INTRODUCTION

Chronology assumes a central role in the process of historical and archaeological reconstruction by allowing us to time the change and development of human societies. Dating provides a framework for linking individual events together. It is the backbone for historical narratives, and connections between environmental and archaeological records on a global scale. However, until today, establishing a reliable chronology for ancient human societies and civilizations using pottery has remained one of the most contested topics of scientific discourse. Although the field of chronology has been revolutionized by modern historical and archaeological critical methods, through assessing historical sources and material...
culture, alongside with advances in science such as ¹⁴C-radiocarbon dating, many crucial chronological questions have still remained unsolved. Any new attempts to clarify the foundations of chronological dating for ancient societies and their artifacts therefore deserves the utmost scientific attention and requires concerted efforts in its methodological development.

One class of artifacts that is of particular interest to archaeologists is fired-clay objects, or ceramics. Ceramics make up one of the most significant portions of the world’s archaeological record. Since the invention of ceramic technology, already during the Upper Paleolithic times, but mainly, during the last 8000 years, pottery has been an integral and important part of human civilizations across the globe.¹⁻³ Given that fired-clay objects are relatively durable and largely inert, ceramic sherds are often found by the thousands (or more) in large deposits. Ceramics are also often decorated with paint, incisions and appliqué and thus provide a wealth of information about past social identities and cultural interactions. Establishing a reliable absolute chronology for pottery ceramics in archaeological assemblages is therefore of crucial relevance for a reliable reconstruction of historical processes.

Direct radiocarbon dating of pottery may trace, for example, the remains of organic temper (e.g. rice straw, chopped dung), sometimes added to prevent shrinkage and cracking. Such dating is possible but not reliable, as many potential sources of carbon in surviving potsherd should be considered.⁴⁻⁵ Since food residuals may also be incorporated into the clay matrix, clay materials can, in principle, be dated by targeting lipid components.⁶⁻⁷ This methodology, however, is subject to all the uncertainties known to occur in radiocarbon dating. Moreover pottery types that were not used for food consumption and preparation would not leave lipid fingerprints. More reliable information may therefore be expected by evaluating the age of the matrix itself. Several methods, such as Thermoluminescence (TL), Optically Stimulated Luminescence (OSL) and Electron Paramagnetic Resonance (EPR) have been advanced for direct dating, using feldspar, quartz, or other crystals present in the ceramics.⁸⁻¹¹ However, depending on uncertainties in the radiation dosimetry and the influence of water, the general margins of uncertainty for the dates obtained via these methods still remain high, in the 3%–7% range, proportional to the age of the sample.¹²

The archaeomagnetic dating technique provides another alternative. It traces the record of geomagnetic field direction and/or intensity stored within archaeological materials such as fired ceramics or mudbricks.¹³⁻¹⁴ Such data are compared to a geomagnetic secular variation curve, based on synchronization with contemporaneous radiocarbon dates and/or historical records, etc. Since the Earth’s magnetic field also varies according to geographical location, a separate calibration curve is needed for different regions.¹⁵⁻¹⁷ However, detailed secular variation curves for many different regions are not yet well-defined, and archaeomagnetic dating is often not possible.

Another promising technique was proposed in 2009 by Wilson et al.¹⁸⁻²⁰ This new technique, called rehydroxyl- ation (RHX) dating, is based on the fact that ceramic materials begin a chemical reaction with atmospheric water (H₂O) as soon as they are removed from the kiln. However, a decade after its first proposal, the RHX dating method is still far from routine in archaeology. The topic is still the subject of lively and often quite controversial discussions.²¹⁻²³ Researchers for example disagree whether or not the recombination of T₂ (structural OH) and T₁ (H₂O) water is simultaneous over longer timescales; and on the level of uncertainty associated with the power law itself.¹⁸⁻²⁰ There are still deficiencies in our knowledge about the elementary processes giving rise to the underlying phenomenon of hydroxylation in thermally altered clay minerals, upon which RHX dating depends.

These deficiencies are the focus of the present communication. Our study is intended to serve as an introduction to the potential of Infrared (IR) and Nuclear Magnetic Resonance (NMR) spectroscopy to better understand the hydroxylation phenomenon, the basis of RHX dating. Both techniques have proven their effectiveness in investigating the elementary processes of mass transfer in nanoporous materials, leading to a paradigm shift in our understanding of both intracrystalline diffusion and surface permeation.²⁴⁻²⁶ Similarly, they should also be able to provide information about structural and dynamic features of ceramics, which are inaccessible to other techniques.

The establishment of IR and NMR spectroscopy as standard techniques of diffusion measurement in nanoporous materials would have been impossible without a close interdisciplinary collaboration. This included material scientists and chemical engineers, in order to provide the required understanding of the materials under study. The analogous interdisciplinary requirement also applies in the present collaboration involving physicists, material scientists and archaeologists. The techniques presented in this paper are introduced for non-experts in these fields. Our aim is to provide an introduction to the RHX dating method, review the current progress in this area and demonstrate the possibilities and advantages of IR and NMR spectroscopy. We use IR and NMR spectroscopy to study the kinetics of rehydroxylation and H/D exchange of three pure clay minerals, muscovite, illite and beidellite, as analogues for components of ceramics. The implications of the results for RHX dating are then discussed. We show that NMR and IR methods hold significant potential to refine the RHX dating method by understanding the elementary processes of mass transfer and hydroxylation in pure clays.
2 REHYDROXYLATION (RHX) DATING OF ARCHEOLOGICAL ARTIFACTS

2.1 The phenomenon of rehydroxylation in fired clay minerals

After firing, hydroxyl groups (OH) are re-incorporated into the structure of ceramic materials, resulting in their expansion and mass gain. The longer the material is exposed to atmospheric moisture, the more hydroxyl groups are incorporated, and the greater the mass gain and size expansion. It was proposed by Wilson et al.\(^{27}\) that the hydroxylation reaction rate is proportional to the quartic root of time. A suggested explanation of the \(t^{1/4}\) law\(^{27}\) involved diffusion of water molecules within a system of sufficiently narrow channels such that the molecules cannot pass each other. During this so-called single-file diffusion, once a water molecule encounters a hydroxylation site, it is chemisorbed. If the hydroxylation reaction rate is proportional to \(t^{1/4}\), the elapsed time since firing can be determined by measuring the number of chemically recombined OH groups and the RHX rehydroxylation reaction rate.

Water incorporates into the material in two stages. During Stage I, the weakly bound (physisorbed) and the strongly bound (chemisorbed) \(\text{H}_2\text{O}\) water, defined as \(T_0\) and \(T_1\) respectively by Wilson et al.\(^{27}\), are loaded. This is the rehydration stage. \(T_0\) and \(T_1\) equilibrate quickly, and this stage lasts between minutes and weeks. Stage II describes the rehydroxylation or the incorporation of OH hydroxyl groups, denoted as \(T_2\) water. The sample's age is obtained by extrapolating how much time the sample in this Stage II needs to regain the original hydroxyl mass that it had before heating. This corresponds to the time elapsed since the ceramic was originally fired.

The following kinetic law was proposed to describe the Stage II phase of long-term chemical recombination by micro-gravimetric studies.\(^{27}\) In this model, this stage is dominated by RHX, or only \(T_2\) water incorporation:

\[
y = \alpha(T) t^{1/4}. \tag{1}
\]

The fractional mass gain \(y\) describes the rehydroxylation, and \(\alpha(T)\) is a mass gain rate constant. With hours as the time unit, the value of this constant varies from about 0.00018 to 0.00075 \(\text{h}^{-1/4}\) at common environmental temperatures.\(^{18-19}\) The \(\alpha(T)\) value depends on the temperature of original firing,\(^{28}\) since at higher temperatures, the degree of vitrification is increased, and therefore the number of sites available for rehydroxylation are reduced.

2.2 Principle of RHX dating by gravimetry

Based on Wilson et al.,\(^{18-19}\) the principle of RHX dating can be described as follows. In step 1, the initial mass (mass \(m_2\)) of the sample at a constant temperature and relative humidity is determined. Subsequently, the sample is heated at high temperatures (about 500°C or higher). In this way, the OH groups which are combined within the sample's structure since it was first fired, and also molecular \(\text{H}_2\text{O}\), are removed. Furthermore, \(m_4\) is determined, which is the hypothetical mass at complete dehydroxylation, but including molecular \(\text{H}_2\text{O}\). Then in step 2, by using subsequent measurements of mass increase, the rehydroxylation rate constant \(\alpha\) is determined. The \(\alpha\) rate is measured at several different temperatures, and an activation energy is determined for the rehydroxylation reaction. Using this activation energy, \(\alpha\) is then calculated for the estimated effective lifetime temperature \(T_e\), which is representative of the temperature history of a specimen.\(^{20}\) Note that a critical assumption is that it is assumed that \(m_4 = m_2 - m_4\) represents the mass of the OH groups (\(T_2\) water). In this case, the fractional OH mass loss is \(y = m_a/m_4\) and one may rearrange Equation (1) to yield the age since original historical firing as:

\[
t_e = \left(\frac{m_a}{(am_4)}\right)^4. \tag{2}
\]

According to Refs. [18,19] Equation 2 provides an estimate of \(t_e\), the age of the material under investigation. Note that the hydroxylation rate in the historical kiln is not necessarily equal to the currently determined RHX rate, considering uncertainties related to firing temperatures, contamination levels, the effective lifetime temperature, and the quartic root time dependence. However, this equality assumption is inherent to the RHX dating method.

Regarding the effective life time temperature \(T_e\), Wilson et al.\(^{19}\) and Hall et al.\(^{20}\) estimate \(T_e\), relying on regional meteorological data near the location where the sample was found, resulting in large temperature uncertainties. A method by which one may determine \(T_e\) largely independent of meteorological records (SAS—Same Age Samples method) was proposed by Moinester et al.\(^{29}\)

2.3 Assumptions of the RHX dating method by gravimetry

The gravimetric RHX dating method is based on a number of assumptions. First, mass gain is used as a proxy for rehydroxylation rate. Second, it is implied that \(T_2\) water is the only source of mass gain in Stage II, and that the RHX rate constant \(\alpha\) after reheating is the same as experienced after its original firing, and that hydroxylation follows Equation (1) over many centuries. Third, it is assumed that the more strongly bound \(T_1\) water, which is released during heating at temperatures between 100°C and 300°C, have a negligible contribution to long term mass gain.

Gallet and Le Goff\(^{21}\) suggested that the uptake of \(T_1\) and \(T_2\) water does not proceed in succession, such that
chemisorbed water resorbs first and then is followed by rehydroxylation, but rather take place simultaneously. In their model, an extra term is added, describing a different diffusion regime proportional to $t^{1/2}$, and mass gain depends on the two $t^{1/2}$ and $t^{1/4}$ power law processes. They suggest that rehydration and rehydroxylation follow this equation:

$$y = -\beta e^{-t / \tau} + \alpha_1 t^{1/4} + \alpha_2 t^{1/2}.$$  

(3)

The values $\beta$ and $\tau$ describe amplitude and time constant of Stage I, respectively, $\alpha_1$ and $\alpha_2$ are the mass-gain rates for both diffusion mechanisms (single-file and Brownian diffusion), and $\mu$ is the initial value (excluding Stage I) for $t = 0$. The pure logarithmic time dependence of mass gain was previously considered by Cole. A logarithmic time dependence of mass gain was previously considered by Cole. The sorption of T0 water is a short-term and reversible phenomenon (at constant temperature and relative humidity), and equilibrium is established between minutes and weeks. Stage I is reversible and transient. However, how the recombination of T1 and T2 water occurs is still unclear. Does a long-lived uptake of T1 water occur simultaneously with uptake of T2 water? Is there a variation in T1 and T2 processes between different clay minerals? What are the effects of contamination by organic carbon, or processes such as transformation of magnetite into iron hydroxides? In addition, Hare showed that stage II mass gain behavior is strongly influenced by sample size; bigger samples take longer to cool to ambient temperatures, which leads to curvature in stage II mass gain, mimicking two separate processes of T1 and T2 water recombination. The thermal-gravimetric analysis by Shoval and Paz showed that dehydration of prior fired (dehydroxylated) clay ceramic occurs from room temperature to 350°C, see also Kuligiewicz and Derkowski, and dehydroxylation from 350°C to 600°C. The latter is in agreement with studies on dehydroxylated and rehydroxylated pure illite and smectite minerals. In the experiments by Shoval and Paz, mass loss upon reheating a material at 350°C broadly correlated with the age of the ceramic, which would also suggest that recombination of both T1 and T2 water is a long-lived process. They found that the percentage of mass loss due to structural OH removed between 350°C and 600°C also broadly correlated with age, but with a different slope. This points to two separate processes for the recombination of T1 and T2 water, but disentangling the two processes remains a fundamental challenge for gravimetric techniques.

Wilson et al. proposed that $N = 4$ in the assumed power law $t^{1/N}$. But there are considerable uncertainties in this value due to the ambiguities of multi-parameter fits, as discussed by Hare. On considering different clay mineralogical compositions in experiments with archaeological bricks, Barrett noted a significant variation in the power $N$, with $2 < N < 6$. Gallet and Le Goff have suggested that a better universal fit is obtained with $N$ closer to 3 or 2. But Hare showed that goodness-of-fit is high for several choices of $N$. Barrett et al. suggested an approach to obtain accurate fits to the Stage II mass gain by introducing a time offset $\Delta t$ with respect to the time $t_e$ at which the sample is removed from the oven. This should account for cooling effects immediately after the heating stops. They describe this offset as “the time required for mass gain at the age of the temperature to equate to the additional mass gain above the age of the temperature during the cooling of the ceramic post-heating.” Time zero is defined as $t_0 = t_e + \Delta t$. Then the mass gain equation becomes: $m(t) = a(t) (t + t_0)^{1/4} + m_0$. By introducing the time offset in the model, one obtains a curve with a concave-up curvature in the mass gain data, which is very similar to a combination of $t^{1/4}$ and $t^{1/2}$ transport processes as obtained in the measurements of Gallet and Le Goff. However, introducing such time offsets into the fitting procedure has been proven most recently to result in highly inaccurate Ea values and provide misleading results albeit a good fit. The time offset should thus be used with caution only if its physical meaning is independently proven. We also note that an important effect here is the cooling rate. Larger samples take a long time to cool, which also introduces (concave-down) curvature into the mass gain curves via the acceleration of the rehydroxylation reaction. Therefore, the true value of $N$, and its variation within different clay minerals, is yet to be determined.

Considering the limitations and complications summarized in the previous paragraphs, application of RHX still appears to be far from straightforward, as extensively described by Hare et al. RHX analysis by gravimetric studies requires knowledge of the underlying power law with a high accuracy, provided that the T1 water follows a short-lived process. If, however, both T1 water and T2 structural OH groups follow a long-lived process, gravimetric analysis may not be entirely successful in RHX practice. A model based on Equation (3) would then complicate the situation to such an extent that reliable dating would not be possible by gravimetric measurement. RHX dating might, however, still be possible by measuring the mass of the sample after heating to 300°C, following which T0 and T1 water are already gone, as Zhao et al. suggested, although dehydroxylation of the rehydroxylated 2:1 layer structure may start below 300°C.

Several gravimetric studies present contradictory results. This may be due to uncertainties in the $t^{1/4}$ model. Other reasons may be experimental issues, the effects of contamination by organic carbon or processes such as transformation of magnetite into iron hydroxides. Hare et al. also argued that calcite (CaCO3) contamination may interfere with accurate dating using gravimetric measurements. For example, there is a mass loss when calcite decomposes to CaO + CO2 during heating, besides which the CaO becomes a rehydroxylation site via CaO + H2O → Ca(OH)2. Similarly, if heating
of the sample takes place in atmospheric conditions, oxides may be produced which also become RHX sites. However, calcite could be removed in a pretreatment process, and the sample may be heated in a nitrogen environment. The RHX dating method, therefore, is not yet established, and still requires research and development.

In view of all these uncertainties, further investigations of RHX dating should first focus on understanding the associated elementary phenomena, particularly the structural data of the basic compounds, structural changes during the different regimes and the dynamics of mass transfer as a function of time.

3 | MEASURING RHX BY IR AND NMR

Fourier Transform Infrared (FTIR) spectroscopy and Nuclear Magnetic Resonance spectroscopy (NMR) are important spectroscopic tools for further fundamental investigations concerning RHX, because information on the temporal evolution of specific molecules and chemical bonds become directly accessible. However, structure problems can be solved as well. For example, Stevenson and Gurnick43 investigated the structural collapse in kaolinite, montmorillonite and illite clay and its role in the ceramic rehydroxylation by application of infrared (IR) spectroscopy. The IR spectra of clay minerals have now been studied at length for many decades.44-46 The mid IR region (4000−400 cm−1) is of particular interest from a diagnostic point of view because it includes absorption features related to both molecular water, and structural hydroxyl groups. In layer silicates, because there is strong absorption by hydroxyl groups, the region between 3750 and 3500 cm−1 is of special interest. Recent advances in the IR Microimaging (IRM) technique47 allow the spatial distribution of these hydroxyl groups to be imaged within a particular material, and for detailed investigations under both non-equilibrium and equilibrium conditions. Originally introduced for studies of molecular transport in nanoporous materials, this technique also holds great potential for the investigation of fired ceramics and DHX/RHX phenomena. RHX kinetics in ceramics could be clarified by applying this technique to the major constituents of ceramics, pure clay materials.

3.1 | Samples

The ultimate goal of spectroscopic RHX investigations of ceramic materials is the investigation of the mixed and fired clays. We start here with a study of pure clay minerals which are used as composite parts of ceramics. Three chemically similar 2:1 layer type phyllosilicate minerals were selected for the studies: Muscovite, RM30 illite, and SBId-1 beidellite. They are primarily composed of 2:1 layered sandwiches, in which two sheets of Si tetrahedron (T) are joined to a middle alumina octahedron (O) sheet, to form three-sheet T-O-T layered sequences. Muscovite is a trans-vacant dioctahedral true mica (layer charge ~1.0 per formula unit) with the octahedral sheet formed only by Al cations and the interlayer positions entirely occupied by K cations. Illite is a clay mineral, of single-μm crystallite plane size and not more than tens of layers in the c*-axis; it has lower Al substitution in the tetrahedral sheet resulting in layer charge ~0.9448 and lower K occupancy. Beidellite is an expandable clay mineral belonging to the dioctahedral smectite group; with the tetrahedral sheet fully occupied by Al cations. Its layer charge (usually 0.4–0.5 per formula unit49) comes from minor Al substitution in the tetrahedral sheet. Illite is represented by the RM30 sample (trans-vacant 1 M polytype) whereas beidellite is the SBId-1 sample from the Clay Minerals Society Source Clays Repository.50 The SBId-1 sample was purified using chemical methods and underwent cation exchange procedure with Na salts. The beidellite sample contains ~15% of kaolinite impurity.32 With respect to other natural clays, SBId-1 beidellite has low iron content; while RM30 illite has an even lower iron content. Paramagnetic iron is obstructive in NMR studies since paramagnetic ions cause broadening of NMR linewidths and shortening of the transverse relaxation time. The resulting decreased resolution of the different signals makes diffusion experiments impossible. The muscovite flakes are mica sheets (ruby muscovite) purchased from Agar Scientific. Thermogravimetric data of the beidellite, illite and muscovite show two thermogravimetric (TG) plateaus for the dehydration/dehydroxylation process; and maxima in differential thermogravimetry (DTG) at 470°C, 590°C and 850°C, respectively, see Figure S1. Samples for the TG, IR and 1H NMR experiments were not pretreated, if not noted otherwise. The H/D exchange with D2O vapor pressure of 30 mbar at elevated temperatures was performed in an oven, see Figure S2. Samples were then stored in a closed tube until the NMR measurements, which were performed at room temperature.1H and 2H NMR experiments proved that identical spectra were obtained for NMR measurements one hour or three months after treatment at higher temperature.

3.2 | IR spectroscopy and IR imaging

IR micro-spectroscopy and IR Microimaging (IRM) provide unique information in characterizing sample heterogeneities51 and mass transfer phenomena.52-54 IRM is based on measuring the IR transmission spectrum, the wavelength-dependent absorption of infrared light as it traverses the sample. It uses an IR microscope composed of an FTIR spectrometer (which produces an infrared spectrum) and a Focal Plane Array detector that records the transmitted IR signal. The IR microscope with heating cell is presented in
Figure S3. For RHX studies, concentrations of OH or H₂O molecules are proportional to the intensities of their respective measured absorption bands. To further improve accuracy and to separate the contribution of T2 water (hydroxyl groups) from T0 and T1 water, intermittent temperature rises under vacuum may be applied. To reach a maximum level of accuracy, we traced RHX by following the IR band around 3620 cm⁻¹ in thin sheets of fired illite, by IR microimaging in transmission mode (see Figure 1A). To gain information on the uptake of physisorbed T0 and chemisorbed T1 water, the corresponding IR bands in the range of 3500-3000 cm⁻¹ and 1640 cm⁻¹ were followed in parallel.

After exposure to water vapor, RHX kinetics shows a notable OH-signal. By monitoring the time-dependence of the IR signal, subsequent to two fast initial processes, a stable slope is observed after about 720 s, which is well-described by a $t^{1/4}$-dependence. It is important to note that the RHX reaction rate (for a given temperature) is independent of the relative humidity (RH), since RHX requires only a tiny amount of moisture, see Derkowski et al.³⁸ The RH for the Figure 1 measurements at 30°C was 7.1%, since the saturation water vapor pressure at 30°C is 42.5 mbar.

The data points in Figure 1B correspond to the region below a simple cut at 3500 cm⁻¹. This figure shows high-quality evidence for the RHX quartic root time power law, independent of gravimetric data, and is therefore very significant.

The investigation of thin pieces of ceramics reduces thermal effects during cooling after the initial reheating of the material. Also, by use of a vacuum system for sample activation, very precise measurements of the early stages are possible. The sample is kept in the IR cell under vacuum during cooling and is brought into contact with water moisture only when the RHX experiment is initiated. Furthermore, Figure 1B shows that the H₂O hydration region is over in 720 s, faster than in gravitational RHX dating, possibly because the clay film is very thin and cooling proceeds much faster than in samples with more thermal mass.

In another test, the DHX process was investigated by IR microimaging in a thin flake of muscovite (see Figure 2). Interestingly, also after DHX for more than 60 h at 800°C under vacuum, stripe patterns of residual OH-groups are evidenced in the IR image (Figure 2B). Similar patterns are also seen in the visual image (Figure 2C). These patterns might be caused by impurities or structural defects.

In comparison to muscovite, IR spectra of illite do not appear to show OH-groups after firing at 800°C, whilst kept under vacuum (not shown). But after exposure to water vapor, a notable OH-signal is found.

Although we studied “pure” clay minerals, our analysis demonstrates the exciting potential of IRM to understand how DHX and RHX proceeds in different archaeological ceramic artifacts, if sufficiently thin samples can be prepared. It could, in principle, also be used to improve our understanding of dehydroxylation temperatures in different materials, and also to monitor spatial heterogeneity of the RHX reaction in archaeological ceramics.

IR microimaging of a thin flake of muscovite gives reason to hope that future studies of the spatial-temporal dependence of water and OH vibrations and lattice variations will provide further insight into the fundamental mechanisms operating during DHX and RHX in fired clays and ceramics. By monitoring the time-dependence of the IR signal, it is apparent that RHX kinetics proceeds via fast initial processes, and achieves a stable slope after about 720 s, which is well-described by a $t^{1/4}$-dependence. This

**FIGURE 1** (A) IR spectra of a thin illite layer (ca. 50 µm) as measured by IR microimaging at different stages of the test experiment. A strong OH-signal is seen after preparation of the layer (blue and red lines). There is no indication for OH-groups after firing at 800°C (green line). After exposure to water vapor (3 mbar) a small but notable OH-signal is found (black line). (B) Example of RHX kinetics by monitoring the time-dependence of the IR signal in the region of 3620 cm⁻¹ (not corrected for contribution of T0 and T1 water). Initially, there are two fast processes: up to 3 s ($t^{1/4} = 1.3$; region I), and 3-720 s ($t^{1/4} = 1.3−5.2$; region II). A stable slope is established after about 720 s ($t^{1/4} > 5.2$; region III), which is well-described by a $t^{1/4}$-dependence. Measurements were performed at 30°C. More experimental details are given in FIGURE S3 and the related paragraph below [Color figure can be viewed at wileyonlinelibrary.com]
is another potential advantage of the IR method, because it appears to reduce the time taken to measure the rehydroxylation rate constant $\alpha$.

3.3 | Solid-state NMR spectroscopy and NMR diffusometry

NMR is a powerful spectroscopic technique, which has wide application in studies of internal mobilities and structural changes in solids. NMR is based on the fact that a nucleus $i$ with an odd number of protons and/or neutrons, for example, $^1\text{H}$, $^2\text{H}$, $^{13}\text{C}$, $^{27}\text{Al}$ and $^{29}\text{Si}$, behaves like a tiny bar magnet having a field strength characterized by its nuclear magnetic dipole moment $\mu_i$. The moment $\mu_i$ is proportional to the nuclear angular momentum $J_i$ of the nucleus $i$. We have

$$\mu_i = \gamma_i J_i,$$

where the gyromagnetic ratio $\gamma_i$ is the proportionality constant between $\mu_i$ and $J_i$. The moment $\mu_i$ experiences a torque in an external magnetic field $B_0$, which causes it to precess with the Larmor frequency $\nu_{Li}$ at particular angles around the external magnetic field direction:

$$\nu_{Li} = \frac{\gamma_i}{2\pi} B_0.$$

Superconducting magnets now provide for NMR spectroscopy external magnetic fields covering a range from 7 T to 25.9 T, corresponding to $^1\text{H}$ Larmor frequencies of 300 to 1100 MHz, respectively. Higher external fields provide a better spectral resolution and sensitivity. A field of 17.6 T was applied in the present study, corresponding to $\nu_L \approx 750$ MHz for $^1\text{H}$ nuclei. Deuterium ($^2\text{H}$), composed of a proton and neutron, often labeled D, has a Larmor frequency lower by a factor of 6.4 compared to $^1\text{H}$. Since OH and OD hydroxyls have similar chemical behavior, $^2\text{H}$ is used as a tracer of hydroxyl transport and diffusion.

Solid-state NMR signals are, in contrast to liquid NMR signals, strongly broadened by dipolar interactions for all nuclei and by quadrupolar interactions for nuclei having significant quadrupole moments, like $^2\text{H}$ and $^{27}\text{Al}$. The usual plot of an NMR spectrum is the signal intensity as a function of the chemical shift $\delta$, given in ppm. It is the relative change in the frequency of a signal relative to the signal of a standard which is fixed by the IUPAC convention for all nuclei and applied external fields. The shift $\delta$ is caused by the interactions of the nucleus with its electron environment. It depends on its local environment; it gives information about the position in tetrahedral or octahedral crystal sheets, the distance from central Al atoms in the tetrahedra or octahedra, the interlayer space between T-O-T sheets, the binding partners, the bond lengths, the angles between bonds, etc. So chemical shifts $\delta$ and their NMR signal intensities are diagnostic of the crystalline structure. NMR is a quantitative spectroscopy in which the areas under the resonance lines due to different hydrogen signal types (T0, T1, T2) correspond to their relative concentrations.

In solid-state NMR, line narrowing is achieved by fast spinning of the sample within a ceramic cylinder around a “magic-angle” axis, the so-called magic-angle spinning (MAS). The axis is inclined by an angle of about 54.7° to the direction of the external magnetic field. MAS reduces (theoretically to zero) the line broadening due to dipolar effects and first-order quadrupole effects (important for $^2\text{H}$). The reduction is about 1/3 for second-order quadrupole effects (important for $^{27}\text{Al}$). The NMR signal splits into a central
band and a series of sidebands separated by the spinning frequency, with all peaks having much narrower line widths than “static” signals without sample rotation.

MAS NMR has been extensively used in the past to study the structure of clay compounds. For example, montmorillonite was investigated using $^1$H, $^{27}$Al and $^{29}$Si MAS NMR, as were lattice variations of clay minerals such as kaolinite during dehydroxylation. Mantovani et al. used $^{27}$Al and $^{29}$Si MAS NMR to study the reaction mechanisms of kaolinite to illite/muscovite transformations. Thermal reactions of muscovite up to 1200°C were studied by MacKenzie et al. using $^{27}$Al and $^{29}$Si MAS NMR.

Figure 3 shows the $^1$H MAS NMR of untreated illite, taken with a rotation frequency of 30 kHz. The MAS frequency of 30 kHz allows distinguishing six $^1$H MAS NMR signals in the illite spectra (see Figure S4).

Figure S5 shows a similar spectrum and deconvolution of an illite sample after the H/D exchange at 350°C. Details of the NMR experiment and the deconvolution procedure are described below Figures S4–S5.

It is well-known from NMR spectroscopy of aluminosilicates that, as a rule, non-isolated water species give rise to signals at about 5 ppm, whereas hydroxyl species appear at about 2 ppm. Therefore, the signals with small chemical shifts (2.1 ppm and 0.8 ppm) are assigned to hydroxyl groups and the signal at 6.7 ppm may be explained by interlayer T1 water and the signal at 4.5 ppm corresponds to physisorbed T0 water. By comparing the intensities of the peaks for untreated illite and illite treated with 30 mbar D$_2$O vapor for 24 h at 350°C, we estimate that after 24 h of treatment, about slightly more than 50% of both T2 species (signals at 2.1 ppm and 0.8 ppm) have exchanged, whereas 80% of interlayer water (6.7 ppm peak) and almost all of the physisorbed T0 water (4.5 ppm) have exchanged with the surrounding atmosphere.

Figure 4 compares the $^1$H MAS NMR spectrum of pristine beidellite (“untreated” sample) with the spectra obtained after a contact time of 24 h with the surrounding atmosphere of deuterated water, kept at a vapor pressure of 30 mbar, at temperatures up to 500°C. All spectra appear as a superposition of two peaks, which may be deconvoluted into two symmetric lines, with the line widths of approximately 2.8 ppm. The intensities of both lines decrease dramatically with increasing temperature, corresponding with a dramatic acceleration of the exchange between the sample and the surrounding. The spectral resolution is worse compared to illite, because the sample contains more iron. We have already mentioned that the variety of species as detectable by MAS NMR, increases with decreasing iron content. Setting the total concentration of hydrogen atoms in the untreated sample to 100%, the signals at 2.0 and 4.8 ppm each correspond to about 50%. These values decrease for the sample pretreated at 500°C to approximately 7.5%. From these data, we may estimate that at 500°C about 85% of the water molecules contributing to these signals have exchanged with the surrounding atmosphere. Based on the rule that non-isolated water species give rise to signals at about 5 ppm and hydroxyl species appear at about 2 ppm (see above), we suggest that the 2.0 ppm signal corresponds to T2 hydroxyl water, and the 4.8 ppm signal corresponds to a superposition of a physisorbed T0 water and T1 interlayer water signal.
Several NMR techniques can be used for studying the mobility of species in a solid. NMR diffusometry is the common term for NMR studies of the diffusion of molecules, including the species moving in a solid host framework. The most frequently applied method of NMR diffusometry is the pulsed field gradient (PFG) technique, which provides direct access to the averaged propagator of molecular diffusion. In PFG, very short duration magnetic field pulses are applied to the sample in addition to the constant field $B_0$. The pulse has a constant field gradient, so that the magnetic field intensity varies linearly over the sample. The Larmor frequency for a resonance is then directly proportional to its position within the sample. Thereby, one can measure the translational (diffusion) motion of the hydroxyls, by imaging the spatial distribution of their nuclear magnetic moments as a function of time, for example as $^1$H nuclei change their location.

However, the time scales in RHX studies (years) and in usual PFG NMR studies (milliseconds) are hugely different. Thus, PFG NMR diffusion studies are only able to cover the mobility of T0 water. The application of conventional PFG NMR is hindered, because the static signal of T0 water is also superimposed by the signals of other species. The weak signal at 4.5 ppm in Figure 3 was attributed to physisorbed T0 water and allows the application of $^1$H MAS PFG NMR diffusometry. It is worthwhile mentioning that this option may only be provided by the combination of MAS and PFG NMR, since conventional PFG NMR is unable to provide such selective measurements. In this way, the self-diffusion coefficient of the molecules contributing to this signal can be determined to be $(3.8 \pm 0.8) \times 10^{-9}$ m$^2$ s$^{-1}$ at room temperature.

A different technique of NMR diffusometry is the tracer diffusion technique. By adding D$_2$O to the sample and monitoring the $^1$H NMR spectrum, we can monitor the transport of OD hydroxyls within clay minerals and ceramic materials. We observed in the present study the increase of the 4.8-ppm signal in the $^1$H MAS NMR spectrum of a beidellite sample after loading 8 mg D$_2$O into the MAS rotor. Exchange of this deuterated water with the water present in the sample increases the 4.8-ppm signal in the $^1$H MAS NMR spectrum and gives for the exchange a mean time constant of $\tau = 125$ s $\pm$ 35 s by means of an equation similar to Equation. (6) below. The mean time of diffusion-limited exchange between a sphere of radius $R$ and its surroundings obeys the relation $D_{intra} = R^2/(15\tau_{intra})$, (see Ref. [64] p. 378). With $(8 \pm 4)$ µm as powder particle diameter ($2R$, determined by optical microscopy), the diffusivity of the water species under study is thus estimated to be $D \approx 8.5 \times 10^{-15}$ m$^2$ s$^{-1}$. We know only one previous NMR diffusion study of interlayer water. Considering that the uncertainties of $\tau$ and $2R$ give $D = 1.7-26.7 \times 10^{-15}$, the present value for beidellite is consistent with the value of $10^{-15}$ m$^2$ s$^{-1}$ obtained for illite in a similar experiment. This self-diffusion coefficient describes the diffusivity of interlayer water T1. Since illite is a non-swelling material, we were unable to apply this method to illite.

$^1$H MAS PFG NMR experiments gave results concerning the diffusivity of T0 water; whereas the diffusivity of interlayer water T1 could be measured by $^2$H MAS MR tracer diffusion experiments, but diffusivity of physisorbed T0 or interlayer T1 water is not the core problem. The resulting time scales and diffusivities cannot be associated with the diffusion phenomena of relevance for RHX dating, which has time scales over millennia. We have rather to develop measurement techniques for much slower mass transfer phenomena. Therefore, we use a method which is similar to the NMR tracer diffusion technique. It is the $^2$H MAS NMR spectroscopy of samples, which were treated at elevated temperatures under a pressure of 30 mbar D$_2$O vapor.

The $^2$H NMR spectrum is strongly broadened by first-order quadrupole interaction of the $^2$H nucleus with the electric field gradient of the surrounding electron environment. $^2$H MAS NMR spectra are superior to “static” $^2$H NMR spectra, because they have a better signal-to-noise ratio and can resolve signals with different chemical shifts. Figure 5 shows that the broadening amounts to about 2000 ppm, which corresponds to 230 kHz at magnetic field 17.6 T. The spectrum consists of many spinning sidebands, 87 ppm (10 kHz) apart. A deconvolution of the signal into T0, T1...
TABLE 1 Activation energies of H/D exchange for illite and beidellite, as obtained from NMR. The temperature range was chosen so that the structure of the material still remains intact.

| Sample | $T^\circ$C | $E_a$/kJ mol$^{-1}$ |
|--------|------------|---------------------|
| RM30   | 300–350    | 39 ± 4              |
| SBld−1 | 200–260    | 36 ± 4              |

and T2-species is necessary, because the broadening varies for different species. The deconvolution is demonstrated in Figure S7. In an early study,$^71$ the $^2$H MAS NMR spectrum of a water-containing zeolite has been referred to the contribution of several hydrogen species. Three of them were water species, single AlOH groups and structural hydroxyl groups in SiOHAl sites. The latter shows spinning side bands, similarly as on the left and right side of Figure 5, which are better demonstrated by the broad deconvoluted signal in Figure S7. We consider for the exchange behavior only the intensities of both maximum wings of the spectra (the broad deconvolution signal in Figure S7) in order to obtain dynamic data concerning the $^1$H/$^2$H exchange of the T2 hydroxyl groups. These intensities are a measure for the concentration of deuterated OD hydroxyl groups which substituted OH groups in T2.

The relative concentration of deuterated hydroxyls may be represented by an exponential increase

$$I_{rel}(t) = \frac{I(t)}{I(t=0)} = \left(1 - e^{-\frac{t}{\tau}}\right),$$

with $I(t)$ denoting the intensities of deuterated hydroxyls groups within the sample after an exchange time $t$. The relative intensity $I_{rel}(t)$ is directly accessible by MAS NMR. Fitting Equation (6) to the intensity of the wings of the signal in Figure 5 gives a mean exchange time at 350°C of $\tau = 64$ h. Using the time constants obtained from the fit at temperatures of 350°C and 300°C, the activation energy obtained for illite is $E_a = (39 \pm 4)$ kJ/mol. A similar experiment was done for beidellite at 260°C and 200°C, yielding an activation energy of the H-D exchange of $E_a = (36 \pm 4)$ kJ/mol, see Table 1. This so-called “apparent” activation energy describes the minimum amount of energy needed for this reaction exchange to take place. A common approximation is that the temperature dependence of the exchange rate follows the Arrhenius relation $\tau \propto \exp \left(\frac{E_a}{RT}\right)$, with $R$ denoting the ideal gas constant. Under the questionable assumption that this activation energy also applies to a larger temperature range, the mean exchange time at room temperature would be $\tau = 842$ d.

The time scale of the present study is much smaller than archaeological time scales. We began by considering the elementary phenomena of mass transfer occurring on the scale of seconds and nanometers relevant in material sciences, and we have reached the scale of days and microns. It is important to note that there is no fundamental limitation that prohibits the detection and the monitoring of slower phenomena, relevant to far larger time spans. Already the present investigations have brought us into time and size scales that are far beyond the range of conventionally studies of mass transfer. This will hopefully pave the way towards an investigation of those mass transfer phenomena which are crucial for providing the microphysical foundation of RHX dating.

4 | CONCLUDING REMARKS

Over the last decade, increasing attention has been given to the idea to utilize rehydroxylation of fired-clay objects as a dating method. RHX dating is based on the observation that, during hydroxylation of archaeological artifacts, their mass increases in proportion with the quartic root of time (i.e., $\propto t^{1/4}$). To the extent that this correlation is valid, the time dependence of such a mass increase may be used to estimate its age, that is, the time span elapsed since its delivery from the kiln.

At this stage, it is important to emphasize that a clear explanation of the proposed quartic-root dependence is still missing. There is indeed an impressive analogy with so-called single-file systems, i.e., with ensembles of particles in one-dimensional arrangement, that are unable to pass each other.$^{72-75}$ It has been suggested that such a scenario might occur in the structure of dehydroxylated clay minerals, as H$_2$O molecules enter the octagonal aluminum sheets, through the ditrigonal cavities of silica tetrahedral sheets,$^{72}$ but further investigation is necessary to better understand the link with time-dependence in single-file systems.

The present study has introduced two techniques well suited for investigating materials of relevance for RHX, namely IR and NMR spectroscopy. In the past, both techniques have been most successfully applied to the investigation of mass transfer phenomena in nanoporous host-guest materials, giving rise to a completely new understanding of mass transfer phenomena in such systems. We applied both techniques to the investigation of three pure clay minerals. Our IRM results show that RHX kinetics is well described by a $t^{1/4}$-dependence. It is an important result since the quartic root time dependence was previously only seen from TG studies. Furthermore, MAS NMR investigations reveal the possibility to distinguish the different types of water (T0, T1 and T2). This could shed light on the conundrum as to which types of water are present during RHX dating measurements. By monitoring the H/D exchange, we are able to also obtain the relevant activation energies and exchange times. Although the ultimate goal is the investigation of mixed clays, the results here are an important stepping stone in the applicability of IR and NMR to RHX. The possibilities of both techniques to explore the
modes of mass transfer and hydroxylation are illustrated. The eventual goal is to develop a reliable methodology for RHX dating of archaeological ceramics.

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