Results on a XRF study of the Mosaic at the house of Neptune and Amphitrite at Herculaneum. A collaborative project between Pratt, RWTH, University of Aachen, and the Herculaneum Conservation Project

Part i

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Location of analysis note numbers(zoom in to see numbers):

Bruce Kaiser insight

So I did a bunch of plots of your data with some of data I have from some other sources. I am having problems with your "glass" data.

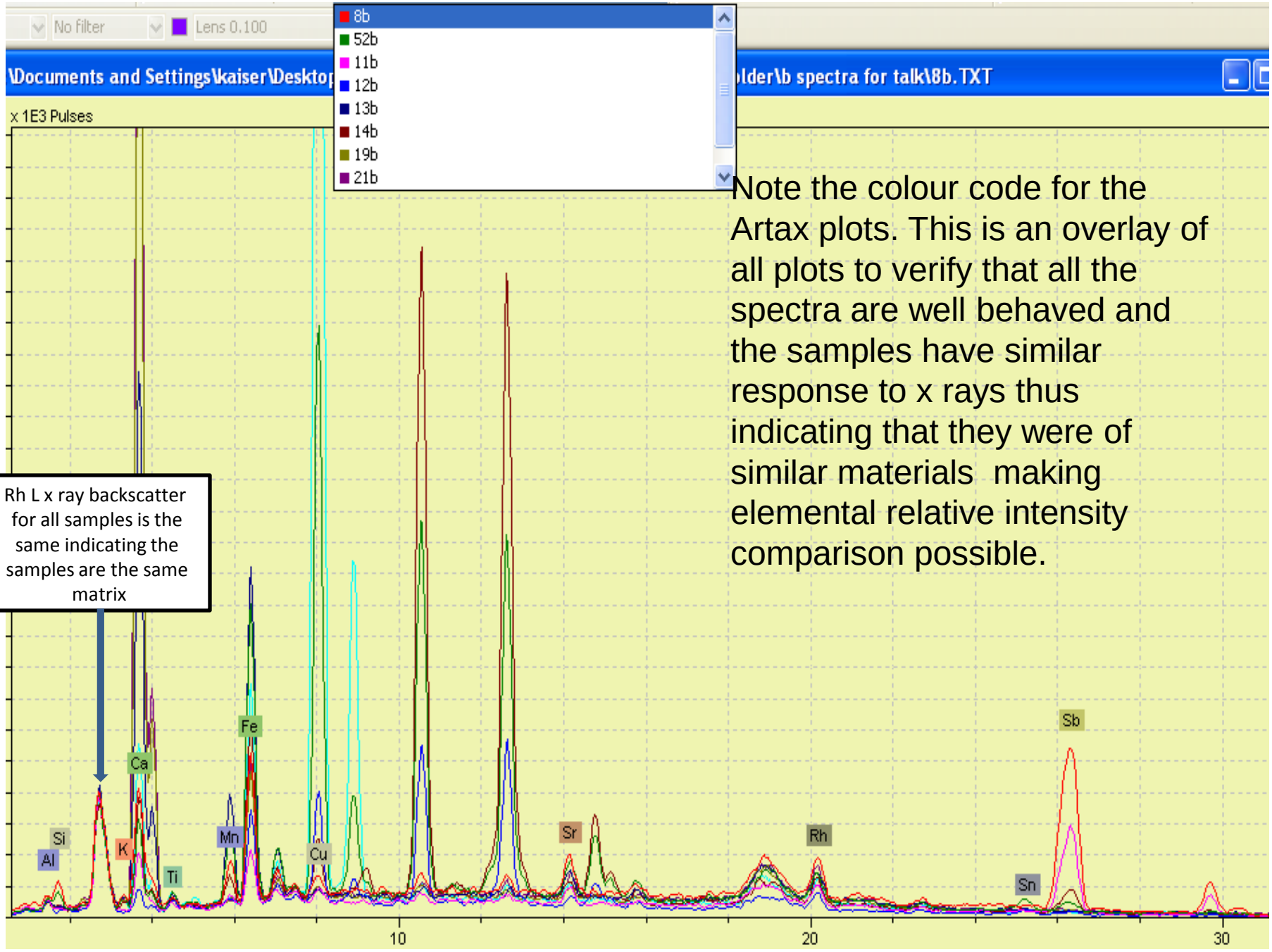
The Si signal is too low in your b spectra. And when there is Pb in your samples there is a very low Pb M peak. This indicates that their was something between your mosaic and the analyzer or the "glass" . It has been covered with a wax or varnish that stops the low energy x rays from getting out.

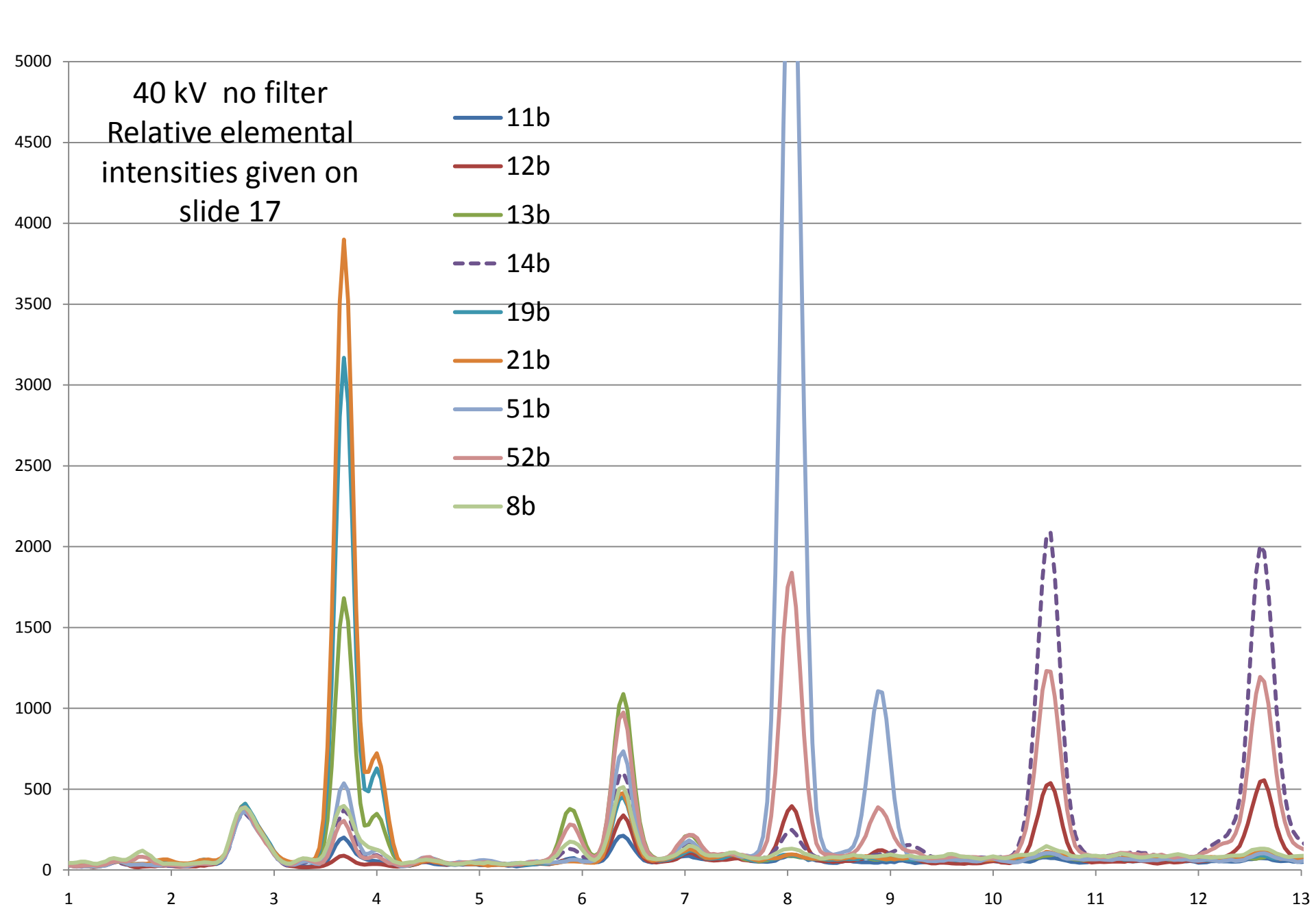
Also I did a semi quant comparison of elemental content of b spectra.

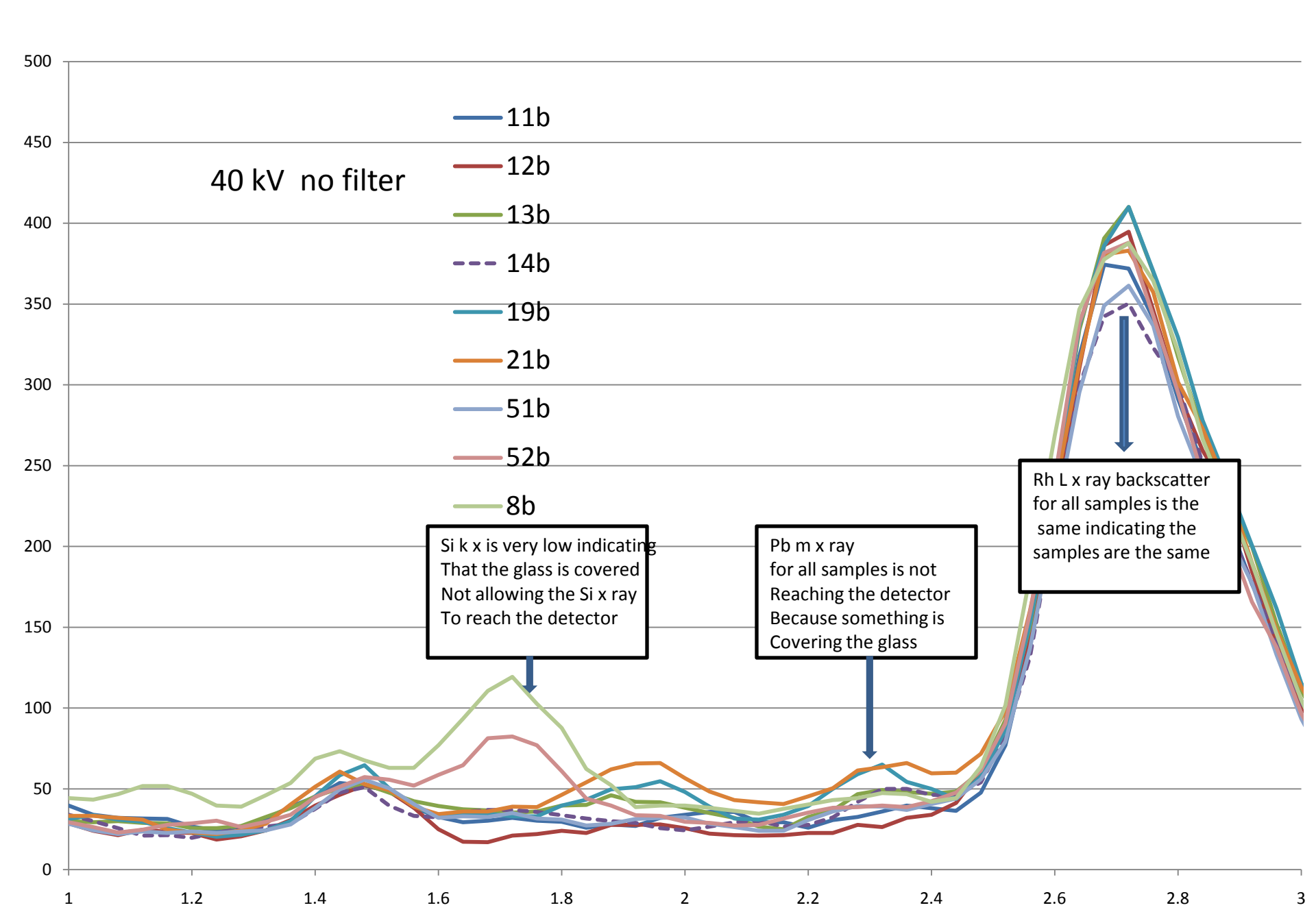
Glasses begin as mixtures of **oxides**. Their compositions can be represented by listing the weight percentages of their components. Compare the percentages for **1**, a typical, modern soda-lime-silica glass (used to make bottles and windows); **2**, laboratory and some baking ware; **3**, optical, high lead crystal; **4**, 96% silica glass (can withstand very high temperatures); **5**,a typical, ancient Roman soda-lime-silica glass.

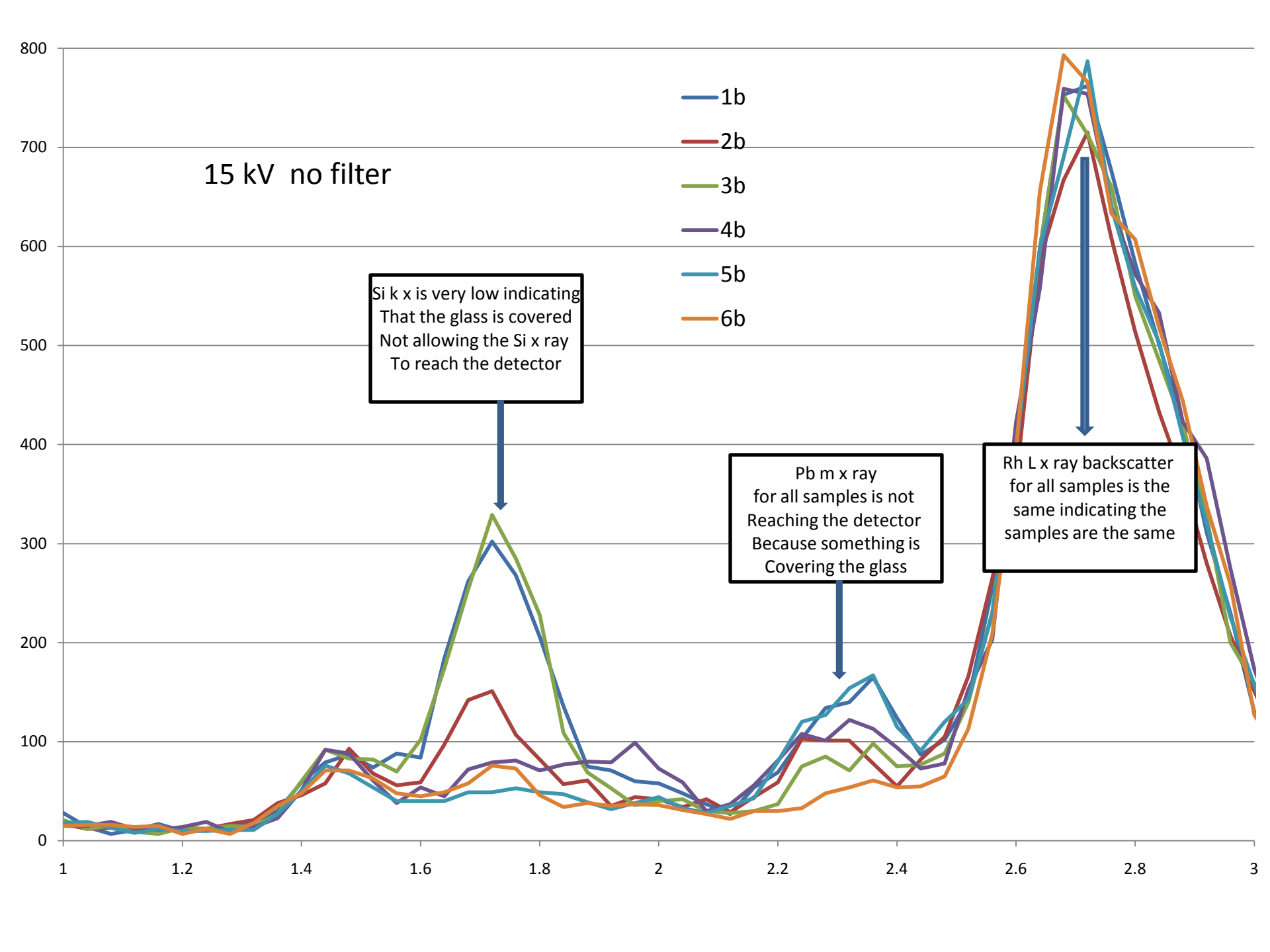
		1	**2**	**3**	**4**	**5**
Silica	SiO_2	73.6%	80.0%	35.0%	96.5%	67.0%
Soda	Na_2O	16.0	4.	--	--	18.0
Lime	CaO	5.2	--	--	--	8.0
Potash	K_2O	0.6	0.4	7.2	--	1.0
Magnesia	MgO	3.6	--	--	--	1.0
Alumina	Al_2O_3	1.0	2.0	--	0.5	2.5
Iron Oxide	Fe_2O_3	--	--	--	--	0.5
Boric Oxide	B_2O_3	--	13.0	--	3.0	--
Lead Oxide	PbO	--	--	58.0	--	0.01

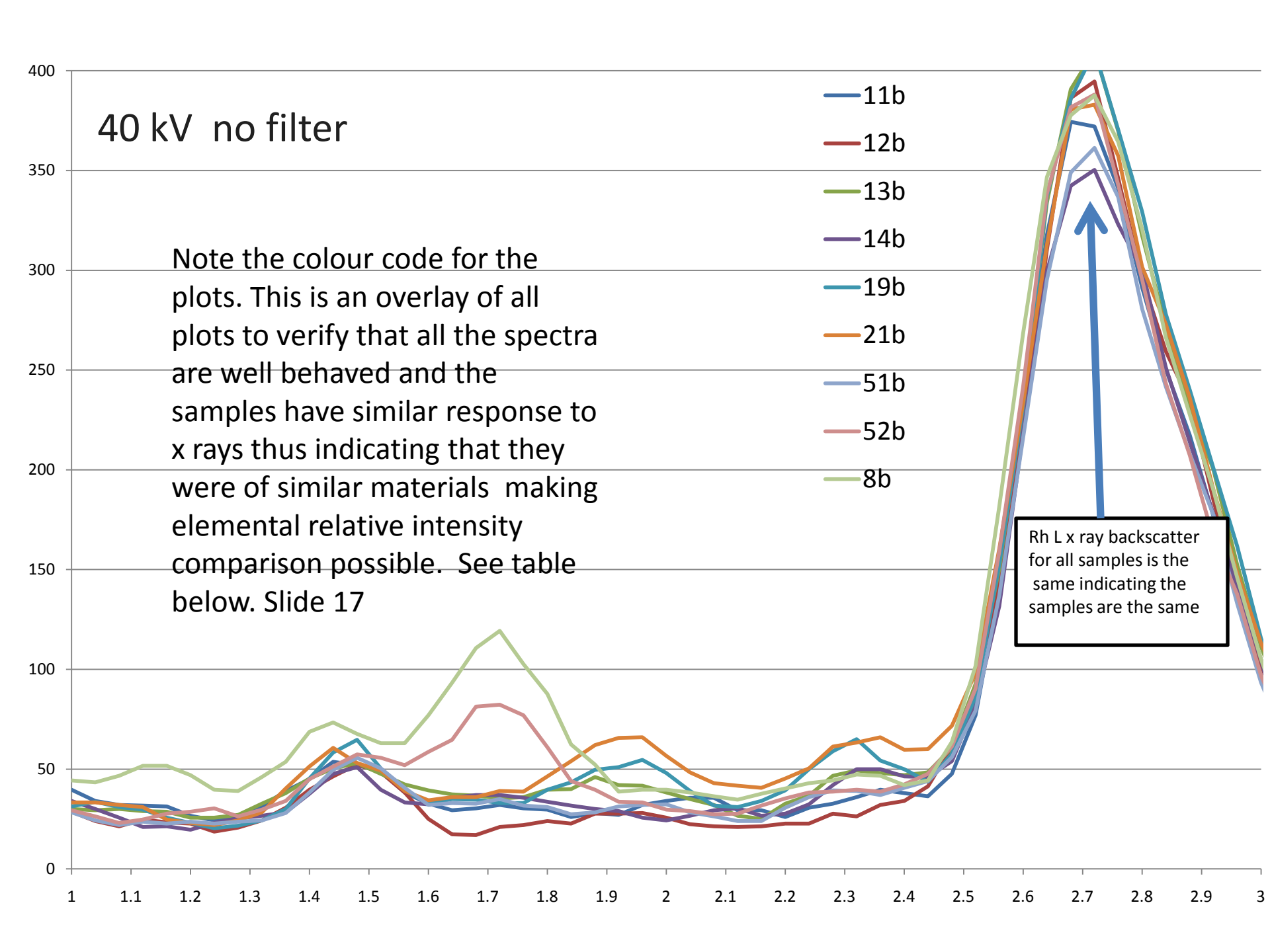
	Colourant	Content	Comments	Furnace Conditions
'Aqua'	Iron(II) oxide (FeO)		‘Aqua’, a pale blue-green colour, is the common natural colour of untreated glass. Many early Roman vessels are this colour.[6]	
Colourless	Iron(III) oxide (Fe_2O_3)		Colourless glass was produced in the Roman period by adding manganese oxide.[1] This oxidised the iron (II) oxide to iron (III) oxide, which although yellow, is a much weaker colourant, allowing the glass to appear colourless. The use of manganese as a decolourant was a Roman invention first noted in the Imperial period; prior to this, antimony-rich minerals were used.[1]	
Amber	Iron-sulfur compounds	0.2%-1.4% S[1] 0.3% Fe	Sulfur is likely to have entered the glass as a contaminant of natron, producing a green tinge. Formation of iron-sulfur compounds produces an amber colour.	Reducing
Purple	Manganese (such as pyrolusite)	Around 3%[1]		Oxidising[1]
Blue and green	Copper	2%-13%[1]	The natural ‘aqua’ shade can be intensified with the addition of copper. During the Roman period this was derived from the recovery of oxide scale from scrap copper when heated, to avoid the contaminants present in copper minerals.[1] Copper produced a translucent blue moving towards a darker and denser green.	Oxidising[1]
Dark green	Lead		By adding lead, the green colour produced by copper could be darkened.[1]	
Royal blue to navy	Cobalt	0.1%[1]	Intense colouration	
Powder blue	Egyptian blue[1]			
Opaque red to brown	Copper lead	>10% Cu 1% - 20% Pb[1]	Under strongly reducing conditions, copper present in the glass will precipitate inside the matrix as cuprous oxide, making the glass appear brown to blood red. Lead encourages precipitation and brilliance. The red is a rare find, but is known to have been in production during the fourth, fifth and later centuries on the continent.[20]	Strongly reducing
White	Antimony (such as stibnite)	1-10%[1]	Antimony reacts with the lime in the glass matrix to precipitate calcium antimonite crystals creating a white with high opacity.[1]	Oxidising
Yellow	Antimony and lead (such as bindheimite).[1]		Precipitation of lead pyroantimonate creates an opaque yellow. Yellow rarely appears alone in Roman glass, but was used for the mosaic and polychrome pieces.[1]	

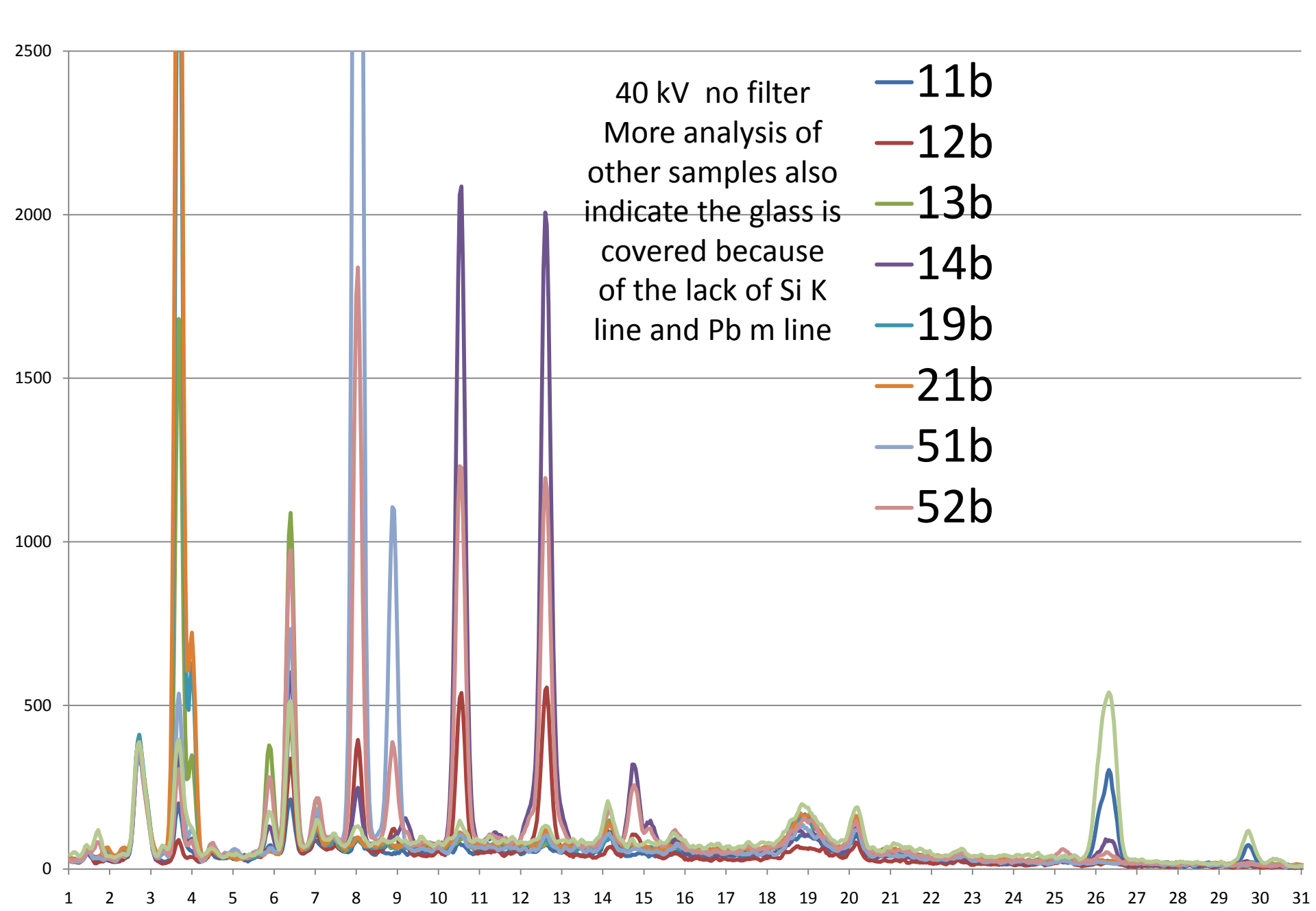

No filter
Lens 0.100
8b
52b
11b
12b
13b
14b
19b
21b
\Documents and Settings\kaiser\Desktop
lder\b spectra for talk\8b.TXT
x 1E3 Pulses
Rh L x ray backscatter for all samples is the same indicating the samples are the same matrix
Note the colour code for the Artax plots. This is an overlay of all plots to verify that all the spectra are well behaved and the samples have similar response to x rays thus indicating that they were of similar materials making elemental relative intensity comparison possible.
Si
Al
K
Ca
Ti
Mn
Fe
Cu
Sr
Rh
Sn
Sb
10
20
30

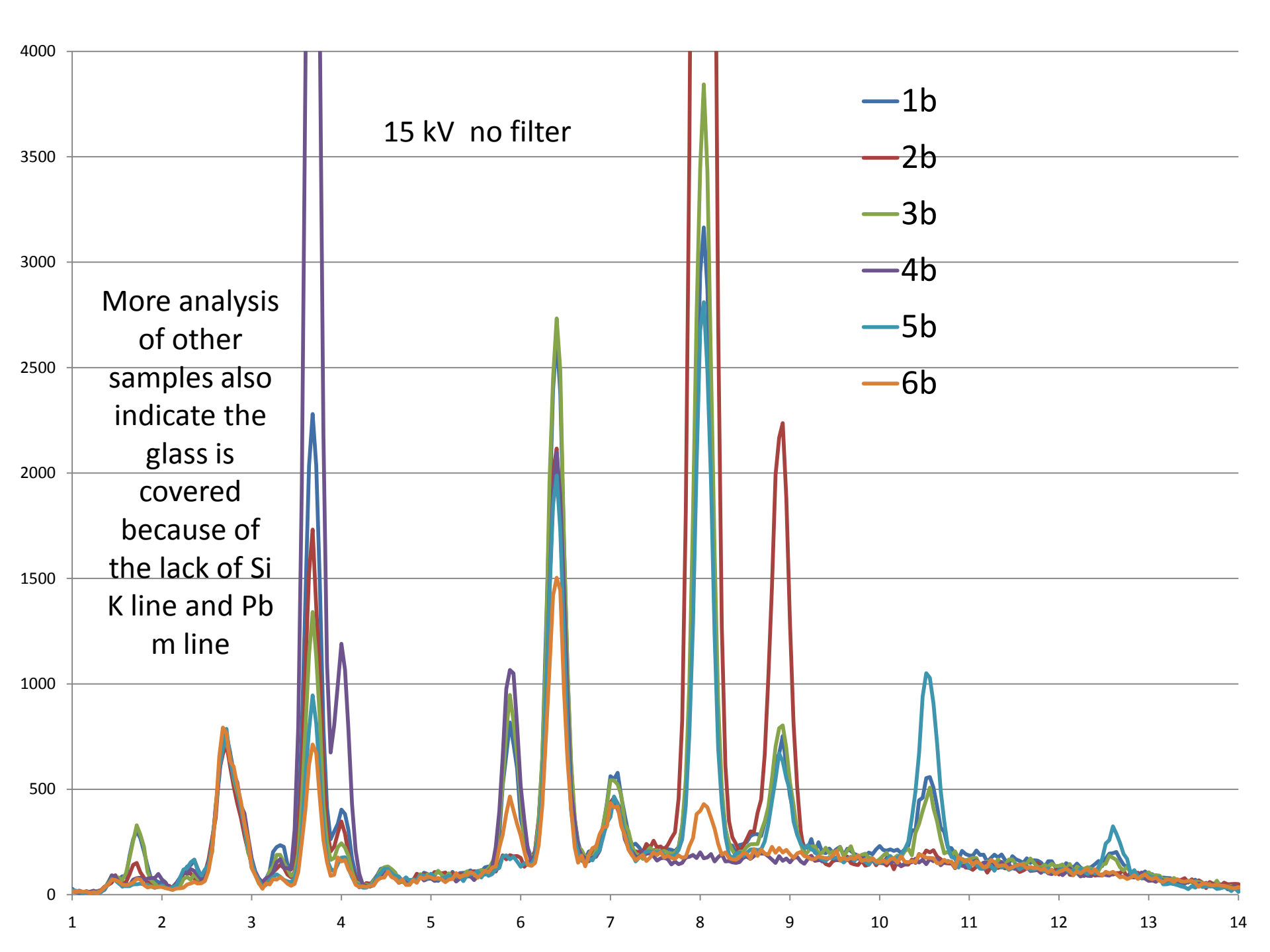

40 kV no filter
Relative elemental intensities given on slide 17
11b
12b
13b
14b
19b
21b
51b
52b
8b
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1
2
3
4
5
6
7
8
9
10
11
12
13

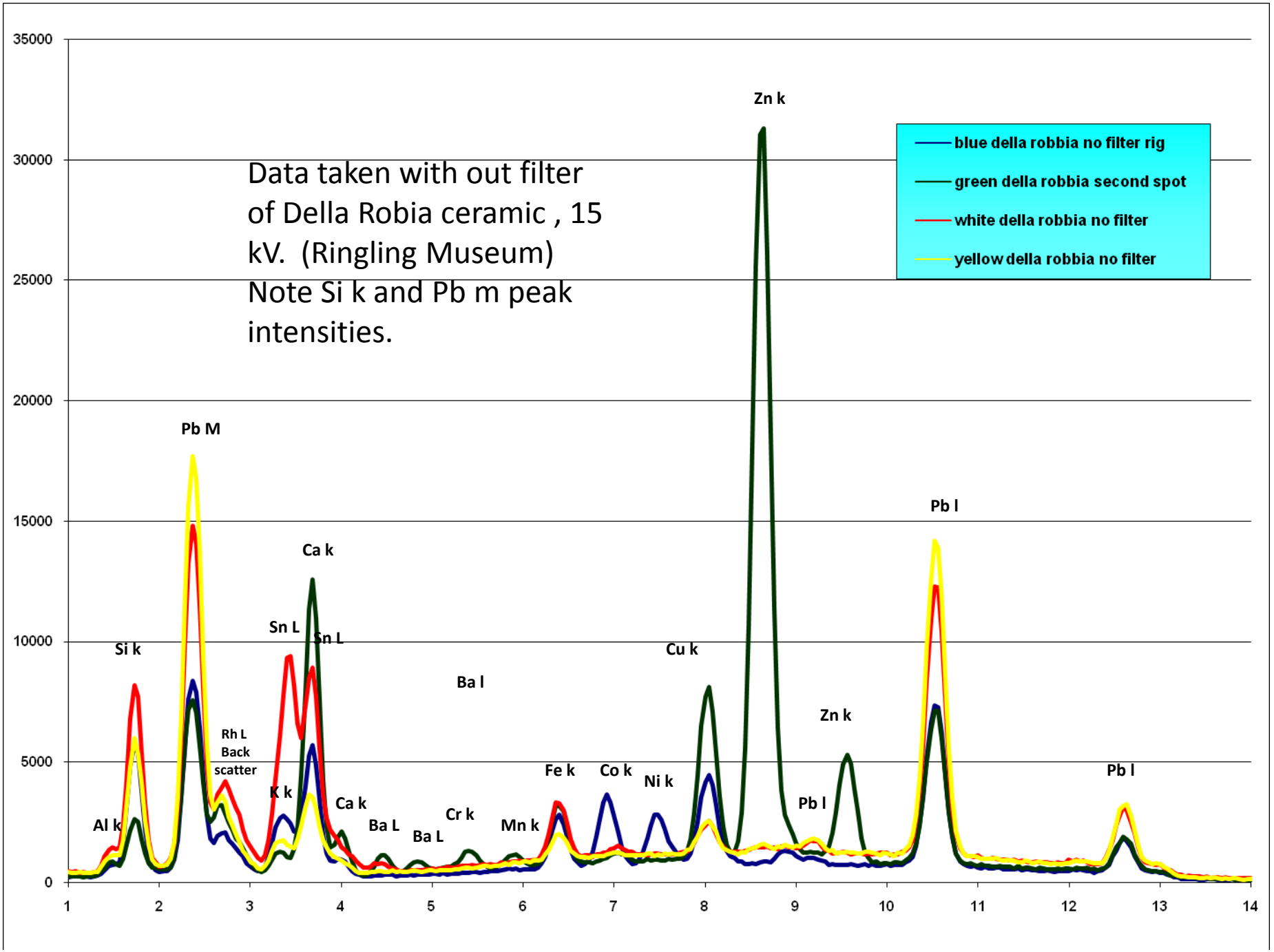

40 kV no filter
11b
12b
13b
14b
19b
21b
51b
52b
8b
Si k x is very low indicating
That the glass is covered
Not allowing the Si x ray
To reach the detector
Pb m x ray
for all samples is not
Reaching the detector
Because something is
Covering the glass
Rh L x ray backscatter
for all samples is the
same indicating the
samples are the same
500
450
400
350
300
250
200
150
100
50
0
1
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3

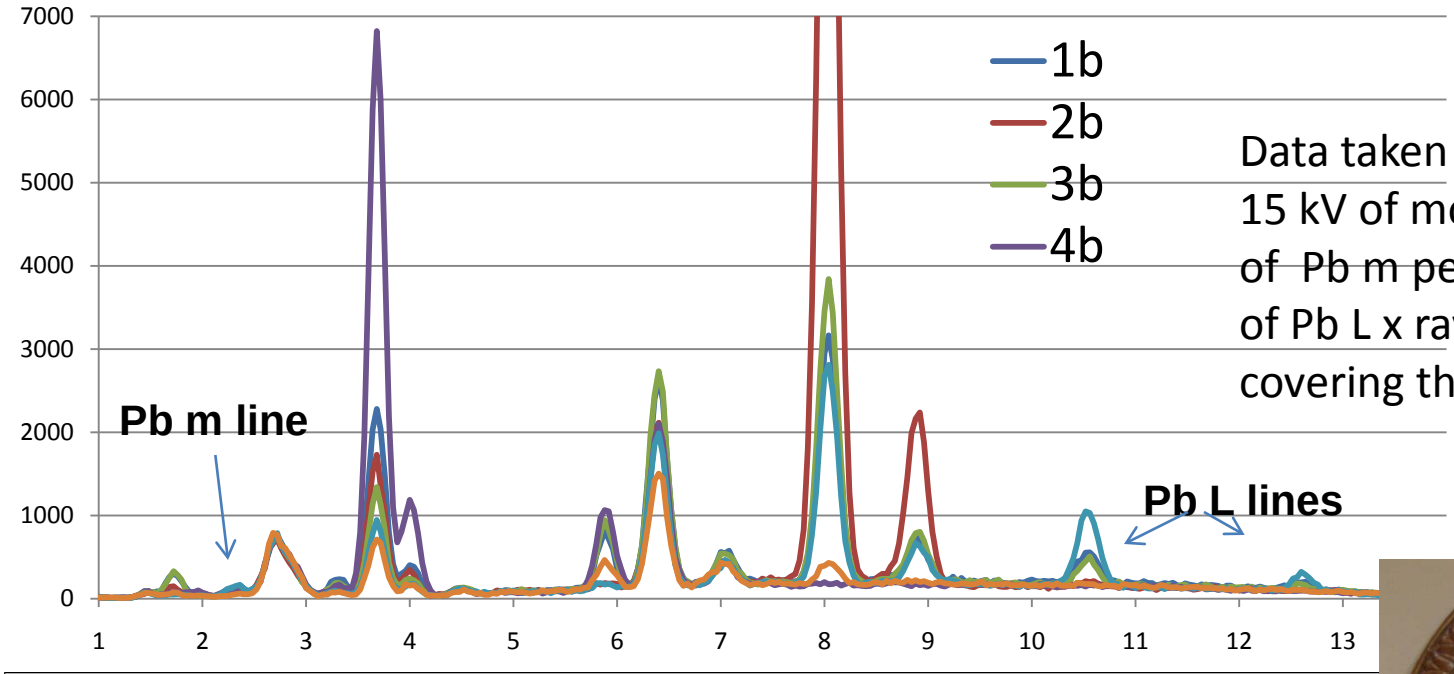

15 kV no filter
1b
2b
3b
4b
5b
6b
Si k x is very low indicating
That the glass is covered
Not allowing the Si x ray
To reach the detector
Pb m x ray
for all samples is not
Reaching the detector
Because something is
Covering the glass
Rh L x ray backscatter
for all samples is the
same indicating the
samples are the same
800
700
600
500
400
300
200
100
0
1
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3


40 kV no filter
Note the colour code for the plots. This is an overlay of all plots to verify that all the spectra are well behaved and the samples have similar response to x rays thus indicating that they were of similar materials making elemental relative intensity comparison possible. See table below. Slide 17
11b
12b
13b
14b
19b
21b
51b
52b
8b
Rh L x ray backscatter for all samples is the same indicating the samples are the same
400
350
300
250
200
150
100
50
0
1
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3

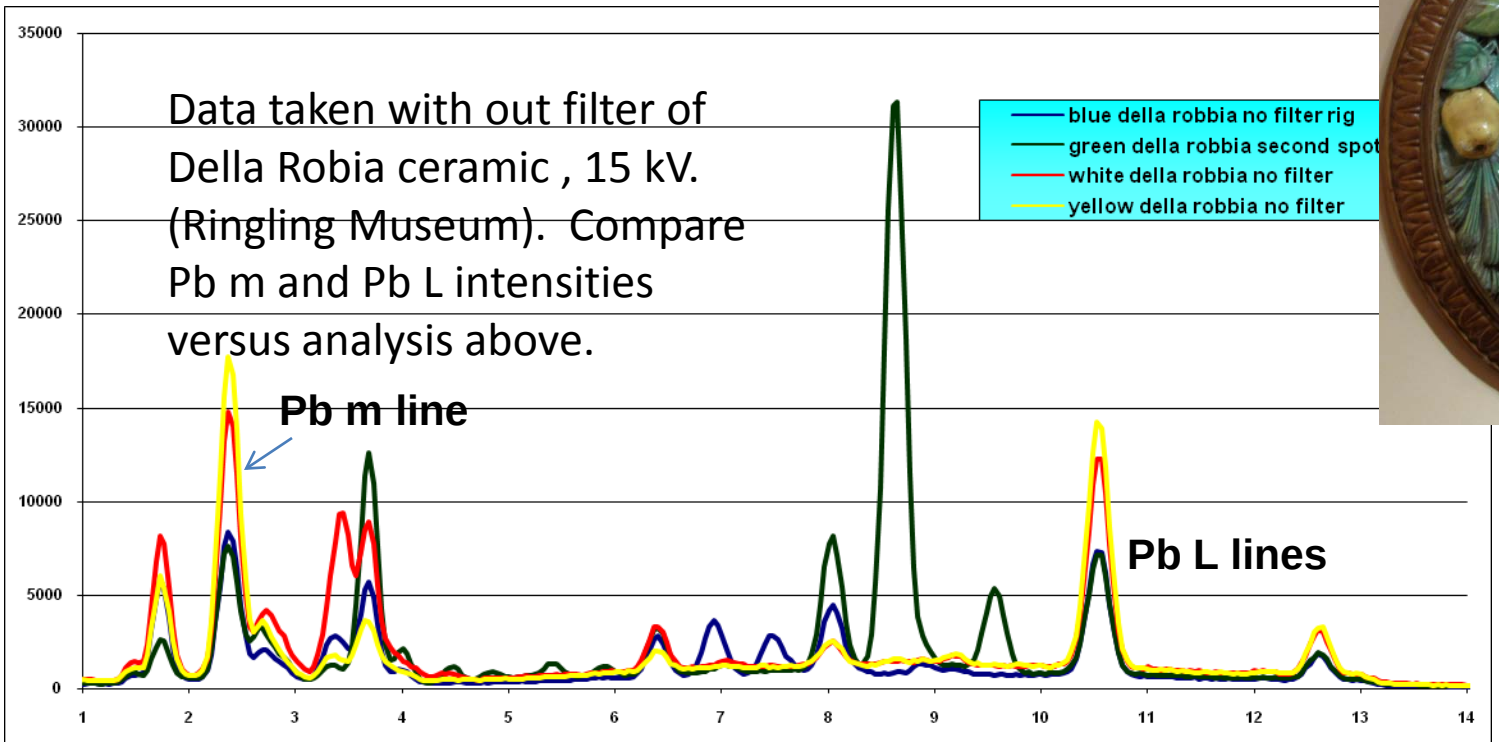

40 kV no filter
More analysis of other samples also indicate the glass is covered because of the lack of Si K line and Pb m line
11b
12b
13b
14b
19b
21b
51b
52b
2500
2000
1500
1000
500
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31


15 kV no filter
1b
2b
3b
4b
5b
6b
More analysis of other samples also indicate the glass is covered because of the lack of Si K line and Pb m line
4000
3500
3000
2500
2000
1500
1000
500
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14


Data taken with out filter of Della Robia ceramic , 15 kV. (Ringling Museum)
Note Si k and Pb m peak intensities.
blue della robbia no filter rig
green della robbia second spot
white della robbia no filter
yellow della robbia no filter
Al k
Si k
Pb M
Rh L Back scatter
K k
Sn L
Ca k
Sn L
Ca k
Ba L
Ba L
Ba l
Cr k
Mn k
Fe k
Co k
Ni k
Cu k
Zn k
Pb l
Zn k
Pb l
Pb l
35000
30000
25000
20000
15000
10000
5000
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14



Data taken with out filter 15 kV of mosaic. Note lack of Pb m peak and yet lots of Pb L x rays. Something is covering the glass



Data taken with out filter of Della Robia ceramic , 15 kV. (Ringling Museum). Compare Pb m and Pb L intensities versus analysis above.

The following is a net area analysis of the b spectra using Artax software.

Note that this method is only effective at comparing a given element from sample to sample, NOT element to element within a sample.

This also only is effective when the samples are of the same matrix so the response to the x ray beam is similar, in this case all are glass.

Note Rh is not present in the glass, it is a backscattered x ray from the instrument and is monitored to assure that the material is consistent, i.e. same backscatter same material type.

Element	Line	Energy/keV	8 white	52 med Dark Green	21 Beige	19 orange	14 yellow	13 l brown	12 red	11 med blue
Al	K12	1.486	42	1	14	56	40	22	91	49
Si	K12	1.74	346	242	4	20	53	25	1	3
Ca	K12	3.692	1861	1395	21574	17203	1832	9030	373	1032
Mn	K12	5.9	764	1355	71	115	482	1919	117	194
Fe	K12	6.405	2623	5283	2498	2379	3290	5819	1639	982
Ni	K12	7.48	195	148	196	162	159	200	104	234
Cu	K12	8.046	394	10875	173	187	1069	180	2015	273
Sr	K12	14.165	1009	727	547	314	372	719	198	438
Zr	K12	15.775	289	341	94	134	209	215	110	90
Rh	K12	20.216	1108	849	936	819	625	847	423	538
Rh	L1	2.697	1907	1826	1751	1853	1696	1869	1893	1799
Sn	K12	25.271	91	361	44	78	135	139	169	41
Sb	K12	26.359	6442	311	114	110	869	54	140	3159
Ba	L1	4.466	111	222	145	153	156	247	137	113
Pb	L1	10.551	553	8147	397	358	13895	257	3391	329

white

med dark green

biege

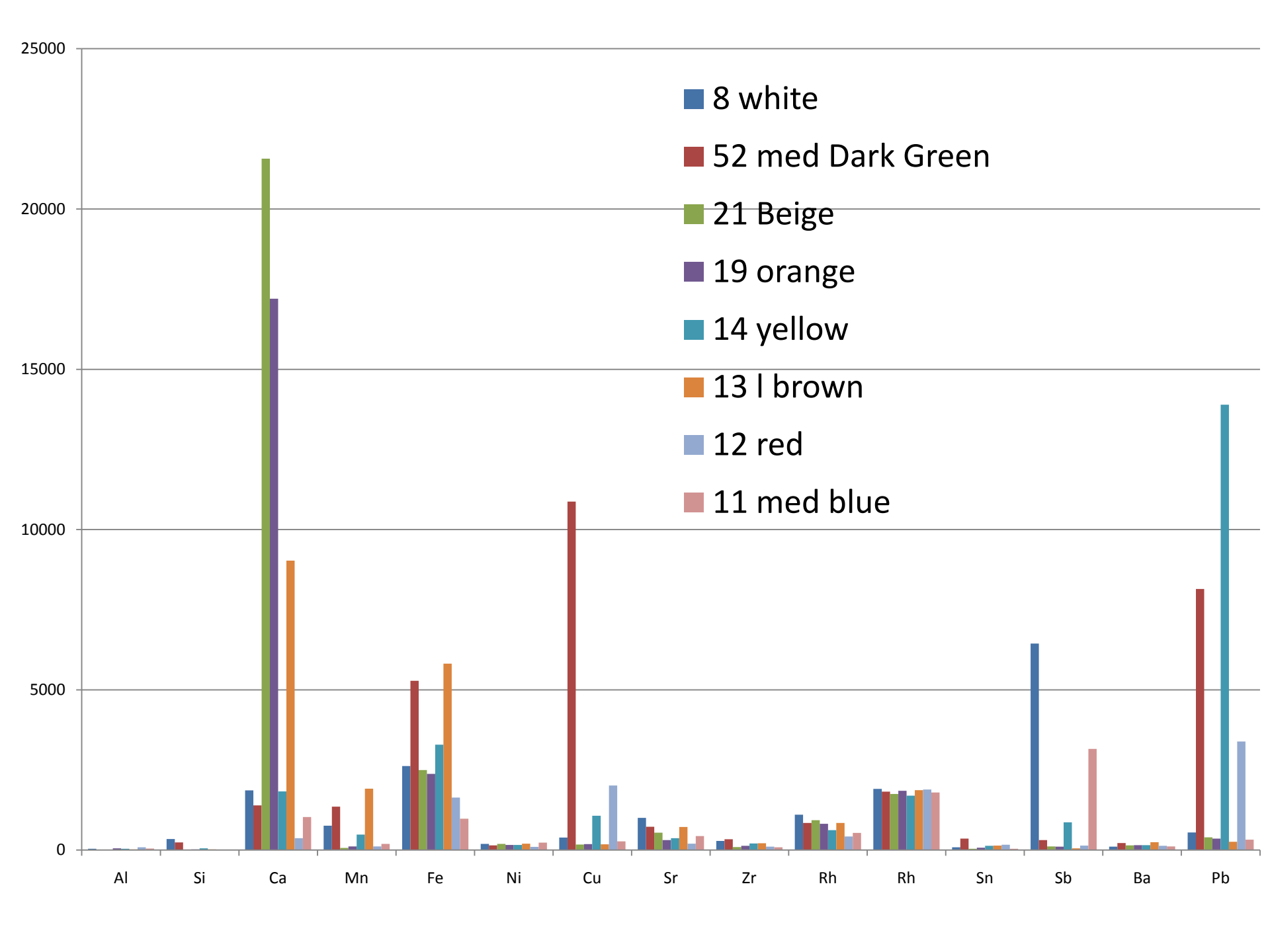
orange

yellow

l brown

red

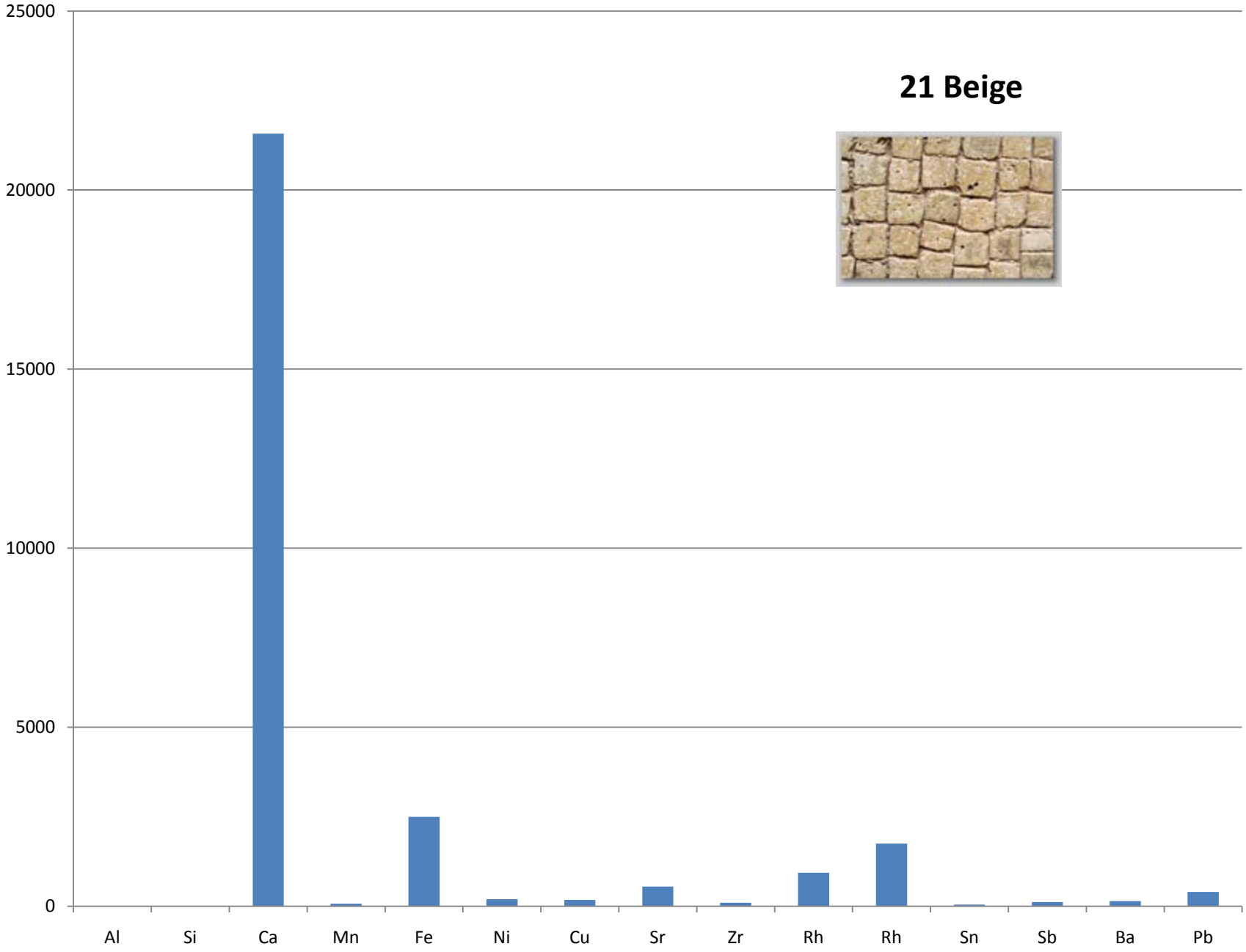
med blue


25000
20000
15000
10000
5000
0
8 white
52 med Dark Green
21 Beige
19 orange
14 yellow
13 l brown
12 red
11 med blue
Al
Si
Ca
Mn
Fe
Ni
Cu
Sr
Zr
Rh
Rh
Sn
Sb
Ba
Pb

8 white

7000
5000
4000
3000
2000
1000
0
Al
Si
Ca
Mn
Fe
Ni
Cu
Sr
Zr
Rh
Rh
Sn
Sb
Ba
Pb

52 med Dark Green


21 Beige
25000
20000
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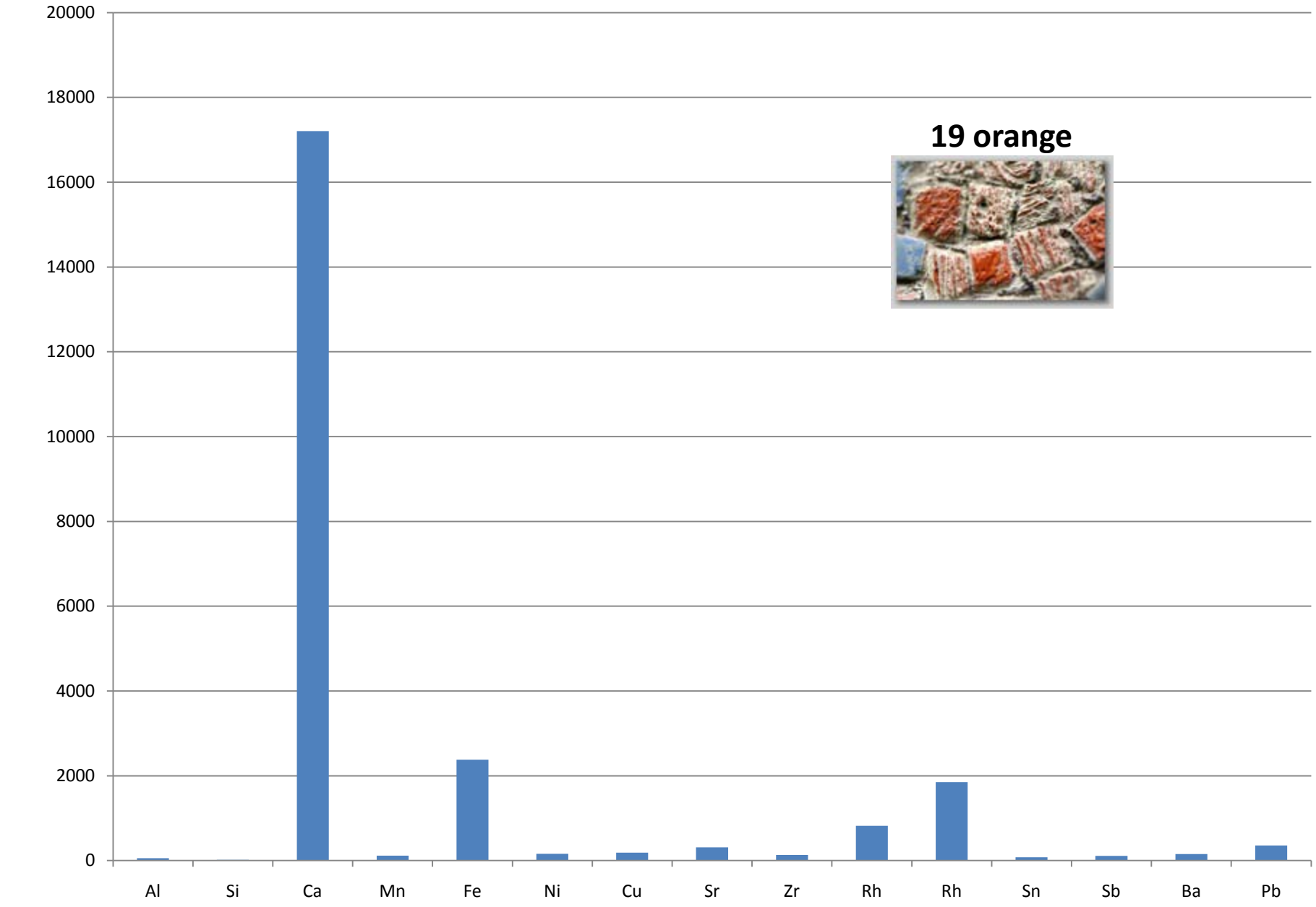
Al
Si
Ca
Mn
Fe
Ni
Cu
Sr
Zr
Rh
Rh
Sn
Sb
Ba
Pb


19 orange
20000
18000
16000
14000
12000
10000
8000
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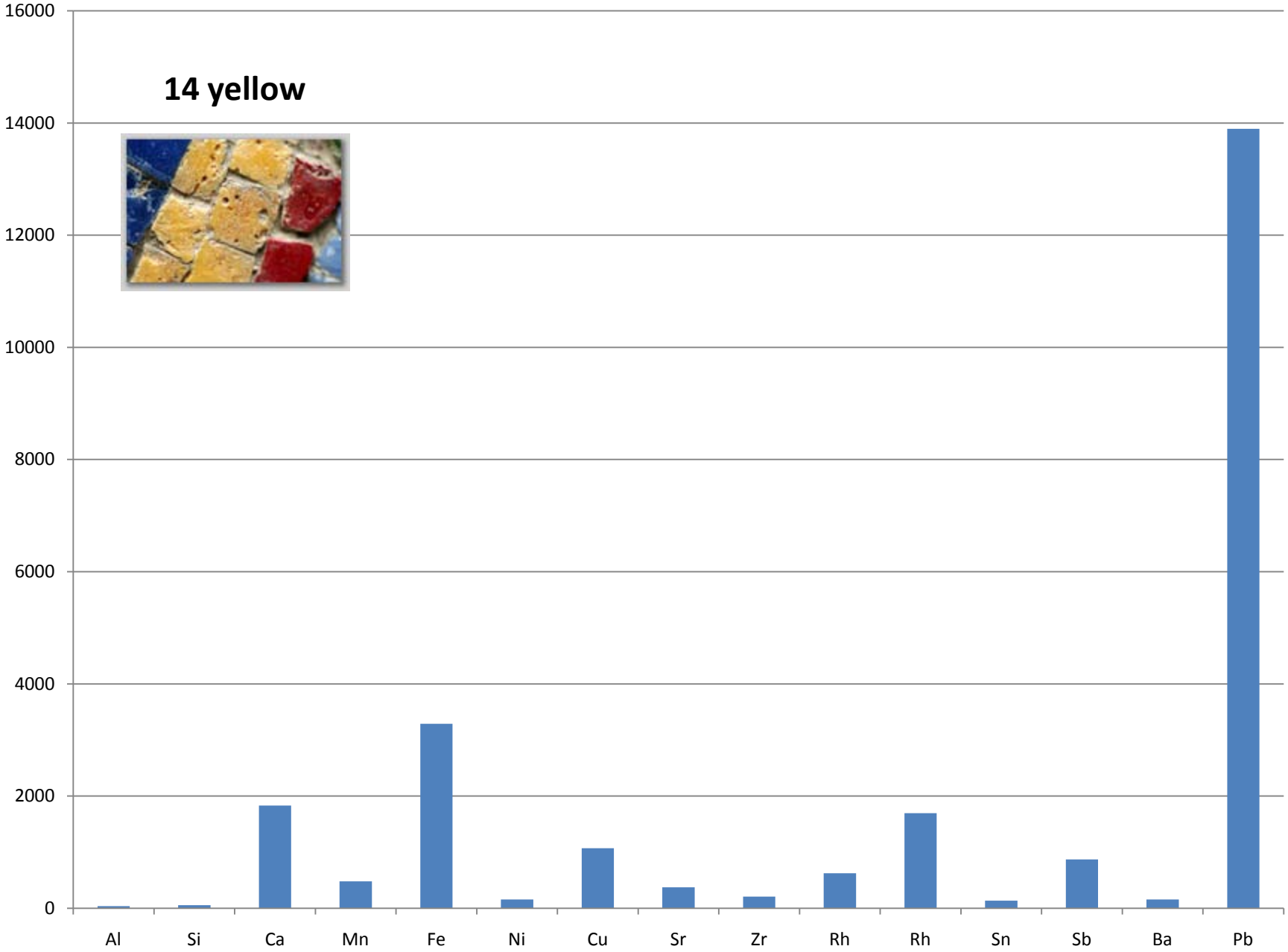
4000
2000
0
Al
Si
Ca
Mn
Fe
Ni
Cu
Sr
Zr
Rh
Rh
Sn
Sb
Ba
Pb


14 yellow
16000
14000
12000
10000
8000
6000
4000
2000
0
Al
Si
Ca
Mn
Fe
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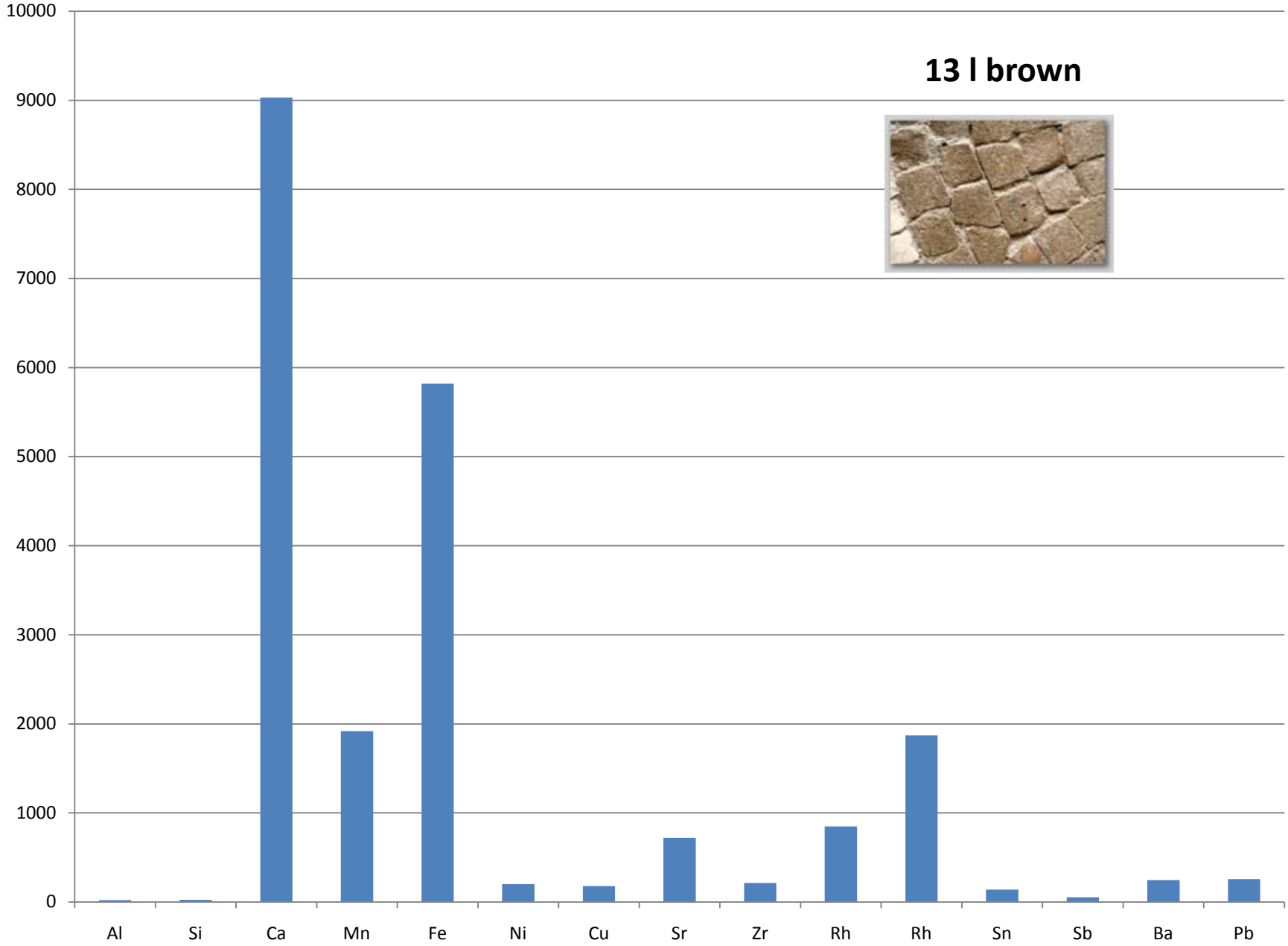
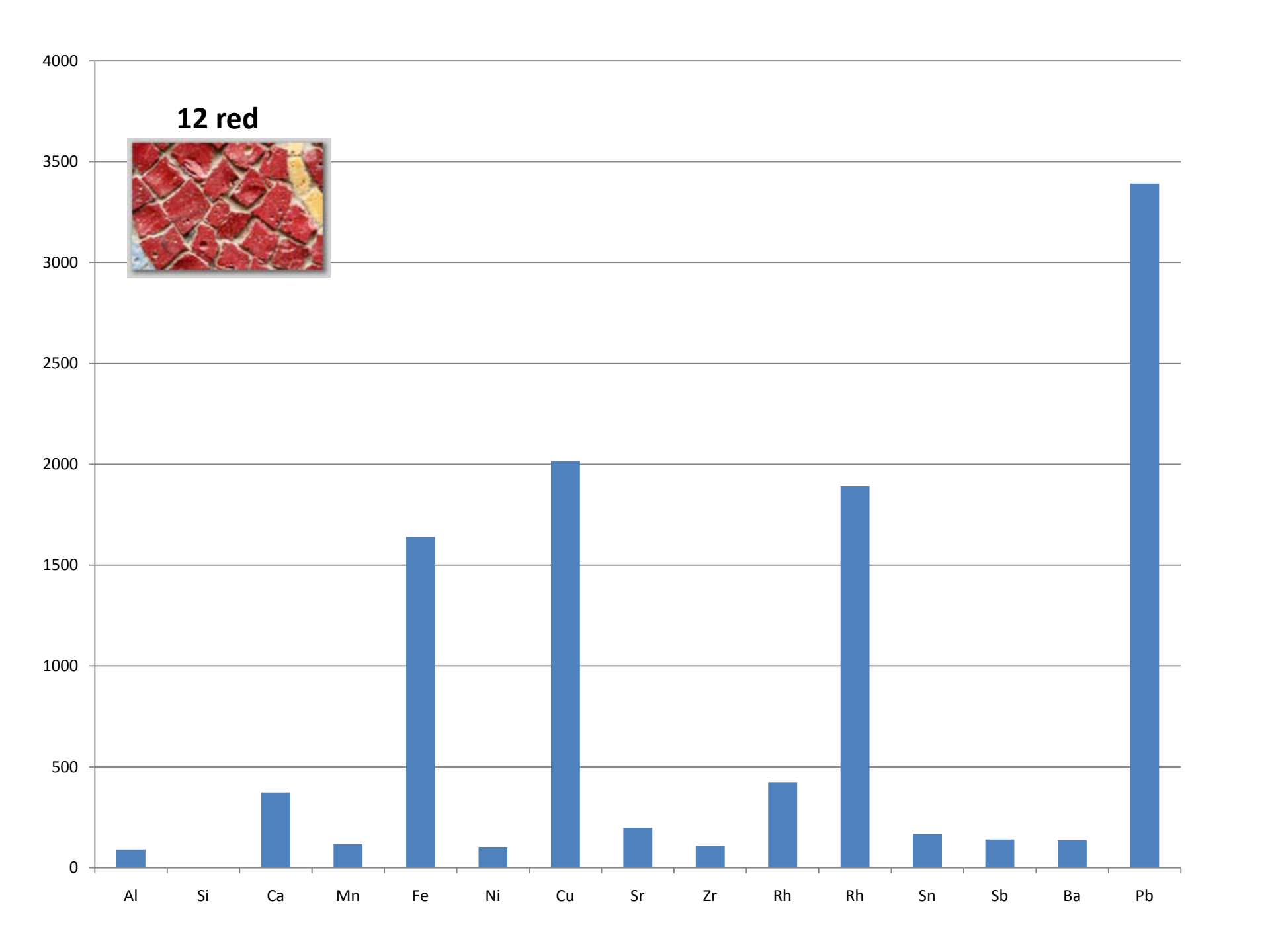
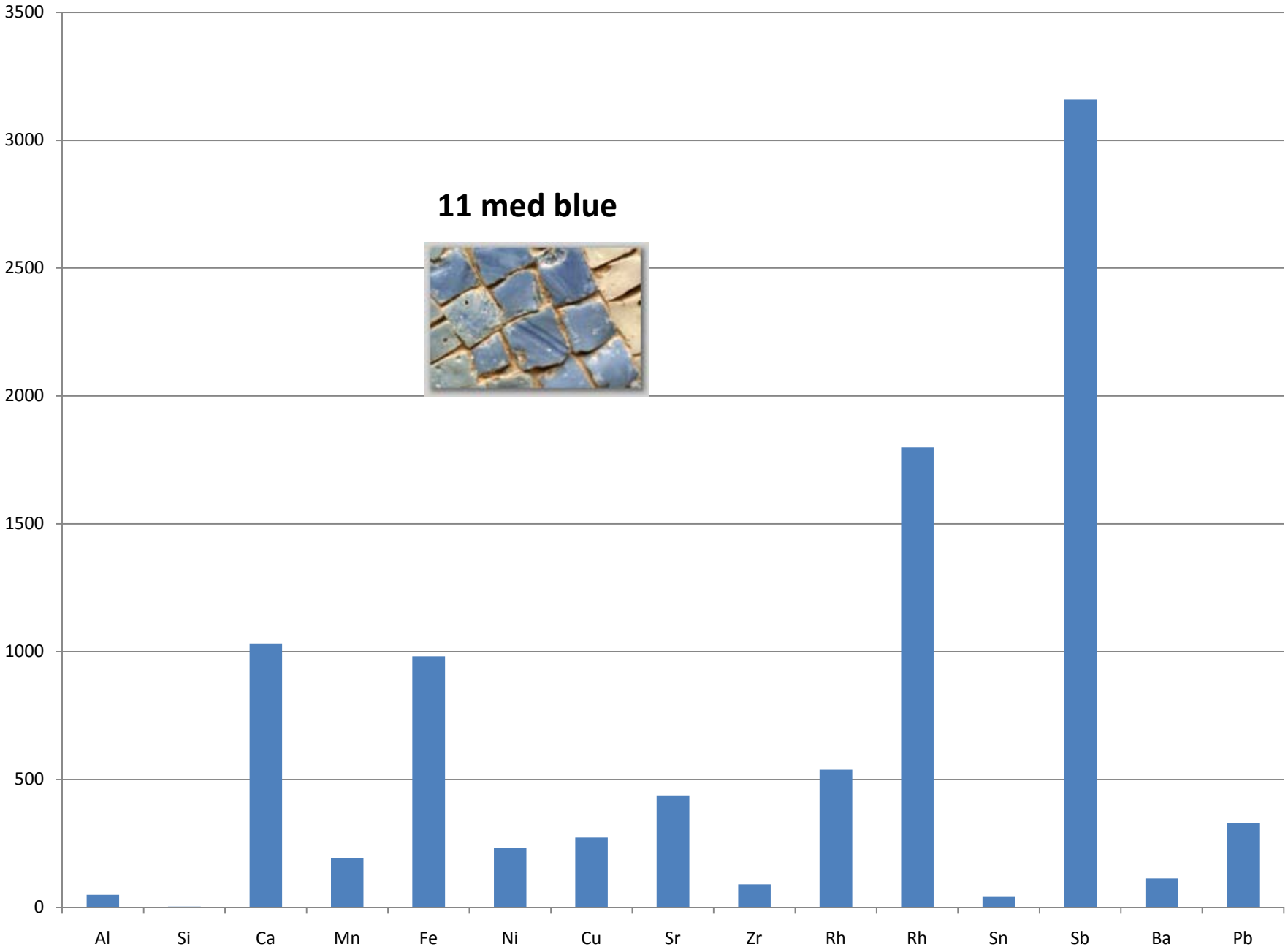
Cu
Sr
Zr
Rh
Rh
Sn
Sb
Ba
Pb


13 l brown
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Al
Si
Ca
Mn
Fe
Ni
Cu
Sr
Zr
Rh
Rh
Sn
Sb
Ba
Pb


12 red
4000
3500
3000
2500
2000
1500
1000
500
0
Al
Si
Ca
Mn
Fe
Ni
Cu
Sr
Zr
Rh
Rh
Sn
Sb
Ba
Pb


11 med blue
3500
3000
2500
2000
1500
1000
500
0
Al
Si
Ca
Mn
Fe
Ni
Cu
Sr
Zr
Rh
Rh
Sn
Sb
Ba
Pb