Testing the $(\text{time})^{1/4}$ diffusion law of rehydroxylation in fired clays: evidence for single-file diffusion in porous media?

Vincent J. Hare,[1] *Jörg Kärger,*[2] *Murray Moinester*[3], *Eli Piasetzky*[3]

[1] Research Laboratory for Archaeology and the History of Art, University of Oxford, U.K.
[2] Fakultät für Physik und Geowissenschaften, Universität Leipzig, Germany
[3] R. & B. Sackler Faculty of Exact Sciences, School of Physics and Astronomy, Tel Aviv University, Tel Aviv, Israel 69978.

Corresponding author: Vincent Hare, Research Laboratory for Archaeology and the History of Art, University of Oxford, South Parks Road, Oxford OX13QY, U.K.
E-Mail: vincent.hare@keble.ox.ac.uk

Abstract

Fired clay minerals rehydroxylate after firing, a phenomenon that causes the long-term mass gain and expansion seen in archaeological ceramics. During rehydroxylation, fired clay minerals react with H_2O to form structural hydroxyl (OH). Recent models propose that rehydroxylation is described by a quartic root ($t^{1/4}$) time dependence, which has led to a dating method based on the process (RHX, rehydroxylation dating). The time dependence has been interpreted as an indication of a transport process of single-file diffusion of H_2O molecules along restricted pathways in clay mineral, as theory predicts that the associated root mean square displacement is proportional to $t^{1/4}$. However, dating trials have led to alternative models, and the process is still poorly understood. Here we outline currently outstanding problems found in different experimental studies, and propose novel ways of investigating the phenomenon. These include (i) gravimetric analyses using pure clay ceramics which are free of calcite and other minerals, and reducing cooling effects by using thin samples; (ii) high-resolution nuclear magnetic resonance (NMR) with aluminum and silicon as well as with protons (hydroxyls, water) for exploring structure and dynamics, and pulsed field gradient (PFG) NMR for exploring water/proton diffusivities; (iii) IR spectroscopy, and micro-IR imaging to explore the spatial-temporal dependence of rehydroxylation of fired clay and (iv) structural investigations by high-resolution electron microscopy and X-ray diffraction.

Keywords

Rehydroxylation, clay minerals, single-file diffusion, ceramics, RHX dating

1. Introduction

Fired-clay objects are ubiquitous in the archaeological record and the modern built environment, and determining their age is of great importance to archaeological and historical research. Therefore, it is surprising that the ability to date these materials with both precision and accuracy has been a long-standing, and as yet, arguably unachieved goal of the sciences. A UK materials science group [1,2,3] recently proposed a new technique for precisely dating fired bricks and pottery using a method called rehydroxylation (RHX) dating. It is based on a proposed empirical law [4] that describes the chemical kinetics of two related phenomena in fired clays: slow irreversible moisture expansion, and mass gain. Several studies [e.g. 5,6,7] found that both these phenomena are caused by slow long-term chemical rehydroxylation. Wilson et al. [4] first proposed that the rehydroxylation reaction is described by a $(\text{time})^{1/4}$ power law dependence. In this model, rehydroxylation is controlled by diffusion of water molecules within the structure of clay minerals, which contain rehydroxylation sites. It was suggested [6] that the $(\text{time})^{1/4}$ dependence reflects a transport process of single-file diffusion of H_2O molecules along restricted pathways within clay minerals, since theoretical models [8] predict the associated root mean square displacement $<x^2>^{1/2}$ is proportional to $t^{1/4}$.

The RHX dating method relies on the fact that fired clay minerals begin chemically reacting with atmospheric moisture as soon as they are removed from the kiln. The rehydroxylation reaction continues over the ceramic's lifetime, causing it to expand and to increase in mass – the older the material, the more hydroxyl groups are incorporated into the clay minerals and the greater the mass gain. If the kinetics of the rehydroxylation reaction are proportional to $(\text{time})^{1/4}$, then the amount of hydroxyl chemically combined with the ceramic material provides an 'internal clock' that can be read by precision mass measurements to determine the elapsed time since it was fired. Besides very strongly bonded chemisorbed hydroxyls, the ceramic sample also incorporates very weakly-bound physisorbed H_2O and strongly physiochemically bound H_2O over its lifetime.

RHX dating proceeds by heating the sample (preferably under N_2 gas flow) to sufficiently high temperature (~500°C or higher) for sufficient time (many hours) to drive off H_2O (dehydration) and hydroxyls (dehydroxylation, DHX). The high temperature heating is necessary to achieve DHX, while weakly- and strongly-bound water may be dehydrated at lower temperatures (e.g., between 105 °C and 300 °C). H_2O rehydration and rehydroxylation begin after heating, when the sample is exposed to environmental humidity. Mass gain measurements are carried out at fixed and very stable temperature and humidity conditions to track these reactions over time. Time zero for thin samples may be taken as the time at the completion of the heating process. Ideally, these mass gain measurements should be carried out at the Effective Lifetime Temperature [9,10] that the ceramics experienced over its lifetime. Wilson et al. [15] claim that weakly- and strongly-bound H_2O rather quickly equilibrate (Stage I rehydration) with the ceramic material. The measured RHX reaction rate (during Stage II rehydroxylation, following Stage I) depends on temperature, and is assumed to equal the hydroxylation reaction rate experienced by the sample during its lifetime. The ceramic's age corresponds to the amount of time necessary (determined by Stage II extrapolation) for the sample to regain the original hydroxyl mass that it had prior to heating, which equals the elapsed time (age) since the ceramic was originally fired.

Several studies [11,12,13] have attempted to apply this method to archaeological ceramics, with limited and contradictory results. This may be due to experimental issues, or the effects of organic carbon, carbonates, and humic acids [14]. On the other hand, it may also be due to inaccuracies in the $(\text{time})^{1/4}$ RHX model. A robust protocol for RHX dating therefore remains elusive.

One important question that has not received much attention is how the rehydroxylation time dependence relates to the proposed mechanism of diffusive transport, or the underlying clay structure. Currently, there is no clear microstructural evidence for restricted pathways in fired clays, and a more detailed investigation of these underlying mechanisms is clearly needed.

In this paper we discuss the unique challenges posed by rehydroxylation measurements in fired clays, identifying the limitations posed by different techniques, and key questions which have arisen from recent work. To help address the current impasse, we then suggest novel experimental strategies to investigate rehydroxylation directly.

2. Rehydroxylation phenomena: magnitude, models and a dating method

When clay minerals are first fired, they lose weakly- and strongly-bound H_2O, as well as structural OH from the aluminosilicate lattice. After firing, the reverse process occurs: the minerals, in altered form, begin to take up both weakly- and strongly-bound H_2O, as well as chemically-bonded structural OH. Wilson et al. [4,6] reported that mass gain and moisture expansion occur in two distinct stages after firing. During the first stage, uptake of weakly- and strongly-bound H_2O accompanies rapid rehydroxylation. The weakly-bound water is physically bonded via van der Waals, capillary effects, and surface-water interactions; and has been variously called ‘physisorbed’/‘T0 water’/‘capillary water’/adsorbed water/‘pore water’/‘interplanar water’ [15,11]. It diffuses rapidly into the micron-scale pores and inner surfaces of the fired clay matrix, and establishes dynamic equilibrium with ambient humidity (at constant temperature). The strongly-bound water is physiochemically bonded via chemical bonds and water interacting via hydrogen bonds forming with hydroxyl groups on the surface of the ceramic matrix; and has been variously called ‘chemisorbed’/‘T1 water’ [15]. It also establishes dynamic equilibrium with ambient humidity (at constant temperature). In their model, Stage I is rapid and transient, and caused by the superposition of mass gains due to uptake of both T0 and T1 H_2O *and* chemical recombination of structural OH groups within the ceramic matrix (‘T2 water’, rehydroxylation). Once equilibrium is obtained with the weakly- and strongly-bound H_2O, Stage I ends (after a few hours or days). Rehydroxylation then begins to dominate mass gain and moisture expansion, obeying a $t^{1/4}$ relationship over the lifetime of the ceramic.

Micro-gravimetric studies propose that the following kinetic law describes this second phase of long-term chemical recombination:

$$y = \alpha(T)t^{1/4}, \qquad (1)$$

where y represents fractional mass gain due to rehydroxylation, and $\alpha(T)$ a mass gain rate constant. The value of this constant (with units of time in hours) varies from about 0.00018 to 0.00075 $h^{-1/4}$ at common environmental temperatures [1,2]. Its value depends on the temperature of original firing [16], as higher temperatures increase the degree of vitrification, and therefore reduce the number of sites available for rehydroxylation.

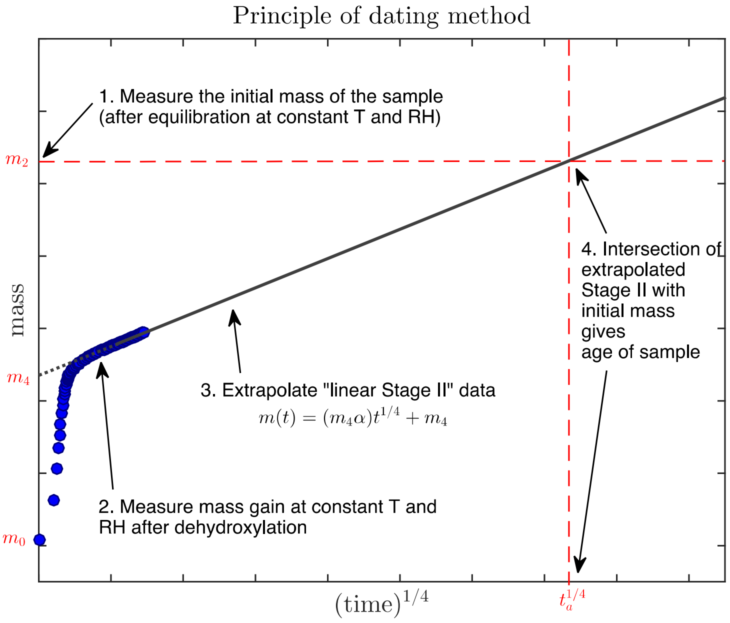

Figure 1: Schematic of RHX dating of archaeological fired-clay objects (redrawn from [31]).

Figure 1 summarizes the Wilson et al. [1,2] method of RHX dating. After having determined the initial mass of sample at constant temperature and relative humidity (mass m_2, step 1), the sample is heated to temperatures high enough to remove structural OH that has combined with the matrix since original firing. By using subsequent measurement of mass increase (step 2) to characterise the rehydroxylation rate constant α, one assumes that the original rate of rehydroxylation after the first firing is equal to that observed after reheating. The mass gain after this reheating is measured at the same constant temperature and relative humidity as step 1. The mass gain data display two stages; first, Stage I shows a rapid uptake of weakly-bound water (referred to as "physisorbed water", "T0 water" etc.), concurrent with the incorporation of chemically-bound ("T2") water. Second, after sorption of T0 water is complete, Stage II shows continuous uptake of T2 water over many decades (rehydroxylation). α and m_4 (the hypothetical mass at complete dehydroxylation, along with T0 water) are obtained from a linear least-squares fit performed on the Stage II data plotted against $(\mathrm{time})^{1/4}$ (step 3). If only T2 water has contributed to the mass lost upon reheating (an assumption which may not always be true), then the fractional mass loss y is therefore $(m_2\text{-}m_4)/m_4$, and one may rearrange Eq. 1 to yield the age since first firing as $t_a=[(m_2-m_4)/(\alpha m_4)]^4$, which is a measure of the time taken for the mass of the sample to reach the initial mass of the sample m_2. According to [1,2] this equation provides, with the values of m_2, m_4, and α measured by mass gain experiments, an estimate of t_a, the age of the artifact under investigation (steps 3 and 4). However, this assumes that (i) T2 water is the only source of Stage II mass gain, (ii) the rate α is the same as that originally experienced by the sample over its effective lifetime temperature, and (iii) that rehydroxylation accurately obeys Eq. 1 over many centuries.

We illustrate the magnitude of changes relevant for this procedure and, thus, the required accuracy with the following example. Consider a sample of fired clay that has a mass of ~10 g. Let us assume that $\alpha(T)$ is 0.00075 $h^{-1/4}$ at the effective lifetime temperature to which the ceramic was exposed during its lifetime, which is assumed to be constant. Then the percentage change in mass within the first hour after firing should be 0.075%, or about 7500 µg. The mass change in the 100th hour will be equal to $\alpha(100^{1/4}\text{-}99^{1/4})$, which is 59 µg – about two orders of magnitude smaller. This represents a scenario where α is very high. At the other extreme (α=0.00018 $h^{-1/4}$), we can expect approximately 1800 μg within the first hour, and ~14 μg in the 100th hour.

Additionally, in most clay minerals more strongly-bound forms of water exist which are lost upon heating to temperatures significantly above 100 ºC, but below 500 ºC, for example ~300 ºC. Wilson et al [2] label this 'T1 water' to distinguish it from 'T2 water', which is assumed to be structural OH water that is lost upon heating at ~500 ºC. In their model, the contribution of T1 water to long-term mass gain is generally assumed to be negligible.

Gallet and Le Goff [11] propose a similar model, with the addition of an extra term that describes a normal diffusion regime (i.e. $t^{1/2}$). However, their model envisages a scenario where uptake of T1 water continues alongside T2 water over timescales of several months/years. In terms of long-term fractional mass gain, this means that the observed time dependence is therefore neither $t^{1/4}$ nor $t^{1/2}$, but some combination of the two:

$$y(t) = -\beta e^{-t/\tau} + \mu + \alpha_4 t^{1/4} + \alpha_2 t^{1/2}, \qquad (2)$$

where β and τ are respectively the amplitude and time constant of the first rapid stage of mass gain, and α_4 is the same as the α in Eq. (1) for a $t^{1/4}$ process. Bowen et al. [12] proposed a similar approach to combining sources of mass gain, Δm:

$$\Delta m(t) = b(1 - e^{-at}) + \gamma t^{1/4}. \qquad (3)$$

Here the first term is related to the uptake of weakly-bound (T0) water, and they do not include terms associated with $t^{1/2}$ behaviour. To evaluate the hypothesis that there is fast uptake of weakly-bound water, based on Eq. 3, these authors calculate the theoretical time to 99% complete uptake as $t_{0.99} = 4.6/a$. Using the range of values of a (0.87h^{-1} -0.28 h^{-1}) fitted to experimental data, they find $t_{0.99}$ between 5 and 16 hours for a range of pottery samples between ~0.9 and ~1.7 g. By contrast, Cole [17] described the mass gain by a logarithmic time dependence.

It would seem that mass gain studies agree that the sorption of T0 water is short-lived and reversible, and that equilibrium (at constant relative humidity and temperature) is established within a couple of hours.

3. Questions arising from experimental studies

3.1 Does recombination of 'T1 water' and structural OH occur together?

Where the above models currently disagree is the extent to which the recombination of T2 (structural OH) and T1 water is simultaneous over longer timescales. This is implied by Eq. (2), but not by Eq. (1) or Eq. (3). Gravimetric data recently presented by Gallet and Le Goff [11] appear to show that archaeological ceramics exhibit continuous mass gain (in fractional terms ~42 ppm of sample mass) for up to 26 days after being reheated at between 60 ºC and 105 ºC to remove T0 weakly-bound water. They also note a systematic increase in this rate up until 450 ºC, whereupon the rate stabilizes for higher reheating temperatures. The result was interpreted as a progressive release upon reheating of a large number of sites previously occupied by T1 water, making subsequent recombination with T1 water more efficient. Similar mass gain data has been reported elsewhere [18], which lends support to a long-lived process running alongside structural rehydroxylation. We also note that thermal analysis conducted on ancient pottery [19] indicates that the percentage of mass-loss for material reheated to 350 ºC (removing mainly T1 water) is broadly correlated with known ages of pottery up to 6500 years old. Separately, the percentage of mass loss due to structural OH removed between 350 – 600 °C is broadly correlated with age, but with a different slope. This seems to add good evidence for separate, long-lived temporal processes for the recombination of both components. Additionally, Fourier transform infra-red spectroscopy of reheated brick [20] shows that peak area associated with both structural OH (3620 cm^{-1}) *and* T1/T0 water (the broad region between 3600 and 2600 cm^{-1}, and the ~1640 cm^{-1} deformation band) increase over several weeks after refiring, although the 3620 cm^{-1} peak seems to dominate after some time. However, it is not clear from this study whether T1 water properly stabilises, since the authors do not calculate specific peak areas – instead, they consider the entire envelope from 3800 to 2600 cm^{-1}.

On the other hand, the systematic non-linearity observed by [11] might reflect a *time-offset* that represents the additional time required for mass gain at a specific *aging* temperature to equate to the additional mass gained above this aging temperature during cooling of the sample post-firing/reheating. Simulations of the mass gain curves expected during post-firing/reheating cooling highlight the significant effect of this mass gained during cooling and provide excellent agreement with experiment. Simulations also suggest that the two-stage structure in the mass gain curves observed might be better explained as largely the result of a single $t^{1/4}$-based process (Arrhenius in temperature dependence) across both stages; Stage I results from mass gained during cooling with Stage II resulting from mass gained during static temperature conditions. The overall implications for the dating method are that a non-linear Stage II mass gain (as a function of $t^{1/4}$) is expected and that an improved time-offset model provides a solution while removing issues of subjectivity in isolating the *Stage II* mass gain rate.

In the case of classical isotherm sorption measurements using gravimetry, several weeks are also sometimes needed to obtain equilibrium; Ref. [21, p. 44] shows that the equilibration time is proportional to the sample thickness squared. Could non-linearity in long term Stage II mass gain be caused by thick samples, and/or long cooling times?

We note briefly that there should be some natural limit to the amount of both structural OH and T1 water, when all available sites are occupied, and so neither process can continue indefinitely. If N is known, this defines a chemical lifetime, $t_{\max}$, for a fired clay, which is the time taken until all available sites are occupied. Recently, a theoretical expression for $t_{\max}$ has been presented [22], which depends on the number of available sites, the activation energy of the rehydroxylation reaction, and the effective lifetime temperature. The theoretical model suggests that this should lie in a range between 10^5 years and 10^3 years for common environmental temperatures.

3.2 What is the uncertainty in the (time)$^{1/N}$ power law?

Another key question is the level of uncertainty associated with the power law itself. Several authors have suggested that long-term data are best fit by a $t^{1/N}$ power law model with N closer to 3 or 2 [23,12], as opposed to N=4 obtained for the same datasets by [4,24]. Here we point out that there are essentially two factors which complicate the accurate determination of N. First, multi-parameter fits (with only two measurands) of the form of Eq. 2 and 3 are prone to overfitting. Goodness-of-fit statistics are high for several choices of N, such that the uniqueness of N is unfounded. Second, slow cooling of thick samples from 500 °C to standard laboratory temperatures introduces a time-offset Δt with respect to the time t_e at which the sample is removed from the oven, such that t in Eqs. 1-3 should be replaced by t-Δt. That is, the definition of time-zero t_0 for time measurements is given as $t_0 = t_e + \Delta t$. Using t_e instead of t_0 for time measurments results in an accelerated effect of all processes in the early stages after reheating [13]. This acceleration leads to a noticable curvature in mass gain data which is identical to a combination of $t^{1/4}$ and $t^{1/2}$ transport processes.

3.3 What is the relationship between the power law and diffusion mechanisms?

Perhaps the most interesting question is how processes of diffusive transport might give rise to such behaviour in fired clays. The possibility of correlating the time dependence of rehydroxylation with a particular mechanism of anomalous diffusion (namely, single-file diffusion) has been proposed because both the apparent mass increase during rehydroxylation (e.g. Eq. 1) and molecular mean displacement during single-file diffusion scale with the square root of time (i.e. during stochastic mass transfer within a one-dimensional arrangement of elements with conserved order). Conventionally, single-file diffusion is implied to occur within channels where the particle diameter d_P is bigger than half the channel diameter d_T [25-28]. For a single particle in such a system of infinite length, theory [8,25-27] gives the time dependence as:

$$\left\langle x^2(t)\right\rangle_{sf} = 2Ft^{1/2} \ , \qquad (4)$$

where F is the single-file mobility, which is related to the diffusion coefficient of a single particle, and the ratio of particles in the queue to the number of available sites. It was suggested by [4] and [6] that such a queue exists in fired clays, and that molecules diffuse along pathways sufficiently small enough that they cannot pass one another, and that when the leading H_2O molecule encounters a site of rehydroxylation, it is removed from the queue. They suggest that this allows the entire file to advance a set distance until the next reaction site, which leads to $t^{1/4}$ kinetics because the root mean square distance travelled by the queue of molecules is proportional to the number of reactions (and therefore mass gain).

At present it is totally unknown, however, what exactly the restricted pathways in clay minerals might be. Considering that clay minerals are of layer structure with interlayer spacings of typically 3 to 4 Å, varying among different clay minerals, and have even larger (nm-scale) lamellar structure [29], it is a challenge to find intra-particle scenarios which might comply with the requirements of single-file diffusion. The situation may be complicated by the occurrence of occasional mutual exchange between the positions of adjcent particles, which are well-known to annnihilate genuine single-file behaviour [30].

3.4 Implications for archaeological dating

What are the implications of these questions for RHX dating? If T1 water is found to be short-lived (hours/days), then RHX dating by gravimetric analysis might be possible. Monte Carlo analyses [31,22] recently showed that high precision dates (~30 years at 1 σ) should be obtainable, provided that the power law obeys N=4 universally. Sub-decade precision as well as the unknown effective lifetime temperature could then be determined using as the same-age-sample (SAS) protocol proposed by [31], as yet untested. If T1 water follows a long-lived $t^{1/2}$ process, and structural OH follows a similarly long-lived $t^{1/4}$ process, then clearly a gravimetric method of RHX dating cannot work, unless the amounts of T0/T1/T2 water can be determined independently by thermo-gravimetric analysis, or it is possible to measure the archaeological mass after heating to 300 °C to drive off T0 and T1 water, as suggested recently [32]. The models that describe these concurrent processes of mass gain (Eq. 2 and Eq. 3) are arguably too complex to be used in any inversion to determine a date. Calcite contamination will also make accurate dating using mass measurements problematic, although pretreatment strategies might be designed to remove calcite.

On the other hand, IR spectroscopy or NMR might offer an advantage over conventional RHX dating by mass gain. Although these methods might be less precise, they should be able to separate the contributions of T1 water and structural OH (T2). If both of these follow known diffusion regimes, and both run together indefinitely as suggested by [11,5,6], then we note that these measurement techniques might be used for RHX dating. The T1 and T2 peak areas might be measured before heating, and the collapse of the peaks might be monitored during heating to ensure all forms of water are totally removed, and then afterwards the rate of peak growth can be measured immediately. The ratio of the rate of peak growth to the original peak area may then be used to date the ceramic sample. Both T1 and T2 process might provide a more robust age determination, because two separate, consistent age determinations would be possible if the two processes are independent of one another. The assumptions of this method would be (i) that there is a good signal-to-noise ratio from IR measurements, (ii) separate fits can be made to each peak, (iii) preparation of thin films for transmission IR does not remove T1 or T2 water and (iv) the diffusion processes are accurately characterised and understood.

In view of all these uncertainties, any in-depth investigation of rehydroxylation dating should first focus on understanding the associated elementary phenomena, particularly the modes of mass transfer and structural chances during the different regimes, both as a function of time and spatial dimensions. A short review of the experimental techniques applicable for this purpose is presented in the remainder of this contribution. .

4. Techniques of recording mass transfer and their potentials for investigating rehydroxylation

4.1 Gravimentric analysis

Most previous studies of rehydroxylation have used micro-gravimetric measurements of archaeological fired clays. However, large times are needed for samples to reach isothermal conditions after reheating, and humidity has to be kept constant to avoid fluctuations of T0 water, which distort measurements of rehydroxylation. The result is that the $t^{1/4}$ process can only be investigated at large times (several weeks) after reheating, when the process is extremely slow (e.g. ppm/hr). Microbalances offer the resolution to determine changes of ~10-60 µg (the predicted range of mass change for 10 g samples at 100 hrs). However, the complication is that multi-parameter fits to models such as Eq. 2 and Eq. 3 (with only two measurands) are prone to overfitting. Most ceramics contain calcite and other minerals which thermally decompose (e.g. to CaO) or oxidise upon reheating. These oxides then hydrate, and contribute to mass gain over and above the proposed transport processes. Removal of carbonates and organic matter [14], and measuring rehydroxylation in a N_2 atmosphere is therefore mandatory for archaeological ceramics before RHX dating.

Since mass measurements are a proxy for *all* sources of mass gain, it is impossible to determine the different mechanims of diffusive transport. We suggest that this can only be remedied by (i) using pure clay ceramics which are free of calcite and other minerals, (ii) by reducing the cooling effect by using thin samples, or (iii) by using spectroscopic methods.

4.2 IR spectroscopy and micro-IR imaging

In general, spectroscopy holds the potential to answer these questions because it provides information about the temporal behaviour of *specific* molecules. Recent advances in high-precision IR spectroscopy [33], have opened up particularly promising possibilities of observation under both non-equilibrium and equilibrium conditions. The technique clearly has great potential for fired clay minerals. One disadvantage of IR methods, particularly standard methods like diffuse reflectance infra-red Fourier spectroscopy [e.g. 20], is that they lack the precision afforded by gravimetry. We propose measuring rehydroxylation by monitoring the ~3620 cm^{-1} peak in thin films of fired clay, by micro-IR imaging in transmission mode, which should allow the maximum level of precision. Simultaneously, this technique would also allow us to monitor the T1/T0 water regions (the 3600-2600 cm^{-1} region, and the ~1640 cm^{-1} deformation band), and obtain spatial information about each transport process.

An advantage of IR spectroscopy is that the thermal effects of cooling rate in the early stages will be minimised by the use of thin clay films, which should cool significantly faster, and obtain equilibrium with T0 water more quickly. The use of pure clay minerals would allow correlations to be made with interlayer spacing, if these are measured independently by X-ray diffraction, or by high-resolution electron microscopy.

Notably, the application of spatially-resolved IR spectroscopy has proved a powerful technique for the exploration of sample heterogeneities [34,35] and of mass transfer phenomena [36-39]. This technique, also refered to as IR microimaging, becomes particularly powerful if applied to mass transfer phenomena associated with chemical transformation [40]. On investigating, in this way, molecular uptake of a benzene-hydrogen mixture by a nanoporous glass with nickel as a hydrogenation catalyst, in addition to recording the penetration front of benzene, it has also been possible to record the spatial-temporal dependence of concentration of cyclohexane emerging as a product of this process of hydrogenation within the host material [41]. It is clearly worthwhile considering whether, in analogy, IR microimaging might be applied for tracing the spatial-temporal dependence of lattice variations during the rehydroxylation of fired clay.

4.3. NMR diffusion measurements

In contrast to microimaging, where information on mass transfer is gained by recording the evolution of the distribution of molelcular guest species within the host system, NMR measurements using the pulsed field gradient (PFG) technique provide direct access to the so-called propagator of molecular diffusion, i.e. to the probability density $P(z, t)$ that, during a time interval t (typically milliseconds), an arbitrarily selected molecule (giving rise to the NMR signal considered) is shifted over a distance z (typically micrometers) into the direction of the gradient of the magnetic field applied in these studies [28,39,42]. The propagator of guest molecules determined by PFG NMR would become directly comparable with its counterpart as to be expected for single-file systems [43]. Given the largely different time scales (milliseconds in PFG NMR vs. years in rehydroxylation studies), the transport phenomena recorded by PFG NMR cannot be anything more than a particular step within the larger series of events which lead to the mass gain due to rehydroxylation. Determining how the particular steps recorded by PFG NMR relate to the overall process of rehydroxylation is therefore a fascinating task and a great challenge for future research.

It is worth mentioning that NMR has already been successfully used to study lattice variation of clay minerals such as kaolinite [44] during dehydroxylation, notably under the conditions of magic angle spinning (MAS) with ^{27}Al and ^{29}Si. Combination of MAS and PFG NMR is well known to improve the potentials of NMR diffusion measurement [45-47], and therefore this combination may be useful to investigations of de- and re-hydroxylation phenomena in fired clays.

5. Conclusion

Several studies have attempted to investigate the time dependence of rehydroxylation in archaeological ceramics, with limited and contradictory results. In part, this may be due to the limitations of gravimetric methods. We suggest that novel high-resolution spectroscopic methods are now needed to better understand transport processes in fired clays, and to resolve important questions identified by different models. The techniques of micro-IR imaging and PFG/MAS NMR, coupled with mineralogical characterisation by XRD (among other techniques) may hold the key to understanding how transport mechanisms relate to underlying mineralogy and structure. In this regard, we may expect to gain deeper insight into the extent to which the proposed $t^{1/4}$ process for mass gain of fired clays is associated with the phenomenon of single-file file diffusion, as first noted by [6]. Last but not least, better understanding might enable the development of more robust methods of archaeological dating, and improve our knowledge of the long-term stability of fired clays, which are of very great practical importance.

Acknowledgements

We thank J. Caro, C. Chmelik, D. Dikken, D. Freude, C. Hall, Y. Gallet, M. Le Goff and M. A. Wilson for helpful discussions and critical comments.

References

[1] M. A. Wilson, *et al.,* Proc. Roy. Soc. A. 465 (2009) 2407-2415.
[2] M. A. Wilson, *et al.*, Proc. Roy. Soc. A. 468 (2012) 3476-3493.
[3] C. Hall, A. Hamilton, M. A. Wilson, J. Arch. Sci. 40 (2013) 305-312.
[4] M. A. Wilson *et al.*, Phys. Rev. Lett. 90 (2003) 125503.
[5] F. Clegg *et al.*, J. Am. Ceram. Soc. 42 (2012) 314-318.
[6] S. D. Savage *et al.*, J. Eur. Cer. Soc. 91 (2008) 3396-3398.
[7] C. Hall, W. D. Hoff, J. Am. Ceram. Soc.95 (2012) 1204-1207.
[8] D. G. Levitt, Phys. Rev. A. 8 (1973) 3050-3054.
[9] A. Hamilton, C. Hall, J. Am. Ceram. Soc. 95 (2012) 2673-2678.
[10] M. Moinester, E. Piasetzky, M. Braverman, J. Am. Ceram. Soc. 98 (2014) 913-919.
[11] Y. Gallet, M. Le Goff, J. Am. Ceram. Soc. 98 (2015) 2738-2744.
[12] P. K. Bowen, J. Drelich, T. J. Scarlett, J. Am. Ceram. Soc. 96 (2013) 885-891.
[13] G. T. Barrett, J. Arch. Sci. 40 (2013) 3596-3603.
[14] M. Nümrich *et al.,* J. Arch. Sci. 57 (2015) 92-97.
[15] M. A. Wilson, *et al.,* Archaeometry 56 (2014) 689-702.
[16] L. Tosheva, B. Mihailova, M. A. Wilson, M. A. Carter, J. Eur. Cer. Soc. 30 (2010) 1867-1872.
[18] G. Cultrone, *et al.,* J. Eur. Cer. Soc. 24 (2004) 547-564.
[17] W. F. Cole, Nature 196 (1962) 431-433.
[19] S. Shoval, Y. Paz, Appl. Clay. Sci. 82 (2013) 113-120.
[20] F. Clegg *et al.,* J. Am. Ceram. Soc. 95 (2012) 416-422.
[21] L. N. Bell, T. P. Labuza, Moisture sorption: practical aspects of isotherm measurement and use, Am. Ass. Cereal Chemists, St Paul, Mn. p. 44.
[22] V. J. Hare, Royal Society Open Science (2015) DOI: 10.1098/rsos.140372
[23] M. Le Goff, Y. Gallet, J. Am. Ceram. Soc. 98 (2014) 398-401.
[24] C. Hall, M. A. Wilson, W. D. Hoff, J. Am. Ceram. Soc. 94 (2011) 3651-3654.
[25] K. Hahn, J. Kärger, V. Kukla, Phys. Rev. Lett. 76 (1996) 2762–2765.
[26] V. Kukla *et al.,* Science, 272 (1996) 702–704.
[27] C. Lutz, M. Kollmann, P. Leiderer, C. Bechinger, J. Phys.-Condes. Matter. 16 (2004) S4075-S4083.
[28] J. Kärger, D. M. Ruthven, D. N. Theodorou, Diffusion in nanoporous materials, Wiley-VCH, Weinheim, Germany, 2012.
[29] F. Bergaya *et al.*, J. Mat. Sci. 31 (1996) 5069-5075.
[30] K. Hahn, J. Kärger, J. Phys. Chem. B. 102 (1998) 5766-5771.
[31] M. Moinester, J. Kärger, E. Piasetzky, V. J. Hare, Poster, Diffusion Fundamentals VI - Dresden, Germany, 23–26 August 2015, http://www-nuclear.tau.ac.il/~murraym/RHXdiffusion.pdf

[32] S. Zhao, P. K. Bowen, J. W. Drelich, T. J. Scarlett, J. Am. Ceram. Soc. 98 (2015) 3367-3372.
[33] J. Kärger *et al.*, Nat. Mater. 13 (2014) 333–343.
[34] F. Schuth, Journal of Catalysis,143, (1993) 388–394.
[35] F. Schueth, J. Phys. Chem., 96 (1992) 7493–7496.
[36] C. Chmelik *et al.,* ChemPhysChem., 10 (2009) 2623–2627.
[37] C. Chmelik *et al.,* Phys. Rev. Lett., 104 (2010) 85902.
[38] C. Chmelik, J. Kärger, Chem. Soc. Rev., 39 (2010) 4864–4884.
[39] J. Kärger, ChemPhysChem. 16 (2014) 25-51.
[40] J. Kullmann *et al.*, Chemie Ingenieur Technik., 85 (2013) 1768–1773.
[41] T. Titze *et al.,* Angew. Chem. Int. Ed., 54 (2015) 5060–5064.
[42] J. Kärger, W. Heink, J. Magn. Reson., 51 (1983) 1–7.
[43] K. Hahn, J. Kärger, J. Phys. A., 28 (1995) 3061–3070.
[44] D. Massiot, P. Dion, J. F. Alcover, F. Bergya, J. Am. Ceram. Soc. 78 (1995) 2940-2944.
[45] S. Beckert *et al.*, J. Phys. Chem. C., 117 (2013) 24866–24872.
[46] D. Freude *et al.*, Micropor. Mesopor. Mater., 172 (2013) 174–181.
[47] M. Fernandez *et al.*, Micropor. Mesopor. Mater., 105 (2007) 124–131.