CHARACTERIZATION OF GEOLOGICAL AND ARCHAEOLOGICAL STONES TO IDENTIFY THE PROVENANCE OF ROCKS FROM THE ARCHAEOLOGICAL PARK OF SIBARI (CALABRIA-ITALY)

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This research has been planned in order to improve the knowledge of stones used for the construction of buildings in the Archaeological Park of Sibari. So far, the study on the origin of the stones of the Archaeological Park of Sibari focused on the architectural structures of great value such as marble columns, but no researches have been conducted on the provenance of carbonate rocks used as building blocks in the city walls. Indeed, the knowledge about the provenance of ancient stones makes possible to identify the quarry locations. This information is quite important for several issues concerning ancient human activities devoted to: i) the research for natural resources; ii) the commercial routes; iii) the supply of materials useful for the restoration.

The carbonatic rocks are ideal materials for the buildings, thanks to their favourable physical, mechanical and technical features. One problem in the identification of the provenance of natural stones regards the difficulty to find rocks with different macroscopic characteristics in the same quarries; but also the possibility to find the same macroscopic characteristics in stones from different quarries. For these reasons the studies should be developed on archaeometric bases. Furthermore, a lot of analytical methodologies must be used simultaneously for getting the best results.

In order to identify the quarries that should be sampled, a preliminary study for the macroscopic characteristics of the rocks found in the Archaeological Park of Sibari was necessary. Putative quarries were identified on these bases: they should be near the site, or near rivers which were formerly used for carrying materials. Sampling was performed on places that belonged to the former Sybaris area. In total, we sampled five quarries (Francavilla Marittima, Timpone Arcomano, Cerchiara di Calabria, Spezzano Albanese, and Cassano). For each quarry, we collected about ten samples. For each sample, we performed X-ray fluorescence spectrometry (XRF), X-ray diffractometry (XRD), the thermal analyses DSC (differential scanning calorimetry) and TG (thermogravimetric), calcimetry, spectrophotometric colorimetry, Fourier transform infrared spectroscopy, mercury porosimetry, and polarized optical microscope analysis.

In the Archaeological Park of Sibari we collected a total of 10 samples. These were taken from some areas of the theatre, along the road NS, and in an area used for storing ancient findings that belonged to the theatre.

Sampled rocks are micritic limestones, with a high concentration of calcite and relatively low concentration of quartz feldspar and clay materials. In the quarry of Cassano only we sampled dolomites that were characterized by high concentration of dolomite and low concentration of calcite.

In order to verify the possibility of separating unambiguously all five quarries, the data were processed by multivariate statistical techniques, in particular the discriminant analysis was used. For data processing, was used the software “statistica”. The first step was to build a data matrix, in which were included as variables the results obtained from different analytical methods (X-ray fluorescence, colorimetric spectrophotometer, mercury porosimetry, thermogravimetric). The colorimetric results were

seen across the spectrum of reflectance over the brightness (L) and chromaticity coordinates (a* b*) and porosimetry analysis, in addition to the value of porosity, were considered as variables the mean diameter of pores, pore area, real density, apparent density and tortuosity. Data obtained from these methods were added to the results obtained from Fourier transform infrared spectrophotometer, whereas all of the information contained in the IR spectrum and not only on individual peaks, therefore, were considered as variable numbers wavelength (about 3000) at which was measured the second derivative of transmittance.

The data matrix, consisting of about 4000 variables, was developed through discriminant analysis, which allowed to find the ideal combination of variables that better separate the various quarries, the "discriminant functions".

The search for variables that can separate the various caves occurred in stages and through iterative combinations. The first attempt was to calculate discrimination functions that take into account only the XRF data. Through the statistical treatment of major and trace chemical elements can be separated only the quarry of Timpone Arcomano and Spezzano Albanese, but the other quarries are not perfectly discriminable. Then considered all the variables from the IR analysis alone, but by combining the results of Fourier transform infrared spectrometry is not possible to separate the five quarries. Combining XRF with those from chemical analysis by thermogravimetric analysis and mercury porosimetry are discriminated only the quarries of Timpone Arcomano and of Spezzano Albanese. By combining the results of chemical analysis and Fourier transform infrared spectrometry, we discriminated the quarry of Cassano only.

Combining the results of thermogravimetric, spectrophotometric colorimetry and mercury porosimetry, can be separated from the others, the quarry of Cassano optimally, and at a less extent the quarry of Spezzano Albanese and of Timpone Arcomano.

By combining the results of thermogravimetric, spectrophotometric colorimetry, mercury porosimetry and chemical analysis is able to separate quite well the quarry of Spezzano Albanese and Cerchiara.

The statistical combination of results of thermogravimetric and mercury porosimetry made possible a separation of the Cassano quarry and a less one of the quarries of Spezzano Albanese and Timpone Arcomano.

After several iterations the ideal combination of Variable-that separates perfectly the five slots is uniquely given by the following variables: MgO, CaO, Fe_2O_3, MnO, P_2O_5, Nb, Sr, Ce, the chromaticity coordinates L* a* b and second derivatives of the transmittance at the wavenumber 2841 cm^{-1}, 2840 cm^{-1}, 2833 cm^{-1}, 2692 cm^{-1}, 2672 cm^{-1}, 2189 cm^{-1}, 1968 cm^{-1}, 1068 cm^{-1}, 962 cm^{-1}, 887 cm^{-1}, 870 cm^{-1} and 591 cm^{-1} (Fig. 1).

The variables that allowed to discriminate the five pits were used to determine the membership of the archaeological remains to the different quarries. The analysis established that the SIR1 sample, taken at the base of a wall in the Hemicycle-Theatre, comes from the quarry of Francavilla Marittima. The archaeological SIR2, taken inside in the Hemicycle-Theatre between the seventh and eighth column, comes from the quarry of Francavilla Marittima (Fig. 2). The sample SIR3, taken in the Hemcycle-Theatre in between the seventh and eighth column comes from the quarry of Spezzano Albanese (Fig. 3). The archaeological samples SIR4 within the Hemcycle-Theatre between eighth and ninth column comes from the quarry of Timpone Arcomano (Fig. 4). The sample SIR5 taken within the Hemicycle-Theatre at the top of the trunk of the eighth column, belongs to the quarry Timpone Arcomano. SIR6 sample taken at the base of a wall in the Hemcycle-Theatre, belongs to the quarry of Cerchiara (Fig. 5). The

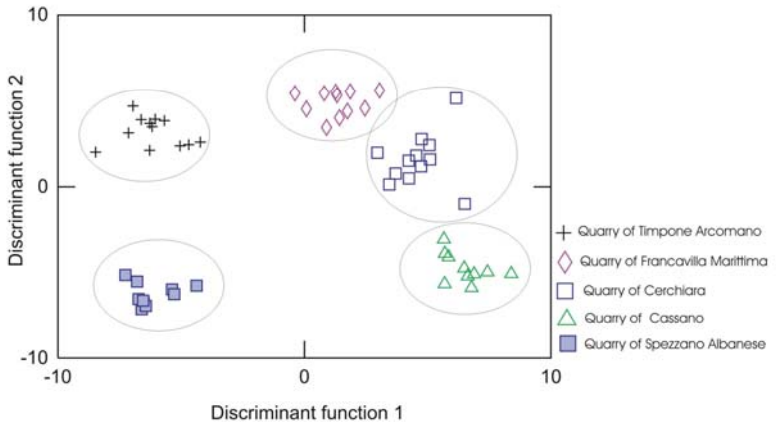

Fig. 1 - Discriminant diagram of quarries.

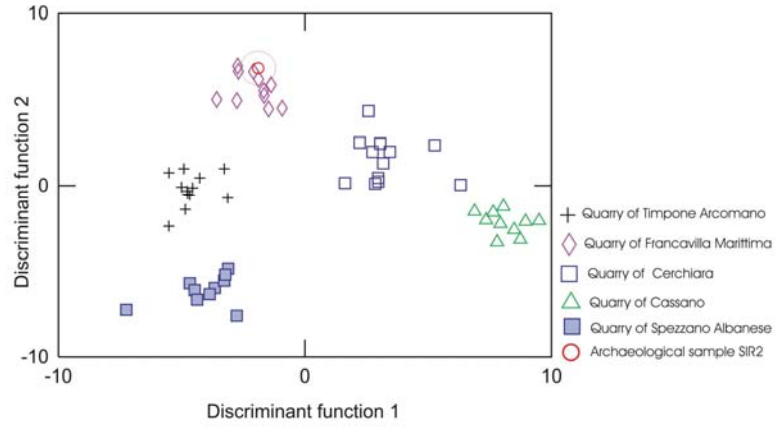

Fig. 2 - Discriminant diagram of archaeological sample SIR2. The sample SIR2 belongs to the quarry of Francavilla Marittima.

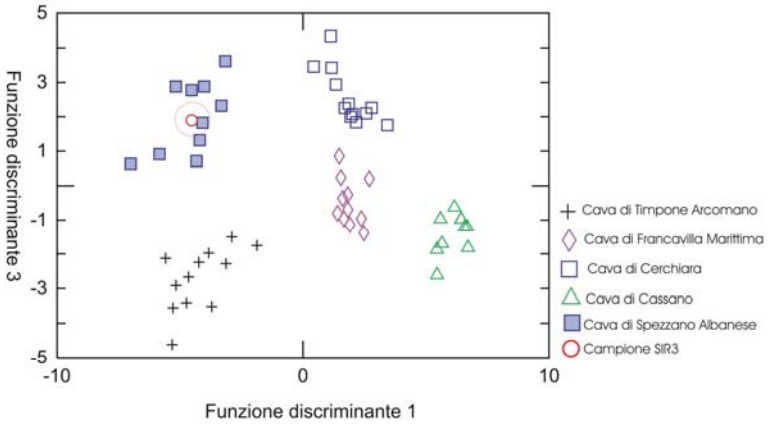

Fig. 3 - Discriminant diagram of archaeological sample SIR3. The sample SIR3 belongs to the quarry of Spezzano Albanese.

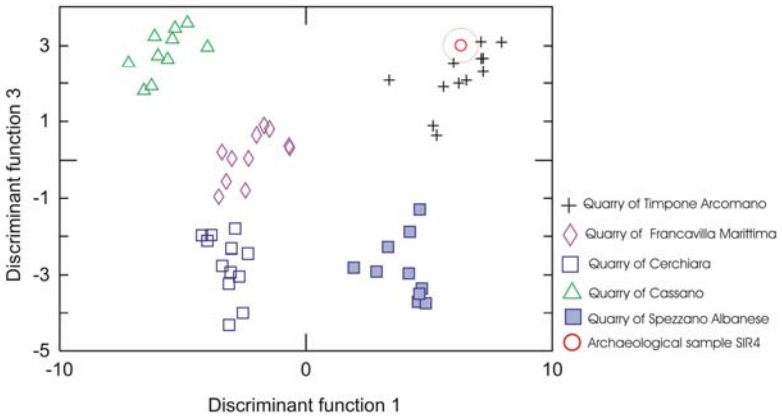

Fig. 4 - Discriminant diagram of archaeological sample SIR4.
The sample SIR4 belongs to the quarry of Timpone Arcomano.

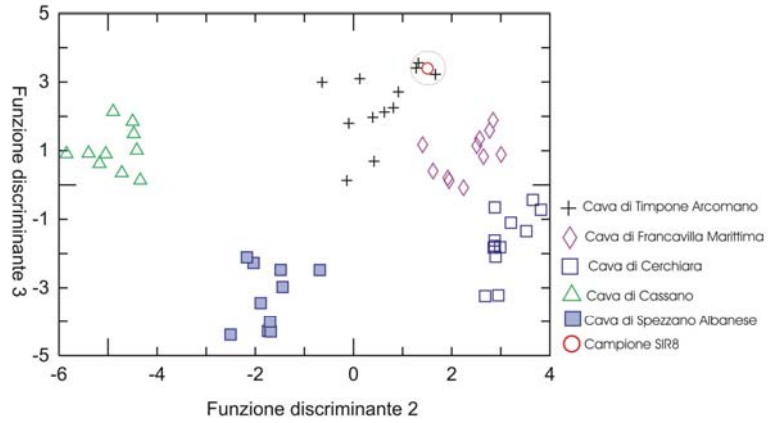

Fig. 5 - Discriminant diagram of archaeological sample SIR6.
The sample SIR6 belongs to the quarry of Cerchiara.

archaeological SIR8 league along the road connecting NS, comes from the quarry of Timpone Arcomano. The sample SIR9 taken along the road connecting NS, belongs to the quarry of Timpone Arcomano. The archaeological SIR10, taken from the area used to the store the findings within the Hemcycle-Theatre belongs to the quarry of Timpone Arcomano. Finally, the archaeological SIR11 sampled in a yard for the storage of specimens taken in the Hemcycle-Theatre, comes from the quarry of Timpone Arcomano.

The results of Fourier transform infrared spectrometry play a key role in the separation of the quarries and in the identification of archaeological findings on the basis of their origin. From a first observation of the spectra it does not seem possible to perceive any differences; however, applying magnification, in correspondence to the wavelengths that allow the separation of the five quarries, you

can see that in each spectrum the intensity of the peaks vary from sample to sample. This fact can explain why certain values of transmittance at a given wave number are essential for the discrimination of different quarries.

This study made possible to determine unequivocally the origin of the stone materials for the construction of the Archaeological Park of Sybaris. The separation in different quarries of archaeological findings was possible through the development of a new analytical procedure based on multivariate statistical analysis, combining data simultaneously from the IR spectra (used to consider all the information in the spectrum and not only on peaks) and other analytical methods (XRF, colorimetry, TG, Porosimetry). This procedure allows to discriminate strongly homogeneous rocks such as quarries and in the Hemicycle-Theatre. The development of a new analytical approach was necessary because the single application of classical methodologies, such as X-ray fluorescence, the microscopic analysis in thin section, XRD analysis etc. did not allow to separate rocks strongly homogeneous, such as quarries.

The Fourier transform infrared spectrometry has not produced significant results for the discrimination of carbonate rocks highly homogeneous. However, this is only because the variables obtained by this technique had never been combined in a statistically rigorous method with those from other analytical methods and the spectral information was not used throughout.

The work has shown that the materials used to develop the Archaeological Park of Sybaris come from areas close to the archaeological site. Perhaps the ancient people of this area used the river Esaro to move westward, and the river Crati to move to south. The two rivers were the only roads; indeed along the valleys of Esaro and of Crati, were found remains of shrines that were probably used as zones of exchange and market places. For materials from the quarry of Spezzano Albanese it can be assumed that the transport route has been the river Crati, while the stone from the quarry of Timpone Arcomano probably have been transported across the river Esaro.