THE FINISHING TECHNIQUE OF THE STONE MONUMENTS OF PERSEPOLIS: FURTHER STUDIES AND NEW FINDINGS THROUGH THE USE OF NON-DESTRUCTIVE ANALYTICAL TECHNIQUES*

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The studies on the finishing technique of the stone monuments in Persepolis (Iran) are part of the archaeological project jointly launched in 2008 by Iran and Italy, named ‘From Palace to Town’. The first experimental results, obtained on a very limited number of samples, revealed that the Achaemenid builders and sculptors used a white pigment, a kind of bone white, calcium fluorapatite, obtained by burning animal bones, to hide the dark grey colour of the stone. In order to verify these unexpected results, a new campaign was implemented to analyse a much larger number of samples. XRF spectrometry, a non-destructive technique, was used and the experimental results were further elaborated by PCA. The presence of a white superficial layer was confirmed, and the use of fluorapatite was confirmed as well, but only on monuments attributed to the Xerxes period or later, while in the earlier monuments the white layer was obtained using gypsum.

KEYWORDS: PERSEPOLIS, STONE FINISHING, BONE WHITE, FLUORAPATITE, XRF SPECTROMETRY, PCA ANALYSIS

INTRODUCTION

Persepolis is one of the most representative sites of the Achaemenid Persian empire (sixth to fourth century BC). It was Darius the Great (r. 522–486 BC) who decided to build this monumental citadel within the town of Pârsa as a huge artificial Terrace, to celebrate the power of his kingdom. The sovereigns who followed Darius further enriched the site with other magnificent, richly decorated, buildings.

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In the year 330 BC, Alexander the Great reached Fars (Persia) and conquered the city of Pārsa, and then, after four months, set fire to the magnificent buildings on the Terrace (Briant 2002). After many centuries of abandonment, it was only in 1931 that systematic excavations and studies were initiated by the Oriental Institute of the University of Chicago (Herzfeld 1929–30, 1941; Schmidt 1953, 1957, 1970).

In 2008, a five-year project for Persepolis was launched jointly by Iran (Shiraz University and Iranian Centre for Archaeological Research) and Italy (University of Bologna and IsIAO), named ‘From Palace to Town’ (Askari Chaverdi and Callieri 2012). One of the important aims of the project was to contribute to the conservation of the stone monuments of the imperial site. As in all conservation projects, and also for the Persepolis monuments, the first step concerned the knowledge of the stone materials and a careful observation of their condition, in order to collect information that would be useful in planning and implementing a new conservation policy. In 2008, an Iranian–Italian team led by G. Guidi and H. Rahsaz carried out a general survey of the site (Guidi et al. 2012); this survey was followed by a study on specific diagnostic problems, directed by M. Laurenzi Tabasso. Part of the latter study was dedicated to investigating the nature of a white layer that was very frequently visible, but had never been studied, nor even documented, on the external surface of the stone, often covered and concealed by a rather thick pinkish encrustation produced along the centuries by the spontaneous deposit of earthy components, rich in silicate and iron oxides. XRD and SEM/EDS analyses were carried out in 2011–12 on a few samples that could be collected at that time. They revealed that such a white layer was mostly composed of fluorapatite and calcite, a kind of ‘bone white’, the use of which in ancient times, however, earlier than the first millennium, had never been described (Thompson 1936; Harley 1970). Traces of a further white layer with barium sulphate were also detected in one sample. This totally unexpected finding was reported and discussed in a previous paper, which has recently been published (Askari Chaverdi et al. 2016). However, these results were obtained on too small a number of samples to have a real statistical value. Therefore, it was necessary to increase the number of samples in order to confirm, or to reject, the hypothesis of finishing layers applied on the stone surface on purpose. In order to have a statistically significant sampling without any damage to the original stone surfaces, a non-destructive analytical technique was needed. X-ray fluorescence spectrometry (XRF) is, without any doubt, the most suitable technique to meet the specific needs of this analytical problem. A new mission was organized within the same Iranian–Italian project so as to perform an extensive analytical campaign in which some portable equipment—an EDXRF (energy-dispersive X-ray fluorescence) spectrometer, powered by dry batteries, specifically designed for the purpose by Ars Mensurae (an Italian private company)—could easily be used all over the site (Fig. 1).

In order to detect a large number of elements, from the lighter ones to the heavier ones, the analyses were carried out in two different conditions: at low energy (max 6.4 keV, iron lines), and at high energy (up to 30 keV). In this latter condition, heavier elements up to tin and antimony (K lines), if present, can be detected; while in the former condition, low-Z elements can be detected, up to iron.

The preliminary results of the 2011–12 campaign indicated that in the case of the few samples that were analysed, the white layer is characterized by the presence of fluorapatite, the characteristic element of which is phosphorus (P), which is a rather light element (Z = 15). In order to enhance the sensitivity of XRF, a set of measures were also carried out in the absence of air, replacing air with helium, through the use of small Mylar® (DuPont Teijin Films, USA) balloons filled with helium at the moment of the measurement. In this way, the interference of argon (a rare gas present in air) could be eliminated and the sensitivity increased (Ridolfi in press).
The portable EDXRF system was calibrated daily, making use of standard samples to define the energy–counts relationship, and to define the mutual sensitivity of the X-ray tube–detector as defined in handbooks of practical EDXRF (Ridolfi 2012).

The main goal of the campaign was to study the white surface finishing but, being aware that the Achaemenid monuments were frequently coloured, at least in the most significant parts, we also tried to check the presence of some remains of those polychrome surfaces. We were only able to see a few traces of colour in the undercut of the stone in the South-West Gateway, on the southern side of the Hundred Column Palace, and some fragments of coloured mortars in the Darius Palace. We therefore analysed these traces using our non-destructive equipment, looking for elements that could be suggestive of mineral pigments.

Finally, a limited number of animal bones from a previous archaeological excavation (in the year 2008) were analysed to check the hypothesis that fluoroapatite could have been obtained by calcined bones (to obtain a kind of bone white). As expected, the presence of phosphorus was confirmed.

A total of 36 areas were analysed on different monuments attributed to the different periods of life at Persepolis.

EXPERIMENTAL RESULTS

As described in the Introduction, X-ray fluorescence spectrometry (XRF) was the non-destructive method of analysis. The measures were carried out at low energy to enhance elements from aluminium to calcium, and at high energy those from calcium to antimony. In the latter condition, heavier elements up to tin and antimony (K lines), if present, can be detected; while in the former condition, low-Z elements can be detected, up to iron.
In both cases, the XRF data were expressed as the number of counts for a fixed time interval, for each sample. Just as an example, two results from the XRF analyses are shown. On the detail of the Treasury’s ‘Darius’ relief (Fig. 2), the presence of sulphur and the absence of phosphorus indicate the occurrence of gypsum; while on the capital in front of the Museum entrance (Fig. 3), the absence of sulphur and the presence of phosphorus indicate the occurrence of fluorapatite.

DISCUSSION OF THE RESULTS

The experimental results achieved through the non-destructive XRF analysis were further elaborated in order to understand how the different elements are linked together to give chemical

Figure 2  A carved detail of the Treasury’s ‘Darius’ relief (sample 1), where the white layer was obtained by the use of gypsum, and the XRF spectrum of the same sample where the peak for sulphur is visible. [Colour figure can be viewed at wileyonlinelibrary.com]
compounds. Actually, XRF gives information on the chemical elements present at the point of analysis but not on the compounds (Ridolfi 2012). Unfortunately, when the mission to Persepolis was planned, it was impossible to also include, mostly for budgetary reasons, the collection of samples and their analysis by XRD and SEM/EDS. This would have allowed a more complete identification of the components of the surface layers. While lacking this possibility, however, we worked in a very cogent way to find the right correlation among the XRF data.

The counts of sulphur and the rate of Ca/S were used to give an indication of the presence of gypsum. However, gypsum is not the only sulphate present on the stone surfaces, as barium was detected in some samples, and a previous SEM/EDS analysis of a sample collected in 2011

Figure 3 A carved detail of the capital in front of the Museum entrance (sample 14), and the XRF spectrum of the same sample with the peak for phosphorus. In this case, the white layer was obtained by the use of fluorapatite. [Colour figure can be viewed at wileyonlinelibrary.com]
revealed the presence of barium sulphate. It must be stressed that the experimental conditions adopted for the portable XRF equipment used in the present study can hardly distinguish the presence of barium from that of titanium, a ubiquitous element in the Persepolis stone. This gives a certain degree of incertitude when evaluating the presence of barium, unless it is rather abundant.

The following logical criteria were used for discussing the experimental results:

- When the counts of sulphur are very high ($\geq 3000$) and the rate of the Ca/S counts is low ($\leq 100$), the presence of gypsum is considered to be certain.
- When the counts of sulphur are high (in the range 3000–1000) and the rate of the Ca/S counts is in the range 100–300, the presence of gypsum is considered to be probable.
- When the counts of sulphur are low ($\leq 500$) and barium is detected or considered probable, the presence of barium sulphate (barite or baritine) is considered to be certain or probable as well.

Further to the above interpretation of the experimental data, principal component analysis (PCA) was also applied. PCA is a statistical procedure that is useful in studying the possible correlations among a set of observations (Gigante et al. 2012; Visco et al. 2015; Caponetti et al. 2017). In the specific case of our analysis, PCA was used to better understand the correlations among the following elements: aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), chlorine (Cl), potassium (K) and calcium (Ca)—and to verify the correctness of the adopted criterion. From the experimental data obtained at low energy, a matrix with seven columns (variables) and 37 rows (objects) was considered and diagrams with the combination of the 1–2, 2–3 and 1–3 components were produced, considering the regularity of good correlations on the screen plot of the eigenvalues (Fig. 4).

The results of the PCA analysis stress the very good P/Cl correlation; this can be interpreted as the presence of a phosphate (namely fluorapatite) containing chlorine. Fluorine cannot be detected by $\textit{in situ}$ XRF analysis, but this good P/Cl correlation now allows us to hypothesize that fluorine is partially substituted by chlorine in the fluorapatite used by the Achaemenids to obtain the white layer. The Ca/S correlation is also good, thus indicating that in some monuments, gypsum was used instead of fluorapatite to hide the black colour of the stone. In fact, the monuments where phosphorus was detected are different from (and later than) the monuments where gypsum was used. The two elements are never present together.

It is interesting to underline the good Si/K correlation (with $R^2 = 0.65$), also confirmed by the PCA analysis: this indicates with good probability that the presence of K is due to silicate minerals, such as mica-illites, which are secondary components of the stone. The good correlation observed for S and Al is more difficult to explain. Probably, deeper analyses of the experimental data and, perhaps, other analytical techniques that require collecting some samples from the monuments are needed.

In Table 1, the analytical results (expressed as the number of counts for the different elements) are grouped with respect to the monument where the XRF measures were implemented.

From the results given in Table 1, the differences among the surface finishing of monuments pertaining to the earlier period of Persepolis and those attributed to later periods are very evident:

- In the earlier period, the dull grey or even black stone was made clearer by the application of a layer containing gypsum (when the surface was accurately cleaned, as, for instance, for sample 2, sulphur is very low, as the white layer was cleaned away in past cleaning treatments). In the Apadana staircases, the construction of which was finished during the kingdom of Xerxes, gypsum is either confirmed or, at least, probable. Phosphorus was never detected, thus indicating that fluorapatite was not used.
Figure 4  PCA diagrams, with the combination of the 1–2, 2–3 and 1–3 components. [Colour figure can be viewed at wileyonlinelibrary.com]
In the later monuments, phosphorus is always present, thus confirming the results of the previous study and indicating the use of fluorapatite as pigment to obtain a white layer that hides the blackish stone surface. In some samples, the presence of small amounts of Ba and S indicate the probable use of a barium sulphate mineral, such as barite or baritine. It seems probable that the Xerxes kingdom was a period of transition between the two finishing techniques.

The reasons for the technological shift from the use of gypsum (available in that period only as a mineral, a naturally occurring material) to fluorapatite (which had to be obtained from the...
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The burning of animal bones still need to be understood and further study is deserved on other Achaemenid monuments, not only in the same area of Persepolis, along with investigations on gypsum ores that could have been exploited by those architects and sculptors.

The XRF analyses at high energy for the detection of heavier elements were made on a limited number of samples, where the presence of coloured pigments was considered probable or possible (samples 37, 38, 39, 40, 41, 42, 43 and 44). The most interesting results were obtained on the South-West Gateway, on the southern side of the Hundred Column Palace, and on the floors of Darius’ Palace. A possible interpretation is proposed in Table 2. The pigments are listed in order of the number of counts of the most relevant elements (e.g., Hg for cinnabar or Cu for Egyptian blue but, of course, this is only a very rough evaluation).

The few analyses made for the detection of pigments allow to hypothesize the use of Egyptian blue and different red pigments: red ochre, realgar and cinnabar. On the basis of these few results, it is impossible to guess whether they were mixed on purpose or if impure mixtures were unintentionally used. Apart from Egyptian blue, all these pigments could have been available in nature, as minerals, for the Achaemenid artists (Guineau 2005; Various Editors 1986–2007).

CONCLUSIONS

The combined use of XRF spectrometry by portable equipment specially developed for low atomic number elements and the analysis of the collected data by PCA has confirmed the results previously obtained on a limited number of samples by the use of XRD and SEM/EDS on polished cross-sections and has increased the knowledge on the coating technique of the Achaemenid stone monuments of Persepolis and on its evolution with time. This coating technique was unknown until the study performed within the above-mentioned Iranian–Italian archaeological research project. It is important to stress that all this was achieved in a totally non-destructive way.

The few traces of colours still visible in the studied monuments were also characterized by the same non-destructive analytical technique.

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