SUPPLEMENTARY MATERIAL

Application of near infrared spectroscopy (NIR), X-Ray Fluorescence (XRF) and chemometrics to the differentiation of marmora samples from the Mediterranean basin

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ABSTRACT
Near Infrared (NIR) and X Ray Fluorescence (XRF) spectra were recorded for 15 different samples of marmora, from the Mediterranean Basin and of different colors. After appropriate pre-treatment (SNV transform + second derivative), the results were subjected to Principal Component Analysis (PCA) treatment with a view to differentiating them. The observed differences among the samples were chemically interpreted by highlighting the NIR wavelengths and minerals, respectively, contributing the most to the PCA models. Moreover, a mid-level data fusion protocol allowed integrating the information from the different techniques and, in particular, to correctly identify (based on the distance in the score space) three test samples of known type. Moreover, it should be stressed that positive results on the differentiation and identification of marmora were obtained using two completely non-invasive, non-destructive and relatively inexpensive techniques, which can also be used in situ.

KEYWORDS
Marmora; Near infrared spectroscopy (NIR); X-Ray Fluorescence (XRF); Principal component analysis (PCA); Chemometrics.
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| Samples                     | Inhomogeneity      | Provenance | Dominant Colour       |
|-----------------------------|--------------------|------------|-----------------------|
| Giallo antico (1)           | Inhomogeneous      | Africa     | Pinkish               |
| Breccia verde (2)           | Highly Inhomogeneous | Asia     | Grey/Green            |
| Serpentino (3)              | Highly Inhomogeneous | Asia     | Dark green            |
| Portosante (4)              | Highly Inhomogeneous | Asia     | Burgundy              |
| Cipollino (5)               | Slightly Inhomogeneous | Asia     | Grey/light green      |
| Bordiglio (6)               | Inhomogeneous      | Italy      | Light grey            |
| Calcare (8)                 | Slightly Inhomogeneous | Italy     | White/yellowish       |
| Basalto (9a and 9b)         | Inhomogeneous      | Italy      | Brown/light green     |
| Porfido rosso (10)          | Inhomogeneous      | Africa     | Dark red              |
| Africano (11)               | Highly Inhomogeneous | Africa     | Light green/reddish   |
| Granito grigio (12)         | Fairly Inhomogeneous | Africa     | Green                 |
| Breccia grigia delle Alpi (13) | Highly Inhomogeneous | Italy     | Black                 |
| Rosso antico (14)           | Fairly Inhomogeneous | Africa     | Fire brick            |
| Travertino (16)             | Slightly Inhomogeneous | Italy     | Very light yellow     |
Figure S1 - PCA analysis on NIR spectra after SNV and first derivative preprocessing. Spectral-like graphical representation of the variable loadings onto the first two components.
Figure S2 - PCA analysis on XRF data after autoscaling preprocessing: Loadings plot for the first two components.
Figure S3 – Picture of the 15 analyzed marmora samples. Sample numbering corresponds to the one reported in Table 1: Giallo antico (1); Breccia verde (2); Serpentino (3); Portosante (4); Cipollino (5); Bordiglio (6); Calcare (8); Basalto (9a and 9b); Porfido rosso (10); Africano (11); Granito grigio (12); Breccia grigia delle Alpi (13); Rosso antico (14); Travertino (16).
Figure S4 – NIR spectra collected on marmora samples before (a) and after (b) pretreatment by SNV and first derivative; (c) XRF spectra collected on marmora samples (the inset contains a magnification of the low energy region). Legend: black continuous line – reference marmora; red dashed line - test samples.