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Title:

Rehydroxylation (RHX) Dating: Trials on Post-Medieval Brick using a Component Based Approach

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Abstract:

Rehydroxylation dating trials were conducted on post-medieval ceramics (bricks) of known age, testing a new *component based* approach. Age estimates were produced using both a $t^{1/4}$ and a more generalised $t^{1/n}$ model for describing the *Stage 2* mass gain, the latter providing a more satisfactory description of the mass gain curves. Despite this, the estimated ages are generally too old for agreement with known ages; the magnitude of the discrepancies suggest issues beyond the particular models used. The effect of uncertainties associated with the effective lifetime temperature (ELT) of the ceramic were explored, aided by the generation of *age-temperature* curves; while potentially a strong contributor, the large age discrepancies can not be explained by ELT issues. The mass of organic matter removed during reheating (estimated from the organic carbon content) is more problematic, suffering from considerable uncertainties on account of a poorly defined organic matter to organic carbon (OM/OC) ratio of 1.4-2.5; again, the large age estimates can not be explained by this factor alone. Additional factors, including incomplete drying, mineral alteration, and short term elevated temperature events (STETEs), are outlined as potential contributors to age discrepancies and uncertainties, further complicating assessment of the results and method. Because of this, the results are considered inconclusive with respect to evaluating in full the effectiveness of the component based approach. However, these results highlight a range of practical difficulties and problematic effects that must be eliminated or minimized in future RHX dating trials; suggestions are made in this regard.

Keywords:

Rehydroxylation, Dating, Post-Medieval, Brick, Component Based Approach

1. Introduction

Rehydroxylation dating is a gravimetric technique that attempts to exploit the long term mass gain of fired clays due to the uptake of environmental moisture. Its potential was first pointed towards by Wilson et al. (2003) in the first research to attributed a $time^{1/4}$ law to the expansive strain increase in modern and ancient clay bricks following firing (prior to this a logarithmic model was frequently used (Cole and Birtwistle 1969, see also Hall et al. 2011 for model comparisons)); this was later supported by observations of similar behavior for mass gain (Savage et al. 2008a; 2008b). Despite early promise (Wilson 2009), few ceramics have been dated to a satisfactory level (11 based on Wilson et al. 2009; 2012) and significant issues have arisen with various aspects of the technique: the ages calculated have been poor (for example, Burakov et al. 2013; Le Goff and Gallet 2015a; Numrich et al. 2015); the $t^{1/4}$ model is considered unsatisfactory (for example, Bowen et al. 2011; 2013; Le Goff and Gallet 2014; 2015a; 2015b) with non-linearity in the second stage suggesting the use of a $t^{1/n}$ based model may be more appropriate (for example, Bowen et al. 2011, Gallet and Le Goff 2015; Le Goff and Gallet 2015b); equilibrium following drying is not observed (Le Goff and Gallet 2014; 2015a); contaminants are problematic (Numrich et al. 2015). Also, along with considerable difficulties encountered with experimental determination of key variables involved (for example Bowen et al. 2011; Zhao et al. 2015), serious question have been posed with regard to earlier successful dating trials (Le Goff and Gallet 2015a).

This work assesses the RHX method and possible issues with its application, presenting dating trial results from Barrett (2015), a larger assessment of the rehydroxylation dating technique, as well as drawing upon results from a companion paper that examines mass loss issues (Barrett 2017). The use of an alternative *component based* approach and various factors that contribute to uncertainties are evaluated. The component based approach (*Section 2.1.2*) is motivated by an issue with prolonged $t^{1/n}$ -like mass gain following drying that has been identified in the present work and observed elsewhere (Le Goff and Gallet 2015a; Gallet and Le Goff 2015); this property renders the original RHX method of Wilson et al. (2009, 2012) inapplicable. Gravimetric analysis (Barrett 2013) is conducted on eighteen samples of varied known ages and contexts, aged at three temperatures (25°C, 35°C, 45°C), following both drying and reheating. Mass gain curve analysis and age estimations are made using both the $t^{1/4}$ and $t^{1/n}$ models; only twelve of the eighteen samples were suitable for providing age estimates. Simulated lifetime mass gains (using surface air temperature

histories) are generated to calculate *effective lifetime temperatures* (ELT) for use in age estimation calculations. Age-temperature curves are also generated to examine variability in age with the *effective lifetime temperature* (ELT) used. Age estimation results are principally evaluated and discussed in consideration of the models used, the suitability of the ELTs, and the effect of organic matter not removed during drying (using results from Barrett 2017). A broader but brief consideration of other potential contributing factors and issues is also conducted, with suggestions made regarding future RHX dating trials.

2. Method

2.1 RHX Dating and a Component Based Approach

2.1.1 Basic Equations

Following firing of a clay to a hard ceramic, or subsequent reheating above (500°C), the ceramic gains mass in two distinct stages (Savage et al. 2008a), *Stage 1 (S1)* and *Stage 2 (S2)*, *Figure 1(a)*. The initial and rapid *S1* mass gain (excluding the contribution that is ongoing into *S2*) can be attributed to physisorption processes (Barrett 2015), with the slower, prolonged, and indefinite *S2* due to chemisorption and rehydroxylation processes, dependent on the drying/heating temperature (Gallet and Le Goff 2015, Barrett 2015). The rate of chemisorption/rehydroxylation mass gain in *S2* is well described by a $time^{1/4}$ (Wilson et al. 2009; 2012) or $time^{1/n}$ (e.g. Bowen et al. 2011; Le Goff and Gallet 2014; Barrett 2015) power law of more general form:

$$m(t) = a(T)t^{\frac{1}{n}} + m_0 \quad (1)$$

with $m(t)$ the sample mass, t the time since heating, m_0 the intercept mass of the *S2* mass gain, a the mass gain rate (T the aging temperature), $1/n = 4$ (Wilson et al. 2009; 2012) or variable otherwise.

The mass gain rate has an Arrhenius (exponential) temperature dependence (Wilson et al. 2009) and can be described by the following equation (generalized from Hall and Hoff 2012; Hall et al. 2013):

$$a(T) = Ae^{-\frac{E_a}{nRT}} \quad (2)$$

with A the pre-exponential factor, E_a the activation energy, R the gas constant, T the temperature, and $n = 4$ for $t^{1/4}$ model.

Where the mass gain rate is estimated for a range of temperatures, the activation energy can be calculated from:

78

$$\ln\left(\frac{a}{a_0}\right) = -\frac{E_a}{nRT} + \frac{E_a}{nRT_0} \quad (3)$$

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with a_0 the mass gain rate at some reference temperature T_0 .

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Figure 1: (a) Illustration of the general RHX dating approach (Wilson et al. 2012); mass gain and equilibration following drying to constant mass at 110°C (blue); rehydroxylation related mass gain following heating at 500°C (red). (b) Illustration of the component-based dating approach; mass gain following drying to constant mass at 130°C (blue); mass gain following heating at 500°C (red). The Stage 2 linear mass gain following heating at 500° is the sum of two components, the mass gain due to processes related to heating to 130°C and the processes related to heating between 130-500°C (RHX/chemisorption-attributed processes).

If the rehydroxylation-related mass, m_{RHX} , gained over the lifetime of the ceramic can be estimated together with a suitable effective lifetime temperature (ELT, see Hall et al. 2013), then the age of the ceramic follows from rearrangement of equation (1):

$$t = \left(\frac{m_{RHX}}{a(T_{elt})} \right)^n, [n = 4] \text{ (Wilson et al. 2009; 2012)} \quad (4)$$

2.1.2 Component Based Approach

The need for an adaptation of the method of Wilson et al. (2012) was driven primarily by the following observations and assumptions, supported in other work (e.g. Le Goff and Gallet 2014; 2015a):

1. Heating at low temperatures (110-130°C), followed by aging/equilibrating at 25°C, 35°C, 45°C (relative humidity of 75%), results in a two-stage mass gain behaviour, with S2 following a $t^{1/4}$ or $t^{1/n}$ equation (Barrett 2015), *Figure 1(b)*.
2. The mass gain curve (*Stage 2*) following heating at 500°C (500C component henceforth) is assumed to be the sum of the 130°C component and an RHX component, the former due to processes related to uptake of moisture (chemisorption) following drying at 130°C, the latter due to processes related to a combination of chemisorption and rehydroxylation following heating between 130°C and 500°C (see Barrett 2015 for discussion).

The component based approach then makes use of the following properties, (see *Figure 1(b)*):

- a. The RHX mass gain rate (rate due to moisture removal between 130-500°C), a_{RHX} , can be obtained by a simple subtraction of the 130C mass gain rate, a_{130} , from the 500C mass gain rate, a_{500} . This assumes the 130°C component follows the same $t^{1/4}$ or $t^{1/n}$ behaviour as the 500°C component; this is supported in Barrett (2015) but the work of Gallet and Le Goff (2015) may suggest variability of $1/n$ with heating temperature.
- b. Similarly, the RHX mass (mass of moisture removed between 130-500°C), m_{RHX} , can be obtained by subtracting the 130°C intercept, m_{130} , from the 500°C intercept, m_{500} . This mass is interpreted as the mass gained during the lifetime of the ceramic by mass gain rates associated with long term chemisorption/rehydroxylation processes that are removed at temperatures between 130-500°C (this mass is assumed to be

a combination of chemisorbed and rehydroxyl associated water but is referred to in the present work as the RHX mass, m_{RHX} , for simplicity).

$$a_{RHX} = a_{500} - a_{130} \quad (5)$$

$$m_{RHX} = m_{130} - m_{500} \quad (6)$$

2.2 Samples and Preparation

The samples consisted of 18 samples: 14 brick samples from the island of Ireland (11 from Northern Ireland, 3 from the Republic of Ireland); 2 pottery samples from Northern Ireland; and a piece of Etruscan and Roman pottery (see *Table S.1-2* in supplementary materials for details, as well as Barrett 2015). The brick and pottery samples were of post-medieval age (see *Table 3*) and were retrieved from a mixture of buried (9) and non-buried (9) contexts (*Table S.2*). Samples were characterized using XRD, FTIR, BET, petrographic and surface area (BET) analysis (Barrett 2015, see summary of results included in *Tables S3-11*). The brick samples provided all 12 samples eventually used to produce age estimates. These bricks were likely produced from local residual/boulder clays (rich in quartz and feldspars and generally low or negligible in calcium content) that are interpreted as mostly having been well-fired above 850°C, evidenced by the presence of minerals associated with high temperature phase transitions (see *Table S.7*), e.g. cristobalite, spinel, mullite (see Dunham 1992); temperatures approaching and above 1000°C are also suggested by the level of vitrification (bloating/melting) found in many brick samples under petrographic analysis. These samples also had lower surface area ($< 5\text{m}^2/\text{g}$), and often calcium content, than more problematic *abnormal* samples (mostly $>14\text{m}^2/\text{g}$) that were unsuitable for dating trials; these samples, *Por*, *Lan*, *Dow1*, *Dow2*, *Etr* and *Rom*, are likely to have been affected by pore condensation issues during mass gain trials leading to mass curves unsuitable for modelling and dating (this beyond the scope of the current work but dealt with elsewhere in Barrett 2015).

For brick, approximately 12 cubes (20-40g) were wet-cut and surface layers (2-4mm) were removed (for pottery sherds were cut into manageable pieces). Pre-drying ($<80^\circ\text{C}$) was conducted over 2 weeks to remove wet-cutting moisture and bulk/capillary moisture that, if removed more rapidly at higher temperature could cause structural changes within the ceramic (issues associated with pre-drying are dealt with in Barrett 2015).

The samples were granulated and sieved to a size 2-5.6mm (approx. 0.05-0.15g per granule). This was carried out to allow mixing and homogenizing of sample material, originally quite heterogenous in composition, in advance of future

splitting of the sample into three subsamples for dating trials. The total granulated material from all cubes (subsherds) were thoroughly mixed for each sample and spread out on aluminium trays for drying.

2.3 Experimental

2.3.1 Drying

Granulated samples were dried in an oven at 130°C for 2 months with the mass monitored almost daily. A constant equilibrated mass did not occur and the projected time for this event was considered indefinite. Drying was stopped and, instead, the drying mass loss curves would be modelled to estimate remaining moisture content; the issue of incomplete drying is dealt with elsewhere (Barrett 2015) but will be commented upon later. Each sample was assigned three Pyrex beakers into which a portion of granules (15-25g), the subsample, was placed.

2.3.2 130°C Stage Mass Gain

Subsamples were assigned to sample boxes (humidity controlled using saturated salt solution of NaCl (74-76%RH, Greenspan 1976)), later used for both storage during aging in environmentally controlled (EC) chambers and transfer to an environmentally controlled glove box arrangement (GBA) for mass measurements (Barrett 2013; 2015 for greater detail).

Following drying, beakers were moved immediately into a desiccated container to minimize mass gain during cooling (Barrett 2013). Following cooling for 1hr 15 minutes in room temperature conditions, the subsamples to be aged at 25°C were transferred, via samples boxes, to the GBA (25°C and 75%RH for all mass gain measurements) and weighed repeatedly over a period of 6-7 hours, during which *Stage I* was observed to have completed in a majority of samples. Then the 25°C samples were moved to the corresponding 25°C environment chamber and over an approximate duration of two months, periodically moved to the GBA for weighing (detailed in Barrett 2015). For the 35°C and 45°C aged samples, *Stage I* monitoring was not carried out and beakers only required 15 minutes in desiccated conditions prior to placement in sample boxes and environment chambers at 35°C and 45°C respectively. Again, the mass was monitored over a period of two months.

2.3.3 500°C Stage Mass Gain

Following 130°C stage weighing, the subsamples were placed in a furnace, the temperature ramped to 500°C, at a ramp rate of 1°C/min, and heated for approx. 72 hours. This reheating duration exceeds or matches the longest durations used in previous RHX work (67-72 hour conducted on larger sized (2-4g) samples, Le Goff and Gallet 2014; 2015a; Numrich et al. 2015). It was also selected based on preliminary trials that involved repeated reheating (500°C) and weighing of *Mac* and *Ria* bulk samples (cubes) at 6-12 hour intervals) until additional mass loss was no longer certain. This duration is assumed to be sufficient for complete dehydroxylation of the ceramic to have occurred; however, the author would note that without the use of a more precise thermogravimetric method during reheating, complete dehydroxylation can not be guaranteed (see Gallet and Le Goff 2015 for heating temperature and duration effects). The subsequent mass gain procedure follows that above for the 130°C stage.

2.4 Mass Gain Analysis and Age Estimation

2.4.1 Mass Gain Curve Analysis

Modelling of *Stage 2* was conducted in *MATLAB* using a timespan analysis approach (Le Goff and Gallet 2015) that is described more comprehensively in Barrett (2015). For the $t^{1/4}$ model, because of curvature issues (Barrett 2015), modelling was generally conducted over the entire EC-GBA measurement period. For sample that suffered from high surface area capillary condensation issues (*Etr*, *Por*, *Lan*, *Dow1*, *Dow2*, and *Rom* to some extent, see Barrett 2015), modelling with a $t^{1/n}$ approach was problematic or unsuccessful, and attempts at dating abandoned.

For the $t^{1/n}$ modelling, timespan analysis was applied to each of the six data series (130°C/500°C, three temperatures) of each sample, providing six $1/n$ values. These were then averaged to obtain a constant $1/n$ value, $1/r$ say. Then modelling was repeated on all six data series with the $t^{1/r}$ model. Conformity of the $1/n$ values for all curves to the same value is a necessary assumption in order to apply the component based approach using the $t^{1/n}$ model; the validity of this assumption is discussed later.

Mass gain rates were normalized relative to the intercept mass, m_{500} . The RHX mass gain rate, a_{RHX} , is calculated using *Equation 5* above.

The complete mass loss due to heating between 130-500°C, m_{RHXC} (Equation 6), was estimated for each aging temperature pair. The average was then taken to be m_{RHXC} for dating. Again, normalization was taken with respect to m_{500} .

To obtain the mass loss attributable to rehydroxylation alone, m_{RHX} , the mass of loose water, m_{lw} , not removed during drying, and the mass of organic matter, m_{OM} , removed during firing, are subtracted from m_{RHXC} . Their estimation is covered in the companion article Barrett (2017) and also in Barrett (2015); $m_{OM} = m_C \times OM/OC$, where m_C is an estimate of the carbon content of the sample removed during heating and OM/OC is the organic matter to organic carbon ratio (1.95).

Activation energy calculations follow Barrett (2013), using Equation 3 above, and were estimated for both the 130°C (E_{a130}) and 500°C (E_{a500}) components separately, as well as for the RHX component, E_{aRHX} using the three RHX mass gain rate estimates (i.e. at each aging temperature). This was carried out for both the $t^{1/4}$ and $t^{1/n}$ approaches, where possible.

2.4.2 Age Estimation

The estimated age of the ceramic, t_{age} , was calculated using Equation 4 above for a range of possible ELTs, from 7-24°C in 0.5°C steps, and including the ELT estimated from simulations, T_{ELT} , described below. Curves of the estimated age as a function of temperature (*age-temperature curves*) were generated.

The effect of uncertainty in the organic matter/organic carbon (OM/OC) ratio was examined for a range of OM/OC ratios (from 1.4-2.5, see Barrett 2017 for details on organic matter present in samples).

Age-temperature curves were also generated using the upper and lower limit (1σ) confidence intervals of the activation energies.

The quantity the RHX mass gain is out by for the estimated, t_{age} , and known, t_d , ages to agree (i.e. the difference between the mass of hydroxyls, m_{RHX} and the simulated mass, m_{sim} , see below), m_{out} , the value the organic matter/organic carbon ratios needs to be for the dates to agree, OM/OC_w , and the ELT for which the estimated dates work, T_w , were all estimated.

2.4.3 Temperature History Construction

Temperature history construction was limited to that of the surface air temperature (SAT) in the locality of the sample over its lifetime; age-temperature curves permitted examination of the suitability of this approximation. The general approach is illustrated in *Figure 2* and outlined below with a detailed method provided in Barrett (2015). A modern local short instrumental record is used as a baseline for calibration/tuning of longer records. Then a longer regional instrumental record is calibrated against the local short instrumental record. If the instrumental series covers the period of the known age of the ceramic, the monthly data must be converted into daily temperature data, described below.

Where the long instrumental records do not extend back far enough, long seasonal temperature reconstruction records were used (Luterbacher et al. 2004). These were calibrated against the adjusted long temperature records. Following calibration of the long seasonal temperature reconstruction, this adjusted data must then be converted into daily temperature data.

Figure 2: Top: Example diagram of site and its relationship to records used in local SAT temperature history reconstruction. There is geographical overlap of all three groups: short local instrumental record, long regional instrumental record and long regional temperature reconstruction. The long records are tuned/calibrated to the short local record. Bottom: Construction of temperature history records by calibration of longer regional instrumental/reconstruction records by shorter more local/accurate instrumental records.

To convert the monthly/seasonal data into daily data, on a year by year basis the tuned data series were fit using the sine function. The coefficients from this fit were then used to generate daily data on a year by year basis.

Due to issues with the *Etr* and *Rom* samples, discussed later, it was not necessary to reconstruct long temperature histories. Nonetheless, daily temperature data was generated from the Luterbacher et al. (2004) 500 year old reconstruction to examine the likely scale of effects associated with the ELT.

2.4.4 Simulated Mass Gain and Effective Lifetime Temperature Estimation

The mass gained by the ceramic over its lifetime was simulated following methods used in Barrett (2013, 2015 *Appendix G*). The critical input required for this simulation was the SAT temperature history described above, the initial year, and the mass gain rate, activation energy, and $1/n$ data obtained from modelling of the mass gain curves. The simulation was carried out for all samples using both a $t^{1/4}$ and $t^{1/n}$ model. The mass gain was also calculated for each year of the ceramics lifetime using the mean lifetime temperature (MLT) since firing.

The mean lifetime temperature is simply the average temperature over the period of lifetime of the ceramic that is under consideration. If used in age estimates the MLT fails to take account of the non-linear Arrhenius temperature dependence of the mass gain rate; this dependence results in exponentially greater quantities of mass gain at higher temperatures and means that the ceramics experiences an effective lifetime temperature (ELT) that is above the MLT (see Hall et al. 2013; Barrett 2015). If both the lifetime mass gain and age of the ceramic are known, then the ELT can be estimated. Using the simulated mass gain, m_{sim} , and the known age of the samples, t_a , along with *Equation 4* above, the ELTs were estimated. Because of issues with poor activation energy plots or modelling of $t^{1/4(n)}$, ELTs were not estimated for *Por* or *Dow2* for either model or additionally for *Etr*, *Dow1*, *Lan* and *Cal* with the $t^{1/n}$ model.

It is worth emphasizing that the temperature history estimation, while involved, does not consider the effect of burial conditions, internal building thermal effects, and storage conditions. A rigorous temperature history reconstruction for all samples was beyond the scope of the present work and merits further examination. However, some comments are worth making. The effect of burial condition has been looked at by Hall et al. (2013); they demonstrate that burial dampens the effects of thermal oscillations (i.e. diurnal and annual temperature cycles which are a major source of the difference between the ELT and MLT), with the ELT drifting towards the MLT for deeper burials. Therefore, the ELT of a sample that has been buried can be considered approximately bound by the mean lifetime temperature (lower

bound) and the ELT estimated from local surface air temperature records/reconstructions (upper bound), both of which can be assessed using the age-temperature curves or working temperature, T_w , described above. For other factors, such as periods of elevated temperatures associated with the particular lifetime use/context of a brick, the age-temperature curves permit interpretations regarding these factors to be scrutinised, at least in terms of likely, plausible, or unacceptable working ELTs, T_w , particularly where the temperature history is ambiguous or reconstructions are not possible.

3. Results

3.1 Curves and Behaviour

Examples mass gain curves (excluding the initial *Stage 1* measurement period for the 25°C curves) are presented in *Figure 3*; the complete set can be found in Barrett (2015). Samples were regarded as *well-behaved* (12 of 18 samples) and suitable for dating (e.g. *Joy* and *Esp*), or *abnormal* (6 of 18 samples) and unsuitable for dating (e.g. *Etr* and *Por*), dependent on the behaviour of the curves. Well-behaved samples have two stages of mass gain, the first a rapid increase that has normally reached completion within 24 hours and often less than 5 hours, and have a clear Arrhenius temperature dependence; these properties are observable following heating at both 130°C and 500°C.

Figure 3: Fractional mass gain curves of *Joy*, *Esp*, *Por*, *Etr* (clockwise from top left) samples, following heating at 130°C (blue) and 500°C (red) and aging at temperatures of 25°C (square), 35°C (triangle), and 45°C (circle), presented across the period of ECC-GBA transfer and weighing. Imposed dashed lines on well-behaved samples, *Joy* and *Esp*, correspond to linear fits across this period. For abnormal samples *Etr* and *Por* interpolated lines are included for visual purposes.

Abnormal samples (*Rom, Etr, Lan, Por, Dow1, Dow2*, with *Cau* and *Bel* considered borderline) display very long *Stage 1* durations (typically > 1 week) and magnitude, have no certain Arrhenius temperature dependence, and, following heating at 130° for many samples, the curves appear to flatten and possibly tend towards an equilibrium value. The curves also suffer from greater levels of random scatter on account of their increased sensitivity (on account of higher specific surface areas and the high %RH used) to small variations in %RH levels during mass measurements. The problematic abnormal behaviour is associated with capillary condensation issues arising from high surface areas (*Table S.6*), evidenced through hysteresis behaviour in nitrogen sorption curves of the aforementioned samples that are elaborated upon in Barrett (2015); it is believed that running the experiment at a lower %RH may help, particularly with regard to the high levels of scatter (75%RH was an experimental setup constraint of the present work).

The magnitudes of the fractional mass gain rates (and 95% uncertainties) for well-behaved samples are illustrated in *Figure 4, left*, together with the RHX rate estimates, *right*; this is for the $t^{1/4}$ model and is included to illustrate both the large variation in rates dependent on the sample and the lower magnitudes of values for the RHX component (this chart is not presented for the $t^{1/n}$ modelled rates as these samples each have different units of measurement, $\text{hrs}^{-1/n}$, due to variation in the $1/n$ values). The fractional RHX rates are typically in the range $2\text{--}12 \times 10^{-5} \text{ hrs}^{-1/4}$.

Figure 4: Fractional mass gain rate (*Stage 2*) following 25°C aging of 130°C (blue) and 500°C (red) heated samples, *left*, and the RHX rate (25°C) estimated from both, *right*. For *Stage 2* of well-behaved samples modelled using the $t^{1/4}$ approach (2σ uncertainties included)

The total fractional mass loss estimates, m_{RHXC} , and the mass loss attributed solely to RHX processes, m_{RHX} , are presented in *Figure 5* for both the $t^{1/4}$ and $t^{1/n}$ approaches. The magnitudes of the RHX mass loss component are typically of the order of 0.1-0.5% of the ceramic mass. The contribution of organic matter, removed during heating, to the total fractional mass loss can also be noted as significant.

Figure 5: Ranking of total fractional mass loss between 130-500°C, decomposed into rehydroxyl (green), organic matter (brown), and loose water (blue) components. For $t^{1/4}$ model (left) and $t^{1/n}$ model (right) using 12 and 11 samples, respectively, from dating trials. The total fractional mass loss is the average of three estimates at each aging temperature, with the uncertainties (error bars) corresponding to the standard deviation of these three values.

Typical Arrhenius plot examples are presented in *Figure 6*, with the estimated RHX activation energies, relevant to dating trials shown in *Figure 7*. The R^2 values from Arrhenius plots are found in *Table 1*. The R^2 values were typically approx. 0.99 for well-behaved samples for both the 130°C and 500°C components, using both models. However, issues were encountered with *Nic* ($R^2 = 0.79$ and 0.51 for $t^{1/4}$ and $t^{1/n}$, respectively, 130°C component), *Bel* ($R^2 = 0.967$ for $t^{1/n}$, 130°C component) and *Cau* (Arrhenius plot could not be produced for the 130°C component). The R^2 values were weaker for the RHX plots, but typically greater than 0.95 for well-behaved samples. *Bel* ($R^2 = 0.567$, $t^{1/n}$) is problematic.

Figure 6: Arrhenius plots, $t^{1/4}$ (left) and $t^{1/n}$ (right), for 130°C (blue), 500°C (red) and RHX (green) mass gain rates for Joy (top) and Esp (bottom). Uncertainties are at 2σ .

Figure 7: Activation energies calculated for RHX component for $t^{1/4}$ (purple) and $t^{1/n}$ (orange) models of dating trial samples. Included are the 2σ uncertainties.

Table 1: R^2 value of Arrhenius plot linear fits ($t^{1/4}$ and $t^{1/n}$ model). Red font marks samples with poor quality fits. o = samples for which fits were not suitable.

	$t^{1/4}$			$t^{1/n}$		
	130°C R^2	500°C R^2	RHX R^2	130°C R^2	500°C R^2	RHX R^2
Ann	0.999	0.999	0.998	0.999	0.999	0.991
Esp	0.999	0.999	0.99	0.999	0.993	0.936
Nic	0.791	0.991	0.962	0.511	0.993	0.972
Mac	0.999	0.999	0.98	1	0.999	0.971
Ria	0.998	0.996	0.923	0.999	0.999	0.977
Rat	0.995	0.995	0.993	0.988	0.997	0.981
Cal	0.999	0.999	0.977	0.999	0.998	0.986
Joy	0.999	0.997	0.981	0.998	0.998	0.999
Cau	o	0.997	0.995	o	o	o
Bel	0.993	0.999	0.859	0.967	0.992	0.567
Tur	0.999	0.999	0.99	0.999	0.999	0.982
Ted	0.994	0.994	0.994	0.997	0.999	0.987

The RHX component activation energies, E_{aRHX} , can be observed to differ dependent on the model used, *Figure 7*. The particular values are samples dependent and vary from extremes of 23.5kJ/mol to 295kJ/mol but most are in the approximate range 75-200kJ/mol for $t^{1/4}$ and 50-125kJ/mol for $t^{1/n}$. These values are of similar magnitudes to values previously reported and associated with rehydroxylation in fired clays (e.g. 57-119kJ/mol in Clelland et al. 2015; 47-119kJ/mol in Stevenson and Gurnick 2016).

The degree of curvature ($1/n$) for all dated samples is presented in *Figure 8* (see also *Table S.9*), broken down into the average of the three modelled curves for both drying and reheating together with the combined average. It can be observed that there is reasonable agreement between the 130°C and 500°C groupings (*t-test* of paired samples produced $p=0.2$ and therefore the null hypothesis of no difference cannot be rejected). The $1/n$ values (combined average) can also be observed to vary with the sample and take on a range of values from approximately 0.16-0.45 or more loosely $1/6 < 1/n < 1/2$. The curvature is generally $> 1/4$ with only *Bel*, *Esp*, *Nic*, *Cau* the exceptions; of these, *Bel* and *Cau* are samples that were considered borderline *abnormal* for reasons mentioned earlier.

Figure 8: Curvature of samples based on $1/n$ values for 130°C component (average of 3 aging temperatures) and 500°C component (average of 3 aging temperature) and both components (average of modelled results from 6 curves). Black dashed line indicates $1/n=0.25$. Purple dotted equals average curvature for all well-behaved curves (excluding *Cau*). Error bars represent one standard deviation.

3.2 Simulated Mass Gain and ELTs

An example of the simulated mass gain (and ELT variation with time) for sample *Joy* is provided in *Figure 9* (top) for *Joy*, with the inset permitting observation of the effects of annual temperature cycles. The ELT estimates for dating trials are provided in *Table 2* and can differ considerably (0.5-2.0°C are common, activation energy dependent) from the mean lifetime temperature used.

Figure 9: Top - Simulated fractional mass gain as a function of time since firing based on SAT temperature history (red) and mean lifetime temperature (green) for *Joy* using the $t^{1/4}$ model. An early portion of the simulated curve is enlarged to highlight annual temperature cycle effects. Bottom - The ELT (red) and mean temperature (green) as a function of the year since firing of the sample *Joy* for $t^{1/4}$ model. Insert is enlarged portion of the early period, highlight the effects of annual temperature cycles.

Table 2: Mean lifetime temperature and ELT values based on SAT based temperature histories for all samples and both models, where simulation could be applied.

	T_{mt} (°C)	$(t^{1/4})$ T_{elt} (°C)	$(t^{1/n})$ T_{elt} (°C)
Ann	9.41	10.66	10.33
Esp	9.3	9.99	10.01
Nic	9.05	10.89	11.31
Mac	9.13	11.6	11.22
Ria	8.96	10.59	10.09
Etr	11.46	12.08	o
Rom	11.46	11.93	11.51
Rat	9.18	10.93	10.19
Cal	9.12	9.98	9.7
Lan	9.29	10.09	o
Joy	8.77	9.67	9.6
Cau	8.31	9.31	o
Bel	8.45	8.82	8.65
Dow1	9.13	9.53	o
Tur	8.55	9.96	9.35
Ted	9.13	10.18	9.69

3.3 Age Estimates, Age-Temperature Curves and Uncertainty Effects

Age estimates are presented in *Table 3* along with the working temperature, T_w , and the working OM/OC ratio, OM/OC_w (minimum/maximum values required for an estimated age to fall within the uncertainty limits of the known age). The effects of uncertainty in the OM/OC ratio (1.4-2.5) and the RHX activation energy ($E_{aRHX} + 1\sigma$ to $E_{aRHX} - 1\sigma$) on the estimated age of the samples are provided in *Table 4*.

To examine the effect of variability in ELT on the age estimates, age-temperature curves were produced for each sample. These are provided in full in Barrett (2015) with an example below, *Figure 10* (left). Similar curves were also generated to examine the effect uncertainties in the OM/OC ratio and RHX activation energy have on the age-temperature curves, *Figure 10* (right, for $t^{1/4}$).

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459 **Table 3: Table of age estimates based on ELTs and both the $t^{1/4}$ and $t^{1/n}$ models. Also included are OM/OC_w and**
 460 **T_w , conditions of OM/OC and temperature under which the age calculation will fall within the uncertainty**
 461 **bounds of the known age.**

		$t^{1/4}$			$t^{1/n}$		
	Known Age (Yrs)	Age Estimate (Yrs)	OM/OC_w	T_w (°C)	Age Estimate (Yrs)	OM/OC_w	T_w (°C)
Ann	110 ± 14	680	3.12	20.2	109	1.94	10.1
Esp	141 ± 6	268	2.53	15.7	589	2.96	22.6
Nic	398 ± 2	55965	10.51	28.1	1024358	12.03	32.1
Mac	228 ± 2	555199409	16.41	49.7	9148913	16.15	45.6
Ria	339 ± 25	153820	9.65	35.4	4869	7.85	26.0
Rat	245 ± 2	1752430	11.39	47.7	4910	9.5	31.7
Cal	182 ± 9	2660	10.4	33.2	194	2.35	10.5
Joy	412 ± 2	399	1.86	9.4	179	<1	3.0
Cau	399 ± 4	528	2.45	11.2			
Bel	395 ± 3	864	2.32	22.3	4390	2.675	97.1
Tur	229 ± 35	48052	8.06	34.9	423	3.8	14.2
Ted	339 ± 25	215	<1	7.3	18	<1	-21.0

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Table 4: Examples of the effect of uncertainties in OM/OC ratio and the activation energy on the age range estimates. For $t^{1/4}$ model (top) and $t^{1/n}$ model (bottom). Italicised and bold correspond to age ranges that overlap with known age.

		Age Range (Yrs) (OM/OC)		Age Range (Yrs) ($\pm \sigma E_{aRHX}$)		Age Range (Yrs) (OM/OC $\pm \sigma E_{aRHX}$)	
	Known Age (Yrs)	OM/OC (2.5)	OM/OC (1.4)	$-\sigma E_{aRHX}$	$+\sigma E_{aRHX}$	OM/OC (2.5) $-\sigma E_{aRHX}$	OM/OC (1.4) $+\sigma E_{aRHX}$
$t^{1/4}$							
Ann	110 $\pm$ 14	319	1283	563	821	265	1549
Esp	141 $\pm$ 6	<i>147</i>	<i>452</i>	209	342	<i>115</i>	<i>577</i>
Nic	398 $\pm$ 2	46440	66885	15118	207161	12546	247585
Mac	228 $\pm$ 2	477321093	642239904	146945777	2097687937	126333562	2426549592
Ria	339 $\pm$ 25	122179	191242	28561	828418	22686	1029959
Rat	245 $\pm$ 2	1415987	2145539	1073622	2860419	867501	3502076
Cal	182 $\pm$ 9	2337	3014	1744	4057	1532	4598
Joy	412 $\pm$ 2	<i>321</i>	<i>489</i>	<i>263</i>	<i>604</i>	<i>211</i>	<i>742</i>
Cau	399 $\pm$ 4	<i>388</i>	<i>704</i>	412	678	<i>302</i>	<i>903</i>
Bel	395 $\pm$ 3	<i>258</i>	<i>2178</i>	490	1522	<i>147</i>	<i>3840</i>
Tur	229 $\pm$ 35	36508	62139	28231	81789	21449	105766
Ted	339 $\pm$ 25	174	263	166	278	<i>135</i>	<i>339</i>
$t^{1/n}$							
Ann	110 $\pm$ 14	<i>59</i>	<i>182</i>	<i>80</i>	<i>148</i>	<i>43</i>	<i>247</i>
Esp	141 $\pm$ 6	284	1115	296	1170	<i>143</i>	<i>2216</i>
Nic	398 $\pm$ 2	820437	1267480	241745	4342090	193586	5371703
Mac	228 $\pm$ 2	8113299	10271317	2565101	32631307	2274744	36634569
Ria	339 $\pm$ 25	4150	5660	2655	8929	2263	10378
Rat	245 $\pm$ 2	4343	5517	3080	7827	2724	8794
Cal	182 $\pm$ 9	<i>177</i>	<i>212</i>	<i>155</i>	<i>244</i>	<i>141</i>	<i>266</i>
Joy	412 $\pm$ 2	152	208	163	196	138	228
Bel	395 $\pm$ 3	774	17058	2140	9009	<i>377</i>	<i>35002</i>
Tur	229 $\pm$ 35	359	494	286	627	<i>242</i>	<i>731</i>
Ted	339 $\pm$ 25	16	21	15	23	12	26

Figure 10: Left - Age-temperature curve for *Esp.* Solid black line – $t^{1/4}$ model. Solid blue line – $t^{1/n}$ model. Solid red line - known age midpoint. Dashed black – ELT of $t^{1/4}$ and $t^{1/n}$ models. Right – Age-temperature curve for *Joy*, $t^{1/4}$ model, with uncertainties associated with OM/OC ratio (green dashed) and activation energies (red dashed dotted, 1σ). Dashed black – ELT. Solid red – known age midpoint.

3.4 Mass Discrepancies and Relationships

The differences between m_{RHX} and m_{sim} , a mass discrepancy, m_{out} , is presented in *Figure 11* as a percentage of the total fractional mass loss, m_{RHXC} , and the RHX fractional mass loss, m_{RHX} . The mass discrepancy varies considerably with the sample, often in excess of 50% of the RHX fractional mass loss. Attempts to correlate this mass discrepancy with the mass of loose water, m_{lws} , and the mass of organic matter, m_{om} , resulted in no statistically significant relationships ($R^2 < 0.05$ typically, see Barrett 2015).

Figure 11: For $t^{1/4}$ (left) and $t^{1/n}$ (right) model, the mass discrepancy, m_{out} , as a percentage of the RHX fractional mass (red), m_{RHX} , and the total fractional mass (blue), m_{RHXC} .

4. Discussion

4.1 Component Based Approach and Appropriate Models

An area of difficulty in RHX dating has been the issue of whether or not the *Stage 2* mass gain is better described by a $t^{1/4}$ model (e.g. Wilson et al. 2009; 2012; 2015; Hall et al. 2011) or a more general $t^{1/n}$ model (e.g. Bowen et al. 2011; 2013). The results supporting the latter model being more suitable (but not necessarily ideal) have grown and are convincing (e.g. Le Goff and Gallet 2014; 2015a; 2015b; Gallet and Le Goff 2015). The modelling results of the present work (*Figure 8*, but see also Barrett 2015) would also argue for preferring a $t^{1/n}$ approach, finding a range of $1/n$ value, from approximately 1/6-1/2, that are similar to those observed previously (e.g. 1/6-1/3 in Le Goff and Gallet 2014, 1/4-1/2 in Le Goff and Gallet 2015b).

Despite this, it was decided that it would be constructive to conduct all of the dating analysis in the present work using both models for several reasons, most notably: (a) dependent on the uncertainties involved and the validity of the component based approach, an improvement in the results would be expected, and provide some validation, for the use of the more appropriate ($t^{1/n}$) model with respect to the less appropriate ($t^{1/4}$) model; (b) it is of interest, given the successful results of Wilson et al. (2009; 2012), to examine the extent to which the use of the less appropriate model ($t^{1/4}$) might produce age estimates that could be considered successful or in reasonable agreement with known ages (note that strong results and arguments which raise serious questions surrounding the validity of the successful dating trials of Wilson et al. have been put forward by Le Goff and Gallett (2015a; 2015b), see also the review of Barrett 2015). The component based approach itself would only be considered successful if the $t^{1/n}$ model produced both accurate dating results and, dependent on the magnitude of the uncertainties, a significant improvement in results when compared with those of the $t^{1/4}$ approach.

The use of a component based approach is supported by the linearity of Arrhenius plots acquired using the RHX mass gain rates estimated from the difference in the components (130°C and 500°C) for three different aging temperatures, e.g. *Figure 6*, *Figure 7* and *Table 1*. The agreement in the estimates of the RHX mass, m_{RHX} , for different aging temperatures, see the small uncertainties in *Figure 5*, also provides some support. However, for the twelve samples on which dating was carried out, the results are mixed and often poor, *Tables 3-4* and *Figure 9*. Some samples provide age estimates that agree well with the known ages, for example *Joy* ($t^{1/4}$, known age 412yrs, estimated age 399yrs) and *Cal/Ann* ($t^{1/n}$, known ages 110/182, estimated ages 109/194, respectively) but other samples produce estimates

that are extremely poor, for example *Mac*, *Nic* (500Myrs and 56kyrs, respectively for $t^{1/4}$, 9Myrs and 1Myrs, respectively for $t^{1/n}$).

Considering certain uncertainties (OM/OC ratio and activation energy), *Tables 4* and *Figures 9* for example, for the $t^{1/4}$ model agreement between the estimated and known ages is the case for 5/12 samples (*Esp*, *Joy*, *Cau*, *Bel*, *Ted*) with 4/5 of these (*Esp*, *Joy*, *Cau*, *Bel*) feasible when the OM/OC range is permitted to vary from 1.4-2.5 (see Barrett 2015; 2017), 1/5 (*Joy*) feasible for the RHX activation energy uncertainty range, and *Ted* only feasible if both uncertainties are considered.

For the $t^{1/n}$ model, 3/12 samples (*Ann*, *Cal*, *Tur*) produce feasible ages under specific uncertainty conditions. Within the OM/OC uncertainty range 2/3 are feasible (*Ann*, *Cal*) with *Tur* only finding agreement when the full range of uncertainties is permitted. For some of these feasible samples the age range is considerable when the uncertainties are considered, for example 258-2178yrs for *Bel* with OM/OC=1.4-2.5 ($t^{1/4}$), whereas for others the effects are relatively small, for example 177-212yrs for *Cal* with OM/OC =1.4-2.5 ($t^{1/n}$).

Often large uncertainties are required for agreement and this is clearly unsatisfactory; in these instances ‘feasible’ is better interpreted as implying that agreement between age estimates and known ages can not be ruled out. Certainly, the large uncertainties in *Table 4* that arise on account of the significant quantities of organic matter present in all samples, *Figure 5*, and the imprecise range of the OM/OC factor would make assessment of the validity of the method difficult even if all the estimates were in agreement with the known ages. The issue of organic matter has previously received attention by Numrich et al. (2015) and is examined in greater detail (for the above samples) in Barrett (2017), yet more focussed work is still needed to understand how this (false) contributor to RHX mass estimates can be removed or more accurately estimated, particularly given its ubiquity regardless of retrieval context for the sample (*Table S.8*).

As well as the above factors affecting the date ranges, there is the issue of samples which have previously been considered problematic: *Cau* and *Nic*, for issues with their 130°C mass gain behaviour and poor Arrhenius plots (see Barrett 2015), and *Mac* and *Bel* for issues with *Stage 1* differences and the possible removal of gypsum related moisture (Barrett 2017). When these are removed and samples with unreasonably large uncertainties are ignored, then for the $t^{1/4}$ model only *Esp*, *Joy*, provide good or feasible agreement, and for the $t^{1/n}$ model *Ann* and *Cal* seem to be the

only positive results. Then only two of out eight suitable samples (differing with the model despite strong evidence and arguments favouring the $t^{1/n}$ model, Barrett 2015; Gallet and Le Goff 2015) provide reasonable ages.

The main points to be taken from these results are that, on account of a range of issues discussed further below, (a) the component based approach could not be validated (but should not yet be considered invalidated), (b) the $t^{1/n}$ model could not be demonstrated to provide improved results and, (c) reasonable ages were produced for 25% of the most suitable samples using the $t^{1/4}$ model (as for the $t^{1/n}$) model. The last point demonstrates that poor models can produce results that, falsely, could be interpreted as reasonable. This highlights the need for running and presenting the results of multiple different samples (to examine and make clear the rate of success), the testing of multiple approaches (allowing the robustness of each to be assessed further), and the need for minimising uncertainties considerably in order to lessen the tolerance for what is considered a reasonable age; this in turn will help clarify both how trustworthy the rate of success is and how effective one model is in relation to another.

A final point needs to be made in relation to the component based approach, regarding its application using a $t^{1/n}$ model. For this model to be used, it was assumed (and necessitated) that the $1/n$ values conform to the same value for all aging temperatures, following both drying and reheating. Work by Gallet and Le Goff (2015) found variation in the $1/n$ value as a function of the drying/reheating temperature. In the present work, no statistically significant differences in curvature between the curves produced following drying/reheating were found (this was also generally the case between aging temperatures (*Table S.9*) but it is worth remembering that three subsamples of the original sample (corresponding to the three aging temperatures) were used so some variation is expected). However, the author accepts the possibility that differences may exist but are hidden by the level of the uncertainties in the modelling results (the typical uncertainty in $1/n$ is ± 0.03 at 95% confidence for each modelled curve) or that the two temperatures chosen, 130°C and 500°C, result in mass gain behaviours with very similar $1/n$ values (conceivable given the curve in Figure 5 of Gallet and Le Goff). Future work on the variation of $1/n$ is needed to confirm a dependence drying/reheating temperature for a wider range of sample types. If this dependence is real, then the component based approach is useless in its present form.

4.2 ELTs and Temperature Histories

The results in *Table 2* demonstrate the variation in ELT with sample and model; the difference between the mean lifetime temperature (MLT), T_{mlt} , and the ELT, T_{elt} , can be quite small, for example the ELT is larger by +0.2°C for

Bel ($t^{1/n}$), or large, for example +2.47°C for Mac ($t^{1/4}$). The effect uncertainty in the ELT, can have on the estimated ages can be examined through the age-temperature curves, e.g. *Figure 10* (full curve set in Barrett 2015). For example, for Ann ($t^{1/n}$) the estimated ages at ELTs of 9°C and 10°C were approx. 130yrs and 115yrs, respectively. For this same temperatures, for Joy ($t^{1/4}$), *Figure 10*, the ages are approx. 440yrs and 380yrs, respectively. There is considerable dependence on the gradient of the age-temperature curve in the region of interest. These examples are typical (for samples that produced more reasonable ages) and highlight uncertainties that can be of the order of 10-15% of the age of the ceramic per 1°C uncertainty, in line with theoretical predictions (Hare 2015). It is difficult to put an estimate on the uncertainty in the ELT itself, but where temperature reconstructions are used and where the temperature history of the ceramic is well described by surface air temperatures, then the present author is of the opinion that a minimum uncertainty of $\pm 0.5^\circ\text{C}$ is likely (discussed with regard to Wilson et al. 2012 in Barrett 2015), corresponding to age uncertainties of the order of $\pm 5\%$ (see Barrett 2015 for more detailed discussion on aspects of ELT and their estimation/use).

A more rigorous temperature history reconstruction (for example, with consideration of the effect of burial conditions, internal building thermal effects, and storage conditions) was beyond the scope of the present work and merits future examination when other factors can be better eliminated. Despite this, the samples (*Table S.8*) in this work can be considered and discussed in groups according to their probability of having elevated ELTs, above ELTs based on SATs alone, the effects of which might be observable in the dating results and working temperature, T_w . The probability of elevated ELTs will not be influenced much by whether the sample was retrieved from a buried (*Ann, Esp, Mac, Ria, Ted*) or non-buried (*Nic, Rat, Cal, Jor, Cau, Bel, Tur*) context, as discussed earlier in relation to MLT and ELT bounds. Instead, the exposure to elevated temperatures on account of the functional location of the ceramic during its lifetime, e.g. *Ria* (recovered in close proximity to a fireplace) and *Tur* (an internal brick from a kitchen), is more likely to have be problematic (see the discussion on short term elevated temperature events in Barrett 2015). In this respect samples can be subjectively grouped as having a weak (*Ann, Esp, Rat, Cal, Joy, Bel, Ted*), medium (*Nic, Mac, Cau, Tur*), or strong (*Ria*) probability of elevated ELTs, based on the lifetime use/location of the brick (see *Table S.7 and S.8*), when considering working temperatures, T_w , in *Table 3*.

Then it appears that *Joy* and *Cau* are plausible T_w (9.4°C and 11.2°C, respectively), *Esp* and *Ted* are borderline plausible (15.7°C and 7.3°C, respectively) and *Bel* very unlikely (22.3°C) for the $t^{1/4}$ model. For $t^{1/n}$, both *Ann* and

Cal are good ($T_w = 10.1^\circ\text{C}$ and 10.5°C , respectively) and *Tur* is plausible (14.2°C). But then there are other samples, e.g. *Nic*, *Mac*, *Ria* and *Rat*, which produced absurdly early ages that would require having lifetime ELTs, T_w , that are highly unlikely to have been the case (28.1°C , 49.7°C , 35.4°C and 47.7°C , respectively, for $t^{1/4}$ and 32.1°C , 45.6°C , 26.0°C , and 31.7°C , respectively, for $t^{1/n}$). While *Ria* might be excused on account of an expected elevated ELT (although that proximity to a fireplace could have this large an effect is uncertain and can not be modelled on account of too many unknowns), the large age estimation issues with these samples, regardless of the model used, can not be explained.

Note also that the above working temperatures are based on other factors remaining fixed, for example the OM/OC at 1.95 (Barrett 2017); if this is permitted to vary, the working temperature can also be permitted to find a more acceptable value, introducing more difficulty in assessing the quality of the age estimates.

In any case, while some discrepancy in the age estimates of certain samples (buried or likely to have experienced elevated temperatures) may be partially attributed to issues in the ELT estimation, as discussed in terms of working temperatures, uncertainties in ELTs do not explain the large discrepancies with most dates.

4.3 Sources of Issues and Recommendations

Excessive ages and associated positive mass discrepancies, m_{out} (the difference between the RHX mass estimate and the simulated (expected) mass), *Figure 10*, may suggest an overestimate of the RHX mass m_{RHX} ,¹ an underestimation of the mass gain rates, or an over estimation of the activation energy (which would result in an underestimation of the mass gain rate at lower temperatures).

An underestimation of the mass gain rate is likely for the $t^{1/4}$ modelling of samples with positive curvature. If a sample has positive curvature the modelled mass gain rate increases as the period over which the curve is modelled is reduced (by incremental removal of the earlier data points). For the example of *Ann* (see *Figure 7.23* of Barrett 2015) the mass gain rate increases by approx. $0.0002\text{g/hrs}^{1/4}$, or 6% of the original rate. For the $t^{1/4}$ model, the mass gain rate required for the estimated and known ages to agree, a_w , can be estimated as a ratio of the mass gain rate at the ELT, a_{elt} . Based on the above reasoning, it would be expected that the greater the curvature the more pronounced this ratio will be. The ratios are presented below in *Table 5* with their relationship to curvature ($1/n$) shown in *Figure 12*. The ratios are

¹ Note, however, that for the $t^{1/n}$ model the mass discrepancy is negative for 3/8 non-problematic samples.

generally far too large (positive or negative) to be explained as the result of modelling the wrong portion of the curve and there is poor correlation with the level of curvature. Also the ratio should be <1 for samples such as *Esp* and *Bel* with negative curvature (accepting that *Bel* is a problematic sample). Such issues with rates should also not be applicable to the $t^{1/n}$ model for which large ages were also recorded.

	$1/n$	a_w/a_{elt}
Ann	0.33	1.58
Esp	0.19	1.17
Nic	0.2	3.44
Mac	0.32	39.5
Ria	0.39	4.61
Rat	0.45	9.20
Cal	0.38	1.96
Joy	0.39	0.99
Bel	0.16	1.22
Tur	0.44	3.80
Ted	0.37	0.89

Table 5 and Figure 12: Relationship between curvature and the ratio of the working mass gain rate, a_w , and the mass gain rate at the ELT, a_{elt} .

$t^{1/4}$	E_a (avg. 130C and 500C) (kJ/mol)	Age (yrs)
Ann	93	287
Esp	39	111
Nic	90	4115
Mac	95	15843939
Ria	127	77786
Rat	108	401647
Cal	80	2771
Joy	99	535
Bel	42	787
Tur	114	21658
Ted	86	148

Table 6: Age estimates using RHX activation energies calculated from the average of the 130C and 500C component activation energies.

An underestimation of the mass gain rate could result from overestimation of the RHX activation energy (or slope of the Arrhenius plot). The quality of the Arrhenius plots for the RHX activation energies do not generally suggest any systematic issues (problems with *Cau*, *Nic*, and *Bel* aside). Nonetheless, with the $t^{1/4}$ model, for which the activation energies are higher than the $t^{1/n}$ model and the *Stage 2* modelling may be less appropriate, the age estimates were recalculated using activation energies that were the average of the 130°C and 500°C activation energies in order to explore the effects. Presented in *Table 6*, it can be observed that the issue of large ages is not resolved. The more likely source of issues with large ages is an overestimation of the RHX mass gain, m_{RHX} , either through some fundamental flaw in the component based approach, modelling issues, or possible components of mass that are either not accounted for or incorrectly estimated.

Attempts to correlate the mass discrepancies, m_{out} , the difference between the RHX mass and the simulated RHX mass, *Figure 11*, with other sources of uncertainty beyond this work (e.g. loose water, organic matter, mineral alteration, short term elevated temperature events (STETES), discussed in detail in Barrett 2015), merit some comments. While the relative severity of these factors on estimate ages could be explored (with STETEs and the alteration of gypsum strongly problematic), it generally proved difficult to attribute issues with estimated ages to specific causes on account of the sensitivity of RHX dating to the wide range of contributing factors and their varied effects. Unless these factors can be remove, minimised or very well quantified, then assessing the techniques (including the particular mass gain models used) validity will remain clouded and inconclusive. A collection of problematic factors can be outlined as follows:

- *Better environmental control and higher temporal resolution data:*

The sensitivity of samples to environmental conditions caused a considerable level of noise in the data of high surface area samples. The effects on the modelling of data can be significant – continuous and automated recording of the mass gain under better-controlled environmental conditions would improve the statistics and data used in modelling, and one aging temperature should be run close to the ELT (not possible with the present setup).

- *Temperature history a minor contributor to dating issues but significant source of uncertainty in the estimated ages:*

A 1°C uncertainties in the effective lifetime temperature leads to uncertainties typically of the order of 10-15% of the age of the ceramic, highlighting the need for a very well stringent understanding of the temperature history. However, the uncertainties in the ages associated with the ELT uncertainties were not major contributors to the problematic ages in the present work.

- *Organic matter was present in all samples in significant quantities and is a serious problem for RHX dating (Barrett 2017):*

All samples investigated had significant quantities of organic matter present (most likely humic-substances or coke). This contributed anywhere between 10-50% of the total mass loss during heating, *Figure 5*. Because of large uncertainties in the organic matter to organic carbon ratios used to estimate the organic matter mass, the uncertainties in the age ranges of samples were considerably affected, varying from 20-50% of the ages of the best behaved samples, *Table 4*. Therefore, the presence of organic matter is a very serious source of uncertainty in RHX dating and, unless the organic matter to organic carbon ratio can be refined, samples with high levels of carbon should be screened or have attempts made at the organic matter's removal, as suggested in previous work (Numrich et al. 2015). The uncertainties due to organics were not of an order to explain the large age issues with samples.

- *Loose water not removed during drying is an issue if due to physisorbed water but less so if associated with a long term chemisorption effect (Barrett 2017):*

Loose water was found to contribute up to 2% of the total mass loss during heating at 130-500°C (*Figure 5*). If attributed to physisorbed water, uncertainties in this quantity can lead to an error of approximately 10% of the estimated age (Barrett 2015). If, alternatively the loose water is due to removal of chemisorbed water, provided the chemisorption process is long term (lifetime of the ceramic), then its effect is arguably taken care of by the use of a component based approach (Barrett 2015; 2017). In any case, uncertainties in the quantity or its interpretation were only minor contributors to the large issues with the dating results.

- *Gypsum is a potential problem in brick samples (Barrett 2017):*

For two samples of brick (*Mac, Bel*), gypsum (or less hydrated form bassanite) was found to be present. It was revealed by XRD and FTIR that dehydration to anhydrite occurred during heating at 130-500°C and this was

associated with a lower level of *Stage I* physisorption (of approximately one quarter that observed for the 130°C mass gain). The removal of water during heating as well as a lower level of physisorption will contribute both to an overestimation of the RHX mass and the age of the ceramic. It was shown that this issue with gypsum can explain partially, if not completely, the issue of large ages for these two samples (Barrett 2015).

- *Short term elevated temperature effects (STETE) are potentially a major source of age estimation issues and a considerable problem for the dating of samples with high RHX activation energies (Barrett 2015):*

It was found that short term elevated temperature events, such as the period of cooling of a ceramic post-firing and the heating/cooling of a sample as part of the RHX dating methodology, could contribute significant quantities of mass gain and additional age to a ceramic, particularly for activation energies exceeding 130kJ/mol. For the present dating trials, the STETE effects were less pronounced for the $t^{1/n}$ model, where lower RHX activation energies were obtained for the samples. For both models, the pre-drying of samples for two weeks was shown to have potentially been a major contributor to the large age estimate issues. However, this was not definitively demonstrated and is dependent on RHX mass gain proceeding to high temperatures > 75°C, an area that requires future work and clarification. Nonetheless, for archaeological dating of samples with moderate to high activation energies, exposure to elevated temperatures even for a very short duration may lead to problematic dating results.

This is not a comprehensive list of issues in RHX dating, instead representing factors affecting the estimated ages that were presented in the present (for example, no issue with goethite dehydration (Burakov and Nachasova (2013) was encountered); while detailed examination and discussion of all of these factors is beyond this article they can be found elsewhere, with mass loss issues (incomplete drying, organic matter contamination, mineral alteration) covered in Barrett (2017) and all issues detailed in Barrett (2015, openly accessible); a detailed examination of STETE effects will also be presented in future work.

Any combination of the factors listed above will complicate the assessment of any future dating trial results, prompting the following recommendations with regard to samples, conditions and method:

- Samples have low surface area (< 2.5m²/g); this will improve experimental precision and help avoid any condensation effects (higher fired samples are desirable in this regard). This can be screened for with BET analysis.

- Samples have low RHX activation energies (<130kJ/mol); this will help minimise any STETE effects. For screening purposes a rapid assessment of difference in mass gain rates at low and high temperatures may be necessary.
- Samples have very simple and well defined temperature histories; external structural post-medieval bricks (< 300-400 years old) retrieved from their original locations are still considered desirable in this regard as their temperature history should strongly reflect that of local SATs for which instrumental records may exist (lower ELT uncertainties).
- Samples free of organic contaminants; if not, either a suitable chemical pre-treatment (see Numrich 2015) or an accurate means of estimating the mass contribution using mass spectrometry approaches is required (perhaps GC-MS methods used in organic residue analysis, Evershed 2008); estimates of carbon content alone are insufficient as OM/OC ratios are too variable.
- Screening for gypsum (XRD or FTIR); avoids unaccounted gypsum related mass loss and variation in level of physisorption.
- One aging temperature near the estimated ELT should be used to reduce uncertainties in the associated mass gain rates used in age estimates. However, multiple aging temperatures are valuable where the ELT is in doubt, for interpretative reasons (age-temperature curves), and also in relation to providing multiple estimates of the RHX mass loss.
- Ideally samples are weighed *during* both drying and reheating (i.e. thermogravimetric analysis); this ensures constant mass is reached (potentially not necessary in relation to drying, see Barrett 2015). Removal/replacement from/to heating environment should be avoided to minimise STETE effects. As well as this, after drying/reheating samples must be cooled in a moisture free environment to avoid STETE effects as well as their associated curvature effects (*time-offset* effects, Barrett 2013) in the *Stage 2* mass gain.
- Mass gain experiments are run at low %RH (reduce magnitude of RH related fluctuations) and with high frequency sampling (automated) to improve the data quality.

5. Conclusion

For the present RHX dating trial, conducted on eighteen varied samples (mostly post-medieval brick), eight samples proved well-behaved and suitable for providing age estimations: six samples were problematic due to very high surface area and possible pore condensation (capillary) issues with further issues in four samples associated with gypsum dehydration, high surface area and poor activation energy estimation (Barrett 2015). The remaining eight samples were well-behaved with no obvious problematic behaviour but generally produced poor ages; only two samples provided good dates for either mass gain model tested (these samples differing for each model).

The factors contributing to poor age estimates are varied and include: the presence of organic matter or gypsum, incomplete drying, short term elevated temperature events, experimental setup restraints, and inadequate temperature histories. Because of these complicating factors, the merit or suitability of the component based RHX dating approach used (with both $t^{1/4}$ and $t^{1/n}$ models examined) is difficult to validate or discredit. The sources of uncertainty need better understanding and, ideally, removal or minimising in future work before a more complete assessment can be made. As the original RHX method is no longer considered suitable, this alternative component based approach merits further examination as a potential avenue to the development of an RHX dating method.

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