Mineralogical reconstruction of complex sulfide ore and Ge-Ga critical metals investigation using LIBS mapping

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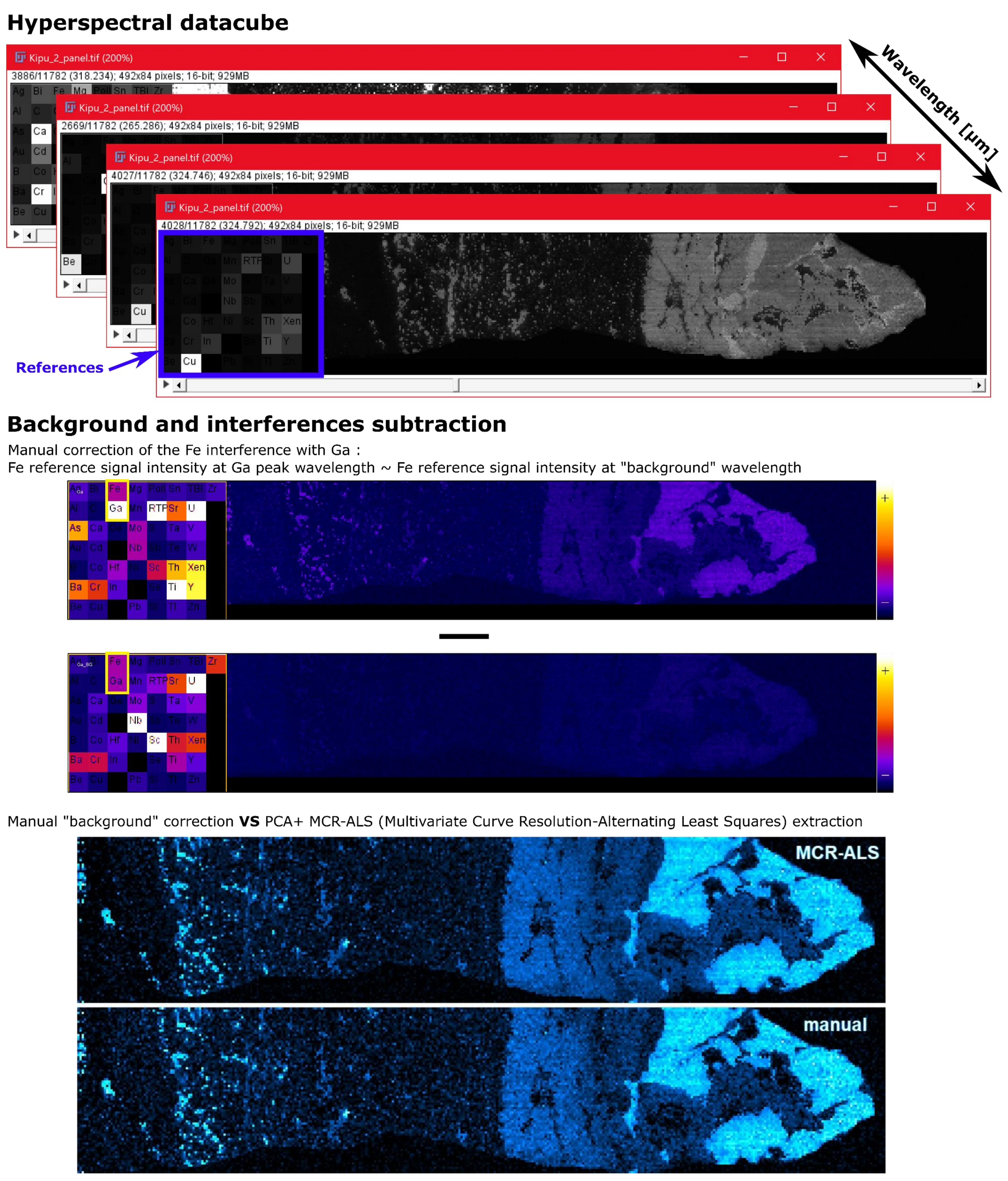
Introduction

LIBS mapping has been performed on several complex sulfide ore samples from Kipushi mine (D.R. Congo). The interest for these geomaterials resides in their **complex and diverse assemblages of mineral species.** Most of them are Cu-Zn-Pb sulfides, some of which containing germanium and gallium as major component or as traces. The detection and location of Ge and Ga, both critical metals of high economic importance and high supply risk, are crucial for the optimization of their mining and beneficiation (mineralurgical and metallurgical processes).

Previous experiments highlighted the **great detection capabilities of Ge and Ga** (along with many other elements) **using LIBS** in other ore samples from various locations. That led us to investigate this material with two objectives:

- Derive the mineralogy of the ore based on elemental data.
- Detect Ga and Ge and map their distribution across large (up to 10 cm) samples.

Data extraction and processing

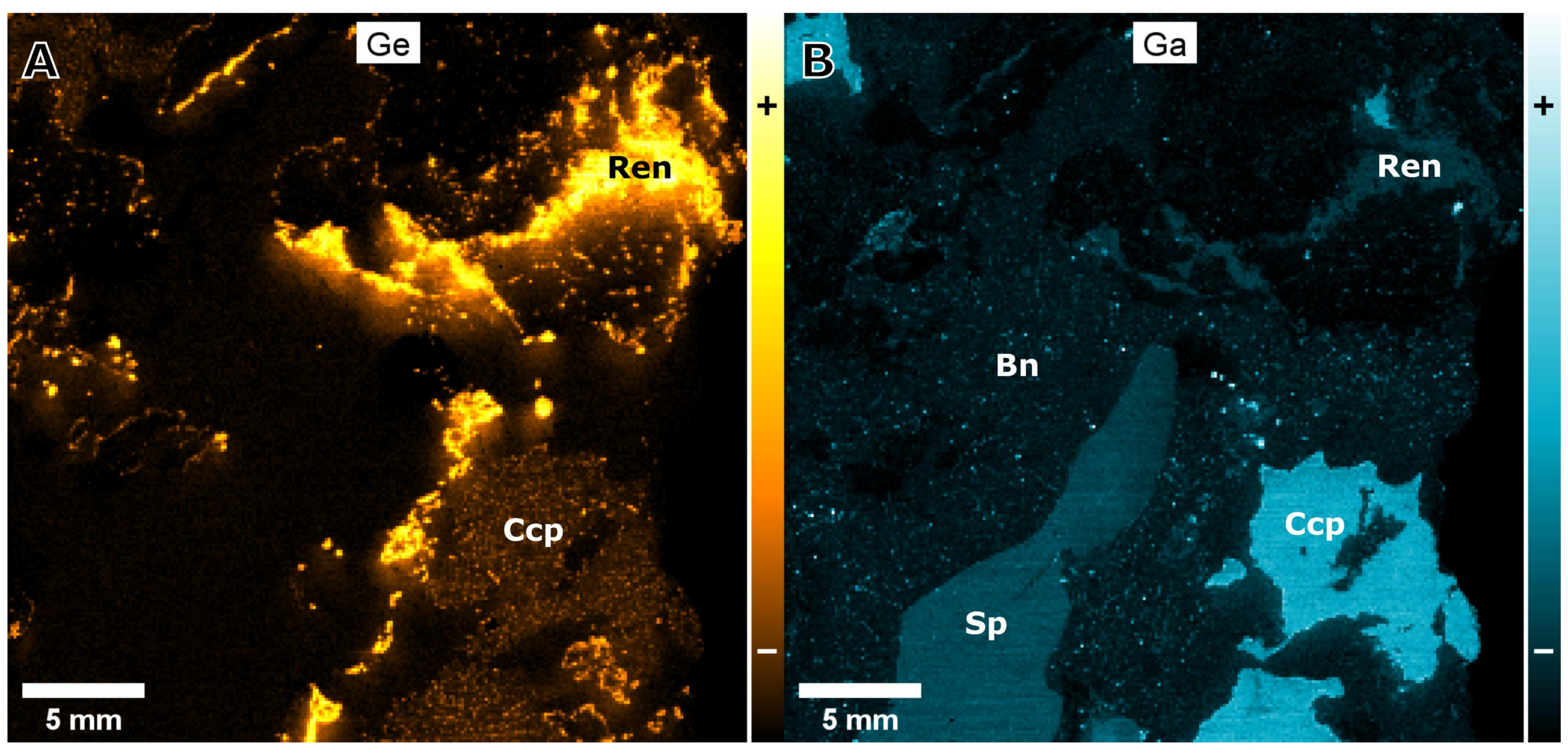


Germanium and gallium distribution

LIBS is capable of detecting **major, minor and trace elements** at the same time. In this particular case, germanium and gallium were both represented at various concentrations depending on the mineral phase:

Ge is mainly detected in the renierite [Ren] (a Ge-bearing mineral) and as scattered inclusions in both chalcopyrite [Ccp] and bornite [Bn].

Ga is present as major element in sub-pixel to pixel sized gallite grains. It is homogeneously detected as traces in chalcopyrite, renierite and sphalerite [Sp]. Ga-bearing disseminated inclusions are also observed in bornite.



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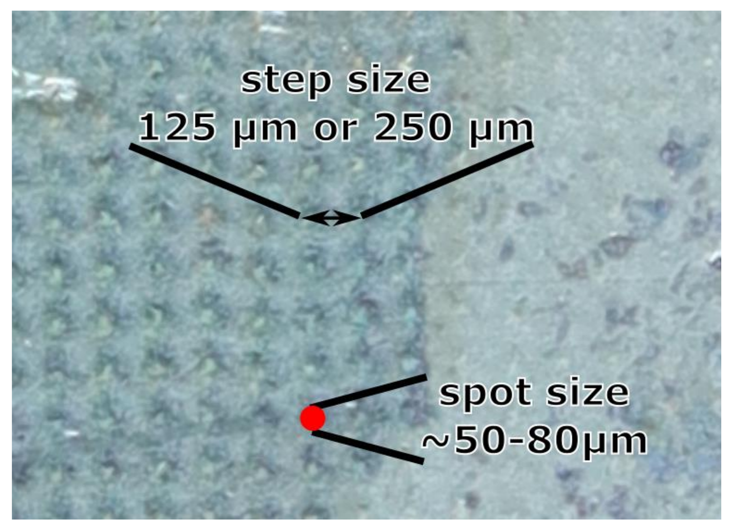
Materials and methods

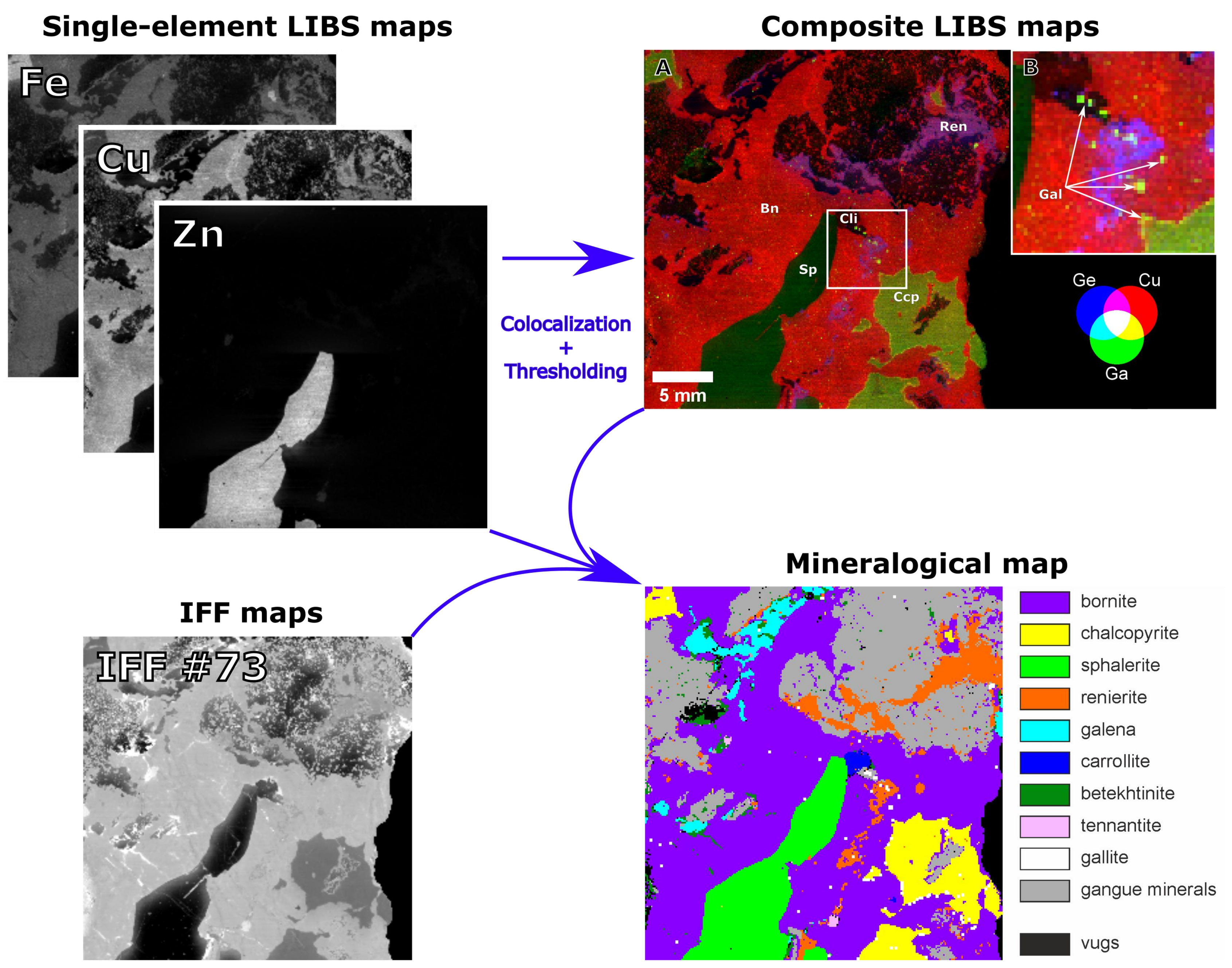
The LIBS system developed at UMONS is based on a **Lumibird/Quantel QSmart450 Nd:YAG laser** with 5 ns pulse duration, 20 Hz repetition rate, 266 nm wavelength and 10 mJ pulse energy. A **Spectral Industries IRIS spectrometer**, with Echelle design and CMOS detector, was used for this study.



The samples were minimally-prepared by sawing and levelling the surface with a lapping machine to ensure uniform surface rugosity and to minimize lens-to-sample distance fluctuations.

Mineralogy

Single-element and composite LIBS maps + IFF (Interesting Features Finder) maps were used to determine the mineral composition of the ore samples. Colocalization and signal intensity were studied to identify minerals from a list of described species found at Kipushi. **Twelve mineral species** were identified in our samples.



SEM-EDS analysis showed excellent agreement with the LIBS data. These analyses also demonstrate that LIBS has a great capability of detecting several elements such as Ge and Ga in mineral inclusions smaller than the laser spot size.

Ore mineral species	Formula	Sample						Trace-elements		
		K1	K2	K3	K4	K5	K6	Ge	Ga	Ag
Betekhtinite	$Pb_2(Cu,Fe)_{22\text{-}24}S_{15}$	1.4				1.6	0.1			
Bornite	Cu_5FeS_4	66.7	5			47.9	10.9		incl.	
Carrollite	$CuCo_2S_4$					0.3	0.01			
Chalcocite	Cu_2S	27.8								
Chalcopyrite	$CuFeS_2$		15.1		19.9	6.8	0.9	incl.		
Galena	PbS		0.1	2.2	0.1	3.1	0.02			
Gallite	$CuGaS_2$					0.1				
Pyrite	FeS_2				12.1					
Renierite	$(Cu^{1+},Zn)_{11}Fe_4(Ge^{4+},As^{5+})_2S_{16}$	2.7	25.4	55.8		6				
Sphalerite	ZnS			37.4	66.4	8.8	14.9			
Tennantite-(Zn)	$Cu_6(Cu_4Zn_2)As_4S_{12}S$	0.4	0.6	1		0.3	0.07			
Tungstenite	WS_2	0.1	1.3	1				?		
Gangue minerals	(carbonates, silicates)	0.9	52.5	2.6	1.5	25	73.1			

Values in vol%

Conclusion

LIBS mapping is a powerful tool for the geochemical and mineralogical investigation of **complex ores** at large (macroscopic) scale, with the following advantages:

- minimal sample preparation
- fast data acquisition and processing
- simultaneous multi-elemental detection
- multi-scale results (sub-microscopic to pluri-centimetric)
- provides a wealth of information from **the same analytical dataset,** including geochemistry, mineralogy and texture.