archaeometry

Archaeometry **55**, 5 (2013) 794–805 doi: 10.1111/j.1475-4754.2012.00712.x

DETECTING AND QUANTIFYING HEAT TREATMENT OF FLINT AND OTHER SILICA ROCKS: A NEW NON-DESTRUCTIVE METHOD APPLIED TO HEAT-TREATED FLINT FROM THE NEOLITHIC CHASSEY CULTURE, SOUTHERN FRANCE*

P. SCHMIDT,[1]† V. LÉA,[2] PH. SCIAU[3] and F. FRÖHLICH[1]

[1]*Muséum national d'histoire naturelle, Département de Préhistoire UMR 7194, Centre de spectroscopie infrarouge, CP 57, 57 rue Cuvier, 75231 Paris Cedex 05, France*
[2]*TRACES—UMR 5608, Université Toulouse II le Mirail, Maison de la Recherche, 5 allée A. Machado, 31058 Toulouse CEDEX 9, France*
[3]*CEMES—UPR 8011, Université de Paul Sabatier, 29 rue Jeanne Marvig, BP 94347, 31055 Toulouse CEDEX 4, France*

Heat treatment of lithic raw material is known from the Middle Stone Age to the Neolithic. These findings require archaeometric techniques and methods for detecting the heat-induced effects within lithic artefacts. However, the existing methods are often cost-intensive and time-consuming, and most of them are destructive. Here, we present a new method using the infrared spectroscopic measurement of the strength of H-bonds formed between surface silanole groups (SiOH) and H_2O molecules held in open pores of the samples. The reduction of H-bond strength in chalcedony is shown to be strongly correlated with the loss of open pores induced by heat treatment. Hence, the method is based on measuring one of the transformations aimed for by the instigators of the heat treatment: the reduction of porosity that modifies the rock's mechanical properties. A first application to heat-treated material from the Neolithic Chassey culture (southern France) shows that flint was heated to temperatures between 200°C and 250°C in this period. This has important implications for the study of the procedures used and the heating environments. Our new method is non-destructive, rapid, cost-effective and allows for detection of the used annealing temperatures.

KEYWORDS: HEAT TREATMENT, FLINT, CHALCEDONY, CHASSEY CULTURE, CHASSÉEN, POROSITY LOSS, NEAR-INFRARED SPECTROSCOPY, SILANOLE (SIOH)

INTRODUCTION

Intentional heat treatment of lithic raw material—that is, the deliberate transformation of the rock's mechanical properties by the action of heat—has been recognized from a large number of archaeological contexts, such as North American Palaeo-Indian groups (Crabtree and Butler 1964; Pavlish and Sheppard 1983), the European Upper Palaeolithic Solutrean culture (Bordes 1969; Tiffagom 1998), the South African Middle Stone Age (Brown *et al*. 2009; Mourre *et al*. 2010) or the Southern European Neolithic (Binder 1984; Léa *et al*. 2007). These findings require reliable methods that allow the detection of heat-induced transformations in lithic artefacts. To date, the only method able to prove the intentionality of heat treatment is the macroscopic assessment of a greasy surface lustre that appears on the fracture surfaces (Crabtree and Butler 1964). This surface gloss is caused by structural and crystallographic transformations that alter

---

*Received 10 April 2012; accepted 18 June 2012
†Corresponding author: email schmidt@mnhn.fr

the material's fracture properties (Schmidt *et al.* 2012) and can therefore be observed only on fracture surfaces of flakes struck after heating. However, taphonomic processes (glossy surface due to taphonomy, patina etc.) can alter an artefact's surface in such a way that the heat-induced surface gloss may not be recognized; or, inversely, in such a way that unheated artefacts may be mistaken for heat-treated ones (Olausson and Larsson 1982; Griffiths *et al.* 1986). This problem can be overcome if one single side of an artefact shows both glossy and dull fracture negatives that can be directly compared, hence indicating that one part of the previously knapped flakes was removed before heat treatment and another part afterwards. Unfortunately, such unambiguous artefacts are rather rare and in order to exclude a taphonomic origin of the observed gloss, many cases require the nature of the surface lustre to be verified by an archaeometric approach that allows for an assessment of the heat-induced transformations in the material. Several authors have proposed such archaeometric techniques for recognizing heat treatment of artefacts, on the basis of the physical, chemical or magnetic properties of materials. These include thermoluminescence (TL) (Göksu *et al.* 1974; Melcher and Zimmerman 1977), electron spin resonance (ESR) using quartz crystal defects (Robins *et al.* 1978) or trace elements (Robins *et al.* 1981; Griffiths *et al.* 1982, 1986), and the magnetic susceptibility of impurities in the rocks (Borradaile *et al.* 1993; Rowney and White 1997). However, none of these methods allow for quantification of the transformations aimed for by the instigators of the heat treatment (i.e., the transformation of the material's properties), for all of them are based on the measurement of impurities, defects or elements that occur in minor amounts in the rocks. Additionally, most of them are cost-intensive, time-consuming and partially or completely destructive. Here, we present an improved version of the method proposed by Schmidt (2011). This new method is based on the infrared spectroscopic measurement of the processes directly causing the transformations aimed for by the instigators of the heat treatment. It is non-destructive, rapid (1–2 min per sample) and cost–effective.

This method is applied to the Neolithic Chassey culture from southern France, for it is during this period, between 4100 cal BC and 3500 cal BC, that heat treatment of flint was systematically used for producing pressure-flaked bladelets (Léa 2005), thus becoming a key element in the lithic reduction sequence. Heat treatment may even have been the reason for the widespread success of the flint from the Vaucluse that was found across all of southern France, and in the regions of Tuscany (Italy) and Catalonia (Spain). The reduction sequence includes heat treatment of large volumes of flint shaped into pre-cores (preforms) that could attain 7 cm in diameter. The recent discovery of the lithic production site of Saint-Martin in the Vaucluse region (southeastern France, excavated by V. Léa), where large preforms were heat-treated, shows that this treatment was conducted by specialists who did not seem to have shared their know-how (Léa 2004). To date, it has not been possible to experimentally heat-treat such large preforms, partly because of a lack of knowledge of the heating temperatures used by the Chassey artisans. Thus, a first application of this new method for detecting and quantifying heat treatment to the Chassey culture is of particular interest, because (1) it can be tested on unquestionably heat-treated artefacts and (2) the determination of the heating temperatures may shed light on the processes used by these specialized artisans.

THEORETICAL BACKGROUND

Flint is a chemically precipitated sedimentary silica rock consisting mostly of length-fast (LF) chalcedony. The term 'chalcedony' is used here in its mineralogical sense (Michel-Levy and Munier-Chalmas 1892) and does not refer to the macroscopic description of a material (a translucent colourless rock) as it often does in archaeology. LF-chalcedony is a cryptocrystalline framework of α-quartz (SiO_2) crystallites of a size of 50–100 nm (Rios *et al.* 2001) that line up to form fibres. The quartz *c*-axis is oriented normal to the fibre axis. This type of chalcedony can contain up to 2 wt% of 'water' (Flörke *et al.* 1982; Graetsch *et al.* 1985) that is subdivided into molecular water (H_2O) and chemically bound hydroxyl (silanole, SiOH). Typically, flint contains 0.5–0.8 wt% of SiOH and 0.3–0.6 wt% of H_2O, strongly retained in liquid inclusions, crystal defects and grain boundaries (Schmidt *et al.* 2011). LF-chalcedony can also absorb 0.2–0.4 wt% of molecular water within a network of open pores (Schmidt *et al.* 2011). Upon heat treatment, silanole is lost from 200°C upwards and new Si–O–Si bonds are created according to the following reaction (Schmidt *et al.* 2012):

$$\text{Si-OH HO-Si} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}.$$

This chemical reaction is responsible for the observed mechanical transformations of the rock (the increase of its hardness and a reduction of its fracture toughness) and contributes to the closing of almost all of its open pores (Schmidt 2011; Schmidt *et al.* 2012). The loss of porosity and other silanole-related defects also results in a more homogeneous rock that permits a better force transmission during debitage.

One way of quantifying these water-related transformations in LF-chalcedony upon heat treatment is near-infrared spectroscopy (NIR). The NIR absorption spectrum of chalcedony shows two combination bands caused by a molecular water OH stretching/HOH bending combination mode at ≈5200 cm^{-1} and a silanole OH stretching/SiOH bending combination mode at ≈4500 cm^{-1} (Aines *et al.* 1984; Kronenberg 1994). Working on opal ($SiO_2 \cdot nH_2O$), Langer and Flörke (1974) deconvoluted the silanole combination band into a high-energy component on its high-frequency side and a low-energy component on its low-frequency side. For LF-chalcedony, Schmidt (2011) showed the total number of components of the SiOH band to be three. In the hydrated state of the samples (i.e., the samples contain molecular water in their open porosity), these three components have their absorption maxima at 4545 cm^{-1}, 4469 cm^{-1} and 4345 cm^{-1} (Schmidt 2011). Figure 1 shows the NIR H_2O and SiOH combination bands and the three components of the silanole band. Schmidt *et al.* (2011) showed the intensities of these high- and low-energy components to be different depending on whether the samples are in the 'hydrated state' or the 'dehydrated state'. In the 'dehydrated state' (i.e., the sample's open porosity is devoid of molecular water), the high-energy component at 4545 cm^{-1} is the most intense band under the absorption envelope, whereas the low-energy component at 4469 cm^{-1} is the most intense band in the 'hydrated state'. This can be explained by the different involvement of the sample's silanole groups in H-bonding in both states. In the 'hydrated state', water molecules retained in pores interact with the surface silanole groups of the pore walls, forming H-bonds. Since the low-energy components of the SiOH band correspond to silanole groups forming H-bonds (Langer and Flörke 1974), the combination band's absorption maximum lies near 4470 cm^{-1}. In the 'dehydrated state', the $SiOH \cdots OH_2$ interaction is not possible. The high-energy component that corresponds to silanole groups that do not form H-bonds is more intense and the combination band's absorption maximum lies near 4545 cm^{-1}. This variation is the cause of the modification of the SiOH band's morphology in both states (Fig. 1). In the case of heat treatment of the flint samples, the shape of the SiOH combination band is also modified (Schmidt *et al.* 2011, 2012). As stated earlier, the volume of the water-absorbing pores is progressively reduced upon rising temperatures. A reduction of the pore volume means a reduction of water molecules that can form $SiOH \cdots OH_2$ hydrogen bonds. Hence, the high-frequency component of the band becomes more

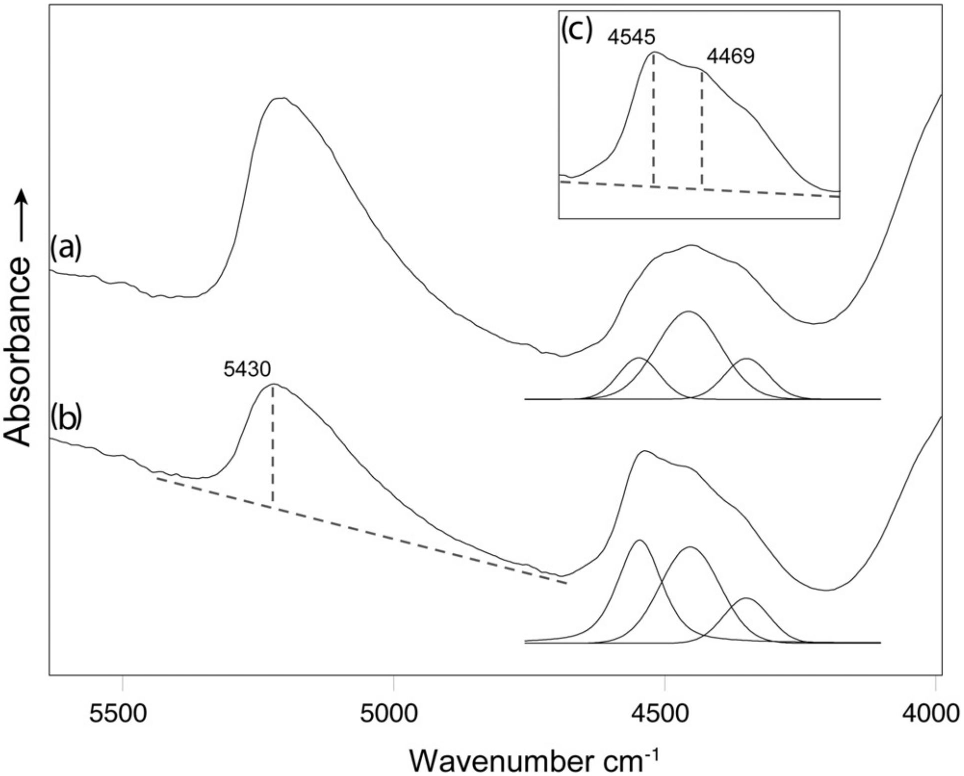

Figure 1 *A comparison between the NIR spectra of VC-12-01 in its hydrated (a) and dehydrated (b) states: sample thickness 1280 ± 5 µm, spectra displaced vertically. Notice the difference of the ≈5200 cm^{-1} H_2O combination band's intensity in the two states and the different shape of the SiOH band at ≈4500 cm^{-1}. The bands under the SiOH absorption envelope were obtained using a pseudo-Voigt deconvolution model and correspond to the three different components of the combination band. The high-energy component at 4545 cm^{-1} is caused by free SiOH, whereas the two low-energy components at 4469 cm^{-1} and 4345 cm^{-1} are caused by SiOH groups involved in H-bonding. Free SiOH is relatively more abundant in the 'dehydrated state', modifying the overall shape of the SiOH combination band. The broken line shows the baseline for the linear absorption measurement at 5430 cm^{-1} (H_2O). (c) The baseline and positions for the measurement of the linear absorption values that are used for calculating the 4545/4469 cm^{-1} ratio.*

intense with reducing pore volume. The transformation of the SiOH combination band's shape is therefore an indirect measure of the water-retaining pore volume of the flint samples and can be used to quantify their heat-induced transformations.

In order to measure the SiOH band shape, Schmidt *et al*. (2011) proposed the ratio between two linear absorptions measured at 4545 cm^{-1} and 4469 cm^{-1}. This ratio was shown to be a good measure of the hydrogen bond strength of the sample's silanole groups. The 4545/4469 cm^{-1} ratio is a relative measure and is therefore independent of the optical pathway in the analysed sample. Moreover, because of the proximity of the two measured frequencies, heterogeneous intensity loss at different frequencies due to surface relief can be neglected. Thus, the ratio can be measured through any part of a sample, regardless of its surface. The sample has to be thin enough not be completely opaque in the NIR and thick enough for the SiOH combination band not to be too weak. The ideal thickness was experimentally found to be between 0.5 and 4 mm. Most cutting edges of archaeological flakes and blades lie within this range of thickness at their distal parts. Such an analysis of a flake is completely non-destructive for the analysed material. In order to test the potential of this method for determining the heat-induced reduction of pore volume in flint, we applied the measurement of the 4545/4469 cm^{-1} ratio to an archaeological assemblage of 41 heat-treated and not-heated flint flakes from the Neolithic Chassey culture.

SAMPLES AND EXPERIMENTAL

Forty-one archaeological flakes and two geological samples, of a light brown flint from the Barremian or the lower Abtian (Bedoulian), were used to test the potential of the method presented here. This flint is locally known as 's*ilex blond barrémo-bédoulien*'. Its mineralogy was assessed by microscopic observations of petrographic thin sections (30 µm, polarized light) cut from the geological samples. The flint is made up of approximately 85% length-fast chalcedony and up to 15% length-slow chalcedony (LS-chalcedony or quartzine). Very few isolated detritic quartz grains could be observed. The sample numbers and descriptions are summarized in Table 1. The geological samples were collected at Combes de Veaux, at the foot of Mont Ventoux (Vaucluse, France), because this area has previously yielded several lithic workshops dating from the Chassey culture (Léa 2004). The 41 archaeological samples were unearthed during the 2010 excavation of a 2 m^2 measuring pit (sector 1) in the northern part of the Chasssey culture lithic production site of Saint-Martin at Malaucène (Vaucluse, France). They are made of the same flint as the geological samples. The sediments dating from the Chassey culture have a thickness of approximately 80 cm at this site and can be subdivided into four sub-horizons. All of the analysed flakes are shaping flakes, and their sizes are summarized in Table 1. Heat-treated flakes could be easily distinguished from flakes that were not heat-treated, on the basis of the presence of a well-developed greasy surface lustre on their fracture surfaces. On this basis, the assemblage was separated into two groups: 16 not-heated flakes and 25 heat-treated artefacts.

The two geological samples were cut into ≈1.2 mm thick slabs and diamond polished on both sides. Their analysis was based on an approach elaborated by Schmidt *et al.* (2011, 2012), using near-infrared (NIR) spectroscopy and an experimental protocol aiming to reproduce heat treatment at different temperatures.

NIR transmission spectra were acquired at normal incidence using a Bruker Vector 22 FTIR spectrometer. Data was recorded between 5600 and 4000 cm^{-1} with a resolution of 8 cm^{-1} and unpolarized radiation. Spectral acquisition was repeated 200 times in order to obtain spectra with a good signal-to-noise ratio. During analysis, samples were individually mounted on a 5 cm large metal plate that slides into the standard sample holder. A circular aperture of 8 mm in diameter cut into the plate delimited the analysed area on the samples. The fixation of the slabs and archaeological flakes on the metal plate was realized using tape outside of the aperture's perimeter. The baseline for absorbance measurements of the two combination bands (H_2O at 5430 cm^{-1} and SiOH at 4545 cm^{-1} and 4469 cm^{-1}) was a straight line between the two lowest points on either side of the absorption bands (Fig. 1). H_2O concentrations were calculated using the linear absorption coefficient $\alpha = 1.14$ L mol^{-1} cm^{-1} (Scholze 1960), applied to the absorbances measured at 5430 cm^{-1}. Error bars were calculated by repeating spectral acquisition 30 times on one sample.

The experimental heat treatment temperatures were as follows: 110°C, 150°C, 200°C, 250°C, 300°C, 350°C, 400°C, 450°C, 500°C, 550°C and 600°C. The expected transformations are essentially completed after 50 min of annealing at a given temperature (Fukuda and Nakashima 2008; Schmidt *et al.* 2012), but the samples were held at each of these temperatures for 2.5 h. NIR spectra were recorded in the 'dehydrated state' immediately after the samples had cooled to

Table 1 *Sample numbers and descriptions*

Sample number	*Thickness (μm)*	*Description*
Geological samples		
VC-12-01	1280 ± 5	Light-brown to yellowish homogeneous flint from solid limestone; Barremian to lower Abtian; 85% LF-chalcedony, 15% LS-chalcedony; minor macro-quartz
VC-12-02	1200 ± 5	

Sample number	*Dimensions (mm)*			*Short sample number*
	*Thickness**	*Breadth*	*Length*	
Archaeological samples previously identified as not heated				
MAL2010-I1-1902	1	12.5	9.5	1
MAL2010-I1-1903	1.5	8.5	20	2
MAL2010-I1-1905a	2.5	23	49.5	3
MAL2010-I1-1905b	3	13	20	4
MAL2010-I1-1905c	2	16	16.5	5
MAL2010-I1-1905d	2	10	16.5	6
MAL2010-I1-1905e	2.5	14	36	7
MAL2010-I1-1905f	2.5	14	23.5	8
MAL2010-I1-1905g	3.5	20	15.5	9
MAL2010-I1-1905h	2.5	14	21.5	10
MAL2010-I1-1905i	1	14	21.5	11
MAL2010-I1-1905j	2.5	19.5	12.5	12
MAL2010-I1-1905k	2.5	10	11.5	13
MAL2010-I1-1905l	2	11	16	14
MAL2010-I1-4302	2	17.5	10	15
MAL2010-I1-4303	2	22.5	42	16
Archaeological samples previously identified as heat-treated				
MAL2010-I1-1899a2	2.5	9	20	17
MAL2010-I1-1899a	1.5	14.5	24.5	18
MAL2010-I1-1899b2	2	8	16.5	19
MAL2010-I1-1899b	2.5	21.5	10	20
MAL2010-I1-1899c2	2	8	12.5	21
MAL2010-I1-1899c	2.5	14.5	15	22
MAL2010-I1-1899d	3.5	12	18	23
MAL2010-I1-1899e	2	9	11.5	24
MAL2010-I1-1899f	1.5	9.5	15.5	25
MAL2010-I1-1899g	1.5	9	8.5	26
MAL2010-I1-1899h	3	9	15.5	27
MAL2010-I1-1899i	2.5	15.5	17.5	28
MAL2010-I1-1903c	2.5	10	17.5	29
MAL2010-I1-1903d	2	11.5	18.5	30
MAL2010-I1-1903e	1.5	12.5	16	31
MAL2010-I1-1903f	2	14.5	11	32
MAL2010-I1-1903g	1.5	14	10.5	33
MAL2010-I1-1903h	1.5	8	14.5	34
MAL2010-I1-1903i	1	11	14	35
MAL2010-I1-1903j	2	12.5	11.5	36
MAL2010-I1-1903k	3	19.5	20	37
MAL2010-I1-1903l	1.5	10	14.5	38
MAL2010-I1-1903m	2	10	12	39
MAL2010-I1-2056a	2	15	15	40
MAL2010-I1-2056b	3	12.5	32	41

*Unlike the breadth and length, the thicknesses are not the maximum thicknesses of the flakes, but average thicknesses measured at the zone where the infrared transmission measurements were acquired.

room temperature. The samples were then rehydrated in deionized H_2O for 24 h at 1 bar and 21°C and a second spectrum was acquired in the 'hydrated state'. After this, the samples were heated to the next higher temperature and the measuring protocol was repeated. The ramp rate for all temperature steps was 10°C min^{-1}. In order to measure the content of H_2O retained in open pores of the samples, the 5430 cm^{-1} H_2O band's absorption in the 'dehydrated state' spectra was subtracted from the band's absorption in the 'hydrated state' spectra. The value thus obtained corresponds to water absorbed by open pores of the rock.

The archaeological samples were dehydrated at 110°C for 3 days in order to allow water and other substances held in open pores to 'evaporate'. This first dehydration is important because open pores of the samples may retain substances due to cleaning and post-excavation treatment (acetone, ethanol) or substances due to taphonomic agents. The dehydrated samples were then hydrated in deionized H_2O for 24 h at 1 bar and 21°C before the NIR spectra were recorded. The parameters for spectral acquisition were the same as for the polished slabs of the two geological samples. Mostly, parts with a thickness between 1.5 and 2.5 mm were analysed (Table 1).

RESULTS

Geological samples

Figure 2 is a plot of the temperature-dependent evolution of the 4545/4469 cm^{-1} ratio for the two geological samples. The values remain unchanged below 200°C in both samples and increase from 200°C upwards. For sample VC-12-01, the increase of the ratio is strongest between 200°C and 300°C, and then again from 400°C upwards. This evolution seems less clear for VC-12-02, but the overall shape of the plot indicates the same tendency. A comparison of these 4545/4469 cm^{-1} ratio values with the thermal evolution of water-retaining open porosity of the samples (Fig. 3) clearly shows that the first increase of the value between 200°C and 300°C coincides with the loss of open pores. Both samples lose almost all of their open pores between these temperatures (VC-12-01, from 0.22 wt% at 200°C to 0.015 wt% at 300°C—i.e., a reduction of 93%; VC-12-02, from 0.34 wt% at 200°C to 0.034 wt% at 300°C—i.e., a reduction of 90%). Thus, the increase of the 4545/4469 cm^{-1} ratio at these temperatures can be correlated with the loss of water-retaining open porosity in the LF-chalcedony of the flint. The increase of the ratio at temperatures above 400°C can most probably be attributed to the accelerated loss of silanole (Flörke *et al.* 1982; Graetsch *et al.* 1985; Schmidt *et al.* 2011, 2012), causing a reduction of the H-bond strength between vicinal silanole groups at defect sites and grain boundaries.

Archaeological samples

Figure 4 is a plot of the 4545/4469 cm^{-1} ratio values obtained from the 41 archaeological samples. The values are also summarized in Table 2. Samples that were previously identified as not heated (samples 1–16) have values between 0.75 and 0.79, with one exception. Samples that were previously identified as heat-treated (samples 17–41) have higher values (between 0.83 and 0.92). Three exceptions (samples 29, 36 and 37) show values similar to those of not-heated artefacts. As can be seen from the theoretical considerations in the 'Theoretical background' section and the experimental results obtained from geological samples, the increase of the ratio values in heat-treated artefacts is a measure of their porosity loss. Both groups, heat-treated and not heated, can easily be distinguished through their 4545/4469 cm^{-1} ratio values, thus indicating that the measurement of this ratio is a reliable method for determining archaeological heat treatment.

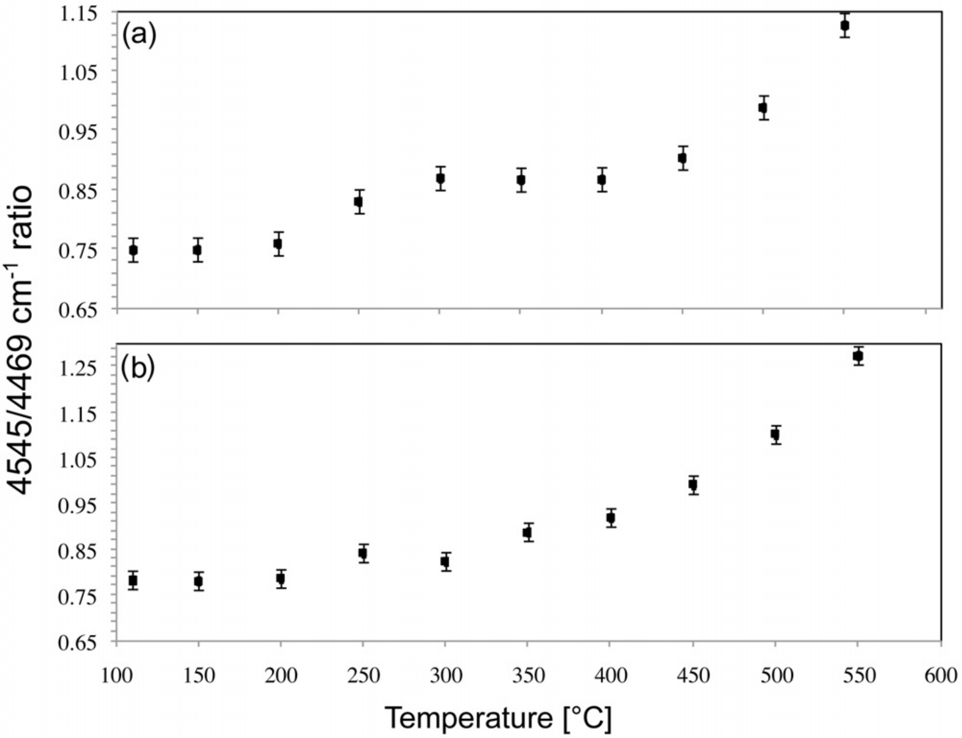

Figure 2 *Two plots of the value of the 4545/4469 cm^{-1} ratio as a function of temperature, for VC-12-01 (a) and VC-12-02 (b). The ratio is obtained by dividing the value of the linear absorption measured at 4545 cm^{-1} by the value of the linear absorption measured at 4469 cm^{-1}. It expresses the strength of H-bonds formed by the sample's SiOH groups. The value increases for a first time from 200°C upwards and again from 400°C upwards. A comparison of Figures 2 and 3 shows the value's increase between 200 and 300°C to be strongly correlated with the loss of open pores in the samples.*

DISCUSSION

The relatively low ratio values for samples 29, 36 and 37 may be due to their erroneous assignment to the group of heat-treated artefacts. However, two of the flakes show both glossy and dull fracture negatives on their dorsal side, clearly emphasizing that they were indeed heat-treated. The low 4545/4469 cm^{-1} ratio values must therefore have a different origin. This ratio expresses the capacity of the rock's pores to rehydrate. Thus, it is strongly correlated with the sample's total open pore volume. Internal fractures or structural heterogeneities within the rocks (microfossils, macro-porosity) may artificially lower the ratio. In fact, two of the three flakes exhibit visible internal fractures that might have been induced by overheating. It appears possible that the low values are due to a different type of open pore, caused by fracturing or crazing. This phenomenon is fairly rare in the studied sample (3 out of 24 heat-treated flakes) and does not conflict with the usefulness of the method for determining heat treatment of flint artefacts. However, it clearly appears that this method must be applied to a statistically significant sample.

The artefact's heating temperatures may be estimated by comparing the 4545/4469 cm^{-1} ratio values obtained from the experimental heating sequence (geological samples) and the values

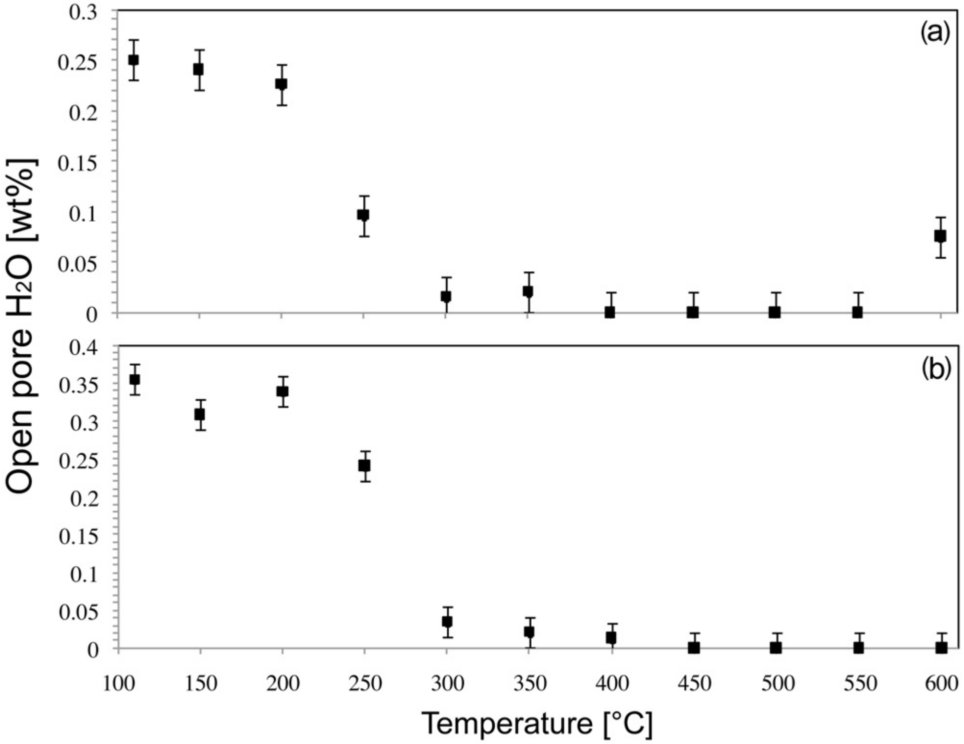

Figure 3 *Two plots of the content of H_2O held in open pores of samples VC-12-01 (a) and VC-12-02 (b) as a function of temperature. The open-pore H_2O content is expressed as the weight percentage of the total samples, and is obtained by subtracting the value of the linear absorbance measured at 5430 cm^{-1} on 'dehydrated state' spectra from this same value measured on 'hydrated state' spectra. The resulting value corresponds to the absorbance caused by water held in open pores of the sample, which can be dehydrated and rehydrated. The figure shows open pores to be essentially lost between 200 and 300°C, indicating a good correlation with the increase of the 4545/4469 cm^{-1} ratio shown in Figure 2.*

measured from the heat-treated Chassey flakes. However, the absolute values of the ratio may also be influenced by taphonomic processes contributing to the loss of open pore volume in the samples. These taphonomic processes may have been different in the sample's post-depositional history, causing slightly different ratio values for geological and archaeological samples. The heat-induced transformations are expected to add to this ratio value. Thus, only the difference between the values of not-heated and heated samples can be taken into account. Applied to the Chassey flakes, this means the following.

The mean of the not-heated artefact's values is 0.773, whereas the average of the heat-treated flake's values is 0.851, producing a difference of 0.078. The ratio of VC-12-01 shifts from 0.748 before heat treatment to 0.829 after annealing at 250°C, producing a difference of 0.081. The comparison between the experimentally obtained ratio shift (0.081) with the artefact's ratio shift (0.078) indicates an average heating temperature between 200 and 250°C for the analysed Chassey flakes.

This temperature interval corresponds to the lower part of the effective temperature range for heat-induced transformations in flint (Schmidt *et al*. 2012). Most flint samples begin to lose open pores at slightly higher temperatures than the samples in the present study (Schmidt *et al*. 2011).

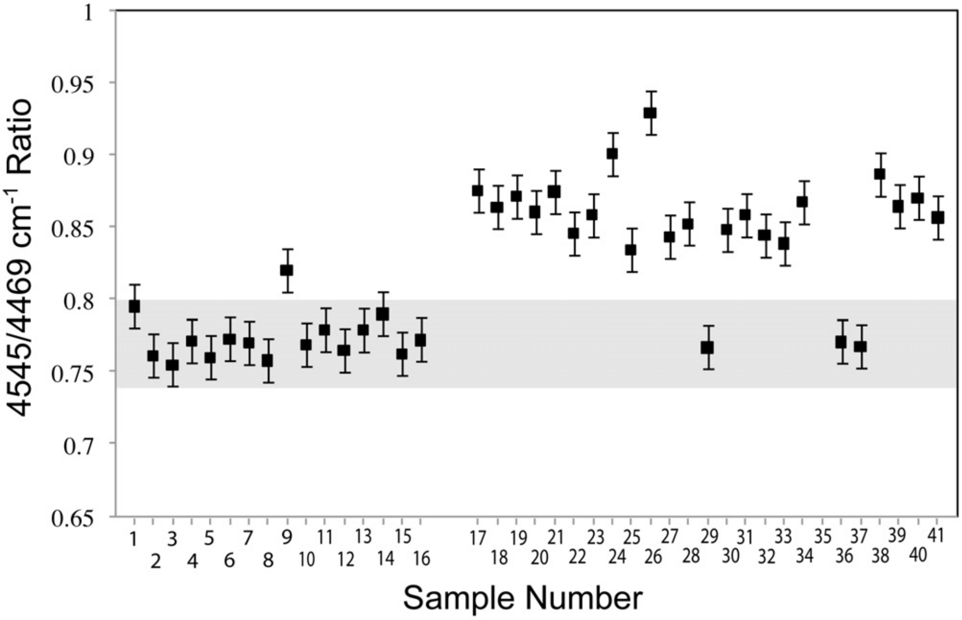

Figure 4 *A plot of the values of the 4545/4469 cm^{-1} ratio obtained from archaeological Chassey culture samples. Samples are named using the short sample numbers shown in Table 1. Samples 1–16 were previously identified as not heated and samples 17–41 as heat-treated. Both groups are clearly distinguished by their 4545/4469 cm^{-1} ratio value. Not-heated samples have an average value of 0.773, while heat-treated samples have an average value of 0.851.*

Table 2 *Values of the 4545/4469 cm^{-1} ratio for the archaeological samples: for complete sample numbers, see Table 1*

Sample number	*Value*	*Sample number*	*Value*	*Sample number*	*Value*	*Sample number*	*Value*
1	0.795 ± 0.015	12	0.765 ± 0.015	23	0.858 ± 0.015	34	0.867 ± 0.015
2	0.761 ± 0.015	13	0.779 ± 0.015	24	0.900 ± 0.015	35	1.215 ± 0.015
3	0.755 ± 0.015	14	0.790 ± 0.015	25	0.834 ± 0.015	36	0.771 ± 0.015
4	0.771 ± 0.015	15	0.762 ± 0.015	26	0.929 ± 0.015	37	0.767 ± 0.015
5	0.760 ± 0.015	16	0.772 ± 0.015	27	0.843 ± 0.015	38	0.886 ± 0.015
6	0.773 ± 0.015	17	0.875 ± 0.015	28	0.852 ± 0.015	39	0.864 ± 0.015
7	0.770 ± 0.015	18	0.864 ± 0.015	29	0.767 ± 0.015	40	0.870 ± 0.015
8	0.758 ± 0.015	19	0.871 ± 0.015	30	0.848 ± 0.015	41	0.856 ± 0.015
9	0.820 ± 0.015	20	0.860 ± 0.015	31	0.858 ± 0.015		
10	0.769 ± 0.015	21	0.874 ± 0.015	32	0.844 ± 0.015		
11	0.779 ± 0.015	22	0.845 ± 0.015	33	0.838 ± 0.015		

This may be explained by the relatively high percentage of LS-chalcedony in the samples. LS-chalcedony essentially shows the same heat-induced transformations as LF-chalcedony, but the effective temperatures are in all cases 50–100°C lower (Schmidt 2011). Thus, it appears possible that the approximately 15% of LS-chalcedony lowers the reaction temperature of the material. A relatively lower effective temperature for this type of flint raw material has broad implications for research concerning the procedures used and the heating environments. Further experimentation, trying to reproduce the heat treatment of large blocks of the *silex blond barrémo-bédoulien*, may make use of a temperature interval between 200 and 250°C.

CONCLUSION

This new technique makes possible the detection and quantification of heat-induced transformations in silica rocks containing chalcedony. It directly assesses the transformations aimed for by the instigators of the heat treatment; it is non-destructive, rapid (1–2 min per sample) and the cost of an infrared spectrometer is fairly low. Nonetheless, the results have to be interpreted cautiously, because the measured phenomenon is the potential of the samples to rehydrate, which may also be influenced by taphonomic factors. The technique has to be applied to a sample large enough to be of statistical relevance and, additionally, a reference of not-heated material, one that has experienced the same taphonomic processes as the heated samples (typically coming from the same sediment layers), is needed for internal calibration. These requirements present no problems in normal archaeological contexts, because heat-treated artefacts are usually associated with not-heated ones. The determination of the heating temperatures used requires an additional approach based on experimental heat treatment of a geological sample of the same rock. The potential applications of this new method are numerous. It will allow for the study of the role of heat treatment during different chronocultural periods, the procedures used and the heating environments.

ACKNOWLEDGEMENTS

We thank Jean Milot from the Géosciences Environnement Toulouse (GET) for his help in accessing the collection of thin sections cut from the geological samples used for our analyses. We are indebted to the programme ANR-09-BLAN-0324-01 ProMiTraSil for financial support of the fieldwork at the Chassey culture site of Saint-Martin at Malaucène.

REFERENCES

Aines, R. D., Kirby, S. H., and Rossman, G. R., 1984, Hydrogen speciation in synthetic quartz, *Physics and Chemistry of Minerals*, **11**(5), 204–12.

Binder, D., 1984, Systèmes de débitage laminaire par pression: exemples chasséens provençaux, in *Préhistoire de la pierre taillée, 2: économie du débitage laminaire: technologie et expérimentation: III^e^ table ronde de technologie lithique. Meudin-Bellevue, octobre 1982* (eds. J. Tixier, M. L. Inizan and H. Roche), 71–84, Cercle de Recherches et d'Etudes Préhistoriques, Paris.

Bordes, F., 1969, Traitement thermique du silex au Solutréen, *Bulletin de la Société préhistorique française*, **66**(7), 197.

Borradaile, G. J., Kissin, S. A., Stewart, J. D., Ross, W. A., and Werner, T., 1993, Magnetic and optical methods for detecting the heat treatment of chert, *Journal of Archaeological Science*, **20**(1), 57–66.

Brown, K. S., Marean, C. W., Herries, A. I. R., Jacobs, Z., Tribolo, C., Braun, D., Roberts, D. L., Meyer, M. C., and Bernatchez, J., 2009, Fire as an engineering tool of early modern humans, *Science*, **325**(5942), 859–62.

Crabtree, D. E., and Butler, B. R., 1964, Notes on experiment in flint knapping: 1 heat treatment of silica materials, *Tebiwa*, **7**, 1–6.

Flörke, O. W., Köhler-Herbertz, B., Langer, K., and Tönges, I., 1982, Water in microcrystalline quartz of volcanic origin: agates, *Contributions to Mineralogy and Petrology*, **80**(4), 324–33.

Fukuda, J., and Nakashima, S., 2008, Water at high temperatures in a microcrystalline silica (chalcedony) by *in-situ* infrared spectroscopy: physicochemical states and dehydration behavior, *Journal of Mineralogical and Petrological Sciences*, **103**, 112–15.

Göksu, H. Y., Fremlin, J. H., Irwin, H. T., and Fryxell, R., 1974, Age determination of burned flint by a thermoluminescent method, *Science*, **183**(4125), 651–4.

Graetsch, H., Flörke, O. W., and Miehe, G., 1985, The nature of water in chalcedony and opal-C from Brazilian agate geodes, *Physics and Chemistry of Minerals*, **12**(5), 300–6.

Griffiths, D. R., Seeley, N. J., and Symons, M. C. R., 1986, Investigation of heating conditions using ESR spectroscopy, in *The scientific study of flint and chert. Proceedings of the Fourth International Flint Symposium held at Brighton Polytechnic, 10–15 April 1983* (eds. G. de G. Sieveking and M. B. Hart), 259–62, Cambridge University Press, Cambridge.

Griffiths, D. R., Robins, G. V., Seeley, N. J., Chandra, H., McNeil, D. A. C., and Symons, M. C. R., 1982, Trapped methyl radicals in chert, *Nature*, **300**(5891), 435–6.

Kronenberg, A. K., 1994, Hydrogen speciation and chemical weakening of quartz, in *Silica: physical behaviour, geochemistry and materials applications* (eds. P. J. Heaney, C. T. Prewitt and G. V. Gibbs), 123–76, Reviews in Mineralogy 29, Mineralogical Society of America, Washington, DC.

Langer, K., and Flörke, O. W., 1974, Near infrared absorption spectra (4000–9000 cm^{-1}) of opals and the role of 'water' in these $SiO_2 \cdot nH_2O$ minerals, *Fortschritte der Mineralogie*, **53**(1), 17–51.

Léa, V., 2004, Centres de production et diffusion des silex bédouliens au Chasséen, *Gallia préhistoire*, **46**, 231–50.

Léa, V., 2005, Raw, pre-heated or ready to use: discovering specialist supply systems for flint industries in mid-Neolithic (Chassey culture) communities in southern France, *Antiquity*, **79**, 1–15.

Léa, V., Binder, D., Vaquer, J., and Briois, F., 2007, Le Chasséen méridional à Lamelles d'Arnal: évolution de notre perception des industries lithiques, in *26ème Congrès de la Société Préhistorique Française—20–25 septembre 2004, Avignon, supplément BSPF*, 263–76, Paris.

Melcher, C. L., and Zimmerman, D. W., 1977, Thermoluminescent determination of prehistoric heat treatment of chert artifacts, *Science*, **197**(4311), 1359–62.

Michel-Levy, A., and Munier-Chalmas, C. P. E., 1892, Mémoire sur les diverses formes affectées par le réseau élémentaire du quartz, *Bulletin de la société minéralogique de France*, **7**, 159–95.

Mourre, V., Villa, P., and Henshilwood, C. S., 2010, Early use of pressure flaking on lithic artifacts at Blombos Cave, South Africa, *Science*, **330**(6004), 659–62.

Olausson, D. S., and Larsson, L., 1982, Testing for the presence of thermal pretreatment of flint in the Mesolithic and Neolithic of Sweden, *Journal of Archaeological Science*, **9**(3), 275–85.

Pavlish, L. A., and Sheppard, P. J., 1983, Thermoluminescent determination of Paleoindian heat treatment in Ontario, Canada, *American Antiquity*, **48**(4), 793–9.

Rios, S., Salje, E. K. H., and Redfern, S. A. T., 2001, Nanoquartz vs. macroquartz: a study of the α–β phase transition, *The European Physical Journal B*, **20**, 75–83.

Robins, G. V., Seeley, N. J., McNeil, D. A. C., and Symons, M. R. C., 1978, Identification of ancient heat treatment in flint artefacts by ESR spectroscopy, *Nature*, **276**(5689), 703–4.

Robins, G. V., Seeley, N. J., Symons, M. C. R., and McNeil, D. A. C., 1981, Manganese (II) as an indicator of ancient heat treatment in flint, *Archaeometry*, **23**, 103–7.

Rowney, M., and White, J. P., 1997, Detecting heat treatment on silcrete: experiments with methods, *Journal of Archaeological Science*, **24**(7), 649–57.

Schmidt, P., 2011, Traitement thermique des silicifications sédimentaires, un nouveau modèle des transformations cristallographiques et structurales de la calcédoine induites par la chauffe, Unpublished doctoral thesis, Muséum national d'histoire naturelle, Paris.

Schmidt, P., Badou, A., and Fröhlich, F., 2011, Detailed FT near-infrared study of the behaviour of water and hydroxyl in sedimentary length-fast chalcedony, SiO_2, upon heat treatment, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **81**(1), 552–9.

Schmidt, P., Masse, S., Laurent, G., Slodczyk, A., Le Bourhis, E., Perrenoud, C., Livage, J., and Fröhlich, F., 2012, Crystallographic and structural transformations of sedimentary chalcedony in flint upon heat treatment, *Journal of Archaeological Science*, **39**(1), 135–44.

Scholze, H., 1960, Über die quantitative UR-spektroskopische Wasserbestimmung in Silikaten, *Fortschritte der Mineralogie*, **38**(2), 122–3.

Tiffagom, M., 1998, Témoignages d'un traitement thermique des feuilles de laurier dans le Solutréen supérieur de la grotte du Parpalló (Gandia, Espagne), *Paléo*, **10**, 147–61.