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On the effect of organic carbon on rehydroxylation (RHX) dating

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ABSTRACT

Scientific dating is an invaluable tool to understand the development of human civilizations from prehistoric to historic times. Ceramics is the most abundant material recovered from archaeological excavations, but a satisfactory scientific dating method is still lacking. So called rehydroxylation (RHX) dating promises precise age information, but the validity of the method still has to be proven. We have investigated one possible obstacle imposed by the presence of organic carbon in the samples. Such a contamination can lead to significant deviations of the dating result. The amount of CO_2 released from the following samples was determined: A medieval clay brick from Alkoven, Austria; two authentic archaeological samples from the Iron Age from Megiddo, Israel; a 1600 AD earthenware sherd from Enkhuizen, Netherlands, which had been successfully dated with RHX at another laboratory. We investigated several possibilities to remove such contamination.

1. Introduction

Ceramics cannot be dated by ^{14}C, and thermoluminescence dating (Aitken, 1985) does not reach a competitive precision (e.g. (Liritzis et al., 1996)). Since ceramics is the backbone of many archaeological chronologies, an additional dating tool would have significant impact on the field of archaeology. Wilson et al. (2003, 2009) observed that the mass gain of a fired-clay material by chemically bonded hydroxyl water followed a strict power law with time ($t^{1/4}$), suggesting a new tool for absolute dating of ceramics, now generally called rehydroxylation (RHX) dating. However, the method is still in its infancy, and has not yet been applied to many real archaeological samples.

The RHX method to date fired-clay ceramics (Wilson et al., 2009) utilizes the mass gain of the ceramic due to uptake of hydroxyl molecules OH^- over a time scale ranging from days to millennia. This mass gain, $m_{OH}(t)$, is assumed to follow

$$m_{OH}(t) = \alpha_m \times t^{1/4} \tag{1}$$

where α_m is a material and temperature dependent constant (see Equation (2) below). This chemical process, in which water is assumed to be converted to hydroxyl molecules and chemically bound to the crystal lattice of the clay particles, is called rehydroxylation and is reset during the initial firing of the ceramic. When the sample is again fired at temperatures above 500 °C, the OH^- will be removed, and the mass loss is used to determine the age. Of course, the mass change is only a proxy measurement for the change in hydroxyl content, which cannot be measured directly.

The simple principle is complicated by the necessity to determine the rehydroxylation mass gain rate α_m for each sample and by the temperature dependency of this parameter. The influence of the temperature on α is given by the Arrhenius equation (Hall and Hoff, 2012; Hall et al., 2013).

$$\alpha_m = \alpha_{m,0} \exp\left[-\frac{E_a}{4R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{2}$$

Here, R denotes the universal gas constant $R = 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$, E_a the material-dependent activation energy and $\alpha_{m,0}$ the rehydroxylation mass gain rate at a temperature T_0 (measured in K). The sample's mass gain rates at different temperatures have to be measured in order to derive the value of the activation energy (Wilson et al., 2009).

To correct for the temperature dependency, the method requires the knowledge of the so called effective lifetime temperature T_{EFF}, at which the sample was actually stored. This is estimated from the archaeological evidence and climate data (Hall et al., 2013).

The surprisingly simple $t^{1/4}$-law is typical for so called single-file diffusion (Lizana and Ambjörnsson, 2008; Savage et al., 2008), and

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is theoretically predicted for one-dimensional diffusion processes where particles cannot bypass each other, fairly independent of the details of the underlying process. In ceramics, the diffusion of hydroxyls seems to be restricted to one-dimensional pathways along available reaction sites, which are occupied one after the other (Richards, 1977; Lizana and Ambjörnsson, 2008). Strictly speaking, the explanation in terms of restricted diffusion is still speculative, and to our knowledge not supported by any microphysical analysis in ceramics; therefore, the observed ($t^{1/4}$) law is essentially empirical.

It should be noted that if the strongly nonlinear $t^{1/4}$ law is indeed valid over millennia, it allows to determine the properties of the rehydroxylation process within a few weeks, which are then used to extrapolate over the historical time range to determine the sample age.

However, any concurrent process leading to a mass change during firing can obscure the relatively small (de-)hydroxylation effect. The influence of loosely bound, "adsorbed" water has been intensively studied by several authors (e.g. Wilson et al., 2012; Wilson et al., 2014; Drelich et al., 2013). This water is in equilibrium with ambient humidity. It is removed together with the hydroxyl water during firing, and replenished with an equilibration time constant on the order of hours to days. Control of environmental parameters and equilibration protocols are necessary to make sure that the amount of adsorbed water is constant during weighing and thus cancels out. Also other processes, like the transformation of magnetite into iron hydroxides through chemical weathering (Burakov and Nachasova, 2013) can lead to a mass change during firing.

In a preparatory and feasibility study to implement capabilities for rehydroxylation dating at our laboratory, we have investigated the technical requirements and possible pitfalls of the method with existing or provisional instrumentation. Special emphasis was put onto the so called non-refractory compounds (NRCs), i.e. substances other than water which are lost during firing at 500 °C. Especially organic carbon compounds, which are present as environmental contamination, will pyrolize at temperatures between 350 and 450 °C, and can lead to wrong determination of the hydroxyl mass. Wilson et al. (2012) did measure the organic carbon of one sample (denoted as L1 in that publication) analytically, and made a correction for 0.67 wt.% carbon in the age calculation. The importance of NRCs for RHX dating is recognized in the available literature (see also e.g. (Hamilton and Hall, 2012)), but so far only cursory instructions to cope with this difficulty are given.

2. Samples

The majority of the investigations were performed on a medieval clay brick, which was kindly provided by the Landesmuseum of Upper Austria. The particular brick was retrieved from the soil during excavations coordinated by archaeologists from the Landesmuseum at the site of a supposed Roman settlement in today's municipality of Alkoven. It has been used at the Atominstitut (Vienna University of Technology) for thermoluminescence dating in the students' lab over several years. Corresponding to these measurements, it is 1000 ± 150 years old, thus not of Roman origin, but medieval. Since excavation in 2002, the brick was stored in darkness at a temperature of about 22 °C at the Atominstitut in Vienna.

To ensure realistic conditions based on true archaeological samples, we obtained pieces from two bowls from an excavation at Megiddo, Israel. The samples were supplied by Israel Finkelstein from Tel Aviv University, and were stratigraphically dated to belong to the Iron Age (IA/IIA).

Moreover, we had the possibility to analyse a sample of Werra earthenware from Enkhuizen, Netherlands, which has been successfully dated by the RHX method by Wilson et al. (2012). In that publication, it has been denoted as W 1-3. The age is known to be 1605 AD (see Wilson et al., 2012).

3. Methods

Our procedure generally follows the protocols applied by (Wilson et al., 2012; Drelich et al., 2013; Bowen et al., 2011, 2013). The cleaned object is heated to 110 °C in a drying oven to remove adsorbed water (Clegg et al., 2012). The time to reach constant weight depends on the individual sample and lies between some hours and some days for samples of 500 mg and 2–4 g, respectively (Wilson et al., 2012; Bowen et al., 2011, 2013). Our samples of ~2.4 g were heated for 48 h at 110 °C. No investigations were carried out that this duration is sufficient for the sample actually used, however, we chose a duration close to the maximum suggested in the available literature. The formulation of a reliable criterion when equilibration is complete is a known problem of the method so far (Le Goff and Gallet, 2014).

In the next step, the sample is exposed to controlled humidity and temperature till equilibration conditions is reached (i.e. no more mass change visible) and the sample is weighed. This constant mass is denoted m_2 in the literature (see Wilson et al., 2012). The sample is then fired at 500 °C in a muffle furnace (Wilson et al., 2009; Tosheva et al., 2010; Clegg et al., 2012) to remove the hydroxyl water and thus reset the "inner clock" of the ceramic. The duration required for this process again depends on the particular ceramic and lies between 4 and 12 h (Wilson et al., 2009; Bowen et al., 2011, 2013) and 74 h (Barrett, 2013). We fired our samples for 72 h at 500 °C.

In the last step, the sample is once more exposed to the same controlled conditions as before the firing. Once lightly adsorbed water reaches equilibrium, the rehydroxylation process alone is assumed to continue. Monitoring the mass gain allows to determine the constant α_m and to determine the sample mass without the hydroxyl mass (denoted as m_4 in (Wilson et al., 2012)) by back-extrapolation to the moment of firing. The mass gain $m_a = m_2 - m_4$ is attributed to the hydroxyl mass m_{OH} and is typically on the order of 10^{-3} g per g of ceramics.

The importance of precise control of temperature and humidity during sample conditioning has been emphasized previously by several authors. First tests with the medieval brick showed that especially variations of the relative humidity in the laboratory have a significant influence on the mass determined by weighing: at a temperature of 23 °C, an increase of 1% in relative humidity lead to a relative mass increase of about 2×10^{-5}. It was evident that active control of temperature and humidity of the environment in which the measurements are carried out is needed. All experiments reported here were performed in a small laboratory at the group for Isotope Research and Nuclear Physics (University of Vienna) which is equipped with a balance (Sartorius 1712 MP 8, precision 10 µg). The accuracy was checked in every measurement series with an external calibration weight made from stainless steel, which in fact reproduced the same result within the last digit. A provisional regulation of both relative humidity and temperature using electronic household devices (Xavax FS20HGS and eQ-3 HM-CC-TC) was implemented. The temperature was regulated by controlling the existing room heating or cooling, while a stable relative humidity was ensured by an air humidifier (Venta 7045501) or dehumidifier (Oasis 165HGXI). The setup provides two independent measurements of both moisture and temperature, which allows to estimate the regulation accuracy. During the experiments, the relative humidity was kept at (59.5 ± 1.0) % RH whereas the temperature was kept at (22.9 ± 0.5) °C. Equilibration, storing, and weighing of the samples were carried out in this controlled room, while they were moved to a regular lab for cleaning, drying, and firing.

The samples were handled in small seggars folded from gold foil throughout the whole procedure, to make sure that no material would be scratched off the samples during handling. Empty seggars showed no mass change after firing at 500 °C.

This provisional implementation did not allow to perform experiments at vastly different temperatures, as required to estimate the temperature dependence of the rehydroxylation mass gain rate. Therefore, a real dating was not possible, but we found that many aspects of methodology could be studied with good precision.

Our laboratory is especially equipped with instrumentation for the elemental analysis of small amounts of carbon (Liebl et al., 2010), which includes a specialized unit to combust and extract carbon as CO_2, coupled to a residual gas analyser (RGA, Type Balzers Instruments QME 200, which is a quadrupole mass spectrometer with an electron impact ion source). Additionally, the extracted CO_2 can be converted to graphite and analysed for radiocarbon content by accelerator mass spectrometry (AMS).

4. Experiments

Rehydroxylation mass gain curves were obtained for two samples from the medieval brick (XMN 40 and 41, Table 1). Considering the strong influence of ambient humidity on the measured sample mass, three unfired samples (XMN 37–39) were used as mass reference for the two other samples (XMN 40, 41). The reference samples were preheated and equilibrated exactly as the dating RHX test samples, but were not heated to 500 °C. We assumed that any mass change of the reference samples indicates a similar mass change of the RHX test samples, which is not related to rehydroxylation. A "nominal" mass of each reference sample was thus determined initially. For later measurements, the ratio between the actually measured and the nominal mass was used to calculate a correction factor, by which the measurements of the RHX test samples were divided. This procedure reduces the scatter of the data significantly (see Fig. 1). The samples XMN 40 and 41 were first heated to 110 °C for 48 h and equilibrated to measure m_2 for 172 h (Fig. 1). Thereafter, the samples XMN 40-41 were reheated at 500 °C for 72 h and then equilibrated while monitoring the mass gain. The mass gain is shown in Fig. 2.

To decide when the initial equilibration is complete and the data starts to follow the $t^{1/4}$ law is a well known problem studied in several publications (e.g. Bowen et al., 2011; Barrett, 2013). This topic is beyond the scope of this work, we just decided by visual judgement of the graphs. The results for the two medieval brick samples are given in Table 1. The masses were obtained at $T_0 = (22.9 \pm 0.5)$ °C and (59.5 ± 1.0) % RH. m_{OH} is derived assuming that the mass of NRCs is zero: $m_{\mathrm{OH}} = m_a = m_2 - m_4$. The respective values for the normalized rehydroxylation rate α, which is given by $\alpha = \alpha_{\mathrm{m}}/m_4$ are in good agreement with each other, as expected for two aliquots from the same brick. The values are comparable to those given in Wilson et al. (2012) for different materials (Werra earthenware, samian ware, and a fired clay loomweight).

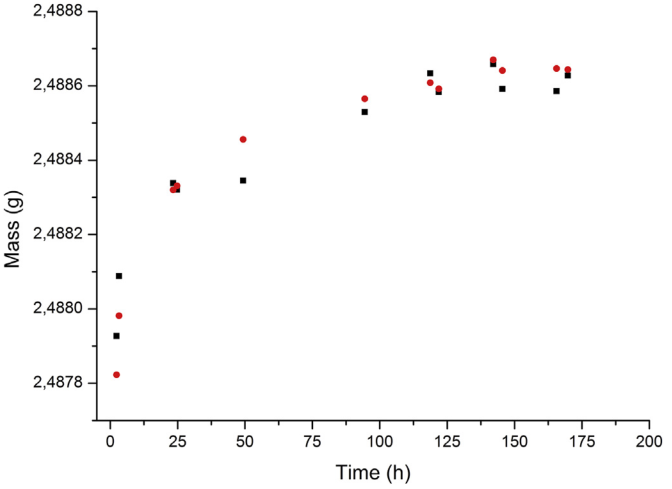

Fig. 1. Mass gain of sample XMN 40 from the medieval brick after heating to 110 °C and then storing in controlled conditions. The red data points indicate the corrected data, where the mass change in the three untreated calibration samples has been considered. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Without the possibility to change the temperature of the laboratory significantly, it was not possible to determine the activation energy E_a. To obtain a sample age, we thus assume not only an effective lifetime temperature $T = T_{\mathrm{EFF}}$ of 10 °C, but also an E_{a} of 83 kJ mol^{-1}, which is a typical value according to Wilson et al. (2012) as well as Hall et al. (2013).

The RHX age, t_{a}, is calculated with

$$t_{\mathrm{a}} = \left(\frac{m_{\mathrm{OH}}}{\alpha_{\mathrm{m}}}\right)^4. \tag{3}$$

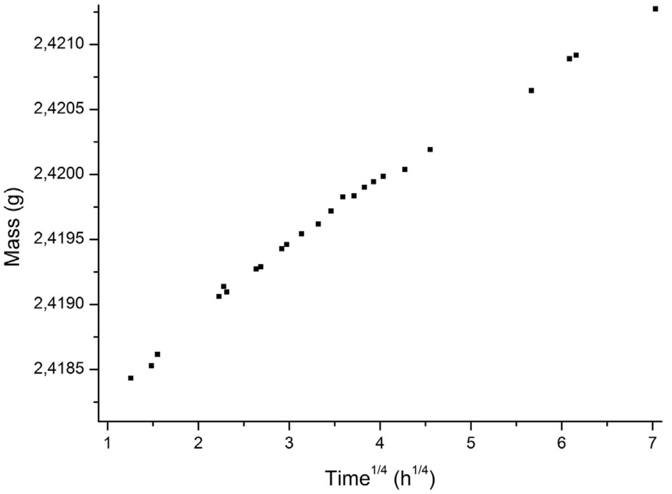

Fig. 2. Mass gain of sample XMN 41 at T_0 – corrected according to the calibration samples – plotted against time$^{1/4}$. The data was obtained at (22.9 ± 0.5) °C and (59.5 ± 1.0) % RH. Linearity is observed (by eye) after about 4 $h^{1/4}$ (~1 week). The slope of this part is $\alpha_{\mathrm{m},0}$.

Table 1
Components of the mass for samples XMN 40 and 41. In column 6, α_{m} is derived from equation (2), using T_{EFF} and E_{a} as given below.

Sample	Equilibrated mass m_2 (mg)	Mass m_4 (mg)	Apparent hydroxyl mass m_a (mg)	$\alpha_{\mathrm{m},0}$ (mg $h^{-1/4}$)	$\alpha = \frac{\alpha_{\mathrm{m}}}{m_4}$ ($h^{-1/4}$)
XMN 40	2488.63 ± 0.08	2454.44 ± 0.03	34.19 ± 0.09	0.423 ± 0.006	0.000118 ± 0.000002
XMN 41	2462.98 ± 0.15	2418.24 ± 0.03	44.74 ± 0.15	0.431 ± 0.007	0.000121 ± 0.000003

However, the resulting rehydroxylation ages are 22,200 and 62,400 years, which is certainly too high (Table 2).

Moreover, it is not possible to force the rehydroxylation age to the thermoluminescence value of about 1000 years by choosing other, suitable values for E_a and T_{EFF}. A negative activation energy or an unreasonable effective lifetime temperature above 30 °C would be necessary. It should be noted, however, that our assumed T_{EFF} of 10 °C could be significantly too low if the brick has not been buried for most of his lifetime, but has been incorporated in a building for an extended duration; the effective lifetime temperature is not simply the average temperature, but has to take into account the stronger influence of high-temperature periods (Hall et al., 2013).

4.1. Mass-spectrometry of released, non-refractory compounds (NRCs)

A possible explanation for the overestimated age of the medieval brick is an additional mass loss during heating at 500 °C due to the presence of NRCs, which will mimic a larger hydroxyl content. Organic material present in the samples would be such a NRC. To assess its relevance, we have analysed the gaseous emissions during firing at 500 °C for all three kinds of samples.

From each sample, a small aliquot was fired inside a quartz vial at 500 °C. The evolving gases were led over copper oxide heated to 900 °C. This ensures complete oxidation of volatile organic compounds to CO_2, but also releases a small amount (10–20 mbar) of O_2 which expands back to the sample to enhance oxidation. A pressure measurement records the sum pressure of O_2 and any released gases.

A small amount of the produced gas was bled through a precision valve into the RGA. The mass spectra obtained reveal that a substantial amount of CO_2 is produced when the sample is heated. The RGA does not allow to determine the released water, due to a large water background in the instrument. RGA measurements are only semi-quantitative, and to increase the accuracy of the results, all data were normalized to the mass 32 (O_2^-) peak.

A first test using 0.727 g of the medieval brick sample clearly showed an increased CO_2/O_2-ratio when it is fired at 500 °C, so it is indeed carbon that gets out of the fired sample (see Fig. 3). After cryogenic separation, the amount of CO_2 was manometrically determined to correspond to about 2 mg carbon. For the typical carbon content of humic acids (the most likely organic contamination of a brick buried in soil) of about 50% (Pospíšilová and Fasurová, 2009), this corresponds to a mass fraction of 0.55% of organic material in the brick. This is on the order of mass needed to reconcile the rehydroxylation date of the brick with the thermoluminescence age.

The CO_2 produced was collected for a radiocarbon measurement. Additionally, another small aliquot was flame sealed together with copper oxide in a quartz vial, and combusted at 900 °C. The ^{14}C content of the released carbon was measured by AMS. Calibrated age ranges (95.4% probability) from 1430 to 1950 AD and 1655 to 1950 AD were obtained for the flame sealed sample and the sample measured with the RGA, respectively. The results indicate a post-medieval origin. Obviously, contamination with carbonaceous material took place well after the brick was manufactured.

Table 2
RHX ages derived by using the data given in Table 1.

Sample	t_a (yr)
XMN 40	22,200
XMN 41	62,400

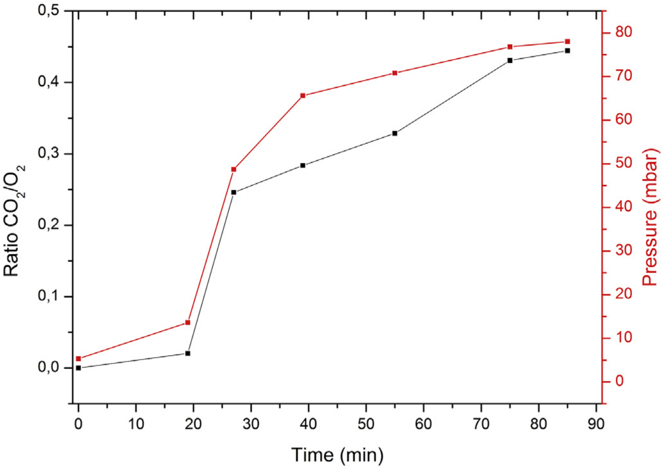

Fig. 3. Ratio of CO_2 to O_2 (black) as well as pressure in the combustion setup (red). The ovens were set to 500 °C at time = 20 min. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.2. Removal of organic carbon

To investigate the possibility of obtaining meaningful rehydroxylation dates for ceramics contaminated by organic carbon, we tested methods to remove carbon-related m_{NRC} before the measurement, without losing the hydroxyl water. Based on our experience with radiocarbon dating, where removal of carbon contamination is also essential, we applied acid and base leaching and wet oxidation to the available sample materials. Acid treatment removes carbonates, base treatment dissolves humic acids usually present in soils, while wet oxidation can destroy organic compounds.

As a first step, all samples were reduced in size to pieces with a maximum diameter of 4 mm. Three to five such pieces were taken from each sample, and rinsed with ultrapure water (Milli-Q) in order to remove any friable material. Table 3 shows the different procedures tried out for the different samples. The steps “A” and “B” stand for Acid-treatment (1 M hydrochloric acid HCl, 60 °C, 30 min) and Base-treatment (0.1 M sodium hydroxide NaOH, 60 °C, 30 min), respectively. The “Ox”-step stands for oxidation with hydrogen peroxide (H_2O_2) for different durations as given in Table 3. The “piranha”-treatment stands for the usage of a stronger oxidation agent, peroxymonosulfuric acid (60 °C, different durations, see Table 3). This acid was made of 18 M sulphuric acid H_2SO_4 and 9.79 M hydrogen peroxide H_2O_2 in a 3:1 ratio. Between individual pretreatment steps, the samples were rinsed several times with ultrapure water.

Finally, the samples (treated and untreated) were measured for organic carbon content as described above. In Table 3, the results for the different samples and the different treatments are given. The percentage of the organic material was estimated by assuming that it contains 50% carbon.

All untreated samples release carbon during firing; the Austrian medieval brick shows the highest contamination (0.55% or 0.41%, in two independent measurements, respectively) and the Megiddo bowl 1 the lowest (0.05%). When pretreated, the organic content of the samples generally drops and in a few cases seems to be removed completely. The combination of acid and oxidation with H_2O_2 seems to yield the best results, and a longer duration of the oxidation is usually better. The Piranha solution, despite a certainly much stronger oxidizing agent, could not remove the carbonaceous contamination, or left other non-refractory compounds (e.g. sulphates) behind. Also the HCl and NaOH used in the A and B treatment could in principle introduce such residues.

Table 3
Carbon contamination in the investigated samples.

Sample	Sample mass (g)	Pretreatment	Carbon mass (µg)	Percentage organic material (%)
Medieval Brick	0.727[a]	None	2000	0.55
	0.15400	None	313	0.41
	0.20012	Piranha (60 min)	283	0.28
	0.16383	Piranha (130 min)	273	0.33
	0.09986	A-B-A-B-A	57	0.11
	0.10404	Ox (395 min)	92	0.18
	0.05840	A-Ox (395 min)	0	0.00
	0.09727	A-B-A-B-Ox (240 min)	12	0.02
	0.07269	A-B-A-B-Ox (360 min)	22	0.06
	0.10437	A-B-A-B-Ox (660 min)	4	0.01
Werra Earthenware	0.14239	None	78	0.11
	0.13341	Piranha 60 min	58	0.09
	0.15769	Piranha 130 min	31	0.04
	0.11261	A-Ox (395 min)	99	0.18
	0.06183	Ox (570 min)	2	0.01
	0.06918	Ox (755 min)	3	0.01
Megiddo bowl 1	0.33797	None	87	0.05
	0.37003	A-B-Ox (120 min)	31	0.02
Megiddo bowl 2	0.33762	None	152	0.09
	0.31864	A-B-Ox (120 min)	95	0.06

[a] This is actually the measurement presented in Fig. 3.

Correcting m_a in Table 1 by the mass of the organic material detected by the RGA measurements shows "better", i.e. younger dating results as shown in Table 4.

The results differ strongly between the two samples and the amount of organic content used for the correction. It must be emphasized that there are numerous uncertainties in obtaining these corrected estimates. Neither the activation energy E_a nor the effective lifetime temperature T_{EFF} is known; the determination of the carbon released as CO_2 provides only a rough estimate of the organic carbon mass, as its composition can vary significantly. The results suggest that the carbon content may vary from sample to sample of nominally similar material.

5. Conclusions

The so called m_{NRC} imposes one obstacle for an accurate measurement with the RHX method. We found in all investigated samples a significant release of carbon during heating, which can explain the too-old rehydroxylation age obtained for a medieval brick in our preparatory experiments. It should be noted that the apparent hydroxyl mass m_a of the two samples from this brick differ by 25 per cent, while the normalized rehydroxylation rates α are very similar. This may support the idea that a variable contribution to m_a from contaminants is responsible for the age deviation. The estimated mass fraction of organic material of 0.55% and 0.41% found is similar to the 0.67% found in a loom weight by Wilson et al., 2012.

The carbon contamination of the Iron-age samples from the Meggido excavation site and of the 400-year old piece of Werra earthenware dated in Wilson et al., 2012 is smaller, but still significant. If we correct the data from Wilson et al., 2012 by the carbon mass we have measured, the resultant age changes from 1577–1624 AD to 1767–1784 AD, which reduces the agreement with the inscribed age of 1605 AD.

Table 4
RHX ages derived after correcting m_{OH} for the observed organic content.

Sample	t_a (yr) 0.55 % Organic content	t_a (yr) 0.41 % Organic content
XMN 40	2865	5367
XMN 41	14,734	22,411

In our opinion, removal of contamination prior to a rehydroxylation measurement is mandatory. Cleaning with acid followed by oxidation with H_2O_2 showed promising results. To gauge the success of cleaning, the gas composition and the amount of CO_2 produced during firing should be determined routinely as quality control for all samples. If the amount is large, the sample has to be discarded. If the CO_2 amount is small, and a sufficiently precise measurement can be achieved, a correction to the mass m_{OH} might be applied. The qualitative result obtained with the RGA in this work does not provide this precision, but e.g. isotope dilution techniques with isotopically enriched compounds could lead to significant improvements.

Ideally, one would like to measure the evolving gases on the same aliquot which is used for RHX age determination. However, this was not possible with our provisional setup, as the maximum ceramic mass which can be handled by our carbon determination is below 1 g, which was too small to perform an accurate determination of m_{OH}, given the precision of our balance. A balance with a resolution of 1 µg to allow smaller samples and an enlarged combustion volume to extract carbon are required. The necessity to perform the equilibration, storing, and weighing at two significantly different temperatures suggests to install two glove boxes with regulated temperature and humidity, with a similar balance in each.

Generally, treatments to remove NRCs could also alter the mineralogy or morphology of the ceramic, and it is unclear whether this will adversely affect the dating result. Potentially, these treatments could also remove some hydroxyls, or lead to additional hydroxylation. Since the mechanism behind the RHX mass gain is still speculative, these questions have to be answered by further investigations.

It should be emphasized that carbon compounds in the sample constitute only one methodical difficulty for accurate RHX dating. Burakov and Nachasova (2013) identified chemical weathering of magnetite Fe_3O_4 into iron hydroxides as another reason why the determination of the hydroxyl mass m_{OH} can fail, and suggest screening of samples for iron minerals to ensure reliable dating. More pitfalls may be connected to the chemistry, mineralogy or porosity of the samples (compare (Wilson et al., 2014)), which may require additional analytical techniques to gauge the suitability of samples.

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