REHYDROXYLATION OF FIRED-CLAY CERAMICS: FACTORS AFFECTING EARLY-STAGE MASS GAIN IN DATING EXPERIMENTS*

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To obtain accurate results in the RHX dating of ceramics, it is essential that the RHX measurements are continued until the rate of mass gain is constant with (time)$^{1/4}$. In this paper, we discuss how the initial stages of mass gain are affected by the specific surface area (SSA) of the ceramic material. The paper provides guidance on experimental protocols to avoid dating results being distorted by relatively early-time mass gain data.

KEYWORDS: RHX, REHYDROXYLATION DATING, FIRED-CLAY CERAMICS

INTRODUCTION

In the manufacture of clay products, the raw clay is shaped and then dried, thus releasing liquid water. When the dried clay is fired, the constituent minerals and amorphous fraction lose chemically combined water (*first dehydroxylation*). As soon as the fired material is removed from the kiln, its moisture content equilibrates with its surrounding environment and at the same time it begins to chemically combine with atmospheric moisture (*first rehydroxylation*). The rehydroxylation reaction results in a progressive increase in mass and an accompanying expansion of the material (Hamilton and Hall 2012). We have shown that both mass gain and expansion involve two processes (Stages I and II) and that the Stage II reaction in both cases occurs at a rate that is proportional to the fourth root of time ($t^{1/4}$) (Wilson *et al*. 2003; Savage *et al*. 2008). The term 'Stage I' denotes the transient equilibration; and the term 'Stage II' denotes subsequent mass gain, which is due to rehydroxylation. Initially, the two processes occur simultaneously. The crossover from Stage I to Stage II occurs when short-term transient equilibration is complete, and thereafter continuing mass gain is due solely to rehydroxylation.

It is well established that chemically combined water can be removed by heating the fired clay at 500°C (*the second dehydroxylation*) (Robinson 1985). The mass lost on second dehydroxylation, hereafter referred to as 'reheating', is equal to the mass of water that has chemically combined with the material over its lifetime. Following reheating at 500°C and after cooling, the

material begins to rehydroxylate (*the second rehydroxylation*) and once again gains mass in accordance with the $t^{1/4}$ law (Wilson *et al.* 2003). It does so at the same rate as in the freshly fired material (Tosheva *et al.* 2010). This is the basis of RHX dating (Wilson *et al.* 2009, 2012): the $t^{1/4}$ law defines precisely the rate at which the rehydroxylation reaction proceeds (the RHX rate constant, α_m); from this, the time that it would take for the material to recover the mass lost on reheating is calculated and this corresponds to the time elapsed since firing. Since the RHX reaction is temperature-dependent, measurement of mass gain following reheating must be carried out at the same temperature (the 'measurement temperature') that the material has experienced over its lifetime. This is its effective lifetime temperature, or ELT (Hall *et al.* 2013). If measurements are carried out at a different temperature from the ELT, then a correction may be applied to the results, provided that an accurate value of the activation energy for rehydroxylation in that material is known (Wilson *et al.* 2009, 2012).

The purpose of this paper is to examine the underlying physicochemical processes that contribute to the two-stage form of RHX mass gain and to examine the influence of specific surface area (SSA), measurement temperature and relative humidity on the mass gain following the second dehydroxylation at 500°C. The archaeological materials examined so far exhibit a much larger range of SSA values than the bricks and tiles first used in the development of the RHX dating technique. It has been found that both lower and higher SSAs can result in greatly extended RHX mass gain measurement times and we explain why this should be so.

An operational explanation of the components of both the mass *loss* during reheating at 500°C and the subsequent mass *gain* following reheating is given in Wilson *et al.* (2012). Briefly, we defined three types of water: T0 is adsorbed H_2O, which is removed on heating at 105°C; T1 is chemisorbed H_2O, which is removed between 105°C and 500°C (at around 300°C: Clegg *et al.* 2012) [this is described by Drits and McCarty (2007) as H_2O bonded to both the internal surfaces and within the interlayers of the mineral structures]; and finally T2, the molecularly combined rehydroxylation component, which is removed at 500°C (Robinson 1985). We now believe that this distinction is not sharp and will differ from sample to sample; therefore we would now describe T0 as physically bonded water molecules (van der Waals, capillary effects and surface–water interactions); T1 as physicochemical bonding of water (weak chemical bonds and water interacting only via hydrogen bonds forming with hydroxyl groups on the surface of the ceramic matrix) and T2 as rehydroxlyation, where groups bond within the ceramic matrix (single-file diffusion into the ceramic matrix).

Therefore, during heating at 500°C, the T01 mass loss (loss of both T0 and T1 water) is due to dehydration, and the T2 mass loss to dehydroxylation. Following reheating at 500°C and subsequent exposure to atmospheric moisture, the T0, T1 and T2 mass gain rates will all increase with measurement temperature, but the amount of T0 water adsorbed at equilibrium decreases with temperature. It is hypothesized that the amount of T1 water at equilibrium is independent of the temperature at which the mass gain is measured. Furthermore, the T0 component, the only source of 'free' water available, will continuously vary in response to any fluctuations in measurement temperature and/or relative humidity (RH). For these reasons, it is necessary to maintain constant temperature and RH during the rehydroxylation mass gain measurement.

EXPERIMENTAL WORK

The detailed RHX methodology described in Wilson *et al.* (2012) was followed for sample preparation, dehydroxylation and rehydroxylation mass gain. In this work, we measured mass gain following reheating at two different temperatures and RH values for published samples

Table 1   *The temperature, relative humidity and corresponding absolute humidity for the environmental conditions used in the microbalance measurements of mass. Absolute humidity was calculated for nitrogen gas at an atmospheric pressure of 1013.25 mbar (Vaisala 2012)*

Temperature (°C)	Relative humidity (%)	Absolute humidity (g m^{-3})	Material
11	30	3.01	*Opus spicatum*
11	60	6.03	Low-fired ceramic
50	20	16.6	Low-fired ceramic
11	50	5.02	Samian
50	10	8.3	Samian

(Wilson *et al*. 2012): a low-fired Anglo-Saxon loom-weight and a sample of high-fired samian ware with a slip layer. These are compared with a Roman tile material, *opus spicatum*, the dating results for which were published in Wilson *et al*. (2009). The measurement conditions of temperature and humidity used in the experimental work are summarized in Table 1. The lower measurement temperature of 11°C (±0.1°C) in each case corresponds to the nominal UK outdoor mean temperature. As RH is temperature dependent, for purposes of comparison and to clarify the effect of RH we shall use the term 'absolute humidity'. Absolute humidity is defined as the amount of water vapour present in a gas, expressed as g m^{-3}. Since the relative humidity in the microbalance chamber is controlled by mixing wet and dry nitrogen streams, the values of absolute humidity have been calculated for nitrogen rather than air. A full explanation of relative and absolute humidity, and the significance of temperature, are given in the Appendix.

Specific surface area (SSA) measurements were carried out on a ~5 mm^3 bulk sample of each material by BET nitrogen sorption. Each sample was purged overnight in helium at 100°C in a Micromeritics Flow Prep 060 to remove liquid water and weighed to four decimal places. It was then placed into a Micromeritics Gemini 2360 Series surface area analyser, chilled in liquid nitrogen and the nitrogen adsorption measured. Each result was obtained from a multi-point determination of five. The SSA was calculated (in units of m^2 g^{-1}) using standard software to four decimal places and quoted to two.

EXPERIMENTAL RESULTS AND DISCUSSION

Rehydroxylation mass gain data

The standard data form: opus spicatum   Figure 1 shows mass versus (time)$^{1/4}$ data for the *opus spicatum* tile material measured in the microbalance at 11°C and 30% RH following reheating at 500°C. We use this graph of mass gain versus (time)$^{1/4}$ to illustrate what may be considered 'ideal' data: the transition from Stage I to Stage II (Fig. 1 (a)) is rapid; the Stage II gradient becomes constant after a relatively short time; and the entire experiment lasted ~45 h. The onset of the constant Stage II gradient in Figure 1 (a), in this case at $t^{1/4}$ = ~1.75 h$^{1/4}$ (corresponding to t = ~9.5 h), was determined by plotting the gradients of consecutive segments of the m ($t^{1/4}$) data as shown inset in Figure 1. For comparison purposes later in the paper, we consider the RHX rate constant for this material to be defined accurately by the gradient of the interval $t^{1/4}$ = 1.75–2.25 h$^{1/4}$ (an interval in $t^{1/4}$ of 0.5 h$^{1/4}$), which corresponds to a time interval of ~16 h (i.e., 2.25^4 – 1.75^4). Therefore, in this example, we did not use the data collected over the last 20 h of the experiment to calculate α_m.
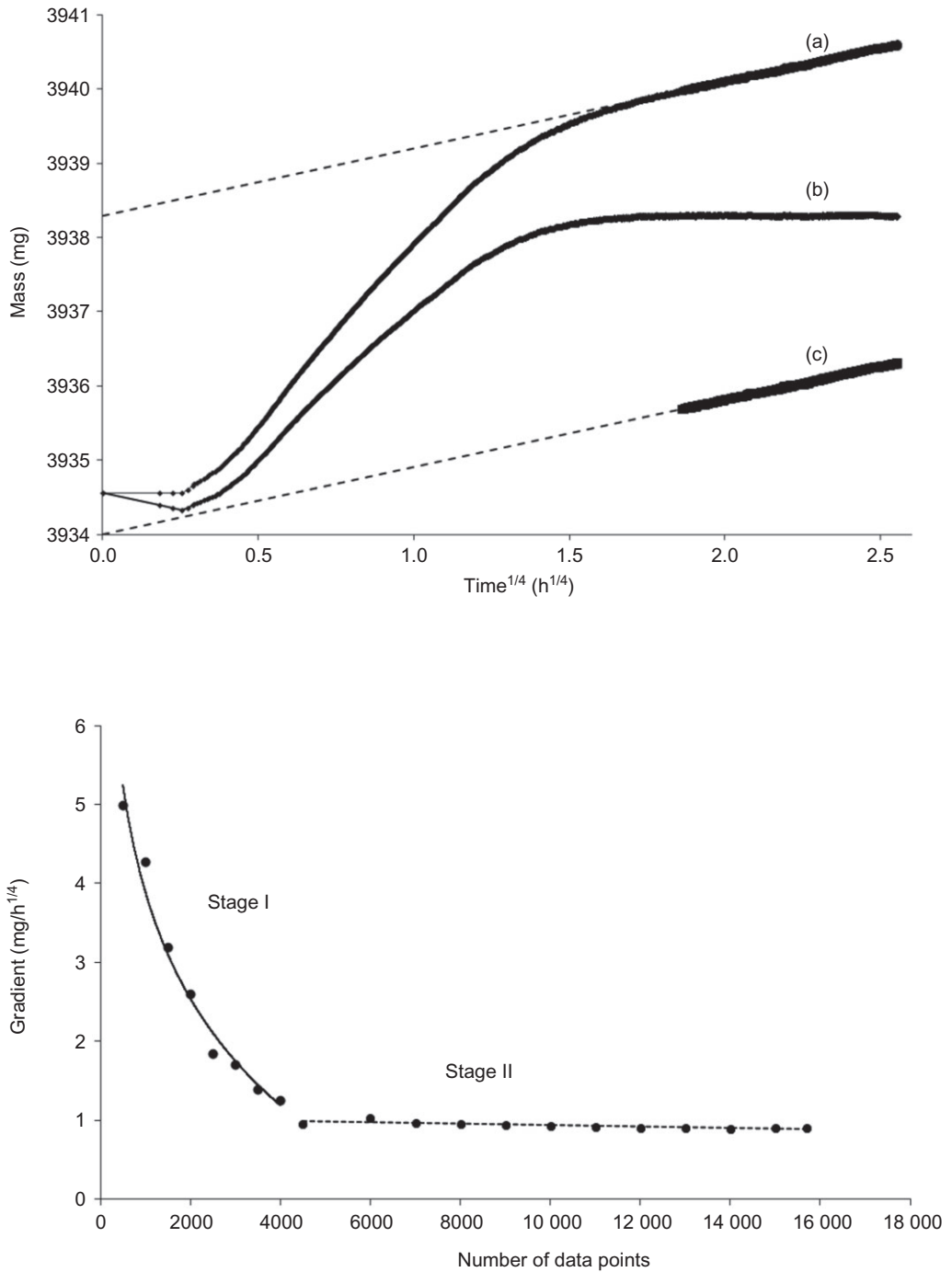
Figure 1   *Mass gain versus (time)$^{1/4}$ following reheating at 500°C for the* opus spicatum *floor tile (upper graph): (a) combined mass gain T0 + T1 + T2 (T012) (~27 000 data points); (b) mass gain due to T0 + T1 (T01) only; (c) mass gain due to the T2 rehydroxylation component only. The gradients of consecutive segments of* m (t$^{1/4}$) *data (lower graph), illustrate that Stage II had been reached. The microbalance has a resolution of 0.1 μg.*

The gradient of the least-squares fit to the Stage II linear region of (a) defines the RHX rate constant, α_m, and the mass gain over this region is due solely to the continuing RHX reaction. If this line is back-extrapolated to the *y*-axis, as shown by the upper dashed line in Figure 1, and the intercept subtracted from the ordinate of each Stage II data point, these data then pass through the origin, as shown by line (c) in Figure 1. This line corresponds to the mass gain due to the RHX component alone. It is assumed here that the rehydroxylation reaction commences at $t = 0$. Subtracting the RHX mass gain (c) from the total mass gain (a) produces line (b), which corresponds to the mass gain due to the T0 and T1 components. The horizontal region of (b) shows that there is no further T0 or T1 contribution beyond the time at which the Stage II gradient becomes constant.

Stage I consists of the T0 + T1 mass gain as the material equilibrates with its environment *in addition to* the rehydroxylation (T2) mass gain which must occur simultaneously. Once T01 equilibrium has been reached, the RHX reaction will continue indefinitely thereafter, with the continuing mass gain due to T2 only. Therefore, the RHX rate equation (Wilson *et al*. 2009) only applies to mass gain due to T2, and it is inappropriate to attempt to fit this function to the entire data set (as per Bowen *et al*. 2011), as there is currently no term to describe the mass gain due to T01.

High specific surface area material: the Anglo-Saxon loom-weight   The first type of departure from ideal behaviour that we have observed, associated with materials of comparatively high SSA, is characterized by an m ($t^{1/4}$) plot, which we describe as 'convex', in which the transition from Stage I to Stage II is so slow that there is an extended non-linear (curved) region. We have observed that this behaviour is also symptomatic of the presence of calcite in the material, and a full discussion of this will be presented in a separate paper. Figure 2 shows the results of mass measurements carried out at 11°C and 60% RH, and 50°C and 20% RH on the same sample of loom-weight following reheating at 500°C. The values of absolute humidity corresponding to these measurement conditions are given in Table 1.

What is immediately striking in Figure 2 is the much greater mass gain of the sample measured at the lower absolute humidity. The reason for this is that the lower measurement temperature increases the T0 component. In contrast to this, the higher measurement temperature will result in more rapid uptake of T1 mass, more rapid and also greater uptake of T2 mass, but a reduction in T0 mass gain. This is further illustrated in Figure 3, in which both sets of data in Figure 2 are separated into their constituent mass components as in Figure 1. From Figure 3, it can be seen that the T01 component at 11°C and 50% RH (corresponding to an absolute humidity of 6.027 g m^{-3}) is 20 mg. Since the lower measurement temperature enhances adsorption, T0 must be the dominant component in Stage I. At 50°C and 20% RH (corresponding to an absolute humidity of 16.601 g m^{-3}), there is a T01 mass of only around 5 mg, despite there being nearly three times more water available. We are not suggesting that RHX dating experiments should be carried out at such high temperatures, but this demonstrates the impact of temperature on the time required to reach Stage II.

The combination of large SSA, low absolute humidity *and* low measurement temperature therefore increases the time for T1 equilibration. This possibly occurs at the expense of T0 equilibrium, which, at lower temperatures, requires a greater quantity of water to be available. Under such conditions, the T0 mass gain is likely to be supply-limited due to the low absolute humidity. In contrast, a high amount of water vapour in combination with a high measurement temperature will accelerate T1 equilibration and also result in more rapid T0 equilibrium. It is hypothesized that the total T1 requirement is the same at each measurement temperature. The
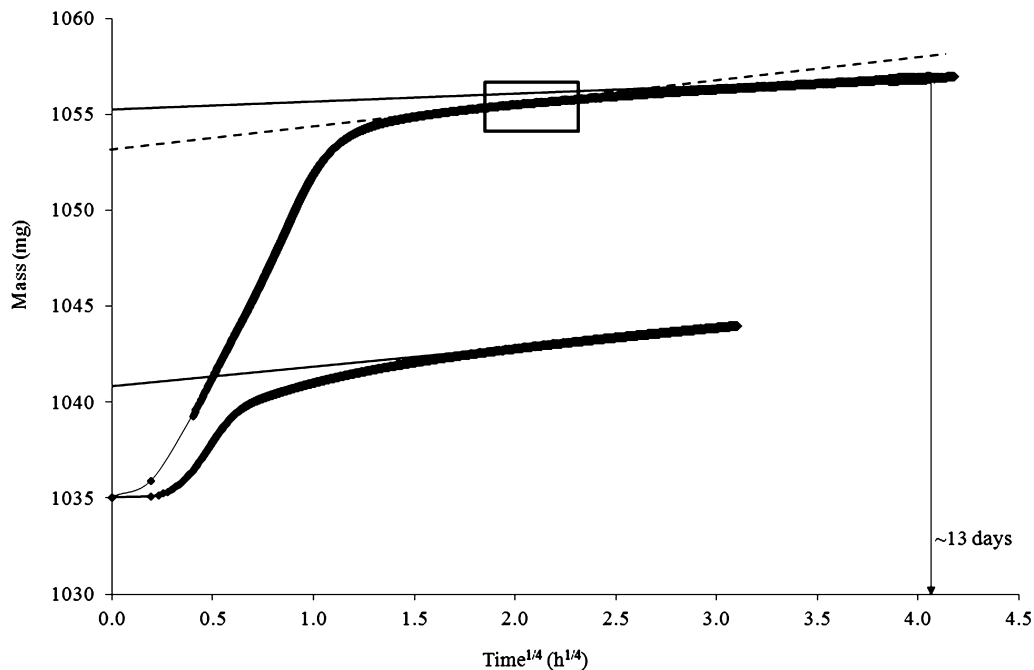
Figure 2   *Mass versus (time)$^{1/4}$ following reheating at 500°C for the same sample of loom-weight measured at 11°C and 60% RH (upper graph) and 50°C and 20% RH (lower graph). The first points of each data set are coincident. The least-squares fits to the linear Stage II region of each are* m = 0.4111t$^{1/4}$ + 1055.2000 *(upper graph) and* m = 1.0266t$^{1/4}$ + 1040.8223 *(lower graph). Data are reported to four decimal places, as the microbalance has a resolution of 0.1 µg. The rectangle on the upper graph indicates the interval* t$^{1/4}$ = 1.75–2.25 h$^{1/4}$ *and the dashed line is the linear least-squares fit to the data over this interval, clearly illustrating the underestimate of age.*

long transition period to Stage II seen with this material at 11°C suggests there is a large difference in the time for each component to equilibrate.

The implications of these results for RHX dating experiments are as follows. Consider the sample measured at 11°C: Stage II becomes linear at $t^{1/4} \approx 3.7$ h$^{1/4}$, or ~187 h, compared to only 9.5 h for the *opus spicatum* of Figure 1. Assuming that we wish to standardize the RHX dating methodology to obtain stable Stage II data over a defined interval of, say, $t^{1/4} = 0.5$ h$^{1/4}$, the sample has to be left in the microbalance for a further 124 h [in this case $(4.2^4 - 3.7^4)$] to collect sufficient Stage II data to define the RHX rate constant, α_m. The consequence of this is a dating experiment requiring uninterrupted, constant environmental conditions of nearly 13 days' duration. Further, because of the $t^{1/4}$ kinetics, the reaction slows monotonically, so that the data quality will degrade as the measurement time is increased.

Consider now the lower graph in Figure 3, which shows the mass gain recorded for the same sample of loom-weight material (also following heating at 500°C) at the higher measurement temperature of 50°C and an absolute humidity of 16.6 g m^{-3}. The increased measurement temperature results in a linear and stable Stage II gradient at a *much* earlier time: 2.5 h$^{1/4}$, or 39 h, compared with 187 h at the lower measurement temperature. Further, to collect Stage II data over an interval of $t^{1/4} = 0.5$ h$^{1/4}$, only 42 h of further measurement is required ($3.0^4 - 2.5^4$) to define α_m.
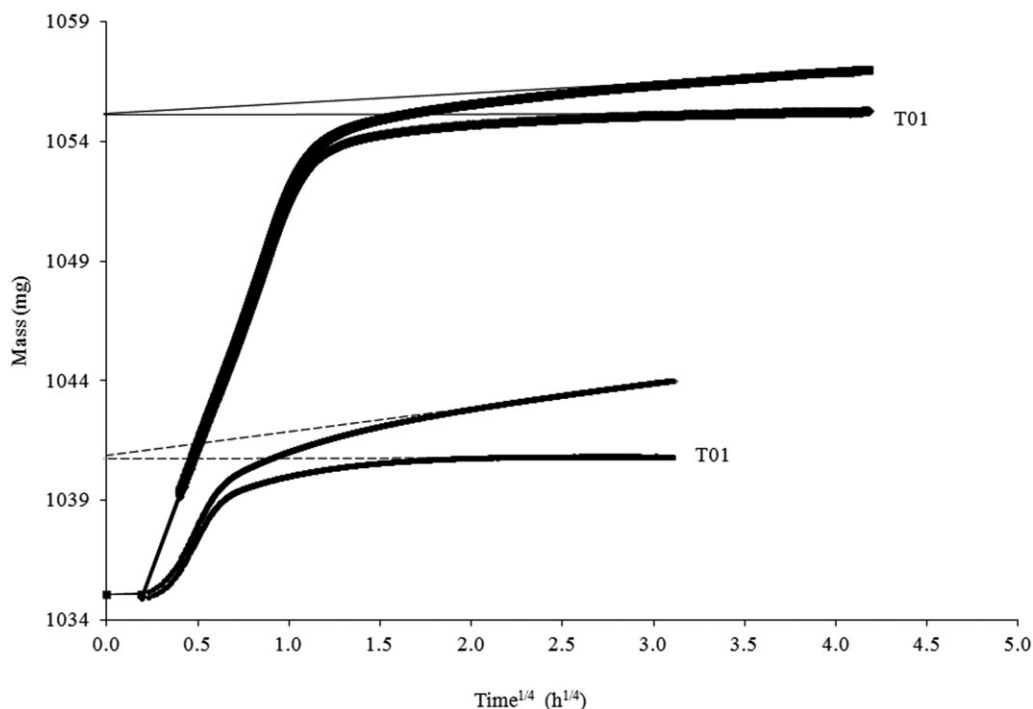
Figure 3 *The data of Figure 2 separated into their constituent components of mass: the same sample of loom-weight measured at 11°C and 50% RH (upper graph) and 50°C and 10% RH (lower graph).*

Clearly, in the case of high SSA materials, taking the $m/t^{1/4}$ gradient before T0 and T1 have stabilized will result in an underestimate of the sample's age. This is illustrated in Figure 2, which shows that the gradient, if measured over the same time interval as Figure 1 ($t^{1/4} = 1.75$–2.25 h$^{1/4}$), will clearly lead to an underestimate of sample age.

Low surface area material: samian ware The second type of behaviour, which is associated with low-SSA materials, is the highly distinctive data form that we have described as 'concave', shown in Figure 4. This shows the mass gain measured at 11°C and 50% RH, and at 50°C and 10% RH, on a sample of samian ware following reheating at 500°C. The associated values of absolute humidity are given in Table 1.

The data are separated into their constituent components and shown in Figure 5. As in the previous case, the mass gain is greater at the lower measurement temperature and the Stage II gradient becomes linear at a much earlier time at the higher measurement temperature. At 11°C the T01 component equilibrates at $t^{1/4} \approx 3.5$ h$^{1/4}$, or ~150 h, and the sample has to be left in the microbalance for a further 106 h ($4^4 - 3.5^4$) to obtain stable Stage II data. The consequence of this is the same as observed with the high-SSA material: a dating experiment of nearly 13 days duration.

As was observed with the high-SSA material, when the low-SSA material was measured at 50°C and 10% RH, a linear and stable Stage II gradient, due to the uptake of T2 only, occurs at a *much* earlier time: 2.5 h$^{1/4}$, or 39 h, compared to 150 h at the lower temperature. In addition, to collect Stage II data over an interval of $t^{1/4} = 0.5$ h$^{1/4}$, another 42 h of data collection were required
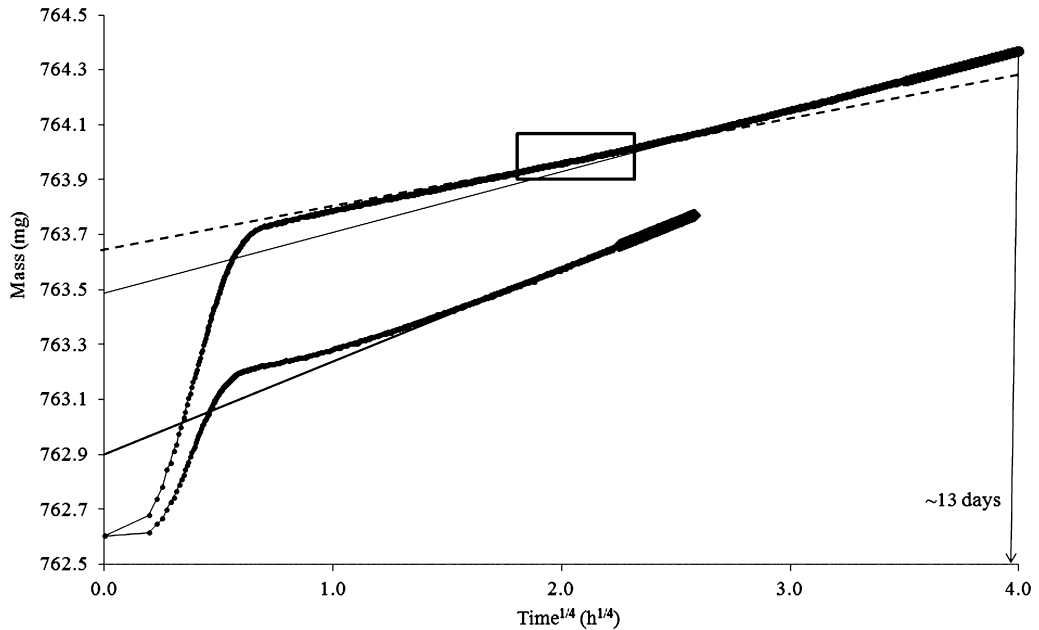
Figure 4   *Mass gain versus (time)$^{1/4}$ following reheating at 500°C for the same sample of samian ware measured at 11°C and 50% RH (upper graph) and 50°C and 10% RH (lower graph). The first points of each data set are coincident. The least-squares fits to the linear region of each are m = 0.2201t$^{1/4}$ + 763.4900 (upper graph) and m = 0.3373t$^{1/4}$ + 762.9000 (lower graph). Data are reported to four decimal places, as microbalance data have a resolution of 0.1 µg. Again, the rectangle on the upper graph indicates the interval t$^{1/4}$ = 1.75–2.25 h$^{1/4}$ and the dashed line is the linear least-squares fit to the data over this region, which illustrates, in this case, the potential overestimate of age.*

($3.0^4 - 2.5^4$ h) to define α_m. In the case of materials with low SSA, taking the $m/t^{1/4}$ gradient before Stage II has stabilized would result in an *overestimate* of the sample's age. It can be clearly seen from the upper graph in Figure 4 that taking the gradient of the line over the interval $t^{1/4} = 1.75–2.25$ h$^{1/4}$ would result in too low a value of α_m. This is emphasized in Figure 4, which shows how taking the gradient over the same time interval as Figure 1 ($t^{1/4} = 1.75–2.25$ h$^{1/4}$) would result in an overestimate of the samples age.

What is unexpected about the data from material with low SAA is that the T01 component reaches a maximum at about $t^{1/4} = 0.5$ h$^{1/4}$. Following this, there is a gradual decrease in mass before T01 equilibrium is reached. This effect can be explained by Figure 6, which shows the T01 component at each measurement temperature with superimposed plots of the recorded values of RH. In each case, it can be seen that substantial mass gain occurs during the time taken for the RH to reach its set point. The sample becomes 'over-wet' and exceeds its eventual equilibrium mass. This excess water must be lost by drying, and this occurs more quickly at the higher measurement temperature and is further facilitated by the constant flow of gas through the microbalance chamber (Hall *et al.* 1984).

The concave data form is therefore an artefact of the measurement conditions. The RH set point is reached in about 0.75 h in each case, with an overshoot of only a few per cent before it stabilizes. It is envisaged that this effect will be much more pronounced if saturated salt solution in a sealed container is used for RH control, since the air is stagnant. Further, if there is a large mismatch between ambient and container temperature and RH, each time the sample is removed
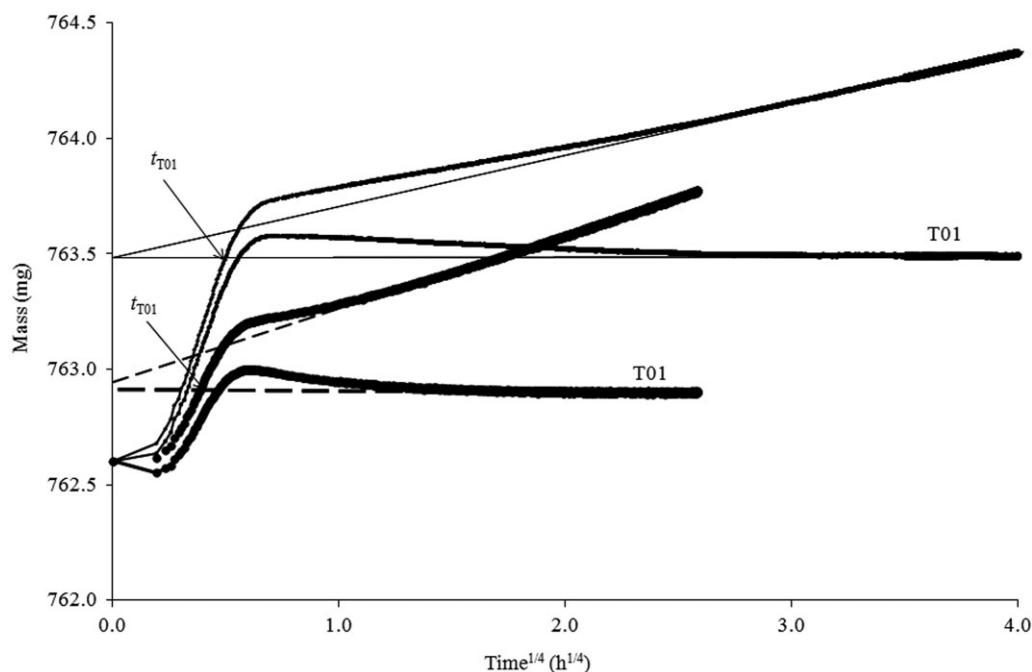
Figure 5   *The data of Figure 4 separated into their constituent components of mass: the same sample of samian ware measured at 11°C and 50% RH (upper graph) and 50°C and 10% RH (lower graph). The time to T01 equilibrium, indicated by* t_{T01}*, is obtained from the intersection of the back-extrapolated linear least-squares fit to the stabilized T01 data and the T012 total mass gain.*

for weighing, the container environment will take a long time to re-equilibrate. Figure 6 also demonstrates that T01 equilibrium is actually reached quite quickly—at about $t^{1/4} = 0.3$ $h^{1/4}$ (~0.5 min). The time at which T01 equilibrium is achieved was established by determining the time at which the T01 equilibrium mass was *first* reached, prior to being masked by the excess initial uptake and subsequent evaporation of T0 water. This is done as shown in Figure 5: the time to *first* T01 equilibrium, indicated by t_{T01}, is obtained from the intersection of the back-extrapolated linear least-squares fit to the stabilized T01 data and the early-time T012 total mass gain.

Specific surface area

The specific surface area measurements are summarized in Table 2. The data in the first four rows of Table 2 were obtained from the brick and tile materials first dated in Wilson *et al.* (2009). It can be seen that these SSAs, which range from 1.4 to 3.0 m^2 g^{-1}, show striking similarity. By comparison, the SSAs of the samian ware and loom-weight, at 0.78 and 35 m^2 g^{-1}, respectively, are the lowest and highest yet encountered. These differences in SSA may be attributed to the temperature and duration of the original firing, with samian ware being highly fired in a kiln and the loom-weight most likely being heated on an open fire (Wilson *et al.* 2012). This is supported by evidence of a systematic reduction in the SSA of fired kaolinite, as both temperature and duration of firing are increased (Mesbah 2011). The SSA value for the Werra pottery (Wilson *et al.* 2012) is included in Table 2 for completeness.
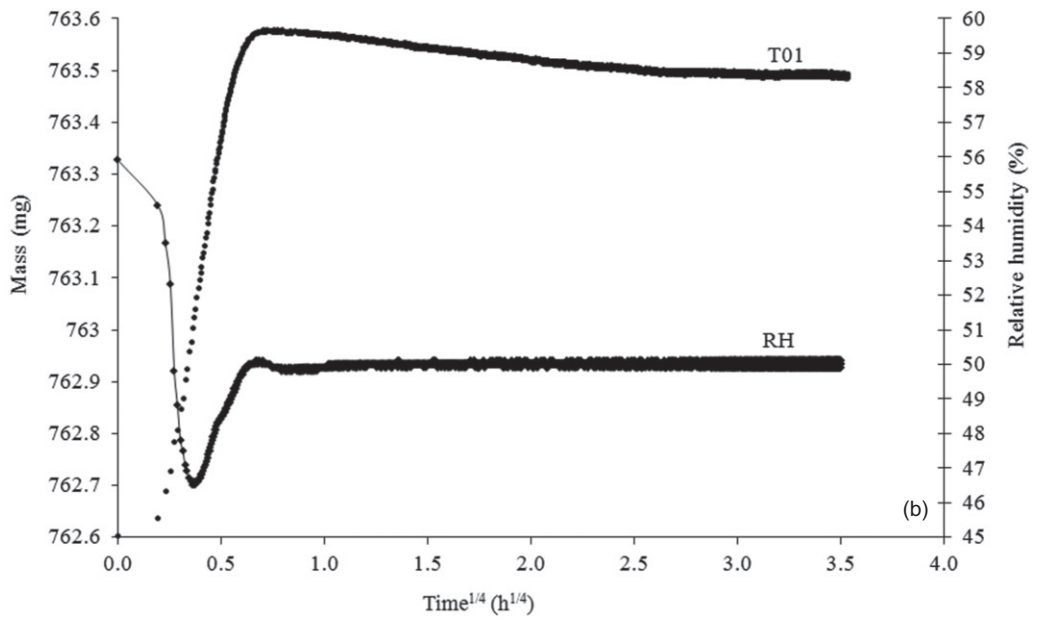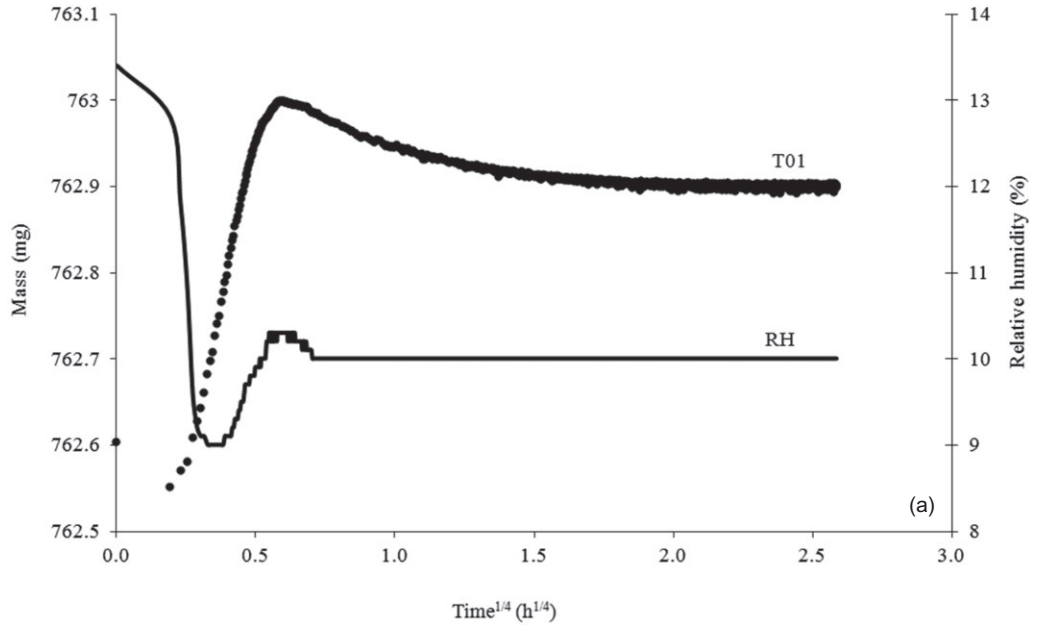
Figure 6 *The T01 components of Figure 5 with relative humidity superimposed at 11°C and 50% RH (upper graph) and 50°C and 10% RH (lower graph).*

Table 2 *Measured values of specific surface area for the range of fired-clay materials examined, together with the time to reach Stage II*

Sample	Function	Specific surface area ($m^2\ g^{-1}$)	Time to end of Stage I (h)	Time to onset of linear Stage II (h)
Greeenwich*	Brick	1.37	1.00	4
Canterbury*	Brick	2.07	1.00	29
*Opus spicatum**	Floor tile	2.33	2.00	10
Westminster*	Floor tile	2.97	2.80	13
Samian ware†	Dish	0.78	<0.5	150
Werra pottery†	Plate	5.00	3.80	24‡
Low-fired ceramic†	Loom-weight	35.00	2.00	187§

*Material dated in Wilson *et al*. (2009).
†Material dated in Wilson *et al*. (2012).
‡Mean of three data sets.
§These data are complicated by the presence of organic carbon.

It can be seen from the fourth column of Table 2 that the time to the end of Stage I (equivalent to the time taken for T01 equilibrium) increases systematically with SSA, with the exception of the loom-weight (so far, the only low-fired ceramic material analysed). Figure 7 shows how at 30% RH the time to the onset of linear Stage II also increases with SSA. In practical terms, these results show that the SSA is a useful indicator of the likely duration of a dating experiment. In all cases shown in Figure 7, mass measurements were carried out at 11°C and 30% RH. The variation in mass across these samples (160 mg to 4 g) suggests that it is the specific surface area rather than the surface area/volume ratio that is of most significance.

CONCLUSIONS

In both cases of the departure of mass/time$^{1/4}$ data from 'ideal', increased temperature produces the same effect: T0, T1 and T2 recombination is accelerated, leading to a more rapid equilibration of the T01 component and a greater contribution from T2 during Stage I. We are not suggesting that mass gain measurements are carried out at higher temperatures, only that the capacity for T0 adsorption is, however, reduced at higher temperatures, leading to a more rapid equilibration of this component. This also explains why the T01 mass is lower at the higher measurement temperature in each case. Mass gain measurements at elevated temperatures, such as 50°C, are carried out for the purpose of calculating the activation energy of the material using the Arrhenius equation, not for the purposes of dating.

In summary, measuring samples with SSAs outside the range 1–9 $m^2\ g^{-1}$ at 11°C and 30% RH will result in greatly extended measurement times, but for completely different reasons. Lower-SSA materials have fewer T0 sites, which, even at low absolute humidities, will become more rapidly occupied. This will lead to a more rapid transition to the linear Stage II process, *provided that the T01 equilibrium mass is not exceeded in the process.* Higher-SSA materials have a large number of T0 sites, the occupation of which, at low absolute humidities, will be supply-limited, leading to an extended transition to Stage II. In either case, a low measurement temperature will require a greater amount of T0 for equilibrium. In the case of low SSA materials, 'concave' data are caused by the material getting wetter (exceeding its eventual equilibrium mass) during early
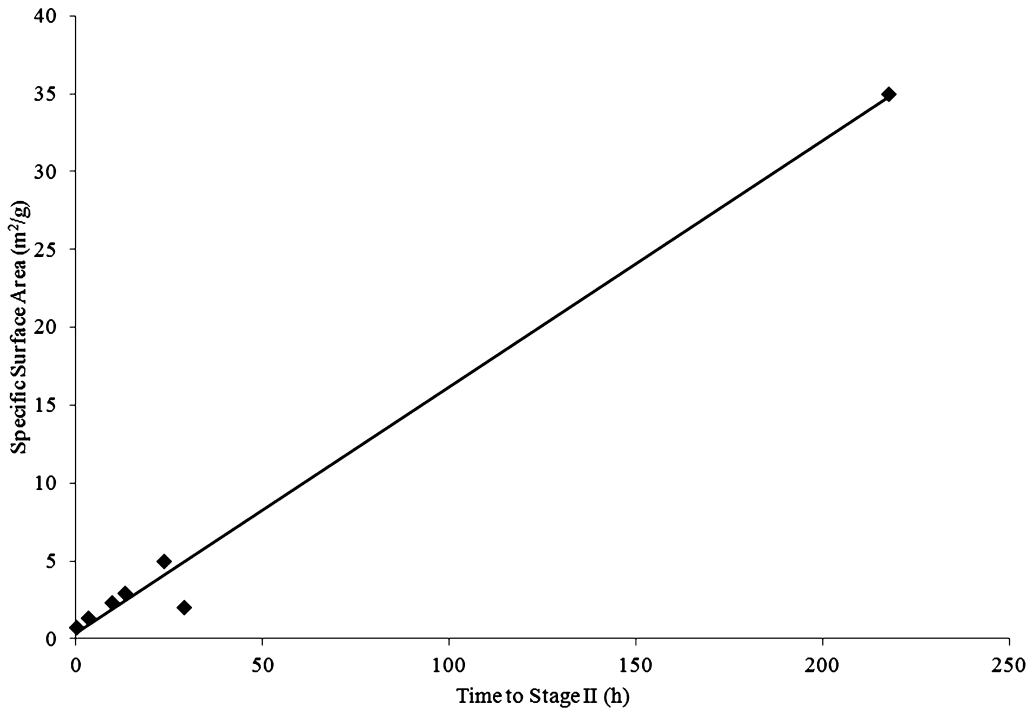
Figure 7 *Specific surface area versus time to the onset of stable and linear Stage II at 11°C and 30% RH.*

stages of mass measurement after dehydroxylation. High-SSA material, on the other hand, takes a long time to reach a linear Stage II because of the time it takes to satisfy the combined T0 and T1 demand.

This new understanding of the RHX process suggests that Stages I and II are not two separate processes. Stage II is solely the uptake of T2, which continues after the T0 and T1 demands of the specimen have been met. Therefore, Stage I represents the uptake of T0, T1 and T2 water. In order to accurately measure the rehydroxylation rate constant of the material, and so date fired-clay ceramic, it is important to continue measurement beyond the point at which T0 and T1 have stabilized, and the time that this will take relates to the SSA of the material.

It is suggested that the variation in SSA seen in archaeological material relates to the type of clay and method of production; in particular, the firing conditions. On the basis of the SSA dependency reported in this paper, we suggest that 30% RH at all measurement temperatures is not likely to be optimal for RHX dating. The lower the measurement temperature, the higher the RH will have to be to satisfy T01 demand within a reasonable timescale. The higher the SSA, the worse this effect will become, and it will be further exacerbated by low measurement temperatures. It is hypothesized that the amount of T1 water at any temperature is constant for any material and that, for a given measurement temperature, an increase in RH will only result in an increase in the amount of T0 water present in the sample. Any T0 water in excess of that required to initially satisfy the T1 demand and thereafter sustain the RHX reaction will simply reside in the material as a non-reacting constituent of mass. In practical terms, this means that the rehydroxylation rate is not affected by the water content of the depositional environmental (e.g., waterlogging), or by soaking or washing post-excavation. In the case of low-SSA materials,

'concave' data may be obtained if the material becomes 'over-wet', so exceeding the eventual equilibrium mass, immediately following the 500°C dehydroxylation step. We also believe that acquiring mass gain data of sufficient quality for calculating α_m is further facilitated by the constant flow of gas through the microbalance chamber.

In conclusion, the specific surface area provides a preliminary indication of the likely duration of a dating experiment; it does not directly affect the accuracy or precision of the RHX date. The results presented here suggest that an optimum range of SSAs for RHX dating experiments carried out at 11°C and 30% RH on fired clay is about 1–9 $m^2\ g^{-1}$, so that the time taken to reach Stage II is not so long that the quality of the measured Stage II mass gain data is compromised. For materials of excessively high SSA, it is more efficient to hold the sample (following dehydroxylation at 500°C) in an environmental chamber under the same conditions of temperature and RH at which its Stage II mass will be measured in the microbalance. It is worth acknowledging the scale of the processes being measured in these experiments: even the early stage mass gain is only 0.2% of the sample's mass, and RHX dating is trying to reproduce in the laboratory a process that has been occurring over historical timescales.

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APPENDIX: RELATIVE HUMIDITY

Air is a mixture of various gases (O_2, N_2 etc.) and water vapour. For completely dry air, the water vapour content is zero and the relative humidity (RH) is zero. For air that is saturated with water vapour, the RH is 100%. The maximum amount of water present at any given temperature is equal to the vapour pressure of water, and this increases rapidly with increasing temperature. An alternative way of expressing this is by *absolute humidity*, which is the water content of the air at a fixed temperature, expressed as *g m^{-3}*. Air at 40°C contains 51.22 g m^{-3} of water at saturation; air at 20°C contains 17.34 g m^{-3} at saturation. Any value of RH, between 0 and 100%, corresponds to the percentage of the amount of water vapour that can be held by that air at saturation. RH is therefore a measure of the percentage water vapour content *relative* to that which could be supported at saturation. Thus air at 40°C and 30% RH contains *much* more water vapour (15.37 g m^{-3}) than air at 20°C and 30% RH (5.20 g m^{-3}).

Values of absolute humidity may be obtained using a calculator such as the Vaisala Humidity Calculator (www.vaisala.com). For example, at the time of writing, the conditions in Cairo are 22°C and 53% RH, whereas in Manchester they are 8°C and 87% RH. The corresponding absolute humidities in Cairo and Manchester are 10.32 and 7.22 g m^{-3}, respectively, which leads to the somewhat counterintuitive result that a volume of air at a perceived 'hot and dry' location contains more water than the same volume of air at a 'cold and wet' location.

A further consideration is the effect of atmospheric pressure on the relative (and therefore absolute) humidity. Atmospheric pressure over the past 12 months has varied between 950 and 1020 mbar (ATIS 2012). This corresponds to a fluctuation in absolute humidity of 7.1×10^{-4} g m^{-3} and this is negligible; even were it not, it would be compensated for by the RH controller in the microbalance chamber.

In terms of RHX dating, the interplay of RH and temperature has consequences for the level of environmental control required. A change in RH at constant temperature will cause a change in the absolute humidity of the atmosphere and thus a change in sample mass due to a change in the T0 component. The consequences of changes in temperature at constant RH are more complex: an increase in temperature will reduce the T0 component, but increase the rate of mass gain due to T2 recombination; a decrease in temperature will have the opposite effect. Lack of control of either parameter over the duration of an experiment will therefore cause simultaneous fluctuations in different components of the sample mass. Although it has not been possible to determine the relative masses of T0 and T1 from the data presented here, it seems reasonable to assume that, since T1 water is removed on heating to ~300°C and is therefore immobilized at ambient conditions, there will be no variation in this component with fluctuations in environmental conditions.

The broader significance of these results is that during a sample's lifetime, fluctuations in both RH and temperature will cause fluctuations in sample mass by the same mechanism: changes in the amount of T0 water present will be superimposed on, but completely independent of, the mass gain due to the RHX reaction, the rate of which will itself respond only to fluctuations in temperature.