Double Digit Megapixel Elemental Imaging at >1 Megapixel per Hour

15 Megapixel Deep Ocean Polymetallic Nodule Images Collected at 1.6 Megapixels per Hour

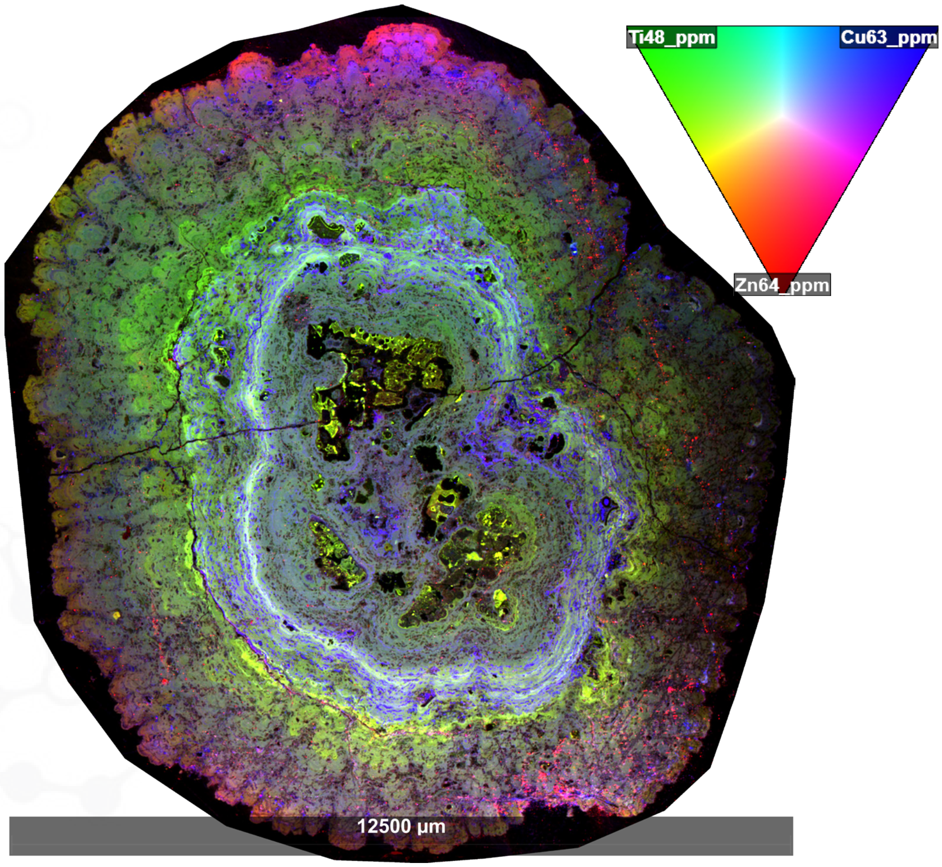


Figure 1. Elemental image of Ti, Cu and Zn concentrations (ppm) across a deep ocean polymetallic nodule. Image is >15 MPx at 3µm resolution, with an imaging speed of 1.6 MPx per hour.

Brief

The combination of fast washout laser ablation (LA) systems [imageGEO193 and imageBIO266] and time of flight mass spectrometry (LA-ICP-TOF-MS) has pushed elemental imaging capabilities beyond 1000 pixels per second. The sample chamber single pulse response (SPR) and the cycle time of the mass spectrometer are key areas that have received significant development in recent years e.g. the TwoVol3, DCI2, etc. However, total analysis time for defect free imaging is affected by many other factors such as stage precision, correlation of laser triggering with the transient data, robust instrument communication, and an optimised duty cycle for both instruments. Here we detail the first double-digit megapixel elemental map (>15 MPx) collected at a rate far in excess of the "golden barrier" of 1 million pixels per hour: 1.6 MPx/hour - using the imageGEO193 with pixel resolution of 3 µm.

Deep Ocean Polymetallic Nodules

With increasing demand for technology-critical metals, efforts to find and characterise new deposits with lower environmental impact and greater yield are of critical strategic and economic importance. Deep ocean polymetallic nodules offer a favorable alternative to terrestrial mining as their chemical composition is controlled by their formation process; uniquely, a single nodule will likely contain high concentration of multiple critical metals (Mn, Fe, Co, Cu, Ti, Ni, etc.). During exploration the characterisation of these nodules, e.g. the metal concentration and their distribution throughout the nodule, are key in determining the economic viability of mining these resources.

Instrumentation – the imageGEO193

The imageGEO193 has been designed to tackle the demanding needs of fast, high-resolution elemental imaging:

- The TwoVol3 chamber provides the Single Pulse Response (SPR <1 ms in combination with the DCI2) necessary to differentiate individual packets of sample material whilst high precision stages ensure accurate and reproducible shot placement (via encoder driven closed-loop feedback) to ensure maps are complete and artefact free.
- A high repetition rate laser and rotatable beam delivery optics ensure long optic lifetime whilst maintaining stable energy delivery throughout long imaging campaigns.
- A high-resolution camera and bespoke microscope provide clear sample viewing for accurate focus of the laser on the sample, ensuring good data quality whilst also providing capture of sample mosaics to overlay on subsequent elemental maps.
- Robust and fast communication between the laser and ICP-TOF-MS for continuity of measured signals and experiment meta data e.g. sample ID, spot size, repetition rate, XYZ coordinates, etc. collated and linked in iolite4 data processing/reporting.

Table 1. Sampling Parameters for the imageGEO193

imageGEO193 Parameters	Value
Repetition rate	950 Hz
Translation rate	2850 µm·s-1
Spot size	15,059,659 pixels 3 x 3 µm square (dosage 1)
SPR	<1 ms
Helium flow	Chamber - 160 mL/min; Cup – 250 mL/min
Cup Spacing	600 µm
Area	4592 lasso lines covering 12.69 x 13.78 mm
Acquisition time for sample	9 hours 11 minutes
ICP-TOF-MS	**Value**
Ar nebulizer gas	1180 mL/min
RF power	1300 W
Integration time	0.22 ms

Automatic Single Pulse Response Optimisation – TV Tuner

ESL's TV Tuner automatically optimizes sample chamber gas flows and sample-to-cup spacing for the shortest SPR (<1 ms); simplifying experimental setup for users and maximizing performance for each sample type. An experimental design, populated within ActiveView2, is sent via plugin or WCF communication to the ICPMS. Bi-directional triggering provides unattended analysis, and progression through all experimental conditions whilst allowing for stabilization of chamber pressure. Chronicle retrieves the transient MS data (typically CSV or native TOFWERK and Nu Instruments data formats) whilst TV Tuner processes the single peak response, to produce a heat map of signal metrics e.g. peak height, peak width, etc. and allows users to select their optimum operating conditions.

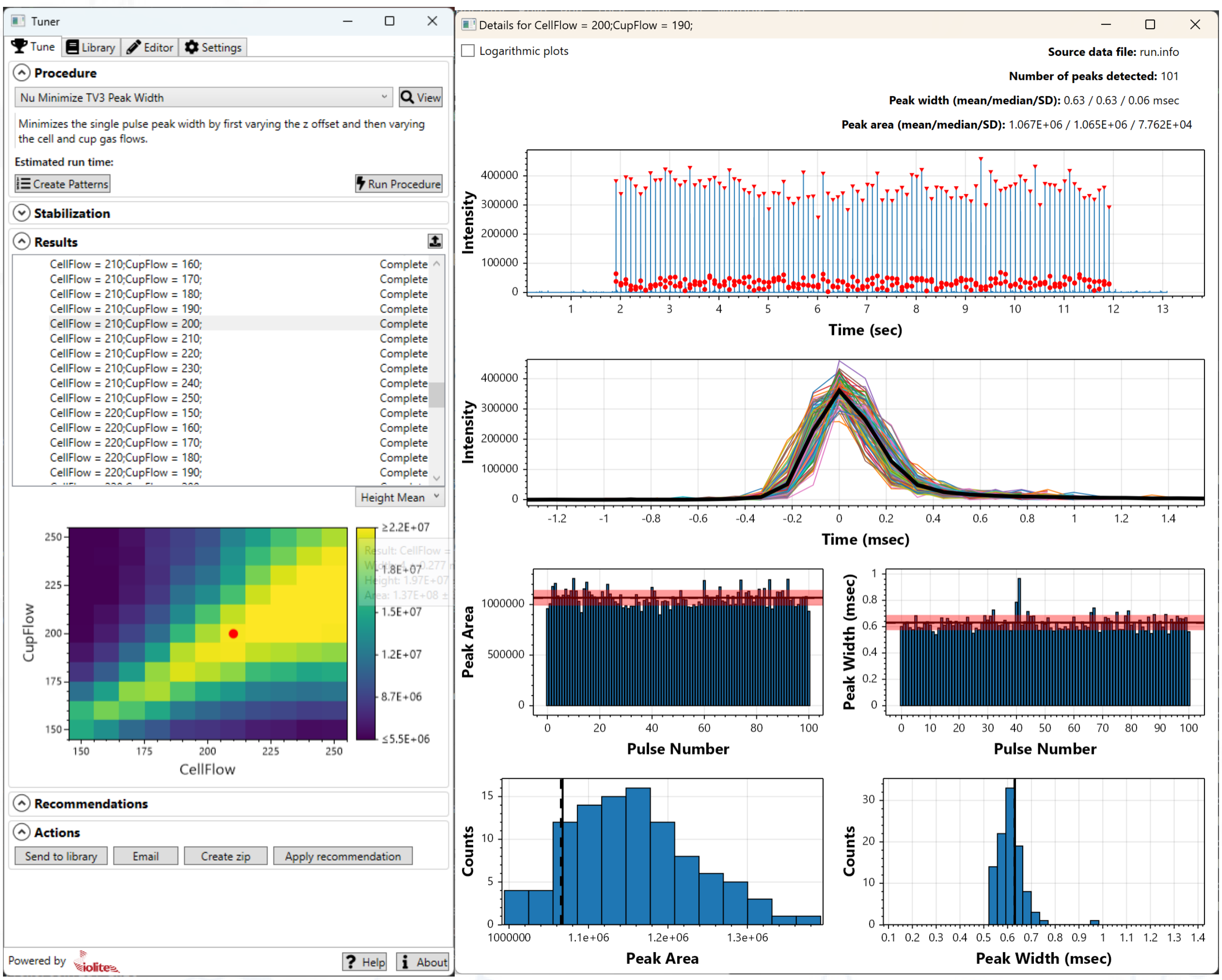


Figure 2. TV Tuner SPR optimization. [Left] Optimization conditions list and resulting heat map for peak mean height. [Right] Single pulse metrics from optimum conditions.

Samples

Samples were collected during a scientific maritime expedition by the Guangzhou Marine Geological Survey (GMGS) Research Vessel Haiyangliuhao, from the eastern Mariana Trench and western Marcus Wake Seamount Chain of the Western Pacific Ocean. The sample analyzed here is a polymetallic nodule (CY1) collected at 4500 m water depth by using box cores from the Northwest Pacific basin (18.9 N, 160.3E) during a 2017 cruise expedition. This sample was previously analyzed using LA-ICP-TOF-MS by Peng *et al.* [1]

Quantified and Drift Corrected Elemental Maps

The sample map was bracketed by SRM 610 for semi-quantitation of the elemental concentration. Using Iolite4, spline fitting between the replicate measurement of the standard (being analysed every 500th line of the sample map) provided a means to drift correct with respect to time.

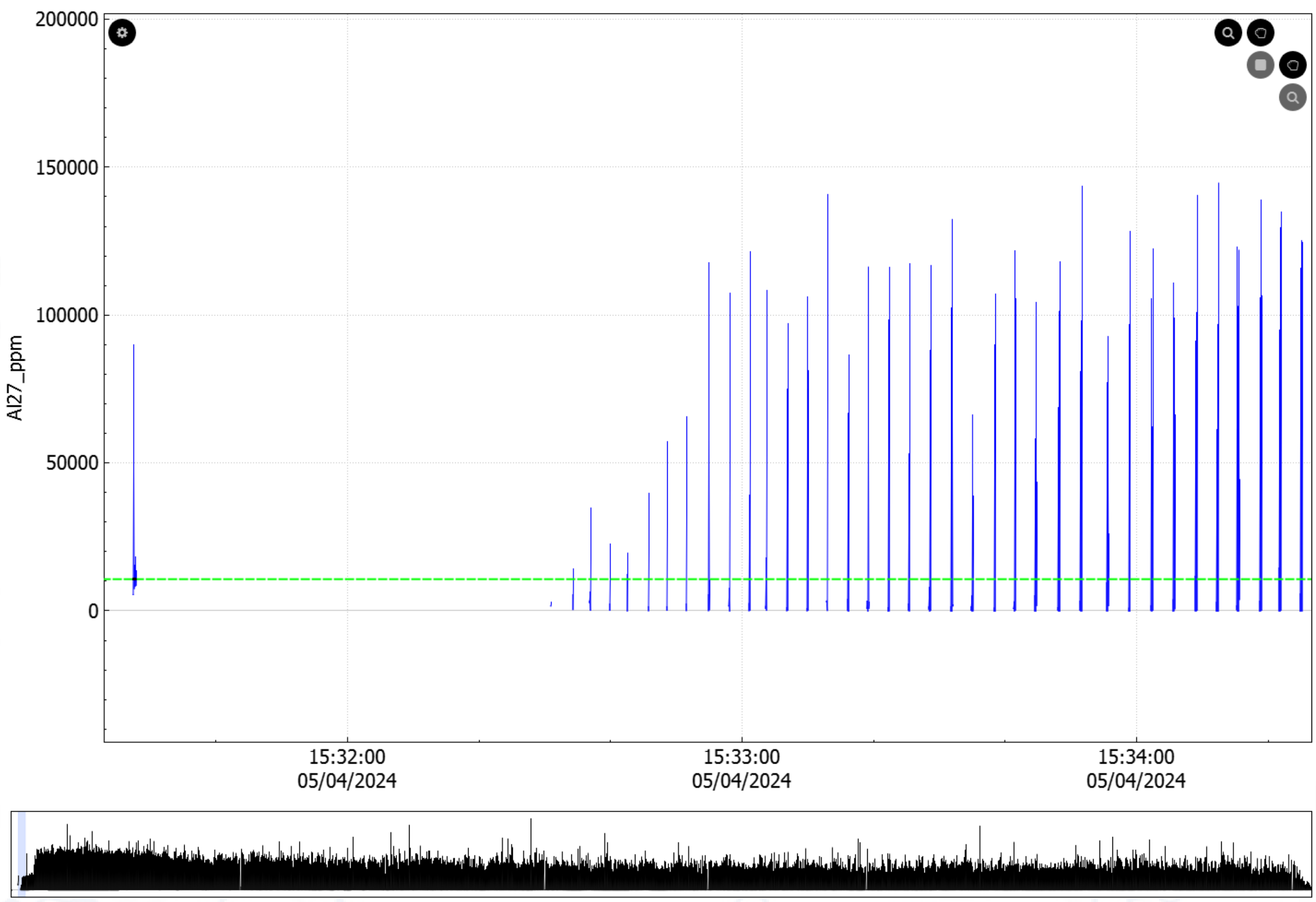
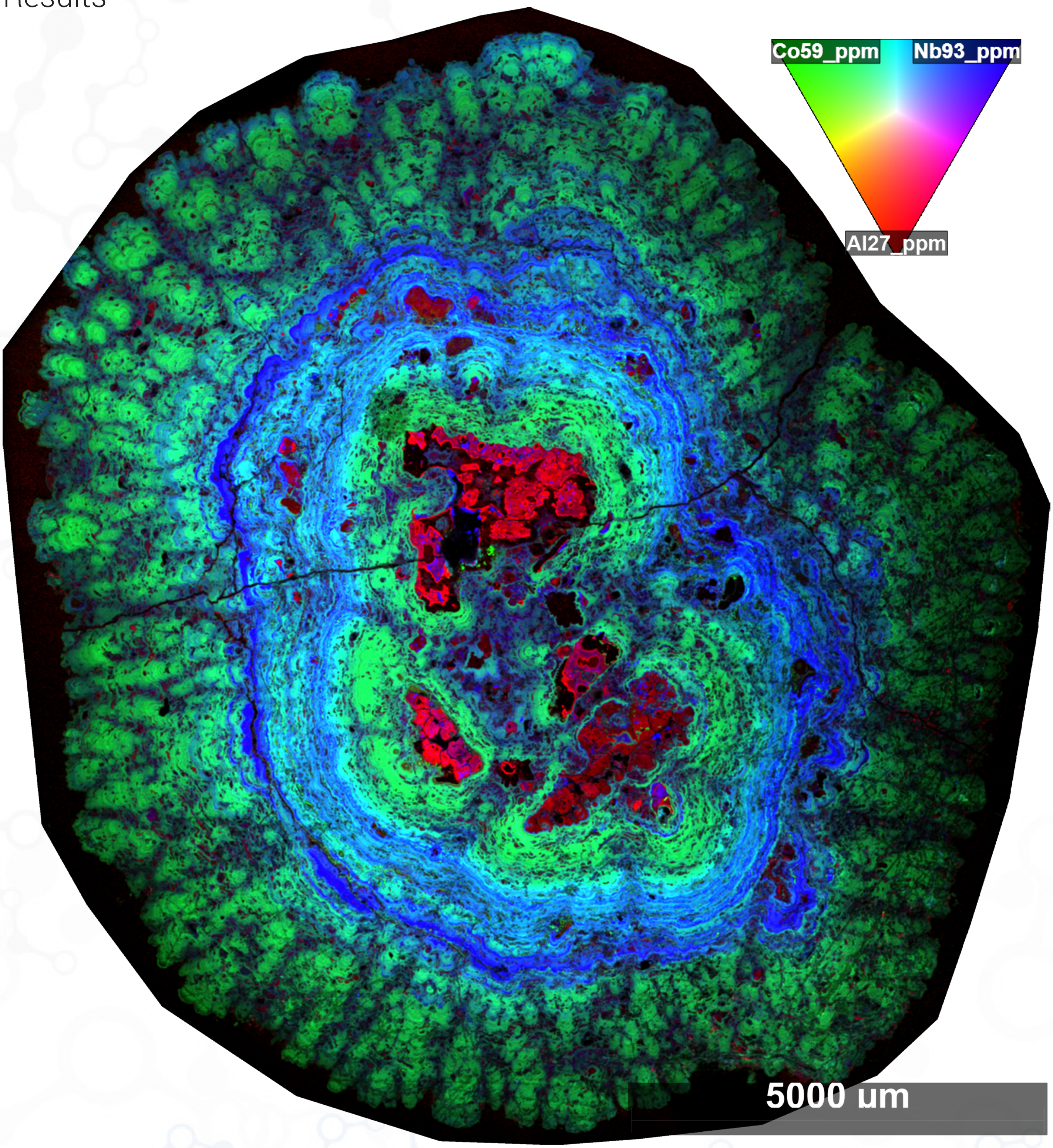
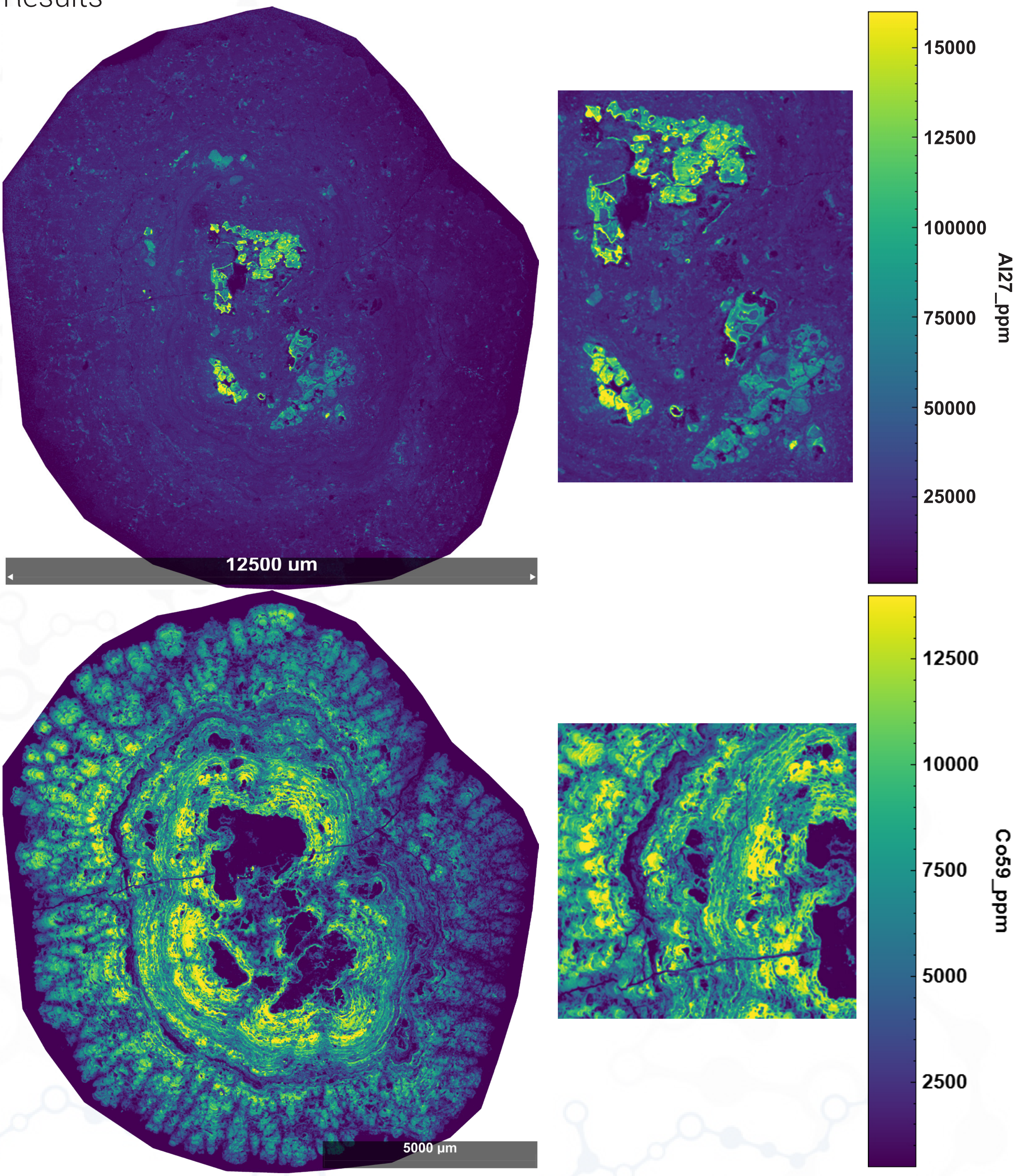


Figure 3. Iolite4 transient signal viewer, displaying Al concentration for a single line ablation of SRM610 (NIST) and the subsequent ablation lines across the deep ocean polymetallic nodule. Note the green line represents the interpolated sensitivity curve across the analysis (using standard bracketing with SRM610).

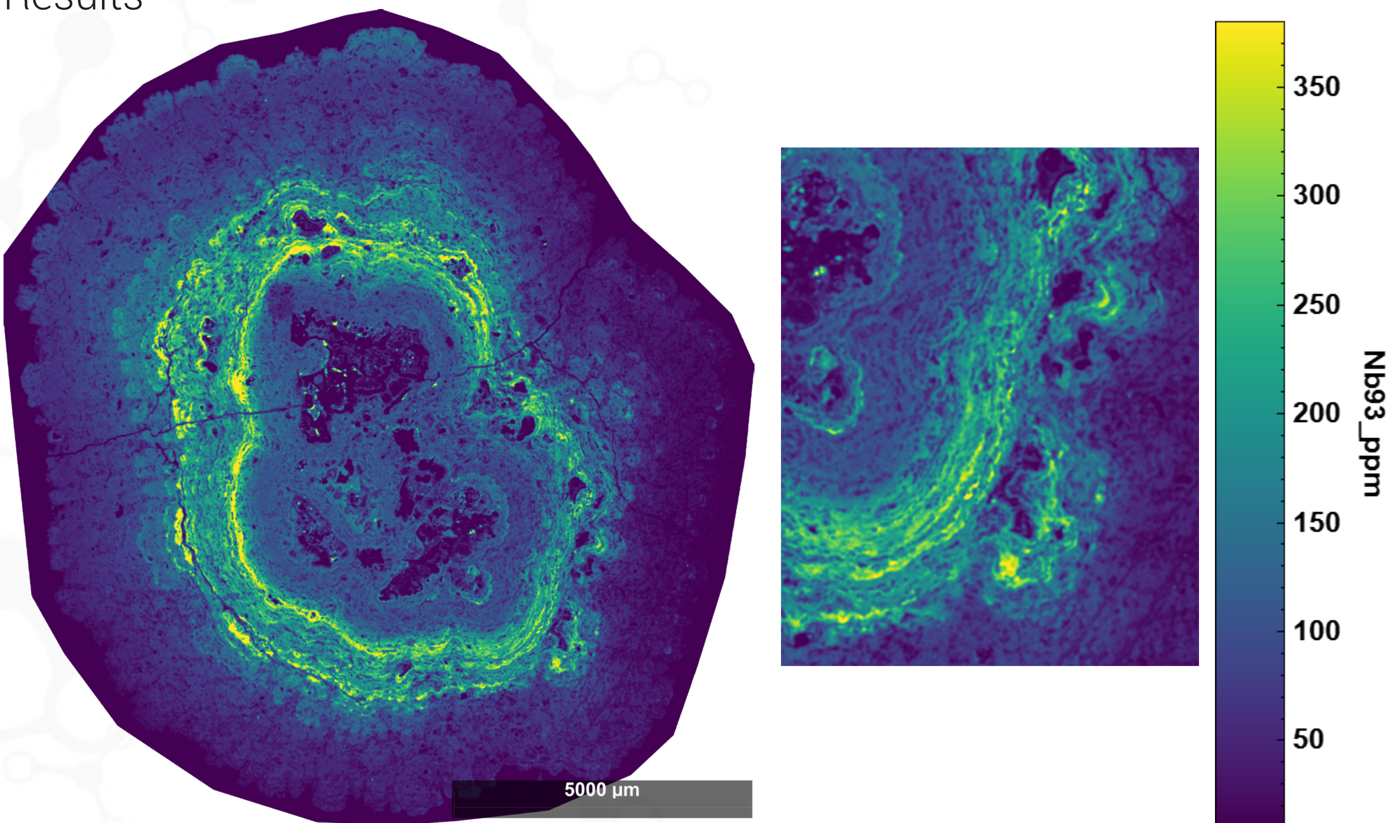
Results

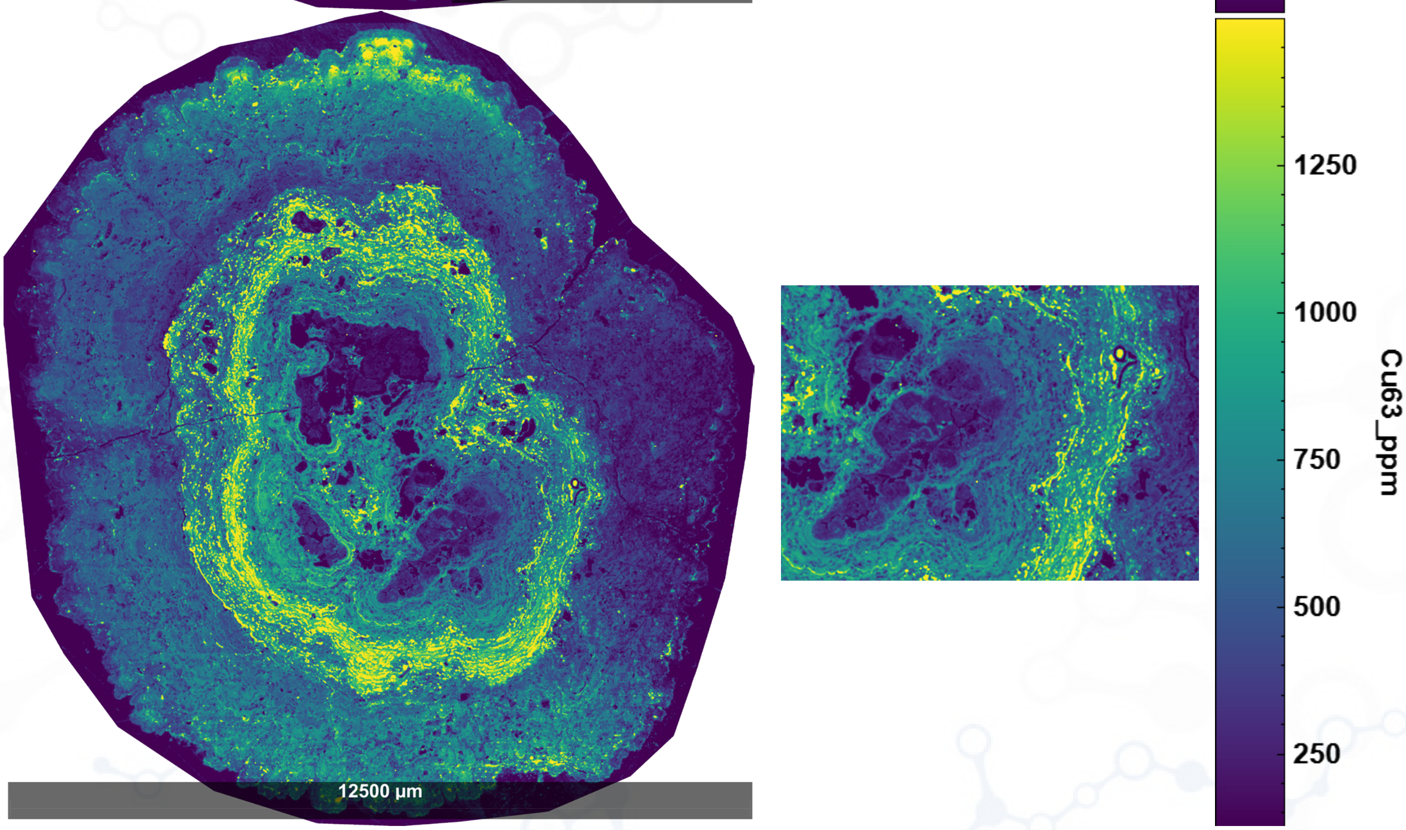


Results

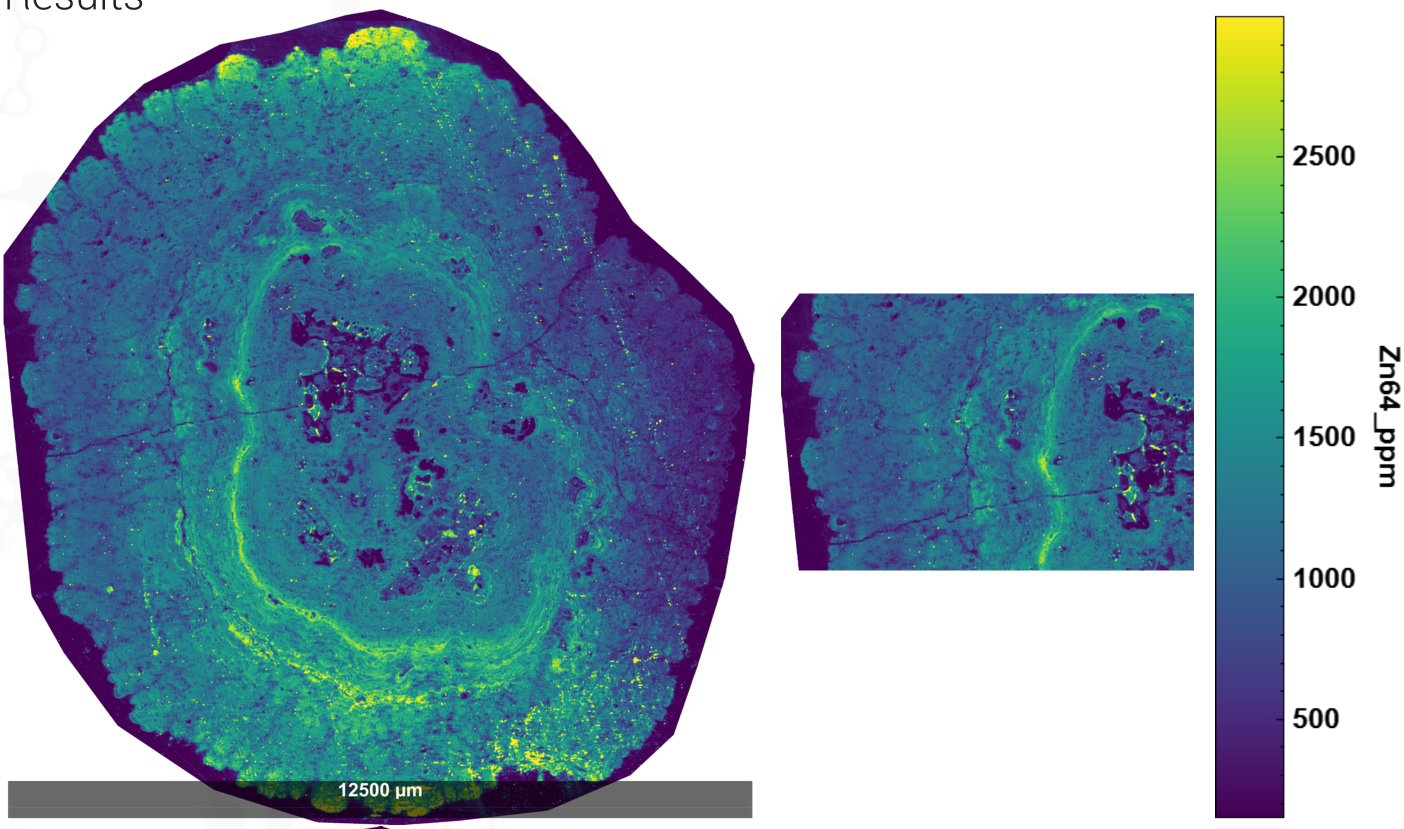

12500 um
15000
12500
100000
75000
50000
25000
Al27_ppm
5000 µm
12500
10000
7500
5000
2500
Co59_ppm

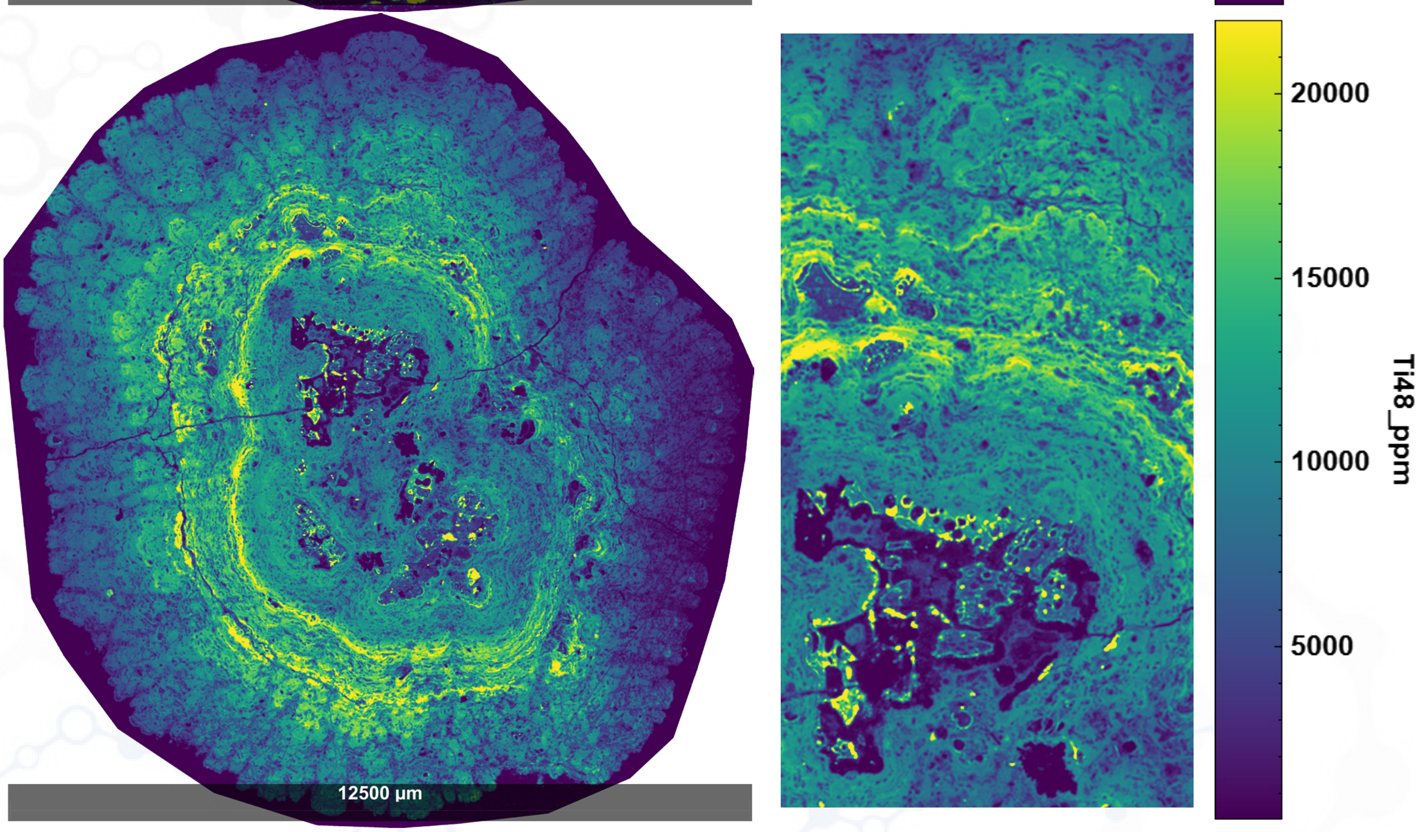
Results


5000 µm
350
300
250
200
150
100
50
Nb93_ppm


12500 µm
1250
1000
750
500
250
Cu63_ppm

Results


12500 µm
2500
2000
1500
1000
500
Zn64_ppm


12500 µm
20000
15000
10000
5000
Ti48_ppm

Elemental Scientific LASERS
INNOVATION TO ILLUMINATE

Conclusion

The imageGEO193, coupled to an ICP-TOF-MS, was used to map a deep ocean polymetallic nodule area of 12.69 x 13.78 mm in 9 hours and 11 minutes. At a spot size of 3 μm and >15MPx this equates to an imaging speed of 1.64 MPx/hour, a significant improvement compared to that previously reported[1] whilst also improving image quality. At this resolution and speed, distinct zones of critical metals are clearly visible and quantifiable. With area information and concentration data, total metal content can be estimated and economic viability of collecting the nodules assessed.

References

1. J. Peng, D. Li, P. Hollings, Y. Fu and X. Sun, Visualization of critical metals in marine nodules by rapid and high-resolution LA-ICP-TOFMS mapping, Ore Geol. Rev., 2023, 154, 105342 (https://doi.org/10.1016/j.oregeorev.2023.105342)

Acknowledgements

Elemental Scientific Lasers LLC would like to thank Jinzhou Peng, Dengfeng Li, Pete Hollings, Yu Fu and Xiaoming Sun for the providing the polymetallic nodule and thank Lukas Schlatt and Phil Shaw of Nu Instruments for collaboration on this project and use of their Vitesse Instrument (Wrexham).

Tel: 406-586-3159 | lasers@icpms.com | www.icpmslasers.com