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EVIDENCE FOR COMPLEXITIES IN THE RHX DATING METHOD*

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The rehydroxylation (RHX) dating method applicable to virtually all baked clay fragments still requires testing and new developments. Here, we have obtained new weighing measurements from Syrian medieval ceramic fragments. In particular, they allow us to illustrate the scatter in RHX behaviour that may exist between different potsherds of the same age and found at the same archaeological site, thus having experienced the same effective lifetime temperature, and even between samples collected from the same artefact. Thanks to a so-called time-span analysis, we also report on some complexities in data sets previously obtained by Wilson et al. *(2009, 2012, 2014).*

KEYWORDS: REHYDROXYLATION DATING METHOD, CERAMIC, SYRIA, STABILIZATION OF ARCHAEOLOGICAL SAMPLE MASS, TIME VARIATION AND SCATTER IN REHYDROXYLATION RATE

INTRODUCTION

The dating method relying on rehydroxylation processes in archaeological baked clays proposed by Wilson *et al*. (2009) could be a major discovery for all of the archaeological sciences. For this reason, it deserves to be tested and studied in order to make it efficient, reliable and usable by different teams. The very positive characteristic of the rehydroxylation (RHX) dating method, as described by Wilson *et al*. (2009), is its relatively easy and rapid implementation, only requiring high-precision weighing measurements in stable and controlled environmental (temperature and relative humidity, RH) conditions. That it is applicable to virtually all baked clay fragments whatever their mineralogy or porosity, thus reducing the number of parameters to be considered, is also a major strength (Wilson *et al*. 2009, 2012).

However, since the description of the RHX dating method by Wilson *et al*. (2009), with 10 remarkably successful dating results from baked clay fragments of known ages, only five new results have been obtained by Wilson's team (Wilson *et al*. 2012). This number is surprisingly small considering the major interest that has been expressed in this new dating method. Several other groups around the world have implemented the RHX dating method, or a variant of it, but with no satisfactory dating results up to now (e.g., Bowen *et al*. 2011; Burakov and Nachasova 2013; Le Goff and Gallet 2014). The most recent studies by Wilson's team have been rather more focused on particular aspects of the method, such as the estimate of the mean 'lifetime' temperatures experienced by the samples since their last archaeological firing (referred to as the effective lifetime temperature, or ELT; Wilson *et al*. 2012; see also Hall *et al*. 2013), or the use of the specific surface area (SSA) of the studied samples to constrain the duration of laboratory

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rehydroxylation measurements (Wilson *et al.* 2014). Even though these aspects are important, they should not mask several other points, which must be further analysed and constrained so that the RHX dating method becomes efficient (e.g., Le Goff and Gallet 2014).

Le Goff and Gallet (2014) developed a new experimental device allowing weighing measurements to be performed automatically in the very same environmental conditions on a series of 10 samples at a time. This ability of our system has important implications for testing and evaluating the reproducibility and the scatter in RHX results, independently of the influence of some of the key parameters, such as the ELT. The present study aims to illustrate this aspect thanks to the acquisition of new RHX data from medieval ceramic fragments, all collected at the same archaeological site in eastern Syria. We further take the opportunity of this study to make a point on the complexities that we encountered in our own RHX experiments (Le Goff and Gallet 2014, and this study) and on those we also observed from a new analysis of some of the data previously obtained by Wilson *et al.* (2009, 2012, 2014). The resolution of these complexities would clearly mark an important step in the development of the RHX dating method.

NEW WEIGHING MEASUREMENTS FROM SYRIAN MEDIEVAL CERAMIC SAMPLES

Most details on the principles of the rehydroxylation dating method and on the experimental protocol involved can be found in Wilson *et al.* (2009, 2012) (Supplementary Fig. A). We adopted the very same experimental strategy, with a first heating of the samples at 105°C in order to determine their archaeological masses and a second heating at 500°C in order to determine the rehydroxylation rates (also referred to as rehydroxylation/RHX slopes, gradients or α), the coefficient of the time$^{1/4}$ power law (e.g., Wilson *et al.* 2003; Savage *et al.* 2008; Hamilton and Hall 2012). All of our experiments were carried out in stable temperature (~16°C) and RH (~31%) conditions, using the device described in Le Goff and Gallet (2014); note that the chosen temperature is not a critical parameter for the purpose of our study.

The fragments of ordinary ceramics analysed in the present study, which were quite probably produced locally, were found during excavations conducted at Tell Guftan (latitude ~35.2°N, longitude ~40.3°W), a rural medieval settlement in the middle valley of the Euphrates River, ~15 km downstream of the modern city of Deir-ez-Zor, in eastern Syria (e.g., Berthier 2001). They were collected in two distinct archaeological contexts (Guibert *et al.* 1998; Berthier 2001; Rousset 2001), referred to as occupation layer 409 of Period III in the Euphrates valley (the Mirdãsid period), dated to between AD 975 and AD 1100 (fragments 06, 07 and 08 from site Lot 40) and pit 214 of Period IV (the Zankid period), dated to between AD 1100 and AD 1175 (fragments 01 and 05 from site Lot 41). Using a non-magnetic diamond core drill bit cooled with water, we prepared from each fragment several cylindrical samples, 1.2 cm in diameter and ~1.5 cm in height, and with a mass of ~2–3 g. To avoid spurious effects on mass behaviour due to the presence of organic contaminants or mineralogical alteration on the surface of the fragments, ancient surfaces were removed from all samples. Considering the self-calibrated nature of the RHX dating method (Wilson *et al.* 2009), we assumed that it was unnecessary to perform mineralogical analyses on our fragments. Following Le Goff and Gallet (2014), however, we performed thermomagnetic analyses to select our fragments. They all possess a univectorial magnetization component, indicating a single high-temperature ($\gtrsim$600°C) heating, principally carried by magnetic grains in the (titano)magnetite family, with no evidence of hydroxides, such as goethite or lepidocrocite, that would otherwise reveal the occurrence of weathering suffered by the fragments since their last firing (e.g., Burakov and Nachasova 2013). Moreover, the good reversibility observed between heating and cooling low-field magnetic susceptibility versus temperature curves obtained from the studied fragments shows that their magnetic mineralogy remains stable after heating at 500°C; that is, the temperature used for the dehydroxylation experiments (see Supplementary Fig. B and further discussion in Le Goff and Gallet 2014).

Mass measurements were carried out on series of five pairs of twin samples (one pair for each fragment). The 10 samples were placed in a rotating carousel (see the description of our apparatus in Le Goff and Gallet 2014). It is worth mentioning that owing to the time necessary for the Mettler–Toledo XP26 balance to stabilize (note that this balance does not deliver any mass value prior to its stabilization), each mass determination, including the zeroing of the balance, took about 20 s. The complete rotation of the carousel thus lasted for about 4 min. Interestingly, we insist on the fact that all of the fragments, being collected from the same archaeological site, were most probably produced using the same clay source and they probably experienced the very same ELT. We will see below that the mass variations obtained from these samples show a rather large scatter in rehydroxylation behaviour, which may originate from a significant variability in the energy of activation of the samples (e.g., Wilson *et al.* 2009), even between samples collected from the same fragment.

According to Wilson *et al.* (2009, 2012, 2014), the heating of baked clay samples at 105°C allows the removal of the molecular and weakly bound adsorbed water from the medium. The mass evolution of these samples, measured in controlled and constant environmental conditions, would then be characterized over 1 or 2 days by a rapid gain in mass, principally by capillarity, before the sample mass attained stabilization—defining the so-called archaeological mass (m_A, see Supplementary Fig. A). A first series of 10 samples were heated at 105°C for 11 h before being placed in our experimental device. The mass behaviours first conform to the expected evolution, with rapid mass gains in the first hours, which decreased significantly afterwards (Fig. 1 (a)). But, as previously observed by Le Goff and Gallet (2014) for other (French) fragments, the Syrian samples did not show any stabilization of their archaeological masses after 1 week of weighing measurements in stable environmental conditions. We analysed a second series of 10 samples from the same fragments, which were heated at 105°C for 14 days. In spite of the much longer duration of heating, the second set of mass data exhibits the same behaviour as that of the first series of samples—that is, non-stabilization of the mass samples even after more than 5 weeks of weighing measurements—hereby confirming the significance of this observation (Supplementary Fig. C).

The samples from the first series were next heated at 500°C for more than 2.5 days (67 h) and weighing measurements were conducted over 3 weeks (527 h) in the same environmental conditions as previously. We note that those conditions remained very stable, with maximum variations reaching only ±0.1°C in temperature and ±0.15% in RH. The results are displayed in Figure 1 (b). These results illustrate the different behaviours recently described by Wilson *et al.* (2014). Two samples from the same fragment, Lot 41-08, show a behaviour that can be qualified as normal, with apparently only the two stages referred to by Wilson *et al.* (2009) as stages I and II. In contrast, the other samples show more complex mass evolutions, with both concave (twin samples from fragments Lots 41-01, 41-05 and 40-07) and convex (twin samples from fragments Lot 40-06) behaviours. It is worth mentioning that the observed concavity and convexity in mass evolution do not coincide in time with perturbations in the environmental conditions in our climatic chamber. Therefore, contrary to the data reported in Barrett (2013) (we note, using larger cubic samples than ours, with 25 mm sides) and Wilson *et al.* (2014), these two behaviours most probably result from intrinsic properties of the studied samples, rather than from particular disturbances in the environmental conditions at the beginning of the experiments (see Wilson *et al.* 2014, fig. 4, and discussion in the next section).

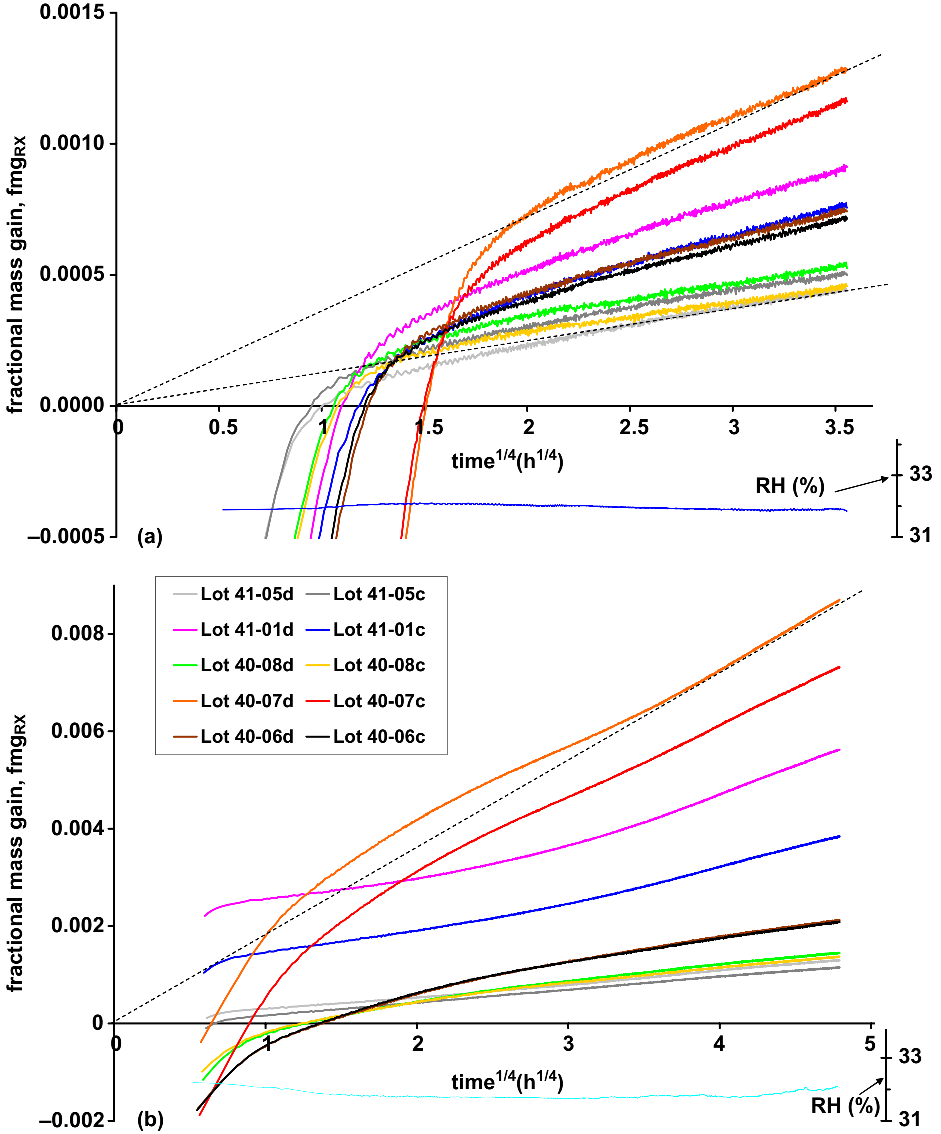

Figure 1 *The weighing measurements obtained for a series of 10 Syrian medieval samples (five different fragments; see text). (a) Fractional mass-gain (fmg) variations relative to* m_{RX} *after heating of the samples at 105°C. The data are reported against time in* $h^{1/4}$. *We recall that* m_{RX} *is the initial sample mass derived from stage II–type mass variations extrapolated to time*$^{1/4}$ = 0 *(Le Goff and Gallet 2014; see also Supplementary Fig. A). (b) Fractional mass-gain variations relative to* m_{RX} *after heating of the samples at 500°C. The data are again reported in* $h^{1/4}$. *Measurements were performed over ~3 weeks. The corresponding variations in RH during the weighing measurements are also reported below the two panels. The dotted lines displayed only for the two extreme fractional mass-gain variation curves in (a) and (b) are shown to help the readers judge of the regularity of the mass behaviours against time*$^{1/4}$. *(See online for a colour version of this figure.)*

The rehydroxylation data shown in Figure 1 (b) also clearly indicate that two samples collected from the same fragment—that is, possessing the same mineralogical assemblage—may not reveal the same behaviour (i.e., the same rehydroxylation rates), although the samples experienced the very same environmental conditions during the weighing measurements. Owing the fact that these samples further experienced the same ELT, this observation has important implications for the applicability of the RHX dating method (see discussion in the next section).

We next explored for each sample the stability of the rehydroxylation rates during the weighing measurements shown in Figure 1 (b). For this, we conducted what we call a time-span analysis, consisting of deriving a succession of RHX dating results (see the formula in Supplementary Fig. A) from the values of the RHX gradients computed using time$^{1/4}$ intervals that were progressively decreasing up the end of the experiments. Here, the highest values obtained at the end of the weighing measurements after heating at 105°C were considered as being the best estimates of the archaeological sample masses. Ideally, each curve should reach a plateau and the data scatter at this level should provide an estimate of the age uncertainties. Using this very convenient way of showing the RHX dating results (Fig. 2 (a)), we observe that the data from our Syrian samples indeed reach roughly constant values, mostly after 4.0 h$^{1/4}$, which may argue for the suitability of our analysed samples. However, the 'plateau' ages are scattered at both the fragment and site levels. Each pair of samples gives ages with fairly strong differences of several tens of years (between 8 years and 470 years), which is due to the different rehydration/rehydroxylation behaviours at the fragment level previously mentioned. Finally, it is worth pointing out that the 'plateau' ages are often (but not always) far too young relative to the expected archaeological ages (dashed lines in Fig. 2 (a)), which may indicate the need to perform ELT corrections (Wilson *et al.* 2012; see discussion below).

Additional weighing measurements obtained from the same fragments (again two samples each) were also used to illustrate the varying sensitivity of the sample masses to fluctuations in humidity. Drelich *et al.* (2013), in particular, highlighted the fact that sporadic RH variations had only a negligible effect on the water component involved in the rehydroxylation process. This allows a clear distinction to be made between the RH-dependent and RH-independent water components existing in the samples over time. We show in Figure 3 that the variations in sample mass related to weak fluctuations in RH could be corrected to the first order. Our experiments were as follows: after 2 weeks of rehydroxylation weighing measurements, we stopped the control of the environmental conditions in the climatic chamber for 18 days, which led to a slow increase of RH by ~1.5% (see the curve at the bottom in Fig. 3 (a)) while the temperatures remained stable. We then added salt (of course, without opening the climatic chamber), which allowed us, in 2 days, to bring the environmental conditions inside the climatic chamber back to the initial ones. This clearly provoked a change in the sample mass evolution (see inside the oval, in Fig. 3 (a)). Taking both into account the mass and the RH variation curves, it was then possible, using a simple linear equation, to correct the mass evolution of the different samples, with correction coefficients of ~30 to ~110 ppm per % of RH according to the samples, as if the latter had been maintained in constant RH conditions (here, 31.6%; i.e., the mean RH level monitored during the weighing measurement after the heating at 105°C). The different curves are now much more regular and no longer reveal a kink as previously observed (Fig. 3 (b)). This approach may thus help to improve the determination of the rehydroxylation rates, provided that the RH variations are weak during the weighing measurements.

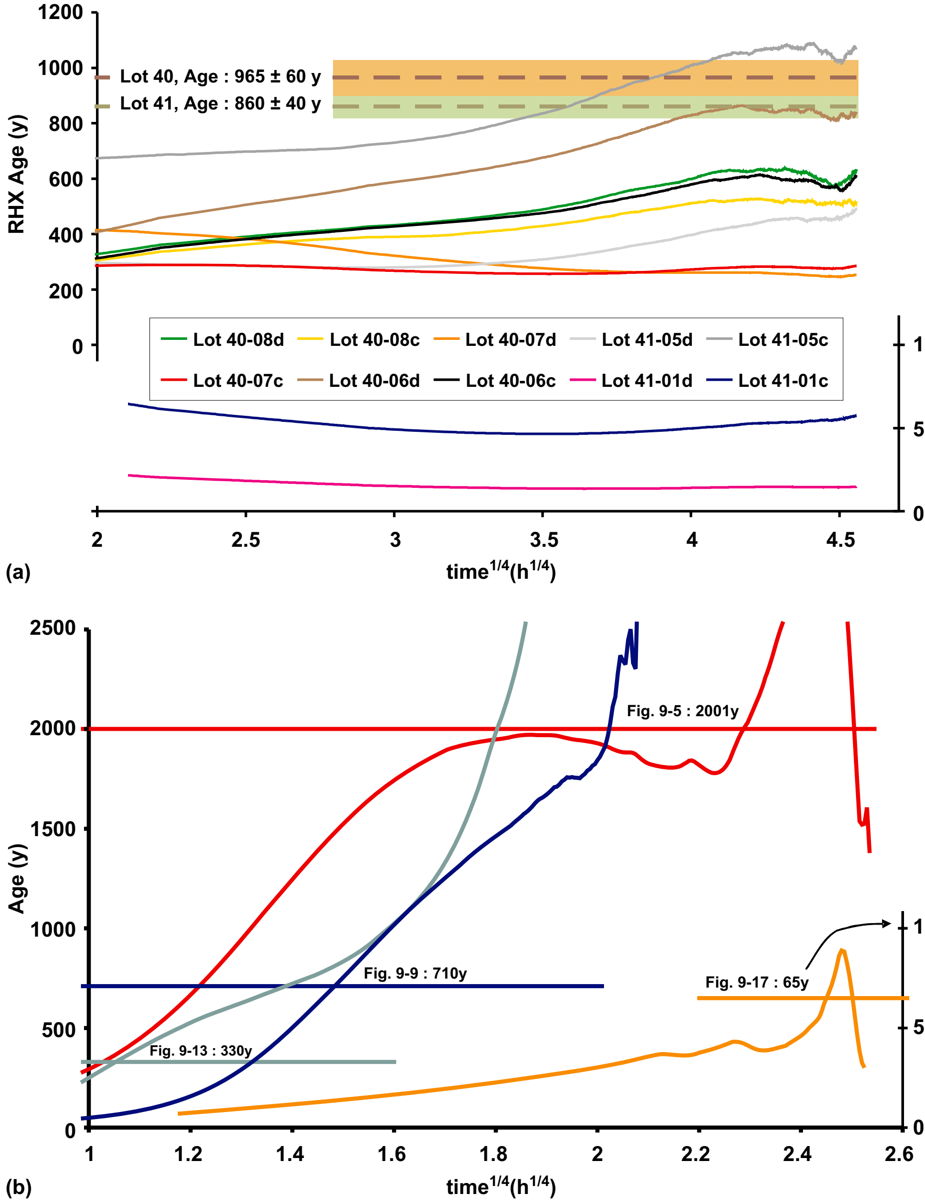

Figure 2 *Variations in RHX dating results due to the evolution in rehydroxylation rates during the weighing measurements. The variations in the rehydroxylation rate and in* m_{RX} *were computed for each sample using time*$^{1/4}$ *intervals that decreased progressively up the end of the experiments. The dashed lines and the two associated bands indicate the expected ages. (a) Dating from the Syrian series (Fig. 1). (b) Dating from Ince's (2009) samples (same samples as in Wilson* et al. *2009 and in Fig. 6 of the present study). (See online for a colour version of this figure.)*

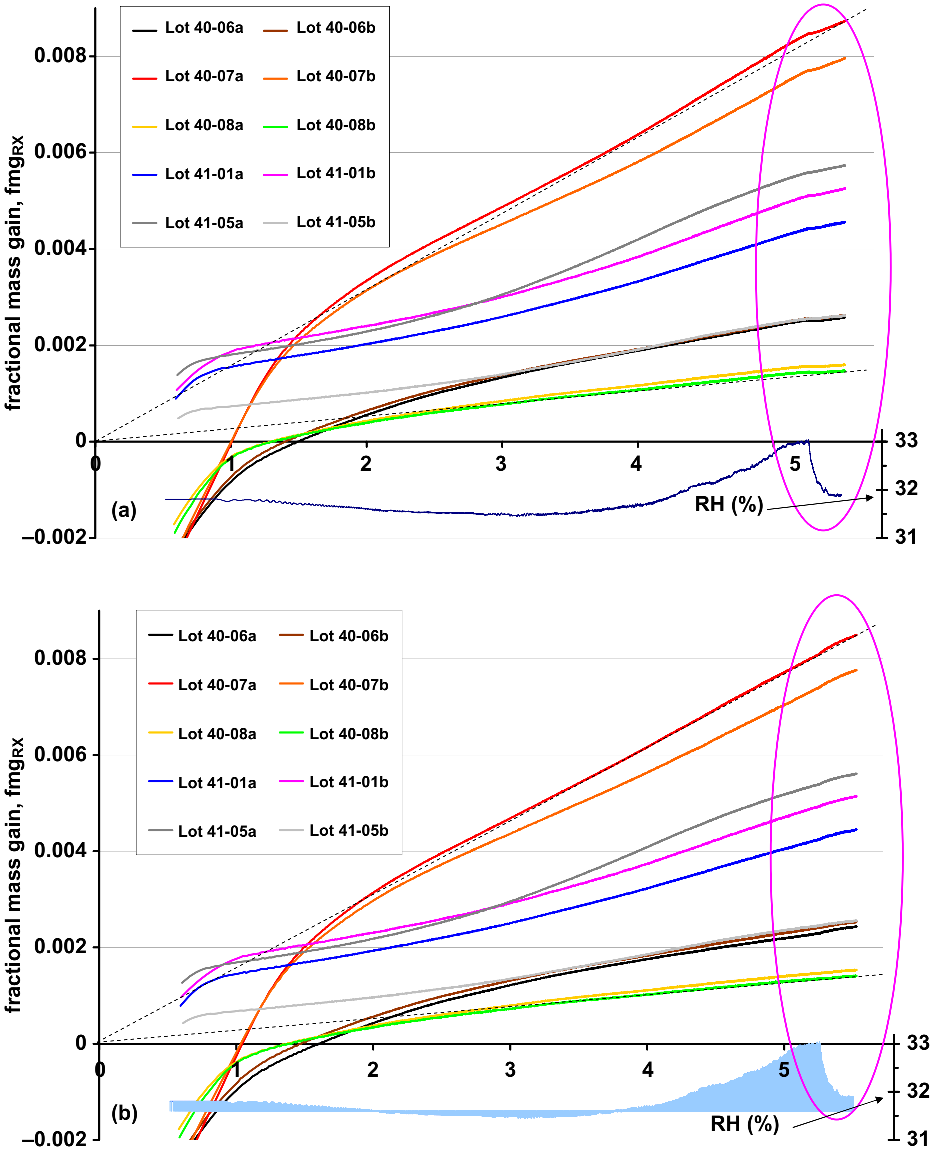

Figure 3 *An example of correction to first order of the sample mass evolution from fluctuations in RH. (a) Fractional mass-gain (fmg) data relative to* m_{RX} *obtained from our new Syrian samples while relatively significant variations occurred in the RH (the curve at the bottom of the panel) during the weighing measurements. (b) Corrected fmg data, as if the RH values remained constant, at 31.6%, during all the weighing measurements (see text). The dotted lines displayed only for the two extreme fractional mass-gain variation curves in (a) and (b) are shown to help the readers judge of the regularity of the mass behaviours against time*$^{1/4}$*. (See online for a colour version of this figure.)*

DISCUSSION

Here, we report on the main difficulties encountered when we applied the original RHX dating method, and on some complexities that we detected in the data sets previously used by Wilson *et al.* (2009, 2012, 2014).

On stabilization of the archaeological mass after drying at 105°C

This stabilization is an essential parameter of the RHX dating method, the determination of which is assumed by Wilson's team to be very straightforward as soon as satisfactory experimental conditions are met (i.e., constant mass reached at 105°C, and constant temperature and RH conditions during weighing measurements). From their experiments, however, Wilson's team did not provide much quantitative information on the duration of heating at 105°C necessary for a 'sufficient' drying (so that samples reach a constant mass at 105°C) and how much it varies according to the type of baked clay material (see the discussion in Le Goff and Gallet 2014, relying on the dependence of mass levels on heating duration). The RHX experiments conducted by Le Goff and Gallet (2014) also showed a systematic complexity whatever the use of short (~1 h or a few hours) or long (up to a week) heating durations at 105°C. The new data reported in this study confirm this complexity, which persists even after 2 weeks of heating. It consists of the non-stabilization of the archaeological masses, even after 3–4 weeks of continuous weighing measurements. The mass measurements obtained from ~100 different samples of different ages and origins (Le Goff and Gallet 2014; this study and unpublished data) are always slightly increasing—according, we note, to a law very similar to that considered for the rehydroxylation process (the results obtained from seven series of 10 samples are shown in Fig. 4). Importantly, this behaviour can clearly not be explained by time-varying (systematically increasing) temperature and RH values during our experiments, since it was observed both when the environmental conditions remained very stable and when they were slightly unstable over short time intervals (within ~0.3%), including sporadic increases *or* decreases in RH. A significant point to note is that all these measurements were obtained in dynamic conditions, as the samples were placed in a rapidly rotating carousel (our apparatus also includes a fan in the climatic chamber; Le Goff and Gallet 2014), thus avoiding stagnant air in the vicinity of the weighing site, which would increase the equilibrium (i.e., mass stabilization) times.

A question is, therefore, why this behaviour was not observed or documented by Wilson's team and how frequent it is. Thanks to S.-J. Clelland and M. Wilson (pers. comm. 2013), we have had access to data obtained but only partially reported in Wilson *et al.* (2012). Some of the weighing data obtained after drying at 105°C are shown in Figure 5 (see online for a colour version). For comparison, we have also reported in Figure 5 some of our results, all showing a trend towards slightly increasing masses. From four samples (the heavy lines in Fig. 5) studied by Wilson's team, one in black (the weighing companion of Werra sample W2, which was eliminated but not described in Wilson *et al.* 2012) clearly does not reach mass stabilization. Another one (W1, the heavy red line) exhibits scattered results, with a distinct mass decrease at the end of the experiments. For the two others (W2 and W3, the heavy orange and brown lines), there is also a very appealing change in curvature just before their mass stabilization (see the orange curve in particular), which may argue for a sudden change in the ongoing behaviour/process. It is worth recalling that good RHX dating results were nevertheless reported for the latter three samples (Wilson *et al.* 2012). At this step, this change in mass evolution cannot be explained in the context of a single rehydration phase of the samples after their heating at 105°C, while the experimental

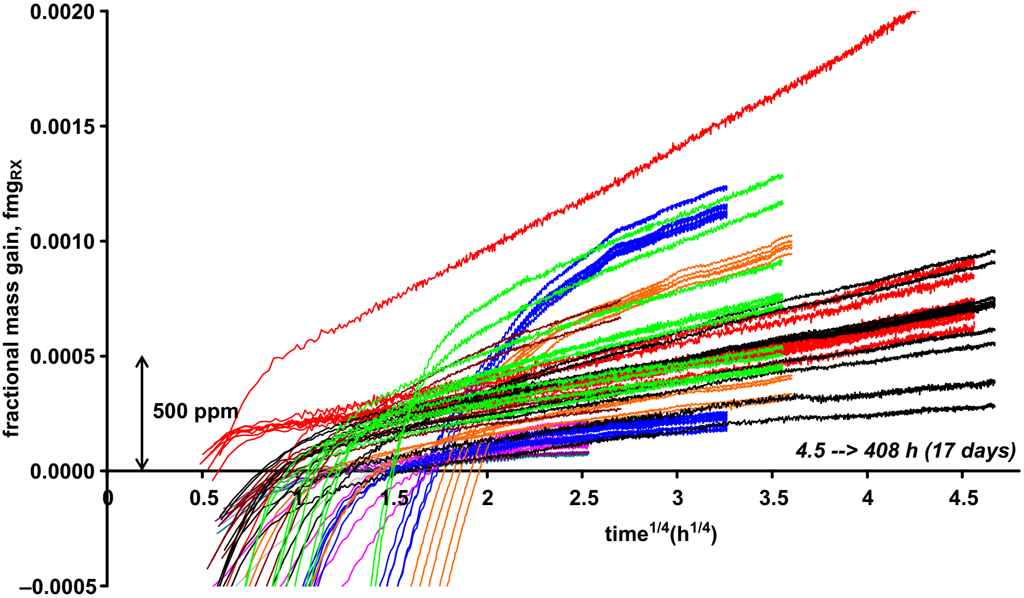

Figure 4 *A synthesis of the weighing measurements obtained for seven series of 10 samples after their heating at 105°C (Le Goff and Gallet 2014; this study). Fractional mass-gain (fmg) variations are plotted against time in h$^{1/4}$, and they all show a non-stabilization of fmg even after several weeks of weighing measurements. (See online for a colour version of this figure.)*

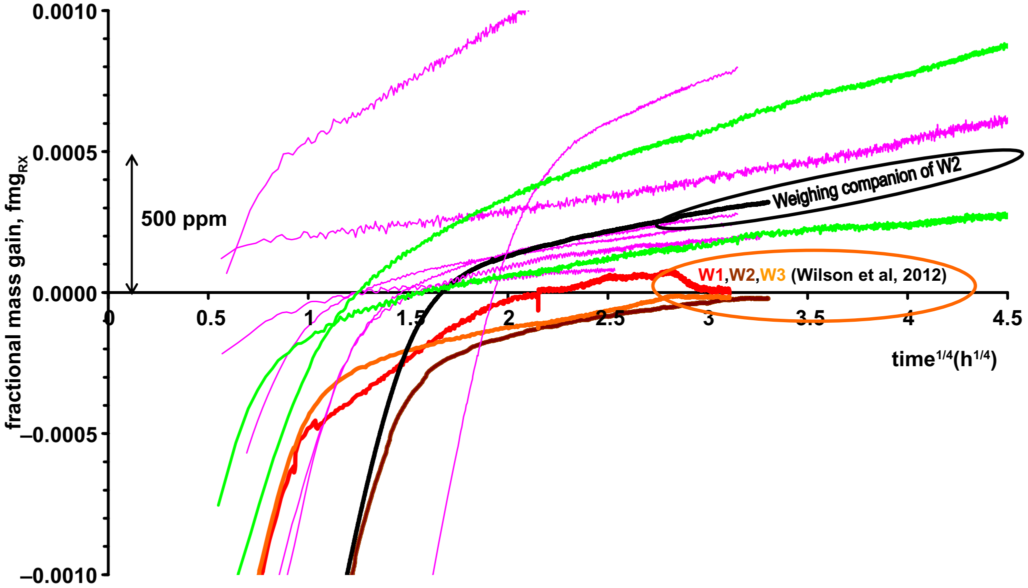

Figure 5 *Examples of fractional mass-gain (fmg) data relative to m_{RX} obtained after heating at 105°C from some of our samples (the pink and green curves) and from four samples previously analysed by Wilson* et al. *(2012), referred to as samples W1, W2 and W3 and the weighing companion of W2. The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

conditions apparently remained very stable during all of the measurements. Another point to note is that before this change, the mass behaviour is similar to that observed in our experiments.

From the available data, it seems to us that the stabilization of the archaeological sample masses after heating at 105°C is not experimentally sufficiently well documented and that it should be substantiated by further analyses.

On concavity in mass-gain evolution

In Wilson *et al.* (2012, 2014), the presence of three water components is mentioned: T0 water, which is the weakly held molecular water removed after a 105°C heating/drying cycle; T2 water, the water involved in the rehydroxylation process after heating at 500°C; and intermediate type T1 water, which is a water component with a 'reset' temperature between 105°C and 500°C (~200–300°C according to Wilson *et al.* 2012). The consequence of this combination of more than two water components may be discussed in the light of the recent study by Wilson *et al.* (2014), in which the authors describe three mass evolutions, intermediate between 'true' stage I and 'true' stage II evolutions, that are referred to as normal (ideal), convex and concave. These different forms of behaviour have been related to the range of specific surface areas (SSA)—note, however, that the values reported in table 2 and fig. 7 of Wilson *et al.* (2014) do not coincide, and that for the two samples showing the longest time to onset of linear stage II, they are not consistent with the dating determinations previously performed by Wilson *et al.* (2012). High values of SSA would be associated with the convex behaviour, while lower values would be associated with the concave one. However, to explain the latter, Wilson *et al.* (2014) have to further invoke large perturbations in the environmental (RH) conditions at the beginning of their experiments (previously not mentioned), due to introduction of the samples in the small climatic chamber of their weighing device, leading to an 'unexpected maximum reached by T1'; that is, an excess of mass gained during stage I (Wilson *et al.* 2014; see also the discussion in Barrett 2013). Regarding this perturbation, the laboratory-built measurement device described by Le Goff and Gallet (2014), with the use of an airlock system for placing the samples on the rotating carousel, presents the advantage of keeping the environmental conditions at the beginning of the weighing measurements and during all of the measurements (with RH variations <1% due to the large volume of the climatic chamber used) very stable. For this reason, the concavity in mass-gain evolution previously reported by Le Goff and Gallet (2014) from Roman Lezoux samian ware samples—that is, of the same type of material showing a concave behaviour as studied by Wilson *et al.* (2014) (see their fig. 4), and again observed from our newly analysed Syrian ceramic samples (Fig. 1 (c))—cannot be explained by a spurious effect provoked by significant and sporadic variations in RH at the beginning of the experiments. Rather, this behaviour seems related to intrinsic properties of the studied material that could make a clear distinction between stages I and II more difficult. The consequences could be significant. First, the rehydroxylation process observed in this case could be reasonably well fitted by a power law with exponent ~1/3 (Le Goff and Gallet 2014), unless it is considered that it reflects a 'disturbed' time$^{1/4}$ power law instead. Second, the RHX behaviours could strongly depend on the mineralogical assemblages present in the samples (e.g., Bowen *et al.* 2011, 2013; Le Goff and Gallet 2014), while Wilson *et al.* (2009) insisted on the self-calibrated nature of the method, which *a priori* avoided the need for any foreknowledge of the mineralogy of the studied samples. Such dependence (or independence) still requires testing.

On the variability and long-term stability of the rehydroxylation process

The new RHX data from Syrian potsherds allow us to illustrate the scatter in rehydroxylation behaviour existing between samples collected from different fragments dated to the same age and discovered at the same archaeological site—and thus having experienced the very same ELT—and even between samples collected from the same fragment. This scatter is appealing for two main reasons. The first reason is that the results of the time-span analysis conducted on these samples, with relatively convincing 'plateau' ages, argue for the suitability of the studied fragments for RHX experiments. The second reason is that to obtain consistent and correct RHX dating results from our data, we would need to make various corrections of ELT effects, which supposes that the energy of activation (EA; see Wilson *et al.* 2009, 2012) characterizing these samples significantly varies with the fragments (even though they were most probably produced using the same clay source), and, more surprisingly, even with the samples analysed from the same fragments. The direct consequence is that in future work, EA should be systematically determined for each sample, and of course the dating determination should be performed on the same sample. As suspected by Le Goff and Gallet (2014), the RHX measurements would thus be much longer, and the experimental protocol more complex than previously envisaged.

Considering our previous time-span analysis and the recommendation of Wilson *et al.* (2014) to extend the weighing time until a linear mass-gain evolution is reached as a function of time$^{1/4}$ (defining stage II), we also found it interesting to re-analyse some of the RHX results reported in Wilson *et al.* (2009), which are at present the only 'good' examples proving the suitability of the RHX dating method. Such an exercise was possible due to Ince's (2009) thesis, in which all the data used by Wilson *et al.* (2009) can be found and which contains, in particular, the graphs of the various rehydroxylation weighing experiments. Because the figures were drawn with full coordinate vector graphics, we were able to retrieve the weighing measurements of four samples after their heating at 500°C (see chapter 9 in Ince's thesis). These samples are from a Roman *opus spicatum* paving brick, from a Westminster floor tile, and from bricks of the King Charles II Building in Greenwich and of the Whitefriars Priory site in Canterbury (see Ince's thesis, figs 9-5, 9-9, 9-13 and 9-17; note that the data from fig. 9-5 were displayed by Wilson *et al.* 2014 in their fig. 1). These four data sets are reported in Figure 6 (see online for a colour version) as a function of time$^{1/4}$ (the heavy blue curve in Fig. 6). Regression lines computed from the data within the time ranges selected by Ince (2009) (the light black vertical lines in the different panels) are shown (i) in blue for the regression established using the parameters reported in Ince's thesis (but not all reported in Wilson *et al.* 2009), and (ii) in red for the regression derived from the digitized data. In each case, the very good consistency observed between the blue and red regression lines proves the reliability of the data shown in Figure 6. The green curves display the variations of the rehydroxylation rates (α) computed using both a constant time$^{1/4}$ interval (light green; 'running slopes') and varying time$^{1/4}$ time intervals (dark green; 'slopes from the end'). The green dashed lines define the ±10% limits about the α values considered by Ince (2009); taking into account error propagation, these correspond to age uncertainties of ±40%.

If the sample from the *opus spicatum* brick (Fig. 6 (a)) appears as a convincing case ('ideal data'; Wilson *et al.* 2014), the three others show results that are clearly not compatible with the recommendation on slope stabilization adopted by Wilson *et al.* (2014). In particular, the selection of the time$^{1/4}$ range providing the 'best fit' for the α determination that excludes the data obtained at the end of the experiments, which normally should provide the 'best' data of stage II, has no clear justification, since no perturbation in environmental conditions was observed (or mentioned) during the experiments. Using a similar time-span analysis as previously conducted

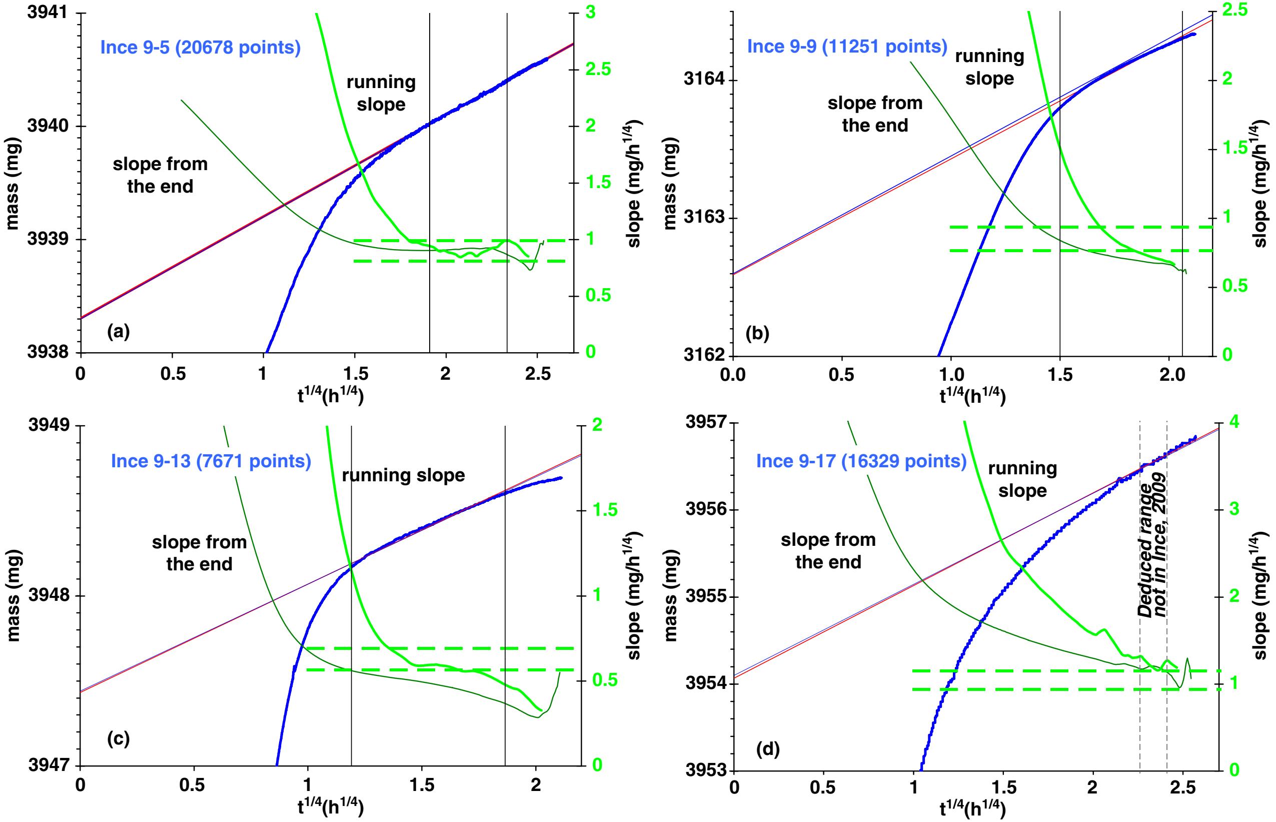

Figure 6 *Mass evolution for four samples previously studied by Ince (2009) and Wilson* et al. *(2009) after heating at 500°C (the blue curves in the various panels). These data, reported in h$^{1/4}$, were digitized from four figures provided in Ince (2009)'s thesis: (a) from fig. 9-5, (b) from fig. 9-9, (c) from fig. 9-13 and (d) from fig. 9-17. See the reference to the samples in Ince's thesis, in Wilson* et al. *(2009) and in the text. The red and blue lines in the various panels show, respectively, the linear regressions computed from our recovered data sets and from the parameters given by Ince (2009), also using the same time ranges as selected by Ince (2009) (see the vertical lines; note, however, that this information was lacking for the fourth sample but could be deduced from the data). The light green and dark green curves in the various panels show, respectively, the variations of the rehydroxylation rates computed using a constant time$^{1/4}$ interval sliding up to the end of the experiments ('running slopes') and using time$^{1/4}$ intervals progressively decreasing up to the end of the experiments ('slopes from the end'). The green dashed lines indicate the 10% limits about the rehydroxylation rate values considered by Ince (2009). (See online for a colour version of this figure.)*

for our Syrian samples (Fig. 2 (a)), the variations in rehydroxylation rate shown in Figure 6, together with the fluctuations in sample mass extrapolated to $t = 0$ (m_{RX}; see Supplementary Fig. A), were next taken into account to highlight the uncertainties in RHX dating resulting from the variations (Fig. 2 (b)). From this analysis, we find no evidence for well-defined 'plateau' ages. This data representation underlines the difficulty in these cases in choosing the 'correct' ages, and thus the poor reliability of at least some of the determinations made by Wilson *et al.* (2009).

CONCLUSIONS

As described in Wilson *et al.* (2009), the rehydroxylation dating method could appear to be a very straightforward method, easy to implement and providing high-precision dating results. After having designed a new measurement device for RHX determinations and conducted numerous experiments in the past 2 years (Le Goff and Gallet 2014; this study), we consider that this method is much more complicated than previously thought, and that it still requires significant developments and tests. Up to now, we have been unable to obtain any successful dating results from ~100 analysed ceramic and brick fragments of different ages and origins (and thus with different clay sources). In the present study, we have illustrated the scatter in rehydroxylation behaviour existing between samples collected from different potsherds of the same age and found at the same archaeological site, and even between samples collected from the same fragment. As all our samples experienced the same ELT, to derive satisfactory RHX dating results from these data, it would be necessary to determine the energy of activation for each sample, and also to conduct these long-lasting experiments on the same samples as those used for dating estimates. Hence, in requiring numerous and time-consuming measurements, the RHX dating method would lose much of its simplicity. We also note that Wilson *et al.* (2009, 2012, 2014) obtained experimental results that share many similarities with our own series of weighing measurements, but that were analysed using different approaches—in particular, concerning the data selection. Here, we have shown that the selection of data must obey strict and undisputable selection criteria taking into account all available data. For this reason, we have used a new data representation relying on a time-span analysis in order to scrutinize and demonstrate the stability of the long-term rehydroxylation process, a mandatory condition for obtaining satisfactory RHX dating results. We suggest that future users of the RHX dating method conduct such a similar time-span analysis when reporting their own results. All RHX data used in this study, and the related computations, are available upon request.

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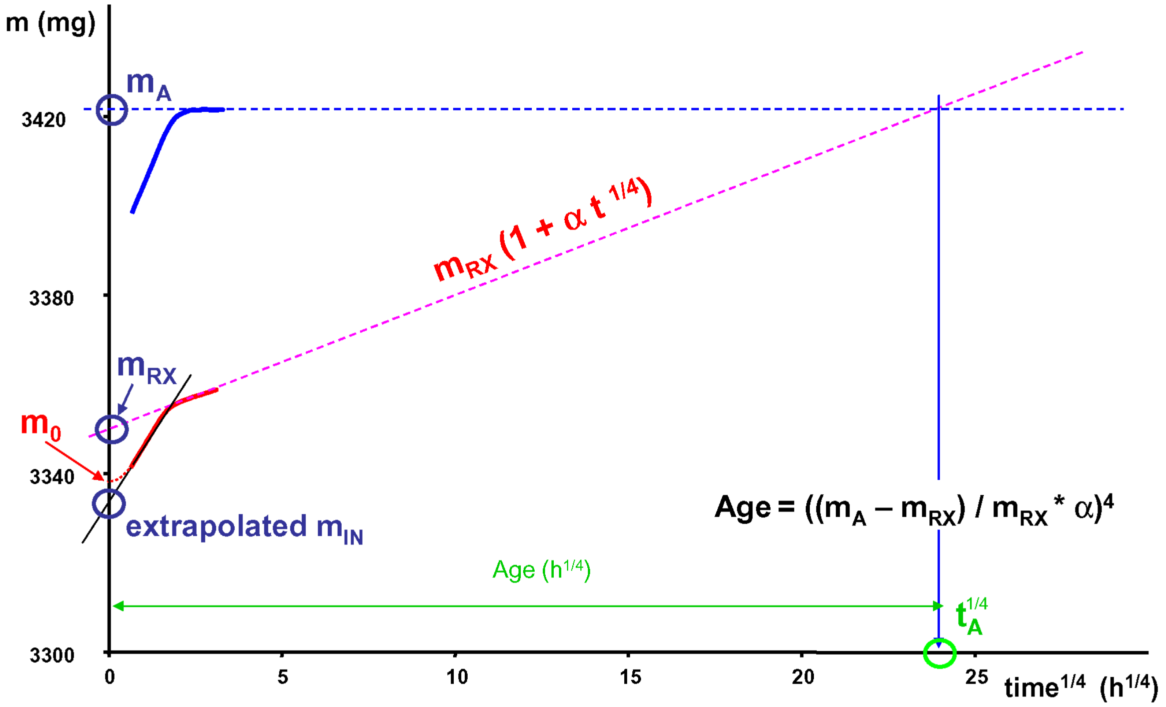
SUPPORTING INFORMATION

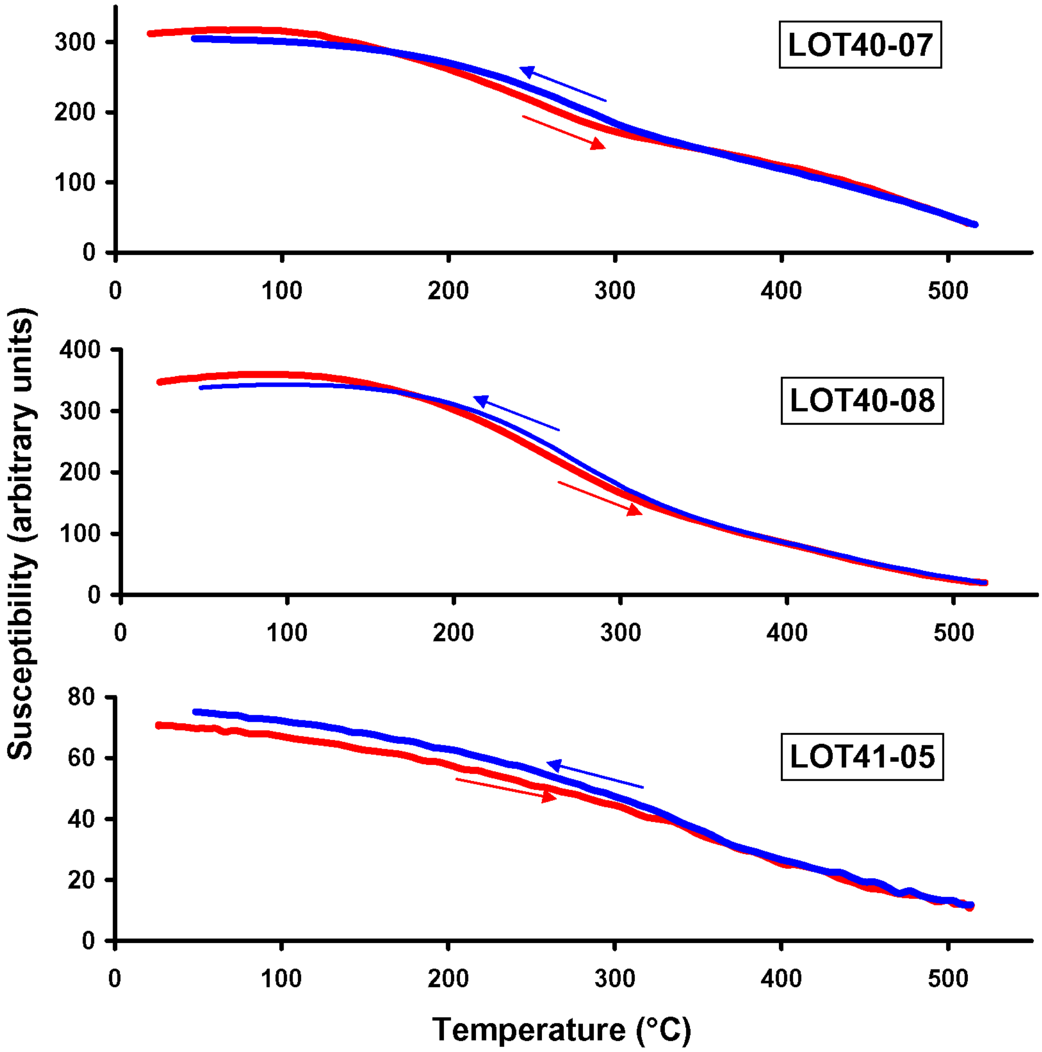
Additional Supporting Information may be found in the online version of this article at the publisher's web-site:

Supplementary Figure A
Supplementary Figure B
Supplementary Figure C



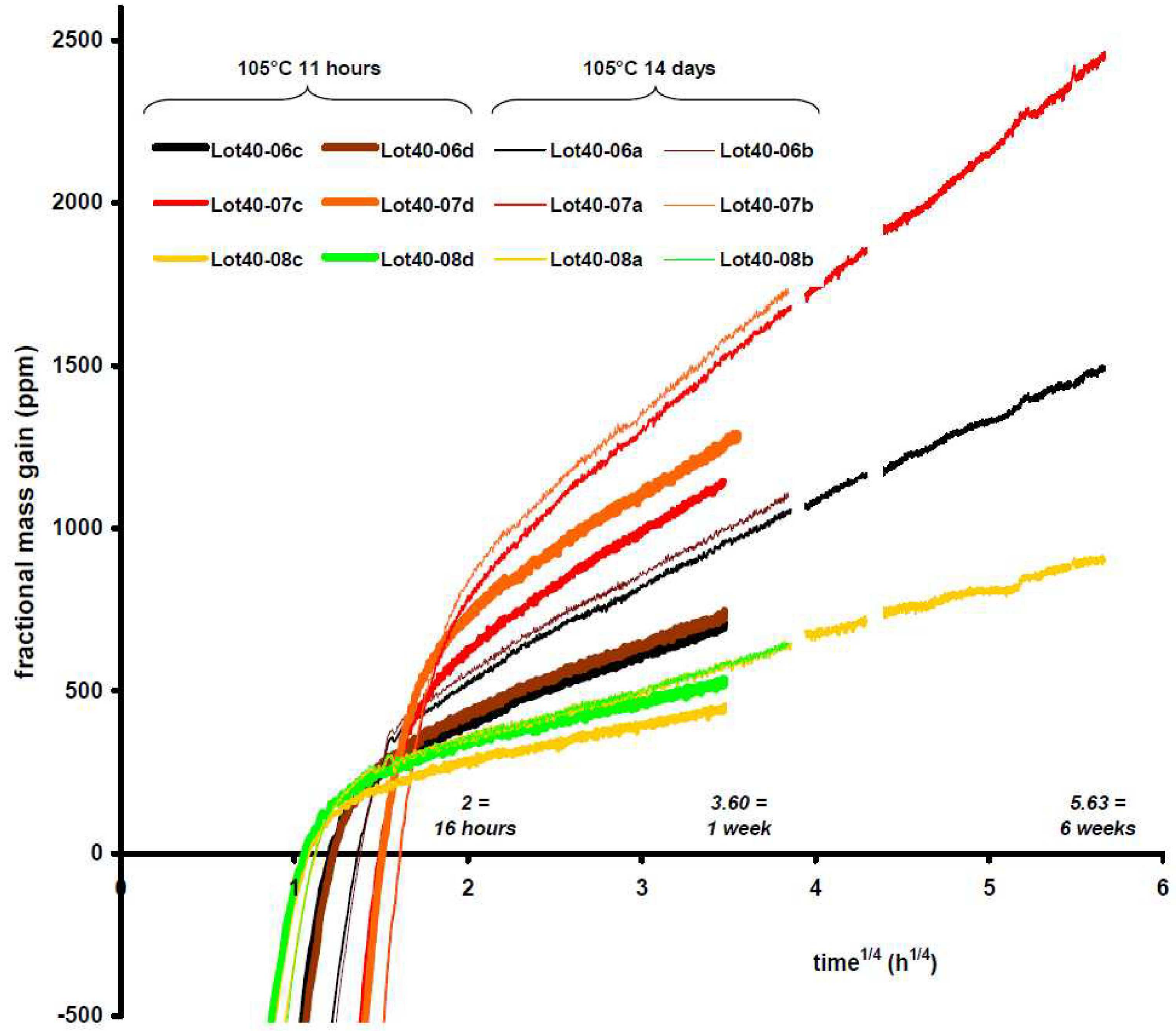
Supplementary Figure A.

Principles of the rehydroxylation dating method (Wilson et al. 2009; from Fig. 1 in Le Goff and Gallet 2014). The blue and red curve show the mass data obtained in constant environmental conditions (temperature and relative humidity) for one sample after its heating at 105℃ and 500℃, respectively. The data are reported against time in $hours^{1/4}$. After the heating at 105℃, the mass data become constant after ~2.5 $hours^{1/4}$, defining the so-called sample archaeological mass (m_A). After the heating at 500℃, the mass values show a linear trend after ~2 $hours^{1/4}$, i.e. after the so-called stage I (see text), in accordance with a slow rehydroxylation process (stage II, Wilson et al. 2009); the extrapolation of this behaviour to m_A gives the archaeological age of the studied sample (t_A, in $hours^{1/4}$; see the formula on the Figure). The two values m_{IN} and m_{RX} are the initial sample mass derived from stage I and stage II-mass variations, respectively, extrapolated to $time^{1/4}=0$; m_0 is the "true" initial mass value measured immediately after heating the sample at 500℃ (Wilson et al. 2009). Note that our terms m_A and m_{RX} are referred to as m_2 and m_4 by Wilson et al. (2012).



Supplementary Figure B.

Low-field magnetic susceptibility versus temperature curves acquired up to ~500℃ obtained for three fragments (Lot40-07, Lot40-08 and Lot41-05) using a KLY-3 Kappabridge coupled with a CS3 thermal unit. The good reversibility between the heating (in red) and the cooling (in blue) curves indicates the absence of alteration of the magnetic mineralogy on heating.



Supplementary Figure C.

Examples of fractional mass-gain variations relative to m_{RX} obtained for two series of samples collected from the same set of three fragments (site Lot40, samples #06, 07 and 08), the first series after heating of the samples at 105°C during 11 hours ("c" and "d" samples; see Fig. 1(a)), the second series after heating at 105°C during 14 days ("a" and "b" samples). See colour code on the figure. The data are reported against time in hours$^{1/4}$.