

# Klimt artwork: material investigation by backscattering Fe-57 Mössbauer and Raman spectroscopy

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**Abstract** The long lost painting “Trumpeting Putto” was discovered and now is not only in the focus of art historian, but has also scientific interest too. We underwent this rare case of an inorganic layered artwork a non-destructive material investigation by employing Raman and MIMOSII Fe-57 Mössbauer spectroscopy. First results indicate several layers, where two layers of different pigments are on an inorganic background layer stabilised by a metallic wire within a wooden frame structure

**Keywords** Trumpeting Putto Klimt artwork · Mössbauer spectroscopy · Raman spectroscopy · Pigments · Corrosion

## 1 Introduction

Two days before the 150th birthday anniversary of Gustav Klimt, the long lost masterpiece of art “Trumpeting Putto” was discovered in Upper Austria in a garage (see Fig. 1). The artwork was created in the early 1880’s and used as a representative masterpiece in the

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**Fig. 1** Selection of the Klimt artwork “Trumpeting Putto” with top layer from the 1950’s (below restoration borderline, e.g. belly) and partially restored original layer from the 1880’s (above restoration borderline, e.g. wings). (colour on-line)

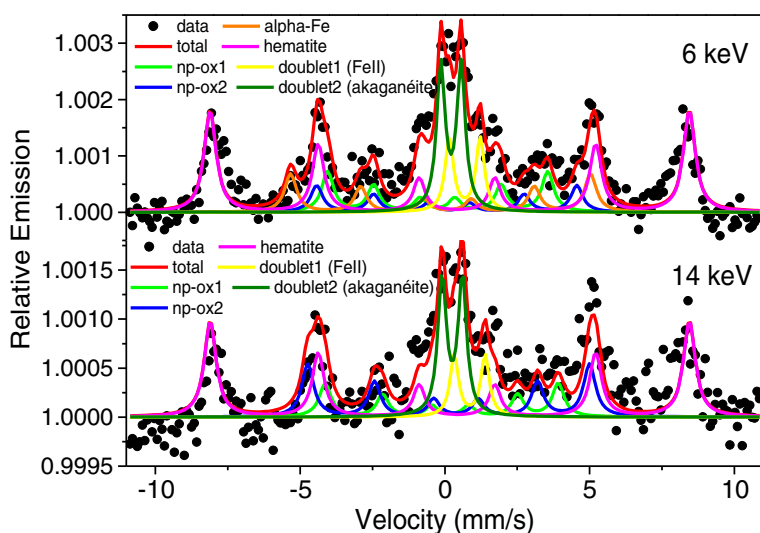
entrance of the “Künstler-Compagnie” from 1883 till 1892 in the Sandwirtgasse 8 in Vienna [1]. The “Trumpeting Putto” welcomed the visitors at the entrance and survived at least until 1969 there [1], before the artwork’s trace got lost in time and space. Today, the “Trumpeting Putto”’s place is taken by an elevator: Art replaced by technique, beauty lost for convenience.

In the 1950’s, in a dilettantish restoration attempt the artwork was painted over in a different technique.

In the work presented here, we performed non-destructive Raman and MIMOSII Fe-57 Mössbauer spectroscopy on selected spots of the “Trumpeting Putto” artwork, in order to elucidate its natural-historical composition and other scientific facts as a foundation for art-historical considerations and interpretations.

## 2 Experimental procedure

The MIMOSII Fe-57 Mössbauer Spectroscopy [2] was applied to identify the iron containing materials in the artwork. Mössbauer spectra were recorded at room temperature with a MIMOS II spectrometer detecting both 6 keV and 14.4 keV radiation in gamma-ray backscattering mode, and a  $^{57}\text{Co}(\text{Rh})$  source with an activity of about 80 mCi. No sample preparation was done to carry out the measurements. Several points of the painting, corresponding to different colour pigments were measured. Also, both non restored and restored locals of the painting were chosen for analysis. The rear side of the painting was also studied.



**Fig. 2**  $^{57}\text{Fe}$  Mössbauer backscattering spectra taken at a point on the Red Scarf of the painting. (colour on-line)

The fitting procedure of the spectra was carried out using a set of Lorentzian lines and parameters determined by least squares method. The isomer shifts are given relative to  $\alpha$ -Fe at RT.

Raman spectra were taken at several points of the artwork with two portable spectrometers. One, a prototype based on the development for Exomars mission illuminated at 532 nm. The spectrometer covers the spectral range of  $150\text{--}4000\text{ cm}^{-1}$  with a spectral resolution of  $6\text{ cm}^{-1}$ . The second is based on commercial components illuminated at 785 nm (BWTEK BRM-OEM-785) and with a spectrometer covering the spectral range  $200\text{--}3000\text{ cm}^{-1}$  (BWTEK Prime T BTC661E-785CUST) with a spectral resolution of  $5\text{ cm}^{-1}$ . The optical probe head was coupled with the spectrometer by an optical fibre and the spot size on the sample in both cases was around 100 microns diameter. In both cases the irradiance on the sample was kept below the thermal damage threshold which was visually and spectrally controlled. The pigments showed in general high fluorescence when illuminated with the 532 nm excitation and the 785 nm instrument was used in preference.

### 3 Results and discussion

We present results on a point of the Red Scarf of the artwork that has been covered with new paint in the restoration. Figure 2 shows Mössbauer spectra collected with 6 keV radiation as well as with 14.4 keV radiation. Table 1 gives the hyperfine parameters obtained in the fitting procedure.

As pigments, iron oxides have always been very important. The natural iron oxide red and yellow pigments are termed ochre. The relative amount of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) or goethite ( $\alpha\text{-FeOOH}$ ) is a factor determining whether an ochre has a red or a yellow colour [3, 4]. Also, the particle size plays an important role accounting for the range of colours seen [3, 4].

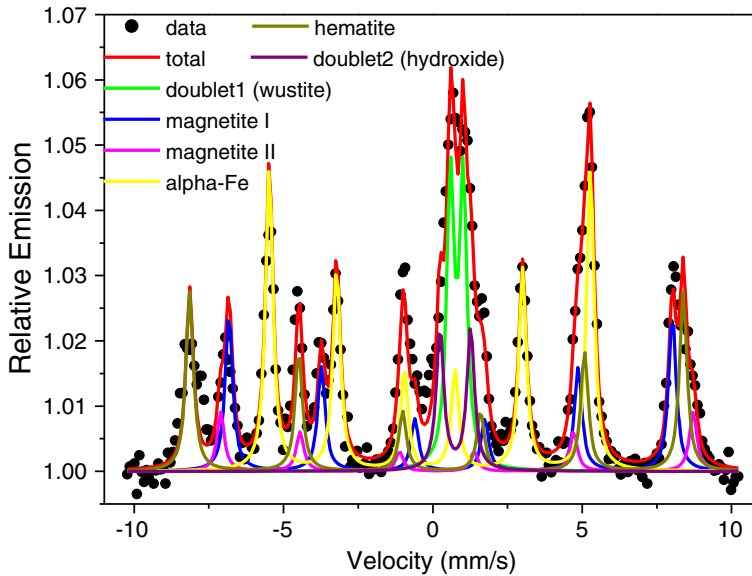
**Table 1** Hyperfine parameters obtained in the fitting of the spectra shown in Fig. 2 and site occupancies (%). IS is given relative to  $\alpha$ -Fe. The term np-ox refers to nanoparticle goethite, as explained in the text

IS (mm/s)	QS (mm/s)	H (T)	$\Gamma$ (mm/s)	%	
6 keV					
-0.15(1)	0.01(4)	23.6(4)	0.50(1)	14.20	np-ox
0.21(3)	-0.07(4)	27.8(6)	0.50(1)	9.4	np-ox
0.08(2)	-0.24(4)	32.1(5)	0.50(1)	13.51	Alpha-Fe
0.40(2)	-0.25(2)	51.3(1)	0.50(1)	35.81	Hematite
0.79(3)	1.07(1)	-	0.35(1)	9.19	Fe <sup>II</sup> Hydroxide
0.32(1)	0.70(1)	-	0.35(1)	17.89	Akaganéite
14 keV					
0.14(2)	-0.29(4)	24.9(5)	0.50(1)	13.25	np-ox
0.37(2)	-0.25(3)	30.1(5)	0.50(1)	20.95	np-ox
0.30(3)	-0.25(2)	51.3(1)	0.50(1)	37.97	Hematite
0.96(2)	1.07(1)	-	0.35(1)	8.58	Fe <sup>II</sup> Hydroxide
0.36(2)	0.70(1)	-	0.35(1)	19.25	Akaganéite

**Fig. 3** Mössbauer measurement at a point of the Metal Cross belonging to the structure frame at the rear side of the artwork. (colour on-line)

Variation of particle size (and also of impurities like clays for instance) results in a distribution of hyperfine fields and sometimes also in superparamagnetism [5–8].

The two different radiations used in the study of the Red Scarf of the artwork, provide depth selective information on surface layers and substrate layers. It is observed that in the surface layer the iron pigments are not the same as in the substrate (original painting). The new painting pigments have metallic iron as well as different nanoparticles oxides (np-ox). The magnetic subspectra with low magnetic fields must be related to goethite with small



**Fig. 4**  $^{57}\text{Fe}$  Mössbauer backscattering spectrum taken at a point of the Metal Cross at the rear side of the painting. (colour on-line)

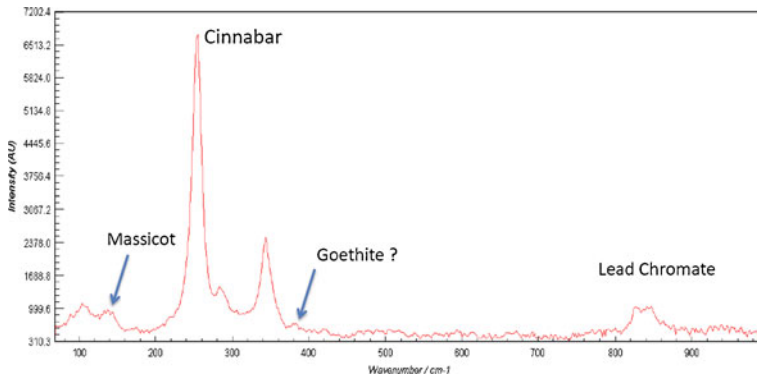
**Table 2** Hyperfine parameters obtained in the fitting of the spectrum shown in Fig. 4 and site occupancies (%). IS is given relative to  $\alpha\text{-Fe}$

IS (mm/s)	QS (mm/s)	H (T)	$\Gamma$ (mm/s)	%	
0.91(1)	0.43(2)	–	0.30(1)	15.57	Wüstite
0.69(2)	0.027(2)	46.0(1)	0.30(1)	17.13	Magnetite (site I)
0.58(1)	0.67(1)	49.0(1)	0.30(1)	6.49	Magnetite (site II)
0.002(2)	0.006(2)	33.3(1)	0.30(1)	33.27	Alpha-Fe
0.32(1)	–0.17(2)	51.2(1)	0.30(1)	19.68	Hematite
0.87(1)	1.03(2)	–	0.30(1)	7.85	$\text{Fe}^{\text{II}}$ Hydroxide

particle size [4]. The doublets obtained in the fitting procedure have been ascribed to an  $\text{Fe}^{2+}$  hydroxide, probably  $\text{Fe}(\text{OH})_2$  and to akaganéite ( $\beta\text{-FeOOH}$ ).

Figure 3 shows a selection of the rear side of the studied artwork, where a Mössbauer measurement with MIMOS II can be observed on the metal cross. Figure 4 shows the spectrum taken at that point, and Table 2 gives the hyperfine parameters obtained in the fitting procedure. The metal cross has a  $\alpha\text{-Fe}$  substrate covered with corrosion products. The main corrosion product is magnetite, but hematite as well as probably wüstite is observed. The hydroxide that is also seen must have appeared due to long-term oxidation process of metallic substrate in a humid environment. This hydroxide ( $\text{Fe}(\text{OH})_2$  or  $\text{FeO}\cdot n\text{H}_2\text{O}$ ) is usually the primary corrosion of metallic iron.

Figure 5 shows a Raman spectrum obtained in a point of the Red Scarf. Massicot (lead oxide) whose colour is yellow to reddish yellow, and cinnabar (red mercury sulphide), a



**Fig. 5** Room temperature Raman spectrum taken at a point of the Red Scarf. (colour on-line)

pigment also called vermilion, have been detected with this analysis. Spectra obtained at several spots of the Red Scarf confirm that cinnabar is the main component.

#### 4 Conclusions

The long lost Klimt masterpiece “Trumpeting Putto” was discovered and is in the focus of our scientific research interest. We underwent a non-destructive material investigation in this rare case of an inorganic layered Klimt artwork by employing MIMOSII backscattering Fe-57 Mössbauer and Raman spectroscopy. First results indicate several layers, where two layers of different pigments are on an inorganic background layer stabilised by a spider-net-like-grid-metallic wire within and between an octagon and spherical wooden frame structure. Preliminary results indicate that there is apparently a significant higher visible emission rate in the lower layer, which indicates a difference in age of more than *ca* 50 years. This is supported by the Mössbauer spectroscopy observation in the rear side at the metal cross (see Fig. 4 and Table 2) showing some aging effects in the form of corrosion products. Further work on this is in progress and will be published in a separate publication.

As internal reference side, the metal-cross mounted to the wooden framework on rear side of the artwork (see Fig. 3) has a  $\alpha$ -Fe substrate covered with corrosion products. The main corrosion products magnetite and hematite appeared due to a long-term oxidation process of the metallic substrate in a humid environment indicating a substantially older backside.

Among the observations done by Raman spectroscopy, there is indication of Massicot (lead oxide) and cinnabar (mercury sulphide) pigments. Both will be used for further natural- and art-historical analysis.

Hence Klimt’s “Trumpeting Putto” is hidden behind a second layer. The over-painting occurred shortly before or after the Second World War in a rather dilettantish style. We imagine a restoration attempt covering the influence of time and space. Fortunately, the original Klimt and the painted over layer are significantly different in technique as well as in pigments. It is very likely that the photograph of Klimt’s “Trumpeting Putto” in Nebehays book [1] from 1969 depicts only the top layer and was taken after the dilettantish restoration attempt.

More detailed further work on the age of the different pigment layers are in progress and will be published in the future. Furthermore, it is apparently necessary to develop physical and chemical methods to rescue Klimt's hidden "Trumpeting Putto" and preserve it as a cultural treasure for mankind.

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