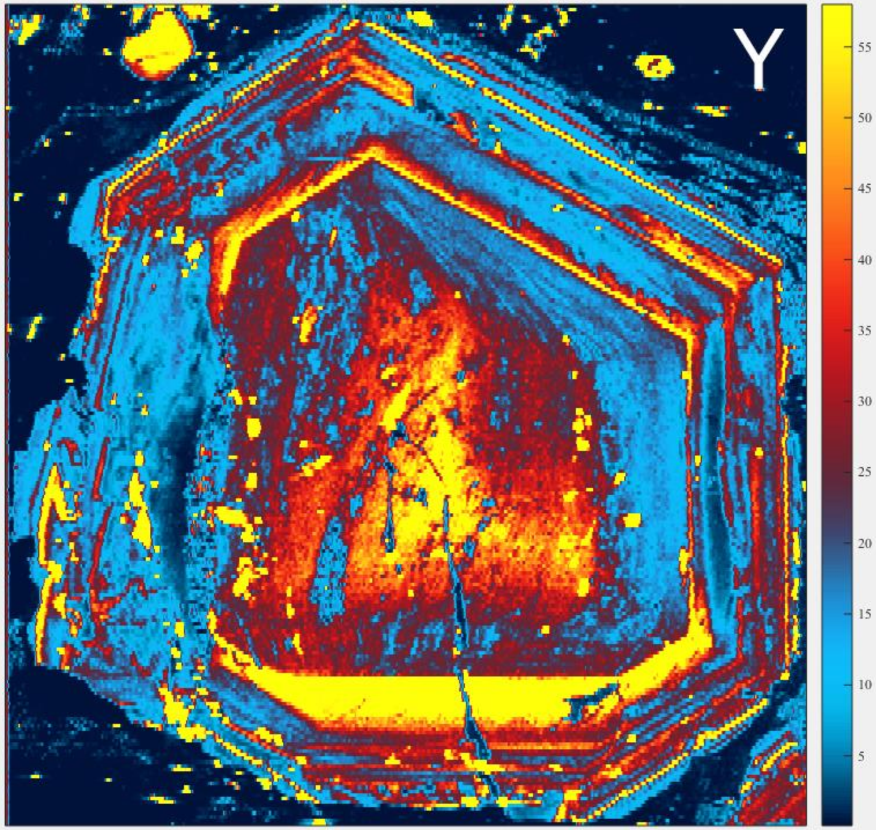


Fe (cps)

Trace element distributions – advanced functions



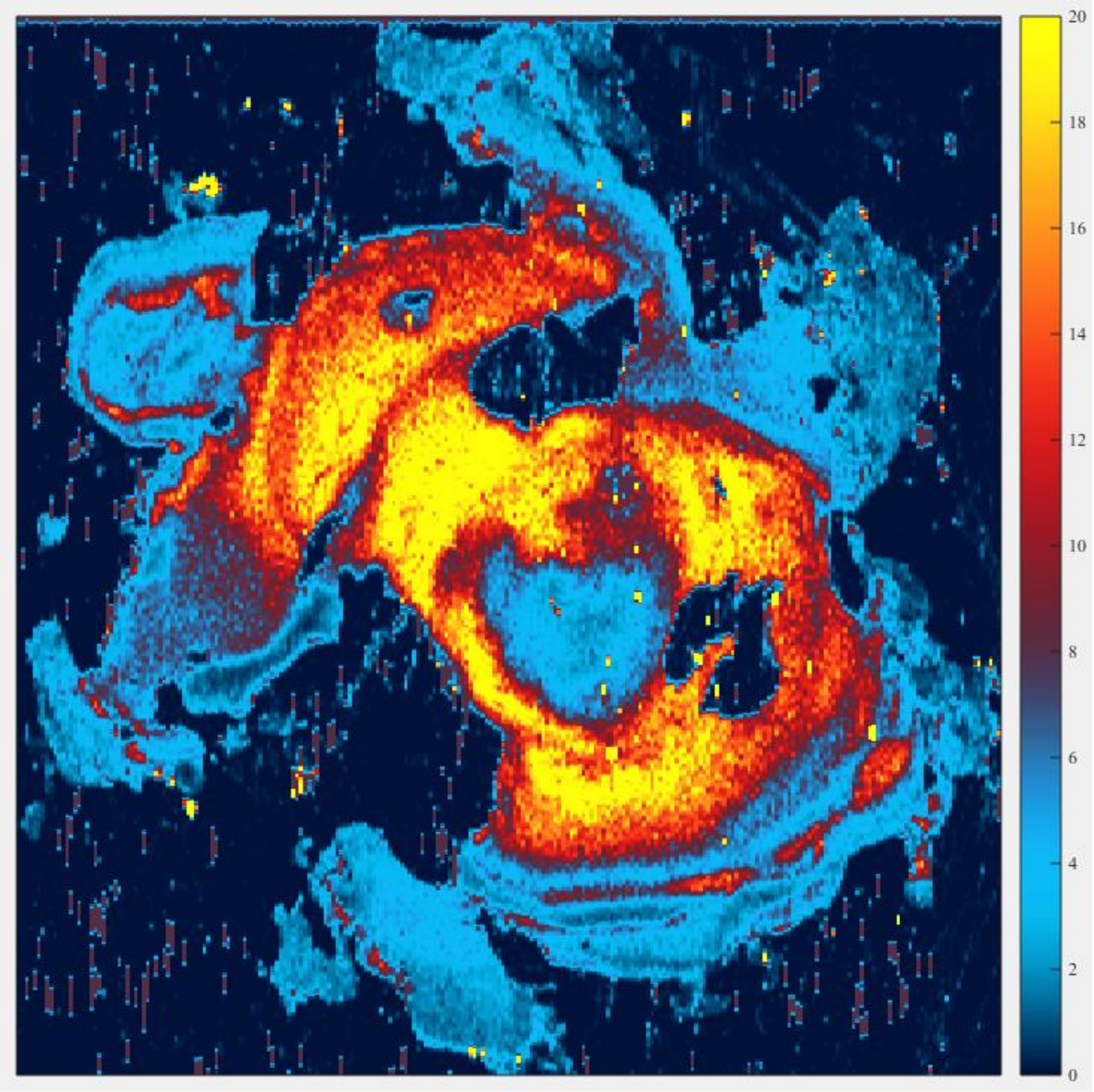
^{55}Mn



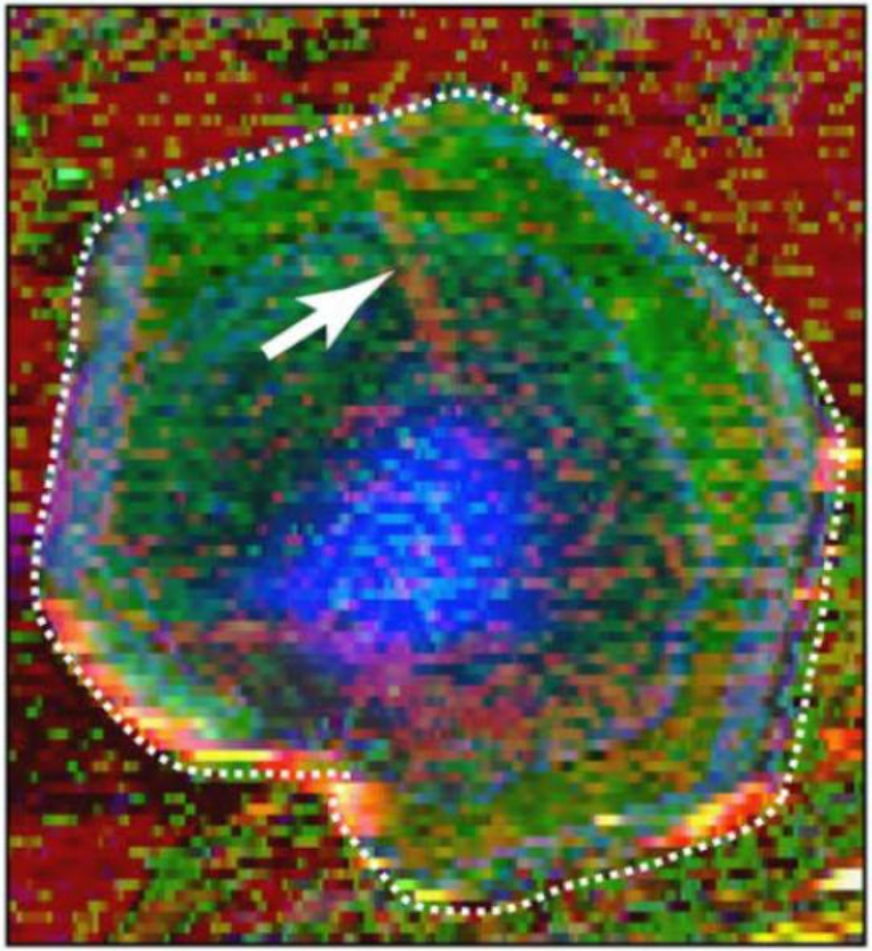
^{89}Y

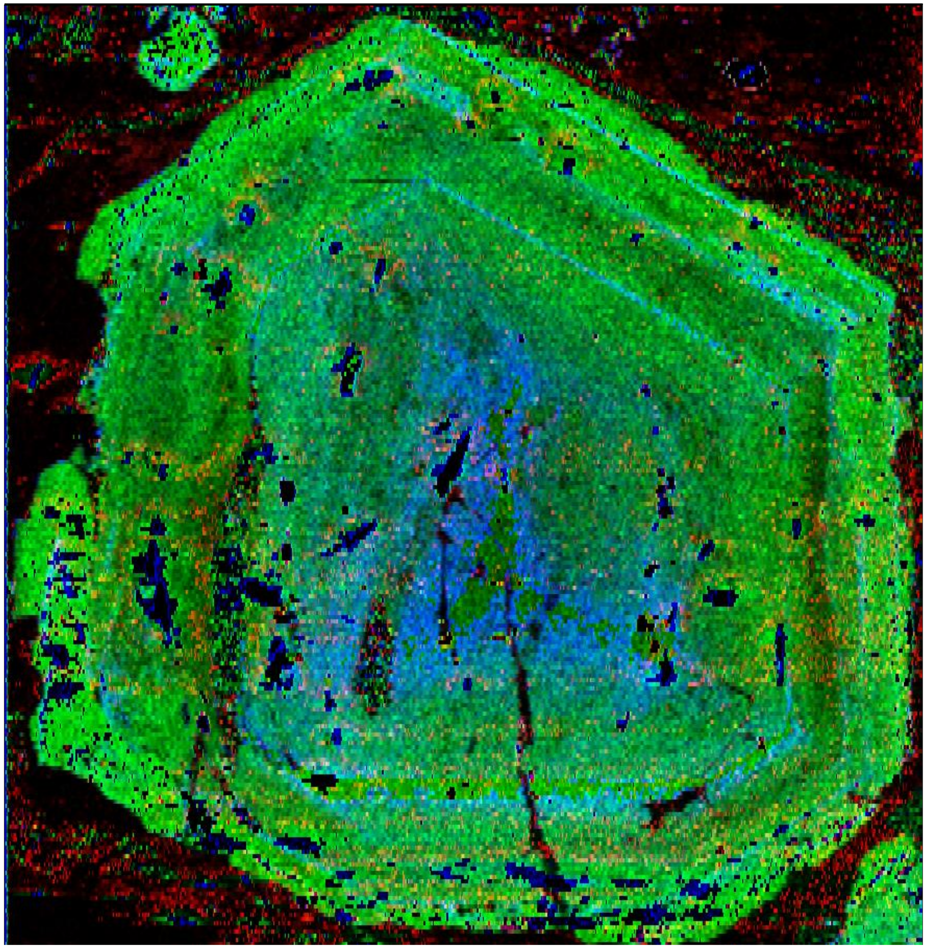
Trace element distributions – advanced functions

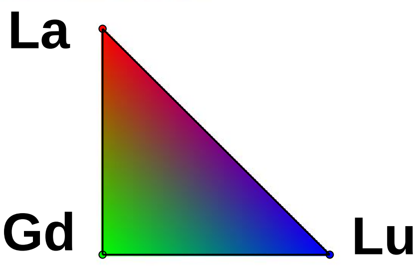
^{165}Ho



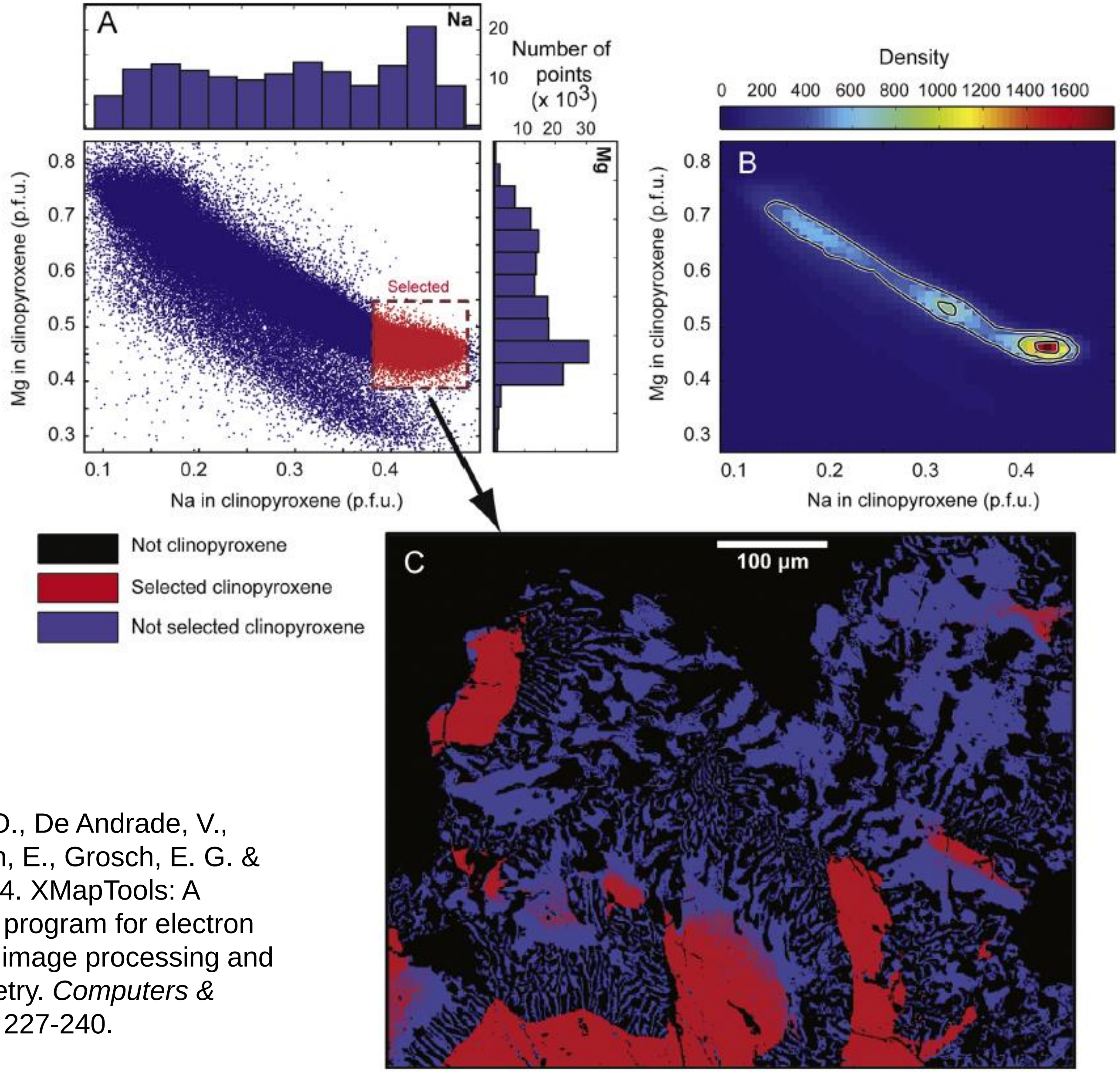
RGB module





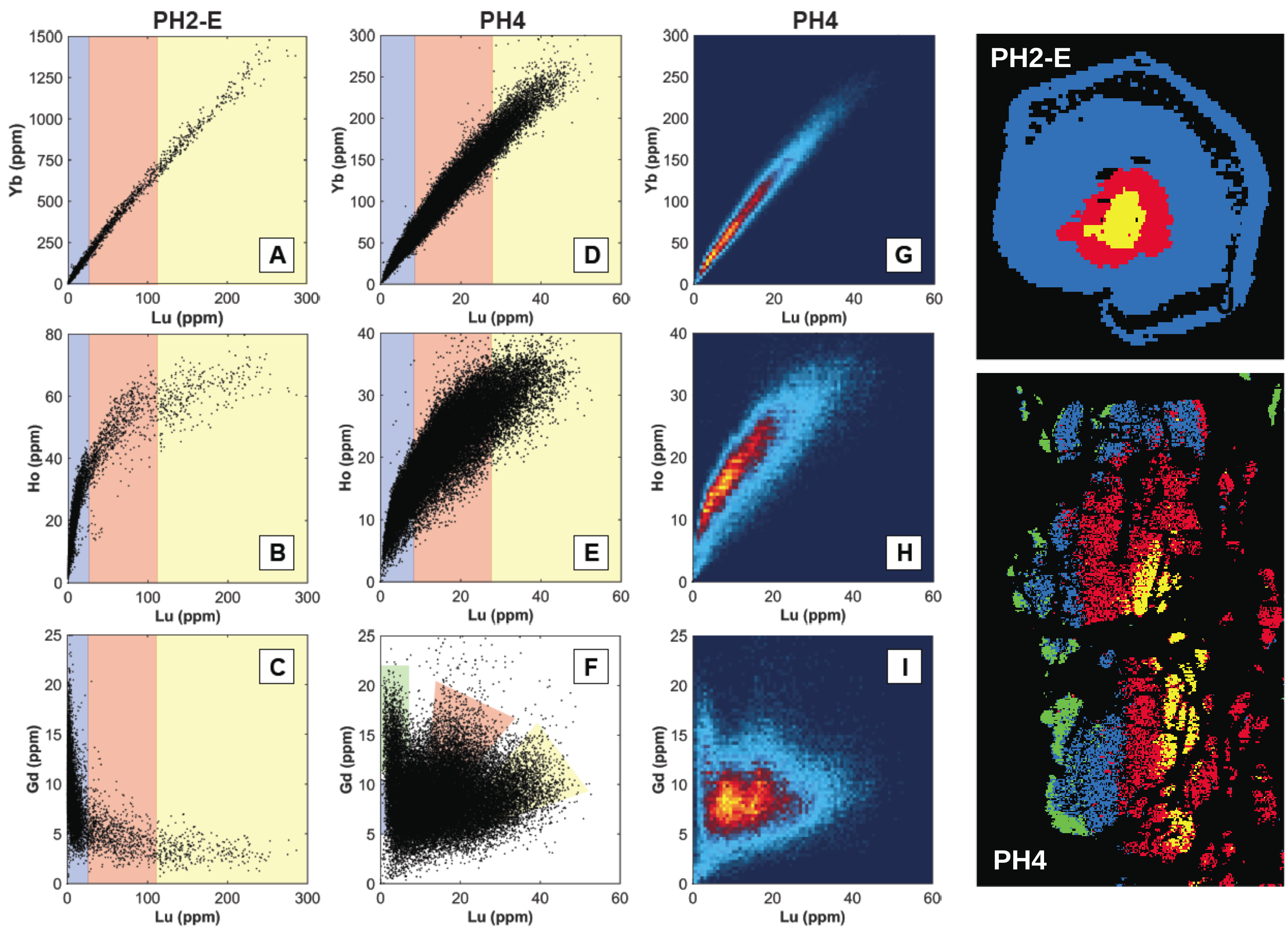


Binary module

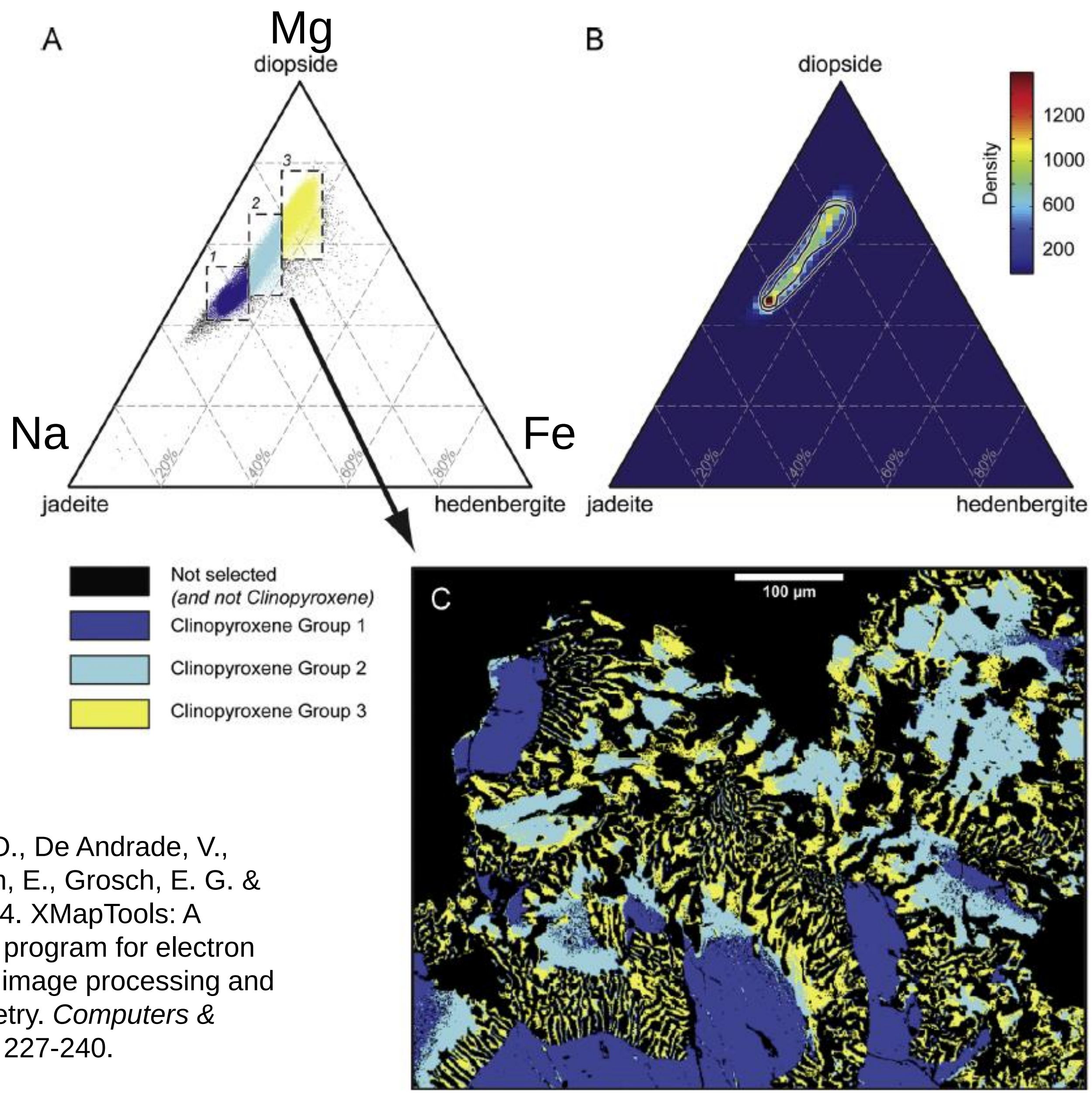


Lanari, P., Vidal, O., De Andrade, V., Dubacq, B., Lewin, E., Grosch, E. G. & Schwartz, S., 2014. XMapTools: A MATLAB©-based program for electron microprobe X-ray image processing and geothermobarometry. *Computers & Geosciences,* 62, 227-240.

Binary module

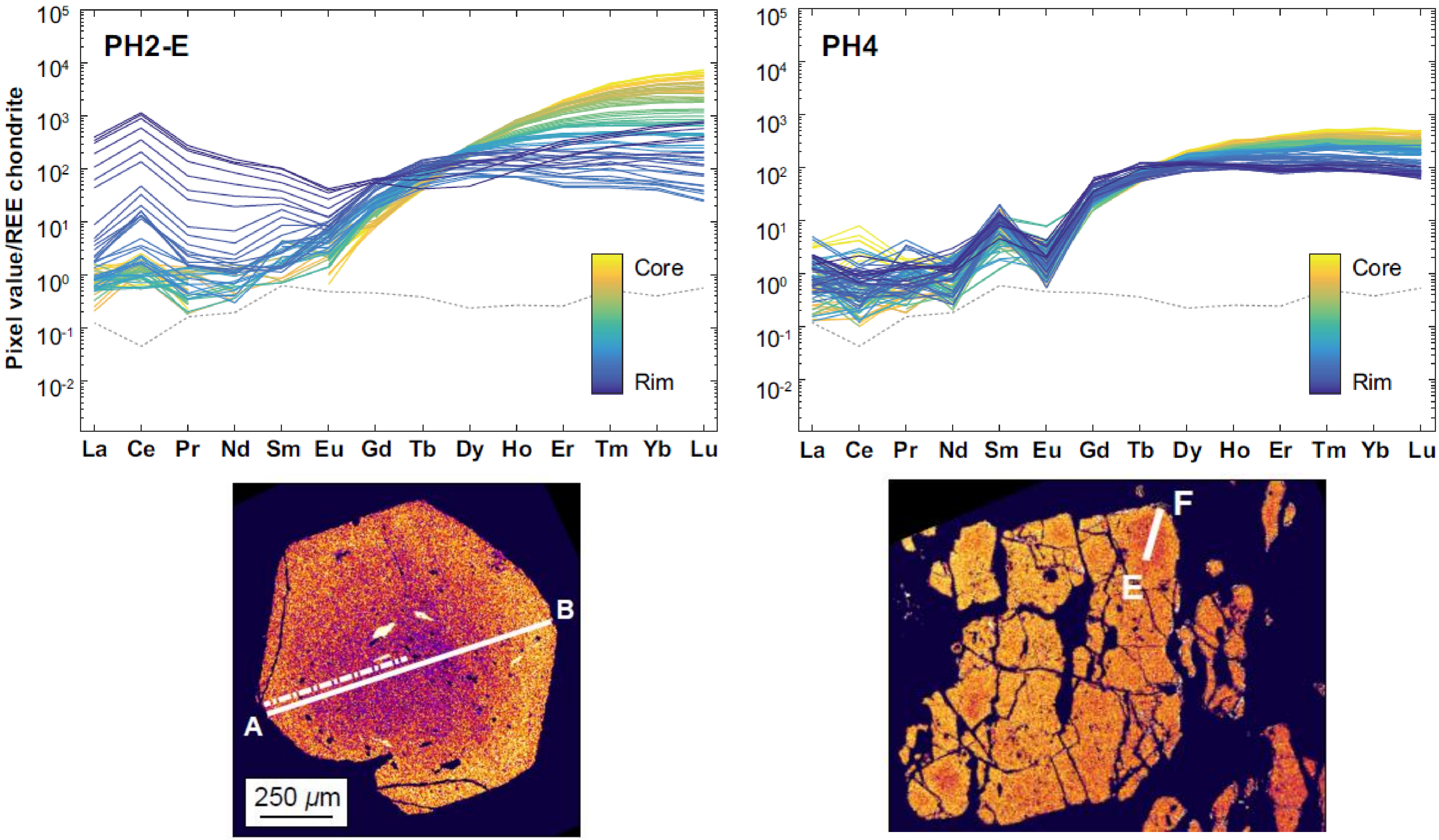


TriPlot3D module



Lanari, P., Vidal, O., De Andrade, V., Dubacq, B., Lewin, E., Grosch, E. G. & Schwartz, S., 2014. XMapTools: A MATLAB©-based program for electron microprobe X-ray image processing and geothermobarometry. *Computers & Geosciences,* 62, 227-240.

Spider module



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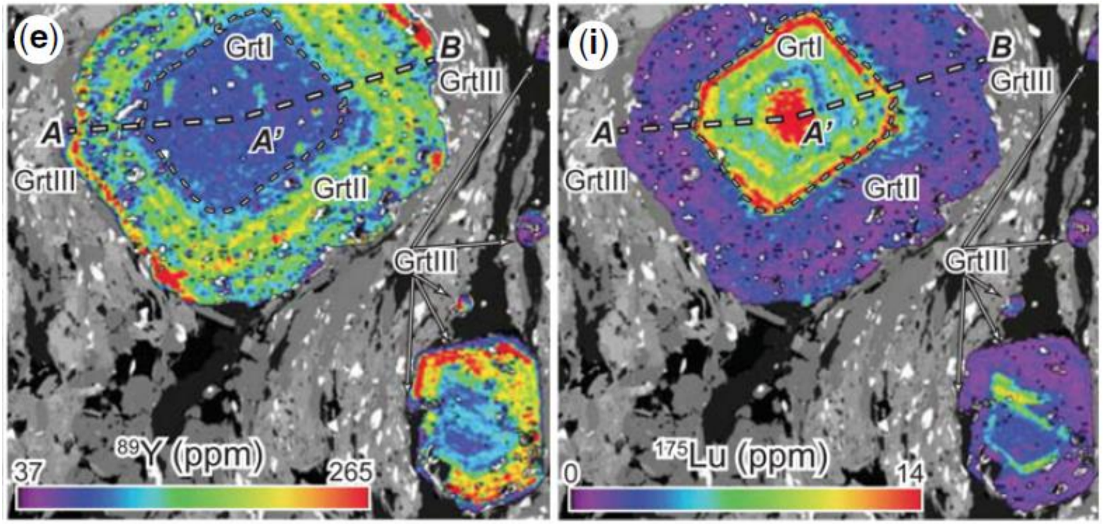
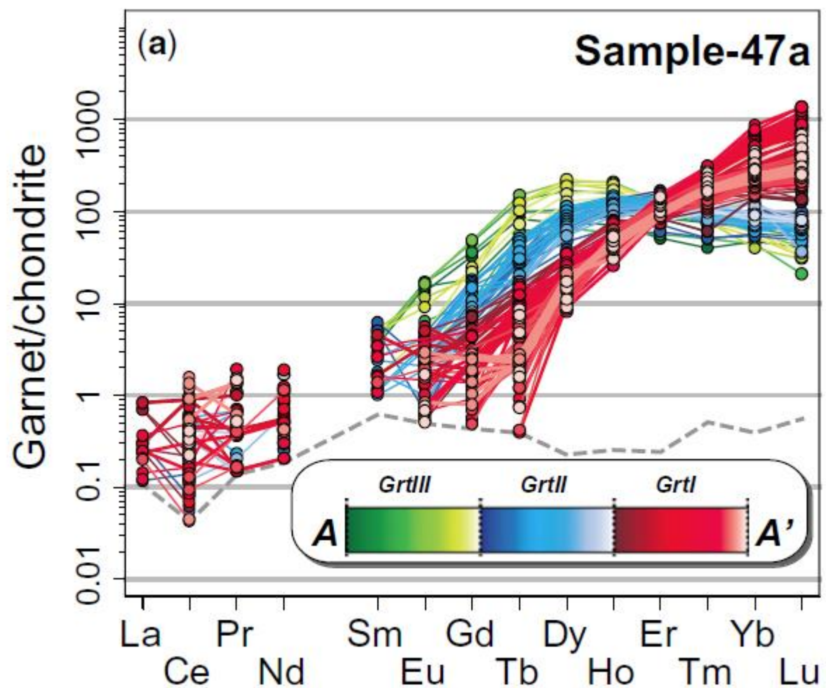
Spider module





Hyppolito, T., Cambeses, A., Angiboust, S., Raimondo, T., García-Casco, A. & Juliani, C. (2018). Rehydration of eclogites and garnet-replacement processes during exhumation in the amphibolite facies. *Geological Society, London, Special Publications,* 478.

Summary

- Contrasting trace element distributions revealed by LA-ICP-MS mapping highlight the complexity of geochemical mobility in garnet through multiple superimposed events
- Trace element mapping is employed to place garnet evolution in a specific paragenetic context and derive absolute age information by integration with existing U–Pb monazite and Sm–Nd garnet geochronology
- Remarkable preservation of original growth zoning and its subtle modification by subsequent re-equilibration is used to ‘see through’ multiple superimposed events
- LA-ICP-MS mapping technique offers a powerful means to visualise and interpret compositional zoning patterns produced during metamorphism, deformation, alteration and mineralisation
- It can also be an effective technique for screening samples likely to give meaningful Lu-Hf/Sm-Nd ages, plus a more robust method for interpreting the geological significance of such ages once obtained

Practical demonstration

Trace element mapping by LA-ICP-MS: Advanced image processing modules

- Application of custom LA-ICP-MS modules in petrology and petrochronology
- Image masking
- Binary & Triplot3D modules
- RGB images
- Spider diagrams and image ratios

QUESTIONS / DISCUSSION