

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

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Determining the absolute chronology of ceramic artifacts has significant implications for archeological and historical research. Wilson, Hall *et al.* recently suggested a new technique for direct absolute dating of archeological ceramics based on a moisture-induced chemical reaction, called rehydroxylation (RHX) dating. RHX dating proceeds by measuring the mass of chemically combined water in the ceramics in the form of OH hydroxyls, and the mass gain rate at the Effective Lifetime Temperature (ELT) that the ceramics experienced over its lifetime. To date, ELT determinations have been based on estimates of the ceramic's lifetime temperature history; taking into account weather and climate data and the depth at which the artifact was found. The uncertainty in determining the ELT can be a major component of the overall dating uncertainty. Here, we propose an alternative method which relies minimally on weather and climate data, and provides more precise determinations of the ELT and the ceramic age. The proposed method (SAS: Same Age Samples) involves a minimum of four measurements of the RHX mass gain rate constant for two ceramic samples of the same age at two temperatures. We show via simulations that the proposed SAS method can determine the ELT with a precision of 0.2 K which is comparable to the best ELT determination based on lifetime temperature history, and also comparable to available microbalance temperature resolutions of around 0.1 K. The corresponding percent age error is then 1.4%, or 43 yr for a 3000-yr-old ceramic. The proposed SAS method should be tested with ceramic samples of different ages, whose ELT are well-known.

## I. Introduction

THE firing of pottery during manufacture drives out all chemically combined water in the form of OH hydroxyls from the clay:  $2\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$ . Rehydroxylation (RHX) dating relies on the fact that fired-clay oxide materials begin chemically reacting slowly with environmental water as soon as they are removed from the kiln. The reaction has been termed RHX and is a super slow special diffusion chemical reaction. It causes a small increase in mass and appears to continue indefinitely. Wilson, Hall *et al.*<sup>1–8</sup> established that the kinetics of this reaction depends on the quartic (fourth) root of the elapsed time (time)<sup>1/4</sup>; and suggested that the RHX process may be used as an “internal clock” to establish the age of archeological ceramics; that is, the time elapsed since the ceramic pottery was fired.

Figure 1 shows the notation and illustrates the RHX dating method.<sup>6</sup> The measurements should be carried out at the Effective Lifetime Temperature (denoted  $T_e$  or ELT) that the ceramic experienced over its lifetime. The mass  $m_2$  represents

the mass of the sample and all the chemically combined rehydroxylated water which has accumulated over the sample's lifetime; while the sample is at equilibrium with a conditioning environment at the ELT and at a fixed relative humidity. The mass  $m_2$  is labeled “initial” in the figure only in the sense that it represents the initial step of the dating procedure. The sample is heated to  $\sim 500^\circ\text{C}$  for sufficient time to drive off all of its chemically combined and molecular water until it reaches constant mass, after which it is returned to the same conditioning environment as was used for measuring  $m_2$ . The sample mass  $m_4$  represents the mass of the sample with all the rehydroxylated water removed at the conditioning environment. With respect to rehydroxylated water, it corresponds to the ceramic mass at the moment that the ancient craftsman removed it from the kiln.

The mass-time dependence due to the RHX reaction is described by the following equation:

$$m(t) = m_4 + \alpha(T)t^{1/4} \quad (1)$$

where  $\alpha$  is the RHX rate constant that describes the rate of RHX mass gain (in units  $\text{g}\cdot\text{h}^{-1/4}$ ) at temperature  $T$ , and the constant  $m_4$  is the intercept on the mass axis, as shown in Fig. 1. Note that in many RHX publications,<sup>4</sup> the notation  $\alpha$  rather refers to a relative mass gain rate relative to  $m_4$  (in units  $\text{hr}^{-1/4}$ ). Savage *et al.*<sup>1</sup> showed that water sorption proceeds in two well-defined stages. Figure 1 shows a rapid Stage I, in which the macropore structure of the fired ceramic body fills with molecular water in the form of capillary or weakly bound  $\text{H}_2\text{O}$ ; and a much slower Stage II, in which this molecular water chemically reacts with the adjacent, dehydroxylated clay components of the ceramic fabric. The transition from the first to the second stage usually takes

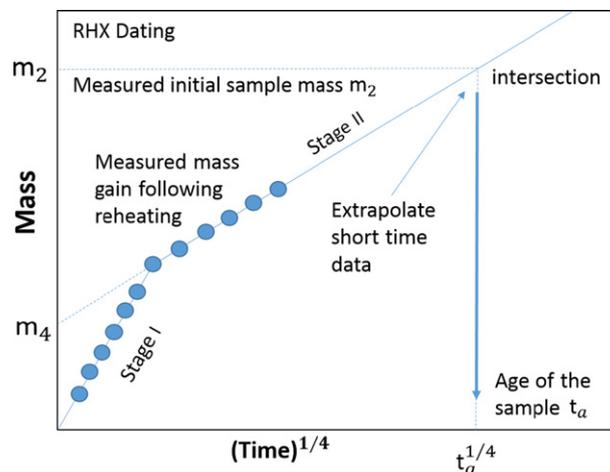


Fig. 1. Schematic of RHX dating method. Data show characteristic two-stage mass gain process, Stage II of which is used for the RHX age determination.

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about one day. After this time, the RHX mass gain follows the quartic root time dependence.

From Fig. 1, the mass of rehydroxylated water  $m(\text{H}_2\text{O})_{\text{rhx}}$  is as follows:

$$m(\text{H}_2\text{O})_{\text{rhx}} = m_a = m_2 - m_4 \quad (2)$$

The ceramic's age is determined via:

$$t_a = (m_a/\alpha(T_e))^4 \quad (3)$$

Here  $\alpha(T_e)$  is the RHX rate constant at the ELT  $T_e$ . The gradient  $dm/dt^{1/4}$  at temperature  $T_e$  is tested until it becomes constant with (time)<sup>1/4</sup>, after which  $\alpha = dm/dt^{1/4}$ . The value  $t_a$  is the deduced elapsed time (age) since the ceramic was originally fired. Although Eq. 3 is often written<sup>4</sup> in terms of fractional mass ( $y = m_a/m_4$ ) and a relative mass gain rate, the form above is used here for simplicity.

## II. Determination of the Activation Energy

The RHX Arrhenius equation<sup>7</sup> gives the temperature dependence of the RHX rate constant  $\alpha$ , verified experimentally<sup>4</sup> as:

$$\alpha(T) = A \exp(-E/4RT) \quad (4)$$

The reaction rate depends on activation energy  $E$ . The temperatures are measured in kelvin (K). The activation energy is the minimum energy required to start the chemical reaction.<sup>8</sup> The universal gas constant is  $R = 8.3144621 \text{ J}\cdot(\text{K}\cdot\text{mol})^{-1}$ . The prefactor  $A$  has been calculated<sup>9,10</sup> as the product of the collision frequency of reactants and the reaction probability. The Arrhenius equation that describes the temperature dependence of the reaction rate of a chemical reaction is generally written without the factor of 4 shown in Eq. (4). Hall *et al.*<sup>7</sup> explain that the factor 4 arises for the RHX reaction since  $[\alpha(T)/m_a]^4$  is the effective rate constant in inverse time units, for example,  $\text{h}^{-1}$ . Typical activation energies for RHX in ceramics are 40 000–80 000 J/mol.

Equation (4) may be used to compare rate constants at two different temperatures. For example, for sample b, the rate constant  $\alpha_b(T_e)$  at temperature  $T_e$  may be determined from measurements of the rate constant  $\alpha_b(T_1)$  at temperature  $T_1$ , if the activation energy is known, via:

$$\begin{aligned} \alpha_b(T_1)/\alpha_b(T_e) &= \exp(-E_b/4RT_1)/\exp(-E_b/4RT_e) \\ &= \exp[E_b(1/T_e - 1/T_1)/4R] \end{aligned} \quad (5.1b)$$

The rate constant ratios  $\alpha_b(T_2)/\alpha_b(T_e)$ ,  $\alpha_c(T_1)/\alpha_c(T_e)$ , and  $\alpha_c(T_2)/\alpha_c(T_e)$  are similarly determined by Eqs. (5.2b), (5.1c), (5.2c), as given in Appendix 1. The Eq. (4) prefactors  $A$  factor out<sup>4</sup> in these ratios.

The activation energy  $E_b$  of sample b could be determined from the measurements of the RHX rate constants at two temperatures  $T_1$  and  $T_2$  via<sup>3,4</sup>:

$$\alpha_b(T_1)/\alpha_b(T_2) = \exp(-E_b[1/T_1 - 1/T_2]/4R), \quad (6b)$$

$$E_b = 4R \ln(\alpha_b(T_1)/\alpha_b(T_2))/(1/T_2 - 1/T_1) \quad (7b)$$

In practice, activation energies have been determined from measurements of RHX reaction rates at three or more temperatures.<sup>3,4,8</sup> In this work, as described later, we rather

focus on how to determine activation energies, ELTs and ages from measurements at only two temperatures.

## III. Determination of the Effective Lifetime Temperature and RHX Age

Wilson, Hall *et al.*<sup>3,7</sup> Calculate the ELT of a ceramic sample from estimates of its lifetime temperature history, based on regional meteorological records near the location where the ceramic was recovered. The resulting ELT uncertainty contributes significantly to the overall ceramic age uncertainty.

Here, we describe how to determine the ELT for ceramic samples independently of meteorological records. That is, we ask two different ceramics samples (b & c) having the same age but different activation energies to reveal their common ELT. The simplest version of the method is to measure the RHX rate constants  $\alpha_b$  and  $\alpha_c$  at two temperatures ( $T_1$  and  $T_2$ , differing for example by  $\sim 10$  K) of two ceramic samples of the same age, where the two samples have different activation energies  $E_b$  and  $E_c$ . The samples may come, for example, from the same archeological stratum; provided by an archeologist who determines, based on excavation information, that they have the same age. Clelland *et al.*<sup>8</sup> found that even ceramic sherds broken from some particular plates had activation energies that differed significantly from one another. This is hardly surprising considering the great mineralogical variability in pedogenic clays and the different firing temperatures of the different parts of the same vessel (e.g., the base and the rim). Notice that this is not an obstacle to the standard RHX dating because the activation energy is measured for each sample. In the case of SAS, it is especially beneficial as this method requires a few samples having the same age and different activation energies. When there is large variability in activation energies of different parts of the same ceramic artifact, the SAS method age and activation energy requirements are both conveniently satisfied.

The RHX rate constants of the chosen two samples (at  $T_1$  and  $T_2$ ) are labeled  $\alpha_b(T_1)$ ,  $\alpha_b(T_2)$ ,  $\alpha_c(T_1)$ , and  $\alpha_c(T_2)$ . Measuring the rate constants at temperatures  $T_1$  and  $T_2$ , using  $t_a = [m_a/\alpha(T_e)]^4$  from Eq. (3); with  $\alpha_b(T_e) = \alpha_b(T_1)\exp[E_b(1/T_1 - 1/T_e)/4R]$  and  $\alpha_c(T_e) = \alpha_c(T_1)\exp[E_c(1/T_1 - 1/T_e)/4R]$  from Eqs. (5.1b) and (5.1c), defining  $m_{ab} = m_{2b} - m_{4b}$  and  $m_{ac} = m_{2c} - m_{4c}$ , the ages  $t_{ab}(T_1)$  and  $t_{ac}(T_1)$  from samples b and c data at  $T_1$  are as follows:

$$t_{ab}(T_1) = m_{ab}^4 \exp[E_b(1/T_e - 1/T_1)/R]/\alpha_b(T_1)^4 \quad (8.1b)$$

$$t_{ac}(T_1) = m_{ac}^4 \exp[E_c(1/T_e - 1/T_1)/R]/\alpha_c(T_1)^4 \quad (9.1c)$$

The ages  $t_{ab}(T_2)$  and  $t_{ac}(T_2)$  from samples b and c data at  $T_2$  are given in Appendix 1 as Eqs. (8.2b) and (9.2c). Although these age equations are written in terms of  $T_e$ , its value is not necessarily yet known. Altogether, Eqs. (8) and (9) comprise four equations to determine the age, all of which should give the same age within the uncertainties. The SAS age is then taken as the statistical average of the four determinations.

We now derive an equation that gives  $T_e$  (ELT and its uncertainty) as a function of the variables  $\alpha_b(T_1)$ ,  $\alpha_c(T_1)$ ,  $m_{ab}$ ,  $m_{ac}$ ,  $T_1$ . Equating Eq. (8.1b) to Eq. (9.1c), and solving for  $T_e$ , one obtains:

$$T_e = \frac{E_b - E_c}{4R \ln \frac{\alpha_b(T_1)}{\alpha_c(T_1)} + 4R \ln \frac{m_{ac}}{m_{ab}} + \frac{E_b}{T_1} - \frac{E_c}{T_1}} \quad (10.1)$$

Similarly, equating Eq. (8.2b) to Eq. (9.2c) yields a second equation for  $T_e$ , Eq. (10.2), expressed explicitly in terms of  $T_2$ , as given in Appendix 1.

Equation (10.1) derived above is the key to the application of the SAS method. It is appropriate therefore to list and address here the implicit assumptions that enter the derivation of this equation. These assumptions can be divided into two categories: those relevant to the RHX method in general, and those that are specific to the SAS method.

A discussion of the implicit assumptions of the RHX method and the experimental evidence that support them is behind the scope of this study. We therefore just list the essential assumptions, as described, for example, in the most recent RHX review article<sup>4</sup>: (1) The mass-time dependence follows the power law given in Eqs. (1) and (2) The RHX rate temperature dependence is described by the Arrhenius Eqs. (4) and (3) The usual RHX Arrhenius equation prefactor does not depend on any possible heating-induced mineralogical changes in the sample as a result of RHX protocol reheatings, (4) Any different thermal conductivity or preferential exposure to sunlight of parts of the ceramic samples do not change the ELT.

Regarding SAS implicit assumptions, it is assumed that two samples with the same age and the same temperature history have the same ELT [assumption used in Eqs. (8) and (9)]. This assumption is precisely true only if both samples were at a constant temperature over their entire lifetimes<sup>7</sup> (C. Hall, private communication, 2014). Actually, if two ceramic specimens have different activation energies and the same variable temperature history, their ELTs will not be equal. The reason is that the ELT rate constant is given as the fourth power mean (FPM) of the different rate constants at the different temperatures over the lifetime history.

Since  $\alpha(T) = A \exp(-E/4RT)$  by Eq. (4), the FPM rate constants  $\alpha_b(T_c)$  and  $\alpha_c(T_c)$  will differ from each other if the activation energies  $E_b$  and  $E_c$  differ from each other, even if the rate constants were equal to each other at one particular measurement temperature.

A calculation for such a situation as given in Appendix 5 shows, however, that samples b and c would have ELTs that differ by  $\sim 0.06^\circ\text{C}$ ; if their activation energies differ by 15 000 J/mol, and they were subjected to temperature variations of order  $5^\circ\text{C}$ . For most archeological ceramic samples, away from the top few meters, the temperature variations are less than  $5^\circ\text{C}$ . Therefore, the dependence of the ELT on activation energy effectively increases the ELT uncertainty as found from Eqs. (10) by less than  $0.1^\circ\text{C}$  in quadrature, which comprises a very small effect. Such a small difference does not affect the validity and applicability of Eqs. (10).

The SAS method requires using samples of equal age. This can best be ensured by selecting the samples from exactly the same vessel. This is a practical procedure, as there is often a large variation in activation energy even between different parts of the same ceramic vessel. In archeological sites, the context often allows obtaining ceramic samples from different vessels that have very high probability of being of the same age. This is the case, for example, for simple cooking or eating pottery that are found on the same living floor in the same location.

Note that in Eqs. (10), the activation energies  $E_b$  and  $E_c$  are not independent variables, but are rather given by Eqs. (7) as functions of  $\alpha_b(T_1)$ ,  $\alpha_c(T_1)$ ,  $\alpha_b(T_2)$ ,  $\alpha_c(T_2)$ ,  $T_1$ ,  $T_2$ . From Eqs. (10), data for each pair of ceramic samples gives two determinations of the ELT. By measuring more samples, one can gain precision, and also check for systematic errors. Age determination via the SAS method is based on Eqs. (8) and (9) in which  $T_c$ ,  $E_b$ , and  $E_c$  are not independent variables, but are rather given by Eqs. (7) and (10).

#### IV. Estimating ELT and Age Uncertainties

The ELT and age uncertainties of the proposed SAS method are estimated via simulations. We consider first the mass and  $\alpha$  rate resolutions. All  $\sigma$  values in this report refer to standard deviations ( $\sim 68\%$  confidence intervals). The Aquadyne DVS Gravimetric Water Sorption Analyzer has been successfully

used to produce published RHX dates.<sup>3,8</sup> It comprises a double microbalance.<sup>11,12</sup> It is designed to simultaneously measure the mass gain of two samples (b & c for example). Each microbalance has a capacity of 5 g, a mass resolution of  $0.1 \mu\text{g}$ , and an accuracy of  $1 \mu\text{g} \pm 0.001\%$  of the suspended mass (therefore,  $\sim 50 \mu\text{g}$  accuracy for a 5 g mass). The accuracy of the instrument should not affect the RHX dating precision because only differences between mass measurements are relevant (for  $m_a$  and  $\alpha$ ). That is, any constant mass bias should cancel out. The quoted  $\sigma(m) = 0.1 \mu\text{g}$  resolution is larger than the smallest increment of the A/D converter scale division of its readout. The relevant mass resolution is therefore expected to be close to the quoted resolution. The instrument can achieve a range of temperatures  $10^\circ\text{C}$ – $80^\circ\text{C}$ , for which the temperature is controlled to  $\pm 0.1^\circ\text{C}$ . RHX Dating may alternatively be carried out with a high precision top loading microbalance inside an environmentally controlled chamber, in which a robotic arm or carousel is used to consecutively manipulate a series of samples without any operator intervention.<sup>13</sup> Here, we use the quoted Aquadyne instrument resolutions as a guide to estimate mass and mass gain rate uncertainties in the simulation studies described below.

We now estimate the statistical precision that may be achieved for the RHX rate constant  $\alpha$ . The  $\alpha$  resolution  $\sigma(\alpha)$  scales with the  $\sigma(m)$  mass resolution; and improves as the total Stage II measurement period and the number of measurements  $N$  taken during the measurement period increase. It is valuable therefore to take frequent measurements over a longer period of time. The instrument continuously monitors the sample mass and the user can determine the frequency with which it records the mass, the shortest interval is every 5 s. To help understand sensitivity limits, we conservatively choose  $\alpha \sim 0.26 \text{ mg}\cdot\text{h}^{-1/4}$  for the simulation. This value is lower than the lowest published RHX rate constant<sup>2,3,12</sup> by a factor of  $\sim 3$ , and therefore more challenging to measure. Appendix 2 describes what  $\alpha$  resolution can be achieved via mass measurements over a typical 16 h time period ( $\Delta t^{1/4} = 2 \text{ h}^{1/4}$ ). The result is that  $\sigma(\alpha) \sim 10^{-7} \text{ g}\cdot\text{h}^{-1/4}$  if mass gain measurements are made with  $\sigma(m) \sim 0.1 \mu\text{g}$ . This  $\sigma(\alpha)$  resolution is used in the following simulations.

#### V. Simulation Results

We will compare the RHX dating uncertainty  $\sigma(t_a)$  that can be achieved when the ELT ( $T_c$ ) is estimated using (1) the ceramic's lifetime temperature history, and (2) the proposed SAS method. For the simulation, we choose the ELT to be  $T_c = 286 \text{ K}$  for two samples that have age  $t_a = 3000 \text{ yr}$ . Simulation input data are summarized in Appendices 3a and 3b. For comparison, some of the simulation data follow RHX simulations of Hare,<sup>14</sup> not related to determining the ELT.

#### VI. ELT via Lifetime Temperature History

The standard RHX age determination uses ELTs calculated from an estimate of the ceramic's lifetime temperature history<sup>3,7</sup>. Regional meteorological records are first used to estimate the mean annual air temperature. One must also take into account that the mean annual ground temperature is higher by approximately 1 K.<sup>15</sup> Otherwise, the estimated ELT will be too low, which would lead to a large error. A correction should also be made to account for local and global climate variations<sup>16</sup> over the past millennia. Also, as different samples come from different depths, one should take into account the time dependence of the depth and the depth dependence of the average temperature. The cumulative ELT uncertainty  $\sigma(T_c)$  considering all of these variables is, however, difficult to estimate accurately.

How does the ELT uncertainty  $\sigma(T_c)$  affect the RHX age uncertainty  $\sigma(t_a)$ ? This question can be answered by simulating the RHX age determination using Eq. (3) for measurements taken at  $T_c$  and Eq. (8.1b) for measurements taken

2 K higher at  $T_1$ , with the simulation data of Appendix 3a. Figure 2(a) shows simulation results for  $t_a$  based on  $10^7$  samplings of Eq. (3). The age uncertainty is found to be  $\sigma(t_a) \sim 5$  yr, an artificially low value that reflects the uncertainty due only to mass and rate constant measurements at  $T_e$ , with no contributions from ELT uncertainties and from related temperature extrapolations. Figure 2(b) shows simulation results for  $t_a$  based on  $10^7$  samplings of Eq. (8.1b). The result  $\sigma(t_a) = 65$  yr corresponds to  $\sigma(t_a)/t_a = 2.2\%$  for  $t_a = 3000$  yr. This uncertainty characterizes the lifetime history method, and is due mainly to the temperature related uncertainties. Here, it is assumed as shown in Appendix 3a, and following Ref. [8], that the activation energy is measured separately by a series of mass gain measurements at typically four different temperatures.

The above simulations, however, do not take into account that  $\sigma(T_e)$  may be significantly larger than the estimated  $\sigma(T_e) = 0.18$  K, even as large as  $\sigma(T_e) = 1$  K. In this method, there is no way to test by measurements that the estimated ELT is correct. Therefore, the age error could even reach as much as 10%, 300 yr for a 3000-yr-old ceramic, as discussed in the following section in greater detail.

Table I summarizes simulation results for different uncertainties  $\sigma(\alpha)$  and  $\sigma(T_e)$ . The  $\sigma(t_a)$  values shown are based only on Eq. (8.1b). For  $\sigma(T_e) = 0.5$  K, even if  $\sigma(\alpha) = 10^{-7}$  g·h $^{-1/4}$ , the per cent age error is as large as  $\sim 5\%$ , or  $\sim 150$  yr for a 3000-yr-old ceramic sample. This corresponds to approximately a 1% error per 0.1 K ELT error.

## VII. ELT Via Proposed Same Age Samples (SAS) method

The new proposed SAS method requires a minimum of four measurements of RHX mass gain rate for two ceramic samples (b & c) of the same age at two temperatures ( $T_1$  and  $T_2$ ). Simulation data input are shown in Appendix 3b. We selected simulation data to be  $T_e = 286$  K for two samples having age  $T_a = 3000$  yr: sample b and sample c. In practice, one temperature ( $T_1$ ) would be chosen close to the ELT as estimated by weather station data, and the second ( $T_2$ ) roughly 6°C–10°C removed. This choice minimizes uncertainties associated with the temperature extrapolation based on the Arrhenius equation.<sup>9,10</sup> Note, however, that measure-

**Table I. Simulation Results  $\sigma(t_a)$  for Different Uncertainties  $\sigma(\alpha)$  and  $\sigma(T_e)$**

$\sigma(\alpha)$ g·h $^{-1/4}$	$\sigma(T_e)$ K	$\sigma(t_a)$ yr	$\sigma(t_a)/t_a$ (%)
$10^{-7}$	0.18	*65	2.2
	0.5	158	5.3
	1.0	314	10.4
$10^{-6}$	0.18	78	2.6
	0.5	165	6.5
	1.0	317	10.6

Figure 2(b) shows \* results.

ments at any two appropriate temperatures would in principle determine the ELT.

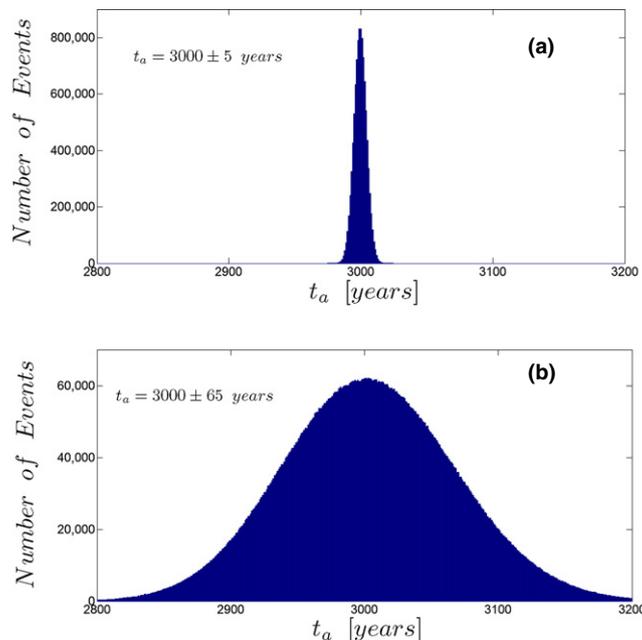
The simulations are carried out by  $10^7$  successive random samplings of all the independent variables:  $\alpha_b(T_1)$ ,  $\alpha_c(T_1)$ ,  $\alpha_b(T_2)$ ,  $\alpha_c(T_2)$ ,  $T_1$ ,  $T_2$ ,  $m_{ab}$ ,  $m_a$ , taken to be normally distributed. The dependent variables are calculated from each sampling. Eqs. (8) and (9) are used to simulate ages, Eqs. (7) are used to simulate activation energies, and Eqs. (10) are used to simulate ELTs. The simulated distributions determine mean values and uncertainties.

Activation energies and uncertainties were found to be  $E_b \sim 70\,000 \pm 12\,500$  J/mol and  $E_c \sim 85\,000 \pm 15\,000$  J/mol. Note that  $E_b$  and  $E_c$  may be determined via measurements that are taken simultaneously or consecutively at each temperature for both samples b and c. Errors in  $E_b$  and  $E_c$  for such measurement due to temperature uncertainties would therefore be correlated for both samples. This correlation reduces the uncertainty of age and ELT determinations, compared to the situation in which  $E_b$  and  $E_c$  are independent variables.

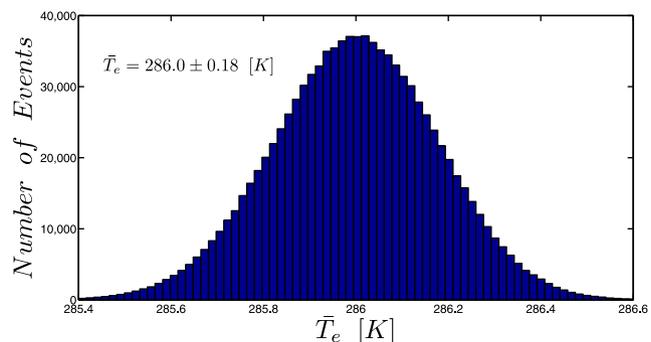
Simulations were carried out to determine the ELT uncertainty  $\sigma(T_e)$  as a function of the variables  $\alpha_b(T_1)$ ,  $\alpha_c(T_1)$ ,  $\alpha_b(T_2)$ ,  $\alpha_c(T_2)$ ,  $m_{ab}$ ,  $m_{ac}$ ,  $T_1$ ,  $T_2$ . The results  $\bar{T}_e = 286.00$  and  $\sigma(\bar{T}_e) = 0.18$  are the mean values from Eqs. (10.1) and (10.2). Figure 3 shows the corresponding  $T_e$  distributions.  $T_e$  in Fig. 3 is calculated using random draws of all the variables in Eqs. (10), where  $E_b$  and  $E_c$  are functions of all the variables, as given by Eqs. (7). In contrast, if  $E_b$  and  $E_c$  are known from independent uncorrelated measurements with uncertainties  $\sigma(E_b)$  and  $\sigma(E_c)$ , then when Eqs. (10) are sampled,  $T_1$  and  $T_2$  are taken from separate draws for normal distributions of  $E_b \pm \sigma(E_b)$  and  $E_c \pm \sigma(E_c)$ . In that case, for sample b for example,  $\sigma(T_e) = 0.3, 0.24, 0.17$  K for  $\sigma(E_b) = 1250, 1000, 500$  J/mol, respectively. The uncertainty  $\sigma(T_e)$  may be slightly higher in this case, but still very good.

Simulations were also carried out to determine the  $\sigma(T_e)$  uncertainty as a function of the rate constant uncertainty  $\sigma(\alpha)$ . For  $\sigma(\alpha) < 2.0 \times 10^{-7}$  g·h $^{-1/4}$ ,  $\sigma(T_e)$  is less than 0.2 K. The corresponding age uncertainty  $\sigma(T_a)$  is less than 45 yr for  $t_a = 3000$  yr. The uncertainty  $\sigma(T_e)$  increases sharply for  $\sigma(\alpha) > 2.0 \times 10^{-7}$  g·h $^{-1/4}$ .

Figure 4 shows simulation results for  $t_a$  based on  $10^7$  samplings of Eqs. (7–10). The sampled variables were  $\alpha_b(T_1)$ ,  $\alpha_c(T_1)$ ,  $\alpha_b(T_2)$ ,  $\alpha_c(T_2)$ ,  $m_{ab}$ ,  $m_{ac}$ ,  $T_1$ , and  $T_2$ . The results



**Fig. 2.** Simulated values for age  $t_a$  based on (a) Eq. (3) and (b) Eq. (8.1b). Input data for the simulations are summarized in Appendix 3a.



**Fig. 3.** Simulated ELT ( $T_e$ ) in K based on Eqs. (10) and Appendix 3b data.

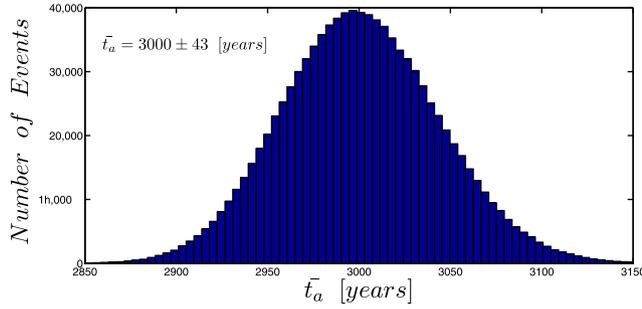


Fig. 4. Simulated Age ( $\bar{t}_a$ ) in years based on Eqs.(8) and (9) and data of Appendix 3b.

$\bar{t}_a = 3000$  yr and  $\sigma(\bar{t}_a) = 43$  yr are the mean values from all four equations [Eqs. (8) and (9)], corresponding to  $\sigma(\bar{t}_a)/\bar{t}_a = 1.4\%$  for  $\bar{t}_a = 3000$  yr. Table II summarizes simulation results for different uncertainties  $\sigma(\alpha)$ . Table II results are in good agreement with previous estimates<sup>7</sup> of  $\sigma(t_a)$ , as described in Appendix 4.

Note that the SAS age resolution in Table II for  $\sigma(\alpha) = 10^{-7}$  g·h<sup>-1/4</sup> is  $\sigma(\bar{t}_a) = 43$  yr, while the corresponding lifetime history method age resolution in Table I is  $\sigma(t_a) = 65$  yr. The difference reflects the fact that the SAS method result is based on two sample measurements at two temperatures, whereas the lifetime history method result is based on one sample measurement at one temperature. A more significant difference is that the SAS method actually measures  $T_e \pm \sigma(T_e)$ ; whereas the lifetime history method is not able to test by measurements that the estimated ELT is correct. This is potentially a significant advantage of the SAS method.

All error estimates considered above do not include systematic errors that may arise, for example, from nonlinearities of the measured mass gain data versus the quartic root time dependence  $t^{1/4}$ , the possibility that the time dependence exponent is not exactly  $1/4$ , and that the temperature dependence does not exactly follow<sup>9,10</sup> the RHX Arrhenius Eq. (5).

### VIII. Application to Climate Studies

Burakov and Nachasova<sup>17</sup> compared archeomagnetic and RHX dating of fired-clay ceramics to study climate change over millennia. Referring to Eq. (8),  $t_a = m_a^4 \exp[E(1/T_e - 1/T_1)/R]/\alpha(T_1)^4$ , they calculate  $T_e$  based on knowing  $E$ ,  $T_1$ ,  $\alpha$  ( $T_1$ ), and knowing  $t_a$  from archeomagnetic dating. Their results represent a first attempt to draw conclusions about climate change based on RHX dating. Eqs. (10) in this work are advantageous for climate studies as they allow a determination of the ELT without the need to independently determine the age  $t_a$  of the ceramic being studied. For climate studies, it is important to note, however, that the deduced ELTs represent a log-time integral of environmental temperature since original firing; and also reflect burial rates and the depth dependence of temperature. Such considerations are, however, beyond the scope of the present investigation.

### IX. Conclusions

A new Same Age Sample (SAS) method is proposed here that allows a precise determination of the effective lifetime temperature of archeological ceramics for RHX dating. We

Table II. Simulation Results for Different Uncertainties  $\sigma(\alpha)$

$\sigma(\alpha)$ g·h <sup>-1/4</sup>	$\sigma(\bar{t}_a)$ yr	$\sigma(\bar{t}_a)/\bar{t}_a$ (%)
$10^{-7}$	*43	1.4
$2 \times 10^{-7}$	85	2.8
$5 \times 10^{-7}$	219	7.3
$10^{-6}$	544	18.1

Figure 4 shows \* results.

study via simulations how well the SAS method can determine the ceramic age and ELT as a function of the uncertainties of mass  $\sigma(m)$ , mass gain rate  $\sigma(\alpha)$ , and measurement temperature  $\sigma(T_m)$ . The dominant uncertainty affecting the ELT and age precisions is  $\sigma(\alpha)$ . For  $\sigma(\alpha) \leq 2 \times 10^{-7}$  g·h<sup>-1/4</sup>, the ELT is determined with a precision of order 0.2 K. The corresponding per cent age error is then 1.4%, or 43 yr for a 3000-yr-old ceramic. This new proposed SAS method should be tested with different microbalance setups and with ceramics samples of different ages, whose ELT are well-known independently.

### Appendix 1: Supplementary Equations

$$\alpha_b(T_2)/\alpha_b(T_c) = \exp[E_b(1/T_c - 1/T_2)/4R] \quad (5.2b)$$

$$\alpha_c(T_1)/\alpha_c(T_c) = \exp[E_c(1/T_c - 1/T_1)/4R] \quad (5.1c)$$

$$\alpha_c(T_2)/\alpha_c(T_c) = \exp[E_c(1/T_c - 1/T_2)/4R] \quad (5.2c)$$

$$\alpha_c(T_1)/\alpha_c(T_2) = \exp[-E_c(1/T_1 - 1/T_2)/4R] \quad (6c)$$

$$E_c = 4R \ln(\alpha_c(T_1)/\alpha_c(T_2))/(1/T_2 - 1/T_1) \quad (7c)$$

$$t_{ab}(T_2) = m_{ab}^4 \exp[E_b(1/T_c - 1/T_2)/R]/\alpha_b(T_2)^4 \quad (8.2b)$$

$$t_{ac}(T_2) = m_{ac}^4 \exp[E_c(1/T_c - 1/T_2)/R]/\alpha_c(T_2)^4 \quad (9.2c)$$

$$T_c = \frac{E_b - E_c}{4R \ln \frac{\alpha_b(T_2)}{\alpha_c(T_2)} + 4R \ln \frac{m_{ac}}{m_{ab}} + \frac{E_b}{T_2} - \frac{E_c}{T_2}} \quad (10.2)$$

### Appendix 2: $\sigma(\alpha)$ resolution

We first estimate what resolution  $\sigma(\alpha)$  can be achieved with this instrument via two mass measurements, one at the beginning and the second at the end of the measurement time period  $\Delta t^{1/4}$ . We find that if mass measurements are made with  $\sigma(m) = 0.1$   $\mu$ g, based on only these two measurements,  $\sigma(\alpha) \sim 0.7 \times 10^{-7}$  g·h<sup>-1/4</sup> for a ceramic sample for which RHX mass gain measurements are carried out over a typical 16 h time period ( $\Delta t^{1/4} = 2$  h<sup>1/4</sup>). The reason is that the difference  $\Delta m$  of these two measurements is determined with resolution  $\sigma(\Delta m) = 0.14$   $\mu$ g. Since  $\alpha = \Delta m/\Delta t^{1/4}$ ,  $\sigma(\alpha)/\alpha = \sqrt{[\sigma(\Delta m)/\Delta m]^2 + (\sigma(\Delta t^{1/4})/\Delta t^{1/4})^2}$ . Time intervals are measured very precisely, with  $\sigma(\Delta t^{1/4})/\Delta t^{1/4} \ll \sigma(\Delta m)/\Delta m$ . Therefore, based on Eq. (1),  $\sigma(\alpha)/\alpha \sim \sigma(\Delta m)/\Delta m \sim 0.14/\Delta m \sim 0.14/\alpha \Delta t^{1/4}$ , and therefore  $\sigma(\alpha) \sim 0.14/\Delta t^{1/4} \times 10^{-6}$  g·h<sup>-1/4</sup>.

For a typical quartic root time measurement period of  $\Delta t^{1/4} = 2$  h<sup>1/4</sup>, Eq. (13) gives  $\sigma(\alpha) \sim 0.7 \times 10^{-7}$  g·h<sup>-1/4</sup>.

Table A2. Resolutions  $\sigma(\alpha)$  as a Function of  $\sigma(m)$  and  $\Delta t^{1/4}$

$\sigma(m)$ $\mu$ g	$\Delta t^{1/4}$ h <sup>1/4</sup>	$\Delta t$ h	$\sigma(\alpha)$ $10^{-7}$ g·h <sup>-1/4</sup>
0.1	2	16	0.7
0.2	2	16	1.4
0.5	2	16	3.5
1.	2	16	7.0
0.1	3	81	0.47
0.2	3	81	0.94
0.5	3	81	2.4
1.	3	81	4.7

Table A2. shows uncertainties  $\sigma(\alpha)$  as a function of  $\sigma(m)$  and the measurement time  $\Delta t^{1/4}$ .

In fact, for a 16 h Stage II measurement, taking a mass measurement every 6 min, a total of  $N = 161$  data points would be taken. Determining  $\sigma(\alpha)$  by a least-square fit of all these data points, rather than only two, considering only statistics, would improve  $\sigma(\alpha)$  resolution by a factor of  $\sqrt{N} \sim 9$ . However, systematic uncertainties associated with the intrinsic microbalance resolution would impose limitations that cannot be overcome just by increasing the number of measurements  $N$ . Still, increasing  $N$  should help to approach the ultimate  $\alpha$  resolution possible with this instrument, a value estimated to be in the range  $\sigma(\alpha) \sim 0.5 \times 10^{-7} - 7 \times 10^{-7} \text{ g}\cdot\text{h}^{-1/4}$ .

### Appendix 3a: Simulation Data for Lifetime History Method

$$m_{2b} = 5.118342 \pm 10^{-6} \text{ g}, m_{4b} = 5.1000 \pm 10^{-6} \text{ g},$$

$$m_{ab} = m_{2b} - m_{4b} = 0.0183426 \pm 1.414 \cdot 10^{-6} \text{ g}$$

$$\alpha_b(T_e) = 0.256142 \cdot 10^{-3} \pm 10^{-7} \text{ g} \cdot \text{h}^{-1/4}$$

$$\alpha_b(T_1) = 0.269573 \cdot 10^{-3} \pm 10^{-7} \text{ g} \cdot \text{h}^{-1/4}$$

$$\alpha_b(T_2) = 0.3284 \cdot 10^{-3} \pm 10^{-7} \text{ g} \cdot \text{h}^{-1/4}$$

$$T_e = 286.00 \pm 0.18 \text{ K}$$

$$T_1 = 288.0 \pm 0.1 \text{ K}$$

$$T_2 = 296.0 \pm 0.1 \text{ K}$$

$$E_b = 70,000 \pm 1250 \text{ J/mol}$$

### Appendix 3b: Simulation Data for SAS Method

$$m_{2b} = 5.118342 \pm 10^{-6} \text{ g}, m_{4b} = 5.1000 \pm 10^{-6} \text{ g},$$

$$m_{2c} = 4.017077 \pm 10^{-6} \text{ g}, m_{4c} = 4.0000 \pm 10^{-6} \text{ g}$$

$$m_{ab} = m_{2b} - m_{4b} = 0.0183426 \pm 1.414 \cdot 10^{-6} \text{ g}$$

$$m_{ac} = m_{2c} - m_{4c} = 0.0170776 \pm 1.414 \cdot 10^{-6} \text{ g}$$

$$\alpha_b(T_e) = 0.2561 \cdot 10^{-3} \pm 10^{-7} \text{ g} \cdot \text{h}^{-1/4}$$

$$\alpha_b(T_1) = 0.2695 \cdot 10^{-3} \pm 10^{-7} \text{ g} \cdot \text{h}^{-1/4}$$

$$\alpha_b(T_2) = 0.3284 \cdot 10^{-3} \pm 10^{-7} \text{ g} \cdot \text{h}^{-1/4}$$

$$\alpha_c(T_e) = 0.2384 \cdot 10^{-3} \pm 10^{-7} \text{ g} \cdot \text{h}^{-1/4}$$

$$\alpha_c(T_1) = 0.2537 \cdot 10^{-3} \pm 10^{-7} \text{ g} \cdot \text{h}^{-1/4}$$

$$\alpha_c(T_2) = 0.3225 \cdot 10^{-3} \pm 10^{-7} \text{ g} \cdot \text{h}^{-1/4}$$

$$T_e = 286.0 \text{ K}$$

$$T_1 = 288.0 \pm 0.1 \text{ K}$$

$$T_2 = 296.0 \pm 0.1 \text{ K}$$

### Appendix 4: Previous Estimates of $\sigma(t_a)$

Previously, Hall *et al.*<sup>7</sup> estimated the systematic error  $SE(t_a)$  in the deduced age  $t_a$  due to a systematic error in estimating the ELT. Define

$$SE(t_a) = t'_a - t_a, \quad (4.1)$$

where  $t_a$  is the age calculated via Eqs. (10) and (11) using the actual  $T_e$ , while  $t'_a$  is calculated using an incorrect value  $T'_e$ . The systematic error has been estimated as<sup>7</sup>:

$$SE(t_a)/t_a = -E \cdot SE(T_e)/RT_e^2 \quad (4.2)$$

where  $SE(T_e) = T'_e - T_e$ .

For  $t_a = 3000 \text{ yr}$ ,  $T_e = 286 \text{ K}$ ,  $R = 8.3144621 \text{ J(Kmol)}^{-1}$ ,  $E = 70\,000 \text{ J}$ ,  $T_e = 285.5 \text{ K}$  corresponding to  $SE(T_e) = -0.5 \text{ K}$ ,

$$SE(t_a) = 0.0515t_a = +154 \text{ yr} \quad (4.3)$$

The negative sign in Appendix Eq. (4.2) signifies that when  $SE(T_e)$  is negative (ELT underestimated),  $SE(t_a)$  is positive (age overestimated). Table II for  $\sigma(T_e) = 0.5 \text{ K}$  and  $\sigma(\alpha) = 10^{-7} \text{ g}\cdot\text{h}^{-1/4}$  gives  $\sigma(t_a) = 158 \text{ yr}$ , in agreement with the Eq. (4.3) estimate, considering that Eq. (4.2) does not include the statistical error due to mass uncertainties.

### Appendix 5: Weak Dependence of the ELT on Activation Energy

Consider a temperature history where a sample is at  $T_1 = 10^\circ\text{C}$  (283.15 K) and  $T_2 = 15^\circ\text{C}$  (288.15 K) for fractions  $f_1$  and  $f_2$  of its lifetime, respectively. The ELT rate constant  $\alpha(T_e)$  is given as the FPM over the lifetime history<sup>7</sup> of  $\alpha(T_1)$  and  $\alpha(T_2)$ , as follows:

$$\alpha(T_e) = A \left[ f_1 \exp\left(-\frac{E}{RT_1}\right) + f_2 \exp\left(-\frac{E}{RT_2}\right) \right]^{1/4} \quad (5.1)$$

Since from Eq. (4),  $\alpha(T_e) = A \exp(-E/4RT_e)$ , it follows that:

$$T_e = \frac{-E}{R \cdot \ln \left[ f_1 \exp\left(-\frac{E}{RT_1}\right) + f_2 \exp\left(-\frac{E}{RT_2}\right) \right]} \quad (5.2)$$

which depends on the activation energy  $E$ . For  $f_1 = 0.5$  and  $f_2 = 0.5$ , for example, the ELTs are  $12.80^\circ\text{C}$ ,  $12.86^\circ\text{C}$  for  $E = 70\,000 \text{ J/mol}$ ,  $E = 85\,000 \text{ J/mol}$ , respectively.

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### References

- Savage, M. A. Wilson, M. A. Carter, W. D. Hoff, C. Hall, and B. McKay, "Moisture Expansion and Mass Gain in Fired Clay Ceramics: A Two-Stage (Time)<sup>1/4</sup> Process," *J. Phys. D: Appl. Phys.*, **41**, 055402, 4pp (2008).
- M. A. Wilson, M. A. Carter, C. Hall, W. D. Ince, S. D. Savage, B. McKay, and I. M. Betts, "Dating Fired-Clay Ceramics Using Long-Term Power Law Rehydroxylation Kinetics," *Proc. Roy. Soc.*, **465**, 2407–15 (2009).
- M. A. Wilson, A. Hamilton, C. Ince, M. A. Carter, and C. Hall, "Rehydroxylation (RHX) Dating of Archaeological Pottery," *Proc. Roy. Soc.*, **468**, 3476–93 (2012).
- A. Hamilton and C. Hall, "A Review of Rehydroxylation in Fired-Clay Ceramics," *J. Am. Ceram. Soc.*, **95**, 2673–8 (2012).
- F. Clegg, C. Breen, M. A. Carter, C. Ince, S. D. Savage, and M. A. Wilson, "Dehydroxylation and Rehydroxylation Mechanisms in Fired Clay Ceramic: A TG-MS and DRIFTS Investigation," *J. Am. Ceram. Soc.*, **95**, 416–22 (2012).
- M. A. Wilson, S. Clelland, M. A. Carter, C. Ince, C. Hall, A. Hamilton, and C. M. Batt, "Rehydroxylation of Fired-Clay Ceramics: Factors Affecting Early-Stage Mass Gain in Dating Experiments," *Archaeometry*, **56**, 689–702 (2013).
- C. Hall, A. Hamilton, and M. A. Wilson, "The Influence of Temperature on Rehydroxylation [RHX] Kinetics in Archaeological Pottery," *J. Archaeol. Sci.*, **40**, 305–12 (2013).
- S.-J. Clelland, M. A. Wilson, M. A. Carter, and C. M. Batt, "RHX Dating: Measurement of the Activation Energy of Rehydroxylation for Fired-Clay Ceramics," *Archaeometry*, doi: 10.1111/arc.12118 (2014).

- <sup>9</sup>K. J. Laidler, "The Development of the Arrhenius Equation," *J. Chem. Educ.*, **61**, 494–8 (1984).
- <sup>10</sup>J. R. Hulett, "Deviations from the Arrhenius Equation," *Quart. Rev., Chem. Soc.*, **18**, 227–42 (1964).
- <sup>11</sup>A. Mangel, "Applications of CI Microbalances," *J. Therm. Anal. Calorim.*, **71**, 107–11 (2003).
- <sup>12</sup>Quantachrome Instruments, Available at [http://www.quantachrome.com/vapor\\_sorption/aquadyne\\_dvs.html](http://www.quantachrome.com/vapor_sorption/aquadyne_dvs.html) (accessed 8 November 2014).
- <sup>13</sup>M. Le Goff and Y. Gallet, "Evaluation of the Rehydroxylation Dating Method: Insights from a New Measurement Device," *Quat. Geochronol.*, **20**, 89–98 (2014).
- <sup>14</sup>V. Hare, "Theoretical Aspects of Uncertainty Estimation in Rehydroxylation Dating"; University of Oxford, M.Sc. thesis (2014), (submitted to Royal Society Open Science).
- <sup>15</sup>J. Busby, A. Kingdon, and J. Williams, "The Measured Shallow Temperature Field in Britain," *Quart. J. Eng. Geol. Hydrogeol.*, **44**, 373–87 (2011).
- <sup>16</sup>M. E. Mann and P. D. Jones, "Global Surface Temperatures over the Past Two Millennia," *Geophys. Res. Lett.*, **30**, 1820–3 (2003).
- <sup>17</sup>K. S. Burakov and I. E. Nachasova, "Archaeomagnetic Study and Rehydroxylation Dating of Fired-Clay Ceramics," *Izvestiya, Phys. Solid Earth*, **49**, 105–12 (2013). □