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APPLICATION NOTE

ChemiSEM for Geochronological Studies

New trace mineral identification workflow combines large-area ChemiSEM mapping with cathodoluminescence imaging

Introduction

U-Pb dating is the most commonly applied age-determination method in metamorphic and igneous rock research. U-Pb data is unique, as the target minerals are typically long-lived and tend to preserve complex age domains that, in turn, preserve the history of geologically important events.

Geochronological studies, however, often have a bottleneck: the extraction and location of dateable minerals. In fact, samples may have few, small, or multiple populations of dateable phases. Finally, the difficulty in locating all datable populations of phases may lead to sampling bias that could impact the interpretation of U-Pb ages, particularly when looking at provenance studies. Finding ways to rapidly locate phases of interest during routine investigations would help improve the number of datable minerals identified and create more confidence in relating the textural, chemical, and deformation histories of each mineral. Techniques such as scanning electron microscopy (SEM) provide higher resolution, and the addition of energy dispersive X-ray (EDS) analysis provides an ideal framework for improving the productivity of analysis.

Methods

This application note describes a new zircon and monazite dating protocol for small minerals (5–60 µm). It has been developed using the Thermo Scientific™ Axia ChemiSEM, which offers a new and different concept of EDS analysis that provides quantitative EDS mapping acquired simultaneously with the SEM imaging. The new protocol takes advantage of native image montage creation in combination with the unique compositional mapping capabilities of the Axia ChemiSEM. The combined result is an automated method to survey a large area of a sample to locate zircon and monazite grains on a polished geological sample.

With the integrated and always-on EDS, the possibility to scan a large portion of the sample of interest has been combined with the quantitative elemental information of the Axia ChemiSEM to localize the different zircons, monazites, and titanites. This overview is used as a map for further analyses, such as cathodoluminescence images and higher magnification EDS quantifications.

The workflow highlighted in this application note is comprised of the following steps:

1. Low-magnification SEM-EDS phase mapping—automated acquisition of a large-scale overview with chemical information displayed, with the possibility to highlight the position of the zircon, monazite, and titanite by visualizing only the elements of interest, such as Zr, Ce, La, and Ti.
2. High-magnification backscattered electron (BSE) imaging and ChemiSEM phase mapping— overview serves for point-and-click navigation for higher magnification elemental analyses with point & ID quantifications.
3. Cathodoluminescence (CL) imaging on specific minerals— integration of CL-imaging in the workflow allows you to gain additional textural information for zircon analysis, which is key for complex igneous and metamorphic samples that may contain multiple phases of zircon growth.

The large-scale BSE overview, higher magnification BSE imaging and ChemiSEM characterization have been acquired at 25 keV in order to properly identify both Kα (at 15.7 keV) and Lα peaks (at 2.04 keV) of the Zr and avoid misidentification with the phosphorous, whose Kα peak is at 2.01 keV and overlaps with the Lα peak of Zr.

CL imaging has been performed with lower acceleration voltage (10 keV) using the retractable solid-state cathodoluminescence detector, composed of four different channels: red, green, blue, and panchromatic. Each of the channels is treated as a separate detector, and the information will be acquired in the form of four different images. R-G-B channels can then be combined to obtain one image in which the different contributions are recolored and showed in red, green, and blue, respectively.

This workflow's main advantage is that it combines the SEM imaging and the identification of the area of interest via EDS. The X-ray collection is coupled to the SEM imaging. Before being displayed, the EDS signal is processed and quantified. During this live quantification, the spectral peaks are deconvolved, the background is removed, and artifacts such as peak overlaps are automatically corrected. The result is a live, compositional image that is free from artifacts and which can be interpreted without further post-processing.

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Discussion

Figure 1 shows a typical large-scale overview (navigation montage) acquired using the BSE.

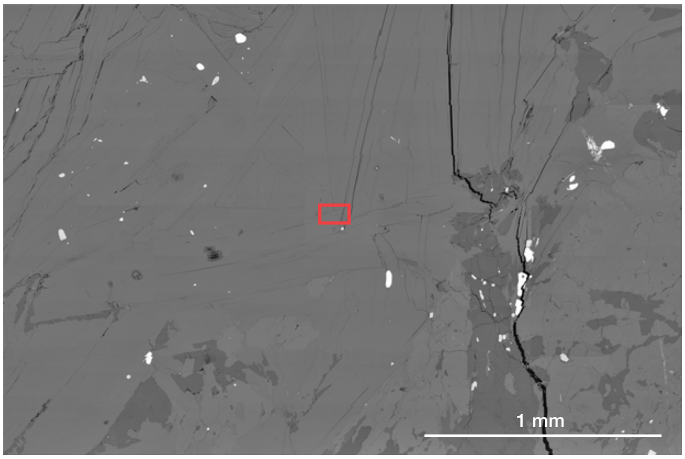

Figure 1. Large-scale overview of a 2.8 mm x 2 mm area (Acc. voltage 25 keV, beam current 15 nA). The red box shows the size of a typical SEM FOV with a magnification of approximately 1,000x.

The information provided by the backscattered electron detector gives an overview of the compositional variations in the area analyzed. The grayscale image is an indication only of the location of crystals (the higher the atomic number, the brighter the object), but this is not enough to precisely localize the zircons and monazites.

However, the **Axia ChemiSEM** delivers the same large-scale overview, with the addition of chemical information overlaid on the high-resolution imagery. This allows you to skip several steps; as Figure 1 does not contain compositional information, the next step would require choosing—in the dark—areas of interest, with the risk to spend time on useless minerals.

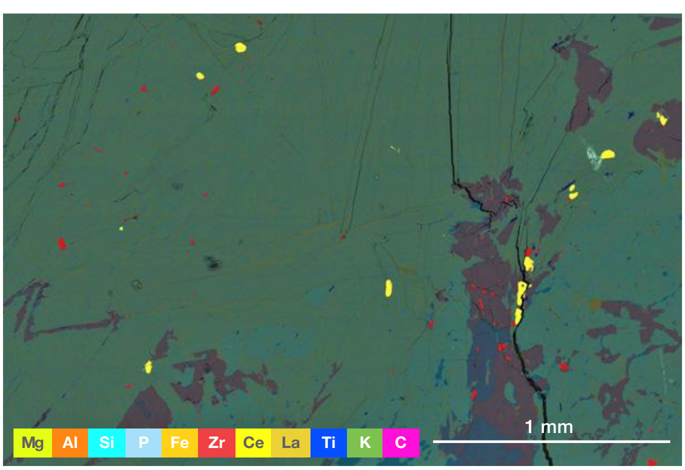

Figure 2. ChemiSEM montage with 9x9 tiles (Acc. voltage 25 keV, beam current 15 nA).

The ChemiSEM map presented in Figure 2, with respect to the grayscale image, already adds what is needed to discriminate between the different minerals: several grains that had the same contrast in the backscattered electron image (due to the similar mean atomic number) are now colored differently depending on their composition.

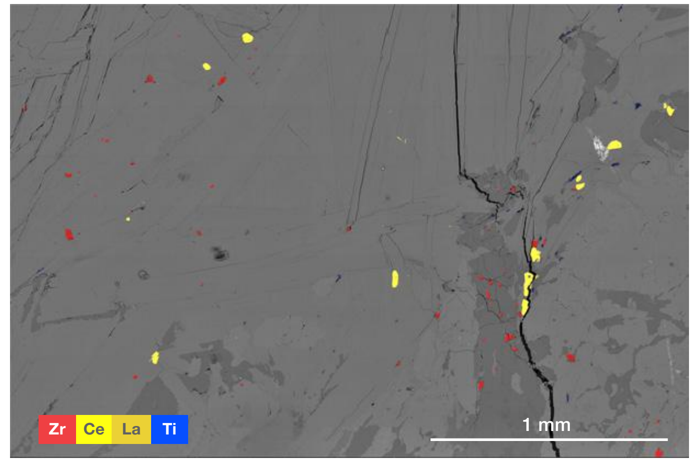

Figure 3. ChemiSEM montage showing the localization of Zr, Ce, La, and Ti.

The positions of zircons, monazites, and titanites can be further highlighted by hiding the unwanted elements and displaying only the typical elements to identify the above-mentioned minerals, such as Zr, Ce, La, and Ti (see Figure 3).

Thanks to its navigation function, the montage offers a precise way to move along the scanned area and center a feature of interest by automatically driving to its stage position. In addition, the large-scale image also provides the textural context of each grain of interest.

Different areas have been selected for high-magnification characterization. Zircons with various sizes, between 5 µm and 50 µm, have been further characterized using the live quantitative elemental information of the **Axia ChemiSEM**, where acquisition is done simultaneously with the SEM image. In addition, CL images have been acquired. CL investigation of zircon is of special interest, as CL provides information on the internal structure of zircons, which are often not visible or detected with other imaging techniques. In addition, CL is crucial to relate the textural petrogenesis to the geochronological interpretation of U-Pb data.

The results on two different areas are presented Figure 4.

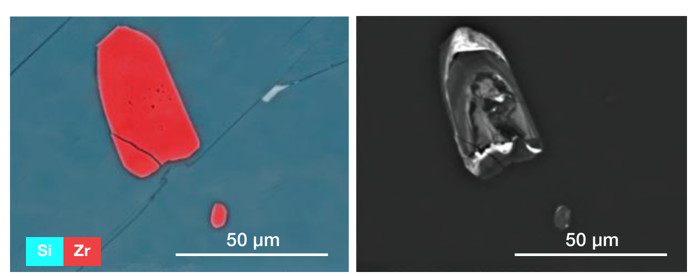

Figure 4. ChemiSEM image of zircons showing the Si and Zr distribution in the imaged area. Right image presents CL-Pan image (Acquisition parameters: ChemiSEM image acc. voltage 25 keV, CL image acc. voltage 10 keV).

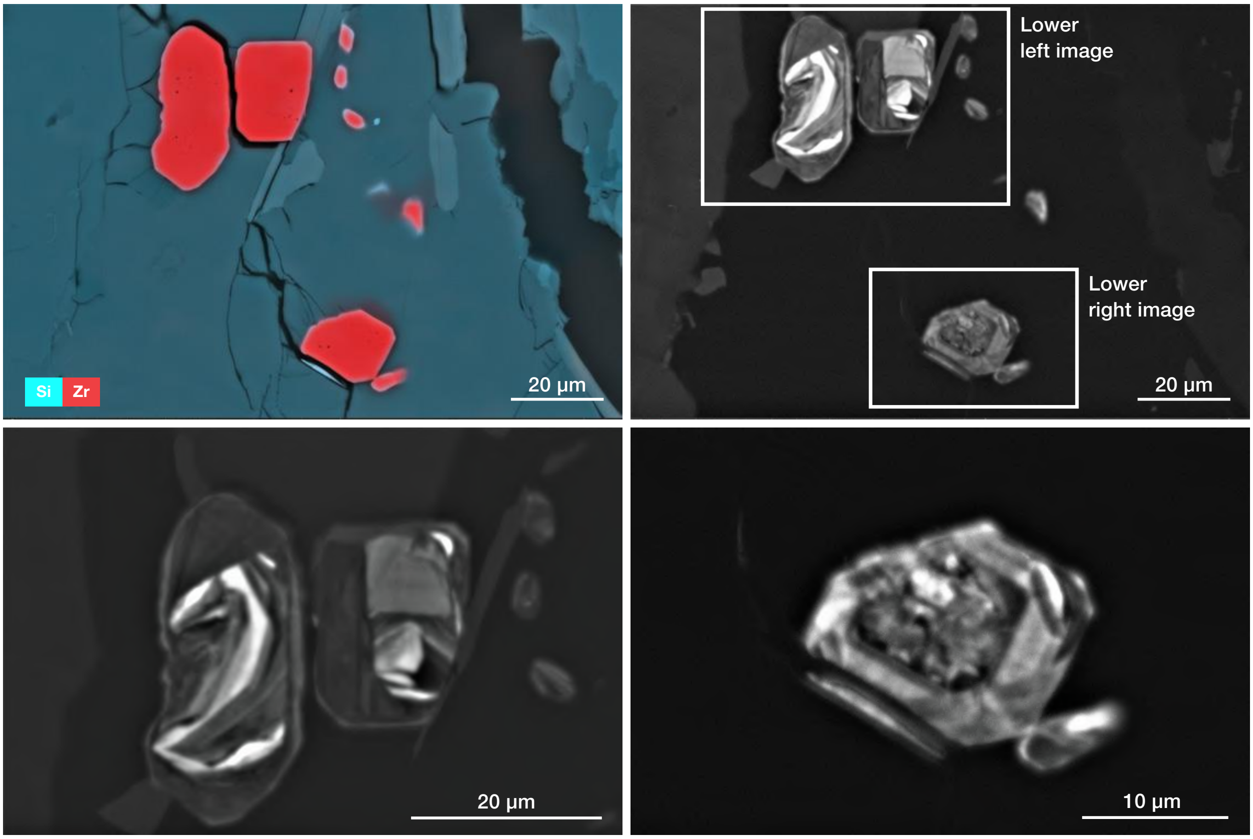

Figure 5. ChemiSEM image of zircons showing the Si and Zr distribution in the imaged area. Top right image presents CL-Pan image; bottom line images are higher magnifications of the different zircons (Acquisition parameters: ChemiSEM image acc. voltage 25 keV, CL image acc. voltage 10 keV).

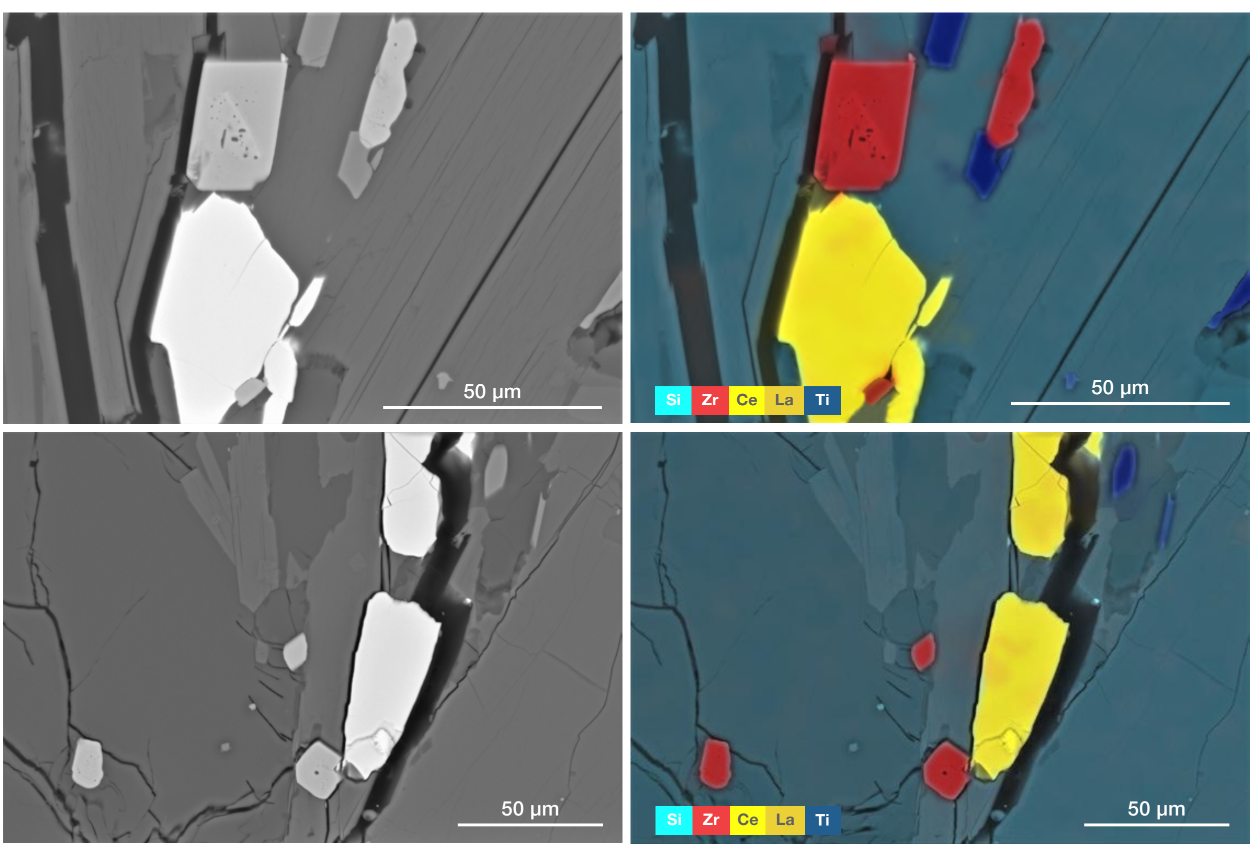

Figure 6. Left images show the BSE image and right images show the ChemiSEM image with the elements of interest ON. Elements signal from the background have been unselected (Acc. voltage 25 keV, beam current 0.26 nA).

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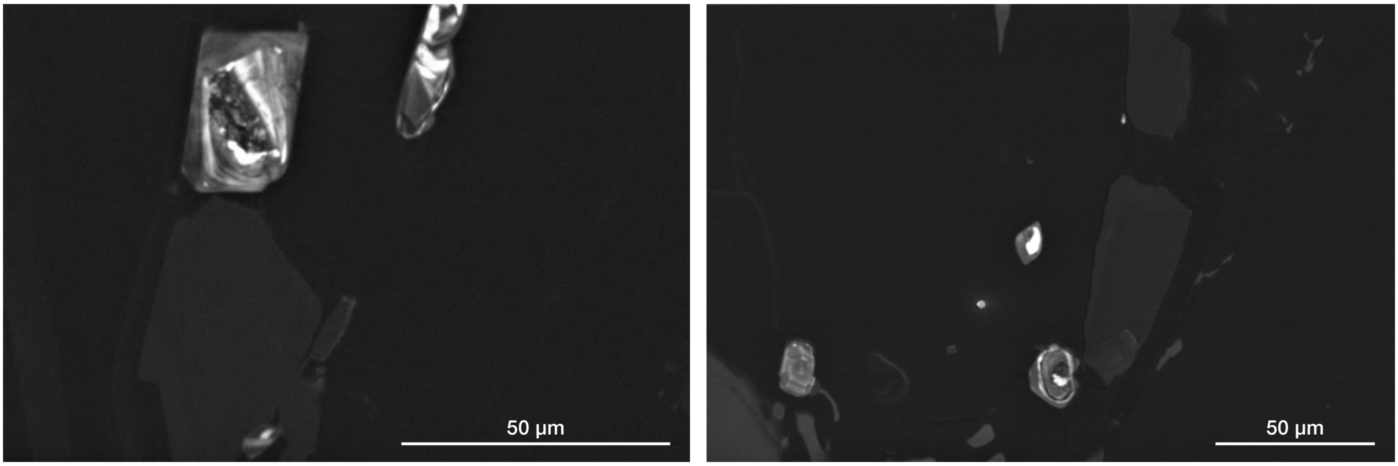

Figure 7. CL images of the areas shown in Figure 6 (Acc. voltage 10 keV, beam current 0.76 nA).

One of the most common features provided by the CL characterization of zircons is growth zoning. A key feature observed in this sample is that nearly all zircons observed contain complex core structures, with faceted late-stage rims. The action of collecting the data has, in minutes, created a digital catalog of target phases, their textural context, and their internal structure.

Transmitted light is conventionally used to distinguish zircons from monazites. Still, it is not easy to discriminate between them, as both can have similar optical properties, especially in samples where zircons lack clear facets. With the instant quantitative chemical information provided by the Axia ChemiSEM, a clear distribution of all the elements in place is provided, within the time required to acquire a conventional SEM image.

The BSE images in Figure 6 show different minerals. From the different gray levels, it is evident that some of them have different compositions. With the ChemiSEM image, the composition and the distribution of the elements of interest are shown. The image shows the distribution of Zr and Si (to highlight the location of zircons), the distribution of Ce and La for monazites, and Ti for titanites.

CL images have been acquired in both areas presented in Figure 6, and they are shown in Figure 7.

Conclusion

SEM has long been used to locate zircons and monazites. However, the activity can be tedious, as traditional workflows require manual operation of the microscope, constant switching between different user interfaces for elemental identification, and then manually cataloging the locations of each grain found. In this application note, we present a workflow that provides rapid access to chemical information over large areas of a polished thin section.

The proposed workflow permits rapid identification of both zircon and monazite. Titanite, apatite, and other potentially datable phases can also be easily discriminated with this approach. The unique live compositional mapping capabilities of the Axia ChemiSEM provide instant access to chemical information. Consequently, when compared to conventional methods ,the Axia ChemiSEM enables significant time savings and increased throughput, allowing more samples to be analyzed.

In a practical sense, you can move from locating a large number of target phases directly to either more detailed compositional mapping, line scans, or spot analyses. In addition, the easy-to-use, solid-state CL detector available on the Axia ChemiSEM fills in the final bits of information for fast and accurate characterization of geological samples.

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

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