

Raman spectroscopy analysis of Palaeolithic industry from Guadalteba terrace river, Campillos (Guadalteba county, Southern of Iberian Peninsula)[†]

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A representative set of eight lithic tools suitably selected among the very rich Palaeolithic industry collected over the past years in different archaeological sites of the Guadalteba County (Málaga, Spain) has been nondestructively investigated by means of Raman spectroscopy using both portable and benchtop Raman spectrometers. This article reports on the first archaeometric Raman analysis of these archaeological samples with the scope of checking if these readily available, nondestructive, fast and cheap vibrational spectroscopic techniques, which in addition do not require a preliminary sample preparation, could provide any meaningful information for characterizing the mineral composition of chert artefacts and ultimately some specific arguments about their assignment to distinctive groups of raw materials of a particular provenance. On the basis of the vibrational data, it was confirmed that α -quartz was the raw material in all the cases, although a small amount of moganite was also evidenced as a distinctive fingerprint in these chert samples. On the other hand, crusts were mainly made of calcite in all the cases, sometimes accompanied by other minerals such as barite or anatase. This first Raman spectroscopic study on chert and sandstone artefacts from the Guadalteba county reveals that there are good premises for a further and more thorough archaeometric investigation of these lithic tools based on sets of Raman measurements (Raman mapping) on each specimen rather than on single-point Raman experiments such as in the present case, given the wide macroscopic heterogeneity of this kind of samples (colour, grain size, transparency, etc.). The Raman-mapping archaeometric analyses of bulks and crusts would be also complemented with X-ray diffraction and X-ray fluorescence data. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: Raman microscopy; portable Raman spectrometer; archaeometry; lithic tools

Introduction

An abundant human occupation existed in the low terraces of the Guadalteba River (Málaga, Spain), which show a continuous chronologic sequence of human occupation extending from the Middle Pleistocene to the Middle Ages. The present work

is related to the intensive field work developed over the past 10 years in various archaeological sites of this territory promoted by the 'Guadalteba County Consortium' through the 'Escuela Taller de Peñarrubia' for assessing the very rich archaeological heritage of this Andalusian area (Fig. 1); field works mainly consisted in the cleaning and collection of

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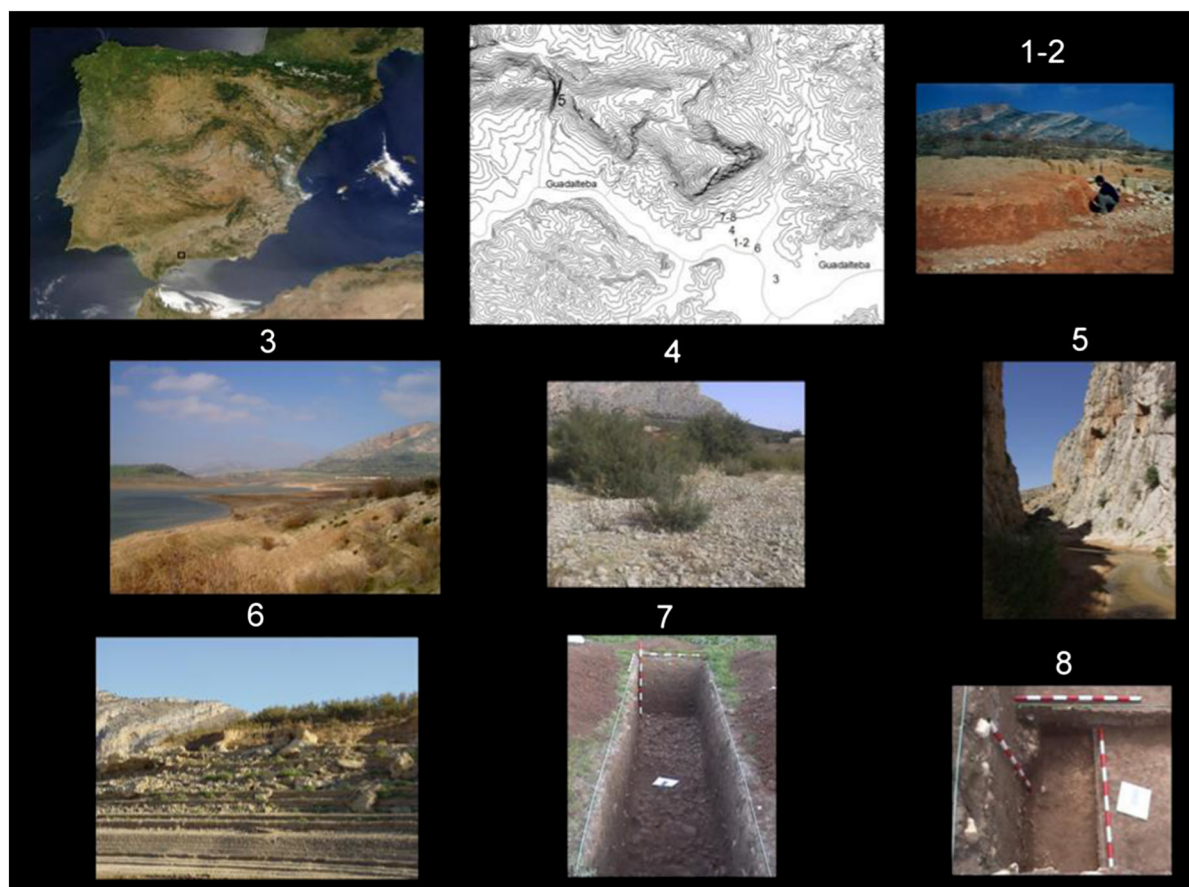


Figure 1. (a) Geographic setting of the Guadalteba County (Málaga, Spain). (b) Location maps and photographs of the different archaeological sites of finding of the eight lithic tools subject of Raman study: (1–2) 6th terrace of the Guadalteba River (specimens TP-TP6-S-395-09 and TP6A1-Niv-006-01); (3) left terrace of the Guadalteba River (specimen TG-S-008-03); (4) TP4 level of the terraces of the Guadalteba River (specimen TP-TP4-S-PL-007-11); (5) karst complex of 'Las Palomas Cave' in Teba, as viewed from La Venta River, in a place known as 'Tajo del Molino' (specimen CP-LZ17-1-004-09); (6) terraces near the confluences of the Guadalhorce, Guadalteba and Turón rivers (specimen EP-C7-S-1792-02); (7–8) excavations works in TP1 zone of 'Parque Guadalteba', in the nearby of the 'Escuela Taller de Peñarrubia' (specimens TP-APC-I13-3-074-01 and TP-APC-G8-4-006-00).

archaeological and faunal records within the karst site of 'Las Palomas' cave in Teba,^[1] works in the terraces of the low basin of the Guadalteba river and in a necropolis and a lithic production workshop rather close to the 'Escuela Taller de Peñarrubia'. These preliminary prospection and excavation works together with those performed in the 'Ardales cave' over the past 25 years has finally allowed for the recent approval in 2011 of a multidisciplinary research project by part of the Junta de Andalucía named 'The Guadalteba Project for Prehistory'. One of the main aims of such research project is the routinary use of modern archaeometric techniques, which may help the scientific investigation of the very rich archaeological heritage of the Guadalteba County in a nondestructive way.

Raman spectroscopy is a valuable technique for the easy and quick detection, without almost no sample manipulation, of organic and/or inorganic compounds or their mixtures in a wide range of areas of application, such as chemistry, archaeological, biological and geological sciences, pharmaceutical, forensic, and uses for medical diagnostics, or extraplanetary exploration, among others.^[2–11]

Nowadays, the trade-availability of many portable Raman spectrometers has allowed for on-field analyses in archaeological excavations, prehistoric caves, art museums, crime scenario, police stations, etc. However, the necessary miniaturization that compromises the instrumental characteristics and capabilities of any portable Raman spectrometer (in particular the spectral

resolution, spot-size, wavenumber region and laser power at the sample) could still allow for the successful identification of main components in simple mixtures, but could be detrimental for the unambiguous analysis of complex mixtures.^[9,12–15] On the other hand, the advantages of such portable Raman instruments have been actually proved in cases when samples cannot be easily moved to the laboratory such as the analysis of prehistoric pictographs, wall paintings in historical buildings, extraplanetary exploration and so on.^[15–19]

In this work, we analyse a number of lithic tools collected in the low terraces of the Guadalteba River (Fig. 1). These lithic tools comprise both unifaceted and multifaceted instruments showing colours from brown, yellowish, grey, black, white to pinkish. Almost all the specimens were also partially covered by a patina or crusts (Fig. 2).

We also survey the capabilities of three different Raman spectrometers: one of them a portable handheld instrument and the other two a benchtop micro-Raman system and a Fourier transform-Raman system. The results obtained when Raman spectra are recorded by means of a portable Raman spectrometer are of a particular significance for us in regards to the future *in situ* archaeometric studies related to the aforementioned 'The Guadalteba Project for Prehistory', provided that nowadays many miniaturized Raman instruments are commercially available but with different capabilities (laser excitation wavelength, laser power adjustable or not from 0 to full power,

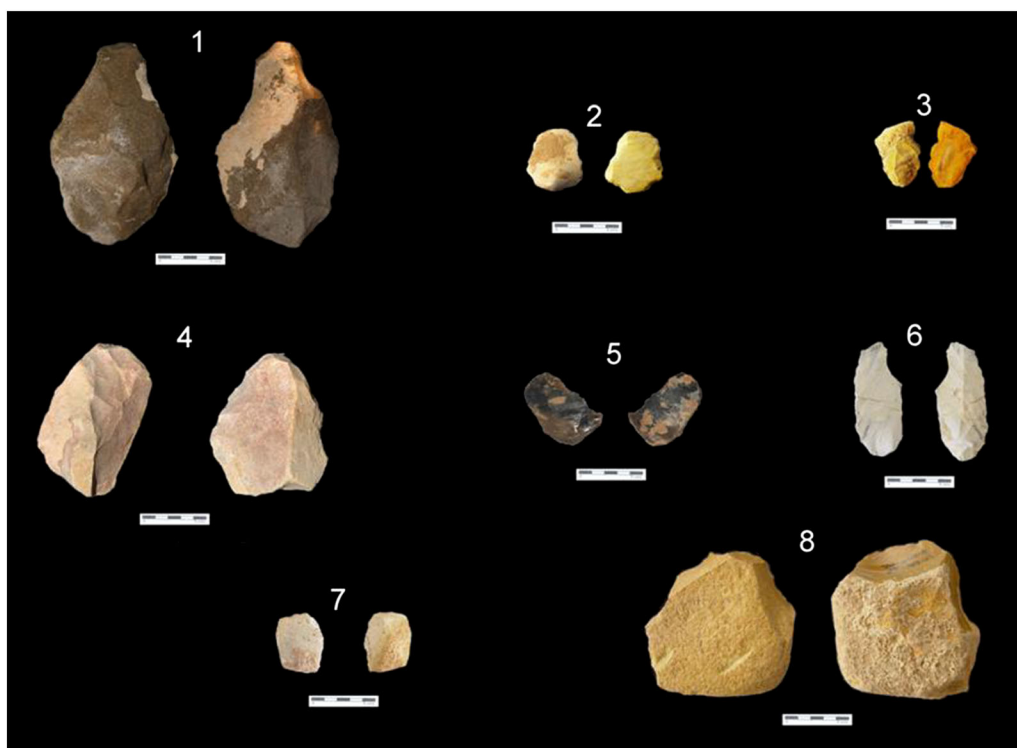


Figure 2. Photographs of the eight lithic tools subject of Raman analysis: (1) TP-TP6-S-395-09 (Acheulean Core-BN1G, Mode II); (2) TP6A1-Niv-006-01 (Denticulate-BN2G-D23nokp, Mode III); (3) TG-S-008-03, (Notch-BN2G-D21, Mode III); (4) TP-TP4-S-PL-007-11 (Bipolar Core-BN1G, Mode II); (5) CP-LZ17-1-004-09 (Internal Flake BP-I, Mode III); (6) EP-C7-S-1792-02 (Scraper on levallois flakes, BN2G-R21nokp, Mode III); (7) TP-APC-I13-3-074-01 (BP-I-Internal Flake, Mode II); (8) TP-APC-G8-4-006-00 (BN1G-Unipolar Core, Mode II). Lithic technology analysis of the roughing and retouched specimens are based on the models proposed by Carbonell *et al.* and Laplace, respectively.^[25,27]

optical and spatial resolutions, spectral coverage, availability or not of a rechargeable battery, etc), at the time that presumably many of the archaeological samples we must investigate, such as wall paintings in caves, could not be carried out to the laboratory.

Geographical setting of the Guadalteba County

The Guadalteba County, with an extension of 722 km², constitutes the natural path between Antequera Depression (at the East) and the Guadalquivir Depression (at the West). It is delimited at the South by a mountain chain (with an average height of 1200 m) crossing the province of Málaga from the Southwest to the East, which separates the inlands from the sea coast (Fig. 1). These lands are bordered on the Northwest and Northeast by the valleys of the Guadalquivir and Genil rivers, respectively, and irrigated by the Guadalhorce river and a number of other small streams that interconnect the Guadalteba County with the fertile and rich lowland areas of Antequera and Campillos. The drainage network is mainly represented by the Guadalhorce River and its two tributaries at the right side, Turón and Guadalteba rivers, which flow into it from the nearby reservoirs that supply water to Málaga City.

Geological, geomorphological and historical context

We study here eight lithic tools collected in various archaeological sites through seven different sequential levels of the Quaternary

terraces of the Guadalteba River, with a height distribution as follows: +80, +80–60, +40–35, +30, +20, +15–7, and +3–2 m. Of them, the first two levels belong to the Early Pleistocene; the next two to the Middle Pleistocene; the following two to the Late Pleistocene, and the last one to the Holocene. The archaeological sites under study are also close to the limestones of the Sierra de Peñarubia,^[20] and to outcrops of quartz-rich sedimentary formations, such as the Numidic or Aljibe sandstones.^[21] The provenance of all lithic specimens must be related with local or regional sources of raw materials, such as the Subbetic mountains and inner zones of the Betic mountain chain in the case of flints and radiolarites,^[22–24] or with Tertiary siliceous materials such as Aljibe sandstones. All raw materials may also occur as pebbles in the Quaternary terraces of the Guadalteba River.

Over the past 10 years, around 70 000 lithic tools have been found during the systematic and exhaustive stratigraphic study of the low terraces of the Guadalteba River, and among them there exist several specimens attributed to the Acheulean industry (cores, flakes, bifaces and retouched products),^[25–27] which were also documented as belonging to Mode II - Old Iberia Acheulean and Plenum Iberian Acheulean.^[28–31] There are also many stone tools of Mode III-Mousterian technology (cores, levallois flakes, and among the retouched products: scrapers, notches and points). The huge number of stone tools and other archaeological findings already found in these privileged lands (such as human bones, wall paintings and engravings in caves, stone lamps and some remains of fire-linked activities and so on) are indicative of an abundant and continuous occupation of this territory by Preneanderthal hunter-gatherer societies and Neanderthals, who lived in the middle and high Guadalhorce River, hunting large mammals.

Experimental

Samples

For this first Raman spectroscopic analysis of the lithic industry from Guadalteba, we suitably selected eight different tools of which six samples were made of various types of coloured flints, whereas the other two specimens were made of a compacted or silicified sandstone/quartzite and an oolitic siliceous rock. The bulk colours of the different samples ranged from white, grey, black, reddish, brown, beige to greenish; while crusts were, mainly, white, beige, orange, brown and reddish in some areas. The selection of these eight lithic tools was aimed at analysing to what extent their variable colouration could affect the quality of the Raman spectral information, thus allowing or not for their full mineralogical characterization. We understand that this aspect is of a prime importance to conveniently choose a portable Raman spectrometer suited enough for *in situ* studies of this type of archaeological findings.

Photographs of the eight lithic tools subject of Raman analysis together with their archaeological notation (according to their stratigraphic records of finding) and of the different archaeological sites where they were found are provided in Figs 1 and 2.

Instrumentation

Both, lithic instruments and patinas were analysed using a portable Delta-Nu Inspector Raman spectrometer of 2.3 kg weight, working with a 785 nm wavelength diode laser. Infield Raman spectra were achieved by means of a Nuscope microscope attachment, with 100× magnification. Samples were placed on a manually mobile platine and no optical fibre was used. In all the cases the laser power was kept as low as possible (it ranged from very low, low to medium intensity, but no other specifications were supplied by the technical service to know the precise intensity value at the sample in each step). The spot size on the sample was nearly 35 μm². Wavenumber spectral range extended from 100 to 2000 cm⁻¹. Several tests were achieved by using different exposure times, number of accumulations and spectral resolutions with the aim of determining the best analytical conditions to obtain good-quality Raman spectra, while optimizing also the time of acquisition and energy consumption, aspects which are of prime importance for *in situ* studies.

For laboratory analyses, we used a Bruker RamanScope micro-Raman spectrometer at the SCAI of the University of Málaga, operating upon a 1064 nm laser excitation and a 20× magnification. We also used a Bruker RamII FT-Raman module attached to a Vertex FT-IR spectrometer. In both cases, the laser power was kept fixed to the lowest possible value to avoid mineralogical changes. Typically, 3000 Raman scans were averaged in each case to improve the signal-to-noise ratio, and a spectral range between 100 and 1800 cm⁻¹ was recorded.

Results and discussion

Flint usually forms irregular nodules in sedimentary rocks. A thin white layer can surround the flint nodules. The outer layer, generally white, is sometimes denoted as cortex. Quite often the cortex shows a powder-like appearance. Remains of this cortex layer can be seen in some of the specimens subject of Raman analysis (see Fig. 2). Flint and radiolarite patinas are also present in most of the studied samples; but in general the areas

of the lithic tools with a knapping display a fresh and clean surface. Patinas are the result of different physico-chemical transformations on the outer surface of siliceous material stone tools after their knapping process because of exposition to weathering and burial during long periods of time.

Thickness and compositional features of stone tools will depend on the type and composition of the original raw materials (flint, radiolarite, sandstone) and the environmental physico-chemical factors to which they have been subjected during their transport, sedimentation or burial. Quite often, a decrease of the rock density, lost or reprecipitation of silica with different morphologies or a dehydration process can occur. Furthermore, these processes can be quite heterogeneous, so different data can be derived from the point of the surface subject of analysis.^[31]

In first place, we analysed the most adequate exposure time–accumulation ratio of our portable Delta-Nu Inspector Raman spectrometer for the infield studies through the comparison of the Raman spectra recorded upon different experimental conditions. In Fig. 3, we compare two sets of Raman spectra obtained by using either the 5 or 10 s exposure time options; for each exposure time, we also acquired spectra as the average of 1, 5 or 10 scans by keeping always the best spectral resolution possible (8 cm⁻¹). All the spectra showed the typical Raman signature of α-quartz at 465 cm⁻¹. We also observed that the option of a 10-s exposure time improves a bit the signal-to-noise ratio, but it is not yet sufficient for the clear detection of other weaker α-quartz Raman bands, such as that at 206 cm⁻¹.

Regarding the number of accumulations, no significant differences were noticed when Raman spectra were acquired as the average of 1, 5 or 10 scans while keeping the same exposure time (Fig. 3). However, we should remark that sometimes, and for some of the samples, the use of a 10-s exposure time saturated the detector response, thus making it impossible to record the corresponding Raman spectrum. To avoid this, we finally decided to use, as an experimental protocol for the subsequent infield studies, a 5-s exposure time and five accumulations. The selection of these two parameters allowed us to optimize both the time needed to analyze a given sample and the energy consumption

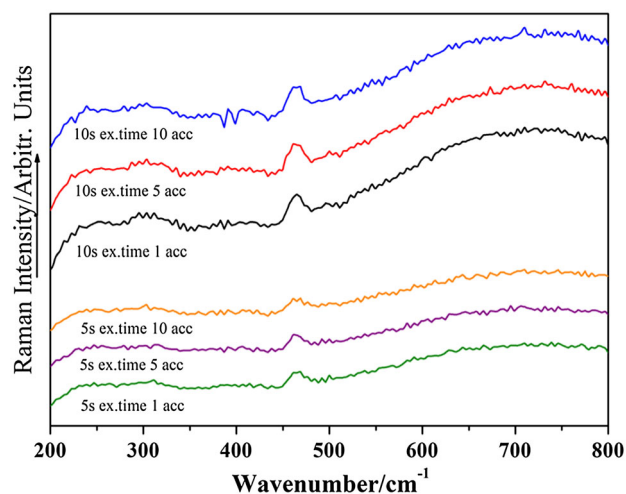


Figure 3. Comparison between the Raman spectra collected by means of the portable Delta-Nu Inspector Raman spectrometer of the bulk of sample EP-C7-S-1792-02 upon exposure times of 5 or 10 s. For each exposure time, Raman spectra were also recorded as the average of 1, 5 or 10 scans. The spectral resolution was always kept fixed to the best value possible (8 cm⁻¹).

of the instrument (in portable Raman spectrometers battery life is a key parameter).

Figure 4 displays four Raman spectra recorded upon changing both the spectral resolution (8 or 12 cm^{-1}) and number of scans (1 or 10), while keeping fixed the exposure time to 5 s. The spot analysed was the same in all the cases and the presence of α -quartz (465 cm^{-1}), calcite (1086 and 281 cm^{-1}) and barite (989 cm^{-1}) was evidenced by their characteristic Raman features. On the other hand, by comparing the four spectra, it becomes clear that some spectral noise is smoothed by mathematical operations when the 12 cm^{-1} spectral resolution is used. However, in such cases, the spectral features in the background could be misunderstood and even wrongly assigned to Raman vibrations, particularly in the spectral range between 600 and 900 cm^{-1} , which could lead to an erroneous mineral identification by nonexperts in Raman spectroscopy. To avoid this, it is desirable to choose the best spectral resolution available, 8 cm^{-1} in the case of our Delta-Nu Inspector spectrometer.

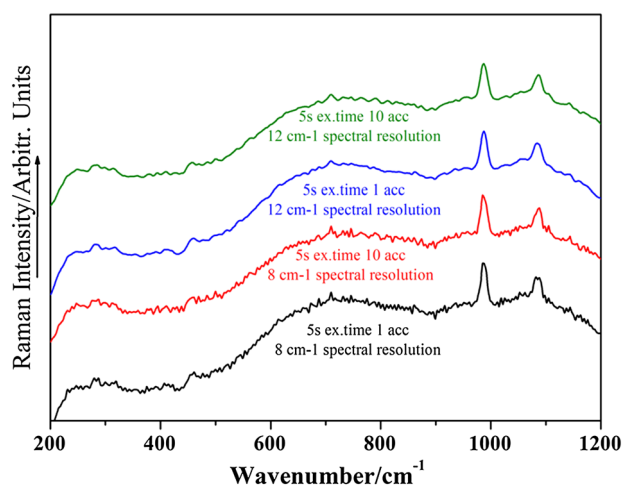


Figure 4. Comparison between the Raman spectra recorded with the Delta-Nu Inspector Raman spectrometer of the crust of sample EP-C7-S-1792-02 upon changing both the spectral resolution (8 or 12 cm^{-1}) and the number of scans (1 or 10), while keeping fixed the exposure time (5 s).

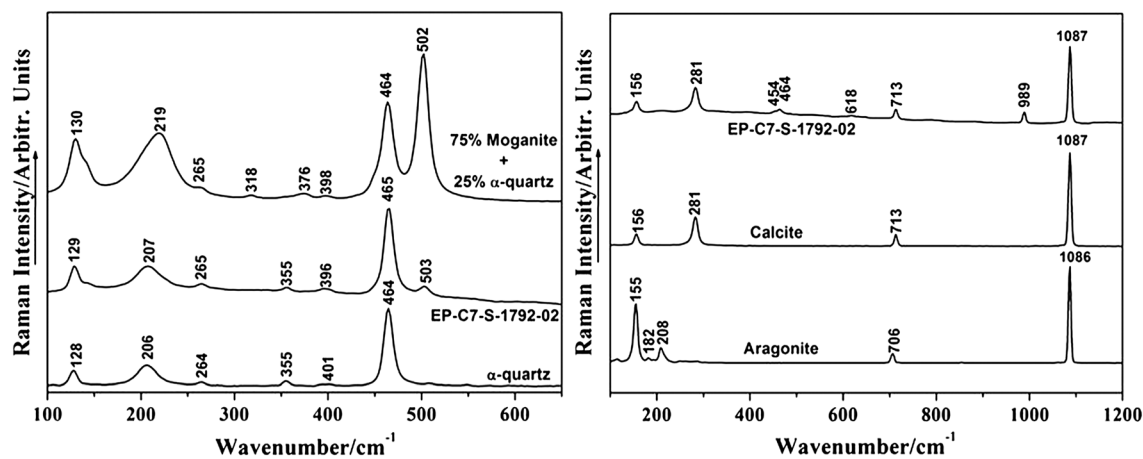


Figure 5. Raman spectra of the bulk (left) and crust (right) of sample EP-C7-S-1792-02 taken as a prototypical case. For comparison purposes, the Raman spectra of α -quartz and of a sample from Gran Canaria Island containing nearly 75% moganite and 25% α -quartz are also displayed in the figure at the left side, whereas the Raman spectra of calcite and aragonite are also plotted together with the crust-Raman spectrum in the figure at the right side.

As for the results derived from the Raman spectroscopic analyses in the laboratory, α -quartz is the mineral that constitutes the bulks of the eight samples, as identified from its characteristic strong Raman scattering at 465 cm^{-1} because of the symmetric stretching vibration of SiO_2 , and other two weaker features at 206 and 128 cm^{-1} . For comparison purposes, the Fourier transform (FT) Raman spectrum of α -quartz is also plotted in Fig. 5 as a reference.

The bulks of the lithic tools under study also showed another Raman scattering at 502 cm^{-1} because of moganite, a naturally abundant silica polymorph, which was initially found in 1976 in a nearly pure form from secondary precipitates within rhyolite ignimbrite flows in Mogan (Gran Canaria Island, Spain).^[32–35] It later turned out to be identical with lutcite, a so-called length-slow silica, and was definitively accepted as a member of the silica system in 1999 (IMA No 99–035). Moganite can also be distinguished from α -quartz by XRD analysis on the basis of their different diffraction patterns (i.e., lattice parameters at room T: $a = 8.7465(5)$ Å, $b = 4.8694(3)$ Å, $c = 10.7255(6)$ Å and $\beta = 0.18(1)$ Å, with a final R_{wp} of 2.71%).^[36–38] Moganite is now recognized as a common intergrowth within unaltered microcrystalline silica varieties, such as chert and chalcedony,^[39] and it has been actually found in many types of cherts used as raw materials during prehistoric times in different locations of the Iberian Peninsula.^[23,40–43] A high concentration of moganite in sedimentary cherts (> 20 wt%) is a strong indicator of crystallization in evaporitic environments.^[44] The FT-Raman spectrum recorded for a nearly '75% moganite + 25% α -quartz' sample from Gran Canaria is also displayed in Fig. 5 as a reference.

The Raman analyses of the crusts showed the presence of calcium carbonate in all the samples, independently of the nature of the bulk (flint, quartzite or oolitic flint). We could identify it as calcite because of its strong and medium Raman features at 1087 and 281 cm^{-1} , respectively (see for instance the Raman spectrum recorded for the crust of EP-C7-S-1792-02 in Fig. 5). The Raman band at 281 cm^{-1} is particularly useful to differentiate between calcite and its polymorph, aragonite, for which the corresponding lattice vibration appears at 208 cm^{-1} . In the same crust-Raman spectrum of specimen EP-C7-S-1792-02 another weak feature of calcite is measured at 713 cm^{-1} , while its counterpart in aragonite is measured at 706 cm^{-1} (Fig. 5). This finding is in

agreement with the presence in almost all the lithic tools under study of a caliche crust because of a diagenetic process. The FT-Raman spectra recorded on various spots of the crust of sample EP-C7-S-1792-02 stone tool made up of a bulk of white flint partially covered in some surface areas by a white crust composed of two clearly distinguishable layers (Fig. 2), also showed three other additional weak Raman signatures at 989, 464 and 454 cm⁻¹, attributed to barite, in the first layer of the crust in direct contact with the white flint bulk, under the outer calcite crust layer (Fig. 5). On the other hand, some Raman spectra recorded on different spots of the crust of specimen TP-TP4-S-PL-007-11 also displayed three other weak Raman features at 639, 396 and 143 cm⁻¹, characteristic of anatase; what could result from an eventual presence of small grains of this heavy mineral in the mineralogy of quartz compacted sandstones.

Finally, a few lithic tools, particularly those with brown and reddish colours, showed a strong fluorescence background upon laser excitation in the visible spectral region at 633 or 785 nm, but those problems were fully overcome by recording their FT-Raman spectra at 1064 nm.

Conclusions

Eight Palaeolithic stone tools from the Guadalteba County (Málaga, Spain) have been analyzed by means of Raman spectroscopy. Regarding the archaeometric analysis of bulks, α -quartz was the main mineral found in all the cases, although a small amount of moganite was also evidenced as a distinctive feature of these chert samples. As for the micro-Raman analyses of crusts and patinas, calcite was found to be the most common mineral in all lithic tools, although barite was also detected in one of the samples and anatase in another specimen. Thus, anatase and barite could be also used to identify the possible origin of the raw materials or their geological setting.

With regard to the capabilities of our current portable Raman spectrometer, it actually served in the preliminary identification in the field of the main mineral components of both bulks and patinas without any significant difference upon changing the exposure time, number of scans or spectral resolution. However, other minor mineral components, such as moganite in the present case, cannot be satisfactorily detected by means of our current handheld Raman spectrometer. Thus, we must note that, although many miniaturized or portable Raman instruments are nowadays available in the trade, the 'successful detection of moganite' in the particular case of these chert samples could be used as a suitable 'quality test' prior to deciding on choosing and purchasing a new portable Raman spectrometer with improved capabilities.

Portable Raman technology cannot replace at all the much more accurate benchtop Raman instrumentation, which would be also complemented with the use of other archaeometric techniques, such as X-ray diffraction or energy dispersive X-ray fluorescence, for the precise identification of every minor mineral component. In this regard, a further archaeometric study is currently underway to carry out a comparative Raman, X-ray diffraction and energy dispersive X-ray fluorescence analysis of both archaeological and geological chert samples from the Guadalteba County to get a more thorough insight into the provenance of the different types of chert raw materials used to fabricate the very many lithic tools found there up to date. In this regard, we also would like to perform some 'line scans' with high

resolution micro-Raman spectroscopy on polished thin sections of geological cherts to analyze the 'local' moganite content at different spots on the clean surface of the different types of cherts and the spatial variation in the moganite-to-quartz ratios in going from the rim or cortex to the core of the different samples, with a lateral resolution within the μm range.

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