APPLICATION NOTE

Malachite characterization with Axia ChemiSEM

Introduction

Malachite is a copper carbonate hydroxide mineral ($Cu_2(CO_3)$ $(OH)_2$). Its external form is conditioned by the way in which crystals grow together into an aggregate. Malachite has different forms with different chemistry, and they are established by external factors (i.e. environmental conditions of mineral formation).

As a secondary mineral of copper, malachite is formed when copper minerals are altered by other chemicals. During its formation, other elements such as Mg, Al, Si or Fe can be carried by leaching processes, and can appear in the structure in the form of inclusions. Tracking the relationships of chemistry and microstructure are key to interpreting the history of secondary mineralization. The goal of these investigations is to understand the spatial chemical and textural relationships controlling the mineralization and properly interpreting the relative timing of crystal growth.

Analytical techniques, such as EDS (energy dispersive X-ray spectroscopy), can be used as a first step in gaining a general overview of mineral phase variability. It can also be used to link these phases with more detailed microstructural features. However, these approaches are not optimized for such analysis, require specialized knowledge and are typically slow.

This application note demonstrates how the Thermo Scientific™ Axia™ ChemiSEM provides an efficient and fast way to evaluate the chemical variability of minerals on a large scale. It also demonstrates the capabilities of this system to easily unveil the chemical nature of specific details.

Methods

Scanning electron microscopy (SEM), coupled with traditional EDS systems, has shown limitations in its ability to screen the sample of interest to provide chemical information on a large field of view. This is crucial in deciding where to point for more specific characterization.

In a conventional SEM-EDS workflow, imaging the sample has always been separated from elemental characterization, making the whole process long and tedious. In addition, in traditional EDS systems, the choice of the area of interest for further analysis is not guided by the chemical information. This can often lead to wasting time hunting around the sample for features/regions of interest. With Axia ChemiSEM, quantitative elemental information is blended with the electron images during acquisition, providing near instant access to quantitative compositional maps

The Axia ChemiSEM offers a completely new method for minerals characterization. A general overview of the elemental distribution on a large-scale sample provides a clear picture of the localization and distribution of chemically unknown inclusions along the sample. As such, it serves as a guideline for more detailed analyses.

Analysis

As previously mentioned, malachite formation is a secondary mineralization process. Its compositional variations on a large scale are heavily dependent on the interaction between copper phases, other surrounding minerals and water.

In order to gain an initial understanding of the chemical variability and distribution of the elements in the sample of interest, a large-scale overview has been acquired combining the navigation montage and the live quantitative information. In fact, as the X-ray collection happens in the background during image acquisition, compositional changes can be easily tracked across the sample by creating maps of elemental distribution on large areas of the surface.

Navigation montage is a built-in function of the SEM, which allows easy navigation on large samples. It automatically collects multiple neighboring images, creating a low magnification image that provides a large-scale overview of the sample in a short period of time. In addition, it can be used as a map to navigate the sample surface, or center a feature of interest, by automatically moving to the stage position in one click.
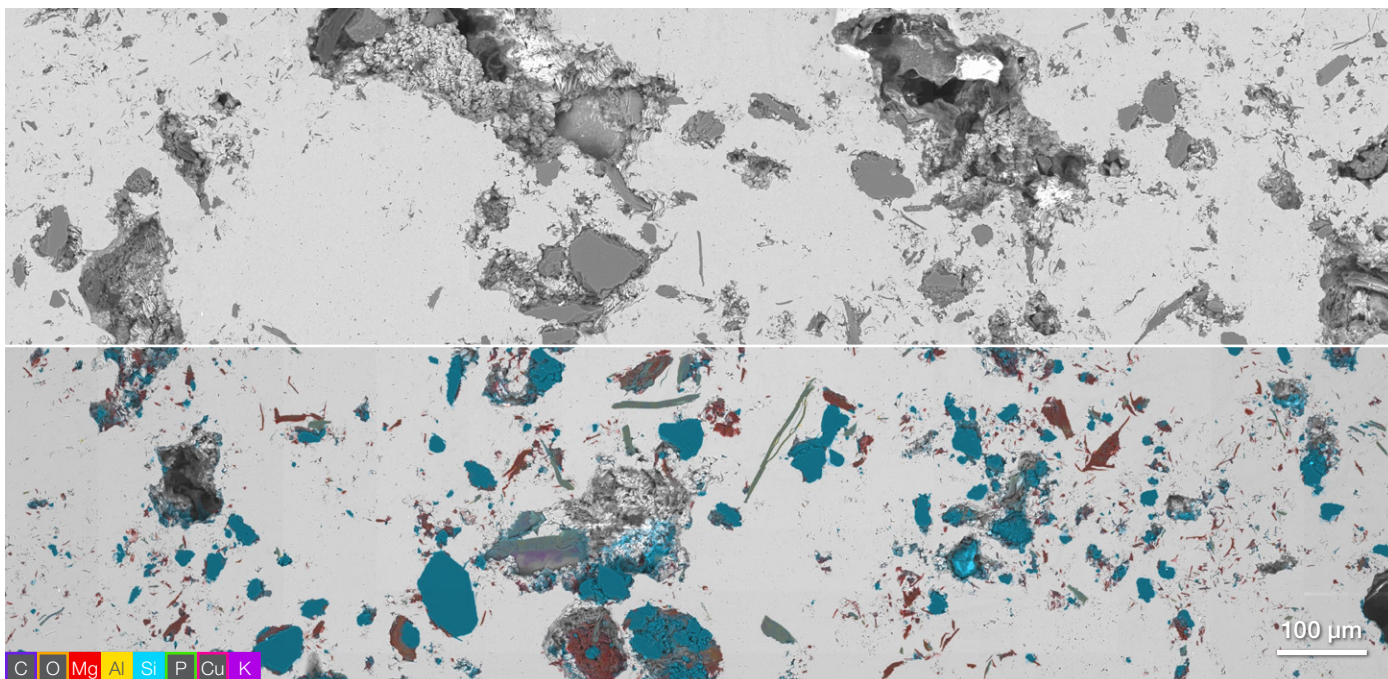
Thermo Fisher
SCIENTIFIC

Figure 1. Large-scale overview of the sample without (top) and with (bottom) the elemental information. These montages have been acquired starting from a magnification of 1500x. 15x15 tiles have been automatically collected.

The figure above shows two different navigation montages of the same sample. One shows a conventional backscattered electron image and the other shows the respective quantitative elemental map, also containing compositional information of the entire scanned surface.

The conventional grayscale image contains information on the distribution (as well as size and shape) of the different inclusions along the surface. However, it only partially gives information on their composition (darker gray level in the backscattered electron image suggests the inclusions are lower in atomic number than the malachite matrix).

The same montage acquired with the addition of the quantitative elemental information provides a much higher level of detail. It immediately correlates the morphological aspect with the chemical data. In this way, the user has more information to help them select the right area.

After the ROI selection, a more detailed characterization can be executed using the traditional approach to any SEM imaging session. With Axia ChemiSEM, you have a workflow-free approach that allows you to seamlessly obtain all needed information without changing your way of working.

Figure 2 shows one of the first steps of a conventional SEM imaging session, which is the acquisition of a backscattered electron (BSE) image of a selected area.
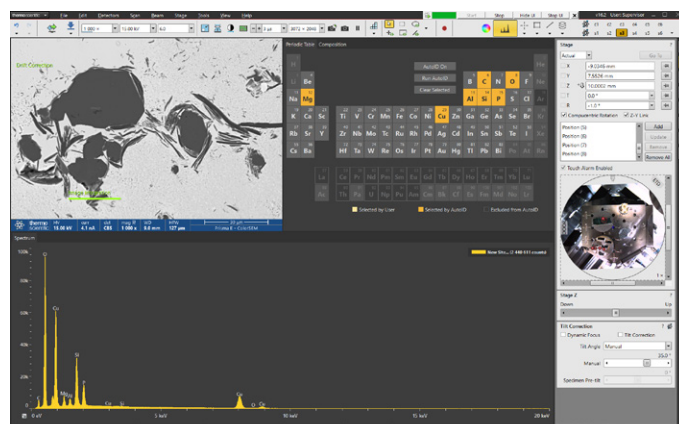

Figure 2. Axia ChemiSEM analytical layout integrated in the graphical user interface showing the acquisition of a BSE image and the spectrum related to the area acquired.

With Axia ChemiSEM, the EDS is fully integrated into the SEM graphical user interface. This means the acquisition and processing of the quantitative elemental information happens live, and X-rays are continuously acquired (Figure 2).

A first overview of the elemental distribution is obtained by simply activating the quantitative elemental mapping after acquiring an image. It will show which elements are present in the area of interest (Figure 3).
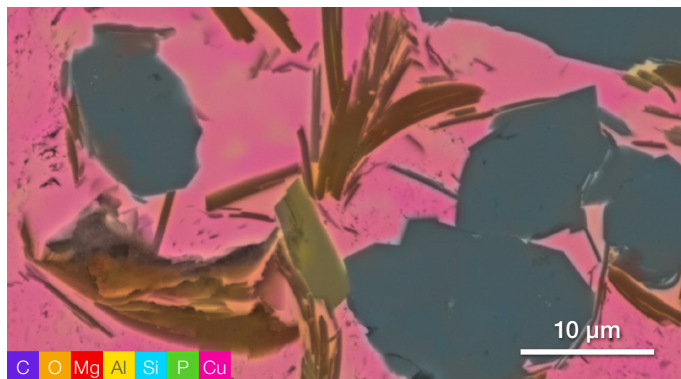

Figure 3. Quantitative elemental image of the area presented in Figure 2.

Within the same acquisition, by deselecting some of the elements, we have the option to highlight that the composition of the inclusions in the image is not the same for all objects in the ROI (Figure 4).
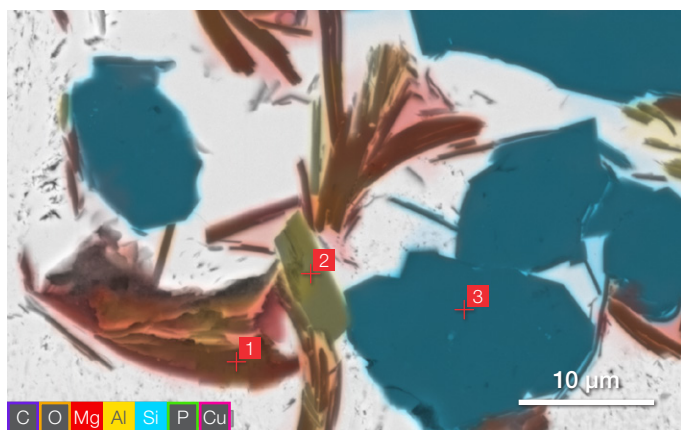

Figure 4. Image in Figure 3, with C, Cu, P and O deselected. Point analyses acquisition parameters: acc. voltage 15 keV, beam current 0.44 nA, average count rate ≈ 10 kcps, acquisition time 60 s per point.
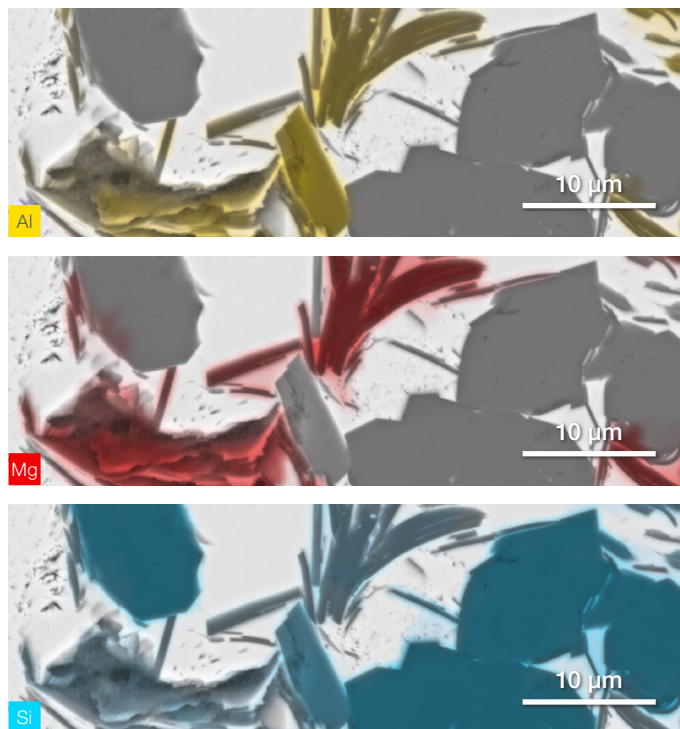

Figure 5. From top to bottom: Al, Mg and Si distribution.

The set of images in Figure 5 immediately shows at least three different phases, where not all of the elements found are present. Without the quantitative elemental information provided by the Axia ChemiSEM this would go unnoticed. This is because the contrast (provided by the backscattered electron image) is not enough to infer compositional differences within inclusions with the same gray levels in the image. Interacting with these tools directly in the microscope UI means the focus of the investigation (imaging the sample) is always at the center of the analysis.

For a comprehensive characterization of the inclusions presented in Figure 5, Point&ID analyses were acquired by simply selecting the point mode analyses, and then selecting the point of interest (their location is shown in Figure 5). This is done without needing to switch software or re-collect the image.

The signal from each point has been acquired for 60 s, and the results are presented below.
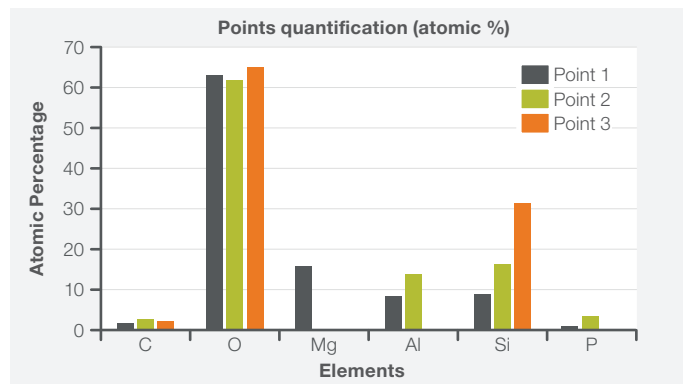

Figure 6. Quantification from the three points highlighted in Figure 4. Acquisition parameters: acc. voltage 15 keV, beam current 0.44 nA, average count rate ≈ 10 kcps, acquisition time 60 s per point.

A rapid comparison of the three points acquired is possible by selecting the three spectra immediately after their acquisition. Overlaying the different spectra quickly provides more information about the composition of the points analyzed (Figure 7).
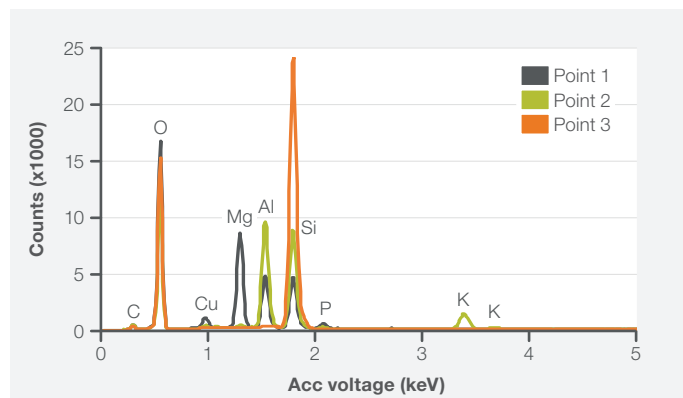

Figure 7. Spectra comparison from Point 1, Point 2, Point 3.

The subsequent Point&ID analysis supported what was previously anticipated from the elemental image: Point 1 has the highest content of Mg, with almost 10% Al and Si. The inclusion analyzed by Point 3 appears to be (most likely) made of silica. Analysis of the central inclusion, the composition of which is shown in Point 2, shows the presence of K.

Potassium localization is then further clarified by re-acquiring a quantitative elemental image, and including it in the elements selected during image acquisition (Figure 8).
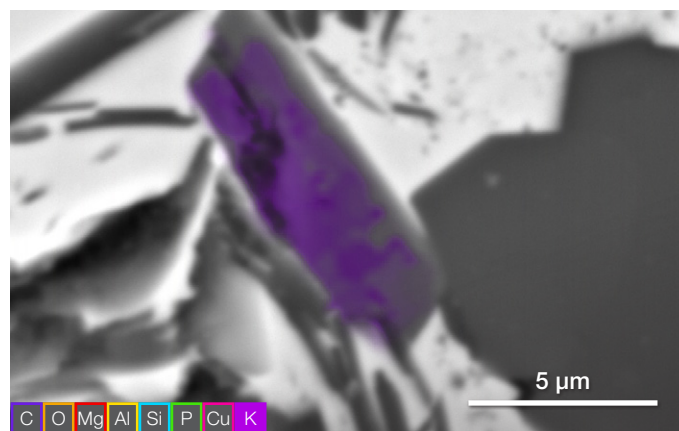

Figure 8. K quantitative map of the area of interest.

Conclusion

Axia ChemiSEM can provide an impressive amount of information about unknown inclusions in minerals, as malachite. The combination of wide area imaging and high-quality EDS mapping makes it an ideal tool for investigating chemical/textural derived processes.

By approaching our work as a conventional SEM imaging session, we were able to analyze chemical information, which included elemental distribution within inclusions of the same compositional contrast. This was done with a short time-to-data, and without switching between software programs or changing workflows.

Find out more at **thermofisher.com/Axia-ChemiSEM**

Thermo Fisher
S C I E N T I F I C