Description and characterization of the natural alteration of chert artefacts from Atapuerca (Burgos, Spain), Cansaladeta (Tarragona, Spain) and Orgnac 3 (Ardèche, France)

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Abstract

Even though several authors have discussed the causes and mechanisms of chert alteration, a methodological description of the alteration itself hasn’t been done. This fact has contributed to a conceptual and terminological confusion. Trying to shed light on this problem, we undertook a description of chert alteration, at a different scale and using various techniques (macroscopic analysis, stereoscopic light microscopy, ESEM, EDX and density analysis) of both fresh and altered chert samples from the sites of Sierra de Atapuerca (Burgos, Spain), Cansaladeta (Tarragona, Spain) and Orgnac 3 (Ardèche, France). Based on the results of this study, we propose a terminology and a protocol of description for this kind of chert alteration.

Keywords: chert alteration, white patina, desilicification, Atapuerca, Cansaladeta, Orgnac 3.

Introduction

In some archaeological sites such as those of Sierra de Atapuerca (Burgos, Spain), Cansaladeta (Tarragona, Spain), or Orgnac 3 (Ardèche, France), highly degraded chert artefacts appear (Carbonell et al., 1999; Angelucci et al., 2004; Moncel, 1999). Due to their degradation, many of these chert tools must be treated before they are studied by technologists. In the field of Conservation, the alterations of stone tools have been poorly studied. However, in the field of Archaeology, various natural chert alterations have been described. Examples of these natural modifications are white patina, desilicification, glossy patina, wind patina or desert varnish (e.g., Schmalz, 1960, Hurst & Kelly, 1961; Rottländer, 1975; Texier, 1981; Luedtke, 1992:99-112). The problem of these studies is that the information related to the alterations is fragmentary: some authors study chert natural alterations to not misrepresent them with use-wear traces (e.g., Stapert, 1976, Plisson & Mauger, 1988); others study them to obtain information about formation processes of sites (e.g. Burroni et al., 2002); finally, some others, study them for chronological issues (e.g. Hurst & Kelly, 1961). The differences between approaches and objectives have prevented the existence of accurate terminology and a proper methodology of description of chert alterations. Also, in these studies, when an alteration is described or mentioned, an image of the alteration is almost always lacking; and this fact complicates the comprehension of the alteration.

The objective of this work is to describe, characterize and graphically document natural chert alteration, as well as to propose an adequate terminology and a description method. For this purpose, we have analyzed materials of the sites of Atapuerca, Cansaladeta and Orgnac 3.

Materials and methods

The present study includes the analysis of altered chert samples coming from the sites of Gran Dolina and Sima de Elefante (7), Cansaladeta (9) and Orgnac 3 (38), as well as of fresh chert samples coming from the potential areas of captation of these sites (from Sierra de Atapuerca (6), from Francoli river (5) and from Aven Lien dit Fouillose (7) respectively). The description and characterization of the alteration of chert was based on the comparison between a fresh geological reference sample, and the altered archaeological material. From this comparison,
we noted changes in the visible, physical-mechanic and chemical properties that the chert has suffered.

First of all, we completed the macroscopic examination of all the samples (72). We took into account visible properties such as coloration, grain size or compactness. Also we paid close attention to other properties like fragility and weight that were qualitatively determined through simple observation or suspension. We took macroscopic photographs with an Olympus Camedia C-5050 Zoom 4 Mega Pixels camera. We controlled the coloration of the photographs with a reference colour scale.

We studied all the samples using x4 to x40 stereoscopic light microscopy (Olympus SZ-11). We took photographs with an Olympus SZ-PT Infinity camera connected to the microscope and to a computer.

A selection of samples (15) was analysed using two different ESEM equipments: a FEI company QUANTA 600 ESEM with an EDAX INCA X – Sight Oxford Instruments model 6427 detector, and a Philips XL 30 Series ESEM with an EDX EDAX Company detector. We worked at high and low vacuum, to a distance between 20 to 9 mm, and to 10 to 25 K. We took photographs from 50 to 500 magnifications. We also did elemental analysis of the samples with EDX to a distance of 10mm. We obtained spectrums, mappings and relative percentages of the elements, as well as back-scattered electron images.

We then calculated the density of 16 samples, all of them from Orgnac 3 and Aven lien dit Fouillose, using the formula \( d = \frac{m}{v} \) (where \( d \) = density, \( m \) = mass, and \( v \) = volume). The sample’s mass (in g) was obtained with a Sartorius MC 1 Laboratory LC 6200S scale precision. The volume of the samples was calculated through the fluid displacement technique. We put a controlled quantity of water in a graduated recipient, in which the samples were submerged. The samples were covered with plastic film to avoid the absorption of water, which could provoke an erroneous calculation. The displacement of water in the recipient after the introduction of the sample was calculated (in ml) with a pipette that has an error rate of ± 10ml.

**Results**

**Chert of Atapuerca**

**Fresh geological sample of Atapuerca.**

Most of the samples of fresh neogene chert that we studied are grey and white. In general, the samples are opaque, with little brightness. Their surfaces have a heterogenic grain size, although this can vary between samples: while some surfaces are irregular and have many empty spaces and impurities, others are very fine-grained and smooth (e.g. Fig. 1A).

![Fig.1](image)

*Fig.1.* General macro images of fresh geological chert samples from Atapuerca (A), Francolí River (B) and Aven Lien Dit Fouilllose (C). The boxes indicate the areas shown in Figures 2A, 2B and 2C.

When observed under ESEM, the samples of fresh neogene chert of Atapuerca have very irregular and rough surfaces (e.g. Fig. 2A). These surfaces have some grain accumulations, some microfractures and important holes and empty spaces. In some of the holes of some samples we observed big grains with a well defined geometrical morphology. One of the samples observed have a more regular and fine-grained surface (the morphology of its grains can’t be appreciated below 250-300 magnifications). Despite this fact, this surface has many well defined micro fractures and other irregularities.
The EDX analysis of the fresh neogene chert samples of Atapuerca analyzed show that they are composed essentially by Si and O. Ca and Al also appeared in these samples, but always with percentages below 2 wt %.

**Altered archaeological sample of Gran Dolina and Sima del Elefante.** The altered archaeological chert samples of Atapuerca have a whitish coloration. In general, they are light and very fragile. They present a differential state of preservation: while their external surfaces look well preserved (they are commonly compact and preserve their original morphology -its edges, extractions, etc.-), their inner part is very powdery (Fig. 3A). This difference between the external part and the inner part is especially appreciable when samples are observed in section. The transition of the outside and the inside varies between different samples, but in general, is relatively gradual.

At a low magnification (x50), the external surface of the single sample that we analyzed using ESEM seems to preserve the aspect of the fresh chert. Even so, when observed up to 100 magnifications, a slightly different surface is appreciated: it doesn’t have grains with well-defined geometrical shapes and its microfractures and others irregularities are not so marked. The inner part of the sample is presented as an extremely irregular, rough and porous material. Up to 50-100 magnifications we can appreciate that the grains are rounded and have no cohesion. Many empty spaces and big holes can also be noticed. When observed in section, some parts of the sample have a very abrupt change between the external and the internal part. In other parts this change is more gradual. In transition areas we have observed many fissures that show the fragility of the sample (Fig. 4A).

The elemental analysis of the external part of the sample that we have analysed under the ESEM has shown that it is composed mainly by Si and O. However, important quantities of Ca and Al have been detected, as well as small quantities (less than 5 wt %) of P, K, Ti and Fe where the sediment is present. The internal part of the sample is also composed mainly by Si and O. However it has small percentages (less than 5 wt %) of other elements as Ca, Al, Fe, Zr, In, Sb or Tb due to the presence of sediment.
**Chert of Cansaladeta**

**Fresh geological sample of Francolí River.** The fresh Francolí River chert samples have colours ranging from white/grey to dark brown, passing through yellow, orange and purple colorations. The samples vary in terms of opacity, grain size and composition. While some surfaces are smooth and homogeneous, others are very rough and irregular, and have important grain-size, many impurities and many predetermined fracture planes. In general, the samples show a brighter type of chert than the neogene chert samples of Atapuerca that we have studied (e.g. Fig. 1B).

The ESEM shows great variability among Francolí River samples in terms of grain size and compactness. Some of them have more heterogeneous and rough surfaces than the samples of neogene chert of Atapuerca. In these areas numerous accumulations of large geometric and well-defined shapes can easily be observed at low magnification (e.g. 2B). Other pieces have much finer, more homogeneous and compact surfaces than those of the fresh chert of Atapuerca.

The main analysis of the river Francolí chert samples analyzed under ESEM, has shown that the smoother surfaces of these are formed only by Si and O. In the roughest surfaces of the samples there have been small amounts of Ca detected, but in very low percentages (always less than 5% in weight).

**Altered archaeological sample of Cansaladeta.**

The archaeological altered samples of Cansaladeta present different rates of conservation. There are some samples that still preserve some of the original colorations of the well-preserved fresh chert. Even though these samples have a different state of preservation between their inner and outer part, they are more consistent than the altered archaeological chert samples of Atapuerca (e.g. 3B). Within the most altered pieces of Cansaladeta, the internal part also varies in terms of compactness. However it never reaches the extreme fragility, porosity and lack of cohesion that the archaeological samples of Atapuerca present. Many samples of Cansaladeta, unlike the Atapuerca ones, present numerous ancient fissures and fractures.

The observation with ESEM revealed no major differences between the surfaces of the altered samples analyzed and the samples of fresh chert of the Francolí River when observed up to 50 magnifications. However, as happened with the chert of Atapuerca, when magnification increases up to around 100 magnifications a less compact surface can be observed. The inner part of the chert of Cansaladeta is very altered, similar to the chert of Atapuerca. It is presented as an irregular, not compact and porous mass, where the grains are totally rounded. But the difference between the chert of Cansaladeta and the chert of Atapuerca is that the holes and the porosity in general of the first one are not so big. We have also observed some grains slightly rounded, that are not fixed but preferably deposited in the holes of the inner part of the altered chert of Cansaladeta. When observed in section, a very marked change in appearance between the outer and the inner part of the sample analyzed can be observed (Fig. 4B). This outer layer has a thickness of about 250µm approx., and it is very well defined, unlike the Atapuerca altered sample. This outer layer is compact, has few cracks and presents well defined geometric forms that show that it is in relatively good condition.

The electron probe microanalysis for the sample of altered flint of Cansaladeta observed with ESEM has shown Si and O as major elements in both the external and the internal part of it. Also, it appeared in the spectrum important amounts of Ca (20 wt %, approx.) and of Al, Fe, Mg, S, Cl or K (in percentages of less than 2 wt %) due to the presence of sediment.

**Chert of Orgnac 3**

**Fresh geological sample of Aven lien dit Fouillose.** Fresh chert samples of the Aven lien dit Fouillose have several colours (black, brown, maroon, gray, beige, etc.). In general, they are translucent. Its composition and grain size is variable: although there is a predominance of fine grain, bright and very homogeneous surfaces, there are also rough and irregular surfaces with large crystallizations and fossils of different types and dimensions (Fig. 1C).

When observed with ESEM, the surfaces of the samples of Aven lien dit Fouillose are compact, and have a very fine and homogeneous grain (these grains are not observed below 500 magnifications) (e.g. 2C). These surfaces do not have empty gaps or holes. But there are others that are more porous, rough and irregular, that contain quartz grains of geometrical shape of
about 200µm, and thin layers with fossils and negatives of fossils.

The elemental analyses have shown that the smoother surfaces of the samples of flint of Avenlien dit Fouillose consist exclusively of Si and O, while the areas that have fossils and other inclusions have a significant presence of Ca. The average density of the pieces of Avenlien dit Fouillose analyzed with a volume exceeding 10 ml, gave 2.67, being 2.42 and 2.79 the lowest and highest densities respectively.

Altered archaeological sample of Orgnac 3. The archaeological altered samples of Orgnac 3 are characterized by its variability in terms of state of conservation. Despite the fact that they are all virtually altered, at least they are patinated (they are white), some of them are in good condition (their weight is apparently similar to that of the fresh chert, they preserve some original colorations, etc.). The most altered samples present a different rate of conservation between their surfaces and their inner part: while their surface is in good condition, their interior is totally altered, just like altered chert samples of Atapuerca and Cansaladeta. However, the interior part is much more compact (even in the more altered samples of Orgnac 3), the grain is finer and it is less porous than the Atapuerca and Cansaladeta archaeological samples analyzed (e.g. 3C).

The samples of Orgnac 3 that were observed under ESEM, present a very different state of conservation between them. Some of them show a clear distinction between the outer layer (very smooth and uniform) and the internal part (powdery, very irregular and porous). However, the outside-inside transition of the five samples of Orgnac 3 analyzed under ESEM is more gradual than the transition of the chert samples of Atapuerca and Cansaladeta analyzed (e.g. 4C). In some cases there is almost no transition, which means that the surface is very thin. Regarding the interior part, it is more compact and homogeneous than the interior part of the samples of Atapuerca and Cansaladeta; its holes are smaller as well as its grains. However, in some parts of the samples we noticed large holes that are full of small and very rounded grains that lost their cohesion. We also noted some small fossils as well as negatives of fossils both in the outer and the inner part of the chert samples of Orgnac 3.

The elemental tests have shown that the five samples of altered chert of Orgnac 3 that were analyzed under ESEM are composed primarily of Si and O, both in their inner and the outer parts. However, other elements have appeared in percentages below 1wt %, such as Ca, Al, Cl, K or Fe. On the surface of some samples have come out rates between 2 and 3 wt % of Al and Fe, in areas where sediment is present.

The density of the archaeological altered chert of Orgnac 3 analyzed goes from 1.23 to 2.10 (in samples whose volume exceeds 10ml). The average density of these samples gave 1.84, well below the value of geological fresh chert (2.67).

Discussion

This work has aimed to describe and characterize a specific type of alteration of chert that is present in the sites of Atapuerca, Cansaladeta and Orgnac 3. This alteration seems to correspond, by description, to white patina. However, other terminology as “desilicification”, “dissolution of silica”, “opalization” or “cacholong” have also been used to refer to this kind of alteration.

Firstly, the term “patina” normally refers to a superficial modification. So we think that the term “white patina” should not be used to refer to the alteration of the chert of Atapuerca, Cansaladeta and Orgnac 3, because it is not only superficial; it is also damaging the inner part of the chert.

Secondly, the terms “desilicification” or “opalization” are processes of alteration. So we think that they can only be used when we are sure that what has provoked the alteration has been exclusively a process of desilicification or opalization (which is not clear yet; a process of desilicification -that is, a dissolution of silica- could have occurred, but also the dissolution of other components as impurities). The term “cacholong”, used by authors as Merino (1994) and Moncel (1999), is used in English to name a variety of opal. Then, the use of this term to refer to a chert alteration involves accepting that the chert has altered becoming a different material. We did some x-ray microdiffraction of altered chert, and the resulting diffractograms showed that cherts are formed mainly by quartz; not by opal.

Therefore, we only accept the term patina when the alteration is superficial. We refuse all
terms that refer to a process or mechanism of alteration, because of its inherent ambiguity. We defend the use of the terms “superficial alteration”, which is equivalent to patina, and “total alteration”, when it affects to the entire object. However, we emphasize the need to attach a good description of the alteration to these terms.

Studies about chert alteration that have been completed in the field of Archaeology have been focused more on finding the causes and mechanisms of the alteration, than on providing an accurate description of this alternation. This fact has provoked, apart from terminological confusions, conceptual confusions about chert alteration, which, at the same time, has not allowed the comparison between alterations of different assemblages.

Although some authors have attached ESEM photographs to the description of a specific alteration (ex: Rottländer, 1975, Stapert, 1976, Texier, 1981), these have not been sufficient to know exactly what kind of modification is being referred to by each author.

As we have seen in this study, many differences between altered and fresh chert samples have been observed (see Table 1). We could deduce many characteristic traits of the alterations that we have studied: the white coloration, the different state of conservation between the inner part (very powdery) and the outer part (more compact), the weight loss and the increase of fragility compared to the well preserved chert, etc. These differences between the altered and the non-altered chert are more evident when they are analyzed macroscopically and using stereoscopic light microscopy, than when they are analyzed under ESEM or EDX (this last technique, the EDX, has shown no differences between altered and fresh chert samples). However, the ESEM has been very useful to describe and characterize the alteration of chert when it has been used in combination with the macroscopic analysis; specifically with macroscopic colour photographs as references. Meanwhile, the density calculations have provided very good results, showing quantitatively the loss of density (and of weight) of the altered chert, that could be appreciated at a glance.

So we defend that the most objective method to describe and characterize the alteration of chert is the combination of different techniques (macroscopic analysis, stereoscopic light microscopy, ESEM and density calculations) together with a good graphic documentation of the alterations and its characteristic traits at different scales. This method of description allows an easier comparison between alterations of chert of different assemblages.

Following the observations outlined in this study we propose that the description of chert alteration should include:

- An allusion to whether the alteration is superficial or total.
- A reference, if needed, to other traits as fractures, fissures, etc.
- It should be clarified if the external part of the sample preserves the original morphology (edges, extractions, etc).
- If any, the differences between the inner and the outer part of the samples should be described, indicating the thickness of each one of them. The transition between the two parts should also be described, specifying whether this transition is gradual or abrupt.
- A description of the coloration, compactness, lack of cohesion and porosity of both, the internal and the external part.
- A reference to the loss of weight, and better if it is accompanied with a density calculation.

The description should be complemented with graphic documentation of the traits that have been described: always macroscopic photographs, and microscopic images when possible.

Conclusions

A kind of natural chert alteration, called white patina, has been analyzed by many authors. This alteration seems to correspond with the alteration that we have studied, and that can be found in chert tools of Atapuerca, Cansaladeta and Orgnac 3. The lack of agreement on the terminology and the lack of documentation towards this type of alteration make it difficult to know whether the alteration that we are studying is the same as the one described by other authors or not. Therefore we propose a description for this alteration based on certain parameters, mainly macroscopic, that include a reference to the superficiality or not of the alteration and a good graphic documentation.
<table>
<thead>
<tr>
<th>TYPE OF CHERT</th>
<th>Macroscopic analysis and stereoscopic light microscopy</th>
<th>MERA</th>
<th>EDX</th>
<th>Density calculations</th>
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</thead>
</table>
| Fresh geological chert of Atapuerca | Number of samples analyzed: 6  
Light colour (white, grey and beige); opaque; variability in terms of grain size and compactness. | Number of samples analyzed: 3  
Predominance of irregular and heterogenic surfaces; presence of accumulations of grains with a geometrical shape very well defined; high presence of holes and empty spaces. | Number of samples analyzed: 3 - Principal elements: Si and O.  - Other elements: Ca and Al (less than 2 wt %). |
| Altered archaeological chert of Gran Dolina and Sima del Elefante, Atapuerca | Number of samples analyzed: 7  
Low variability in terms of state of conservation; whitish coloration; high fragility; different state of conservation in a same sample (outer part well compact and well preserved, and inner part very powdery). | Number of samples analyzed: 1 - External surface: smooth and rounded (the edges and fissures are not very well defined; there is an absence of well defined geometrical forms).  - Inner part: very irregular and rough; presence of big cavities and holes, rounded and detached grains.  - Transition: variable; presence of fissures that prove the fragility of the chert. | Number of samples analyzed: 1 - Predominance of Si and O in both the internal and the external en la part of the sample, and presence of Ca, Al, Fe, Zr, In, Sb and Tb (< 5 wt %) where sediment is present. |
| Fresh geological chert of Francoli river | Number of samples analyzed: 5  
Light colour (grey, beige); variability in terms of opacity; variable in grain size (little predominance of big grain); high presence of impurities and preferential plains of fracture. | Number of samples analyzed: 3 - Variability in terms of grain size and compactness; combination between smooth and rough surfaces. | Number of samples analyzed: 3 - Principal elements: Si and O.  - Other elements: Ca (less than 5 wt %). |
| Altered archaeological chert of Cansaladeta | Number of samples analyzed: 9  
Variability in terms of state of conservation; whitish coloration in general, although sometimes the samples preserve some colorations of the fresh chert; different state of conservation (outer part well compact and well preserved, and inner part very powdery although not as much as that of the archaeological chert of Atapuerca); presence of ancient fractures and fissures. | Number of samples analyzed: 1 - External part: rounded (the edges and fissures are not very well defined; there is an absence of well defined geometrical forms).  - Inner part: irregular, rough, powdery, but not as much as that of the archaeological chert of Atapuerca.  - Transition: very marked (thick external part, in which there are grains with a very well defined geometrical shape). | Number of samples analyzed: 1 - External part: Si and O  - Inner part: Si and O  - Presence of Ca (near to 20 wt %) and of Al, Fe, Mg, S, Cl or K (< 2 wt %) in areas where sediment is present. |
| Fresh geological chert of Aven Lien Dit Fouillose | Number of samples analyzed: 7  
Variability in coloration (black, brown, grey, etc.); translucent; variability in grain size and composition; combination of fine grain and smooth surfaces with rough surfaces that have impurities and inclusions (fossils, quartz crystallizations, etc.). | Number of samples analyzed: 2 - Predominance of fine grain, and of smooth and homogenised surfaces. Although that, there is and important presence of fossils, impurities and big crystallizations. | Number of samples analyzed: 7 - Smooth surfaces: Si and O  - Rough surfaces with fossils: high presence of Ca. |
| Altered archaeological chert of Orgnac 3 | Number of samples analyzed: 38  
High variability in terms of the state of conservation; variability in coloration (predominance of white, but presence of the colours of the fresh chert); variable fragility; different state of conservation in a same sample (outer part well compact and well preserved, and inner part very powdery but with less holes than those of the altered chert samples of Atapuerca and Cansaladeta) | Number of samples analyzed: 5 - External part: smooth and rounded; predominance of fine grains; presence of some crystallizations and impurities; low presence of fossils.  - Inner part: compact but powdery; very fine grained; low presence of fossils.  - Transition: not very marked (the external surface is very thin). | Number of samples analyzed: 5 - External part: Si and O  - Inner part: Si and O  - Areas with sediment: presence of Ca, Al, Fe, Mg, S, Cl or K (< 5 wt %). |

Tab.1. Resume of the principal results obtained through the analysis of the different chert types (fresh geological chert of Atapuerca, altered archaeological chert of Gran Dolina and Sima del Elefante, fresh geological chert of Francoli river, altered archaeological chert of Cansaladeta, fresh geological chert of Aven lien dit Fouillose and altered archaeological chert of Orgnac 3) using different analytical techniques (macroscopic analysis, stereoscopic light microscopy, ESEM, EDX and density calculations).
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Bibliographie


