HORIBA Scientific

JEOL

Raman Spectroscopy

Colocalized microscopy techniques for pyrite mineral spatial characterization

Application Note

Geology RA84

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Abstract: A complete microscopic characterization of certain geological samples is very complex, particularly on studies related to their spatial distribution of the mineral phases and inclusions composition. Indeed, structural, elemental and chemical variations on the micro- or nano-scale are hard to observe by a single instrument, like a simple optical microscope, or even a scanning electron microscope (SEM). A comprehensive evaluation by multiple techniques is key for a good understanding of the material properties. However, multi-technique studies generally lead the user to physically move the sample among different instruments. This approach can become even more difficult if the user is interested in evaluating a specific area or pattern. The identification at a precise localization on such a sample remains essential for a complete interpretation of the sample. HORIBA Scientific developed a new technology, called navYX™. Based on nanoGPS technology, navYX™ can precisely relocalize the specific areas in the sample from one instrument to another with a high degree of accuracy, rapidly and easily.

Keywords: Raman, SEM, Cathodoluminescence, EDS, SXES, colocalized, mineral, pyrite, nanoGPS, correlative microscopy.

Introduction

In this study we have chosen to study pyrite and its surrounding minerals in order to identify the different mineral phases as well as the chemical variations from micro- to nano-scale. Pyrite is a brass-yellow mineral with a bright metallic luster. It has a chemical composition of iron sulfide (FeS_2) and is the most common sulfide mineral. It forms at high and low temperatures and occurs, usually, in small quantities associated with other sulfides or oxides in quartz veins, organic-rich sedimentary rocks, and metamorphic rock, as well as a replacement mineral in fossils.

The selected pyrite occurs in a crysotile vein intersecting a serpentinite meta-arkose. This type of metamorphic rock is the result of the interaction between sea water and peridotites, which are the rocks that make up the earth's mantle. We have used here Raman and Scanning Electron Microscopies (SEM) to study such a sample provided by French BRGM laboratory.

The Scanning Electron Microscope (SEM) scans the surface of a sample with an electron beam and detects the information produced by the sample via an image displayed on a computer. By irradiating the sample with an electron beam, secondary electrons, backscattered electrons and characteristic X-rays are generated. Scanning Electron Microscopy can be equipped with several different detectors for complementary analysis of the specimen. SEM detectors such as BSE-EDS-SXES and hyperspectral Cathodoluminescence play a key role for a comprehensive chemical characterization of such complex sample. Thanks to their own specificities combined with a good spatial resolution, each of these techniques bring crucial information for mineral investigations. Secondary electrons (SE) reflect the fine topographic structure of the sample, while backscattered electrons (BSE) reflect the compositional distribution on the sample surface. X-rays are used to determine which elements are included in the sample and how they behave.

Raman Microscopy is based on a spectrograph attached to an optical confocal microscope. It is a powerful and non-destructive characterization tool to study minerals. It has the capability of characterizing the molecular chemical distribution of the material, as well as its various mineral phases, and unveiling the mixtures of solid, gas and liquids trapped in micrometric inclusions.

A critical point on this type of correlative microscopy study is the ability to measure a specific area or artefact of the sample at the same location between the SEM to the Raman Microscope. Being co-localized allows a comprehensive characterization of the sample and a precise superimposition of all the images. The nanoGPS Suite™ overcomes this challenge by providing an accurate relocalization between different instruments (navYX™), and a software able to position the multimodal maps in the same coordinates system (graphYX™).

In this particular example, it allowed to record every point of interest on the large pyrite sample on SEM and revisit them immediately - even small inclusions which proved very difficult to find - on optical microscope. Raman microscopy on the other hand, enables identification of compounds present in those small inclusions, where SEM technique failed to determine their molecular compositions.

Thanks to the nanoGPS Suite™, the users can precisely relocalize the points of interest at the microscale and superimposing all generate images among different microscopy techniques.

Methodology

In order to perform a complete characterization of the sample and provide information about the spatial distribution, a set of multi-approach and complementary studies were conducted.

Sample

A thin section of a geological chrysotile vein in a serpentinite was chosen. Within the chrysotile vein is pyrite surrounded by different mineral phases that appear to have variable chemical compositions observed with an optical microscope. This area was therefore selected for the identification and distribution of the different elemental assemblages. The sample was generously provided by *Bureau de Recherches Géologiques et Minières* (BRGM).

Raman Spectroscopy

Raman spectroscopy is based on the detection of photons scattered when the sample is illuminated by a laser source (UV-visible-IR). The energy gain or loss of the photons emitted is translated on the Raman spectrum.

HORIBA LabRAM Soleil™ is a Raman multimodal microscope offering the highest throughput with no compromise on resolution, thanks to the high efficiency dielectric mirrors, coupled with high quality gratings. The instrument comes with specially designed edge filters and a motorized kinematic filter holder to guarantee 30 cm^{-1} cut-off, making it the perfect instrument for molecular analysis of complex samples (Figure 1). Mapping is up to 100 times faster than a conventional Raman, thanks to the innovative SmartSampling™ technology. The patented QScan™ feature offers lightsheet confocal Raman imaging.

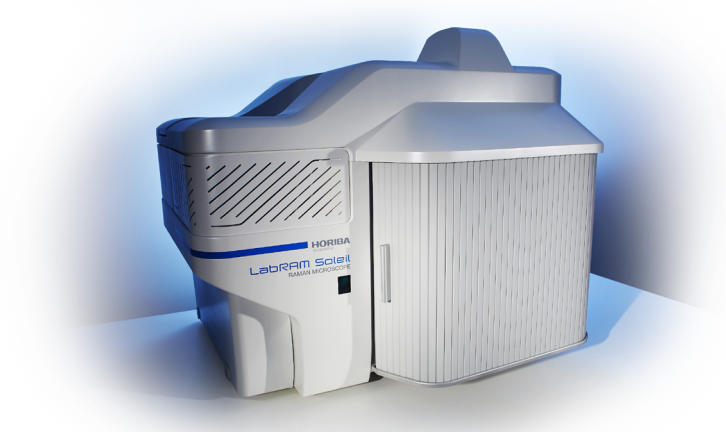


*Figure 1: HORIBA **LabRAM Soleil™** Raman microscope*

HORIBA LabSpec 6 is the complete software solution starting from the instrument control/data acquisition, going through the data pre-processing and data analysis, thanks to the software module MVA+ and xSTaiN™, and ending on a powerful spectra identification, thanks to the comprehensive database, Know it All™, powered by Wiley.

SEM-BSE Image

Backscattered electrons (BSE) are high-energy electrons that are produced by the elastic scattering of the primary beam electrons of the SEM with the atom nuclei. The yield of BSE, that is the ratio of the number of emitted BSE and the amount of primary beam electrons, depends on the atomic number: the higher the atomic number, or the heavier the element, the brighter the contrast. All SEM-BSE experiments were conducted using the SEM instrument, model JSM-IT800 from JEOL.

EDS Analysis

Energy Dispersive X-ray Spectroscopy (EDS) is based on the detection of the characteristic X-ray emitted from the sample, which measures the signal and interprets it using SEM operator software from JEOL. The elemental information can be visualized in several ways including elemental mapping and associated spectrum. In this way, X-rays can be used to identify the chemical composition of a sample, including what elements are present as well as their distribution and concentration. All SEM-EDS experiments were conducted by using the SEM instrument from JEOL, equipped with EDS add-on detector.

SXES Analysis

Soft X-Ray Emission Spectroscopy (SXES) is a complementary SEM technique developed by JEOL using high spectral resolution grating and a CCD detector for X-Rays, allowing to differentiate various phases of elements, such like iron alpha and beta phases (in this study) at the nanoscale. All SEM-SXES experiments were conducted by using the SEM IT800 instrument from JEOL, equipped with SXES add-on detector.

SEM-CL Spectroscopy

All SEM-CL experiments were conducted by using the SEM instrument from JEOL, equipped with the HORIBA F-CLUE add-on detector (Figure 2). Using the scanning electron beam as an excitation source, the attainable resolution is on the order of a few tens of nanometers. In addition, SEM-CL analysis offers the advantage of a high sensitivity to variations in chemical composition on a lower detection limit than techniques based on X-ray fluorescence analysis. Therefore, it is advantageous over conventional SEM-EDX and SEM-WDX analyses for detecting trace elements. HORIBA CLUE CL systems are also capable of performing hyperspectral images providing high spatial resolution of a region of interest based on the emitted light.

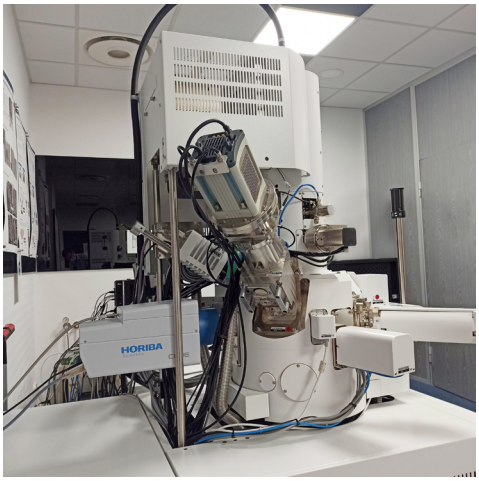


Figure 2: HORIBA F-CLUE Cathodoluminescence instrument coupled to SEM system from Jeol.

navYX™ Relocalization Technology

navYX™ is a relocalization method based on machine readable, small-patterned tags fixed on the samples or their substrates. The patterns include an imaged-based position sensing technology, for which an image of a small part of the tag can be automatically interpreted into absolute coordinates and angular orientation. Taking a single snapshot on the tag with an imaging instrument provides the correspondence between sample and moving stage coordinates. This correspondence is a crucial information to guarantee the colocalization of images when using different objectives or different instruments, bringing a huge benefit for the user being able to fully characterize their sample at the same localization (Figure 3).

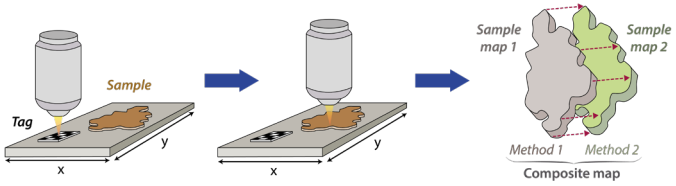


Figure 3: HORIBA navYX™ relocalization technology. 1st step: Start the session on the tag; 2nd step: generate the POIs and 3rd step: Superimpose all generated images.

Results

In this section we will present the SEM-BSE-EDS-CL and micro-Raman results, showing the complementarity information obtained by analyzing at the same localization with different techniques, thanks to navYX™, the innovative relocalization technology powered by HORIBA. Detailed SXES results can be found in a separate poster available through JEOL website https://www.jeol.fr/produit/sxes/

BSE imaging shows chemical composition variation on the observed area. On Figure 4a and 4b, a contrast and brightness difference can be easily observed and indicates the differences in chemical composition. On BSE, imaging offers an easy and quick visualization of the specimen chemical variation, however, no chemical identification and characterization can be performed with this method. For this reason, the need of complementary techniques is crucial for a complete understanding of the sample proprieties.

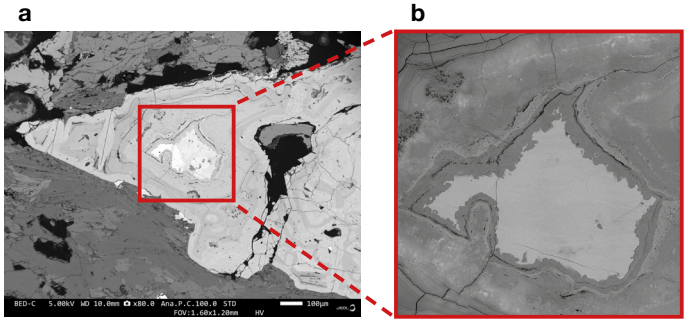


Figure 4: BSE image of the thin section of a chrysotile vein in a serpentinite. (left) BSE image generated at 80x magnification and (right) 300x magnification.

The first complementary technique applied to the sample was EDS mapping, which can bring information about the elemental composition, distribution and concentration (Figure 5 and 6). It's possible to observe the spatial distribution and the associated density of each chemical element detected by EDS. Additionally, the EDS spectrum shows several peaks, representing the different elements presented on the analyzed area. Other EDS maps in different areas and magnifications were carried out, where some small particles at nanometer scale (Al and Ca) were identified.

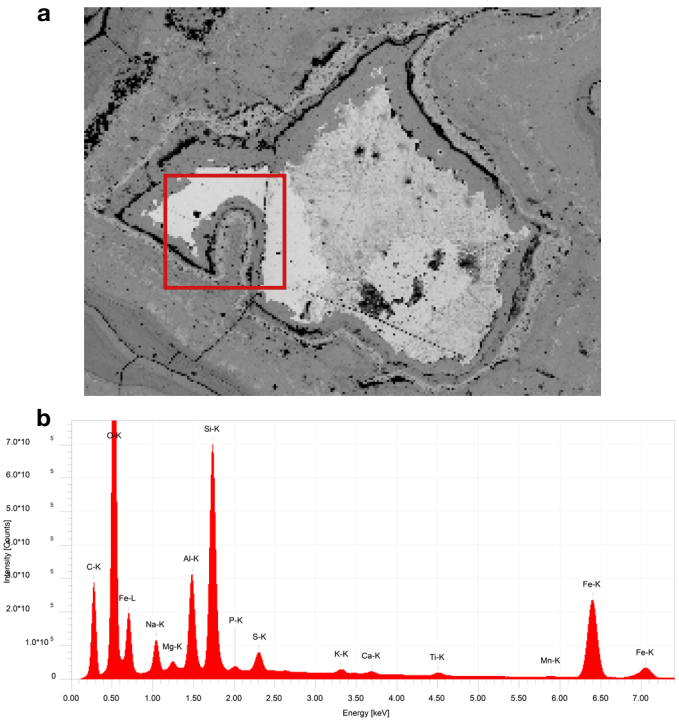


Figure 5: (a) BSE image showing the analyzed area. (b) EDS spectrum

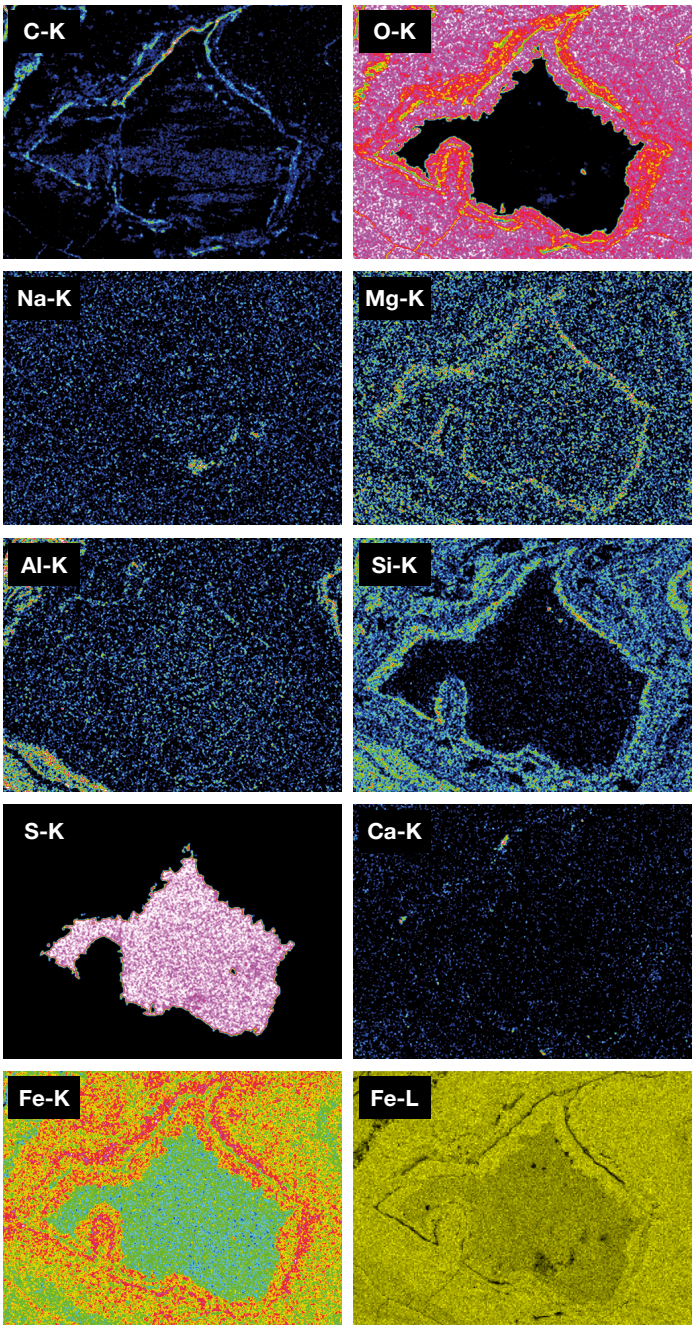


Figure 6: EDS maps representing the different elements detected on the analyzed area.

A further characterization of the sample was carried out by Raman spectroscopy and differently from the previous used technique, where the technique is built-in on the SEM platform. To perform Raman analysis on the sample, the physical movement of the sample from the SEM chamber to the motorized stage of the Raman microscope is needed. Thanks to navYX™ technology it`s possible to automatically and precisely relocalize the point of interest, enabling the Raman measurement at the same localization (Figure 7). In this study, the mineral phases identification was based on EDS and on the Raman spectra. The EDS analysis helped to sort between all matching results in the Raman database.

A complementary technique was applied for the identification of inclusions on the sample. Cathodoluminescence is a built-in technique on the SEM platform, offering high-sensitivity and nanometric spatial resolution.

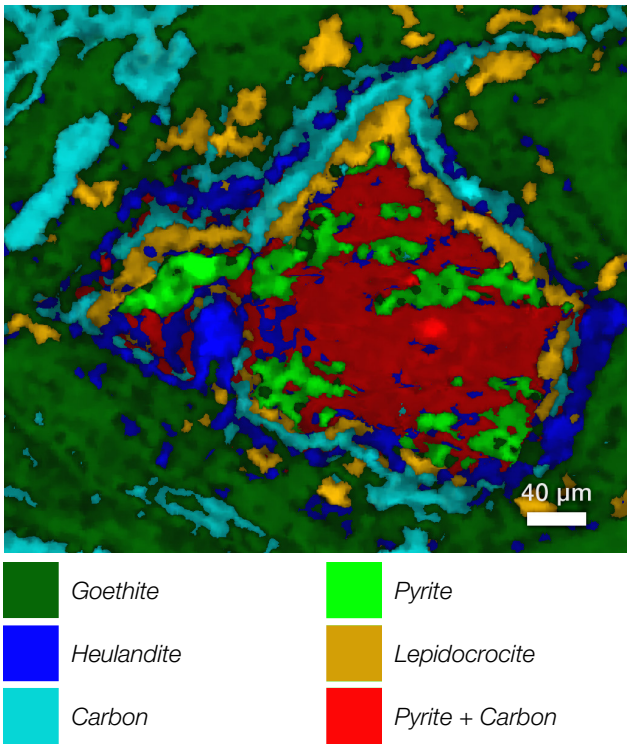


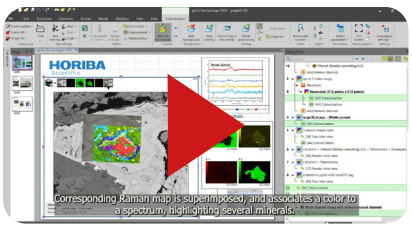
Figure 7: Raman mapping of the thin section of a chrysotile vein in a serpentinite.

CL mapping provides valuable information about the sample's luminescence. Thanks to navYX™ technology, it`s possible to easily place back the sample on the SEM chamber and relocalize the point of interest used before.

In this study, a 10 µm Al inclusion was identified with the CL, including the bubbles inside that were characterized (Figure 8b). The same inclusion was revealed by EDS, but not precisely identified if it was an oxide or a metal, mainly because the inclusion was located in an iron oxide region. However, CL spectrum reveals the inclusion and the chemical assignment of the aluminum oxide.

Based on the new information about the inclusion provided by CL, a new point of interest was generated and saved. The sample was once more moved from the SEM chamber to the Raman instrument and the same 10 µm-inclusion and their inside bubbles were relocalized, thanks to navYX™ and its relocalization accuracy. A new Raman high-spatial resolution map was performed on the same area to fully characterize the inclusion on the sample (Figure 8c).

All generated results from the different techniques leads to a better understanding of the sample. However, been at the same localization on the different techniques, really brings an enormous advantage to not only understand the different proprieties of the sample, but also the correlation of the results between them and the advantage to extract the technical benefits from each technique and associate them for the sample evaluation.



graphYX software: how to combine chemical images for a comprehensive characterization.

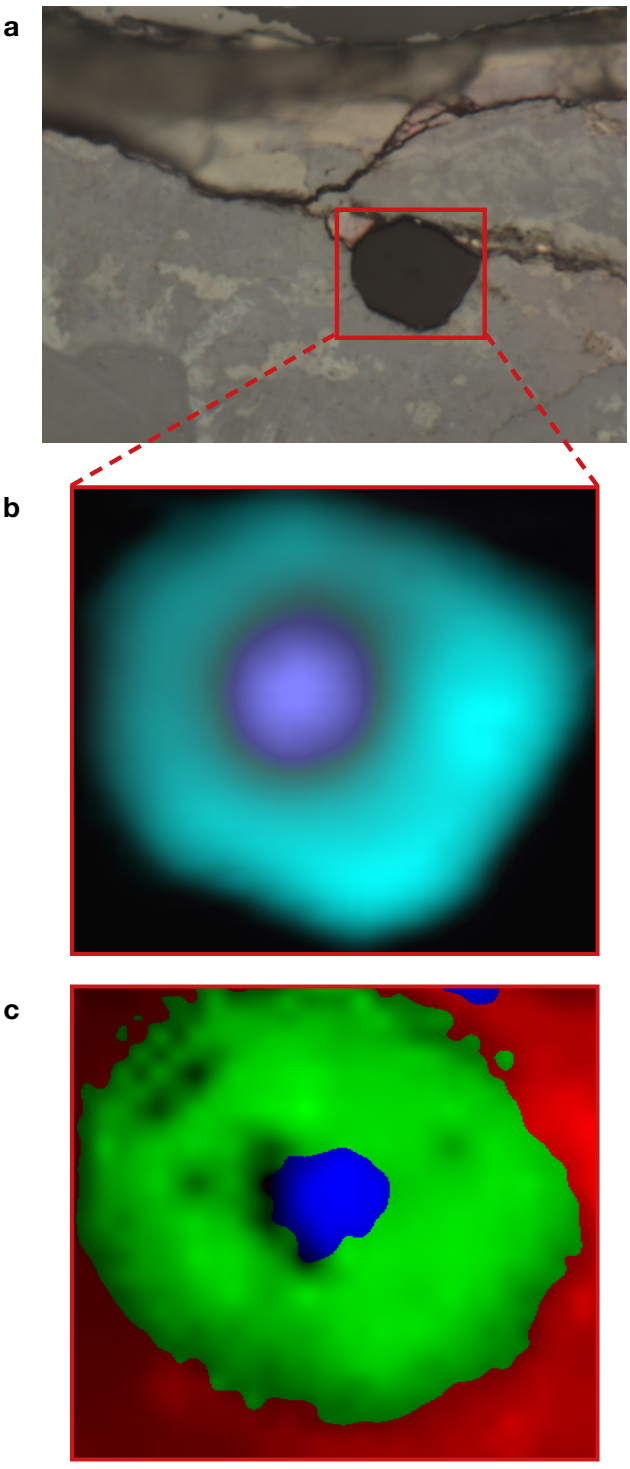


Figure 8: (a) Optical image showing the inclusion analyzed, (b) CL image and (c) Raman mapping of the inclusion.

Conclusions

Following this set of multi-approach analyses, several general conclusions can be drawn. The BSE images, the EDS mapping and the Raman measurements identified the presence of several mineralogical compositions surrounding the pyrite. Furthermore, Raman measurement results associated with EDS mapping allowed the identification of the different minerals in the rings around the pyrite, proving the benefits of navYX™ technology to easily relocalize the point or area of interest. The CL revealed inclusions with strong luminescence that were not detected by BSE images and low magnification EDS mapping. In order to identify the chemical composition of these inclusions as well as to have a high-resolution maps, Raman and CL were performed on this new point of interest. The result is a very heterogeneous elemental distribution both spatially and in density.

This multi-approach study highlights the real benefits of navYX™ as a relocalization tool between various microscopy instruments. Not only were the complementary results observed, but also a colocalized measurement, illustrating an extremely precise elemental identification and density, a high-resolution spatial distribution, as well as the chemical composition of the studied area. nanoGPS tags can be imaged with different microscopes, over a wide range of magnification. A relocalization accuracy of a few µm up to 10 µm is routinely observed, and the orientation error is negligible. This is sufficient to avoid any ambiguity in colocalized observations. navYX is expected to save time and to open new opportunities to researchers. Spotting the same areas of interest without waste of time means more time for the research.

The colocalization of different techniques and the complementary information leads to a complete knowledge of the specimen in question.

Acknowledgements

Many people participated in this collaborative study and we thank them all warmly. The BRGM, and more particularly Guillaume Wille, are thanked for the loan of the chrysotile thin section (250,000th thin section of the BRGM!) that served as a case study for these analyses. We also thank them for their constructive discussions regarding the interpretation of the different results. Finally, we would like to thank the application engineers from JEOL and HORIBA for their patience, their professionalism and their pertinent remarks without which the study would not have been as successful.

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