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Raman identification of cuneiform tablet pigments: emphasis and colour technology in ancient Mesopotamian mid-third millennium

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Abstract

Cuneiform tablets tell the life and culture of Sumerian people in a sort of black and white tale because of the binary engraving technique. A leading question arises: did Mesopotamian people apply some kind of colour to decorate their tablets or to put emphasis on selected words? Some administrative and literary Sumerian cuneiform tablets of mid-third Millennium B.C. from the site of Kish (central Mesopotamia, modern Iraq) were dug up in twentieth-century and stored at the Ashmolean Museum of the Oxford University. Non-destructive micro-Raman spectroscopy is a powerful technique to detect the presence of residual pigments eventually applied to the engraving signs. Yellow, orange, red and white pigments have been detected and a possible identification has been proposed in this work. In particular yellow pigments are identified as Crocoite (PbCrO_4), Lead stannate (Pb_2SnO_4); red

pigments – hematite (Fe_2O_3) and cuprite (Cu_2O); White pigments – Lead carbonate (PbCO_3), calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), titanium dioxide (TiO_2), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); orange pigment a composition of red and yellow compounds. These results suggest that Sumerian people invented a new editorial style, to overcome the binary logic of engraving process and catch the reader's eye by decorating cuneiform tablets. Finally, the coloured rendering of the tablet in their original view is proposed.

Keywords: Analytical chemistry, Physical chemistry, Archaeology

1. Introduction

In the modern age, there is a large number of ways to manage a written text, from bolding or underlining some words with the preferred PC editing software down to animated gifs or emoticons for short edited text of mobile messaging and social posting. The task is to catch the eye and rapidly convey the important message. Besides the almost endless opportunities of high-tech displays, to put emphasis on a text written on a hard support mainly relies on changing the editing style, by applying bold, italic or underline style to selected words or phrases and exploiting the characteristic of human eye to be sensible to the change of brightness into a written text [1, 2, 3]. The main employed strategy in typographic art, for example, is to emphasize the words by operating on the “blackness” of the characters composing the text. The result implies more emphasis in the written content and the possibility to change also the logic process of the text [1]. By the use of different colors, the possibilities to obtain different grade of emphasis in the text are practically infinite. Indeed, the use of different colored inks is well documented across the centuries, especially to create notes or to highlight part of a manuscript (see, for example, the reproduction of the books by monks) [4, 5].

As for the high-tech solutions, the use of different writing styles depends on the support where the text is going to be written (paper, parchment, papyrus, canvas etc.). However, this kind of supports, able to absorb different colored inks, was not continuously used in the course of the writing evolution. We could ask to ourselves “What happened when Sumerian people wrote on clay tablets? How the Sumerians did manage to emphasize their written text?” Since the writing process followed a binary condition, carved (written) or not carved (not written), how could they emphasize or underline different part of the text? A possibility can be found in the use of different pigments used as “style marker” for a writing support in which the blackness manipulation of a character cannot be used. In the present work, we analyzed by Micro Raman Spectroscopy some literary and administrative cuneiform tablets dated back to the mid-third millennium B.C to ascertain the presence of pigments. Raman spectroscopy, being a sensitive, non-destructive and, in the present case, portable technique, was successfully applied to investigate

potteries and ancient painted walls to analyze the composition of the color [6, 7, 8]. Recent paper dealing with cultural heritage samples performed with visible excitation light, pointed out how it is possible to reach high resolution on inorganic samples [9, 10]. However, the choice of near infrared excitation (1064 nm), prevents the excitation of fluorescence and represents a suitable non-destructive choice to detect organic components [7].

In addition, the use of a microscopy technique allows changing the focal plane to analyze both the surface and the depth of the engraving signs.

The aim of the paper is to establish if and to what purpose colors were applied in the studied Sumerian cuneiform tablets.

2. Materials and methods

Micro-Raman scattering measurements were carried out in back scattering geometry with the 1064 nm line of an Nd:YAG laser. Measurements were performed in air at room temperature with a compact spectrometer B&W TEK (Newark-USA) i-Raman Ex integrated system with a spectral resolution of less than 8 cm^{-1} . All the spectra were collected with an acquisition time of about 60 s (5 replicas) and power excitation between 10 mW to 30 mW concentrated in a spot of 1 mm^2 of dimension through the BAC151B Raman Video Micro-sampling System equipped with a $20 \times$ Olympus objective to select the area on the samples ($50 \times$ objective used for investigations in the depth of the signs). Each measurement area is identified in the figures with a letter representing a sampling surface of about 1 cm^2 .

2.1. Archaeological and historical samples

Analyses have been carried out on six cuneiform tablets (Fig. 1), identified as administrative and literary typology and written in Sumerian language, kept in the Ashmolean Museum of the University of Oxford (AN 1924.462, 464, 465, 466, 468, 469) [11, 12, 13]. The objects come from the site of Kish in central Mesopotamia, Iraq, and are dated to the mid-third Millennium B.C. The site of Kish was excavated by the joint archaeological expedition of Oxford-Field Museum, Chicago, from 1923 to 1933. Only occasionally do we know the actual find spot of the tablets since in most cases this is not reported in the records, though we know at least the mound where they were found. The location is Inghara, Mound D and Mound W, in some case Dilbat or Barguhiat.

The text presented constitutes a part of the administrative and literary texts in the collection of the Ashmolean Museum dating to what is commonly called the Early Dynastic Period. The Early Dynastic period (abbreviated ED period or ED) is an archaeological culture in southern Mesopotamia that is generally dated to

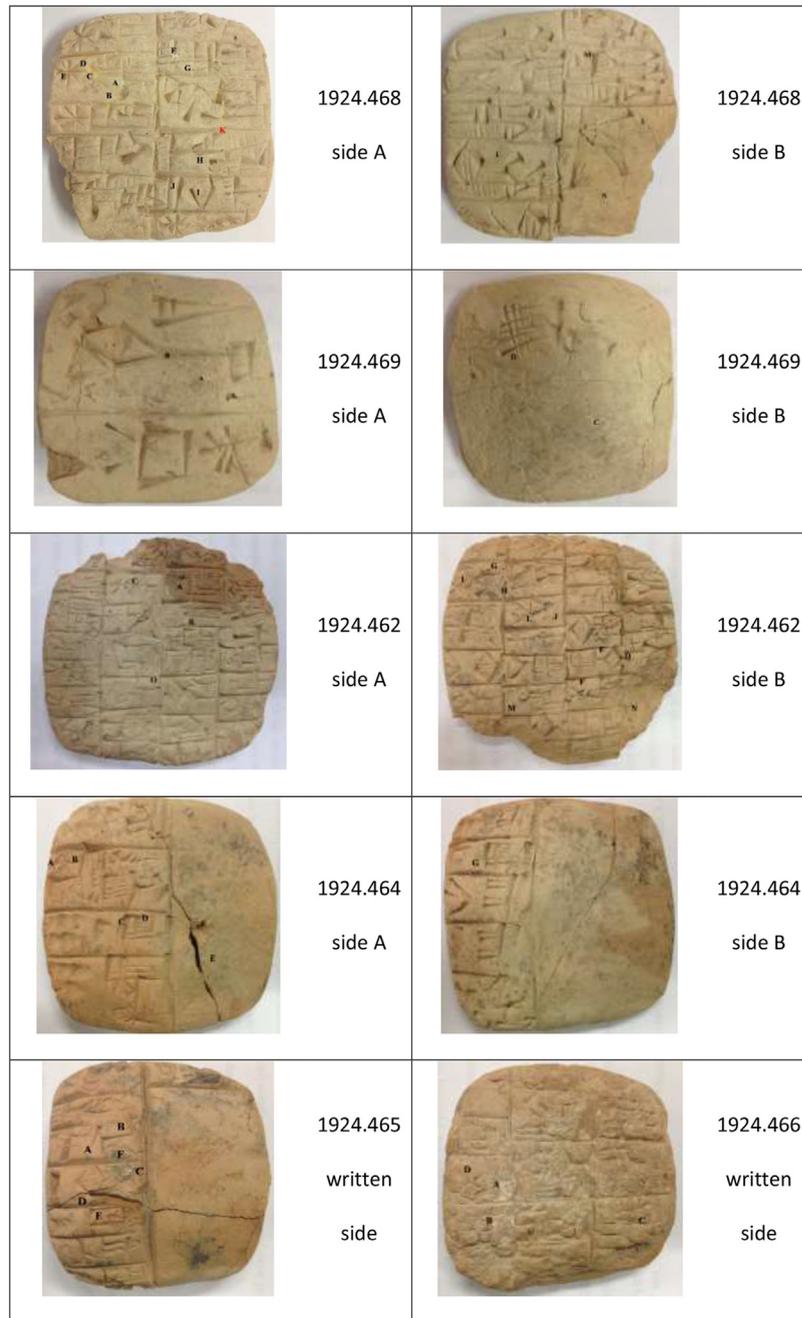


Fig. 1. Analyzed cuneiform tablets from Ashmolean Museum – Oxford.

2900–2350 BC. It was preceded by the Jemdet Nasr period and followed by the Akkadian period. The ED period is divided into three sub-phases, termed Early Dynastic (ED) I–III, with the ED III period being further subdivided into ED IIIa and ED IIIb. The Early Dynastic IIIa period, also known as the Fara period, is when syllabic writing began. Administrative records and a non-deciphered logographic script existed before the Fara Period, but the full flow of human

speech was first recorded around 2600 BC at the beginning of the Fara Period [14, 15, 16]. All the samples are catalogued in a database of 2480 objects inscribed in the collections of the Department of Antiquities, Ashmolean Museum of Art and Archaeology, University of Oxford and are contextualized during the ED IIIa period (ca. 2600–2350 BC). The collection is presently the subject of a digitisation project, a cooperative effort of the Ashmolean Museum and the Cuneiform Digital Library Initiative (CDLI), an international research project based at the University of California, Los Angeles. Their main value lies in the mass data they provide for the reconstruction of the economic, legal and social life of that historical period. In addition, there are useful for toponymy and “onomasticon” purposes, allowing to trace population movements, and to reconstruct the historical geography of Mesopotamia [15, 16].

All the tablets are constituted of clay, not exposed to any fire operation since the writing procedure was realized in wet-clay condition. Once carved, the tablets were dried under sun exposition [13, 14, 16]. The low temperature drying procedure, was not implemented with any further exposition at high temperature (no traces of blazes).

3. Results

3.1. Experimental results

For sake of brevity, we report the results of only those tablets where pigments were detected (tablet 1924–468 and 1924–462). Additional information about all the investigated samples and experimental methods are reported into the Supplementary Material.

3.2. Tablet 1924–468

This tablet presents written text in both sides (see Fig. 2). The side A is divided in 2 columns composed by 5 and 6 rows (column 1 and column 2, respectively), whilst the side B, divided in 2 columns, presents 5 rows for each column. The side B is damaged and a part of the text is lost. The transliteration process is not yet completed, but it is possible to clearly distinguish in the text the logographic character “dingir” (a sort of star) in different positions. The ancient Sumerian sign “dingir” is found on clay tablets since the Uruk IV period (3300–3200 BC) and represents one of the most known elements of the earliest writing system in the world [15, 17]. On the Uruk IV tags it signifies “star” or “sky” or “god” and was apparently pronounced “AN” or “DINGIR”. The logographic sign is used to credit to another sign the meaning of deity, being carved before the name of the deity.

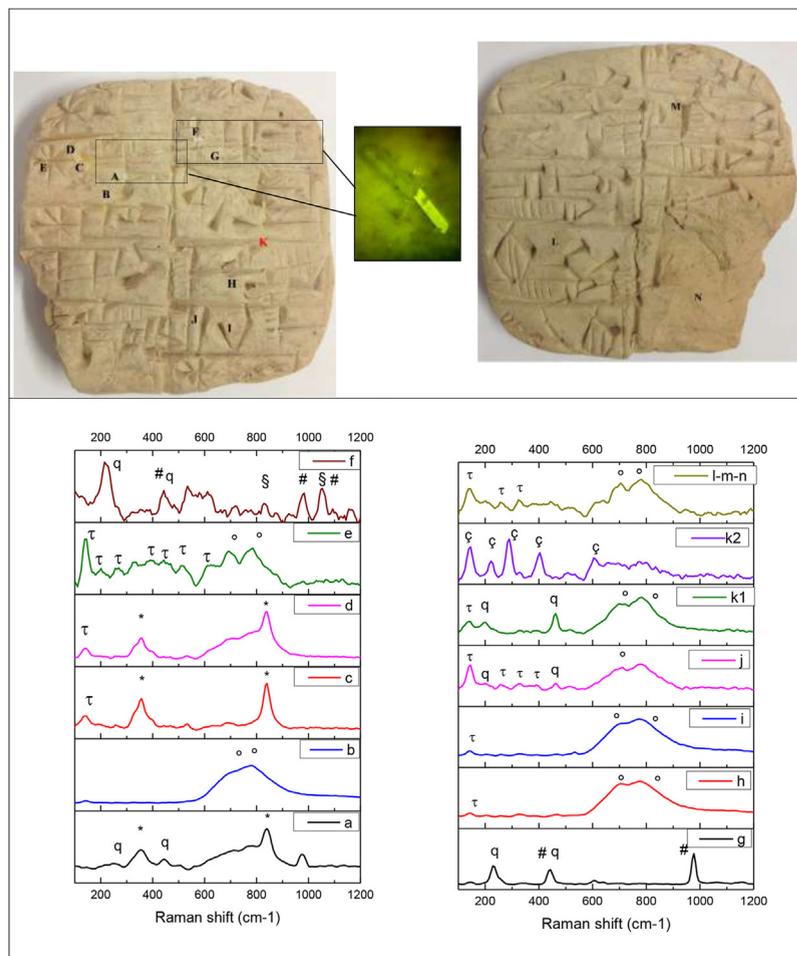


Fig. 2. Tablet 1924–468 (both sides) and collected Raman spectra in representative points (q = Quartz; # = Calcium Phosphate; § = Cerrussite; τ = Titanium Oxide; \circ = Calcium oxide/hydroxide; * = Crocoite; ζ = Hematite). Inset: Quartz crystals on the surface.

The presence of this particular sign into the text suggests its interpretation as a list of “deities” indicated in the tablet. Presently, no other information are available on the content of the rest of the written text, probably referred to the deeds of the gods.

The Fig. 2 shows the sample 1924.468 and the points where the Raman spectra were collected (also reported in the figure). Table 1 summarizes the results obtained in the whole set of samples. We point out that we sampled the zone all around the indicated spot to increase the statistical meaning of the recorded data and to exclude local artifacts.

Concerning the composition of the tablets, we found in the clay two broad bands at 700 and 780 cm^{-1} , common to all the spectra acquired. The two bands are assigned to the Calcium oxide/hydroxide (probably with different grade of carbonation as indicated in the reference [8]). The presence of Calcium hydroxide confirms the marl composition of the Kish ceramic as found in references [7, 13, 18].

Table 1. Identified compounds and pigments in tablets. Sample 468 refers to Fig. 2, sample 465 refers to Fig. 3. Detail on samples 469, 462, 464 and 466 are reported in the Supplementary Material (SM).

Sample	Pigment/compound With references	Symb. in figures	Formula	Colour	Main peaks (cm ⁻¹)	Points in figures
468	Chrome Yellow (Crocoite) [24]	*	PbCrO ₄	PigmentYellow	355, 844	a,c,d
	Quartz [26]	q	SiO ₂	PigmentWhite lucent	463, 510	a,g
	Calcium oxide/hydroxide [8]	°	CaO/Ca(OH) ₂		690, 780	b,h,i,j,l,m,n
	Titanium oxide (Anatase/Rutile) [22]	τ	TiO ₂	PigmentWhite	145, 198, 235, 399, 445, 516, 610, 640	e,h,i,j
	Lead White (Cerussite – Hydrocerussite) [23]	§	PbCO ₃	PigmentWhite	1053, 830	f
	Calcium Phosphate [21]	#	Ca ₃ (PO ₄) ₂	PigmentWhite	975, 430, 1054	g, f
	Hematite [25]	ç	Fe ₂ O ₃	PigmentRed	224, 291, 407, 494, 610	k
465	Quartz	q	SiO ₂	White lucent	463, 510	a,b
	Calcium oxide/hydroxide	°	CaO/Ca(OH) ₂	Clay	690, 780	a,b,d,e
	Calcite/Vaterite [8]	@	CaCO ₃	PigmentWhite	283, 1087	a,b,c,
	Lead Tin Yellow [28]	+	Pb ₂ SnO ₄	PigmentYellow	125, 197	d
	Gypsum [30]	&	CaSO ₄ .2H ₂ O	PigmentWhite	1007, 1140	d
	Cuprite [29]	x	Cu ₂ O	PigmentRed	228, 410	d
	Titanium oxide (Anatase)	τ	TiO ₂	PigmentWhite	145, 198, 399, 516, 640	e
469 (see SM)	Calcium oxide/hydroxide		CaO/Ca(OH) ₂	Clay	690, 780	a,b,c,d
462 (see SM)	Calcium oxide/hydroxide		CaO/Ca(OH) ₂	Clay	690, 780	all points
	Hematite		Fe ₂ O ₃	PigmentRed	224, 291, 407, 494, 610	i
464 (see SM)	Calcium oxide/hydroxide		CaO/Ca(OH) ₂	Clay	690, 780	a,b,d,g
	Hematite		Fe ₂ O ₃	Clay	224, 291, 407, 494, 610	a,b,d,g,e,f
	Calcite		CaCO ₃	PigmentWhite	283, 1087	c
466 (see SM)	Calcium oxide/hydroxide		CaO/Ca(OH) ₂	Clay	690, 780	a,b,c,d

In different points, the Raman analysis reveals the presence of various pigments or compounds as here briefly listed:

- *White pigments*: the Raman spectra, presenting a main intense band at 975 cm^{-1} , with other less intense peaks at 430 and 1054 cm^{-1} , fits with the Raman spectra of beta wollastonite [19, 20] and with Calcium phosphate [21]. Beta wollastonite is a very common calcium silicate of clay in potteries [19], however, the peaks at 975 , 430 and 1054 cm^{-1} have been found only in spectra collected into some signs and not in the spectra acquired from the surface. This fact indicates that the compound is related to engraving procedure and it is not included in the clay. In addition the Si-O-Si bending mode at $600\text{--}650\text{ cm}^{-1}$ [19, 20] is absent in the experimental spectra. On the other hand, the main peak of Calcium phosphate is shifted through the lower wavenumber in the literature spectra (965 cm^{-1}). This variation can be due to impurities in the samples that affect the spectral position of the PO vibration mode and to resolution limit of the instrument. This pigment was found in the second row of column 2 (side A). Other Raman bands in the spectra could be associated to the presence of titanium oxide in both the Anatase (the intense band at 145 cm^{-1}) and Rutile (the bands in the $250\text{--}650\text{ cm}^{-1}$ region) phases [22]. It is worth noting that TiO_2 was not spread all over the clay but within the engraving sign in the E point. Finally, Raman spectra collected in the point F (second row col. 2–side A) revealed the presence of Lead carbonate in the cerussite phase (intense band at 1053 cm^{-1} and medium at 830 cm^{-1}), also known as Lead White pigment [23].
- *Yellow pigment*: the vibrational bands at 355 and 844 cm^{-1} identify the mineral Crocoite, often associated to the Chrome Yellow pigment [24]. This pigment was detected in the second row of column 1 (side A), especially in the sign “dingir”. The presence of Chromium yellow pigment is unusual for that period whilst it was largely diffused as a synthetic material in the 19th century for tablet reading purposes. However, the contamination of the samples can be excluded as a first instance. The museum archives assure that the samples were taken from the excavation site and moved without any other management directly to the museum. Moreover, in a consolidated practice, artifacts due to the use of colored chalk to facilitate the reading of the inscriptions could be detected also in other signs and/or samples, and it is not the case. In the same spot the Raman features of quartz powders were also detected (see below).
- *Red pigment*: traces of hematite pigment (Raman bands at 224 , 291 , 407 , 494 , 610 cm^{-1}) [25] localized in a point on the surface (not an engraving sign) was revealed (point K).
- *Quartz microcrystals*: in a vast area of the second row (col. 2) and in the right part of the second row (col. 1) mixed to the yellow pigment (see above), the presence of quartz micro-crystals encapsulated on the surface was revealed.

Raman spectra show the typical bands at 206 cm^{-1} and 463 cm^{-1} (strong) associated to SiO_2 -quartz [26]. In some spectra (a and k) the presence of the band at 510 cm^{-1} (very weak) indicates a more disordered silica, leading us to consider the chalcedony or flint phase [26]. In the column 2, the silica crystals appear as encapsulated in the clay (not in the depth of the sign), suggesting that this material was applied above the surface when the clay was still hydrated and fresh, after the carving procedure.

3.3. Tablet 1924-465

This tablet presents written text only in one side (see Fig. 3) divided in two columns composed by 7 and 1 rows (column 1 and column 2, respectively). For this tablet the transliteration process is completed and reported in Table 2.

It represents an administrative account book in which different amount of products are assigned to some people and registered in the tablet. Englund explained exhaustively the administrative management and registration in cuneiform tablets [27]. It is well known that the administrative tablets were divided in different sections, in order to have a sort of account balance of the products. We checked the presence of pigments possibly applied with the purpose to emphasize some parts of the text.

Fig. 3 shows the carved sides of the tablet 465 and the representative points where Raman spectra were collected. As compared to the previous tablet, the clay shows a diffuse presence of calcite (or vaterite) in addition to the calcium oxide/hydroxide previously commented. In different points, the Raman analysis reveals the presence of an orange/red compound and the one of quartz microcrystals:

- Orange pigment (Fig. 3 point D): the raman spectra reveals a compound with intense Raman bands at 125 cm^{-1} (strong), 197 cm^{-1} , 228 cm^{-1} (strong), 263 cm^{-1} , 410 cm^{-1} , 1007 cm^{-1} . The vibrational spectrum could be assigned to the combination of lead stannate Pb_2SnO_4 (bands at 125 and 197 cm^{-1} [28]), cuprite Cu_2O (bands at 228 , 410 cm^{-1} [29]; the band at 630 cm^{-1} is not clearly identified because of the intense broad band of Calcium Hydroxide) and calcium sulfate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (bands at 1007 and 1140 cm^{-1} [30]). The presence of lead pyrochlore solid solution (Naples Yellow) as well hematite cannot be totally excluded due to the overlapping the related Raman bands at 125 cm^{-1} and 228 cm^{-1} [31] and 228 and 410 cm^{-1} peaks, respectively. The resulting orange pigment is obtained by mixing Lead Tin Yellow (Pb_2SnO_4 – Yellow), Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – White) and Cuprite (Cu_2O – Red) [32]. The pigment was detected on the row 5 (col.1) both in the engraving signs and the administrative division line.
- Quartz microcrystals (Fig. 3 points A and B): a small presence of quartz (206 cm^{-1} and 463 cm^{-1} bands) was revealed in the second row (col. 1).

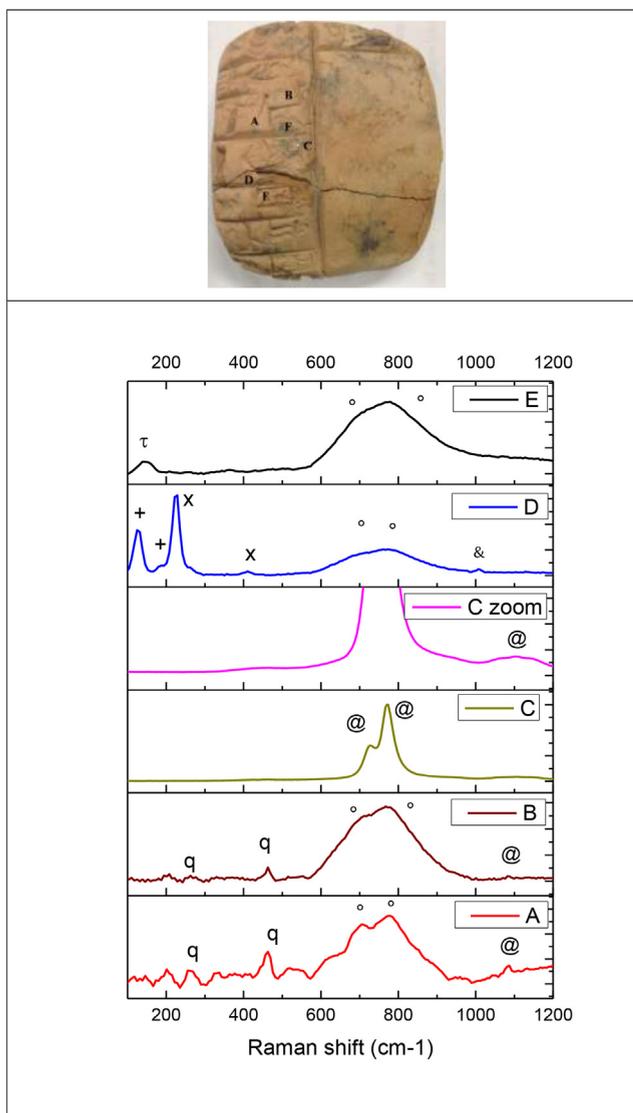


Fig. 3. Tablet 1924–465 (only written side) and collected Raman spectra in representative points (q = Quartz; τ = Titanium Oxide; $^{\circ}$ = Calcium oxide/hydroxide; + = Lead Stannate; X = Cuprite; @ = Vaterite; & = Gypsum).

4. Discussion

The presentation of experimental data clearly indicates that pigments were applied on written Sumerian tablets. Besides the classical pigments already known in this historical period to ornate decorative potteries or grave goods, such as Hematite, Gypsum, Calcium phosphate [7, 33], the presence of lead based compounds appears quite significant. Indeed, we found Crocoite (PbCrO_4), Cerussite (PbCO_3), Lead stannate (Pb_2SnO_4) pigments, which arises the question about the knowledge of lead based compounds in the ancient Mesopotamia.

Table 2. The transliteration process for Tablet 1924–465.

Column 1	Column 2
1. 7(barig@c) zi ₃	1. 1(asz@c) x x x
2. lugal-a ₂ -mah	blank space
3. 1(barig@c) har-tu	
4. 3(asz@c) lGA ₂ xHAL	
5. x-sag	
6. 3(asz@c) lGA ₂ xHAL	
7. me-x-su#-x	

The use of lead antimonate (Pb(SbO₃)₂) was previously ascertained; its related mineral pigment, bindheimite, dates back to the 16th century BC, and, although quite rare, it was used as a pigment [34]. In addition, many historical sources confirm the use of Lead (galena, argentiferous lead ores, antimonates etc.) in the ancient Mesopotamia [33]. Anatolia was the primary source of the lead minerals, other possible sources being Syria and Iran. Famous is the use of raw materials from Elam (Iran) to produce cosmetic kohl, imported as antimonates [33].

Cerussite (lead carbonate) is an important, widely distributed secondary ore mineral of lead formed by the action of carbonated waters on galena [33].

The use of Crocoite in ancient Mesopotamia is here reported for the first time, to the best of our knowledge. However, the application of this mineral as yellow pigment was found, for example, in precious funerary relics belonging to Egypt (1600 BC) [35, 36]. Moreover the use of Lead- based minerals as pigments, especially Lead Chromate, has been conducted during the centuries (Crocoite and Mimetite – Palmyra 200 BC [37]; Crocoite – North Bohemia 1300 BC [24]; Crocoite, Lead Tin yellow, Lead antimonate – Renaissance [38]) until the modern age when the synthetic production was developed [32]. The evidences here reported indicate that Sumerian people did know lead based mineral compounds and used them to colour their clay tablets. The micro-Raman analysis also allows us to elucidate how the pigments were applied and to exclude external successive origin, such as post-excavation restoration. Indeed, we sampled the tablets all around the mapped spots and we recovered the presence of the pigments in most cases in the engraving signs. In a few cases, the pigments were detected on the surface of the tablets. Thus, we may argue that the pigments were applied when the tablets were hydrated and still soft, during the engraving procedure. A hypothetic successive restoration, eventually carried out with colored pigment, could be excluded for three reasons. First reason, the pigment unlikely could fill the sign in the depth and would be detected all over the surface. Second, a superficial coating

with an external pigment, applied *a posteriori*, would cover completely the quartz microcrystals detected on the clay surface (see tablet 1924.468). Finally, it would be quite difficult to explain the use of different pigments in different spots of the tablets. All these arguments support the idea that the tablets, or at least a few parts of them, were colored by the Sumerian scribes. The Fig. 4 reports a reconstruction of the two tablets to show how they should appear on the basis of the detected pigment.

At this point, the question is “why” the tablets were colored. We can only speculate that the colors were applied to put in evidence some words or some parts of the tablets. It is known, for example, the presence of red dots in cuneiform tablets with the purpose to highlight an entire row, especially when the mentioned dots were found in administrative tablets containing a list. In other cases these dots are used for identify the boundaries between minimal metrical units in poems [39, 40]. It was reported that other administrative cuneiform tablet dated in the Ur III period were structured with divisions: debit sections (previous debit, increased debit and total debit), credit sections (milling, agricultural work, bala work, offtime, total) and balance (new debit) [27]. If a similar division was applied in the analyzed tablet, the color could be used to put emphasis on the in the tablet. Indeed, in the administrative tablet we analyzed, we found that the entire row separating the list of credits and debts from the resulting sum was decorated with red pigment, as to better separate the two parts of the tablet or to put in evidence the results of the administrative registration.

As concerns the literary tablet, we found four pigments in different regions, red, white, white and yellow both with added microcrystal of quartz. The most

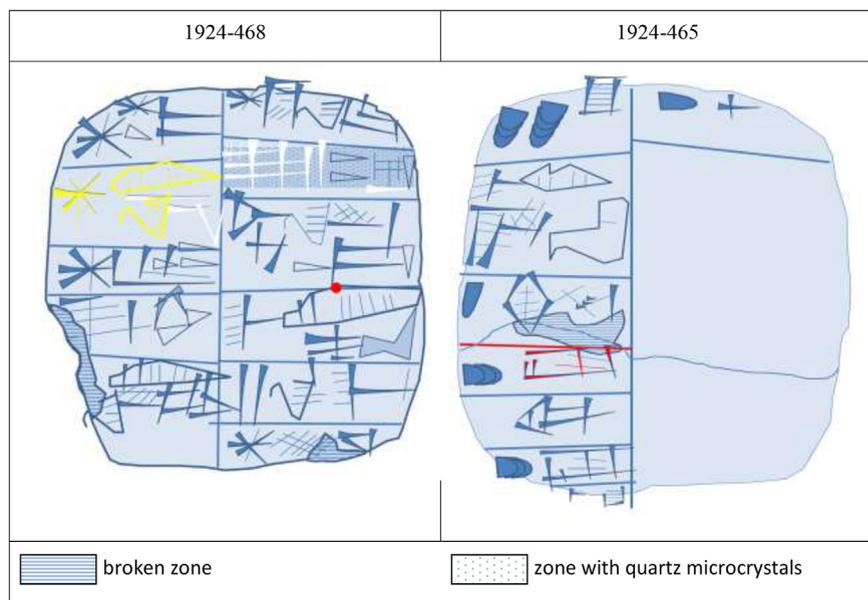


Fig. 4. Proposal of coloured rendering of the tablet 1924–468 and 1924–465.

impressive one is the yellow pigment with quartz microcrystals we detected in the “DINGIR” logograph, used to indicate a deity. The compound recalls for both color and gleam the features of gold, the precious metal always associated to gods and kings. We do not know why this specific deity is signaled with the yellow pigment among the gods present in this tablet, we could not exclude that some other deity had the same colored sign perhaps lost during time. We can only argue that this particular god deserved to be evidenced among the others, and the selected color is the color of deity. This last consideration, together with the presence of the brilliant quartz crystals, suggest a final conjecture regarding the different colors. We hypothesize that they were applied for different purposes of emphasis, in a scale of increasing highlighting from plain text (no emphasis) to red, white, brilliant white and brilliant yellow (maximum emphasis).

5. Conclusions

In this paper, we reported the analysis by micro Raman spectroscopy of Sumerian cuneiform tables of the collection of the Ashmolean Museum (Oxford University), aiming to ascertain the presence of ancient pigments. We identified in two specific tablets (one literary and one administrative) three different colors, red, white and yellow, in some cases (white and yellow) mixed to brilliant quartz microcrystals. The colors were discovered both in the depth of some specific engraving sign and on the surface of a selected part of the tablet. In the literary tablet the brilliant yellow compound was detected in one sign, *dingir*, a logograph associated to identify a deity. The other colors were detected in different zones of the tablets, but the meaning is not clear since the transliteration is not completed. In the administrative tablet, an orange color (composed by yellow, red and white pigment) was found in the row traced to separate the list of debts and credits from the results. Besides of the meaning, the main result is that colors were applied by Sumerian scribes to decorate cuneiform tablets. In addition, the detected mineral pigments indicate that Sumerian people did know lead based colors and were able to obtain lead containing minerals to produce their color. As regards the use of the colors, we hypothesize that the pigments allowed to put emphasis on specific words or zones of the tablets, applying different colors according to the degree of stress the scribe was looking for. Thus, Sumerian people should be given credit of the invention of a new editorial style, to overcome the binary logic of the engraving process and catch the eye of the reader by marking specific signs.

Declarations

Author contribution statement

Daniele Chiriu, Pier Carlo Ricci, Carlo Maria Carbonaro, Davide Nadali, Andrea Polcaro, Paul Collins: Conceived and designed the experiments; Performed the

experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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