Mössbauer studies of subfossil oak

Uwe van Bürck · Friedrich E. Wagner · Anton Lerf

Abstract Subfossil oak wood found in a dried-up bog in Bavaria, Germany, was studied by Mössbauer spectroscopy. The bog oaks contain substantial amounts of iron taken up from the bog waters and presumably forming complexes with the tanning agents in the oak wood. The iron is mainly Fe^{3+} and much of this exhibits an uncommonly large quadrupole splitting of up to 1.6 mm/s that can tentatively be explained by the formation of oxo-bridged iron dimers. Only rarely, mainly in the dense wood of the roots of bog oaks, was divalent iron found. When the wood was ground to a powder the divalent iron oxidized to Fe^{3+} within hours. This suggests that iron is taken up from the bog water as Fe^{2+} and oxidizes only when the wood emerges from the water and comes into contact with air.

Keywords Mössbauer spectroscopy · Subfossil oak · Oak wood · Bog wood · Tannin · Polyphenols

1 Introduction

Wood may be preserved for thousands of years when buried under wet and anaerobic conditions in swamps, bogs, riverbeds or elsewhere below the groundwater table [1–3]. Oak wood in particular is often found exceptionally well preserved, presumably due to its high content of tanning agents. After slow drying to prevent cracking, such subfossil oak wood is highly appreciated for its hardness and durability, as well

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as for its appealing dark colour. It is used for making furniture and veneers, sculptures, musical instruments, tobacco pipes and various ornaments. Its popular name is bogwood or bog oak. Subfossil oaks are also the basis of the European dendrochronological oak tree calendar [4–8].

Subfossil oak wood often is rich in iron taken up from the groundwater. Its dark colour, which ranges from brown over brownish green to deeply black, results largely from reactions of the iron with the tanning agents in the oak wood. These reactions may be similar to those made use of in the production of ferro-gallic inks [9–13].

The iron content is often high enough for measuring Mössbauer spectra. We here report on a Mössbauer investigation of subfossil oak wood from a dried up bog in southern Germany. Besides being of interest in its own right, such studies may also shed light on other fields of iron-tannin chemistry, like the preservation of old manuscripts from iron-gall ink corrosion [11], or the development of rust converters and anti-corrosion agents for steel on the basis of tannic acids [14–16].

2 Samples and experiments

The subfossil oak samples investigated in the course of our studies are of central European provenance, either from bogs or from the flood plains of rivers, and were either directly collected in the nature or obtained from wood sculptors, veneer factories, or other sources. In this paper we discuss only specimens from a bog dried up for agricultural use, called the Donaumoos, which is situated south of the Danube near the towns of Neuburg and Ingolstadt in Bavaria, Germany. After drainage was started in the late 18th century, the water level slowly fell and the bog oaks dried slowly and are now often found in the course of building activities.

Usually, the outer parts of trunks of bog oak are strongly weathered, while in the interior hard solid and often nearly black wood is found. Usually solid samples from the interior with air dried densities between 0.8 and 0.9 g/cm^3 and thicknesses between 5 and 15 mm were taken for Mössbauer spectroscopy. The Mössbauer measurements were performed with sources of ^{57}Co in Rh. For measurements at 4.2 K, a liquid He bath cryostat was used in which the source was also cooled to 4.2 K. Measurements at 160 K were taken with only liquid nitrogen in the cryostat. All samples were measured within a small (4 mm/s) and a large (11 or 15 mm/s) velocity range to get the inner part with good resolution as well as the magnetically broadened part of the spectra. The spectra of the same sample were fitted simultaneously with suitable superpositions of Lorentzian lines.

3 Results

The Mössbauer spectra of most samples exhibit only ferric iron (Fig. 1 and Table 1). The RT spectra exhibit two ferric quadrupole doublets, one with splittings of about 0.8 mm/s and the other with rather large splittings of 1.3 to 1.6 mm/s. The relative intensity of the two components changes from sample to sample. At 4.2 K a substantial fraction of the iron splits magnetically into a sextet with broadened lines and mean hyperfine fields of 53 to 55 T and a broad, structureless magnetic background. The sextet component exhibits nearly no electric quadrupole shift. It is
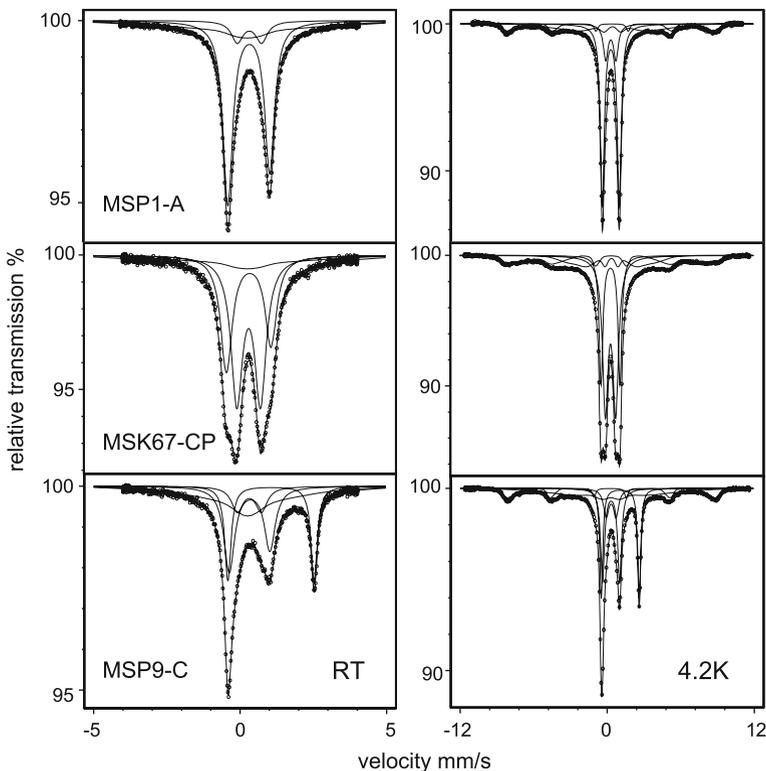
Fig. 1 Mössbauer spectra of some bog oak samples taken at ambient temperature (RT) and at 4.2 K. The corresponding Mössbauer parameters are compiled in Table 1

attributed to ferric iron exhibiting slow paramagnetic relaxations, an interpretation that is supported by the observation of the broad structureless background. Such a broad structureless component was also observed at 160 K and even at RT in the spectra taken with a large maximum velocity. It is attributed to magnetic relaxation phenomena in the regime intermediate between slow and fast relaxation. In the spectra shown in Fig. 1 the broad magnetic components were approximated by static Gaussian distributions of magnetic hyperfine fields.

At RT the quadrupole doublet with the larger quadrupole splitting in all cases shows a pronounced asymmetry, the line at negative velocity being considerably stronger than that at positive velocity (Fig. 1). At 4.2 K this asymmetry is practically absent, which suggests that it is due to an anisotropy of the Lamb-Mössbauer factor rather than to texture. The absence of texture was also established by measurements with a $1 \times 1 \times 1$ cm^3 cube of wood through which the γ rays were passed in a radial, tangential and axial direction, which revealed no differences in the doublet asymmetry. The doublet with the smaller quadrupole splitting did not show any noticeable asymmetry. The asymmetry must thus be considered as typical for the bonding situation of the iron giving rise to the large quadrupole interaction.

Ferrous iron was observed only in a few cases, most prominently in a sample of very dense wood from the roots of a bog oak (Fig. 1). When this wood was ground

Table 1 Isomer shifts (IS) relative to the ^{57}Co:Rh source having the same temperature as the absorber, electric quadrupole splittings (QS), FWHM linewidths (W) and relative areas (A_{rel}) for the quadrupole doublets observed in some bog oak specimens at RT and 4.2 K

Sample	T (K)	IS (mm/s)	QS (mm/s)	W (mm/s)	A_{rel} (%)
MSP1-A	298	0.31(1)	1.42(1)	0.40(2)	66.2(5)
		0.33(1)	0.83(1)	0.48(2)	10.2(3)
	4.2	0.29(1)	1.38(1)	0.39(2)	56.9(4)
		0.29(1)	0.83(1)	0.46(2)	13.1(3)
MSK67-CP	298	0.29(1)	1.52(1)	0.48(2)	36.2(7)
		0.30(1)	0.81(1)	0.48(3)	50.0(5)
	4.2	0.28(1)	1.54(1)	0.54(2)	24.9(3)
		0.28(1)	0.84(1)	0.36(3)	44.6(3)
MSP9-C	298	0.32(1)	1.38(1)	0.44(2)	33.2(14)
		0.32(1)	0.82(3)	0.58(3)	11.8(8)
		1.05(1)	2.94(3)	0.26(1)	24.5(3)
	4.2	0.31(1)	1.39(1)	0.38(1)	27.6(8)
		0.31(1)	0.80(2)	0.51(2)	10.9(8)
		1.06(1)	3.09(1)	0.29(1)	25.2(2)

The A_{rel} values do not add up to 100%, the balance being the components exhibiting broadening or magnetic splitting attributable to slow paramagnetic relaxation

to a powder, the ferrous iron oxidised to ferric iron within hours. When the sample that yielded the spectrum shown in Fig. 1 was re-measured after 5 years during which it was kept in a closed vessel in a nitrogen atmosphere, the intensity of the Fe^{2+} component had diminished by about 30 %. A similar sample kept in air for 5 years did no longer show any Fe^{2+}. These observations support the notion that the iron is deposited in the wood from the bog waters as Fe^{2+} and oxidises only after the wood falls dry and is exposed to air. In the very dense wood of roots the air apparently penetrates slowly enough for Fe^{2+} still to be found.

The total area under the spectra is about 3 times larger at 4.2 K than at RT, indicating a strong temperature dependence of the f-factors. This apparently affects all components in roughly the same way, since the relative intensities do not change much (Table 1). The iron contents of the samples can be estimated from the intensities at 4.2 K assuming that there the mean f-factor is the same as that of hematite, which was used for calibration. One of the highest iron contents was found in sample MSP9-C with 1.3 wt. %.

4 Discussion

In bog waters, the conditions are anaerobic, i.e., reducing, the pH is rather acidic and the iron is dissolved as Fe^{2+}. When iron penetrates into the waterlogged wood, it is expected to react with the polyphenols of the tannic substances, of which oak wood is particularly rich. While the iron is still divalent, it presumably forms monomeric complexes by binding to phenolic OH groups. This is presumably the iron we saw in the root of a bog oak. When a waterlogged tree falls dry, oxygen will penetrate into the wood and the iron will oxidise. One would then expect to observe ferric compounds like those obtained in the laboratory in reactions between iron and tannic substances. In such studies [14–16] ferric compounds with QS ≈ 0.8 mm/s have been

observed, which may explain the component with the small quadrupole splittings in bog oaks (Table 1). However, quadrupole splittings of more than about 1.2 mm/s were not observed in the products of such reactions. This raises the question what gives rise to the component with the large quadrupole splitting in bog oak.

Possibly, under oxidising conditions and when the pH rises, there is a tendency for forming small particles of oxyhydroxides [17]. On the way towards these, dimers like $[(H_2O)_4FeO_2Fe(H_2O)_4]^{4+}$, $[(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{6+}$ or $[(H_2O)_5FeOFe(H_2O)_5]^{5+}$ may form. At still higher pH values, these species would further polymerise and form iron oxyhydroxides. In the presence of polyphenols, this process may be hindered by complexation of the iron with polyphenols instead of water, and the polymerization process may stop at the stage of dimers or other rather small oxo-clusters. Rather large ferric quadrupole splittings have, indeed, been observed in a number of oxo-bridged dimers [18–21], which renders such clusters probable candidates for the component with the large quadrupole splitting in bogwood.

The reason for the large electric field gradients (EFG) in such dimers is the strong covalency of the bonds with the bridging oxygen due to the short iron-oxygen distances [22]. This is expected to give rise to a negative EFG. The strong axial bonds in oxo complexes may also cause an anisotropy of the f-factor, which should be larger along the molecular axis and hence the axis of the EFG than perpendicular to it. The asymmetry of the quadrupole doublets observed in the Mössbauer spectra of bog oak is in agreement with this and a negative value of the EFG, which supports the presence of clusters of the kind described.

The slowly relaxing ferric component in the Mössbauer spectra could not be clearly identified. The iron that yields the sextet pattern at 4.2 K may, in fact, become the heavily broadened component at 160 K and at RT and thus never appear in the spectra as a quadrupole doublet.

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