Highlighting liquid water trapped in Neolithic Chassey flints using Neutron Scattering

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Abstract. A specific lithic manufacturing of flints has emerged in the South of France from 4200 to 3500 ca B.C. This treatment involving a smooth thermal exposure procures an improvement of the ease of detachment and of the cutting properties of the flints. The origin of these new properties remains misunderstood. High resolution large angle neutron scattering (Barotron detector) is used to describe the structural modifications occurring after the thermal treatment. The comparison of the scattering exhibited by native silica flints and flints treated at the Neolithic age does not show a structural change but indicates a significant increase of the quantity of liquid water trapped in the treated flint. It is suggested that the Neolithic treatment was proceeded in several steps including a prior wetting of the flint and then a thermal treatment closing the porosity and trapping the liquid water inside the silica flint.

Introduction

Neutron Scattering is a powerful means particularly adapted to the investigation of cultural heritage objects. Indeed this low energy neutron radiation is non-destructive and non-invasive and provides information on the volume because of its deep penetration length. Offering a unique contrast between elements such as close hydrogen or deuterium, between nuclei of metals or metalloids as silica, neutron scattering can give access to new insights and key information about the structure, the content, the provenance or the history of these precious objects from the past. In this paper, we present the first neutron scattering analysis evidencing that the thermal treatment carried out by the Neolithic societies produces deep physical transformations in the silica flints. Stone tools belongs the first prehistory tools developed by the human activity. These remains of the past have undergone several specific evolutions during millennia. At the end of the 5\(^{th}\) millennium (Cal. BC) an important change occurred in the fabrication of the flint tools, which is related to a more pronounced craft and the development of long distance trade. In archaeological terms, this is particularly visible in the southern Chassey culture across the south of France. An exceptional dissemination of specialized lithic flint productions has been identified from the Vaucluse: they are found on nearly 1000 Chassey culture consumer sites and in most cases constitute 99% of the tools. The magnitude of these exchange networks reaches the European scale with the identification of products in Italy and in Catalonia [1]. Recent archaeological researches [2] on Barremo-Bedoulian flints demonstrated that physical transformations take place at a surprisingly moderate temperature around 250\(^{\circ}\)C. The thermal treatment modifies the original gloss of flint, its roughness and its mechanical properties [3]. The first modern flint heating replicative...
experiments were performed by Crabtree and Butler in 1964 [4] and subsequent studies have been performed by various authors in order to assess the response and transformations of flint on a wide range of siliceous rocks, with different sizes and heating rates [5]. Recently, studies have tried to clarify the heat-induced transformations occurring in Barremo-Bedoulian flints at rather low temperature (around 250°C) [11-12]. They revealed that the transformation was due to the loss of silanols (Si-OH) and the formation of new Si-O-Si bonds which led to a “closure of the pores” and an improvement of the mechanical resistance at the grain boundaries leading to a more homogeneous distribution of mechanical strength. The production of flint bladelets by a pressure technique is thus facilitated, and the sharpness of the blades (cutting properties) is also improved. The aim of this study is to detail the physical changes occurring in Barremo-Bedoulian flints when it is heated at low temperature, in particular the role and the presence of the water during these transformations. We therefore sought to detect the presence of water in the Neolithic flints treated by the Chassey culture and to compare with native flints. For this, the study by neutron is particularly relevant since this technique is sensitive to light elements such as liquid water while X-Ray scattering is strongly dependent on heavy elements. With an incoherent cross-section of 80 barns, Hydrogen has the largest scattering interaction with neutrons of all the elements of the periodic table making neutron scattering ideal to detect the presence of natural water (Table 1). In addition the long mean free path of the neutron enables to probe silica samples in the depth.

Table 1. Incoherent neutron cross sections (in barn) of the constituents of the silica flint:

| Isotope | Incoherent cross sections: |
|---------|---------------------------|
| H       | 80.26                     |
| O       | 0.0008                    |
| Si      | 0.004                     |

**Experimental**

Neutron scattering experiments are carried out using a new instrument available at the Laboratoire Léon Brillouin. Initiated about a couple of years ago [6], the concept “Barotron” has evidenced the possibility of using CCD cameras and now of CMOS technology as a mean to explore the reciprocal space by neutron scattering. This two-dimensional position sensitive detector couples the advantages of a solid scintillator in terms of excellent spatial resolution to an excellent efficiency of detection and with the possibility of permanent upgrading of the charge-coupled detection device or of the CMOS technology [7]. This solid-PSD uses a coupling of a photoemission means (LiFZnS solid scintillator) adapted for the neutron radiation, a cooled low-light level charge-coupled detection device and a light amplifier. This setup is advantageous with respect to ICCD (intensified charge coupled devices) and enables a full well capacity of at least 65000 e-/pixel. The LiFZnS solid scintillator is chosen for its very low rate of detection of gamma, its high and fast photoconversion rate of neutrons (about $10^5$ photons/neutron) and its fast relaxation time (about 200 ns). The resulting two-dimensional neutron detector displays a large and versatile detection area (260 mm x 260 mm), a high spatial resolution (250000 pixels of 0.35 mm x 0.35 mm), a very low detection threshold (<1 neutron/cm²/s), a true 16 bits dynamic range that ensures a linear intensity measurement. The performances compete with the best conventional gas chamber detectors in terms of detection efficiency with a spatial resolution of the quality of X-Ray or synchrotron radiation 2D-detectors. Additionally, the compact size of this new neutron detector allows a high versatility including the use in neutronography mode (neutron imaging).
and data viewable *in situ* during the acquisition. The detector is coupled to crystalline monochromator delivering a wavelength of $\lambda = 2.36$ Å with bandwidth of less than $\Delta \lambda / \lambda < 2\%$.

The sample of silica flints are cut in thin slices of 1mm thickness for the neutron scattering experiments. They are optically opaque and thus exclude the possibility to use optical means to study the inner structure. The chemical composition of flints originating from Chassey contents more than 99% of SiO$_2$ in weight, 1% being impurities and a certain amount of water, chemically bound hydroxyl (silanole, SiOH) or free molecular water (0.3-0.6%). The present study describes the results obtained by neutron diffraction on two samples: a native flint and a flint sample originated from Chassey and treated at the Neolithic age. Both are compared at room temperature.

**Results- Discussion:**

Flint is a chemically precipitated sedimentary silica rock. This cryptocrystalline $\alpha$-quartz (SiO$_2$) is made of nanometre sized crystallites [8] assembled to form fibers. The native silica flint contains about 0.3%-0.6% of molecular water retained in voids, crystal defects and grain boundaries [9]. A small amount of water (0.5%-0.8%) is reacting with the silicon forming Si-OH bonds. At temperatures higher than 200°C, the heating is supposed to regenerate the silicon oxide (Si$_2$O) following the reaction:

$$\text{Si-OH} + \text{Si-OH} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O} \quad (1)$$

This chemical reaction, which produces molecular water is responsible for the changes of mechanical properties such as the increase of hardness, an ease of cutting and lowers the fracture ability [10]. The co-product, H$_2$O, is evaporated from the surface but hardly migrate from the thickness of the mineral. Therefore the question is to know if the crystalline structure is changed during the heating and how much the molecular water remains within the mineral. A first study using infrared spectroscopy has enabled measuring the ability of the samples to rehydrate. The identification of weak chemical transformations during heating has enabled the determination of the working temperatures used at the Neolithic. These latter are estimated between 200 and 250°C [11]. However, the method discriminates hardly the differences between native and archeological flints in terms of hydration. The present neutron scattering experiments are carried out on these native and archaeological minerals and complete the infrared study.

Because of its high cross-section (Table 1), the hydrogen nucleus has a high probability of intersection with the incident neutrons making neutron scattering a sensitive probe to detect this light atom.

Figure 1 displays the two-dimensional pattern produced by a 1mm thick flint sample treated at the Neolithic age. The isotropic scattering (rings) indicates that both treated and the native (not represented here) flints are a powder structure without texture indicating a fine-grained structure. The peak of highest intensity corresponds to the Si-Si distance.
Figure 1: 2D neutron pattern of wide angle neutron spectrum exhibited by silica flints at room temperature (raw data without correction, smoothing or binning. Barotron detector: sample-detector distance: 60mm, $\lambda = 2.36\text{Å}$, 4mm diaphragm, wavelength dispersion $\Delta\lambda/\lambda \approx 2\%$, acquisition time: 900s, incident flux: $6.10^5$ neutrons/cm$^2$/s). The scattering indicates that both treated and the native (not represented here) flints are a powder structure without texture.

The neutron scattering profiles corresponding to the native and to the treated Neolithic flints are displayed in Figure 2. Both native and treated Neolithic flints display a similar structural pattern with identical peak positions. The thermal treatment has not physically or chemically fundamentally modified the flint; its crystalline structure and the crystallite size are kept (the FWHM corrected from the instrumental resolution of the intense reflection at $Q = 1.87$ Å$^{-1}$ indicates a short range for the domain of coherence of about 70 Å - no significant structural change is observed before and after the thermal treatment within the accuracy). However the background level is significantly different. The treated sample displays an increase of the background in the whole scattering range with respect to the native one. This increase can be interpreted by a higher proportion of hydrogen in the treated sample; i.e. the Neolithic flint contains a more pronounced quantity of liquid water. From the quantitative comparison of the background levels, the rate of hydrogen is increased of 7% in the sample submitted to the thermal treatment with respect to the native sample; i.e. 7% of about 1.3% of water contained in a native flint. It should be thus concluded that the thermal treatment closes the porosity of the flint and traps a part of the water molecules within the sample. Moreover, since the thermal process (reaction (1)) consists in a release and recombination of hydrogen in water molecules, no increase of the rate of hydrogen should be noticeable. The present observation suggests that a prior wetting or an immersion of the native flint precedes the thermal treatment.
Figure 2: Neutron scattering profile (corrected from the dark and normalized by Vanadium) corresponding to the native and to the treated Neolithic flints. The red points describe the scattering produced by the native flints containing 1.3% of water and the blue points correspond to the scattering exhibited by the treated Neolithic flint. Both samples display a similar structural pattern (identical peak positions) indicating that the thermal treatment did not have chemically modified the flint and that the crystalline structure is kept. The background level is significantly different indicating that the treated sample contains a more pronounced quantity of liquid water.

Conclusions

We present here a pioneering neutron scattering study of the cultural heritage objects: the silica flints of Neolithic age manufactured by the Chassey societies. The present results identifying the presence of molecular water trapped in archaeological crafted objects would not have been obtained by other radiation than neutron scattering. Because of the strong incoherent scattering length of the hydrogen atom, the presence of water (in its liquid or crystalline form) can be easily detected by neutron scattering. Here it is evidenced by two-dimensional high resolution large angle neutron scattering that the thermal treated flints of the Neolithic age by the Chassey civilizations contain a higher concentration of water. The observation of a higher hydrogen concentration in the treated flint compared to the native one, might suggest a wetting of the flint prior the thermal treatment. The thermal procedure then induces a closure of the porosity trapping the liquid water in the mineral. These slight modifications provide important mechanical properties of the treated flints in terms of cutting. Other studies on the Neolithic flints are needed to complete this preliminary study and confirm the suggested scenario.

The present study points out the interest of intermediate and wide neutron scattering angles to characterize condensed matter objects. While conventional X-Ray scattering are available and used for years in many museums and laboratories, offering an accurate spatial resolution, the analysis with neutron scattering is rarely explored. It provides a different contrast particularly for light nuclei as hydrogen. The penetration length of the neutrons is deep in dense and thick materials as minerals. In this respect and in addition to techniques as X-Ray tomography or neutronography (neutron imaging), neutron scattering provides a powerful non-destructive investigation of heritage objects. Moreover, the adaptation of a technology based on optical sensors to two-dimensional neutron scattering procures an unrivaled high spatial resolution together with a fast speed reading (for example CMOS) extends the
possibilities to characterize reduced size samples with a high dynamic which is an advantage when the material is rare or precious.

Acknowledgements
The authors thank V. Lea for the archaeological specimens and F. Porchet for crystallography data. This work was supported by the programme ANR-09-BLAN-0324-01 ProMiTraSil.

[1] Lea V., Roque-Rosell J., Torchy L., Binder D., Sciau P., Pelegrin J., Regert M., Cousture M.-P., Roucau C., 2012 *Craft specialization and exchanges during the Southern Chassey culture: an integrated archaeological and material sciences approach*, Rubricatum, 5 (Numéro spécial dédié aux actes du colloque de Gava, Networks in the Neolithic. Exchange of raw materials, products and ideas in the Western Mediterranean (VII-III millennium BC) 2011, M. BORRELL, F. BORREL, J. BOSC, X. CLOP & M. MOLIST Ed.

[2] Binder D., 1984. Systèmes de débitage laminaire par pression : exemples chasséens provençaux. in *Préhistoire de la Pierre Taillée II, économie du débitage laminaire* (Table ronde de technologie lithique 3; Meudon-Bellevue octobre 1982) 71-94. CREP, Paris, Pelegrin J., 1988. *Débitage expérimental par pression; “du plus petit au plus grand”*. In: Tixier J. (dir.) Technologie préhistorique (Notes et Monographies Techniques du CRA, n°25), 37-53. Ed. CNRS, Paris.

[3] Lea V 2005 *Antiquity* 79 51.

[4] Crabtree D.E., Butler B.R. 1964 *Tebiwa* 7 1.

[5] Mercieca A, Hiscock P 2008 *J. of Archaeological Sci.* 35 2634.

[6] Baroni P, Noirez L (patent) Two-dimensional detection system for neutron radiation in the field of neutron scattering spectrometry. 2006 PCT WO2006/095013 A.

[7] Baroni P, Noirez L 2014 *Am. J. of Appl. Sci.* 11 1558.

[8] Rios S, Salje E.K.H., Redfern S.A.T. 2001 *EPJ B* 20 75.

[9] Schmidt P, Badou A, Fröhlich F, 2011 *Spectrochimica Acta, Part A.: Mol. and Biomol. Spectroscopy*, 81 552.

[10] Schmidt P, Masse S, Laurent G, Slodczyk A., Le Bourhis E, Perrenoud C, Livage J, Fröhlich F, 2012 *J. of Archaeol. Science* 39 135.

[11] Schmidt P, Léa V, Sciau Ph, Fröhlich F, 2013 *Archaeometry*, 55 794.

[12] Schmidt, P., Slodczyk, A., Lea, V., Davidson, A., Puaud, S. & Sciau, P. (2013b). *Phys. Chem. Minerals* 40, 331-340.