Diffusion Fundamentals VI

Diffusive Spreading in Nature, Technology and Society

Basic Principles of Theory, Experiment and Application

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Testing the (time)1/4 diffusion law of hydroxylation in fired clays: evidence for sub-diffusion in porous media?

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INTRODUCTION

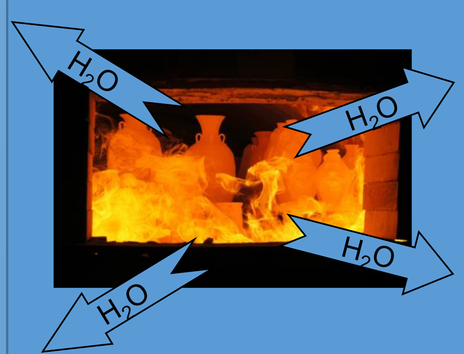
Absolute dating of ceramics is important for archaeological and historical research. Radiocarbon dating is limited to organics, and cannot therefore be used. All fired clays hydroxylate after firing; the slow uptake of structural (OH) hydroxyls in collapsed phyllosilicates continues over millenial timescales. Hydroxylation causes ceramics to expand and to increase in mass, the older the material, the more hydroxylated the ceramics and the greater the mass gain. **RHX Dating** was proposed [1,2] as a technique for dating ceramics, based on the observed ***quartic root (time)$^{1/4}$*** dependence of rehydroxylation. This may be the first experimental evidence for anomalous sub-diffusion in porous nanomedia. However, the 1/4 power law is not currently verified, and it is not known how it relates to underlying mineralogy and diffusion mechanisms in fired clays.

RHX Dating proceeds by measuring the hydroxyl mass, and the mass gain rate at the ***Effective Lifetime Temperature (ELT)*** that the ceramics experienced over its lifetime. The **ELT** can be determined using weather/climate data or the higher precision **SAS method** [3], based on RHX rate measurements at two temperatures of two ceramic samples having the same age.

RHX DATING

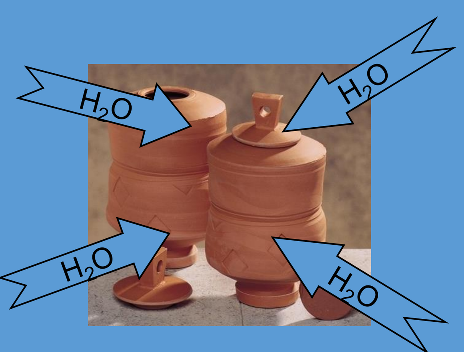
① Firing ceramic pottery in kiln removes OH hydroxyl radicals. CaO shown as example.

$Ca(OH)_2 \rightarrow CaO + H_2O$



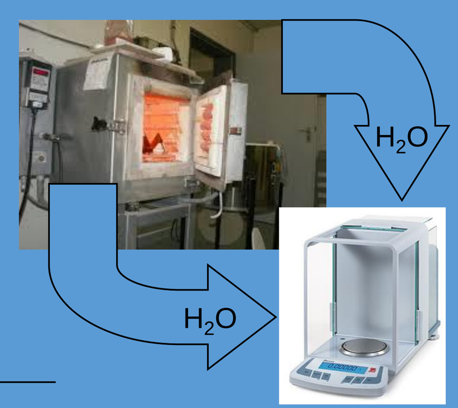
② Clay ceramics oxides and environmental moisture undergo lifetime hydroxylation

$CaO + H_2O \rightarrow Ca(OH)_2$

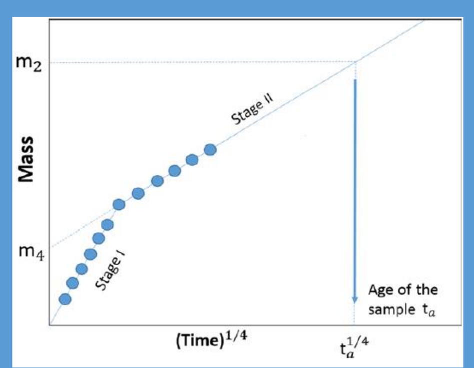


③ Dehydroxylate (DHX) sample by heating years later to measure lifetime collected OH mass.

$Ca(OH)_2 \rightarrow CaO + H_2O$



Mass gain after firing occurs in two stages [1,2].



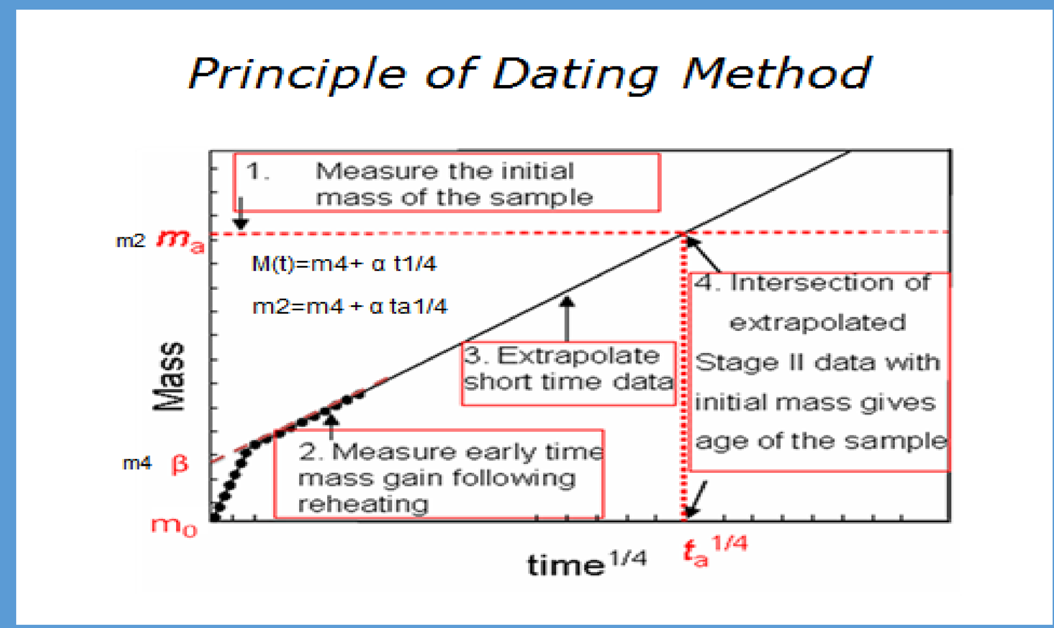
•Stage I – **rapid** (~ 2 days), Physisorbed water, weakly hydrogen-bound water molecules.

•Stage II – **very slow**, Chemisorbed water, structural hydroxyl (OH) groups.

StageII RHX mass-time dependence follows quartic root ***(time)$^{1/4}$*** time law [1,2]:

$$\Delta m = \alpha(T) \cdot t^{1/4}$$

Sample's lifetime OH mass gain Δm and mass gain rate α during rehydroxylation (RHX) at the ELT determine the sample age t_a, as shown below. "Initial" mass m_a is mass before DHX.



Sample age

$$t_a = \left(\frac{\Delta m}{\alpha(T_e)} \right)^4$$

$\Delta m = m_a - \beta$ equals lifetime OH mass gain

α(Te) is the RHX mass gain rate at the ELT (Te).

Testing the diffusion law

We do not understand the reason for the quartic root time dependence. It indicates a restricted diffusion process with constrained path to the RHX sites [4]. Anomalous (sub-diffusion) Single File Diffusion was suggested [1,2], but there is no known microstructural evidence in ceramics for such restricted pathways.

Testing Methods

We plan to test the (time)1/4 law by carrying out diffusion measurements [5]:

(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.

RHX DATING STATUS

- RHX occurs universally in all fired clay ceramics [1,2].
- Evidence for $t^{1/4}$ RHX time dependence [1,2]. But results to date are still ambiguous. Validation studies in progress.
- RHX Dating "Same Age Samples" method [3] provides more precise determinations of the Effective Lifetime Temperature and ceramic Age.
- Diffusion measurements [4,5] may clarify underlying physics mechanisms responsible for the $t^{1/4}$ dependence.
- RHX Dating has potential to resolve chronological questions related to history and archaeology worldwide.

REFERENCES

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