

## Dating fired-clay ceramics using long-term power law rehydroxylation kinetics

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Fired-clay materials such as brick, tile and ceramic artefacts are found widely in archaeological deposits. The slow progressive chemical recombination of ceramics with environmental moisture (rehydroxylation) provides the basis for archaeological dating. Rehydroxylation rates are described by a (time)<sup>1/4</sup> power law. A ceramic sample may be dated by first heating it to determine its lifetime water mass gain, and then exposing it to water vapour to measure its mass gain rate and hence its individual rehydroxylation kinetic constant. The kinetic constant depends on temperature. Mean lifetime temperatures are estimated from historical meteorological data. Calculated ages of samples of established provenance from Roman to modern dates agree excellently with assigned (known) ages. This agreement shows that the power law holds precisely on millennial time scales. The power law exponent is accurately 1/4, consistent with the theory of fractional (anomalous) 'single-file' diffusion.

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Dating methods are of paramount importance in the earth and environmental sciences, palaeontology, archaeology and art history. Laboratory-based dating of any material depends on identifying and measuring a physico-chemical property, which changes in a predictable way with time, thus providing the material with an internal clock (as in radiometric dating). It is established (Cole 1962; Wilson *et al.* 2003) that the fired-clay ceramics produced in the manufacture of bricks, tiles and pottery gain mass and expand continuously from the time of firing as a result of chemical recombination with environmental moisture (here described as rehydroxylation). Furthermore, these ceramics can be returned to their initial as-fired condition by heating to a suitable high temperature. We have shown (Wilson *et al.* 2003; Savage *et al.* 2008) that in experiments lasting up to a few weeks both mass gain and expansion increase linearly with (time)<sup>1/4</sup>. There are

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also indications (Wilson *et al.* 2003) that this relation holds over much longer time scales. We now exploit this  $t^{1/4}$  power law to provide a method of determining the age of ceramic artefacts. The measurement of mass gain kinetics, together with total mass gain since manufacture (obtained by reheating), provides an accurate self-calibrating method of archaeological ceramic dating. Our experimental data show the significance of environmental temperature on the kinetics of mass gain, with activation energy consistent with a chemical recombination mechanism. Our highly precise mass gain data coupled with the correctness of our dating results show the validity of the  $t^{1/4}$  law over all practical time scales. The results on a series of specimens of known age up to 2000 years demonstrate the power of what we term *rehydroxylation* dating.

A wide variety of clay raw materials is used in making brick and tile but, most commonly (Prentice 1990; Hall 1996), the main clay mineral components are kaolinite, illite and chlorite. During firing, the green clay first loses weakly bound molecular water and then at temperatures in the range 450–900°C water is lost from the octahedral sheets by chemical dehydroxylation  $2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}^{2-}$ . At higher temperatures, further reactions occur to form anhydrous minerals such as spinels, mullite and wollastonite (Rodriguez-Navarro *et al.* 2003; McConville & Lee 2005; Traoré *et al.* 2006). However, in heavy clay ceramics these reactions are evidently incomplete (Cultrone *et al.* 2001; Bauluz *et al.* 2004). After cooling, slow rehydroxylation of partially reacted material occurs (Cole 1962; Heller *et al.* 1962; Shoval *et al.* 1991). Studies of individual pure clays (Grim & Bradley 1948; Wang *et al.* 2002; Carroll *et al.* 2005) show that the dehydroxylation temperature depends on the mineralogy and in particular the stereochemistry of the clays, *trans*-vacancy *tv* hydroxyl structures being more easily dehydrated than *cis*-vacancy *cv* configurations (Drits *et al.* 1995; Stackhouse *et al.* 2004; Molina-Montes *et al.* 2008). It is accepted that for kaolinite, illite and montmorillonite there is a structural reorganization on dehydroxylation (Muller *et al.* 2000) so that when dehydroxylated clay is rehydroxylated the reformed structure is predominantly *tv*, and in any subsequent heating cycle the dehydroxylation occurs at around 450–550°C.

It is now established that the rate of rehydroxylation of ceramics is described by a (time) $^{1/4}$  power law (Wilson *et al.* 2003). Two distinct stages are seen (Savage *et al.* 2008) when ceramics, both in the freshly fired state and after reheating, react with environmental moisture. The brief first stage, which lasts only for a few hours, is much more rapid than the second stage, which continues indefinitely. Figure 1 shows mass gain data obtained on a reheated medieval fired-clay brick which show these characteristic features. A careful analysis of these high-precision data shows that the power law exponent is indeed accurately  $1/4$ , not  $1/2$  as expected for a classical Brownian diffusion process. Such anomalous diffusion is often found where particles move in highly restricted geometries or are subject to long waiting times between jumps caused by trapping. In particular, in single-file diffusion on a linear structure, the motion of each particle is impeded by the neighbouring particles in the file and for this particular case (Richards 1977; Lizana & Ambjörnsson 2008), the root mean square particle displacement grows as  $t^{1/4}$ . In such a fractional diffusion process, after a transient at early times, the cumulative absorption (Gerolymatou *et al.* 2006) of an initially empty system with a constant concentration boundary condition scales as  $t^{1/4}$  as we observe. In these fired-clay ceramics, water as vapour or

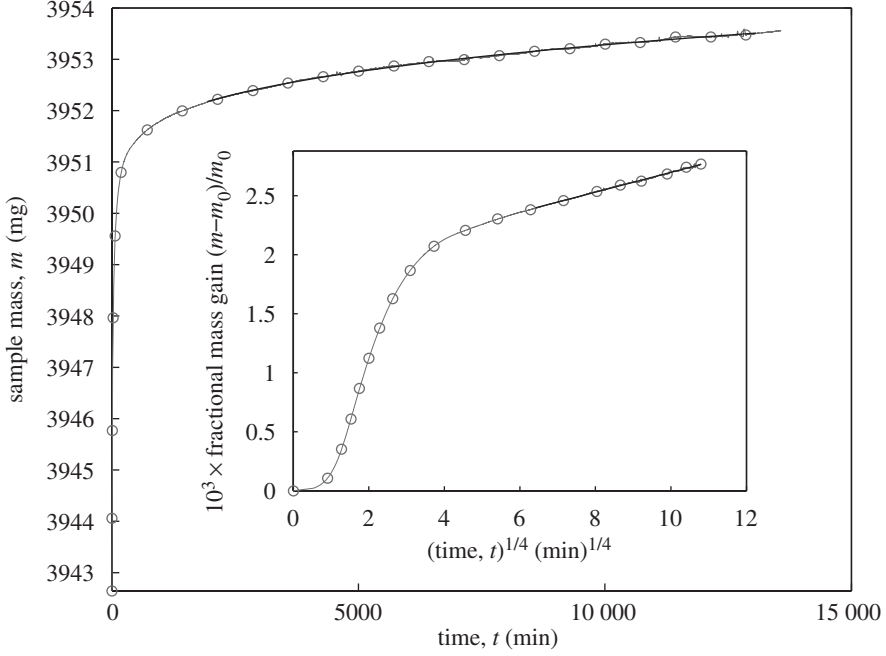


Figure 1. Rehydroxylation kinetics of reheated fired-clay brick. Main figure: mass  $m$  versus time  $t$  for a fired-clay tile during rehydroxylation; sample from St Bride's Church, Fleet Street, London, UK (Museum of London, WFG62 Penn floor tile), assigned date AD 1350–1390. Mass  $m$  at 25°C and 35% relative humidity recorded over a period of 9.1 days.  $m(t)$  measured at 30 s intervals (continuous light line); sample of equally spaced data points (circles). Heavy black line is the least-squares fit of data from 1.3–9.1 days to equation  $m - m_0 = at^b + c$  with parameters  $a = 0.3117$ ,  $b = 0.254$ ,  $c = 3950.0$  mg. Inset figure: data of main figure plotted as fractional mass gain  $(m(t) - m_0)/m_0$  against  $t^{1/4}$ ; sample of equally spaced data points (circles).

liquid readily permeates the entire macropore system to maintain this boundary condition. The rate-determining rehydroxylation reaction must proceed by ultra-slow nanoscale solid-state transport from the macropore surfaces into amorphous or clay dehydroxylate components.

As far as the dating process is concerned (and likewise for engineering applications of the  $t^{1/4}$  law, such as the calculation of moisture expansion stress in brick structures), it is the measurement of the rate of rehydroxylation in the second stage that is critical. We write the following kinetic equation for the second stage:

$$y = \frac{m(t) - \beta}{m_0} = \alpha(T)t^{1/4},$$

where  $m(t)$  is the sample mass,  $m_0$  the sample mass after reheating,  $\alpha$  a kinetic constant and  $t$  the elapsed time. The quantity  $\beta = m_1 - \alpha t_1^{1/4}$ , where  $m_1$  is the sample mass at the end of the first stage at  $t = t_1$ . We obtain  $\beta$  most easily as the intercept of the second stage line at  $t = 0$ . The rehydroxylation rate constant  $\alpha$  is insensitive to water vapour pressure at all normal environmental

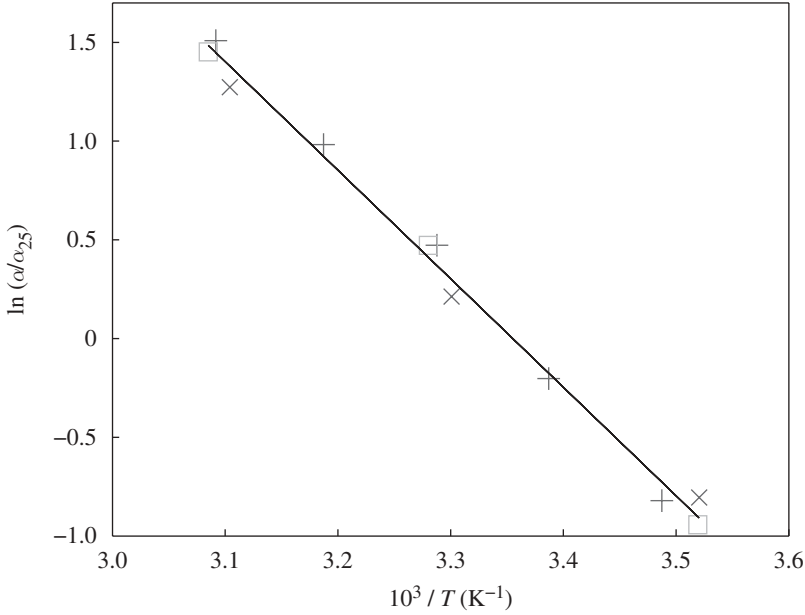


Figure 2. Arrhenius plot: effect of temperature on rehydroxylation mass gain rate. Normalized stage 2 slope  $\ln(\alpha/\alpha_{25})$  plotted against  $10^3/T(\text{K}^{-1})$ , where  $\alpha_{25}$  is the interpolated slope at  $25^\circ\text{C}$ , for three fired-clay brick and tile samples. +, Roman *opus spicatum* clay paving brick, London; x, ‘Westminster’ clay tile, Merton Priory; □, clay brick, King Charles II Court, Greenwich. For full details of provenance of specimens, see figure 4.

levels (Wilson *et al.* 2003). This is because the long-term uptake of water is both small and slow so that the water demand is extremely modest; and because the rehydroxylation rate is controlled entirely by internal processes and does not increase when water is available in excess in the microenvironment. However, the rate does increase markedly with temperature.  $\alpha$  measured from  $14$  to  $50^\circ\text{C}$  shows Arrhenius behaviour (figure 2). We find that the derived activation energy  $E_a = \mathbf{R} d \ln(\alpha^4) / d(1/T)$  is  $182 \pm 5$  (s.e.,  $n = 11$ ) kJ/mol for three different fired-clay brick ceramics ( $T$ , absolute temperature;  $\mathbf{R}$ , gas constant). The magnitude of  $E_a$  indicates a chemical rate-determining process. Similar activation energies have been reported for the high-temperature dehydroxylation reactions in kaolinite (Bellotto *et al.* 1995) and illite (Gualtieri & Ferrari 2006).

We show the principle of the dating method in figure 3. The measured initial mass of the sample is the sum of the original mass of the as-fired material and the mass of water that has chemically combined with it over its lifetime. The older the sample, the greater is the mass it has gained by slow rehydroxylation and thus the greater is the mass it loses during heating at  $500^\circ\text{C}$  as a result of dehydroxylation. Following re-exposure to environmental moisture, the material once again gains mass in accordance with the two-stage (time) $^{1/4}$  law. The age of the sample is established by extrapolating the second-stage mass data to find the time needed to regain the mass lost during heating. The method is thus self-calibrating, and the influence of firing temperature, mineralogy and microstructure is consequently eliminated.

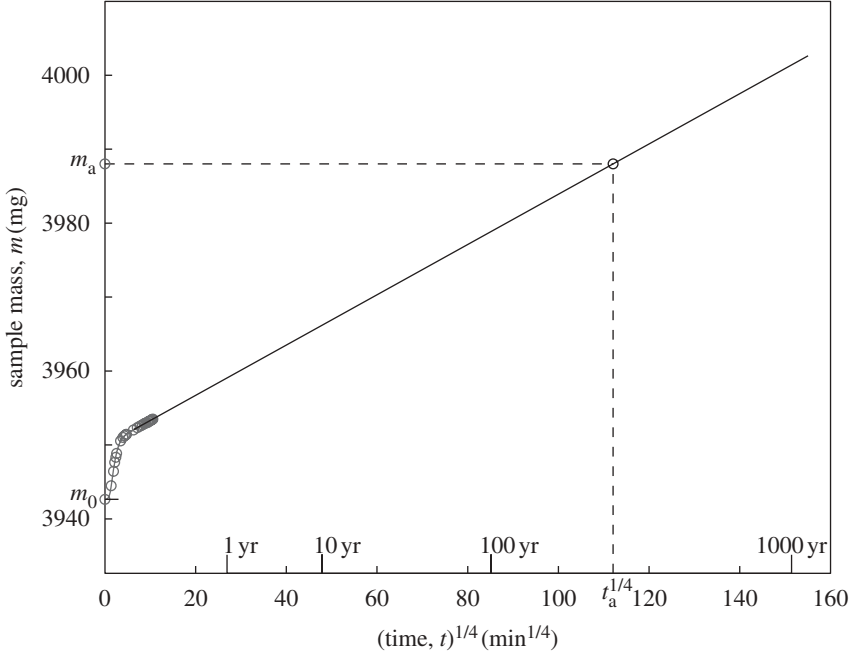


Figure 3. Schematic of rehydroxylation dating method. Typical experimental mass gain data (circles) show linear dependence of  $m$  on  $t^{1/4}$ . The calculated age  $t_a$  (here 300 years for illustration only) is obtained by extrapolating to the initial mass  $m_a$ .

The dating methodology follows directly. We take a sample of ceramic material (typically 3–5 g) and after removing any loose debris condition it to remove capillary water by heating at 105°C to constant (‘initial as-received’) mass  $m_a$ . The sample is then heated to 500°C for 4 h. The mass after reheating is  $m_0$ . Next, the sample is transferred to a microbalance where it cools and is exposed to water vapour (at controlled temperature and relative humidity) to determine the kinetics of mass gain by recombination with water. Data are collected for sufficient time (typically 2–4 days) to allow the mass gain rate to become constant. We use an ultra-high accuracy recording microbalance (CiSorp Water Sorption Analyser, CI Electronics) with a capacity of 5 g, weighing to 0.1  $\mu$ g under precisely controlled conditions of relative humidity (normally  $30.0 \pm 0.1\%$  RH) and temperature ( $\pm 0.2^\circ\text{C}$ ). The chamber and sample temperatures are matched to the long-term mean temperature  $T_a$  that the ceramic material has experienced since manufacture. Here we have considered data (Parker *et al.* 1992) for mean annual ground and air temperatures at several stations in southern England and set  $T_a = 11^\circ\text{C}$ . We calculate from these experimental quantities the kinetic constant  $\alpha(T_a)$  using the equation. The estimated age of the sample  $t_a$  is then  $(y_a/\alpha)^4$  where  $y_a = (m_a - \beta)/m_0$ .

In figure 4, we show the fundamental dating relation where  $t_a^{1/4} = (y_a/\alpha)$  is plotted against (assigned age)<sup>1/4</sup> for brick and tile samples of widely different ages. All samples fall close to the master line. The excellent agreement between calculated and assigned ages provides direct evidence that the  $t^{1/4}$  kinetic law extends to times as great as 2000 years. On a clay brick specimen (c in figure 4)

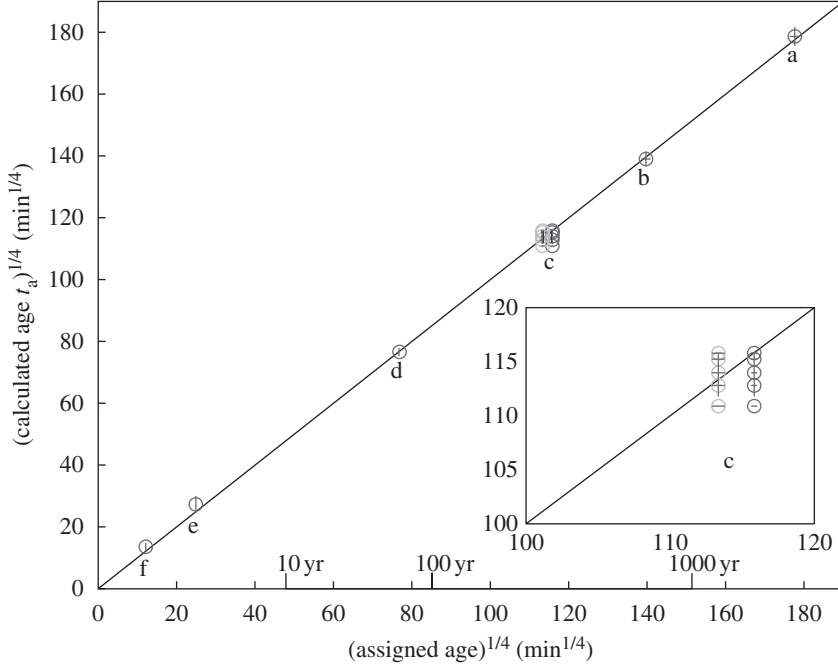


Figure 4. Master plot of ages: comparison of calculated and assigned ages.  $(\text{calculated age } t_a)^{1/4}$ ,  $y_a/\alpha$ , is compared with archaeologically assigned ('known') age for fired-clay brick and tile samples. Horizontal bars indicate the range of assigned ages; vertical bars show the probable error,  $\pm 1$  s.d., based on statistics of replicate determinations. a: Roman *opus spicatum* clay paving brick, 12 Arthur Street, London, UK (Swift 2008) (Museum of London, AUT01 fabric 2452), assigned date AD 50–160;  $\alpha$   $2.3042 \times 10^{-4} \text{ min}^{-1/4}$ ,  $m_0$  3.9345 g. b: Westminster floor tile (Betts 2002), Augustinian Priory of St Mary Merton, Surrey, UK (Miller & Saxby 2007) (Museum of London, MPY86), assigned date AD 1250–1300;  $\alpha$   $2.7008 \times 10^{-4} \text{ min}^{-1/4}$ ,  $m_0$  3.1580 g. c: Clay brick, King Charles II Building, Greenwich, UK (Museum of London), construction AD 1664–1669, reconstruction AD 1690s; mean  $\alpha$   $1.4648 \times 10^{-4} \text{ min}^{-1/4}$ , mean  $m_0$  3.9394 g ( $n = 5$ ). d: Clay brick recovered in AD 2003 from an archaeological investigation of Whitefriars Priory site, Canterbury, UK (Museum of London);  $\alpha$   $2.6573 \times 10^{-4} \text{ min}^{-1/4}$ ,  $m_0$  3.9405 g. Surface vitrification of sand suggests that the brick had, at some time, been exposed to fire. The rehydroxylation dating age of approximately 66 years is consistent with the specimen having been heated to at least 500°C in AD 1942, when the site was subject to intense incendiary and high explosive bombing on 31 May/1 June. e: Chester Red clay brick, Ibstock Brick Ltd, UK; age determined 268 days after date of manufacture (May 2005) following storage under ambient laboratory conditions;  $\alpha$   $1.1327 \times 10^{-4} \text{ min}^{-1/4}$ ,  $m_0$  1.28007 kg (moisture regain measurements made on a whole brick over 15 days also under ambient laboratory conditions using a top loading balance). f: Westminster tile (as b above), dated 15 days after reheating;  $\alpha$   $3.4343 \times 10^{-4} \text{ min}^{-1/4}$ ,  $m_0$  3.8412 g. The inset shows replicate determinations of the age of sample c plotted against the alternative assigned ages.

in five repeat determinations of the quantities  $m_a$ ,  $m_0$  and  $\alpha$ , we obtained an estimated age of  $318 \pm 22$  years (s.d.,  $n = 5$ ), corresponding to a rehydroxylation date of AD  $1691 \pm 22$ . The sample, provided as a blind test by the Museum of London, originated from the King Charles II building in Greenwich, constructed in 1664–1669, and altered to some extent by Wren in the 1690s. Our result

tends to indicate that the material was from the reconstruction. The estimate of uncertainty is of course based solely on repeatability. This is the type A uncertainty of Bailiff (2007). The choice of mean lifetime temperature provides the main other source of uncertainty, but we are unable to quantify the uncertainty in this temperature at present.

The dating method described has several valuable features. These offer the prospect of some advantages over established but complex luminescence methods for ceramic dating (Bailiff 2007). Being a gravimetric technique, it is rather simple. It is essentially self-calibrating, and is based on a precise kinetic law. The rehydroxylation process is so slow that it is readily sustained by minimal concentrations of environmental moisture. In these respects, the method may be superior to obsidian dating of glass (Rogers 2008). The only ancillary information needed to calculate the age of the sample is an estimate of its mean lifetime temperature. As we show, it appears that regional meteorological records are adequate for this purpose. On the other hand, for samples of known age the method can be inverted to provide an estimate of the mean lifetime temperature through the Arrhenius behaviour of the rate constant. Such an estimate may itself have value, for example in climate studies. We note also that for materials that have been exposed to extreme heat or fire conditions during their lifetime (temperatures greater than 500°C: for example, sample d, figure 4) the dating clock is reset.

We emphasize also that the agreement between calculated and assigned ages provides powerful evidence that the kinetic power law holds precisely for time scales of several thousand years. Thus, remarkably, the underlying anomalous diffusion also operates on a millennial time scale. Over such a period, the total rehydroxylation mass gain is typically 1–2% of the sample mass. This is considerably less than the ultimate rehydroxylation capacity of a fired-clay ceramic estimated from the known dehydroxylation mass loss (Gualtieri & Ferrari 2006; Heide & Földvari 2006), so that dating of material of greater ages (say, at least 10 000 years) is entirely possible.

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