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Analytical report

Date: 20.09.2014

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Object: Mercator Globes (16th century)

Analytical question: Pigment identification (red, green, blue(?), brown, black (print), black (paint))

Internal service No.: HKB14061016Ext

Methods applied: Raman (pigment), FTIR (binder), SEM-BSE/EDS (elements)

Operator(s): Dr. Nadim Scherrer, Dr. Stefan Zumbühl

Sample material

Microsamples were collected on 19.06.2014 at UNIL by N. Scherrer under supervision of Micheline Cosinschi. Globe Terrestre (GMT) p01 (red), p02 (green), p03 (brown/black); Globe Celeste (GMC) p01 (red), p02 (green), p03 (yellow-green), p04 (orange) sample lost on mismanipulation.

Methods

The sample material was observed optically using a microscope and then analysed sequentially using Raman spectroscopy (785nm), Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) with elemental analysis (SEM-EDS).

Instrument details

Reflected light microscopy: Leitz DMRB, equipped with Vis and UV (Osram HBO 103W/2) illumination and different filters:

- DF	=	dark field		
- BF	=	bright field		
- A	=	UV	BP340-380	LP430
- I3	=	Blau	BP450-490	LP515

BP = Bandpassfilter (excitation)
LP = Longpassfilter (edge)

Polarisationsmicroscopy (PLM): Olympus BH 2

Stereomicroscopy (ST): Leica Z16 Apo Zoom

Digital microscope camera: Jenoptik ProgRes Speed XT Core 3, pixel resolution 2080x1542

Digital microscopy: Keyence VHX-1000 with 54MP camera (max. 15 images/sec.) equipped with

- Objective: VH-Z20W (20-200x)
- Objective: VH-Z100W (100-1000x), dark field, bright field and bright field with x-polarisers
- Stage: VH-S50 with motorised Z-axis (1µm step)

Infrarot spectroscopy (µ-FTIR):

Perkin Elmer System 2000:

- single element LN-MCT detector 7500-580cm⁻¹ / settings: 16 scans / 4 cm⁻¹ resolution / range 4000-580cm⁻¹;

Bruker Hyperion 3000:

- single element LN-MCT-D 10000-400cm⁻¹ / settings: 32 scans / 4cm⁻¹ resolution / range 4000-450cm⁻¹
- multi-element FPA 64x64 detector (32x32µm area), 4500-900cm⁻¹, ATR-20x objective A677-B10 250µm

Bruker Tensor 27:

- 10000-50cm⁻¹ / A225/QI Platinum ATR module

Scanning Electron Microscopy (SEM): Zeiss EVO MA 10 (2014), W-Kathode, variabler Druck (VP-Modus) 10 bis 400 Pa (0.1mbar - 4mbar), SE-Detektor, LM 5SBSD-Detektor; Beam deceleration kit (to put bias voltage on a single holder); Framestore 3072x2304 pixels; Beamsleeve-1000 (to minimise skirt effect in VP); Acceleration Voltage = 0.2 to 30kV; Probe Current: 0.5pA to 5µA; 5-axes stage: X=80mm, Y=100mm, Z=35mm, T=-10 to 90°, R=360°, max. Probenhöhe=100mm; 3DSM Surface Modelling.

Energy Dispersive Spectrometry (EDS): Thermo NORAN System 7 (2014), peltier cooled ULTRADRY Detector 30mm², 129eV; COMPASS & XPHASE Software.

C-coating: Cressington Carbon Coater 108C with carbon rods at 0.01mbar chamber pressure

Au-Bedampfung: - Au-Evaporation coater: Edwards E12 E2

- Au-Sputter coater Edwards S150 with Ar-Plasma

Dispersive Raman spectroscopy: Renishaw InVia (2007) system, 250mm focal length, maximum spectral resolution achievable (depending on wavelength and grating) ~1-0.5cm⁻¹

- Laser 785nm (Diode-type): Renishaw HP NIR785 (300 mW), grating 1200l/mm, edge filter, 110-3200cm⁻¹
- Laser 633nm (He-Ne-type): Renishaw RL633 (17mW), grating 1800l/mm, std edge filter, 100-4000cm⁻¹
- Laser 514nm (Ar-type): Spectra-Physics (24 mW), grating 1800l/mm, sup edge filter, 100-4000cm⁻¹
- Prior motorised stage x-y-z (nominal microstep movement is 0.04microns)
- N-PLAN Objectives 5x (NA 0.12 - WD 13.2mm), 20x (NA 0.40 - WD 1.10), 50x (NA 0.75 - WD 0.37), 100x (NA 0.90 - WD 0.27), LWD 50x (NA 0.55 - WD 8.00) on Leica DM LM microscope
- Extendable sampling arm for in-situ measurements outside sample chamber (larger objects)

Results:

Sample	Method	Result
GMT p1 red	Raman 785nm	red lead Pb3O4 [550s, 391, 313, 225, 151, 120vs cm-1], traces of hematite Fe2O3 [291s, 225m cm-1] and carbon-based black [1600br, 1325br cm-1]
	SEM-EDS	Pb (lead-based red pigments); ± Ca (calcium carbonate)
	FTIR	Red paint: protein, resin (likely varnish), traces of oil cannot be excluded due to the presence of lead carboxylates, yet not confirmed due to spectral overlaps of the organic compounds. There is also some basic lead carbonate (lead white) and some gypsum. Transparent particle: protein, with a minor waxy component.
GMT p2 green	Raman 785nm	copper-based pigment with chlorine (compare SEM-EDS results). The spectral information is weak [1341, 547, 440cm-1] and so far not identified
	Raman 514nm	No success (fluorescence)
	SEM-EDS	Cu, Cl (copper chloride based pigment or degradation product)
GMT p3 brown/black	Raman 785nm	brown/red iron oxide particles identified as hematite [409w, 291 s, 225m cm-1]. An additional black phase with a response at [1366br, 1247w, and 613s] is not yet identified.
	SEM-EDS	Fe (iron oxides); Si, Al, Ca, Mg, ±P (silicate); Ti, Si, Ca. The combination of elements and phases suggests the use of natural ochre.
GMC p01 red	Raman 785nm	(orange/yellow PbO) and darker red lead (Pb3O4). Green areas (sample GMC p2) seem to be painted with a copper-based pigment, giving no response with 514nm excitation, but identifying copper oxalate dehydrate on 785nm excitation.
	SEM-EDS	Pb (PbO + Pb3O4); Ca, S (gypsum); ± Fe (iron oxides)
GMC p02 green	Raman 785nm	copper oxalate dihydrate [1513, 559cm-1]
	Raman 514nm	No success (fluorescence)
	SEM-EDS	Cu, Cl
	FTIR	contains oil. potentially protein, however not confirmed due to spectral overlaps. Oxalates (support Raman identification of copper oxalates), calciumcarbonate, silicates.
GMC p03 brown/black	Raman 785nm	No success (fluorescence)
	SEM-EDS	Si, Al, K (silicate); Fe (iron oxide); Cu±Cl (green copper pigment); Ca±Mg ±S (Ca-carbonate, gypsum)

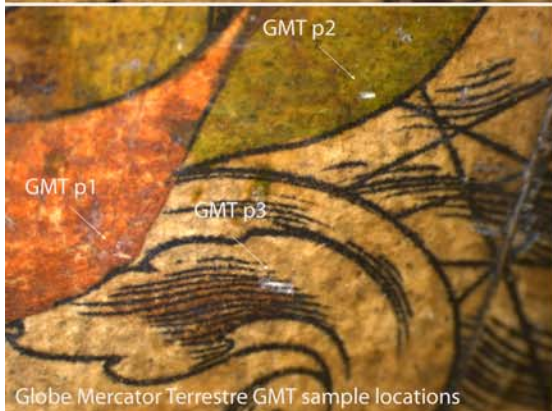
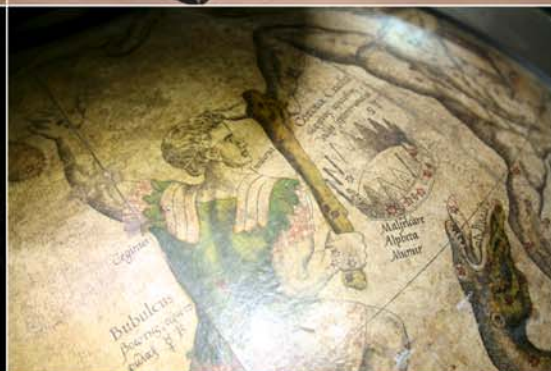
Tab. 1: Summary of samples and analyses performed on samples taken from the Globes Mercator Terrestre (GMT) and Celeste (GMC) with results and interpretation.



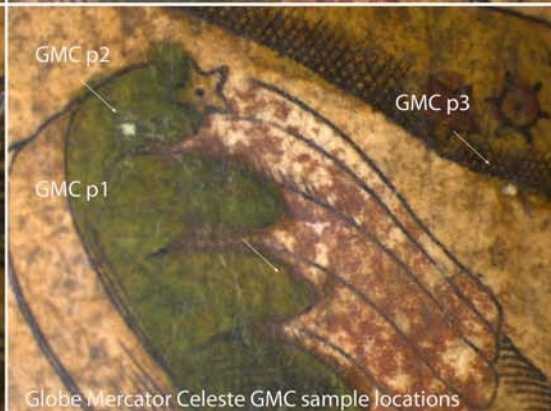
Globe Mercator Terrestre GMT



Globe Mercator Celeste GMC



Globe Mercator Terrestre GMT sample locations



Globe Mercator Celeste GMC sample locations

Fig. 1: Overview images of objects, Globe Mercator Terrestre (GMT top left) and Globe Mercator Celeste (GMC top right). Orientation of sampling area (middle images) and exact sampling locations, before and after sample taking (bottom).

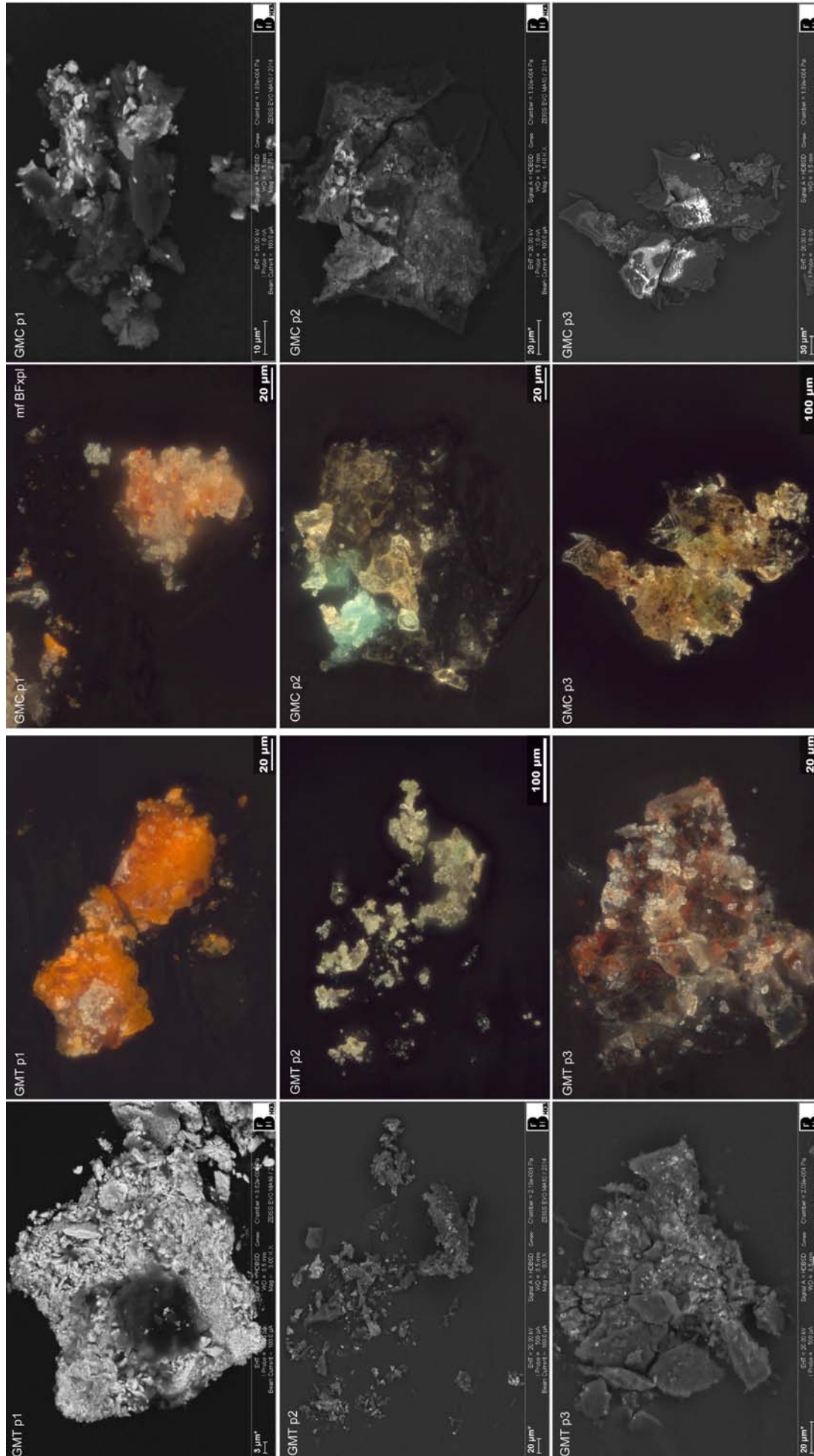


Fig. 2: SEM-BSE and corresponding multifocus LM images with BFExpl illumination for colour and density information. Sample locations can be seen in Fig. 1. GMT (terrestre on left, GMC celeste on right).

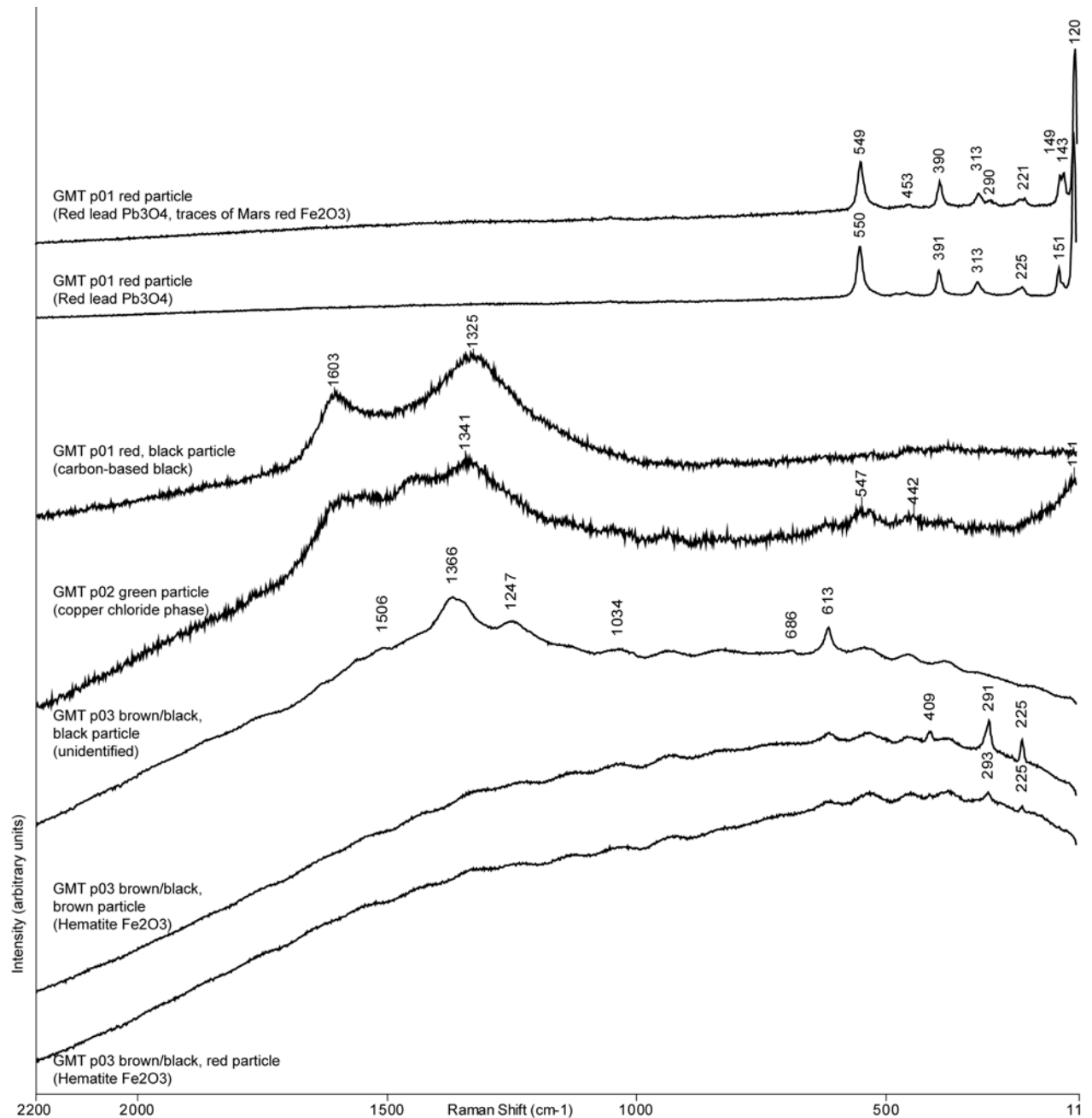


Fig. 3: Raman analyses of GMT samples using 785nm excitation. Within the sample GMT p1 red, at least 3 components can be found - red lead Pb₃O₄ [550s, 391, 313, 225, 151, 120vs cm⁻¹] (Bell 1997, Burgio 2001), traces of hematite Fe₂O₃ [291s, 225m cm⁻¹] (Das, 2011) and carbon-based black [1600br, 1325br cm⁻¹]. GMT p2 green contains a copper-based pigment with chlorine (compare SEM-EDS results). The spectral information is weak [1341, 547, 440cm⁻¹] and so far is not identified. 514nm excitation did not deliver any result on the green. GMT p3 brown/black is made up of brown/red iron oxide particles identified as hematite [409w, 291s, 225m cm⁻¹] (Das 2011). An additional black phase with a response at [1366br, 1247w, and 613s] is not yet identified.

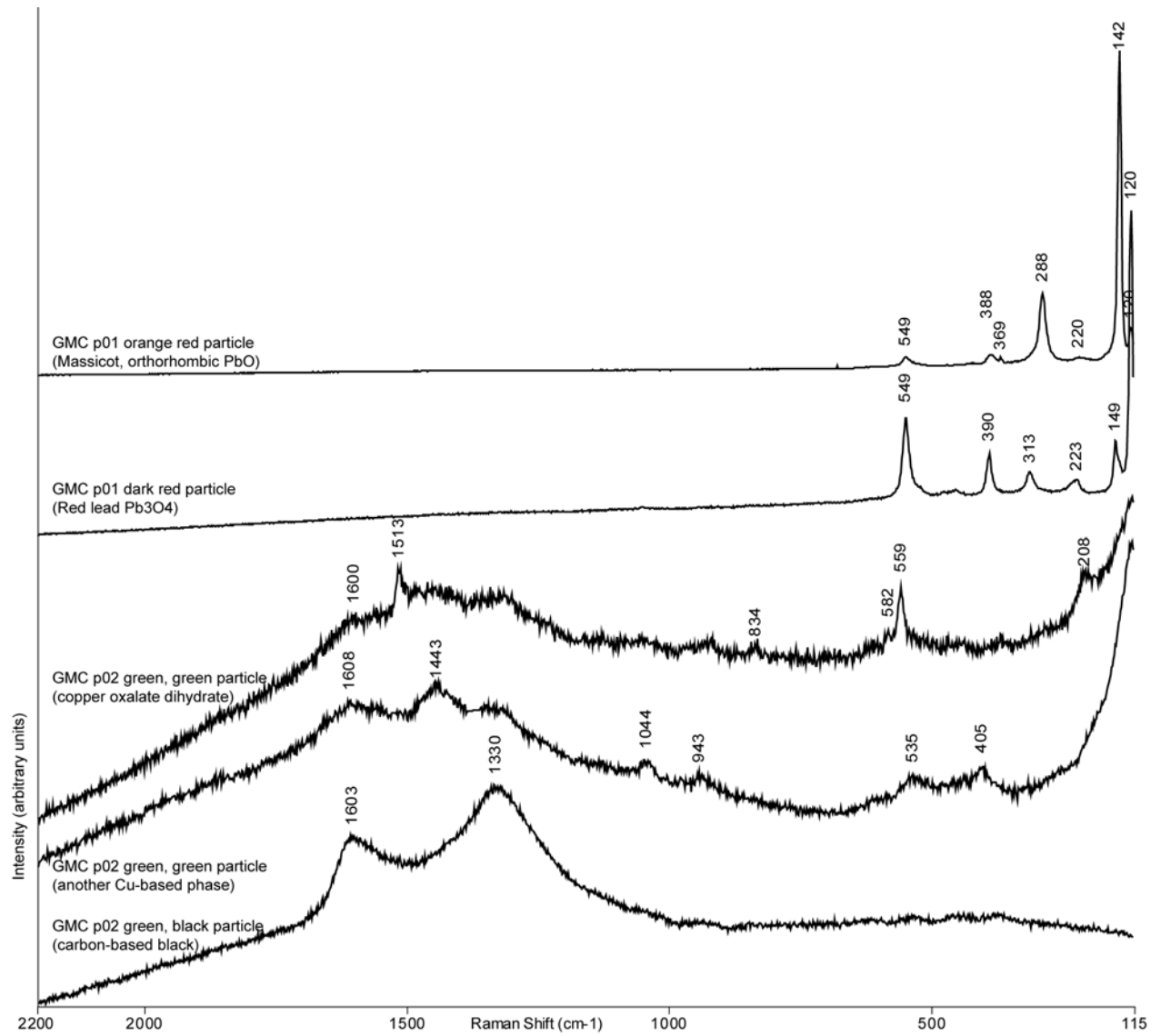


Fig. 4: Raman analyses of GMC samples using 785nm excitation. Sample GMC p3 was non-responsive using any of the laser sources available. The red paint in sample GMC p1 contains a mixture of Massicot (orange/yellow PbO) and darker red lead (Pb₃O₄). Green areas (sample GMC p2) seem to be painted with a copper-based pigment, giving no response with 514nm excitation, but identifying copper oxalate dihydrate [1513, 559cm⁻¹] on 785nm excitation (Burgio 2001, Castro 2008, Miller 2010, Zoppi 2010).

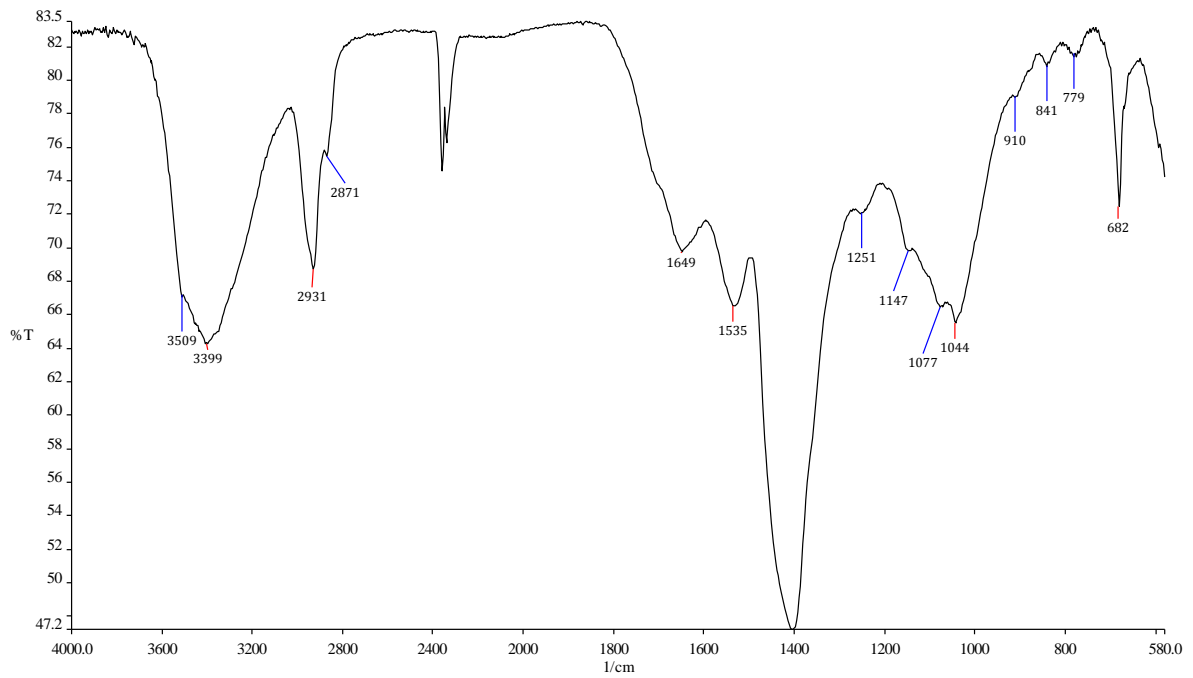


Fig. 5: FTIR of GMT p1 red: protein, resin (likely varnish), traces of oil cannot be excluded due to the presence of lead carboxylates, yet due to spectral overlaps of the organic compounds it can neither be proven. There is also some basic lead carbonate and some gypsum.

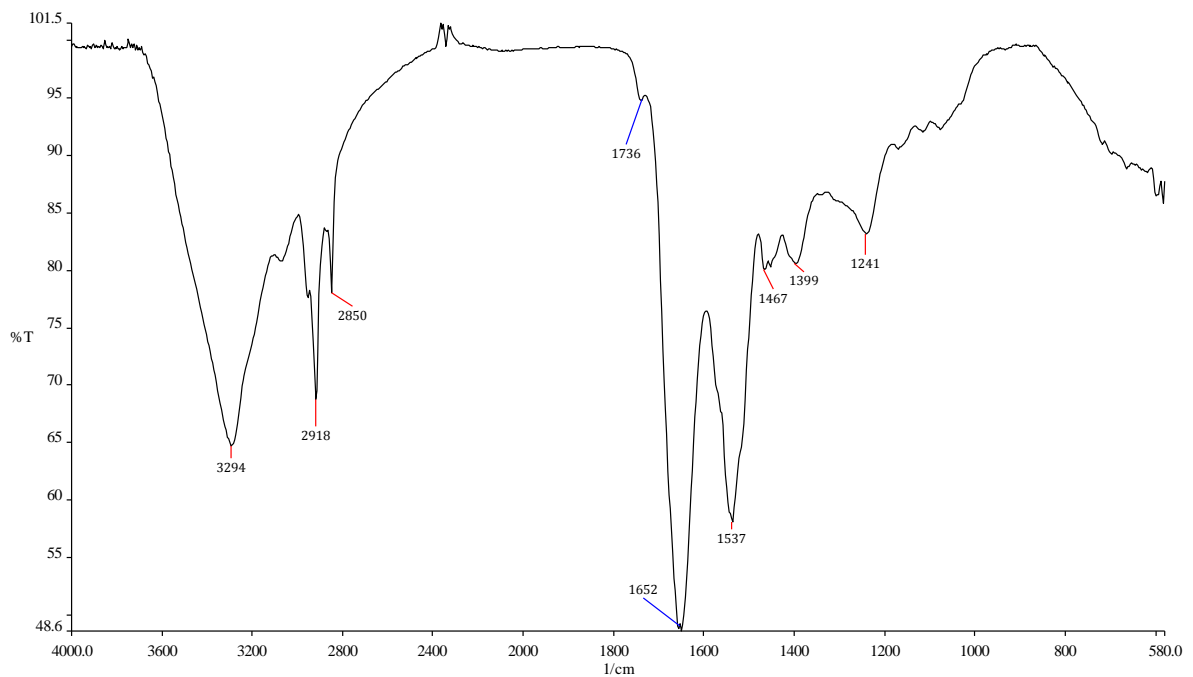


Fig. 6: FTIR of transparent particle in GMT p1 red: protein, with a minor waxy component.

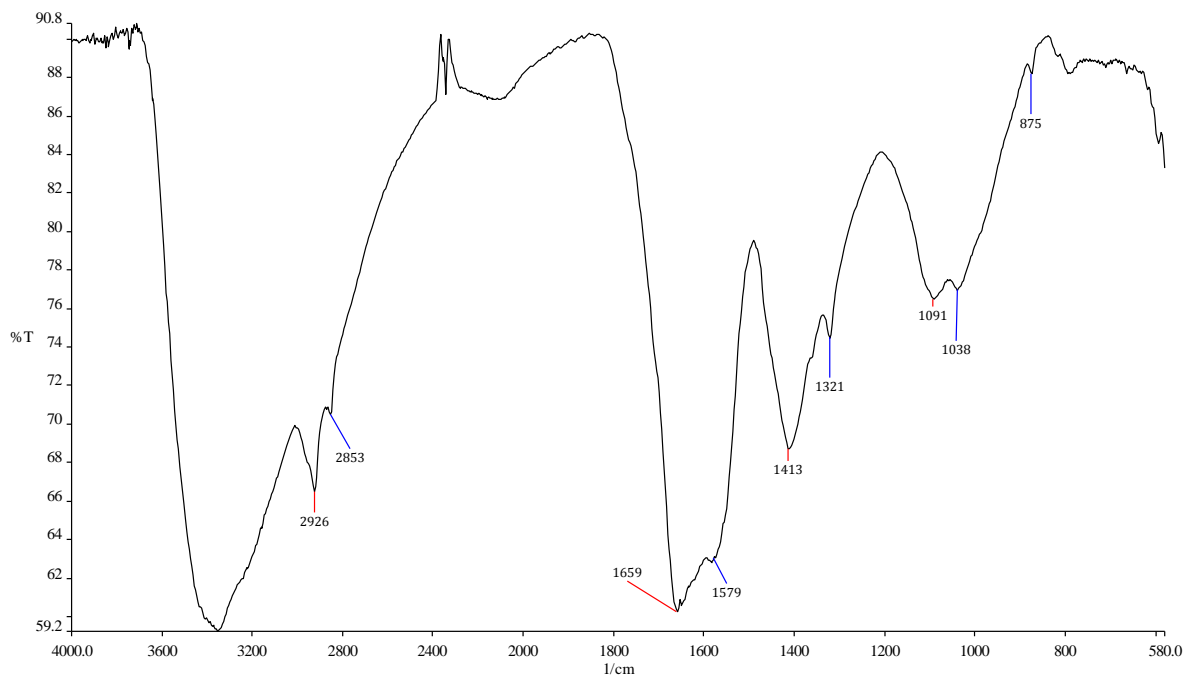
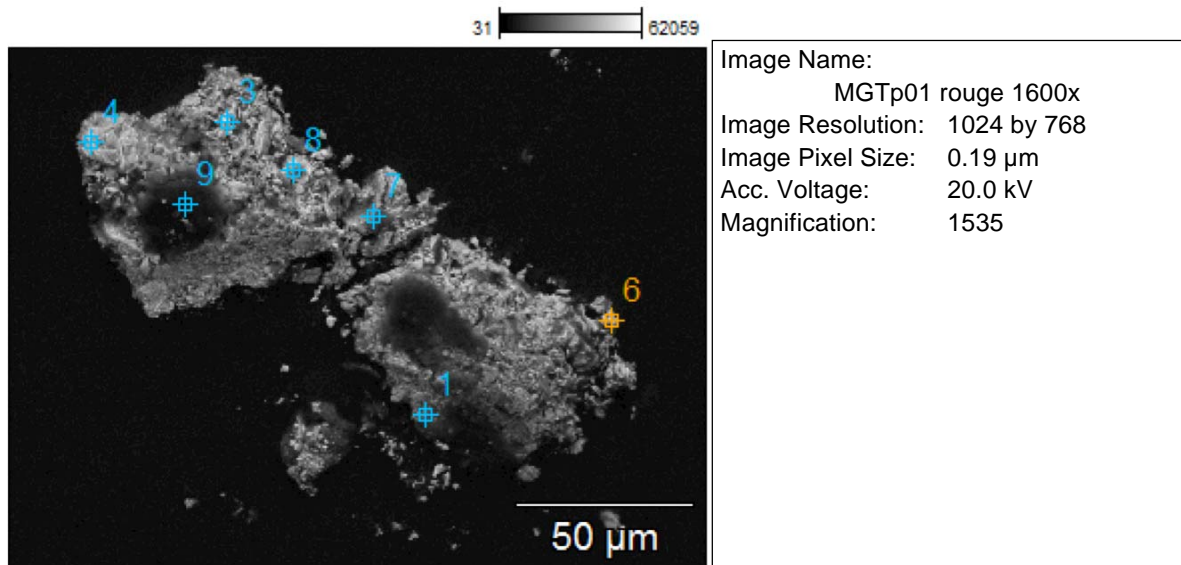


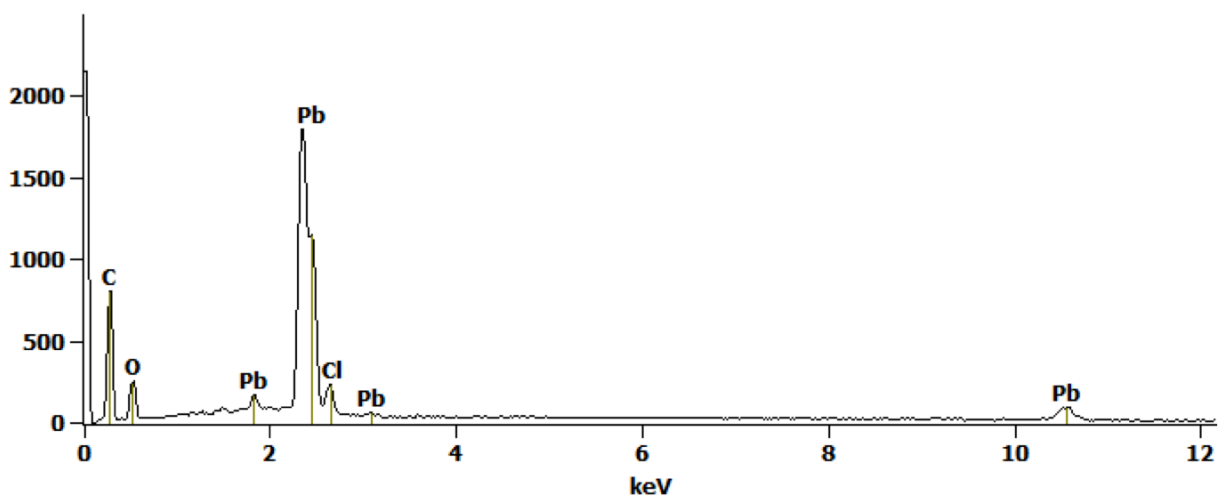
Fig. 7: FTIR of sample GMC p2 green: contains oil, with potential protein, however not confirmed due to spectral overlaps. Oxalates (support Raman identification of copper oxalates in GMC p2, Fig. 4), calciumcarbonate, silicates.

MGTp01 rouge 1600x



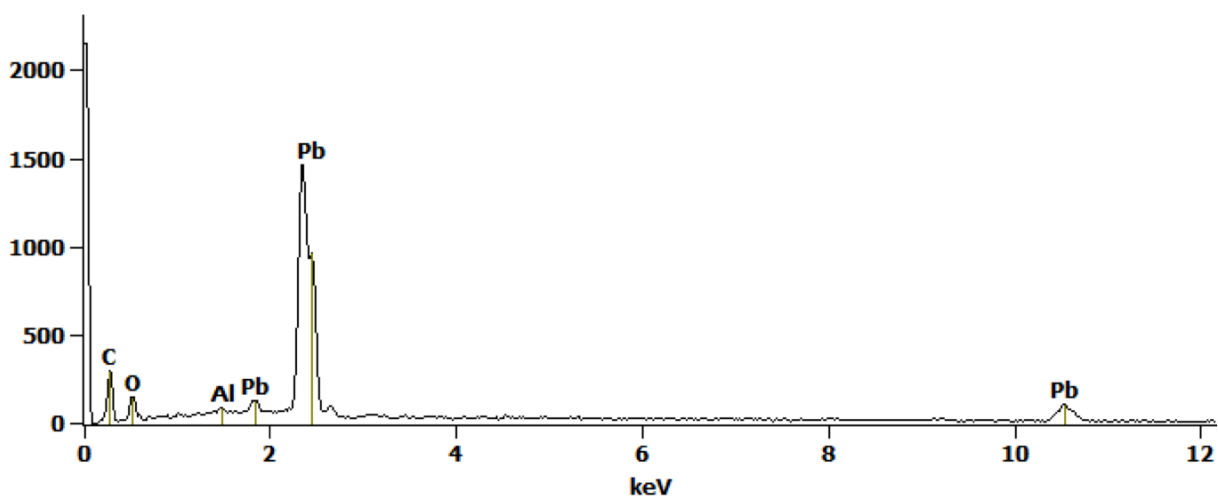
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MGTp01 rouge 1600x_pt1



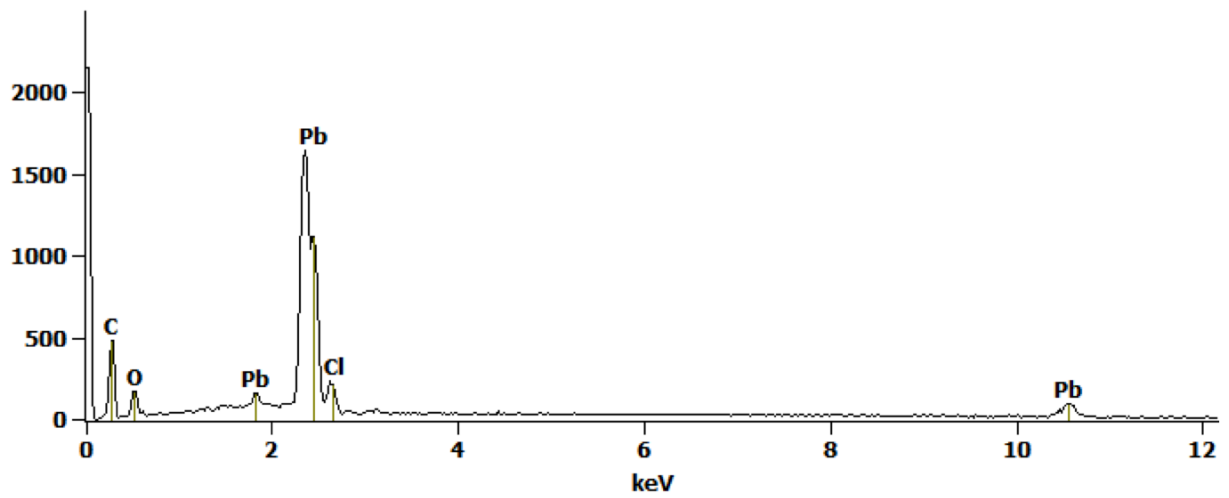
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MGTp01 rouge 1600x_pt3



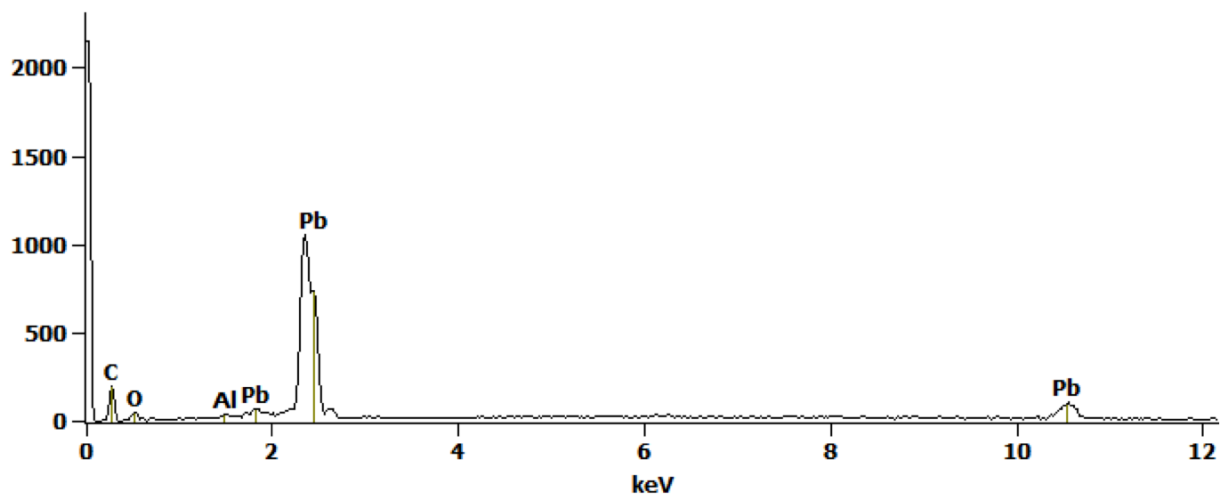
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MGTp01 rouge 1600x_pt4



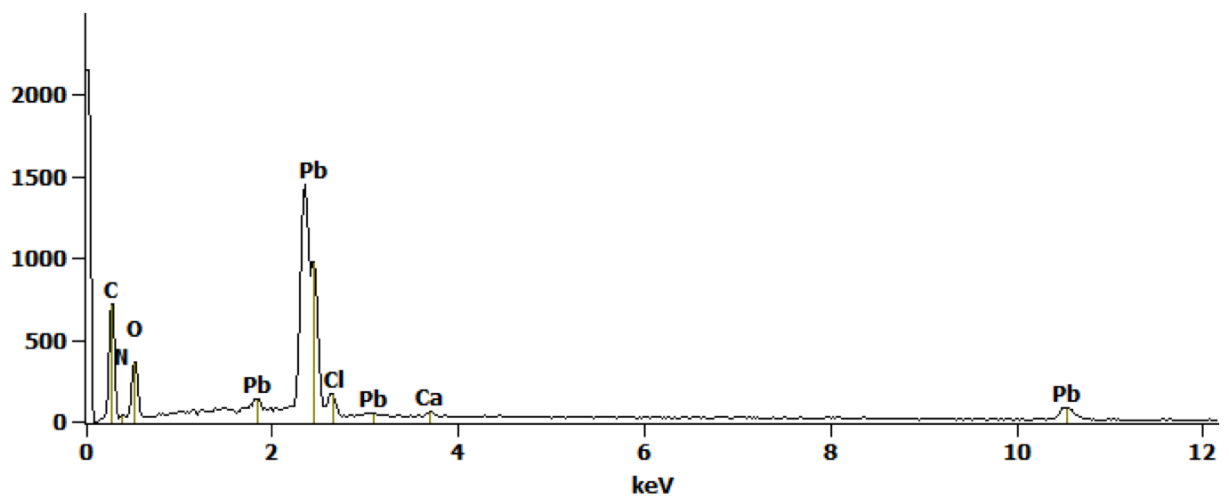
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MGTp01 rouge 1600x_pt6



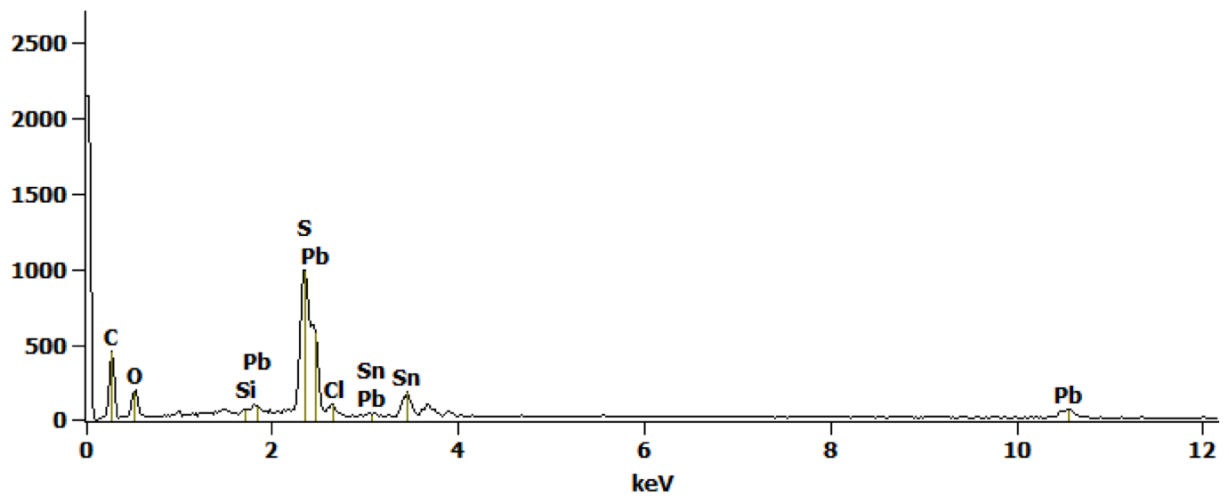
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MGTp01 rouge 1600x_pt7



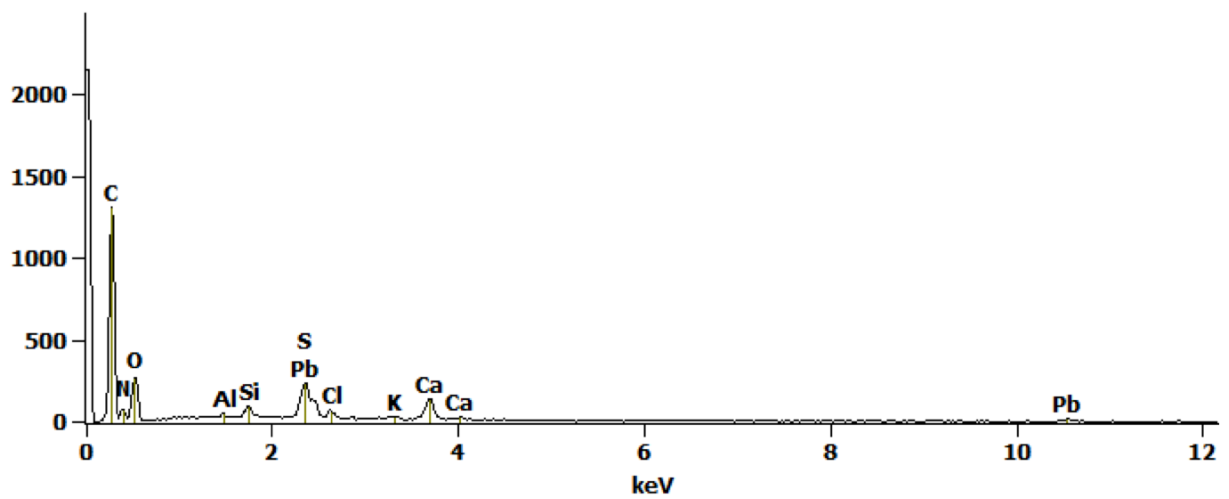
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MGTp01 rouge 1600x_pt8



Full scale counts: 2147

MGTp01 rouge 1600x_pt9



MGTp02 vert 600x

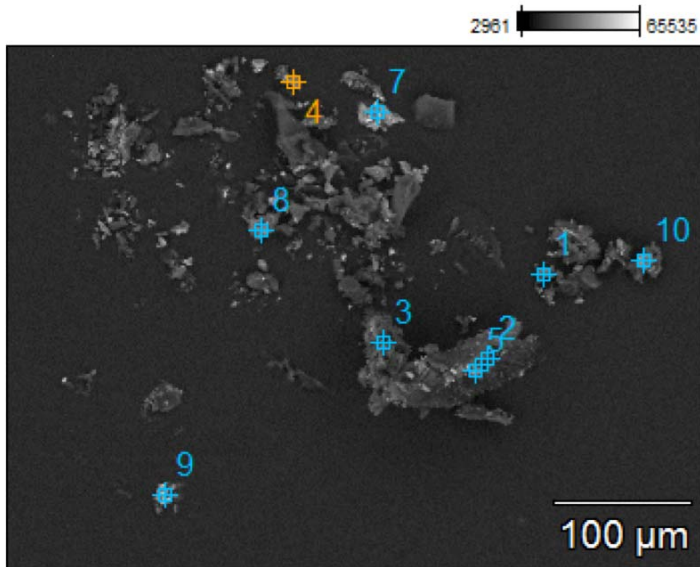
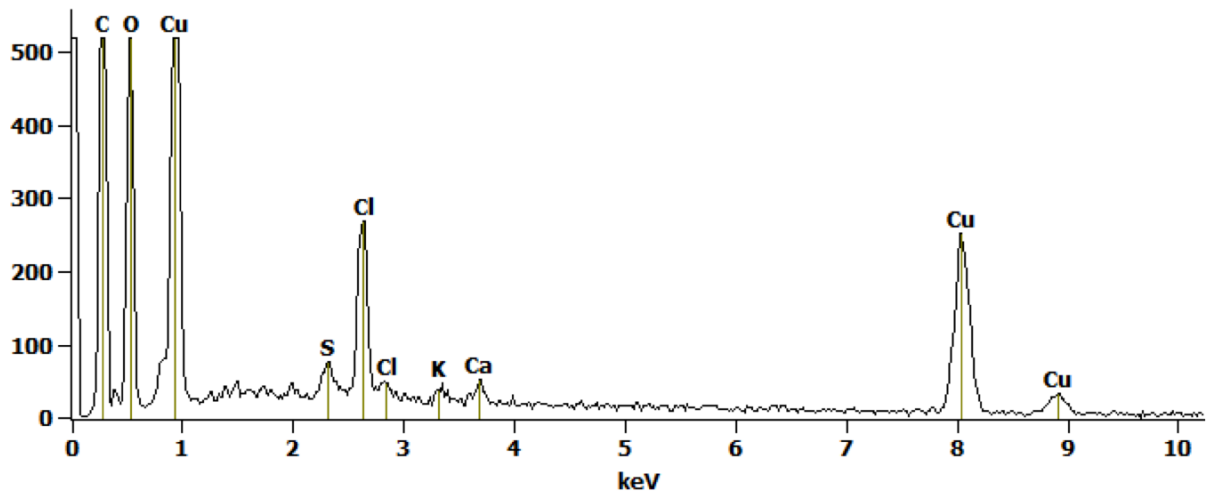


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Acc. Voltage: 20.0 kV
Magnification: 600

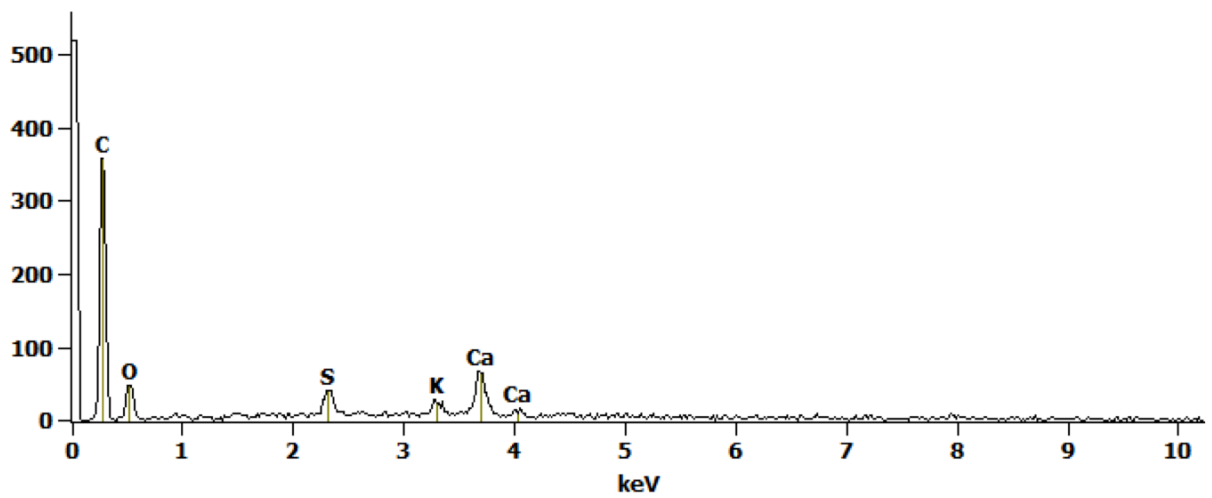
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MGTp02 vert 600x_pt1



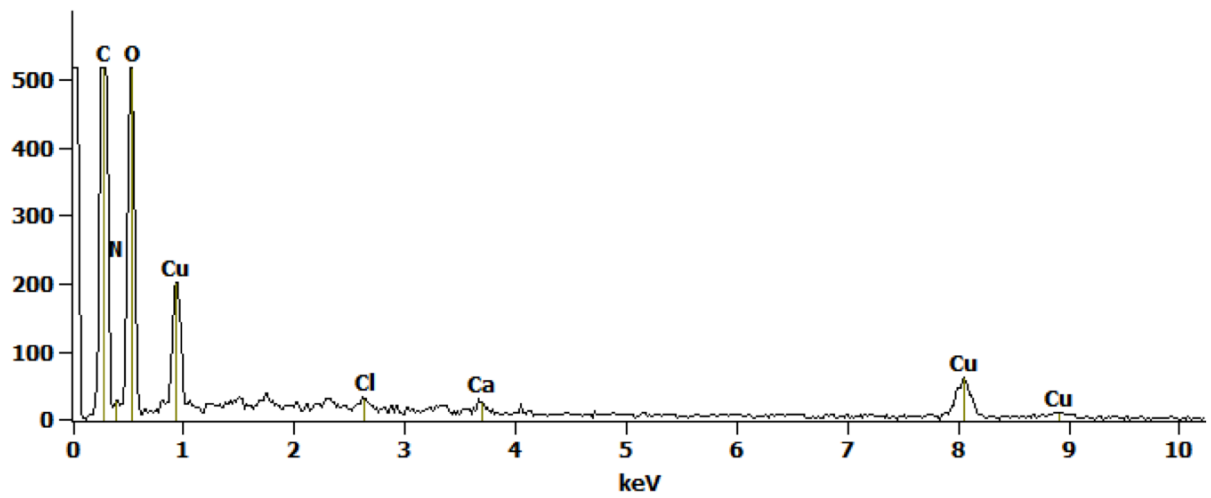
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MGTp02 vert 600x_pt2



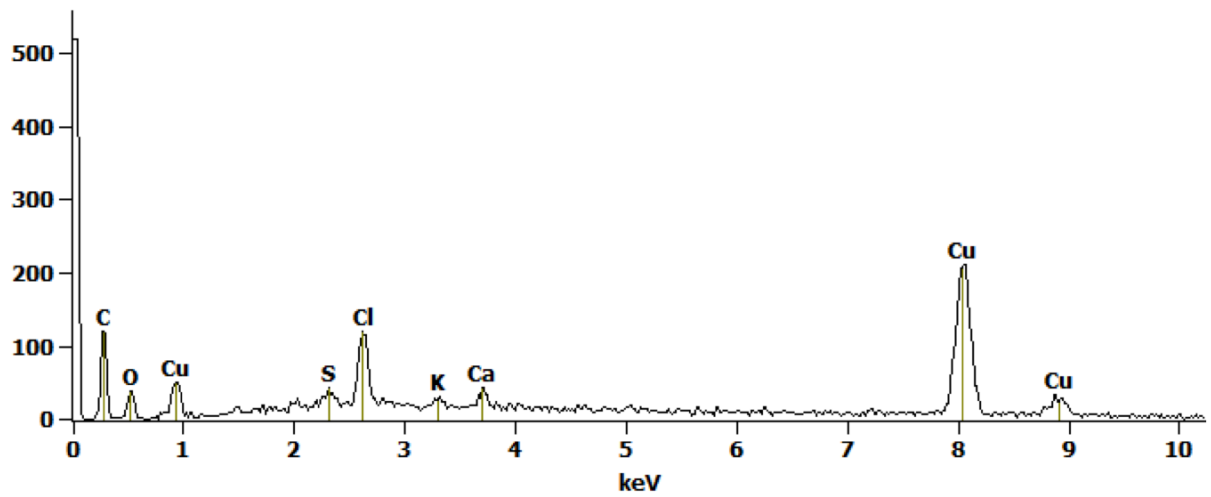
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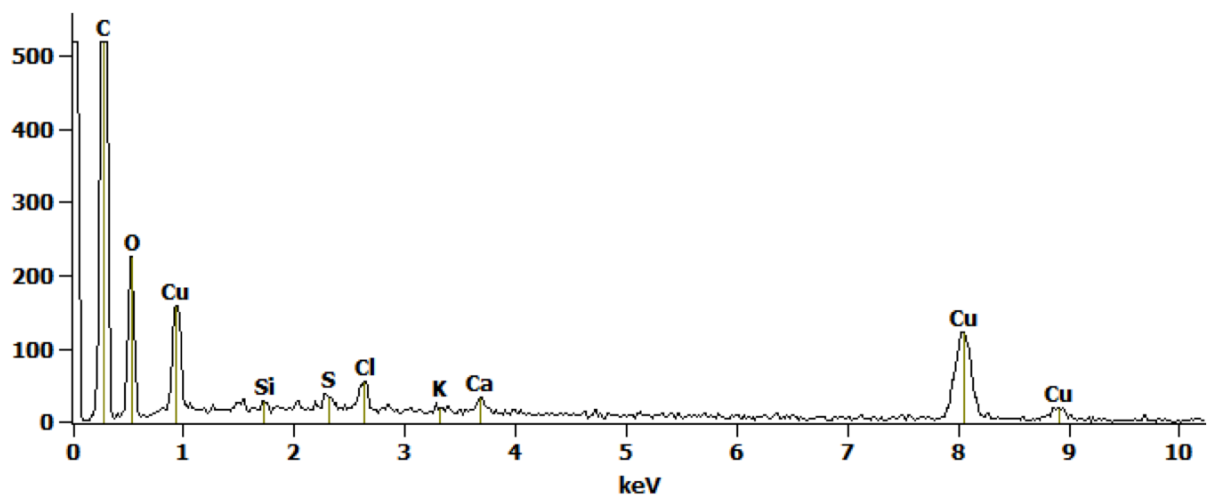
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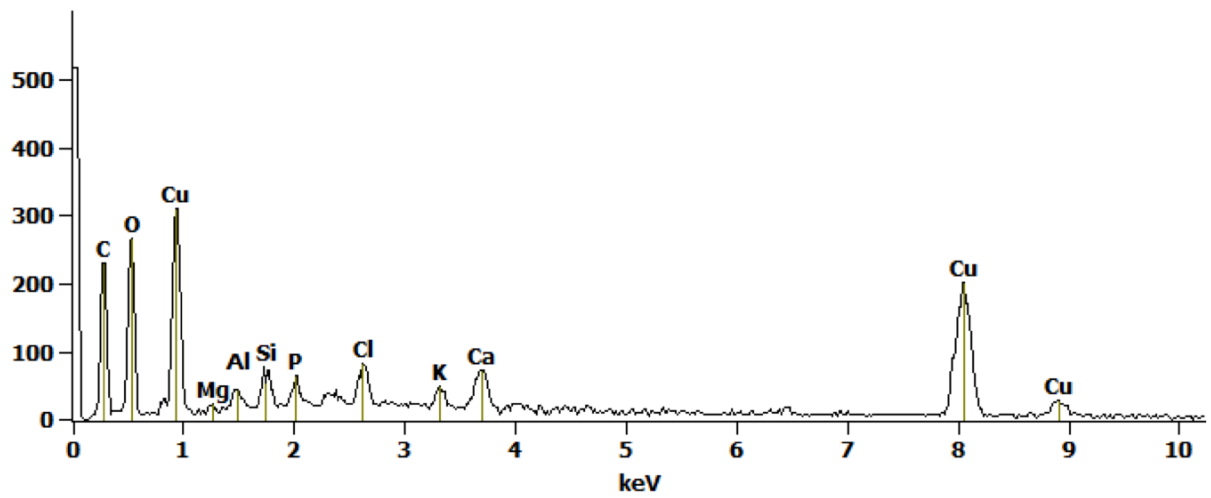
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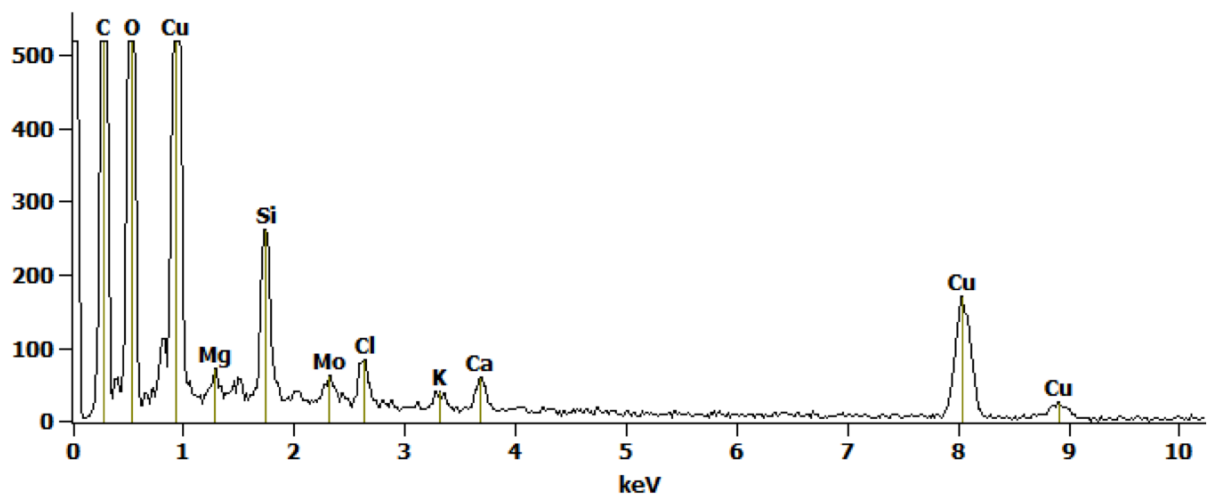
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MGTp02 vert 600x_pt7



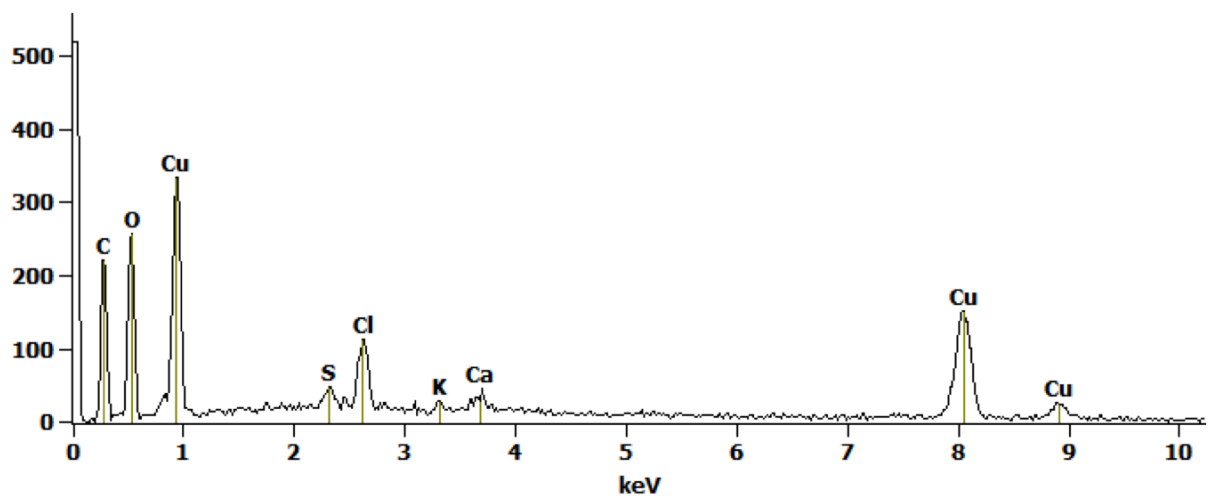
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MGTp02 vert 600x_pt8



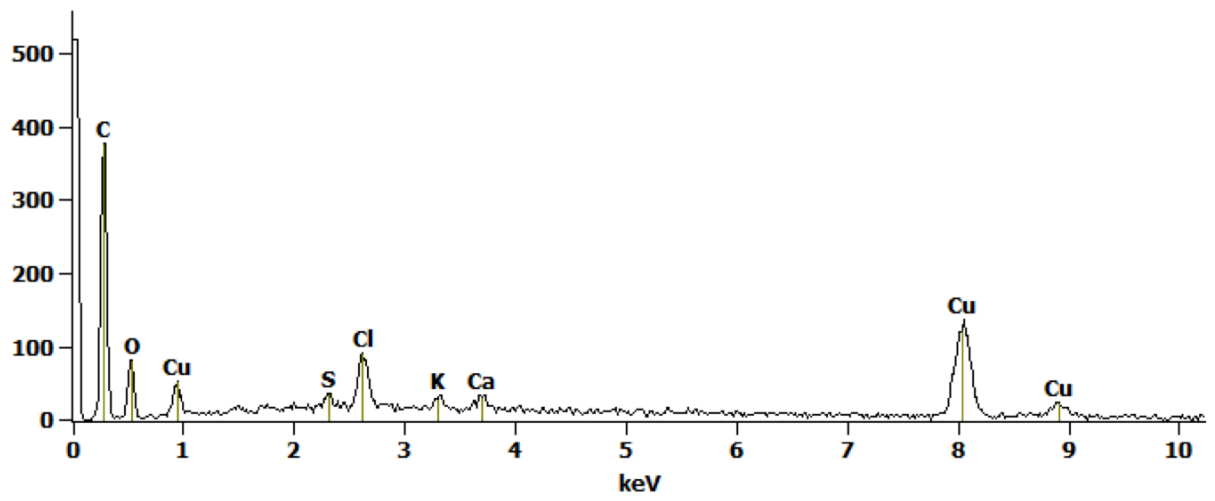
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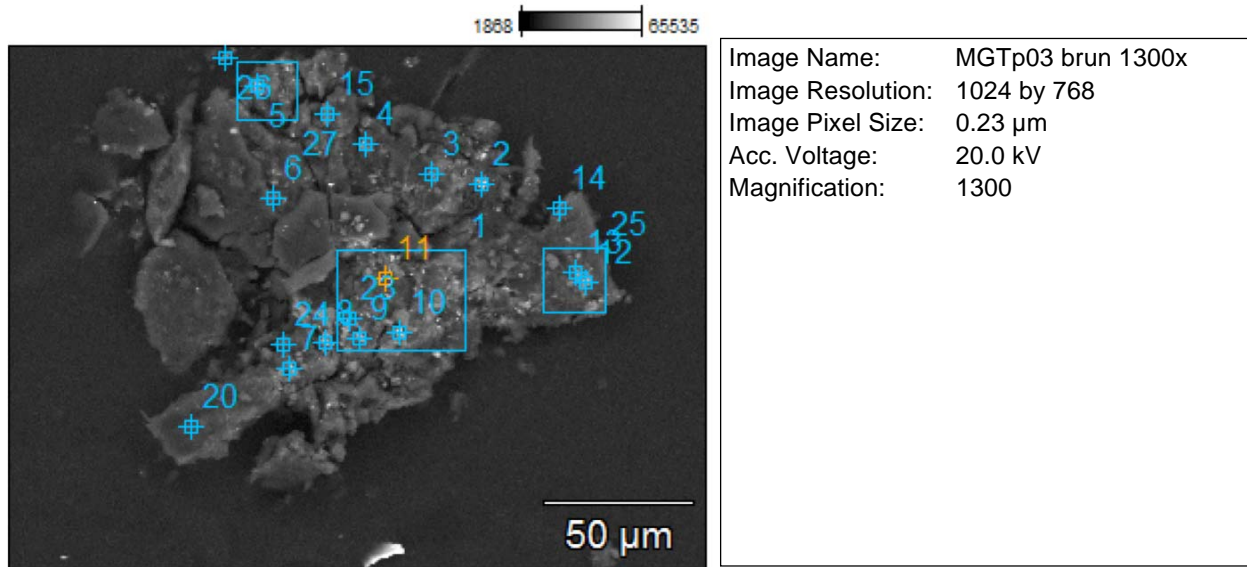


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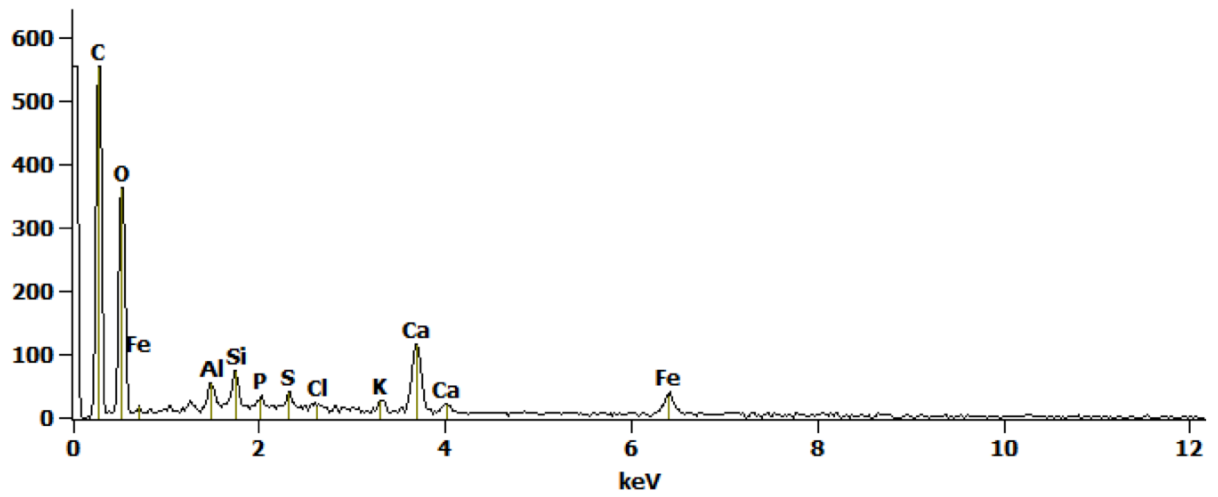


MGTp03 brun 1300x



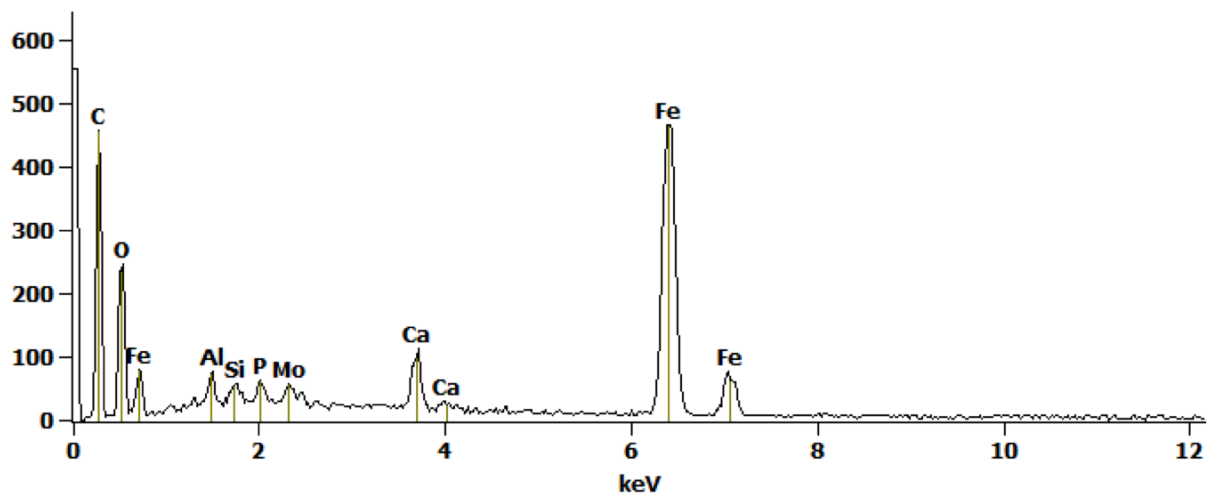
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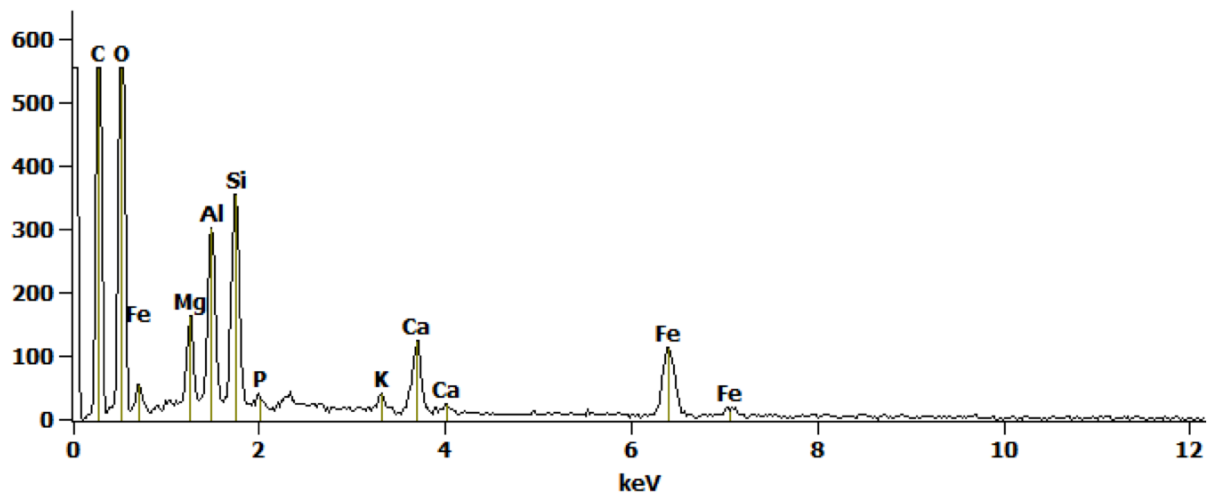
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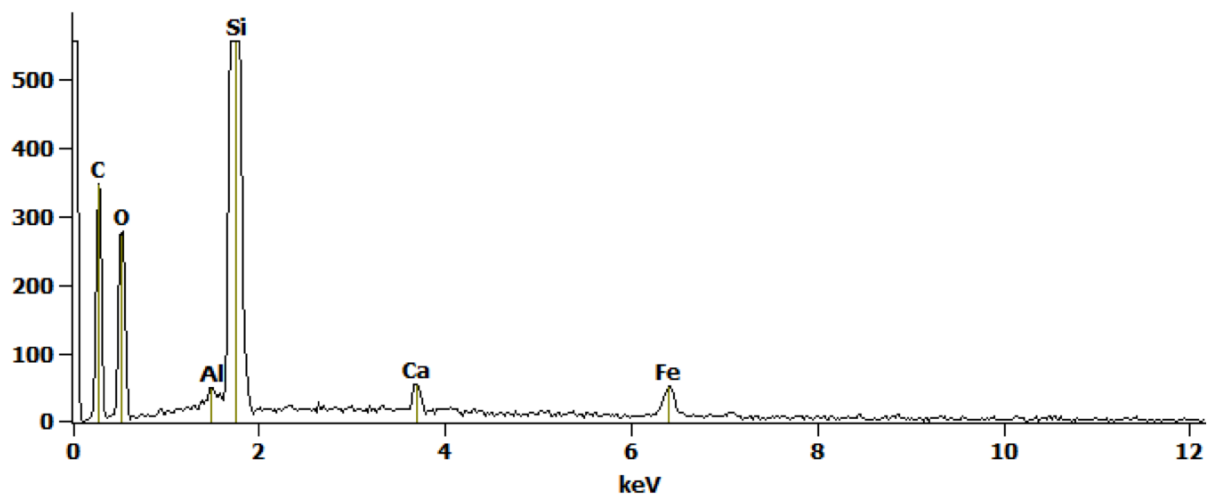
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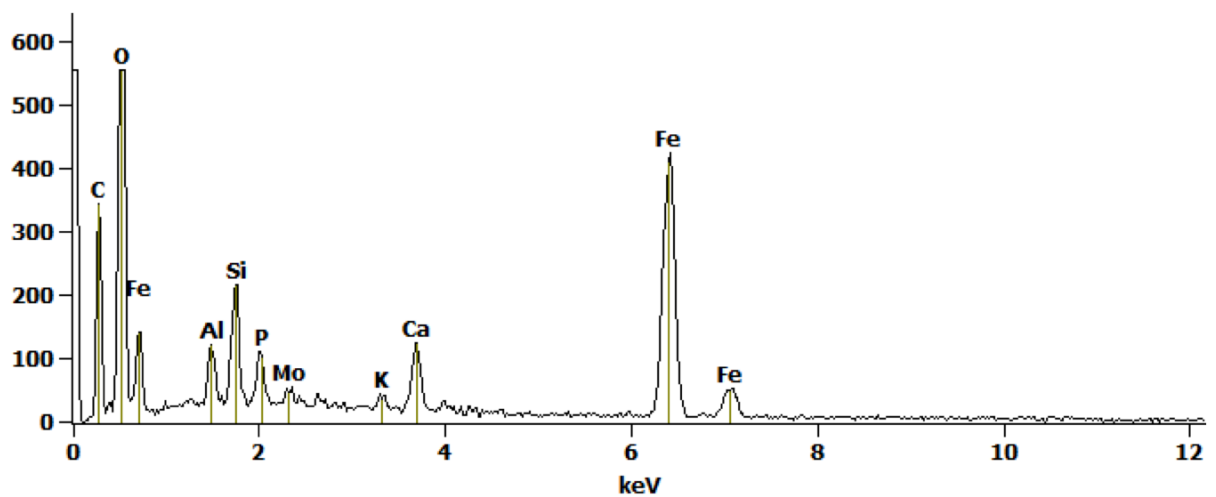
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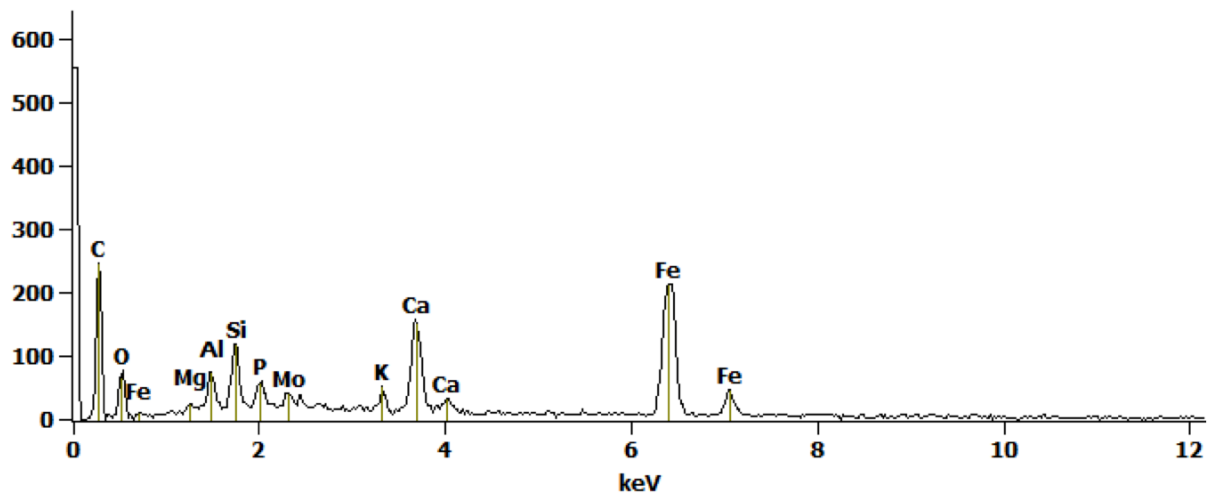
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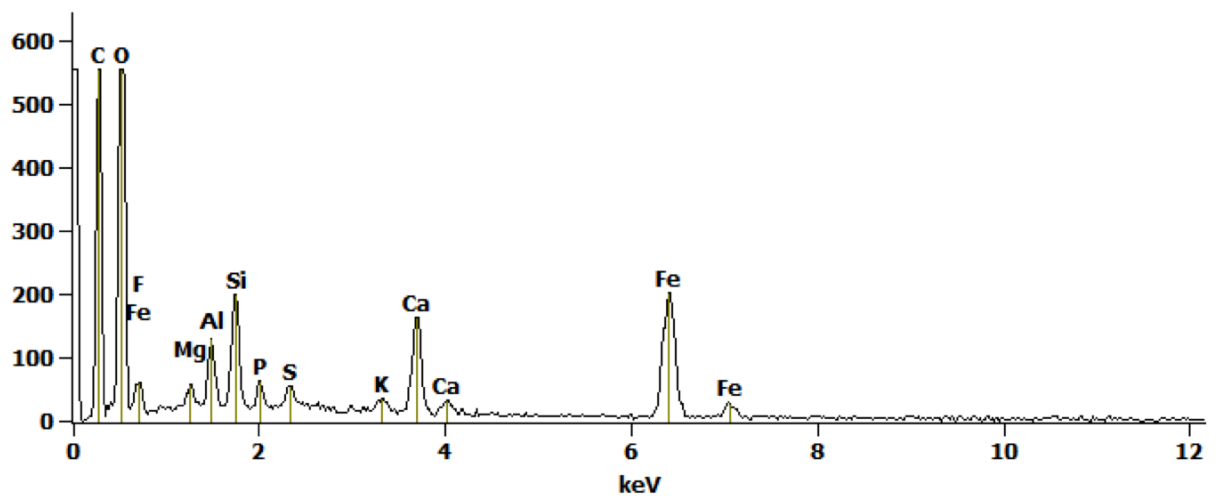
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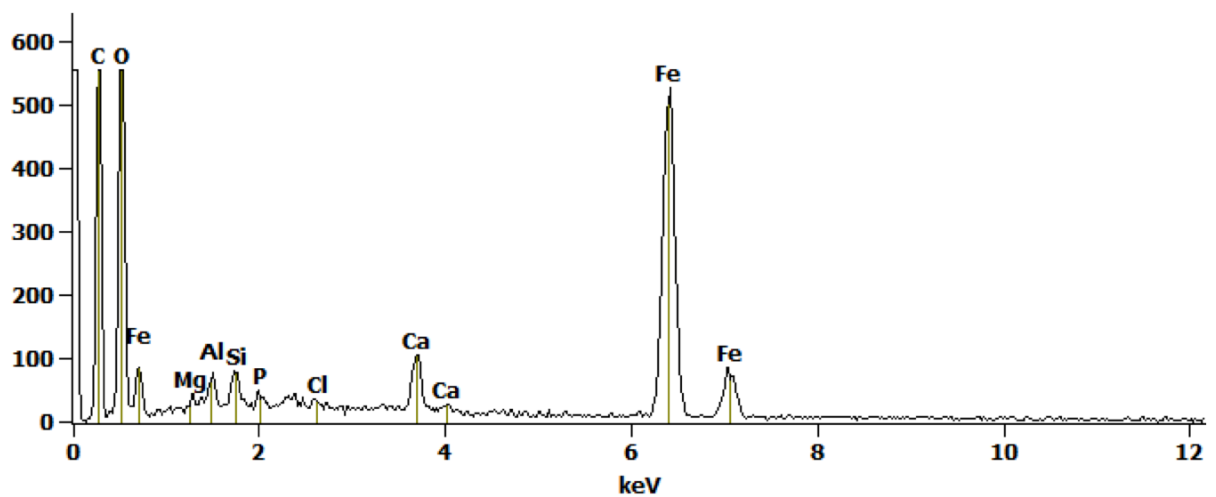
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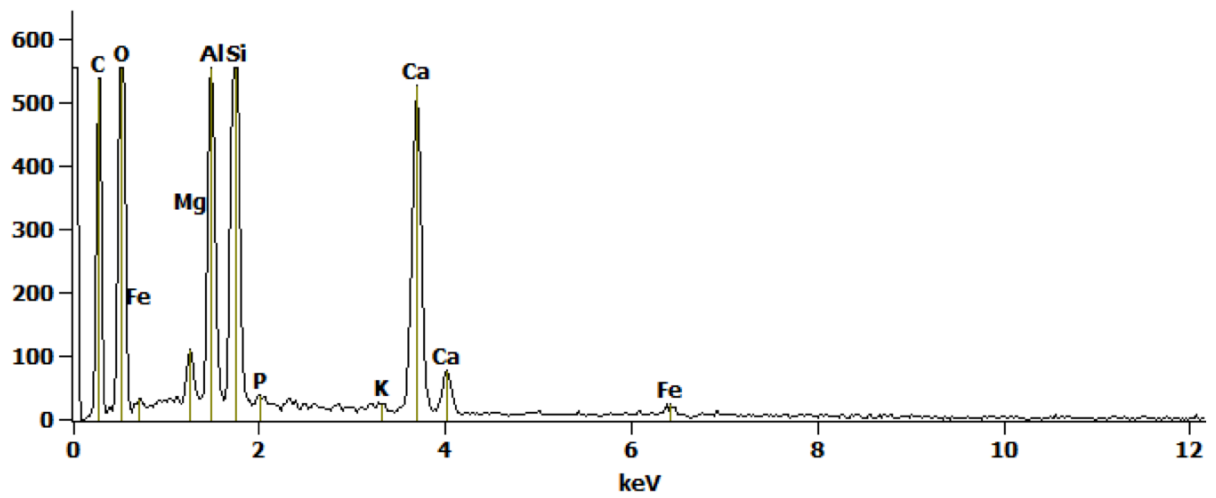
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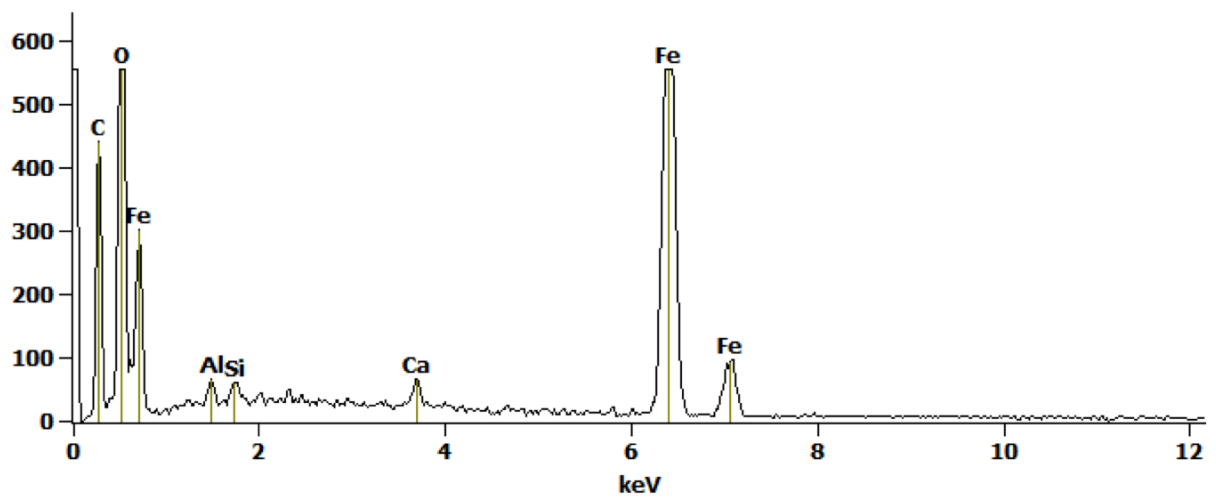
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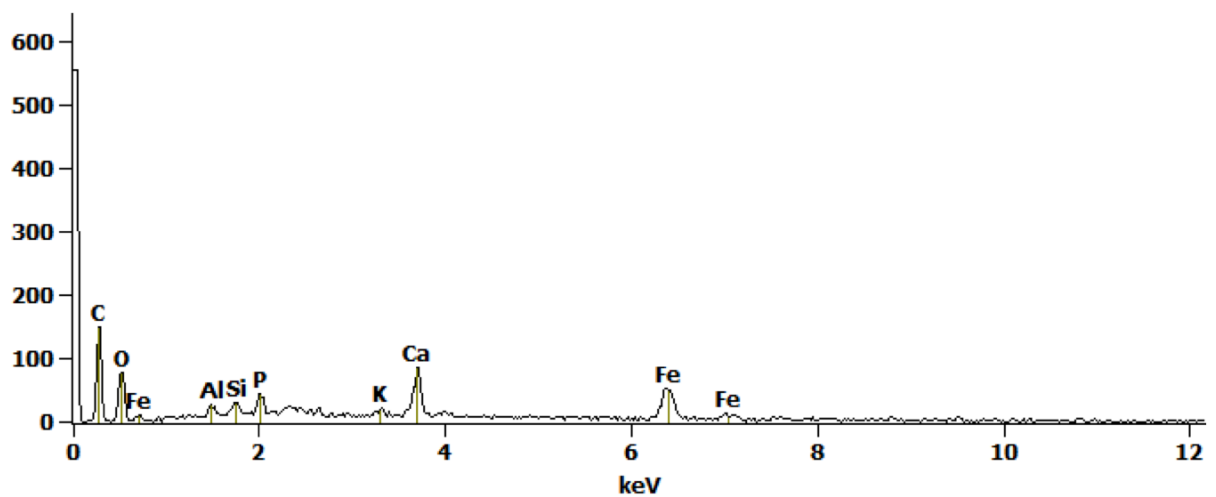
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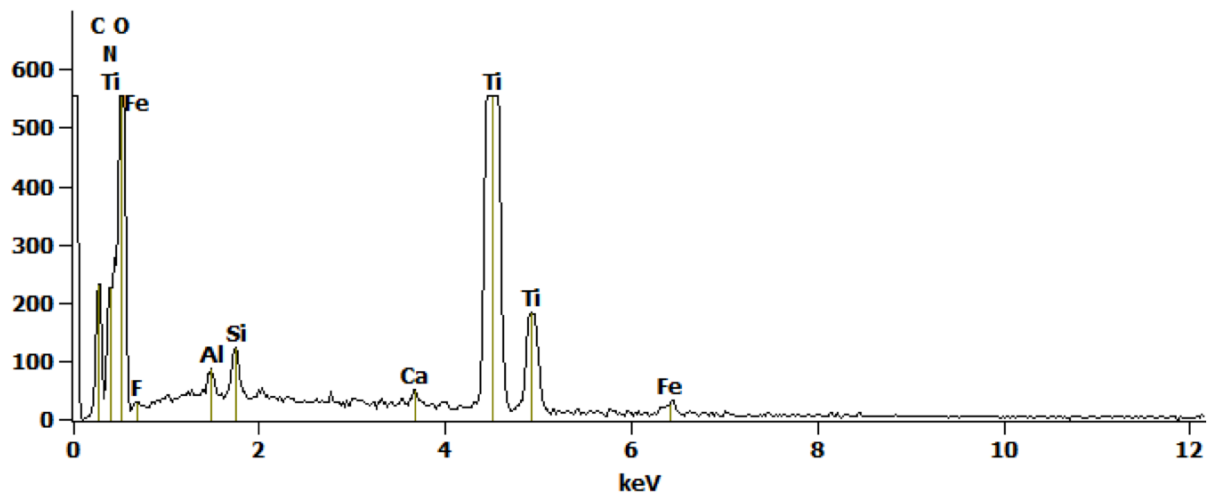
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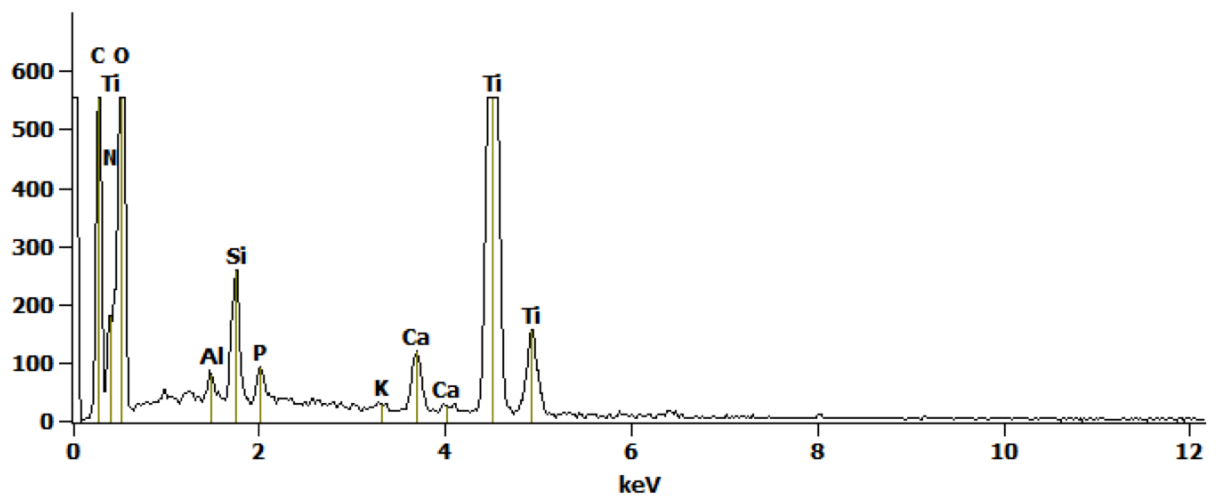
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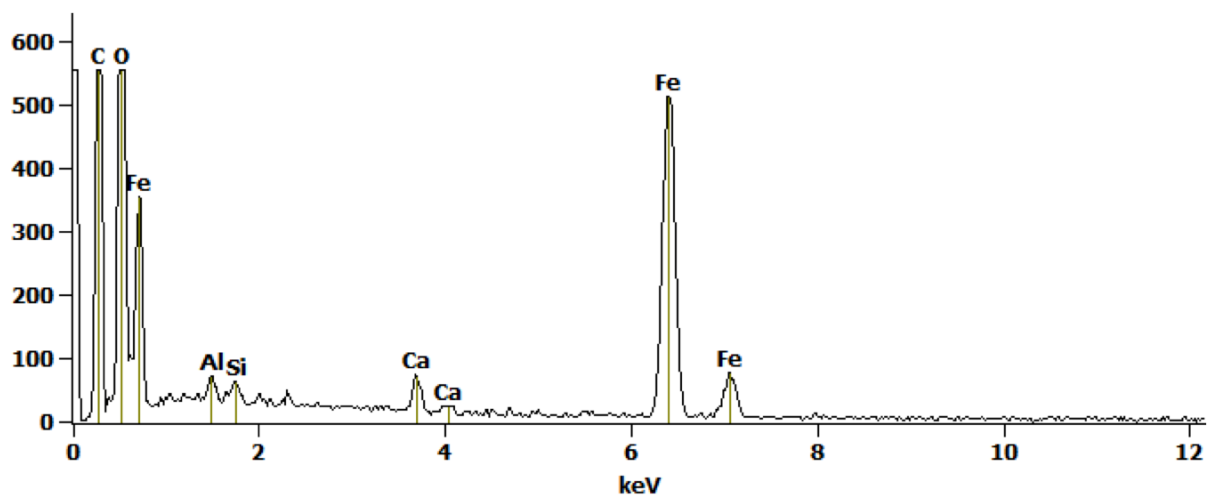
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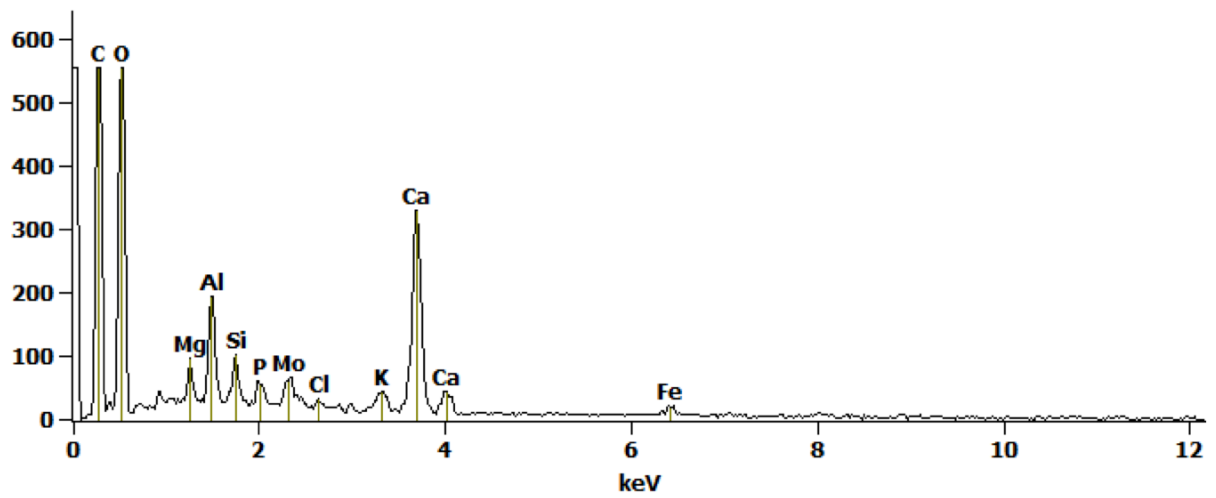
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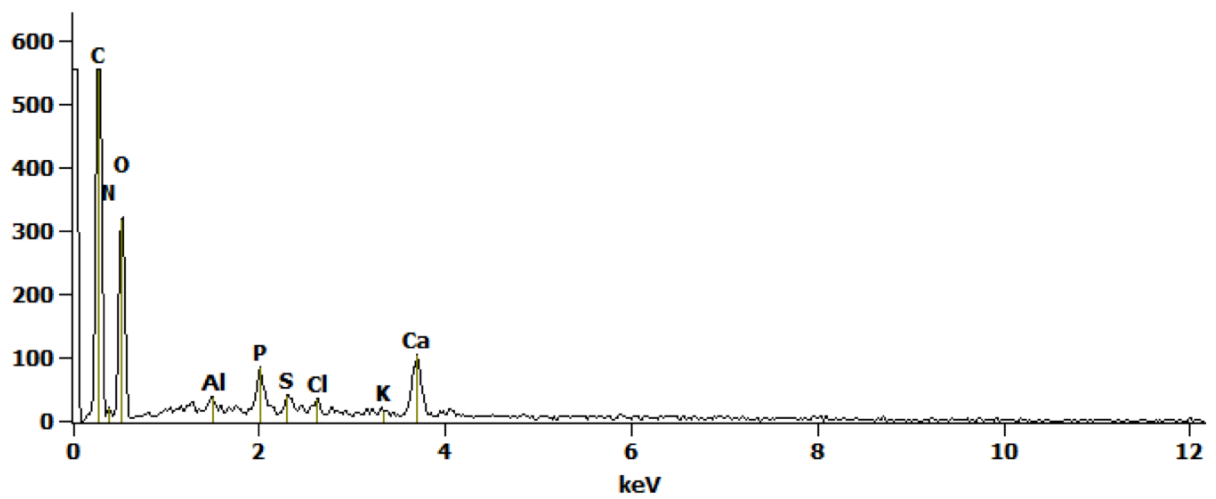
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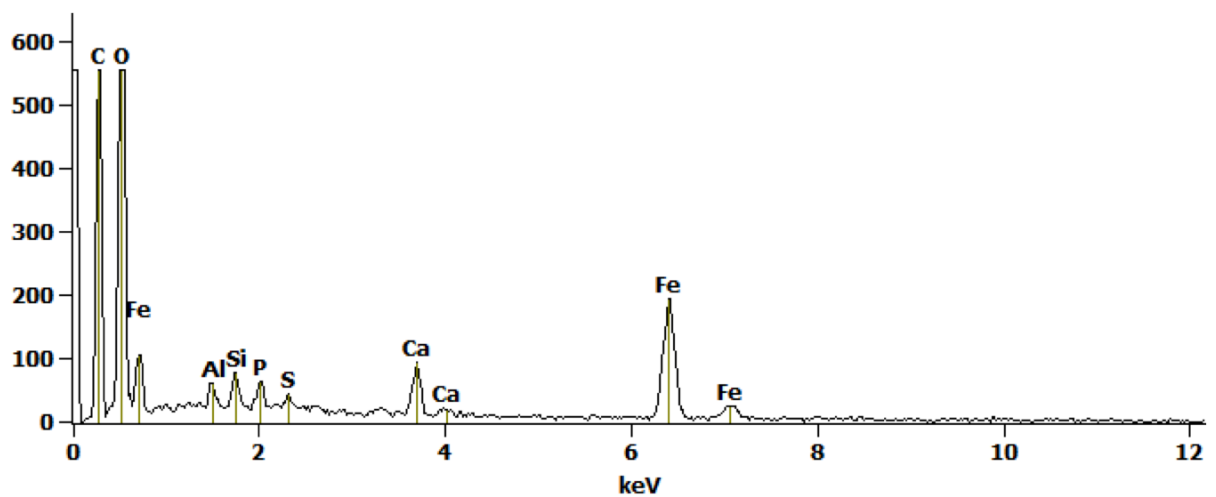
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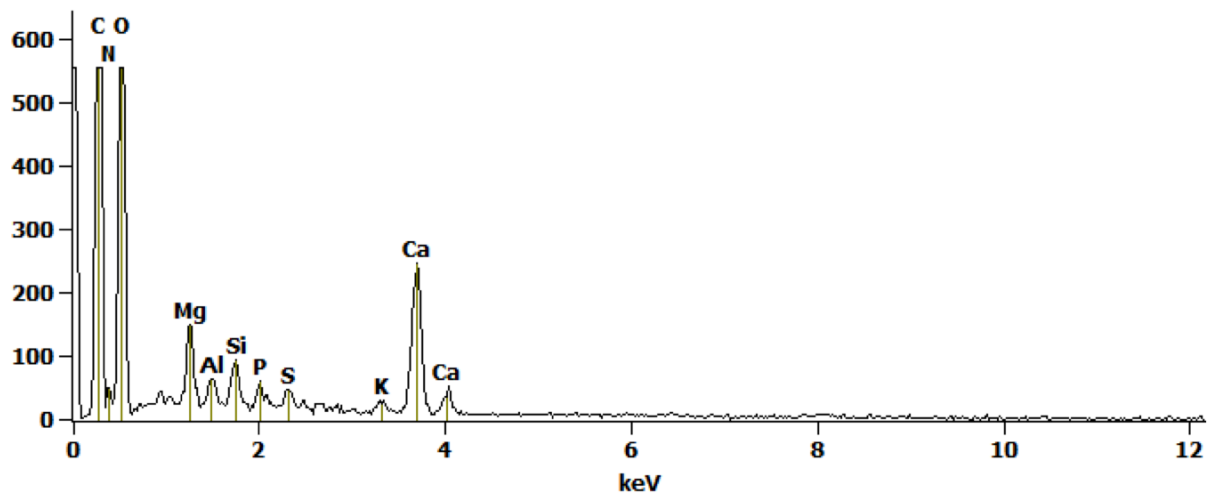
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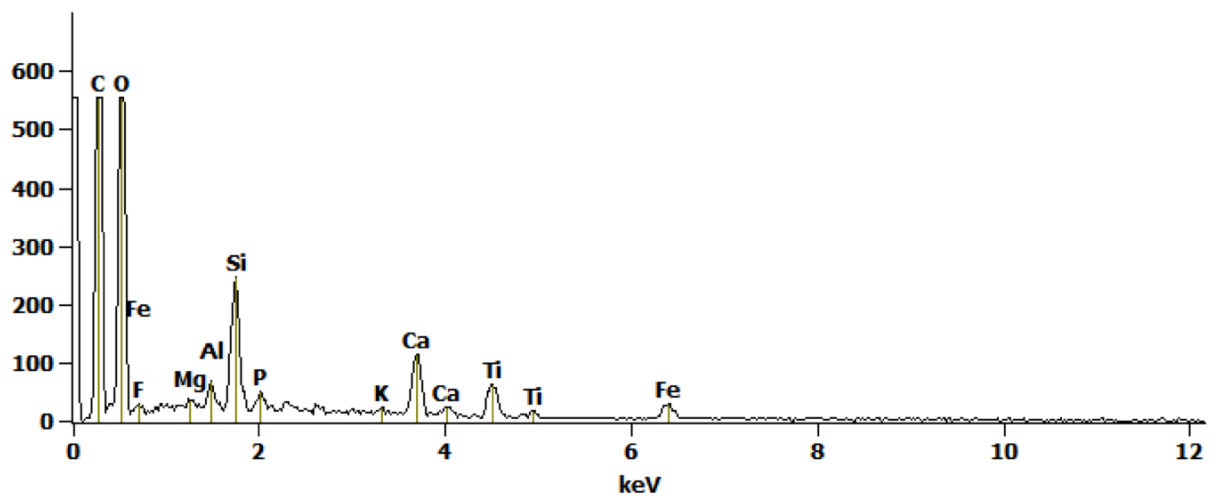
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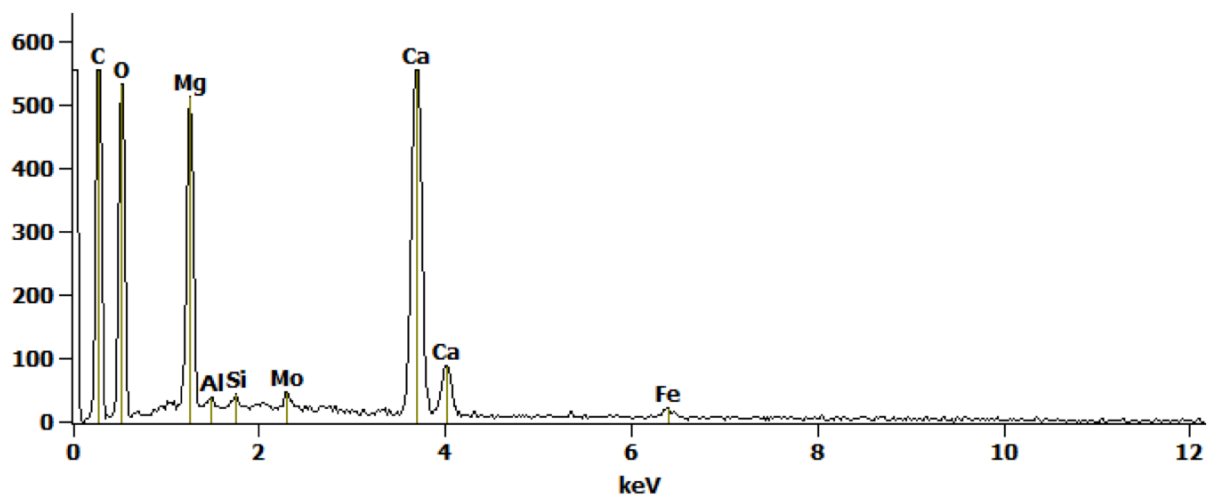
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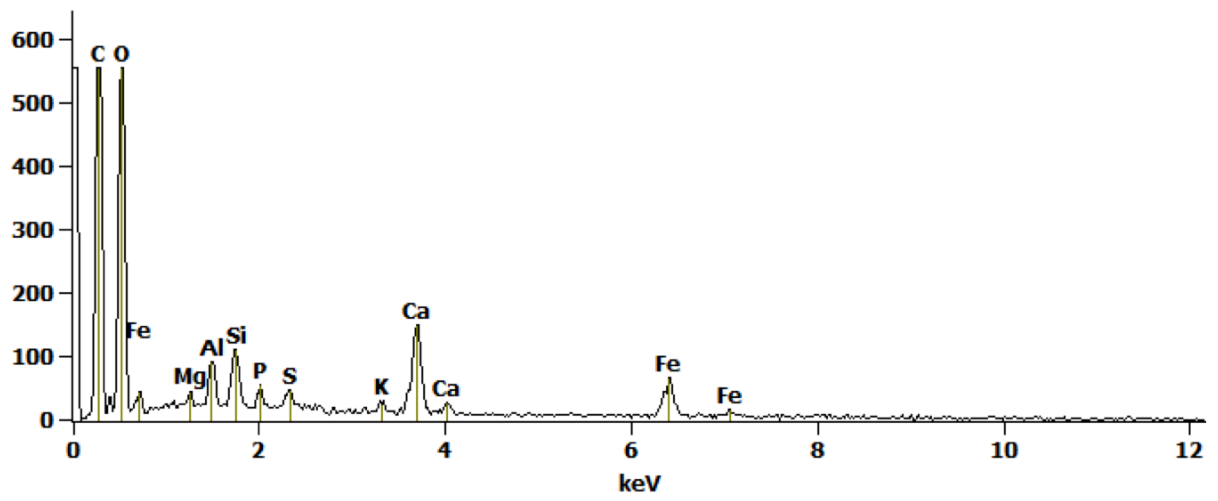
Full scale counts: 554

MGTp03 brun 1300x_pt26



Full scale counts: 554

MGTp03 brun 1300x_pt27



MGCp01 rouge 2750x

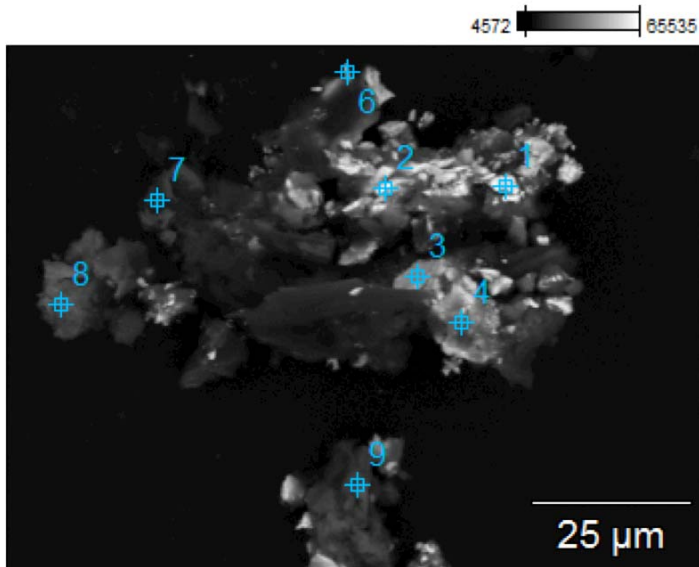
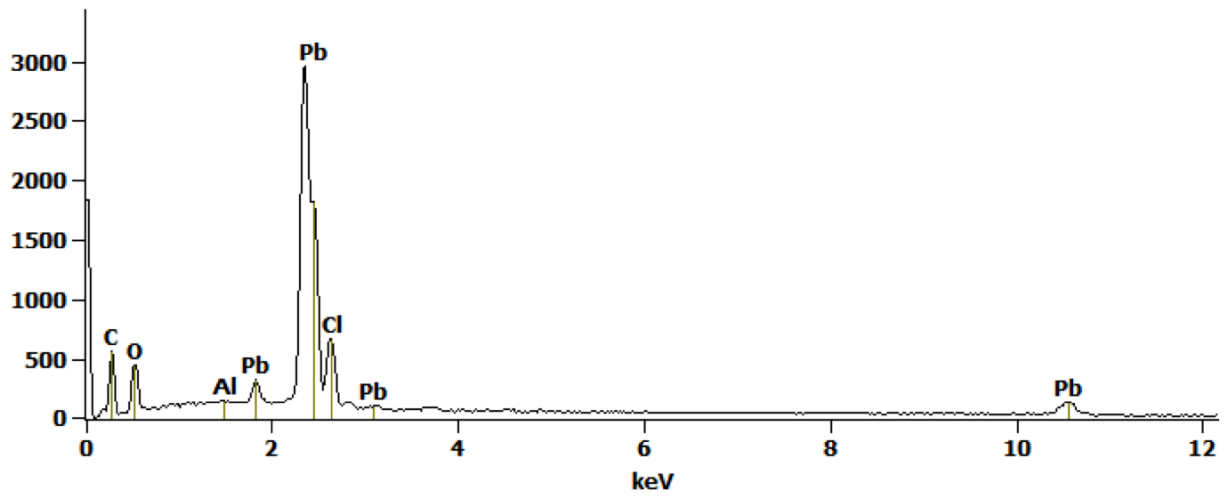


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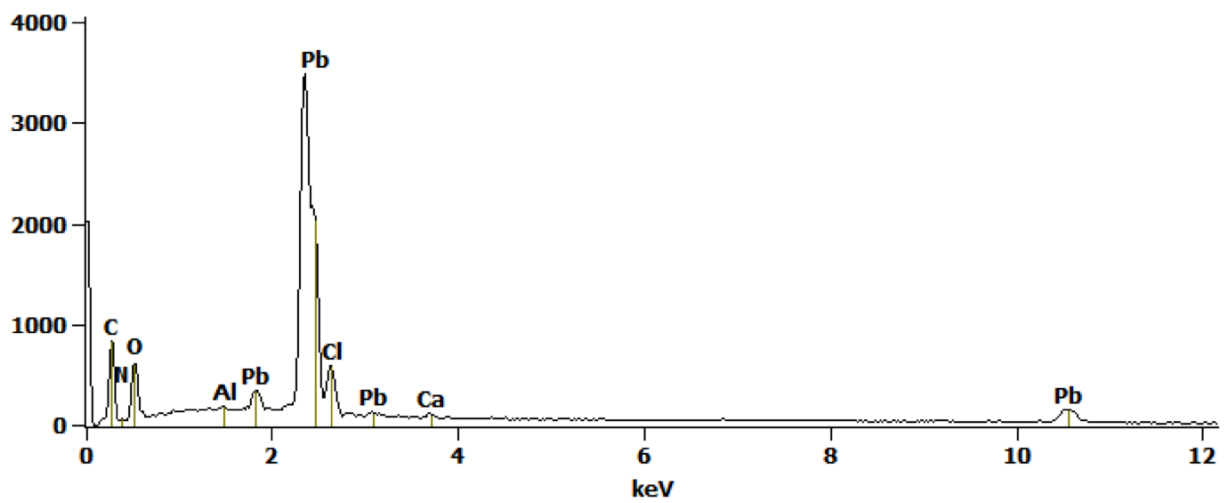
Full scale counts: 2958

MGCp01 rouge 2750x_pt1



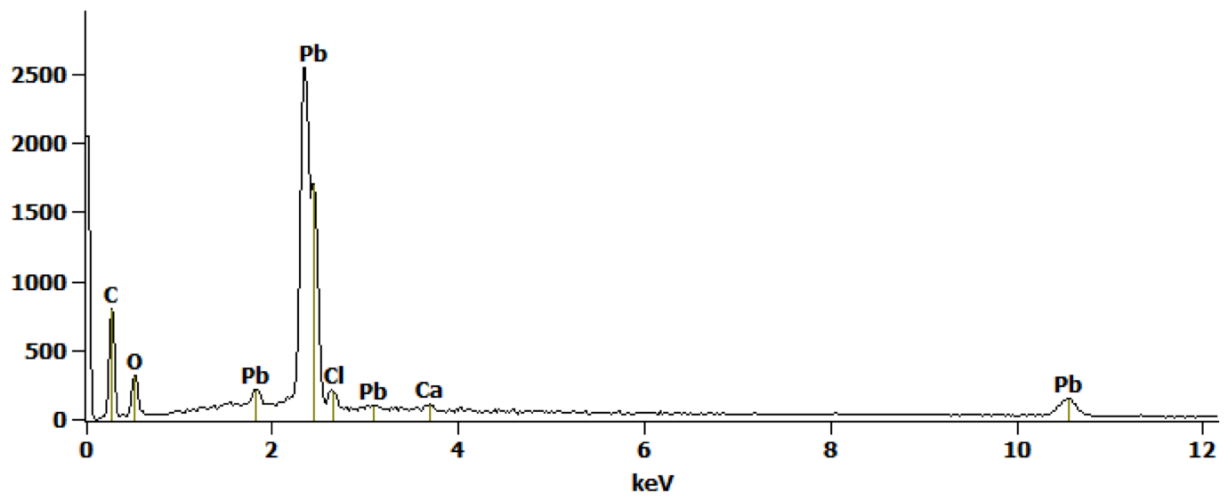
Full scale counts: 3488

MGCp01 rouge 2750x_pt2



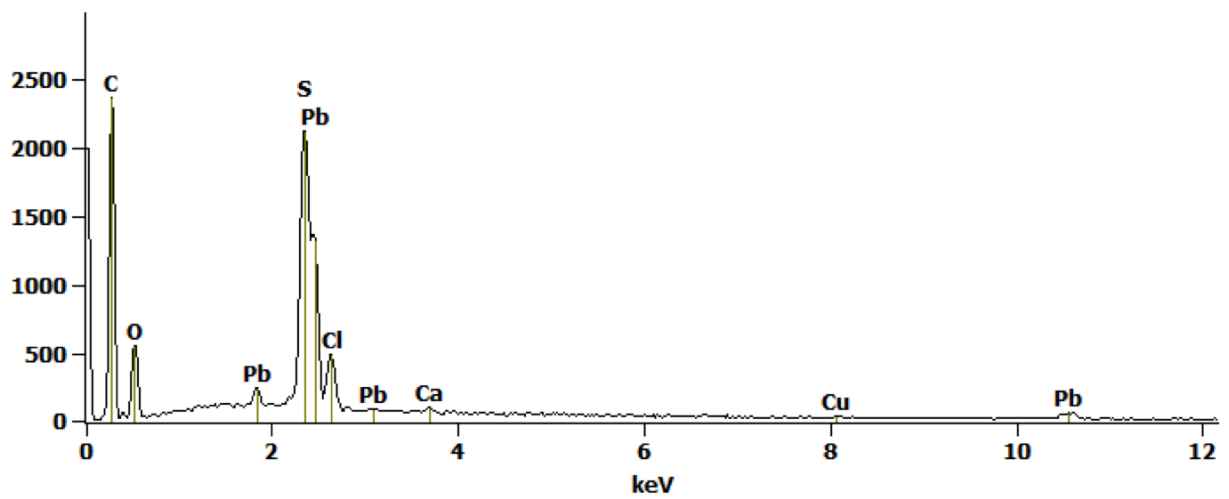
Full scale counts: 2541

MGCp01 rouge 2750x_pt3



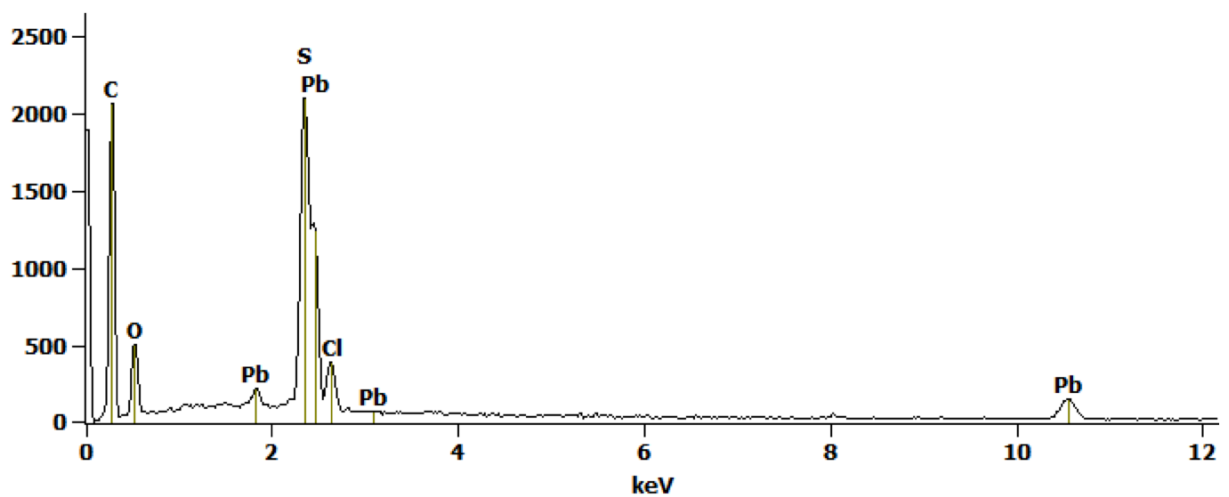
Full scale counts: 2363

MGCp01 rouge 2750x_pt4



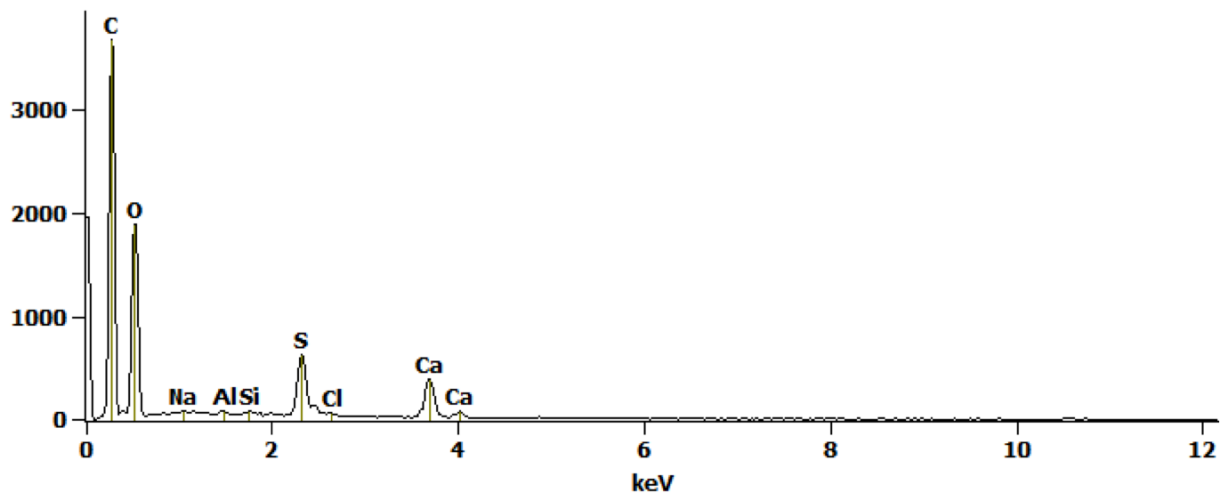
Full scale counts: 2095

MGCp01 rouge 2750x_pt6



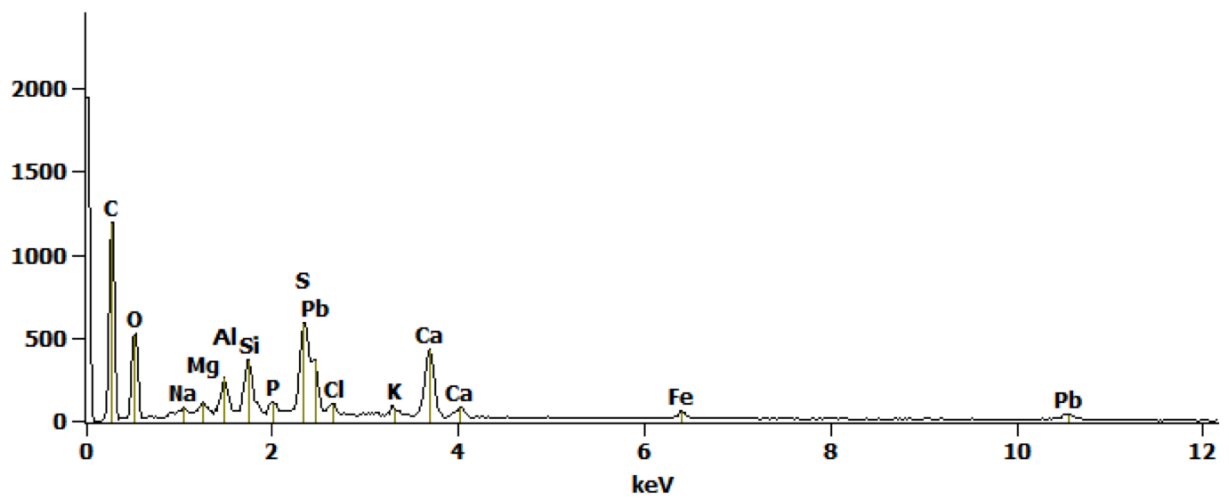
Full scale counts: 3662

MGCp01 rouge 2750x_pt7



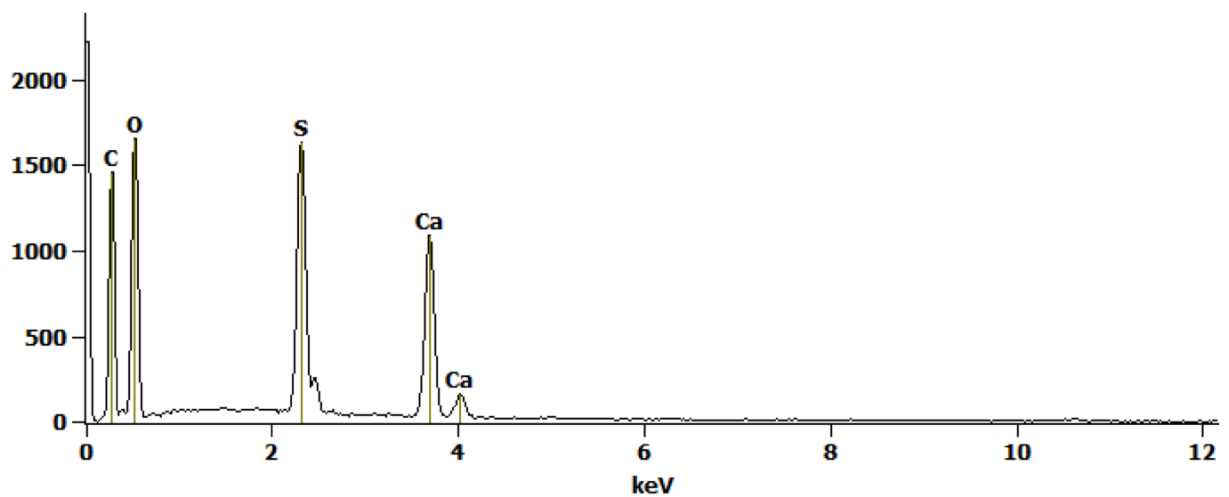
Full scale counts: 1942

MGCp01 rouge 2750x_pt8



Full scale counts: 2218

MGCp01 rouge 2750x_pt9



MGCp02 vert 1400x

4222 65535

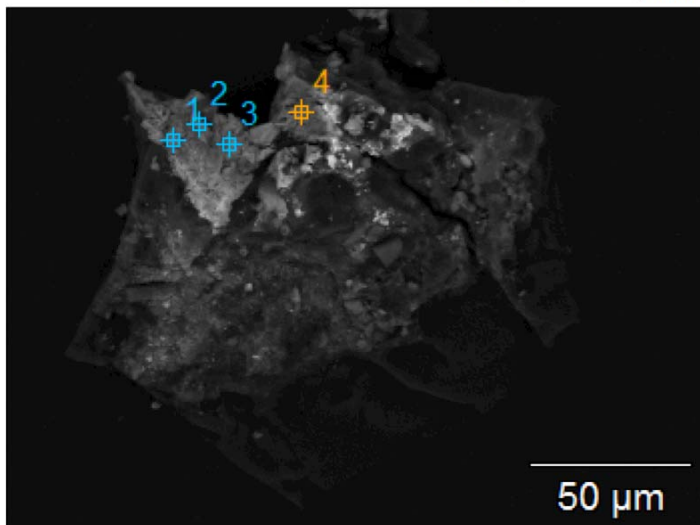
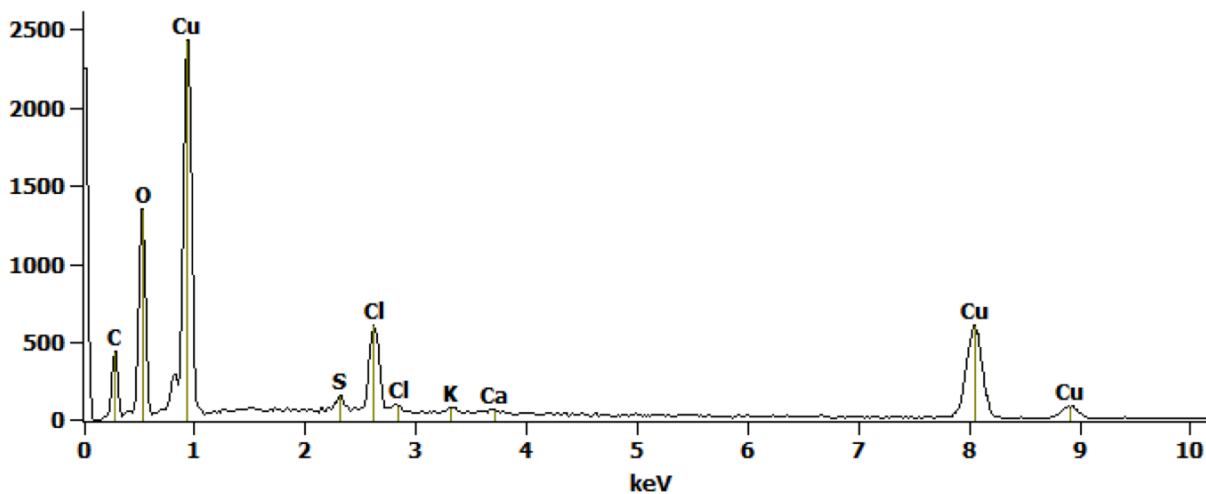


Image Name: MGCp02 vert 1400x
Image Resolution: 1024 by 768
Image Pixel Size: 0.21 µm
Acc. Voltage: 20.0 kV
Magnification: 1400

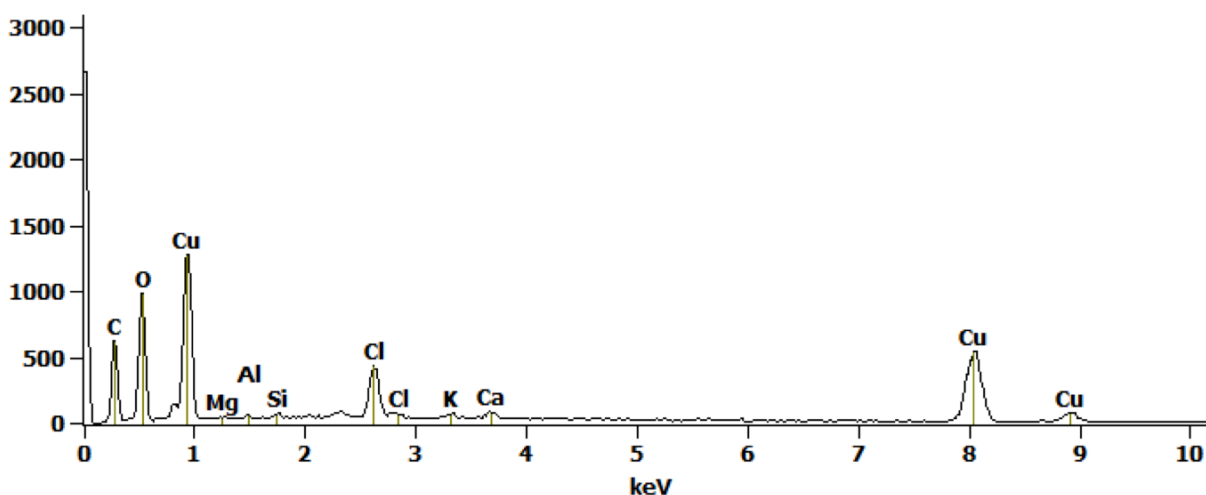
Full scale counts: 2429

MGCp02 vert 1400x_pt1



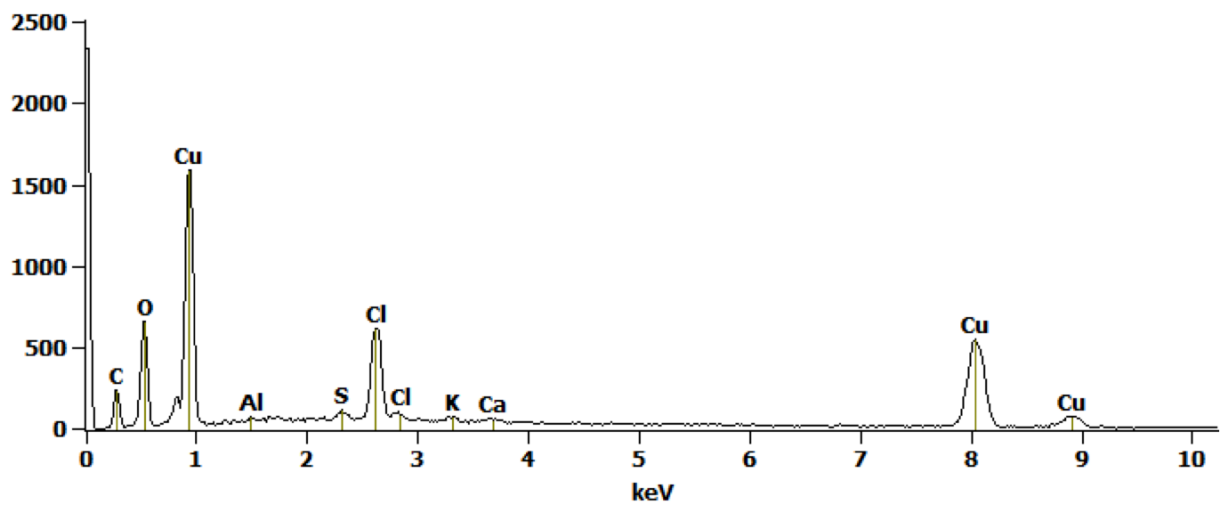
Full scale counts: 2667

MGCp02 vert 1400x_pt2



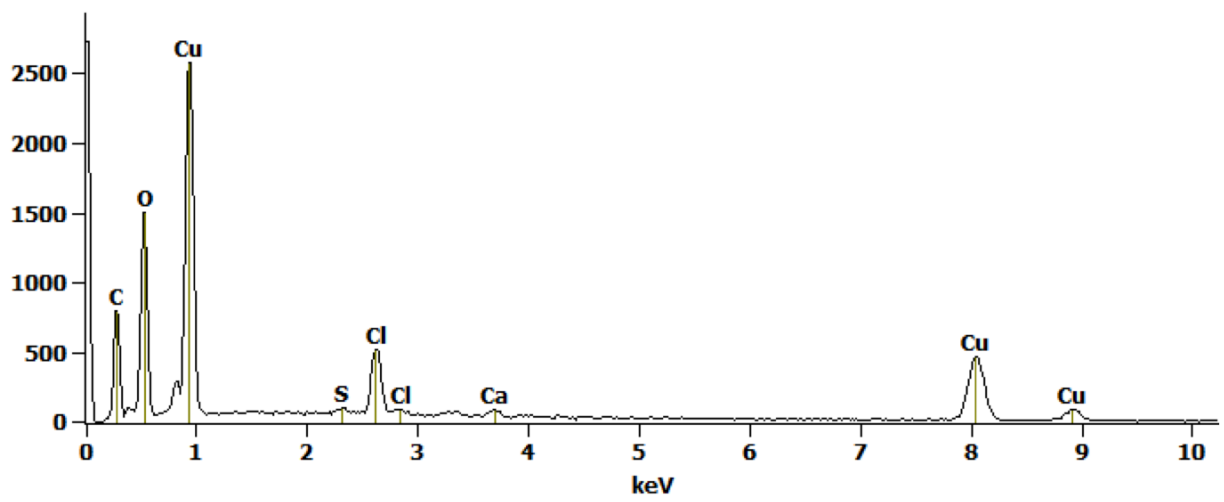
Full scale counts: 2334

MGCp02 vert 1400x_pt3



Full scale counts: 2727

MGCp02 vert 1400x_pt4



MGCp03 brun 500x

7270 85535

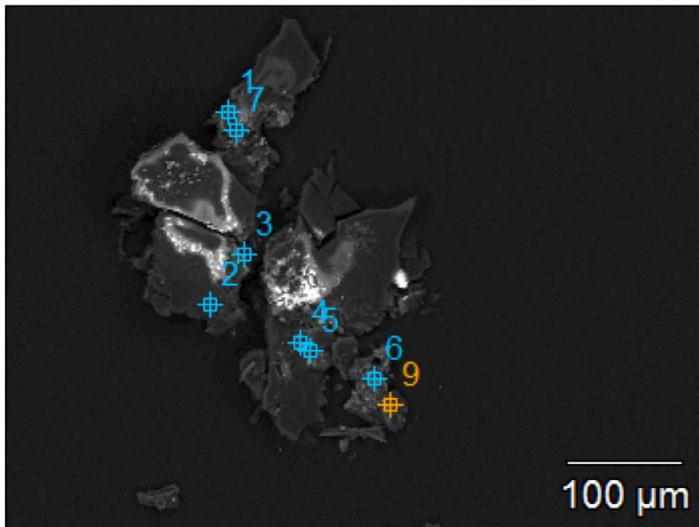
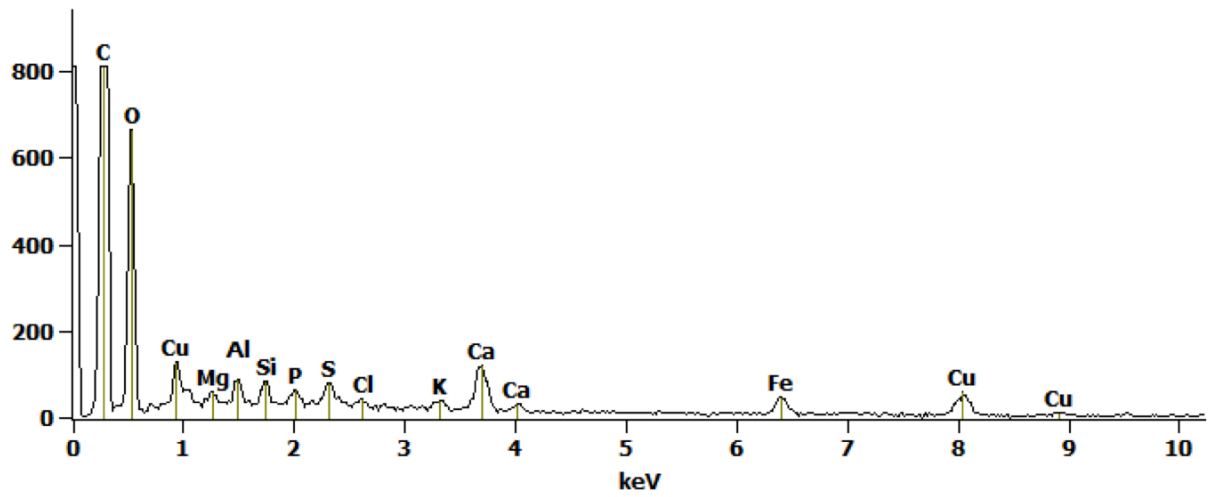


Image Name: MGCp03 brun 500x
Image Resolution: 1024 by 768
Image Pixel Size: 0.59 µm
Acc. Voltage: 20.0 kV
Magnification: 500

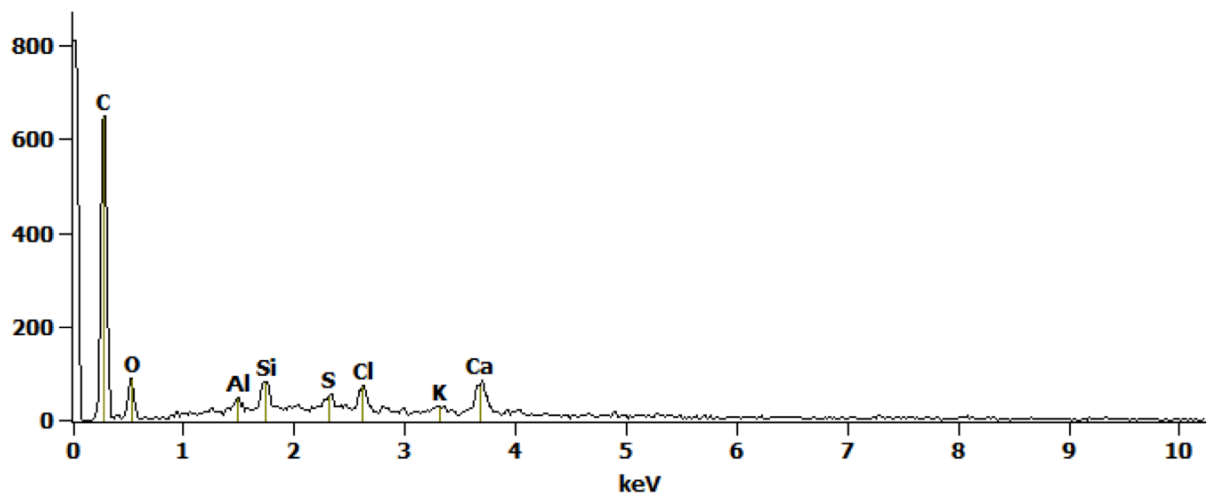
Full scale counts: 810

MGCp03 brun 500x_pt1



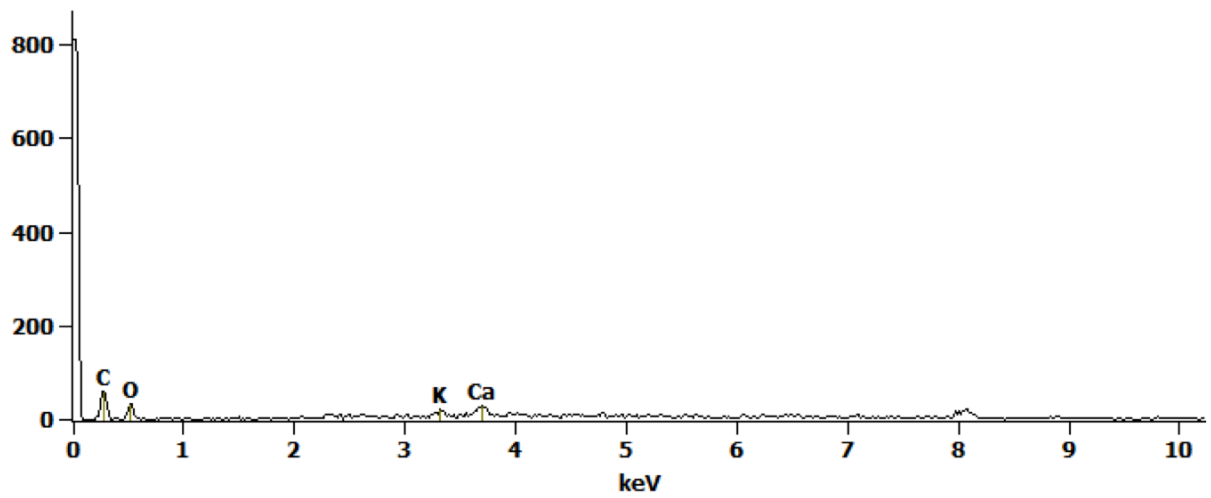
Full scale counts: 810

MGCp03 brun 500x_pt2



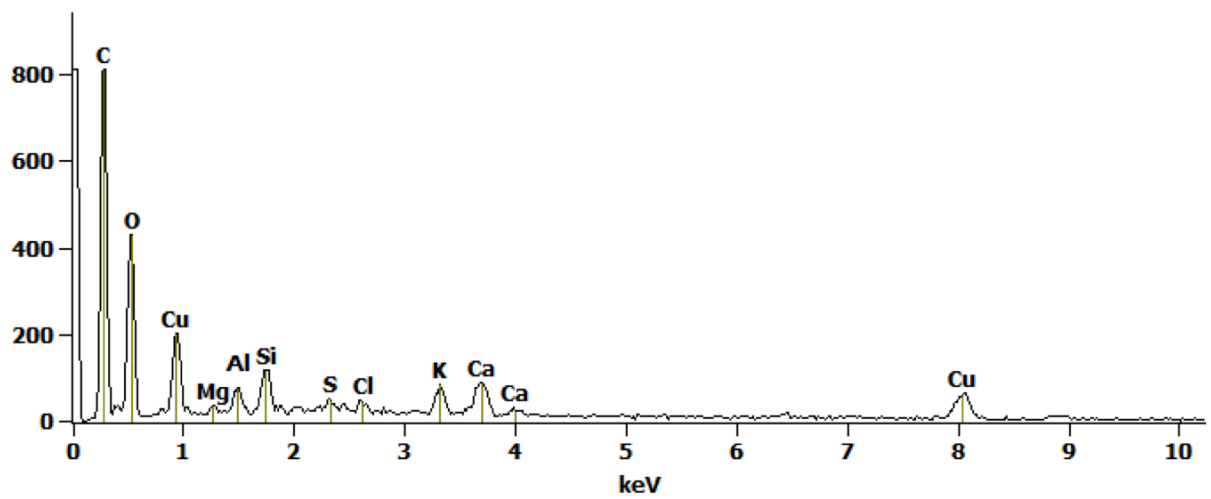
Full scale counts: 810

MGcP03 brun 500x_pt3



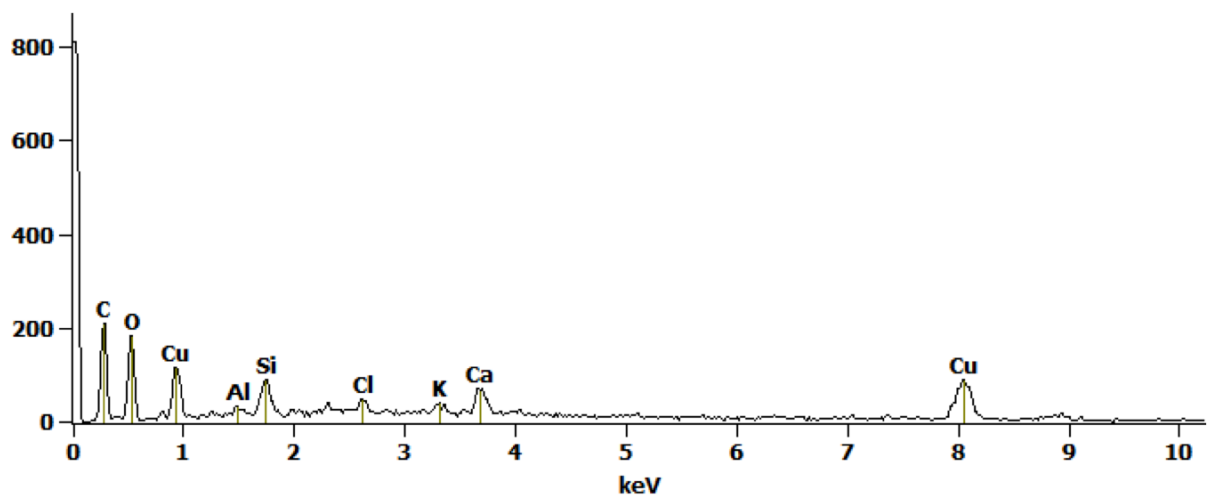
Full scale counts: 810

MGcP03 brun 500x_pt4



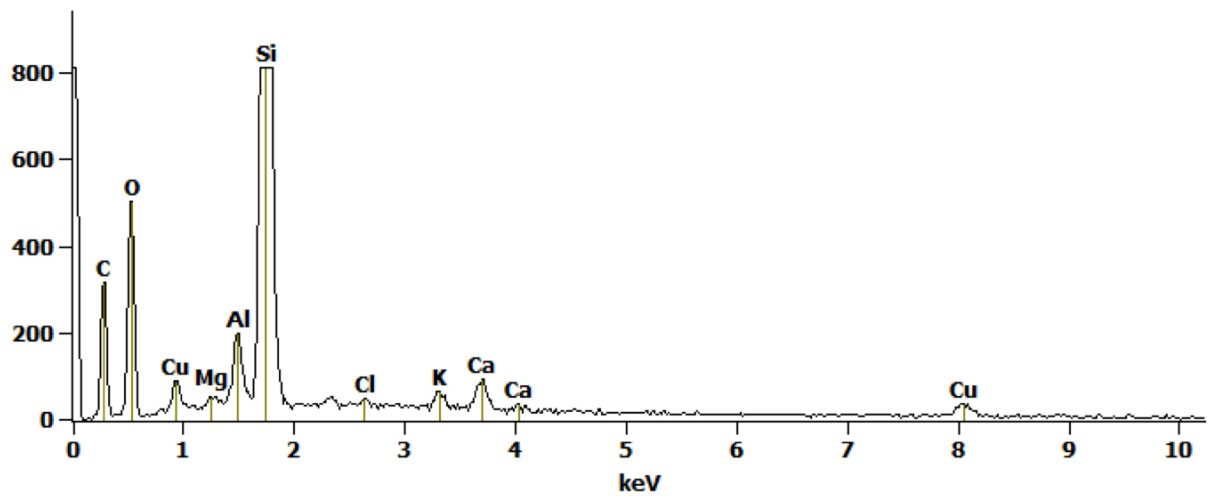
Full scale counts: 810

MGcP03 brun 500x_pt5



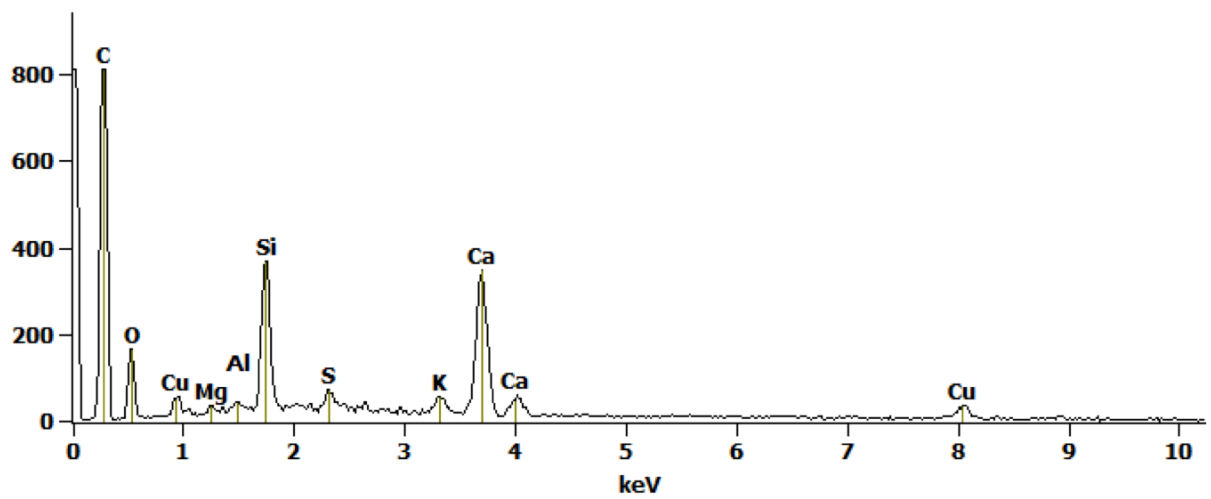
Full scale counts: 810

MGCp03 brun 500x_pt6



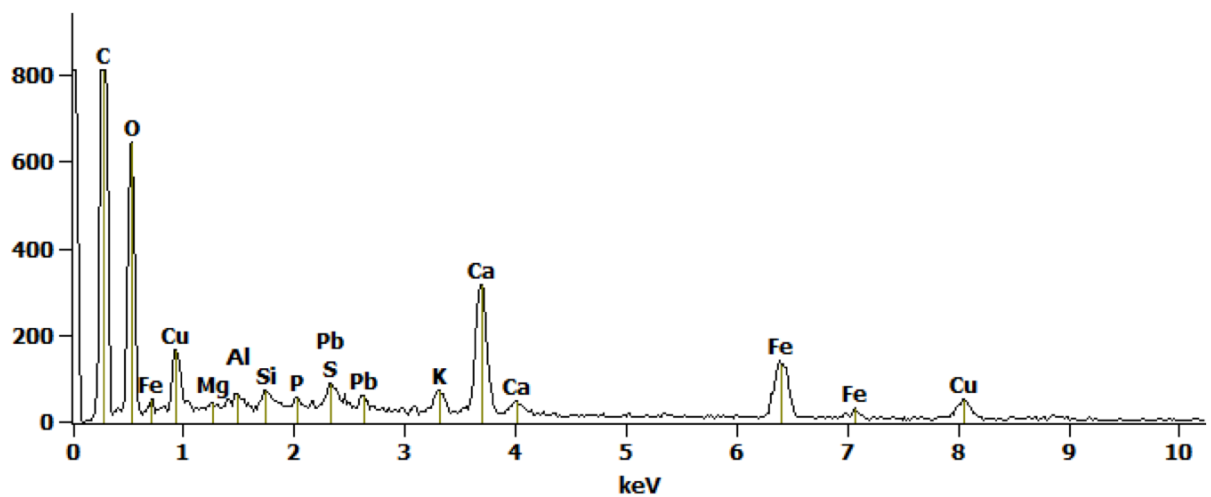
Full scale counts: 810

MGCp03 brun 500x_pt7



Full scale counts: 810

MGCp03 brun 500x_pt9



Interpretation

All of the components identified were available at the time of the suggested origin (around 1540). The combination identified on this Mercator Terrestrre/Celeste pair does, however, not completely match the pigment set apparently identified on another Mercator Terrestrre/Celeste pair, documented by Peters (1995). The article, however, was published in 1995 and does not state the source of the pigment identification. The copper oxalate identified in the green painted areas could possibly be a secondary product from (bio-)degradation of other copper pigments (Miller 2010, Zoppi 2010, Castro 2008). Raman spectra within the green particles do vary, such as do relative ratios of Cu to Cl in SEM-EDS analyses across the greenish particles. This heterogeneity suggests either degradation or use of a mineral product.

References

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- Das & Hendry 2011: Application of Raman spectroscopy to identify iron minerals commonly found in mine wastes. *Chemical Geology*, 290 (3-4), 101-108.
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- Zoppi et al. 2010: Metal oxalates in paints: a Raman investigation on the relative reactivities of different pigments to oxalic acid solutions. *Anal Bioanal Chem*, 397, 841-849.

The results relate exclusively to the sample material taken on-site. The analyses have been performed to current lab practices and are delivered without manipulation. Interpretation may depend on experience, knowledge and databases available at the time, and thus we do not take any financial liability for consequences arising from the use of this analytical data.

We hope to deliver helpful information to your satisfaction.

Yours sincerely,

Dr. Nadim Scherrer
HKB Art technological Laboratory