High-resolution spatial distribution of chemical composition on a pyrite surrounded by oxide / hydroxide phases

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Introduction

Context

In the world of microscopic studies, the **identification of the spatial distribution** of certain mineral phases and inclusions **remains complex**. Indeed, variations in **chemical composition** on a scale that can sometimes be very small remain **difficult to observe** with a simple optical microscope and even with the use of a scanning electron microscope (SEM). The **identification** and the **precise localization** of these differences of chemical nature remain however **essential for the good understanding** and the interpretation of the sample, and those, even on a **very small scale** (going to the order of the hundred or even of the ten nanometer).

Case of study

In this study, a geological thin section of a **meta-arkose in a serpentinite** was chosen. This sample comes from the Bureau de Recherches Géologiques et Minières (BRGM). This type of metamorphic rock comes from the interaction between sea water and peridotites, which are the rocks that make up the earth's mantle. Within the meta-arkose rock is **a pyrite surrounded by different mineral phases** that appear to have **variable chemical composition**. This area was therefore selected for the **identification and distribution of the different elemental assemblages**.

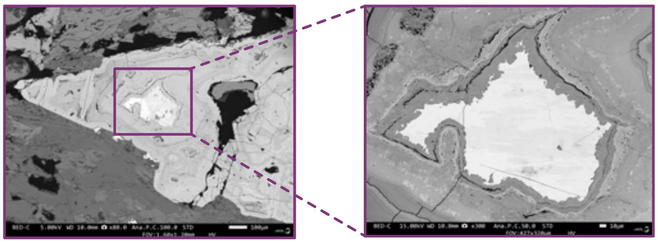
Methodology

In order to better answer the questions of chemical identification and spatial distribution, a **set of multi-approach and complementary studies** was conducted between JEOL and HORIBA companies. It includes the use of a **SEM** IT800HL of the JEOL brand to which were added three other tools, namely an **Energy Dispersive X-Ray Spectroscopy** (EDS) and a **Soft X-Ray Emission Spectrometer** (SXES) of the JEOL brand as well as a versatile hyperspectral **cathodoluminescence** (CL) F-CLUE of the HORIBA brand. In addition, the sample selectioned for this study was analyzed by **RAMAN** with the LabRAM Soleil™ Raman Microscope from HORIBA.

Main results

SEM - BSE image

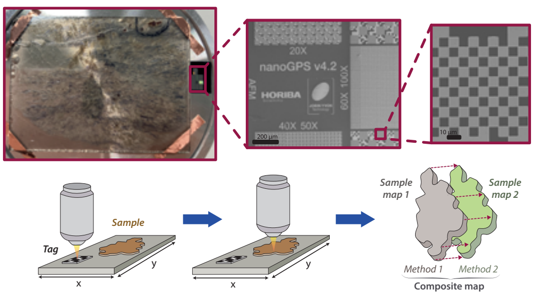
Backscattered electrons (BSE) are high-energy electrons that are produced by the elastic scattering of the primary beam electrons of the SEM with the atom nuclei. The yield of BSE, that is the ratio of the number of emitted BSE and the amount of primary beam electrons, **depends on the atomic number**: the higher the atomic number, or the heavier the element, the brighter the contrast.



In this study, BSE imaging allows to see the **difference of chemical composition** on the observed area. Thus, this study area showing **important contrasts**, sign of **important chemical variation**, is selecting for additional on complementary analysis.

Nano GPS NavYX

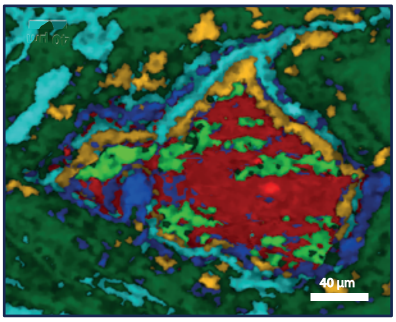
This GPS allows to spot the same points of interest with a **high degree of accuracy** and **simplicity** using different microscopes. It is based on **patterned tags** fixed to the samples. An image of a part of the tag can be automatically **converted to absolute coordinates** and **angular orientation** which will provide a **correspondence** between the **sample** and the coordinates of the **moving stage**.

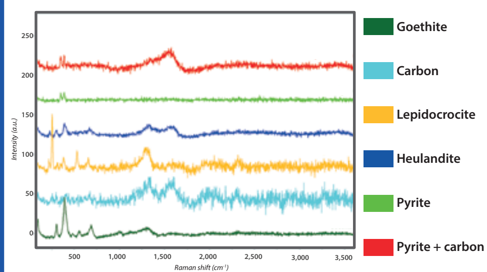


With NavYX, maps from different microscopic techniques are **co-localized** and **overlaid** to create **composite maps**. Thus, we can perfom **correlative measurements** on the same observation area.

Raman mapping

Raman photons are emitted when the sample is illuminated by a laser source (UV-visible-IR) through an inelastic light scattering phenomenon. The **gain or loss of energy** of the inelastic photons emitted compared to the incident photons is translated on the **Raman spectra by a frequency shift**. The Raman bands observed at a frequency shift correspond to the **energy gap between the vibrational levels of the analyzed molecule**.

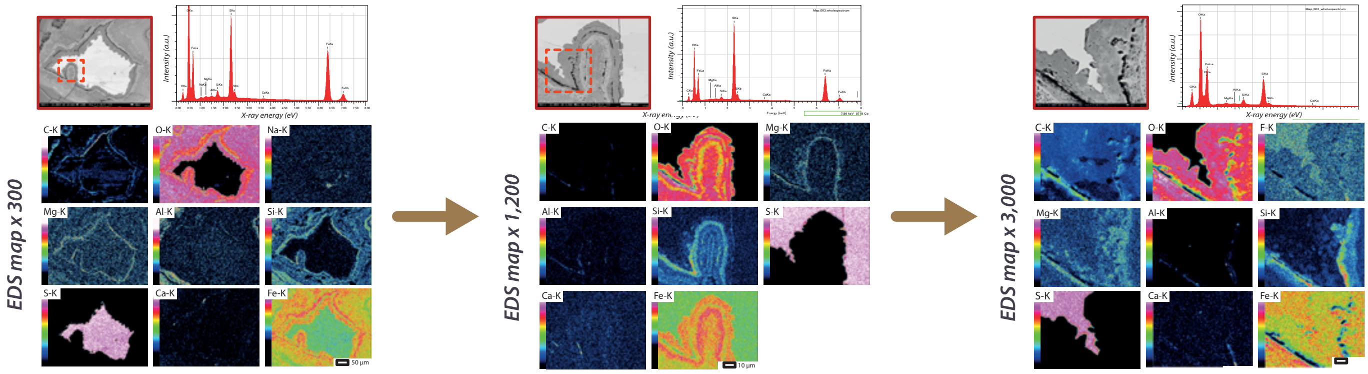




In thi study, the RAMAN **allows the identification of the main minerals** composing and surrounding the pyrite as well as their **general spatial distribution**.

EDS Mapping

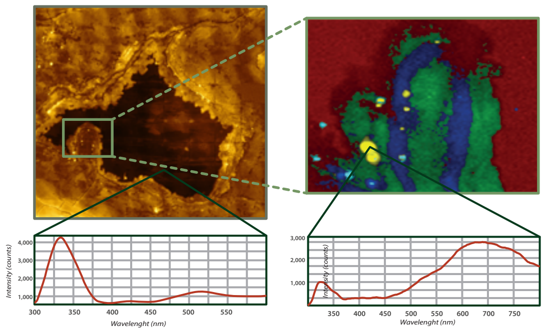
The X-rays emitted from the sample are collected by a detector, which measures the signal and interprets it using software. The elemental information can be visualized in several ways including **elemental mapping and associated spectrum**. In this way, X-rays can be used to identify the **chemical composition of a sample**, including what elements are present as well as their **distribution and concentration**.



This mapping allows to visualize the **spatial distribution** and the **associated density of each chemical element** detected by EDS from low event to high magnification. With high magnification, some **small particles at nanometer scale** (Al and Ca) are clearly identified.

Cathodoluminescence

CathodoLuminescence is a non-destructive technique providing **maps of optical and electronic properties of many kinds of materials with a nanometric spatial resolution**. The CL is similar to Photoluminescence (PL) technique, but the excitation by high energy electron beam can produce all the transitions to the higher energy excitation states and induce **light emission from deep UV to near-infrared**.



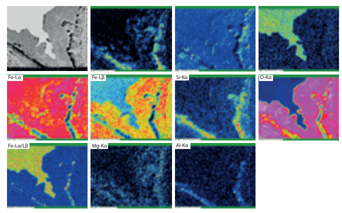
The CL mapping shows the differences in luminescence in the observed area. In this study, **inclusions with very strong luminescence** that were not detected by RAMAN, BSE imaging and low magnification EDS mapping were identified thanks to the CL.

SXES

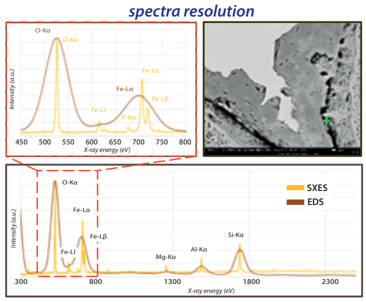
Characteristic X-rays are generated by the electron beam from the sample and guided, by the focusing mirror, to the newly developed **diffraction varied-line-spacing grating**. X-rays diffract from the grating according to their wavelength; **different characteristic X-rays** are detected simultaneously by a parallel detection system (CCD camera) and **displayed as a spectrum**.

The SXES analysis provide **an extreme spectral resolution** compared to EDS results, even for **light elements** (F). In addition, **different chemical states of iron** (Fe) could be **clearly identified and separated** compared to EDS results.

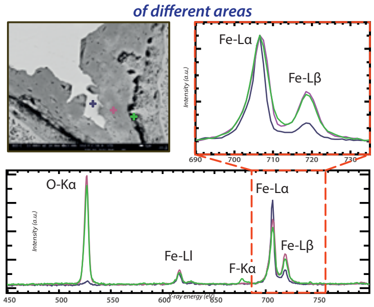
SXES mapping



Comparison between the EDS and SXES spectra resolution



Dissociation of different Fe states on the spectra of different areas



Conclusion

Following this set of **multi-approach analyses**, several general conclusions can be drawn. First, thanks to the nano GPS NavYX correlative technology, the **location of the areas of interest** were found without difficulty and allowed a **precise analysis** through different microscopes.The BSE images, the EDS mapping and the RAMAN spectrometry identified and show **various mineralogical compositions** surrounding the pyrite. Furthermore, RAMAN coupled with EDS mapping allowed the **identification of the different minerals** in the rings around the pyrite. The CL **revealed inclusions with strong luminescence** that were not detected by BSE images, RAMAN and low magnification EDS mapping. In order to **identify the chemical composition of these inclusions** as well as to have a **high resolution rendering of the elemental spatial distribution**, high magnification EDS mapping and SXES analysis were performed. The result is a **very heterogeneous elemental distribution** both **spatially** and in **density**. Moreover, the SXES analysis allowed the **identification of different chemical states of some elements** such as iron (Fe), which are indistinguishable in EDS analysis, and **different levels of elemental concentration** depending on the selected analysis areas.

This multi-approach study highlights the complementarity of the different analysis techniques used through results illustrating extremely precise elemental identifications, a high resolution spatial distribution as well as a precise variation of the elemental density in the selected observation area.