

Supporting information for “Dual Isotope System Analysis of Lead-white in Artworks”

Laura Hendriks^{1,2,‡}, Stefan Kradolfer^{2,‡}, Tiziana Lombardo³, Vera Hubert³, Markus Küffner⁴, Nara-yan Khandekar⁵, Irka Hajdas¹, Hans-Arno Synal¹, Bodo Hattendorf^{*,2}, Detlef Günther^{*,2}.

¹Department of Physics, ETH Zurich, Otto-Stern-Weg 5, 8093 Zurich, Switzerland.

²Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland.

³Laboratory for Conservation Research, Collection Centre, Swiss National Museum, Lindenmoosstrasse 1, 8910 Affoltern am Albis, Switzerland.

⁴Swiss Institute for Art Research (SIK-ISEA), Zollikerstrasse 32, 8008 Zürich

⁵Straus Center for Conservation and Technical Studies, Harvard Art Museums, 32 Quincy Street Cambridge, MA 02138, USA

This PDF file includes the supporting information divided in 3 sections:

1. Sampling and material characterization

Figures S-1 and S-2 provides an overview of the sampling location and sampled amount of material from Swiss artist objects, while Figure S-3 displays the canvas clipping of the British objects.

Material characterization data for objects from Swiss respective British artists are reported in Table S-1 and Table S-2 respectively.

2. ¹⁴C-data

Table S-3 and Table S-4 contain an overview of the radiocarbon data measurements

3. Lead isotope measurements

Table S-5 provides the parameters for the digestion of the remaining material after ¹⁴C dating.

Table S-6 and S-7 are giving the ICPMS parameters, Q-ICPMS and MC-ICPMS

Table S-8 and S-9 are providing data concerning the long-time stability of the MC-ICPMS data

Fig. S-4, S-5 and S-6 are showing the influence of additional matrices in the samples as CaCO₃ load respectively acid and oil additives.

Table S-10 reports all the numeric lead isotope ratio results of the samples from Swiss and British artists.

Figure S-7 shows the ²⁰⁶Pb/²⁰⁴Pb- vs. ²⁰⁷Pb/²⁰⁴Pb-data for all the samples (Tab. S-10)

Figure S-8 shows the calculated LIRI-values against the signed date for all the samples

Figure S-9 shows the ²⁰⁷Pb/²⁰⁶Pb- vs. ²⁰⁸Pb/²⁰⁶Pb-data for all the samples, separated based on the century of their signed date.

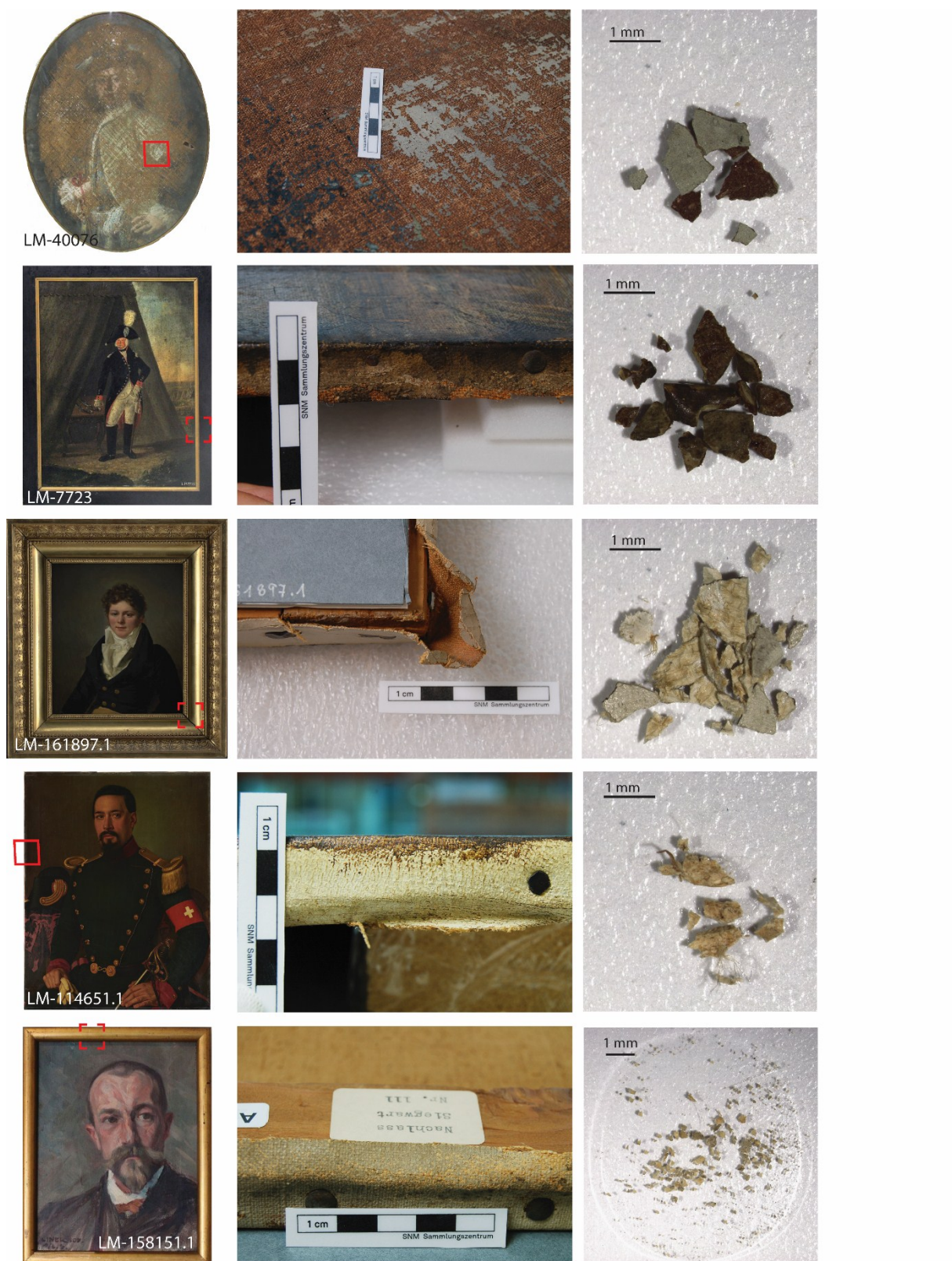


Figure S-1: Sampling overview from the Swiss objects. (Left) Picture of the paintings (Copyright: Swiss National Museum) where the red box indicates the sampling location, (middle) close-up of the sampling area, (right) actual sampled amount of material.



Figure S-2 Sampling overview from the Swiss objects (continued). (Left) Picture of the paintings (Copyright: Swiss National Museum) where the red box indicates the sampling location, (middle) close-up of the sampling area, (right) actual sampled amount of material.



Figure S-3 Sampling overview from the canvas tacking margins belonging to paintings by British artists and provided by the Harvard Art museums. (A) Marco Ricci, (B) PH Hill, (C) Joshua Reynolds, (D) Richard Wilson, (E) Georges Romney (a), (F) Georges Romney (b), (G) Samuel Alken, (H) John Francis Sartorius, (I) John Warkup Swift, (J) William Meadows, (K) Henry Tanworth Wells, (L) Sir Arthur Stockdale Cope.

Material characterization was conducted by combining XRF, FTIR and Raman spectroscopy. XRF analyses were carried out directly on the paintings at the Collection Centre (SNM, Affoltern a. A., Switzerland) using a Bruker AXS ARTAX 800 system equipped with a Rh target and achieving an excitation spot of 80 μm . Spectra were collected with the following settings: generator voltage 50 kV, current 600 μA , ambient conditions, and acquisition time 120 s (Bruker, Karlsruhe, Germany). FTIR analyses were conducted in ATR mode on a Spotlight 200i FTIR spectrometer (Perkin Elmer, Massachusetts, USA). The acquisition spectral range covered 4000–580 cm^{-1} with a resolution of 4 cm^{-1} and 8 scans. The evaluation and interpretation of the FTIR spectra was based on in house reference database, as well as the online IRUG spectral database¹ and published data (Vahur et al., 2016)². Raman measurements were performed on an ARAMIS Raman spectrometer (Horiba Jobin Yvon, Germany) equipped with a microscope (Olympus BX41) which allows visualizing the sample. The spectra were acquired with a 785 nm laser source (Laser diode controller Pilot PC500, Sacher Lasertechnik, Germany) and recorded using a laser power between 3 to 15 mW on sample, 100x magnification, 600 g/mm grating and measurement time between 30 and 200 s. Raman spectra evaluation was based on published data^{3–8} Table 1 and 2, material characterization for samples

Table S-1 Summary of the material characterisation results conducted on the Swiss paintings.

Code	Title/object - artist	Date	Method	Laboratory data	Interpretation
LM-161897	Eric Magnus Louis Grand Hauteville By anonymous after Amélie Munier Romilly	1813	XRF	Pb	Lead white
			FTIR	3535, 1387, 1045, 837, 678	Lead white (basic)
				2922, 2851, 1736, 1616, 1164, 772	drying oil
				1511	lead stearate
				2517, 1798, 1387, 1092, 872, 712	Calcium carbonate
				1616, 772	Calcium oxalate · H ₂ O
			Raman	1050, 102	Lead white (basic)
				1388, 1597	Carbon black
				143, 282	Litharge/Massicot/Naples yellow
LM-114651	Adolphe Morand By Jh. Lorette	1863	XRF	Pb, Ca, Fe	Lead white, calcium carbonate, earth pigment
			FTIR	3535, 1391, 1045, 833, 679	Lead white (basic)
				2923, 2852, 1734, 1167, 854, 768	drying oil
			Raman	56, 70, 102, 151, 1053	Lead carbonate
				988	Barium sulfate
				145	Litharge/Massicot/Naples yellow
LM-158151	Hugo Siegwart By Carl August Liner	1907	XRF	Pb, Zn, Ca, Fe	Lead white, calcium carbonate, earth pigment

			FTIR	3530, 1395, 1053, 846, 670,	Lead white (basic)
				3290, 1624	Proteinous material
				2920, 2851, 1734, 1160, 1115,	Drying oil
				1023, 605	Bone black
				2515, 1798, 1395, 871, 712	Calcium carbonate
				1624, 773	Calcium oxalate · H ₂ O
			Raman	546	Lazurite
				152, 1085	Calcite
LM-161803	Preliminary design for “die Wiege der Eidgenossenschaft” By Charles Giron	1899-1902	XRF	Pb, Zn, Ca, Fe	Lead white, calcium carbonate, earth pigment
			FTIR	3538, 1393, 1047, 835, 678	Lead white (basic)
				2926, 2853, 1734, 1709, 1241, 1163, 1082	Drying oil
				1531	Carboxylates
				872, 713	Calcium carbonate
				1622, 778	Calcium oxalate · H ₂ O
			Raman	143, 287	Litharge/Massicot/Naples yellow
				1319, 1586	Carbon black
				71, 102, 1048, 1052	Lead white
				979	Anglesite PbSO ₄
				154, 1080	Calcite
LM-40076	Giambattista Somazzi By anonymous	1733	XRF	Pb, Fe, Mn, Ca	Lead white, calcium carbonate, earth pigment
			FTIR	3696, 3653, 3620, 1087, 1030, 1006, 940, 912, 795, 735	Kaolinite
				3536, 1396, 837, 678	Lead white (basic)
				2921, 2851, 1710, 1166,	Drying oil
				1514	Lead stearate
				1396, 873, 711	Calcium carbonate
				1615, 1314, 778	Calcium oxalate · H ₂ O
			Raman	226, 244, 291, 410, 495, 613, 1314	Heamatite
				1050	Lead white

				1315, 1562	Carbon black
LM-7723	Salomon Ruppert By Caspar Bachmann	1797	XRF	Pb, Ca, Fe	Lead white, calcium carbonate, earth pigment
			FTIR	3696, 3654, 3619, 1115, 1084, 1030, 1006, 939, 912, 796, 752	Kaolinite
				3536, 1399, 837, 677	Lead white (basic)
				2920, 2850, 1710, 1169	Drying oil
				1518	Lead stearate
				1399, 873, 711	Calcium carbonate
				1616, 1314, 778	Calcium oxalate · H ₂ O
			Raman	225, 244, 293, 410, 495, 610	Heamatite
				1306, 1590	Carbon black
				150, 1080	Calcite
LM-52427	Marie Regine Krus-Guérmand By Johann Melchior Joseph Wyrsh	1783	XRF	Pb, Fe, Ca	Lead white, calcium carbonate, earth pigment
			FTIR	3698, 3650, 3619, 1096, 1030, 1006, 941, 912, 798,	Kaolinite
				3532, 1399, 839, 678	Lead white (basic)
				2924, 2853, 1702, 1162	Drying oil
				1514	Lead stearate
				1399, 874, 711	Calcium carbonate
				1620, 1316, 778	Calcium oxalate · H ₂ O
			Raman	463	Quartz
				1098	Dolomite
				225, 248, 293, 411, 611, 1312	Heamatite
				57, 73, 102, 151, 1056	PbCO ₃
SIK-98511 a)	Bildnis Margrit mit roter Jacke und Konzertkleid by Franz Rederer	1962	XRF	Zn, Pb, Ti, (Cr, Ca, Mn, Fe, Co, Cu)	ZnO, TiO ₂ , PbCO ₃
			FTIR	2925, 2853, 1741, 1458, 1162	Linseed oil
				3542, 1405, 1043, 839, 681	Lead white (basic)
			Raman	141s	TiO ₂ -anatase
				587, 547s, 374	Ultramarine

				1542s, 1341, 1218, 775, 741, 686	PG7 (traces)
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a) Data already published in Hendriks et al. (2018)⁹

Table S-2 Summary of the material characterisation results conducted on the target margins from British paintings.

Artist	Signed date	Method	Laboratory data	Interpretation
Marco Ricci	1711	FTIR	3535, 1392, 1045, 833, 680	Lead white
			2923, 2852, 1707, 777	Drying oil
			1517	Lead stearate
			1392, 1095, 871, 711	Calcium carbonate
			722	Dolomite
		Raman	57, 72, 100, 1053	Lead white
			153, 283, 711, 1086	Calcite
			288, 402	Heamatite
PH Hill	1795	FTIR	2923, 2852, 1707, 1629, 1176, 780	Drying oil
			2513, 1798, 1392, 1087, 871, 712	Calcium carbonate
			1046, 830, 681	Lead white
			1629	Lead oxalate
		Raman	1310, 1595	Carbon black
			85, 103, 252, 287, 343	Vermillion
			88, 203, 245, 299, 390, 554	Goethite
Joshua Reynolds	1765	FTIR	3537, 1392, 1045, 837, 680	Lead white
			2922, 2851, 1733, 1702, 1167, 1097, 773	Drying oil
			1508	Lead stearate
			2514, 1796, 1392,872, 712	Calcium carbonate
			3290, 1633, 1530, 1403	Proteinous material
			1152, 1104, 1080, 1032	Silicates
		Raman	1310,1585	Carbon black
			82,138	Massicot/Litharge/Naples yellow

			88, 103, 254, 283, 342	Vermillion
Richard wilson	1761	FTIR	3535, 1391, 1045, 839, 679	Lead white
			2924, 2852, 1707, 1170, 1108	Drying oil
			2514, 1796, 1391, 871, 712	Calcium carbonate
			1618, 777	Calcium oxalate · H ₂ O
		Raman	1313, 1592	Carbon black
			252, 343	Vermillion
Georges Romney (a)	1770	FTIR	3539, 1388, 1051, 837, 678	Lead white
			2921, 2851, 1732, 1703, 1163	Drying oil
			2515, 1796, 1388, 1097, 871, 712	Calcium carbonate
			1622, 777	Calcium oxalate · H ₂ O
		Raman	71, 85, 143, 284	Massicot
			222, 238, 287, 403, 491, 605, 1306	Haematite
			1316, 1585	Carbon black
Georges Romney (b)	1770	FTIR	3539, 1388, 1051, 837, 678	Lead white
			2921, 2851, 1732, 1703, 1163	Drying oil
			2515, 1796, 1388, 1097, 871, 712	Calcium carbonate
			1622, 777	Calcium oxalate · H ₂ O
		Raman	1310, 1580	Carbon black
			71, 85, 142, 281	Massicot
Samuel Alken	1795	FTIR	3532, 1389, 1046, 681	Lead white
			2927, 2851, 1705, 1160, 1108	Drying oil
			2514, 1796 1389, 1087, 871, 712	Calcium carbonate
		Raman	732, 750, 1334, 1545	Phthalocyanine
			154, 282, 1085	Calcite
			140, 278	Massicot/Litharge/Naples yellow
			1313, 1585	Carbon black
			226, 245, 293, 411, 496, 613,	Heamatite
JF	1803	FTIR	3532, 1390, 1045, 680	Lead white

Sartorius			2922, 2852, 1707, 1159, 1060	Drying oil
			2514, 1796, 1390, 872, 712	Calcium carbonate
			1615, 776	Calcium oxalate · H ₂ O
			1517	Lead stearate
		Raman	1310, 1585	Carbon black
			82, 138	Massicot/Litharge/Naples yellow
			108, 1051	Lead white
			154, 1080	Calcite
JW Swift	1840	FTIR	3533, 1391, 1045, 838, 680	Lead white
			2926, 2853, 1729, 1174	Calcium carbonate
			2516, 1798, 1391, 1085, 871, 712	Calcium carbonate
			1525	Lead stearate
			1620, 776	Calcium oxalate · H ₂ O
		Raman	1315, 1585	Carbon black
			153, 1088	Calcite
			223, 290, 407	Heamatite
			76, 106, 1054	Lead white
			622, 1002	Gypsum
William Meadows	1868	FTIR	3535, 1384, 1045, 837, 678	Lead white
			2921, 2851, 1729, 1176	Drying oil
			2513, 1796, 1384, 1089, 872, 712	Calcium carbonate
			1510	Lead stearate
			(1620), 776	Calcium oxalate · H ₂ O
		Raman	1315, 1585	Carbon black
			82, 112, 151, 276, 2095, 2122, 2157	Prussian blue
			76, 222, 287, 404, 493, 605	Heamatite
			1013	Anhydrite
			85, 104, 254, 286, 343	Vermillion
			72, 105, 1051	Lead white

Henry Tanworth Wells	1874	FTIR	3535, 1392, 1045, 837, 680	Lead white
			2920, 2852, 1733, 1711, 1176	Drying oil
			2518, 1796, 1392, 872, 712	Calcium carbonate
			1509	Lead stearate
			1620, 775	Calcium oxalate · H ₂ O
		Raman	1313, 1590	Carbon black
			75, 106, 1052	Lead white
			225, 244, 292, 409, 496, 609	Heamatite
			91, 244, 300, 393, 478, 549, 1378	Goethite
Sir Arthur Stockdale Cope	1901	FTIR	3357, 1393, 1045, 680	Lead white
			2920, 2851, 1738, 1703, 1166, 1101	Drying oil
			1514	Lead stearate
			928, 852	Earth pigment
			(1620), 769	Calcium oxalate · H ₂ O
		Raman	239, 485, 844, 904, 1164, 1190, 1222, 1293, 1331, 1359, 1484, 1520	Alizarin krapplack PR83
			69, 86, 142, 282	Massicot
			536, 827	Lazurite/ultramarine
			110, 156, 673, 1053	Lead white
			672, 535	Cerulean blue
			1319, 1576	Carbon black
			220, 293, 407, 1310	Heamatite

Table S-3 Overview of the radiocarbon data collected on the samples from the Swiss paintings provided by the Swiss National Museum (CH) as well as Margrit's portrait by Franz Rederer from the SIK-ISEA collection (CH). The results are summarized as sample code, title of object and respective artist, signed date, ETH laboratory code, targeted material (lead carbonate, organic binder of the paint, canvas textile), the measured ^{14}C ages with 1σ uncertainty and corresponding fraction modern $F^{14}\text{C}$, the measured amount of carbon and the respective calibrated calendar ages using the calibration software Oxcal v.4.3.2 ^{10,11} with Intcal13 calibration curve ¹² and post-bomb atmospheric NH1 curve¹³.

Code	Title/object - artist		Date	ETH Nr.	Targeted Material	^{14}C Age [yr BP]	σ	$F^{14}\text{C}$	σ	C mass [μg]	Calibrated age interval (95.4% confidence interval)
LM-161897	Eric Magnus Louis Grand Hauteville By anonymous in style of Amélie Munier Romilly		1813	96797.1.1	carbonate	227	63	0.972	0.008	63	Mean value: 251 +- 45 1493-1602 & 1615-1684 & 1734-1807 & 1930 - 1954
				96797.2.1	carbonate	274	63	0.966	0.008	75	
				96798.1.1	paint	206	54	0.975	0.007	144	Mean value: 257 +- 41 1493-1602 & 1615-1682 & 1738-1754 & 1762-1803 & 1937-1950
				96798.2.1	paint	322	62	0.961	0.007	279	
				96799.1.1	textile	151	20	0.981	0.002	990	1667-1698 & 1724-1783 & 1796-1816 & 1834-1879 & 1916-1954
LM-114651	Adolphe Morand By Jh. Loretti		1863	96800.1.1	carbonate	-71	151	1.009	0.019	11	1637-1956
				96801.1.1	paint	-149	96	1.019	0.012	15	1680-1764 & 1801-1957
LM-158151	Hugo Siegwart By Carl August Liner		1907	96802.1.1	carbonate	312	70	0.962	0.008	29	1440-1680 & 1764-1801 & 1939-1950
				96803.1.1	paint	247	129	0.970	0.016	14	1451-1894 & 1905-1950
LM-161803	Preliminary design for "Die Wiege der Eidgenossenschaft" By Charles Giron		1899 - 1902	96804.1.1	carbonate	226	326	0.972	0.039	9	1183-1950
LM-40076	Giambattista Somazzi By anonymous		1733	96806.1.1	carbonate	261	80	0.968	0.010	25	1449-1699 & 1721-1818 & 1833-1879 & 1916-1950
				96807.1.1	paint*	316	55	0.961	0.007	107	N/A
LM-7723	Salomon Ruppert By Caspar Bachmann	1797		96808.1.2	carbonate	132	64	0.984	0.008	55	1665-1785 & 1793-1950
				96809.1.1	paint*	291	55	0.964	0.007	1201	N/A

LM-52427	Marie Regine Krus-Guérmand By Johann Melchior Joseph Wyrsh	1783	96810.1.1	carbonate	154	76	0.981	0.009	25	1642-1954
			96811.1.1	paint	266	55	0.967	0.007	84	1469-1684 & 1735-1806 & 1931-1950
SIK-98511	Bildnis Margrit mit roter Jacke und Konzertkleid by Franz Rederer	1962	57442.2.1	Canvas ^{a)}	-888	25	1.117	0.004	997	1957-1958 & 1993-1997
			69024.1.1	paint ^{a)}	-183	30	1.023	0.004	398	1955-1956
			69024.4.1	carbonate ^{b)}	25724	223	0.041	0.005	93	Industrial process, > 19th century
			69024.9.1	carbonate	5261	93	0.519	0.006	67	Industrial process, > 19th century
			88907.3.1	carbonate	5713	94	0.491	0.006	66	Industrial process, > 19th century

^{a)} Data published in Hendriks et al. (2018)⁹

^{b)} Data published in (Hendriks et al., 2019)¹⁴

* not calibrated, as ¹⁴C age is biased due to presence of carbon black.

Table S-4 Overview of the radiocarbon data collected on the samples from the British paintings clippings provided by the Harvard museum (USA). The results are summarized as artist, signed date, ETH laboratory code, targeted material (lead carbonate, organic binder of the paint, canvas textile), the measured ¹⁴C ages with 1sigma uncertainty and corresponding fraction modern F¹⁴C, the measured amount of carbon and the respective calibrated calendar ages using the calibration software Oxcal v.4.3.2^{10,11} with Intcal13 calibration curve¹² and post-bomb atmospheric NH1 curve¹³.

Artist	Date	ETH Nr.	Targeted Material	¹⁴ C Age [yr BP]	σ	F ¹⁴ C	σ	C mass [μg]	Calibrated age interval (95.4% confidence interval)
Marco Ricci	1711	95049.1.2	carbonate	-9	54	1.001	0.007	42	1688-1730 & 1809-1927 & 1954-1956
		95050.1.1	paint	177	59	0.978	0.007	420	Mean: 203 +-43
		95050.2.1	paint	232	61	0.971	0.007	249	1637-1706 & 1719-1820 & 1832 -1882 & 1914-1950
		95051.1.1	textile	96	20	0.988	0.002	988	1691-1729 & 1810-1923
PH Hill	1795	95052.1.1	carbonate	12	69	0.998	0.008	31	1680-1764 & 1801-1939 & 1954-1956
		95053.1.1	paint*	389	71	0.952	0.008	56	N/A
		95054.1.1	textile	164	20	0.980	0.002	994	1666-1695 & 1726-1785 & 1795-1814 & 1838-1843 & 1852-1868 & 1917-1950
Joshua Reynolds	1765	95055.1.1	carbonate	-78	55	1.010	0.007	37	1693-1728 & 1812-1920 & 1954-1957
		95056.1.1	paint*	435	64	0.947	0.007	69	N/A

		95056.2.1	paint*	421	55	0.949	0.006	182	N/A
		95057.1.1	textile	193	20	0.976	0.002	997	1660-1681 & 1735-1806 & 1932-1950
Richard Wilson	1761	95061.1.1	carbonate	-30	53	1.004	0.007	35	1691-1730 & 1810-1925 & 1954-1957
		95062.1.1	paint*	477	74	0.942	0.009	68	N/A
		95063.1.1	textile	221	21	0.973	0.003	981	1645-1680 & 1764-1801 & 1939
		95064.1.1	carbonate	13	53	0.998	0.007	33	Mean: 2 +- 36 1695-1727 & 1812-1854 & 1867-1919 & 1954-1957
Georges Romney	1770	95064.2.1	carbonate	36	76	0.996	0.009	33	
		95064.3.1	carbonate	-35	61	1.004	0.008	45	
		95065.1.1	paint*	413	65	0.949	0.008	111	N/A
		95066.1.1	textile	168	20	0.979	0.002	984	1665-1694 & 1726-1785 & 1793-1814 & 1918-1950
Georges Romney	1770	95067.1.1	carbonate	86	55	0.989	0.007	43	1677-1777 & 1800-1941
		95068.1.1	paint*	523	59	0.937	0.007	347	N/A
		95069.1.1	textile	158	20	0.980	0.002	997	1666-1697 & 1725-1784 & 1796-1815 & 1836-1877 & 1916-1950
Samuel Alken	1795	95070.1.1	carbonate	4247	79	0.589	0.006	24	N/A
		95070.2.1	carbonate	4448	177	0.575	0.013	17	N/A
		95071.1.1	paint	256	72	0.969	0.009	81	1692-1729 & 1811-1920
		95071.2.1	paint	126	77	0.985	0.009	21	1663-1950
		95072.1.1	textile	92	20	0.989	0.002	982	1692-1729 & 1811-1920
JF Sartorius	1803	95073.2.1	carbonate	-78	82	1.010	0.010	22	1681-1739 & 1745-1763 & 1802-1938 & 1954-1957
		95074.1.1	paint*	390	66	0.953	0.008	173	N/A
		95074.3.1	paint*	278	55	0.966	0.007	186	N/A
		95075.1.1	textile	201	20	0.975	0.002	979	1652-1684 & 1736-1805 & 1935-1950
JW Swift	1840	95076.1.1	carbonate	64	52	0.992	0.006	37	1680-1764 & 1801-1939 & 1954-1955
		95077.1.1	paint*	362	67	0.956	0.008	85	N/A
		95078.1.1	textile	99	20	0.988	0.002	983	1691-1730 & 1810-1925
William Meadows	1868	95079.2.1	carbonate	121	57	0.985	0.007	36	1669-1781 & 1798-1945 & 1954-1955
		95080.2.1	paint*	480	58	0.942	0.007	47	N/A

		95081.1.1	textile	91	20	0.989	0.002	995	1692-1729 & 1811-1920
Henry Tanworth Wells	1874	95082.1.1	carbonate	178	65	0.978	0.008	21	Mean: 169 +- 60
		95082.2.1	carbonate	120	148	0.985	0.018	10	1649-1894 & 1905-1950
		95083.1.1	paint*	566	67	0.932	0.008	89	N/A
		95083.2.1	paint*	362	57	0.955	0.006	39	N/A
		95084.1.1	textile	102	20	0.987	0.002	998	1690-1730 & 1810-1926
Sir Arthur Stockdale Cope	1901	95085.1.1	carbonate	-100	50	1.012	0.006	61	Mean: -40 +- 35 1697-1724 & 1814-1835 & 1877-1918 & 1954-1957
		95085.3.1	carbonate	68	60	0.992	0.007	33	
		95085.4.1	carbonate	-88	83	1.011	0.010	32	
		95086.1.1	paint*	338	64	0.959	0.008	411	N/A
		95086.2.1	paint*	320	63	0.961	0.008	481	N/A
		95086.4.1	paint*	231	53	0.971	0.006	297	N/A
		95087.1.1	textile	103	20	0.987	0.002	986	1689-1730 & 1809-1926

* not calibrated, as ¹⁴C age is biased due to presence of carbon black.

Table S-5: Digestion parameter for the following ICPMS-measurements: The provided sample were digested upon addition of 2 ml water (milli-Q) and 2 ml nitric acid (sub-boiled, in-house), which was carried out over 30 minutes in a turboWAVE microwave assisted digestion system (MLS GmbH, Leutenkirch, Germany) at 220 °C and 40 bar

Instrumentation	turboWAVE microwave assisted digestion system (MLS GmbH, Leutenkirch, Germany)
Parameter	
Media	2 ml Water (milli-Q), 2 ml Nitric acid (sub-boiled, in-house
Time	30 min
Temperature	220 °C
Pressure	40 bar
Microwave assistance	1200 W

Table S-6: Technical parameter for the quantification by Q-ICPMS (Agilent7500, Agilent Technologies, Santa Clara, USA).

Parameter:	ICPMS
RF power	1450 W
Plasma gas flow	15.2 l/min
Carrier gas	0.91 l/min
Make-up gas	0.1 l/min
Nebulizer gas	0.1 l/min
Cone material	Ni
Dwell time	50 ms
Measured isotopes	²⁰² Hg, ²⁰³ Tl, ²⁰⁴ Pb, ²⁰⁵ Tl, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²⁰⁹ Bi
Internal standard	²⁰⁵ Tl
Calibration approach	External Calibration

Table S-7: Operating conditions for the Nu plasma HR MC-ICPMS

RF-power	1350 W		
Plasma gas flow	13.0 L min ⁻¹ Ar		
Auxiliary gas flow	0.9 L min ⁻¹ Ar		
Nebulizer gas pressure	33.0 PSI		
Cone material	Ni		
Blocks	5		
Measurements	10		
Integration time	5 s		
Assignment to Faraday cup detector*	(Hg)	(200)	(L3)
	Hg	202	L2
	Tl	203	L1
	Pb	204	Ax
	Tl	205	H1
	Pb	206	H2
	Pb	207	H3
	Pb	208	H4
Nebulizer type	Meinhard type		
Sample uptake	80 uL min ⁻¹		

Data processing: The data were corrected for instrumental background using ESA deflection and for isobaric overlap of ²⁰⁴Hg via the measurement of ²⁰²Hg (<http://hbcponline.com>, 08.2019). Measured isotope ratios that were out of the range of the mean plus or minus two times the standard deviation were considered as outliers and discarded. Mass discrimination correction was performed against the previously calibrated thallium standard using the exponential model¹⁵ and periodically verified against SRM NIST981 (NIST, USA) published values^{16,17}.

The thallium correction was performed based on frequent measurements of NIST SRM981 (400 ppb) with the addition of thallium (200 ppb), either a liquid standard (Inorganic ventures, D2-TL01114) or NIST SRM991, in minimum prior and after every measurement set. The two different sources of Tl-standard solutions showed negligible differences in the resulting Tl-ratio. The Tl isotope-ratio was calculated from Pb isotope analyses of SRM 981 after mass correction for mass discrimination using the exponential model.¹⁵ The $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratio given by the NIST SRM981 was used as a basis to calculate the adjusted Tl-ratio for all the measurements. In table S-8 the average $^{205}\text{Tl}/^{203}\text{Tl}$ -ratio from the long-term stability of the measurements (41 samples) and with just the samples containing SRM991 (14 samples) are given.

Table S-8: Long-term stability of the thallium ratio determined from SRM981 measurements given as a means with standard deviation, standard error and the confidence intervals. The numbers are given calculated with the lead isotope ration from the $^{207}\text{Pb}/^{206}\text{Pb}$ and the $^{208}\text{Pb}/^{206}\text{Pb}$ data. The long-term stability includes 41 measurements including 14 samples with SRM991 and 27 measurements with a liquid Tl-standard solution.

	Mean	SD	SE	CI (0.95)
$^{207}\text{Pb}/^{206}\text{Pb}$				
$^{205}\text{Tl}/^{203}\text{Tl}$ – long term	2.388583	$3.8 \cdot 10^{-4}$	$8 \cdot 10^{-6}$	Upper 2.388603 Lower 2.388570
$^{205}\text{Tl}/^{203}\text{Tl}$ – SRM991	2.388445	$3.9 \cdot 10^{-4}$	$1.5 \cdot 10^{-5}$	Upper 2.388475 Lower 2.388415
$^{208}\text{Pb}/^{206}\text{Pb}$				
$^{205}\text{Tl}/^{203}\text{Tl}$ – long term	2.388641	$3.6 \cdot 10^{-4}$	$8.2 \cdot 10^{-6}$	Upper 2.388657 Lower 2.388624
$^{205}\text{Tl}/^{203}\text{Tl}$ – SRM991	2.388554	$5.5 \cdot 10^{-4}$	$2.18 \cdot 10^{-5}$	Upper 2.388597 Lower 2.388511

Stability over Time

The overall stability during the measurement session was controlled by frequent standard measurements and is listed in Table S-9. Given with the correspondent literature values. One has to be aware the mass bias correction is based on the empirical determined Thallium ratio which is based on these standard measurements and contains therefore a circular logic.

Table S-9: Mean values of lead isotope abundance ratios for SRM 981 (NIST, USA) measured during all measurement sets

	Mean	RSD %	Literature values ¹⁶
$^{208}\text{Pb}/^{206}\text{Pb}$	2.16774(16)	0.007	2.16701
$^{207}\text{Pb}/^{206}\text{Pb}$	0.914813(34)	0.004	0.91464
$^{208}\text{Pb}/^{204}\text{Pb}$	36.7106(75)	0.02	

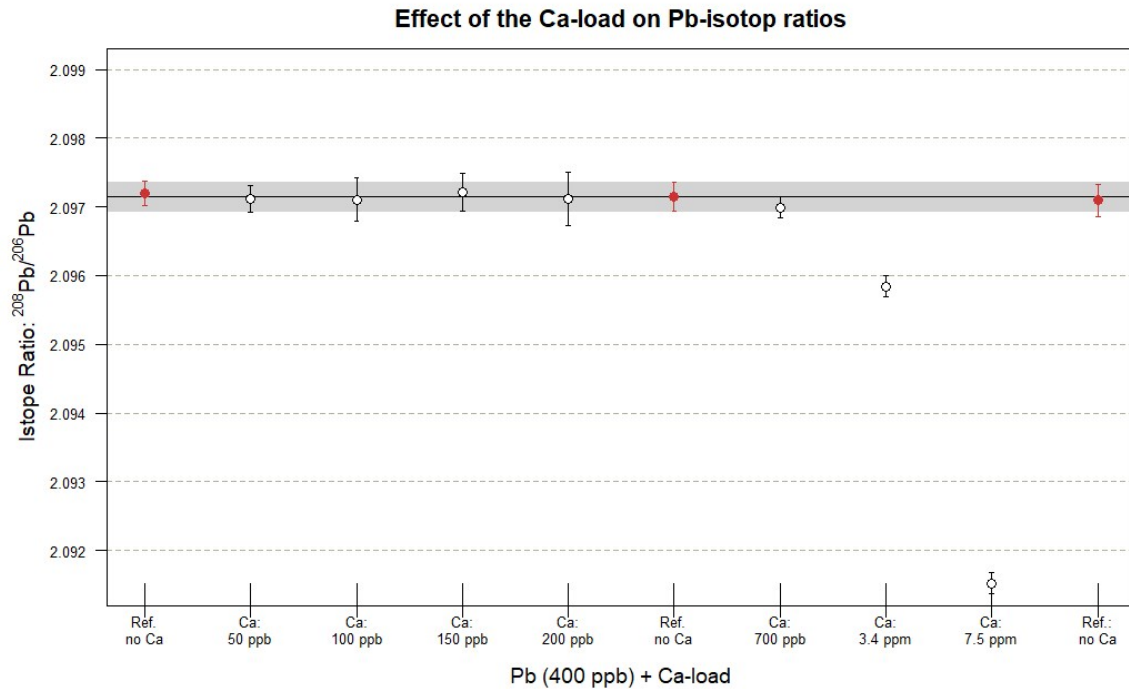


Figure S-4: Influence of additional Ca (white points, in form of added CaCO_3 prior to the digestion: 50, 100, 150, 200, 700, 3'400 and 7'500 ppb, Kremer Pigmente GmbH & Co, Aichstetten/Allgau, Germany) in Pb-Samples (400 ppb, #46000, Kremer Pigmente GmbH & Co, Aichstetten/Allgau, Germany) in regards to the determined Pb-isotope ratios (shown $^{208}\text{Pb}/^{206}\text{Pb}$) given with the standard deviation. The black line ($2.097143 \pm \text{SD}$ (grey area)) is the average from the control measurements, "Ref. no Ca" (red). A Ca-load of >700 ppb rel. to 400 ppb Pb results in high deviation to the true value by keeping a low SD.

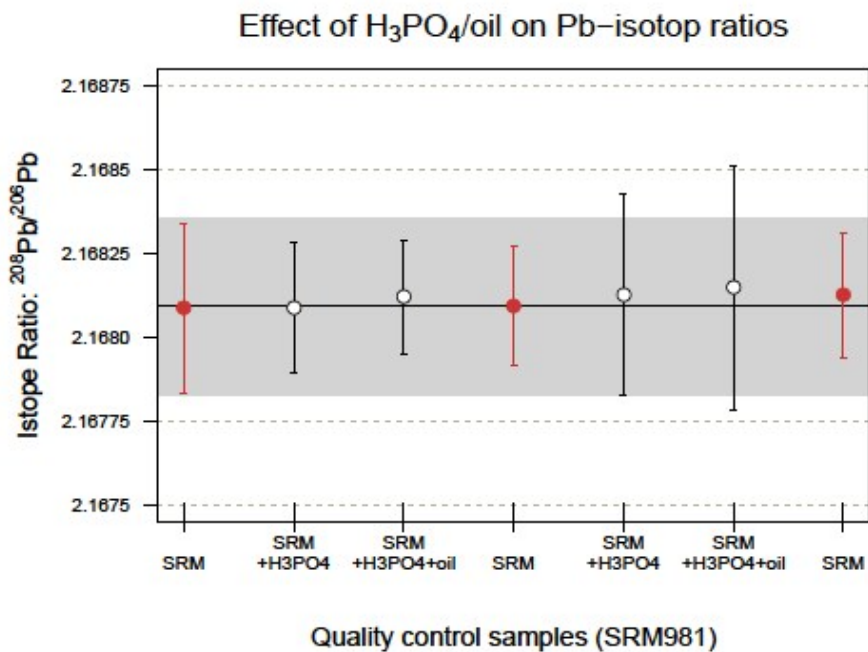


Figure S-5: Effect of the addition of up to 1% H_3PO_4 (+ acid) and linseed oil (+ oil) (white points, #73504, Kremer Pigmente GmbH & Co, Aichstetten/Allgau, Germany) to a Pb-Solution (400 ppb, NIST SRM981) in regards to the isotope ratios after digestion and dilution. The pure Pb-solution is given in red with the individual SD and the mean of the three measurement (black line) with SD (grey box).

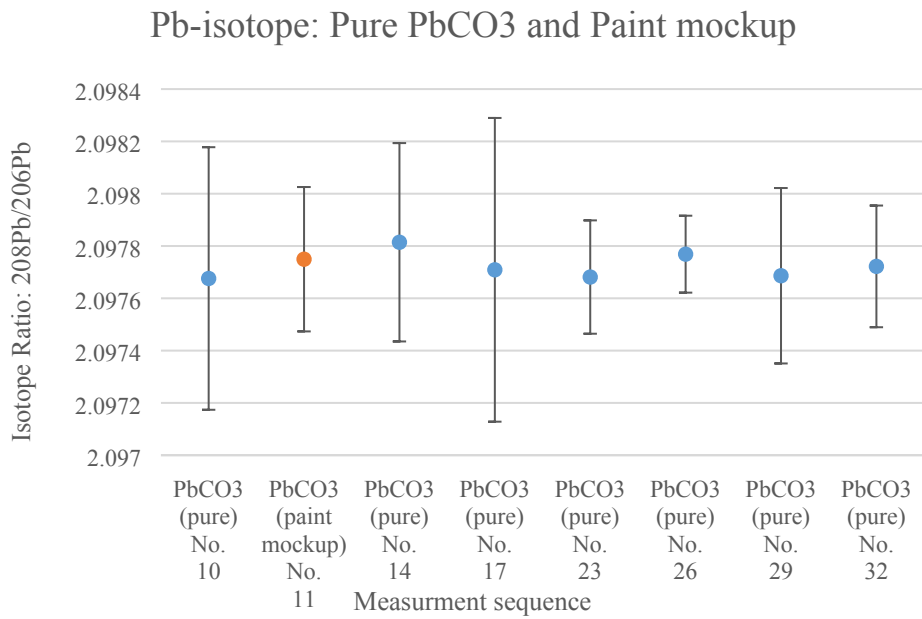


Figure S-6 Effect on the Pb-isotope ration under the addition of linseed oil (#73504, Kremer Pigmente GmbH & Co, Aichstetten/Allgau, Germany) to pure PbCO₃ (#73504, Kremer Pigmente GmbH & Co, Aichstetten/Allgau, Germany) to reconstruct a lead white oil paint. The samples were digested and further diluted to a Pb-Solution (400 ppb) with the addition of 200 ppb Tl. The results for the pure Pb-solution (only PbCO₃) is given in blue over a measurement series indicated by the measurement number (No.) with the individual SD. The paint mockup is given in orange with the SD (No. 11).

Table S-10 Overview of the lead isotope ratios for all the investigated samples, namely $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ with the corresponding RSD (1s, in %). They are summarized as artist, signed date, ETH laboratory code, the lead isotope ratios, the delta value Δ (in %) to the corresponding not Hg-corrected ratios and additional comments if necessary. *A high load of CaCO_3 in the samples (>64%) has an influence on the true lead isotope ratios and the data has therefore to be discarded.

Artist	Signed date	ETH No.	$^{208}\text{Pb}/^{204}\text{Pb}$		$^{207}\text{Pb}/^{204}\text{Pb}$		$^{206}\text{Pb}/^{204}\text{Pb}$		Delta to the not Hg-corrected value (Δ)	Comments / Explanation
Marco Ricci	1711	95049.1.1	38.4226	0.017%	15.6291	0.016%	18.4752	0.016%	0.06%	
		95049.2.1	38.4296	0.015%	15.6323	0.011%	18.4767	0.010%	0.11%	
PH Hill	1795	95052.1.1	38.4360	0.018%	15.6226	0.019%	18.4553	0.017%	0.06%	
Joshua Reynolds	1765	95055.1.1	38.4302	0.016%	15.6300	0.016%	18.4726	0.014%	0.13%	
		95055.2.1	38.4327	0.015%	15.6302	0.014%	18.4727	0.013%	0.11%	
Richard wilson	1761	95061.1.1	38.4411	0.015%	15.6116	0.016%	18.4517	0.015%	0.01%	
		95061.2.1	38.4667	0.019%	15.6220	0.018%	18.4636	0.018%	0.02%	
Georges Romney (a) / (b)	1770	95064.1.1	38.4061	0.020%	15.6202	0.014%	18.4584	0.011%	0.07%	
		95067.1.1	38.4060	0.029%	15.6220	0.035%	18.4613	0.018%	0.01%	
		95064.3.1	38.4309	0.026%	15.6290	0.017%	18.4704	0.014%	0.02%	
		95067.2.1	38.4275	0.015%	15.6295	0.015%	18.4706	0.013%	0.01%	
Samuel Alken	1795	95070.1.1	38.4157	0.017%	15.6111	0.016%	18.4284	0.015%	0.01%	*Ca-load too high
		95070.2.1	38.4422	0.018%	15.6210	0.016%	18.4403	0.015%	0.01%	*Ca-load too high
JF Sartorius	1803	95073.1.1	NA	NA	NA	NA	NA	NA	NA	
		95073.3.1	38.4283	0.019%	15.6216	0.017%	18.4293	0.016%	0.01%	
JW Swift	1840	95076.1.1	38.4390	0.021%	15.6279	0.018%	18.4382	0.018%	0.01%	
William Meadows	1868	95079.1.1	38.4288	0.017%	15.6245	0.015%	18.4326	0.014%	0.03%	
		95079.1.1	38.4449	0.018%	15.6278	0.016%	18.4358	0.015%	0.00%	
		95079.2.1	38.4552	0.014%	15.6310	0.014%	18.4337	0.013%	0.01%	
Henry Tanworth Wells	1874	95082.1.1	38.4117	0.021%	15.6295	0.015%	18.3764	0.016%	0.04%	
		95082.2.1	38.4206	0.013%	15.6330	0.015%	18.3816	0.014%	0.01%	

Sir Arthur Stockdale Cope	1901	95085.1.1	38.5513	0.012%	15.6642	0.011%	18.4389	0.010%	0.01%	
		95085.3.1	38.5298	0.031%	15.6585	0.020%	18.4287	0.018%	0.01%	
		95085.3.1	38.5379	0.019%	15.6617	0.016%	18.4324	0.016%	0.03%	
		95085.5.1	38.5435	0.017%	15.6645	0.017%	18.4358	0.015%	0.01%	
Title/object - artist										
Eric Magnus Louis Grand Hauteville – By anonymous in style of Amélie Munier Romilly	1813	LM-161897	38.4395	0.019%	15.6258	0.017%	18.4418	0.015%	0.01%	
		LM-161897	38.4366	0.019%	15.6252	0.017%	18.4410	0.017%	0.01%	
		LM-161897	38.4311	0.029%	15.6234	0.030%	18.4393	0.028%	0.01%	
Adolphe Morand – By Jh. Loretti	1863	LM-114651	38.3668	0.019%	15.6253	0.019%	18.3794	0.018%	0.02%	
Hugo Siegwart – By Carl August Liner	1907	LM-158151	38.7349	0.019%	15.6618	0.019%	18.5291	0.017%	0.02%	*Ca-load to high
Preliminary design for “die Wiege der Eidgenossenschaft” – By Charles Giron	1899-1902	LM-161803	NA	NA	NA	NA	NA	NA	NA	Sample amount not sufficient for analysis
Giambattista Somazzl – By anonymous	1733	LM-40076	38.4100	0.020%	15.6308	0.020%	18.4468	0.019%	0.29%	
Salomon Ruppert – By Caspar Bachmann	1797	LM-7723	38.4181	0.028%	15.6242	0.016%	18.4341	0.014%	0.40%	
Marie Regine Krus-Guérmand – By Joseph Wyrsch	1783	LM-52427	38.4288	0.016%	15.6268	0.019%	18.4422	0.017%	0.11%	
Margrit – by Franz Rederer SIK-98511	1962	88907.3.1	38.5654	0.031%	15.6525	0.031%	18.4167	0.035%	0.01%	
		69024.9.1	38.5662	0.035%	15.6526	0.030%	18.4152	0.029%	0.02%	
Artist	Signed date	ETH No.	²⁰⁸Pb/²⁰⁶Pb		²⁰⁷Pb/²⁰⁶Pb					Comments / Explanation
Marco Ricci	1711	95049.1.1	2.07970	0.007%	0.845971	0.004%				
		95049.2.1	2.07989	0.007%	0.846047	0.004%				
PH Hill	1795	95052.1.1	2.08266	0.006%	0.846506	0.005%				

Joshua Reynolds	1765	95055.1.1	2.08039	0.006%	0.846115	0.004%				
		95055.2.1	2.08051	0.007%	0.846122	0.004%				
Richard wilson	1761	95061.1.1	2.08331	0.005%	0.846083	0.004%				
		95061.2.1	2.08336	0.006%	0.846100	0.005%				
Georges Romney (a) / (b)	1770	95064.1.1	2.08066	0.010%	0.846235	0.004%				
		95067.1.1	2.08034	0.012%	0.846181	0.004%				
		95064.3.1	2.08068	0.007%	0.846171	0.004%				
		95067.2.1	2.08046	0.005%	0.846180	0.004%				
Samuel Alken	1795	95070.1.1	2.08459	0.005%	0.847125	0.004%				*Ca-load too high
		95070.2.1	2.08469	0.005%	0.847116	0.004%				*Ca-load too high
JF Sartorius	1803	95073.1.1	NA	NA	NA	NA				
		95073.3.1	2.08516	0.009%	0.847641	0.005%				
JW Swift	1840	95076.1.1	2.08475	0.007%	0.847587	0.004%				
William Meadows	1868	95079.1.1	2.08480	0.011%	0.847642	0.006%				
		95079.1.1	2.08533	0.006%	0.847685	0.004%				
		95079.2.1	2.08614	0.007%	0.847964	0.005%				
Henry Tanworth Wells	1874	95082.1.1	2.09029	0.013%	0.850533	0.005%				
		95082.2.1	2.09015	0.007%	0.850470	0.004%				
Sir Arthur Stockdale Cope	1901	95085.1.1	2.09078	0.006%	0.849517	0.004%				
		95085.3.1	2.09080	0.011%	0.849702	0.005%				
		95085.3.1	2.09078	0.008%	0.849683	0.005%				
		95085.5.1	2.09070	0.007%	0.849675	0.004%				
Title/object - artist										
Eric Magnus Louis Grand Hauteville – By anonymous in style of Amélie Munier Romilly	1813	LM-161897	2.08438	0.008%	0.847302	0.004%				
		LM-161897	2.08430	0.006%	0.847298	0.004%				
		LM-161897	2.08419	0.009%	0.847276	0.006%				
Adolphe Morand – By Jh. Loretti	1863	LM-114651	2.08748	0.006%	0.850150	0.004%				

Hugo Siegwart – By Carl August Liner	1907	LM-158151	2.09048	0.007%	0.845257	0.005%				*Ca-load to high
Preliminary design for “die Wiege der Eidgenossenschaft” – By Charles Giron	1899-1902	LM-161803	NA	NA	NA	NA				Sample amount not sufficient for analysis
Giambattista Somazzl – By anonymous	1733	LM-40076	2.08220	0.006%	0.847351	0.004%				
Salomon Ruppert – By Caspar Bachmann	1797	LM-7723	2.08406	0.006%	0.847597	0.012%				
Marie Regine Krus-Guérmand – By Joseph Wyrsh	1783	LM-52427	2.08372	0.007%	0.847336	0.004%				
Margrit – by Franz Rederer SIK-98511	1962	88907.3.1	2.09410	0.004%	0.849932	0.007%				
		69024.9.1	2.09425	0.006%	0.849982	0.007%				

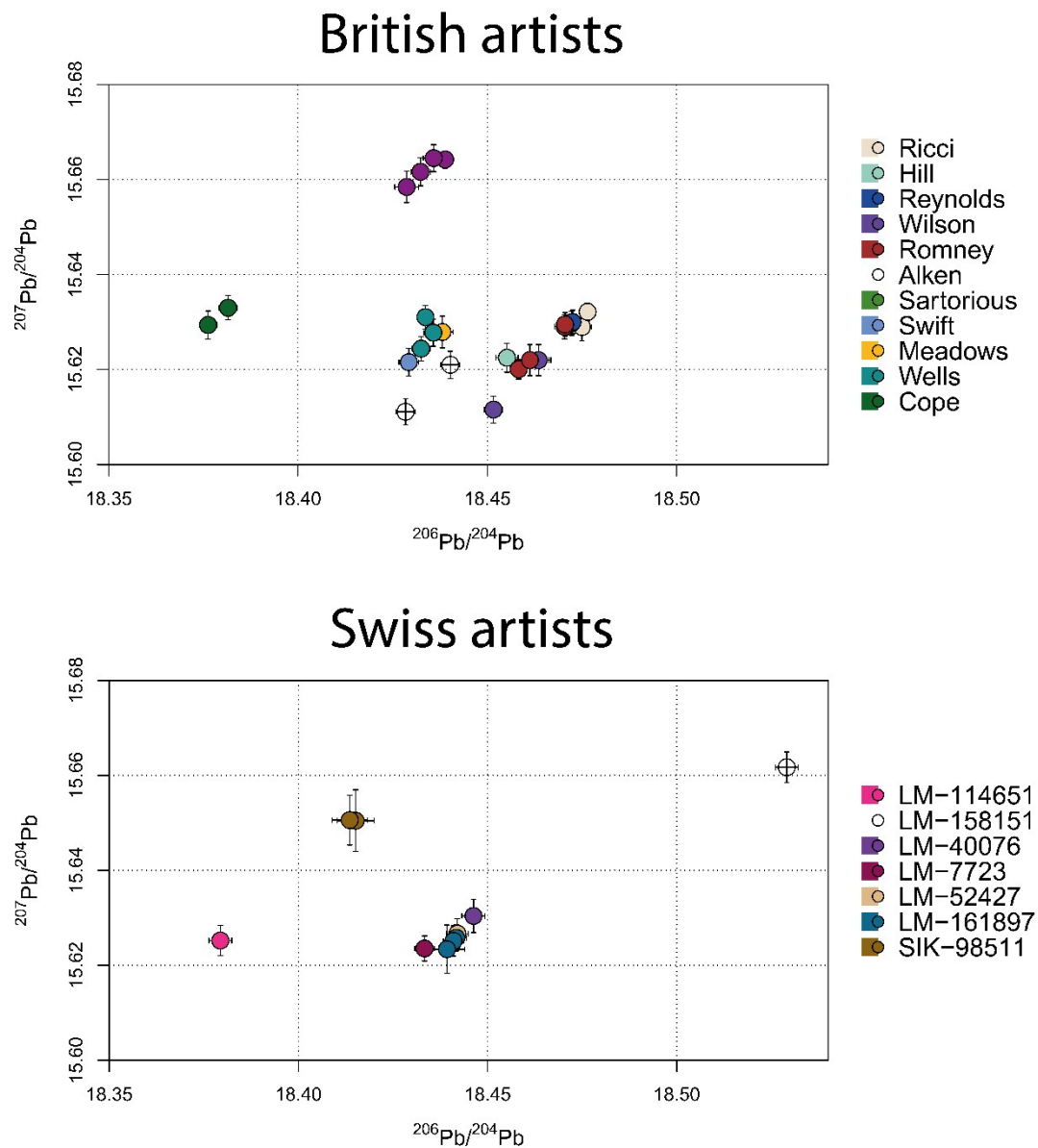


Figure S-7 Lead isotope ratios ($\pm$ standard deviation) determined for all the analyzed paintings ($^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$): orange from British artist (top) and blue from Swiss artists (bottom). They are individually color-coded given by the labels on the side. The empty data points are represent samples where the CaCO_3 -load can likely bias the lead isotope ratio determination.

Classification based on Keisch et al. 1976

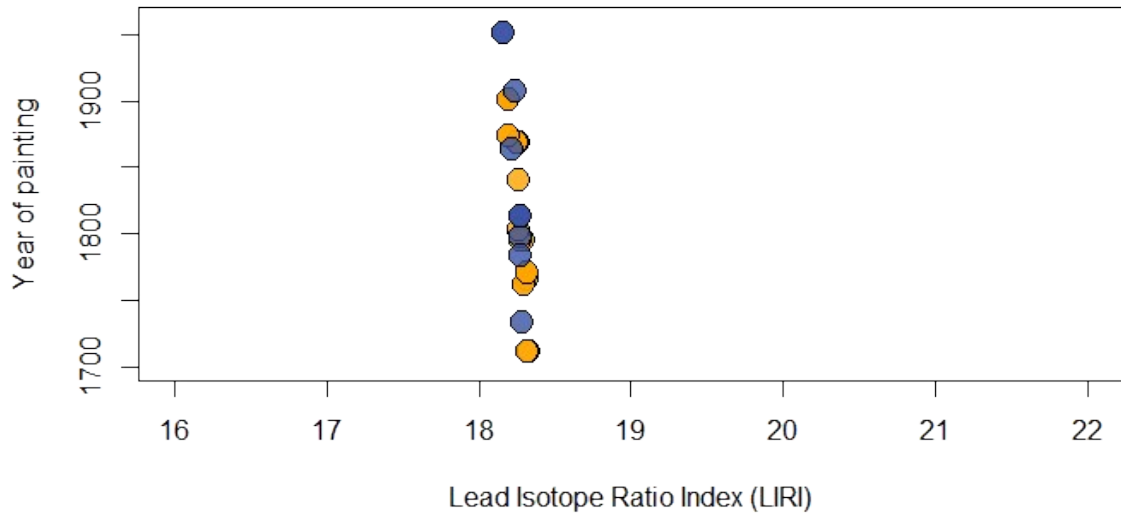


Figure S-8 Results from the LIRI-data of all the investigated samples (based on Keisch 1976)¹⁸ against the signed date of the paintings; British artists: orange, Swiss artists: blue. The data is lying on a straight line and shows no spread after 1850 as expected from literature^{18,19}. The LIRI was calculated based on the following formula: $LIRI = 35.385 + 0.4729 * (^{206}\text{Pb}/^{204}\text{Pb}) - 0.5519 * (^{206}\text{Pb}/^{204}\text{Pb} * ^{207}\text{Pb}/^{206}\text{Pb}) - 8.2561 * (^{208}\text{Pb}/^{206}\text{Pb})$.

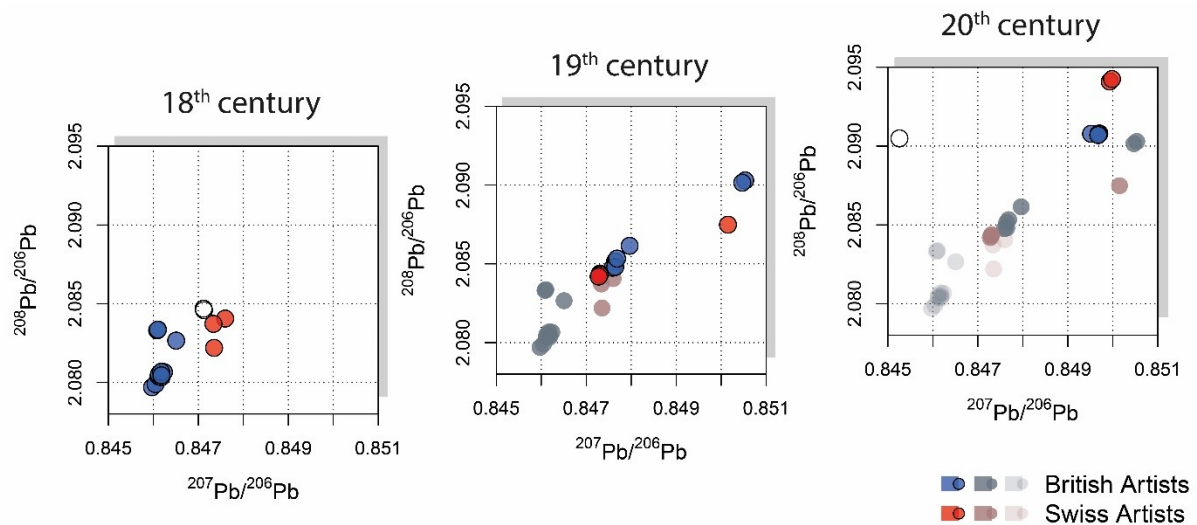


Figure S-9: Lead isotope ratios for the sample collection of this project ($^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$). The paintings from British artist are labelled blue, the ones from Swiss Artists are red. The three different plots are separated based on the century of the signed date to the corresponding painting given with the older data points in increasing transparency. The empty data points had to be disregarded, based on their CaCO_3 -load which affects their true lead isotope ratios. Although these were determined, no error bars representing the standard deviations from the individual measurements are shown in this plot due to their small value compared data points font size.

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