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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.

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; Burroni 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

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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 clear-white, 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).

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 Rruff 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 × 660 μm representative surface were performed with a Sensofar S neox Confocal Imaging Profiler (Sensofar, Barcelone). The surfaces