Analysis by Scanning Electron Microscopy and Microanalysis of Sandstones in Bologna, Petra and Mtskheta

SEM analysis combined with the EDXRS system are performed on many types of artistic and historical assets, in order to obtain information about the materials and their deterioration, the artistic techniques, the presence of damage, etc. This work reports the results of a study carried out on samples coming from the Orsi-Marconi palace in Bologna (Italy), from the Khazneh (House of the treasury) in Petra (Jordan), and from the Holy Cross monastery of Jvari in Mtskheta (Georgia). All these buildings are made of sandstone, the peculiarity of which is the change in colour, due to the different concentration of oxides in their composition

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Introduction

Electron microscopy analysis is a very useful method in the Cultural Heritage field, allowing to identify artistic techniques and giving important data for restoration and conservation of works of art. *Scanning Electron Microscope (SEM)*, with respect to traditional optical microscopes, can provide three-dimensional images, with higher magnification. Moreover, SEM analysis, once combined with an *Energy Dispersive X-Ray Spectrometry* (EDXRS) system, can be used to detect X-rays emitted by the atoms of the analyzed elements and to yield the chemical composition of the sample.
Many applications of the SEM analysis combined with an EDXRS system are performed on paintings and frescos, stained glasses, sculptures as well as archaeological findings and many other types of artistic and historical assets, in order to get information about the materials and their deterioration, the artistic techniques, the presence of cracks, damage or weaknesses. All these data can be essential for a proper dating of the works of art, or for their attribution to a certain artist, and are very important for the selection of the most appropriate restoration and conservation actions.
This work reports the results of a study, carried out by SEM analysis combined with an EDXRS system, on samples coming from the *Orsi-Marconi* palace in Bologna (Italy) and from two UNESCO world heritage sites, the Khazneh *(House of the treasury)* in Petra (Jordan) and the *Holy Cross monastery of Jvari* in

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Mtskheta (Georgia). All these buildings were realized employing sandstone, a sedimentary rock produced by the gradual accumulation and sedimentation of small grains of sand. A particular feature of sandstones is the change in colour, from yellow ochre to red to white, due to the different concentration of oxides in their composition.

Stereo Microscopy and SEM/EDXRS Analyses

The Orsi-Marconi Palace

The *Orsi-Marconi palace* (Fig. 1) is one of the most noteworthy architectures in Bologna: it was realized by the famous Antonio Terribilia in the middle of the XVI century, having a monumental façade decorated with many sandstone ornaments.

During the recent restoration works, some samples were taken from the ornaments to yield chemical composition and identification of the materials by scanning electron microscopy combined with EDXRS system, giving conservators useful data for the selection of both the restoration method and the suitable products to be employed.

SEM analysis shows a characteristic fine grain microstructure, with silicate cluster formed by some small and round quartz elements in a carbonate matrix (Fig. 2a). This morphological appearance confirms the hypothesis that the analyzed sandstone originated from the reworking of oldest *terrigeni* sediments. The sandstones have a yellow-grey colour due to the presence of quartz crystals and to small concentrations of limonite dispersed in the matrix (Fig. 2b).

The microanalysis confirmed the chemical composition of the sample as sandstone, showing the high concentration of carbon of the carbonate matrix and the presence of silica and also calcium (Fig. 3). This

FIGURE 1 The Orsi-Marconi Palace: The main façade
Source: ENEA

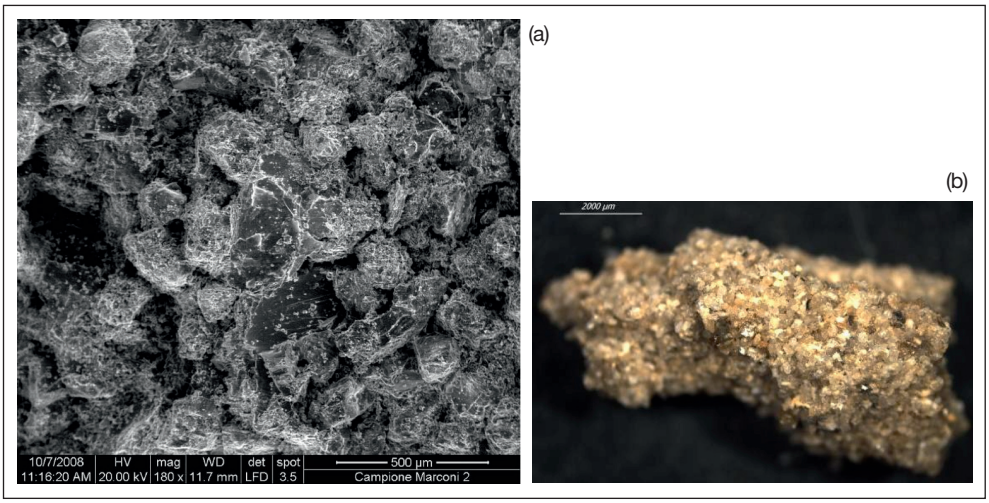


FIGURE 2 SEM (a) and Stereomicroscopic (b) images of sandstone sample n. 2, collected from the ornaments of the Orsi-Marconi building windows
Source: ENEA

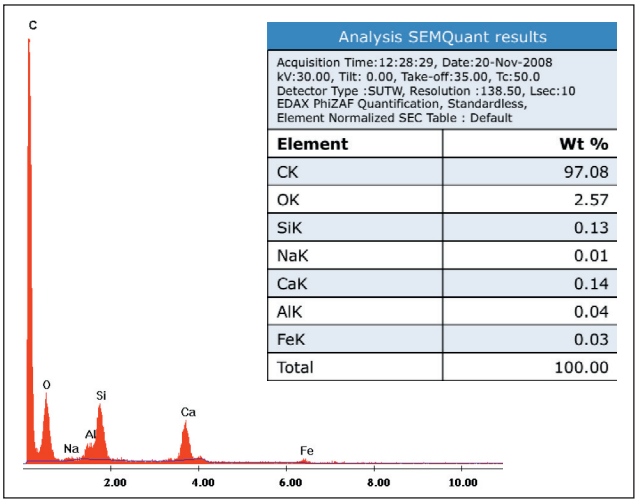


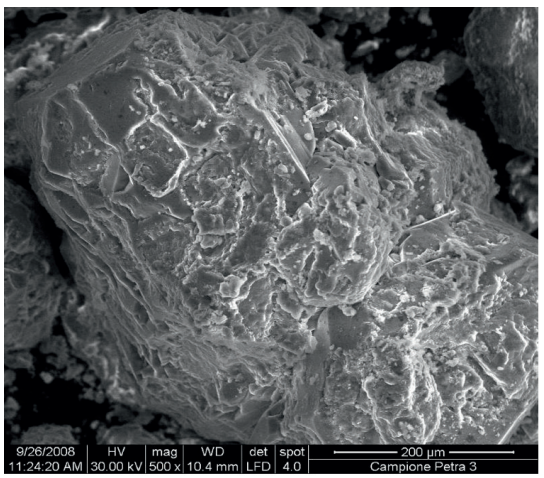
FIGURE 3 EDXRS microanalysis of sandstone sample n. 2
Source: ENEA

FIGURE 4 The Khazneh of the Nabataea city of Petra (Jordan)
Source: ENEA

mineralogical composition is typical of the Bolognese Apennines' sandstones, characterized by a high concentration of calcium carbonate. According to Luigi Fantini, a renowned Bolognese archaeologist, this yellow sandstone comes very probably from the Varignana quarry, near Castel San Pietro Terme, as the present analyses confirm on the basis of comparisons between the sandstones of the building and those extracted from the ore. This kind of sandstone was used in the Bolognese area since the Romans' age both for structural and decorative purposes, and can be found in many other artistic monuments in Bologna.

The Khazneh (House of the Treasury)

UNESCO declared the Nabataea city of Petra World Heritage on 6th December, 1985 (Fig. 4): moreover, in 2007 Petra was declared one of the seven wonders of the world. One of the most important monuments of Petra



(a)

(b)

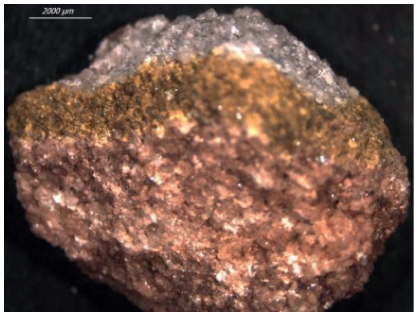


FIGURE 5 SEM (a) and Stereomicroscopic (b) images of a sample taken from the Khazneh
Source: ENEA

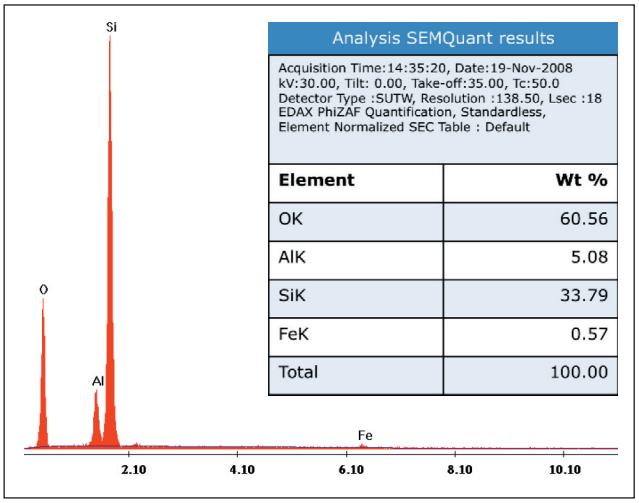
is the Khazneh (meaning the Treasury), an elaborate building 30 m wide and 43 m high, directly carved out of a sandstone rock face. Spectacular colour changes, due to the different oxides included in the sandstone during its formation, are visible on the façade and on the ceilings of many buildings of Petra, including the Khazneh.

Some samples were taken from the Khazneh and then analysed by scanning electron microscopy (SEM) combined with the EDXRS system.

The morphological analysis shows a structure with sand grains formed by some small and round quartz elements (Fig. 5a).

The analyzed sample is characterized by the colour changes typical of the Petra sandstone: Three different layers are recognizable and were analyzed: gray, yellow and red (Fig. 5b).

The microanalysis results confirm the presence of quartz grains, detecting a high concentration of silicon and the presence of aluminium in each layer (Figs. 6-7-8). Also iron is always present, but its concentration varies in the different layers from 0,57 Wt%, in the gray area of the sample (Fig. 6), to 2,65 Wt% in the red one (Fig. 7). Thus, the iron concentration and its oxidation state can be related to the different colours of the sample: the lowest iron concentration corresponds to the gray layer, the highest one corresponds to the red layer; finally, the intermediate concentration corresponds to the yellow layer (Fig. 8).

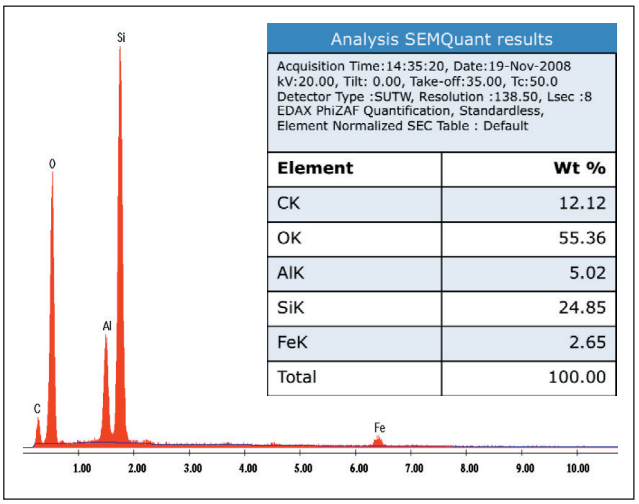


Element	Wt %
OK	60.56
AlK	5.08
SiK	33.79
FeK	0.57
Total	100.00

FIGURE 6 EDXRS microanalysis of the gray layer
Source: ENEA

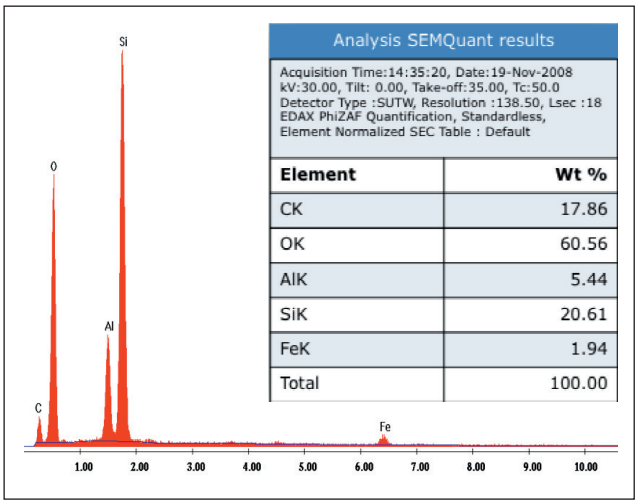
The Holy Cross Monastery of Jvari

Jvari Monastery (Fig. 9) stands on a mountain facing Mtskheta, right at the confluence of the Mtkvari and



Element	Wt %
CK	12.12
OK	55.36
AlK	5.02
SiK	24.85
FeK	2.65
Total	100.00

FIGURE 7 EDXRS microanalysis of the red layer
Source: ENEA



Element	Wt %
CK	17.86
OK	60.56
AlK	5.44
SiK	20.61
FeK	1.94
Total	100.00

FIGURE 8 EDXRS microanalysis of the yellow layer
Source: ENEA

FIGURE 9 Holy Cross Monastery of Mtskheta (Georgia): a view from the Aragvi river
Source: ENEA

the Aragvi rivers. After the conversion of the Kartli region, a large wooden cross was erected on top of this mountain and, between 545 and 586 a.C., a little church was built next to the cross; it is cruciform inside and rectangular outside, while the cross vault is now fallen in. A bigger church was then built between 586 and 605 a.C., enclosing the wooden cross in the interior. This *Church of the Holy Cross* is one of the best examples of the Georgian early architecture and had a deep influence on the further developments of it: Its structure is a four-apse domed building, where walls are faced with smoothly finished sandstone blocks. The octagonal drum has four windows; it is worth remarking that the Holy Cross Church was the first Georgian church to be amply decorated with sculptures. In the XVII-XVIII centuries, a wall was built around the Holy Cross Monastery in order to protect it from invasions by the Caucasian people.

Some samples were taken from **Jvari**, in particular from the arch ornaments of main façade, and then analysed.

The stereomicroscopic observation (Fig. 10a) shows various colorations, from tan to yellow: the three dimensional observation with SEM (Fig. 10b) shows a slightly different morphology, with silicate cluster formed by small sharp quartz elements in a carbonate matrix.

The microanalysis by combined EDXRS system confirmed this composition, showing the presence of silicon and of some oxides as iron and aluminium (Fig. 11). Unlike the samples collected in Bologna and in Petra, magnesium, sodium and potassium where detected too.

Conclusions

The analyses carried out on the samples collected in Bologna, Petra and Mtskheta show a composition

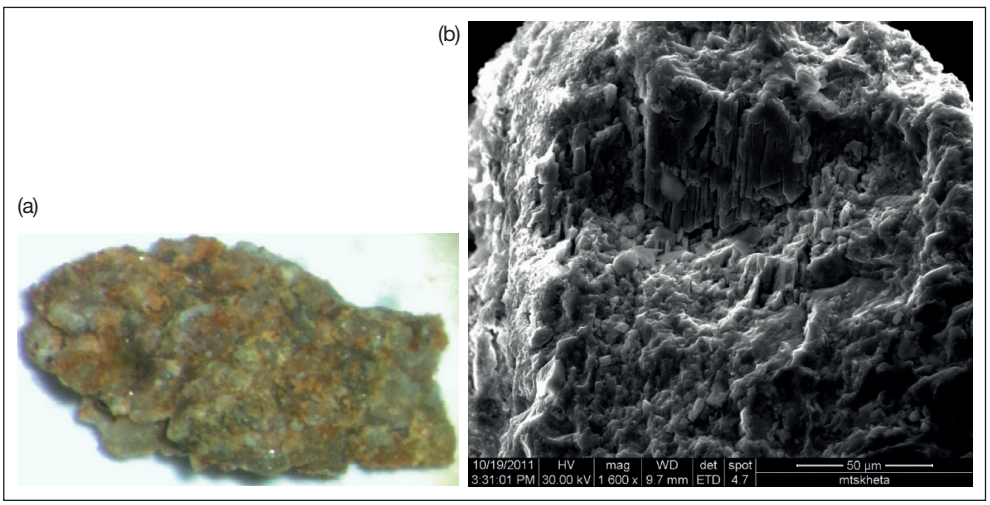


FIGURE 10 Stereomicroscopic (a) and SEM (b) images of a sample taken from the Holy Cross monastery of Jvari
Source: ENEA

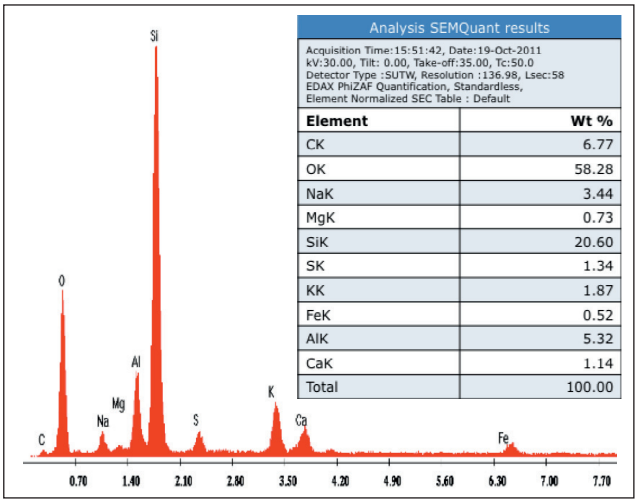


FIGURE 11 EDXRS microanalysis of a sandstone sample
Source: ENEA

basically similar, being the sandstone a sedimentary rock composed fundamentally by sand grain (quartz, feldspar, and/or micas) immersed in a carbonate matrix. The different concentration of the oxides observed in the samples confers a particular colouration to the rock in the three sites of origin: the larger concentration of iron oxide imparts a reddish tint to the samples coming from Petra, whereas the yellow tint of the Orsi-Marconi samples is due to the presence of limonite (small iron concentration). The large number of different oxides detected in the Georgian samples could be responsible for the tint shifting from tan to yellow.

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