Supporting Information

Artificial Vitriols: A Contemporary Interpretation of Historical Ingredients

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Ancient sources

Text 1. Bayerische Staatsbibliothek, 2 Inc.s.a. 907, Nicolaus Salernitanus and Mesuë. *Antidotarium.* Straßburg: [Johann Prüss], 1478. fol. 74r, col. 2, ll. 3-7

Normalization and translation: G. Montanari

[...] et discernitur illud quod est alteratum cum vitriolo ponendo ipsum in lamina ferrea supra igne, et si continet aliquid vitriolum qui erit combustum, ustum fiet rubeum.

[...] and what is altered with vitriol is known by placing it on an iron sheet over a fire, and if it contains any vitriol that will be burnt, the burned remains will be red.

Text 2. AAVV, *Antidotarium Collegii Medicorum Bononiensis*, Venice: [Niccolò Pezzana], 1773, p. 153

Normalization and translation G. Montanari

VITRIOLUM RUBIFICATUM sive Colcothar

Vitrioli calcinati ad albedinem - quantum placet

Tractetur igne reverberii, dum colorem acquirat obscure rubentem. Est etiam verum Colcothar id quod remanet in retorta ab extractione Spiritus et Olei Vitrioli.

Reddened Vitriol or Colchotar

Vitriol calcined to whiteness - as you like

Treat it with a reverberating fire, until it acquires a dark red color. It is also true Colchotar what remains in the retort after the extraction of Spirit and Oil of Vitriol.

List of phases for identification retrived in COD (Crystallographic Open Database)

Phase	COD Ref. Code	Reference
Melanterite	9007482	Baur, W. H. Baur, *Acta Crystallogr.*, 1964, **17**, 1167-1174
Rozenite	9007473	Baur, W. H. Baur, *Acta Crystallogr.*, 1962, **15**, 815-826
Szomolnokite	9009370	M. Wildner, G. Giester, Neues Jahrbuch fur Mineralogie, Monatshefte, 1991, **1991**, 296-306
IS(OH)	9003662	G. Johansson, *Acta Chem. Scand.*, 1962, **16**, 1234–1244

Hematite	2101167	E. N. Maslen, V. A. Streltsov, N. R. Streltsova, N. Ishizawa, Acta Crystallogr. Sec. B, 1994, **50**, 435-441
Mikasaite	9008258	P. C. Christidis, P. J. Rentzeperis, Zeitschrift fur Kristallographie, 1976, **144**, 341-352

Table S1. COD reference codes for the structural data used as a starting point in the Rietveld refinements.

Rietveld refinements

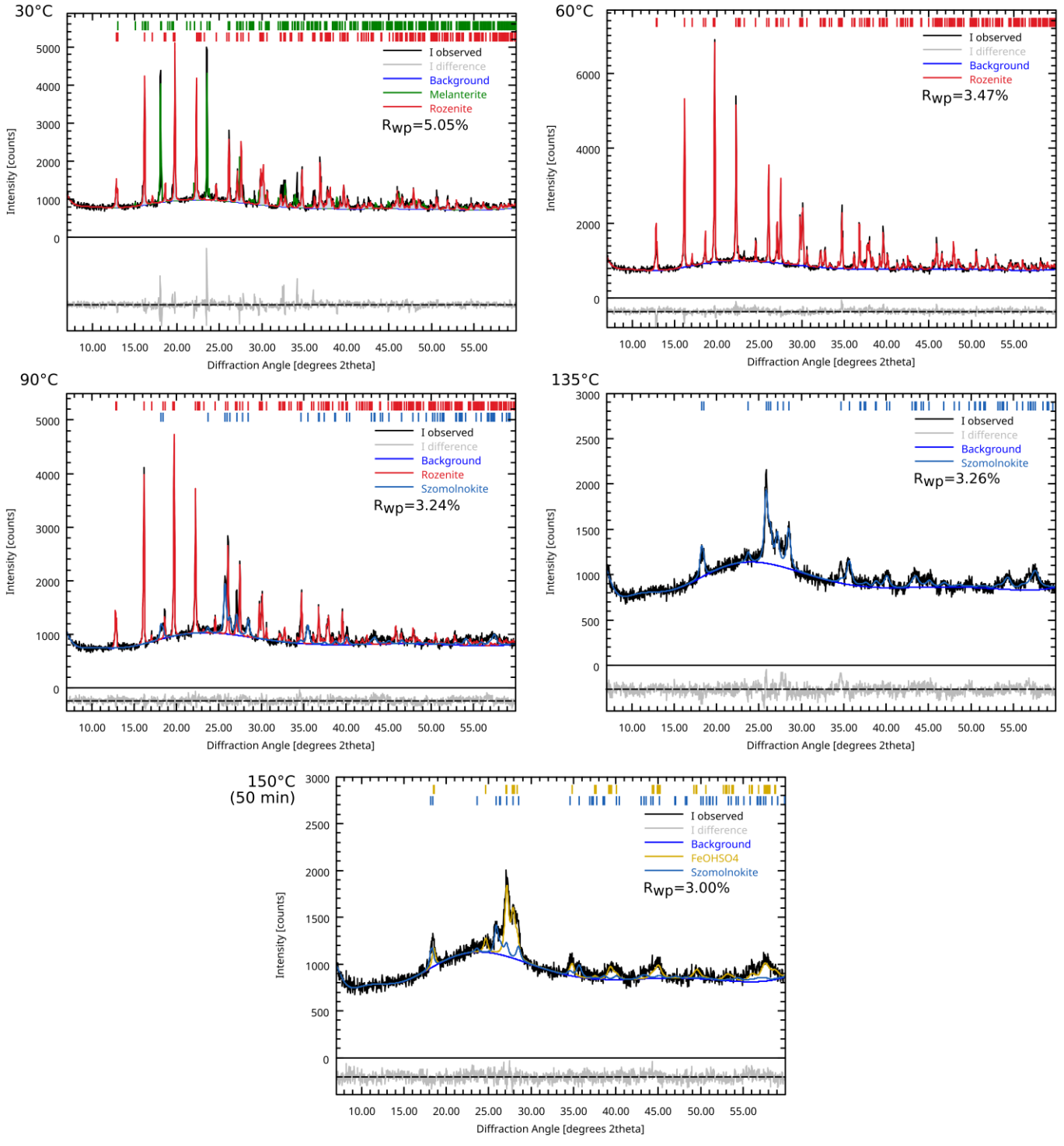

Figure S1. Selected XRPD pattern from the VTXRPD experiment; the structural data necessary to perform the Rietveld refinements were taken from the Crystallographic Open Database (reference codes given in Tab. S1).

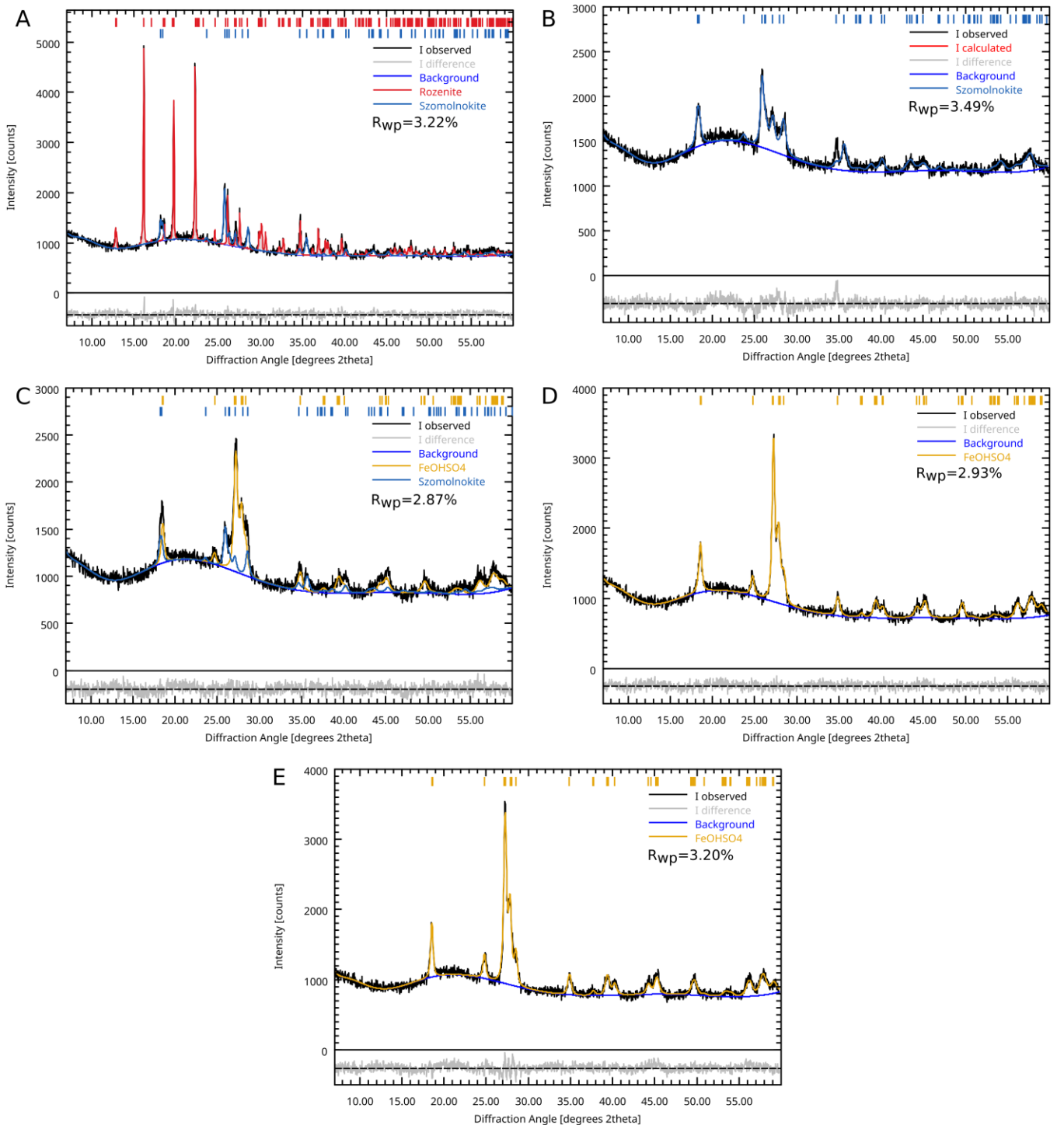

Figure S2. XRPD patterns of samples A-E from the Kofler bench. Rietveld refinement for each phase was performed using COD structural data (see Tab. S1)

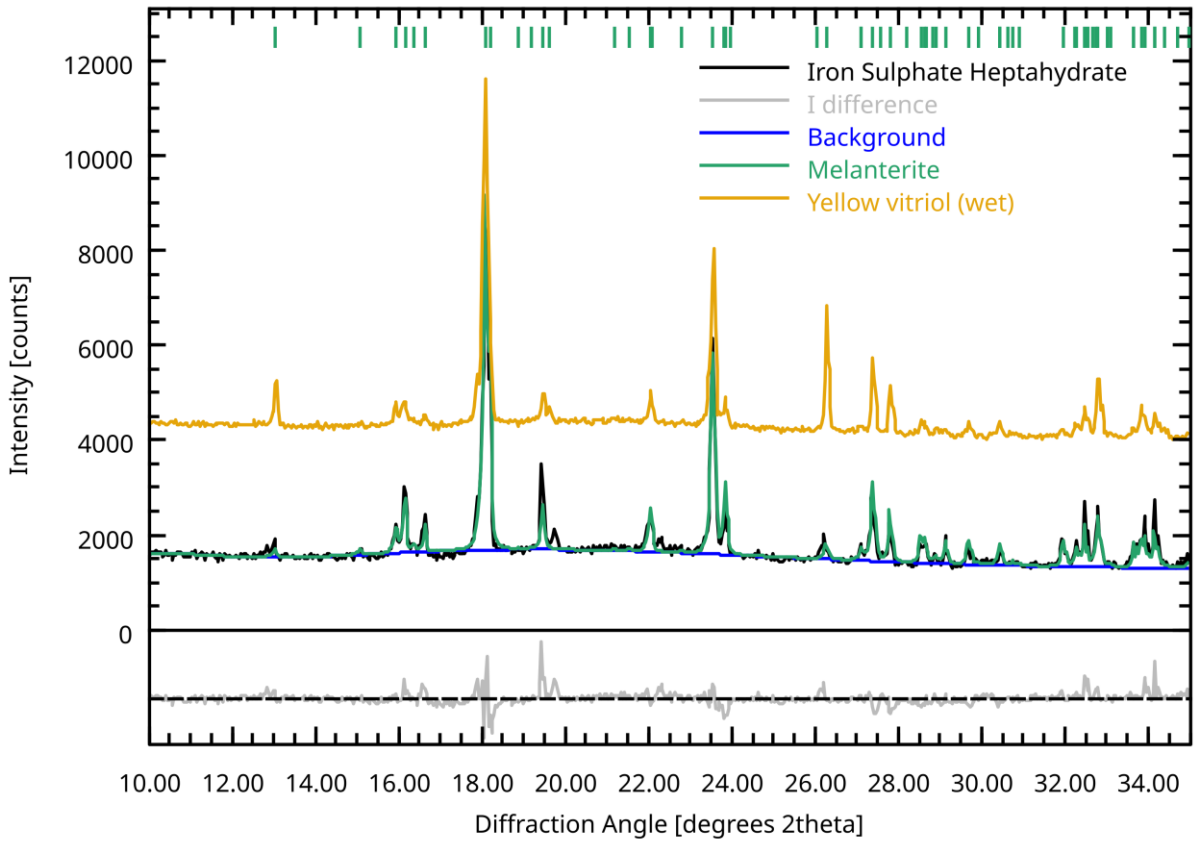

Figure S3. XRPD pattern comparison between iron sulphate heptahydrate starting material (black) and yellow vitriol obtained by wet method (yellow). Starting material was identified as melanterite (green); the melanterite phase was refined with the Rietveld method (see Tab. S1 for COD ref. code) against the starting material pattern with an R_{wp} of 5.55%, and against the yellow vitriol with an R_{wp} of 8.20%; this worse parameter is seemingly due to a marked preferred orientation for the (h00) planes, (13.05°, 19.65°, and 39.90°2θ respectively), in the product.

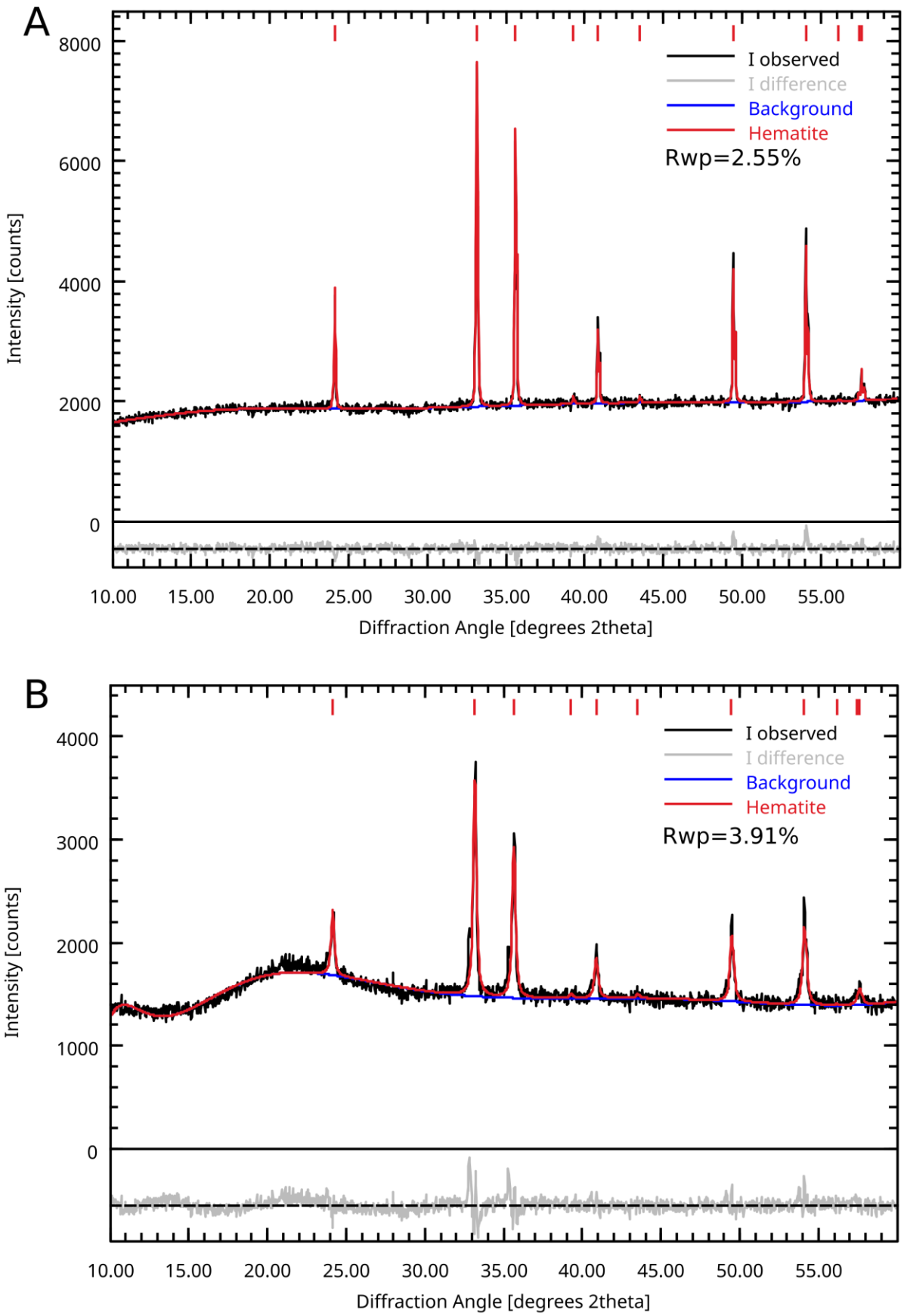

Figure S4. XRPD patter of "black" vitriol before (A) and after (B) grinding. Both were identified as hematite (ref. codes reported in Tab. S1)

Thermogravimetric Analysis

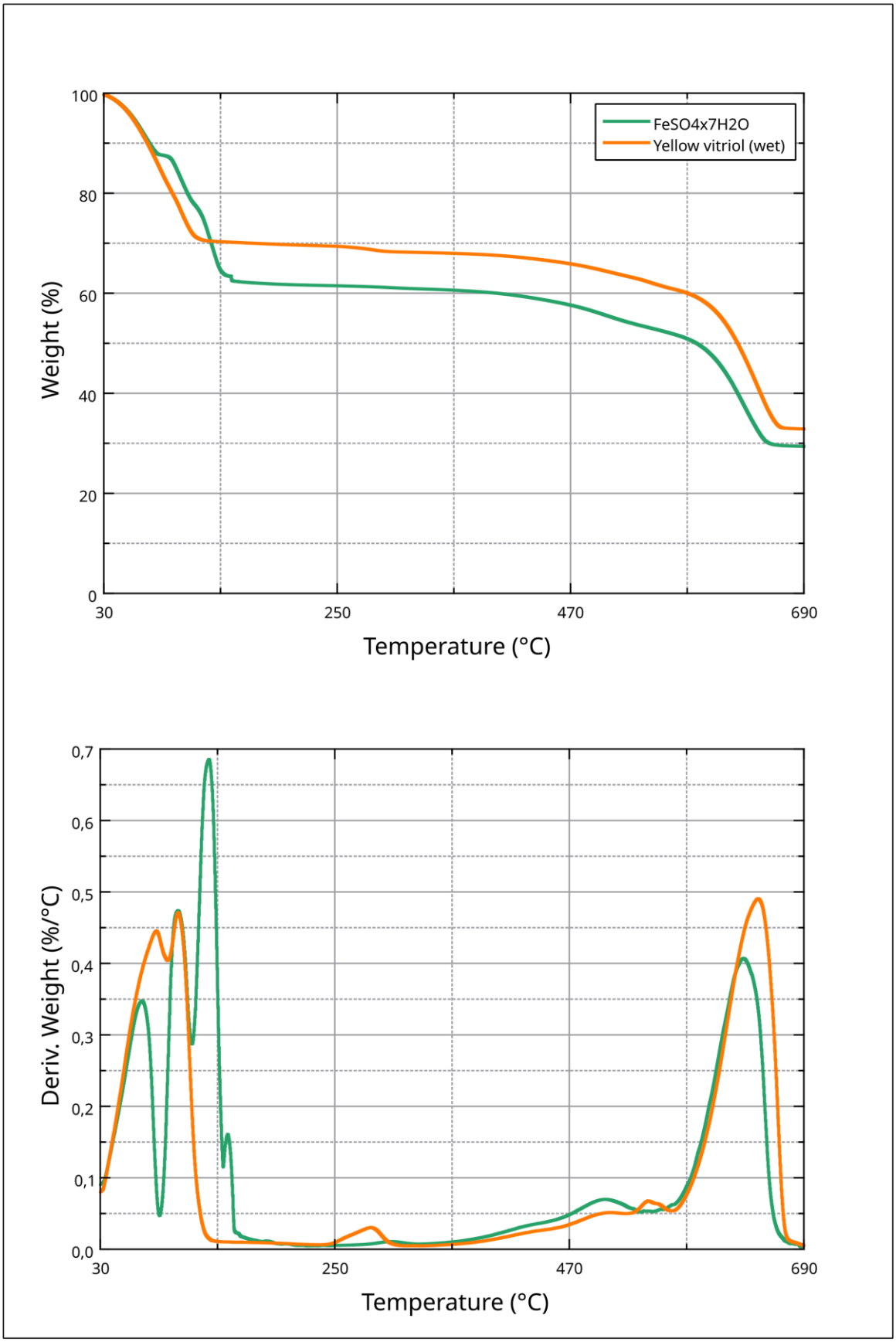

Figure S5. TGA of melanterite and yellow vitriol obtained from the wet method.

	Theoretical Mass Loss (melanterite)	Iron sulphate heptahydrate	Theoretical mass loss (iron sulphate hexahydrate)	Yellow vitriol (wet)
30°C-200°C	38.9%	38.0%	34.5%	30.0%
200°C-560°C	5.0%	8.4%	5.0%	9.1%
560°C-690°C	27.4%	24.0%	29.8%	27.8%
Total mass loss	71.3%	70.4%	69.3%	66.9%

Table S2. Percentage mass loss of Fe(II) sulphate heptahydrate and yellow vitriol (obtained from the wet method) during TGA from 30°C to 700°C, 10°C/min, under air flow.

Presuming the initial starting composition to the same in both sample (ferrous sulphate heptahydrate), the major difference between the two scans lies in the initial water loss, which is consistent with 6 water molecules for melanterite (greenline) (38.0%, compared to a theoretical 38.9%), while for the yellow vitriol (yellow line) is of only 5 water molecules (30.0%). The TGA suggest that the yellow vitriol is closer to an hexahydrate.

Between 200°C and 560°C the scans show several, poorly defined, small thermal events which can be ascribed to the release of the remain water molecules and the partial oxidation of the sample, with the addition of atmospheric oxygen (see Eq. 2).

The final mass is due to the presence of Fe_2O_3; therefore, considering the total stoichiometry and the iron oxide molecular weight (159.69 g/mol), the calculated total mass loss is 71.3%. The starting material sample behaves exactly as expected, with a total mass loss of 70.4%, while total mass loos of 66.9% of the yellow vitriol sample more closely matches the hypothetical Fe(II) sulphate hexahydrate.

Additional Photos

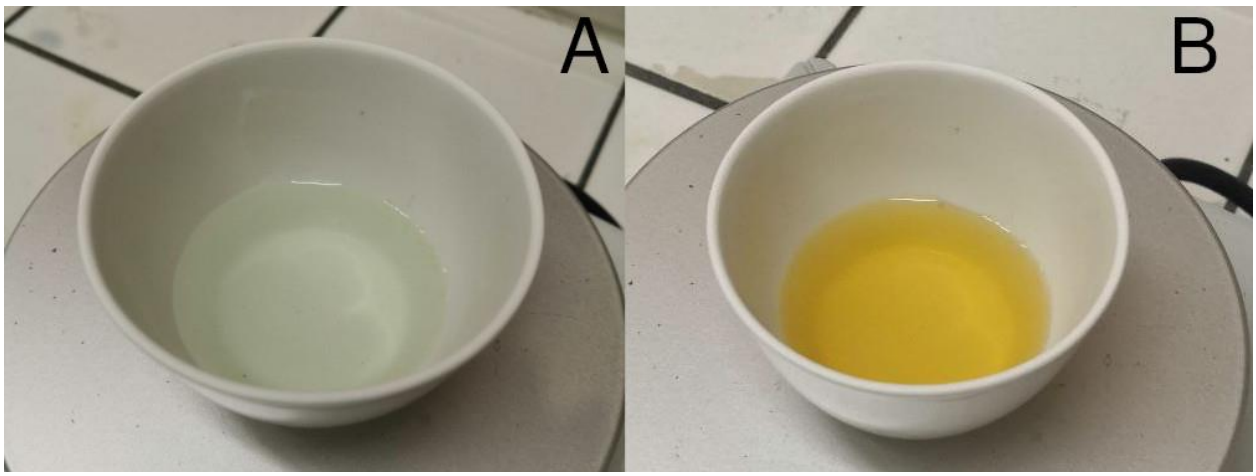

Figure S6. Iron (II) sulphate solution before (A) and after (B) heating.