LIBS analysis to define the alteration processes on the surface of ancient stones: the case study of Romanesque medieval monuments (Italy)

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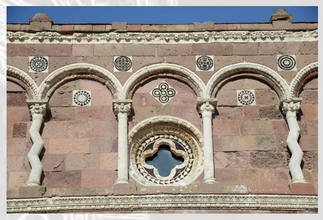
Abstract

Weathering and bio-deterioration processes frequently affect the chromatic aspect of the stones used in the monuments. The surface alteration involves both physical modifications (e.g., increase of porosity) and chemical-mineralogical transformations of the rock, with formation of new secondary phases and deposition of the organic substances and inorganic solid phases (amorphous or crystalline particles).

This research aims to study the surface films of stones (i.e., basalts, pyroclastic rocks) used in some historical-cultural relevant Sardinian Romanesque churches (XII century) using LIBS and XRD analyses. These latter, together with petrographic analysis by polarized light microscopy on thin section, are useful to reconstruct the micro-stratigraphic aspects of different film levels.

Santa Maria del Regno di Ardara
(consecrated in 1107)

Nostra Signora di Tergu
(consecrated in 1117)



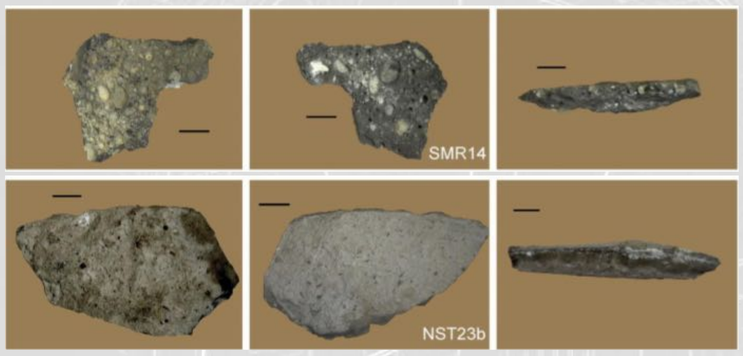
Sample	Provenance	Lithology
SMR14	S. Maria del Regno di Ardara (SS)	“Basalts”
NST23b	Nostra Signora di Tergu (SS)	Pyroclastite

X-Ray diffraction

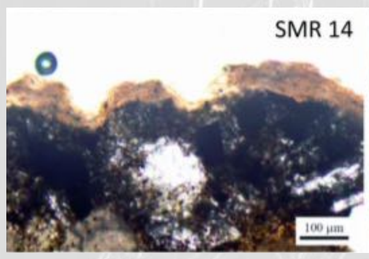
SMR14: the upper yellowish part is made up by whewellite - $Ca(C_2O_4)\cdot H_2O$, quartz - SiO_2, gypsum - $CaSO_4\cdot 2H_2O$, and carbonate-hydroxyapatite - $Ca_5(PO_4)_{2.5}(CO_3)_{0.5}(OH)$.

NST23b: in the upper part, sanidine - $K(AlSi_3O_8)$, quartz - SiO_2, cristobalite - SiO_2, gypsum (tr.) - $CaSO_4\cdot 2H_2O$, weddellite (tr.) - $Ca(C_2O_4)\cdot H_2O$ were identified.

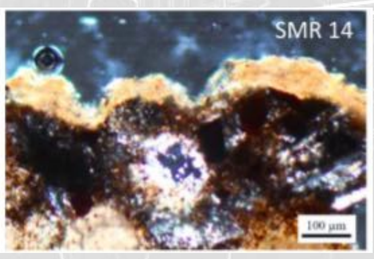
Macro photos



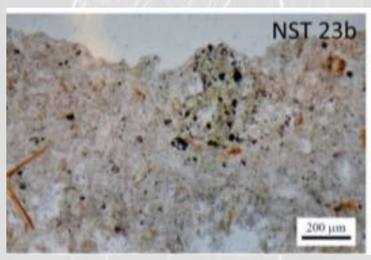
Micro photos



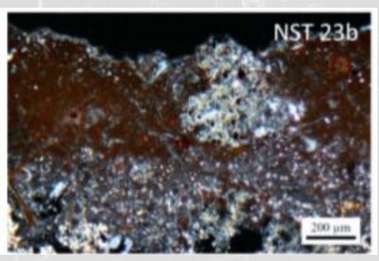
Parallel nichols



Crossed nichols



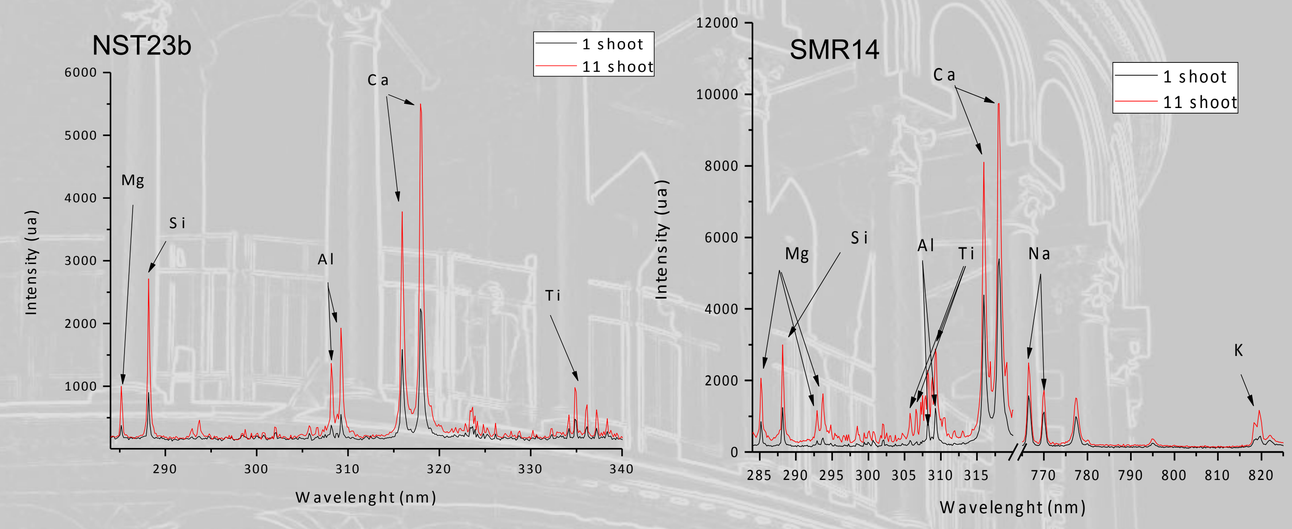
Parallel nichols



Crossed nichols

SMR14 (from the deepest layer to the superficial one): effusive rock, low crystalline basalt with small plagioclase and pyroxene crystals.
NST23b (from the deepest layer to the superficial one): pyroclastite substrate with a thick (about 350 µm) and compact deposit of microcrystalline gypsum with rare brownish ocher and traces of calcium oxalate.

Laser-Induced Breakdown Spectroscopy (LIBS)



LIBS is an elemental analytical technique that use an high power pulsed laser to generate a plasma on the surface of the sample and to analyze it by mean of a spectrometer. Analysis on the two selected samples shows:

NST23b (upper layer): presence of Ca, Si, Mg, Ti and Al compatible with the minerals recognized by means of optical microscopy and XRD.

SMR14 (upper layer): presence of Ca, Si, Mg, Ti, Al e Fe compatible with the minerals recognized by means of optical microscopy and XRD.

In the two case the laser can not penetrate the alteration patina due to its thickness.

Conclusion

The LIBS analysis is a fast and highly reproducible method for elementary identification of alteration phenomena due to degradation patinas on geomaterials of interest for cultural heritage. The subsequent analyses in optical microscopy and XRD allow us to accurately and exhaustively characterize the aforementioned alteration patinas. The ability to go deep into the sample for several microns helps to draw depth profiles in the elemental composition of the alteration patinas, while allowing the study of the layer and its interaction with environmental pollutants.

Reference

Columbu, S., Piras, G., Sitzia, F., Pagnotta, S., Raneri, S., Legnaioli, S., … Giamello, M. (2018). Petrographic and mineralogical characterization of volcanic rocks and surface depositions on Romanesque monuments. Mediterranean Archaeology and Archaeometry, 18(5), 37–63.

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