

Thibault Brulé, Jocelyne Marciano, Sofia Gaiaschi, Céline Eypert, Catalina David.
HORIBA FRANCE SAS, Palaiseau, France.

Abstract: In this article, we present how our Raman and X-Ray Fluorescence microscopies can be combined to shed some light on the origins of the universe. We show some examples on a meteorite piece and on water inclusion in quartz matrix.

Keywords: Raman, X-Ray Fluorescence, meteorite, inclusion, correlative microscopy.

Introduction

Among all information investigated in mineralogy, meteorites play a vital role in the understanding of our universe. The history of life and the pathways to form habitable worlds, can be unveiled by studying these objects.

Optical micro-spectroscopies such as Raman microscopy and X-Ray Fluorescence (XRF), offer a very high specificity combined with a good spatial resolution, two critical specifications for geological investigations, as for this application the features of interest can sometimes be lost in large matrices. Moreover, these characterization techniques are non-destructive, a crucial point as the artifacts involved in these studies are rare and precious.

The main interest in combining measurements of X-Ray Fluorescence and Raman microscopy arises from the information provided by these techniques: while the first one gives direct access to the elemental distribution, the latter provides information about the molecular one, enabling a complete characterization of the artefacts.

In this application note, we present two examples: a polished meteorite and a gas inclusion in quartz, showing how Raman microscopy and X-Ray Fluorescence can help provide a better comprehension of our universe and the origins of life.

Instruments and methods

Raman microscopy

Raman spectroscopy is a non-destructive and non-invasive vibrational spectroscopy technique that provides information about the molecular structures, crystal phases, polymorphism, and much more. When coupled with

optical microscopy, the technique offers the advantage of a high magnification visualization of a sample and the Raman analysis can be performed with a microscopic laser spot. Various imaging modes (e.g. brightfield, darkfield, polarized light,...) are available to separate the feature of interest and its environment.

LabRAM Soleil™ is the perfect instrument for the molecular analysis of complex geological samples. This system offers a high sensitivity, based on its specific optical design, coupled with a high spatial resolution guaranteed by the motorized true confocal pinhole on the detection pathway.

X-Ray Fluorescence

XRF is a non-destructive emission spectroscopy technique able to provide qualitative and quantitative elemental information. The advantage of the micro-XRF is the XY



Figure 1. **LabRAM Soleil™** Raman microscope (top) and **XGT-9000** X-ray Fluorescence microscope (bottom)

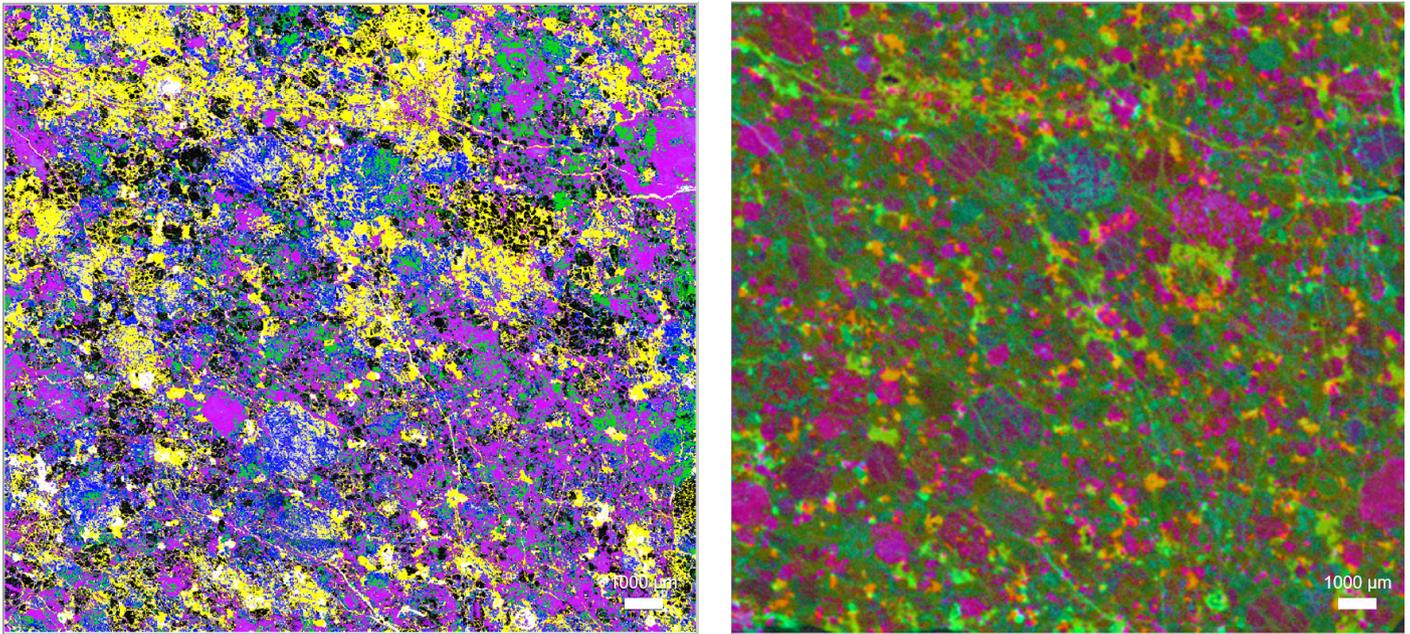


Figure 2: Maps of meteorite. (Left) Chemical Raman map. (Right) Elemental X-ray Fluorescence map.

motorized stage, which provides the possibility to acquire a pixel-by-pixel spectrum from which X-ray elemental images of large areas, as well as small details, can be reconstructed. Various illumination modes (coaxial, circular or combined) allow a better localization of the areas of interest.

The new XGT-9000 is the perfect tool to perform a large mapping of heterogeneous samples. As many metallic elements are present in a meteorite, several X-ray peaks are generated in the same energy range. The software is equipped with the peak separation (PS) function, which allows to perform the deconvolution of the general

spectrum pixel-by-pixel, clearly separating the interfering peaks. Furthermore, major elements, as well as traces are detected thanks to the high sensitivity of the silicon drift detector. All these features make the XGT-9000 an easy, fast and sensitive tool to acquire scientific information on mineral samples.

Meteorite

Raman microscopy and X-Ray Fluorescence were combined for the analysis of a polished section of a meteorite. Both techniques rely on the acquisition of a point-

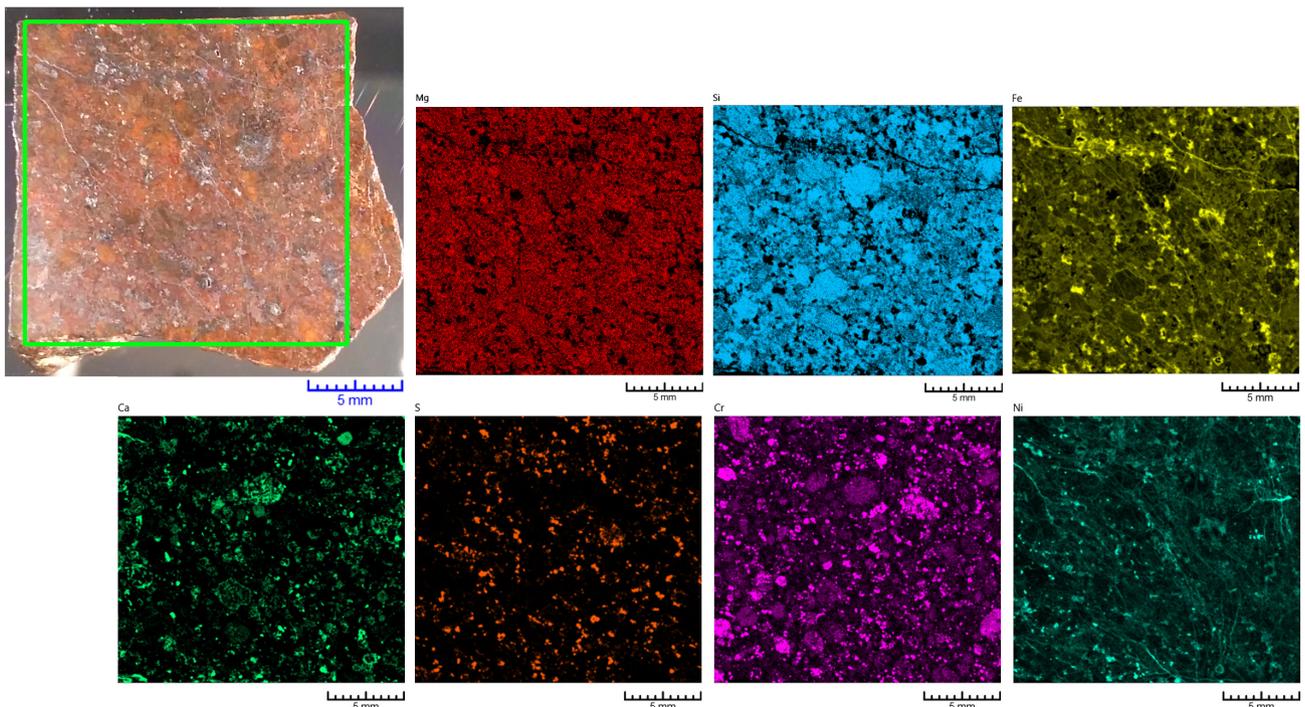


Figure 3: Elemental maps of meteorite obtained by X-Ray fluorescence. (From left to right) Top: Video image, Mg, Si, Fe element distribution. Bottom: Ca, S, Cr, Ni element distribution.

by-point spectrum, in order to obtain the hyperspectral images, presented on Figure 2 (chemical map – Raman and elemental map - XRF).

The Raman map was obtained applying multivariate analysis (Multivariate Curve Resolution – MCR - in this case), which provides a good discrimination between the different molecular compounds present in this meteorite. Thanks to this analysis we can discriminate between enstatite, pargasite, picropharmacolite, actinolite, and more other alloys and oxides.

Moreover, the X-Ray Fluorescence map was obtained by the superposition of the single elemental mappings presented in Figure 3. Each element is displayed based on the intensity of the region of interest in the measured X-ray spectrum. Thus, we observe that some of the main elements in the meteorite are Si, Mg, Cr and Fe, with some Ca and Ni contributions and some S inclusions.

These element distributions, coupled with the Raman map, can lead to the classification of this meteorite as a Chondrite LL5, as we see a lot of olivine and pyroxene compounds (chondrite class) and low levels of iron and metals with low resolved chondrules (LL5 specification).

Gas and liquid inclusion

Raman microscopy was also applied on a gas and liquid inclusion. This sample is a typical one in the research of water traces, as it witnesses of the presence of water at a given period of the time, providing useful information on the origin of life. More precisely, the analyzed sample is a quartz matrix with a CO₂ and water inclusion. Due to the high confocality and high sensitivity achieved with our LabRAM Soleil™ Raman microscope, it has been possible to characterize how the gas (blue color) and the water (red color) have been captured in the quartz, as shown in Figure 4.



Figure 4: Raman map of water and CO₂ inclusion in quartz matrix. (30x30x40µm)

Conclusion

In this application note, we demonstrated how the investigation of the origin of the universe and life itself can benefit from the powerful combination of Raman microscopy and X-ray Fluorescence. These results were possible thanks to the high throughput performance of the LabRAM Soleil™ and the XGT-9000.