

What causes failure (overheating) during lithic heat treatment?

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Abstract Heat treatment of lithic raw material, i.e. the intentional alteration of silica rocks for improving their knapping quality, is a process that may require great care and precisely controlled conditions in order to avoid failure due to overheating. The physical causes of overheating remain poorly understood leading to problems in the interpretation of heat-treated artefacts and/or fire-related taphonomic alteration of different types of silica rocks. This driving force of overheating is investigated by a set of experimental heat treatment sequences with different ramp rates and different volumes of flint with a well-defined mineralogical composition, porosity and water content. The results of this experiment show the main cause of heat-induced fracturing to be the vapour pressure in fluid inclusions within the rocks. Heterogeneous thermal expansion could be discarded. The interdependence between volume and heating rate is also shown. These results have implications for the study of archaeological heat-treated rocks, the understanding of taphonomic heat-induced fracturing of silica rocks and experimental flint knapping.

Keywords Heat treatment · Thermal alteration · Overheating · Flint · Flint knapping · Lithic raw material

Introduction

Heat treatment of lithic raw material is the intentional alteration of rocks for improving their knapping quality. The

process is known since the Middle Stone Age in South Africa (Brown et al. 2009; Mourre et al. 2010) and prominent examples are known from the European Upper Palaeolithic and Mesolithic (Bordes 1969; Tiffagom 1998; Eriksen 2006), the American Paleo-Indian period (Crabtree and Butler 1964; Wilke et al. 1991) and the European Neolithic (Binder 1984; Léa 2005).

The technique is normally applied to silica rocks like flint, chert or silcrete that are composed of quartz in the form of chalcedony or micro-quartz. The major heat-induced transformations in these rocks have recently been shown to be (1) the loss of chemically bound water (hydroxyl, silanol, SiOH) located on pore walls and defect sites in the quartz crystallites and (2) the ‘synthesis’ of molecular water (H₂O) (Schmidt et al. 2011; Schmidt et al. 2012; Schmidt 2013). At sites where the distance between two of these hydroxyl defects is sufficiently small, the silanol loss results in the formation of new Si–O–Si bonds according to the reaction: $2\text{SiOH} \rightarrow \text{Si–O–Si} + \text{H}_2\text{O}$. The resulting molecular water is evacuated from the rock through its open pores. The formation of new Si–O–Si bridges causes the increased hardness (Schmidt et al. 2012) and reduced fracture toughness (Schindler et al. 1982; Domanski et al. 1994) that can be measured in silica rocks after heat treatment. However, another result of this reaction is the gradual loss of the network of open pores (Roqué-Rosell et al. 2010; Schmidt et al. 2011), making it increasingly difficult for H₂O to be evacuated.

Numerous authors found that heat treatment, especially of homogenous silica rocks like flint, has to be performed cautiously for it to be successful (Olausson et Larsson 1982; Ahler 1983; Rick et Chappell 1983; Hanckel, 1985). Too rapid heating rates or excessive temperatures can result in failure of the rocks, occurring in the form of cracking, crazing, pot-lid fractures or falling to pieces of the entire rocks. This phenomenon is often termed overheating. In a detailed experimental study involving heat treatment of different volumes of chert and silcrete at varying temperatures,

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Mercieca and Hiscock (2008) found that the success or failure due to overheating was ‘...determined by the interaction between specimen volume and raw material as well as temperature and the rate of heating,’ (op. cit., p. 2637). Large volumes were found to show signs of overheating at relatively lower temperatures and slower heating rates than smaller volumes. The physical causes of the overheating were not discussed in this paper. This physical driving force of overheating has often been admitted by archaeologists to be the thermal expansion of the heated materials:

In their pioneer study about lithic heat treatment, Crabtree and Butler (1964) had already described that smaller volumes of flint were easier to heat-treat than larger ones. The reason for this was stated as ‘The thicker pieces do not heat or cool evenly...’ (op. cit., p. 2); implying that overheating was due to differential stress in a rock that is not homogeneously heated. This statement gave rise to the theory that failure during heat treatment was mainly caused by differential thermal expansion creating such irregular stress in the rocks. The theory has since been widely accepted and can frequently be found in the literature about heat treatment (Purdy 1974; Anderson 1979; Price et al. 1982; Patterson 1995; Inizan and Tixier 2001). The ‘differential thermal expansion theory’ also implies the need for slow cooling rates in order to avoid failure. However, some authors challenged this theory by describing that very abrupt cooling (Anderson 1978) or even abrupt heating (Inizan et al. 1976; Griffiths et al. 1987; Schmidt et al. 2013) of certain silica rocks does not produce failure.

An alternative explanation of overheating may come from the model of heat-induced structural transformations of silica rocks proposed by Schmidt et al. (2012). According to this model, it might be expected that fluid inclusions and the vapour pressure within them play an important role in failure during heat treatment. The aim of this article is to test which theory, (1) differential thermal expansion or (2) vapour pressure, allows for the best explanation of the observed experimental data.

Samples and experimental protocol

Samples and sample preparation

All samples used for the experiments described here come from one single nodule of black Turonian flint of approximately 15 kg that was collected in the north of the town Tours, France. The flint nodule was cut with a water-cooled diamond saw into 16 regular cubes: eight cubes with a volume of $\approx 37 \text{ cm}^3$, four cubes with a volume of $\approx 12 \text{ cm}^3$ and four cubes with a volume of $\approx 4 \text{ cm}^3$ (with an edge length of $\approx 3.3 \text{ cm}$, $\approx 2.3 \text{ cm}$ and $\approx 1.6 \text{ cm}$, respectively). The eight 37 cm^3 -cubes were subdivided into two groups of four cubes

each, one of which was kept in a drying oven at $110 \text{ }^\circ\text{C}$ for 3 weeks meanwhile the other group was kept at room temperature and ambient air humidity together with the 12- and 4-cm^3 cubes. The only difference between the 37-cm^3 cubes that were held at $110 \text{ }^\circ\text{C}$ and the ones that were held at room temperature is that the open pores of the dried cubes were emptied from molecular water that is adsorbed in the pores of flint at room temperature (Schmidt et al. 2011).

Heating experiment

Four heat treatment sequences with different ramp rates, 0.1, 0.5, 1 and $10 \text{ }^\circ\text{C}/\text{min}$, from room temperature to a maximum temperature of $350 \text{ }^\circ\text{C}$ were programmed in an electrical furnace (furnace atmosphere with free access to oxygen). During each of these four sequences, one dehydrated 37-cm^3 cube, one not-dehydrated 37-cm^3 cube, one 12-cm^3 cube and one 4-cm^3 cube were heated in order to test which ones of the volumes withstood the different speeds. Once the maximum temperature of $350 \text{ }^\circ\text{C}$ was reached, the samples were held at this temperature for 3 h before the furnace was allowed to slowly cool down to room temperature during 5 h. After heating, all cubes were examined for signs of cracking crazing or any other heat damage with a $10\times$ hand loupe. Before heat treatment, all cubes were weighted using a balance with a precision of 10^{-5} g and, if they did not suffer any damage during the treatment, they were again weighted after they had cooled to room temperature. Cubes that broke or cracked during heat treatment were not weight after the procedure because it could not be determined with certainty whether small sized pieces had fallen off or not.

Mineralogy and water content of the samples

A standard thin section was cut from the flint nodule and observed using a petrographic microscope (polarised light). The moganite content of the sample was determined by X-ray powder diffraction (grain size $4\text{--}15 \text{ }\mu\text{m}$) and subsequent Rietveld refinement of the diffractogram acquired with a Bruker D2 PHASER diffractometer. The diagram was recorded between 0 and $65^\circ 2\theta$ with a step size of 0.2 s° (using the $K\alpha$ line of a Cu anode, no incident beam monochromator and a sample holder in constant rotation during acquisition).

The water content of the flint was determined by near-infrared spectroscopy using a $790\text{-}\mu\text{m}$ -thick polished sample slab according to the protocol described in Schmidt et al. (2011). This protocol provides three values relevant to this study: (1) SiOH content, (2) H_2O strongly retained in closed pores and at defect sites in the rock and (3) H_2O adsorbed and held in the network of open pores of the rock. For this, spectra were acquired between $5,600$ and $4,000 \text{ cm}^{-1}$ (spectral resolution of 8 cm^{-1}) using a Bruker VECTOR 22

Table 1 Masses of the cubes before and after heat treatment in grams. Cubes that showed heat-induced damage like cracking, breaking or crazing could not be accurately weighed after heat treatment and are listed as ‘Failed’

	4 cm ³	12 cm ³	37 cm ³	37 cm ³ dried
0.1 °C/min	Before, 10.36151	Before, 32.28762	Before, 95.3074	Before, 97.9023
	After, 10.33239	After, 32.2157	Failed	After, 97.8742
0.5 °C/min	Before, 10.85417	Before, 30.97148	Before, 97.1423	Before, 97.0905
	After, 10.83593	After, 30.93629	Failed	Failed
1 °C/min	Before, 10.48471	Before, 28.52292	Before, 96.5721	Before, 96.9156
	After, 10.47208	Failed	Failed	Failed
10 °C/min	Before, 10.16953	Before, 31.61162	Before, 96.2276	Before, 95.7639
	Failed	Failed	Failed	Failed

spectrometer in direct transmission mode at normal incidence. The analytical procedure for calculating the H₂O and SiOH concentrations is detailed in Schmidt et al. (2011).

Results

Mineralogy and water content of the material

The black Turonian flint's mineralogical composition as determined by X-ray diffraction and Rietveld refinement is 89 wt% quartz and 11 wt% moganite. The microscopic examination of the thin section showed only short-fibred length-fast chalcedony. Its silanol concentration is 0.79 wt%, the structural H₂O content is 0.39 wt% and the sample's open pores contain 0.31 wt% H₂O. Thus, regarding its mineralogy and water content, the sample can be considered as representative of common European flint (Schmidt et al. 2011; Graetsch and Grüberg 2012).

Heating experiment

The mass of each cube before and after heat treatment is listed in Table 1. All four 37-cm³ cubes that were not dehydrated shattered during heating, indicating that even the slowest heating speed of 0.1 °C/min is too fast for a not dried 37-cm³ volume. The previously dehydrated 37-cm³ cube withstood the 0.1 °C/min ramp and showed no sign of cracking or any other heat-induced damage. However, ramp rates faster than 0.1 °C/min were too fast for the dehydrated 37 cm³ cubes that broke during heating with rates of 0.5, 1 and 10 °C/min. The 12-cm³ cubes withstood heating rates of 0.1 and 0.5 °C/min but broke at rates of 1 and 10 °C/min. The 4-cm³ cubes withstood rates of 0.1, 0.5 and 1 °C/min and only the one heated with 10 °C/min broke. Thus, a correlation between the tolerated heating speed and the volume is noticeable. Smaller volumes tolerate faster heating rates than larger volumes. Figure 1 shows a matrix illustrating this effect. The figure also shows the values of mass lost during the different heat treatment sequences in wt%. The values

obtained from the 4-cm³ cubes indicate that slower heating rates produce larger weight losses than faster ones. The comparison between values obtained on 4- and 12-cm³ cubes indicates that smaller volumes proportionally lose more weight than larger ones. The value obtained from the dehydrated 37-cm³ cube cannot be compared with the values of the smaller cubes because dehydration already produced some weight loss associated with the loss of water held in the open pores of the cube.

After this first set of experiments, the 4-, 12- and dehydrated 37-cm³ cubes from the 0.1 °C/min heating experiment that had shown no heat damage were reheated with a speed of 10 °C/min. None of the three cubes showed any sign of heat-induced damage after this second heat treatment and the weight losses produced by this second treatment were -0.0004, 0.0009 and 0.0004 wt% for the 4-, 12- and 37-cm³ cubes, respectively. These values correspond to mass differences before and after heating of 4×10⁻⁵ g to 10⁻⁴ g and lie within the range of the measurements' expected error. Thus, it can be concluded that there is no weight loss during this second heating experiment.

	4 cm ³	12 cm ³	37 cm ³ dried	37 cm ³
0.1°/min	0.281	0.223	0.029	Failed
0.5°/min	0.168	0.114	Failed	Failed
1°/min	0.12	Failed	Failed	Failed
10°/min	Failed	Failed	Failed	Failed

Fig. 1 Matrix showing the values of lost mass in wt% during the heating experiments as a function of temperature and volume of the cubes. Cubes that suffered heat damage are reported as ‘Failed’ and were not weighted. Note the correlation between volume and heating rate. For further explanations, see text

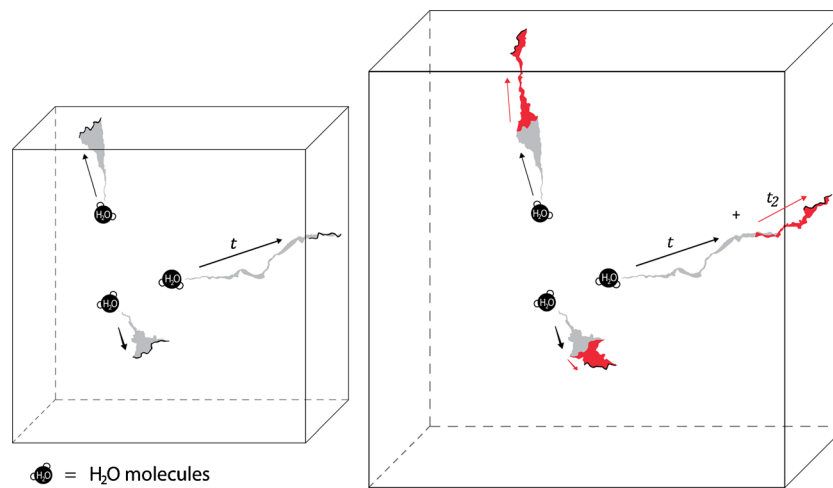


Fig. 2 Schematic illustration of the diffusion of H₂O molecules through open pores of two cubes of flint with different volumes. The pores are illustrated as conduits through which H₂O is evacuated from the centre of the cube to its surface. The time required for this diffusion is represented by the vectors t . Note that, if the volume is greater, the distance H₂O molecules have to travel is longer and their evacuation from the cube

takes more time. Water that cannot be evacuated from the cube will contribute to fracturing it at elevated temperatures. Thus, larger volumes need to be heat-treated with a relatively slower heating rate for the water to have sufficient time to be fully evacuated from the volume before the final heat treatment temperature is reached

Discussion

The gradient of weight losses

The weight losses observed during this experiment can be unambiguously assigned to the loss of different water species in flint (Flörke et al. 1982; Graetsch et al. 1985). At the used heat treatment temperature, 350 °C, especially silanol is lost (Schmidt et al. 2011). During this process, silanol groups form H₂O that is subsequently evacuated from the rock by diffusion through open pores (Schmidt et al. 2012). Simultaneously, these open pores are gradually closed upon heat treatment (Roqué-Rosell et al. 2010; Schmidt et al. 2011; Schmidt et al. 2012). The fact that larger cubes lose proportionally less water than smaller cubes indicates that this evacuation of H₂O through the porosity is more hampered in larger volumes. This can be explained by the fact that the pore's size in flint is in the nanometre range (Micheelsen 1966) and that the H₂O diffusion through these pores must therefore be expected to be a relatively sluggish process. Thus, H₂O formed in the centre of a large cube has to travel a farther distance to the surface, hence taking more time, than it is the case in a smaller cube. However, since pores are continuously closed during this H₂O diffusion, some of the H₂O does not have enough time to be evacuated from the flint before these pores are closed. Hence, the quantity of water remaining in the flint is proportionally greater in larger volumes where the H₂O evacuation takes more time. This theory also explains the observation that slow heating rates produce more water loss than faster heating rates because fast heating causes faster closing of open pores, hence stronger restriction of the H₂O

diffusion. The role of volume in the diffusion of H₂O through open pores of flint is schematically shown in Fig. 2.

The cause of failure during lithic heat treatment

The equilibrium between H₂O evacuation and porosity loss also allows for understanding the cause of failure due to overheating:

The water held within a heat-treated rock will endure the same temperature conditions as the rock itself, resulting in increasing vapour pressure in fluid inclusions (Burnham et al. 1969; McLaren et al. 1983). This vapour pressure is a function of temperature and the size of the fluid inclusions, larger inclusions enduring higher pressure than smaller inclusions (Burnham et al. 1969). Thus, when more water is retained in a rock, as it is the case in larger volumes of flint, the vapour pressure within the rock is higher. The pressure in fluid inclusions of several hundred H₂O molecules, as they can be expected in the pores of flint, can attain several kbar at 350 °C (McLaren et al. 1983), creating forces strong enough to induce fracturing of the rock. The observed pattern (that small volumes can be more rapidly heated than larger volumes and that samples that have already been slowly heated one time can be very rapidly reheated a second time) can only be explained if the driving force of heat-induced fracturing is the vapour pressure in fluid inclusions. If differential thermal expansion were the driving force of heat-induced fracturing, cubes that are reheated should fracture at the same heating rate as cubes heated for the first time because, in the absence of fracturing that could be excluded in this study, thermal expansion is entirely reversible.

Further support for vapour pressure as the mechanism of heat-induced fracturing comes from the current literature

about archaeological heat-treated and burned silica rocks: silcrete, a rock with a significantly lower SiOH content than flint (mostly between 0.1 and 0.3 wt% SiOH (Schmidt et al. 2013)), can be heated with considerably faster heating rates and higher temperatures than flint (Mercieca 2000; Mercieca and Hiscock 2008; Schmidt et al. 2013). In an experimental study based on very rapid heating of silcrete, Mercieca (2000) also found that rocks soaked in water for several days shattered at lower temperatures than dry rocks. This could be explained by the assumption that the increased amount of water in the soaked rocks led to a higher vapour pressure causing failure at relatively lower temperatures (in the absence of water evacuation that was hindered by the very rapid heating during this experiment). Another shortage of the ‘differential thermal expansion theory’ is the finding that similar volumes of very different types of silica rocks experience failure at very different temperatures and heating rates (Mandeville 1973; Inizan et al. 1976; Price et al. 1982; Patterson 1995). All silica rocks are made of the same material, microcrystalline quartz with the same thermal expansion coefficient, and, if it were their thermal expansion that causes the overheating, they should therefore experience overheating at the same conditions. However, different silica rocks may have very different SiOH content and a more or less large network of open pores (compare for example the values given in Schmidt et al. (2011) and Schmidt et al. (2013)). The ‘vapour pressure theory’ could therefore also explain the finding that different rocks made of microcrystalline quartz show different heat-induced behaviour.

Conclusion

These findings make it possible to summarise some principles relevant to successful heat treatment of flint:

- (1) Fracturing of flint during heat treatment or burning is mainly induced by water that cannot be evacuated from the rocks. Rapid thermal expansion or retraction may be expected to play a role for fracturing induced by sudden changes of temperature (quenching or direct exposure to flames) but can be discarded as the cause of overheating during controlled heat treatment.
- (2) Greater volumes need to be heat-treated with slower heating rates than smaller volumes.
- (3) Silica rocks with higher water content (H₂O and SiOH) need to be heat-treated more carefully than rocks with lower water content. More porous rocks can be heat-treated more easily because they allow faster water evacuation.
- (4) Drying of silica rocks before heat treatment allows faster heating rates and/or heat treatment of greater volumes because, if the network of open pores is emptied of water before heating, it may act as a reservoir for H₂O molecules created from SiOH at high temperatures, lowering the overall vapour pressure in the rocks.
- (5) It can be expected that smaller volumes may be heat-treated with relatively higher temperatures than larger ones because part of the water cannot be evacuated from the pores at all (due to closing porosity). The greater the volume, the more water remains in the rock and the higher is the vapour pressure in the fluid inclusions. Hence, the heat treatment temperature of larger volumes needs to be lower, for it has to be a function of the quantity of water retained in fluid inclusions.

These results have implications for the study of heat treatment from the Middle Stone Age to the Neolithic but also for the understanding of taphonomic heat-induced fracturing of silica rocks from archaeological contexts. Experimental flint knappers may also benefit from the understanding of the physical principles behind success or failure of lithic heat treatment.

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