Structural collapse in kaolinite, montmorillonite and illite clay and its role in the ceramic rehydroxylation dating of low-fired earthenware

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ARTICLE INFO

ABSTRACT

The rehydroxylation dating of ancient pottery estimates the age of ceramic manufacture based upon the total hydroxyl (OH) accumulation since initial firing. The diffusion of OH is impacted by the structural porosity of the ceramic that becomes progressively, or suddenly, closed with increasing temperature as the clay structure collapses. Changes in ceramic mineral structure along the temperature continuum occur at certain thermal set points. Infrared spectroscopic analysis of heat-treated kaolin, illite, and montmorillonite reveals that shifts in the Si-O band correlate with the extent of structural collapse occurring between 600 and 1000 °C. Accelerated rehydroxylation experiments reveal that the activation energy of rehydroxylation decreases with greater structural collapse and indicates that the rate of rehydroxylation will be faster for ceramics fired at more elevated temperatures.

1. Introduction

The ceramic rehydroxylation (RHX) dating of bricks, terracotta tiles and archaeological pottery (Tosheva et al., 2010; Wilson et al., 2009, 2012, 2014) has captured the interest of archaeologists who work diligently at developing and refining chronological sequences using ceramic materials from archaeological contexts. Chronology building is especially challenging in locations where earthenware, with modest amounts of surface decoration, are part of the cultural assemblage. Any number of regions in the world can be used as an example whether it is the Woodland Period of the Southeastern United States (Smith and Neiman, 2007) or the prehistoric ceramic sequence of Fiji (Sand et al., 2000). In such contexts, chronological sequences may be categorized simply as early, middle and late, and may constitute periods spanning 200—500 + years. On a larger regional basis, it is difficult to correlate multiple local chronologies or trace evolving historical ceramic traditions with such large temporal periods. Put simply, the poor temporal resolution restricts the ability to evaluate

hypotheses about past behavior and to easily engage in the emerging social archaeology of the present.

Ceramic rehydroxylation dating is a self-calibrating method that provides a rate constant for hydroxyl (OH) diffusion intrinsic to the sample under study. It generates an age assessment for the last heating, or dehydroxylation (DHX), event. This may reflect initial firing, a cooking event, or the disposal and burning of pottery sherds with other domestic refuse. As such, the method has the potential to provide absolute dates for individual contexts and to enhance regional chronological sequences. A recent series of papers have sought to refine the initial rehydroxylation model of Wilson et al. (2009) by the examination of central issues such as environmental temperature estimation (Hall et al., 2013), the impacts of mass gain during cooling (Barrett, 2013), and the impacts of humidity (Bowen at al. 2011; Drelich et al., 2013). In this study, we look at another key aspect of the dating method; that of structural changes in the clay matrix induced during firing and the impact it has on the rehydroxylation process.

2. Background to ceramic rehydroxylation dating

As originally described by Wilson et al. (2009) the DHX/RHX process was discussed for kaolin, montmorillonite, and chlorite clays. During the ceramic manufacturing process raw clay may be

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fired within kilns at temperatures up to approximately 1200 °C. As the temperature is raised above ambient conditions, physically adsorbed water is lost just above 100 °C. Between 105 °C and 500 °C chemisorbed water, or bonded H_2O, is removed from the interlayers and surfaces of any mineral features (Drits and McCarthy, 2007). At 500–900 °C hydroxyl is removed as the dehydroxylation of bonded water takes place ($2OH^- \rightarrow H_2O + O^{2-}$). The temperature at which DHX initiates is dependent upon the structure of the clay matrix. The removal of water is likely a complex reaction that may include both diffusion and first-order kinetics (Ortega et al., 2010).

Once a ceramic is removed from the kiln and allowed to cool, rehydroxylation begins immediately and occurs in two stages. Initially, there is a rapid gain in mass as molecular water and hydroxyl is adsorbed onto the surface and into the pore structure of the ceramic (Stage 1). This process decreases with time and is replaced by a $t^{0.25}$ gain (Wilson et al., 2009; Hall et al., 2013; Hamilton and Hall, 2012) in mass as a result of hydroxyl migration through the boundary layers between the ceramic microcrystalline particles (Stage 2). The exact mechanism of this process is not known but is assumed to be a single-file type of solid state transport. This would account for the slow inward movement of hydroxyl over time. In laboratory mass gain experiments, the amount of available molecular water is arbitrarily restricted (Savage et al., 2008; Wilson et al., 2014) during RHX by exposing the ceramic to a low relative humidity (e.g., 30–35%) that inhibits the adsorption of excess surface water and allows the mass uptake of OH to be tracked. In archaeological contexts additional water may accumulate in the larger pore structure from rain but the excess water does not accelerate the RHX process (Wilson et al., 2009).

Encouraging dating results have emerged from the application of the RHX dating method (Wilson et al., 2009). Follow-up investigations after the initial study have identified significant deviations from the outlined protocols. Several investigations (Bowen et al., 2013; Le Goff and Gallet, 2015) have argued that the $t^{0.25}$ power law that defines the RHX rate is not always observed and that a variable exponent (t^n) is needed to account for variation in the experimental data. In addition, others note that a scrutiny of the completeness of sample drying and dehydroxylation (Le Goff and Gallet, 2014) and the effect of contaminating carbon (Numrich et al., 2015) is needed.

In contrast to advanced ceramic production, prehistoric earthenware was hardened through open firing within pits, or on the ground surface, where the surrounding fuel of wood, or dung, generated temperatures that were several hundred degrees lower than kiln environments. Ethnographic and experimental data indicate that firing temperatures may range between 300 and 900 °C (Shepard, 1976; Gosselain, 1992). In addition, the thermal gradients associated with open firing can be highly variable depending upon the fuel load, number of pots, and their physical separation. Careful monitoring with thermocouples revealed that temperature variation within a firing event may range up to 390 °C (Maggetti et al., 2011). Under such circumstances, and with many observed firing durations under two hours (Smith, 2001), the clay vessels have the potential not be full dehydroxylated, and variable in terms of clay crystalline structure.

This variability in clay structural states has the potential to impact the rate of rehydroxylation for low fired ceramics. While the self-calibrating nature of the dating process compensates for this situation by developing a hydroxyl diffusion coefficient specific to the material state, it is informative to explore the impact of structural collapse on hydroxyl diffusion, since future research may explore the development of a predictive model of RHX based upon ceramic molecular structure. Thus, we look at the dehydroxylation of kaolinite, montmorillonite and illite to determine at what temperatures critical structural changes occur and how we can identify

these temperatures in archaeological materials using infrared spectroscopic analysis. We then show how these structural changes impact the subsequent OH diffusion process as reflected by the changes in activation energy of RHX.

3. Dehydroxylation and structural change in kaolinite, montmorillonite, and illite

Kaolinite, montmorillonite, and illite were some of the most common minerals used in the manufacture of prehistoric ceramics, and as such, understanding structural and mineralogical changes during heating is central to the process. The thermal treatment of clay has been extensively investigated and reveals how the mechanisms of water loss vary between kaolinite, montmorillonite, and illite. We summarize this previous research to identify changes in ceramic molecular structure with temperature and hypothesize how this might impact the RHX process.

3.1. Kaolinite

Kaolinite, a dioctahedral 1:1 clay with the formula $Al_2Si_2O_5(OH)_4$. Its dehydroxylation has been thoroughly studied with a variety of analytical techniques including scanning electron microscopy [SEM] (Felicissimo et al., 2010), X-ray diffraction [XRD] (Marghussian et al., 2009) and Fourier transform infrared spectroscopy [FTIR] (Frost and Vassallo, 1996). This type of clay is known to be an inorganic polymer with a two-dimensional layered structure (Frost et al., 2003). In each layer, a sheet of SiO_2 tetrahedra is bonded at the apices of the tetrahedral to a sheet of aluminum (III) octahedra with four of the six octahedral sites occupied by hydroxyl groups. Two of every three aluminum octahedral sites are occupied resulting in lattice distortion which lowers the crystal symmetry. A direct result of the low symmetry is the rich FTIR spectrum of kaolinite. The intra-layer of the hydroxyls is located in the same plane as the apical oxygen, while the remaining three hydroxyls are directed toward the interlayer space and hydrogen bond with the silica of the adjoining layer. This accounts for the lack of water in the interlayer space.

After the loss of physically absorbed water between 100 and 200 °C, the hydroxyl from the inner and inner-surface migrates to the exterior and dehydroxylates endothermically at temperatures between 450 and 600 °C (Zemenova et al., 2014). This temperature range applies to both ordered and disordered kaolinites (Bellotto et al., 1995). Beginning in this temperature range there is a structural reorganization during DHX where metakaolin is formed. A progressive distortion and collapse of the clay 1:1 structure occurs as OH is removed and the metakaolin nucleates. At this point the interlaminar channels that allow water to be removed are blocked (Ortega et al., 2010; Sperinek et al., 2011). This results in some residual OH remaining in the ceramic. The metakaolin becomes progressively a less layered structure as temperature increases.

The next phase transformation occurs at about 950 °C when spinel is formed. This is followed by a transformation to mullite between 950 and 1100 °C. At the end of this process a nearly water free, highly vitrified ceramic is produced. For ceramics fired at temperatures below 950 °C, we can conceive of the kaolin molecular structure as a continuum exhibiting varying degrees of deformation and channel blockage (Pesova et al., 2010).

3.2. Montmorillonite

Montmorillonites are a type of 2:1 dioctahedral phyllosilicates with the general formula: $(Al_{(2-y)}Mg_y)$ $(Si_{(4-x)}Al_x)$ $O_{10}(OH)_2M_{(x+y)}\cdot nH_2O$, where $y > x$ an M represents interlayer exchangeable cations. These clays are somewhat turbostratic (Viani