



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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ARTICLE INFO

Article history:

Received 10 November 2016

Received in revised form

6 January 2017

Accepted 17 January 2017

Available online 28 January 2017

Keywords:

Ceramics

Rehydroxylation

Dating

Ceramic firing

TGA

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 ($\text{Al}_2\text{O}_3 \cdot n \cdot 2\text{SiO}_2 \cdot m \cdot 2\text{H}_2\text{O}$). 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 α_T = the temperature dependent rate of rehydroxylation. If y and α_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 (α_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

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