



# Are the intensities and durations of small-scale pottery firings sufficient to completely dehydroxylate clays? Testing a key assumption underlying ceramic rehydroxylation dating



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## ABSTRACT

Rehydroxylation (RHX) dating was recently suggested as a simple, cheap, and accurate method for dating ceramics. It depends on the constant rate of rehydroxylation (the slow reintroduction of OH) of clays after they are fired and dehydroxylated (purged of OH) during the production of pots, bricks, or other ceramics. The original firing of the ceramic artifact should set the dating clock to zero by driving all hydroxyls out of the clay chemical structure. To examine whether this assumption holds, especially for pot firings of short duration and low intensity, as those in small-scale traditional settings, we performed thermogravimetric analysis of clay samples of known mineralogy at temperatures and for durations reported from traditional sub-Saharan, American, and South Asian pottery firings. Results demonstrate that in the majority of samples, complete dehydroxylation (DHX) did not occur within, or even beyond, the conditions common in traditional firings. Consequently, between 0.01 and 1.5% of a sample's mass in residual OH may remain after firings analogous to those observed in the ethnographic record. Lack of complete DHX at the scales we have observed can result in the over-estimation of ceramic ages by decades to tens of thousands of years, depending largely on the age of the sample, and the amount of residual OH present. Thus, in many cases, a key assumption underlying current RHX dating methods is unlikely to have been met, introducing considerable error in dates.

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## 1. Introduction

Ceramics are ubiquitous in post-Pleistocene archaeological contexts around the world. They have been used to explore questions that vary in scale from provenance and long-distance trade, to specific communities of practice and identity (Crown, 2014; Michelaki et al., 2015; Sinopoli, 1991; Tite, 2008). Furthermore, their chemical and/or mineralogical makeup, as well as their stylistic variations have often allowed researchers to reconstruct relative chronological relationships in the past (Steponaitis, 1984, 1983). Using ceramics to generate chronologies, however, can be frustrating. For periods or regions characterized mostly by the

production, use, and circulation of undecorated plainware, stylistic variation is not useful and, sometimes, chemical/mineralogical variation may only produce chronological frameworks too coarse to be of use for many archaeological questions. In sites with well-stratified deposits and multiple other lines of evidence, useful chronologies may be possible (Ortman, 2016; Ortman et al., 2007). In sites of lesser integrity, or when encountering assemblages from surface or museum collections detailed and accurate ceramic chronologies can be unattainable. Although luminescence methods have been shown to generate reliable calendar dates when used to date ceramics (Duller, 1995; Dunnell and Feathers, 1994; Feathers, 2003) such methods are complex, expensive, and cannot be used on surface materials or those from unprovenanced museum collections.

In 2009, Wilson et al. argued that a new method, ceramic rehydroxylation (RHX), could allow archaeologists to directly date

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archaeological ceramics in a way that would be accurate, reliable, simple, non-destructive, and inexpensive, requiring only small fragments of the ceramic artifact. This was an exciting proposition that could potentially revolutionize the understanding of prehistory in various parts of the world.

Geologists, material scientists, archaeometrists, and archaeologists alike set out to replicate the Wilson et al. (2009) experiments with the aim to validate and improve the method (e.g., Bowen et al., 2013, 2011; Clegg et al., 2012; Hall et al., 2013, 2011; Hall and Hoff, 2012; Hamilton and Hall, 2012; Moinester et al., 2015; Wilson et al., 2014), yet many were faced with limited success (Le Goff and Gallet, 2015; Le Goff and Gallet, 2014a, b; Numrich et al., 2015; Zhao et al., 2015). By now multiple processes have been put forward as potential confounding factors, which we discuss below. One of these is incomplete dehydroxylation of ceramics during their production (Stevenson and Gurnick, 2016).

Here, we evaluate the potential impacts of incomplete dehydroxylation on RHX dating by 1) evaluating whether archaeologically recovered sherds from small-scale prehistoric settings are likely to have been fully dehydroxylated during their production; 2) estimating the error introduced into the RHX dating method if dehydroxylation is incomplete; and 3) assessing whether that error can account for published inaccurate dates.

### 1.1. Rehydroxylation dating

RHX dating relies on chemical changes that occur in ceramics: first in response to the application of heat during their production, and then in response to the presence of moisture throughout their lifetime, from their use and discard, to their archaeological recovery, and curation.

Clay minerals, the fundamental ingredient of all ceramics, are variable in both chemical composition and physical configuration, but all are hydrous alumina silicates ( $\text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot m\text{H}_2\text{O}$ ). They contain water in the form of hydroxyls (OH) in the alumina silicates and in the form of interlayer water typically found between layers in three-layer clays. This water is chemically bound and present in clays even in their dry state, before potters begin to manipulate them.

The water potters add to make clay plastic is mechanically, rather than chemically, bound to the clay. A freshly made, unfired pot contains both chemically and mechanically bound water. It takes drying at a minimum of 100 °C, and more typically at 200–300 °C, to remove all the mechanically bound water (Rice, 1987: 87). At that point the pot has *dehydrated* and only retains chemically bound, *hydroxylated*, water. During firing at temperatures higher than 300 °C, the hydroxyl and interlayer water are driven from clays as *dehydroxylation* occurs (Rice, 1987: 87). For RHX dating, it is this higher-temperature dehydroxylation that sets the “time-since-firing clock” to zero. Immediately after firing, the pot begins to *rehydrate*, absorbing moisture from the atmosphere, to equilibrate with its environment (Savage et al., 2008). Over time, chemical *rehydroxylation* also occurs as hydroxyls are reintroduced to the chemical structure (Cole, 1962; Shoval et al., 1991).

Wilson et al. (2009) demonstrated that while the process of rehydration is short lived, lasting a few hours after firing is completed, the process of rehydroxylation is very slow, lasting for thousands of years. Furthermore, while the rate of rehydration is influenced by parameters such as relative humidity, the rate of rehydroxylation is an internal chemical process affected by temperature, but not by relative humidity. They described the rate of rehydroxylation as a power law, and stated that mass gain during rehydroxylation increases as the fourth root of the time since last firing, expressing the Rehydroxylation Rate Equation as  $y = \alpha_T t^{1/4}$ , where  $t$  = time since firing,  $y$  = mass gain due to rehydroxylation,

and  $\alpha_T$  = the temperature dependent rate of rehydroxylation. If  $y$  and  $\alpha_T$  can be observed/calculated, then time since dehydroxylation can be calculated as:  $t = (y/\alpha_T)^4$  (Wilson et al., 2009). Through their experiments and observations Wilson and colleagues provided a theory and a methodology for dating the last time any archaeological ceramic material had been fired to the point of complete dehydroxylation, setting the clock to zero.

A RHX date requires two values: The total mass of hydroxyls acquired across the lifetime of a sample, and the rate at which that sample rehydroxylates. These two values are acquired through gravimetric approaches. First, a sherd is fired at 105 °C until its mass stabilizes (after a few hours to several days) and then weighed to acquire the dehydrated mass of the sample. The sherd is then fired at higher temperatures (500 °C) until the sample mass stabilizes after anywhere from 4 (Wilson et al., 2009) to more than 40 h (Clelland, 2013). The sample is then weighed to acquire the dehydroxylated mass of the sherd. The difference between the dehydrated mass, and the dehydroxylated mass should represent the total mass of hydroxyls acquired across the lifetime of the sample ( $y$ ). After the firing process, the sherd is left to rehydrate and rehydroxylate in a temperature and relative humidity controlled chamber, while its mass is being tracked carefully. That rate of mass gain ( $\alpha_T$ ) is used to calculate how much time it would take for the sample to gain the mass of hydroxyls it accrued over its lifetime using the equation  $t = (y/\alpha_T)^4$ .

Since the initial paper on RHX dating (Wilson et al., 2009) both the methodology and the mechanism by which rehydroxylation is expected to work have been revised and questioned (e.g., Le Goff and Gallet, 2014a, 2014b, 2015; Numrich et al., 2015; Zhao et al., 2015). Dehydration and dehydroxylation durations of samples have been extended, since these processes may take several days and even weeks to complete. This is much longer than original protocols by Wilson et al. (2009) suggest (Le Goff and Gallet, 2014a, b, 2015; Zhao et al., 2015). Furthermore, scholars have refined RHX dating models to incorporate mass changes due to both rehydration and rehydroxylation phases rather than attempting to isolate only mass gain due to rehydroxylation (Bowen et al., 2011). However, multiple samples taken from the same ceramic objects, gathered from the same site often show varying RHX rates which leads to scattering of date estimates (Le Goff and Gallet, 2014b). Others have argued small errors from multiple causes may fundamentally limit the accuracy of RHX dating (Hare, 2015). Likely due to some or all of the above factors, few accurate RHX dates have been published, and replication studies are consistently unable to accurately date sherds (Zhao et al., 2015).

One specific cause of dating error is overestimation of  $y$ , the amount of OH that accrued across the lifetime of a sample. During gravimetric stages designed to isolate  $y$ , combustion of organics, and thermal decomposition of calcites may produce mass changes indistinguishable from those due to dehydroxylation without additional analyses (Numrich et al., 2015; Moinester et al., 2015 pers. comm.). Numrich et al. (2015), for example, dated two medieval bricks using the methodology of Wilson et al. (2009). This resulted in ages of 22,000 and 62,000 years ago. They then found that organic material in their bricks may add up to 0.55% of sample mass to  $y$ . The subtraction of that amount of residual material from  $y$  partially accounted for the dating error. The calibrated dates, given 0.55% residual material, were 2865 and 14,734 years ago, significantly predating the medieval period in Europe.

Leftover organic material may not be the only cause of  $y$  overestimation. Stevenson and Gurnick (2016) have suggested that many ceramics recovered from the archaeological record may only have been partially dehydroxylated given the short duration, and low intensity of many ceramic firings in prehistory. This could be another cause of overestimation of  $y$ , and would similarly drive

overestimation of RHX dates.

## 1.2. Ethnographic versus materials science firings

While we know the temperatures at which dehydroxylation occurs in different clays, and that those temperatures are very often met in traditional pottery firings, it is unclear if pots fired in pre-history experienced DHX temperatures long enough to ensure their complete dehydroxylation. During firing, clays lose mechanically bound water first, starting at around 110 °C, and then chemically bound water from their alumina octahedral sheets ( $2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{CO}_2$ ) at higher temperatures, between 450 °C and 900 °C. Materials scientists observing pure clays (Brindley, 1975; Carroll et al., 2005; Grim and Bradley, 1948; Wang et al., 2002), have shown that the temperature range within which individual clays dehydroxylate depends on the mineralogy and stereochemistry of the clays, such that trans-vacancy (tv) hydroxyl structures dehydroxylate faster than cis-vacancy (cv) configurations (Stackhouse et al., 2004; Wilson et al., 2009). For example, kaolinite begins to dehydroxylate between 450 and 600 °C (Zemenová et al., 2014), montmorillonite between 500 and 700 °C (Drits et al., 1995) and illite between 700 and 900 °C (Ferrari and Gualtieri, 2006; Gualtieri and Ferrari, 2006; McConville and Lee, 2005).

The above observations have all been made by firing pure clays in electric laboratory kilns, and for the purpose of detecting the temperatures at which the DHX reaction was initiated, or accelerated. While the process of dehydroxylation does begin at well understood temperatures, it is not necessarily completed once those temperatures are reached.

Others have found that some hydroxyls persist in the clay matrix even after raw kaolinite has been fired at temperatures between 600 °C and 800 °C, the temperature range at which a structural transformation to metakaolinite begins (Stubičan, 1959; Stubičan and Rustum, 1961). In fact, the DHX reaction slows in the case of halloysite and kaolinite once ~90% of OH are evicted (Murray and White, 1955). The speed of dehydroxylation, and therefore, the amount of OH leftover after firing, is also influenced by the size, shape, thickness, and compactness of samples (Brindley, 1975; Brindley and Nakahira, 1957). This pattern led Pampuch (1966) to infer that up to 12% of the OH originally present in kaolinite would remain even after the transition to metakaolinite. Furthermore, Flank (1979) showed that DHX continued to occur for up to 100 min during temperature ramps to 1000 °C and for up to 400 min at temperatures of 400 °C to 900 °C.

Traditional pottery firings, as observed in ethnographic and ethnoarchaeological settings can vary considerably from materials science firings in controlled laboratory conditions. For example, not only do traditional potters use mixed, rather than pure, clays, but also their infrastructure rarely guarantees great control over firing conditions. For our purpose, it is important to examine the maximum temperature achieved, the total firing duration, and the firing duration at high temperatures (those sufficient to dehydroxylate clay) of traditional firings to observe whether their intensity and duration would allow complete dehydroxylation.

Livingstone Smith (2001) compiled data on 80 traditional pottery firings in Africa (Cameroon, Togo, Burkina Faso, Senegal, Burundi, Congo, Namibia, Zaire, Egypt and South Africa), in the Americas (New Mexico, Mexico, and Guatemala), and in India. Excluding one 19-h long firing, the observed firings averaged 77 min (95th percentile = 284 min) with a range between 13 and 550 min (Fig. 1) in duration.

The vast majority of those firings (~91%) ended within 200 min. For the 69 observed firings with maximum firing temperatures above 700 °C, pots reached temperatures above 700 °C for an average of 30 min (95th percentile = 136 min) and for as long as

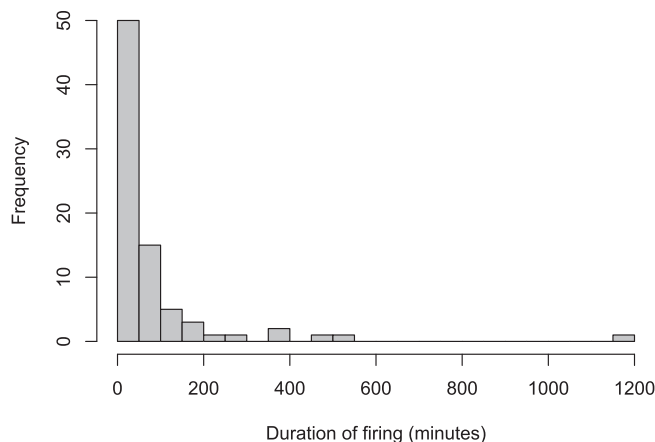


Fig. 1. Duration of pottery firings as reported in Livingstone Smith (2001).

183 min. In only 25% of observed firings did pots achieve temperatures above 900 °C for as long as 20 min and an average of 6 min. Livingstone Smith (2001) reported the time pots spent at temperatures above 700 °C (for 69 of the 80 firings). He did not report the time pots spent at lower temperature ranges at which dehydroxylation occurs in kaolinite and montmorillonite (~450–650 °C). Of the 11 observed firings that did not reach 700 °C, the mean firing temperatures ranged between 560 °C and 690 °C. The heating rate in all firings was typically below 60 °C per minute (mean = 33 °C/min). In summary, ‘traditional’ ceramic firings often lasted for several hours, and reached temperatures at which clays dehydroxylate. However, the amount of time pots spent at those temperatures was often far shorter than the total duration of the firing event.

The short time spent at DHX temperatures is important because both uptake and loss of water and OH can be very slow. If complete DHX of clays does not occur at the time scale of minutes to a few hours, and if residual hydroxyls are removed during sample preparation steps designed to isolate  $\gamma$  (mass gain due to rehydroxylation after firing), then current RHX dating methods will overestimate that value.

## 2. Materials and methods

The clay types selected for this analysis have distinct chemical structures,<sup>1</sup> and were commonly used to produce ceramics in pre-history: kaolinite, illite, and montmorillonite. Our samples were purchased in 2014 from various vendors through Amazon.com in powder form. A sample of each clay type was subjected to bulk, randomly oriented x-ray diffraction at Georgia State University to verify the mineralogy and purity of the clays.

The samples used for our analysis had been formed initially into dried clay tiles. Two hundred milliliters of each clay were added to each of three glass beakers. Fifty milliliters of deionized water were then added to the dry powder. The clays and water were stirred manually and left in the beakers overnight. The following day excess water was removed and the remaining wet material was left uncovered until it dried to the point of being workable. A test tile (12 cm × 2 cm × 1 cm) was then created from each beaker's clay and

<sup>1</sup> Depending on how the aluminas and the silicates are arranged, clay minerals are categorized into: two-layered (1:1) clays - one sheet of silicate tetrahedra ( $\text{SiO}_4$ ) bound to an octahedral sheet of alumina ( $\text{AlO}_4$ ), like Kaolin; three-layered clays (2:1) - two tetrahedral sheets sandwiching a single octahedral sheet -, like illite and montmorillonite; and mixed layered clays, like Chlorite.

placed on a wire rack to dry. Pieces of those tiles were broken off and powdered using an agate mortar and pestle to form samples of kaolinite, illite and montmorillonite (total N = 9).

Each powdered sample of approximately 50 mg was placed into a 200  $\mu$ L titanium crucible and loaded into a thermogravimetric chamber (Setaram TG92) within an inert helium atmosphere replenished at a flow rate of 20 mL/min. The inert atmosphere served to prevent other chemical changes (oxidation and reduction) from occurring that would otherwise influence sample mass. After a temperature ramp phase at a rate of 20  $^{\circ}$ C per minute, each sample was fired at a target maximum temperature (either 500  $^{\circ}$ C, 700  $^{\circ}$ C or 900  $^{\circ}$ C) for 400 min, at which point the TGA chamber began to cool. Mass changes were tracked continuously at 6 s intervals from the beginning of firing during the ramp phase, through the firing at the prescribed maximum temperature, and the cool down period. Across the heating treatments, continued mass loss was interpreted as continuation of dehydroxylation.

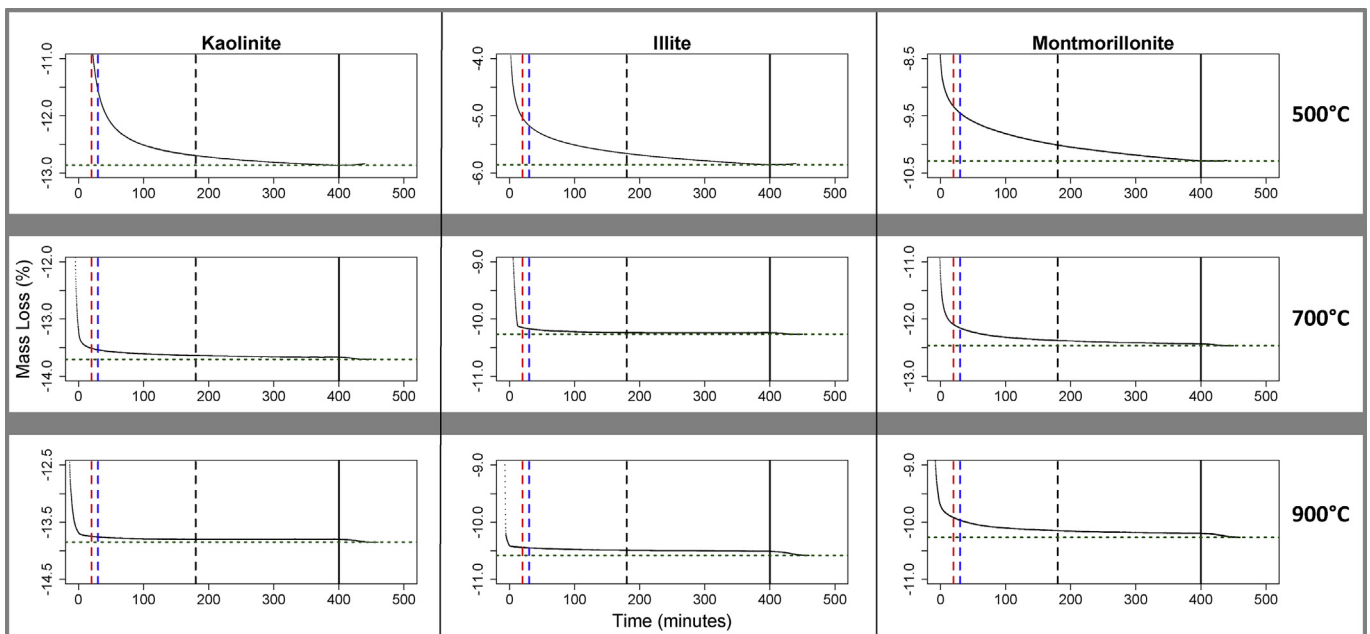
The firing intensities and durations chosen for this experiment cover most seen in Livingstone Smith's (2001) dataset. The maximum temperatures selected cover a range of those seen in ethnographic conditions (500  $^{\circ}$ C, 700  $^{\circ}$ C and 900  $^{\circ}$ C). Although two of 80 pot firings reported in Livingstone Smith (2001) experienced maximum temperatures above 1000  $^{\circ}$ C, each was fired at or above that temperature for only 4 min. The rate of temperature increase experienced by our samples (20  $^{\circ}$ C/min) is lower than the average seen in Livingstone Smith's (2001) dataset (33  $^{\circ}$ C/min), but well within one standard deviation (26  $^{\circ}$ C/min). Our ramp rate was constrained by the Setaram TG92's working range.

Of the firings reported by Livingstone Smith (2001) 96% ended by 400 min and only three of the 80 observations extended beyond 400 min (Fig. 1). However, the average time a pot spent at temperatures above 700  $^{\circ}$ C was 30 min. Likewise, no pot in Livingstone Smith's dataset (2001) was exposed to temperatures above 700  $^{\circ}$ C longer than 180 min in duration (95th percentile = 135 min), and no pot reached temperatures greater than 900  $^{\circ}$ C for more than 20 min. We fired samples at the maximum targeted temperatures

for 400 min (after between 44 and 64 min of ramping to the target temperature from room temperature). The amount of residual OH in each sample was calculated as the difference in sample mass after firing at DHX temperatures for durations representative of the durations at DHX temperatures observed by Livingstone Smith (20, 30, and 180 min) and after further firing until 400 min at the target temperature elapsed. We assume that by 400 min samples are nearly or completely dehydroxylated.

We calculated the amount of error those estimated amounts of residual OH would cause if present in accurately dated samples published by Wilson et al. (2012). These five samples, include two Roman artifacts (a Lambourn loomweight, and a piece of Samian Ware) and three 17th century samples of Werra Ware. Our estimated amounts of residual OH as a proportion of a sample's fired mass ( $r$ ) were added to proportional mass gain due to RHX ( $y$ ) and the dating calculation was changed from  $t = (y/\alpha_T)^4$  to  $t = (y + r/\alpha_T)^4$ . We estimated the difference between accurate RHX dates published in Wilson et al., (2012), and recalculated dates that include residual OH mass. We then assessed whether the amounts of residual OH we identified could help explain too-old dates published by Numrich et al. (2015) by subtracting residual OH amounts from  $y$  for those sample date calculations.

We also calculated the error due to residual OH for RHX methods that model both rehydration, and rehydroxylation (Bowen et al., 2011). We simulated different dating scenarios with a mass gain model used to date a 12.94 g Neolithic sherd (sample RLG20). To remove carbonates and organics we soaked the sample for 24 h in distilled water, then in hydrogen peroxide solution for 24 h, and then in an acetic acid solution for another 24 h, followed by another 24 h in distilled water. We fired the sample for a week at 300  $^{\circ}$ C to acquire the dehydrated mass of the sample, then for 24 h at 500  $^{\circ}$ C to acquire the amount of OH within the sample. We then weighed the sample on a Sartorius microbalance for 20 h at  $3.2 \pm 1\%$  relative humidity (RH), and at 22  $^{\circ}$ C. Using R package *minpack.lm*, the mass gain curve of this sample was used to fit a linear model ( $\text{time} = (y/l)^n$  of mass gain where both the temperature dependent rate of mass



**Fig. 2.** Summary of mass loss in samples at temperatures of 500  $^{\circ}$ C (top row), 700  $^{\circ}$ C (middle row) and 900  $^{\circ}$ C (bottom row) for 400 min. The dashed red line represents maximum duration of firing at or above 900  $^{\circ}$ C observed in Livingstone Smith dataset (20 min). The dashed blue line represents the average duration of firings at temperatures above 700  $^{\circ}$ C (30 min) in Livingstone Smith's dataset (2001). The dashed black line represents maximum duration of firing above 700  $^{\circ}$ C (180 min). The horizontal green line represents the lowest mass the sample achieved in each experiment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

gain, and the exponent (normally  $\frac{1}{4}$ ) is allowed to vary. With this model we calculated dates based on varying two variables:  $y$  (giving different 'dates of manufacture') and  $y + r$  (giving the RHX date, given the date of manufacture, and some amount of residual OH).

### 3. Results

The bulk x-ray diffraction analysis of clay samples confirmed the advertised mineralogy from the vendors. Only the illite sample showed any amount of  $\text{CaCO}_3$  (up to 10%) and none showed evidence for organic contamination. In all TGA firing experiments sample mass decreased rapidly at target temperatures of 700 °C and 900 °C, and more gradually at 500 °C. In all but the cases of Kaolinite fired at 900 °C, and Illite fired at 700 °C, mass loss continued to occur until the end of observations (Fig. 2). This indicates that, even after such a prolonged firing treatment, most samples continued to dehydroxylate, albeit very slowly.

With the exception of montmorillonite, each increase in maximum temperature resulted in a greater proportional loss of OH for kaolinite and illite (Fig. 3).

For example, after 180 min firing at 500 °C, 700 °C, and 900 °C, kaolinite had lost 12.70%, 13.65%, and 13.80% of its mass, respectively. This increase, from identical material, suggests that firing temperature also plays a critical role in the dehydroxylation process. Additionally, in almost all cases, the percentage of mass lost between 180 and 400 min of soaking time varied consistently among clay types. For example, at all three temperatures, montmorillonite always lost proportionally more mass between 180 and 400 min than illite and kaolinite. Illite lost proportionally more mass than kaolinite at 500 °C and 900 °C, but this was reversed at 700 °C. It is possible that this pattern reflects some aspect of clay mineralogy, where montmorillonite is more difficult to dehydroxylate compared to illite and kaolinite.

In all but two samples - illite fired at 700 °C, and kaolinite fired at 900 °C - mass continued to decrease well beyond the maximum duration of firing at 700 °C seen by a pot (180 min) reported in Livingstone Smith (2001). Additionally, all three samples fired at 900 °C continued to lose mass after 20 min, the longest firing time at or above that temperature reported by Livingstone Smith (2001). All three clay samples at all three maximum temperatures continued to lose mass after the average ethnographic firing duration above 700 °C (30 min, 75th percentile).

However, further mass loss beyond the durations seen in ethnographic firings was exceptionally small. For example, the total loss after 180 min of firing at target temperatures averaged approximately 12% of original sample mass. The same samples saw a mean additional loss of 0.10% of original sample mass, and a maximum of 0.31% following an additional 220 min at the maximum temperature. Total loss after 30 min at target temperatures averaged approximately 1.21% with an additional loss of only about 0.45% (1.51% max) following an additional 370 min at maximum temperature. More specifically, 99% of the total mass lost during our experiments was reached between 212 and 316 min of firing at 500 °C, between 16 and 91 min of firing at 700 °C, and between 63 min into the ramp phase and up to 85 min into firing at 900 °C (Table 1; Fig. 2).

Thus most, but not all, of the total mass is lost at time frames seen in small-scale firings. We estimated the residual OH for different firing treatments as the difference in mass between a sample after firing for durations at DHX temperatures as reported by Livingstone Smith (2001) (20, 30, and 180 min) and after firing for 400 min. Residual OH ranges between 0.01% and 1.5% of a sample's mass.

Although our residual OH estimates are very small, these amounts are enough to cause substantial error in RHX dates. For

example, 5 samples published by Wilson et al. (2012) are accurate to the true ages of those samples. If present in low amounts,

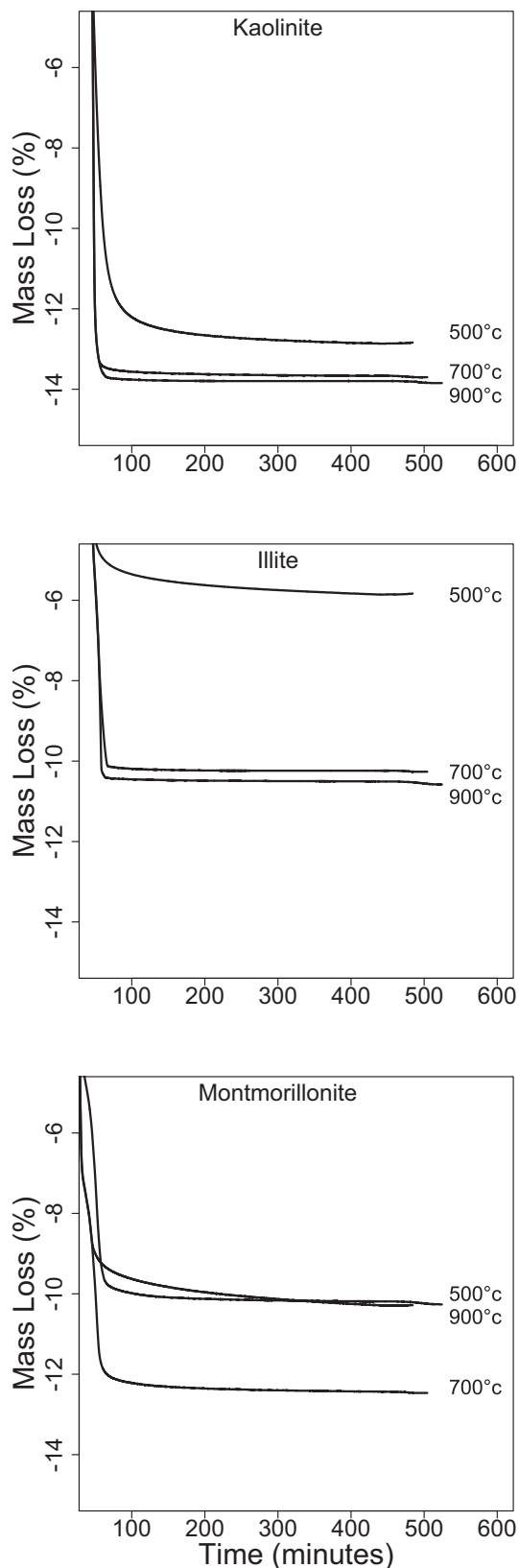


Fig. 3. TGA mass loss curves for kaolinite (top), illite (middle), and montmorillonite (bottom) samples at treatment temperatures of 500, 700 and 900 °C.

residual OH would cause overestimation of RHX dates for those samples, but to a very small degree. Amounts between 0.01%, and 0.05% of a sample's mass may cause overestimation by between 9 and 348 years (mean = 70). However, still conservative estimates of residual OH (0.1% and 0.2% of a sample's mass) result in RHX dates between 102 and 1685 years too old (mean 405). The average estimates for residual OH tend to be greater than 0.2% of a sample's mass. At 0.4%–0.8% of a sample's mass, RHX ages are between 541 and 13,569 years too old (mean 2802). Our maximum estimate for residual OH is 1.5% of sample mass. That amount may cause overestimation of the manufacturing date by between 4994 and 50,642 years. Residual OH in the levels we observed in our clay samples could cause errors at the scale of decades, to tens of thousands of years in Wilson et al.'s samples if it were present (Fig. 4).

Residual OH in the amounts we have observed could help account for some too-old dates. Numrich et al. (2015) found that two medieval brick samples had returned RHX ages of 22,169 and 62,394 years old. When the maximum amount of organic carbon identified in their samples (0.55% of a sample's mass) was controlled for, they calculated RHX ages of 2865 and 14,734

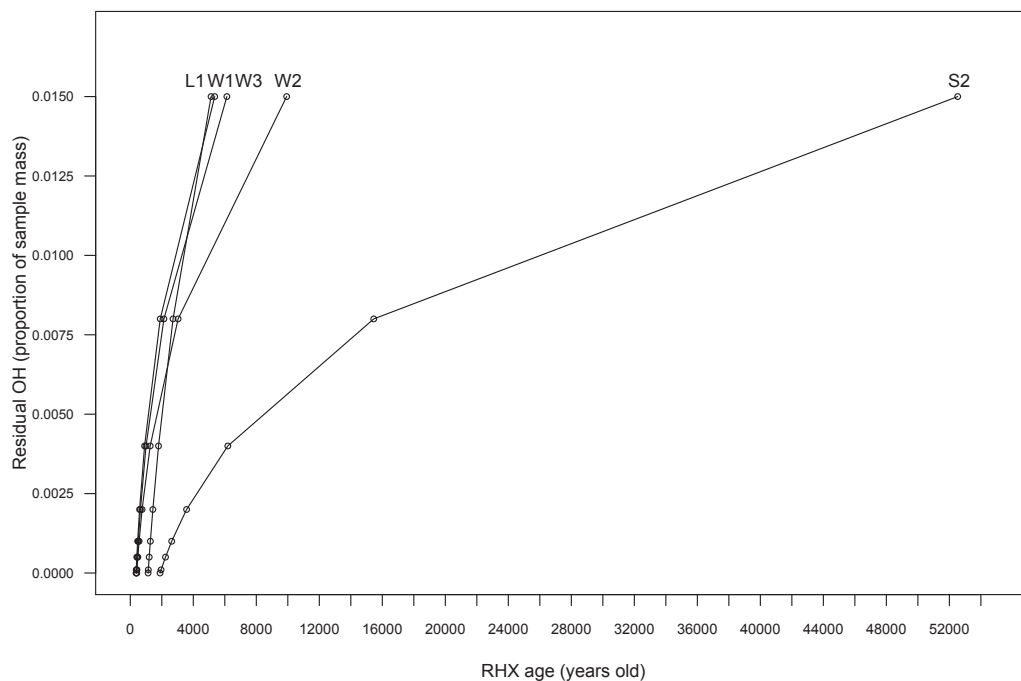
(Table 2). Residual OH estimates subtracted from  $y$ :  $(t = (y-r/\alpha_r)^4$  would need to be ~0.75%–1.2% of a sample's mass to bring those dates back to the medieval period (~1000 years ago). Those values fall within the range of residual OH we have estimated, but smaller amounts of residual OH in addition to organic material identified by Numrich et al. (2015) are more likely causes.

Estimates of RHX dating error due to residual OH are more wide ranging where dates are calculated using a linear model that incorporates both mass gain due to rehydration, and due to rehydroxylation. The most conservative estimates are for samples fired within the past 1500 years with only 0.01% residual OH. These would return RHX dates between 79 and 211 years too old. However, the older a sample is, the greater divergence in dates, and slight increases in residual OH greatly increase that divergence as well. Samples of greater antiquity, (4000–10,000 years old) should return RHX ages between 400 and 1000 years too old with 0.01% residual OH, between 3000 and 6000 years too old with 0.05% residual OH, between 26,000 and 50,000 years too old with 0.1% residual OH, and between 64,000 and 115,000 years too old with 0.2% residual OH (Fig. 5).

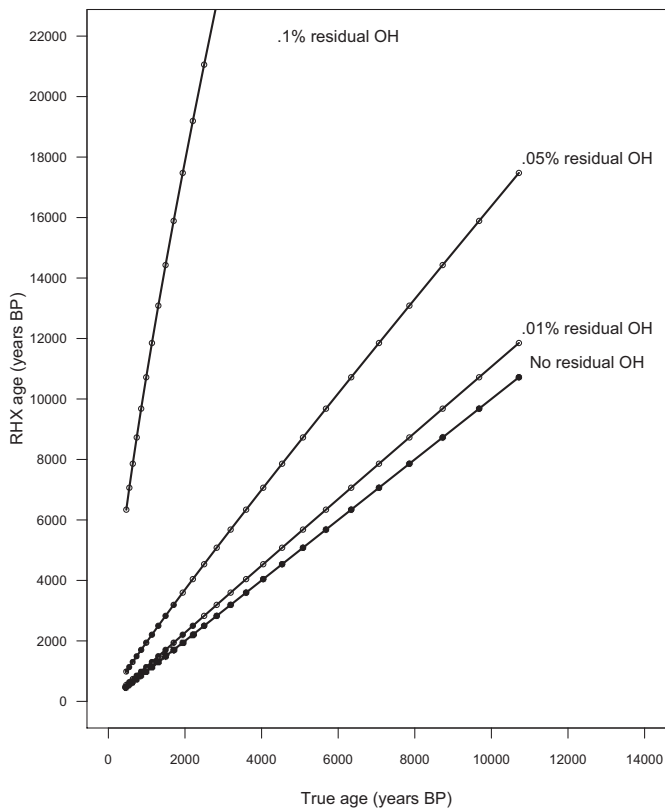
**Table 1**

Thermogravimetric analysis summary. Amount of mass loss after firing samples for 380, 370 and 220 min longer than durations observed in ethnographic firings.

Sample information and treatments				Proportion of sample mass lost at end of ethnographic firing durations.			Additional proportional mass loss between end of ethnographic firing durations and end of firing.		
Clay type	Starting mass (mg)	Mass after firing (400 min. at target temp.) (mg)	Target temp (°C)	20 min.	30 min.	180 min.	Loss between 20 and 400 min.	Loss between 30 and 400 min.	Loss between 180 and 400 min.
Kaolinite	49,830	43,419	500	-0.1325	-0.1457		-0.0151		-0.0020
Illite	49,700	46,788	500	-0.0549	-0.0601		-0.0073		-0.0021
Montmorillonite	49,880	44,749	500	-0.1053	-0.1116		-0.0093		-0.0031
Kaolinite	49,830	43,020	700	-0.1568	-0.1581		-0.0015		-0.0002
Illite	49,910	44,800	700	-0.1133	-0.1141		-0.0008		0.0000
Montmorillonite	49,940	43,730	700	-0.1389	-0.1413		-0.0031		-0.0007
Kaolinite	49,920	43,033	900	-0.1595	-0.1596	-0.1601	-0.0006	-0.0005	0.0000
Illite	49,890	44,648	900	-0.1167	-0.1167	-0.1173	-0.0007	-0.0007	-0.0002
Montmorillonite	50,000	44,905	900	-0.1105	-0.1109	-0.1130	-0.0030	-0.0026	-0.0004



**Fig. 4.** Recalculated RHX ages for samples (L1, W1, W2, W3 and S2) published by Wilson et al. (2012) assuming 0%, 0.01%, 0.05%, 0.1%, 0.2%, 0.4%, 0.8% and 1.5% of sample mass in residual OH.



**Fig. 5.** Results of simulating different dating scenarios with a mass gain model used to date a 12.94 g Neolithic sherd (sample RLG20). Dates were calculated based on that mass gain curve and based on two variables:  $y$  (OH gained since firing giving different “true ages” represented on the x-axis) and  $y + r$  (OH gained since firing plus residual OH amounts of 0, 0.01%, 0.05% and 0.1, giving RHX ages on the y-axis).

#### 4. Discussion

The design of our experiments excluded several chemical reactions from having caused continued mass loss in our clay samples (combustion of organic matter, oxidation, reduction, and thermal decomposition of  $\text{CaCO}_3$  [except in the case of illite]). As a result, continued loss of mass likely reflects the continued process of dehydroxylation. Our experimental data demonstrate continued loss of mass in most clay samples by 400 min of firing at temperatures intense enough to cause dehydroxylation, far longer than the majority of firing durations (regardless of what maximum temperatures they achieved) observed in the ethnographic record.

This pattern is robust, as several aspects of our experiment likely increased the likelihood of complete dehydroxylation compared to ethnographic firings. First, our firing durations at target temperatures were all longer than those reported by Livingstone Smith (2001) from ethnographic observations. Second, our samples were all powdered, meaning that heat was more evenly distributed across each sample, unlike in the case of ceramic pots/sherds that are characterized by a temperature differential between their core and surfaces.

The residual amounts of OH we estimated after different firing durations are minute (0.01%–1.21% of a sample’s mass). However, we have demonstrated that even these small amounts of OH may cause overestimation of RHX from anywhere between a few decades and tens of thousands of years. Our results may seem extreme, but forces that cause error at the scale of tens of thousands of years are necessary to account for some published ages that are far too old (Numrich et al., 2015). We suspect incomplete dehydroxylation

could be one cause among several previously identified (decomposition of calcites, combustion of organics) that may drive overestimation of RHX ages (Numrich et al., 2015). Residual OH is arguably a more severe problem for RHX dating than the presence of calcites or organics, since we do not currently have a tested method to remove or isolate residual OH chemically.

Our work is the first step towards excluding or minimizing residual OH as a cause of error in future replication studies. This is necessary to better isolate potentially more severe factors that are driving error in RHX dating.

There are three ways forward from here. First, without a method of directly measuring residual OH and OH gained across the lifetime of a sample separately, the amount of residual OH would have to be inferred by reconstruction of the firing conditions a pot experienced. This, however, requires accurate and precise reconstructions of the firing conditions pots experienced in prehistory. As we have shown, relatively small variations in temperature, and firing duration will have downstream effects on the amount of residual OH, and the magnitude of dating error. Unfortunately, while we can accurately determine the maximum firing temperature a pot experienced (Rasmussen et al., 2012), we can only very coarsely reconstruct the duration of firings in prehistory, and are currently unable to accurately reconstruct the duration of firing at specific temperatures. We hope that these results are used as further justification for investigating and refining methods of reconstructing firing conditions.

Second, Stevenson and Gurnick (2016) have argued that some residual OH is likely to exist in low fired ceramics, but that this is unlikely to cause error in RHX dates. This argument rests on three proposals: 1) residual OH is strongly bound to the clay matrix because it lays in regions that have not experienced structural collapse; 2) OH gained by pots after rehydroxylation is assumed to be weakly bound; and 3) The relative strengths and weaknesses of these two kinds of bonds are such that only OH gained across the lifetime of a sample is lost at 500 °C.

The above three propositions may be the case. If so, residual OH would only be a problem for vessels fired below 500 °C in prehistory. However, we find those proposed behaviors hard to reconcile with the durations necessary to dehydroxylate ceramic samples in a laboratory setting at 500 °C. If residual OH is not removed at 500 °C, and if lifetime OH is weakly bound in comparison to residual OH such that it is lost at 500 °C, why does the DHX process continue for weeks at that temperature even in young samples (Le Goff and Gallet, 2014a, b)? We suspect that the OH lost over the course of many days at 500 °C may be OH that otherwise would more quickly be driven away at 800 or 900 °C. It may be the case that OH gained after firing really is weakly bound compared to residual OH, but it seems unlikely that residual OH will not be lost, even very slowly, at 500 °C. If it is the case that residual OH is slowly driven out at 500 °C, then current protocols would indeed cause removal of residual OH. Nonetheless, the possibility that residual OH is strongly bound, and will not be driven away at temperatures of 500 °C needs to be formally tested.

Thirdly, dating replication experiments (e.g. Zhao et al., 2015) in the future should attempt to control for residual OH, and other causes of error. Organics and calcites should be removed through chemical treatments (though whether or not chemical treatments will alter rehydroxylation rates in a sample is unknown). Likewise, to exclude mass changes due to oxidation or reduction during sample preparation steps, researchers should dehydroxylate samples in an inert atmosphere. To help reduce the risk of high overestimation due to residual OH, exterior portions of sherds more likely to be completely dehydroxylated, should be targeted. Likewise, samples with a higher intrinsic rate of RHX and younger samples should be less sensitive to date overestimation due to

residual OH or other factors.

Even if we can eliminate the problem of overestimating  $y$ , it would only partially address replicability issues in RHX dating. Incomplete dehydroxylation, or any other phenomenon that causes overestimation of  $y$  has a directional effect on date calculations. Overestimation of  $y$  cannot account for dates that are too young, which are at least as pervasive in replication studies as dates that are too-old (Table 2 supplementary). Overestimation of  $y$  also cannot account for overall scatter in dates from the same samples. Different samples taken from the same artifact may show very different RHX rates, causing scatter in dating estimates according to Le Goff and Gallet (2014b).

## 5. Summary and conclusions

Our results indicate that variations in the maximum temperature, firing duration, soaking time, and clay mineralogy are all factors that must be considered when conducting RHX analyses as each variable contributes to the rate and magnitude of dehydroxylation during ceramic production. While we do not question that some RHX dating protocols do result in complete dehydroxylation of samples, the conditions necessary for full dehydroxylation of clays were likely rare among prehistoric firings. Consequently, it is unlikely that a large number of sherds we find in the archaeological record were completely dehydroxylated during their production. Residual OH in the amounts we have identified may result in overestimation of ages by a few decades to tens of thousands of years.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jas.2017.01.009>.

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