

Quantification of Mineralogy with XRF Microscopy

Efficient trace element detection in materials has become important as the global demand for mineral resources increases. Sigray AttoMap™ series provides mineralogical quantification of minerals from major concentrations to trace-level (ppm-level) quantities and at microns-scale resolution and acquisition speeds of down to 5ms/point.

This white paper will review mineralogical applications of the AttoMap XRF microscope



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

Quantification of Mineralogy with the AttoMap™ Series XRF Microscopes

Author: Dr. Frances Su, Sylvia Lewis | Sigray, Inc.

Introduction: Elemental spatial distribution and relative elemental quantification techniques are essential for mineralogy research in the natural resource (O&G and mining) industries. This information is often needed at trace levels and is used to extract as much valuable material as possible and to inform ore processing¹. The AttoMap's automated mineralogy capabilities complement existing approaches, including: scanning electron microscope (SEM) based systems, laser ablation inductively coupled mass spectrometry (LA-ICP-MS), and nanoscale secondary ion mass spectrometry (nanoSIMS). AttoMap provides down to 3-5 μm resolution, sub-ppm sensitivities, and software featuring machine learning algorithms for quantitative segmentation of grains and open-box extensibility.

Current Mineralogical Approaches: MLA and QEMSCAN

Scanning electron microscopes (SEM) based Automated Mineralogy systems² have become one of the key methods for characterizing mineralogy. In these systems, an electron beam is stepped across a polished sample surface to excite x-ray fluorescence (XRF), which is recorded as a function of the beam position. This results in a mineralogical map at microns-scale resolution as shown in the left-hand side of Figure 1.

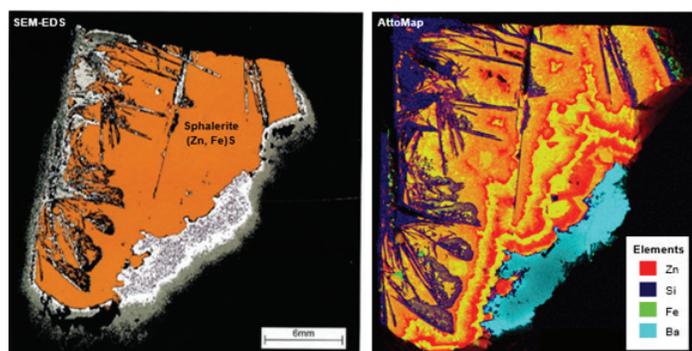


Figure 1: Mapped mineral sample. Left: SEM-EDS result showing sphalerite ((Zn, Fe)S) in orange. Right: AttoMap result showing Zn (red), Si (navy), Fe (green), and Ba (cyan). Note that AttoMap provides an abundance of textural information, showing Zn-rich regions (yellow from green and red overlap) within the region broadly identified as sphalerite by SEM-EDS. Courtesy Dr. Dieter Rammilmair, BGR

The major limitation of these SEM-based techniques is their sensitivity for trace (e.g. <0.1%) elements due to the large

bremsstrahlung background inherent in electron excitation. Often, complementary downstream techniques such as laser ablation inductively coupled mass spectrometry (LA-ICP-MS) and nanoscale secondary ion mass spectrometry (nanoSIMS) are used in addition to SEM-EDS techniques to acquire information about trace minerals. There are some additional challenges to these techniques, including: interference artifacts, matrix dependency, and variability due to conditions (ablation and analytical count times) that can mask or mimic trace element distributions³.

Novel Approach with Sigray AttoMap XRF Microscope

AttoMap microXRF was developed from patented x-ray source and optics technologies to enable synchrotron-like microXRF performance in a laboratory system. The system features several key advantages for mineralogical investigations:

1. A patented **multi-target x-ray source** allows users to

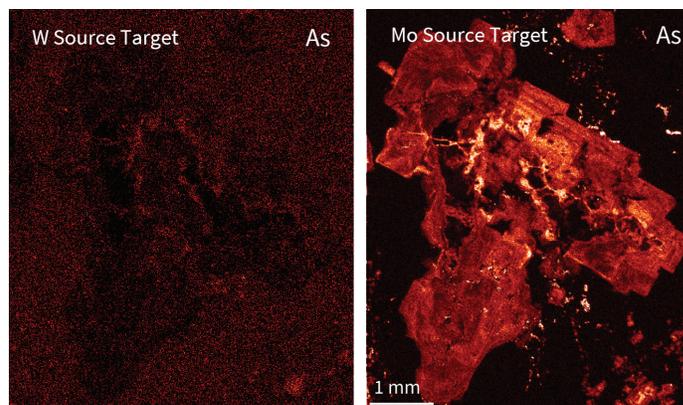


Figure 2: Selection of x-ray source target can dramatically XRF sensitivity. Sigray's patented multi-target source enables optimizing for almost all elements in the periodic table.

optimize fluorescence signals of interest and detect trace elements at the sub-ppm level (see Fig. 2).

2. A **large sample stage**, allowing large, intact specimens to be scanned (up to 300mm travel on the ambient 200 series and 100mm travel on the vacuum 310 series)
3. **Straightforward sample preparation:** The large working distance of Sigray's proprietary optics allows for imaging large samples even having some topography, such as powders and particles, and does not require the polished surfaces

required by SEM-EDS. No additional preparation is required (e.g., resin embedding, polishing, or carbon coating).

4. Variable **spatial resolutions from 5 to 100 μm** , providing flexibility in trading off resolution with FOV/throughput.
5. **Mineralogical software analysis tools:** Sigray's software implements k-means clustering (an unsupervised machine learning algorithm) to segment grain boundaries by mineralogy. Grains can be segmented by XRF data alone or by additionally incorporating the correlative optical microscopy images acquired inside the AttoMap. The suite of tools includes an easy-to-use GUI interface and Jupyter python notebooks, allowing easy extension of algorithms and open source collaboration.

In this applications note, we used an AttoMap-200 ambient system to determine the mineralogical composition of a rock sample courtesy of Dr. Sakthi Chinnasamy, IIT Bombay.

Results and Discussion

A polished thin section of rock containing pyrite and arsenopyrite (sulfides), silicates, and carbonates was imaged. Due to the minerals of interest, a Mo target and optic were selected. A large-field-of-view (LFOV) overview scan was first acquired at 30 μm dwell width and 0.1s dwell time (Fig. 3).

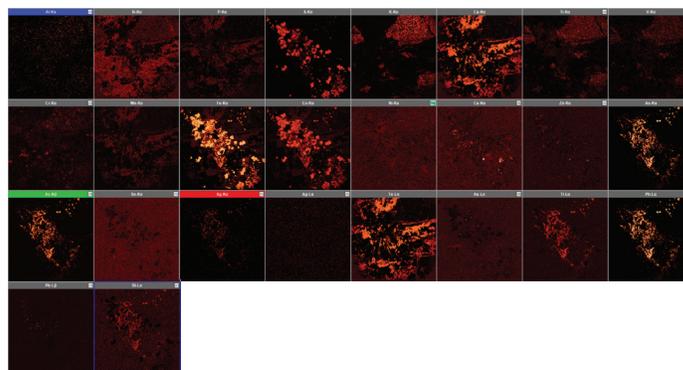
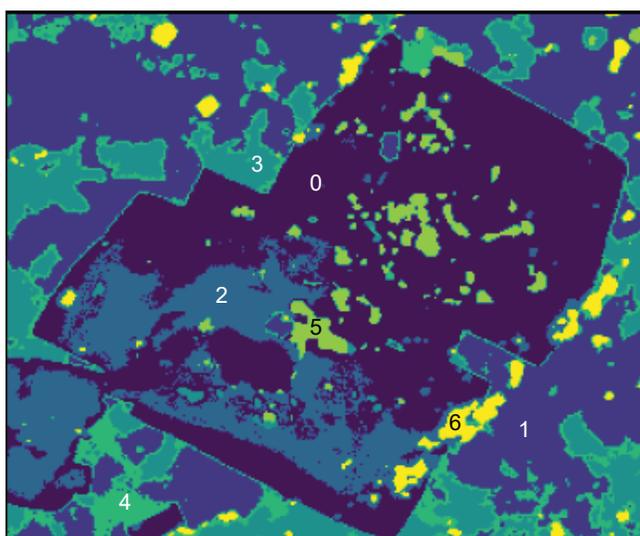


Figure 3: Software view of LFOV at 30 μm dwell width. Multiple elements of interest are acquired simultaneously and displayed as "heat maps".

Clicking on specific subregions of interest queued the ROIs for higher resolution scans performed at 10 μm dwell width and 0.1s dwell time.

For each subregion, machine learning based spectral deconvolution picked out features in the spectra (Fig. 4) and successfully distinguished between certain elements with overlapping energy lines (e.g., As K- α from air and Pb L- α from the sample). Seven regions were identified and relative weight percentages of minerals were calculated for each region based on a fundamental parameters (FP) model.



	Region 0	Region 1	Region 2	Region 3	Region 4	Region 5	Region 6
Arsenic	0.1275	0.1277	1.3008	0.2519	0.2413	0.2083	15.2562
Calcium	0.567	5.8313	0.5578	51.4627	21.127	1.1187	3.8056
Chromium	0.0066	0.1032	0.0182	0.0393	0.0696	0.0265	0.0563
Copper	0.1226	0.0671	0.0703	0.0796	0.0793	9.3215	0.0302
Iron	43.4856	2.0032	42.6952	20.5661	9.9628	37.2082	28.4973
Lead	0.378		0.1226		0.5066	0.2846	
Manganese		0.0516		0.8785	0.2312	0.0522	0.044
Nickel	0.0187	0.0352	0.0279	0.03	0.0286	0.0194	0.0587
Phosphorus	0	0.7844	0.1092	1.4945	0.4294		
Potassium	0.0095	0.3774		0.4249	1.1677		0.2035
Silicon	3.3172	85.8527	2.7076	19.7786	55.2531	4.1562	26.3397
Sulfur	51.9456	4.6494	52.3669	4.8221	10.7366	47.545	25.5782
Titanium		0.0905		0.0615	0.1126		0.1011
Vanadium			0.011	0.0313			
Zinc	0.0215	0.026	0.0126	0.079	0.0542	0.0592	0.0294

Figure 4: K-means clustering with deconvoluted spectra used to pull out the most prominent 7 regions of a selected subregion of interest. Peaks were then fit and a fundamental parameters model was used to approximate the composition of the 7 regions.

1. Warlo, M., et al. (2019). Automated Quantitative Mineralogy Optimized for Simultaneous Detection of (Precious/Critical) Rare Metals and Base Metals in A Production-Focused Environment. *Minerals*, 9(7), 440.
2. Zhou, W., et al. (2006). Fundamentals of scanning electron microscopy (SEM). In *Scanning Microscopy for Nanotechnology* (pp. 1-40). Springer, New York, NY.
3. Prencipe, I., et al. (2015). Energy dispersive x-ray spectroscopy for nanostructured thin film density evaluation. *Science and Technology of Advanced Materials*, 16(2), 025007.
4. Nikonow, W. and Rammlmair, D. (2017). Automated mineralogy based on micro-energy-dispersive X-ray fluorescence microscopy (μ -EDXRF) [...]. *Geoscientific Instrumentation, Methods and Data Systems*, 6(2), 429-437.

REV20210702

SIGRAY

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