



## Research paper

## Evaluation of the rehydroxylation dating method: Insights from a new measurement device



Maxime Le Goff\*, Yves Gallet

*Equipe de Paléomagnétisme, Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Univ. Paris Diderot, UMR 7154 CNRS, F-75005 Paris, France*

## ARTICLE INFO

*Article history:*

Received 2 May 2013

Received in revised form

2 October 2013

Accepted 3 December 2013

Available online 11 December 2013

*Keywords:*

Rehydroxylation dating

Ceramics

Heating duration

Archeology

Archeomagnetism

## ABSTRACT

The recently published rehydroxylation (RHX) dating method applicable to baked clay artifacts potentially represents a major tool for research in geoarcheology and archeomagnetism. We report on a new experimental device customized to conduct RHX experiments on series of ten samples without any operator manipulation. We applied the rehydroxylation method on precisely dated French archeological fragments. Our device provides adequate environmental experimental conditions, yet our observations identified several difficulties. First, based on the published protocol, the “archeological mass” of a sample should be determined following an initial drying at 105 °C when the slope of the mass over time is zero. In all our experiments on ~60 samples, no stabilization of the sample mass is reached even after several weeks of monitoring. This is always true whether the heating at 105 °C was short (a few hours) or long (several days), which may indicate that a slow diffusion process is ongoing even after a low-temperature heating. Second, the initial sample mass following the heating step at 105 °C or 500 °C remained dependent on the duration of heating even though both short and long heating were applied. We demonstrate that the duration of heating at both 105 °C and 500 °C is a critical parameter for the RHX dating method. Further methodological improvements, including the selection of suitable fired clay fragments, are thus required so that the RHX dating method becomes reliable and efficient.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Much effort is currently devoted to the construction of reliable regional and global geomagnetic field models ranging over the past few millennia (e.g. Pavón-Carrasco et al., 2009; Korte et al., 2011; Licht et al., 2013). These reconstructions rely on large compilations of directional and intensity magnetic data obtained from archeological, volcanic and sedimentary materials, for which the parameters of dating are clearly of major importance (e.g. Genevey et al., 2008; Donadini et al., 2009). In particular, the (archeomagnetic) data obtained from archeological baked clays, i.e. from kiln walls, pottery, bricks or tiles are recognized as very suitable for geomagnetic modeling because they often benefit from dating constraints provided by their archeological contexts of discovery, further including the typology of the studied objects, historical accounts and/or by radiocarbon (<sup>14</sup>C) counting.

The dating accuracy, together with the temporal homogeneity of the samples when several fragments collected from different objects (for instance ceramics) are used to define a single dated

archeomagnetic site are very restrictive criteria but essential to ensure the reliability of archeomagnetic data. All themes of research in archeomagnetism, such as the detection and characterization of rapid multidecadal-scale geomagnetic fluctuations (e.g. the archeomagnetic jerks; Gallet et al., 2003, 2009a), the potential link of the latter with atmospheric processes or their use as a dating tool for archeological purposes (e.g. Le Goff et al., 2002; Lanos, 2004; Gallet et al., 2009b) depend on the dating uncertainties attached to the analyzed objects. For this reason, the archeological dating method based on rehydroxylation processes in baked clays recently proposed by Wilson et al. (2009, 2012) offers an exceptional range of applications in archeomagnetism, in particular because the very same objects could both provide archeomagnetic and dating results, and more generally for all fields of research in (geo)archeology. One of the most important aspect of this new dating method, referred below to as the RHX (ReHydroXylation) dating method, is that it would also give the possibility to perform straightforward relative dating between fragments collected from the same archeological sites.

The RHX dating method as described by Wilson et al. (2009), however, is still challenging due to the lack of sufficient testing. There are no other successful dating results than those, not numerous, already proposed by M. Wilson and colleagues (10 data

\* Corresponding author.

E-mail address: [legoff@ipgp.fr](mailto:legoff@ipgp.fr) (M. Le Goff).

reported in 2009 and 5 others in 2012), while Bowen et al. (2011) were unable to obtain satisfactory results from 4 samples and Burakov and Nachasova (2013) underlined complexities from 6 dating attempts. For this reason, it appears essential to explore further the method, its validity considering samples of different ages and origins and its applicability to the domain of archeomagnetism. If successful, the rehydroxylation dating method would allow us to strengthen our collaboration with archeologists and would significantly contribute to the improvement of our knowledge of the geomagnetic field behavior over the past millennia.

The paper is organized as follows. After the present introduction, Section 2 describes the RHX dating method as proposed by Wilson et al. (2009). Section 3 describes a new experimental system we built in order to perform mass gain measurements for series of ten samples at the time in a temperature and relative humidity controlled environment. We present in Section 4 the results of our investigations using samples of different origins and different ages. From these experiments, we address in Section 5 several encountered difficulties, such as the systematic lack of stabilization of the mass of the samples after their heating at 105 °C, even after several weeks of monitoring, or the fact that the initial sample mass following the heating step at 105 °C and 500 °C remained dependent on the heating duration even though both short (a few hours) and long (up to a week) heating were applied. These difficulties, which prevent us to obtain satisfactory RHX dating estimates, are finally summarized in Section 6.

## 2. Description of the rehydroxylation dating method

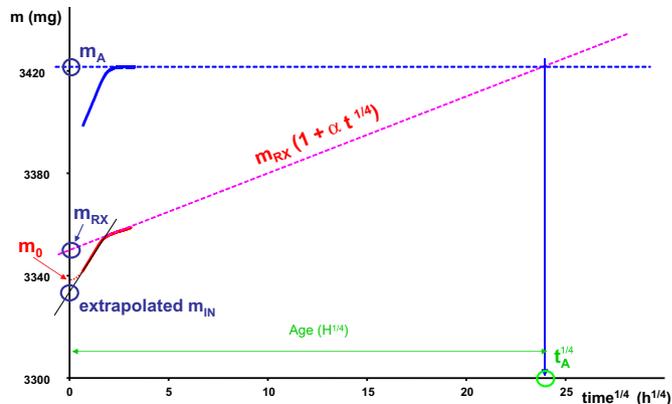
Such as described by Wilson et al. (2009), the overall principles of the rehydroxylation dating method seem to be relatively simple, self calibrated and apparently easy to implement. We present below a rough description of the method but a more thorough discussion on the underlying processes can be found in Wilson et al. (2009, 2012) (see also Savage et al., 2008; Hall et al., 2011; Hamilton and Hall, 2012). When the clays used for making pottery, bricks, etc. are heated to high temperatures (>500 °C), they undergo a complete dehydroxylation, which results in the loss of all water components (e.g. Wilson et al., 2012). This stage defines what can be referred to as the archeological “zero age” to be determined. When the baked clays are subsequently cooled at ambient temperature, they rapidly undergo (in a few hours) an adsorption phase which principally corresponds to the gain of capillary water (defining the brief “stage I” in RHX experiments), followed by a very slow rehydroxylation process, i.e. the diffusive transport of OH groups from the environment into the material (defining “stage II”), with both stages leading to moisture expansion and to a gain of mass of the material (e.g. Hamilton and Hall, 2012). The fundamental observation of Wilson et al. (2003, 2009) (see also Savage et al., 2008) lies in the fact that the increase in mass of a baked clay sample is a function of time following a power law with exponent 1/4 over centennial and millennial time scales (red dashed lines, Fig. 1). According to Wilson et al. (2009), such a behavior may reflect a diffusion process in a restricted environment (see also discussion in Hamilton and Hall, 2012). Using the notation given in Fig. 1, the law is:

$$m = m_{RX} \left( 1 + \alpha t^{1/4} \right) \quad (1)$$

or, in terms of fractional mass gain relative to  $m_{RX}$  (fmg<sub>RH</sub>):

$$\text{fmg}_{RX} = (m - m_{RX})/m_{RX} = \alpha t^{1/4} \quad (2)$$

The RHX dating method derived from the observations above hence comprises the following steps (Wilson et al., 2009, 2012):



**Fig. 1.** Principles of the rehydroxylation dating method. The blue (resp. red) curve represents the mass data obtained for one sample after its heating to 105 °C (resp. 500 °C) and while it remains in constant environmental conditions (temperature and relative humidity). The data are plotted against  $\text{time}^{1/4}$ . After the first heating at 105 °C, the mass data become constant after  $\sim 2.5 \text{ hours}^{1/4}$ , so defining the sample archeological mass ( $m_A$ ). After the second heating at 500 °C, the mass values show a linear trend after  $\sim 2 \text{ hours}^{1/4}$ , i.e. after the so-called stage I (see text), in accordance with a slow rehydroxylation process (stage II, see text); the extrapolation of this behavior to  $m_A$  gives its archeological age ( $t_A$ , in  $\text{hours}^{1/4}$ ). The two values  $m_{IN}$  and  $m_{RX}$  are the initial sample mass respectively derived from stage I and stage II—mass variations extrapolated to  $\text{time}^{1/4} = 0$ ;  $m_0$  is the “true” initial mass value after heating of the sample to 500 °C (Wilson et al., 2009). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

- Heating the sample of a few grams at 105 °C to constant mass in order to remove the capillary water from the pores and weakly bound adsorbed water (Wilson et al., 2012).
- Weighing the sample in imposed and constant conditions of temperature and relative humidity (RH) until reaching a constant mass, hereafter referred to as the archeological mass ( $m_A$ ).
- Heating the sample at high temperature (500 °C; Wilson et al., 2012) during several hours, until reaching a constant mass, in order to perform a complete dehydroxylation of the sample.
- Repeatedly weighing the sample during several weeks in the same constant environmental conditions as those imposed for step “b” until the mass gain rate becomes constant and can be precisely determined (Wilson et al., 2013).
- Defining from RHX mass data of step “d” fitted to a time  $1/4$  power law the parameters  $\alpha$  and  $m_{RX}$ , which allows one through extrapolation to  $m_A$  to determine the time spent since the original (archeological) heating of the sample. This defines  $t_A$  with:

$$t_A = ((m_A - m_{RX})/\alpha m_{RX})^4 \quad (3)$$

It is worth noting that Bowen et al. (2011) used a single power law function to fit all the mass data encompassing both stages I and II. Until now, however, no satisfactory RHX dating results could be derived using this alternative approach (see below).

In the method proposed by Wilson et al. (2009), the stringent parameter is that the kinetic of rehydroxylation after high-temperature heating ( $\alpha$ ) strongly depends on the temperature experienced by the sample (but not on humidity). To obtain a dating, the temperature used for the experiments must be chosen identical or very close to that experienced by the sample during its archeological history (referred to as the mean lifetime temperature by Wilson et al., 2009). Beyond the experimental constraints, which this imposes (no disturbance in temperature and humidity in a climatic chamber during several days up to several weeks), it is thus necessary to precisely know the average climate (average

temperature) of the region where the studied objects have been found, which is far from being trivial (e.g. Wilson et al., 2012). Dating an isolated sample/fragment seems therefore relatively difficult but this difficulty could be circumvented by working on sets of fragments collected from the same archeological sites. In this case, as previously mentioned, the method would at least insure relative dating between the fragments without making any assumption on the temperature to be used during the RHX experiments, but also, if some of the studied fragments are dated, it would then make it possible to adjust the correct temperature applicable to the undated samples. Note that Wilson et al. (2009) showed that the effect of temperature on rehydroxylation rates follows an Arrhenius-type behavior, which permits some *a posteriori* adjustments.

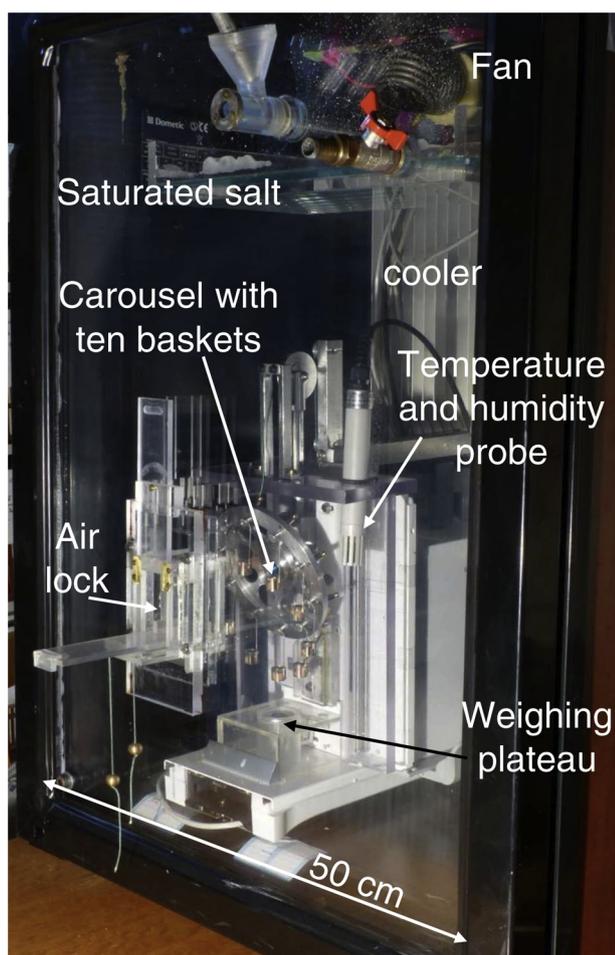
### 3. Description of a new experimental device

In order to adapt the rehydroxylation experiments to our intention of performing both relative and absolute dating, in more direct connection with our archeomagnetic studies, we designed a weighing system for series of ten samples at a time (Fig. 2). This system comprises a microbalance Mettler-Toledo XP26, with an accuracy of  $\sim 1 \mu\text{g}$ , whose motors that normally operate the

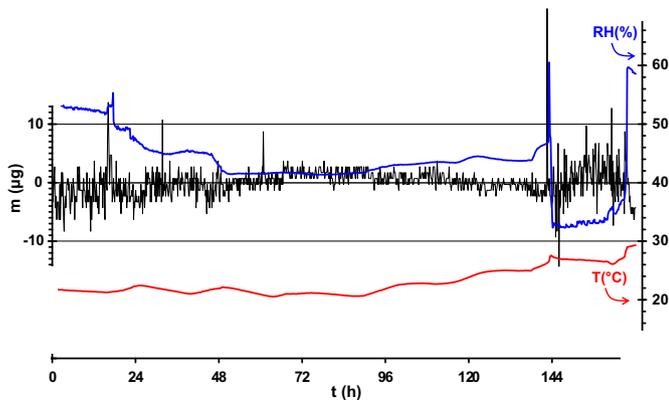
movement of glass doors of protection are now used to drive the rotation of a laboratory-built carousel with 10 samples, 2–3 g each, placed in small baskets hung to a hook on the carousel. These baskets have a cylindrical shape, and can contain samples up to 15 mm in height and 13 mm in diameter. The microbalance is installed in a climatic chamber consisting of a modified wine cellar working according to the principle of absorption, i.e. without any vibration. Inside the climatic chamber, the relative humidity level is controlled by a saturated salt solution (RH  $\sim 32\%$  using Potassium Acetate or  $\sim 42\%$  using Magnesium Chloride), with the possibility to add more solution without the need to open its large door during experiments, which would drastically change the temperature and RH conditions requiring several hours ( $\sim 24$  h) before to reach again their initial values. The samples are placed on the carousel using an air lock with small sliding doors, again avoiding the need to open the main door of the chamber for this operation (Fig. 2). Acknowledging the instabilities in environmental conditions (both in temperature and RH) provoked when introducing hot samples inside the climatic chamber (beginning of steps “b” and “d”), our device benefits from the relatively large interne volume of the climatic chamber ( $\sim 0.15 \text{ m}^3$ ), which thus allows one to minimize that effect (e.g. Barrett, 2013; Wilson et al., 2013). Moreover, thanks to the rapid and repeated rotation of the carousel (15 cm-diameter and 4 cm-vertical movement) during experiments, the air is not stagnant in the vicinity of the samples, which otherwise could cause some spurious effects on mass-gain variations (M. Wilson, pers. com. 2013). For the same reason, a small fan was also placed in the upper part of the climatic chamber.

The performances of our climatic chamber in terms of temperature and humidity stability appear sufficient for RHX experiments (see below), with nearly half-hour periodic low-amplitude oscillations of the order of  $\sim 0.2 \text{ }^\circ\text{C}$  and  $\sim 0.3\%$  RH directly related to the thermal regulation of the climatic chamber. After filtering these oscillations, the mean stability of the environmental conditions is of the same order of magnitude and so, similar to the manufacturer specifications of the equipment used by Wilson et al. (2009, 2012). The latter is a Cisorp Water Sorption Analyser (CI Electronics), which consists in a double microbalance with a very high accuracy ( $0.1 \mu\text{g}$ ) and a small climatic chamber ( $\sim 10^{-3} \text{ m}^3$ ); it thus makes it possible to analyze only 2 samples at a time. In our system, however, changes in weather during the period of RHX experiments (typically 2–3 weeks, sometimes longer; see below) could induce temperature and RH fluctuations with larger amplitudes and longer, daily wavelengths (maximum  $\sim 1 \text{ }^\circ\text{C}$  and  $\sim 1\%$  RH). For this reason, we have dedicated a closed space in our laboratory at Saint-Maur, where the stability of the temperature is controlled by a powerful air conditioning system in addition to a dehumidifier. Since the mass data acquisition is automatic, there is no need to enter this space during the RHX experiments, which further insures the stability of the environmental conditions around and inside the measurement system.

Fig. 3 illustrates the stability of weighing given by the balance used for our experiments. We show the measurements recorded on one of the empty baskets, always the same, during  $\sim 7$  days (values obtained after subtraction of the mass of this basket). These measurements were further carried out with extreme environmental variations, principally in RH (blue curve in Fig. 3), during the phase of development of our instrument, including tests for internal ventilation. We observe that whatever the environmental conditions, the resulting values are always within  $10 \mu\text{g}$ , decreasing to  $\sim 5 \mu\text{g}$  when the conditions are the most stable, i.e. between  $\sim 50$  and  $\sim 90$  h (Fig. 3). The latter value therefore provides a good estimate of the stability of the weighing in normal conditions for RHX experiments (steps “b” and “d”).



**Fig. 2.** New device specially designed for rehydroxylation experiments. Series of ten samples can be weighed at the same time using a carousel driven by the motors of the microbalance (here a Mettler-Toledo XP26). Each sample inside its basket can be suspended at one of the ten carousel's hooks using an air lock system with small sliding doors. The climatic chamber is a modified wine cellar with no-vibration absorption cooling. The relative humidity inside the climatic chamber is controlled by a saturated salt solution. See text for further explanations.



**Fig. 3.** Illustration of the weighing stability of the Mettler-Toledo XP26 microbalance used for the RHX experiments. The grey curve shows the mass measurements obtained during  $\sim 7$  days for one empty basket after subtraction of the (constant) mass considered for this basket. These measurements were intentionally performed while large variations in environmental conditions occurred inside the climatic chamber (RH: blue curve; temperature: red curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

After the heating of the samples either at  $105\text{ }^{\circ}\text{C}$  or at  $500\text{ }^{\circ}\text{C}$ , the time necessary to hang the 10 baskets with their samples on the carousel, via the air lock system, takes at least 2 min but does not exceed 3–4 min. Furthermore, due to the time requested for the stabilization of the balance, comprising a zeroing and the weighing, the weighing of a series of ten samples (i.e. a complete rotation of the carousel), lasts  $\sim 4$  min. These technical constraints hence lead to the loss of the very beginning of steps “b” and “d” (see dashed lines in Fig. 1). Attempts to introduce hot ( $\sim 50\text{ }^{\circ}\text{C}$ ) samples in the climatic chamber did not reveal the early part of these two steps because of convection of hot air, which made impossible a rapid stabilization of the balance. Nevertheless, we note that the initial mass value of step “d”, called  $m_0$  by Wilson et al. (2009), is not taken into account for age computations. In our study, to make comparisons between the different observed mass variations, we will refer to the changes in fractional mass gain (fmg) relative to an initial mass derived for each sample from either its stage I- or stage II-mass behavior extrapolated to  $t = 0$  ( $m_{\text{IN}}$  or  $m_{\text{RX}}$  respectively, Fig. 1).

## 4. First results

### 4.1. Studied fragments

We used precisely dated fragments collected from different French archeological contexts, which in most cases provided suitable archeointensity results (Genevey et al., 2009) (discussion and references therein). A set of samples was obtained from two groups of fragments of the same age collected from sites Bois d’Epense (archeomagnetic site BDE01 dated to 1785–1815 AD; studied fragments from three different ceramics referred to as BDE01-01/04/05 in Genevey et al., 2009) and Ancy-le-Franc (archeomagnetic site ALF03 dated to 1797–1807 AD; studied fragments from two different ceramics referred to as ALF03-01/02 in Genevey et al., 2009), which were faience workshops during the second half of the XVIIIth century and the XIXth century AD. Several samples were also obtained from different pavement brick fragments, whose pavements laid in the Ecoeu castle (archeomagnetic site EC02 dated to 1549–1551 AD, studied fragments from two different bricks referred to as EC02-05/07 in Genevey et al., 2009) and in the “King’s room” of the Hospices de Beaune (archeomagnetic site HB01 dated to 1448–1452 AD; studied fragment from brick no. 09; see photo in Fig. A in supplementary material). We also analyzed a

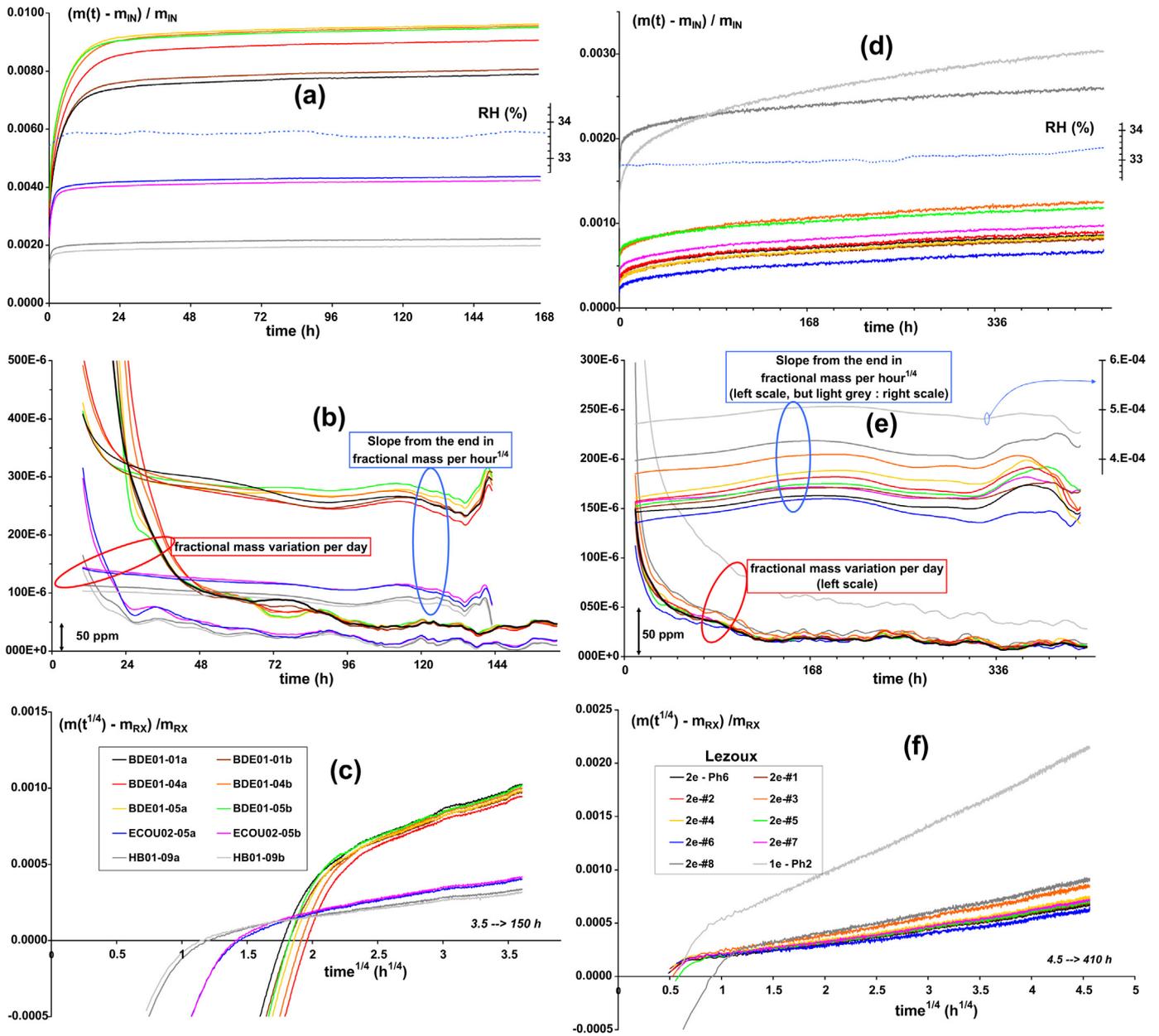
series of 10 fragments of different Roman samian wares produced in Lezoux (Central France) during the second century AD. Lezoux was a famous ceramic production center during the Roman period, in particular during the three first centuries AD, and its mass production was exported to many regions of the Roman Empire (e.g. Bet et al., 1989; Bet, 2012). The dating of these ceramics is generally well constrained within  $\sim 1/3$  century from their morphological attributes, molded decoration and/or marks of potters.

It is worth pointing out that the fragments from sites BDE01, ALF03 and all fragments from Lezoux were found in a production context. For some reasons, for instance because of cracks or deformation induced during their manufacture, the ceramics were thrown out in the close vicinity of the kilns where they were fired. Such a context obviously limits the possibility for secondary heating inducing a partial or complete remagnetization of the studied fragments, otherwise more frequent when the potsherds are found in a use context. A single magnetization component was obtained in all our samples, likely tracing a single heating-cooling event, which is necessary for correctly using the RHX dating technique. This is also an important aspect when testing the reproducibility of the results and the possibility of relative dating offered by the RHX dating method, whatever the exact mean temperature lifetime characterizing the fragments. Finally, we note that all the studied fragments were heated at high temperatures ( $>600\text{ }^{\circ}\text{C}$ ) during their manufacture. X-Ray Diffraction (XRD) analysis carried out on a series of fragments from 4 sites (BDE01, EC02, HB01 and Lezoux; M. Gérard, pers. com. 2013) shows that their composition is dominated by quartz and feldspar and that all clay minerals such as kaolinite underwent a transformation during the heating. The absence of mullite or cristoballite in the XRD results indicate that the maximum temperature reached during the heating was most probably  $<1000\text{ }^{\circ}\text{C}$  (e.g., Holm, 2001; Cultrone et al., 2001).

### 4.2. Determining the archeological mass of the samples (steps “a” and “b”)

We present in Fig. 4 fractional mass-gain measurements for two sets of 10 samples after their heating to  $105\text{ }^{\circ}\text{C}$ . The first series is made of five fragments (BDE01-01/04/05, EC02-05 and HB01-09), two samples each, whereas the second series is constituted by ten samples collected from as many different Lezoux fragments. In fact, all samples underwent two successive heating at  $105\text{ }^{\circ}\text{C}$ , respectively during 4 h and 16 h for the first series of samples and during 66 h and 51 h for those of the second series. Weighing measurements were performed after each heating and the data reported in Fig. 4 are the results obtained after the second heating. For these experiments, the temperature and the relative humidity inside the climatic chamber were chosen close to  $13\text{ }^{\circ}\text{C}$  and 32%, respectively. These conditions are similar to those considered by Wilson et al. (2009, 2012) for their attempts of dating, and the chosen temperature most probably represents a good estimate of the mean lifetime temperature expected for the samples. Note that because of the unexpected behavior observed in the present study (see below), a better estimate of the “true” mean lifetime temperature experienced by our samples was not searched.

Although the environmental conditions have remained stable throughout the experiments (see the blue dashed lines in Fig. 4a,d), a striking feature is that the archeological mass of the samples never reaches a constant value, even after more than 2 weeks of measurements (Fig. 4a,d). This is further shown in Fig. 4b,e where the gradients of the fractional mass gains computed per day are reported (see the curves encircled in the red oval). We observe that the gradients first evolve rapidly and significantly (during  $\sim 2$  and  $\sim 4$  days, respectively), principally due to a rapid gain of mass by capillarity (stage I), and next converge more slowly toward much



**Fig. 4.** Fractional mass-gain (fmg) variations obtained for two series of 10 samples after their heating at 105 °C during 7 and 18 days, respectively. Fig. 4a–c: the set of samples is constituted by three different fragments from the same site BDE01, one fragment from site ECO2 and another fragment from site HB01; two twin samples are analyzed for each fragment (see color code on the figure). Fig. 4d–f: the samples were collected from ten different samian-ware fragments produced in Lezoux. Fig. 4a,d: the fmg are relative to  $m_{IN}$  (see definition in legend of Fig. 1) and plotted against time in hours. The blue dotted lines show the variations in relative humidity (RH) monitored during the experiments. Fig. 4b,e: Temporal variations in fmg behavior observed for the two series of samples. The curves encircled in the red oval exhibit the variations computed per day (i.e. the slopes), while those encircled in the blue oval show the slopes computed in  $\text{fmg}/\text{hour}^{1/4}$  using running time intervals decreasing up to the end of the experiments. Fig. 4c,f: same data as in Fig. 4a,d but the fmg are here relative to  $m_{RX}$  (see definition in legend of Fig. 1) and plotted against  $\text{time}^{1/4}$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lower values, but the latter never achieve zero. This behavior shows no sign of change even after several weeks of measurements. It is important to stress that the same behavior was observed in all (~60) our studied samples, independently of the very small (increase or decrease) sporadic changes in RH, of less than 0.2–0.3%, which sometimes occurred during the weighing experiments (e.g. Fig. 4).

Fig. 4a,d further show that the amplitude of the mass-gain variations, particularly at the beginning of the experiments, appears very different between the two sets of samples. While it is quite significant, between 0.2% and 0.9% for the first series of

samples, it remains much more limited, less than 0.08% (but ~0.2% for two samples) for the second series of samian-ware samples from Lezoux. We note that such a weak porosity for the vitrified pore structure of the samian-ware shards (thus linked to the high temperature of firing of the pottery) has already been mentioned by Wilson et al. (2012).

Fig. 4a also illustrates the differences in mass gain variations occurring between two samples collected from the same fragments (see color code in the inset of Fig. 4c). For the five fragments analyzed here, the differences between the twin specimens remain limited, thus revealing a quite homogeneous behavior (note that

these differences nevertheless induce some uncertainties in RHX dating). During all our experiments, a similar homogeneity was systematically obtained for the fragments made using a fine and homogeneous clay paste. In contrast, the clay paste of pavement brick fragment HB01-09 is clearly coarser (and more reddish), which we think may explain the more heterogeneous mass-gain behavior we observed between several samples from this fragment (but not between the twin HB01 samples shown in Fig. 4a; see Fig. A in supplementary material).

Additional experiments performed on samples partly from the same fragments after their heating at a slightly lower temperature (90 °C and 95 °C) or using different RH levels (41% and 32%) further indicate that the long-term mass behavior mentioned above is not related to these parameters. Moreover, different series of measurements were systematically carried out on the same samples after at least two successive heating at 105 °C during several hours (one or two days each). We observed that the repetition of heating does not change the overall trend of the long-term mass gain variations, but the successive heating causes a systematic, and significant loss of mass (see Fig. B and C in supplementary material).

Our experiments conducted for step “b” therefore show that the accurate determination of the sample archeological mass  $m_A$  after the heating at 105 °C is more complex than initially expected. The fact that for all our samples their masses are continuously increasing after several days and weeks of measurements by much more than one ppm per day (i.e. a threshold value considered by Wilson et al., 2012) may indicate that a slow diffusion process is ongoing even after a low-temperature heating. A simple analysis of the mass-gain rates indicates that they can satisfactorily be modeled by a  $\frac{1}{4}$  power law after the first few days of measurements (Fig. 4c,f), yielding reasonably constant slopes for the fractional mass gain (fmg) computed per  $\text{time}^{1/4}$  (see the curves encircled in a blue oval in Fig. 4b,e). If significant, such a characteristic would clearly bring some confusion with the rehydroxylation process occurring after high-temperature heating (see below).

Independent of the difficulty above, plotting these data against  $\text{time}^{1/4}$  further highlights the effects of weak fluctuations in environmental conditions (RH) on mass-gain variations. Indeed, we observe that during the first series of measurements small variations in RH, with slightly higher values, occurred after ~80 h (Fig. 4a), which contrasts with a small decrease in RH values after around 230 h during the second series of measurements (Fig. 4d). In both cases, the fractional mass-gain variations do not seem to be affected, at least visually, by these very limited environmental fluctuations (see in particular Fig. 4a). However, a clear effect marked by a bump is observed for the samples from fragments BDE01 and EC02 when the data are reported in  $\text{time}^{1/4}$  (~3 hours<sup>1/4</sup> see Fig. 4c). This is clearly not the case for all data from Fig. 4d, and this difference can again be explained by the much weaker porosity of the samian-ware pottery (these samples were thus insensitive to the small temporary RH variations).

#### 4.3. Rehydroxylation experiments (steps “c” and “d”)

Following Wilson et al. (2009), the samples were next heated at 500 °C. The duration of heating was 72 h for the first set of samples and 68 h for the second set (i.e. according to the long heating duration, up to several days, promoted in Wilson et al., 2012). Mass measurements were conducted over more than three weeks (respectively 22 and 26 days; Fig. 5a, c). During these time intervals, the environmental conditions remained stable inside the climatic chamber, i.e. within 0.5% in RH (blue dotted lines in Fig. 5a, c). We note however that for the series of samian-ware samples, an increase in RH by ~0.5% occurred during ~2 days after ~17 days of measurements, which was provoked by a temporary breakdown of

the air conditioning system. Fortunately, this problem apparently had no impact on the mass measurements (Fig. 5c, d), likely because the samian-ware samples are only very weakly sensitive to variations in RH (see Section 4b).

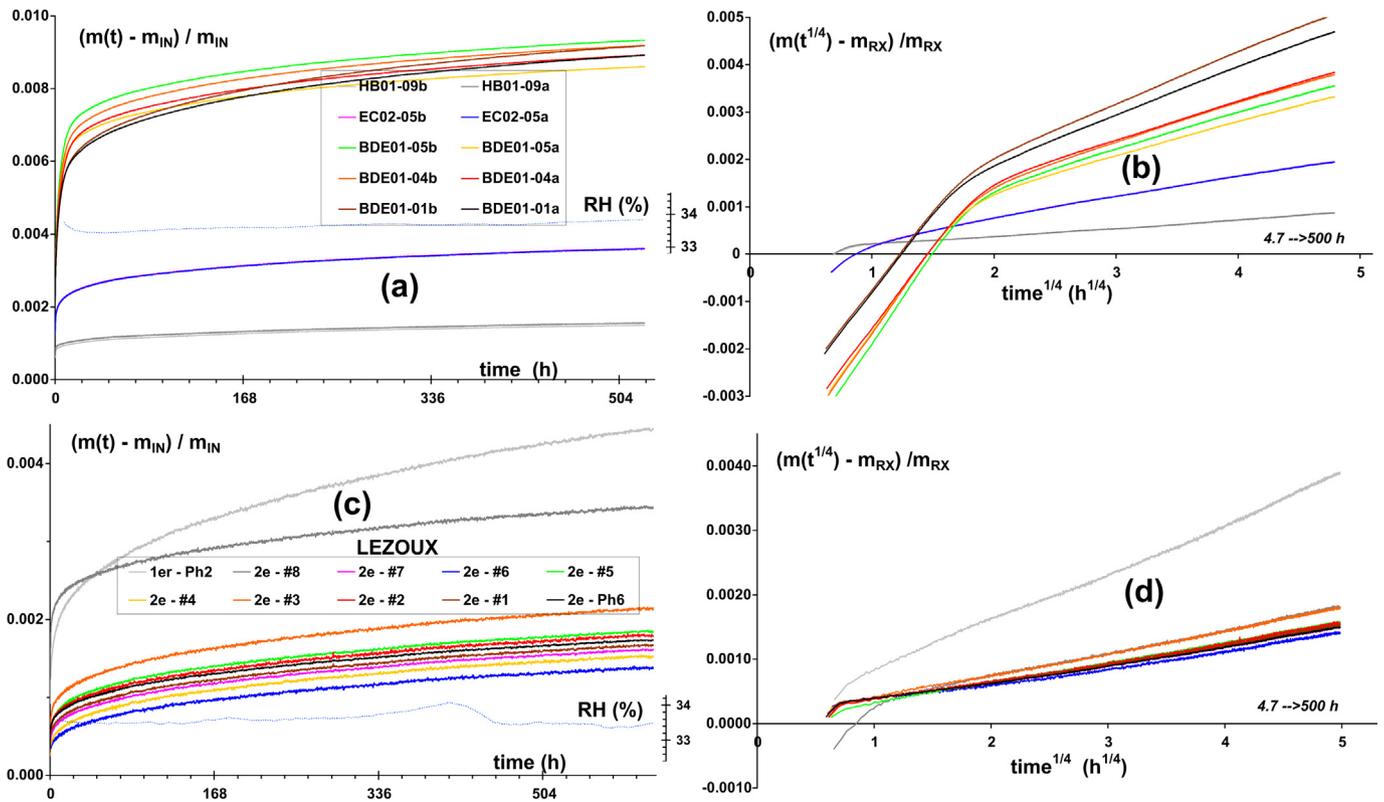
Fig. 5 clearly exhibits the two stages previously described by Wilson et al. (2009, 2012). In both cases, the first stage (stage I) marked by rapid variations occurs during approximately two–three days, and is followed by stage II which is characterized by much slower continuous variations. Concerning the first series of measurements (Fig. 5a), the curves are distinctly grouped according to the origin of the samples. Fig. 5a further indicates a good homogeneity of the behavior between samples from the same fragments (the homogeneity is particularly excellent for fragments EC02 and HB01). For the samian-ware samples, the curves are essentially grouped but two are significantly different (Fig. 5b). When plotted against  $\text{time}^{1/4}$ , data from a large late part of stage II are in good accordance with a linear trend (Fig. 5b, d). Our experiments for step “d” (i.e. the rehydroxylation step) thus appear compatible with the observations made by Wilson et al. (2003, 2009; 2012; 2013) and Savage et al. (2008).

We also conducted several series of measurements after successive heating of the samples at 500 °C (see Fig. C in supplementary material). As previously observed for step “b”, the repetition of heating does not change much the long-term variations of the samples, the latter keeping nearly the same mass-gain rate ( $\alpha$ ) over time, but it again tends to make uncertain the overall magnitude of these variations (referred below to as the “mass level”).

## 5. Discussion

The weighing measurements performed in our study for steps “b” and “d” present a lot of similarities with previous rehydration/rehydroxylation results, in particular the sensitivity of those measurements to humidity except for the Roman samian wares (Savage et al., 2008; Wilson et al., 2009, 2012; Bowen et al., 2011, 2013; Drelich et al., 2013). In spite of the complexities reported in Section 4, Fig. 6 shows the attempts of RHX dating obtained using the archeological masses and the fmg data reported in Figs. 4 and 5, respectively. For both series of samples, we partially took into account the problem in the determination of their  $m_A$  (see Section 4b) by considering the highest values obtained at the end of our step “b”. Fig. 6 clearly shows that the derived ages are generally far too young, in fact very recent, without relationship with the known ages of the analyzed fragments. This is particularly the case for the Roman samples from Lezoux for which ages of less than 20 years are found (Fig. 6c). Only the two samples from site HB01 yield raw ages relatively close (603 and 736 years) to the one expected (560 years). Fig. 6a further shows a grouping of the derived ages according to the origin of the fragments, but again these ages are not in agreement with the true ages. We also observe significant differences up to several tens of years between samples from the same fragments (229/287 years for fragment EC02-05; 10/12 years, 42/59 years, 45/82 years respectively for the three fragments BDE01 of same age, and see above for fragment HB01-09). It is worth mentioning that the RHX and the true ages of the fragments cannot be reconciled either if the archeological masses are derived from the extrapolation of the long-term trends seen in Fig. 4 until the variations in  $m_A$  become smaller than 1 ppm.

At present, the simplest explanation for our unsuccessful dating results is likely to be attributed to the absence of stabilization of the mass levels despite several short and long heating of the samples at 105 °C (between four hours and up to several days) and 500 °C (between two days and up to more than four days). All our experiments thus make it clear that the heating durations at these two



**Fig. 5.** Fractional mass-gain variations versus time for the same two series of 10 samples (see Fig. 4) after their heating at 500 °C. Measurements were performed during 22 and 27 days, respectively. Fig. 5a,c: Temporal variations of fmg relative to  $m_{IN}$  (see definition in legend of Fig. 1). The blue dotted lines show the variations in relative humidity (RH) monitored during the experiments. Fig. 5b,d: same data as in Fig. 5a,c but the fmg are relative to  $m_{RX}$  (see definition in legend of Fig. 1) and plotted against  $time^{1/4}$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

temperatures are crucial parameters for the RHX dating method. This point has, however, not been detailed enough until now by Wilson et al. (2009, 2012). One can find some information in Ince's (2009) thesis and in the RHX patent (Wilson et al., 2010), where it is only specified that these durations are rather short, i.e. of a few hours, whereas more recently Wilson et al. (2012) have mentioned the necessity of conducting longer heating, possibly up to several days, so that the samples can reach a constant mass at 105 °C and 500 °C. Again, we have tried in our study both short and long heating, but without obtaining a stabilization of the mass levels for steps “b” and “d”. These durations should thus be carefully evaluated for each sample, however this will involve time-consuming additional experiments besides the “regular” cycle of RHX measurements.

Another possible effect leading to biased RHX dating results may be related to the mineralogy of the studied samples, even though Wilson et al. (2009) emphasized the self-calibrating nature of the RHX dating method (but see discussion in Bowen et al., 2011), and/or be provoked by possible mineralogical alteration of the fragments since their manufacture, in particular during the laboratory heating. The latter issue was already discussed by Burakov and Nachasova (2013). In order to decipher that possibility, we carried out for the first series of samples measurements of their low-field magnetic susceptibility versus temperature using a KLY-3 Kappabridge coupled with a CS3 thermal unit. We briefly recall that each type of iron oxide is characterized by its own magnetic susceptibility (e.g. Dunlop and Özdemir, 1997) and the reversibility between the heating and cooling curves of susceptibility vs. temperature constitutes a good marker of the stability on heating of the magnetic mineralogy originally present in the

samples. All the mineralogical components are therefore not concerned by this test, but if a modification is detected between the heating and the cooling curves of susceptibility, we could conclude to the transformation, either by oxidation or reduction, of at least a fraction of the iron oxides, slightly changing the water budget in the samples (e.g. Dunlop and Özdemir, 1997; Burakov and Nachasova, 2013). Moreover, our experience in rock magnetism tells us that, when existing, these transformations generally occur rapidly, thus avoiding the need to heat the samples during a long duration to detect them. A point of note is that the information provided by this test is more qualitative than quantitative because the non-reversibility between the heating and cooling susceptibility curves would indicate that the RHX dating results are most probably biased but without us exactly knowing by how much.

In the present study, the susceptibility measurements were performed up to ~500 °C, the same temperature as for step “c”, and the results do not show evidence for any noticeable alteration of the magnetic mineralogy of the studied samples (see examples in Fig. 7). Concerning samian wares, we note that Wilson et al. (2012) have obtained satisfactory results for this very specific type of material (but it is true that the fragment analyzed by Wilson and colleagues was produced from La Graufesenque in southern France and not from Lezoux as in the present study). We therefore did not obtain evidence indicating the occurrence of significant alteration of the samples neither during their heating to 105 °C nor to 500 °C.

Finally, it is also of interest to have some concerns on the  $(time)^{1/4}$  power law proposed for the behavior of the rehydroxylation process. Further confirming the reality of exponent  $1/4$  as found by Savage et al. (2008) and Wilson et al. (2009) is in fact not a

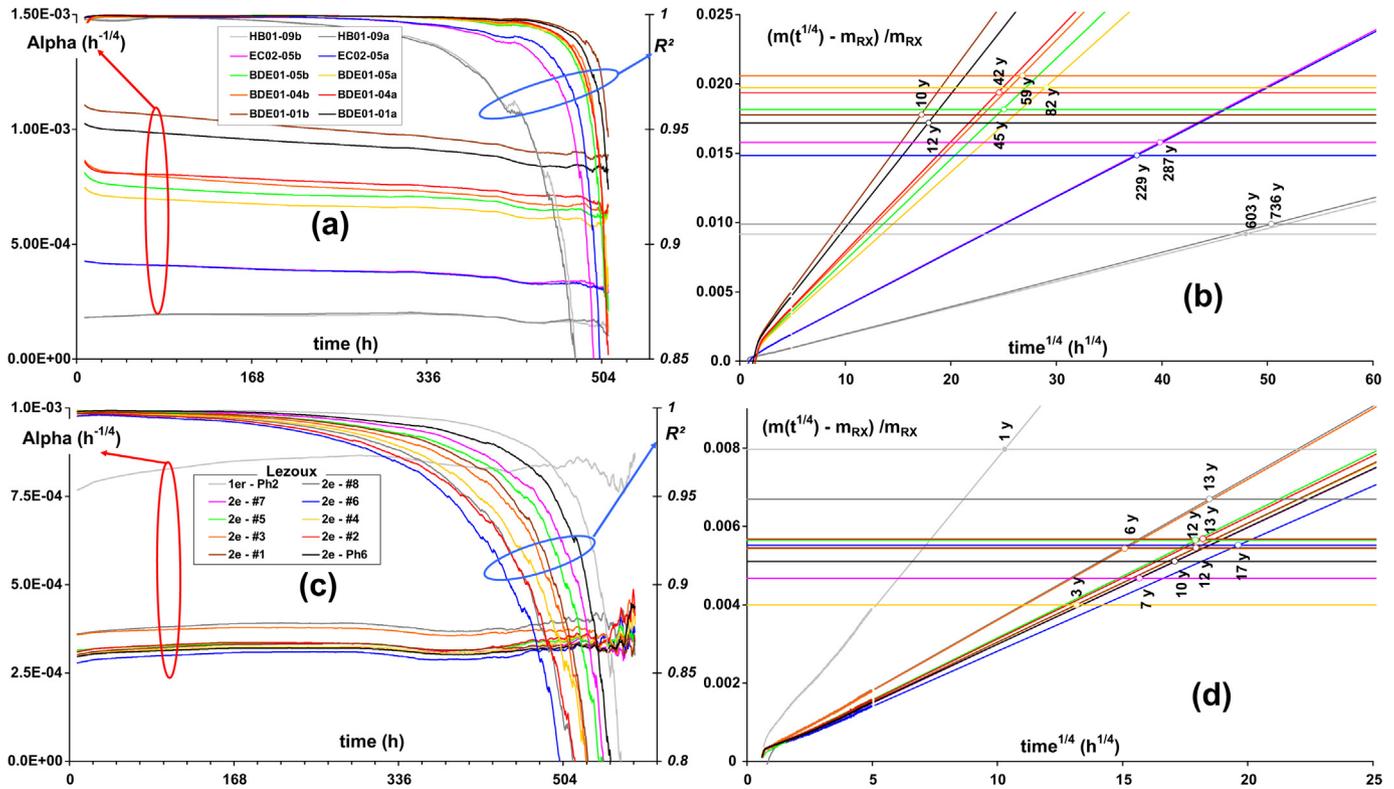


Fig. 6. Dating attempts using the rehydroxylation method. a, c) Variations against  $t^{1/4}$  of the rehydroxylation rates  $\alpha$  (in the red oval; left scale) and of the derived  $R^2$  regression parameters (in the red oval, right scale) computed from the fractional mass gains using running time intervals decreasing up to the end of the experiments. b, d) Rehydroxylation dating of the analyzed samples. The horizontal lines show the fractional archeological mass gains relative to  $m_{RX}$  ( $fmg(m_A/m_{RH})$ ; see Fig. 1), and the thick lines show the extrapolation of the experimental rehydroxylation data until intersection with the corresponding  $fmg(m_A/m_{RH})$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

trivial matter because of the mixing of the two processes leading to phases I and II at the beginning of rehydroxylation measurements.

Considering the fractional mass gains as a function of time, the rehydroxylation process (phase II) yields the general equation:

$$fmg(t) - \mu = \alpha t^{1/N} \tag{4}$$

in which there are three independent parameters: the rate  $\alpha$ , the power  $1/N$  and  $\mu$  which is theoretically null when the  $fmg$  are relative to  $m_{RX}$  (see Equation (2) in Section 2).

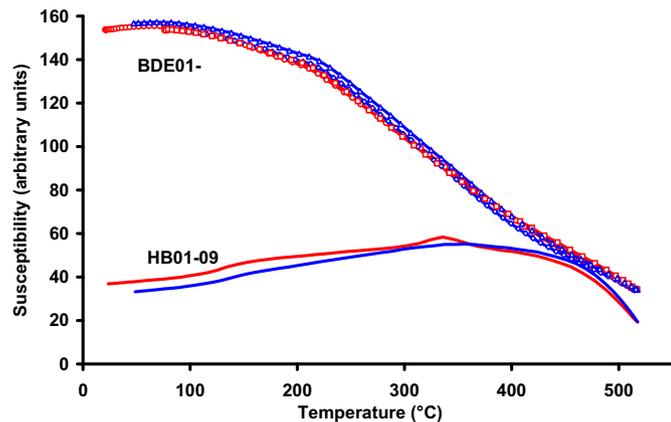


Fig. 7. Low-field magnetic susceptibility versus temperature (up to 500 °C) curves for samples BDE01-04 and HB01-09. Heating (cooling) curves are in red (blue). Sample BDE01-04 was successively heated two times up to ~500 °C. The good reversibility between the heating and cooling curves indicates the absence of alteration on heating of the magnetic mineralogy of the two samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

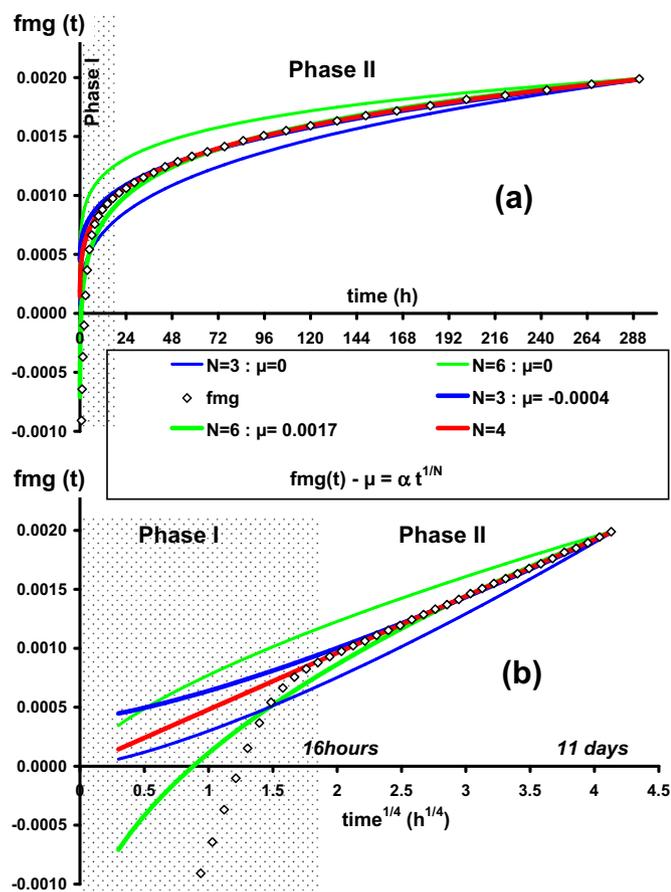
The search of  $N$  can be simplified by considering the logarithm of Equation (4):

$$\log(fmg(t) - \mu) = \log \alpha + (\log t)/N \tag{5}$$

where  $\alpha$  now appears as a translation and  $N$  can be obtained from least-squares calculations by successive adjustments of  $\mu$ .

Using the non-linear algorithm of Levenbeg-Marquardt (e.g. Crescent Software, 1994), we can then fit the three parameters to the mass data. From our 60 experimental data, we obtained values for  $N$  ranging from 2 to 7 (see examples in Fig. D in supplementary material), with a maximum frequency for 3 and 4. These values are generally grouped according to the fragments, but we note that they, of course, also depend on the time chosen for the beginning of the fitted segment (between 1.5 and 3  $h^{1/4}$ ). In order to further illustrate the difficulty of precisely finding a value of  $N = 4$  in the RHX experimental conditions, we constructed a synthetic data set obeying a true  $1/4$  power law succeeding a phase-I like mass behavior (the latter being derived from Equation (6) below; Fig. 8). In this case, we observe that after 2 or 3 days of experiments (i.e. after phase I), values of  $N$  between 3 and 6 provide a very reasonable fit for a large late fraction of the synthetic data.

The range of values of  $N$  obtained is similar to the one previously found by Bowen et al. (2011), although their data appear much more scattered than ours (see their Table 3). It is worth mentioning that Bowen et al. (2011) used another (and unique) function relying on the 1898 Lagergren equation (see for instance Ho, 2004) to fit the mass variations all through the RHX experiments, thus including the mass variations both during phase I and phase II. Considering fractional mass gains, their function can be rewritten as:



**Fig. 8.** Fitting examples of synthetic RHX data (diamond symbols) obeying a  $t^{1/4}$  power law (thick red line) using a power law with exponents  $1/3$  (thin blue curve) and  $1/6$  (thin green curve). Parameters  $\alpha$  and  $\mu$  can be adjusted using Equation (4) so that the curves, whatever the true exponent, become in good agreement with the synthetic data after 2 or 3 days of measurements (thick green and blue curves). The data are reported against time (a) and  $\text{time}^{1/4}$  (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$\text{fmg}(t) = -\beta e^{-t/\tau} + \mu + \alpha t^{1/N} \quad (6)$$

This equation thus introduces two supplementary parameters, the phase-I amplitude  $\beta$  and the time constant  $\tau$ . Not surprisingly, these additional parameters do not allow for a better least-squares determination of  $N = 4$ . Nevertheless, the equation used by Bowen et al. (2011) is particularly interesting because it provides a reasonable fit to the entire data set avoiding the need of considering a rather problematic cutoff between data from phase I and phase II.

At this step, the calculations using three or five free parameters therefore do not permit one to satisfactorily verify a systematic value of 4 for  $N$  (see also discussion in Bowen et al., 2013), which is the *sine qua non* condition for the validity of the RHX dating method. It may be argued that the reason for that could either result from inappropriate conditions of our RHX experiments, in particular because the mass-gain levels remained dependent on the heating duration, or from the unfortunate inadequacy of our analyzed samples for the RHX dating method, for instance because of their specific mineralogical assemblages or of their alteration (but undetected from thermomagnetic experiments) during the heating at 500 °C. Further RHX analyses will be clearly necessary for deciphering this issue.

## 6. Concluding remarks

Our study allows one to describe a new experimental device for RHX experiments, which was designed with the objective to

conduct joint RHX and archeomagnetic analyzes. To this end, our equipment was specially adapted for the automatic weighing of series of ten samples, hence providing the possibility to obtain both relative and absolute dating from the same series of measurements. The results we have obtained so far from more than 60 samples of different origins (clay sources) and different ages underline several recurrent problems. No baked clay fragment gave satisfactory RHX dating results, whether it is for relative and absolute dating. Contemporaneous fragments and/or twin samples collected from the same fragments rarely show the same mass-gain behavior even though the measurements were carried out in the same batch of 10 samples (thus in exactly the same environmental conditions), and so may not give very similar RHX age determination, i.e. within a few tens of years. Our measurements show that besides the “regular” cycle of RHX measurements as described in Wilson et al. (2009, 2012; 2013), the RHX dating technique makes necessary the implementation of additional long measurements, poorly discussed until now, to check in particular the stabilization of the mass levels of the samples after their heating at 105 °C and at 500 °C. We therefore underline the fact that the duration of both heating presently appears as a critical parameter, which is currently poorly controlled in regards to the nature of the studied samples. The definition of specific characteristics allowing a preliminary selection of the samples and giving some information on the way the samples should be analyzed will thus be a crucial stage in the development of the rehydroxylation dating method.

## Acknowledgments

We are very grateful to Moira Wilson and Sarah-Jane Clelland for advices while the authors were constructing the device used in this study. We also thank Vincent Hare, whose motivation encouraged us to perform our experiments. Philippe Bet and Bruno François provided some of the fragments analyzed in the present study (i.e. the samples from Lezoux and from the Hospices de Beaune, respectively). We thank them very much, together with Martine Gérard who performed XRD analyses on our samples and Samuel Taylor for his helpful reading of the manuscript. We are finally very grateful to two anonymous reviewers for their constructive comments on the manuscript. This project was supported by IPGP through a BQR funding and the INSU-CNRS via the PNP program. IPGP contribution no. 3469.

*Editorial handling by:* R. Grun

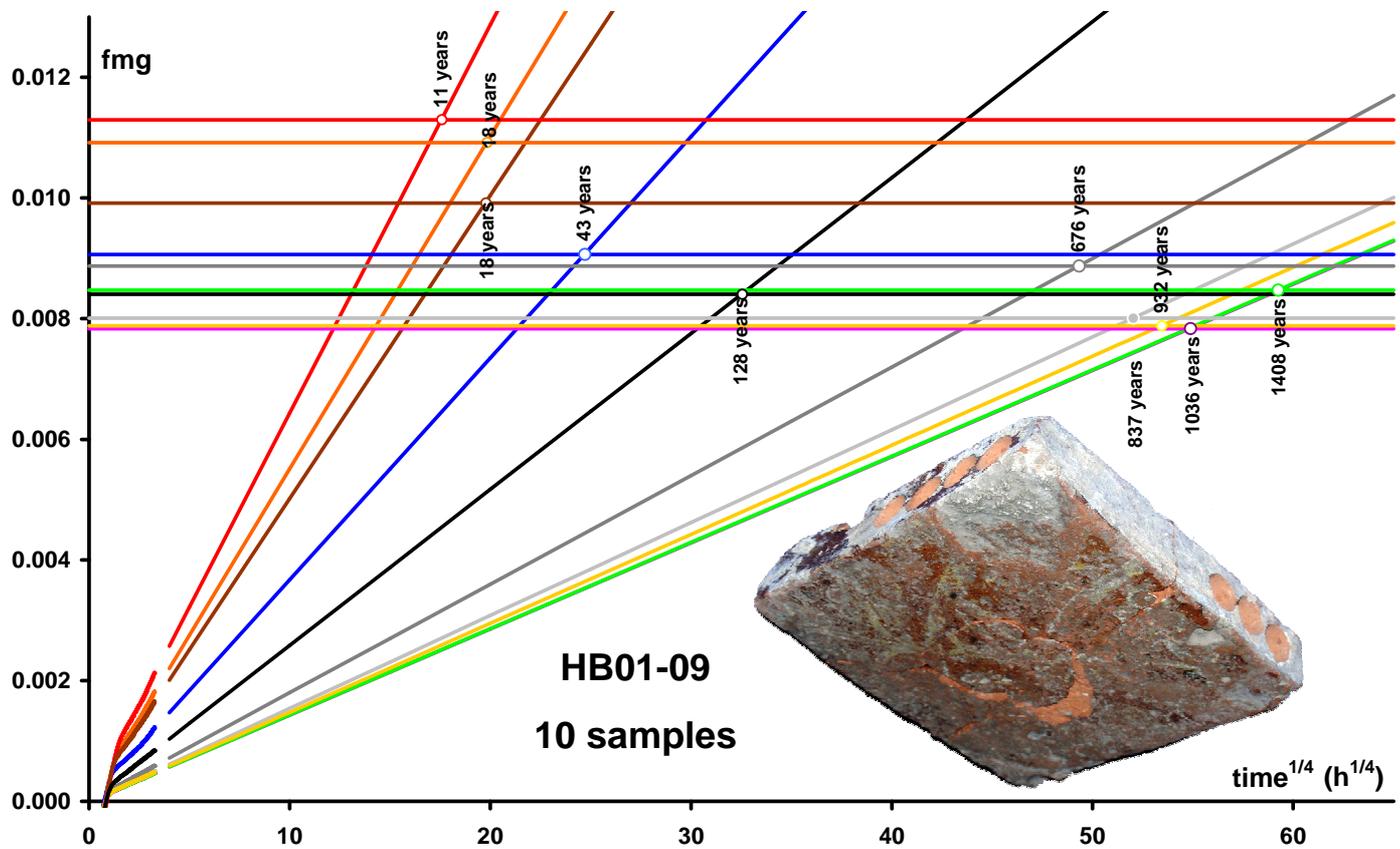
## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.quageo.2013.12.001>

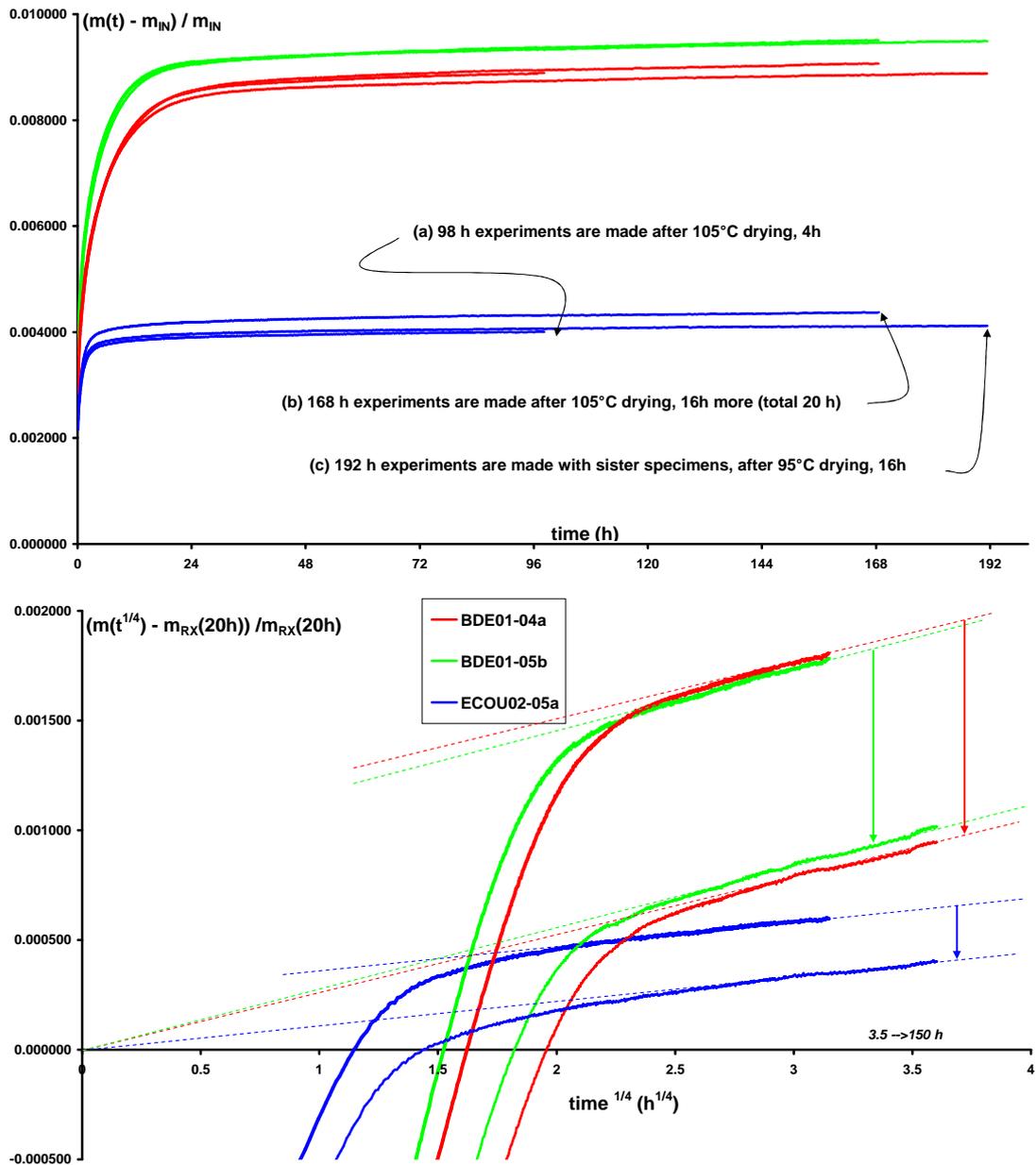
## References

- Barrett, G.T., 2013. Rehydroxylation dating of fired clays: an improved *time-offset* model to account for the effect of cooling on post-reheating mass gain. *J. Archaeol. Sci.* 40, 3596–3603.
- Bet, P., Fenet, A., Counord-Montineri, D., 1989. La typologie de la sigillée lisse de Lezoux. In: *1er-IIIème s. considérations générales et formes inédites, proceedings of the S.F.E.C.A.G. meeting in Lezoux 1989*.
- Bet, P., 2012. De l'argile à la céramique: le centre de production de Lezoux à l'époque romaine. *Géologues* 173, 61–66.
- Bowen, P.K., Ranck, H.J., Scarlett, T.J., Drelich, J.W., 2011. Rehydration/rehydroxylation kinetics of a reheated XIX-century Davenport (Utah) ceramic. *J. Am. Ceram. Soc.* 94, 2585–2591.
- Bowen, P.K., Drelich, J.W., Scarlett, T.J., 2013. Modeling rehydration/rehydroxylation mass-gain curves from Davenport ceramics. *J. Am. Ceram. Soc.* 96, 885–891.
- Burakov, K.S., Nachasova, I., 2013. Archeomagnetic study and rehydroxylation dating of fired-clay ceramics. *Izvestiya Phy. Solid Earth* 49, 105–112.
- Cultrone, G., Rodriguez-Navarro, C., Sebastian, E., Cazalla, O., De La Torre, M.J., 2001. Carbonate and silicate phase reactions during ceramic firing. *Eur. J. Mineral* 13, 621–634.

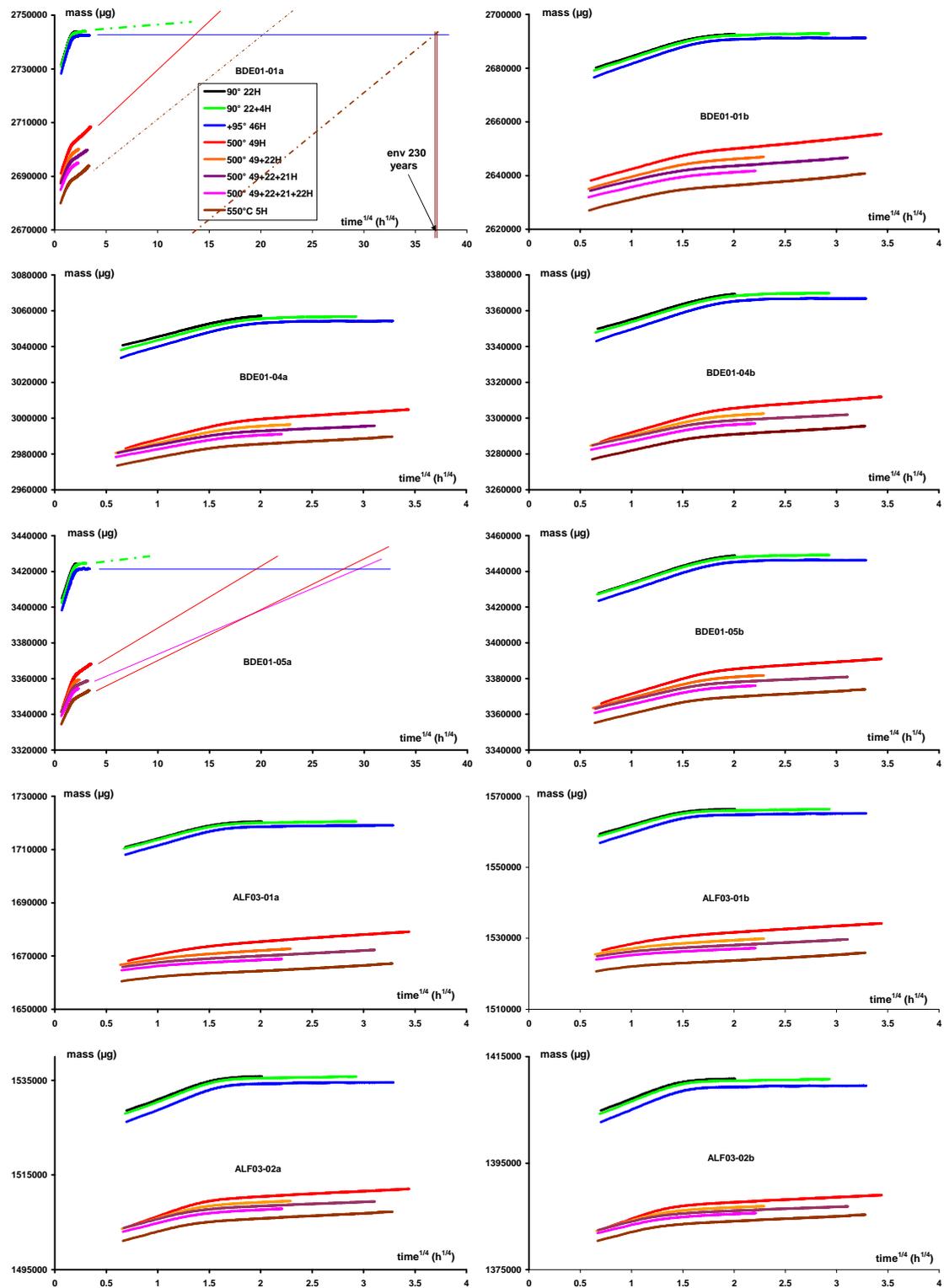
- Crescent Software Inc, 1994. In: QuickPak Scientific. Crescent software, Inc.
- Donadini, F., Korte, M., Constable, C.G., 2009. Geomagnetic field for 0–3 ka: 1. New data sets for global modeling. *Geochem. Geophys. Geosyst.* 10, Q06007.
- Drelich, J., Bowen, P.K., Scarlett, T.J., 2013. Effect of humidity instability on rehydroxylation in fired clay ceramics. *J. Am. Ceram. Soc. Rapid. Com.* 1–4.
- Dunlop, D.J., Özdemir, Ö., 1997. *Rock Magnetism, Fundamental and Frontiers*. Cambridge Univ. Press, New York.
- Gallet, Y., Genevey, A., Courtillot, V., 2003. On the possible occurrence of archaeomagnetic jerks in the geomagnetic field over the past three millennia. *Earth Planet. Sci. Lett.* 214, 237–242.
- Gallet, Y., Hulot, G., Chulliat, A., Genevey, A., 2009a. Geomagnetic field hemispheric asymmetry and archeomagnetic jerks. *Earth Planet. Sci. Lett.* 284, 179–186.
- Gallet, Y., Genevey, A., Le Goff, M., Warmé, N., Gran-Aymerich, J., Lefèvre, A., 2009b. On the use of archeology in geomagnetism, and vice-versa: recent developments in archeomagnetism. *C. R. Physique* 10, 630–648.
- Genevey, A., Gallet, Y., Constable, C.G., Korte, M., Hulot, G., 2008. Archeoint: an upgraded compilation of geomagnetic field intensity data for the past ten millennia and its application to the recovery of the past dipole moment. *Geochem. Geophys. Geosyst.* 9, Q04038.
- Genevey, A., Gallet, Y., Rosen, J., Le Goff, M., 2009. Evidence for rapid geomagnetic field intensity variations in Western Europe over the past 800 years from new French archeointensity data. *Earth Planet. Sci. Lett.* 284, 132–143.
- Hall, C., Wilson, M.A., Hoff, W.D., 2011. Kinetics of long-term moisture expansion in fired-clay brick. *J. Am. Ceram. Soc.* 94, 3651–3654.
- Hamilton, A., Hall, C., 2012. A review of rehydroxylation in fired-clay ceramics. *J. Am. Ceram. Soc.* 95, 2673–2678. <http://dx.doi.org/10.1111/j.1551-2916.2012.05298x>.
- Ho, Y.-S., 2004. Citation review of the Lagergren kinetic rate equation on adsorption reactions. *Scientometrics* 59 (1), 171–177.
- Holm, J.L., 2001. Kaolinites-mullite transformation in different Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> systems: thermo-analytical studies. *Phys. Chem. Chem. Phys.* 3, 1362–1365.
- Ince, C., 2009. *Water Transport Kinetics in Mortar-masonry Systems*. PhD thesis (Chap. 9). The University of Manchester, Manchester, UK.
- Korte, M., Constable, C.G., Donadini, F., Holme, R., 2011. Reconstructing the Holocene geomagnetic field. *Earth Planet. Sci. Lett.* 312, 497–505.
- Lanos, P., 2004. Bayesian inference of calibration curves, application to archaeomagnetism. In: Buck, C.E., Millard, A.R. (Eds.), *Tools for constructing chronologies, crossing disciplinary boundaries*, Lecture notes in statistics, vol. 177. Springer, London, pp. 43–82.
- Le Goff, M., Gallet, Y., Genevey, A., Warmé, N., 2002. On archeomagnetic secular variation curves and archeomagnetic dating. *Phys. Earth Planet. Inter.* 134, 203–211.
- Licht, A., Hulot, G., Gallet, Y., Thébault, E., 2013. Ensembles of low degree archeomagnetic field models for the past three millennia. *Phys. Earth Planet. Inter.* 224, 38–67. <http://dx.doi.org/10.1016/j.pepi.2013.08.007>.
- Pavón-Carrasco, F.J., Osete, M.L., Torta, J.M., Gaya-Piqué, L.R., 2009. A regional archaeomagnetic model for Europe for the last 3000 years, SCHA.DIF.3K: applications to archaeomagnetic dating. *Geochem. Geophys. Geosyst.* 10, Q03013.
- Savage, S.D., Wilson, M.A., Carter, M.A., McKay, B., Hoff, W.D., Hall, C., 2008. Mass gain due to the chemical recombination of water in fired clay brick. *J. Am. Ceram. Soc.* 91, 3396–3398.
- Wilson, M.A., Hoff, W.D., Hall, C., McKay, B., Hiley, A., 2003. Kinetics of moisture expansion in fired clay ceramics: a (time)<sup>1/4</sup> law. *Phys. Rev. Lett.* 90, 125503–125511–4.
- Wilson, M.A., Carter, M.A., Hall, C., Ince, W.D., Savage, S.D., McKay, B., Betts, I.M., 2009. Dating fired-clay ceramics using long-term power law rehydroxylation kinetics. *Proc. R. Soc. A* 465, 2407–2415.
- Wilson, M.A., Hall, C., Hoff, W., Carter, M., 2010. International Application PCT/GB2010/05075. *Archeological Dating Technique*. May 10th 2010.
- Wilson, M.A., Hamilton, A., Ince, C., Carter, M.A., Hall, C., 2012. Rehydroxylation (RHX) dating of archaeological pottery. *Proc. R. Soc. A.* <http://dx.doi.org/10.1098/rspa.2012.0109>.
- Wilson, M.A., Clelland, S.J., Carter, M.A., Ince, C., Hall, C., Hamilton, A., Batt, C.M., 2013. Rehydroxylation of fired-clay ceramics: factors affecting rehydroxylation mass gain in dating experiments. *Archaeometry*. <http://dx.doi.org/10.1111/arc.12038> online May 26th 2013.



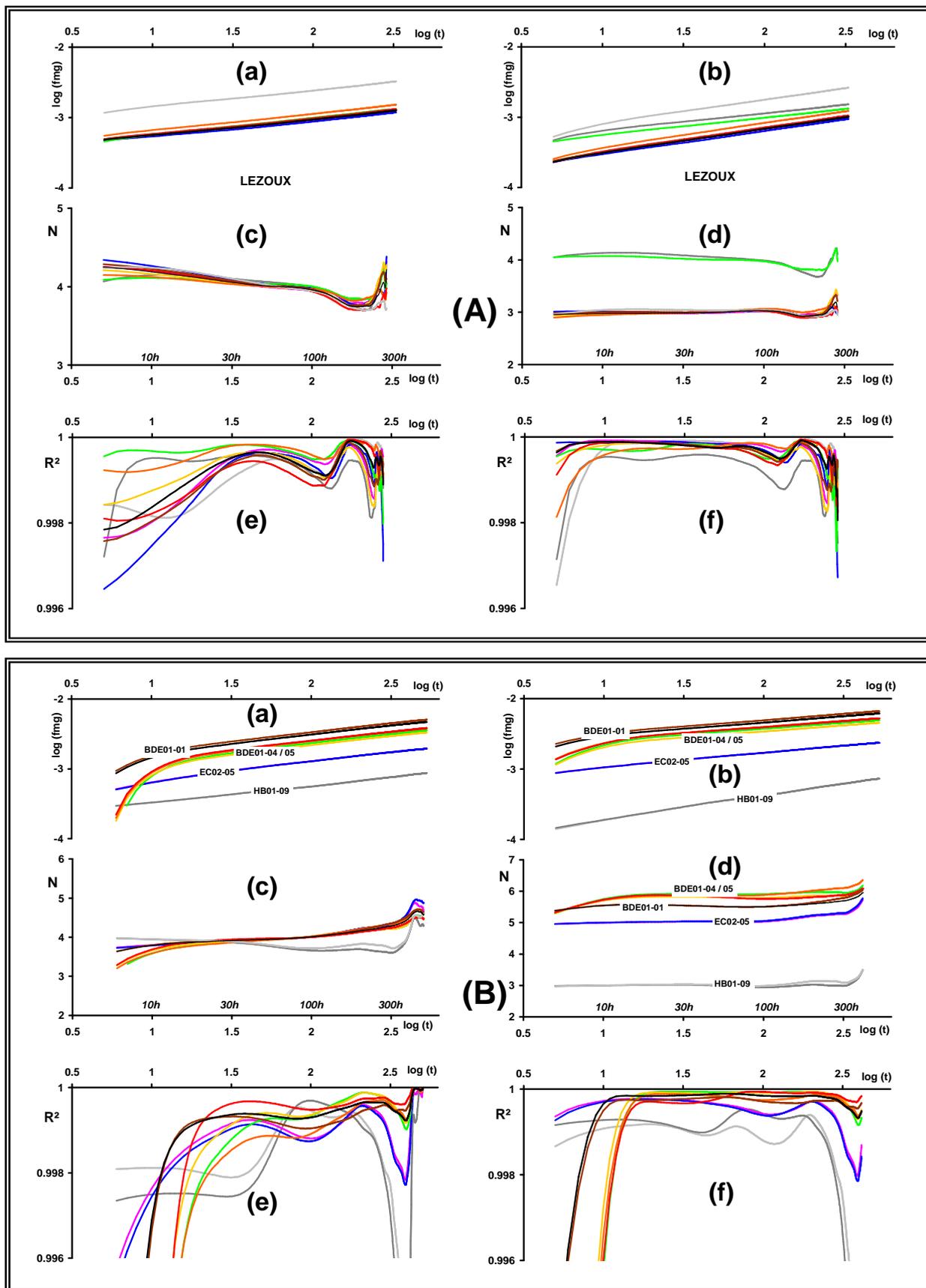
**Figure A.** Examples of scattered RHX dating results obtained from the same pavement brick (see picture), referred to as HB01-09, collected in the “King’s room” of the Hospices de Beaune (1448-1452 AD). The expected time was thus ~560 years (~47 h<sup>1/4</sup>)



**Figure B.** Variations of the mass levels (see text) for three samples from site BDE01 (see color code on the figure) after heating at 95°C and 105°C. Upper panel: variations of fractional mass gains (fmg) relative to  $m_{IN}$  against time in hours; see the description of the three series of experiments on the figure. Lower panel: variations against  $t^{1/4}$  of fmg relative to “pseudo”- $m_{RX}$  obtained after heating at 105°C the same samples as before during 20 hours. For each sample, this figure shows a loss of mass without any change in the overall long-term trend in mass variations, yielding a “pseudo”-RHX behavior at low temperature very similar to the regular high-temperature RHX process.



**Figure C.** Weighing results against  $t^{1/4}$  obtained for two samples collected from three fragments of archeomagnetic site BDE01 and two fragments from site ALF03. Each sample was heated three times at low temperatures ( $90^\circ\text{C}$  and  $95^\circ\text{C}$ ) and five times at high temperatures ( $500^\circ\text{C}$  and  $550^\circ\text{C}$ ) during various time spans (see color code and legends on the figure).



**Figure D.** Testing the  $t^{1/4}$  power law of the rehydroxylation process for a series of Lezoux samples (Frame A) and a series of samples collected from archeomagnetic sites BDE01, EC02 and HB01 (Frame B). Time  $t$  is expressed in hours. (a,b) log-log behavior of the fractional mass gains (fmg) relative to  $m_{RX}$ , which is  $N$  dependent, computed using a  $t^{1/N}$  linear fit over a long time interval ( $t > 20$  h until the end).  $N$  is fixed to 4 in the two panels (a) and is derived from least-square computations in the two panels (b). (c,d) variations of  $N$  recomputed after fitting the previous log-log curves (see equation 5 in text) with time intervals decreasing up to the end of the experiments. (e,f) variations of the  $R^2$  regression parameter for the fits shown in panels (c) and (d), which illustrates the improvement made in that fitting. If the  $N$  used in panels (a) and (b) was indeed the “best value”, the curves should be constant over most of the time interval; this is clearly not the case when using  $N=4$  (except for 2 samples from Lezoux), whereas values of  $N=3$  for the other Lezoux and HB01 samples or  $N=5$  to 6 for the EC02 and BDE samples provide a much better fit for the RHX process.