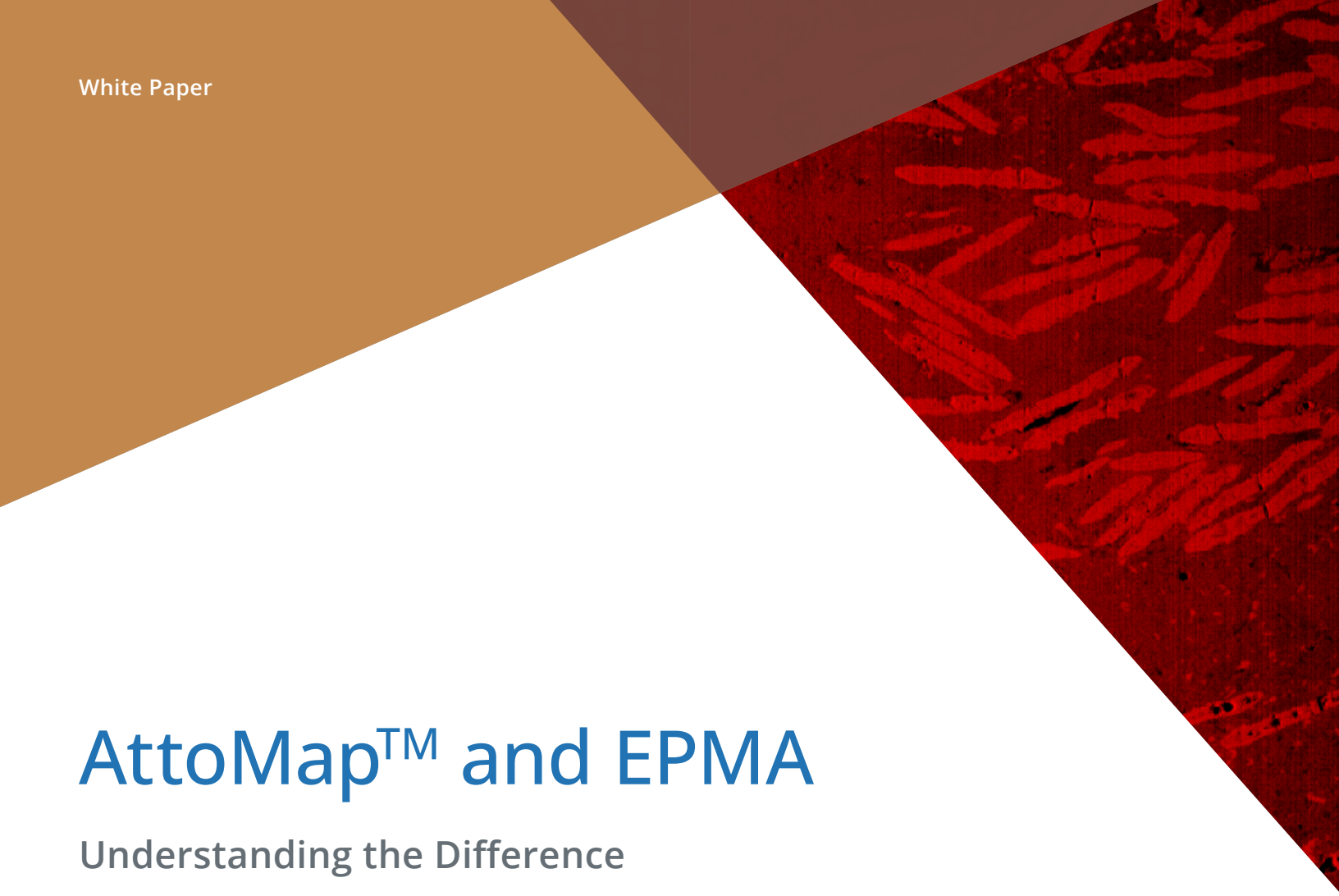
White Paper



AttoMap™ and EPMA

Understanding the Difference

Sigray's AttoMap is an x-ray fluorescence microscope that is rapidly emerging as a complement and alternative to EPMA (electron probe micro-analyzer). Both systems provide elemental imaging capabilities at microns-scale resolution. In this white paper, we will describe the key differences between the approaches and AttoMap's advantages in key applications.

This white paper compares the difference between the novel AttoMap™ approach and EPMA.

SIGRAY

5750 Imhoff Drive, Suite I
Concord, CA 94520 USA
P: +1-925-446-4183
www.sigray.com
info@sigray.com

Understanding the Difference
AttoMap™ and EPMA

Authors: Dr. Michael Lun, Dr.Frances Su, Sylvia Lewis | Sigray, Inc.

Overview: Elemental mapping is essential for a wide range of fields, including: metallurgy, mineralogy and geochemistry, materials science (glass, ceramics, and cements), and metallomics (the study of trace metals in biological specimens). In these fields, EPMA (electron probe micro-analyzer) has been a workhorse instrument. However, there are major limitations in sensitivity, performance for low atomic number (Z) elements, speed and flexibility, and sample type. A newly developed technique, the AttoMap x-ray fluorescence microscope, provides a rapidly growing complement to EPMA.

AttoMap™ X-ray Fluorescence Microscope

AttoMap is based on patented x-ray source and optics technologies that allow unprecedented performance in elemental (compositional) analysis. Similar to EPMA, AttoMap detects the characteristic fluorescent x-rays produced by the sample to determine the elemental composition at microns-scale resolution. The major difference is AttoMap uses x-ray fluorescence excitation, while EPMA uses electron excitation. EPMA therefore suffers from a significant production of Bremsstrahlung background that limits its ultimate sensitivity.

AttoMap has been adopted by a rapidly growing international group of researchers in mineralogy, metallurgy, and geochemistry institutes and companies because of its unique advantages over EPMA, including:

1. **Increased Sensitivity:** AttoMap's lower limit of detection (LLD) is 100X lower (sub-ppm vs. EPMA at 100s ppm).

2. **Superior Light Element Capabilities:** AttoMap is ideal for down to sub-0.01% organics (C, O, N) and other low atomic number elements such as S and P. Such capabilities are critical for accurate mineral identification and biological samples.

3. **Variable Depth Information:** AttoMap can achieve depth information ranging from ~2 to 100s µm.

4. **Improved Separation of Elements:** AttoMap can excite higher energy (L or K lines), which may overlap in the soft/tender x-ray regime for EPMA.

5. **Faster Speed, More Flexibility:** AttoMap acquires at speeds up to >10X faster than EPMA.

6. **Accommodates All Sample Types:** Almost any sample can be placed in the AttoMap, including irregularly shaped samples with topography and biological/polymeric samples.

In many cases, AttoMap is used alongside an EPMA to accommodate samples that the EPMA cannot - or to analyze samples requiring higher sensitivity. The following sections detail the physics behind the performance advantages achieved by AttoMap.

Technical Advantages of AttoMap

1) Increased Sensitivity

In general, LLDs of x-ray fluorescence are 1-2 orders of magnitude better than EPMA [1] because x-ray induced fluorescence does not suffer the Bremsstrahlung background radiation in the same way that electron excitation does (Fig. 1). With the AttoMap-310, this advantage is even further increased because of the AttoMap's patented multi-spectral x-ray source, which tunes the incident x-ray energy to maximize the fluorescence cross-section [ref. 2].

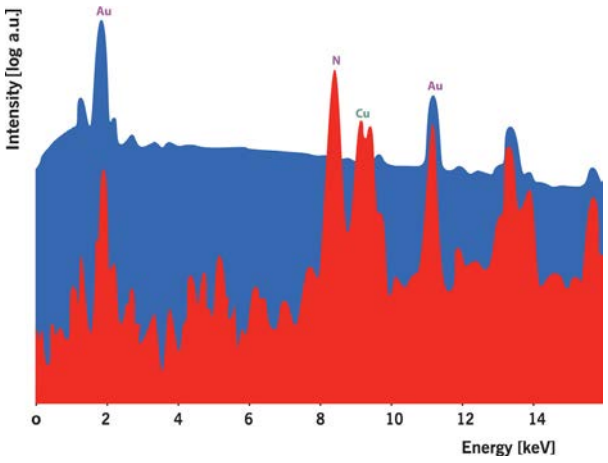


Figure 1: *X-ray excitation (red) does not suffer the bremsstrahlung background of electron excitation (blue), enabling much higher sensitivity*

2) Superior Light Element (Low-Z) Capabilities

AttoMap-310 uses patented x-ray source targets to maximize the fluorescence cross-section for light elements and a silicon drift detector (SDD) designed for direct light element detection. The system provides orders of magnitude better light element performance (Fig. 2) compared to most EPMA, which have drastically reduced light element capabilities due to a combination of: 1) relatively poor reflectivity of analyzing crystals and 2) low sensitivity of the detectors used.

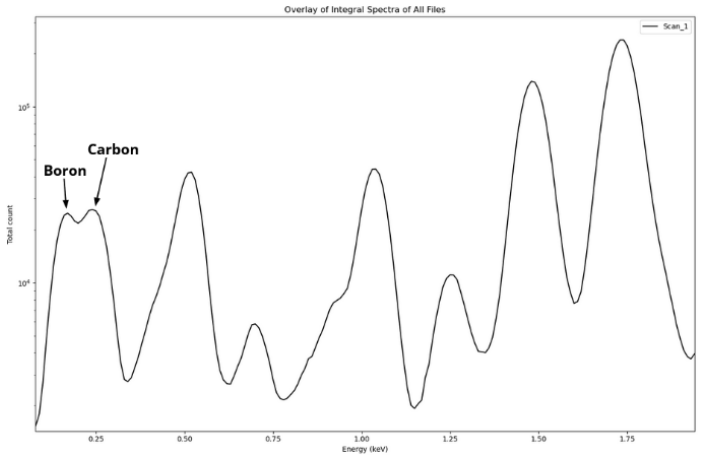


Figure 2: *Example of low-Z detection from the AttoMap-310 of a boron carbide sample showing the detection of both B (183 eV) and C (277 eV).*

Furthermore, AttoMap is relatively insensitive to oxidation and carbon contamination, which present major problems for EPMA because of its surface sensitivity.

3) Variable Depth Information

EPMA is a surface-level technique (typically nm), while AttoMap provides variable sample depths between single-digit microns to millimeters, depending on the matrix and element of interest. Varying the sample depth probed in the AttoMap is achieved by tuning the angle of incidence and x-ray energy for depth-varied information. This can be advantageous when surface-only information presents inaccurate compositional information due to problems such as contamination (e.g., hydrocarbon) or formation of oxides.

4) Improved Separation of Elements

M and L-lines of trace elements can be often difficult to separate from overlapping lines of more dominant elements. For example, trace Rb and Y from the large Si signal in geological samples [3]. AttoMap provides two solutions to this type of problem: 1) a patent-pending approach in which the x-ray target is selected to preferentially excite the lower concentration element to allow peak separation, and 2) the flexibility to operate the x-ray tube at 50 kV to excite the more well-separated K lines.

5) Higher Speed and Flexibility

Due to its increased sensitivity and low bremsstrahlung background, >10X faster acquisitions than EPMA can be achieved, especially for challenging low concentration samples. Moreover, XRF images a wide range of elements simultaneously (e.g., >30 elements vs. only 1-4 for most EPMA, depending on how many WDS attachments are purchased for the EPMA). AttoMap also provides the flexibility to vary spot sizes from 3 to 100 µm depending on the optics paired with the system and/or by varying the angle of x-ray incidence. Larger spot sizes are useful in providing rapid LFOV scans and identifying regions of interest (ROIs), while smaller spot sizes provide fine details within the ROIs.

6) Simple Sample Preparation Requirements

AttoMap has a large, flexible enclosure that can be either operated in ambient or vacuum. It can accommodate samples up to ~200 x 200 mm in lateral dimensions, and 25 mm in height. This resolves several known challenges for EPMA, including:

- The need to reduce the sample size to fit into the analytical position in the EPMA chamber
- Inability to accommodate samples such as:
  - Unpolished samples, such as loose minerals and sand
  - Samples with any topology (e.g., electronics)
  - Biological samples

Summary Table at a Glance

Parameter	AttoMap	EPMA
Highest Spatial Resolution	3-5 µm	2-3 µm
Sensitivity	Sub-ppm	100s ppm
# of Elements Detected	>30-50	4 (limited by # WDS)
Analytical Depth	1 µm to mms	<100s nm
Throughput Gain	>10X	Baseline
Sample Preparation	Simple/None	Polished, Coated

The advantages in summarized in the table above enable a wide variety of applications in metallurgy, geology, archaeology, and biology.

Challenging EPMA Applications Enabled by Sigray AttoMap

Metallurgy and 3D Printing

Low Z elements are of primary interest for metallurgy. As an example, carbon is a key additive to steel alloys to increase hardness and strength. AttoMap has outstanding sensitivity for carbon in steel (e.g., <0.09%) and no sample preparation requirements, leading a major steel manufacturer to purchase the tool (see Fig. 3B, right).

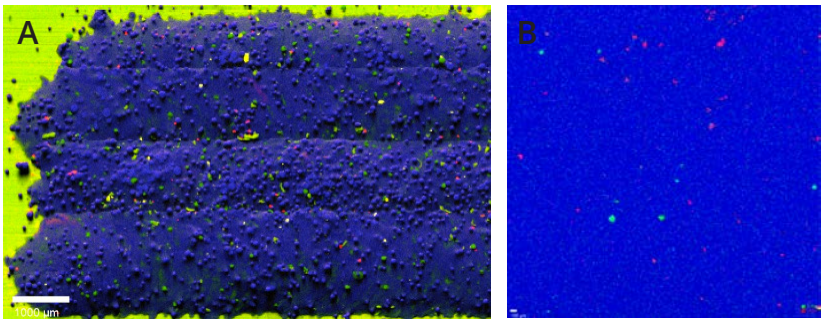


Fig. 3: *A) 3D printed Metal: Ti alloy (Ti6Al4V) showing Al (yellow), Ti (blue), Fe (green), and V (red). B) Carbon (green) and Oxygen (red) distribution on steel.*

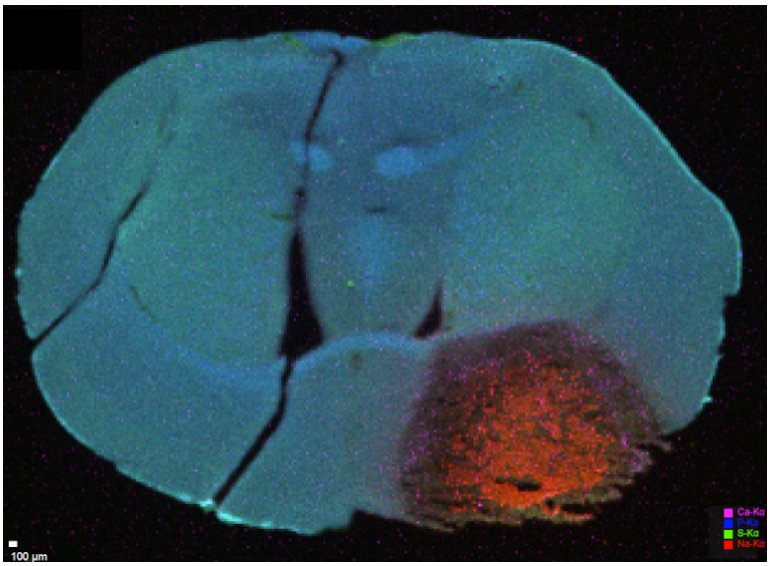


Fig. 4: *XRF mapping of a mouse brain cross-section after an induced stroke. Mapping of Ca (magenta), P (blue), S (green), and Na (red).*

Biology: Metallomics and P, S, Na Mapping

A rapidly growing field in life sciences is the study of the distribution of trace elements (e.g., Cu, Zn, Fe) and metallodrugs (such as Pt chemotherapeutics) in tissue. The abnormal distribution of trace elements has been increasingly understood as a key indicator (and possible cause) of diseases such as Alzheimer's and breast cancer [4,5]. EPMA often cannot image biological samples because they are insulating materials that can charge upon electron beam exposure. AttoMap-310 has the sub-ppm sensitivity for trace elements and outstanding sensitivity that outperforms even most synchrotron beamlines for critical biological elements such as P, S, and Na (see Fig. 4).

Archaeology and Geology

With AttoMap, little to no sample preparation is needed and there are no requirements like flat and polished surfaces as with EPMA. Intact, larger samples of 200×200×25mm can be scanned. Shown Fig. 5 is the AttoMap-310 map of a fossilized fish. O, Al, Ca, and P were selected to simplify the color map of Fig. 5, including C.

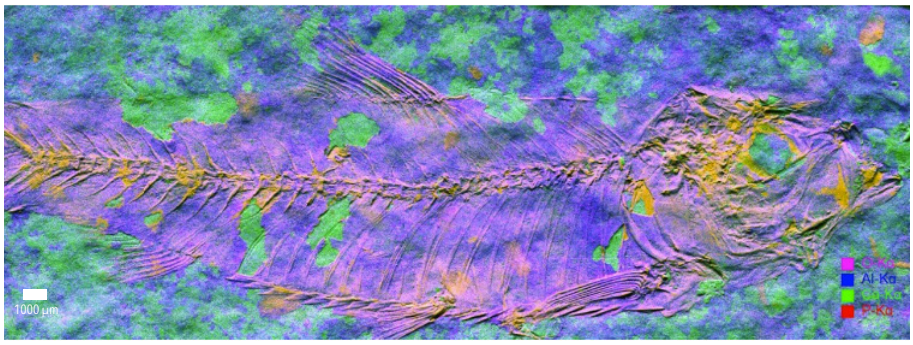


Fig. 5: *XRF scan of a fish fossil taken with the AttoMap-310 showing O (magenta), Al (blue), Ca (green), and P (red) distribution.*

References

1. A Bjeoumikhov, et al. Wiley Anal. 2005.
2. AttoMap White Paper. Email info@sigray.com to acquire a copy.
3. R Wakimoto, et al. Microsc. Microanaly. 26 (2), 2020.
4. MJ Pushi, et al. Metallomics. 2020.
5. T Paunesku, et al. J Cell Biochem. 2006.