

Rehydroxylation (RHX) Dating of Archaeological Ceramics

Murray Moinester, Tel Aviv University
8 March 2017, Leipzig RHX Workshop



Sächsische Akademie
der Wissenschaften zu Leipzig



*Searching for a
Precision Dating Clock
for Archaeological Ceramics*



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

Moira A. Wilson, Margaret A. Carter, Christopher Hall, William D. Hoff, Ceren Ince, Shaun D. Savage, Bernard McKay and Ian M. Betts

Proc. R. Soc. A published online 27 May 2009

doi: 10.1098/rspa.2009.0117

The $t^{1/4}$ model

Moisture expansion obeys model over long time scales:

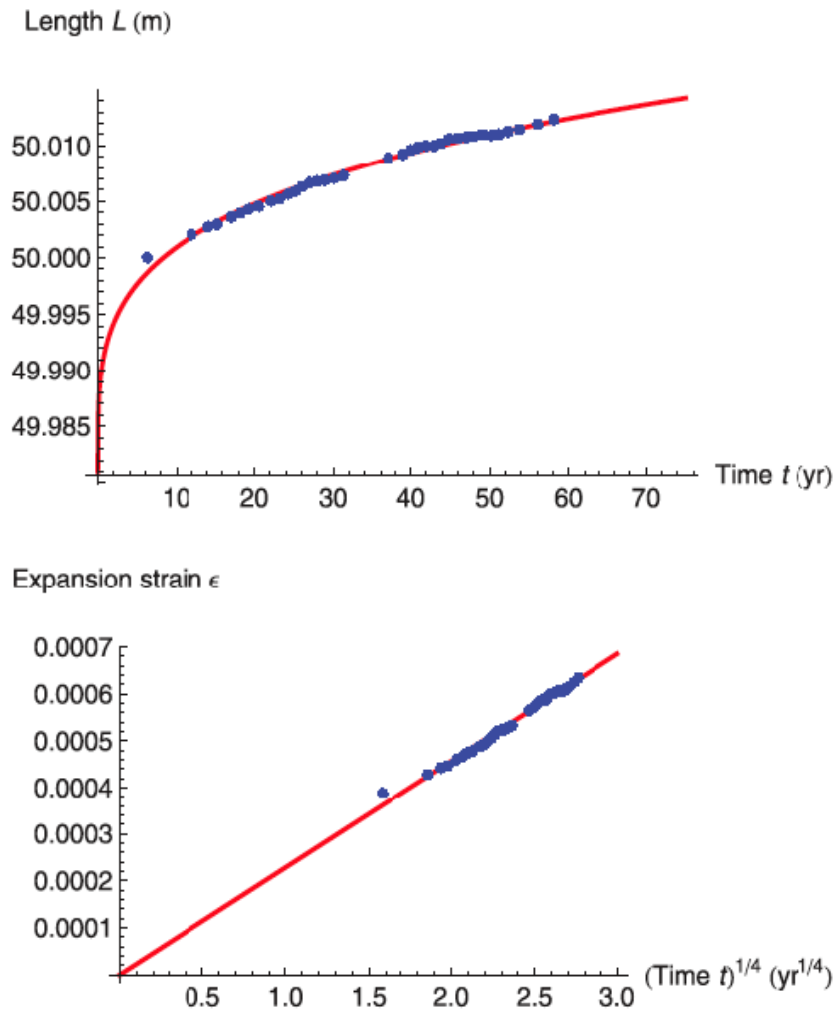


Fig. 6. 58-year moisture expansion of NPL standardizing bench (data of Cole¹⁶ replotted) fitted to the power law model, Eq. 3, with t measured from 1908. Top: Change in 50 m gauge length L versus time t ; fitted curve $L = L_0 + 0.01142t^{1/4}$ with $L_0 = 49.9806$ m. Bottom: Expansive strain ϵ versus $t^{1/4}$; fitted curve $\epsilon = L/L_0 - 1 = 0.0002285t^{1/4}$.

But $1/4$ power difficult to determine by fit!

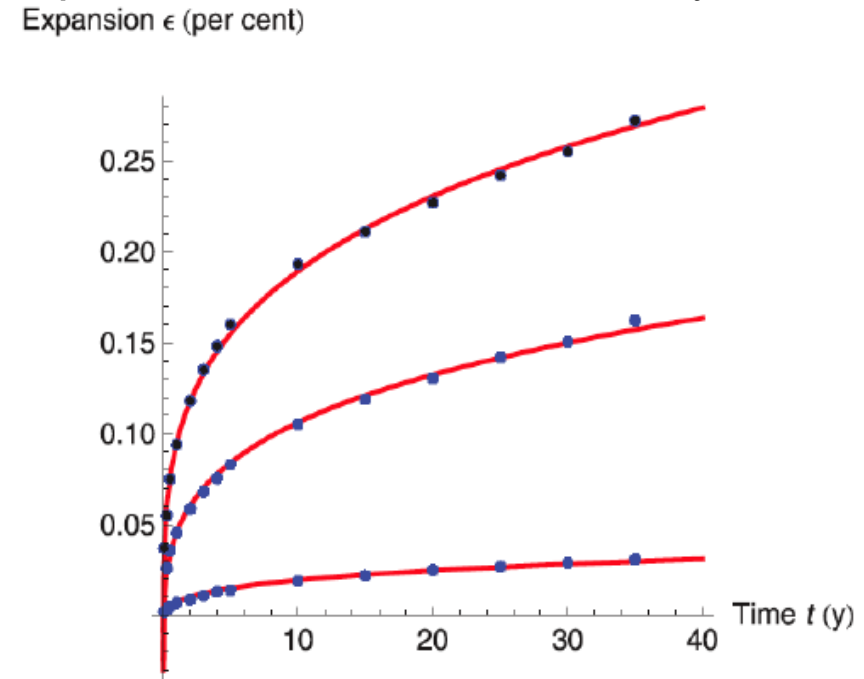


Fig. 1. 35-year moisture expansion of Australian fired-clay bricks: data (points) from Zsembery *et al.*¹⁰ Middle: The mean natural expansion of the entire set of over 300 bricks over 35 years; Top: The mean natural expansion of the group with 0.075% steam autoclave expansion; Bottom: The mean natural expansion of the 0.005% steam autoclave group. The curves are fits to the power law model, Eq. 3.



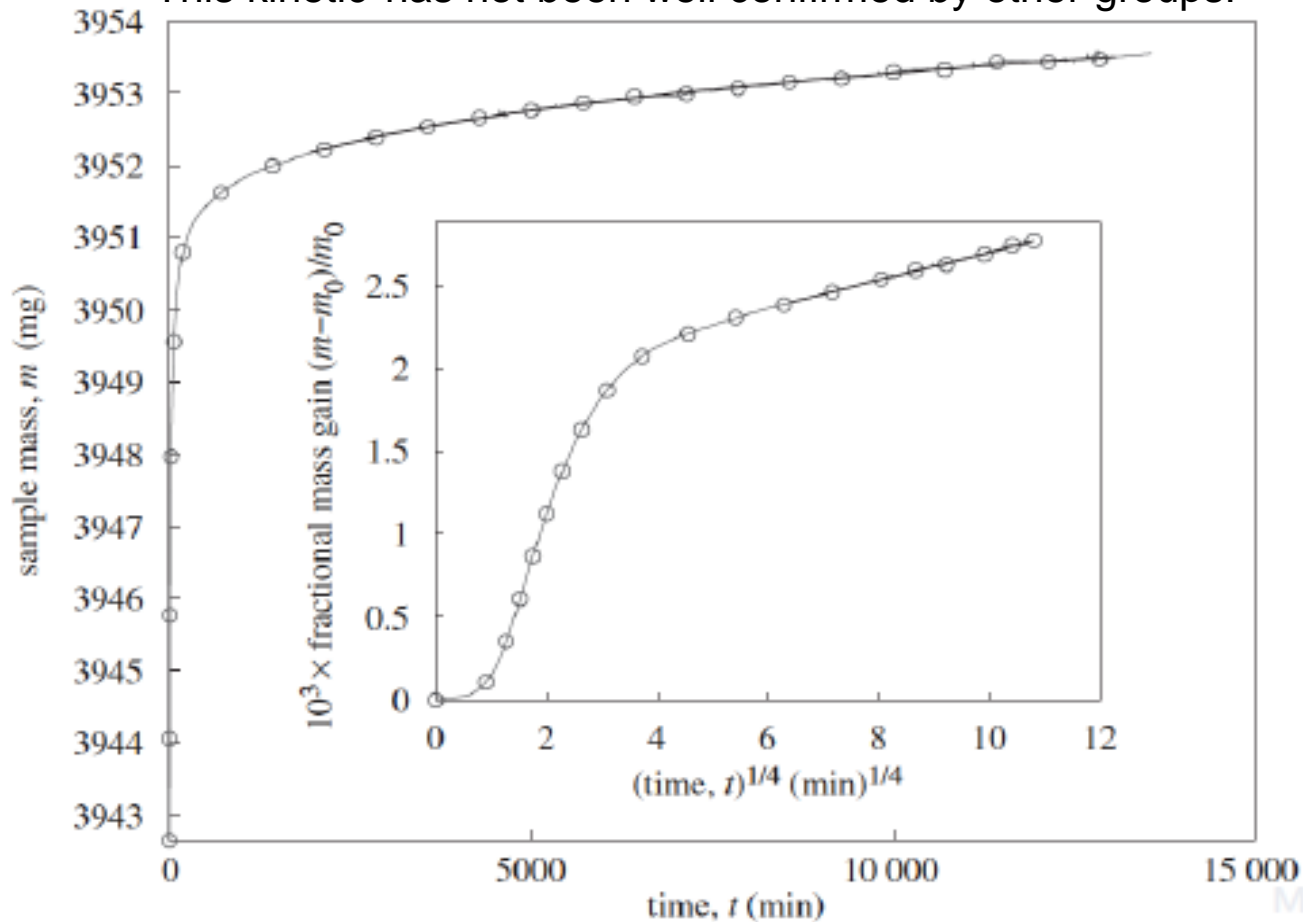
Savage, S. D., Wilson, M. A., et al., 2008.

Mass Gain due to the Chemical Recombination of Water in Fired Clay Brick.

Journal of the European Ceramic Society 91, 3396-3398.

Mass gain also obeys this kinetic model. However, this proceeds in two stages due to rapid initial uptake of weakly-held molecular water.

This kinetic has not been well confirmed by other groups!



A little bit of mathematics...

Given the RHX rate equation for mass gain ' y_a ':

$$y_a = \alpha(T) t_a^{1/4}, \quad (4)$$

and rearranging, we can solve for time:

$$t_a = (Y_a/\alpha)^4$$

The kinetic constant, $\alpha(T)$, depends on temperature. Operationally, this is measured at the effective lifetime temperature of the material, $\alpha(m)$. We also make the approximation that $y_a \approx m_2 - m_4$.

RHX date equation

Actually, Y_a generally is fractional mass gain

$$t_a = ((m_2 - m_4)/\alpha)^4$$

How we currently get m_2 , m_4 and α_m .

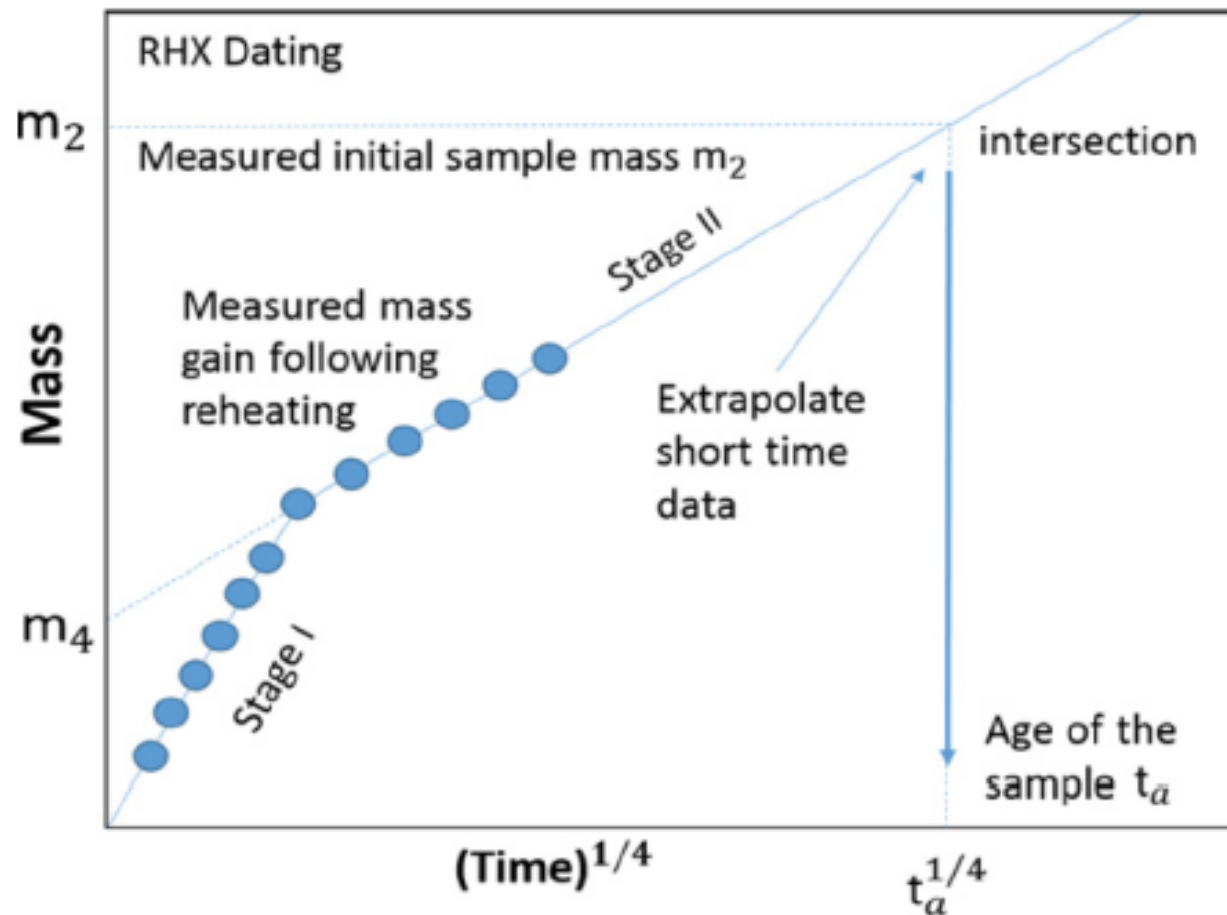


Fig. 1. Schematic of RHX dating method. Data show characteristic two-stage mass gain process, Stage II of which is used for the RHX age determination.

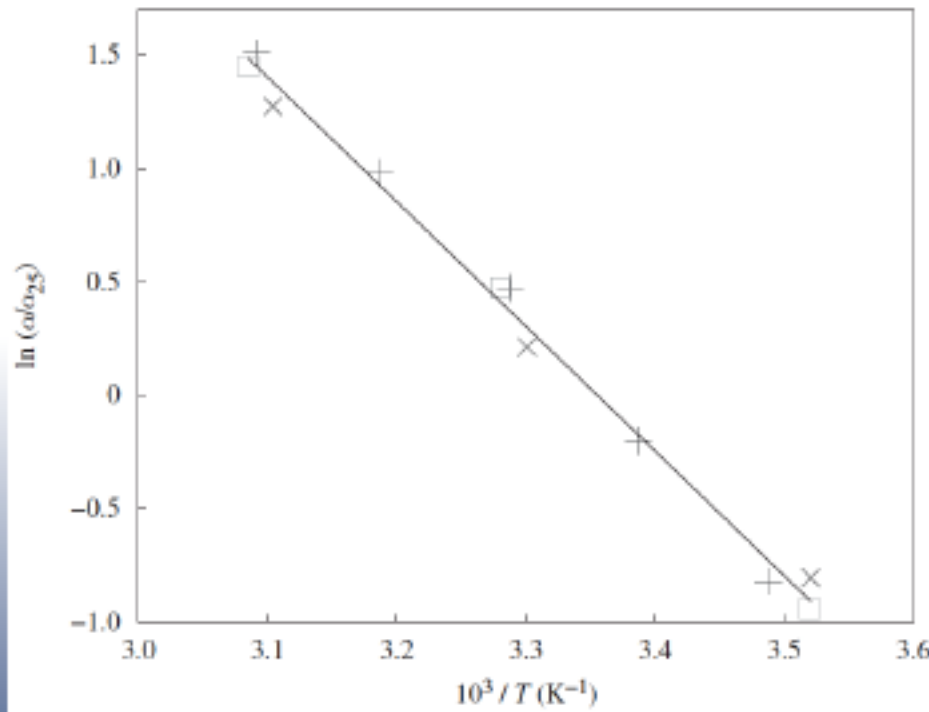
$y_a = m_2 - m_4$ and $m(t) = m_4 + \alpha_m t^{1/4}$ once gradient $dm/dt^{1/4}$ stabilises.

Corrections for temperature history

$$\frac{d \ln \alpha}{d(1/T)} = -\frac{E_a}{4R} \quad (7)$$

Need value at ELT!

$$\alpha(T) = \alpha_m e^{-\frac{E_a}{4R} \left(\frac{1}{T} - \frac{1}{T_m} \right)} \quad (8)$$



From Wilson et al., 2009, provides evidence for sub-diffusive regime, but does not prove quartic root dependence.

Sample Chemical Pre-treatment Required

Potential issues exist with organic burnoff and calcite mass loss, plus other forms of hydration. Can try to remove contaminants by chemical pre-treatment. Numrich et al. studied these issues. However, chemical treatment may affect structural OH, and therefore RHX Dating!

- 1) Acid pre-treatment uses dilute HCL to remove insoluble non-contemporaneous carbonates: $\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$.
Need to prevent decomposition to $\text{CaO} + \text{CO}_2$.
- 2) Wet oxidation removes organic carbon residues to prevent their oxidation when heating to CO_2 , and subsequent mass loss, which affects ya.
Uses Hydrogen Peroxide (H_2O_2) to oxidize Carbon.
- 3) Base treatment uses NaOH to dissolves humic acids, which come from organic constituents of soil produced by biodegradation of dead organic matter.

RHX Dating of Archeological Ceramics Via a New Method to Determine Effective Lifetime Temperature

Murray Moynester,[†] Eli Piasetzky, and Michael Braverman

R. & B. Sackler Faculty of Exact Sciences, School of Physics and Astronomy, Tel Aviv University, Tel Aviv 69978, Israel

NOVEL Effective LifeTime (ELT) Determination

- ELT uncertainty is a major component of the overall dating uncertainty.
- SAS Method (Same Age Samples) determines ELT and Age.
- SAS requires measuring RHX mass gain rate of two Same Age Samples at two temperatures.

SAS Method: Moinester, M., Piasezky, E., & Braverman, M.

(2015). RHX Dating of Archeological Ceramics Via a New Method to Determine Effective Lifetime Temperature, *Journal of the American Ceramic Society*, 98, 913-919.

1) Determine Activation Energy (Sample **b**) by mass gain rate measurements at two temperatures:
 $\alpha(T) = A \exp(-E/4RT)$.

$$\alpha_b(T1)/\alpha_b(T2) = \exp(-E_b[1/T1 - 1/T2]/4R),$$

$E_b = 4R \ln(\alpha_b(T1)/\alpha_b(T2)) / (1/T2 - 1/T1)$, with similar equation for sample **c**.

2) Ceramic's **age** is determined via: $t_a = (m_a/\alpha(T_e))^4$, where $m_a = m_2 - m_4$ (OH Mass).
 $\alpha(T1)/\alpha(T_e) = \exp[E(1/T_e - 1/T1)/4R]$.

$$t_a b(T1) = m_a b^4 \exp[E_b(1/T_e - 1/T1)/R] / \alpha_b(T1)^4$$

$$t_a c(T1) = m_a c^4 \exp[E_c(1/T_e - 1/T1)/R] / \alpha_c(T1)^4 \quad (\text{with } T2, \text{ get 4 Age determinations})$$

3) Effective Lifetime Temperature **ELT (Te) Determination:** Since $t_a b(T1) = t_a c(T1)$,

$$T_e = \frac{E_b - E_c}{4R \ln \frac{\alpha_b(T1)}{\alpha_c(T1)} + 4R \ln \frac{m_{ac}}{m_{ab}} + \frac{E_b}{T_1} - \frac{E_c}{T_1}} \quad \text{Eq. 10.1} \quad \text{with similar equation for } T2$$

For measurements of samples b and c at temperatures T1 and T2, if the two samples have the same age, Te is well determined.

SAS Conclusions:

Age and ELT uncertainties depend on uncertainties in $M(\text{OH})$, mass gain rate $\sigma(\alpha)$, and $\sigma(E)$. Dominant uncertainty is $\sigma(\alpha)$.

For $\sigma(\alpha) \leq 2 \times 10^{-7} \mu\text{g-hr}^{-1/4}$, ELT determined to ~ 0.2 K, per cent age error is 1.4%, 43 years for 3000 year old ceramic.

Test SAS method with ceramics samples whose ELT and Ages are well known independently.

Caveats

Metrology

- ① *Most, if not all structural OH^- groups are removed from the clay mineral lattice in the event of initial firing.*
- ② *Subsequent reheating removes all structural OH^- groups which the material has gained over its lifetime by rehydroxylation.* Proven
- ③ *RHX is accurately described by a $t^{1/4}$ kinetic model, the kinetic constant of which depends only on temperature, provided some moisture is available.* Not Proven
- ④ *The rate of rehydroxylation measured after reheating can be isolated from the uptake or exchange of weakly-bound water, and is the same for successive reheatings.* Highly Likely
- ⑤ *It is possible to measure any additional mass lost upon reheating to combustion of organic matter/diagenetic material which the ceramic has accumulated over its lifetime.* Not Proven
- ⑥ *The lifetime temperature history of the material can be estimated... Or more robust techniques of determining T_e can be found.* SAS

Rehydration and Rehydroxylation in Ancient Ceramics: Yves Gallet and Maxime LeGoff, J. Am. Ceram. Soc., 1–7 (2015)

CAUTION: Failed to consistently observe time^{1/4} dependence. Results **differ** from Wilson, Hall et al. Suggest sorption of chemisorbed and rehydroxylated water occurs simultaneously.

$$mg(t) \sim \alpha_4 \text{ time}^{1/4} + \alpha_2 \text{ time}^{1/2}$$

T0: weakly bound molecular water (H₂O)

T1: chemisorbed water (H₂O)

T2: chemically bound water (OH Hydroxyls)

UK group see only time^{1/4}. Independent studies are needed to understand Gallet/LeGoff results.

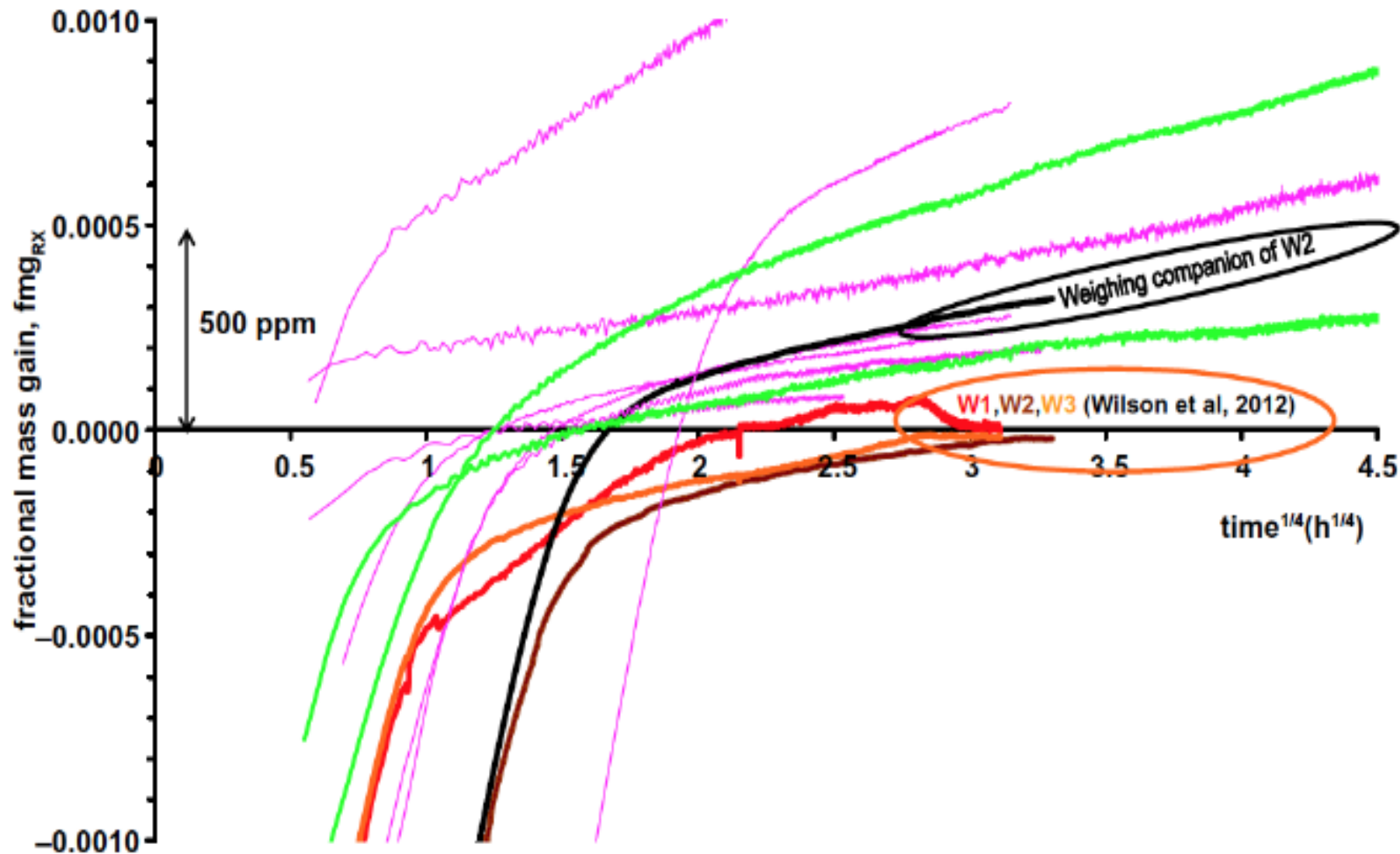


Figure 5 Examples of fractional mass-gain (fmg) data relative to m_{RX} obtained after heating at 105°C from some of our samples (the pink and green curves) and from four samples previously analysed by Wilson et al. (2012), referred to as samples W1, W2 and W3 and the weighing companion of W2. The data are plotted in $h^{1/4}$. The four samples show either an unexplained change in curvature around $2.8 h^{1/4}$ (W1, W2 and W3: the red, orange and brown curves) or a non-stabilization of the fmg data (the weighing companion of W2, black curve). (See online for a colour version of this figure.)

Recent attempts at the method

- As yet, nobody has unambiguously reproduced the results of Wilson et al (2009, 2012).
- Few studies have had adequate RH control and the necessary apparatus to perform measurements.
- This is crucial in determining the “equilibrium mass” m_2 .
- However, there seem to be other effects on m_2 which are not well understood.
- There are also strong effects due to contaminants in archaeological (specifically *buried*) pottery, which affect $m_2 - m_4$.

Testing the (time)^{1/4} diffusion law of rehydroxylation in fired clays: evidence for single-file diffusion in porous media?

Vincent J. Hare,¹ Jörg Kärger,² Murray Moinester³, Eli Piasezky³

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application, 25 (5) (2016), pp. 1–11 (diffusion-fundamentals.org)

We propose novel ways of investigating the RHX phenomenon. These include:

- (i) high-resolution NMR with aluminum and silicon as well as with protons (hydroxyls, water) for exploring structure and dynamics.
- (ii) pulsed field gradient NMR for exploring water/proton diffusivities.
- (iii) micro-imaging by IR and interference microscopy for exploring the spatial-temporal dependence of RHX.
- (iv) structural investigations by high-resolution electron microscopy and X-ray diffraction.

Infrared spectroscopy - Example

IR spectroscopy can trace diffusion of OH and H₂O molecules into a thin film of fired clay ceramics.

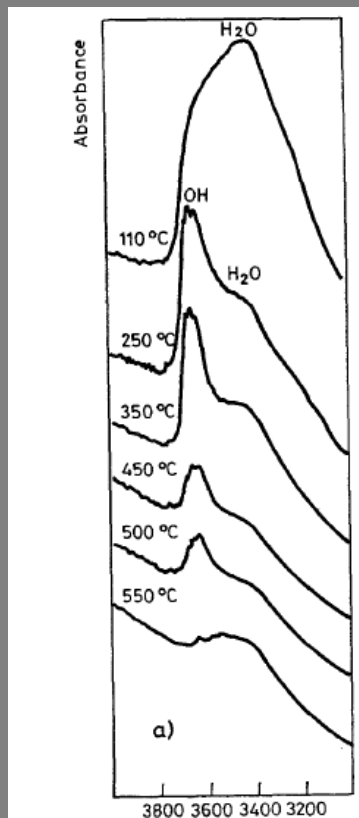
Absorption of IR light vs. wavelength determined by FTIR spectrometry transmission mode. Concentration of particular molecules in thin film proportional to intensity of its “absorption band”. Measure OH concentration (RHX rate) at Leipzig vs. time (at different laboratory temperatures) by monitoring the $\sim 3620 \text{ cm}^{-1}$ OH peak. Simultaneously, monitor T1 & T0 water at $3600\text{-}2600 \text{ cm}^{-1}$ and $\sim 1640 \text{ cm}^{-1}$. Obtain temporal diffusion information of different water types. Square or quartic root power law associated with OH and H₂O diffusion (for RHX Dating) can be tested experimentally.

Moisture expansion is REVERSIBLE



TEL AVIV UNIVERSITY

By FTIR, observe OH and H₂O bands after high temperature (550 C) heating. Absorbed OH removed, expansion strain released, increased size and mass gain lost. (Mars water study method)



Need FTIR studies to optimize heating protocols:

- (1) Weigh sample after initial heating removes H₂O;
- (2) Weigh sample again after 550C heating removes OH.
- (3) Does OH peak area increase as (time)^{1/4} ?

IR spectra of OH and water bands in pottery powder after heating at different temperature

Journal of Thermal Analysis, Vol. 37 (1991) 1579-1592

W a v e n u m b e r, c m⁻¹



Normal Brownian diffusion process $\rightarrow t^{1/2}$

\rightarrow Suggestions have been made based on $N=4$ that RHX follows diffusion in constricted geometries, **But $N=4$ NOT PROVEN**

Need to study how the RHX diffusion process works

- Junctions between sheets in clay ceramics may form restricted random pathways.
- Transport within the interlayers
- Transport along random sub-micron scale pore structures
- Diffusion through atomic lattice to get to Al reaction sites

Conclusions

- RHX process is very common in fired clay ceramics, and is most significant way that these materials undergo long-term change.
- RHX time dependence, $(time)^{1/N}$ requires further experimental and theoretical study.
- Contaminants (organic carbon, carbonates, humic acids) need to be removed for RHX by metrology. Chemicals may affect OH structure.
- Necessary to have climatic temperature data for geographical region to know the ELT, or use SAS.
- Studies planned at Leipzig to test the $(time)^{1/N}$ dependence by carrying out diffusion measurements.
- RHX Dating has potential to resolve chronological questions related to history/archaeology of Bronze & Iron ages worldwide. Knowledge of the underlying process is important for earth sciences and earth history.