INSTITUTO DE RESTAURACIÓN DEL PATRIMONIO
INSTITUTO UNIVERSITARIO DE INVESTIGACIÓN

FIB-FESEM-EDX study of the painted surface of the Mikado 141F engine

R+D Project AICO/2021/095
"Developing strategies against climate change for the preventive conservation of Valencian railway-tramway heritage"

Financial support by *Consellería de Innovación, Universidades, Ciencia y Sociedad Digital. Dirección General de Ciencia e Investigación. Subvenciones para la realización de proyectos I+D+i desarrollados por grupos de investigación consolidados 2021*

Authors:

María Teresa Doménech Carbó
Miguel F. Silva

Date:
Valencia, 13th July 2022

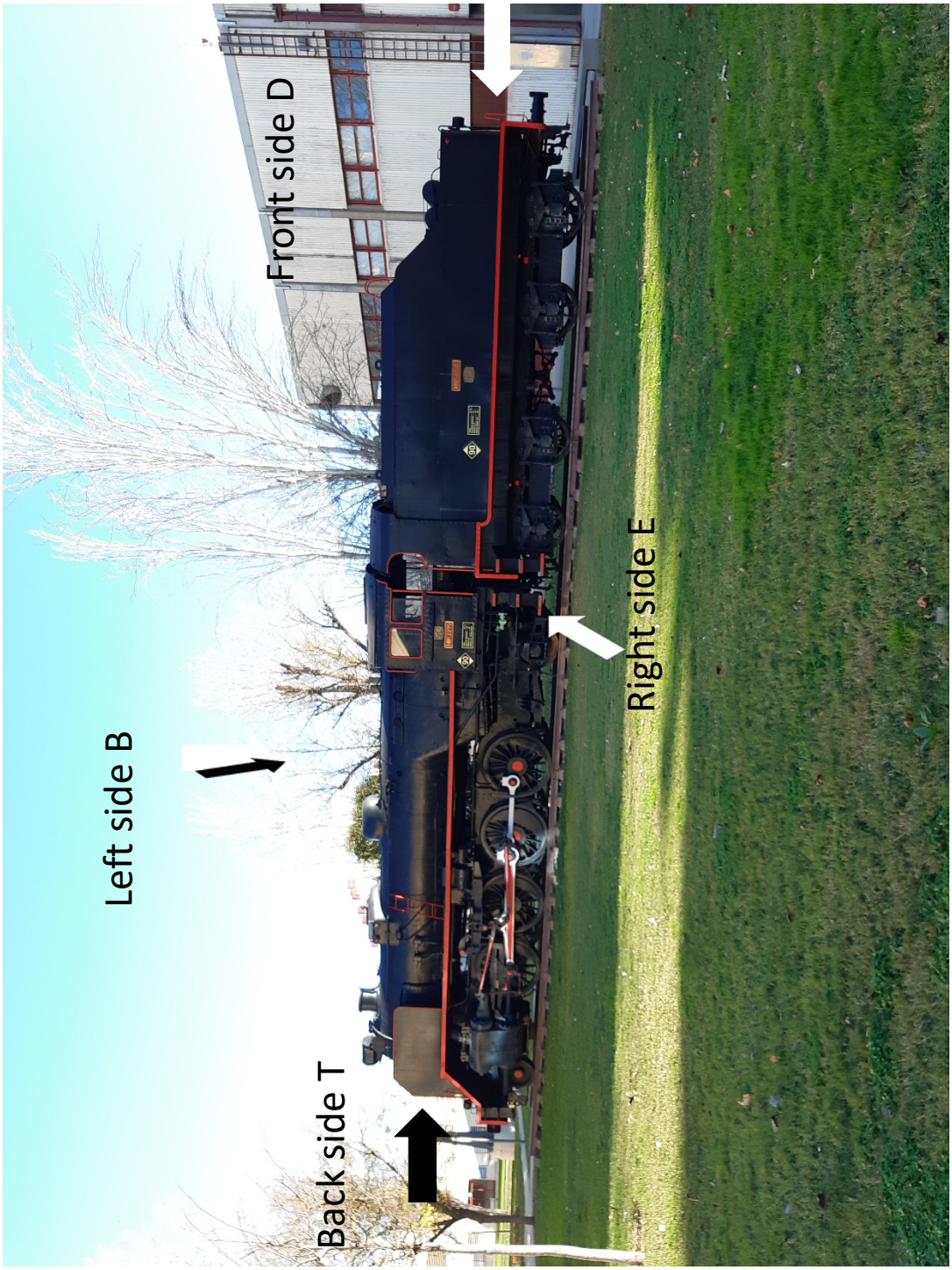
Instrumentation:

Field emission scanning electron microscope coupled to a focused ion beam Zeiss (Orsay Physics Kleindiek Oxford Instruments) model Auriga compact equipment with an Oxford-X Max system controlled by Aztec software.

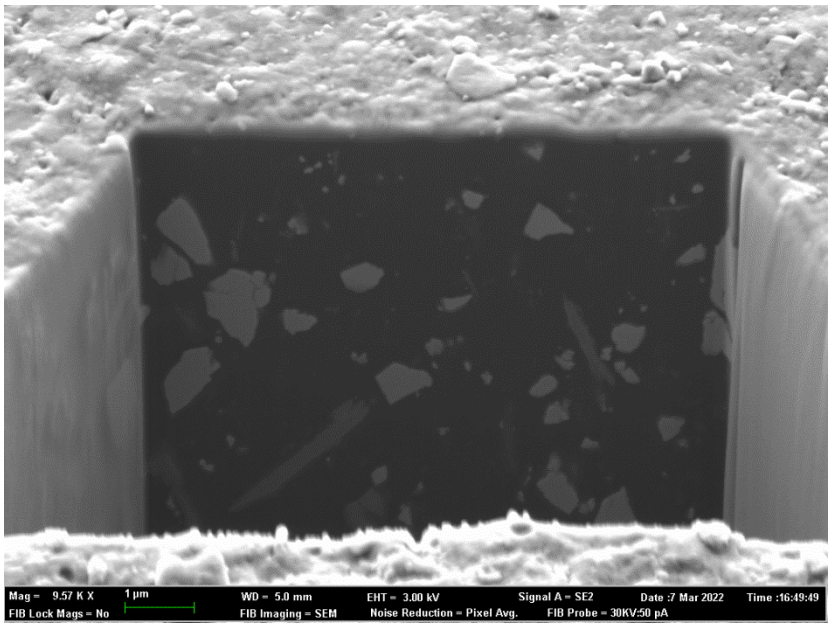
Working conditions:

FIB: voltage, 30 kV and current intensity, 500 μA and 20 nA for generating the focused beam of Ga ions
The Ga beam impacts perpendicularly to the plane of the vertical wall of the trench by tilting 54º the stage where is placed the coin.
FESEM: voltage of 3 kV for acquiring secondary electron images.
FESEM-EDX: voltage of 20 kV, working distance of 6–7 A mm were applied.
ZAF method to correct interelemental effects in semiquantitative microanalysis was carried out.
Counting time of 100 s.
Surface analysis has been carried out performing trenches at ca. (15x15) μm.

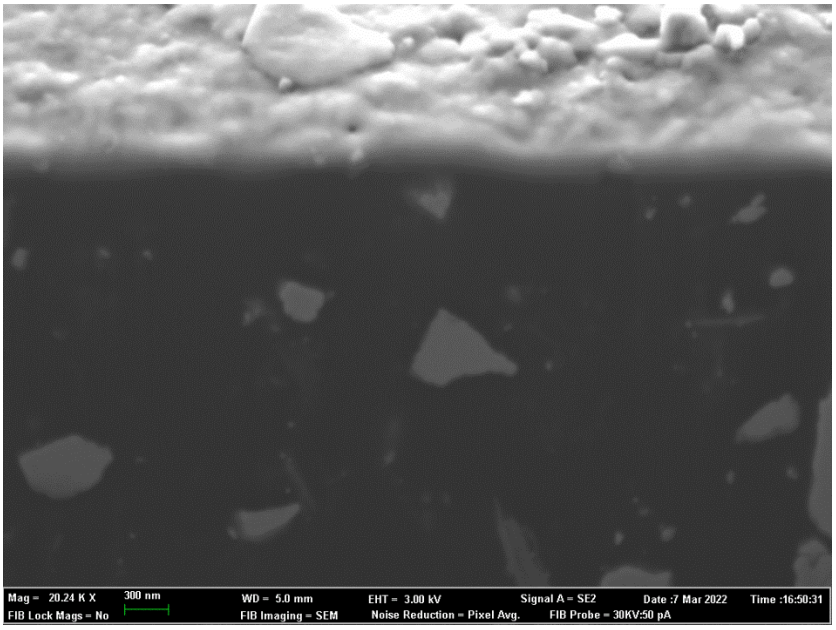
Map of the engine:



Sample: black paint
Ref: MIK-2
Sampling point: side E



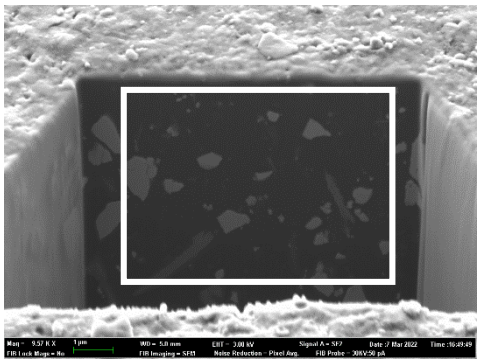
Secondary electron image of the trench



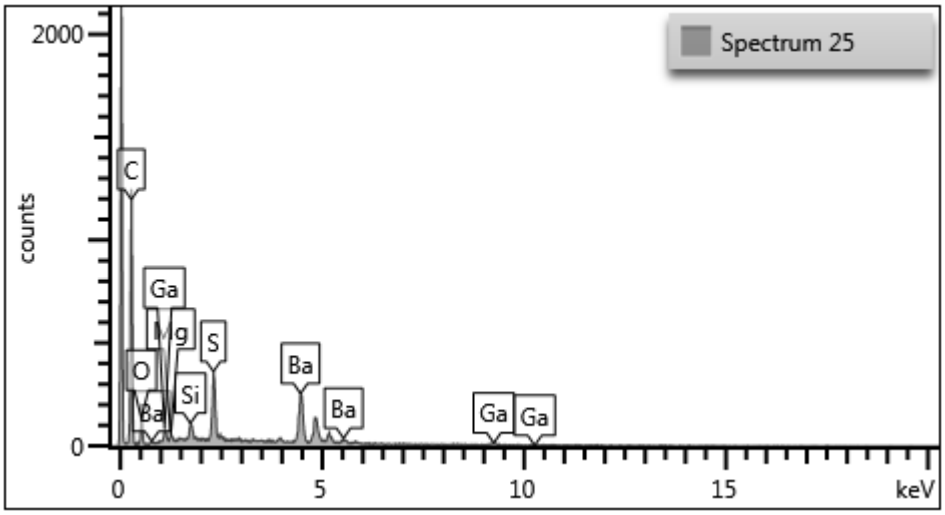
Secondary electron image of the trench. Detail of the upper part of the trench

Sample: black paint
Ref: MIK-2
Sampling point: side E

Acquisition area

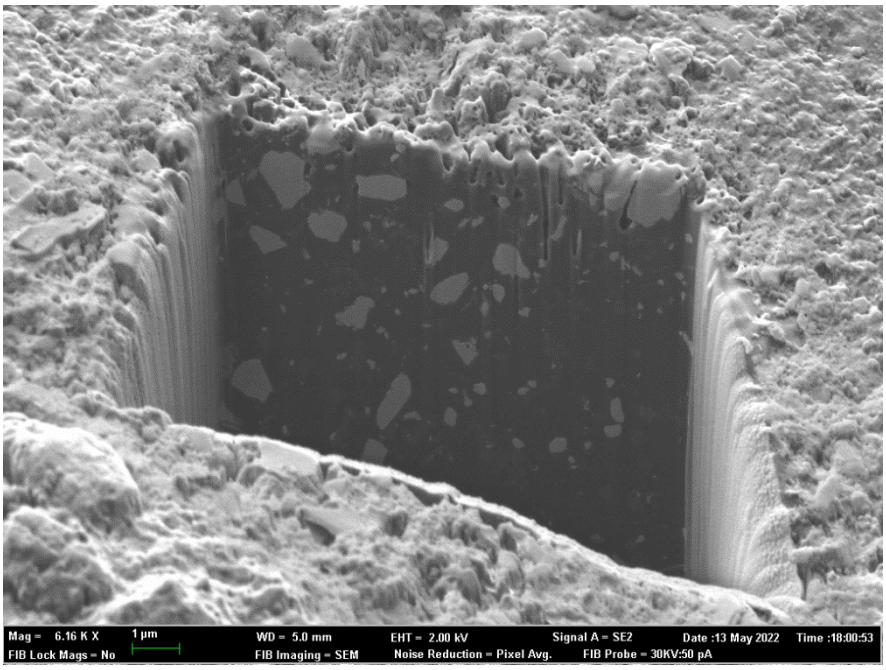


X-ray spectrum

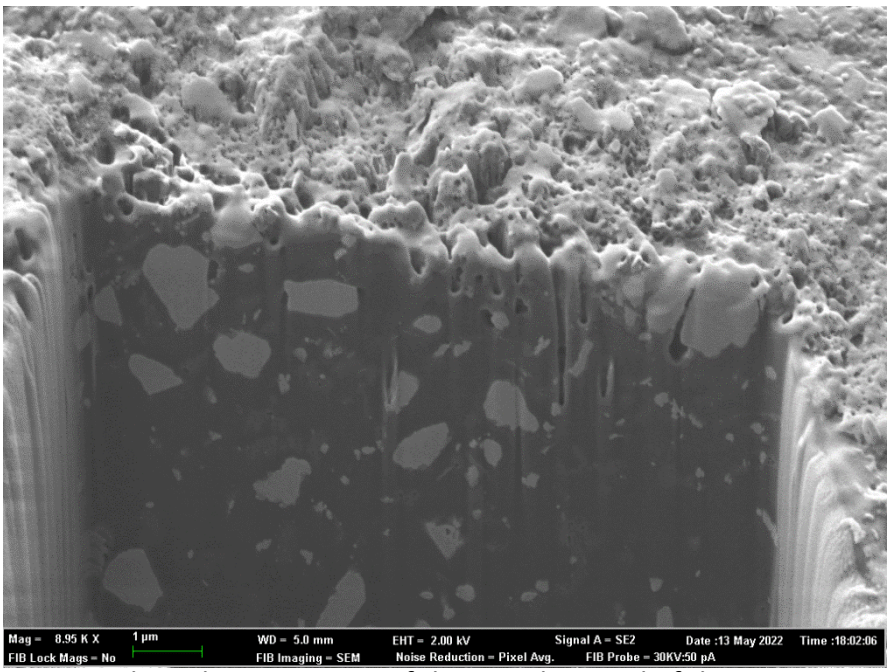


Element	Line Type	Wt%	Wt% Sigma	Atomic %	Oxide %	Oxide % Sigma
C	K series	19,8	0,38	29,15	72,56	1,39
O		60,13		66,46		
Mg	K series	0,21	0,05	0,15	0,35	0,08
Si	K series	0,57	0,06	0,36	1,22	0,13
S	K series	2,97	0,1	1,64	7,42	0,26
Ga	K series	1,05	0,27	0,27	1,41	0,36
Ba	L series	15,26	0,37	1,97	17,04	0,42
Total:		100		100	100	

Sample: red paint
Ref: MIK-3
Sampling point: side E



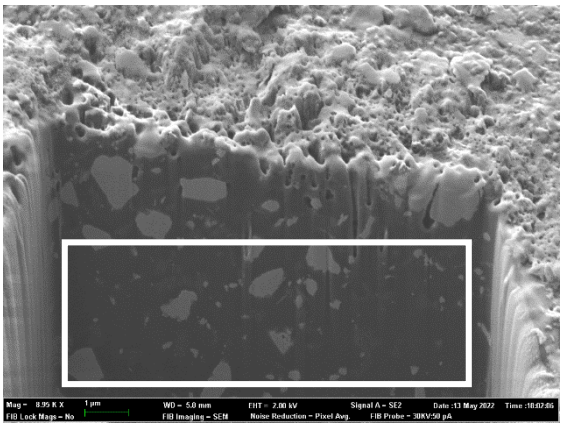
Secondary electron image of the trench



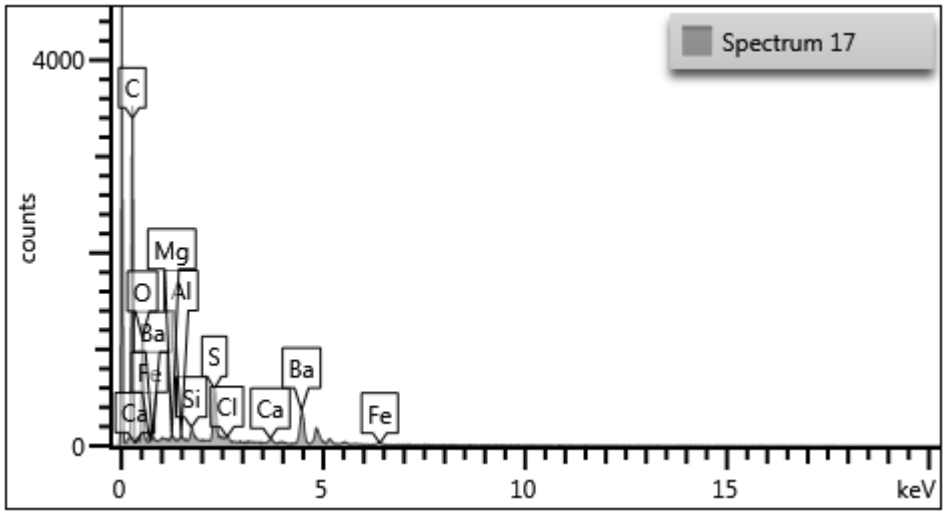
Secondary electron image of the trench. Detail of the upper part of the trench

Sample: red paint
Ref: MIK-3
Sampling point: side E

Acquisition area



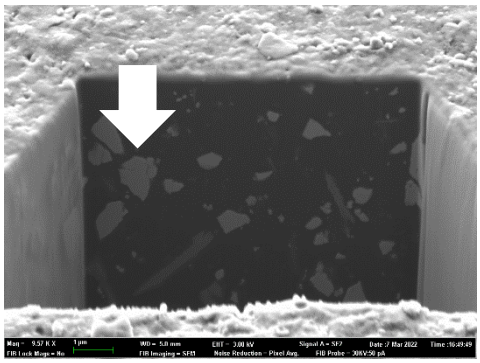
X-ray spectrum



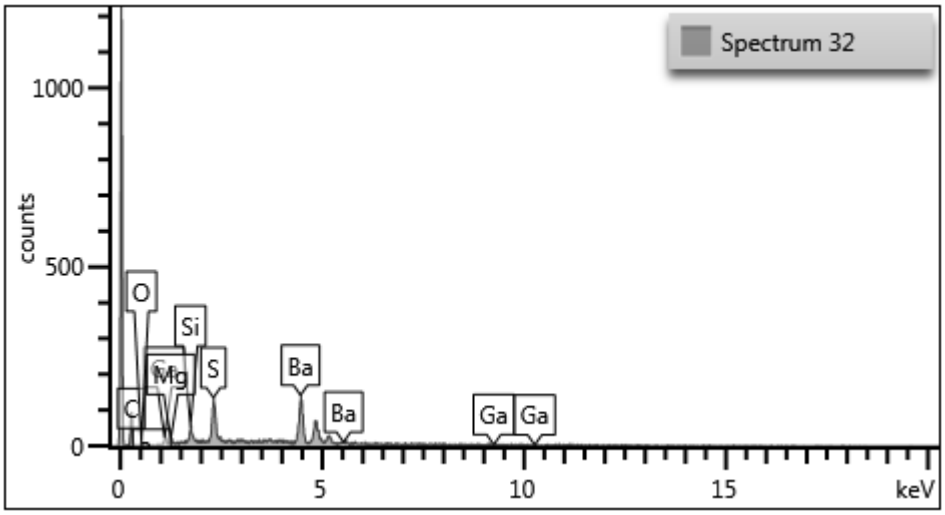
Element	Wt%	Wt% Sigma	Atomic %	Oxide	Oxide %	Oxide % Sigma
O	29,18		64,55			
Mg	0,9	0,19	1,31	MgO	1,5	0,31
Al	0,58	0,18	0,76	Al2O3	1,1	0,34
Si	2,32	0,21	2,92	SiO2	4,96	0,44
S	12,27	0,35	13,55	SO3	30,65	0,88
Cl	1,3	0,2	1,3		0	0,2
Ca	1,57	0,21	1,39	CaO	2,2	0,29
Fe	2,25	0,37	1,43	FeO	2,9	0,47
Ba	49,62	0,76	12,79	BaO	55,4	0,85
Total:	100		100		98,7	

Sample: red paint
Ref: MIK-3
Sampling point: side E

Acquisition point

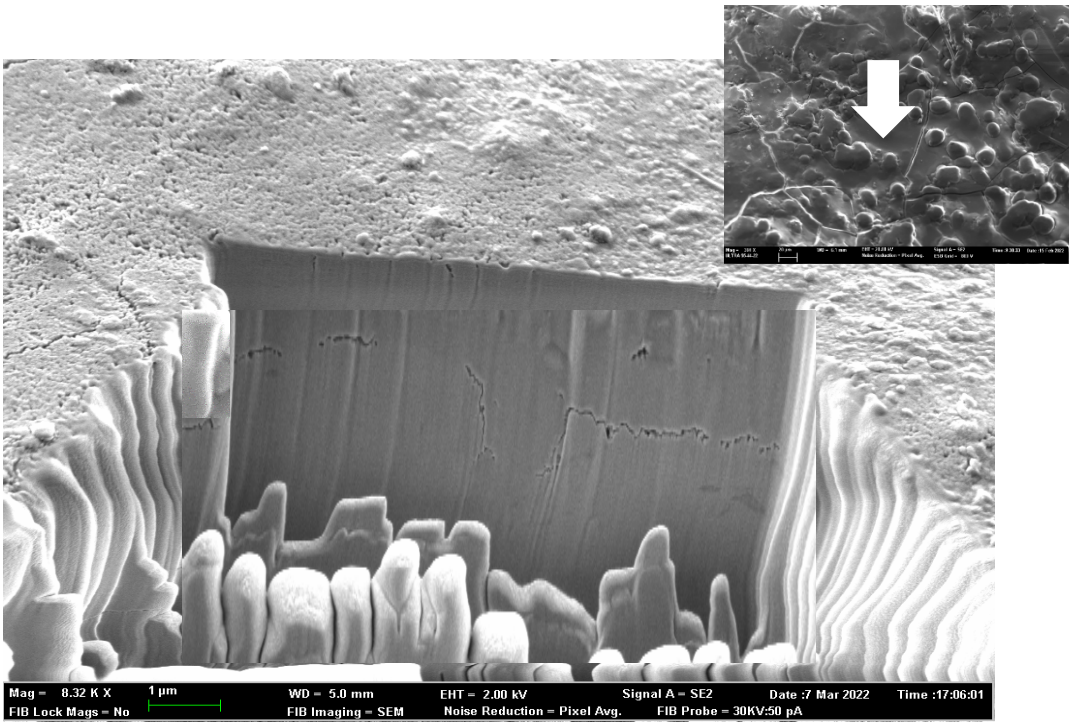


X-ray spectrum

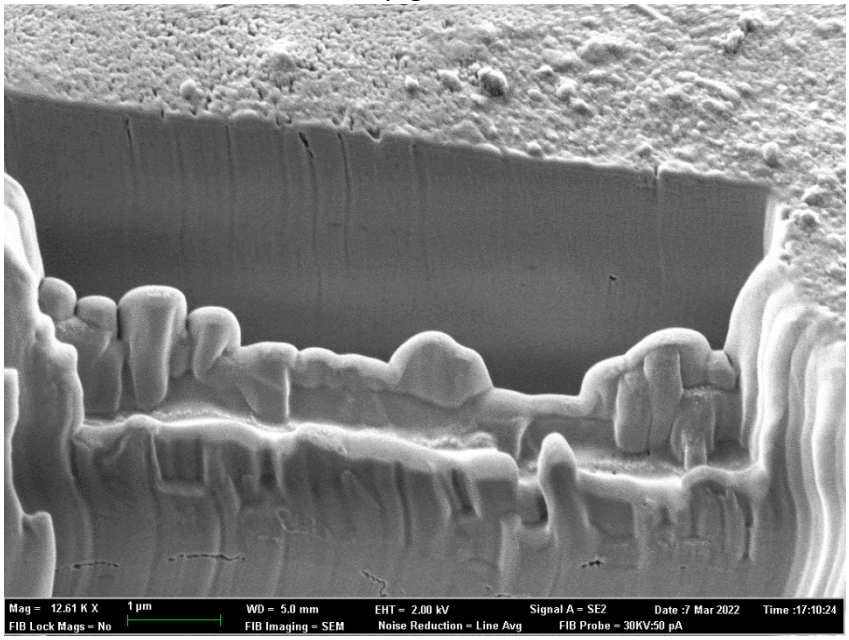


Element	Line Type	Wt%	Wt% Sigma	Atomic %	Oxide %	Oxide % Sigma
C	K series	9,25	0,72	19,82	33,91	2,64
O		40,57		65,25		
Mg	K series	0,9	0,17	0,95	1,49	0,29
Si	K series	1,58	0,23	1,45	3,38	0,48
S	K series	5,68	0,38	4,56	14,18	0,95
Ga	K series	0,58	0,96	0,21	0,78	1,29
Ba	L series	41,44	1,24	7,76	46,27	1,39
Total:		100		100	100	

Sample: red paint
Ref: MIK-5
Sampling point: side E



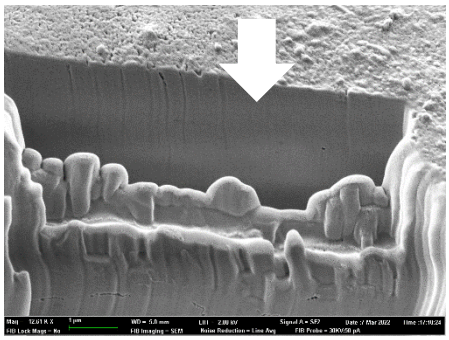
Secondary electron image of the trench performed inside a grain of pigment.



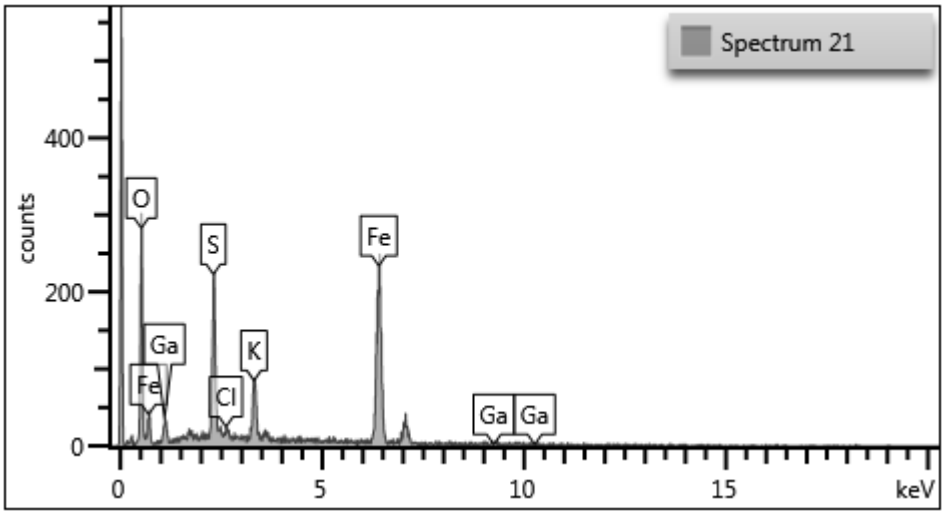
Secondary electron image of the trench. Detail of the upper part of the trench

Sample: red paint
Ref: MIK-5
Sampling point: side E

Acquisition point



X-ray spectrum

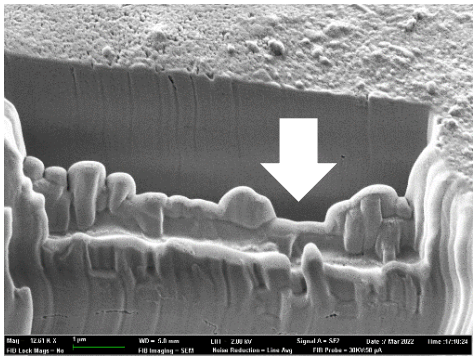


Element	Line Type	Wt%	Wt% Sigma	Atomic %	Oxide %	Oxide % Sigma
O		31,19		58,1		
S	K series	9,92	0,41	9,22	24,78	1,03
Cl	K series	0,71	0,2	0,59	0	0,2
K	K series	5,46	0,35	4,16	6,57	0,42
Fe	K series	50,75	1,02	27,08	65,29	1,31
Ga	K series	1,97	0,83	0,84	2,65	1,12
Total:		100		100	99,29	Fe/S = 2,9

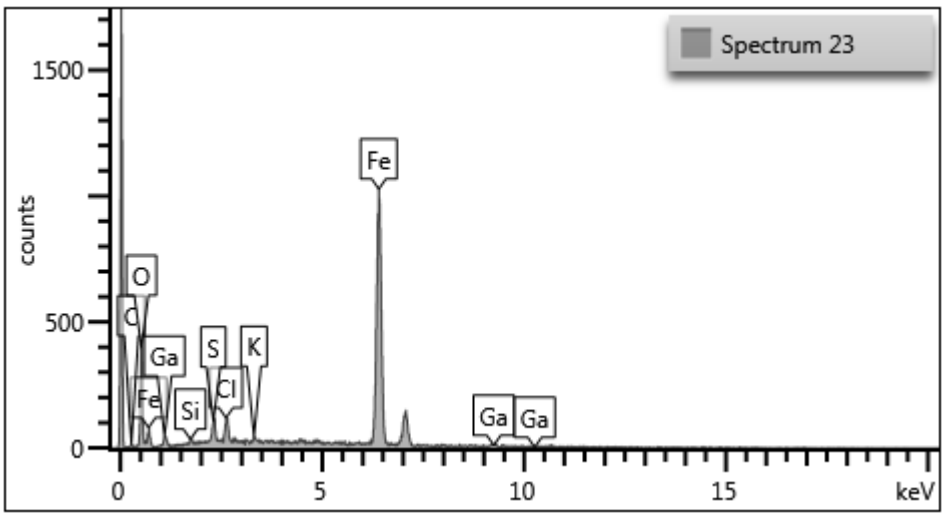
The decreasing value of the Fe/S ratio since the core to the surface of the grain of pigment suggests that the oxidative calcination reaction of the reagent iron(II) sulfate heptahydrate used in the roasting process () of synthesis of iron oxide red (α-Fe_2O_3) has been uncomplete

Sample: red paint
Ref: MIK-5
Sampling point: side E

Acquisition point



X-ray spectrum



Element	Line Type	Wt%	Wt% Sigma	Atomic %	Oxide %	Oxide % Sigma
C	K series	0,61	0,23	1,71	2,23	0,83
O		24,54		51,79		
Si	K series	0,24	0,06	0,29	0,52	0,14
S	K series	1,4	0,11	1,47	3,49	0,27
Cl	K series	1,71	0,12	1,63	0	0,12
K	K series	0,34	0,1	0,3	0,41	0,12
Fe	K series	69,45	0,67	41,99	89,35	0,86
Ga	K series	1,7	0,45	0,83	2,29	0,61
Total:		100		100	98,29	Fe/S = 28,6