Imaging vegetal inclusions in porous clayey materials and ceramics, by impregnation with fluorescent polymers

C. SESTIER[1] R. MARTINEAU[2] E. CHENU[3] A. ELIAS[3] R. GOYDADIN[3] E. LADMIRAL[3]

ABSTRACT The detection and imaging of vegetal inclusions in fired ancient materials has been investigated after treatment with a fluorescent polymer. Impregnation allows voids and matrix to be clearly distinguished as contrasted shapes on the section. Structural organisation and quantitative porosity are thus more easily observable. Qualitative and quantitative studies of reference samples containing chaff, moss and dung have been performed. Archaeological samples of Neolithic sherds and cobs have been treated and compared to the reference samples. Our results confirm the previous interpretation concerning moss tempering of Neolithic pottery from De Spière (Belgium). Moreover, the impregnation technique allows the identification of a greater amount of vegetal inclusion than previously suspected.

1. Introduction

1.1 Preservation of vegetal remains in clayey material and observation of voids left by inclusions

Mixing organic matter with clayey material is a basic recipe for making building material and sometimes pottery. The inclusion of fibres enhances the tensile strength of the wet and dry paste, and improves water exchange through macroscopic porosity (Sestier, 2005). Analysis of the technological choices underlying preparation and use of this kind of composite material requires the identification and quantification of vegetal inclusions, or characterisation of the voids remaining after degradation of organic structures.

Thus, whilst biological degradation generally ceases after drying, partial degradation has been observed in cob after a very long time (Boissinot, 1984). Heating of vegetal inclusions in a clayey matrix obviously produces degradation of the organic matter (Dammers, 1996), a phenomenon which is greatly dependent on temperature and oxygen supply (reviewed in Johnson et al., 1988). Occurrence of organic "ghosts" — voids left by animal or plant remains — in clayey materials (either fired or not) is very frequent. The presence of "positive" objects such as non-lignified structures is rarely observed, unlike lignified remains or seeds (Willcox, 2004), which generally retain their morphology, even after mild carbonization.

One of the aims of this study is to transform vegetal ghosts (namely voids) into positive objects by filling them with fluorescent polymer. Such micromoulds will be easier to observe in the matrix after sawing it.

Small vegetal ghosts become visible after fluorescent polymer impregnation. Interpretation is based on experimental samples used as reference. The final task is to perform a botanical identification, quantitative evaluation is therefore possible. Structural features of the pottery wall may also be revealed. Such features may correspond to incomplete mixing of clay components, incomplete assembly of different parts during the shaping of the pot, or minor cracks produced during drying: these structural features are of the utmost importance for technological interpretation.

1.2. Pottery making and vegetal tempering: past and present use

The technical system, comprising the production, exploitation and transformation of plant matter and mineral ressources, allows a vast range of activities to be described. Within this system, the analysis of hidden interactions may reveal the organisation of the whole, and thus allow missing data to be inferred and modelised.

Many traditional societies use vegetal temper. Some recent studies have underlined the technological function of vegetal temper (Sestier, 2005; Tsetlin, 2003). Despite the fact that vegetal tempering of pots is quite common in some past cultural groups, few studies have been carried out on the use of vegetal temper in Neolithic sherds in western Europe. The lack of a technique adapted to the characterisation of vegetal ghosts in pottery probably explains this.

Nonetheless, vegetal inclusions and temper have been recognised for a long time in the Belgian Michelsberg group (Constantin et al., 1984), as well as in the Epi-Roessen group (Vanmontfort et al., 1997). Recently, C. Constantin refered for more than 30 Neolithic sites in northern France and Belgium (Constantin and Kuijper, 2002), where vegetal tempering of pots has been observed.

Thus, vegetal tempering of earthenware is probably more common than previously thought, which explains our interest and investment in this topic. Plant remains are poorly preserved in most of the excavated sites in western Europe, except for underwater preservation. Investigation of a new technique for the discovery and characterisation of plant remains is the principal motivation for our efforts.

2. Material and methods

2.1a. Archaeological material

Fired material is from Neolithic sites in northern France and Belgium. Sherds from the “De Hel” site near Spiere (dated between 4400 and 3800 cal BC) contain vegetal inclusions, according to B. Vanmontfort: “clays are generally tempered with flint chunks and a vegetal material, at Spiere at least partly consisting of moss” (Vanmontfort, 2001). We also studied sherds from a Michelsberg level (Blicquy, La couture du couvent, sample BCC84, 7-5094). In the same area, a Rubanné level (Blicquy, la petite rosière, sample BPR80, 7-2971) gave pottery and cob samples (Constantin et al., 1984).

2.1b. Reference material

Flint tempering of pottery: Cretaceous flint was fired and crushed into millimetric parts. Loess (more commonly named “limons de plateaux”), which is a clayey aeolian deposit containing very fine silica inclusions, was collected in the Paris Basin. It was mixed with crushed fired flint (30% flint, 70% loess, dry weights).

Samples containing moss were also prepared (30% flint, 10% moss, 60% loess, dry weight). Loess and flint were used in order to mimic the sherds from Spière, as no precise determination of their composition exists at the time of this work. Moss was not cut, but clumps of roots were separated in order to obtain a homogeneous mix with the clay.

Building materials were also obtained by mixing chaff with loess. For this purpose, *Triticum spelta* was grown and harvested after complete ripening. Monogastric (donkey) dung was collected in summer, when grass was scarce, giving a material with a high content in vegetal fibers. It was mixed with loess in serial dilutions (1,25-2,5-5% in dry weight).

2.2. Processing of the samples

2.2.1. Firing of the samples

Samples were fired in oxidising conditions (>750°C, 30 m), in order to obtain complete destruction of organic matter. This was done after having demonstrated that a high organic content of sherds partially inhibited the polymer inclusion process (probably by reducing open porosity). Sample thickness ranged from 1 mm to 10 mm and weighed from 1,5 g to 30 g. Firing was particularly useful for its hardening effect on cob fragments.

2.2.2. Polymer impregnation

Two kinds of polymers were used. Impregnation of samples with a fluorescent Metacrylate resin was performed by Maldaner SA (monomeric solution: IM3000, info@imp-sealants.de). Samples were put into a vacuum chamber (30 millibars) which was filled with the fluid monomer solution containing a fluorescent derivative, and pressure was applied. Sample surface was cleaned with water and polymerisation took place in a water bath (90°C) for 10 m. We also used an Epoxy-fluorescent monomer solution (Juracime, Switzerland). Samples were then sawed and surface was fine-ground before examination under white light (N) or UV light (360 nm).

2.3 Imaging

Digital images were processed using Photoshop® software and Scion Image® freeware, an upgraded version of NIH Image® (ftp: zippy.nimh.nih.gov). Colour was coded as grey levels, and values were inverted and appear black on the picture.

3. Results

3.1. Bibliometric overview of the topic

A basic bibliographic research shows that 95% of the hits matching the subject (vegetal temper, technology, identification, ethnology, archaeology) have been published between the years 1968 and 1984, peaking in 1980. A dramatic decrease in the amount of significant reports from 1980 onward is noticed, probably due to the lack of a convenient technique for imaging vegetal "ghosts" in pottery.

3.2. *Imaging the vegetal ghosts*

3.2.1. Reference material with moss

Structures characteristic of Moos are visible in the fired loess even in the presence of flint temper. The dramatic enhancement in the visibility of structures by the aid of fluorescence is self-explanatory (Fig. 1a and 1b).

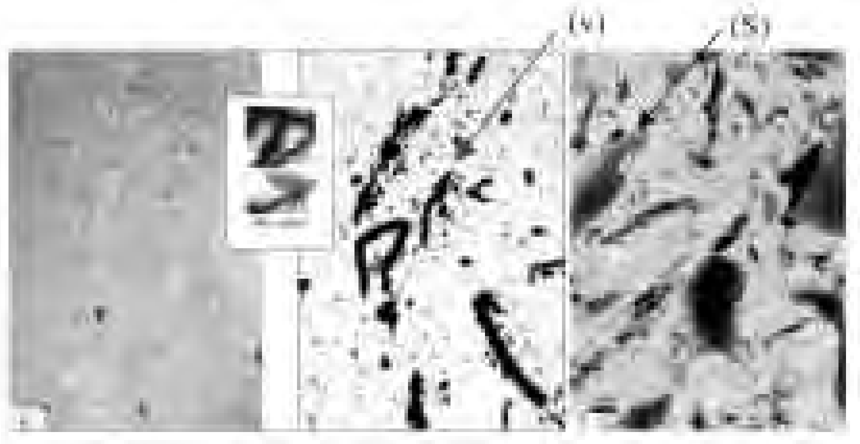

FIG. 1 – Experimental sherds, Loess+Moss. (Fluorescent resin impregnation) a: Under normal light. b: The same polished section under UV illumination (negative imaging, Green layer). c: Loess+10% moss +30% flint, polished section under UV illumination (negative imaging, Green layer). Two mineral inclusions are underlined. Insert: Dried moss. (v) = végétal inclusion, (s) = structure.

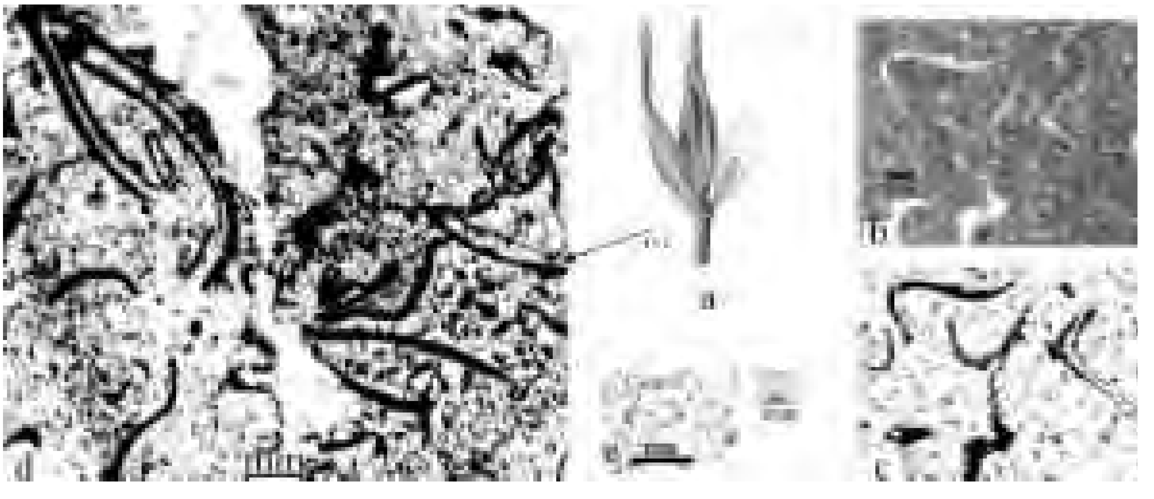

FIG. 2 – Experimental sherd, Loess+Chaff. (Fluorescent resin impregnation) a: anatomy of a cereal ear (partial). b: loess+chaff, polished section under normal light. C: the same part, polished section under UV illumination. d: other parts, polished section under UV illumination. e: background. c and d: Negative imaging, only the Green layer has been treated as a Grey-level image.

Appearance of vegetal inclusions is also modified after incorporation in the plastic paste: leaves are compacted onto the stalk, which appears more massive. Broken stalks are visible, with leaves still attached, sometimes as aggregates. The small, leafy and often tufted stem of this bryophyte is no longer visible (Fig. 3), and roots are present in the shape of isolated rods. Structures (cracks) are also visible. They usually develop around aplastic inclusions during the drying process (see Fig. 5).

3.2.2. Reference material with chaff

"Ghosts" of chaff (*triticum sp.)* and kernel envelopes are visible in the loess sample (Fig. 2) under normal light. The UV illumination of the polymer-treated samples (Fig. 2 c, 2d) dramatically improves the detection of the structures. Fig. 2e is shown as negative control (loess without chaff). Different parts of the plant (0,05-0,025 mm) are also visible with very precise structures, for example curved seed coverings and elongated shapes (glumes).

3.3. Quantitative data

Fig. 3 shows loess sherds containing an increasing amount of Moss. Fibres and stalks appear as small rods, or irregular patches if in transverse section. The elongated parts of the moss probably have prevented the homogeneous mixing with clay, and fibers are aligned with the displacement of clay during mixing. A rough dose-effect is visible, and quantification of non-homogeneous samples may require the analysis of a larger number of images. The same conclusion is drawn from the examination of loess mixed with dung, although showing a much more heterogeneous aspect (not shown).

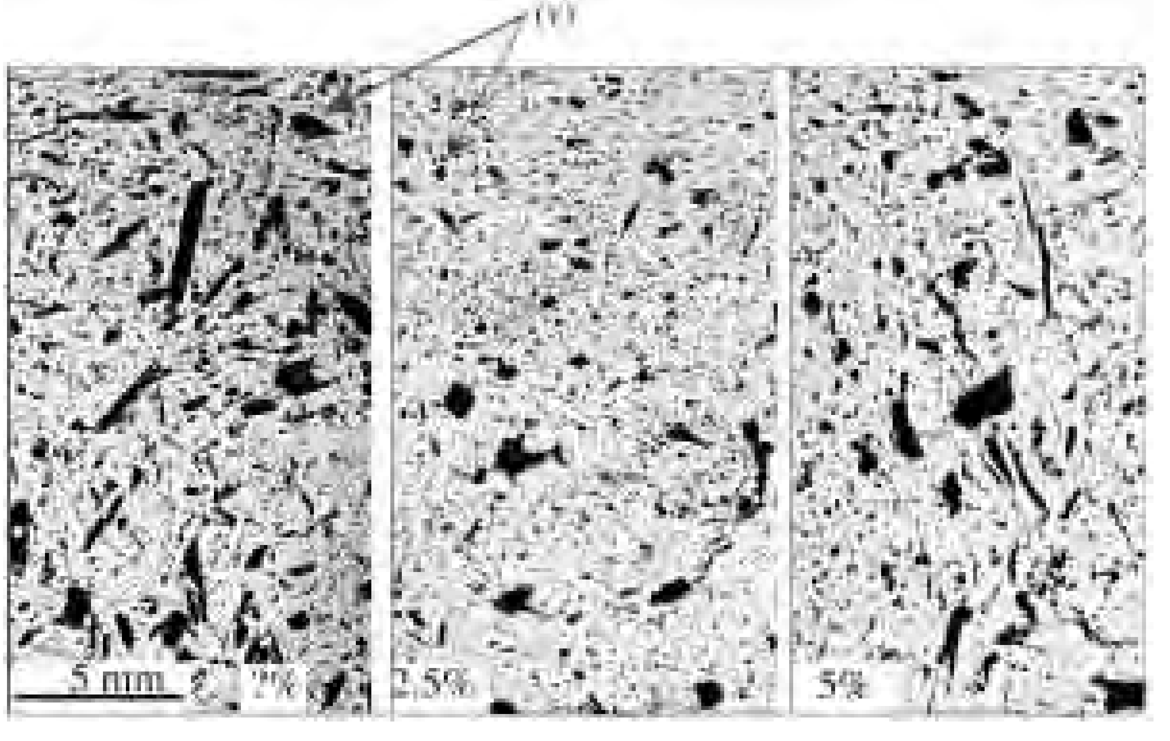

FIG. 3 – Experimental sherds, Loess + Moss. Fluorescent resin impregnation, polished section under UV illumination (negative imaging, only the Green layer has been treated as a Grey-level image). Same scale for the 3 sections. Bottom of the pictures, % of moss, dry weight; a: unknown %, b: 2,5%, c: 5% (% of Moss).

3.4 Archaeological remains

3.4.1. Neolithic sherds from Spière

Examination of the Neolithic sherds from "Spière" by the fluorescent impregnation method also demonstrates the presence of different kinds of vegetal inclusions. Very small holes visible on the broken sherd (4a) may be interpreted as stalks, and has been previously refered as to "hairs", thus the correct determination appeared later in the litterature (Constantin, 1984).

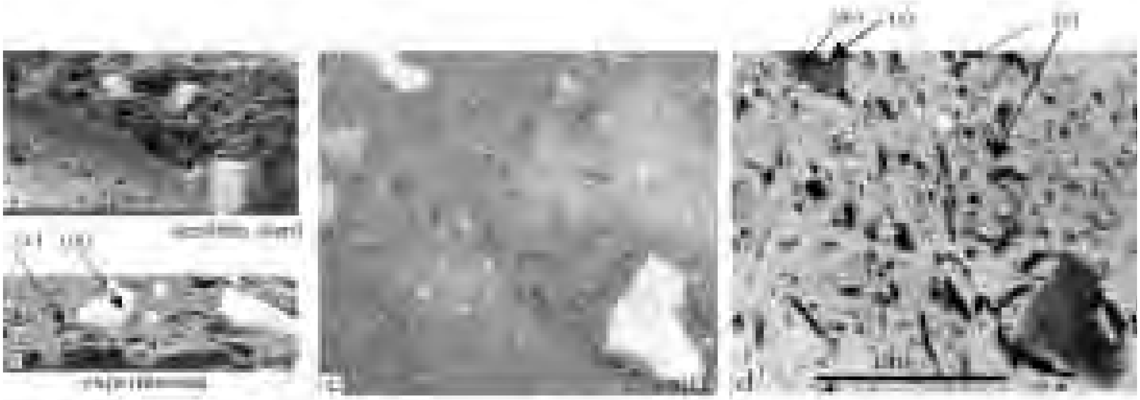

FIG. 4 – Neolithic Sherds, De Spière (vmf3) and *fac-similé*. a: untreated sherd, Spière (vmf3), broken sherd partially sawed. b: experimental sherd, untreated, section. Loess, 30% w/w fired flint, 10% moss. c: fluorescent resin impregnation for vmf3 sherd, polished section under white light. d: the same under UV light (negative imaging, only the Green layer has been treated as a Grey-level image).

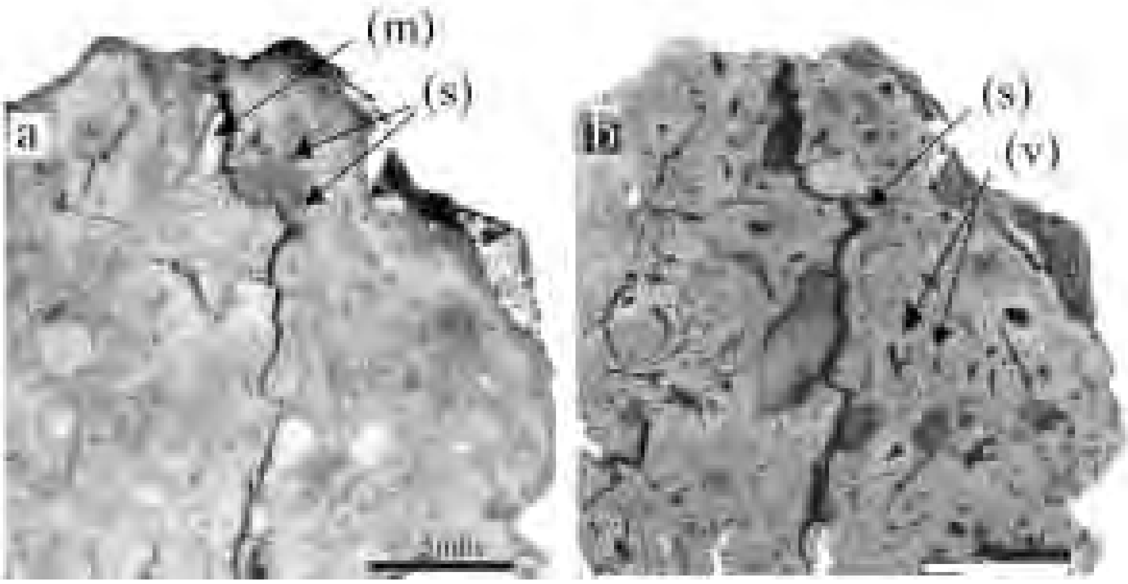

FIG. 5 – Neolithic Sherds, De Spière (vmf8), fluorescent resin impregnation. a: section under normal light. b: the same, UV illumination (negative imaging, only the Green layer has been treated as a Grey-level image). s = structure, v = vegetal inclusion, m = mineral inclusion.

This is confirmed after resin impregnation and imaging of the section, under UV light. Numerous rods are parts of stalk, probably stripped of their leaves during the mixing with clay. The smaller, curved patches are probably leaves. The presence of moss in this sherd is highly probable, but fragments present slight differences in aspect compared to experimental references. Compact mineral inclusions appear as greyish zones finely underlined and bordered by a gap. Some patches of irregular shape do not correspond to any known mineral temper: their origin remains to be determined (wood coal?) by the aid of fluorescent microscopy or thin section examination .

Another sherd (*vmf8*) in Fig. 5 shows numerous drying cracks centred around mineral inclusions. Thus, some patchy zones may correspond to vegetal inclusions, whose origin still has to be precisely determined. Nonetheless, comparison of the "Spiere" sherds at the same magnification (Fig. 6) shows unexpected heterogeneity both for density and distribution of fluorescent inclusions, and for mineral inclusions.

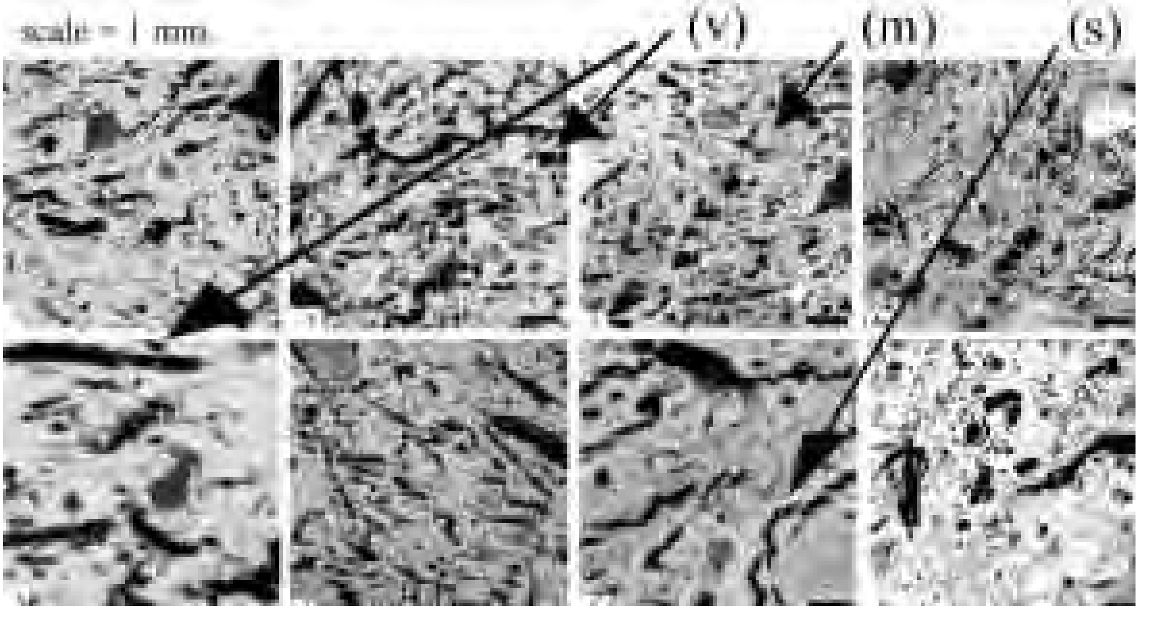

FIG. 6 – Neolithic Sherds, De Spière Fluorescent resin impregnation of 8 separate sherds (vmf, 1-2-3-4a-5-7-8-4b, from left to right and top to bottom). Polished sections under UV light (negative imaging, only the Green layer has been treated as a Grey-level image). Bar = 1 mm. All pictures show the same surface. (v) = vegetal inclusion, (m) = mineral (flint), (s) = structure.

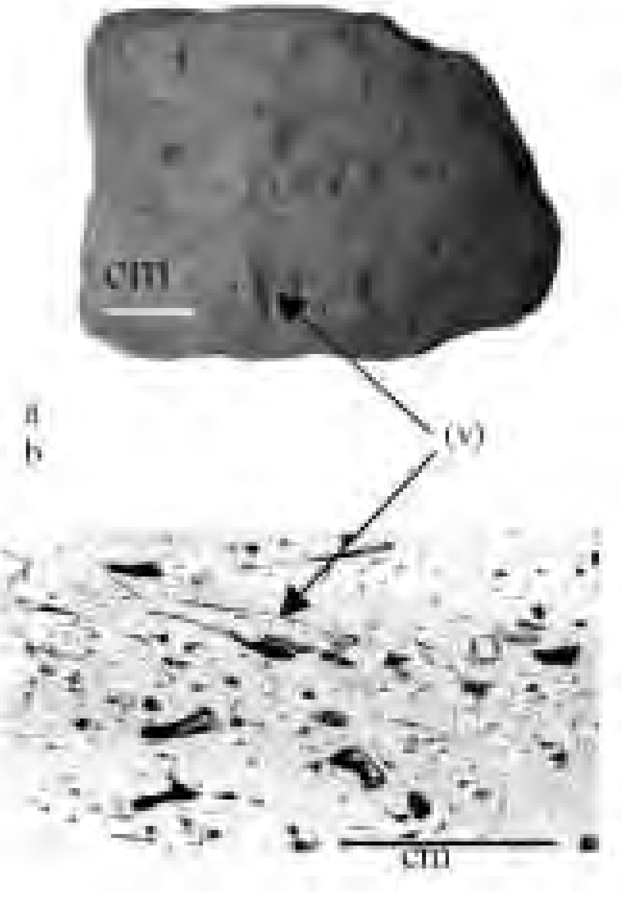

FIG. 7 – Neolithic Cob (Blicquy, la petite rosière BPR80) a: untreated sample, normal light, b: fluorescent resin impregnation, polished section under UV light (negative imaging, only the green layer has been treated as a grey-level image). V = vegetal inclusion.

3.4.2. Neolithic material from "Blicquy"

The cob sample (Fig. 7a) shows evidence of elongated vegetal inclusions, which may correspond to leaves. A polished section on the polymer-treated sample (Fig. 7b) confirms this, and shows other thin and elongated shapes which may remind us to cereal spikelets. At the time of the discovery, this cob was not fired, demonstrating that structures and voids may remain preserved in undisturbed archaeological soil.

4. Discussion

4.1. Signal acquisition

Fluorescent tagging of void's mineral matrix appears as a very convenient way for 2D imaging on polished sections. A high signal/noise ratio is easily obtained, as natural background fluorescence of matrix is usually low.

The problems of reflected light (especially by mineral inclusions) will be resolved either by using a specific narrow band filter or by numerically separating green component of the image.R-G-B image.

A reduction of the background noise is currently being tested. 3D image reconstruction is also possible after sampling serial polished sections. The use of higher magnification with optical fluorescent microscopy may help for a detailed botanical identification (not shown).

Quantitative morphometry usually applied to burnt seeds (Willcox, 2004) may find here new developments, especially for exploiting previously neglected material like as cob and burnt soils.

4.2. Reference material

Our results show that fine structure of vegetal "ghosts", once filled with the polymer, are easily detected. Quantification may remain a difficult task, and will obviously require a correct sampling procedure and additional work.

Our results suggest a great variability in the distribution of organic fragments within the mineral matrix, depending on their size, shape and quantity, and on the paste preparation technique used. Sample heterogeneity has thus to be checked before any quantification.

Complete experimental reference samples are needed for the identification of botanical structures. The process used for paste preparation may influence the shape of vegetal inclusions, for example by breaking or deforming them. Some aplastic inclusions may also give rise to specific structures, e.g. the drying and shrinkage of the clay around the mineral surface.

4.3. Archaeological material

The archaeological samples presented here highlight the three major problems which must still be questioned: sample preparation, creation of experimental references, and contextual interpretation.

Sampling bias may explain great differences in organic concentration observed in sherds obtained from the same location after excavation, because heterogeneity within the same pot and between different pots is possible. Moreover, incorporation of organic matter in only some specific parts of a pot is a true knowledge (Kelso and Thorley, 1943) and may account for a specific distribution of the vegetal temper, to be distinguished from an incomplete mixing of clay and vegetal.

The question of reference material used for interpretation is tremendously important. Plants from the same botanical family may appear very similar after inclusion in a pot and after carbonisation. Voids due to vegetal inclusions are also to be distinguished from structural voids.

4.4. Structures, vegetal ghosts (namely voids) and porosity. Problems in interpretation

The filling of voids with fluorescent polymers allow the imaging of all kinds of structures, reflecting some flaws in the sherd, which are broadly linked to the technical process of paste preparation, paste shaping and paste composition.

Thermally induced modifications (mainly decarbonatation and dehydration), together with differential thermal expansion of mineral inclusions and matrix produce different types of microporosity (Maggetti, 1994; Freestone, 1995). Sometimes, aplastic inclusions have an intrinsic porosity, like grog, bone, volcanic lava, and so on.

Shrinkage of the clay during drying physically dissociates the sticky material from aplastic inclusions, opening the paste and leaving a porosity which is affected by paste composition and thermal factors (Morariu et al., 1977).

Here, we point out that the term *temper* has been confusedly used by some authors, in place of *inclusion*. It is actually more correct to restrict *temper* to the voluntary inclusion of materials in the pottery paste. *Inclusion* refers to an unknown origin, which may be natural.

Flaws in paste cohesion, also observed during the shaping process (where parts are to be joined together) are accentuated after drying. This leaves structural voids which may be used to recognise some technical features, a way to characterize some culturally-transmitted knowledge (Martineau, 2003).

All these parameters account for some of the mechanical properties of unfired and fired pottery, and interact with vegetal inclusions. Technical interpretation for pottery tempering has therefore mainly to deal with interactions between plastic and aplastic inclusions (Sestier, 2004). Interpretation of the porosity revealed by the fluorescent inclusion technique needs an integrated approach and may be an invaluable source of information, revealing functional interaction between mineral and vegetal inclusions.

4.5. General technical comments

We have here to claim that this method fulfils requirements for a basic method of investigation. We also suggest an inexpensive modification of thin section preparation methods, e.g. addition of fluorescent-dye to the resin to be used. Anyway, if some ambiguous "voids" are observed on the thin section, it will be still possible to make observation on some parts of the sample.

Informations concerning the structures are to be treated in analogous ways as those previously studied in soil samples (Etienne and Le Fournier, 1967; Hartmann et al., 1992).

Other structures, whose size and morphology may match vegetal structures, are the basis for quantitative data studies and future experimental work. Interpretation has to be based upon macroscopic examination, in order to decipher if the vegetal ghosts are true tempering material or merely naturally occurring inclusions. Detailed data and diagnostic rules will be published elsewhere. In fact, experimental references must be produced for each case, matching archaeological material. References should be created using equivalent raw materials and similar forming techniques, in order to reproduce phenomena which may modify inclusion shape.

4.6. Technical issue

A planned development is the use of fluorescence microscopy, in order to broaden the range of the study to sub-millimetric objects. Another expected result is the separation of matrix from "micromoulds", by the way of a chemical and mechanical process. Preliminary results have shown this to be possible.

4.7. Archaeological perspectives and applications

Discussion concerning the cultural or technical roots for the tempering of pots is outside the scope of this work. This topic is included in the general field of technical constraints and past technologies. Pottery-making should be considered as a complex activity combining technical and social constraints, and we wish to avoid sterile discussion about the usefulness of materials science investigations. Such debate (Sillar and Tite, 2000) may result from a lack of information about past processes and technical knowledge. Testing the mechanical properties of composite materials and the influence of vegetal on the "workability" of clay (Sestier, 2005) may help in distinguishing true technical recipes from habits without technological effects.

The innovative application presented here may open new avenues in the study of clay technology. It offers a unique opportunity to exploit the numerous and abondant clay building materials which may contain vegetal remains, and should prove to be a valuable contribution to the "Archaeological Ceramic Ecology" approach (Matson, 1965; Kolb, 1989), and ceramic technology (Martineau et al., 2000).

Acknowledgements

C. Constantin and B. Vanmonfort for the kind gift of Neolithic sherds, C.Chateau for her linguistic help, ESIREM for its collaborative support, M-C. Frère-Sautot/APAB-SAPRR (Dijon, France) for her long-lasting help and support, Maldaner SA (France) and Juracime (Switzerland).

NOTES

[1] UMR 5594 " Archéologie, cultures et sociétés ". National Centre of Scientific Research (CNRS)/University of Burgundy/Ministry of Culture 6 bd. Gabriel 21000 Dijon, France. Corresponding author: sestier.flint@infonie.fr.

[2] UMR 5594 " Archéologie, cultures et sociétés ". National Centre of Scientific Research (CNRS)/University of Burgundy/Ministry of Culture 6 bd. Gabriel 21000 Dijon, France. Remi.Martineau@u-bourgogne.fr.

[3] Ecole Supérieure d'Ingénieur en Recherche et Etude des Matériaux (ESIREM, Dijon, France).

BIBLIOGRAPHY

ETIENNE, J.; LE FOURNIER, J. (1967) - Applications des résines synthétiques colorées pour l'étude des propriétés de réservoir des roches en lames minces. *Revue de l'Institut Français du Pétrole*. 22, p. 595-629.

HARTMANN, C.; TESSIER, D.; WILDING, L.P. (1992) - Simultaneous use of transmitted and incident ultraviolet light in describing soil microfabrics. *Soil Science Society of America Journal*. 56, p. 1867-1870.

BOISSINOT, P. (1984) - Les constructions en terre au Ier s.av. J.-C. sur l'oppidum du Baou-Roux (Bouc-Bel-Air, Bouches-du-Rhône). *Documents d'Archéologie Méridionale*. Lattes. 7, p. 79-96.

CONSTANTIN, C.; LE BOLLOCH, M.; DEMAREZ, L. (1984) - Une enceinte Michelsberg à Blicquy (la Couture du Couvent), Hainaut. *Notae Praehistoricae*. 4, p. 109-123.

CONSTANTIN, C.; KUIJPER, W.J. (2002) - Utilisation de mousse comme dégraissant dans des céramiques néolithiques de France et de Belgique. *Bulletin de la Société Prehistorique Française*. Paris. 99:4, p. 775-783.

DAMMERS, K. (1996) - Progressive loss of carbon and nitrogen from simulated daub on heating. *Journal of Archaeological Science*. London. 23, p. 639-648.

FREESTONE, I.-C. (1995) - Ceramic petrography. *American Journal of Archaeology*. Boston. 99, p. 111-115.

JOHNSON, J.-S., CLARK, J.; MILLER-ANTONIO, S.; ROBINS, D.; SCHIFFER, M. B.; SKIBO, J.-M. (1988) - Effects of firing temperature on the fate of naturally occuring organic matter in clays. *Journal of Archaeological Science*. London. 15, p. 403-414.

KELSO, J.L.; THORLEY, J.-P. (1943) - The potter's technique at Tell Beit Mirsim, particularly in stratum A, in « WF Albright, The excavation of Beit Mirsim III, The Iron age ». *Annual of the American School of Oriental Research*. 21-22, 93.

MAGGETTI, M. (1994) - Mineralogical and petrographical methods for the study of ancient pottery. In BURRAGATO, O.; GRUBESSI, O.; LAZZARINI, L., eds. - *1st International Workshop on Archaeological Ceramics*. Roma: Dipartimento di Scienze della Terra, Università degli Studi di Roma "La Sapienza", p. 23-35.

MARTINEAU, R.; CONVERTINI, F.; BOULLIER, A. (2000) - Provenances et exploitations des terres à poterie des sites de Chalain (Jura), aux 31e et 30e siècles avant J.-C. *Bulletin de la Société Préhistorique Française*. Paris. 97:1, p. 57-71.

MARTINEAU, R. (2003) - Methodology for the archaeological and experimental study of pottery forming techniques. In DI PIERRO, S.; SERNEELS, V.; MAGGETTI M., eds. - *Ceramic in the Society, Proceedings of the 6th European Meeting on Ancient Ceramics, Fribourg, Switzerland, 3-6 October 2001*. Fribourg: Département de Géosciences, Minéralogie et Pétrographie, Université de Fribourg, p. 209-216.

MORARIU, V.V.; BOGDAN, M.; ARDELEAN, I. (1977) - Ancient pottery: its pore structure. *Archaeometry*. Oxford. 19:2, p. 187-221.

SESTIER C. (2005) - Utilisation du dégraissant végétal dans des poteries en contexte Néolithique. In LIVINGSTONE SMITH, A.; DOMINIQUE BOSQUET, D.; MARTINEAU, R., eds. - *Acts of the XIVth UISPP Congress, University of Liège, Belgium, 2-8 September 2001 2 Pottery Manufacturing Processes: Reconstitution and Interpretation Colloque/Symposium 2.1*. Oxford: Archaeopress.

SILLAR, B.; TITE, M.-S. (2000) - The challenge of «technological choices» for materials science approaches in archaeology. *Archaeometry*. Oxford. 42:1, p. 2-20.

TSETLIN, Y.-B. (2003) - Organic temper in ancient ceramics. In Di Pierro, S.; Maggetti, M.; Serneels, V., eds. - *Proceedings of the 6th European Meeting on Ancient Ceramics, Fribourg, Switzerland*, oct. 2001, p. 289-306.

VANMONTFORT, B. (2001) - The group of Spiere as a new stylistic entity in the Middle Neolithic Scheldt Basin. *Notae Praehistoricae*. Leuven. 21, p. 139-143.

VANMONTFORT, B.; CASSEYAS, C.; VERMEERSCH, P.M (1997) - Neolithic ceramics from Spiere « De Hel » and their contribution to the understanding of the earliest Michelsberg culture. *Notae Praehistoricae*. Leuven. 17, p. 123-134.

WILLCOX, G. (2004) - Measuring grain size and identifying Near Eastern cereal domestication: evidence from the euphrate valley. *Journal of Archaeological Science*. London. 31, p. 145-150.