

Quantification of Mineralogy with the AttoMap™ series XRF microscopes

Application Note

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Abstract

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 5 ms/point.

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 2. Demonstration of the power of the quantitative phase and subresolution darkfield capabilities applied to an angle-interlock woven CFRP. All three images were acquired simultaneously in the PrismaXRM. Absorption contrast (what is acquired with conventional microCT) has limited contrast, while the other two images provide information on materials, weaves, and fiber orientations. Scalebar is 1 mm.

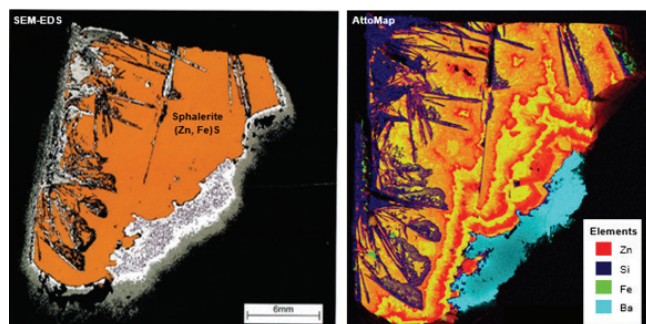


Figure 1: Mapped mineral sample. Left: SEM-EDS result showing sphalerite ((Zn, Fe)S) in orange. Right: AttoMap result showing Zn (red), Si (navy), Fe (green), and Ba (cyan). Note that AttoMap provides an abundance of textural information, showing Zn-rich regions (yellow from green and red overlap) within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

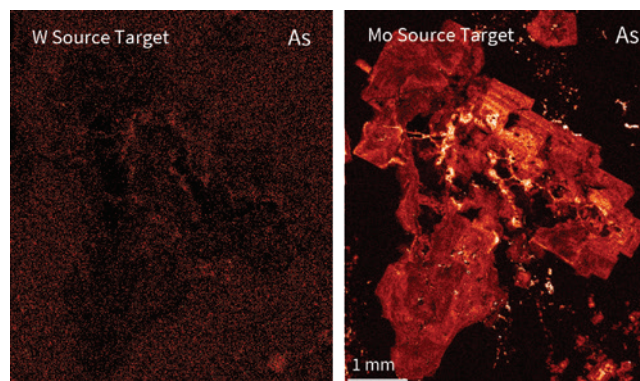


Figure 2: Selection of x-ray source target can dramatically XRF sensitivity. Sigray's patented multi-target source enables optimizing for almost all elements in the periodic table.

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

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3. **Straightforward sample preparation:** The large working distance of Sigray's proprietary optics allows for imaging 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).

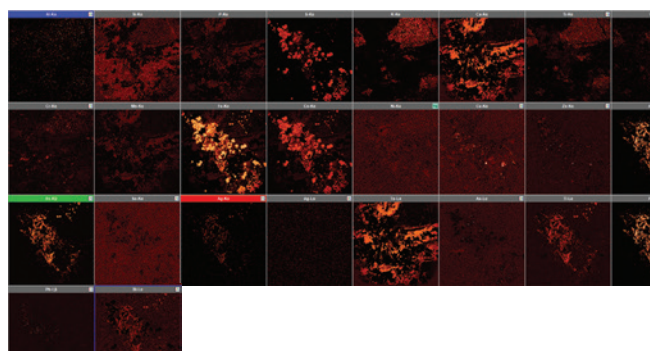


Figure 3: Software view of LFOV at 30 μm dwell width. Multiple elements of interest are acquired simultaneously and displayed as "heat maps".

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 ele-

ments 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.

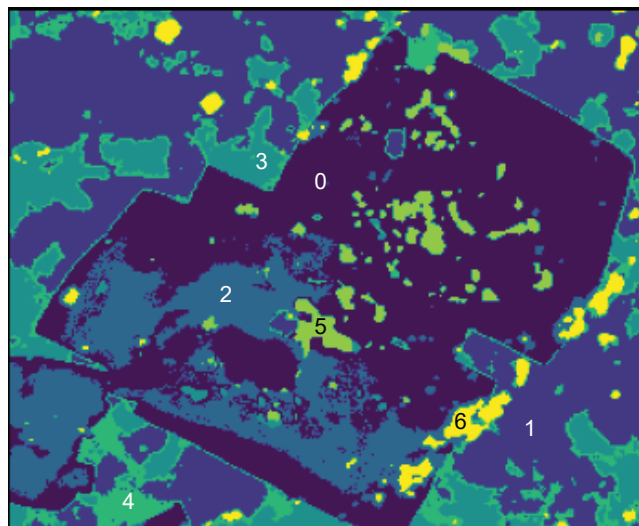


Figure 4: K-means clustering with deconvoluted spectra used to pull out the most prominent 7 regions of a selected subregion of interest. Peaks were then fit and a fundamental parameters model was used to approximate the composition of the 7 regions.

| | 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 |

References

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