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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 generalized $t^{1/n}$ 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 suggests 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.

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 behaviour for mass gain (Savage et al., 2008a, 2008b). Despite early promise (Wilson et al., 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 and Nachasova, 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

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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*), Fig. 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:

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

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

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 Eq. (1) (Wilson et al., 2009, 2012):

$$t = \left(\frac{m_{RHX}}{a(T_{elt})}\right)^n, [n = 4] \quad (4)$$

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), Fig. 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 Fig. 1(b)):

a. The RHX mass gain rate (rate due to moisture removal between 130 and 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 and 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 and

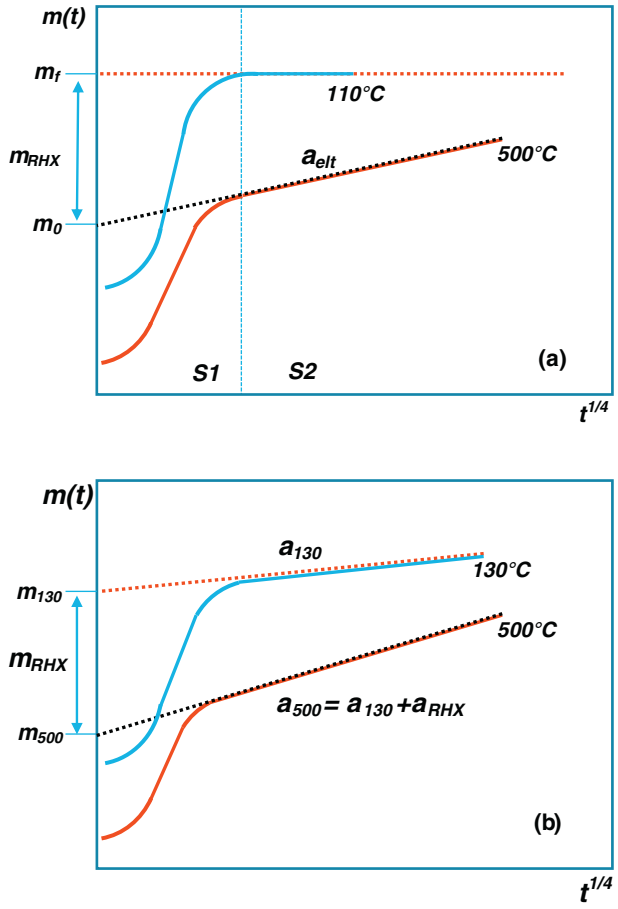

Fig. 1. (a) Illustration of the general RHX dating approach (Wilson et al., 2012); mass gain and equilibration following drying to constant mass at 110 °C (blue); rehydroxylation related mass gain following heating at 500 °C (red). (b) Illustration of the component-based dating approach; mass gain following 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 and 500 °C (RHX/ chemisorption-attributed processes). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)