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FORMATION OF FLUID INCLUSIONS DURING HEAT TREATMENT OF BARREMO-BEDOULIAN FLINT: ARCHAEOMETRIC IMPLICATIONS*

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At the end of the fifth millennium BC, *the development of a specialized lithic industry in the Chassey societies of south-eastern France and its dissemination as far as Catalonia and Tuscany attest to important socio-economic changes in the Mediterranean Neolithic societies. The lithic production was made on barremo-bedoulian flint that was heat-treated to improve the sharpness of the tools produced. Microscopic observations of archaeological and geological, heated and unheated barremo-bedoulian flint samples allowed us to highlight the heat-induced formation of fluid inclusions. Microthermometry analyses showed that these inclusions contain pure* H_2O*, most probably resulting from the dehydration of length-slow (LS) chalcedony and the closure of narrow pores, according to the model proposed by Schmidt et al. (2012). Our results enable us to estimate the heating temperatures used by Chassey artisans to ≈ 230°C. We also propose the 'pressure cooker' model to explain the migration of liquid water in flint nodules heated to 230°C. Then, we discuss the ability of a particular type of flint to be heat-treated, and hence its value for Neolithic society, which depends on: (1) the amount of LS chalcedony that ensures the water release at relatively low temperature; and (2) on the total volume of porosity available to store the dehydration water.*

KEYWORDS: CHASSEY CULTURE, BARREMO-BEDOULIAN FLINT, HEAT TREATMENT, FLUID INCLUSIONS, MICROTHERMOMETRY

INTRODUCTION

The archaeological context

At the end of the fifth millennium BC, Neolithic societies from the north-western Mediterranean area show important socio-economic changes. The increased craft specialization and the development of trade over long distances are two interrelated phenomena that illustrate these changes. The wide dissemination of specialized lithic production made in the Vaucluse region in the south of France (Léa 2005) by Chassey societies (Phillips 1982) from –4100 to –3500 cal. BC attests to this evolution. This production was made from a particular type of light-yellowish flint of Barremian to lower Aptian age, which has sometimes been called 'honey flint' but that we henceforth call 'barremo-bedoulian flint' in analogy to the commonly used name in French. About a

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thousand Chassey sites have been discovered and for some of them, the barremo-bedoulian flint production represents nearly 99% of all tools (Léa *et al*. 2007). These exchange networks cover the north-western Mediterranean coast and reach Tuscany (Italy) and Catalonia (Spain) (Léa 2005). The exceptional development of this lithic industry is certainly due to the systematic heat treatment that was applied to the flint before pressure knapping of bladelets (Binder 1984, 1991, 1998). While there are other examples of heat treatment in prehistory, the high degree of standardization of the process and the regularity with which it was applied to a particular raw material during the Chassey culture are remarkable. Treatment before breakdown is rare and the large scale of this phenomenon in the Chassey culture is exceptional. Even if heat treatment has been identified on Chassey industry since the 1980s, its precise influence on the raw material remained unclear until a recently terminated interdisciplinary research programme (ANR ProMiTraSil, directed by V. Léa).

Between 2003 and 2008, a first collective research programme allowed us to uncover a dozen Chassey production sites near rich flint outcrops in the Vaucluse region (PCR 'Sites producteurs et consommateurs en Vaucluse, France', directed by V. Léa). The major discovery was the site of Saint-Martin, near the town of Malaucène: archaeological excavations began in 2006 and uncovered particularly well preserved evidence of lithic production workshops and Chassey habitats (excavation supervised by V. Léa; cf., Léa *et al.* 2012). The spectacular amount of lithic material found on this site provides information on each of the stages of preparation of flint. The operational sequence of bladelets manufacture was archaeologically identified: it first consists in shaping a flint nodule to create a standard form, heat-treating it according to a standardized protocol, shaping it a second time to remove the outer layer and then knapping this preform by pressure to make bladelets. This knowledge was not shared by all Chassey communities; it was spatially and temporally segmented. The delicate process of shaping flint before and after heating and the heat treatment itself were carried out on the production sites in the Vaucluse, while the bladelet knapping was performed on consumer sites (Binder and Gassin 1988; Binder and Perlès 1990; Léa 2004). Indeed, heat-treated artefacts made from barremo-bedoulian flint can be found all over the Chassey cultural sphere, from central and northern Italy to eastern Spain, and archaeologists have been wondering about the reasons for the exceptionally widespread distribution of this material. What are the properties that explain the systematic use of this flint to make lithic tools? Understanding the heat-induced transformations in barremo-bedoulian flint may help us to understand the reasons for the extent of this phenomenon, which lasted for more than 500 years (Léa *et al*. 2012).

Intentional heat treatment of flint is a phenomenon that has been identified since the 1960s. Palaeoindian populations from North America were shown to deliberately heat-treat flint, and the benefits that this treatment confers to the knapping process have been mentioned (Crabtree and Butler 1964; Bleed and Meier 1980; Schindler *et al.* 1982). The manufacture of objects from intentionally heated flint by the Solutrean culture of Western Europe was reported (Bordes 1969) and the heat treatment was described as a laborious process that required time and good control of the heating temperature. Other studies have shown that heating of flint has been carried out in various parts of the world from about 164 000 years ago up to recent times (Hester 1972; Mandeville 1973; Brown *et al*. 2009; Domanski *et al*. 2009; Mourre *et al*. 2010). In Europe, this practice reached its peak during the Neolithic, especially in the Chassey society of south-eastern France, where large preforms were heated for blade knapping (Binder 1991; Léa 2004, 2005).

The heating of flint can be considered as a technique to produce a 'new man-made material', the knapping qualities of which have been described as being closer to those of obsidian (Crabtree and Butler 1964). The process induces transformations of the fracture pattern, causing an increased lustre on the fracture surfaces and allowing for the production of sharper blades with respect to flint that has not been heat-treated (Léa *et al.* 2012; Torchy 2012; Schmidt *et al.* 2013a). This may partially result from the fact that heat treatment reduces the porosity of flint (Roqué-Rosell *et al.* 2011, Schmidt *et al.* 2011, 2012). In order to better understand the benefits of flint heat treatment, the physico-chemical changes occurring during this process have been investigated over past years. Several authors have tried to explain the heat-induced transformation as being due to the transformation of accessory iron oxides (Purdy and Brooks 1971; Schindler *et al.* 1982), internal fracturing (Flenniken and Garrison 1975) or recrystallization (Domanski and Webb 1992). Most of these hypotheses have more recently been refuted. Other models suggest the fundamental role of water in the heat-induced transformation of silica rocks. Griffiths *et al.* (1987) proposed an improved knapping quality of flint due to water migration, but his explanation was based on the hypothesis of water integration in flint of Micheelsen (1966), which is now mainly refuted (Flörke *et al.* 1982; Graetsch *et al.* 1985). More recently, Schmidt *et al.* (2012) explained the major heat-induced transformation of flint to be the loss of chemically bound water. Water in flint is present as molecular water (H_2O) and chemically bounded hydroxyl (silanol, Si–OH) (Flörke *et al.* 1982). In this model, the loss of silanol causes the formation of H_2O molecules that can be evacuated through a network of interconnected pores, and it eventually allows for the formation of new Si–O–Si bonds that alter the physical properties of the rocks (Schmidt *et al.* 2012).

Flint is normally composed of more than 90% of chalcedony: an arrangement of nanometer-sized quartz crystals that align to form a fibrous-like texture (Michel-Levy and Munier-Chalmas 1892). Two kinds of chalcedony can be distinguished: length-fast (LF) chalcedony is the most common type, and length-slow (LS) chalcedony is a less common type. Schmidt *et al.* (2013b) showed that the heat-induced reduction of silanol occurs at different temperatures in different types of chalcedony: LF chalcedony loses its silanol from 250 to 550°C, while LS chalcedony loses it between 200 and 300°C (Schmidt *et al.* 2013b).

In the present work, we aim to investigate the role of this structural H_2O by analysing fluid inclusions in heat-treated flint. In order to understand the genesis of these inclusions, we investigated heat-treated archaeological and experimentally heat-treated geological samples. Petrographic analyses of the barremo-bedoulian flint microstructure show the distribution of fluid inclusions in heated flint. Microthermometric and Raman spectrometric analyses of fluid inclusions are used to investigate the composition of the water inclusions and to quantify the heat-treatment temperature. Based on our experimental results, we discuss the particular interest of the barremo-bedoulian flint during heat treatments and we propose a model of the thermal behaviour of flint nodules.

Fluid inclusions: theoretical background

The study of fluid inclusions in a rock is commonly applied in mineralogy, where it may provide valuable information on the mode of formation of minerals (Roedder 1984; Goldstein 2003). During the formation of a crystal from a fluid, irregularities in the crystal growth surface can lead to the trapping of small amounts of the fluid. Generally, we call a ‘fluid inclusion’ a microcavity in a crystal filled with a fluid phase, sometimes accompanied by a vapour phase and/or a solid phase. The inclusion may have a sub-microscopic size but can also measure up to several hundred micrometres in diameter. In transparent minerals such as quartz, or transparent rocks such as flint, these fluid inclusions can be observed with an optical microscope. This method allows us to determine whether a trapped fluid was in contact with the mineral during its growth (primary inclusions) or whether it was trapped therein after its formation (secondary inclusions).

Fluid inclusions of the latter kind may have been trapped during subsequent deformation from ductile towards brittle (Siebenaller *et al.* 2013) or during pressure–temperature changes inducing recrystallization (bulging or grain boundary migration recrystallization) of the quartz crystals and coeval trapping of fluids (Urai *et al.* 1986; Drury and Urai 1990; Schmatz and Urai 2011). Fluid inclusions represent closed systems where the physico-chemical properties (composition, density) of the original fluid are conserved. The fluid, trapped in the temperature and pressure conditions of the forming environment, will shrink upon cooling of the rock and a bubble-shaped vapour phase will appear in the inclusion.

The microthermometric study of fluid inclusions allows the tracing of part of the chemical composition of the trapped fluid as well as the temperature and pressure conditions prevailing at the time of trapping (cf., Roedder 1984, fig. 2). This technique consists in cooling and/or heating samples that contain fluid inclusions while observing the inclusions with a microscope and measuring the temperatures during which phase transitions occur (solid, liquid and vapour). The salinity of the inclusion can be measured by cooling the inclusion (step 1) until total freezing (T_{sol}). Upon reheating (step 2), the temperature at the beginning of melting (the eutectic temperature, T_{e}, which is characteristic of the fluid composition) and the temperature at which the inclusion melts completely (T_{m}, which is characteristic of the fluid salinity) are recorded (Bodnar 1993). A supplementary analysis consists in heating the samples until the liquid and vapour phases in the fluid inclusions are homogenized (the homogenization temperature, T_{h}). This change from a heterogeneous two-phase fluid inclusion to a homogenous fluid corresponds to the point at which the isochore intersects the phase transition curve in Figure 1. This temperature corresponds to a minimum temperature for formation of the inclusion. However, the real trapping temperature and pressure of an inclusion lies on the corresponding isochore, and can be constraint by other techniques such as maximum *P–T* for mineral assemblages and other thermobarometers. Isochores represent the evolution of pressure (*P*) and temperature (*T*) conditions for a given fluid inclusion and corresponding molar volume, and can be calculated using the

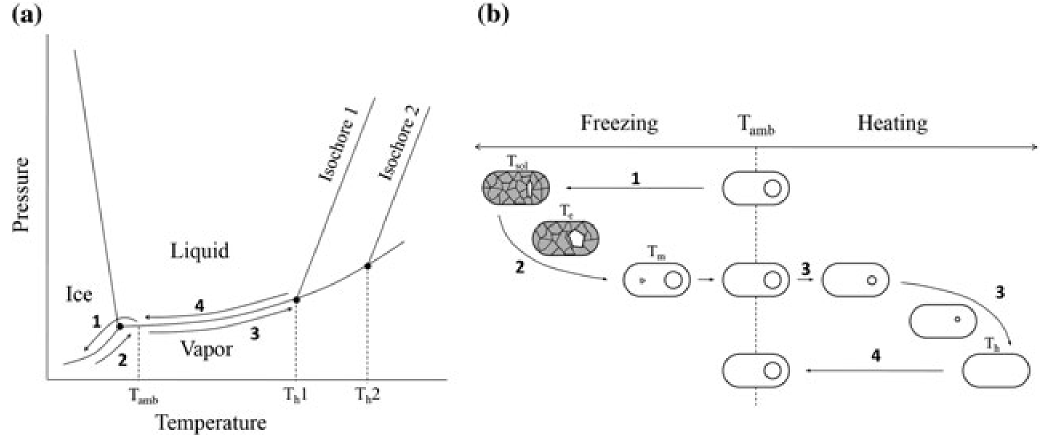

Figure 1 *(a) The P–T diagram of pure water: each isochore curve (1 and 2, respectively) represents the evolution of P and T after homogenization of corresponding inclusions and their specific molar volume at different temperatures* T_h1 *and* T_h2*. (b) The evolution of phase changes of an inclusion from cooling upon heating. Step 1: the inclusion is cooled until total frozen (*T_{sol}*). Step 2: the inclusion is progressively heated:* T_e *and* T_m *correspond to the first droplet appearance and the final ice melting temperature, respectively. Step 3: the inclusion is heated until total homogenization of vapour and liquid (*T_h*). Step 4: the inclusion returns to the ambient temperature (*T_{amb}*) and the vapour phase reappears.*

method of Wagner and Pruss (1993. The trapping *P* and *T* conditions of inclusions are located on these isochore curves (for a review of H_2O inclusions, see Diamond 2003).

Materials

Our work is based on the observation and analysis of archaeological and geological barremo-bedoulian flint samples (Table 1). We selected 17 heated and four unheated archaeological samples unearthed during the excavation of Saint-Martin. Heated artefacts were selected on the basis of the macroscopic observations of the gloss on fracture surfaces. Their size was between 2 and 5 cm, and they were about 1 cm thick. We observed that three of these samples showed signs of thermal cracking. All these archaeological flints are honey-coloured.

Geological flint samples were collected in the Vaucluse during successive survey campaigns and 53 nodules were cut into thin sections (the B-B flint series). Their size varied from 5 to 10 cm.

Additionally, experimental heat-treatment experiments were performed in an electrical furnace. Geological barremo-bedoulian flint samples were first shaped to a size of about 10 cm long by 1–2 cm thick and an unheated witness flake was then taken off each sample. Pieces were buried in a terracotta pot filled with different materials (heating environments), which serve to control the transmission of heat to the flint. A first series of seven flint pieces were heated in sandy clay (A series). This material is abundant and easily available near the site of Saint-Martin. A second series of seven pieces was heated in ochre (B series), which is abundant in the Vaucluse. This material contains clay and iron oxides, mainly goethite (FeO(OH)). During heat

Table 1 *Descriptions of the analysed samples: for more detailed information about the micro-facies of barremo-bedoulian flint and the experimental heat-treatment protocol, see the text*

Archaeological flint

Sample name(s)	*Number of samples*	*Description*
AC1 to AC17	17	Honey-coloured, pieces from the core of heat-treated nodules, 2–5 cm in diameter and 1 cm thick
ANC1 to ANC4	4	Honey-coloured, pieces of unheated nodules, 2–5 cm in diameter and 1 cm thick

Geological unheated flint

Sample name(s)	*Number of samples*	*Description*
B-B flint	53	Nodules of barremo-bedoulian flint, different micro-facies, 5–10 cm in diameter

Geological experimentally heat-treated flint

Sample name(s)	*Number of samples*	*Heating environment*	*Heating mode*	*Description*
B1 to B7 (B series)	7	Sandy clay	170–290°C in an oven (temperature step of 20°C)	Honey-coloured flint pieces, 10 cm long and 1–2 cm thick
B1 to B7 (B series)	7	Ochre		

treatment, ochre turns red because of the transformation of goethite into hematite (Fe_2O_3) at about 250°C (Gualtieri and Venturelli 1999). Thus, we tested here the interest of ochre as a potential natural thermometer in the prospect of future heating experiments in Neolithic conditions.

The principal aim of these experiments was to specify the temperature range for the appearance of fluid inclusions. For this, each sample of both the A and B series was heated to a maximum temperature of 170, 190, 210, 230, 250, 270 or 290°C. Each of these temperature ramp and cooling progressions lasted for 10 h. The maximum heating temperatures were maintained for 6 h. After the heat treatment, each sample was flaked to detect any increased lustre on fracture surfaces, which would indicate that the heat treatment had been efficient. All samples were cut into polished thin sections of 30 μm thickness for petrographic analysis, and into 200 μm thick sections, polished on both sides, for fluid inclusion analysis. Sections were made in the Thin Section Laboratory of Toul, France, and in the GET laboratory of Toulouse, France.

METHODS

Petrographic analysis

Determination of the exact quantity of each type of chalcedony is of great importance for understanding the thermal transformations of barremo-bedoulian flint. For this purpose, we cut standard thin sections for microscopic analysis using a petrographic microscope (Fig. 2). The distinction between LF and LS chalcedony was made using a full wave plate. Petrographic analysis of the samples also allowed us to detect the presence or absence of fluid inclusions.

Fluid inclusions: analytical techniques

The microthermometry analyses were performed in the GET laboratory of Toulouse, France, using a LINKAM THMS600 heating/freezing stage adapted to an OLYMPUS BX 51 microscope, allowing observation at a 1000× magnification, given the small size of the fluid inclusions (< 5 μm). The accuracy of our measurements was ensured by calibration on the freezing point of water (0°C) and the critical point of water (374.6°C) in a synthetic pure water inclusion. We estimate errors of about ±0.2°C for T_m measurements and ±10°C for T_h. Flint sections were first examined under the petrographic microscope, and fragments of the doubly polished sections were then cut to proceed to the heating/freezing experiments.

The freezing protocol consisted in cooling the samples to –100°C with a rate of –30°C min^{-1} (step 1) to ensure total freezing of the fluid inclusions. Subsequent heating of the samples was progressive, by adapting slow heating rates (1°C min^{-1}) when approaching phase changes. T_m was taken to be the temperature at which the last visible ice crystal melted. When this last crystal was not observable, T_m was inferred from the temperature at which the observed vapour bubble started moving freely in the liquid phase.

Raman spectroscopy was used to determine the composition of the vapour phase (Burruss 2003). We applied this method to some fluid inclusions to analyse vapour phases and to detect the possible presence of CO_2, CH_4 and other gases. Raman micro-spectrometric analysis on fluid inclusions was performed at the G2R laboratory, University of Nancy, France. The Raman spectrometer used was a Labram type (Dilor®), equipped with a Notch (Kaiser®) filter and with only one grating (1800 grooves mm^{-1}), which resulted in high optical throughput. The detector was a CCD, cooled at –30°C. The exciting radiation of 514 nm was provided by an Ar^+ laser

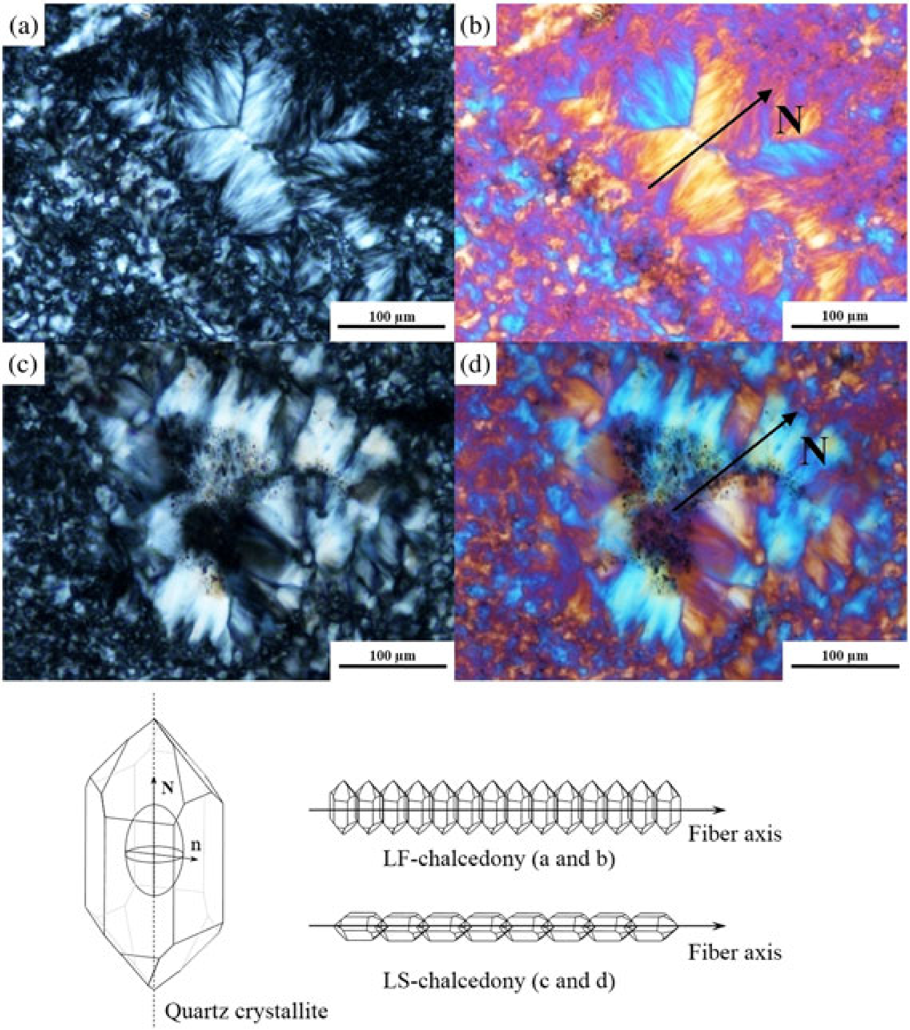

Figure 2 *Sample AC17, cross-polarized microphotographs of LF chalcedony (a, b) and LS chalcedony (c, d). On (b) and (d), the direction N represents the slow direction of the superimposed full wave plate. We can distinguish the orange tint of LF (b) and the blue tint of LS chalcedony (d) on similarly oriented crystals (chalcedony fibres elongated in the SW–NE direction).*

(Spectraphysics® Type 2020). CO_2 and CH_4 were evaluated using the Raman bands at 1200 and 2860 cm^{-1}. The spectral resolution was 2 cm^{-1}.

RESULTS

Micro-facies of barremo-bedoulian flint

The observation of the 53 geological flint nodules (B-B flint series) allowed us to establish a classification based on macroscopic criteria. We distinguished the ‘honey facies’ (light brown colour, translucent appearance, 20 samples), the ‘Bouche-grasse facies’ (grey/blue colour, mat appearance, 13 samples), the 'detrital facies' (grey/honey colour, opaque with a high detrital content, 11 samples), the 'grey facies' (grey colour, milky appearance, six samples) and the 'Murs facies' (black colour, bright appearance, three samples).

These criteria are also related to some of the microscopic characteristics. The samples contain from less than 10% to 50% carbonates, which are responsible for the grey colour and milky/mat appearance. The detrital load is mainly composed of microfossils, mostly sponge spicules and foraminifer remains (orbitolinidae, textulariidae) and accessory minerals, mainly pyrite. Barremo-bedoulian flint contains different forms of silica. Quartz in the form of chalcedony represents more than 90% of the silica, while opal-CT lepispheres represent less than 10%. Detrital quartz grains can occasionally be found in the matrix. The honey facies is the 'purest' type and contains less than 5% of carbonate impurities. However, all our samples, including those of the honey-facies type, contain zones rich in impurities, with variable geometry. These zones enclose coarse porosity and zones of chalcedony with longer fibres (up to 300 µm, while they measure 50 µm at most in the rest of the rocks) (Figs 3 (a) and 3 (b)). Barremo-bedoulian flint contains both LF and LS chalcedony. For the majority of the observed samples, the composition of chalcedony can be estimated to about 85% LF and 15% LS chalcedony.

Results of experimental heat treatment

Both the A and B experimental series, heated in the furnace, were successful and no heat-induced fracturing occurred. No significant difference was observed between samples from the two

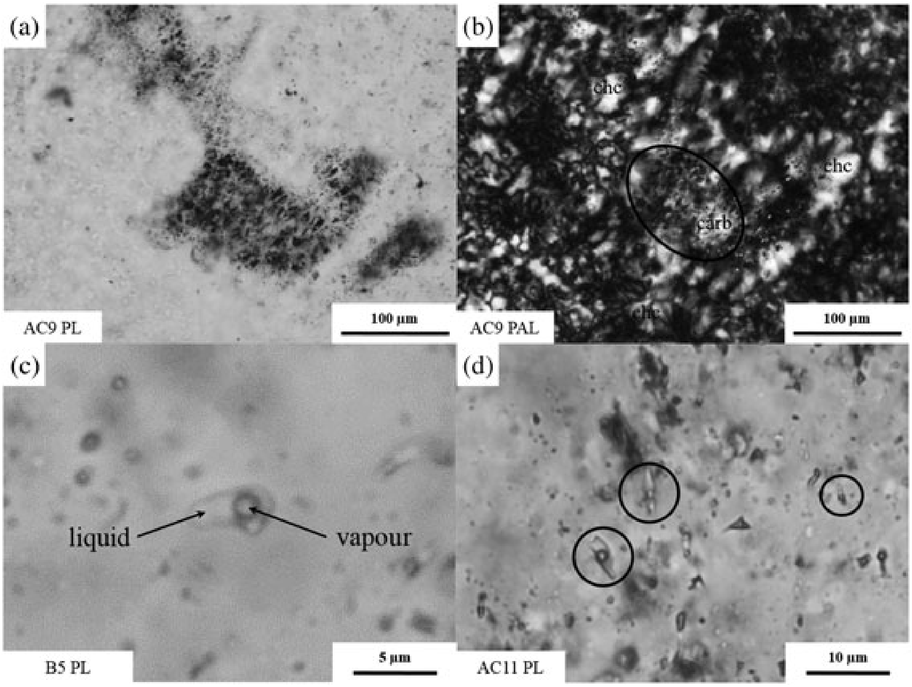

Figure 3 *(a) A porous zone that is favourable for the formation of fluid inclusions in an archaeological heat-treated flint (sample AC9). (b) This porous zone is associated with carbonated impurities (carb) and long fibre chalcedony (chc). (c) A fluid inclusion composed of a vapour and a liquid phase (sample B5). (d) Fluid inclusions of different sizes and shapes in highly porous areas (sample AC11). Microphotographs under plane-polarized (PL) and cross-polarized light (PLA).*

heating environments placed in the furnace. In both cases, we noted that the lustre of the fracture surfaces did not increase for flint pieces heated to 170 and 190°C. At 210°C, the fracture surfaces of the pieces showed a slightly increased lustre. The lustre of the fracture surfaces is strongest from 230°C to higher temperatures.

Fluid inclusion distribution

Fluid inclusions were detected in all heated archaeological samples, while none of the unheated samples contained inclusions. Concerning the flint samples heated in the furnace, no fluid inclusions were observed in the samples heated to 170 and 190°C. However, some fluid inclusions occurred in the samples heated to 210°C, which coincided with a slightly increased lustre of the fracture surfaces. The samples treated at 230 and 250°C contained a large amount of fluid inclusions, but the samples heated to 270°C showed a significantly smaller amount of fluid inclusions. The samples heated to 290°C and the unheated control samples did not contain any fluid inclusions.

Fluid inclusions were observed in small clusters in porous zones, but not as isolated single inclusions. The presence of such zones is not heat-induced, since they can also be observed in unheated flint. The geometry of these porous zones is variable, and fluid inclusions also show variable sizes and shapes (Figs 3 (c) and 3 (d)). All fluid inclusions generally measure less than 5 µm, with an average size of approximately 3 µm. Their estimated degree of liquid with respect to vapour filling varies from 50% to 90%.

Another important feature concerning the distribution of the fluid inclusions is that in the experimentally heated samples, they are abundant in porous zones located in the centre of the pieces, while they are rare in the outer rim of the initial samples. This observation could not be made on archaeological samples, because the exact orientation of the flakes within the original volume of the heat-treated flint is unknown.

The microthermometry of archaeological flint

A total of 53 inclusions from eight archaeological heated flints were selected for analysis from amongst the purest sample sections, since the presence of impurities in the flint makes it difficult to observe fluid inclusions. The results of the freezing and heating runs are shown in Figure 4.

During the cooling runs, the vapour bubble disappeared in all cases and did not reappear before the ice melted. This happened at a T_m value between –0.5°C and 0°C (Fig. 4 (a)). Considering the given error of ± 0.2°C, this temperature range is fairly close to 0°C, and is consistent with pure or almost pure water, with no or only a very small amount of salt.

During heating, the inclusions homogenized (T_h) into a single liquid phase between 225 and 285°C. The great majority homogenized between 230 and 240°C. Six inclusions homogenized above 300°C (Fig. 4 (b)).

Raman analysis was performed on some of the largest fluid inclusions. The results indicate that, at room temperature, the vapour phase is exclusively water vapour. Neither CO_2 nor CH_4 could be detected.

The microthermometry of experimentally heat-treated flint

We performed T_h measurements on experimentally heat-treated flints in order to verify the consistency of the results obtained on archaeological samples with a specific heating temperature. Measurements were performed on 40 fluid inclusions from each B4 and B5 sample, heated to

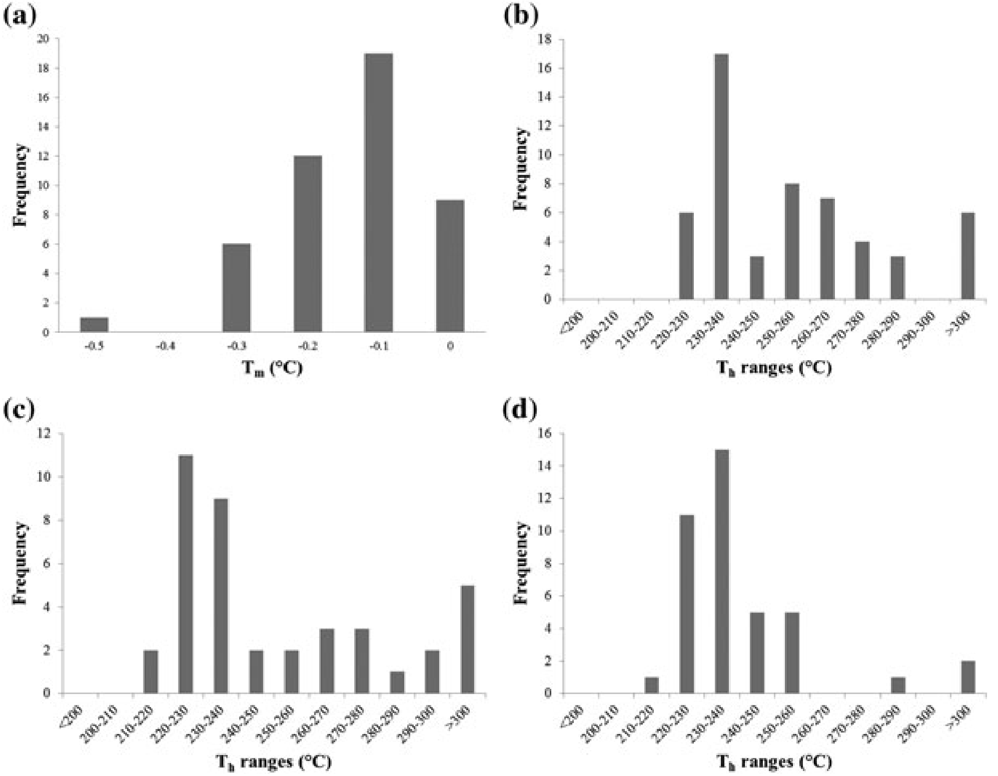

Figure 4 *(a) The distribution of the final ice-melting temperature (T_m) for fluid inclusions in archaeological heated flint samples. (b) The distribution of the homogenization temperature (T_h) of fluid inclusions in archaeological heated flints. (c, d) The distribution of fluid inclusions in geological samples B4 (c) and B5 (d) respectively, heated in an oven at 230 and 250°C.*

230 and 250°C respectively (B series). We selected these two samples because they contain enough fluid inclusions to have a statistical view of the T_{h} distribution. Those heated to lower or higher temperatures did not contain enough fluid inclusions. The T_{h} values of samples B4 and B5 are shown in Figures 4 (c) and 4 (d). Both histograms show a majority of fluid inclusions homogenizing between 220 and 240°C and spreading of higher homogenization temperatures, up to 300°C for some inclusions. Thus, the distribution of homogenization temperatures of inclusions from samples B4 and B5 is similar to that obtained in the archaeological samples.

DISCUSSION

The genesis of fluid inclusions

The T_{m} value of fluid inclusions from archaeological flint was found to be close to 0°C, which indicates the presence of pure water. Knowing that flint had formed in a marine environment, the presence and influence of diagenetic water can be disregarded, because the salinity of sea water would result in a T_{m} value around –2°C. Moreover, diagenetic water inclusions would also be present in unheated flint. Their absence in unheated flint clearly shows that their appearance is a heat-induced phenomenon.

We noted the frequent presence of carbonate fossil relics trapped in the matrix of flint. These carbonates were spatially associated with longer fibres of chalcedony, which is in agreement with the hypothesis of a crystallization of chalcedony replacing carbonate fossil skeletons by an epigenetic phenomenon (Cayeux 1929; Fröhlich 1981). Larger bioclasts that are included in the flint nodules during early crystallization are dissolved during the silicification, creating zones with larger pores in which the development of long fibres of chalcedony is facilitated. However, in barremo-bedoulian flint, this carbonate dissolution is not totally achieved and we observe some carbonate impurities and coarse porosity in the chalcedony (Figs 3 (a) and 3 (b)). These porous areas act as potential traps for the fluids resulting from chalcedony dehydration.

Our results are consistent with the model of Schmidt *et al.* (2012), which proposes the heat-induced water release of flint to be due to the loss of free H_2O and the dehydration of chalcedony by reduction of silanol groups, according to the following reaction:

$$\text{Si–OH} + \text{HO–Si} = \text{Si–O–Si} + H_2O. \tag{1}$$

The first reaction that occurs during progressive heating from 100°C upwards is that free H_2O, held in the network of interconnected pores is evaporated from the flint. At temperatures above 200°C, silanol is dehydrated and the rock's network of open porosity is progressively closed at sites where two silanol groups are sufficiently close on opposite pore-walls to form new Si–O–Si bridges (Schmidt *et al.* 2012). As a result of reaction (1), molecular H_2O is synthesized and must be evacuated through the network of pores leading to the surface of the flint nodule (Schmidt 2014). However, this H_2O evacuation is increasingly hampered as the network of interconnected pores is lost (Schmidt 2014), and the remaining molecular water will be trapped to form fluid inclusions within areas of coarse porosity. The closure of the fine intergranular porosity by the formation of Si–O–Si bonds is responsible for the structural changes of heat-treated flint (Schmidt *et al.* 2012).

Our study shows that fluid inclusions are formed between 200 and 250°C in barremo-bedoulian flint. This is in agreement with Schmidt *et al.* (2013a because we observed this flint to contain approximately 15% of LS chalcedony, which dehydrates at lower temperatures compared to LF chalcedony (approximately 200–300°C) (Schmidt *et al.* 2013b). The presence of LS chalcedony may explain the high reactivity of barremo-bedoulian flint at low temperatures during heat treatment.

Considering that fluid inclusions in flint are secondary inclusions, trapped when the structural water migrates towards porous zones that act as a reservoir during the heat-induced dehydration of chalcedony, the filling of the pores during the heat treatment may not necessarily be complete. Partially filled inclusions, having different total molecular volumes, must be expected to homogenize over a larger range of temperatures. Moreover, microfractures may appear adjacent to completely filled fluid inclusions due to rising temperature and vapour pressure, causing similar effects (Sterner and Bodnar 1989). The series of inclusions that gave the most consistent homogenizing temperature, between 220 and 240°C, can therefore be interpreted as corresponding to fluid inclusions that are totally filled and unaffected by post-entrapment modifications such as microfractures. If this is confirmed, our measurements of these inclusions would represent the temperatures of trapping and, consequently, the heating temperatures applied to the flint during manufacturing by the Chassey artisans. Unusually high homogenization temperatures, of greater than 240°C, may correspond to incompletely filled and/or microfractured cavities, where part of the fluid has leaked out (Bakker and Jansen 1990).

The T_h distribution of the two experimentally heated flint samples B4 and B5 are very similar, and both are centred around 230°C. This distribution was expected for the B4 sample, which has been heated to 230°C, but it is surprising for the B5 sample, heated to 250°C. This similarity of the T_h distributions may be related to the endothermic character of reaction (1). As the reaction evolves, it consumes heat, maintaining a lower temperature within the flint nodule with respect to its enveloping heating environment. Once this reaction is completed, the inner part of the flint will rise in temperature and pressure if the heat treatment persists. A possible explanation for the discrepancy between the actual heating and homogenization temperatures of the fluid inclusions in sample B5 would be that the interior part of the flint nodule remained close to a temperature of 230°C during dehydration of the chalcedony, even though the surface of the rock was heated to a higher temperature. Admitting this hypothesis, the dehydration reaction (1) would be more complete in sample B5 than in sample B4. This could explain why we observe a greater number of fluid inclusions in sample B5.

Furthermore, our study showed that all analysed fluid inclusions homogenize from a liquid–vapour mixture into a homogenous liquid phase, indicating higher trapping pressures compared to the case where such inclusions homogenize into vapour (Diamond 2003). The phase diagram of pure water allows us to estimate a minimum pressure of between 15 and 40 bars, which corresponds to a homogenization temperature range from 200 to 250°C, because the water was trapped in the liquid phase field above the critical curve (Fig. 5 (b)). According to the method developed by Wagner and Pruss (1993, internal pressures of 19, 28 and 74 bars correspond to homogenization temperature of 210, 230 and 290°C. We can then calculate the fluid density and trace isochores on the *P–T* diagram of pure water (Fig. 5 (b)). The increase in temperature leads to higher internal pressure in the inclusions, until a breakpoint called 'decrepitation' is reached. This decrepitation of fluid inclusions causes micron-scale cracks along the grain boundaries and the crystallographic axis of chalcedony, ending up with thermal cracking that runs through the entire nodule. The cracks most probably opened during heating, causing a decrease in thermal diffusivity. Branlund and Hofmeister (2008 have reported that this effect is greatest in samples containing large fluid-filled pores, suggesting that the expansion of pore fluids, and especially in this case the decrepitation of fluid inclusions, could be the main cause of thermal cracking. This results in subsequent pressure drop and vaporization of water once the fracture network is connected to the atmosphere.

The total absence of inclusions homogenizing into vapour at the studied temperatures indicates that the H_2O migrating during heat treatment is exclusively liquid water, which can only occur if the inner part of the flint nodule is under pressure. Elsewise, H_2O would start boiling and be trapped in the typical form of H_2O- and vapour-rich fluid inclusion assemblages. Moreover, porous areas located in the rim of the experimentally heat-treated nodules do not contain any fluid inclusions. Similar porous areas located in the inner core of the rocks contain a large number of inclusions. This characteristic spatial distribution of fluid inclusions may be due to the diachronism of the reaction of chalcedony dehydration. Indeed, flint is a poor heat conductor —according to Horai (1971, the thermal conductivity of quartz is 7.69 W^{-1} m^{-1} K at normal temperature and pressure—and the temperature rises faster in the rim of the nodule than in its core. Thus, dehydration first occurs in the outer part where H_2O cannot be trapped, because the porosity is connected with the external environment. The progressive closure upon heating of that peripheral part of the porosity 'disconnects' the internal part of the porosity from the external environment. Consequently, fluid pressure increases in the core of the nodule when it reaches the dehydration temperature and the released H_2O migrates as a liquid from the finer part of the porosity towards areas of coarser porosity. This is what we call the 'pressure cooker' effect (Fig. 5 (a)).

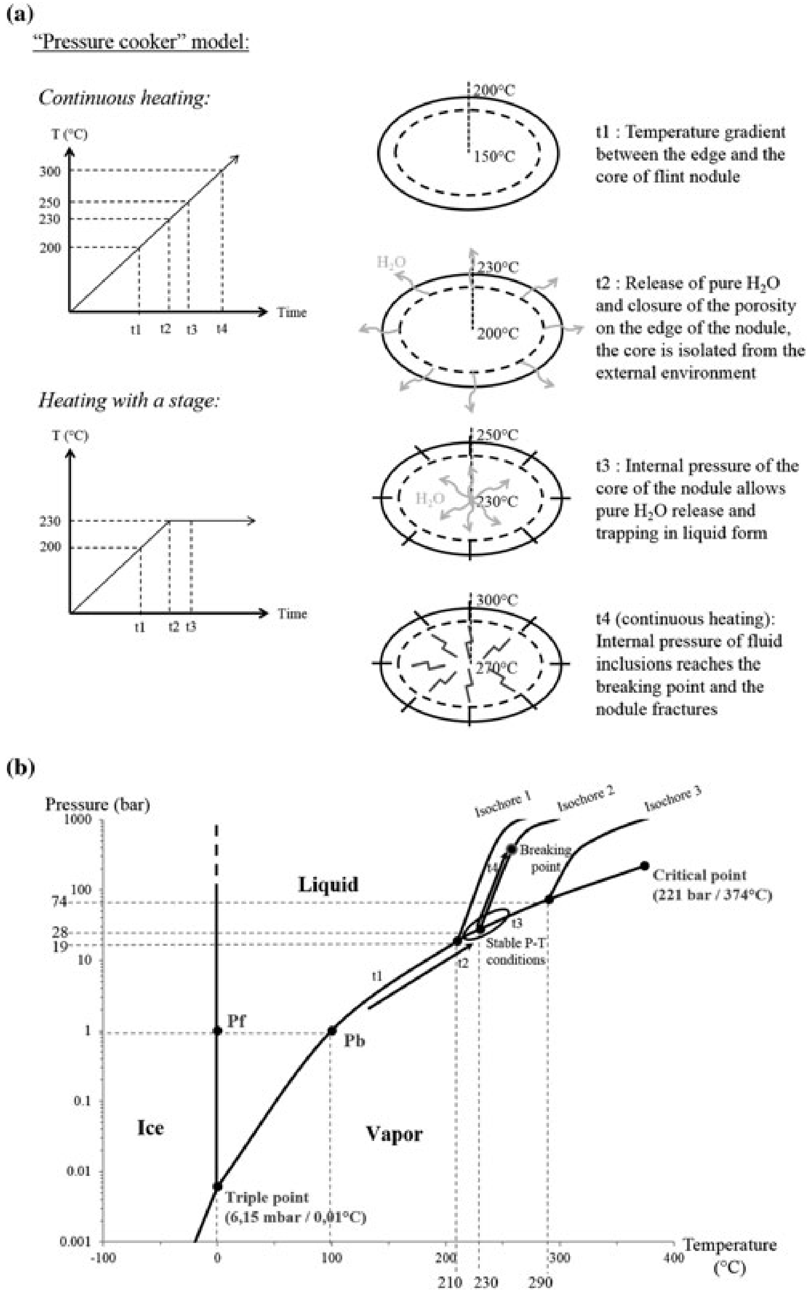

Figure 5 *(a) The 'pressure cooker' model. (i) The case of continuous heat treatment: when the dehydration reaction is completed, the rising temperature induces an increasing pressure in the fluid inclusions until the breaking pressure is reached. (ii) Case of heat treatment with a stage: a stage at 230°C allows the internal pressure of fluid inclusions to be maintained below the breaking pressure of the flint. The temperatures presented here are theoretical temperatures to better illustrate the phenomenon. (b) A general pressure–temperature reconstruction of the conditions prevailing in flint: Pf and Pb, the freezing and boiling points of pure water respectively; isochores 1, 2 and 3, the T and P evolution of inclusions homogenized at 210, 230 and 290°C respectively. The y-axis is on a logarithmic scale.*

Archaeological implications

According to the ‘pressure cooker’ model, the closure of the porosity in the outer part of the flint nodule allows the circulation and trapping of liquid water at 230°C in porous zones in the core of the nodule. In the case of heat treatment that is prolonged after the dehydration reaction is completed, the internal pressure in the inclusions rises up to the breaking point, at which the flint starts to fracture. In the case of heating while maintaining a temperature close to that of the LS chalcedony dehydration, the internal pressure does not exceed the breaking point of flint after the reaction is completed (Fig. 5). However, maintaining a constant temperature may have been difficult in the Neolithic, and a procedure was needed to prevent the temperature from rising too quickly and the flint from fracturing. In view of the extent of the Chassey lithic industry, we suppose than the heating process used was reproducible and standardized. Thus, for a calibrated volume of flint and a constant temperature of the fire (the maximum temperature of embers is about 700°C), only a strict protocol of heat treatment and a specific heating environment could have allowed the flint nodule to be maintained at a precise temperature. The use of ochre, which turns red at about 250°C (Gualtieri and Venturelli 1999) and is abundant in the Vaucluse region, may have helped to control the heating temperature. This underlines the fundamental role of the heating environment and can explain why the heat treatment of flint is a process difficult to control, which was not shared by all of the Chassey communities.

Our results indicate a temperature of heat treatment performed by Chassey artisans of around 230°C. This is in agreement with the results of Schmidt *et al.* (2013a, who found a heating temperature of between 200 and 250°C, and it allows us to further refine the temperature used for heat treatment during the Chassey period. This temperature corresponds to the lower part of the range of activation temperatures for flint heat treatment (Schmidt *et al.* 2012), although we expect that some flint nodules may be heated to higher temperatures, depending on the quantity of porous zones within the rocks and the degree of filling of the resulting inclusions. The ability to heat-treat flint to a given temperature appears to be governed by two factors. First, the amount of LS chalcedony determines the quantity of water released by the dehydration reaction at temperatures below 250°C. The second factor is the amount of intergranular and coarse porosity that acts as a reservoir to store the water produced by dehydration. In the case of flint that contains a lot of LS chalcedony and not enough porosity, fluid inclusions (coarse porosity) will rapidly be saturated after reaching the dehydration temperature and pressure will increase in the rock, causing the flint nodule to fracture. In the opposite case of a low LS chalcedony content and a high volume of coarse porosity, fluid inclusions will be less filled and the internal pressure rise will be limited, preventing the nodule from fracturing. In this latter case, the degree of filling of the inclusions is expected to be very variable, inducing the spread of T_h measurements that we observed in our results.

Flint that is exclusively made up of only LF chalcedony, containing no LS chalcedony, will most probably not react at a temperature as low as 230°C. The LF chalcedony dehydration temperature (250–550°C; Schmidt *et al.* 2013b) would have to be reached so that the nodule reacts to the heat treatment.

The good quality of barremo-bedoulian flint for heat treatment of large precores, as was the case during the Chassey period, may be explained by a proper balance between: (i) the amount of LS chalcedony, which confers a high reactivity to heating at temperatures below 250°C, producing a large quantity of H_2O released at these temperatures; and (ii) the amount of impurities and the degree of silicification that produced the porous space available to store the released H_2O. These combined characteristics generate the rare good ability of the barremo-bedoulian flint to be heated, and the fact that it is only present around a specific area in France may explain the exceptional development of the Chassey specialized lithic industry in the Vaucluse and the value of this flint for Neolithic societies. It may also explain the exceptional expansion of this flint distribution network and the duration of this phenomenon for 500 years.

CONCLUSION

Microscopic observations of different types of barremo-bedoulian flint (archaeological and geological, heated and unheated samples) allowed us to apprehend its petrographic characteristics and to highlight the formation of fluid inclusions during heat treatment. Microthermometric measurements performed on these inclusions showed that the water contained in the inclusions is pure H_2O, although flint is formed in a marine environment. According to the model of Schmidt *et al.* (2012, the heat-induced dehydration reaction of LS chalcedony causes the release of structural H_2O and the closure of the fine porosity. Structural water accumulates in zones of coarse porosity, where it forms fluid inclusions. The closure of the fine intergranular porosity is responsible for the increased knapping ability of heated flint, as noted in Schmidt *et al.* (2013a.

The measurement of homogenization temperatures of fluid inclusions allowed us to access the temperature of heat treatment used by Chassey artisans. The flint nodules were heated to about 230°C, which corresponds to the dehydration temperature of LS chalcedony. Moreover, we noted that all of the inclusions were trapped in liquid phases despite the heating temperature of 230°C. This observation leads us to propose the ‘pressure cooker’ model to explain the dehydration reaction in a flint nodule during heat treatment. The dehydration reaction of chalcedony first occurs in the outer part of the flint, and then in the inner core. The early closure of the porosity of the rim of the nodule isolates the core, which then increases in pressure, allowing the migration of liquid water. Considering the extent of the lithic industry in the Vaucluse, it is probable that the heating process used by the Chassey artisans was standardized and reproducible. Thus, for a calibrated size of flint nodules and a constant heating temperature, only a specific heating environment and a well-controlled set of heating parameters allowed the maintenance of a constant temperature in the flint that was near the dehydration temperature of LS chalcedony.

Depending on the degree of filling of the inclusions, their internal pressure rises more or less rapidly during heating. If this pressure exceeds the breaking point of flint, the decrepitation of the fluid inclusions causes thermal parallel cracking, which runs through the entire nodule. This phenomenon has been identified on several archaeological samples and frequently occurs during heat treatment experiments. Thereby, the capacity of flint to be heated is governed by the quantity of released water and the total volume of pores available to store it. The presence of LS chalcedony in flint ensures its high reactivity to heat treatment and governs the quantity of released water. The purity of flint and the advancement of the silica replacement of carbonated fossils affect the total pore volume of flint. The archaeological interest of the barremo-bedoulian flint and its preciousness in Neolithic society are probably due to its proper balance between these factors. These rare characteristics, combined with a good control of temperature during heat treatment, may have ensured, for the Chassey communities from the Vaucluse region, the great success of their specialized lithic industry.

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