Mössbauer study of Celtic pottery from Bopfingen, Baden-Württemberg, Germany

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Abstract. In the course of a study of pottery from Celtic Central Europe, we report on an investigation of pottery found in the context of a Celtic ditched square enclosure near the modern town of Bopfingen in Baden-Württemberg, Germany. The studied pottery may be visually subdivided into wheel-turned ware, graphite ware, and coarse ware. The Mössbauer spectra are surprisingly uniform, indicating that all types of pottery were fired in a similar manner. Firing in a reducing environment at 800 °C was usually followed by re-oxidation during cooling, which leads to unique features in the low temperature Mössbauer patterns.

1. Introduction

The pottery of the Celtic civilisation in Central Europe exhibits a considerable degree of uniformity. Apparently it was made locally, but the style and methods of production were similar throughout the Celtic world during several centuries before the beginning of the Christian era. An outstanding feature of the Celtic ceramics is the abundance of graphite pottery, which was made by mixing natural graphite into the clay and hence required graphite deposits at a viable distance to the production site. This is probably the reason why graphite pottery is abundant only east of the Rhine.

In the course of an ongoing study of Celtic pottery [1], we studied about 60 pottery fragments found in or near a ditched square enclosure from the 2nd century BC, with features from the preceding 3rd century, excavated near the modern town of Bopfingen in Baden-Württemberg, Germany, during the years 1989-1992 [2]. Bopfingen is situated about 100 km west of the Celtic oppidum of Manching, one of the biggest Celtic settlements in Central Europe. By their appearance, the finds from Bopfingen were classified as graphite ware, wheel-turned ware and coarse ware. The main purpose of this study is to gain information on the material properties of the sherds.

The methods used to study the material are Mössbauer spectroscopy [3, 4], on which this paper will focus, as well as neutron activation analysis (NAA) [5] and thin-section microscopy [6].

2. Samples and Experiments

The sherds were ground in a mortar and absorbers of about 100 mg/cm^2 thickness were prepared. Mössbauer spectra of all samples were recorded at room temperature (RT) and 4.2 K with sources of ^{57}Co in rhodium that were always at the same temperature as the absorber. Isomer shifts are always

given with respect to the source. In some cases, Mössbauer spectra were also taken at temperatures between 4.2 K and RT. Moreover, some samples were re-fired in the laboratory before being subjected to Mössbauer spectroscopy.

3. Results and discussion

About 60 samples were studied in order to obtain a set of representative data. The sherds are mainly dark brown or dark grey; only a few are brick-coloured. NAA showed a rather wide spread of element contents overlapping in part with that of pottery from the oppidum of Manching [7, 8]. Thin section microscopy revealed a rather varied composition of the ceramic material in terms of mineral content, texture and particle size of the constituents.
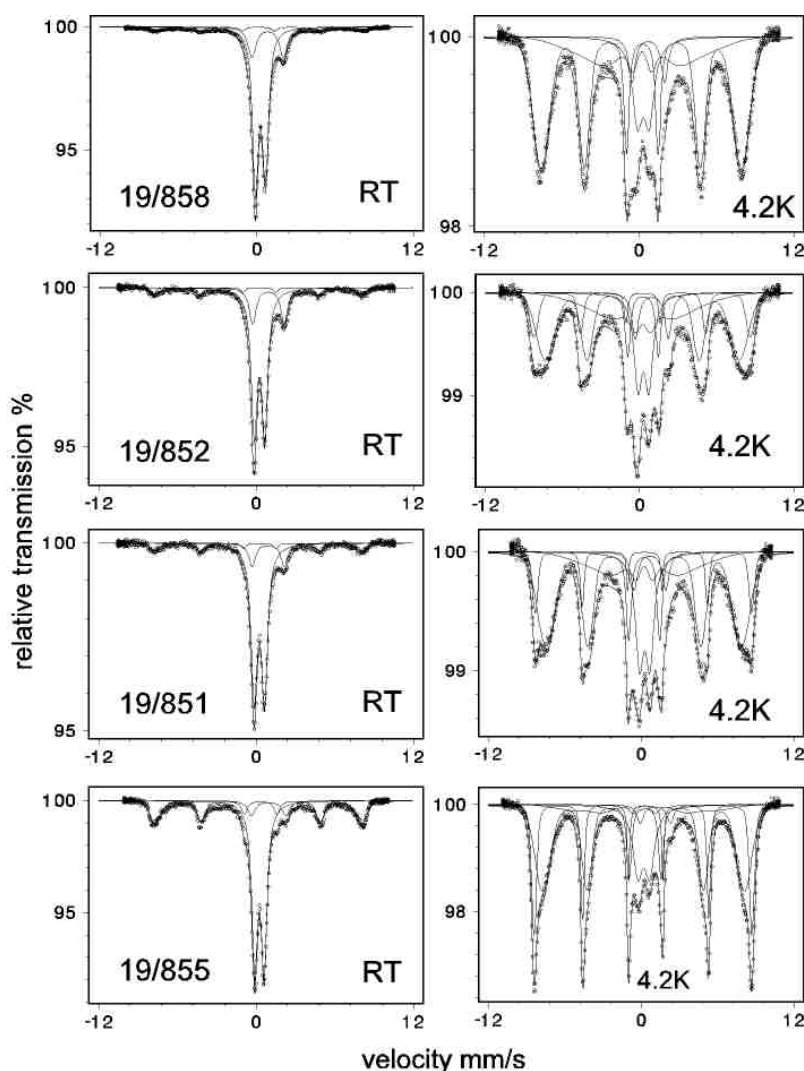

Figure 1. ^{57}Fe Mössbauer spectra of pottery from Bopfingen. RT spectra are shown on the left, 4.2 K spectra on the right. The numbers given on the left identify the individual sherds.

The Mössbauer spectra are, however, remarkably uniform. With very few exceptions, they are all like those shown in figure 1. RT spectra consist of a dominant Fe^{3+} quadrupole doublet with an isomer shift (IS) of 0.33 mm/s and a quadrupole splitting (QS) between 0.7 and 0.8 mm/s. An additional weak Fe^{2+} doublet (IS=1.02 mm/s; QS=2.6 mm/s) has intensities between 10 and 20%. Only in a few cases, more than one Fe^{2+} doublet is present. In all spectra, one also finds a weak (5–15%) magnetic sextet pattern with hyperfine fields between 48.0 and 49.5 T. In some cases this can be identified as hematite

by its quadrupole shift near −0.21 mm/s, but in most cases the quadrupole shift is near zero, which is typical for maghemite. Intermediate values may be due to a mixture of both.

In the 4.2 K spectra one observes mainly a broad magnetic hyperfine pattern that can be fitted assuming a Gaussian distribution of hyperfine fields with mean values of 48 to 49 T and a variance of 3 to 4 T. The quadrupole shift is close to zero, and the IS around 0.22 mm/s. In some spectra, nearly all the Fe^{3+} yielding the doublet at RT splits in this manner, with only a weak Fe^{3+} quadrupole doublet remaining (figure 1, sample 19/858). In most cases, a more substantial fraction of the iron is still paramagnetic at 4.2 K. The temperature dependence of the spectra was studied in detail in two cases, which exhibited a very similar behavior: The intensity of the broad magnetic pattern begins to decrease already at about 25 K; at 40 K its intensity is only about half of that at 4.2 K, and at 70 K it has vanished altogether. While its intensity decreases, the hyperfine field of the remaining magnetically split component is virtually unchanged.

This behaviour is reminiscent of that of 2-line ferrihydrite, which becomes superparamagnetic in the same temperature range [9]. The presence of ferrihydrite in ceramics is, however, difficult to understand, since ferrihydrite converts into hematite at about 300ºC. In pottery it could therefore only be formed during burial by contact with iron-bearing groundwater.

However, the broad magnetic component cannot be ferrihydrite, since a sample that was heated in the laboratory in air to temperatures of 300, 500, 700 and 800 ºC for 24 hours still showed it even on heating to 800 ºC, though with reduced intensity. The sample that was subjected to these re-firing experiments contained 15 % of maghemite according to its RT spectrum. This was found to be still present on heating to 700 ºC; on heating to 800 ºC it had converted to hematite.

The broad magnetic component also occurs in the Mössbauer spectra of pottery from other locations (e.g., [10]), but it is particularly prominent in the pottery from Bopfingen. It thus seems to form easily during firing, but the firing conditions or the clay composition of the ceramics from Bopfingen appear to have been particularly favorable to its formation. It does not seem to be a common iron oxide phase. The distribution of hyperfine fields indicates that it is a spin-glass like magnetic system. In fact, it probably also is a structurally amorphous phase.

When clays are fired at around 800ºC, the sheet silicate structure of the de-hydroxylated clays will collapse into an amorphous state, from which new crystalline phases (pyroxenes, spinels) may crystallize at somewhat higher temperatures. The vitreous state is particularly favored during reducing firing; Fe^{2+} readily dissolves in it. The Mössbauer spectra of this amorphous phase exhibit mainly a Fe^{2+} quadrupole doublet at both RT (QS= 2.6 mm/s; IS=1.03 mm/s) and 4.2 K (QS =2.8; IS = 1.03 mm/s) [7, 11]. When this phase is oxidized at or above 800 ºC, the iron exsolves as hematite. A subsequent reduction at 800 ºC has been found to result in a re-dissolution of the hematite in the amorphous phase. In fact, this process can be repeated many times [11].

When the oxidation occurs at a temperature that is too low for diffusive processes to take place, the iron will remain in the vitreous phase and, when its concentration is sufficiently high, it may order magnetically at low temperatures, probably as a spin glass. The appearance of the amorphous, Fe^{3+}-bearing phase would thus be connected with firing the pottery near 800ºC under reducing conditions and then, at the end of the firing cycle, re-oxidising the material at a lower temperature. This explains the mainly trivalent state of the iron in the spectra of the Bopfingen pottery. The gradual disappearance of the magnetic pattern of the vitreous phase when the temperature is raised above 4.2 K can be understood in terms of a distribution of ordering temperatures, though superparamagnetism of nano-scale ordered regions may also play a role.

In the case of the Bopfingen pottery, the oxidation seems to have taken place at a temperature where only a minor exsolution of iron into oxides would occur. When the oxide formation occurred at a sufficiently high temperature, hematite would form, while maghemite may have formed at lower temperatures. The temperature limit of maghemite formation probably lies somewhere between 700 and 800ºC, since we found maghemite in the Bopfingen ceramics to transform into hematite between 700 and 800ºC. This explains that some of the sherds contain hematite and some contain maghemite.

The described phenomena seem to have occurred in a similar manner in all types of pottery from Bopfingen (graphite ware, wheel-turned ware and coarse ware). Thus, the firing seems to have followed the same procedure for all these types of pottery. The predominance of the vitreous phase containing Fe^{3+} may also be due to the special composition of the clay used to make this pottery. The initially reducing firing was probably chosen because the potters wanted to avoid oxidation of graphite in graphite ware, and the pottery not containing graphite was fired in the same way. The graphite as such does not noticeably influence the Mössbauer patterns of the pottery, which also indicates that the graphite did not contain noticeable amounts of iron.

One should also note that the described process would explain the frequent presence of maghemite in graphite pottery from other locations, like Manching or sites in Bohemia [7, 11]. If the cooling is sufficiently slow, the exsolution of iron may be nearly complete, and maghemite may form if this happens at a sufficiently low temperature. Graphite ware from Manching and Bohemia is, however, often found to contain mainly divalent iron in the amorphous phase [7, 11]. In these cases, the cooling of the pottery in the kiln apparently occurred under persistently reducing conditions.

Laboratory firing experiments intended to test the firing sequence described above are presently under way. First results show that Mössbauer spectra like those observed for the Bopfingen pottery are, indeed, obtained for samples fired in the described manner.

4. Conclusions

One may thus conclude that the firing conditions of the graphite ware, the wheel-turned ware and the coarse ware were quite similar over a wide region of Celtic Europe. Firing apparently occurred at 800 to 850 ºC, and the differences observed in the Mössbauer spectra of the pottery are mainly due to differences in the cooling procedure, i.e., the atmosphere during cooling and the speed of cooling.

For the pottery found at the ditched square enclosure near Bopfingen, even the cooling conditions seem to have been remarkably uniform and favourable for the preservation of the Fe^{3+}-bearing vitreous phase that gives rise to the broad magnetic pattern at 4.2 K and becomes paramagnetic between 20 and 50 K.

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