unisantis

XMF 104 X-ray Micro Analyser

Micro X-ray Investigation on surface laser treatment of ancient calcite

Introduction

Application and utility of Micro XRF in archeology related applications is amply illustrated in this application note.

Several characterization techniques have been employed in the past to verify the effect of laser cleaning on the surface , in order to evaluate the possible damages induced by the ***light beam.***

In this study, it is shown as how micro X-Ray fluorescence (μXRF) provides proper information on the chemical composition of the clean surface, microstructures. These techniques resulted to be effective in assessing the quality of the cleaning process.

Micro X-Ray Fluorescence studies were carried out using the high resolution Unisantis X-Ray Micro Analyser.

Unisantis XMF-104 X-Ray Micro Analyser

Application Background

The use of pulsed laser radiation for removal of extraneous materials from a solid substrate (known as laser cleaning) has evinced keen interest in recent years in several fields including cultural heritages. The combined action of chemical, physical and biological agents often forms a pollution layer of thickness ranging from a few microns to millimeters especially on stone objects.

Even if the interaction of pulsed laser radiation with matter has been extensively studied from a theoretical point of view, its applications concerning cultural heritage samples are usually very complex, since base material is neither homogeneous nor well defined; besides, sample surface is often not regular and covered by multiple layers below encrustations.

Such studies have become a reality with the utility of Unisantis XMF-104 X-Ray Microanalyser. It is mainly possible due to optimal collimatiom of the primary x-ray beam into a very highly intense spot using Kumakhov's polycapillary lens

The present study was carried out on a 4th century BC chamber gravesite in Torricelle, near Nola (Naples) which was cleaned using laser beam.

Instrumentation

Measurements were performed using a Unisantis XMF-104 X-Ray Micro Analyser , equipped with a 50 W Molybdenum tube and a high resolution two–stage Peltier cooled, compact Si-PIN detector.

This reduces the dimensions of the instrument significantly and also eliminates the need for cooling of the detector with liquid nitrogen.

The XMF uses a Polycapillary focusing lens which provides the analyst an intensely focused x-ray beam of very small diameter. Typical dimensions of the focal spot at the exit of the lens vary between 50 and 250 microns.

Results

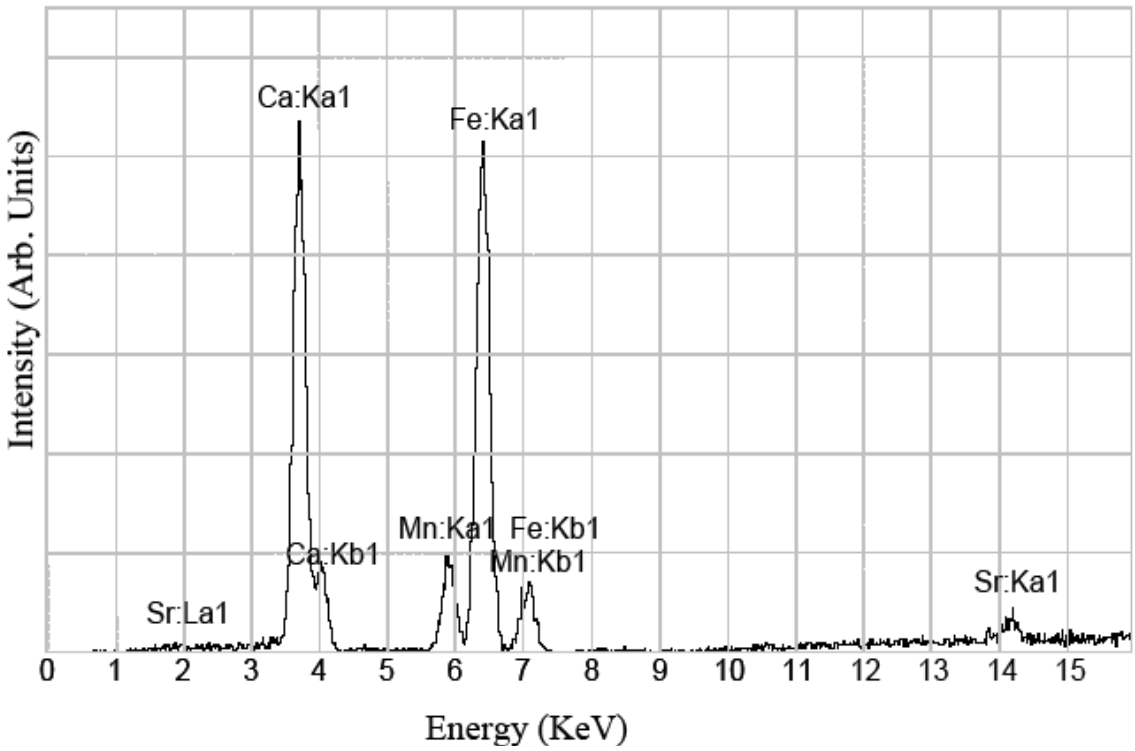

Fig 1. Micro XRF measurement on surface layer

Discussion

The microanalysis EDXRF spectrum obtained from the surface layer is presented in Fig 1. The spectrum indicates strong presence of Calcium and Iron with small amounts of Strontium and Manganese.

x-Ray microdiffraction (not reported here) indicated local recrystallization of the calcite due to the high temperature caused by the laser beam. Moreover, XRD analysis confirmed the presence of both calcite and aragonite, a polymorphic phase of $CaCO_3$. The aragonite is thermodynamically unstable at normal conditions and, when it is chemically pure, it is stable only at high pressures.

Recent geochemical studies on the polymorphic transition of $CaCO_3$ have shown that the complexity of the calcite-aragonite transformation process depends on the metal dopant, concentration, and synthesis pressure. Moreover, among the several factors affecting the formation of calcium carbonate phases, the influence of Sr^{2+}/Ca^{2+} ratio is also a significant one. . Indeed, large cations, such as Ba^{2+}, Sr^{2+}, and Pb^{2+} are mainly accommodated **in** carbonates with aragonite-type structures, although small amounts of these cations can be also incorporated into calcite-type structures. This can justify the fact that in $CaCO_3$ meta-stable aragonite formation is favored by the incorporation of large cations.

Conclusion

From the comparison between micro-XRF and XRD analysis (not reported here), it was observed that the white fly-ash deposit is a mixture of crystalline sulphate phases, comprising mainly of ***$K_2Ca(SO_4)_2 \cdot (H_2O)$ (syngenite),*** *$K_3Na(SO_4)_2$ (aphthitalite), $CaSO_4$* ***(anhydrite) and Pb*** *sulphates. Peaks, of chlorides like NaCl (halite), were also found in the XRD patterns.*

From the Micro XRF study, it is found that the transition between calcite and aragonite is more significant on the surface layer, where a relatively high content of Sr, Fe, Mn was detected.

Thus, Micro-XRF analysis of the surface has been used to identify the presence of elements such as Strontium, Manganese and Iron that are responsible for the transition between Calcite and Aragonite.

The high resolution of UNISANTIS XMF-104 X-Ray micro analyser was useful in obtaining a detailed map of these elements on the surface. It was also possible to study the effect of several laser settings on selected micro areas of the sample due to the sharp and micro beam spot of Unisantis XMF-104.

Other unique advantages of Unisantis XMF-104 are:

- No counter gas
- No external water cooling for x-ray tube
- Small footprint
- Low power tube

Reference; The above study was carried out at Chem4Tech, University of Brescia, Italy under the expert guidance of Dr. L .Depero and her research team.

Unisantis S.A. is a global leader in the development and manufacture of innovative X-Ray analytical instrumentation, complete solutions and software for structure and elemental analysis using proprietary Kumakhov's optics best known for accurate beam collimation. Success in research has enabled Unisantis S.A. to develop new cutting - edge X-ray technology, applications and products for the market. Our products have particular applications in material characterization, life science and industrial analysis.

Unisantis S.A.

Avenue des Morgines 12

1213 Petit-Lancy

Geneva

Switzerland

Tel.: +41 22 879 11 70

Fax: +41 22 792 60 11

sales@unisantis.com

www.unisantis.com