Rehydroxylation: a promising technique for ceramic dating

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Abstract. The kinetics of expansion in ceramic materials due to rehydration and rehydroxylation was investigated since the early XX century as a cause of crazing in glazed ceramics. Since then, the study of expansion and mass gain of ceramic has been studied extending the monitored times and modeling the involved processes. In the last 20 years, the interest in this process grew due to its possible application in the dating field, supporting well-established techniques such as thermoluminescence and optically stimulated luminescence. The principle of the dating technique is based on the fact that after the firing all water and hydroxyl molecules are desorbed from the ceramic structure, and after cooling are slowly adsorbed following a mathematical law. Nowadays, the correlation between time and mass gain is well established, but there is still no agreement on the mathematical model of the rehydroxylation process, and on a reliable protocol to date the materials. However, promising results have been reached, and more efforts must be put into the study of the role of involved parameters (storage temperature, activation energy, experimental setup…). Considerations on the last point will be shown, together with experimental evidence collected at Lambda (Laboratory of Milano Bicocca university for Dating and Archaeometry).

1. Introduction

The effect of water adsorption in ceramic matrices was firstly investigated as the cause for crazing in glazed ceramics [1] and was later studied in bricks and masonry materials. In 2003 Wilson et al. [2] proposed an expansion model in which the dimensions of ceramic samples follow a $t^{1/4}$ linear correlation, opening the way for a new dating technique that could support existing and well-established techniques such as thermoluminescence and optically stimulated luminescence. Following studies related the matrix expansion to a mass gain that could be described as a two-step process [3]: firstly, water molecules are adsorbed by the pores of the structure, and after a transient period the rehydroxylation process begins, where hydroxyl groups chemically bond with the lattice, diffusing in the octahedral sites (figure 1). The kinetics of the diffusion process depends on the activation energy only, which in turn depends on the temperature of the environment.

The main advantage of this technique is its auto consistency: the parameters needed for age evaluation are acquired during the measurement itself, regardless of environmental moisture or chemical composition; moreover, the amount of material needed for the measure is comparable with the powder sampled for thermoluminescence dating. The apparent ease of the technique is

counterweighted by the uncertainty that is still associated with some of the parameters involved in the measure.

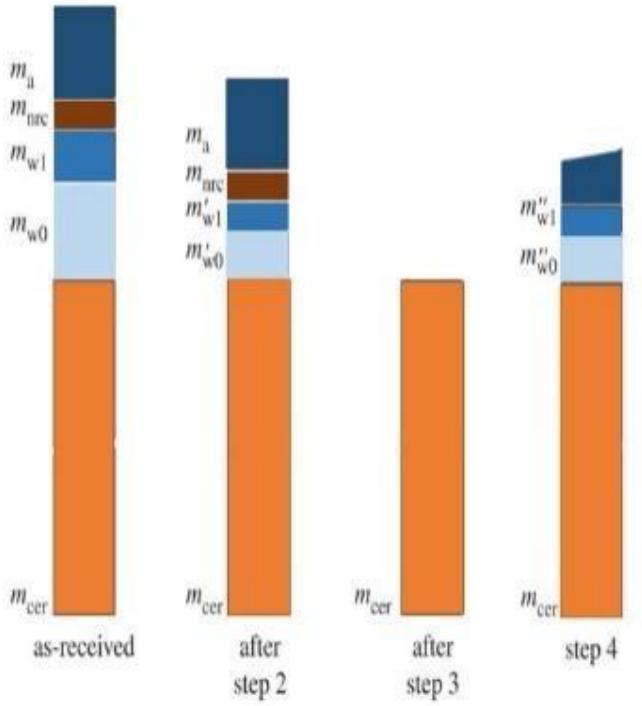

Figure 1: mass fraction in a ceramic sample after each of the dating steps [4]. m_{cer} is the ceramic fraction, m^{x}_{w0} is the physisorbed water fraction, m^{x}_{w1} is the weakly bond molecular water fraction, m_{nrc} is the non-refractory fraction, m_a is the hydroxyl/rehydroxylated fraction

2. Dating principles

The rehydroxylation process can then be applied to ceramic dating. The second stage of the process can be described by the equation:

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

where m(t) is the sample mass at time t, m_0 is the sample mass right after heating, b is the intercept of the linear regression of second stage points, α(T) is the slope of the linear regression.

The experimental steps to achieve a reliable date are:

1. after heating the sample at a temperature of 105-110°C for 24h all the physisorbed water is desorbed and the sample is placed on a balance (sensitivity=0.1μg) and the mass value is recorded until a stable value is reached (figure 1, after step 2). The recorded mass (m_2) represents the mineral mass plus the physisorbed water, the weakly bond water and the strongly bond hydroxyl groups.
2. thereafter, the sample is heated at 500°C for 24h (figure 1, after step 3) and immediately put in the balance to record the mass gain behavior (figure 1, after step 4).

At the beginning of the measure the mass is represented only by the mineral mass, at the end of stage I (figure 2) the mass is the mineral fraction plus the physisorbed water and a little fraction of bonded water and hydroxyl groups. The growth during stage II (figure 2) is due mainly by the

intake of hydroxyl groups that follow the rehydroxylation process. Once the process is stabilized and the mass gain points can be linearly fitted, it is possible to calculate the mass gain of the sample as the difference between m_2 and the intercept of the growth linear fit (m_4); the slope of that fit represents the growth vs. $t^{1/4}$ ratio.
The age of the sample can then be written as

$$t = \left(\frac{m_2 - m_4}{\alpha(T)}\right)^4 \tag{2}$$

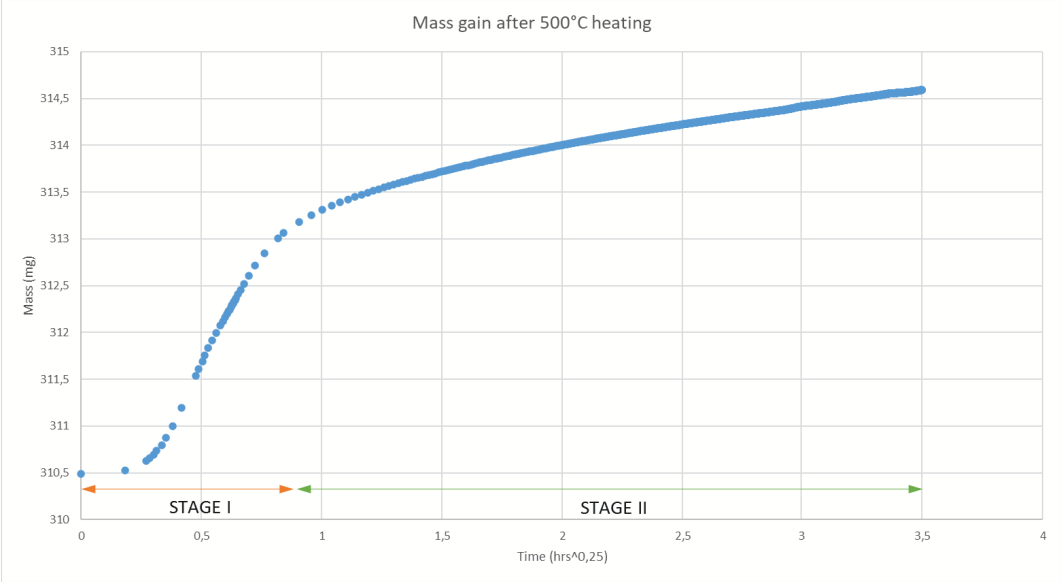

Figure 2: Mass gain behaviour after 500°C heating

3. Open issues

Even if the principle of RHX dating is simple, its application and reliability are still a matter of study, since a lot of variables and error sources are currently being studied. A selection of the most affecting parameters are shown, together with measurement optimizations and error reduction strategies adopted at Lambda. All the experimental data are taken from samples fully described and characterized in [5].

3.1. Activation energy

Activation energy strongly depends on the temperature at which the material was stored after initial heating, since it affects the kinetic of rehydroxylation process (α value), following an Arrhenius law:

$$E_a = \frac{d\ln\alpha}{d(\frac{1}{T})} 4R \ . \tag{3}$$

All the methods used to determine the activation energy imply the measure of mass gain at different temperatures, defining the associated values of α and fitting these values with temperature. Although the correlations are in most cases satisfactory, the obtained E_a values range is wider than expected, with values from 20 kJ mol^{-1} to 110-120 kJ mol^{-1}. Currently the procedure adopted at Lambda aims at finding the behavior of the activation energy with temperature. The sample is kept at 500°C for 24 hours, and then the mass change is recorded every 10 minutes at different temperatures. Every

temperature step lasts 3 days, and then the temperature is increased by 10°C, without resetting the mass to its dry value. The relative humidity is kept constant at 30%.

The result is a mass vs. time to the quarter (TTTQ) curve, with increasing slopes corresponding to different kinetics and different E_a values (figure 3).

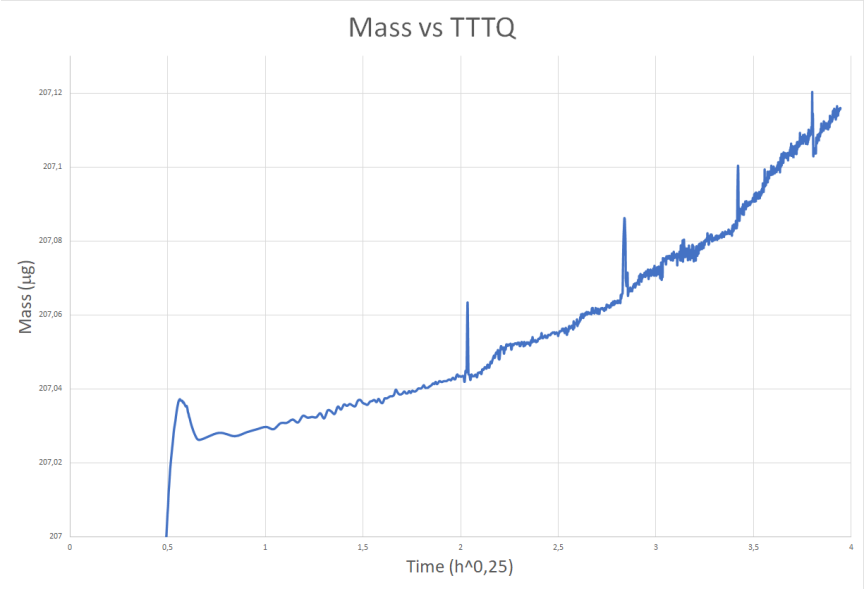

Figure 3: Mass gain vs TTTQ. The temperature is increased sequentially without resetting the water mass in the sample

3.2. Estimated lifetime temperature (ELT)

Fluctuations in environmental temperature heavily affects the water intake in ceramic lattice, especially sudden and prolonged increases. A good climatic model can help reconstructing such variations and finding a reliable mean value (ELT) to be used in the estimation of activation energy. However, when no climate data are available, temperature must be estimated, and the uncertainty in this estimation can dramatically affect the error on the calculated age: considering the Arrhenius behavior of the activation energy an overestimation of the ELT involves a bigger uncertainty on the final estimated age.

Currently at Lambda a specifically written Mathematica algorithm is used to find mean temperature time series of the burial site of the samples for the longest periods available. From these values the fourth root of the mean value of the fourth power is evaluated, giving a good approximation of the ELT value.

3.3. The role of physisorbed water

The determination of m_2 implies a preheating at low temperature (105°C) that removes all the physisorbed water mass fraction. Since weakly-bonded water is released at higher temperatures, it is not removed during this step, and is added to the total adsorbed water value calculated: this may lead to an overestimation of the age. The data reported in figure 4 are related to sample ESP [5]: for every aliquot the first heating step was increased by 100°C, and the trend shows that higher heating temperatures lead to a more accurate evaluation of the age. This trend is under further investigation.

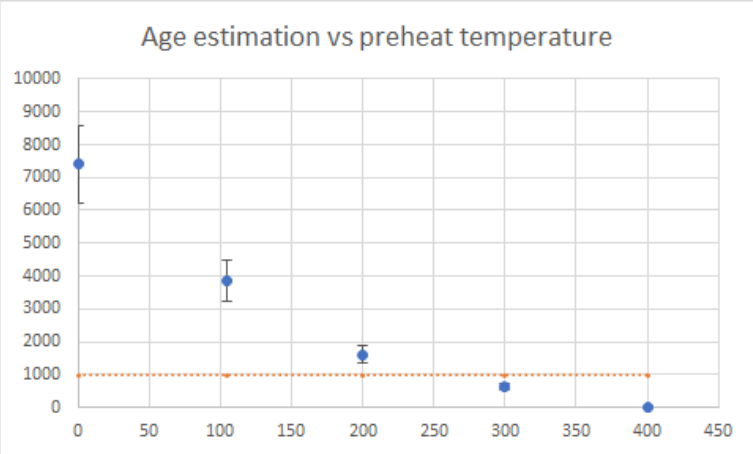

Figure 4: Age estimation trend changing the preheat temperature. Red dotted line represents the expected age

3.4. Exponential law

The first model of rehydroxylation in ceramics assumed that the exponential trend of the mass gain is proportional to $t^{0.25}$ (N=4). However, following studies [6] showed that experimental data can be fit parametrizing N with values between 2 and 6. The value of N is linked to the diffusion mechanism in the ceramic lattice, which is not yet fully clear, and it is still being studied [7]. A better knowledge of the diffusion mechanisms involved in the different rehydroxylation stages would improve the reliability and the precision of the technique. At least, the application of a unique fit model would allow a better replica of the results. At the moment the procedure applied in Milano Bicocca lab refers to the TTTQ model, since an efficient algorithm applicable to all the experimental curves is still under development.

4. Conclusions

The application of the TTTQ rehydroxylation model has been attempted as a dating technique for ceramic materials, in particular bricks. The advantages of this technique reside mainly on its independence from environmental parameters, such as radioactivity or relative humidity. The tests made on known-age samples gave promising results, but some of the principles of the model must be further studied: in particular, the rehydroxylation process is not clearly modeled yet, and there isn't a well established procedure to evaluate the experimental data.

References

[1] Schurecht H G 1928 *J. Am. Ceram. Soc.* **11** 271
[2] Wilson M A, Hoff W D, Hall C, McKay B and Hiley A 2003 *Phys. Rev. Lett.* **90(12)** 125503
[3] Savage S, Wilson M A, Carter M, Hoff W D, Hall C and McKay B 2008 *J. Phys. D* **41(5)**
[4] Wilson M A, Hamilton A, Ince C, Carter M A and Hall C 2012 *Proc. R. Soc. A* **468** 3476-3493
[5] Barrett GT 2015 Rehydroxylation Dating: Assessment for Archaeological Application *Ph.D. Thesis*. Queens University Belfast.
[6] Le Goff M and Gallet Y 2015 *J. Am. Ceram. Soc.* **98(2)** 398-401
[7] Kuligiewicz A and Derkowski A 2021 *J. Archaeol. Sci.* **125**