

Study of archaeological iron objects by PGAA, Mössbauer spectroscopy and X-ray diffraction

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Abstract Archaeological iron objects often corrode rapidly after their excavation, even though they have survived long times of burial in the ground. Chlorine that accumulates during burial is thought to play a major role in this destructive post-excavation corrosion. It is therefore important for the conservation of such objects to determine the chlorine content in a non-destructive manner and, if necessary, to remove the chlorine from the artefacts by appropriate methods. Such methods are leaching in alkaline solutions or heating in a reducing atmosphere at temperatures up to 800 °C. We have studied the efficiency of the heating method using prompt gamma activation analysis (PGAA) for monitoring the Cl content and Mössbauer spectroscopy at room temperature (RT) and 4.2 K as well as X-ray diffraction to study the mineralogical transformations of the rust layers. The heat treatments were performed a N₂/H₂ (90/10) mixture at temperatures up to 750 °C. As test specimens sections of iron rods from the Celtic oppidum of Manching (Bavaria) were used. The initial Cl contents of the pieces varied in the range of several hundred ppm, referring to the iron mass. Annealing for 24 h at 350, 550 and 750 °C was found to reduce the Cl contents of the specimens, to about 70, 30 and 15 % of the original values, respectively. The rust consists mainly of goethite with admixtures of magnetite, lepidocrocite and akaganeite, which is thought to be a major carrier of chlorine, probably together with iron chlorides. Much of the goethite is so fine-grained that it does not split magnetically at RT. Annealing converts the rust mainly

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to maghemite at 350 °C, to magnetite at 550 °C and to wüstite plus magnetite and metallic iron at 750 °C. Pure akaganeite behaves in nearly the same manner.

Keywords Mössbauer spectroscopy · PGAA · XRD · Archaeological iron · Corrosion · Chlorine · Akaganeite

1 Introduction

Archaeological iron artefacts often corrode rapidly after excavation, which causes severe problems for their conservation. This corrosion process has been studied extensively, and chlorine present in the corrosion layer has been identified as the main cause for post-excavation corrosion [1–5]. The presence of chlorine on corroding iron surfaces is explained by a diffusion of Cl^- ions dissolved in the moist surrounding soil towards the iron surface. The chlorine then promotes corrosion after excavation, when the finds are exposed to air [4–6]. The chlorine in the corrosion layer is often present in akaganeite ($\beta\text{-FeOOH}$) which accommodates up to about 15 mol% of Cl in its structure [7, 8], but may also occur as ferrous or ferric iron chloride [4] or ferrous hydroxychloride ($\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$) [9].

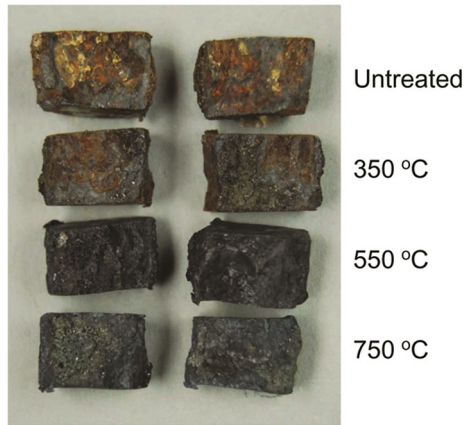
The removal of chlorine from archaeological iron artifacts is considered as important for long-term conservation. Leaching in alkaline hydrous solutions is often used for that purpose [10]. Heating in reducing atmospheres is an alternative, but since it may erase the forging texture of the artefacts, the annealing temperature should be as low as possible, but still high enough to ensure an efficient removal of the chlorine. This requires that the Cl content be determined both before and after the annealing by a non-destructive method. Prompt gamma activation analysis (PGAA) [11, 12] is an ideal method for this purpose: The studied objects are irradiated by an external neutron beam from a nuclear reactor, and the gamma rays that are emitted promptly after the neutron capture processes are detected. This allows for big objects to be analyzed and, in the case of fairly pure iron containing chlorine, the objects become only weakly radioactive and the radioisotopes formed are short-lived, so that one can safely return them to the museum collections within a few weeks after the irradiation. Recently, first experiments using PGAA to study archaeological iron artifacts have been reported [13].

In this paper we report on experiments studying the chlorine extraction by heating in mixtures of hydrogen and nitrogen to temperatures of 350, 550 and 750 °C. The studied samples were pieces cut from a Celtic iron rod excavated at the oppidum of Manching in Bavaria in 1999. The chlorine contents were analyzed before and after the annealing at the PGAA facility at the FRM-2, the research reactor of the Technical University of Munich at Garching, Germany. To study the chemical modifications of the corrosion layers during the annealing, we used Mössbauer spectroscopy and X-ray diffraction.

2 Samples and experiments

The samples were pieces from an iron rod excavated at the Celtic oppidum of Manching in 1999. The rod had a cross section of about $15 \times 6 \text{ mm}^2$ and a length of about 40 cm. From this rod sections of about 15 mm length were cut with a diamond saw. Two parallel samples were used for each firing temperature. Figure 1 shows unfired pieces and the pieces heated in a mixture of 10 % H_2 in N_2 to 350, 550 and 750 °C for 24 h. The furnace used

Fig. 1 Test pieces cut from a Celtic iron rod before annealing and annealed in welding gas (N_2/H_2 90:10) for 24 h



for this treatment is available for the treatment of large amounts of big iron objects at the Archaeological Museum in Munich. It consists of a stainless steel vessel with an inner diameter of 30 cm and a length of 120 cm that can be evacuated and flushed with N_2 gas before the heating in a constant stream of N_2/H_2 . The time to reach the maximum temperature was set to 5 h. When the furnace is switched off, it cools to ambient temperature quite slowly, i.e., within about 24 h.

The Cl content of the specimens was determined before and after the heat treatment at the Prompt Gamma Activation Analysis (PGAA) facility at the research reactor of the Heinz Meier-Leibnitz Research Center in Garching, Germany with a relative accuracy of about 4 % and with a detection limit of about 10 ppm referring to the iron mass.

In order to determine the mineral composition of the original rust layer and of the annealed samples, Mössbauer spectroscopy at room temperature (RT) and at liquid He temperature and X-ray diffraction were used. The Mössbauer experiments were performed with a spectrometer operating with a sinusoidal velocity waveform and a source of about 25 mCi ^{57}Co in Rh. The measurements at 4.2 K were performed in a liquid He bath cryostat in which the source was also cooled to 4.2 K. The XRD patterns were recorded with $Co K\alpha$ radiation using a Philips PW1070 diffractometer equipped with a graphite monochromator.

The rust contains different iron oxides and oxyhydroxides, which are usually quite inhomogeneously distributed. The data shown below are for pieces of rust fallen off during the cutting, which were ground to a fine powder for making the absorbers for Mössbauer spectroscopy (ca. 25 mg/cm²) and for X-ray diffraction. The specimens of the annealed rust layers were material that had detached from the test pieces during the annealing in alumina crucibles. These fragments were only minor fractions of the total amount of rust on the test pieces.

Since a major carrier of Cl in rust is often akaganeite ($FeO_{0.833}(OH)_{1.167}Cl_{0.167}$ [8]), an oxyhydroxide of iron that carries a substantial amount of Cl in its structure, we also studied the annealing behaviour of this compound by heating samples of it together with the iron specimens.

Un-annealed test pieces and pieces annealed at the different temperatures are shown in Fig. 1. The original rust layers are dark brown with lighter brown spots. After annealing at 350 °C the surfaces become black with brown spots, at 550 °C they become uniformly black and at 750 °C they are black with a bluish hue.

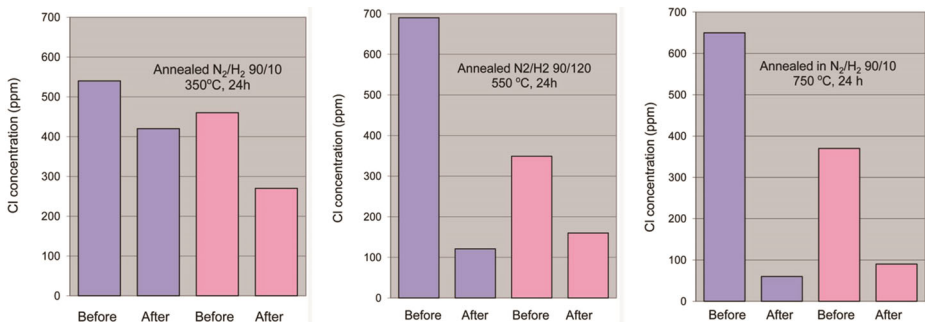


Fig. 2 Results of the Cl determination by PGAA of the iron test pieces before and after annealing

3 Results and discussion

3.1 Prompt gamma activation analysis (PGAA)

In Fig. 2 the results of the PGAA determinations of the Cl content of the samples are shown as determined before and after the heating. As expected one finds that the Cl content decreases with the annealing temperature to a mean value over the two parallel samples of 70 % after annealing at 350 °C, to 50 % after annealing at 550 °C and to 15 % after annealing at 750 °C. The differences between the two parallel samples are, however, considerably higher than expected from the statistical accuracies of the individual Cl determinations. That the parallel samples initially already have widely different Cl contents is due to the inhomogeneous Cl distribution on the surface of the iron. The discrepancies in the efficiency of the Cl extraction may be related with different chemical states of the Cl in the corrosion layer or to inhomogeneous distribution of the Cl on the surface of the individual test pieces, which may affect the results due to the attenuation of the incoming neutrons and the outgoing gamma rays. These effects should be taken into account in order to increase the accuracy in future studies.

3.2 Mössbauer spectroscopy and X-ray diffraction

The Mössbauer spectra of detached rust from the original and annealed iron test pieces and of akaganeite treated together with the test pieces are shown in Figs. 3 and 4. The corresponding X-ray diffraction patterns are shown in Figs. 5 and 6.

The RT Mössbauer spectrum of an untreated rust sample from the rod used in the annealing experiments (Fig. 3) is very similar a spectrum reported previously for rust from an iron nail from the oppidum of Manching [14]. It exhibits the pattern of magnetite with its two sextets, a broad magnetic pattern with a mean hyperfine field of 35 T that is typical for small particle goethite exhibiting strongly broadened lines and a ferric quadrupole doublet with a splitting of $QS = 0.65$ mm/s that may represent goethite with very small particles that shows no magnetic hyperfine splitting or broadening at all at RT. Akaganeite or lepidocrocite would also contribute to the quadrupole doublet. The XRD pattern is more specific in this case, showing (Fig. 5) the presence of all these components. The 4.2 K Mössbauer spectrum (Fig. 3) is not very specific, because all oxides and oxyhydroxides split magnetically a 4.2 K and their patterns do not differ much.

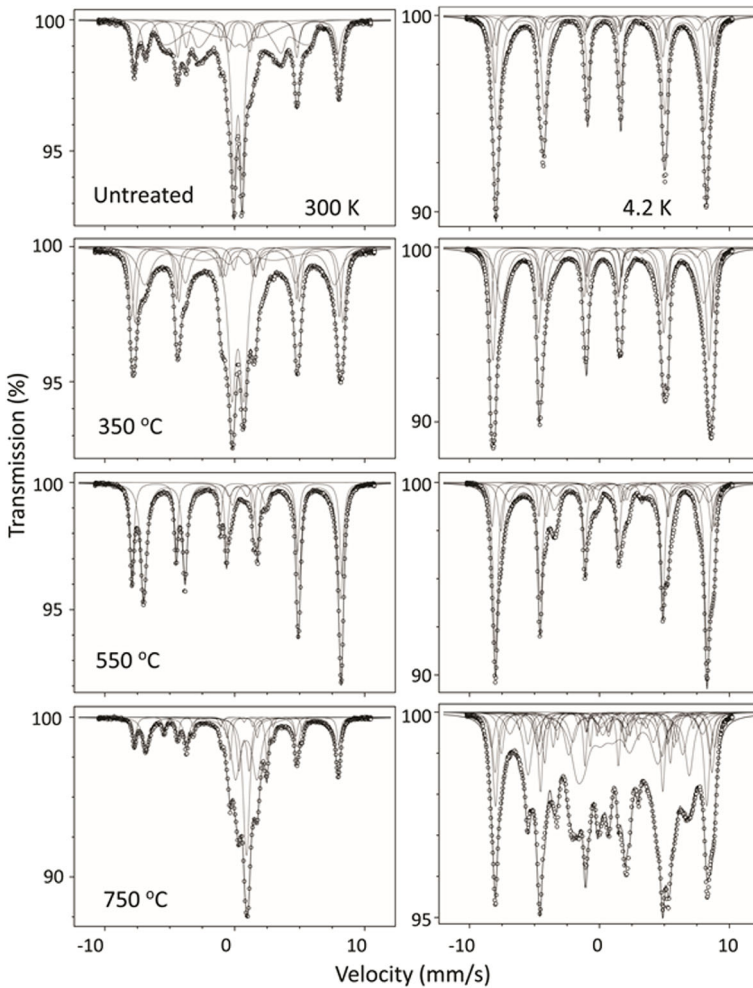


Fig. 3 Mossbauer spectra of rust from the original and the annealed test pieces measured at ambient temperature (*left*) and at 4.2 K (*right*)

Annealing in the H_2/N_2 mixture at 350 °C yields pure maghemite according to the XRD pattern (Fig. 4). The quartz present in all XRD patterns of rust and its annealing products stems from soil that adheres to the rust layers. Both the RT and the 4.2 K Mössbauer patterns of the 350 °C sample exhibit rather broad lines with practically zero quadrupole shift indicating that the maghemite is either impure or not very well crystallized. Annealing at 550 °C yields pure magnetite according to both the Mössbauer and the XRD data. The magnetite is of good stoichiometry as is shown by the intensity ratio of 1.95:1 for the patterns of the mixed valence $Fe^{2.5}$ B sites and the Fe^{3+} A sites. The 4.2 K spectrum is also typical for stoichiometric magnetite.

Annealing at 750 °C results in a mixture of wüstite, magnetite and metallic iron. At RT the wüstite exhibits a broadened single line ($IS = 0.90$ mm/s) with 20 % of the spectral area and three quadrupole doublets with together 44 % of the spectral area, similar to patterns

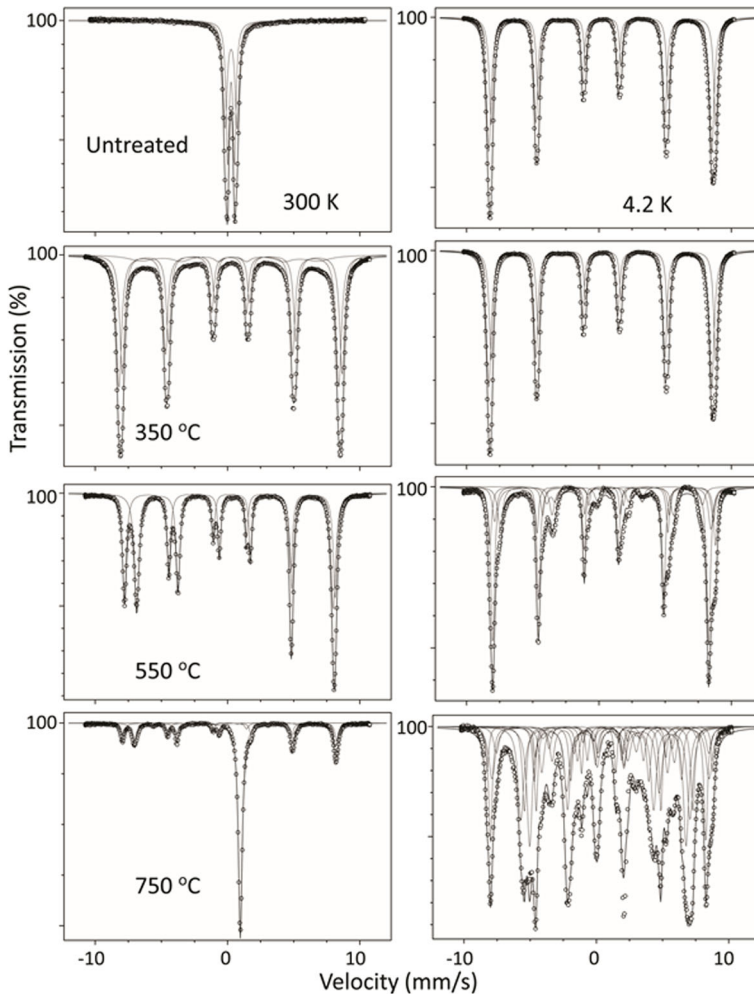


Fig. 4 Mössbauer spectra of synthetic akaganeite and its annealing products measured at RT (*left*) and 4.2 K (*right*)

observed previously for non-stoichiometric Fe_xO ($x < 1$) [15, 16]. It is magnetically ordered at 4.2 K yielding a complicated magnetic hyperfine pattern similar to those observed by McCammon and Price [15]. A least squares fit with five octet patterns with a wide distribution of hyperfine fields between 19 and 38 T gave a reasonable agreement with the data, but is not expected to be a unique solution for the fitting of the spectrum.

The akaganeite that was annealed together with the iron test pieces shows nearly the same behavior as the rust: Both Mössbauer spectroscopy (Fig. 4) and XRD (Fig. 6) show that it converts to pure maghemite at 350 °C, to pure magnetite at 550 °C and to a mixture of magnetite, wustite and metallic iron at 750 °C. In this case the wustite is remarkable since it exhibits a rather narrow line ($W = 0.34$ mm/s) that covers 54 % of the spectral area and has a rather large isomer shift of $S = 0.97$ mm/s. The linewidth is the same as observed by Hentschel [17] for nearly stoichiometric wustite. The isomer shift Hentschel observed is IS

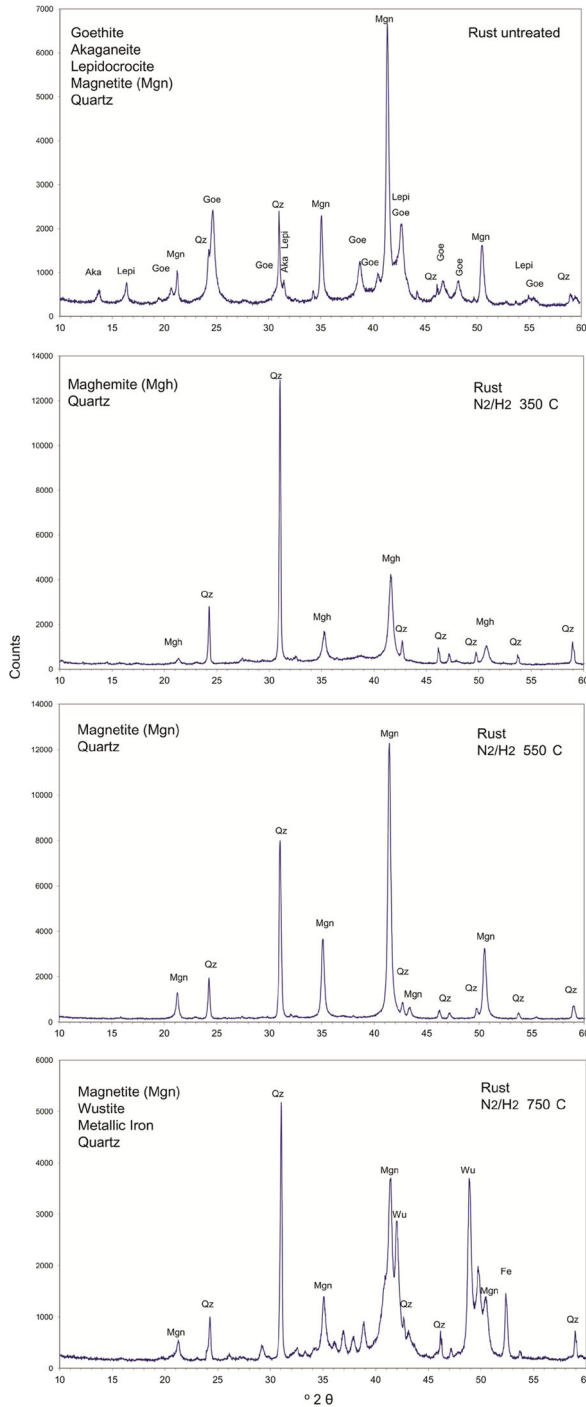


Fig. 5 X-ray diffractograms obtained with Co $K\alpha$ radiation for rust from the test pieces before annealing and after annealing at 350, 550 and 750 °C in a N₂/H₂ (90:10) mixture for 24 h

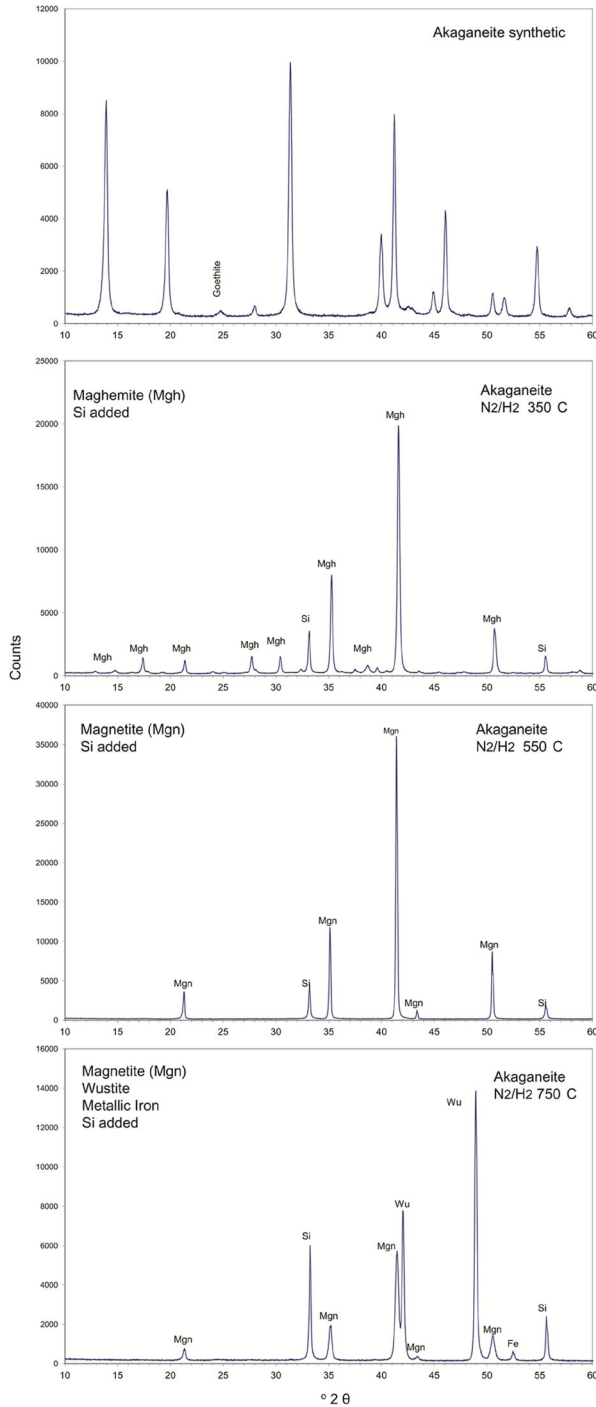


Fig. 6 X-ray diffractograms obtained with Co $K\alpha$ radiation for a synthetic akaganeite before annealing and after annealing at 350, 550 and 750 °C in a N₂/H₂ (90:10) mixture for 24 h

= 1.00 mm/s when converted to a value relative to the $^{57}\text{Co}:\text{Rh}$ source, which is very close to our value. To obtain an accurate value of the lattice constant of this wustite from the X-ray diffractogram, the goniometer was calibrated against silicon added to the sample. The result is $a = 0.4324$ nm for the lattice parameter of the cubic wustite. Using the correlation between the parameter x of Fe_xO given by Hentschel [17], one obtains a value of $x = 0.98$, which is surprisingly close to stoichiometry. Hentschel [17] obtained virtually stoichiometric wustite by prolonged annealing at 225 °C. The slowly decreasing temperature to which the sample was exposed in our case may thus have led to the high value of x .

4 Conclusions

PGAA is an efficient method to obtain data on the reduction of Cl in archaeological iron objects. The scattering of the results may be due to the different thermal stability of the Cl in the rust layer, but some of it may also be attributable to the inhomogeneous distribution of the Cl that affects the accuracy of the determination. The present data show that heating in a mixture of N_2 and H_2 reduces the Cl content of the objects only moderately at 350 °C. At 550 °C about half of the Cl can be extracted and even after heating to 750 °C there is still about 15 % of the initial Cl present.

The Mössbauer and X-ray data show that akaganeite, which is an important carrier of Cl, has already decomposed at 350 °C. This means that the Cl can no longer be incorporated into its lattice. Most of the chlorine is, however, still present after annealing at this temperature. The question where and in what chemical form the Cl that is still present after the different annealing steps will have to be clarified in future studies, as well as the question how detrimental the residual chlorine still is for the conservation of the objects.

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