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Aspects and characterization of chert alteration in an archaeological context: A qualitative to quantitative pilot study

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Abstract

Chert alteration in Paleolithic contexts, generally known as “patina” by prehistorians, has long been recognized. Originally, different types of “patina” were defined as “white patina”, “glossy patina”, or “porcelain-like patina”, all of which involved changes in the color and/or roughness of the initial raw material. Alteration degrees are used in many research fields like taphonomy, petroarchaeology or use-wear analysis; however most of these studies are still based on qualitative descriptions using a wide range of terms that bring about confusion. In this paper, we present first the results of an inter-observer's blind-test where color and roughness are described at macroscopic scale. Secondly, we use quantitative methods to compare archaeological and experimental altered silicifications: light spectrometry and confocal microscopy are used to quantify color and roughness. We show here how macroscopic qualitative descriptions could lead to confusion because of the lack of calibration and the number of terms used differently by each one. We demonstrated the efficiency of quantitative methods as light spectrometry and confocal microscopy that will significantly enhance studies of surface alteration in terms of taphonomy, use-wear analyses, and petroarchaeology issues as well as interdisciplinary discussions.

Keywords: Chert alteration ; Confocal microscopy ; Light spectrometry ; Quantitative analyses ; Taphonomy ; Petroarchaeology

1. Introduction

While often considered immutable on a human time-scale, rocks undergo significant physical and chemical changes over time. Silicifications and particularly flints are no exception, and their alteration in archaeological contexts, generally known as “patina” by prehistorians, has long been recognized (e.g. Boucher de Perthes, 1864; Meillet, 1866; de Mortillet, 1883; Chédeville, 1907). Originally, different types of “patina” were defined as “white patina”, “glossy patina”, or “porcelain-like patina”, all of which involved changes in the color and/or roughness of the initial raw material during its stay inside the sediments (in geological as well as archaeological context). While alteration was initially considered a good age marker of prehistoric flints, experimental research soon showed that it was a complex and largely misunderstood process, resulting from the combination of several factors as pH, sediments' type, weathering, water circulation, etc. (e.g. Meillet, 1866; de Mortillet, 1883; Chédeville, 1907; Sollas, 1913; Hue, 1929; Cayeux, 1929; Bellard, 1930; Curwen, 1940; Mitchell, 1947; Goodwin, 1960; Schmalz, 1960; Hurst and Kelly, 1961; Honea, 1964; Rottländer, 1975; Aubry, 1975; Stapert, 1976; Trauth et al., 1978; Texier, 1981; Masson, 1981). The variability in the degrees of intensity of the “patinas” within a single archaeological collection is still used, however, to test the integrity of an assemblage, and it is now an element in “lithic taphonomy” studies of archaeological site formation processes (e.g. Villa, 1982; Schiffer, 1987; Dibble et al., 1997; Bordes, 2002; Eren et al., 2011; Fernandes, 2012; Glauberman

and Thorson, 2012; Bertran et al., 2017). Moreover, altered flints are also studied and used as control samples in use-wear analyses to distinguish taphonomic alteration from use wear (Semenov, 1964; Tringham et al., 1974; Keeley, 1980; Meeks et al., 1982; Plisson, 1985; Levi Sala, 1986; Asryan et al., 2014; Lemorini et al., 2015). Finally, geological flint alteration is studied in petroarchaeology in order to establish Paleolithic raw material sources (regolith, colluviums, and alluviums) (e.g. Masson, 1981; Demars, 1982; Geneste, 1988; Turq, 1992; Primault, 2003; Fernandes and Raynal, 2006).

In the last decade, progress in the study of siliceous materials has greatly improved our understanding of the alteration process (Howard, 2002; Burrioni et al., 2002; Fernandes, 2012; Glauberman and Thorson, 2012; Fernandes et al., 2007; Graetsch and Grünberg, 2012; Thiry et al., 2014). It appears that alteration results from combinations of phases of desilication and silica recrystallization. Despite this significant theoretical progress, most taphonomical, petroarchaeological, and use-wear analyses are still based on qualitative descriptions using a wide range of terms that could bring about confusion. Firstly, the terminology referring to the raw materials (nature, parts, and classification) and their alteration, has simultaneously developed among several different fields of research (mineralogy, sedimentology, petroarchaeology, lithic technology, and use-wear analysis) and is not always consistent. For example the altered zone of a flint is known as the “cortex” among many geologists and petroarchaeologists (e.g. Cayeux, 1930; Trauth et al., 1978; Thiry et al., 2014) while this term refers to limestone gangue residues for prehistorians. Secondly, there is still no global proposition of terminology for comparing degrees of alteration, and each study uses its own terms. Some use-wear studies have recently focused on the quantitative characterization of use-wear polishes, mainly thanks to the technological development of confocal microscopy (Evans and Donahue, 2008; Stevens et al., 2010; Stemp and Chung, 2011; Ibáñez et al., 2014; Macdonald, 2014). However, taphonomical and petroarchaeological studies are still mainly based on empiric and macroscopic observation.

In this paper, we will study the qualitative to quantitative characterization of altered silicifications. For this, we will compare archaeological and experimental materials at both a macroscopic and microscopic scale, focusing on color and roughness. As alteration depends on the mineralogical composition of the raw material, for this pilot study we have chosen to focus on one single type for which we have correlated geological and archaeological samples from the newly discovered Protoaurignacian site in Le Bois de Milhac, France. After detailing our materials and methods, we shall first of all present the petroarchaeological characterization of the archaeological and geological raw material at macroscopic and microscopic scales. We shall then present the observations made during a 22 observers blind-test to compare macroscopic descriptions of alteration. Finally, we shall give the measurements taken using light spectrometry and confocal microscopy. We show then that quantitative methods will significantly enhance studies of surface alteration in terms of taphonomy, use-wears analyses, and petroarchaeology issues as well as interdisciplinary discussions.

2. Materials and methods

2.1. Archaeological samples

Le Bois de Milhac is a Protoaurignacian site discovered in 2014 after clandestine excavations, which was then properly excavated in 2015 and 2016 (Caux et al., 2015). A significant lithic collection has been documented at the site as well as faunal remains and perforated shells. The lithic industry is largely dominated by a material with a clearwhite, glossy, porcelain-like patina. The majority of lithic industries from Paleolithic sites in the nearby area are composed of the same material (e.g. Champagne and Espitalié, 1967, 1981; Bordes and Labrot, 1967; Bordes, 2002) what has been identified, through

macroscopic observation, as Calcédoine de Bord collected at Domme. It is a light gray to pale yellow chalcedony from a tertiary lake environment that was used as a grindstone in the 18th and 19th centuries, and so the outcrop's location is very well known in Dordogne, France (Grandvoinnet, 1870; Labrot and Rey, 1976; Demars, 1982; Capdeville and Rigaud, 1986; Turq, 1992), being located about 10 km from Le Bois de Milhac. Some archaeological pieces with porcelain patina were broken during clandestine excavations, revealing the cross section of the flakes. We selected all 16 broken pieces to study the internal structure of the altered flakes and 10 complete pieces to complete non-destructive observation (Table 1).

	Blind Test	Petroarchaeological characterization			Quantitative characterization	
		Macroscopic description	Sedimentary contents	Mineralogy (thin sections)	Raman spectroscopy	Light spectrometry
Bois de Milhac						
Complete sample (external surface)	✓		✓			✓
Siliceous film		✓		✓	✓	
Desilication layer (section)		✓		✓	✓	✓
Central part		✓		✓	✓	✓
Geological sample						
Control samples (D0)	✓	✓	✓	✓	✓	✓
NaOH day 3 (D3)					✓	✓
NaOH day 6 (D6)	✓	✓			✓	✓
NaOH day 9 (D9)					✓	✓

Table 1 Crossed recap of samples and methods.

2.2. Experimental samples

We collected geological samples at Calcédoine de Bord outcrops and knapped several flakes, then selected 16 flakes without any cortex (Table 1). We kept 4 flakes as control samples and took the others for experiments. As the most well-known factor in white patina formation appears to be an elevated pH in basic solution (e.g. Meillet, 1866; de Mortillet, 1883; Chédeville, 1907; Sollas, 1913; Hue, 1929; Bellard, 1930; Curwen, 1940; Mitchell, 1947; Goodwin, 1960; Schmalz, 1960; Honea, 1964; Rottländer, 1975; Stapert, 1976) we chose a basic solution, sodium hydroxide (NaOH, 5 mol/l), for observing the development of the patina. We selected 12 non-cortical flakes and placed each of them in a tube containing 2.5 ml of sodium hydroxide. We then placed them for 9 days in a stove set at 50 °C, removing 4 flakes from the experiment at days 3, 6 and 9 (D3, D6 and D9), providing us with 4 samples for each degree of alteration.

2.3. Petroarchaeological characterization

In order to compare the archaeological, experimental, and control samples and gain a better understanding of the alteration of white patina, a petroarchaeological characterization of both the archaeological and geological materials was realized (Table 1). First, we compared the sedimentological content, using 4 archaeological samples and 4 geological samples, describing the part and the nature of the allochems types (e.g. Séronie-Vivien, 1987; Caux and Bordes, 2016). We then compared the mineralogical composition with 30 µm thin sections observed under polarized light and polarized and analyzed light, using 2 thin sections taken from the archaeological samples (broken pieces) and 2 others from geological ones, and also with Raman spectroscopy. The Raman spectra were obtained on a thin, polished section with a SENTERRA confocal microspectrometer (Bruker Optics, Ettlingen, Germany) equipped with a 532 nm exciting line (spectra acquired with 10 mW laser power, 30 co-additions of 10

s excitation). The Raman spectra were then compared with the Ruff database (Lafuente et al., 2016) for quartz and calcite, and Kingma & Hemley (Kingma and Hemley, 1994) for moganite.

2.4. From microscopic to macroscopic characterization: blind-test

As alterations are generally described in qualitative terms based on macroscopic observations, a blind-test with 22 observers (excluding the authors) was organized, mixing experiences levels from non-archaeologists to specialists of lithic industries. The aim of this inter-observer test was to gain a better understanding of the variability in the terms employed and the validity of macroscopic estimation. For this, we selected 3 samples (Table 1): 1 archaeological sample from Le Bois de Milhac (BdM), 1 geological control sample of Calcédoine de Bord with no alteration or cortex (D0), and 1 experimental sample (D6). The observers were not aware of the origin of each sample. We asked them to describe the color and roughness of each sample. Their descriptions were then compared with the light spectrometer and confocal microscopy measurements.

2.5. Light spectrometer measurements

The degree of alteration was quantified using a visible light spectrometer (an Avantes AvaSpec2048 fiber optic spectrometer equipped with a 2048 pixel CCD detector, an AvaLight-HAL as the illumination source, and a Halon D65 white reference). The measurements were translated in a three-dimensional ($L^*a^*b^*$) color space in which “ L^* ” was the luminance index, “ a^* ” the red-green color component, and “ b^* ” the yellow-blue color component, using Avasoft 7.5 software. Ten measurements were taken randomly on each sample.

2.6. Confocal microscope measurements

The microtopography measurements and 3D scanning of a $877 \times 660 \mu\text{m}$ representative surface were performed with a Sensofar S neox Confocal Imaging Profiler (Sensofar, Barcelone). The surfaces were scanned with a $20\times$ objective (0.45 NA) allowing a lateral sam- with soapy water (with the exception of the experimental flakes) and pling interval of $0.645 \mu\text{m}$, a vertical resolution of 8 nm, and an optical alcohol (70% modified) in order to remove any manipulation residues. resolution of $0.31 \mu\text{m}$. Prior to measurements, the surfaces were cleaned We took 10 measurements on each flake scar, where possible on the ventral surface. The surfaces were then analyzed using SensoMap 7.1 software (Sensofar, Barcelone). First, we used automatic leveling correction obtained through the Least Squares Plane Method, then we removed the outliers due to measurement errors and filled the nonmeasured points. Finally, we separated the wavelengths corresponding to roughness from those related to surface form and waviness using a Gaussian filter with a 0.08 mm cut-off. The parameters extracted from the roughness area were taken from the ISO norm 25,178 and each of them corresponded to a specific statistical measurement of an area. We chose to use the two parameters that best characterized the surfaces according to our objectives. The first was S_q (μm), square root mean height, and the second was V_v ($\mu\text{m}^3/\mu\text{m}^2$), void volume, in order to characterize microtopography and microporosity respectively. Outliers in roughness values were removed using boxplots.

3. Petroarchaeological characterization

3.1. Sedimentary content

The sedimentary content of the geological and archaeological samples was very similar (Fig. 1). The geological samples presented less than 10% of allochems: rare gyrogonites, very rare stem fragments of Charophyta, and very rare gastropods. This paleontological content was typical of a lake environment formation and consistent with previous descriptions of Calcédoine de Bord (Capdeville and Rigaud, 1986). The archaeological samples also presented less than 10% of allochems. We observed rare Charophyta gyrogonites, very rare stem fragments and no gastropods. In view of the very small percentage of these fossils in the geological samples and the number of samples observed, there was no significant difference between the geological and archaeological samples.

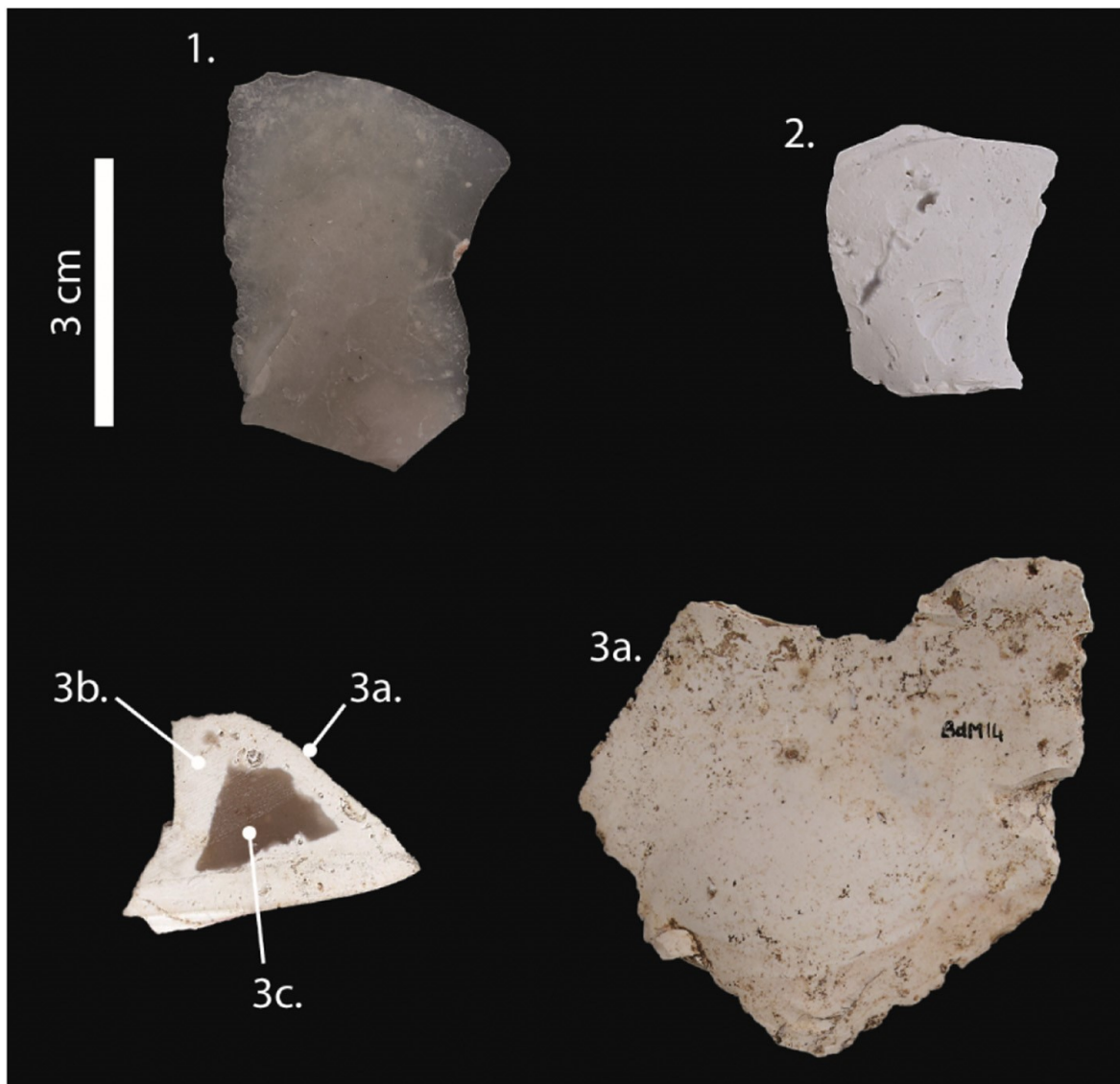


Fig. 1. Macroscopic view of geological and archaeological samples. 1.: Geological sample; 2.: experimental sample (D6); 3.: archaeological samples from le Bois de Milhac (BdM), 3.a.: complete sample/siliceous film; 3.b.: desilication layer; 3.c.: central part.

3.2. Macroscopic description of alteration

Three degrees of alteration can be distinguished on the archaeological samples, mainly depending on the thickness of the pieces. The thickest flakes (approximately over 3 cm) presented low alteration rates, with three alteration phases from the surface: an external patina, composed of a thin, compact, translucent film on the surface; an internal patina, composed of a white, porous layer; and a central part that resembled the white to bluish-white unaltered *Calcédoine de Bord* (Figs. 2 and 3). The medium-sized pieces presented a high alteration rate, with only external and internal patina (no more central part). Finally, the thinnest pieces (approximately under 1 cm) presented a very high alteration rate with an external patina, a thin layer of internal patina, and an internal cavity. Despite these huge structural modifications, it is possible to observe some knapping marks as hackles on the surface of all these pieces.

Surface from D0 to D9 experimental samples also show alteration gradation: the longer the duration of the experiment, the whiter and rougher the altered samples appeared at a macroscopic scale. Moreover, we noticed that the hackles were very clear on D3, visible on D6, but no longer perceptible on D9, whose very rough, porous surface was disintegrating. The cross-sections of the experimental samples showed a central part similar to that of the control flakes (D0) and an altered zone whose thickness increased with the duration of the experiment, up to about 1 mm for D9. This altered zone was similar to the internal patina of the archaeological sample. We observed no film like the external patina of the archaeological samples, however.

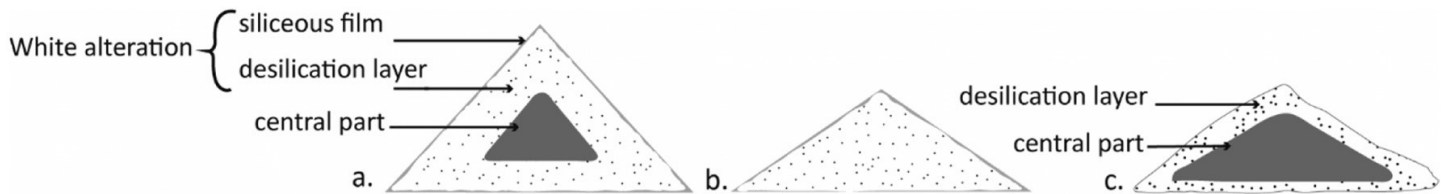


Fig. 2. Schematic representation of altered samples section. 1. and 2.: Archaeological samples from le Bois de Milhac; 3. Experimental sample.

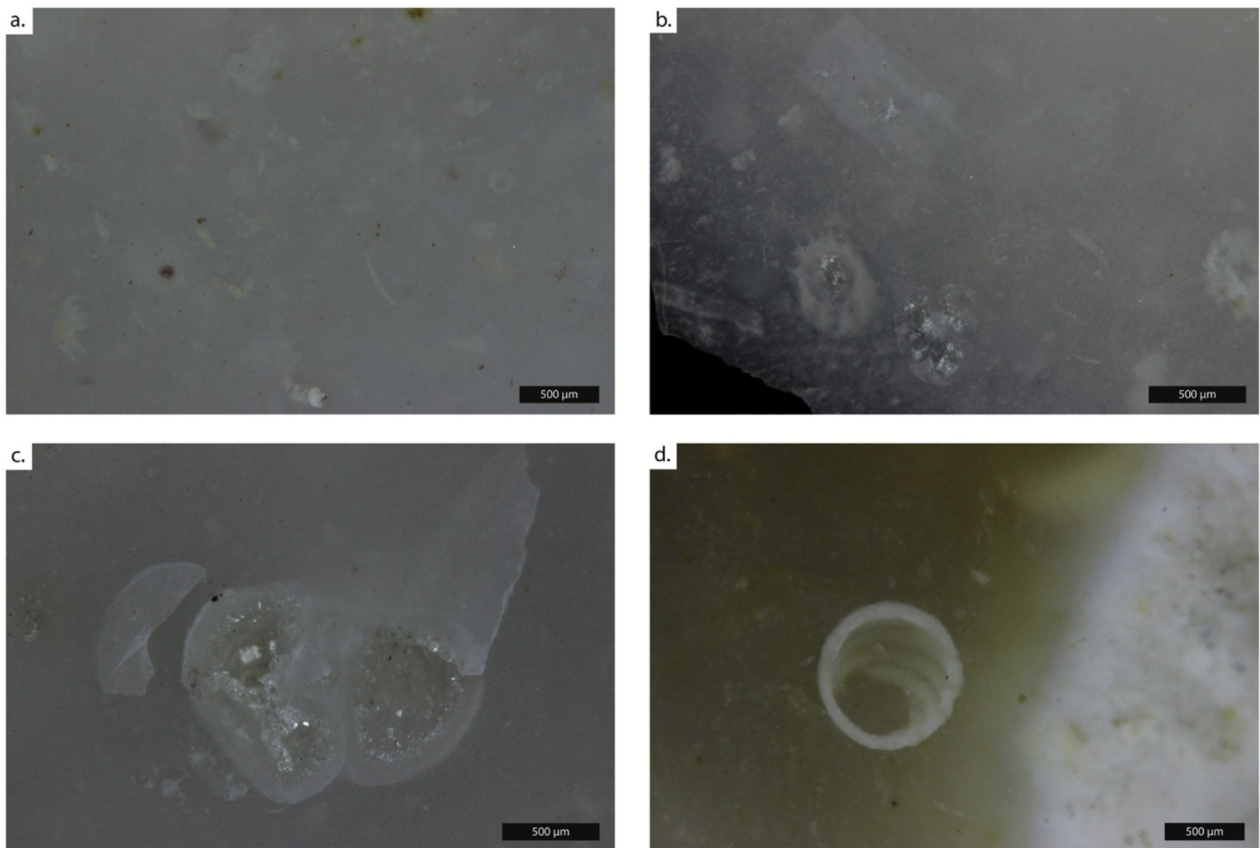


Fig. 3. Sedimentary content. a., b., c.: Geological sample; d.: archaeological sample from le Bois de Milhac. b.: Charophyta stems fragments; c.: gastropod section; d.: Charophyta gyrogonites section.

3.3. Mineralogical characterization

Observation of the thin sections showed a clear correlation between the geological samples and the central parts of the archaeological samples (Fig. 4). All of them presented a microcrystalline to cryptocrystalline texture composed of siliceous crystals with very low birefringence. There were also some calcitic microcrystals and some inclusions of about 1 mm of well-expressed fibrous and radial chalcedony: both these components had to be related to epigeny or the filling of different fossils. The external patina appeared to be a very thin film of uncrystallized material. In the internal patina, we observed a network of pores, coated with a thin film similar to that of the external patina. This network of pores passed through a mixture of cryptocrystalline areas similar to the central part texture and areas with a spherulitic texture.

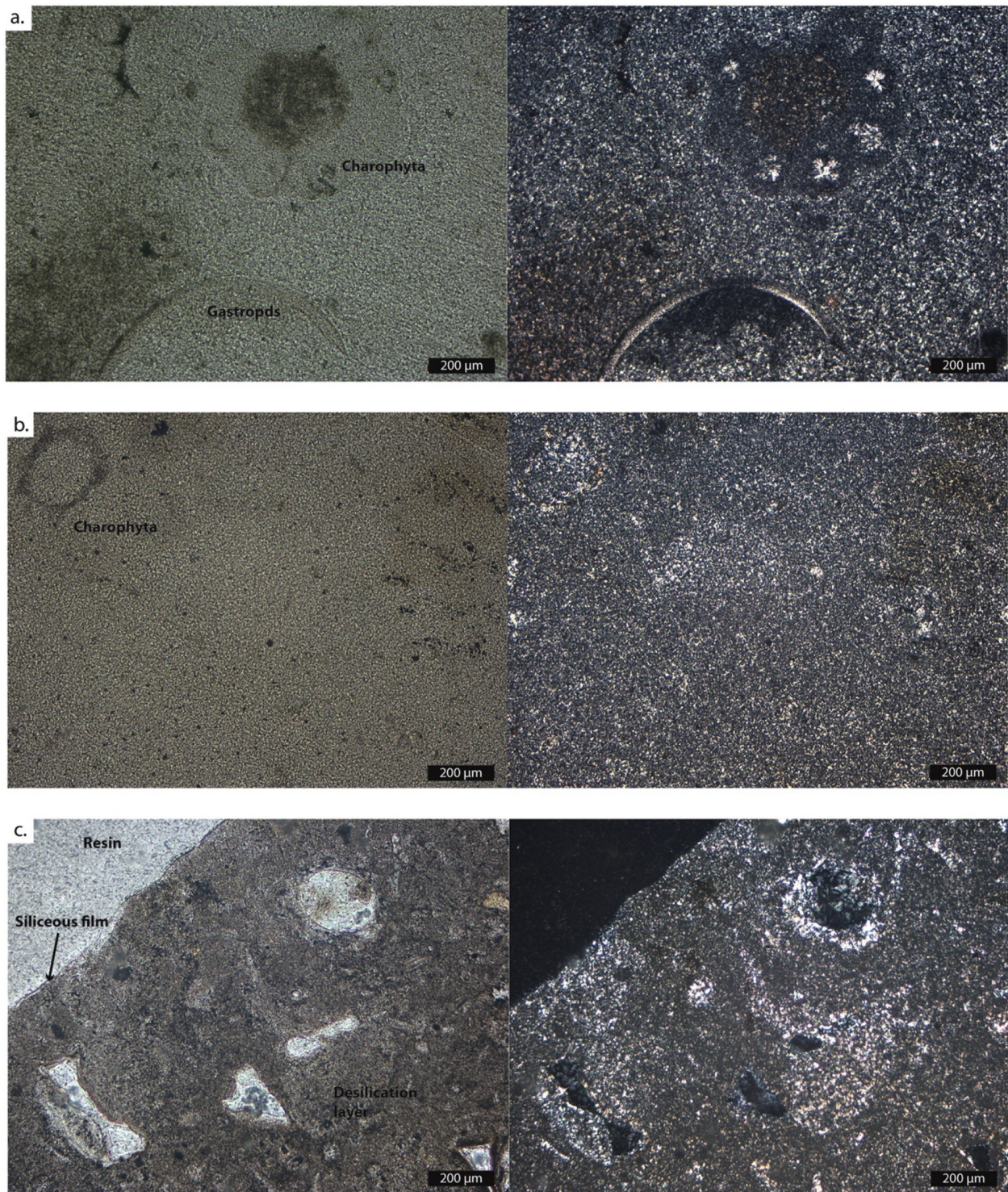


Fig. 4. Mineralogical characterization. a.: Geological sample; b.: archaeological sample, central part; c.: archaeological sample, desilication layer and siliceous film.

The Raman analyses also showed a clear correlation between the geological samples and the central parts of the archaeological samples (Fig. 5) which were mainly composed of chalcedony as shown by the quartz and moganite peak levels (e.g. Heaney and Post, 1992). The external and internal patinas presented the same geochemical composition, with quartz and moganite peaks, as well as a calcite peak (Fig. 5).

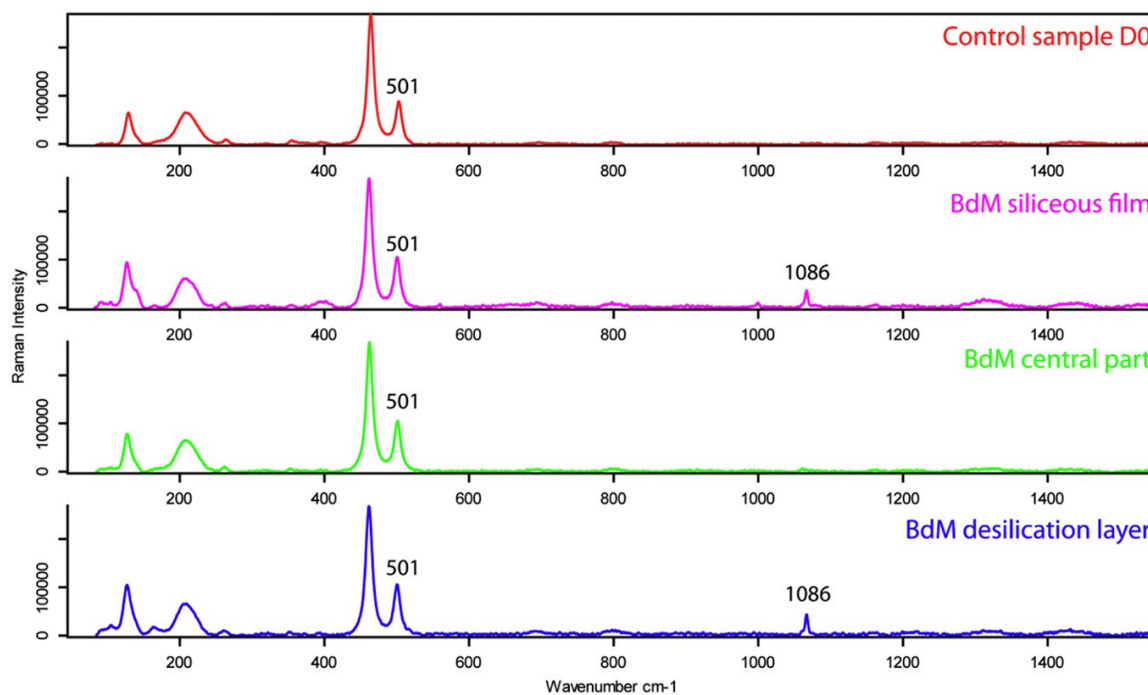


Fig. 5. Mineralogical composition via Raman spectrometer.

3.4. Interpretation and discussion

Firstly, all these methods highlight the correlation between the archaeological and geological samples and thus confirm that the archaeological material was procured at Domme. Secondly, the broken archaeological pieces and thin sections have clarified the internal structure of the altered archaeological flakes from Le Bois de Milhac. These observations regarding the alteration process are comparable to those documented on many archaeological flints such as at PiéLombard (Texier, 1981), as well as geological flints from the Rhone Valley (Fernandes, 2012; Thiry et al., 2014) and the Paris Basin (Thiry et al., 2014). It appears that the alteration processes are similar (desilication with or without precipitation of silica) but the terminology differs substantially (Table 2). We here propose a terminology that aims to be applicable within any research field (Table 2). Regarding the geological terminology we propose to keep “alteration” as a generic term with the possibility of specifying “white alteration”, as the white aspect is the most well-known evidence of alteration in an archaeological context. “White alteration” is a macroscopic characteristic referring to any alteration leading to a white aspect independent of the process(es) at work (desilication with or without recrystallization). In order to enable interdisciplinary discussion we propose to call the white zone an “alteration layer” as it is impossible to call it a “cortex” as this term has been used otherwise for over a century by prehistorians. We then propose to subdivide the “alteration layer” into “desilication layer” for the porous part and “siliceous film” for the external silica deposit. It is also confusing to keep the term “core” for the central part as “core” has already been used for decades in lithic technology.

	Peyrony, 1938; Renard, 1930; Stapert, 1976	Texier, 1981	Fernandes, 2012; Graetsch and Grünberg, 2012	Thiry et al., 2014
(White) alteration layer	Siliceous film White patina or Patina: alteration on the chert's surface	Test Translucent and matt, porcelain-like, about 500 µm	White patina or altered surface: translucent film	Cortex cemented rim: about a few tens of microns thickness, without porosity, film of secondary silica
	Desilication layer	Internal porous part: White and friable material	White patina: Porous and altered zone	Cortex: White and porous, centimetric
Central part	-	-	Core	Core

Table 2. Comparison of silicification alterations' terminology in the bibliography.

4. Results and interpretations: from a qualitative to quantitative characterization

4.1. Inter-observer blind-test

Many different terms were used by the observers to describe color and roughness, which we regrouped into synonyms (Fig. 6). Almost all the observers began by describing the color aspect, as this seemed to be more familiar than roughness. Most of them first described the experimental sample (D6) as “white” or “pure white” as a reference and then tried to characterize the two other samples. The archaeological sample (BdM) was described as “cream”, “off-white” etc. but the observers noticed that the surface had some tiny darker spots giving it a “dirt-like” or “nougat-like” appearance. The geological sample (D0) appeared to be the most difficult to describe, the observers generally focusing on the translucent aspect, which complicated color perception. For all the samples, especially D6 and BdM, a wide range of terminology was used, however most of the terms were congruent as there were a lot of synonyms.

The observers started by describing the roughness of BdM and D6 as references: the former was described as “fine-grained” or “soft” and the latter as “rough”, “porous”, or “coarse” (Fig. 6). D0 was then generally defined as “intermediate”. Despite the redundancy of terms there was not only a clear distinction between the roughness of BdM and D6, but also a gradation was consistently observed as D6 was considered rougher than D0, which was rougher than BdM.

These blind-test results have highlighted the fact that intuitive descriptions of color and roughness are not precise enough for inter-observer characterization as the terminology used was very heterogeneous. There were a lot of synonymous terms, mainly intuitive, sometimes associated with a totally empiric gradation (like “very-finegrain”/“fine-grain” or “white”/“pure white”).

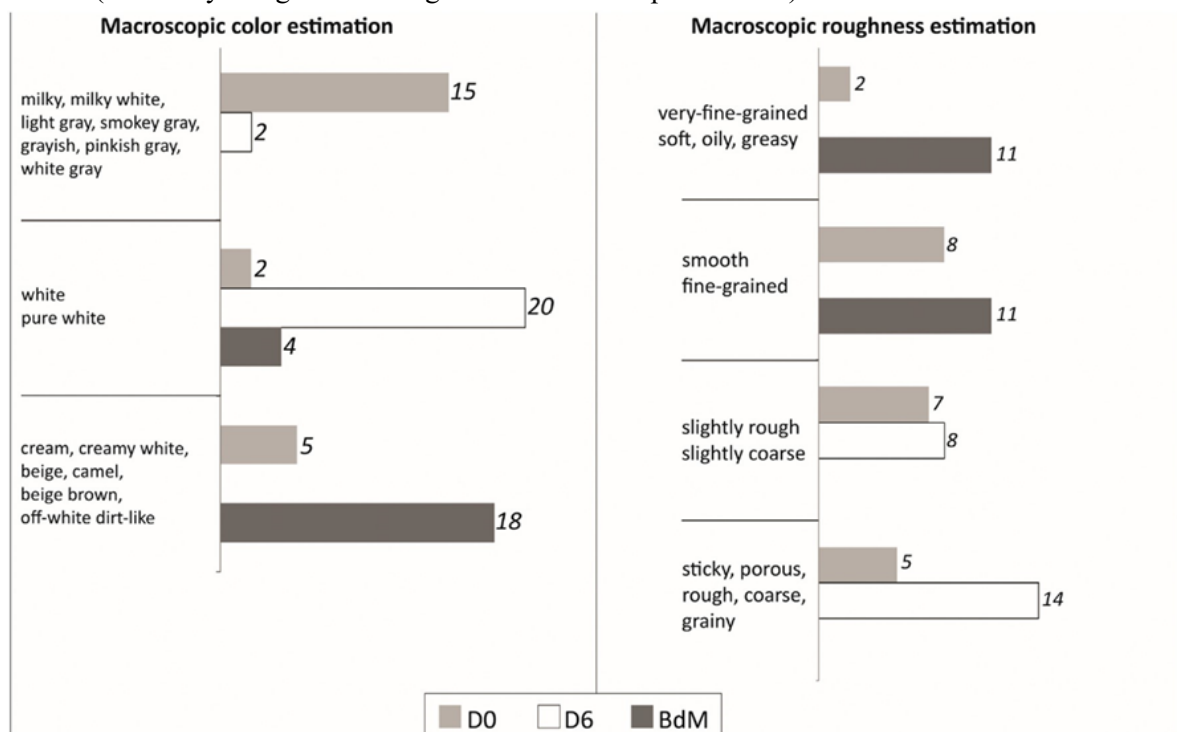


Fig. 6. Macroscopic characterization of color and roughness aspects: blind-test results.

4.2. Quantitative characterization

We then compared the control samples (D0), experimental samples (D3, D6, and D9), and archaeological samples using light spectrometry and then with confocal microscopy. For the archaeological samples, we distinguished three zones for macroscopic observation: the central part, the desilication layer, and the siliceous film. All the measurements included the blind-test samples: D0, D6, and BdM as the siliceous film.

In the $L^*a^*b^*$ color space, the “ a^* ” (green to red) component did not seem to be significant, however the “ L^* ” (lightness), and “ b^* ” (blue to yellow) components showed distinct areas for each sample (Fig. 7). D0 was characterized by a low L^* value (less than 40) and a blue component near zero (b^* between -1 and 0). The BdM central part overlapped with these measurements, however the yellow component was well-expressed. The experimental samples varied from D0 with a significant increase in lightness (D6: $60 \leq L^* \leq 100$). The white alteration area of BdM (desilication layer and siliceous film) differed from D0 in terms of both its very high lightness (over 80) and a significant yellow component that was very well expressed on the siliceous film (b^* between 10 and 45).

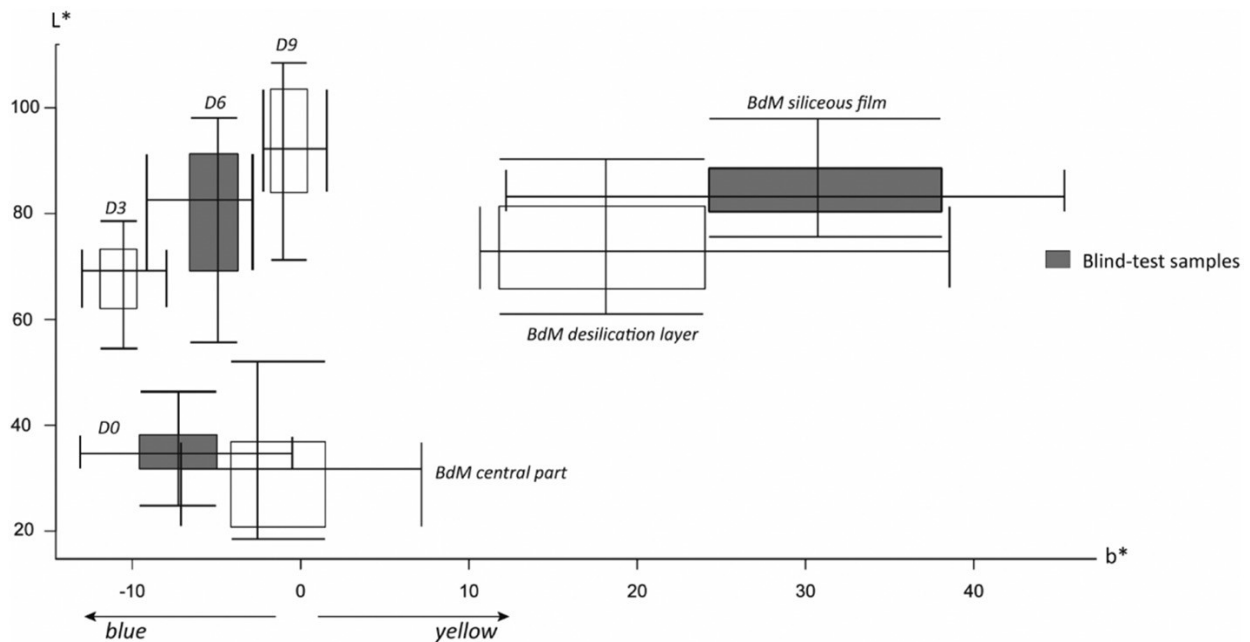


Fig. 7. Quantitative characterization of color with light spectrometry.

The confocal microscopy showed a clear gradation in surface roughness (Figs. 8 and 9). It appeared that the archaeological samples had the smoothest surface (siliceous film: Sq below $0.8 \mu\text{m}$). D0 ($0.5 \leq Sq \leq 1.4 \mu\text{m}$) and the BdM central part were overlapping. However the BdM central part presented a slightly smoother surface than D0. There was also a gradation among the experimental samples: D3 and part of D6 overlapped with D0, then D6 and D9 were increasingly rough (D6: $1.2 \leq Sq \leq 2.0 \mu\text{m}$). The BdM desilication layer clearly had the roughest surface, as Sq was up to $4.6 \mu\text{m}$ and the volume of voids can rise up to $5 \mu\text{m}^3/\mu\text{m}^2$.

We show here that quantitative characterization with light spectrometry and confocal microscopy is appropriate for describing alteration degrees as altered and geological flints are clearly distinguished for both color and roughness measurements. Then, visible spectrometry and confocal microscopy will be useful methods in next taphonomic, petroarchaeological, and use-wear studies.

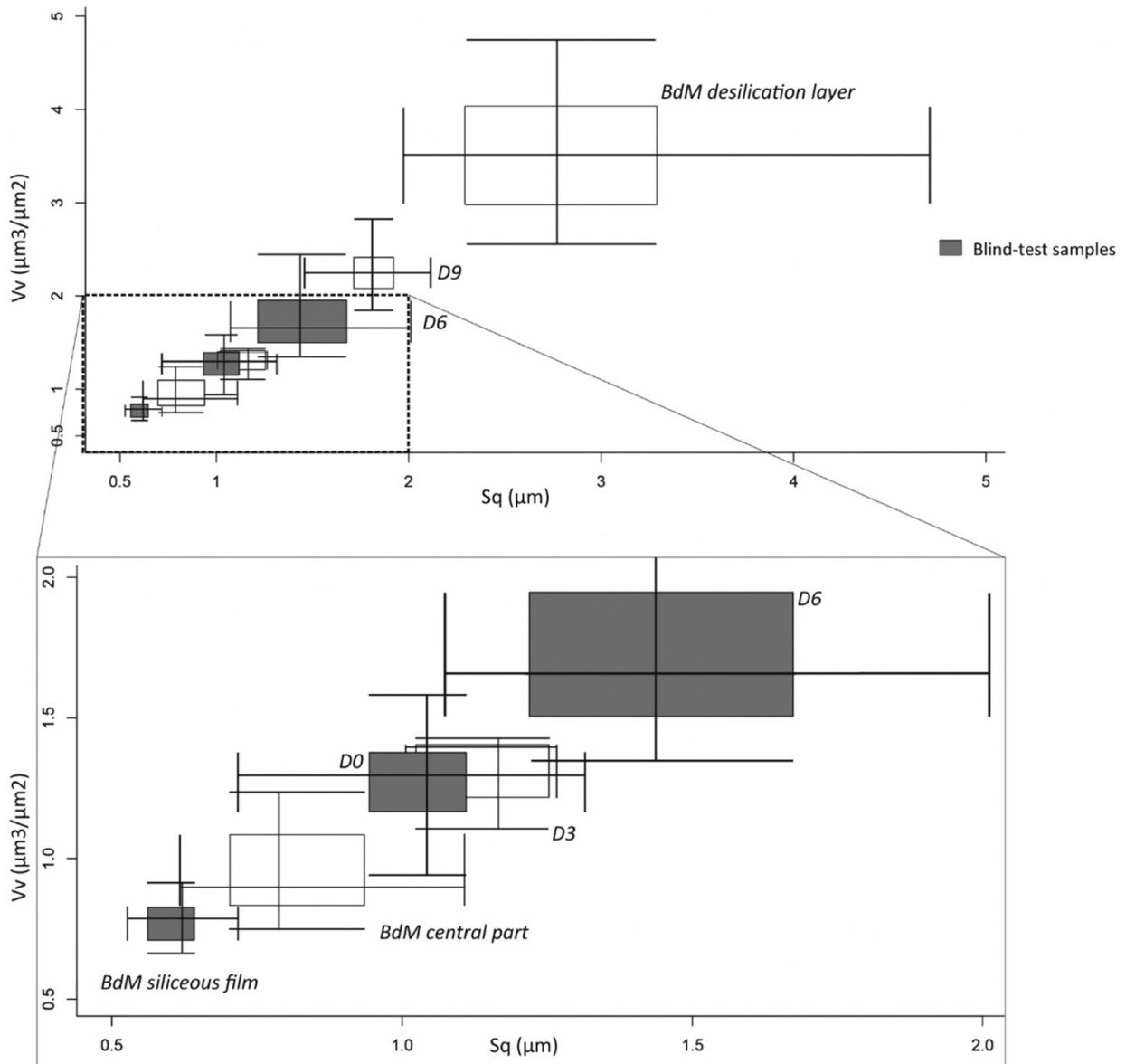


Fig. 8. Quantitative characterization of roughness with confocal microscopy.

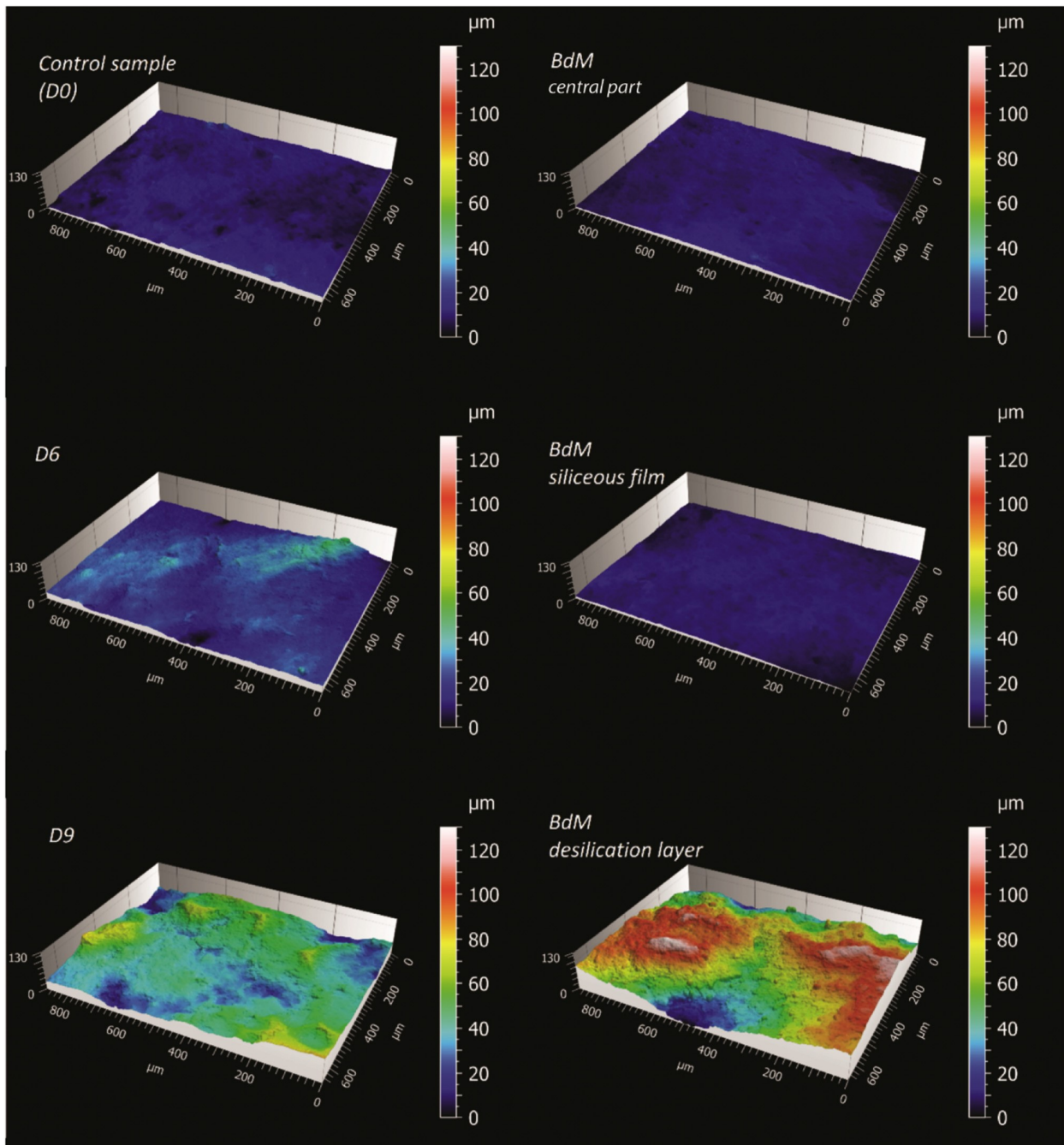


Fig. 9. 3D scans of geological and archaeological samples. 3D scans of $877 \times 666 \mu\text{m}$ surfaces obtained with confocal microscopy (set up at 15% amplification and 50% resolution). Note the amplitude variations of peaks height.

5. Global discussion and conclusion

However, some trends did exist as shown by the grouping of synonymous terms. These trends are perceptible at macroscopic scale and are valid from one observer to another. Secondly, the quantitative characterizations confirm these trends, as the light spectrometry showed a clear and distinct color partitioning of D0, D6, and BdM/ siliceous film (Fig. 7), while the confocal microscopy showed a gradation in roughness from BdM/siliceous film to D0, and on up to D6 (Figs. 8 and 9).

This work highlights the terminology problem in interdisciplinary studies of silicification alteration. Using archaeological and experimental material, we have observed different cases of silicification

alteration and proposed a descriptive terminology (white alteration, siliceous film, desilication layer, and central part) that could be applicable within any research field. We have then demonstrated that macroscopic descriptions are empiric and confusing because of a lack of common and calibrated terminology, and also that, light spectrometry and confocal microscopy are rather both suitable for respectively quantifying the color and roughness of white alteration.

Finally, comparing the archaeological and experimental samples has also raised some further questions that go beyond our main issue. Our study has highlighted the fact that white alteration can involve a combination of desilication and precipitation processes, as in the case of the archaeological collections from Bois de Milhac and Pied-Lombard or geological flints from alluvial deposits; or desilication processes alone, as in the case of the geological flints from the Paris Basin or our experimental samples. The conditions of the precipitation process have already been discussed including pH variations, water flow variations, and climate fluctuations (e.g. Hurst and Kelly, 1961; Howard, 2002; Fernandes, 2012; Glauberman and Thorson, 2012). Most of these studies are based on the observation of geological samples, however following our study, it appears that the complementary observation of archaeological, geological, and experimental samples seems to be the best way to gain a better understanding of the alteration of cherts.

We also identify through Raman analyses that the geochemical composition of the altered zones of the archaeological samples (both the siliceous film and the desilication layer) differs from the central part and control sample in the additional presence of calcite. It can therefore be supposed that the alteration of cherts could include chemical exchanges with the environment, such as the addition of calcite within the cherts' altered zones. It is also possible that these exchanges could explain the variation in b^* toward the yellow hue by incorporation of chemical elements like iron.

Finally we have observed that the BdM central part presented a slightly smoother surface than the geological samples. We suggest that this could be due to the selection of blocks of Calcédoine de Bord by Paleolithic groups, as the finest raw materials have the best knapping qualities. Following this hypothesis, the properties of raw materials could be characterized with confocal microscopy in order to highlight the selection modes used by Paleolithic groups.

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