Analysis of Roman Era archaeological finds from Museo Territoriale del Lago di Bolsena with non-destructive investigation techniques

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Abstract – **The management of the Museo Territoriale del Lago di Bolsena has made various types of archaeological finds available for non-destructive and non-invasive analysis using advanced techniques. The finds date from the Roman period and were collected during the excavation campaigns of the French School in the archaeological area of Poggio Moscini in the town of Bolsena (Viterbo) between 1962 and 1973. The finds on which the analyses focused are: metallic handles, pots and mosaic tiles. The techniques used to carry out this archaeometric study are based on X-ray diffraction (XRD). In addition, Raman and Fourier-Transform IR (FTIR) spectroscopies in the reflection mode have been considered for the characterisation of the finds. The content of this paper is part of the research activity of the project REMEDIAVI (Ricostruzione virtuale ed in realtà aumentata di Volsinii Novi: un approccio avanzato per la fruibilità sostenibile dell'area archeologica di Bolsena).**

I. INTRODUCTION

Archaeometry, also known as "archaeological science", is a discipline that combines knowledge from different fields, i.e. materials science, chemistry and archaeology. The aim of this discipline is to uncover the history of archaeological remains and artefacts through sophisticated laboratory analysis [1]. Using various techniques, it is possible to obtain chemical, physical and morphological information about the artefacts under study, which can reveal new information about the history of the products, such as the production processes used at the time and their historical evolution. The possibility of using non-destructive techniques allows the characterization and study of products and finds without

damaging the samples, and it's a crucial requirement in archaeometry for the high historical value of each sample [2].

The aim of this paper is to present an archaeometric study of different archaeological artefacts from the Roman period (approximately between the 2nd century BC and the 3rd century AD), which were found in the archaeological area of Poggio Moscini in Bolsena and are currently exposed in the Museo Territoriale del Lago di Bolsena [3]. The samples were analyzed using various non-destructive techniques exploiting XRD, Raman and FTIR spectroscopies. In the context of cultural heritage, the use of non-destructive techniques is fundamental to allow further study of archaeological finds without altering their chemical-physical integrity. Furthermore, the importance of using non-invasive techniques is based on the fact that the artefacts will be preserved for future generations. Among the various archaeological finds made available by the Museum's management that have undergone analytical testing are metallic handles, probably from an ancient pot, amphora fragments, fine Roman tableware (Sigillata Italica) and mosaic tiles.

The combination of all these analytical techniques makes it possible to obtain information on the constituent materials of the finds. The aim is to identify the production materials, their origin and to deduce the degradation processes to which the artefacts were subjected over time, in an attempt to increase our knowledge of the civilization of that period [4].

II. MATERIALS AND METHODS

A. Archaeological finds

In the present study, a fragment of an ancient amphora with a red inscription was analyzed to identify the pigment (Fig. 1a). Fig. 1b refers to a handle made of metallic material, probably belonging to an ancient pot. Both artefacts were analyzed by Raman spectroscopy. Another interesting sample is a fragment of the so-called "Sigillata Italica" (Fig. 1c), a type of pottery used as tableware in Roman times. A typical feature of this type of pottery, apart from its typical reddish color, is the presence of relief stamps, also known as "sigilli" (from which the pottery takes its name), which indicate the name of the maker or the place of origin. In addition to the handle shown in Fig. 1b, another similar handle was analyzed by Raman and FTIR (Fig. 1d). Fig. 1e shows part of a mosaic of black and white tiles on a cement base. The sample in Figures 1c and 1e has been subjected to XRD analysis, supplemented by FTIR spectroscopy.
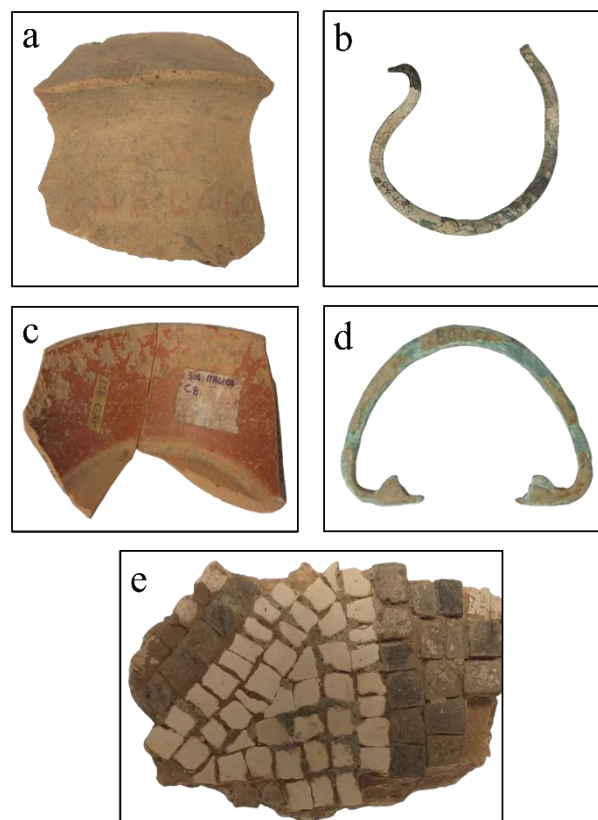

Fig. 1. (a) Fragment of an ancient amphora with a red inscription; (b, d) handles of metallic material, probably belonging to an ancient pot; (c) "Sigillata Italica", a type of pottery used in Roman times as tableware with a characteristic red color; (e) part of a mosaic with black and white tiles.

B. Experimental Setup

Raman spectroscopy

For the Raman analyses, spectra were collected using an inViaTM confocal Raman spectrometer (Renishaw) with a 250 mm focal length. The archaeological finds were analyzed at room temperature and the signal was scattered by an 1800 l/mm holographic grating and collected by a Peltier-cooled CCD detector. The excitation line at 532.1 nm was generated by a Nd:YAG diode-pumped continuous wave solid-state laser (Renishaw) and focused on the sample using a series of 20x, 50x and 100x close-up objectives and a 5x long-distance objective (all Leica Microsystems).
In another setup for Raman analysis, a LabRAM HR Evolution confocal Raman microscope (laser wavelength 633 nm) was used.

FTIR spectroscopy

In this study, FTIR spectroscopy was performed using a Bruker Optics - IFS 66v/S Vacuum FT-IR. The

instrument was combined with a Hyperion 200 IR microscope with 15x objective and used in reflection mode. For each spectrum, 128 scans were acquired with a resolution of 4 cm^{-1} in the range 400 to 6000 cm^{-1}. A gold plate was used as a reference to compensate for possible spectral interferences (water vapor, CO_2). The reflection spectra obtained were processed using the following equation:

$$Abs = -\log\frac{Refl}{R_0} = \log\frac{1}{R} \qquad (1)$$

Where Abs is a quantity proportional to the absorbance, Refl is the reflectance of the sample and R_0 is the reflectance of the gold reference.

X-ray diffraction (XRD)

For XRD analysis, it was used a Bruker D8 ADVANCE. Samples were investigated in various 2Θ range according with the nature of the samples with a size step of 0.0205°/step and molybdenum Kα radiation (0.71 Å) with voltage 45kV and current 35mA. The analyzed samples are: Sigillata Italica, dd3_a_white (white piece of mosaic) and dd3_a_black (black piece of mosaic).

III. RESULTS

Raman spectroscopy

Raman analyses were carried out on three samples: a fragment of an ancient amphora with a red inscription (Fig.1a) and two handles of metallic material (Fig.1b and 1d). For the sample in Fig.1a, the analyzes were carried out with a 532 nm wavelength laser on the inscription in order to determine the chemical composition of the letters painted on the amphora. Among the results obtained from this analysis, one of the spectra (Fig. 2) shows the bands at 144.1 cm^{-1}, 446 cm^{-1} and 611 cm^{-1}, which seem to be the characteristics of rutile, i.e. a mineral composed mainly of titanium dioxide (TiO_2) with a tetragonal crystal structure. The peaks mentioned could correspond to lattice vibrations, Ti-O stretching modes or other vibrations in rutile and such high band intensities are probably influenced by the high cross sectional structure of rutile [5]. However, considering the bands mentioned together with those at 228.2 cm^{-1}, 291.7 cm^{-1} and the most intense band at 1325 cm^{-1}, suggests the presence also of an iron oxide based compound (hematite, Fe_2O_3) with slightly modified bands, probably due to the use of high power lasers. Indeed, hematite presents these characteristic peaks and seems to be the main element characterising the red inscription analyzed [6].
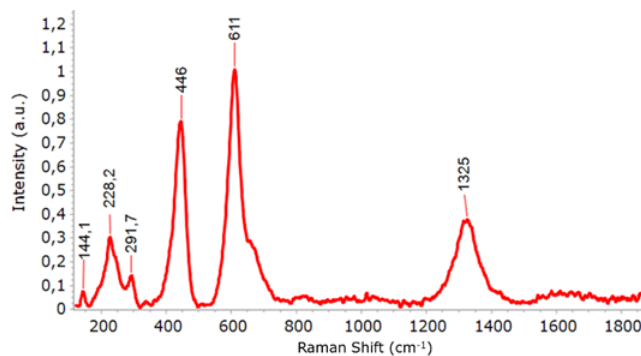

Fig. 2. Raman spectrum (532 nm) of the red inscription on an ancient amphora fragment that seems to show the typical bands of rutile and hematite.

Among the various results obtained from the different analyses of the red inscription, a very repeatable spectrum is the one shown in Fig. 3, which seems to describe characteristic peaks of an iron oxide earth pigment, the burnt sienna, which typically has a reddish-brown color and it is identifiable together with the peaks at 291.5 cm^{-1}, 410 cm^{-1}, 666 cm^{-1} and the one at 1323 cm^{-1}, overlapping the same Raman band as hematite [7]. Their detection is probably related to the presence of iron in the find or in the excavated ground.
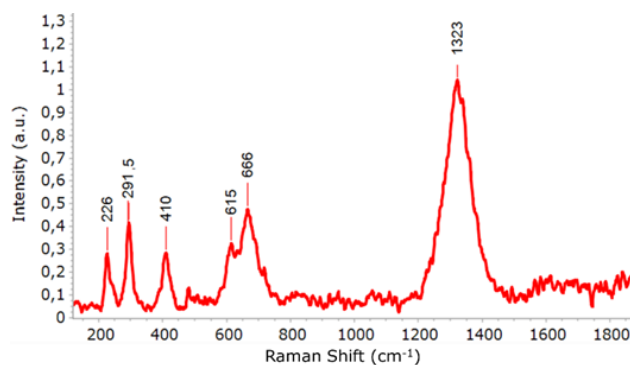

Fig. 3. Raman spectrum (532 nm) of the red inscription on an ancient amphora fragment that seems to show the typical bands of burnt sienna.

The second sample was also analyzed with a 532 nm laser wavelength and it was the handle of a metallic material, probably belonging to an ancient pot. A series of spectra were found that can be related to different phases associated with earthy residues and different types of metal oxides. Among these, the oxide compounds are presumably those of iron, in fact, as shown in Fig. 4, the characteristic bands at 219.2 cm^{-1}, 284.9 cm^{-1}, 398.3 cm^{-1}, 495.3 cm^{-1} and 1303 cm^{-1} seem again to be reminiscent of hematite Fe_2O_3 [6].

Furthermore, the addition of a broad band in the range 580-700 cm^{-1} with a peak at 655.9 cm^{-1} cannot be stated with certainty, but hypothetically it could derive from the contribution of the characteristic peaks of magnetite Fe_3O_4 [8] or maghemite γ-Fe_2O_3.

We cannot exclude the presence of iron sulphides, such as pyrrhotite, whose bands match those shown in Fig. 4 and could be part of the contribution in the detected bands.
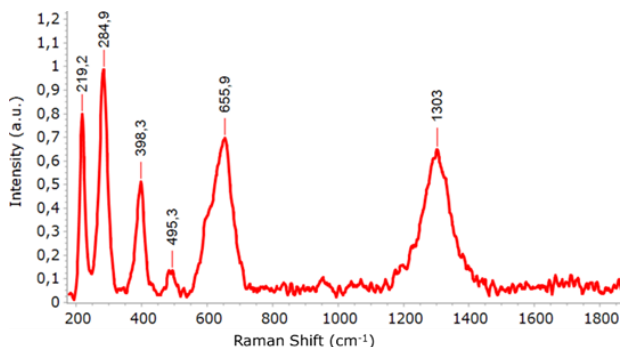

Fig. 4. Raman spectrum (532 nm) of a spot of the metallic handle that show the typical bands of hematite and magnetite.

Raman measurements with laser at 633 nm was also applied to the metallic handle in Fig. 1d, with the aim of characterizing the different patinas observable on its surface (Fig. 5). In the red area on the sample, Raman spectroscopy allowed the clear identification of cuprite Cu_2O through the observation of the characteristic bands at 94 cm^{-1}, 146 cm^{-1}, 189 cm^{-1} (shoulder), 199 cm^{-1}, 219 cm^{-1} and 631 cm^{-1}. On a brown-orange area, instead, the signals at 87 cm^{-1}, 247 cm^{-1}, 298 cm^{-1} and 387 cm^{-1} suggest the presence of goethite $FeOOH$, which could also come from iron contained in the object or from the excavation.
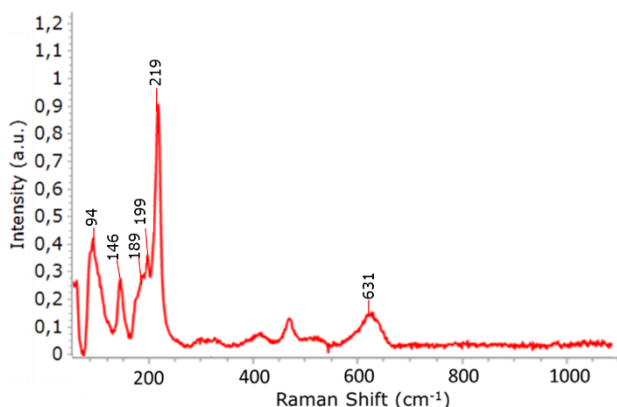

Fig. 5. Raman spectrum (633 nm) of a red area of the metallic handle that show the typical bands of cuprite and goethite.

FTIR spectroscopy

About the FTIR measurements performed on the metallic handle shown in Fig. 1d, it is important to mention that the obtained spectra (Fig. 6) show great reproducibility in correspondence of the area of the same color. In the green area, broad bands at around 745 cm^{-1}, 1115 cm^{-1}, 1150 cm^{-1}, 1400 cm^{-1} and 1650 cm^{-1} are present, while, in the red-brown areas, an evident Reststrahlen band at 615 cm^{-1}, along with another at 1400 cm^{-1}, is observable. In the yellowish parts, a band at 730 cm^{-1} is usually observable,

along with two Reststrahlen bands at around 910 cm^{-1} and 1040 cm^{-1} and two further bands at 1670 cm^{-1} and 3525 cm^{-1}. The interpretation of these spectral data is quite complex.
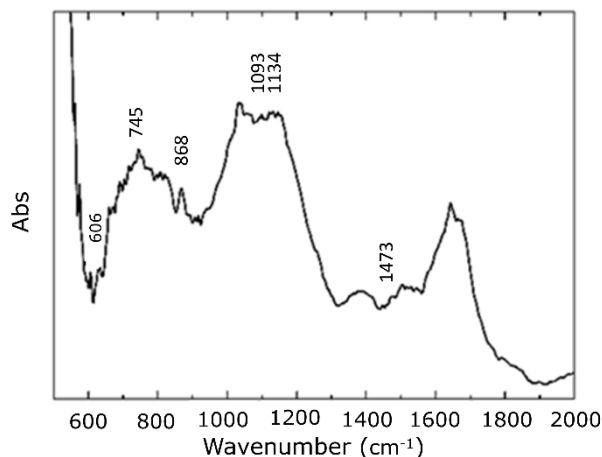

Fig. 6. FTIR spectrum of a metallic handle.

The presence of the bands at 1650-1670 cm^{-1} and 3525 cm^{-1} could be probably attributed to the presence of sulfates, while the Reststrahlen bands at around 910 cm^{-1} and 1040 cm^{-1} could be indicative of silicate materials. Some signals have a certain similarity in the general spectral pattern with those of brochantite: in particular, the signals at 606 cm^{-1}, 745 cm^{-1}, 868 cm^{-1}, 1093 cm^{-1}, 1134 cm^{-1} and at 1473 cm^{-1} are reported in the literature and assigned to this compound (even if in the spectra some bands are broad and no Kramers-Kronig transformation was applied, on the contrary of some studies) [9,10]. Finally, the Reststrahlen band at 615 cm^{-1} is attributable to cuprite.

Regarding the mosaic sample shown in Fig. 1e, two tiles of different color (white and black) were analyzed. Two points were analyzed for each sample. Of these acquired spectra, the spectrum obtained from the white tile is the most significant and is shown in Fig. 7.
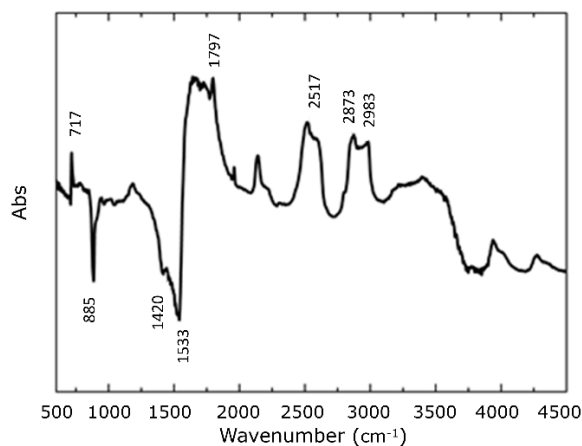

Fig. 7. FTIR reflectance spectrum on a white mosaic tile, where the typical wavenumbers of $CaCO_3$ are highlighted.

For the white tile, the acquired spectrum showed a signal with a maximum at 717 cm^{-1} and a Reststrahlen band with a minimum at 885 cm^{-1}, followed by a second band of the same type with two minima at 1419 cm^{-1} and 1529 cm^{-1}. A set of peaks at 1799 cm^{-1} and 1958 cm^{-1} are observable, followed by a signal at 2141 cm^{-1} with a shoulder at about 2210 cm^{-1} and another peak at 2515 cm^{-1} with a shoulder at 2590 cm^{-1}. Finally, signals at 2875 cm^{-1}, 2983 cm^{-1} and at higher wavenumbers bands: 3221 cm^{-1}, 3402 cm^{-1}, 3944 cm^{-1}, 4014 cm^{-1} (shoulder), 4279 cm^{-1} and 4360 cm^{-1} (shoulder) cm^{-1} are visible. Several of these signals are attributable to the presence of calcium carbonate (in-plane bending at 717 cm^{-1}, out-of-plane bending at 885 cm^{-1}, asymmetric stretching at 1420 cm^{-1} and 1529 cm^{-1}, combination bands at 1799 cm^{-1}, 2515 cm^{-1}, 2590 cm^{-1}, 2875 and 2983 cm^{-1}). The presence of sulfates can be hypothesized from the signals at 2141 cm^{-1} and 2210 cm^{-1}. In particular, the greatest similarities are found with a calcium sulfate compound, such as bassanite, although further analyses are necessary to be able to discriminate the specific mineral.

The spectrum acquired for the black tile (not shown) presents in all points a minimum of Reststrahlen is observed at 1057 cm^{-1}, attributable to the silicate matrix. The characteristic signals of the water are then found at about 1635 cm^{-1} and 3450 cm^{-1} (these signals are more evident and more intense in the black sample with respect to the white one). Furthermore, in the case of the black tile, a low intensity signal is observed at 2510 cm^{-1}, attributable to the calcium carbonate.

In the case of Sigillata Italica, four points were analysed, two on each side. The composition is very similar for the different points and the most significant spectrum is shown in Fig. 8.
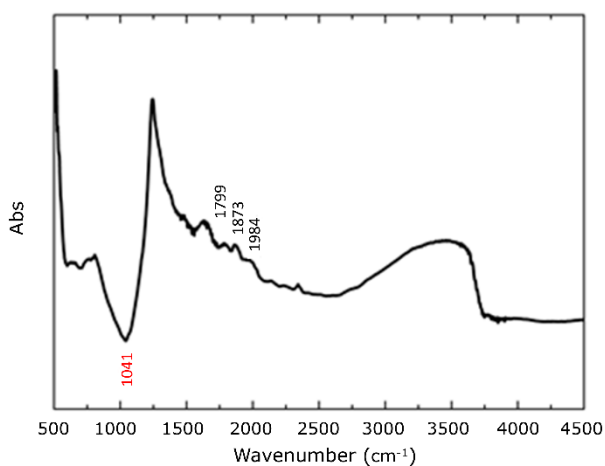

Fig. 8. FTIR reflectance spectrum on Sigillata Italica, where the typical wavenumbers of allumosilicate (red) and silicate (black) are highlighted.

A minimum of Reststrahlen is identified at 1041 cm^{-1}, with a shoulder at about 1072 cm^{-1}, indicative of the aluminosilicate matrix. The presence of quartz is

detectable by the combination and overtone bands of the silica at about 1799 cm^{-1}, 1873 cm^{-1}, 1984 cm^{-1}, 2240 cm^{-1} and 2320 cm^{-1}. The water signals are also observable at approximately 1610 cm^{-1} and 3450 cm^{-1} for two points on the same side. On the opposite side of the Sigillata the water signals are slightly shifted at 1640 cm^{-1} and 3480 cm^{-1}. For one of these points, moreover, two bands are observed at about 3250 cm^{-1} and 3475 cm^{-1}: these are indicative of a certain quantity of water in liquid form. In the spectrum detected for this point, a series of weak signals at approximately 2850 cm^{-1}, 2920 cm^{-1} and 2960 cm^{-1} suggests the presence of organic material. However, the organic material cannot be specifically identified since these signals are indicative of generic C-H stretching typical of aliphatic compounds.

X-ray diffraction (XRD)

Sigillata Italica sample is a piece of pottery. As a such it is expected to be composed mainly by silicates, feldspars, quartz and iron oxides like hematite. The latter imparts the characteristic red color, as shown in the insert of Fig. 9. The peak assignment is also shown in Fig. 9 and the predominant signal is attributed to quartz, although they are also visible silicates and feldspar signals.
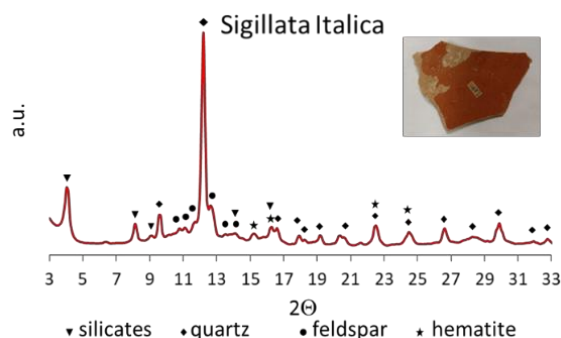

Fig. 9. XRD spectrum of Sigillata Italica sample with the inset showing a picture of the sample.

It is not possible to discriminate the exact species of silicates or feldspars present in the sample just with XRD analysis, since there are many peaks that can be assigned to different compounds, and the complexity of the sample does not allow a further global comprehension.

Tile dd3_a (white tile) sample is taken from the same mosaic. As shown in Fig. 10a, the dd3_a_white sample shows a clear calcareous nature with all peaks assigned to the signals of calcite, which is the most stable polymorph of calcium carbonate.
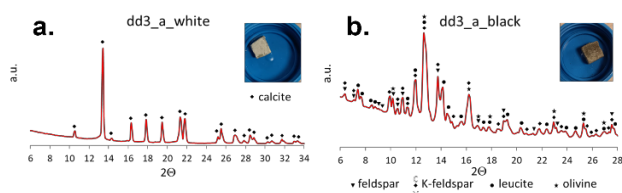
Fig. 10. (a) XRD spectra of dd3_a_white sample and (b) of dd3_a_black sample with insert showing the picture of the tiles.

In Fig. 10b dd3_a_black sample shows a composite nature of both feldspars and potassium-rich feldspars, but also leucite and olivine are present. This composition and the appearance of the sample suggest an igneous nature that could be ascribed to the volcanic activity of Volsinii mounts during Middle Pleistocene. Geological data on the examined region can be found at the web page of Regione Lazio [11].

IV.   CONCLUSIONS

In the field of artistic and cultural heritage conservation, it is highly important to have investigative techniques that do not damage or alter artistic artefacts. Through these techniques, it has been possible to characterize artefacts on a chemical and structural level, understanding part of their manufacture and constituent materials for a set of artefacts found in the archaeological area of Poggio Moscini.
Further research is planned to gain an even more comprehensive overview with additional non-destructive investigation techniques, e.g. X-ray tomography and X-ray fluorescence (XRF), which will allow us to study artefacts both at the level of three-dimensional structure, with 3D reconstruction, and at the chemical level, with elemental analysis.

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