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Gravimetric and spectroscopic studies of the chemical combination of moisture by as-fired and reheated terracotta

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Abstract

The application of microbalance measurements to investigate the chemical recombination of moisture with fired clay ceramics is demonstrated. The kinetics of mass gain at constant temperature and relative humidity (RH) are studied for terracotta fired at temperatures between 800 °C and 1200 °C. The experimental results show that mass gain proceeds in two stages. The second stage mass gain is taken as a measure of the capacity for long-term chemical combination with moisture based on the $(\text{time})^{1/4}$ law. A maximum rate of mass gain is obtained for terracotta fired at 1000 °C. It is shown that reheating a sample of fired terracotta at any temperature between 500 °C and the original firing temperature will return the material to its as-fired state. This is supported by Raman spectroscopy. Exceeding the original firing temperature during reheating alters the subsequent rate of reaction to moisture, suggesting a method for determining the original firing temperature of ceramic artefacts.

Keywords: Rehydroxylation; Terracotta; Microbalance; Fired ceramics; Raman spectroscopy

1. Introduction

It has long been recognised that fired clay ceramics expand upon exposure to the atmosphere[1] and also gain mass due to chemical combination with atmospheric moisture. The moisture induced expansion is a major problem for preserving the integrity of ceramic bodies over long periods of time and can even cause structural failure in brick masonry. Information about long-term moisture expansion is of paramount importance not only for engineering design but also for the conservation of ceramic artefacts. Dimensional changes in fired clay caused by chemical combination with atmospheric moisture have been investigated by previous workers by the long-term measurements of expansive strain under ambient conditions over time periods ranging from several months to more than 10 years.[2–4] Methods such as steaming at either atmospheric pressure or at high pressure in an autoclave have also been developed to accelerate the moisture expansion process.[5–8] These allow data on the potential long-term expansion to be acquired over greatly reduced periods of time. This expansive behaviour is caused by the very slow chemical combination of moisture with the fired clay which causes an increase in mass as first demonstrated by Cole.[8] Mass gain is therefore the more fundamental measure of the underlying process; expansion is a consequence of this. Rates of mass gain are extremely slow but the use of an accurate recording microbalance with controlled sample environment makes the determination of rates of reaction with water vapour by measurement of mass entirely feasible.

Chemical composition and firing temperature are the main factors influencing the chemical combination of moisture with fired clays and these have been extensively studied.[9–12] The reactivity of fired clays is generally associated with the presence of amorphous phases, the amount of these depending on the firing temperature.[2,9] It is often important to estimate past moisture expansion, and this requires reheating of the ceramic to a sufficiently high temperature to return the material to its ex-kiln or as-fired state, *i.e.* the state prior to its exposure to the atmosphere. The choice of such a reheating temperature has long been discussed in the literature and reheating temperatures between 450 °C and 900 °C have been applied.[13]

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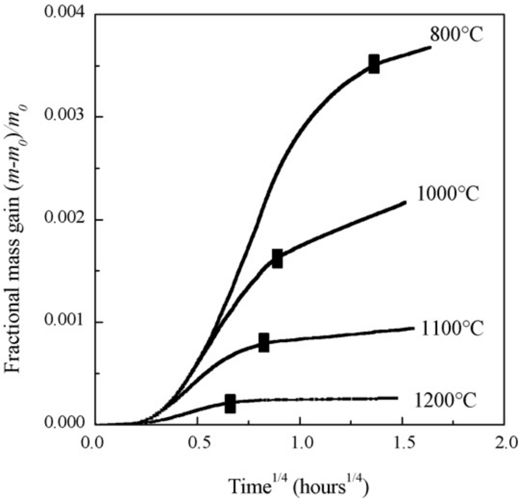

Fig. 1. Fractional mass gain versus (time)$^{1/4}$ for terracotta samples fired at temperatures between 800 °C and 1200 °C and measured at 30 °C and 60% RH. The smooth curves are made up of very closely-spaced primary microgravimetric data points.

Recently, it has been shown that the kinetics of both moisture expansion and mass gain in fired clay ceramics can be described by a (time)$^{1/4}$ law.[14] In further work it has been shown that both moisture expansion and mass gain in freshly fired clays follow a two-stage process, each stage being linear with (time)$^{1/4}$.[15] The main application of this discovery has been a new dating method for archaeological ceramics called “rehydroxylation (RHX) dating”.[16] In this method, fired clay samples are first dried at 105 °C to remove capillary water and then weighed. They are then reheated at 500 °C to remove the chemically combined water. (This choice of reheating temperature is fully justified in Ref. [16].) Following reheating the sample starts to regain mass and rate of mass gain can be determined by precise microbalance measurement at constant temperature and relative humidity (RH). The age of the sample is obtained by the extrapolation of the second stage data to the initial mass of the sample before reheating.

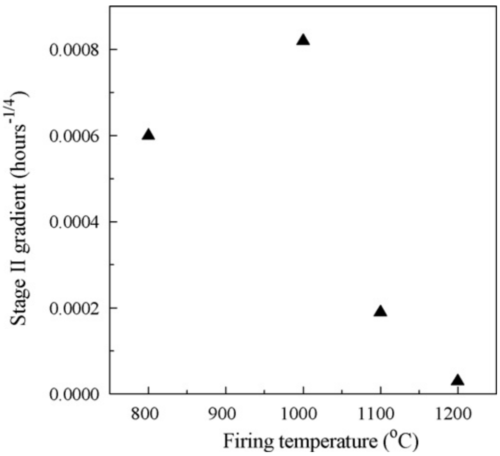

Fig. 2. Stage II gradients derived from the data of Fig. 1 plotted against firing temperature.

In the work reported here, a high accuracy microbalance (Cisorp Water Sorption Analyser, CI Electronics) is used to measure the mass gain in both freshly fired and reheated terracotta. The results show that the technique provides a rapid, simple method for measuring the rate of reaction with atmospheric moisture and therefore for predicting the long-term mass gain and establishing the time since firing. The structural changes following firing at different temperatures were also studied by micro-Raman spectroscopy to complement the microbalance measurements.

2. Experimental

Unfired terracotta was supplied in the form of a slab by Shaws of Darwen Ltd. (UK). The oxide equivalent composition of the terracotta as given by the manufacturer was 61.3 SiO_2, 1.62 TiO_2, 33.4 Al_2O_3, 1.51 Fe_2O_3, 0.12 CaO, 0.32 MgO, 1.47 K_2O, 0.22 Na_2O (wt.%). Small pieces of about 2.5 g were cut from the slab and fired at 800 °C, 1000 °C, 1100 °C and 1200 °C for 12 h after reaching the firing temperature at a rate of 10 °C min^{-1}. Reheating was carried out at 500 °C and higher temperatures using the same heating rate and a dwell time of 4 h. The rate of mass gain for each sample was determined using the microbalance with the sample chamber environment set at 30 °C and 60% RH. The instrument comprises two independent microbalance arms each with a capacity of 5 g, a resolution of $\pm 0.1\ \mu g$ and an accuracy of $\pm 1.0\ \mu g$ plus 0.001% of the suspended mass. Measurement was started immediately after transferring the hot samples from the furnace to specially constructed wire loop sample holders in the microbalance chamber. Mass was recorded at increments of 0.001% mass increase, typically every 5–40 s.

In a further set of experiments a terracotta sample was fired at 1000 °C and then placed in a desiccator at 30 °C containing saturated NaCl solution. The RH over this solution was taken as 75%.[17] After 78 h, the sample was transferred from desiccator to microbalance and the mass gain recorded at chamber conditions of 30 °C and 75% RH. The sample was then reheated at 500 °C,

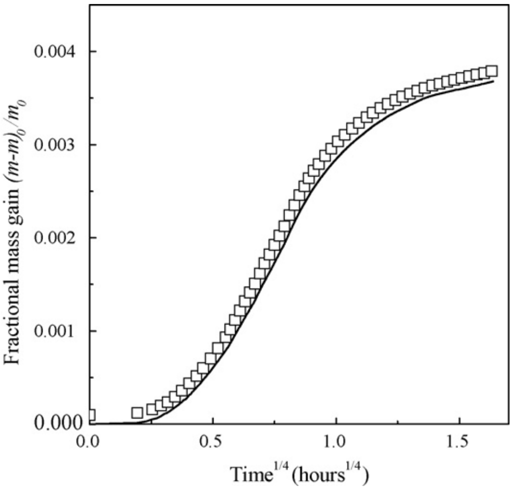

Fig. 3. Fractional mass gain versus (time)$^{1/4}$ for fired terracotta. Solid line: freshly fired at 800 °C and □: the same sample following reheating at 500 °C.

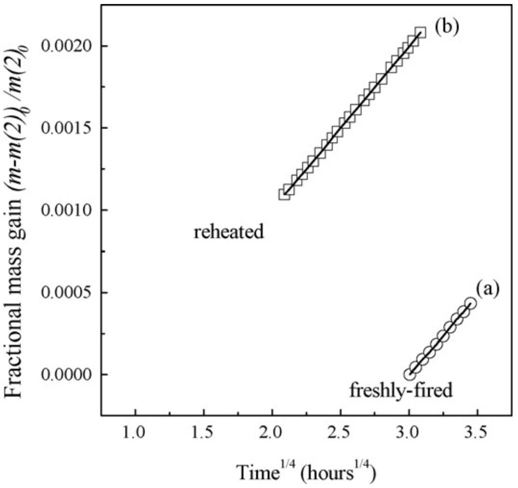

Fig. 4. Stage II fractional mass gain versus (time)$^{1/4}$ measured at 30 °C and 75% RH for: (a) terracotta fired at 1000 °C and stored over saturated NaCl for 78 h prior to measurement; (b) the same sample reheated at 500 °C and placed directly into the microbalance chamber. $m(2)_0$ is the mass at the beginning of Stage II.

transferred directly to the microbalance and its mass measured at chamber conditions 30 °C and 75% RH. The purpose of this experiment was twofold: to investigate the possibility of measuring Stage II data only following storage of the freshly fired sample under controlled environmental conditions, and to further demonstrate that the rate of mass gain in the reheated terracotta was the same as that in the freshly fired material.

For the Raman spectroscopy, a diamond saw was used to cut disc shaped specimens one side of which was polished with an alumina and 0.1-μm colloidal silica suspension. Raman spectra were obtained for each of the four firing temperatures and recorded on a Horiba Jobin-Yvon T64000 spectrometer with an Ar^+ laser operating at 514.532 nm equipped with a confocal Olympus BX41 microscope. The output laser power was 0.1 W, the laser spot size on the sample surface was about 0.5 μm and the achieved spectral resolution was approximately 2.0 cm^{-1}.

3. Results and discussion

3.1. Microbalance measurements

Fig. 1 shows fractional mass gain plotted against time$^{1/4}$ for terracotta samples fired at a range of temperatures between 800 °C and 1200 °C. The smooth continuous lines are not fitted curves but based on closely-spaced primary microgravimetric data. The two-stage nature of the results has been discussed in detail elsewhere.[15] During the first stage (Stage I), the samples quickly combine with moisture resulting in a sharp increase in their mass. Following this, there is a gradual transition to Stage II. Stage II is deemed to have begun when the derivative of the data (*i.e.* mass gain change with time$^{1/4}$) becomes constant. The time at which Stage II commences is shown for each temperature in Fig. 1 by the solid square. It can be seen from Fig. 1 that the fractional mass gain during Stage I as well as the time to reach Stage II both increase as the firing temperature is reduced. Fig. 2 shows the dependence of the Stage II gradient on firing temperature. The Stage II gradient increases with firing temperature above 800 °C but decreases at temperatures greater than 1000 °C. This is consistent with a maximum in the moisture expansion of clays fired at about 1000 °C.[10]

Fig. 3 compares the mass gain in a sample of terracotta fired at 800 °C with that of the same sample following reheating at 500 °C. It can be seen from Fig. 3 that the data almost superimpose indicating that reheating to 500 °C returns the material to its as-fired state in terms of its reactivity to moisture. Similar results were obtained for higher firing temperatures and the same reheating temperature.

The sample fired at 1000 °C, for which the Stage II gradient was the steepest, was used to examine the effect of reheating temperature on the Stage II mass gain. Reheating at any temperature from 500 °C up to the original firing temperature (1000 °C) did not change the Stage II gradient. However, reheating to a temperature greater than the original firing temperature caused a reduction in the Stage II gradient. These results suggest that reheating a ceramic at a temperature greater than the original firing temperature causes an increase in the amount of crystalline material, at the expense of the amorphous material believed to be involved in the rehydroxylation process. This effect has the potential to be used as a method to determine the original firing temperature of ancient fired clay ceramics.[18–21]

A sample fired at 1000 °C was also used to investigate the possibility of eliminating the need to place a hot sample directly into the microbalance chamber from the furnace. Fig. 4 shows Stage II mass gain data obtained for a sample fired at 1000 °C and then stored in a controlled environment of 30 °C and 75% RH for 78 h prior to being placed in the microbalance chamber under the same conditions. This conditioning step also allowed the rapid

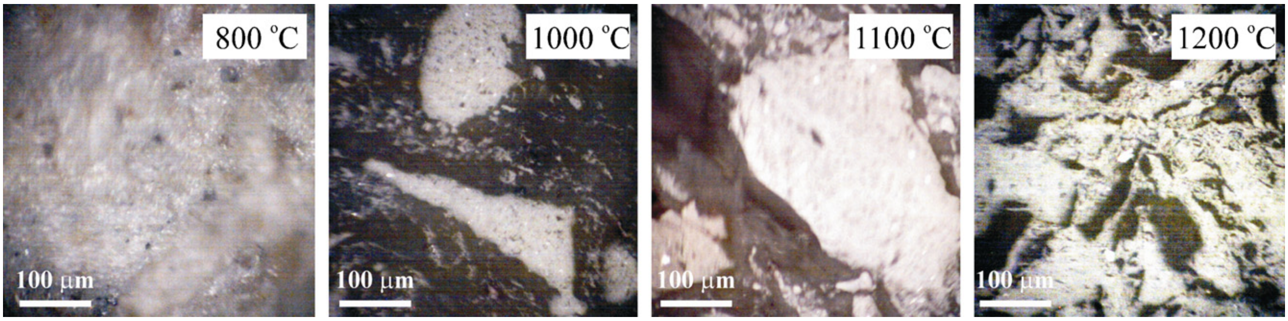

Fig. 5. Optical reflection microscopy images of polished terracotta samples fired at different temperatures.

Stage I mass gain to be bypassed. The same sample was then reheated at 500 °C and placed into the microbalance chamber (at 30 °C and 75% RH) directly from the furnace, as had been the procedure previously. The results shown in Fig. 4 indicate that the Stage II gradients are the same in the freshly fired and reheated material and that it does not matter whether the Stage II data are acquired by transferring the sample directly from the furnace to the microbalance or by holding the sample for several days under the desired measurement conditions before placing in microbalance. The Stage II gradients calculated using Origin Pro8 were 9.75×10^{-4} and $9.72 \times 10^{-4}\,\mathrm{h}^{-1/4}$ for the freshly fired and reheated samples respectively. These results suggest that the procedure for acquiring Stage II data can be greatly streamlined thus saving microbalance time. These results provide further confirmation that the mass gain in a ceramic that has been reheated at 500 °C occurs at the same rate as that in the freshly fired material as already shown in Fig. 3.

3.2. Raman micro-spectroscopy

Raman micro-spectroscopy was applied to provide an insight into the sample structure. Optical microscopic images obtained in reflection mode on polished terracotta revealed that all firing temperatures used produced samples that were not homogeneous, as shown in Fig. 5. The optical inhomogeneity was less pronounced for the sample fired at 800 °C, whereas in the samples fired at 1000 °C, 1100 °C and 1200 °C dark and bright regions were observed with the relative area of the bright region increasing with firing temperature.

The observed Raman peaks were identified using the reference spectra of layer silicates (the main mineral components in fired clay ceramics), silica and titania shown in Fig. 6. The titania polymorphs anatase and rutile are likely to be detected in fired terracotta even though the TiO_2 of the raw material is only 1.62 wt.% since they have a very strong Raman cross-section due to the strong polarizability of the Ti-O bond. Kaolinite, another common layer silicate, also shows strong Raman scattering near 260 cm^{-1}, 340 cm^{-1}, and 420 cm^{-1}.[22]

Representative Raman spectra collected from the bright and dark regions of the optical micrographs are shown in Fig. 7 for the four firing temperatures considered. These spectra are dominated by the Raman signals arising from TiO_2 (both anatase and rutile) and SiO_2 (quartz) phases.[23,24] Layer silicates, which are composed of consecutive sheets of SiO_4 tetrahedra and AlO_6 octahedra, have poor Raman scattering and thus provide a very small contribution to the overall Raman spectra in Fig. 7.

The Raman spectra in Fig. 7 show two main trends: (i) the ratio of anatase to rutile decreases in both dark and bright regions with increasing firing temperature and (ii) the presence of quartz in both the dark and bright regions appears to diminish with increasing firing temperature. This is due to an increase in phases giving rise to Raman scattering near 260 cm^{-1}, 360 cm^{-1} and 410 cm^{-1} and these are marked by asterisks in Fig. 7. These asterisked signals are most likely to originate from layer silicates and, to a lesser extent, from hydrous (opaline) silica.

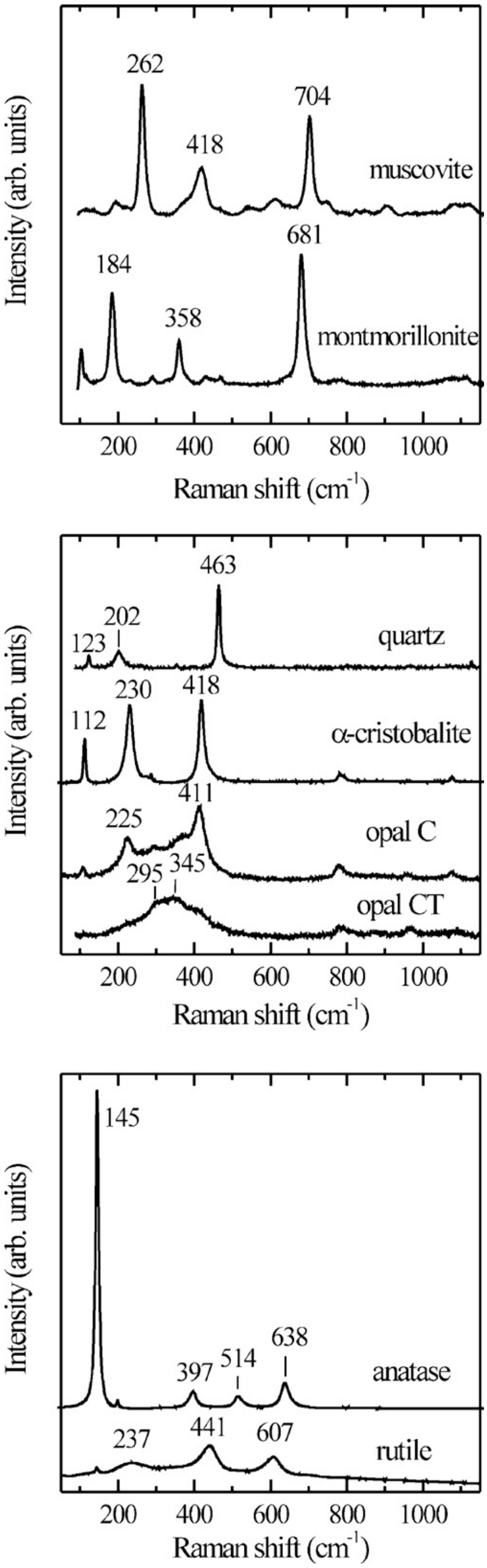

Fig. 6. Raman reference spectra of layer silicate, silica and titania samples. The spectra of montmorillonite and muscovite as representative layer silicates were downloaded from the RRUFF Caltech Raman database (http://minerals.caltech.edu/FILES/raman/).

Comparison between spectra collected from dark and bright regions shows that the intensity of quartz peaks is higher in dark

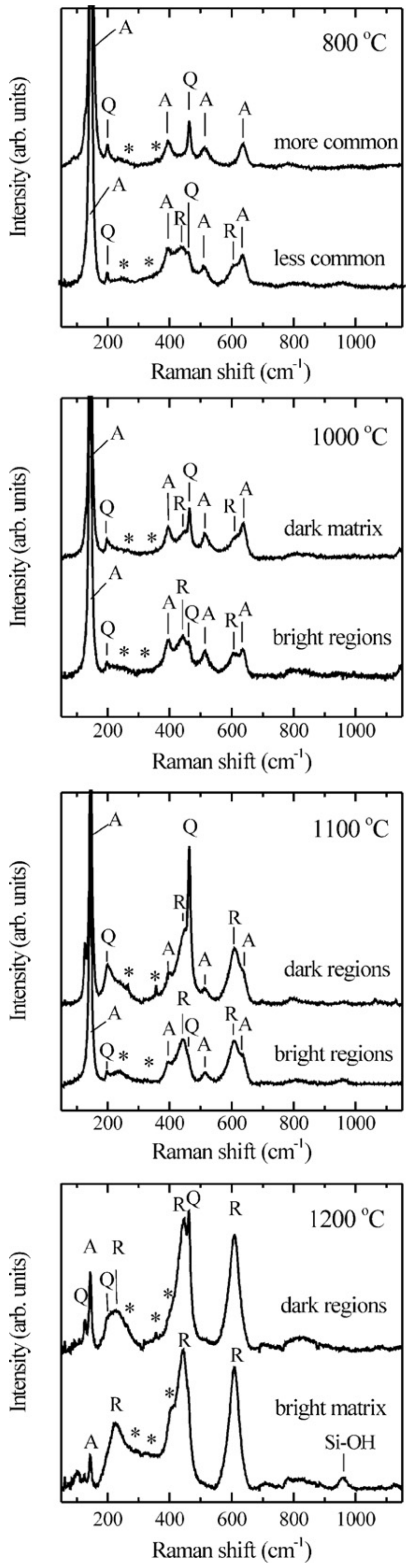

Fig. 7. Representative Raman spectra measured from the bright and dark areas shown in Fig. 5 of terracotta samples fired at different temperatures. The firing temperature is shown in the top right hand corner in each case. The peaks arising from anatase, rutile and quartz are designated as A, R and Q respectively. The contributions from layer silicates and hydrous silica (microcrystalline opal) are marked by asterisks.

regions for samples fired at 1000 °C and above. The signals arising from layer silicates are sharp and resolved in the spectra collected from dark regions, while they are very broad in the spectra collected from bright areas. Raman peak broadening is indicative of structural defects which may facilitate the chemical combination of water. This assumption is supported by the presence of the Si–OH Raman peak near 960 cm^{-1} in the spectra of terracotta fired at 1200 °C collected from bright regions. This sample shows the highest abundance of disordered silica phases according to the Raman intensity in the range 260–410 cm^{-1}. However Raman spectroscopy did not provide evidence for any particular phases in terracotta fired at 1000 °C that might be responsible for the high mass gain rate in Stage II. The high reactivity at this firing temperature is most probably related to the ceramic texture (grain size and distribution, boundary interface and fraction of non-crystalline phases).

Raman spectra from terracotta samples fired at 1000 °C and then reheated at 500 °C and 1200 °C also showed that reheating at the temperature lower than the original firing temperature did not change the Raman features observed in the original fired material. However, reheating at the temperature above the original firing temperature (*i.e.* at 1200 °C) led to Raman scattering similar to that obtained from terracotta fired at 1200 °C.

Raman scattering analysis also indicates that the ratio of anatase to rutile decreases with increasing firing temperature. Because of the extremely high Raman cross-section of TiO_2 phases, the intensity ratio between the signals at 638 cm^{-1} (anatase) and 607 cm^{-1} (rutile) measured on powdered samples in a macrochamber could possibly be used to estimate the firing temperature of a ceramic of unknown manufacturing history provided that the duration of firing does not influence the results.[25]

4. Conclusions

The mass gain due to the recombination of fired terracotta with atmospheric moisture under controlled conditions of temperature and relative humidity has been studied using a recording microbalance. The results show that for samples fired in the range 800–1200 °C, a maximum rate of Stage II fractional mass gain is obtained for material fired at 1000 °C. This maximum in mass gain coincides with the reported maximum in expansive strain.[9]

It has been shown that fired terracotta can be returned to its as-fired state in terms of reactivity to moisture by reheating at 500 °C. The reheated material shows identical $(\text{time})^{1/4}$ kinetic behaviour to that of the freshly fired material. Reheating above the original firing temperature however results in a decrease in the Stage II fractional mass gain rate. We suggest that this effect could be exploited to determine the original firing temperature of some ceramics, with particular application to archaeology.

Excellent agreement was obtained for the rate of Stage II mass gain between fired terracotta placed directly into the microbalance chamber from the furnace and terracotta fired at the same temperature that had been cooled and held for over 3 days at the environmental conditions to be used for microbalance measurement. In practice, fired clays are not used directly following removal from the kiln and changes associated with the rapid chemical combination in Stage I have already finished. It is the Stage II data that are required for the determination of the fractional mass gain rate that is exploited in the RHX dating method. The sample preconditioning presented here greatly speeds up and streamlines the collection of Stage II kinetic data and allows sufficient data to be collected over a period of about 12 h compared to several weeks by the previous method. Further, this methodology comprises a single temperature step.

Raman micro-spectroscopy generally supports the microbalance results for as-fired and reheated terracotta in that the Raman spectra of as-fired and reheated samples were similar as long as the reheating temperature did not exceed the original firing temperature. Further, because of the extremely high Raman cross-section of TiO_2 phases, the intensity ratio between the signals at 638 cm^{-1} (anatase) and 607 cm^{-1} (rutile) could possibly be used to determine the original firing temperature of some ceramics.

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