COBALT ENAMELS THROUGH TIME: ARSENIC'S INFLUENCE AND REMOVAL IN HISTORICAL PRODUCTION TECHNIQUES

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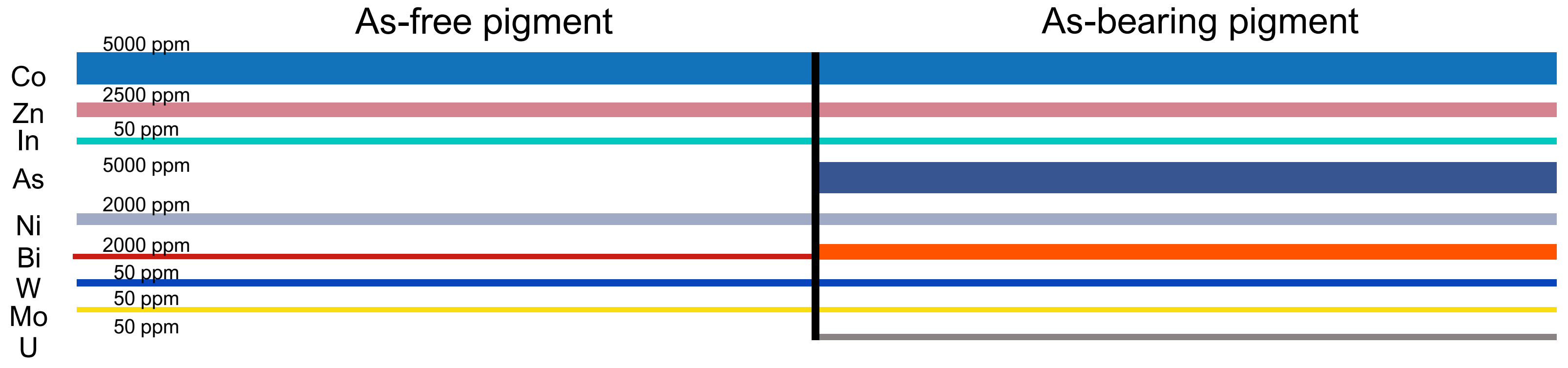
INTRODUCTION

Cobalt blue has been one of the most widely used pigments in the arts, especially in ceramic glazes and glass. In historical times, it was produced from cobalt ores, processed according to various recipes.

Cobalt enamels produced between the 15th and 16th century contain two different types of pigment: i) an As-free, employed until 1520, and ii) an As-bearing type.

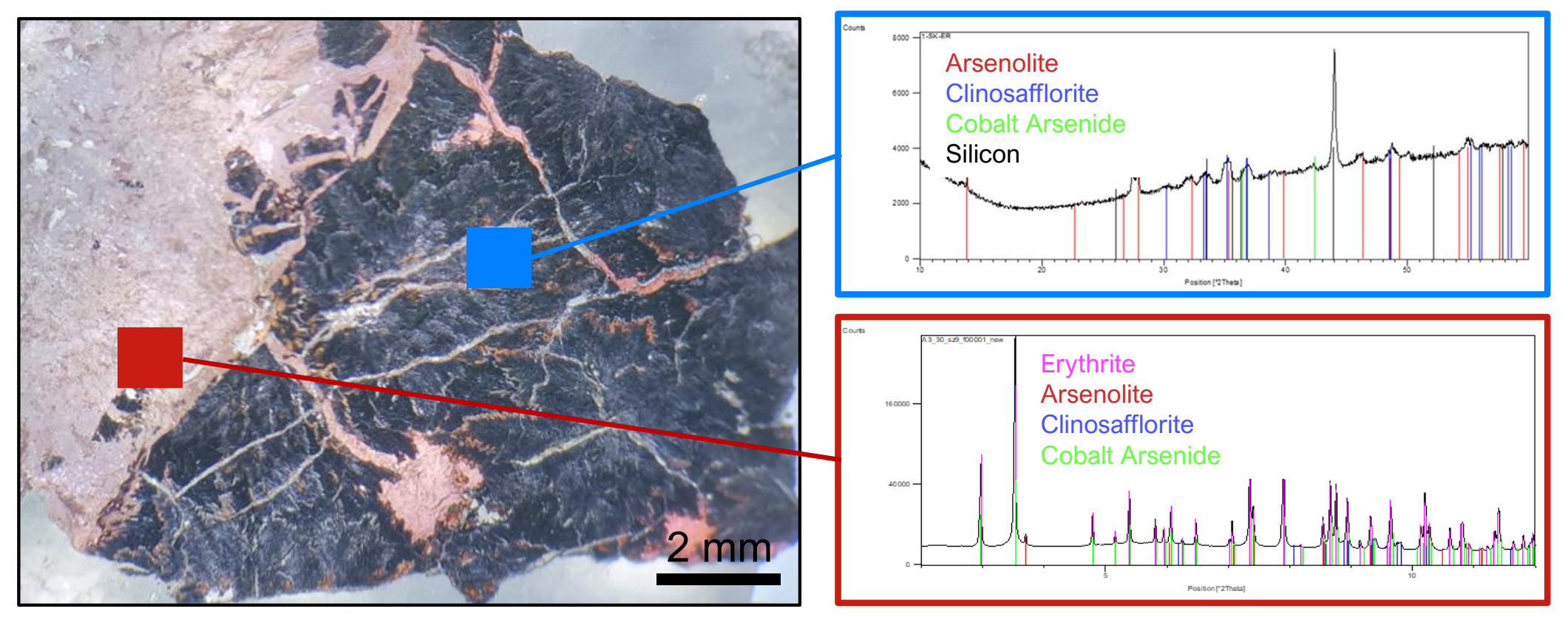


Main cobalt-related elements in blue ceramic glazes analyzed by LA-ICP-MS (Gratuze et al., 1996)

Given the significance of the Erzgebirge mining district for the supply of cobalt between the 15th and 16th century, it is assumed that the raw minerals used for both pigments might origin in the area ores: erythrite, smaltite and skutterudite, all containing arsenic (Gratuze et al., 1996; Soulier et al., 1996). The arsenic might have been removed through mineral roasting, during *saffron* production, or by using fluxes, added to obtain enamel (Meltzer, 1716).

The objective of this research is to assess the feasibility of arsenic removal from erythrite and clinosafflorite, two minerals found in the Ergebirge region, possibly used to produce cobalt blue pigment in historical times.

MATERIALS AND METHODS



A mineralogical sample from Bou Azzer, Morocco was used for this study.

The starting material consists of two main phases: erythrite and clinosafflorite. Arsenolite, skutterudite and annabergite occur in minor amounts.

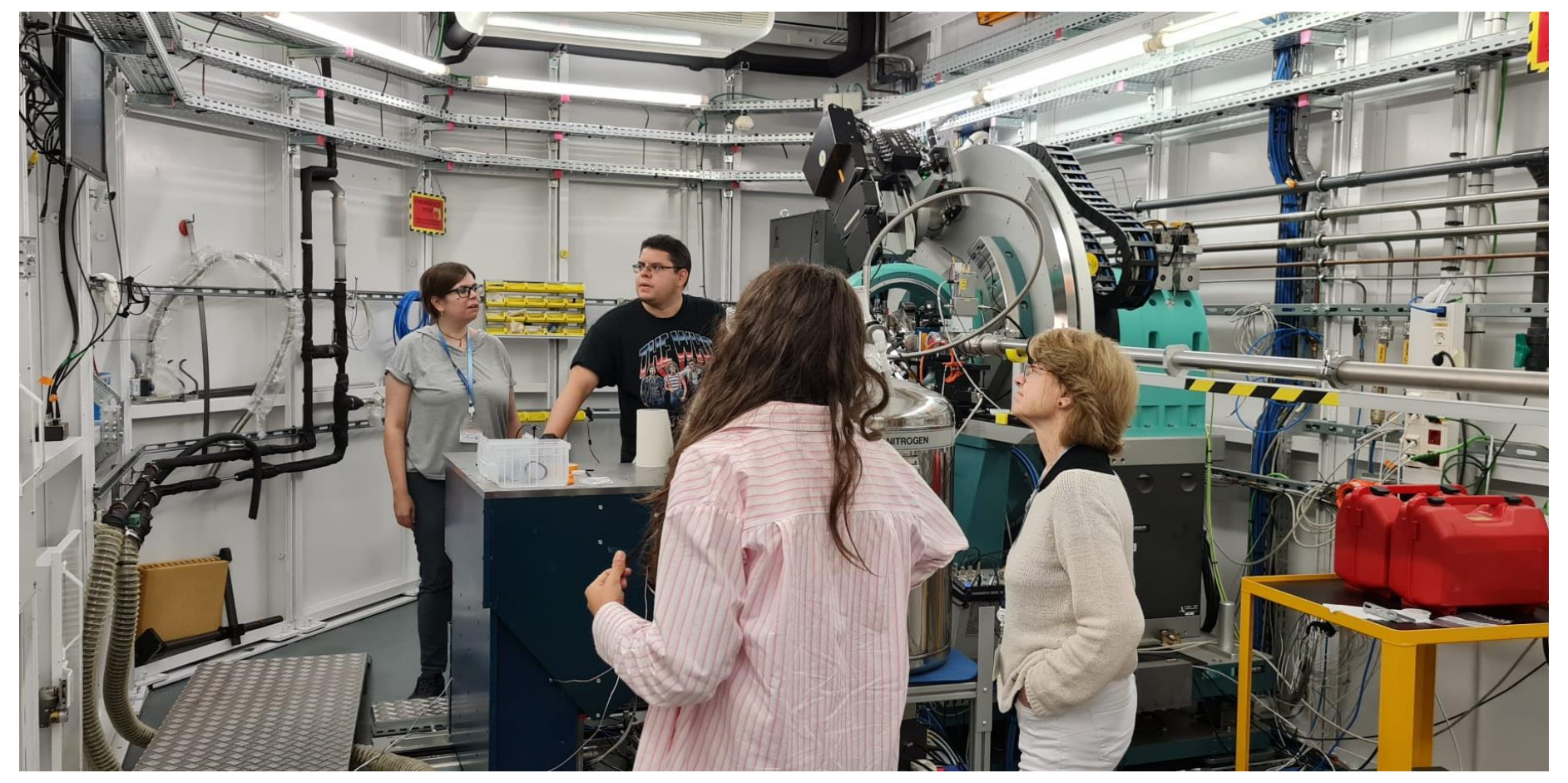
Reflected light OM close up textures, and XRD mineral composition of the ER sample from Bou Azzer

Erythrite and clinosafflorite powders, hand picked from the Moroccan sample, underwent thermal treatment, i)individually and ii)mixed with different fluxes, following ancient recipes.

Pre- and post-roasting characterization of the phases was conducted using OM, SEM-EDS, XRD and XRF.

The firings, aimed at reaching temperatures of 1020°C, were carried out under oxidizing conditions using the TERSID tubular oven and the HOBERSAL forced ventilation oven.

Additionally, some diffraction analyses were performed, under continuous heating (up to 895°C), using synchrotron radiation.

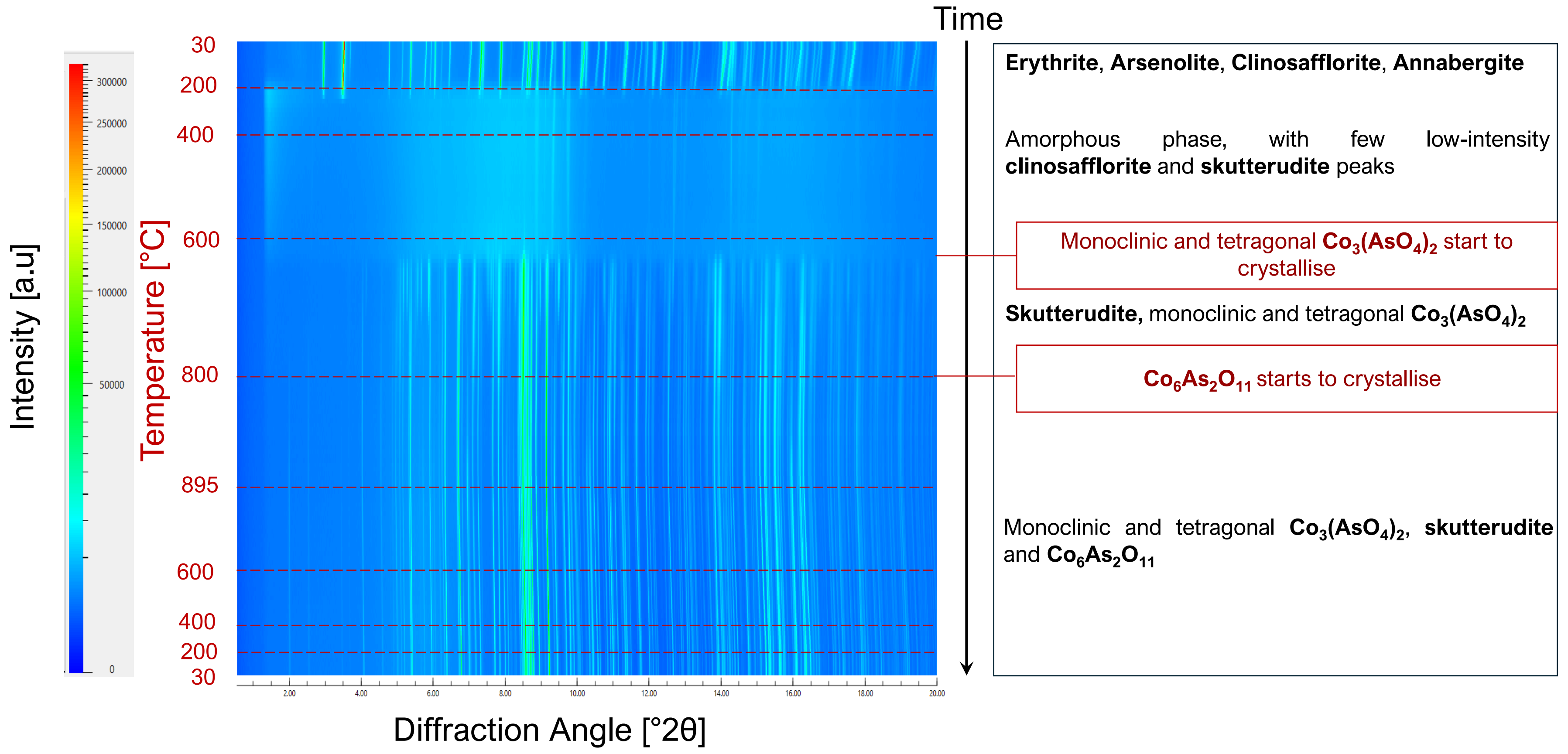


MSPD (BL04) beamline at ALBA Synchrotron

RESULTS

The erythrite powder was roasted in 4 steps until it reached a maximum temperature of 900°C, resulting in a weight loss of 28.29%. XRF analysis revealed that the arsenic quantity reduced progressively, at last corresponding to 22.4% total loss in the bulk.

The ore thermal behaviour investigated by SR-XRD, showed the formation of monoclinic and tetragonal $Co_3(AsO_4)_2$ at *c.* 560°C, replacing the starting phases from the natural ore. The monoclinic and tetragonal cobalt arsenates persist throughout the entire heating and cooling process.



Erythrite, **Arsenolite**, **Clinosafflorite**, **Annabergite**

Amorphous phase, with few low-intensity **clinosafflorite** and **skutterudite** peaks

Monoclinic and tetragonal $\mathbf{Co_3(AsO_4)_2}$ start to crystallise

Skutterudite, monoclinic and tetragonal $\mathbf{Co_3(AsO_4)_2}$

$\mathbf{Co_6As_2O_{11}}$ starts to crystallise

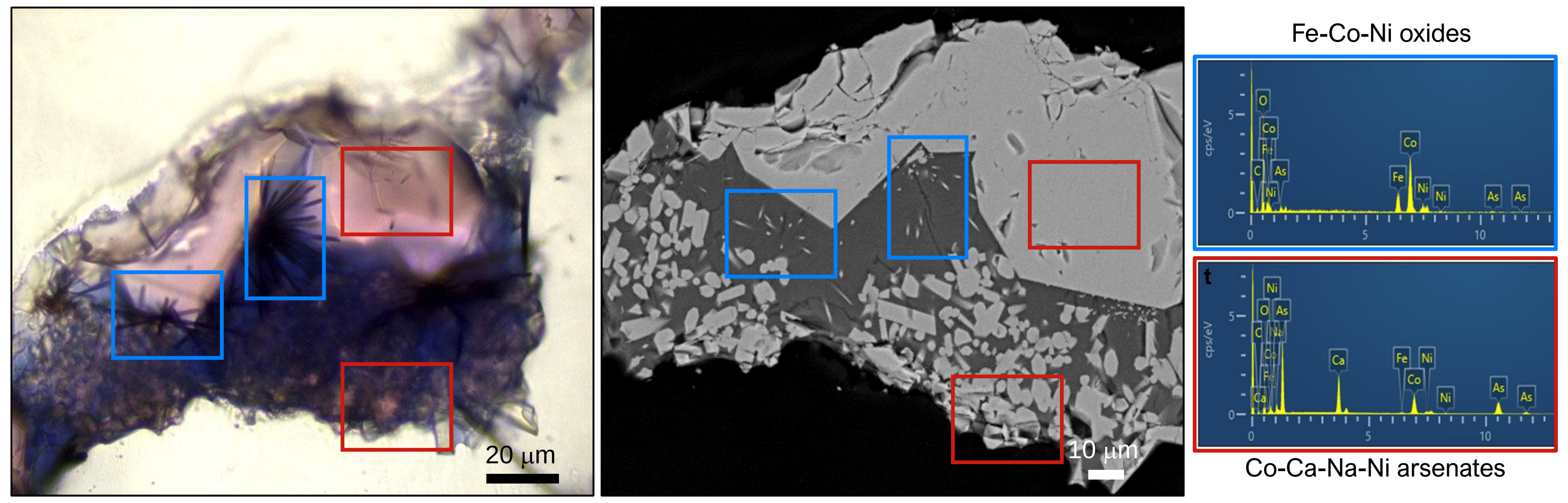
Monoclinic and tetragonal $\mathbf{Co_3(AsO_4)_2}$, **skutterudite** and $\mathbf{Co_6As_2O_{11}}$

Erythrite heating and cooling SR-XRD sequence showing the phase evolution during the thermal cycle

Roasted clinosafflorite powder determined the formation of As-poor cobalt phases with maximum Co/As ratios in atoms of about 329. However, some SEM-EDS analyses, conducted on a wider area, have shown that arsenic persists in the roasted mineral.

Some historical recipes for the production of cobalt blue enamels were replicated, using different fluxes mixed with erythrite and clinosafflorite powders.

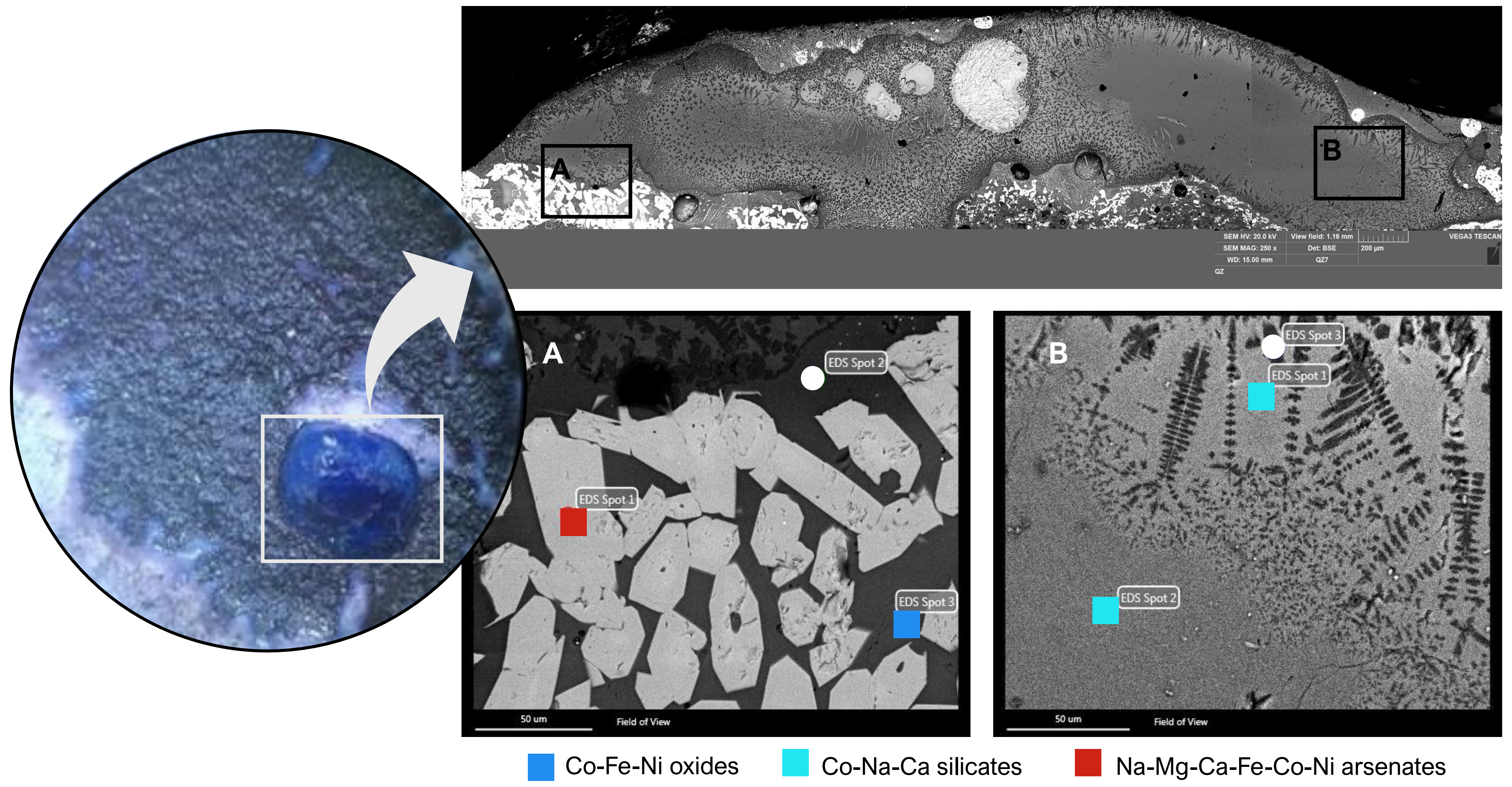
The calcination at 900°C of a mixture made with erythrite, borax and CaO led to the formation of Co-Fe-Ni oxides and Co-Ca-Na-Ni arsenates.



Transmitted light microphotograph, SEM images and SEM-EDS analyses of the erythrite, borax and CaO mixture roasted up to 900°C and the correlation between textures and phases

Roasted clinosafflorite, mixed with plant ash, was re-heated to 1020°C. This resulted in the formation of arsenic-free cobalt phases, however SEM-EDS analyses demonstrated that arsenic is still present in the bulk samples.

In parallel, the reaction and blue colouring of a quartz grain and the formation of different phases of Co-Na-Ca silicates and Na-Mg-Ca-Fe-Co-Ni arsenates were obtained by heating clinosafflorite with borax at 1020°C.



Reflected light OM close up, and SEM images of the quartz grain roasted with clinosafflorite powder and borax up to 1020°C and correlation between textures and phases

CONCLUSIONS

Our experiments demonstrated the difficulty of completely removing arsenic from erythrite and clinosafflorite by roasting individual minerals and/or mixtures although with different fluxes.

However, descriptions in historical treatises assess that thermal analyses carried out on clinosafflorite and mixtures, containing erythrite or clinosafflorite combined with fluxes, led to the formation of separated cobalt (Co-Fe-Ni oxides and Co-Ca-Na silicates) and arsenic phases (mainly Ca, Na and Pb arsenates).

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