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Rehydroxylation (RHX) dating: Issues due to short term elevated temperature events

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ABSTRACT

The long-term uptake of environmental moisture (rehydroxylation) is a property of fired clay ceramics. Rehydroxylation dating (RHX) attempts to provide age estimates for ceramics by measuring the associated mass gain and evaluating the duration over which this gain occurred. Simulations of the potential additional mass gained by fired clay ceramic brick and pottery due to short term (minutes to days) elevated temperature (> 50 °C) events, STETEs, and the effect this has on age estimations as part of rehydroxylation dating trials were explored. These events, including post-firing cooling of a brick, the use of pottery in cooking, and heating/cooling cycles during drying, for example, add considerable quantities of (re)hydroxyl mass to the sample and, particularly for samples with high activation energies (> 130 kJ/mol), the effect on age estimations can in some instances be detrimental (of the order of hundreds or thousands of years); where the activation energy is lower, the effects only become considerable at higher temperatures (e.g. > 75 °C) and over longer durations (days). Simulations of the STETEs for a brick cooling over a range of activation energies and for a variety of post-firing cooling durations and cooling temperature profiles, as well as for a pot undergoing varied numbers of cooking cycles (*stewing* and *boiling*) are presented, highlighting the magnitude of the issue if unaccounted for. STETEs are also shown to be a plausible major contributor to the age discrepancies (resulting in very old ages) between known and estimated ages in associated dating trials. The implications for RHX dating are discussed.

1. Introduction

Rehydroxylation dating (RHX) was first proposed as a direct dating method for archaeological ceramics following investigations into the expansive properties of fired clay bricks (Wilson et al., 2003). When inorganic clays are fired at temperatures in the range 450–900 °C hydroxyls of the clay minerals are converted to water and subsequently evaporated (dehydroxylation), accompanied by a collapse of the crystal structure of the clay (for example, Belloto et al., 1995; Gualtieri and Ferrari, 2006; Wang et al., 2002). Following cooling, a reversal of this process takes place in the hardened ceramic; water from the environment is absorbed and rehydroxylation occurs (for example, Heller et al., 1962; Muller et al., 2000; Shoval et al., 1991). Central to rehydroxylation dating are that (a) the rate at which rehydroxylation occurs can be described by a well-defined equation (a function of *time*$^{1/4}$), (b) the rate has an exponential (Arrhenius) temperature dependence, (c) reheating the ceramic to a sufficiently high temperature (e.g. > 500 °C) for a sufficient duration will dehydroxylate or reset the mass of the ceramic to that of the as-fired state and (d) any subsequent mass gain will replicate the original mass gain following firing, provided the environmental conditions (temperature) are the same (Wilson et al., 2009, 2012). Using gravimetric techniques, rehydroxylation dating (Wilson et al., 2009, 2012) takes advantage of these properties. In principle, by weighing a sample of ceramic (under controlled environmental conditions) before and after reheating, the mass the ceramic has gained since it was originally (or last) fired can be estimated using suitable methods. Following reheating, measuring the mass gain of the sample as it ages in a controlled environment (with a temperature equivalent to that which the ceramic was effectively exposed to during its lifetime, the effective lifetime temperature, ELT), will permit the original rehydroxylation rate to be calculated. With these two quantities, the mass of rehydroxyls and the mass gain rate, the elapsed time since firing can then be calculated.

Despite the promising application of these principles by Wilson et al. (2009, 2012) to date bricks, tiles and pottery up to 2000 years old, there is a growing body of work that demonstrates significant issues with many aspects of the method: aside from the 11 samples dated by Wilson et al. (2009, 2012) age estimations from other works have been unsatisfactory (for example, Burakov and Nachasova, 2013; Le Goff and Gallet, 2015a; Numrich et al., 2015; Barrett 2017a); the *time*$^{1/4}$ model is

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inadequate (for example, Bowen et al., 2011, 2013; Le Goff and Gallet, 2014, 2015a, 2015b; Barrett, 2017a, 2017c) with the use of a *time*$^{1/n}$ model considered an improvement (for example, Bowen et al., 2011; Gallet and Le Goff, 2015; Le Goff and Gallet, 2015b; Barrett, 2017a, 2017c); the presence of contaminants (notably organics and gypsum) that interfere with rehydroxyl mass estimation are also an issue (Numrich et al., 2015; Barrett 2017b). Along with other experimental difficulties (for example Bowen et al., 2011; Zhao et al., 2015), questions surrounding the validity of successful dating trials have also arisen (Le Goff and Gallet, 2015a, 2015b; see also the review of Barrett, 2015).

Little attention has been given to potential problems that arise when a ceramic is exposed to high temperatures ($>$ 50 °C) for short durations (minutes to days), referred to here as short term elevated temperature events (STETEs). Due to the Arrhenius temperature dependence of the rehydroxylation mass gain rate (Wilson et al., 2009; Barrett, 2013; Clelland et al., 2014), a ceramic can gain exponentially greater quantities of mass at higher temperatures. The implications of this for RHX dating have previously been explored both in terms of how diurnal and annual temperature cycles can require corrections to age estimations if a mean lifetime temperature is used (Barrett, 2011), and in terms of estimating an effective lifetime temperature (ELT) which reflects the average mass gain rate the ceramic will have had during its lifetime (Hall et al., 2013). Barrett (2013) demonstrated that for small bulk samples (30-40 g) the mass gained during the cooling period following heating is quite significant and results in a curvature (non-linearity) in the mass gain data as a function of $t^{1/4}$ (applicable to $t^{1/n}$ also); this additional mass gain (i.e. above what would be expected for aging at ambient laboratory conditions alone) was shown to be equivalent to an apparent increase (equivalent to a *time-offset*) in the estimated age of the ceramic if ambient temperature alone was used in age estimation. However, this work did not consider in any detail the implications of this effect on dating trials.

The RHX age estimation, t_{age}, requires an estimate of the quantity of mass the ceramic has gained over its lifetime due to rehydroxylation and an estimate of the ELT the ceramic has experienced. The ELT is calculated using a constructed temperature history of the ceramic and an understanding of how the mass gain rate varies with temperature (see Hall et al., 2013). However, for long temperature histories (hundreds to thousands of years) there is the potential for minor temperature events, occurring on the order of minutes to days, to be overlooked; yet because of the exponential temperature dependence of the mass gain rate it is plausible that a considerable quantity of mass could be gained at high temperatures during such short events. Consequently, the effective lifetime temperature needs to be raised, otherwise age calculations will be overestimated. For example, with a piece of structural brick located on an external exposed face of a building since manufacture, this effective lifetime temperature may be expected to largely reflect local air temperatures; however immediately post-firing the brick may have experienced a considerable period of cooling down (e.g. several days for a downdraught kiln, Brunswick, 1990) during which accelerated mass gain can occur. For pottery that is used in cooking, repeated cycles of heating and cooling might also increase the effective lifetime temperature. Also overlooked is the potential mass gained by the ceramic while heating up and subsequently cooling as part of the drying stage of the RHX methodology.

To examine potential STETE effects on RHX age estimations, simulations of the mass gain due to varied brick cooling durations following initial firing, and also for pots undergoing varied cooking cycles (*stewing* and *boiling*), are conducted for a range of activation energies (and cooking cycles for pots). The effect this additional mass has on age estimations where the ELT is not altered to account for the STETE is examined and discussed.

The work also examines the possible effects of a range of STETEs experienced by post-medieval brick samples used in a recent dating trial (Barrett, 2015). These events cover lifetime use events (post-firing cooling) and RHX methodology events associated with drying. Simulations of the lifetime mass gain by the ceramics without STETEs considered and with STETEs considered are generated. The potential additional age due to STETEs are then used to examine possible discrepancies in ages estimates obtained in the dating trial.

2. Theory and method

2.1. Theory

After firing of a clay and its conversion to a hard ceramic (or subsequent reheating above 500 °C), the ceramic gains mass in two stages (Savage et al., 2008a), *Stage 1* and *Stage 2*. The initial and more rapid *Stage 1* can be largely attributed to physisorption processes (the processes responsible for *Stage 2* are on-going and a lesser contributor to *Stage 1*) and has generally reached completion within 24 h (Barrett, 2017c). The prolonged and indefinite second stage, *Stage 2*, is likely due to both chemisorption and rehydroxylation processes (Gallet and Le Goff, 2015; Barrett, 2017c). The rate at which chemisorption/rehydroxylation takes place in *Stage 2* is well described by a *time*$^{1/n}$ (e.g. Bowen et al., 2011; Le Goff and Gallet, 2014; Barrett, 2015, 2017c) power law of the general form:

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

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 is the *aging* temperature, i.e. the environmental temperature to which the ceramic is exposed and at equilibrium with). A fixed value of $1/n = 4$ was originally proposed and applied with some success (Wilson et al., 2009, 2012) but this has been increasingly shown to be unsatisfactory (e.g. Bowen et al., 2011; Le Goff and Gallet, 2014, 2015a, 2015b; Barrett, 2015, 2017c) with $1/n$ instead observed to be sample dependent and varying between 1/6–1/2 (e.g. Le Goff and Gallet, 2014; Barrett, 2017c).

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

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

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.

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

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

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, T_{ELT} (see Hall et al., 2013), then using the Arrhenius temperature dependence to estimate the rehydroxylation rate at the ELT, $a(T_{ELT})$, the age of the ceramic follows from rearrangement of Eq. (1):

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

2.2. Simulation approach and application

Three groups of simulations were run to examine STETE effects: (a) brick cooling effects, (b) pot cooking effects, (c) dating trial effects. The first two groups are entirely simulation based but use parameters for the ceramic behaviour that are from experimental work (Barrett 2015, 2017a). The third group of simulations is applied to samples (described below) tested in the dating trials of Barrett (2015, 2017a, 2017b) and