Mineralogical study of different mortar types from historical monuments of northern Greece

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ABSTRACT

Red coloured plaster mortars and a masonry mortar sample dated from 5th c. BC to 3rd c. BC were collected from Aiani's archaeological site, northern Greece. The mineralogical composition of the bulk mortars and the mortar surfaces were determined by μRaman spectroscopy and X-Ray Diffraction (XRD) techniques. Calcite, quartz, feldspars, dolomite, Ti-oxides (anatase/rutile) and clay minerals consisted the mortar samples. Serpentine, a mineral characteristic for its local provenance was found, which is related to the ophiolithic complex and the ultramafic rocks of the surrounding area. The red colour of the mortar surfaces is attributable to hematite, the raw material being iron oxides and hydroxides either from an ochre deposit or an iron-rich clay deposit. Black inclusions identified by Raman spectroscopy may be associated with carbonaceous material of an amorphous character and iron oxides and hydroxides (hematite/goethite). The presence of micaceous and clay minerals, corroborates the origin of the raw material from local Fe-rich clays.

INTRODUCTION

Mortars are composite materials, composed of hydraulic or aerial binding material or a mixture of binding materials, aggregates and additives [1-3]. Different kinds of mortars exist: masonry mortars between bricks or stones, mortars as wall finishing materials internally or externally, mortars as foundations for flooring, rubble mortars for the infillings of walls etc. [4]. The chemical, mineralogical and structural characterisation of ancient mortars can shed light to the provenance of raw materials and the production processes, but can also help to match materials from currently accessible sources in the process of renovation or reconstruction of the buildings [5].

The employment of interdisciplinary chemical, geological and physical analytical techniques in the study of archaeological artefacts, such as mortars, is a common practice nowadays. Several analytical methods, both destructive and non-destructive, have been used for the qualitative and quantitative characterisation of ancient mortars, like SEM/EDX, FTIR, DSC/TGA/DTA, microprobe, optical microscopy, XRD, XRF etc. [1, 6-9]. Amongst them, a well established analytical technique used for the analysis of art objects through a non destructive approach is Raman spectroscopy, which has been widely used in the last decades [10,11].

In the present study, the investigation of various types (plaster and masonry) of mortars, collected from the ancient city of Aiani and dated back to archaic/classical (6th c. BC) and hellenistic (3rd c. BC) times is attempted. The study is focused on the mico-molecular and mineralogical characteristics, in an attempt to investigate the raw material used and the technology applied for these types of mortars.

SAMPLING AND ANALYTICAL METHODOLOGY

Three characteristic mortar samples were collected from different places within the archaeological site of Aiani, northern Greece. K5 sample, a red-coloured plaster mortar, was collected from the afore-mentioned cistern. K9, another red-coloured plaster mortar sample was collected from one large public building known as Large Blocks (Megaloi Domoi). Finally, K15 sample, a cream-coloured masonry mortar, was collected from the royal cemetery (in particular from Tomb A, the largest built tomb found). All samples are dated back to archaic/classical and hellenistic periods [12]. The macroscopic views (both surfaces and cross sections) of these samples are shown in Figure 1.

X-Ray Diffraction (XRD) was employed for the semi-quantitative mineral identification of the coloured surfaces and the bulk mortar samples. Samples were carefully placed horizontally on a special self-made holder, so as to analyse non-destructively the coloured surfaces of the mortars. Moreover, ground aliquots were used for the bulk mortar analyses. A Philips PW-1710 powder diffractometer with CuKα radiation was used. Patterns were obtained by step scanning from 3^o to 63^o 2θ, with a goniometer speed of 0.03^o/sec, operating at 30kV and 10 mA. The XPOWDER analytical software was used for the semi-quantitative determination of the mineral phases.

The Raman spectroscopic study was carried out with a Thermo Scientific DXR Raman Microscope. Several experiments were conducted on the surfaces of the mortar samples, applying different power values, laser beams, bleaching time, number of exposures and exposure time, in order to obtain the optimum analytical parameters. The average spectral resolution in the Raman shift range of 100-3000 cm^{-1} was 5 cm^{-1} (grating 400 lines/mm, spot size 2μm). Raman images were obtained using the 20X objective of the con-focal microscope. A 780 nm laser beam was used, and the power value of the of the sample irradiation was 12 mW. Other analytical parameters were as follows: 30sec bleaching time; 5 exposures of 10 sec exposure time. Under the Raman microscope the mortar surfaces could be clearly seen and the area of their spectra could be precisely determined.

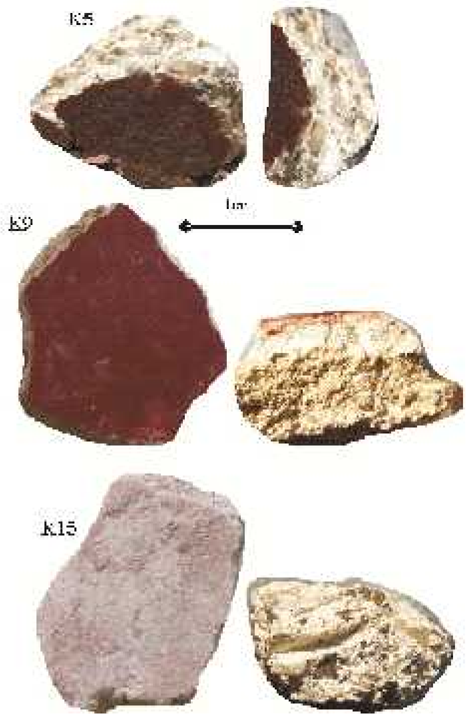

Figure 1. Macroscopic views of the external surfaces and the cross-sections of the plaster mortar samples collected from the cistern (K5) and a building (K9) and a masonry mortar collected from a tomb (K15) from Aiani archaeological site, ancient Upper Macedonia, northern Greece.

Table 1. Semi-quantitative mineralogical composition, using non-destructive X-Ray Diffraction for the mortar surfaces and powder XRD for the bulk samples of the three ancient mortars (K5, K9 and K15) analysed in this study.

	Surface			**Bulk**		
	K5	**K9**	**K15**	**K5**	**K9**	**K15**
Quartz (%) SiO_2	28.6	0.5	24.9	36.7	10.0	23.7
Calcite (%) $CaCO_3$	37.1	16.5	59.6	43.8	44.7	61.1
Feldspars (%) $(K,Na,Ca)AlSi_3O_8$	27.0	-	10.9	13.0	4.0	8.8
Dolomite (%) $CaMg(CO_3)_2$	6.0	68.8	3.6	-	36.1	-
Hematite (%) Fe_2O_3	-	6.5	-	-	-	-
Kaolinite (%) $Al_2Si_2O_5(OH)_4$	-	6.2	-	-	-	-
Illite(%) $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2,(H_2O)$	-	-	-	3.0	1.0	2.0
Serpentine (%) $Mg_3Si_2O_5(OH)_4$	-	-	-	3.0	3.0	4.0
Amorphous (%)	1.3	1	0.9	0.5	1.2	0.4

RESULTS AND DISCUSSION

The mineralogical composition of both the bulk mortar samples and their outer surfaces is shown in Table 1. The main identified minerals in the bulk samples are quartz [SiO_2], feldspars [(K,Na,Ca)$AlSi_3O_8$], calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$] and illite [$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$]. The semi-quantitative results for the bulk mortars are: K5 (36.7% quartz, 43.8% calcite, 13% feldspars, 3% serpentinite and 3% illite,), K9 (10% quartz, 44.7% calcite, 36.1% dolomite, 4% feldspars, 3% serpentine and 1% illite), K15 (23.7% quartz, 61.1% calcite, 8.8% feldspars, 4% serpentine and 2% illite). Calcite, quartz and feldspars are the most abundant minerals in all mortars with minor differentiations in their percentages in each sample. It is evident that these mortars were prepared by crushing local calcareous sedimentary rocks. Secondary calcite may occur due to post-burial depositional processes [13]. During post-burial period, Mg-rich waters could also have replaced Ca and produced dolomite along with calcite. The presence of white colour magnesite deposits in the surrounding area of Aiani is a clear evidence for the magnesium abundance [14,15]. The non-destructive application of XRD technique on the mortar surfaces revealed the following mineralogical composition: Calcite is the most common mineral found in all samples (with concentrations ranging from 16.5 to 59.6 %), while quartz and feldspars are present mainly in K5 and K15 samples. Hematite (with a content of 6.5%) comprised the red-coloured surface of K9 sample, while the other red-coloured mortar K5 did not show the presence of Fe-rich minerals. The high contents of iron in K9 sample may also be related to the presence of iron not only in the pictorial but also to the outer preparation layer, as evidenced in the macroscopic images of Figure 1. The absence of hematite on the XRD results from the K5 red-coloured mortar sample does not necessarily show that it does not exist, since hematite in low quantities (<1%) is adequate for giving a red hue on the ceramics. Phyllosilicate minerals (e.g. (kaolinite) are also present in the K9 mortar sample and might be related to the use of local clays [13, 15-17]. The presence of Mg-rich dolomite minerals in high amounts (68.8 %) is found in one sample (K9) and could be related to the local Mg-rich deposits found in the surrounding area [9, 17] and may be attributed either to a dolomitic lime binder, obtained by the calcinations of dolomitic limestone or to secondary carbonates, due to post-burial depositional processes. It should be noted that some minor mineral phases might not have been identified and the XRD results could not directly be correlated with the results of the other analytical methodologies, since it was not always the same surface area analyzed.

Table 2. Raman peaks assignment (refer to Figure 2) to specific minerals from the surfaces of the three ancient mortars (K5, K9 and K15) analysed in this study.

SAMPLE ID	Peaks (cm^{-1})	Mineral assignment
K5	227,294,411,502,614,697,1326	Hematite
	1088	Calcite
K5 black inclusion	228,274,487,618,	Hematite
	383,548,694	Goethite
	1407,1498,1588	Carbon black
K9	145	Anatase/Rutile
	227,294,412,498,614	Hematite
	1087	Calcite
K15 white	157,283,714,1088	Calcite
K15 grey	158,287,714,1088	Calcite
	397,621	Serpentine
	509	Feldspar

The Raman spectra of all the analysed mortar surfaces along with characteristic micrographs of the red-coloured surfaces of K5 and K9 samples and the cream-coloured surface of K15 sample using the Raman microscope are shown in Figure 2. The identified mineral phases are also presented in Table 2, indicating the characteristic Raman peaks of each mineral. The red-coloured mortar surface of K5 sample seems to be composed of different proportions of hematite and calcite mineral phases. Hematite reveals its main peaks at 227, 294, 411, 502, 614 and 1326 cm^{-1} and calcite is clearly inferred from the 1088 cm^{-1} Raman peak. A black-coloured inclusion is observed on the surface of K5 sample. This black coloured inclusion is comprised of hematite (228, 274, 487, 618 cm^{-1}) and goethite (383, 548, 694 cm^{-1}). Raman peaks at 1407, 1498 and 1588 cm^{-1} are probably attributable to black carbon present in the inclusion. Most probably, red clays rich in iron oxide and hydroxides were carefully mixed with a proper amount of Ca (and occasionally Mg) rich carbonates and organic carbon of plant origin and coat the outer surface of the mortars. The other red-coloured mortar surface

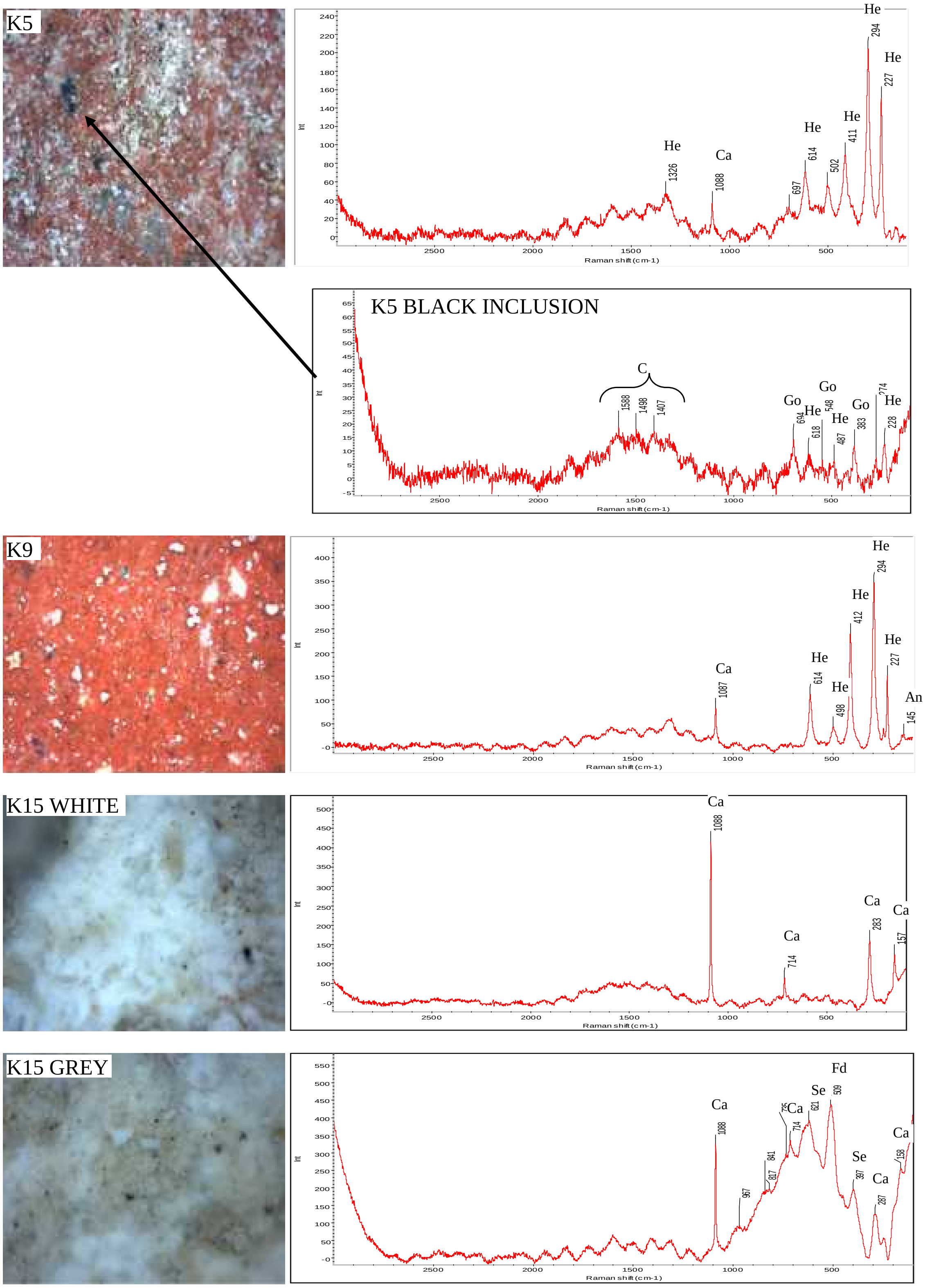

Figure 2. Raman spectra and microphotographs of the red pigments from K5 and K9 samples and the white and grey surface material of K15 mortar sample. (Laser wavelength 780 nm, objective 20X). Labels: He=hematite, Go=goethite, Fd=feldspar, Ca=calcite, An= anatase, C=black carbon, Se=serpentine.

(K9) has shown a Raman peak at 145 cm^{-1}, which is attributed to the vibrational modes of the Ti-oxides (rutile or anatase), being present as an ancillary component of silicates [18]. Hematite is also present with its characteristic peaks at 227, 294, 412, 498, 614 cm^{-1} and calcite with its main Raman band at 1087 cm^{-1} [19-21]. Based on these results, a mixture of iron oxides/hydroxides is proposed for the manufacture of the red coloured plaster. It could be assumed that the different colours are attributed to different percentages of the same minerals. Two hues were evident on the cream-coloured K15 mortar surface, a grey one and a white one. Calcite was prominent by its Raman bands at 157, 283, 714 and 1088 cm^{-1} for the white hue. The grey hue seems to be composed of various minerals. Calcite is the predominant, as shown by its bands at 158, 287, 714 and 1088 cm^{-1}. The bands at 397 and 621 cm^{-1} are probably attributed to serpentine [22, 23] and the one at 509 cm^{-1} to feldspars.

CONCLUSIONS

Two ancient plaster mortars and one masonry mortar from Aiani's archaeological site, northern Greece were comprehensively analysed in this study, using complementary methodologies. The concluding remarks are as follows: The bulk mortar samples are composed of calcite, quartz, feldspar and dolomite. Provenance characteristic minerals, such as serpentine has also been determined and is attributable to the ultramafic rocks of the surrounding area. The Raman spectra of all the red-coloured mortar surfaces revealed hematite as the main constituent. Black inclusions identified by Raman spectroscopy may be associated with carbonaceous material of an amorphous character and iron oxides and hydroxides (hematite/goethite). The raw material for the red painting derives probably from iron oxides and hydroxides either from a local ochre deposit or an iron-rich clay deposit. The presence of mica and clay minerals is consistent with a provenance of local Fe-rich clays.

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