

Prehistoric Anasazi ceramics studied by micro-Raman spectroscopy

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In this project, micro-Raman (μ -Raman) spectroscopy has been used as a means to investigate the pigments employed in decoration of Anasazi pottery. Analysis of Raman spectra revealed the presence of organic (amorphous carbon), iron- and/or manganese-based pigments in line with the known pictorial materials used by Anasazi people. The results were also complemented by studies employing a scanning electron microscope equipped with a microanalysis energy dispersive X-ray detection (SEM/EDX) system, which proved helpful mainly while identifying the manganese-based minerals (i.e. pyrolusite). Knowledge of the pigments augments our understanding of the materials favored by the different production centers and of the artistic skills of ceramic producers. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: Raman spectroscopy; SEM/EDX; pigments; Anasazi; ceramics

INTRODUCTION

This paper reports on the ongoing studies¹ of prehistoric, southwestern Native American ceramics by means of micro-Raman (μ -Raman) spectroscopy. This noninvasive, nondestructive analytical method offers several advantages in the study of ceramics, coming from its inherent selectivity and sensitivity. These include the possibility to obtain direct information on the pigments as well as on the minerals constituting the pottery.^{2–5} Another remarkable benefit of μ -Raman spectroscopy is the possibility to investigate pottery objects as they are and thereby obtain direct information about the structural characteristics of the analyzed artifact without tedious sample preparations.

Despite all the advantages offered by Raman spectroscopy, the complexity of ceramic materials can require the application of other analytical methods also.⁶ X-ray diffraction patterns can be used to study the specific phases of minerals, assuming that these occur in crystalline form.^{7,8} Techniques of elemental analysis such as X-ray fluorescence (XRF),⁶ proton-induced X-ray emission (PIXE),^{9,10} and scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDX)^{8,11–13} can help identify the mineral composition and therefore ensure complete and confident results.

For this project, we had a total of 16 pottery shards at our disposal, kindly provided by Carla Fornasari, a collector

of native American artifacts and founder of the Centre of Studies Red Eagle Woman – American First Nations.¹⁴ The shards were retrieved in the late 1990s from today's Navajo region, namely in the zones of Navajo Mountain and Canyon De Chelly. The goal of our work was to identify the principal pottery groups on the basis of the ceramic formal and stylistic analysis combined with investigations of materials used for the pottery decoration. To organize the shard samples into the different pottery groups, we relied also on the results of our previous work concerning a different set of Anasazi ceramics.¹ In this study, Raman spectroscopy had been employed to obtain the spectral characteristics of the pigments, and SEM/EDX technique as a means to investigate the presence of specific elements.

Historical background – the Anasazi nation

The term Anasazi originates from the Navajo word, literally meaning 'enemy ancestors' or 'ancient people who are not us', used to designate the prehistoric people of Navajo's southwestern area.^{15,16} The Navajo people are related to the Athapaskan tribes of northwestern Canada and came to the Southwest only about the year 1500.¹⁷ Therefore, they are not to be considered blood relatives of the ancestral nations that we refer to in this study. The Anasazi was a pre-historic nation inhabiting the dry land of the Four Corners area where the North-American states of Arizona, New Mexico, Utah, and Colorado meet. The Anasazis settled in the southwestern United States during the Archaic Period (1–500 AD). During the Classic Period (late thirteenth century) the population

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of Anasazi abandoned their settlements¹⁸ and fused with the Zuni lands (western New Mexico) and Hopi mesas (northeastern Arizona).¹⁶ The reasons of the great migration have been greatly debated. In summary, the migration most likely resulted from both environmental (e.g. draught, soil depletion) and religious causes.

The ceramics of Anasazi are considered to be their most developed handicrafts and, therefore, provide an indispensable tool in studies of trade interactions among people, reveal well the changes in events and ideas, and help date archaeological sites.^{15,16} To illustrate the ceramic production technique, it is important to realize that the use of the potter's wheel was unknown to prehistoric people of the Southwest.^{18,19} They used a simple coiling method to make the pots. The principle of pot formation consisted in placing narrow coils of clay on top of each other. The rough pot form was scraped and smoothed with a piece of sandstone to create an even finish. The ceramics were fired in open fires or shallow pits, without using a kiln,^{18,19} in a reducing or oxidizing atmosphere. Additionally, after the paint had been applied, a second firing at a lower temperature was carried out.¹⁸

To follow the temporal development, the earliest Anasazi ceramics were plain gray, brown and redware (~600 AD), which was later (700–900 AD) elaborated into the most characteristic and distinctive Anasazi black-on-white ware. Finally, these wares were slowly replaced by black-on-red, black-on-orange, and polychrome types (from 900 AD).^{16,18} To design the ceramics, Anasazi potters adopted the geometric elements originally used in their basketry; these included lines, bands, hachures, additionally also triangles, scrolls and dots. Typical black-on-white and black-on-red shards studied in this project are displayed in Fig. 1.

EXPERIMENTAL

Sample designation

The ceramics shards are designated by numbers from 168 to 183, which follow the numbering used in the Carla Fornasari ceramic collection. The samples were examined by μ -Raman technique without any sample preparation. From these, four samples (n.169, 170, 173, 174) were prepared as cross sections for SEM/EDX analysis.

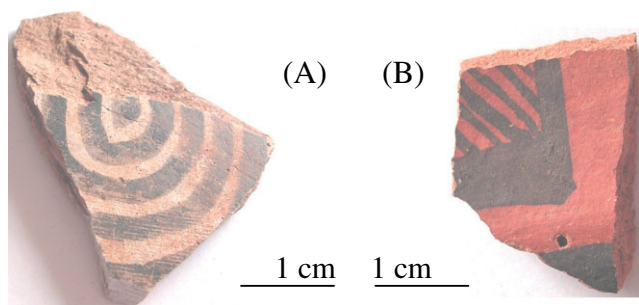


Figure 1. Photographs of the (A) black-on-white (n.170) and (B) black-on-red (n.174) shards.

Micro-Raman spectroscopy

The precise parameters of the Raman Renishaw System 2000 spectrometer coupled to a Leica optical microscope used to study the samples have been described elsewhere.³ Briefly, the 785-nm line of a diode laser was used as the excitation source providing 28 mW laser power at the source. This was reduced by filters and optical components ($\times 50$ objective) to yield powers on samples ranging from 0.2 to 6.9 mW. To separate the Rayleigh signal from the Raman signal, a narrow-band holographic notch filter was employed. The Raman photons were dispersed using a diffraction grating (1200 lines/mm) and detected by a CCD camera. The experimental setup enabled spectral and spatial resolutions of *ca* 3 cm^{-1} and 2 μm , respectively. The spectra are presented as acquired (i.e. untreated).

Scanning electron microscopy with energy dispersive X-ray detection (SEM/EDX)

The four cross sections were prepared by embedding the respective shard chips in an epoxy resin (Epoxicure, Buehler). For the X-ray microanalysis (Philips 515 SEM with EDAX Falcon system), they were treated using standard procedures (i.e. polished with diamond paste and coated with a thin layer of graphite by sputter coating). The accelerating potential of the electrons inducing the sample X-ray emission, and the time to acquire the EDX spectrum were 25 kV and 100 s, respectively. Data treatment allowed a quantitative chemical microanalysis with a detection limit of 0.5% by weight. Elemental relative proportions are reported as the means and the standard deviations from five measurements for each sample.

RESULTS AND DISCUSSION

Pigment analysis

The pigment colors of our samples range from white, red, to black. The results are sorted according to visibly identified colors (starting from black continuing with red to white), and according to the chemical nature of pigments. Examples of Raman spectra obtained on the samples n.169 (black-on-white decoration), n.173 (black/white-on-red decoration), and n.174 (black-on-red decoration) are reported in the following section, as their results are representative of those of the other samples.

Black pigment

To obtain the black color in the prehistoric ceramic decoration, the use of amorphous carbon, magnetite, and pyrolusite is usually considered. While the carbon- and iron-based pigments require firing in a reducing atmosphere to maintain or to reach the black appearance, the color of the manganese-based ones is independent of the firing atmosphere.

Manganese-based pigment

The black pigment of sample n.174 yielded a spectrum with a broad peak around 640 cm⁻¹. Relying on the knowledge of pigments used in the decoration of prehistoric ceramics,²⁰ manganese-based ones come into consideration. All manganese oxides are indicative of spectral domains at 450–600 cm⁻¹ and 600–750 cm⁻¹, stemming from Mn–O bending and stretching vibrations, respectively.²¹ Nevertheless, the identification of manganese-based minerals by Raman spectroscopy is accompanied by difficulties due to their high thermal sensitivity,^{2,21} which causes most of the Mn(IV) oxides (e.g. mineral pyrolusite (β -MnO₂)) to reduce under the laser beam to a more stable phase, bixbyite (Mn₂O₃).²² Together with the existence of manganese in the nonstoichiometric and disordered systems,¹⁰ this leads to the great discordance in the spectral characteristics reported in the literature. On the basis of the fact that the spectrum was not represented by many peaks (Fig. 2), it is impossible to identify the exact nature of black manganese-based pigment. However, the presence of manganese was confirmed by SEM/EDX analysis (Table 1, sample n.174-black), and also by the broad peak around 640 cm⁻¹ that has been previously assigned to manganese (IV) oxides such as pyrolusite or ramsdellite.^{12,23,24} Since all species of MnO₂ have been reported²⁵ to convert to α -Mn₂O₃ above 450 °C, this ceramic object (i.e. sample n.174) has probably undergone a second firing at temperatures lower than 450 °C. Smith *et al.*⁶ have stated that the presence of manganese minerals could be confirmed by XRD. The XRD experiments performed directly on the cross-sectioned samples did not bring satisfactory results, mainly because of the low sensitivity and spatial resolution of available instrument. Nevertheless, more successful results could have probably been obtained by removing a part of black decoration and analyzing it in this form.²⁶

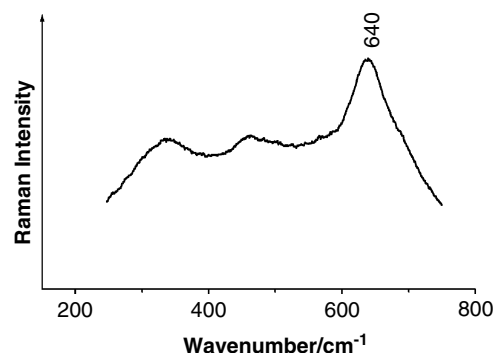


Figure 2. Raman spectrum of manganese-based pigment obtained on sample n.174. Experimental conditions: excitation source, 785 nm; power on sample, 0.9 mW; acquisition time, 140 s; accumulations, 10.

Carbon-based pigment

The Raman spectrum shown in Fig. 3 and obtained on the black decoration of the sample n.169 is that of amorphous carbon. This spectrum consists typically of two broad peaks around 1330 and 1600 cm⁻¹, which are associated with sp³ and sp² carbon hybridization, respectively.²⁷ The characteristic peak of the phosphate group (960 cm⁻¹)^{27,28} is not detected in any spectrum of any sample. For this reason we can exclude this pigment as having been prepared by burning bones. A single narrow peak at ~1600 cm⁻¹ would be characteristic of crystalline graphite² (sp²) but this was not found in our spectra. More likely, various plants served as sources of amorphous carbon (e.g. Beeweed, *Cleome Serrulata*;¹³ Mesquite, *Prosopis glandulosa*¹⁸), having been converted to carbon after firing under reducing conditions. An indirect proof for the carbonaceous character of the decoration has been furnished by SEM/EDX (Table 1, sample n.169). The results demonstrate the low concentration of iron

Table 1. Elementary SEM/EDX analysis performed on sample decorations of white (n.169, n.170) and red (n.173, n.174) ware

Elements (wt %)	White ware				Red ware			
	n.169		n.170		n.173		n.174	
	Black	White	Black	White	Black	Red	Black	Red
Na	1.0 ± 0.1	0.7 ± 0.3	0	3.4 ± 1.4	0	0	0	0
Mg	13.9 ± 1.8	0.9 ± 0.7	3.6 ± 1.1	1.7 ± 0.3	4.0 ± 0.9	0	0	1.6 ± 0.1
Al	66.4 ± 2.2	15.7 ± 4.1	22.1 ± 2.8	20.7 ± 3.9	17.8 ± 1.4	12.1 ± 5.1	21.1 ± 1.2	16.7 ± 1.9
Cl	0.7 ± 0.1	0	0	0	0	0	0	0
S	0	8.0 ± 5.1	0	0	0	0	0	0
Si	66.4 ± 2.2	70.2 ± 3.8	54.5 ± 2.9	62.2 ± 2.4	55.8 ± 6.4	21.7 ± 2.6	42.0 ± 4.4	40.1 ± 10.3
P	0	0	0	0	0	0	0	0
K	16.4 ± 0.2	8.0 ± 5.1	6.2 ± 2.1	5.3 ± 1.4	6.3 ± 1.4	3.1 ± 1.1	3.2 ± 1.1	2.4 ± 1.0
Ca	0	1.8 ± 0.6	3.1 ± 1.1	2.3 ± 1.1	5.6 ± 1.5	0.8 ± 1.3	1.5 ± 0.2	3.0 ± 1.5
Ti	0	0.9 ± 0.3	0.6 ± 0.2	1.3 ± 0.2	0.9 ± 0.2	0	0.8 ± 0.2	0.7 ± 0.2
Mn	0	0	0	0	0	5.1 ± 3.9	19.0 ± 5.0	0
Fe	1.3 ± 0.5	1.4 ± 0.4	9.9 ± 1.3	2.9 ± 0.5	9.7 ± 1.7	57.3	12.5 ± 2.3	35.8 ± 9.7

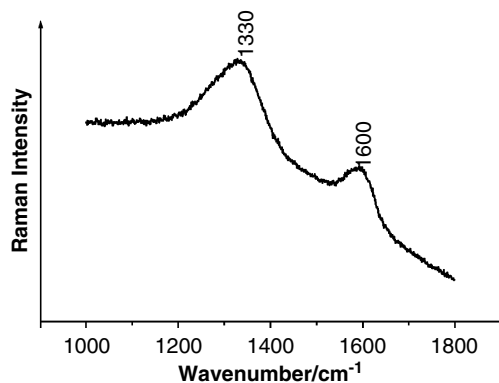


Figure 3. Raman spectrum of amorphous carbon obtained on sample n.169. Experimental conditions: excitation source, 785 nm; power on sample, 6.9 mW; acquisition time, 100 s; accumulations, 1.

Table 2. Identified pottery types together with sample designations (D) and principal decoration characteristic

Ware	D (n.)	Principal decoration characteristics
Little Colorado White	169	Carbonaceous pigment on a thin white slip, well polished, dark body
	172	
	179	
	180	–
	181	–
Cibola White	182	–
	170	Mineral (Fe) based pigment on a white slip, bright body, reducing atmosphere
	175	
Tusayan White	176	Carbonaceous pigment on white slip, reducing atmosphere
Tusayan Grey	183	Rough, not polished finish, no slip, no decor
White Mountain Red	168	Mineral (Fe) and carbonaceous pigment on red slip
	171	
	173	
	177	–
Tsegi Orange	178	–
	174	Mineral (Mn/Fe) based pigment on a red slip, bright body

and the absence of manganese. The amorphous carbon used as a pigment has been detected also in the following samples: n.169, n.172, n.179, n.180, n.181, and n.182, as indicated in Table 2. Additionally, in combination with other pigments (iron oxides), amorphous carbon was found in the samples n.168, n.171, n.173, n.177, and n.178 (Table 2).

These easily accessible carbonaceous materials often employed in the decorations of ancestral ceramics have a long history^{13,18} and their use lasts up to the present time. One of the impacts of our finding is that dating of ceramic samples using ¹⁴C technique seems feasible,^{29,30} even though such experiments are accompanied by a number of uncertainties. The results would indicate the death of trees or plants used to prepare the pigment, at best. In case wood fossils were used, the data would not be directly related to the age of the ceramics. Additionally, as the pigments were not applied in a thick layer, their sampling would significantly affect the character and value of the ceramic shards.

Iron-based pigments

The oxidation state of iron is strongly dependent on the atmosphere under which ceramic was fired.³¹ To obtain black color, a reducing environment must be imposed to form mixed iron oxides (e.g. magnetite). On the other hand, the reddish trivalent iron oxide (e.g. hematite) is formed under an oxidizing atmosphere.⁴

In the spectra reported in Fig. 4 and obtained on the black/brownish decors of sample n.173, one can observe three broad spectral bands centered around 317, 500, and 700 cm⁻¹. This spectrum could represent a reaction intermediate formed during the oxidation or reduction cycles of iron oxides considering the similarities with the position of peaks in spectrum of maghemite (γ -Fe₂O₃) single crystal (broad peaks at ~350, ~500, and ~700 cm⁻¹),³² which correspond to Raman-active T₁, E, and A₁ phonons.³³ The shifts in peak position as well as the changes in their intensities could be due to the material being subjected to various degrees of phase transformation and/or due to the coexistence of various phases giving rise to not-well-defined spectra. The observed disagreement in the lowest wavenumber peak position prevents us from claiming the presence of maghemite phase only, even though the presence of maghemite in ancestral Mesa Verde Pueblo ceramics has been reported by Van der Weerd *et al.*³⁴ with

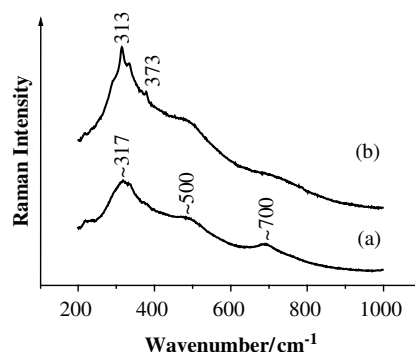


Figure 4. Raman spectra of sample n.173 black decoration at two different points (a) and (b). Experimental conditions: excitation source, 785 nm; power on sample, 0.9 mW; acquisition time, 100 s; accumulations, 10.

~ 316 , ~ 505 , and ~ 706 cm^{-1} Raman band assignments. The Raman spectra of the minerals present are directly related to the degree of crystallinity and reflect the extent of phase transformation.^{32,35} This could probably explain the observed shift in the peak position from 350 cm^{-1} to 317 cm^{-1} .

Wavenumber shifts of the iron oxide Raman bands have been observed in detail by De Faria *et al.*³² and Wang and Saxena³⁵ in the study of pressure-induced phase transformation and have been attributed to the coexistence of α - and γ - Fe_2O_3 phases. Additional peaks at around 313 and 373 cm^{-1} observable in the spectrum in Fig. 4(b) could be associated with the mineral lepidocrocite (γ - $\text{FeO}\cdot\text{OH}$), which often accompanies maghemite.^{32,36} However, the broad spectral feature around 320 cm^{-1} does not allow the differentiation of the second strongest peak at 245 cm^{-1} , typical of the lepidocrocite spectrum.³² The various spectra recorded for the black decoration of this sample were not rigorously consistent (representative spectra are shown in Fig. 4) throughout the examined area; however, a detailed examination of the spectral features of each specific sample is beyond the scope of the current project and would be an interesting subject for future work.

'Maghemite-like' structures were detected also in other samples (n.170 and n.174), and most likely resulted from two processes of thermal transformations (i.e. reduction and oxidation). For the black-on-white sample (n.170), the 'maghemite-like' structures might have been formed by reduction of hematite, starting at a relatively low temperature of 400 $^\circ\text{C}$, and being further reduced to magnetite. For black-on-red sample (n.174) the presence of 'maghemite-like' structures can also result from the reverse process (i.e. the oxidation of magnetite) and would manifest the oxidizing atmosphere and mild temperatures (~ 300 $^\circ\text{C}$).³³ The decoration on sample n.174 nicely demonstrates the skills of the Puebloan potters. The dark decor on this black-on-red shard is mostly due to manganese oxides (Fig. 2), whose color is independent of their oxidation states. This allowed the artists to fire the ceramic items in oxidizing atmosphere under careful temperature control (not allowing complete magnetite-to-hematite transformation) giving rise to the red background while keeping the decor dark.

Even though a precise definition of the observed mineralogical phases is not possible, the presence of iron-based pigment is indicated by SEM/EDX analysis, which yielded higher percentage of iron in the black decors of samples n.170, n.173, and n.174 (Table 1). This supports our interpretation of the spectra in Fig. 4, ascribing them to the iron oxide reaction intermediates that could have been formed during the firing process at mild temperatures.

Red pigment

The red color is essentially intrinsic to the slips (sample n.168, n.171, n.173, n.177, n.178, and n.174), and the decoration of red ware (n.168). Firing in an oxidizing atmosphere was particularly desirable with the red wares, as the slip

ultimately obtained its rich red color upon the oxidation of iron contained in the clay. An example of the spectra associated with the red grains of sample n.174 can be seen in Fig. 5, where the spectral characteristics of the mineral hematite (α - Fe_2O_3), which belong to a space group D_{3d}^6 , were observed as follows: A total of six out of seven possible Raman-allowed modes^{32,35,37} were detected (Fig. 5) in sample n.174, namely, the phonons corresponding to A_{1g} modes (225 and 496 cm^{-1}) and E_g modes (244 , 293 , 410 and 612 cm^{-1}). The 299 cm^{-1} band corresponding to one of the two 'external' (i.e. involving motions of entire Fe_2O_3 units) E_g Raman-active modes, which are easier to be detected at low temperature or under hydrostatic pressure experimental conditions, has not been resolved. The presence of a broader peak around 660 cm^{-1} could be assigned to residual magnetite.⁷ Alternatively, this band could be attributed to the Raman-forbidden LO phonon as observed by Massey *et al.*³⁷ at 660 cm^{-1} . The peak near 1312 cm^{-1} has been previously ascribed to two-magnon scattering and, more recently to a second-order phonon scattering.^{37,38} The band at 144 cm^{-1} is attributed to anatase,^{5,39,40} which could be present as an ancillary component of silicates.

White pigment

The sample n.173 represents the only polychromatic shard. Here, the white stripes, used to accent the black linear decorations, were applied on a red slip. The mineral associated with white pigment gave rise almost constantly to a very intense Raman peak around 144 cm^{-1} . This band together with others (194 cm^{-1} (w), 394 cm^{-1} (m), 514 cm^{-1} (m), and 637 cm^{-1} (m)) can be attributed to the vibrational modes of the anatase structure.^{5,39,40} An example of the spectrum obtained on the white grains of sample n.173 is shown in Fig. 6(a). Anatase represents one of three naturally grown polymorphs of titanium dioxide.⁴¹ While rutile represents the most common naturally occurring phase, brookite is the rarest one.

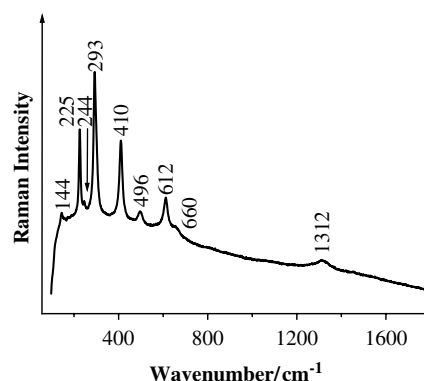


Figure 5. Spectrum of red grains of the ceramic slip (sample n.174). Experimental conditions: excitation source, 785 nm; power on sample, 2.0 mW; acquisition time, 10 s; accumulations, 1 .

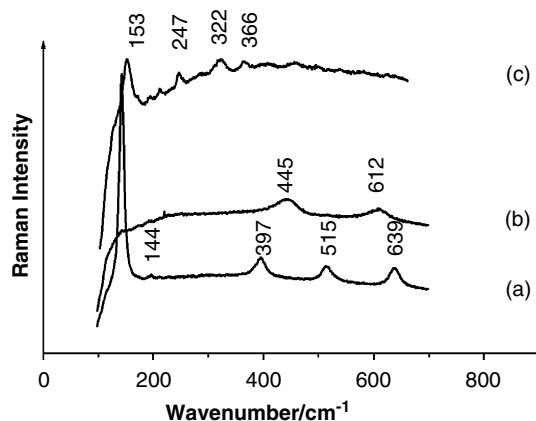


Figure 6. Raman spectra of TiO_2 polymorphs obtained on the white decoration of sample n.173: (a) anatase, (b) rutile, and (c) brookite. Experimental conditions: excitation source, 785 nm; power on sample, 2.0 mW; acquisition time, 100 s; accumulations, 1.

Reports on the use of titanium dioxide pigments in the decoration of ancestral ceramics are rare.²⁶ In fact, anatase is a common component of soil minerals and is often present as ancillary constituent in kaolins.⁴² It has been reported by other researchers^{26,42} that the Raman bands of clay minerals (i.e. silicates) are often masked in presence of anatase. This is due to the fact that the strongly covalent Ti–O bonds give intense Raman bands, while silicates are poor Raman scatterers. Therefore the presence of clay minerals (e.g. kaolinite) in our samples, used both as a pigment and a binder, cannot be ruled out; instead it is also highly probable, and would be in agreement with common pigment palette used by prehistoric people of the Southwest.¹⁸ These results must be considered preliminary since only one sample with white decoration was available for analysis. Additionally, further work is necessary to identify the main component of the white pigment. FTIR spectrophotometry, representing a complementary technique to Raman spectroscopy, could be a very effective tool permitting the more complex spectral characterization of the matrix forming the white decoration.

In the white decoration of sample n.173, anatase (Fig. 6(a)) has been easily distinguished by means of its Raman spectrum from rutile and brookite structures (Fig. 6(b) and (c)), the latter two representing minor phases in our sample. Theoretically, the presence of anatase in ceramics could be used as an indicator of the firing temperatures, as the irreversible thermal anatase/brookite to rutile phase transformation is well known and widely reported.^{5,40,43} Nevertheless, the presence of SiO_2 has been shown to render the anatase-to-rutile conversion more difficult or to inhibit it completely.^{44,45} This makes the argument of TiO_2 phase transformation ambiguous and not uniquely applicable to deduction as to the temperature the ceramics were fired at after the pigment application.

It has to be pointed out that the anatase spectra were linked also with the white slips that serve as the ceramic body base coatings before the application of the decoration.

The rest of the analyzed samples yielded Raman spectra similar to the ones reported in this paper. The study aims at the general understanding of the materials used in the ceramic decorations. To examine more profoundly the fine details in which the spectra of the individual samples might differ as a function of focusing area, a parallel study of the thermal transformation of iron and manganese oxides is planned.

Identification of pottery types

Plog¹⁶ reports the different types and styles of production and pottery design to be distinctive of territorial groups that occupied relatively large areas. To classify different pottery groups, many aspects are to be considered including geographical indications, ceramic typology, and pictorial style. On the basis of our previous work dedicated to a larger set of Anasazi ceramics samples,¹ we collocated the samples examined within the frame of the reported study with different production centers. The results of this collocation, together with the principal sample characteristics, are summarized in Table 2. The visual characterization of ceramic body and paste, the presence of slip (watery clay coating the pottery before decorating), and the chemical nature of applied pigments were used to recognize the pottery groups. The majority of white ware was identified as *Little Colorado White Ware* (n.169, n.172, n.179, n.180, n.181, and n.182). This pottery type is named after a river in northwestern Arizona, where the Anasazi presence was most abundant. Pottery was fired in a reducing atmosphere; the body color is dark gray. The carbonaceous decoration was applied on a well-polished thin white slip. For *Cibola White Ware*, two pottery shards (n.170 and n.175) were found made of white clay, painted with an iron-based mineral on a white slip, and fired in a reducing atmosphere. For *Tusayan White* (n.176) and *Gray Ware* (n.183), an organic base with no decoration was typical. The samples of *White Mountain Red Ware* (n.168, 171, 173, 177, and 178) were decorated using a combination of iron-based and carbonaceous pigments, which was applied on a thick red slip and fired in an oxidizing atmosphere at low temperatures.

The categorization of the pottery is not always straightforward, as various ceramics types are very similar. For example, the *Tsegi Orange ware* (n.174) was difficult to differentiate from *San Juan ware* (no sample identified), as both have many common characteristics (red core, use of manganese- and iron-based pigments, use of oxidizing atmosphere at the end of the firing process). The distinguishing features are: (1) the application of slip for *Tsegi Ware*, and (2) temper (material added to clay to alleviate the shrinking and cracking during drying and/or firing), broken shards for

Tsegi, and sand or crushed rock for San Juan ware. To further support our present classification, the study of sample ceramic bodies is now being elaborated.

CONCLUSIONS

The chemical composition of the materials used in decoration of Southwestern prehistoric ceramics has been studied by μ -Raman and SEM/EDX techniques. The black colors were associated with carbonaceous material of an amorphous character, and iron and manganese minerals. Use of anatase in the role of white pigment was indicated by Raman spectroscopy (using 785 nm excitation source); nevertheless, this result is to be considered preliminary. On the basis of the principal pottery characteristics (visual body characterization, presence of ceramic slip, type of pigment and decoration) the following ceramic types were diagnosed: *Little Colorado White*, *Cibola White*, *Tusayan White*, *Tusayan Gray*, *White Mountain Red*, and *Tsegi Orange Ware*.

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