

## **APPENDIX 5**

### **Archaeo-metallurgy: 49-SIT-963**

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1. Analysis and Metallography of Copper Sheet from Sitka, Alaska (#R5032)
2. Analysis and Metallography of Copper Sheet fragments from the NEVA Survivors' Camp (#R5032/5284-85)
3. Analysis and Metallography of Copper 1 *Kopek* Coins (#R5253-59)

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1. Analysis of Metal Artifacts from Suspected Neva Survivor Camp

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*Metallurgy and Archaeology*

**ANALYSIS AND METALLOGRAPHY OF  
COPPER SHEET FROM SITKA, ALASKA**

**#R5032**

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## **ANALYSIS AND METALLOGRAPHY OF A FRAGMENT OF COPPER SHEET FROM SITKA, ALASKA**

A fragment of copper sheet excavated at Sitka, Alaska was submitted for metallurgical study; the fragment, which measured 55 x 30mm is illustrated as the frontispiece of this report.

It was reported that the sheet came from the location of the camp established by survivors of the wreck of the Russian ship *Neva*, wrecked in 1813. The ship had been built in England as the *Theme* and bought more or less of the stocks by Russia in 1803. It was refitted in St Petersburg in 1807 for a round the world voyage. The primary question to be addressed by this report is the possibility that the copper, with its nail holes, represents a fragment of the sheathing of the *Neva* and, if so, whether the sheathing dates to its construction in England in 1803 or to a possible re-coppering in St Petersburg in 1807-8. Given the usual service life of copper sheathing it is indeed plausible that she was re-sheathed in Russia. If it appears more probable that the copper has a different source the question then is whether comparative databases of 19<sup>th</sup> century and 20<sup>th</sup> century copper analyses can provide a possible dating for this fragment.

### **Sampling and analysis**

A single sample, labelled #R5032, was cut from the edge of the fragment. Analysis was by electron probe microanalysis using wavelength dispersive spectrometry. Operating conditions were an accelerating voltage of 20kV, a beam current of 30nA, and an X-ray take-off angle of 40°. Counting times were 10s or 20s per element, and pure element and mineral standards were used. Eighteen elements were analysed as listed in accompanying table; detection limits were 100-200ppm for most elements, except 300ppm for gold.

Five areas, each 30x50µm, were analysed on the sample. The individual analyses, normalised to 100%, are given in the table; all concentrations are in weight %.

The sample was then examined metallographically (Figures 1-2) in both as-polished and etched states. The etch used was an ammoniacal solution of hydrogen peroxide.

### **The alloy**

The copper is of considerable purity. The most significant impurities were 0.04% nickel and 0.16% arsenic. There were also small traces of cobalt, antimony, silver, lead, sulphur, and, possibly, cadmium although this last identification is not certain. Oxygen is also present as cuprous oxide particles (cuprite, Cu<sub>2</sub>O)(see metallography below) but was not quantified.

For comparison there is, first of all, a database of analyses copper sheathing and fastenings from 18<sup>th</sup> and 19<sup>th</sup> century wooden ships being compiled by the present writer. To this may be added other copper components from wooden ships of the same period, together with copper components from a steam locomotive built in 1857 and lost at sea off Scotland on its delivery voyage to Canada and two copper fragments from the ironclad USS *Monitor* built in 1862 and lost at the end of that year. Also made available were analyses from sheet copper roofs and other applications in the 19<sup>th</sup> century, notably the Statue of Liberty of 1878.<sup>1</sup>

At the time the *Neva* was built in England in 1803 British copper (that is from Cornish and Welsh ores) supplied the great majority of British industrial needs. With the resumption of war with France after the collapse of the Peace of Amiens in 1803 demand for copper for the Navy

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<sup>1</sup>These data were made available to the writer by Dr Jean-Marie Welter

increased and consideration was given in 1807 to importing copper from Russia. However, from 1807, at least 80% of the Navy's need were met by copper from ships being resheathed or scrapped. The copper being recycled in the increasingly efficient metal mill at Portsmouth Dockyard. From the time of the *Neva's* construction we have analyses of copper bolts and sheathing from HMS *Pomone*, launched in 1805 and wrecked in 1811 without being re-coppered, sheathing from HMS *Amethyst*, launched in 1799, last coppered in 1809 and lost in 1811, and from HMS *Primrose*, launched in 1807 and lost in 1809. The compositions of the sheathing from these three ships are included in the table attached to this report and they exemplify the universal composition of British copper at this time with its arsenic, silver, bismuth, and lead impurities, the bismuth and at least some of the arsenic and lead being present as the oxide phase. These compositions are also very different from #R5032 in having significantly higher concentrations of the four similar impurities. It may be added that, based on analyses of contemporary British copper coins and also of Liberty head US cents which were struck wholly from British copper until 1837, that these composition type persists through the 1820s and 1830s.

We now need to consider whether the Sitka fragment could come from the wreck of the *Neva* but have been produced elsewhere. This is technically feasible but so far the evidence is against it. The first reason is that British copper had a dominant position in the Maritime world and key components such as rolled copper bolts in French and Spanish warships were made of it. Less critical components were made from copper from other sources, often with a significant antimony impurity that is absent from British copper. We may also add that Swedish copper does not match #R5032 but at present we do not have analyses of Russian copper, and *Neva* could have been re-coppered in Russia in 1807-08, or at least had her copper repaired. One hint as to the possible composition of Russian copper of the period comes from analyses of Russian bronze ordnance cast in St Petersburg in St Petersburg in 1803-1807.<sup>2</sup> These analyses suggest that the copper available in quantity in St Petersburg in 1803-07 had a an arsenic/antimony/nickel/silver impurity pattern, which is very different from #R5033, and a much higher impurity total. It seems clear, therefore that the Sitka fragment does not come from the *Neva*, and the low impurity total makes it unlikely to relate to local activity in the 1820s to 1840s.

Moving forward in time the table of analyses also includes analyses from copper of the 1850s and 1860s from maritime contexts, including pieces associated with the search for Sir John Franklin's lost expedition, and from copper roofs and also from the Statue of Liberty. These results point to a decline in impurity totals during the second half of the century and metallographic data suggest that the oxide impurities are increasingly just of cuprite. Where results from 20<sup>th</sup> century copper are available the copper is much purer and oxide inclusions smaller and more finely dispersed. On the basis of present knowledge we can suggest that analysis #R5032 represents activity in the second half of the 19<sup>th</sup> century, say up until the time of the Yukon gold rush.

### **Metallography**

To increase our understanding of the Sitka fragment a metallographic study was made (Figure 1). The sample is illustrated only after etching because the ammoniacal hydrogen peroxide etch dissolves any distortions made in the sample surface by the polishing process and the structure is much clearer (Figure 1). The copper is extensively corroded at the surface giving the sample an irregular outline, and there is some penetration within grains in the surviving metal. The bulk of the sample is marked by a dense distribution of rounded cuprite particles. Etching has revealed a

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<sup>2</sup>H. Forshell, 1992: *The inception of copper mining in Falun*, (Stockholm: Archaeological Research Laboratories of Stockholm University, Theses and Papers in Archaeology, B:2), esp. 125-144

fully recrystallised, equiaxed grain structure with no residual cold work; the grain diameter is moderate at about 30µm. The structure indicates that the copper has been cold worked and annealed, probably through several cycles, at a high enough temperature to ensure homogenisation of the arsenic impurity. The structure is typical of a broad variety of worked copper and it is not possible to say whether local re-working of scrap copper is indicated but it may well be that a larger sheet of copper was being converted into these objects.

### **Conclusions**

While it is not possible to say at this stage what the real context of the copper fragment from Sitka actually was but, on the basis of present knowledge, we can be confident that it does not come from the *Neva*. A date in the second half of the 19<sup>th</sup> century is most probable.



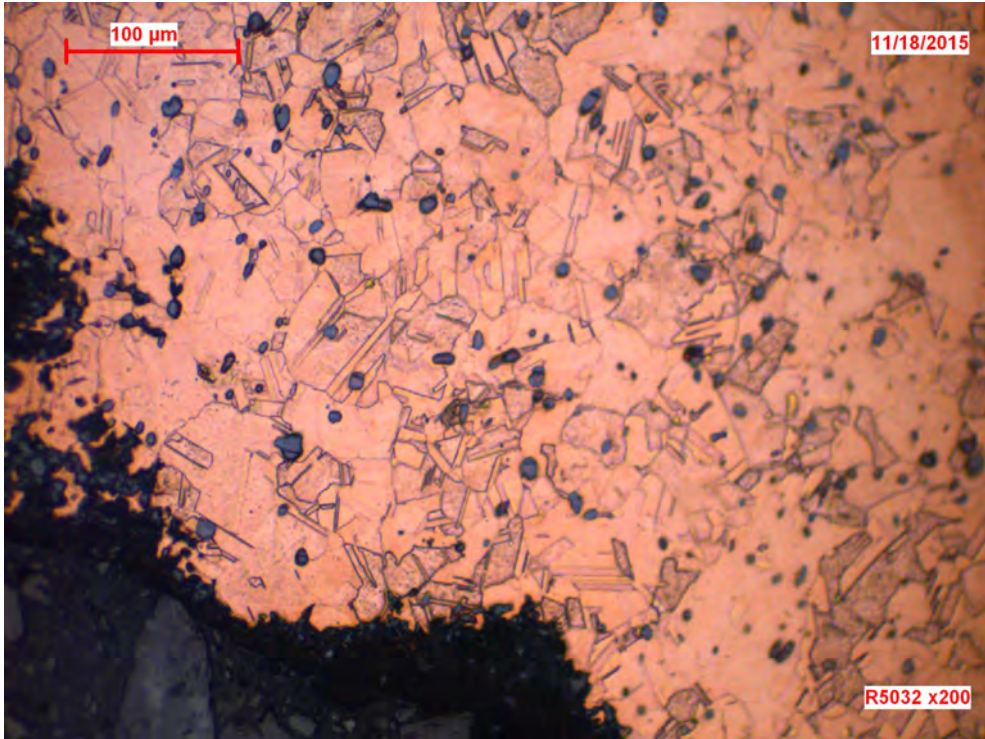


Fig. 1: #R5033, etched



## ANALYSIS OF COPPER SHEET FROM SITKA, ALASKA

Sample	Object	Part	Fe	Co	Ni	Cu	Zn	As	Sb	Sn	Ag	Bi	Pb	Au	Cd	S	Al	Si	Mn	P
R5032/1	Copper sheet from Sitka, Alaska	edge	0.00	0.01	0.04	99.73	0.00	0.16	0.01	0.00	0.00	0.00	0.02	0.00	0.02	0.02	0.00	0.00	0.00	0.00
R5032/2			0.00	0.00	0.06	99.71	0.00	0.16	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00
R5032/3			0.00	0.01	0.00	99.73	0.00	0.20	0.04	0.00	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
R5032/4			0.01	0.00	0.05	99.64	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.04	0.04	0.03	0.00	0.00	0.02	0.00
R5032/5			0.01	0.01	0.06	99.65	0.00	0.13	0.02	0.00	0.03	0.00	0.01	0.00	0.00	0.04	0.00	0.00	0.03	0.00

R5032/Mean	Copper sheet from Sitka, Alaska	edge	0.00	0.01	0.04	99.69	0.00	0.16	0.02	0.00	0.01	0.00	0.01	0.01	0.01	0.03	0.00	0.00	0.01	0.00
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## Sheathing 1800-1815

Sample	Object	Date	Fe	Co	Ni	Cu	Zn	As	Sb	Sn	Ag	Bi	Pb	Au	Cd	S	Al	Si	Mn	P
R5032/Mean	Copper sheet from Neva site	??	0.00	0.01	0.04	99.69	0.00	0.16	0.02	0.00	0.01	0.00	0.01	0.01	0.01	0.03	0.00	0.00	0.01	0.00
R5024/Mean	Copper sheathing from HMS Amethyst	1809	0.00	0.00	0.03	99.28	0.01	0.38	0.04	0.00	0.08	0.14	0.01	0.00	0.00	0.01	0.00	0.00	0.02	0.00
R5025/Mean	Copper sheathing from HMS Amethyst	1809	0.00	0.01	0.06	99.27	0.00	0.42	0.02	0.00	0.08	0.04	0.01	0.03	0.03	0.01	0.00	0.00	0.01	0.00
R5026/Mean	Copper sheathing from HMS Amethyst	1809	0.01	0.01	0.03	99.35	0.00	0.37	0.02	0.00	0.08	0.07	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00
SH 2/Mean	Copper sheathing from HMS Pomone	1805	0.01	0.01	0.03	99.19	0.00	0.46	0.01	0.00	0.08	0.13	0.04	0.02	0.01	0.01	0.00	0.00	0.00	0.00
NW 4/Mean	HMS Primrose	1807	0.00	0.00	0.16	99.08	0.00	0.43	0.07	0.02	0.05	0.03	0.09	0.04	0.01	0.01	0.00	0.00	0.01	0.00
	Deltebre I (before 1813)	Before 1813	0.00		0.00	99.30	0.00	0.36	0.02	0.01	0.09	0.20	0.01							

## Copper components from mid-19th century

Sample	Object	Date	Fe	Co	Ni	Cu	Zn	As	Sb	Sn	Ag	Bi	Pb	Au	Cd	S	Al	Si	Mn	P
R5032/Mean	Copper sheet from Neva site	??	0.00	0.01	0.04	99.69	0.00	0.16	0.02	0.00	0.01	0.00	0.01	0.01	0.01	0.03	0.00	0.00	0.01	0.00
R4887/Mean	Copper sheathing from HMS Investigator	1850	0.01	0.01	0.05	99.29	0.01	0.32	0.03	0.00	0.07	0.10	0.04	0.03	0.00	0.00	0.00	0.04	0.01	0.00
R4888/Mean	Sheet/sheathing from Northumberland House	1850-53	0.01	0.00	0.05	98.75	0.00	0.18	0.04	0.00	0.01	0.01	0.83	0.03	0.03	0.01	0.00	0.05	0.01	0.00
R3915/Mean	Caduceus	1857	0.00	0.00	0.10	99.48	0.01	0.17	0.02	0.00	0.05	0.02	0.09	0.03	0.01	0.01	0.00	0.00	0.01	0.00
NRM 4	Steam pipe from Neilson locomotive,	1857	0.00	0.00	0.04	99.48	0.00	0.17	0.01	0.01	0.07	0.05	0.12	0.03		0.00				
HT 4	Firebox stay bolt deom Neilson locomotive,	1857	0.01	0.01	0.04	98.77	0.01	0.32	0.03	0.01	0.02	0.09	0.63	0.01	0.01	0.03	0.00	0.00	0.00	0.00
HT 1	Copper pipe from USS Monitor	1862	0.01	0.00	0.02	99.53	0.01	0.15	0.04	0.01	0.08	0.02	0.08	0.02	0.01	0.01	0.00	0.00	0.01	0.00
HT 2	Copper wire from USS Monitor	1862	0.01	0.01	0.04	99.45	0.01	0.06	0.01	0.01	0.09	0.02	0.24	0.01	0.01	0.02	0.00	0.00	0.01	0.00

## 19th century copper roofs etc.

Sample	Object	Date	Fe	Co	Ni	Cu	Zn	As	Sb	Sn	Ag	Bi	Pb	Au	Cd	S	Al	Si	Mn	P
R5032/Mean	Copper sheet from Neva site	edge	0.00	0.01	0.04	99.69	0.00	0.16	0.02	0.00	0.01	0.00	0.01	0.01	0.01	0.03	0.00	0.00	0.01	0.00
	Madeleine church, Paris, roof	1835	0.00	0.00	0.05		0.00	0.27	0.01	0.03	0.08	0.00	0.31				0.00	0.00		
	Chartres cathedral, roof	1840	0.01	0.00	0.05		0.01	0.28	0.02	0.03	0.07	0.00	0.36				0.00	0.00		
	Saint-Denis basilica, roof	1844	0.00	0.00	0.16		0.00	0.02	0.11	0.06	0.03	0.00	0.13				0.00	0.00		
	Autun cathedral, roof	1848	0.00	0.00	0.11		0.00	0.66	0.07	0.00	0.06	0.01	0.15				0.00	0.00		
	Ste-Anne de Dijon church, roof	1848	0.00	0.00	0.03		0.00	0.35	0.03	0.00	0.05	0.12	0.12				0.00	0.00		
	Invalides church, roof	1870	0.00	0.00	0.06		0.00	0.16	0.01	0.00	0.02	0.02	0.04				0.00	0.00		
	Statue of Liberty	1878	0.00	0.00	0.01		0.07	0.52	0.01	0.00	0.02	0.02	0.07				0.02	0.00		
	Statue of Liberty	1878	0.00	0.00	0.09		0.03	0.06	0.01	0.00	0.01	0.00	0.00				0.00	0.00		

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**ANALYSIS AND METALLOGRAPHY OF  
COPPER SHEET FRAGMENTS FROM THE  
NEVA SURVIVORS' CAMP**

**#R5032/5284-85**

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## ANALYSIS AND METALLOGRAPHY OF COPPER SHEET FRAGMENTS FROM THE *NEVA* SURVIVORS' CAMP

Three copper sheet fragments from the presumed site of the *Neva* survivors' camp, Kruzof Island, Sitka, Alaska were submitted for metallurgical study.

The primary question to be addressed by this report is the possibility that the copper, with its nail holes, represents a fragment of the sheathing attached to the *Neva* when it was wrecked near Sitka in 1813 and, if so, whether the sheathing dates to its construction in England in 1803 or to a possible re-coppering in St Petersburg in 1807-8. The ship had been built in 1801-02 England as the Thames and bought by Russia in 1803. It was refitted in St Petersburg in 1807 for a round the world voyage. Given the usual service life of copper sheathing it is indeed plausible that she was re-sheathed in Russia. If it appears more probable that the copper has a different source the question then is whether comparative databases of 19<sup>th</sup> century and 20<sup>th</sup> century copper analyses can provide a possible dating for this fragment.

### Sampling and analysis

A single sample was cut from the edge of each fragment of sheet and labelled and identified as follows:-

#R5032	UA2016-063-078 [# added by McMahan]
#R5284	UA2015-237-87
#R5285	UA2016-063-078

The samples were hot-mounted in a carbon-filled thermosetting resin, ground and polished to a 1 $\mu$ m diamond finish. Analysis was by electron probe microanalysis using wavelength dispersive spectrometry. Operating conditions were an accelerating voltage of 20kV, a beam current of 30nA, and an X-ray take-off angle of 40°. Counting times were 10s or 20s per element, and pure element and mineral standards were used. Eighteen elements were analysed as listed in accompanying table; detection limits were 100-200ppm for most elements, except 300ppm for gold. The writer is grateful to Mr Chris Salter of Oxford Materials Characterisation Service for assistance with these analyses.

Five areas, each 30x50 $\mu$ m, were analysed on each sample. The individual analyses, normalised to 100%, are given in Table 1; all concentrations are in weight %. Also included in the table are the mean compositions of contemporary Russian copper coins.

The samples were then examined metallographically (Figures 1-7) in both as-polished and etched states. The etches used were an ammoniacal solution of hydrogen peroxide and an acidified aqueous solution of ferric chloride further diluted with ethanol.

### The alloy

The copper is of considerable purity with a minimum copper content off 99.4%: oxygen is always present as cuprous oxide particles (cuprite, Cu<sub>2</sub>O)(see metallography below) but was not quantified. The first two samples (#R5032, #R5284) are closely similar with 0.04-0.05% nickel and 0.16-0.21% arsenic as the principal impurities, together with possible traces of iron, cobalt, antimony, silver, and sulphur. The third sample (#R5285) has 0.40% arsenic and 0.09% silver as the principal impurities, together with traces of cobalt, nickel, antimony, bismuth, and sulphur.

For comparison there is, first of all, a database of analyses copper sheathing and fastenings from 18<sup>th</sup> and 19<sup>th</sup> century wooden ships being compiled by the present writer. To this may be added other copper components from wooden ships of the same period, together with copper components from

a steam locomotive built in 1857 and lost at sea off Scotland on its delivery voyage to Canada and two copper fragments from the ironclad USS *Monitor* built in 1862 and lost at the end of that year. These comparative data are presented in Table 2.

At the time the *Neva* was built in England in 1803 British copper (that is from Cornish and Welsh ores) supplied the great majority of British industrial needs but with the resumption of war with France after the collapse of the Peace of Amiens in 1803 demand for copper for the Navy increased and in 1807 over 400 tons were imported from Russia. However, the sheathing used by the Navy would have had an increasing proportion of recycled metal: when a ship was docked any marine growths were burned off and the copper returned to the contractors for recycling. From 1797 onwards there were proposals for a Metal Mill at Portsmouth Dockyard to take the recycling in-house. in the increasingly efficient metal mill at Portsmouth Dockyard: this was commissioned in September 1805<sup>1</sup> but by April 1808 there was a stockpile of some 1600 tons awaiting processing, including 414 tons from Russia. The Mill moved to two shifts and recourse was again had to outside contractors, primarily Grenfells.<sup>2</sup> We know much less about what was happening with the merchant fleet but it is to be presumed that worm sheathing would be returned to the suppliers for recycling and that the sheathing fitted to ships would contain a growing percentage of recycled copper.

From the period of the *Neva*'s construction we have analyses of copper bolts and sheathing from HMS *Pomone*, launched in 1805 and wrecked in 1811 without being re-coppered, sheathing from HMS *Amethyst*, launched in 1799, last coppered in 1809 and lost in 1811, and from HMS *Primrose*, launched in 1807 and lost in 1809. From a slightly earlier period there are samples of sheathing from HMS *Colossus*, last re-coppered no later than 1793 and lost in 1798, and from HMS *Sirius*, rebuilt in 1786 for service in the First Fleet to Australia and lost in 1790.

The first comparisons will be made with the contemporary British sheathing, albeit it is from naval rather than merchant vessels. with the results also displayed graphically. The results from the British naval sheathing exhibit the characteristic impurity pattern of British copper at that time with arsenic, silver, bismuth, and lead as the principal impurities, with all of the bismuth and some of the lead and arsenic present as the oxide phase. Inspection of the tables shows that the copper from the survivors' camp tends to have lower levels of silver, bismuth and lead when compared with the known British sheathing although the differences are not necessarily large. On a plot of silver against lead sample #R5285, with the highest arsenic and silver contents, plots very close to three of the samples from HMS *Amethyst* while #R5032/5284 are well separated because of their much lower silver content. The same separation can be seen when impurities are combined in a principal components analysis. There is therefore a good probability that at least #R5285 is British and original to the *Thames* when built, while it is not impossible that the other two also have that origin. It is also very probable that the fragments represented by #R5032 and #R5284 came from the same sheet.

We have noted above how copper was recycled by the metal mill at Portsmouth Dockyard and it is highly likely that this was the source of the copper on the *Amethyst*. Indeed, it is probable that in any given ship, at least those whose hulls were built before 1897, the sheathing was much more likely to be recycled than the copper bolts and, therefore, that there should be systematic differences between the compositions of bolts and sheathing. That this is the case is shown in the next two graphs, scatterplots of silver against lead, bismuth against lead, and lead against arsenic. Combined

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<sup>1</sup>E.A. Forward, 1922: Simon Goodrich and his work as an engineer, *Transactions of the Newcomen Society*, 3(1), 1-15

<sup>2</sup>TNA ADM 354/231/58, Letter from William Wellesley-Pole

these show that the concentrations of all these elements are often much smaller in the sheathing, thereby supporting the contention that the copper from the survivors' camp is indeed original British sheathing from 1803.

Even though we now have a plausible conclusions that at least some of the copper is British we still need to consider whether the came from the wreck but were produced in another European country (the USA did not have a significant copper industry at the time). This is technically feasible but so far the evidence is against it. The first reason is that British copper had a dominant position in the maritime world and key components such as rolled copper bolts in French and Spanish warships were made of it. Less critical components were made from copper from other sources, often with a significant antimony impurity that is absent from British copper. We may also add that Swedish copper does not match the three samples<sup>3</sup> but at present we do now have some analyses of Russian copper in the form of 1 *kopek* coins, and *Neva* could have been re-coppered in Russia in 1807-08, or at least had her copper repaired. Further indications of the possible compositions of Russian copper of the period comes from analyses of Russian bronze ordnance cast in St Petersburg in St Petersburg in 1798-1807.<sup>4</sup> A scatterplot of antimony against arsenic for the *Neva* copper, the *kopeks*, the British sheathing and the Russian ordnance shows the ordnance split into two groups indicating two separate supply streams one of which overlaps with the British sheathing and two of the *Neva* samples. The *kopeks* plot well away from the rest and are clearly very different and, possibly, also diverse. A principal components analysis generally confirms the pattern; two of the samples do plot close to the *kopeks* but that is an effect of the generally low concentrations of all impurities in this copper. From these data we can then conclude that, based on present knowledge, the copper from the survivors' camp is not Russian and that the ship was not re-sheathed in Russia.

A final consideration is whether any of the copper represents later 19<sup>th</sup> century activity on the site - the pattern and size of the oxide inclusions in the copper rules out a 20<sup>th</sup> century date. The available analyses date from the 1850 sheathing of HMS *Investigator* lost in the search fro Sir John Franklin's expedition and 1852 components from the USS *Monitor*. Inspection of Table 2 shows that these samples tend to have either more lead or more bismuth, or both, than the *Neva* samples. The nearest matches are a copper bolt from the British-built *Caduceus* and a copper pipe from the *Monitor*; as the Federal government did not have any large local copper supply in the Civil War this copper may also be British. Overall, the copper from the *Amethyst* is still the best match, especially from #R5485.

## Metallography

The results of the metallographic survey are presented in Figures 1-7. Sample #R5032 has a pitted surface but no inter-or transgranular penetration. Etching has revealed a fully recrystallised equiaxed grain structure with annealing twins but no residual cold work. The dark spots are the location of oxide inclusions: the acid etch has dissolved the inclusions and enlarged the cavities within which they were located. Sample #R5284 (Figure 2) shows larger areas of more general corrosion but little sign of inter-or transgranular attack; under crossed polars (Figure 3) the inclusions glow red indicating that they are cuprite. Etching (Figure 4) again revealed a fully recrystallised, equiaxed grain structure with annealing twins and no residual cold work. The grain size is similar to that in #R5032 which supports the suggestion that the two pieces were originally part of the same sheet. Sample #R5285, which we have already noted has a different composition, is characterised by a network of intergranular corrosion intermittently enlarged into cavities (Figure 5). Under crossed polars (Figure 6) it clear that the distribution of cuprite particles is less uniform. Etching (Figure 7) again

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<sup>3</sup>H. Forshell, 1992: *The inception of copper mining in Falun*, (Stockholm: Archaeological Research Laboratories of Stockholm University, Theses and Papers in Archaeology, B:2), esp. 125-144

<sup>4</sup>H. Forshell, *op. cit.*

revealed a fully recrystallised, equiaxed grain structure with annealing twins and no cold work. These are all typical structures for copper sheathing.

### Conclusions

The compositional analysis and metallography have made it very probable that fragments #R5032 and #R5284 came from the same sheet, while #R5285 was different. The latter almost certainly came from typical British sheathing made from recycled copper and must represent sheathing applied to the *Neva* when she was built in 1803. It is quite that the other two samples did as well but this is not so certain. Within the present state of knowledge they are not Russian but it is possible they come from mid-19th century activity on the site and in that case they could still be British.

**Table 1: Analysis of copper sheet from Sitka, Alaska**

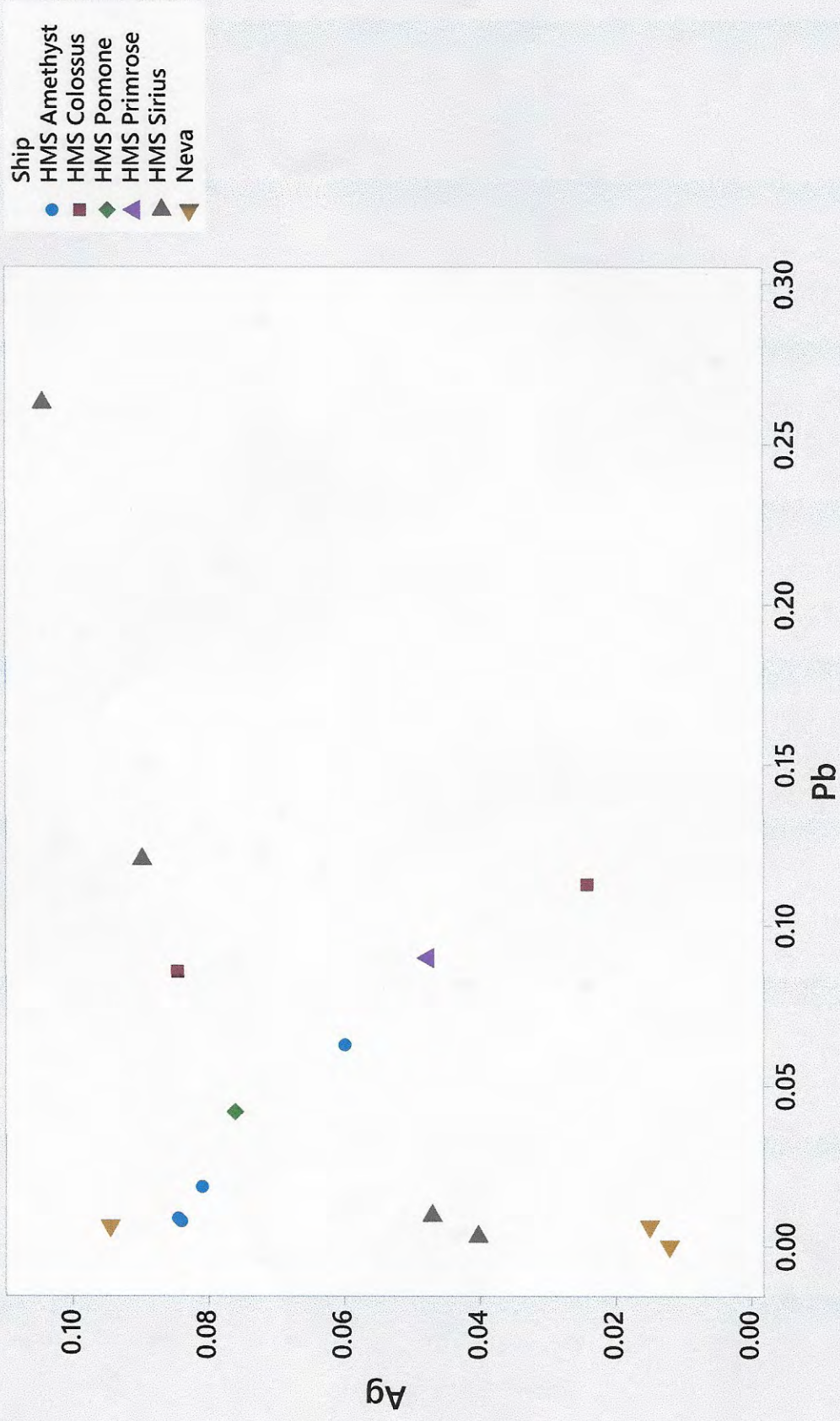
Sample	Object	Part	Fe	Co	Ni	Cu	Zn	As	Sb	Sn	Ag	Bi	Pb	Au	Cd	S	Al	Si	Mn	P
R5032/1	Copper sheet from Sitka, Alaska	edge	0.00	0.01	0.04	99.73	0.00	0.16	0.01	0.00	0.00	0.00	0.02	0.00	0.02	0.02	0.00	0.00	0.00	0.00
R5032/2			0.00	0.00	0.06	99.71	0.00	0.16	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00
R5032/3			0.00	0.01	0.00	99.73	0.00	0.20	0.04	0.00	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
R5032/4			0.01	0.00	0.05	99.64	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.04	0.04	0.03	0.00	0.00	0.02	0.00
R5032/5			0.01	0.01	0.06	99.65	0.00	0.13	0.02	0.00	0.03	0.00	0.01	0.00	0.00	0.04	0.00	0.00	0.03	0.00
R5284/1	Copper sheet from Sitka, Alaska (UA2015-237-87)	edge	0.00	0.00	0.04	99.58	0.07	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.04	0.01
R5284/2			0.02	0.01	0.05	99.59	0.00	0.21	0.00	0.00	0.00	0.08	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00
R5284/3			0.00	0.00	0.05	99.63	0.00	0.27	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
R5284/4			0.00	0.00	0.08	99.64	0.00	0.21	0.01	0.00	0.03	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
R5284/5			0.02	0.02	0.04	99.68	0.00	0.17	0.00	0.00	0.02	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.01	0.00
R5285/1	Copper sheet from Sitka, Alaska (UA2016-063-087)	edge	0.00	0.00	0.00	99.45	0.00	0.40	0.02	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
R5285/2			0.02	0.00	0.03	99.16	0.00	0.44	0.03	0.00	0.17	0.03	0.03	0.03	0.04	0.00	0.00	0.00	0.00	0.00
R5285/3			0.00	0.01	0.00	99.38	0.00	0.41	0.02	0.00	0.11	0.05	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00
R5285/4			0.00	0.01	0.04	99.56	0.00	0.33	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
R5285/5			0.00	0.00	0.00	99.53	0.00	0.40	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
R5032/Mean	Copper sheet from Sitka, Alaska	edge	0.00	0.01	0.04	99.69	0.00	0.16	0.02	0.00	0.01	0.00	0.01	0.01	0.01	0.03	0.00	0.00	0.01	0.00
R5284/Mean	Copper sheet from Sitka, Alaska (UA2015-237-87)	edge	0.01	0.01	0.05	99.62	0.01	0.21	0.01	0.00	0.01	0.02	0.00	0.01	0.00	0.02	0.00	0.00	0.01	0.00
R5285/Mean	Copper sheet from Sitka, Alaska (UA2016-063-087)	edge	0.00	0.01	0.01	99.42	0.00	0.40	0.02	0.00	0.09	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00

**Table 2: Comparative data for Neva copper**

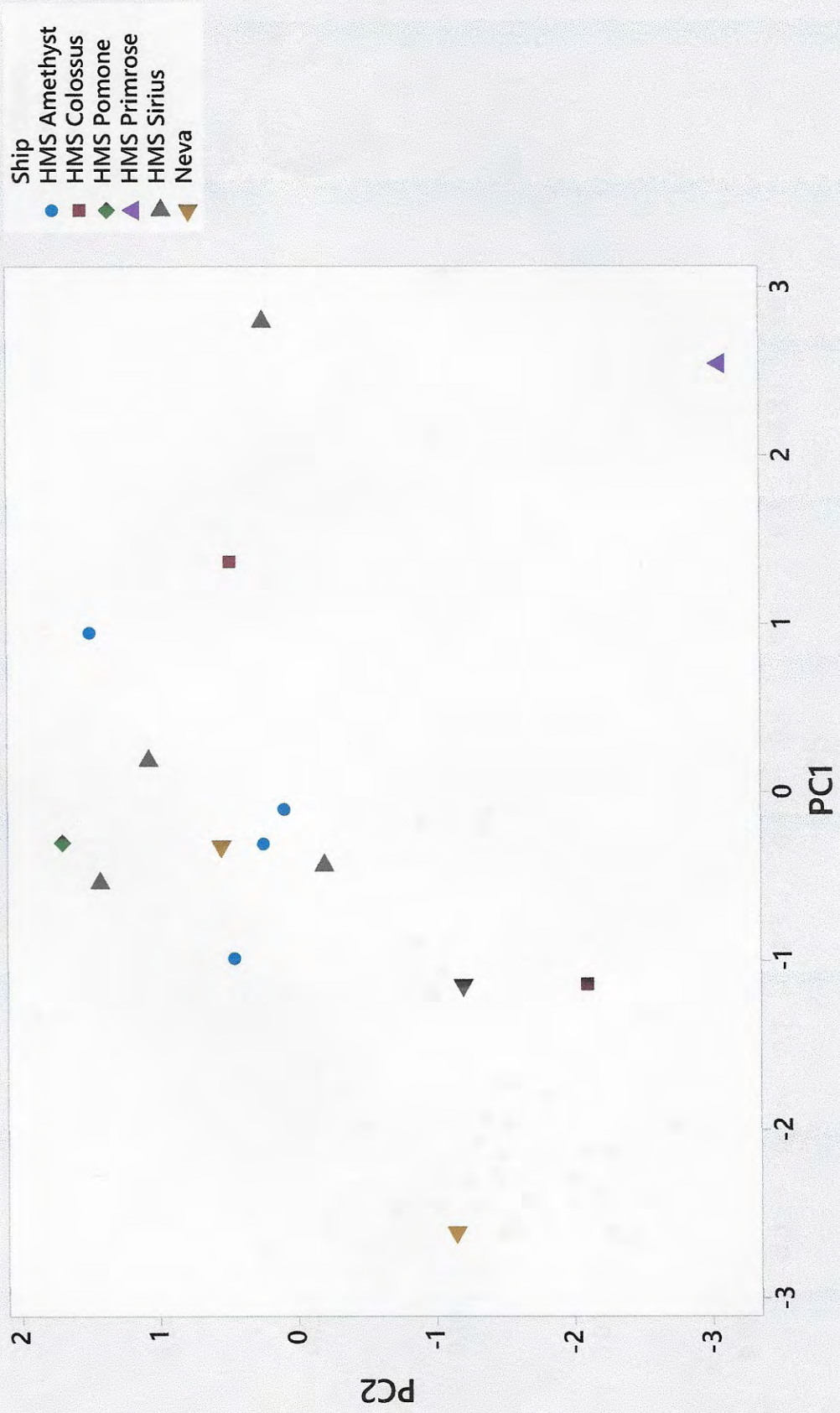
Sample	Ship	Sheathed	Object	Fe	Co	Ni	Cu	Zn	As	Sb	Sn	Ag	Bi	Pb	Au	Cd	S	Al	Si	Mn	P
R5032/Mean	Neva		sheet	0.00	0.01	0.04	99.69	0.00	0.16	0.02	0.00	0.01	0.00	0.01	0.01	0.01	0.03	0.00	0.00	0.01	0.00
R5284/Mean	Neva		sheet	0.01	0.01	0.05	99.62	0.01	0.21	0.01	0.00	0.01	0.02	0.00	0.01	0.00	0.02	0.00	0.00	0.01	0.00
R5285/Mean	Neva		sheet	0.00	0.01	0.01	99.42	0.00	0.40	0.02	0.00	0.09	0.02	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
SI-357/Mean	HMS Sirius	1786	sheathing	0.01	0.01	0.03	99.23	0.00	0.26	0.02	0.00	0.09	0.02	0.12	0.02	0.01	0.02	0.01	0.14	0.01	0.00
SI-465B/Mean	HMS Sirius	1786	sheathing	0.00	0.00	0.05	98.59	0.00	0.98	0.01	0.01	0.04	0.09	0.00	0.00	0.00	0.08	0.00	0.12	0.01	0.00
SI-465/2/Mean	HMS Sirius	1786	sheathing	0.00	0.00	0.02	98.87	0.00	0.39	0.04	0.00	0.10	0.05	0.26	0.02	0.01	0.02	0.00	0.18	0.01	0.01
SI-465/3/Mean	HMS Sirius	1786	sheathing	0.00	0.01	0.04	98.30	0.00	1.04	0.03	0.00	0.05	0.08	0.01	0.02	0.03	0.13	0.02	0.22	0.01	0.00
NW 6/Mean	HMS Colossus	1793	sheathing	0.00	0.01	0.03	99.10	0.00	0.55	0.03	0.01	0.08	0.04	0.09	0.04	0.02	0.01	0.00	0.00	0.00	0.00
NW 11/Mean	HMS Colossus	1793	sheathing	0.01	0.01	0.09	99.40	0.01	0.26	0.02	0.00	0.02	0.03	0.11	0.02	0.01	0.00	0.00	0.00	0.00	0.01
SH 2/Mean	HMS Pomone	1805	sheathing	0.01	0.01	0.03	99.19	0.00	0.46	0.01	0.00	0.08	0.13	0.04	0.02	0.01	0.01	0.00	0.00	0.00	0.00
NW 4/Mean	HMS Primrose	1807	sheathing	0.00	0.00	0.16	99.08	0.00	0.43	0.07	0.02	0.05	0.03	0.09	0.04	0.01	0.01	0.00	0.00	0.01	0.00
R5024/Mean	HMS Amethyst	1809	sheathing	0.00	0.00	0.03	99.28	0.01	0.38	0.04	0.00	0.08	0.14	0.01	0.00	0.00	0.01	0.00	0.00	0.02	0.00
R5025/Mean	HMS Amethyst	1809	sheathing	0.00	0.01	0.06	99.27	0.00	0.42	0.02	0.00	0.08	0.04	0.01	0.03	0.03	0.01	0.00	0.00	0.01	0.00
R5026/Mean	HMS Amethyst	1809	sheathing	0.01	0.01	0.03	99.35	0.00	0.37	0.02	0.00	0.08	0.07	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00
R5162/Mean	HMS Amethyst	1809	sheathing	0.00	0.00	0.03	99.34	0.00	0.35	0.02	0.00	0.06	0.06	0.06	0.03	0.02	0.01	0.00	0.00	0.01	0.00
R3915/Mean	Caduceus	1857	bolt	0.00	0.00	0.10	99.48	0.01	0.17	0.02	0.00	0.05	0.02	0.09	0.03	0.01	0.01	0.00	0.00	0.01	0.00
R4887/Mean	HMS Investigator	1850	sheathing	0.01	0.01	0.05	99.29	0.01	0.32	0.03	0.00	0.07	0.10	0.04	0.03	0.00	0.00	0.00	0.04	0.01	0.00
NRM 4	Neilson locomotive, (1857)	1857	copper steam pipe	0.00	0.00	0.04	99.48	0.00	0.17	0.01	0.01	0.07	0.05	0.12	0.03	0.00	0.00	0.00	0.00	0.04	0.01
HT 4	Neilson locomotive, (1857)	1857	firebox stay bolt	0.01	0.01	0.04	98.77	0.01	0.32	0.03	0.01	0.02	0.09	0.63	0.01	0.01	0.03	0.00	0.00	0.00	0.00
HT 1	USS Monitor	1862	copper pipe	0.01	0.00	0.02	99.53	0.01	0.15	0.04	0.01	0.08	0.02	0.08	0.02	0.01	0.01	0.00	0.00	0.01	0.00
HT 2	USS Monitor (1862)	1862	copper wire	0.01	0.01	0.04	99.45	0.01	0.06	0.01	0.01	0.09	0.02	0.24	0.01	0.01	0.02	0.00	0.00	0.01	0.00
R5253/Mean	Kopek	1798	whole coin	0.01	0.00	0.10	99.70	0.00	0.01	0.02	0.00	0.06	0.01	0.02	0.03	0.01	0.00	0.00	0.00	0.01	0.00
R5254/Mean	Kopek	1799	whole coin	0.00	0.00	0.17	98.67	0.00	0.02	0.01	0.00	0.04	0.00	0.01	0.03	0.02	0.01	0.00	0.00	0.01	0.00
R5255/Mean	Kopek	1810	whole coin	0.01	0.00	0.01	99.82	0.01	0.00	0.01	0.00	0.09	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.00
R5256/Mean	Kopek	1811	whole coin	0.01	0.01	0.16	99.68	0.00	0.01	0.02	0.00	0.07	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.01	0.00
R5257/Mean	Kopek	1812	whole coin	0.01	0.01	0.04	99.49	0.01	0.04	0.12	0.00	0.15	0.03	0.04	0.01	0.04	0.01	0.00	0.00	0.01	0.00
R5258/Mean	Kopek	1817	whole coin	0.01	0.01	0.07	99.65	0.01	0.04	0.07	0.00	0.08	0.00	0.00	0.01	0.02	0.01	0.00	0.00	0.00	0.00
R5259/Mean	Kopek	1842	whole coin	0.01	0.01	0.07	99.74	0.00	0.01	0.02	0.00	0.05	0.01	0.01	0.04	0.01	0.01	0.00	0.00	0.01	0.00
S342	St Petersburg	1803	6 pdr	0.07	0.01	0.10	87.67	1.05	0.23	0.20	9.92	0.06	0.02	0.68	0.00	0.00	0.00	0.00	0.00	0.01	0.00
S330	St Petersburg	1782	3 pdr	0.08	0.01	0.07	87.41	4.47	0.33	0.18	6.57	0.07	0.03	0.81	0.00	0.00	0.00	0.00	0.00	0.01	0.00
S331	St Petersburg	1785	3 pdr	0.04	0.01	0.05	92.11	1.87	0.17	0.02	4.32	0.04	0.02	0.83	0.00	0.00	0.00	0.00	0.00	0.01	0.00
S338	St Petersburg	1789	12 pdr	0.03	0.00	0.11	93.18	1.48	0.10	0.02	4.95	0.04	0.01	0.07	0.01	0.00	0.00	0.00	0.00	0.01	0.00
S337	St Petersburg	1789	12 pdr	0.05	0.01	0.09	89.84	2.03	0.19	0.34	7.21	0.04	0.02	0.19	0.00	0.00	0.00	0.00	0.00	0.01	0.00
S345	St Petersburg	1803	6 pdr	0.03	0.01	0.09	88.72	1.64	0.28	0.16	7.52	0.08	0.02	1.47	0.00	0.00	0.00	0.00	0.00	0.01	0.00
S344	St Petersburg	1803	6 pdr	0.03	0.01	0.11	88.05	0.04	0.34	0.25	10.31	0.08	0.03	0.79	0.00	0.00	0.00	0.00	0.00	0.01	0.00
S343	St Petersburg	1803	6 pdr	0.03	0.01	0.10	88.02	0.08	0.27	0.23	10.35	0.08	0.03	0.80	0.00	0.00	0.00	0.00	0.00	0.01	0.00
S348	St Petersburg	1804	12 pdr	0.02	0.01	0.08	89.39	0.28	0.11	0.17	9.22	0.08	0.03	0.74	0.00	0.00	0.00	0.00	0.00	0.01	0.00
S349	St Petersburg	1804	12 pdr	0.05	0.01	0.11	90.51	0.02	0.34	0.50	7.78	0.06	0.04	0.62	0.00	0.00	0.00	0.00	0.00	0.01	0.00
S352	St Petersburg	1807	6 pdr	0.01	0.01	0.14	88.88	0.05	0.17	0.14	10.13	0.05	0.03	0.36	0.00	0.00	0.00	0.00	0.00	0.01	0.00
S351	St Petersburg	1807	6 pdr	0.03	0.01	0.15	89.26	0.02	0.43	0.04	9.92	0.03	0.03	0.15	0.00	0.00	0.00	0.00	0.00	0.01	0.00
S350	St Petersburg	1807	6 pdr	0.04	0.01	0.15	88.66	0.02	0.54	0.03	10.43	0.03	0.02	0.15	0.00	0.00	0.00	0.00	0.00	0.01	0.00



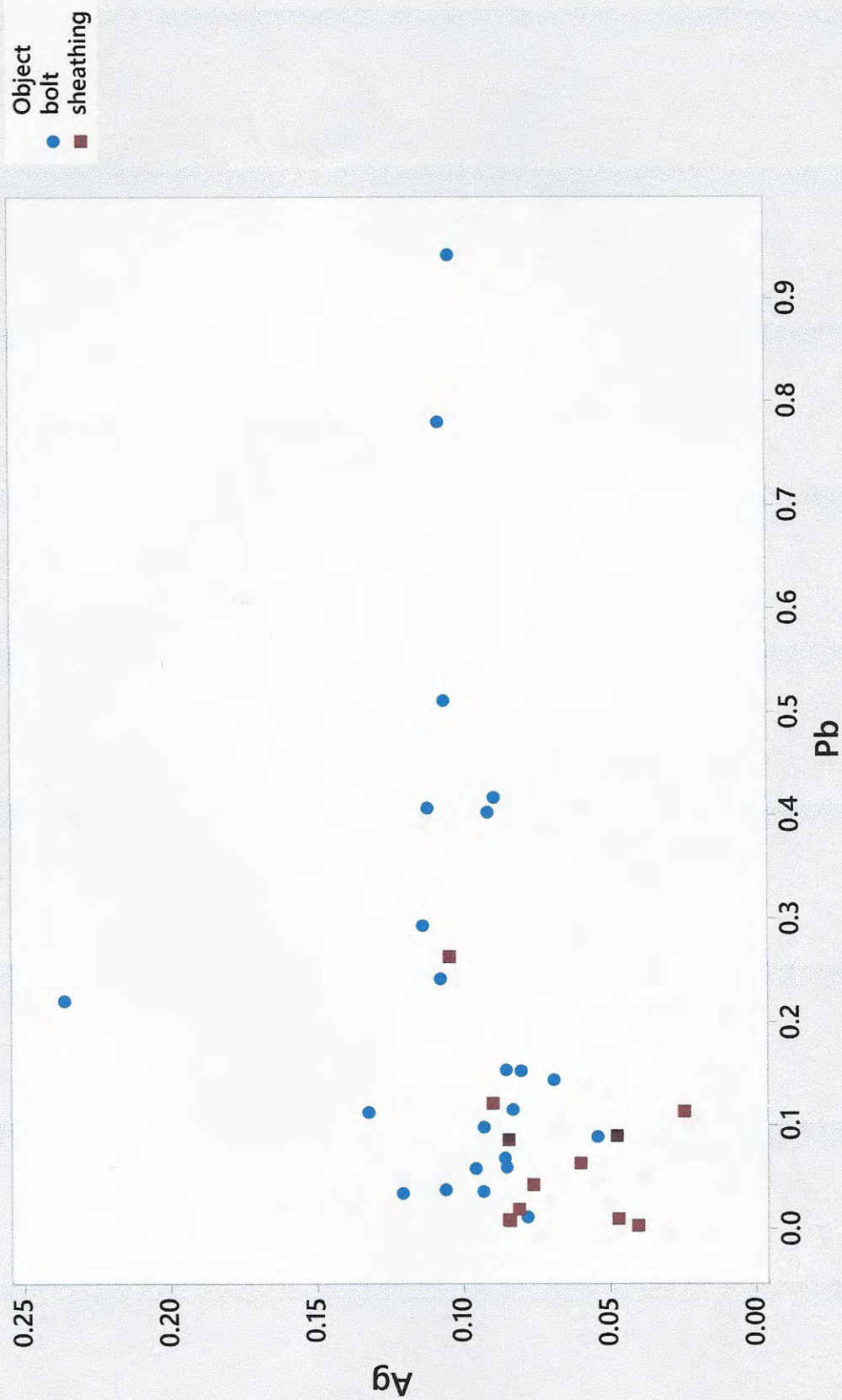
Scatterplot of Ag vs Pb



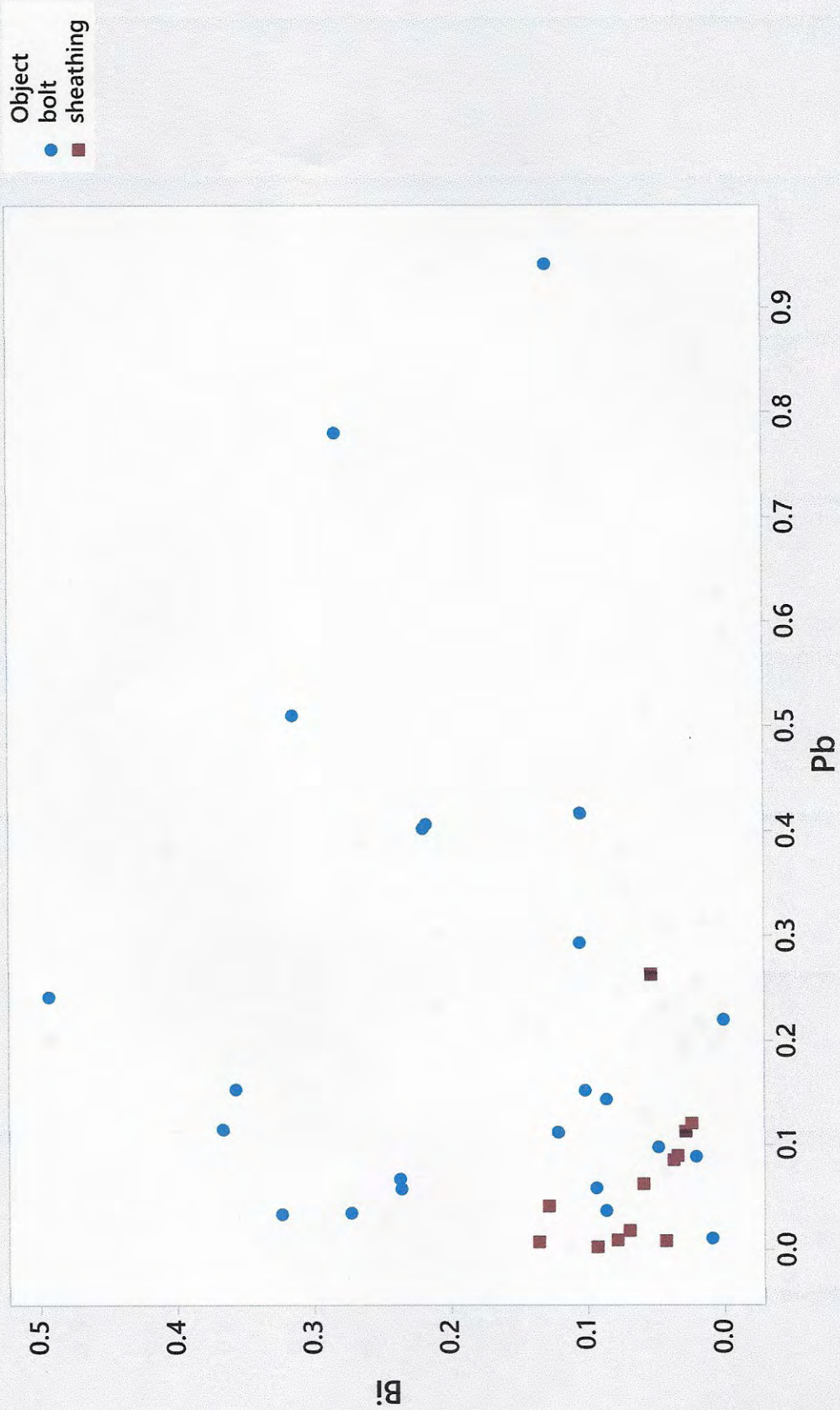
Scatterplot of PC2 vs PC1



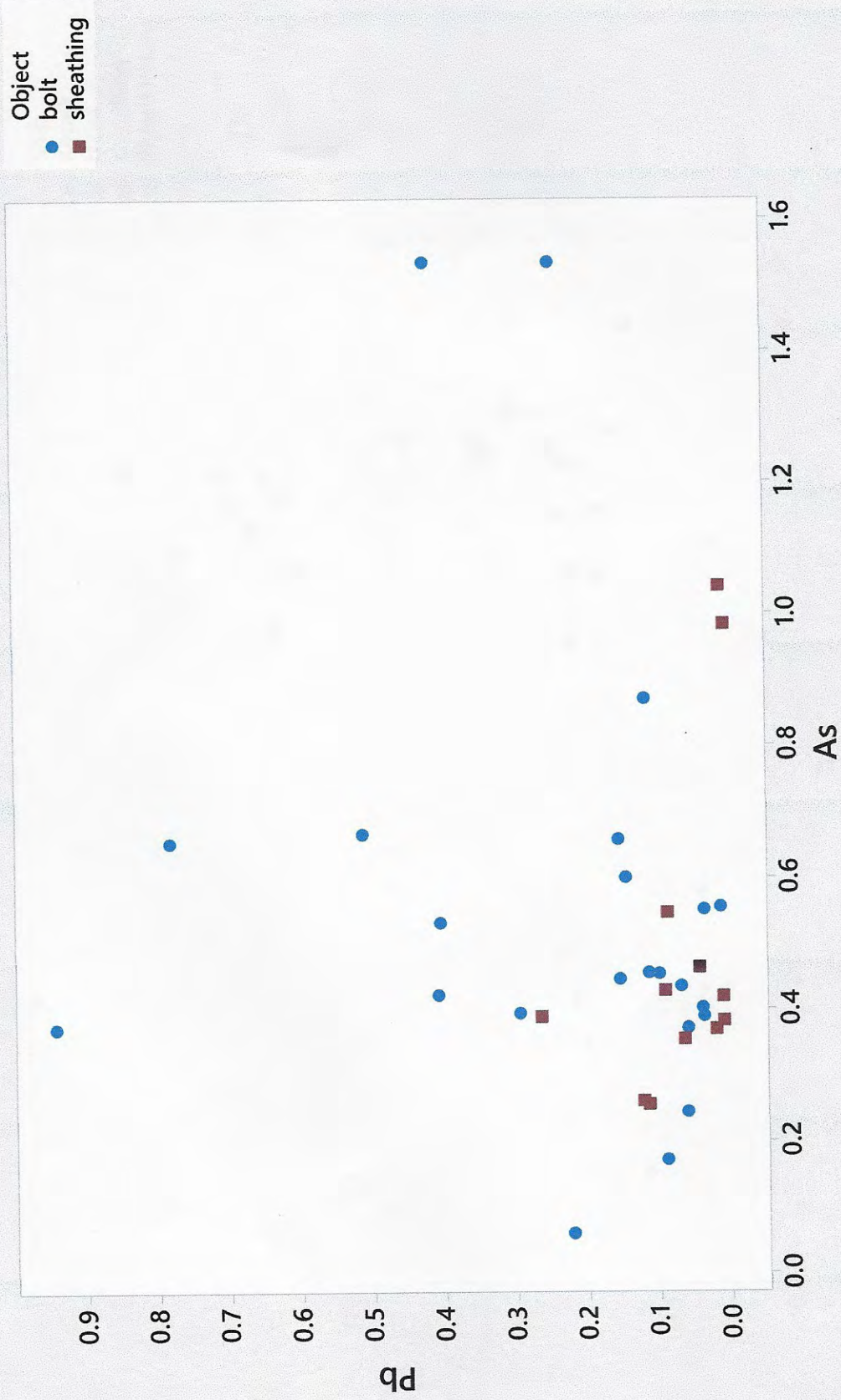
Scatterplot of Ag vs Pb



Scatterplot of Bi vs Pb



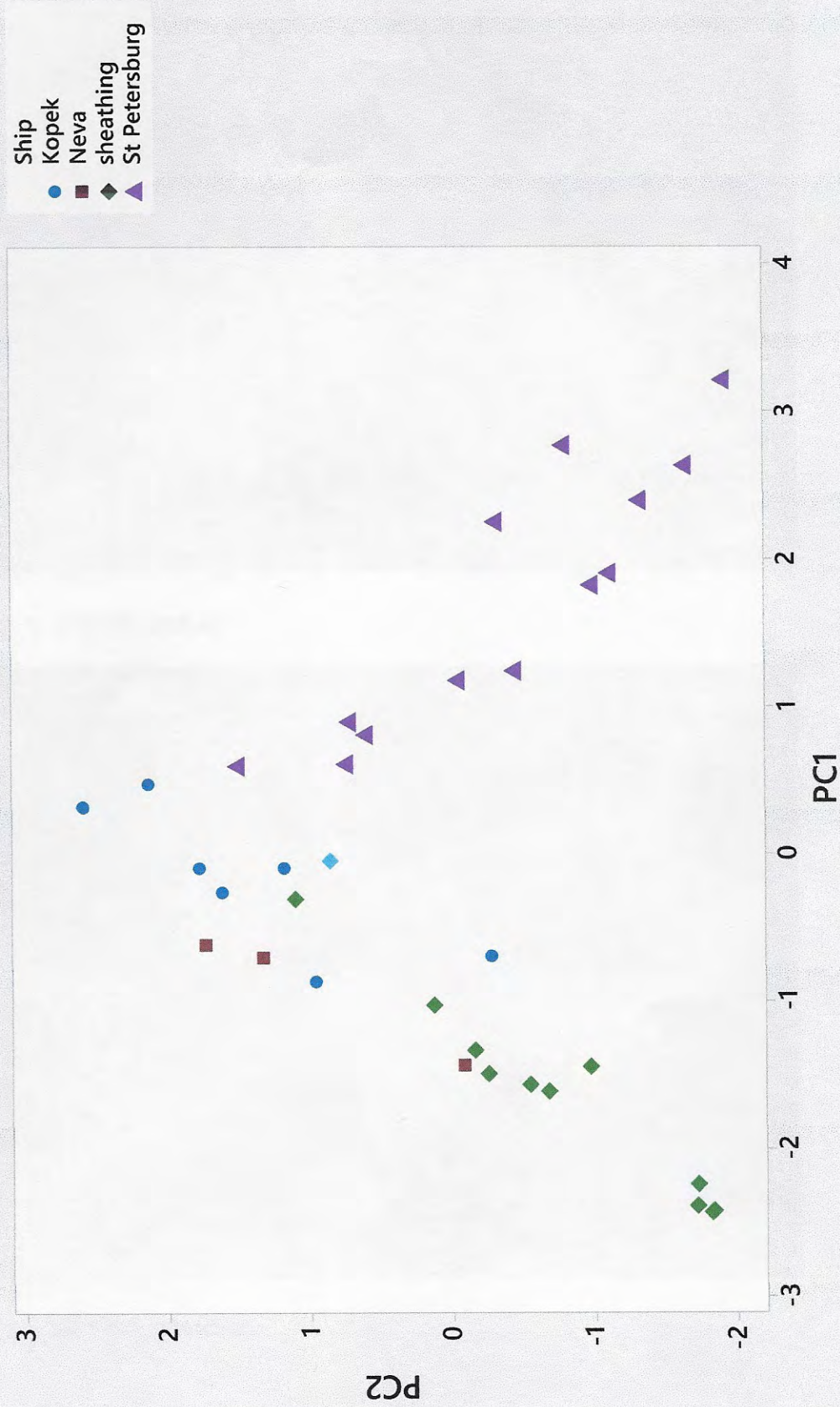
Scatterplot of Pb vs As



Scatterplot of Sb vs As



Scatterplot of PC2 vs PC1



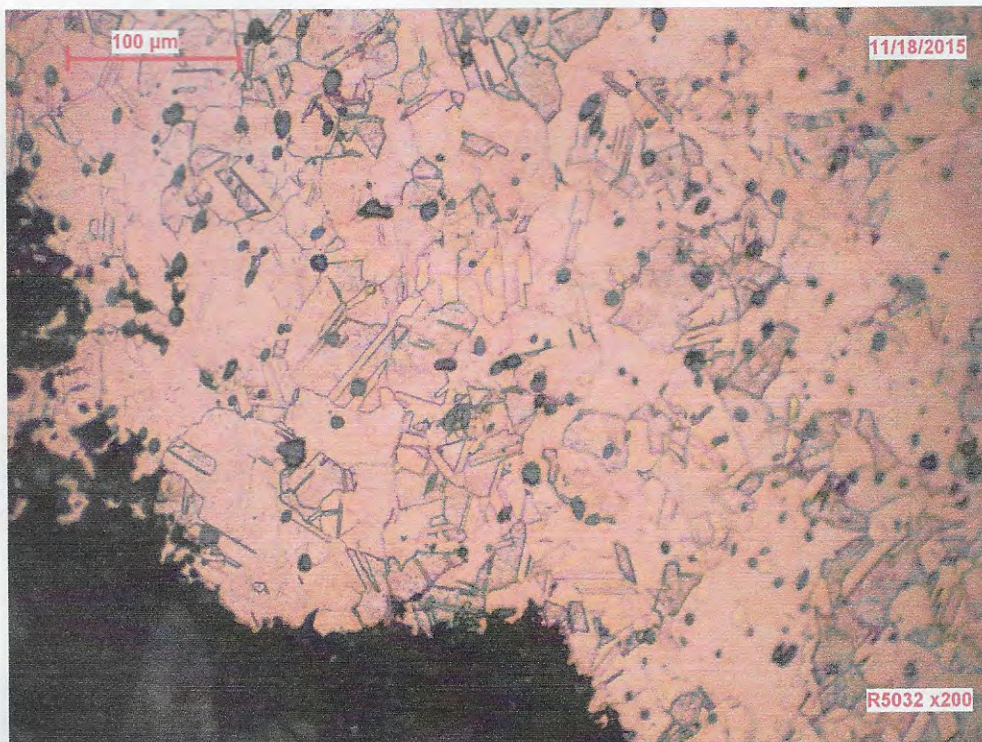


Fig. 1: #R5032, etched

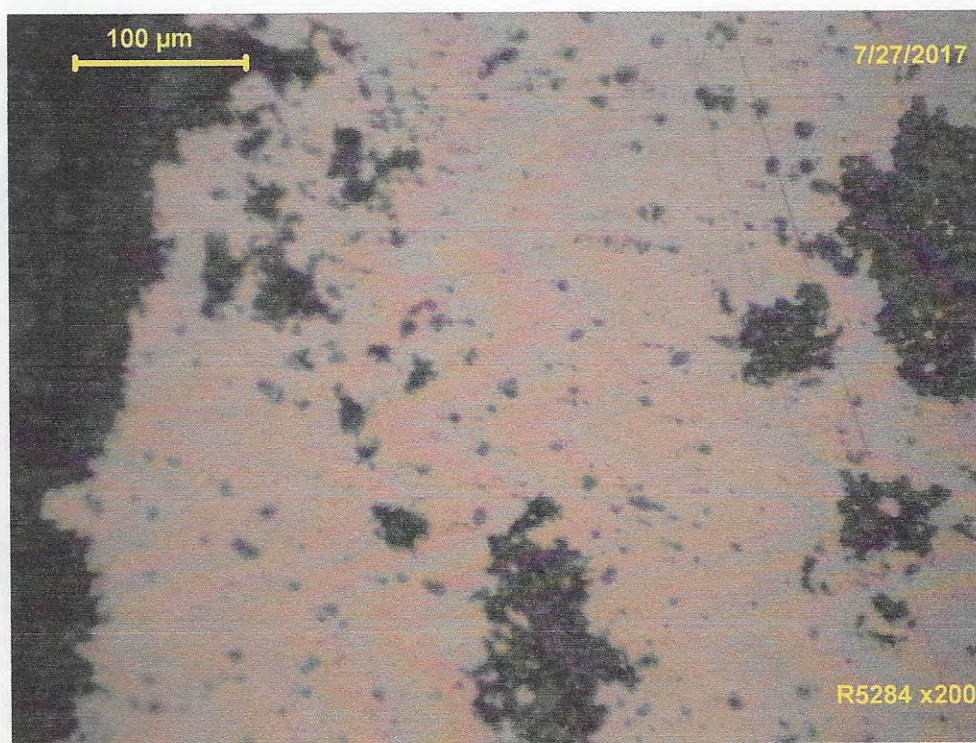


Fig. 2: #R5284, unetched



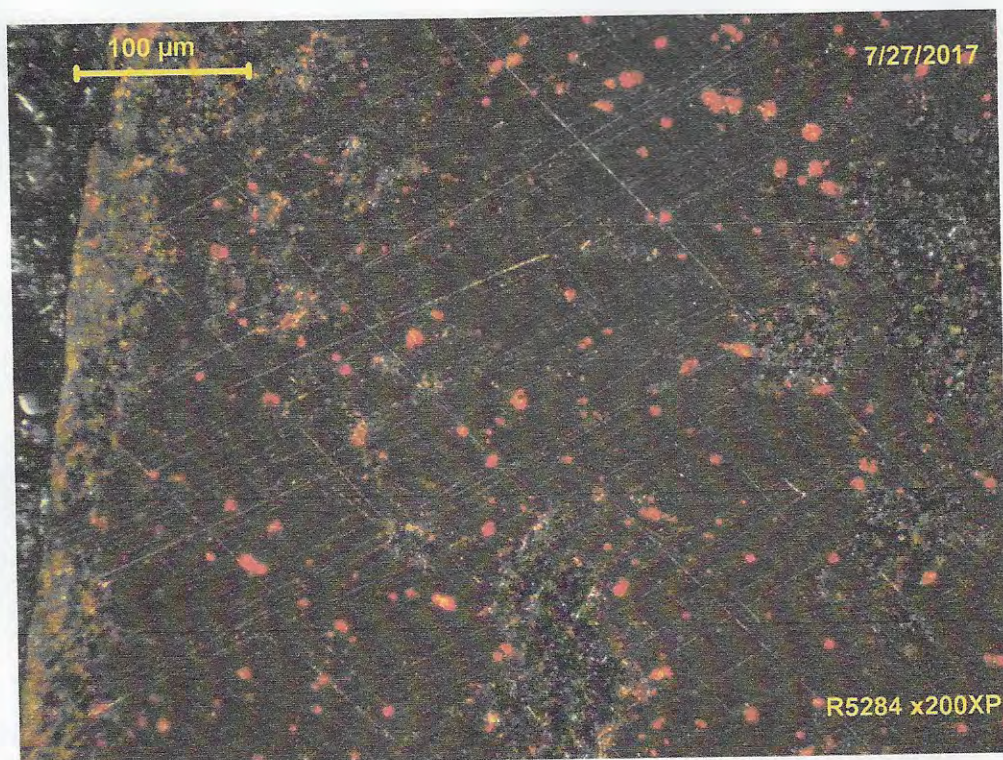


Fig. 3: #R5284, unetched, crossed polars

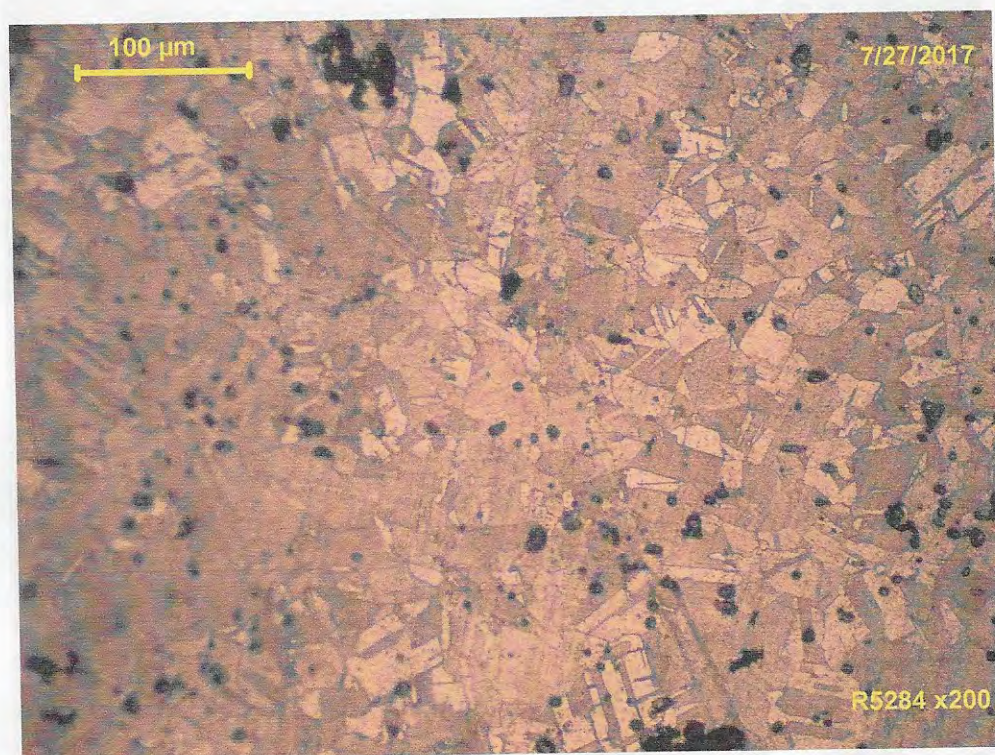


Fig. 4: #R5284, etched

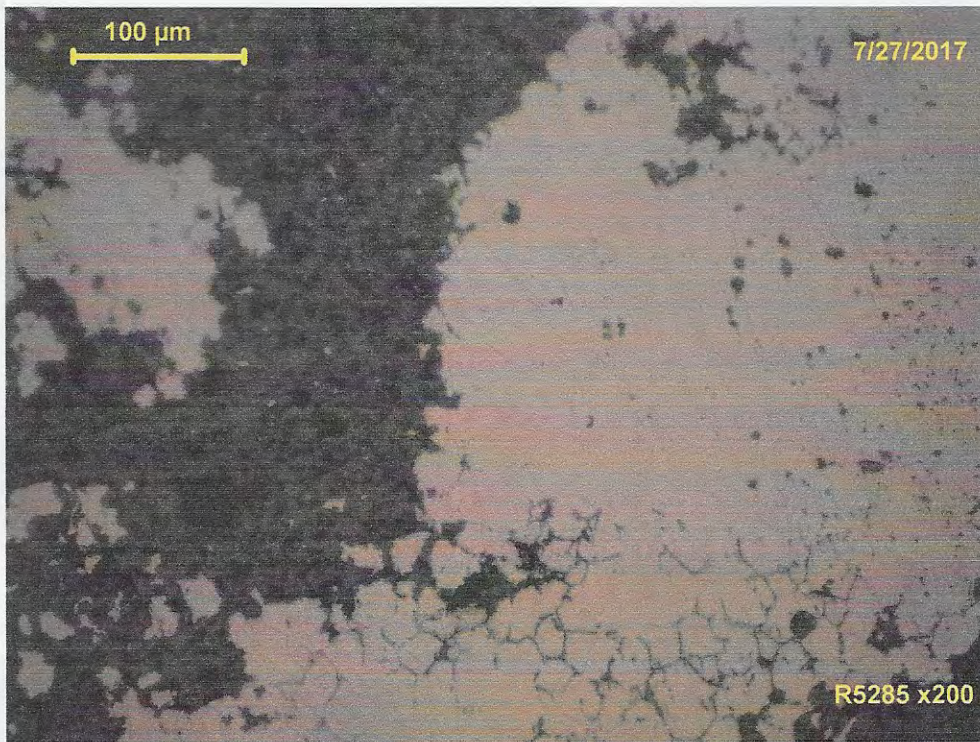


Fig. 5: #R5285, unetched

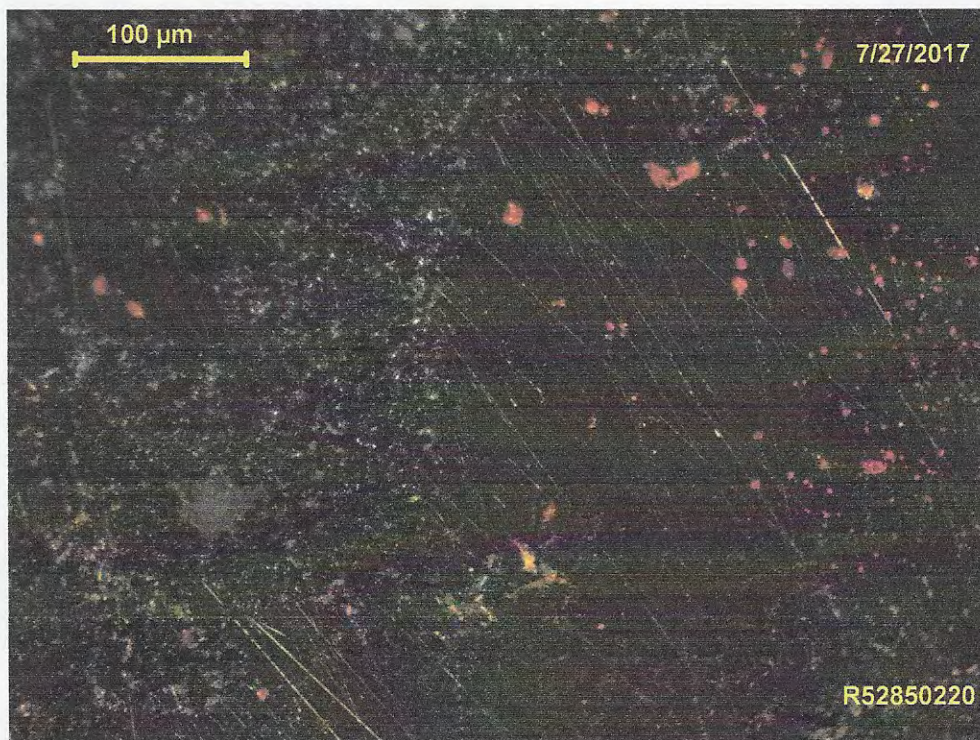


Fig. 6: #R5284, unetched, crossed polars

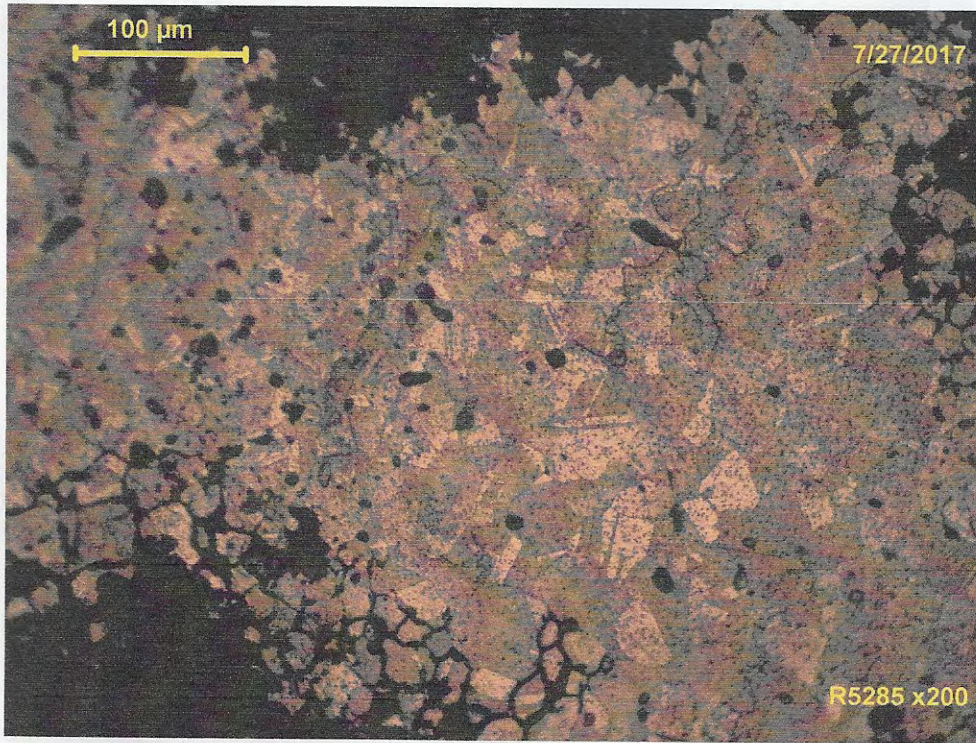


Fig. 7: #R5285, etched

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**ANALYSIS AND METALLOGRAPHY OF  
COPPER 1 KOPEK COINS**

#R5253-59

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## ANALYSIS AND METALLOGRAPHY OF RUSSIAN 1 KOPEK COPPER COINS

Seven Russian 1 *kopek* copper coins were submitted for metallurgical study. The purpose of the study was to provide data on Russian copper in support of the characterisation of three samples of copper sheathing from the presumed survivors' camp associated with the wreck of the *Neva* in 1813 at Sitka, Alaska

### Sampling and analysis

A single radial sample was cut from each coin and identified and labelled as follows:-

#R5253	1 <i>kopek</i>	1798
#R5254	1 <i>kopek</i>	1799
#R5255	1 <i>kopek</i>	1810
#R5256	1 <i>kopek</i>	1811
#R5257	1 <i>kopek</i>	1812
#R5258	1 <i>kopek</i>	1817
#R5259	1 <i>kopek</i>	1842

The samples hot-mounted in a carbon-filled thermosetting resin, ground and polished to a 1 $\mu$ m diamond finish. Analysis was by electron probe microanalysis with wavelength dispersive spectrometry; operating conditions were an accelerating voltage of 25kV, a beam current of 30nA, and an X-ray take-off angle of 40°. Eighteen elements were analysed as indicated in the accompanying table; counting times were 10s or 20s per element and pure element and mineral standards were used. Detection limits for most elements were 100-200ppm, with the exception of 300ppm for gold. The writer is grateful to Mr Chris Salter of Oxford Materials Characterisation Service for assistance with this analysis.

Five areas, each 30x50 $\mu$ m, were analysed on each sample; the individual analyses and their means are given in the accompanying table; all concentrations are in weight %.

After analysis the samples were examined metallographically in both as polished and etched states; the etches used were an ammoniacal solution of hydrogen peroxide and an acidified aqueous solution of ferric chloride further diluted with ethanol.

### The alloy

The analyses discussed here are the first detailed analyses of Russian copper coins of the period known to the writer and they constitute a minuscule sample of a population of coins that must number many millions. It must also be remembered that the period covered by the coins includes the Treaty of Tilsit in 1807 in consequence of which Napoleon tried to include Russia in his "Continental System" and the failure of this attempt because of its impact on the Russian economy. As a result Russia abandoned the treaty which provoked Napoleon's disastrous invasion of Russia. It might therefore be supposed that there were interruptions and changes in the supply of copper to the Russian mint(s) but even so, they share some common features which are of assistance in assessing the material from the *Neva*. This, of course, was also the period in which Matthew Boulton's technicians were erecting a steam-powered mint in St Petersburg which ultimately put its first copper coins into local circulation in 1810.

The coins were all struck in copper of 99.5% purity or better with the majority of impurities at a low level. For comparison there are available analyses of copper coins from the United States of

America, the United Kingdom, and Austria-Hungary, and of late 18<sup>th</sup> century counterfeits of British coins from both sides of the Atlantic.<sup>1</sup> So far no French, German or Italian copper coins have been analysed but analysis of contemporary bronze ordnance can give an idea of the impurity patterns of copper in use in those areas at the beginning of the nineteenth century. One striking feature of all these data is the consistent presence of an arsenic impurity >0.10%, something absent in the *kopek* coins; arsenic is also present in cannon cast in St Petersburg at the beginning of the nineteenth century.<sup>2</sup>

The best way of presenting the discussion of these copper coin compositions is with the aid of a number of graphs. Because of the connection of this project with the study of the *Neva* survivors' camp the three copper analyses from that site are included in the graphs, but are also the subject of a separate report (#R5032/5284-85). The first graph is a log-log plot of antimony against arsenic: this clearly separates the Austro-Hungarian coins from the rest because they are the only group with a significant antimony impurity. The British and USA coins group together which is to be expected because Boulton and Watt supplied the Philadelphia Mint with its blanks until 1837 and also struck the analysed British copper. It is clear that the *kopeks* fit with neither of these groups, while the *neva* copper sits at the lower end of the British/USA grouping. The same pattern can be seen in plots of bismuth against antimony and bismuth against lead. 3D scatterplots, such as that of silver vs lead vs arsenic also emphasise the separation of the *kopeks*, both from the other coins and from the *Neva* copper.

Although the impurities totals in the *kopeks* are low there is still sufficient variation to suggest copper from more than one source, one being characterised by nickel (1798, 1799, 1811, and, possibly, 1842, and another by antimony (1811-12), possibly suggesting a switch in source with time. Whether the copper was Russian is another question and one source of comparison lies in the impurity patterns of Russian bronze ordnance cast at St Petersburg in this period. Plots of antimony against arsenic and silver against lead show no overlap between the *kopeks* and the cannon. Much documentary research will be needed to resolve this question.

### **Metallography**

The results of the metallographic survey are presented in Figures 1-20. They are not discussed in detail here because there are insufficient samples to build up any systematic picture. All samples show parallel rows of cuprous oxide (cuprite) inclusions typical of rolled copper of the period. Grain sizes in the recrystallised grain structures vary considerably suggesting some variation in practice in the production of the blanks.

### **Conclusions**

The copper in the 1 *kopek* copper coins is very different from that in other European coins of the period of the Napoleonic Wars, and its impurity pattern differs from that in contemporary Russian

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<sup>1</sup>J.P. Northover and N. Wilcox, 2012: Matthew Boulton's copper, in K. Quickenden, S. Baggott and M. Dick, eds. *Matthew Boulton: enterprising industrialist of the Enlightenment*, (Farnham: Ashgate Publishing Ltd), 101-110

<sup>2</sup> J. Riederer, *Waffen und Kostümkunde*, 14, 1972, 49-56

J. Riederer, *Berliner Beiträge zur Archäometrie*, 2, 1977, 27-40

H. Forshell, *Bronze cannon analysis: alloy composition related to the corrosion picture*, (Armémuseum, Rapport No. 2, Stockholm, 1984)

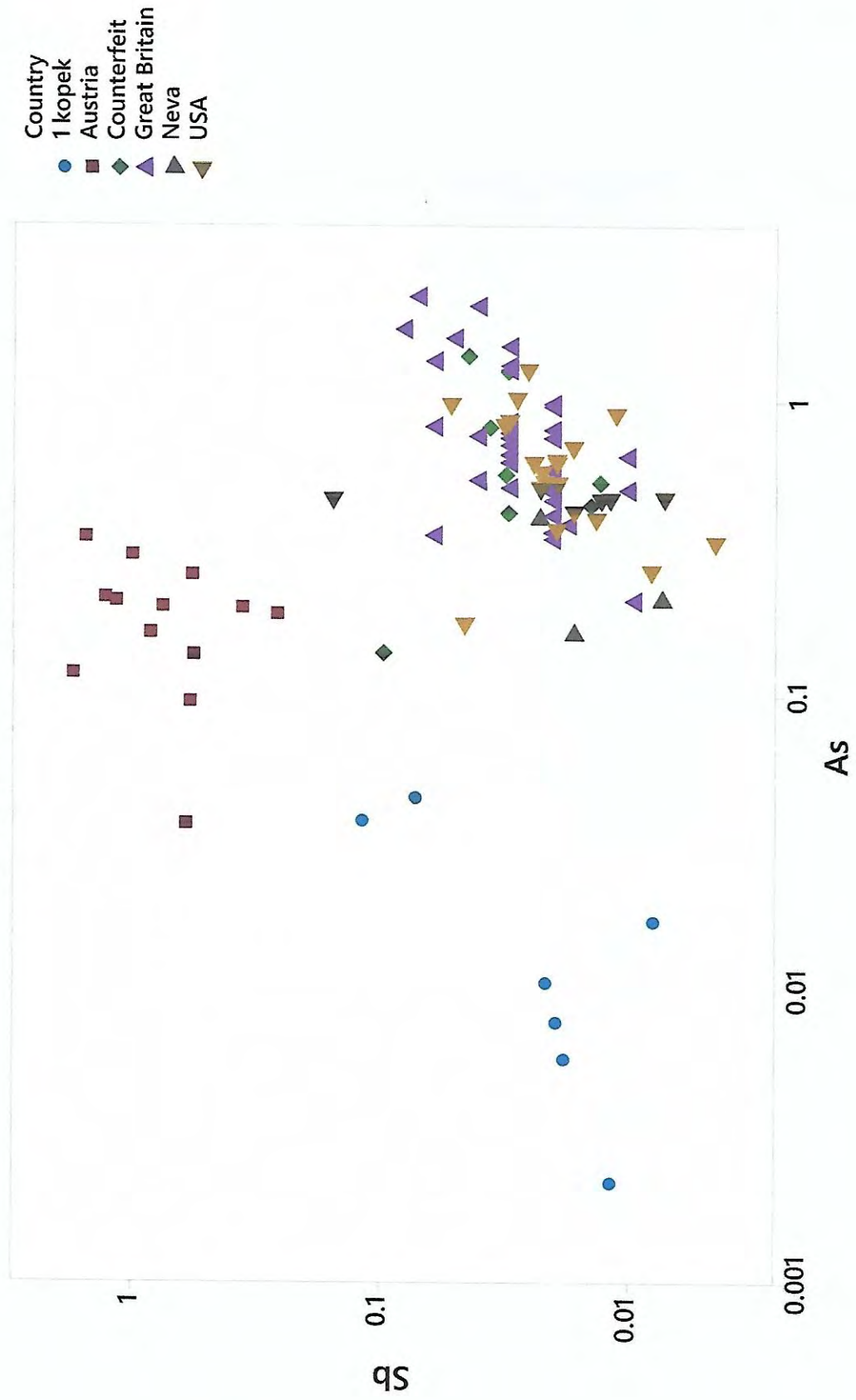
H. Forshell, *The inception of copper mining in Falun*, *Theses and Papers in Archaeology B:2*, (Stockholm: Archaeological Research Laboratory, Stockholm University), 1992, 119-144

copper alloy ordnance. The compositions also suggest that the source of the copper may have changed with time.

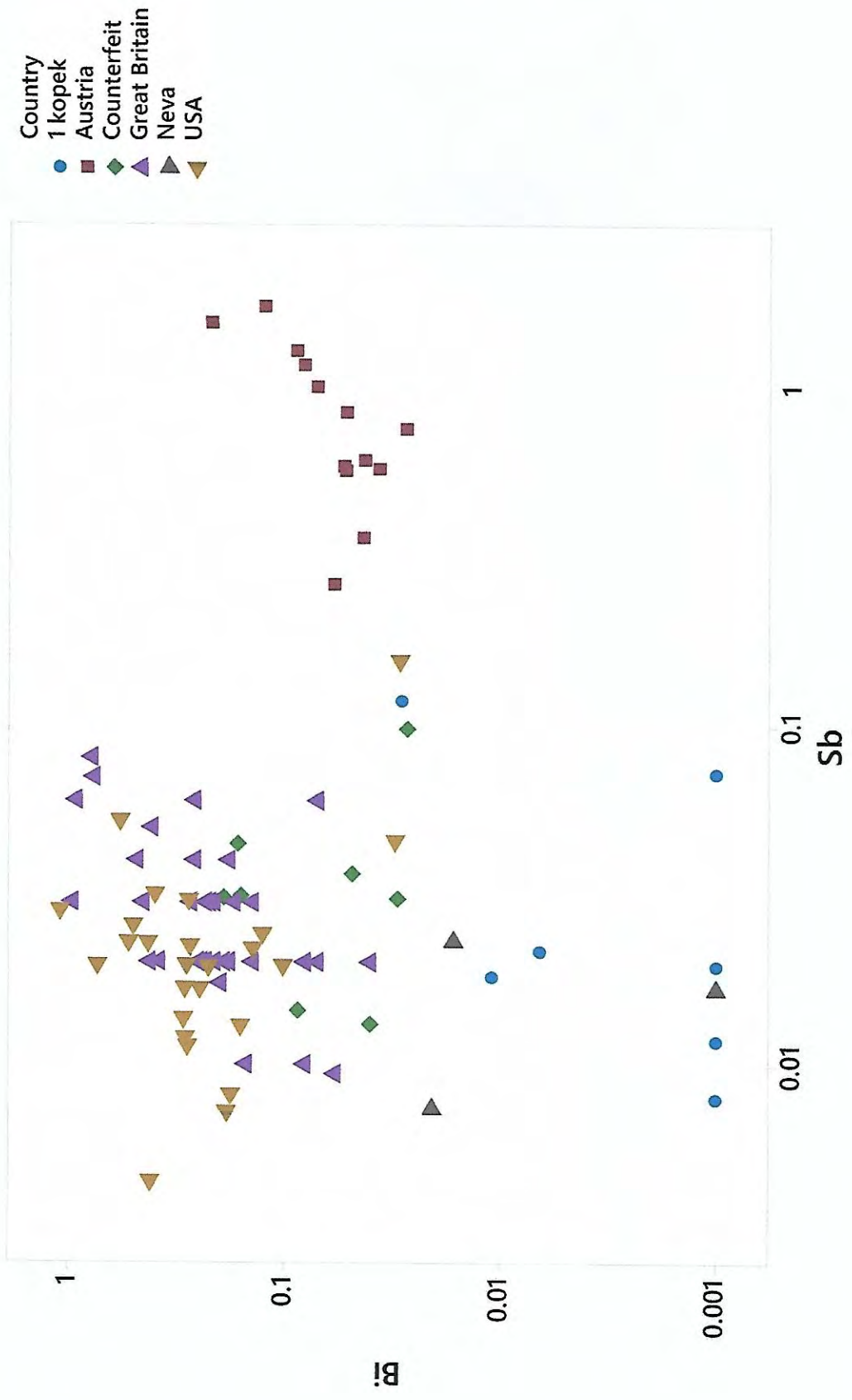




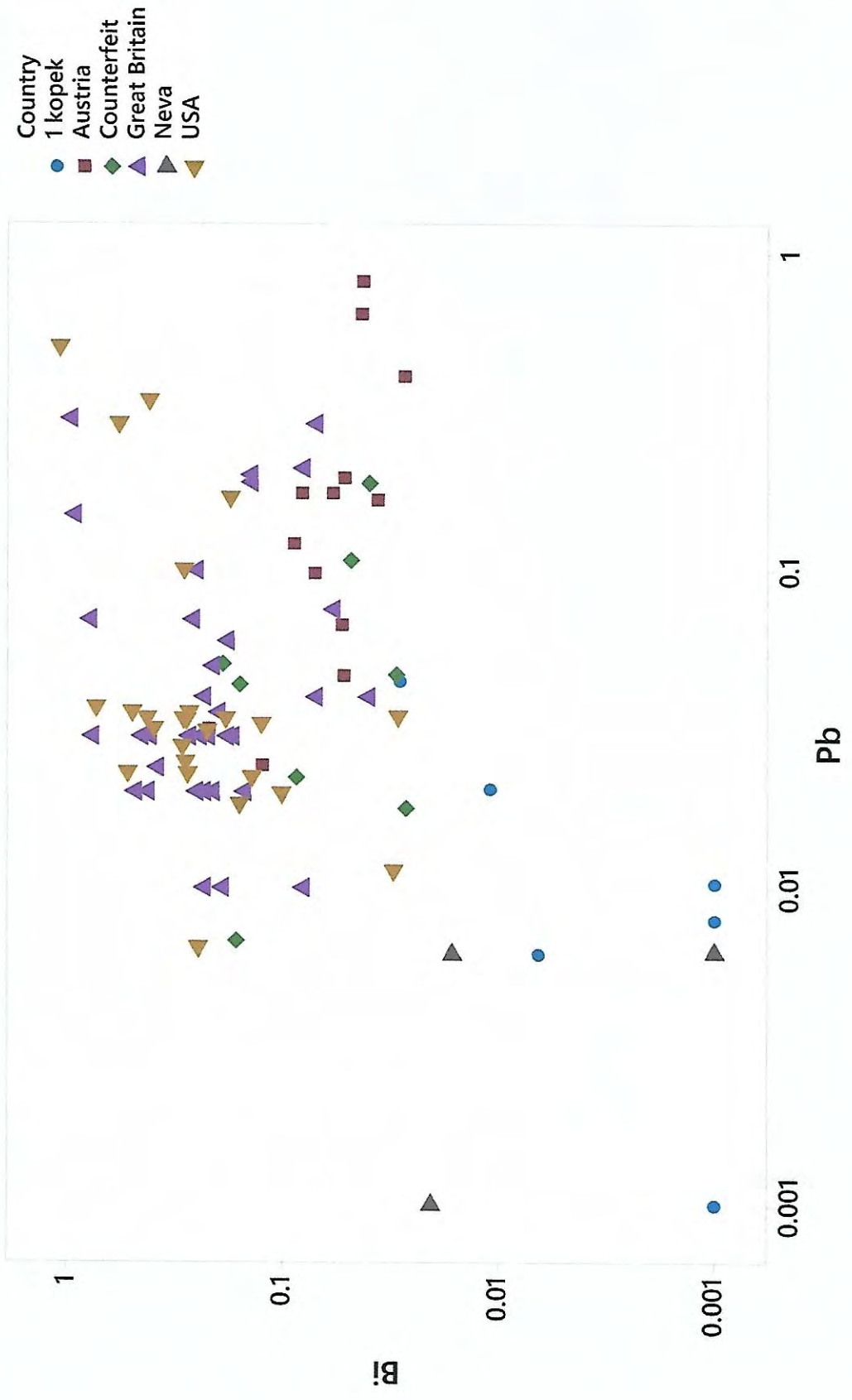
Scatterplot of Sb vs As



Scatterplot of Bi vs Sb

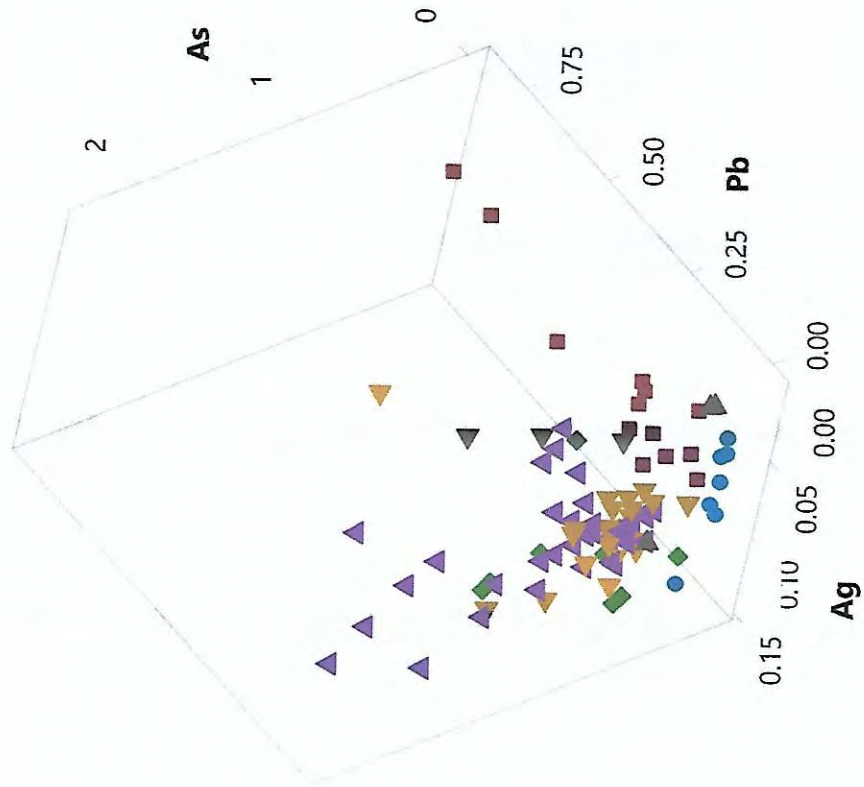


Scatterplot of Bi vs Pb

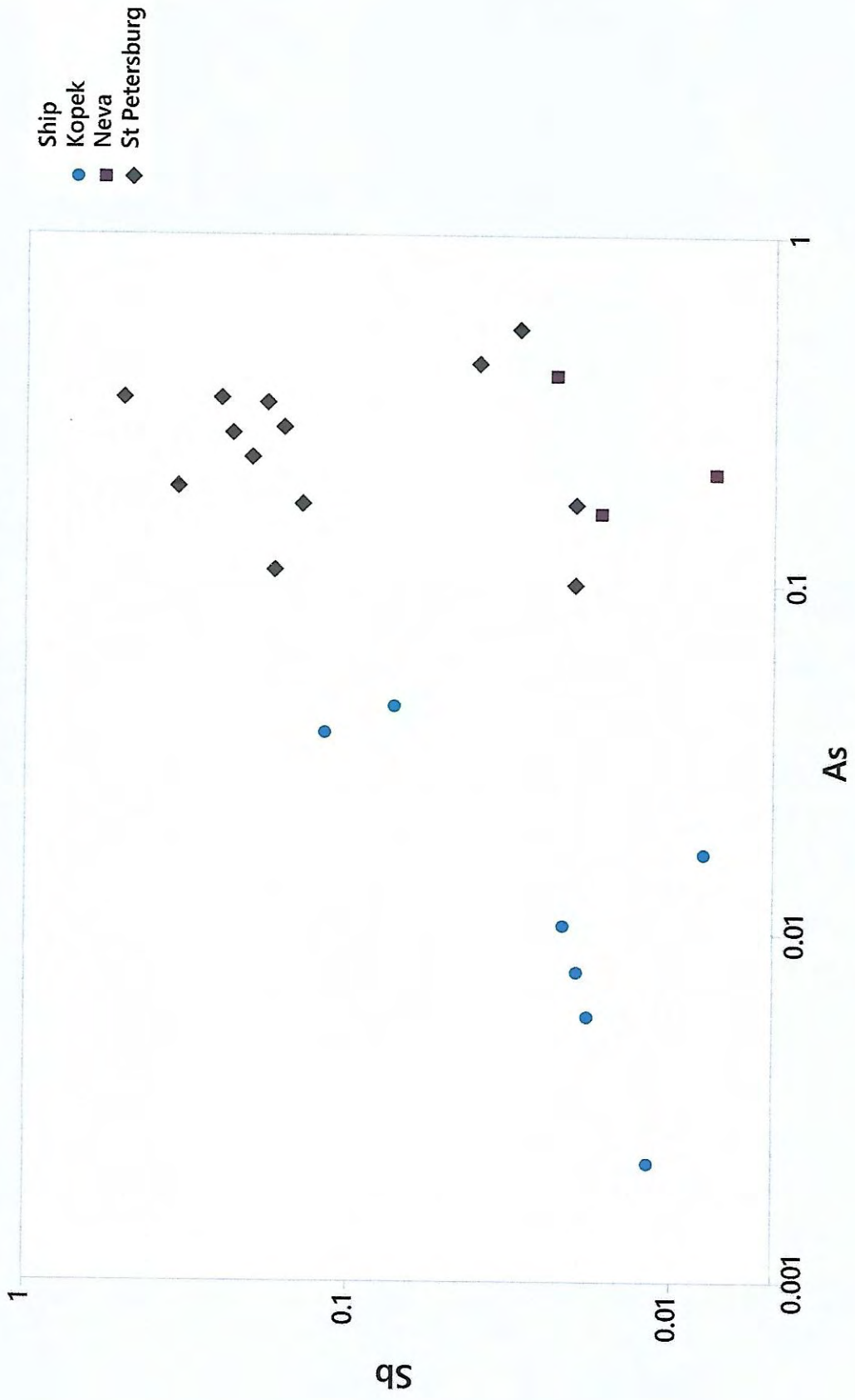


### 3D Scatterplot of Ag vs Pb vs As

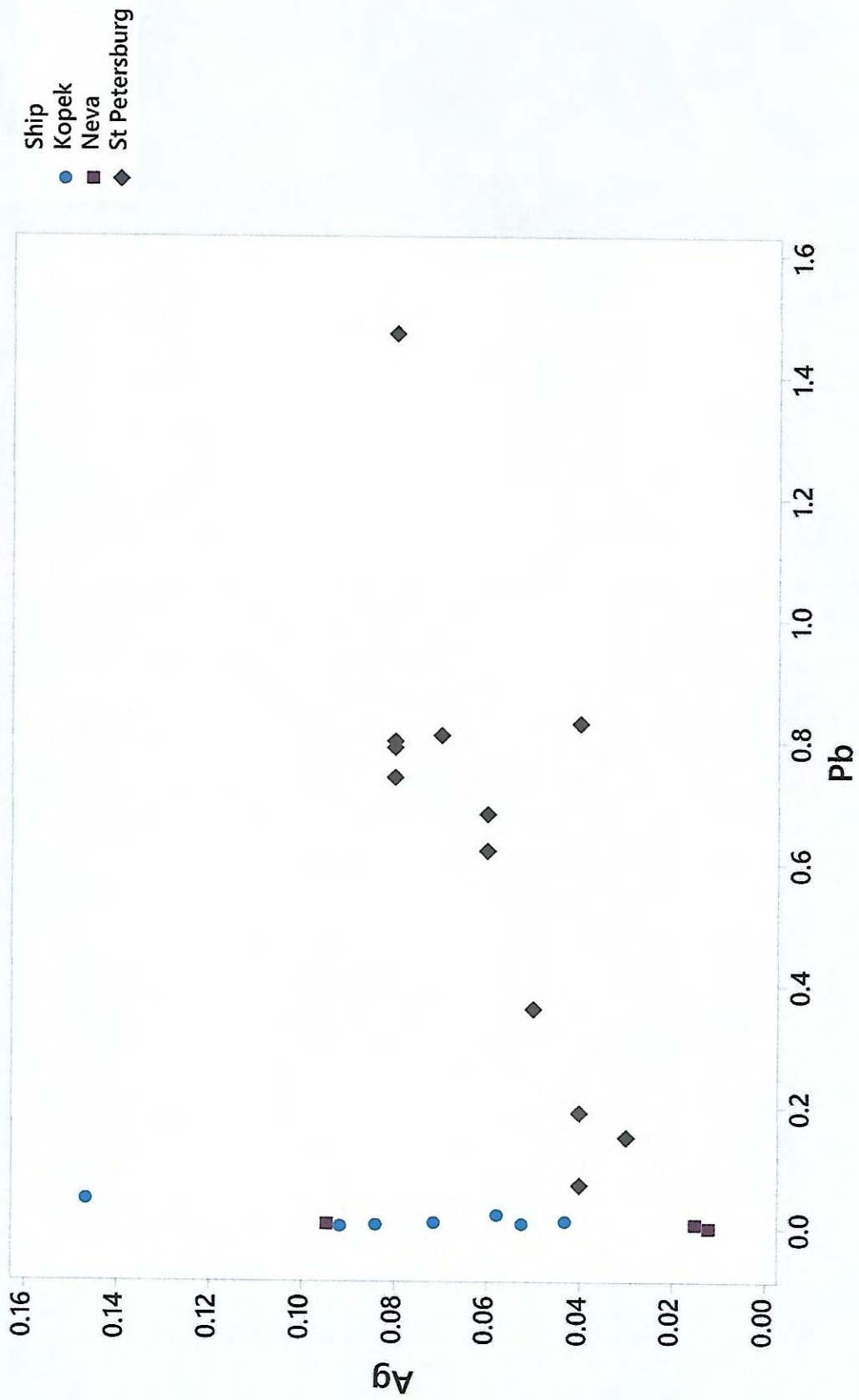
- Country
- 1 kopek
  - Austria
  - Counterfeit
  - Great Britain
  - Neva
  - USA



Scatterplot of Sb vs As



Scatterplot of Ag vs Pb



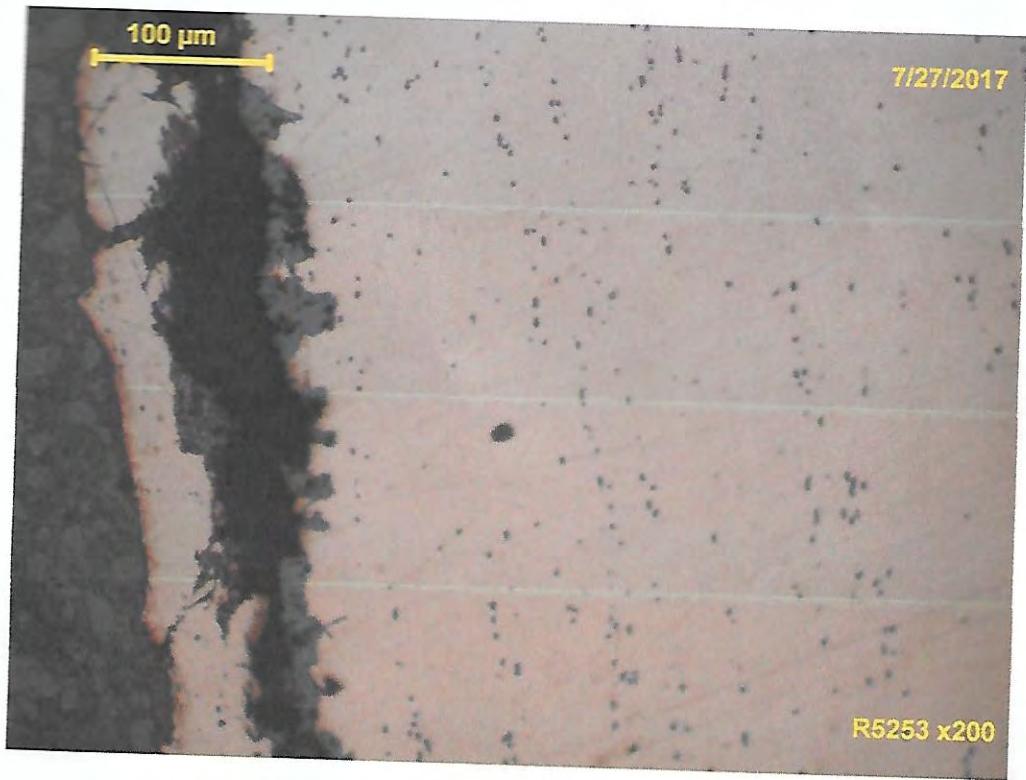


Fig. 1: #R5253, unetched

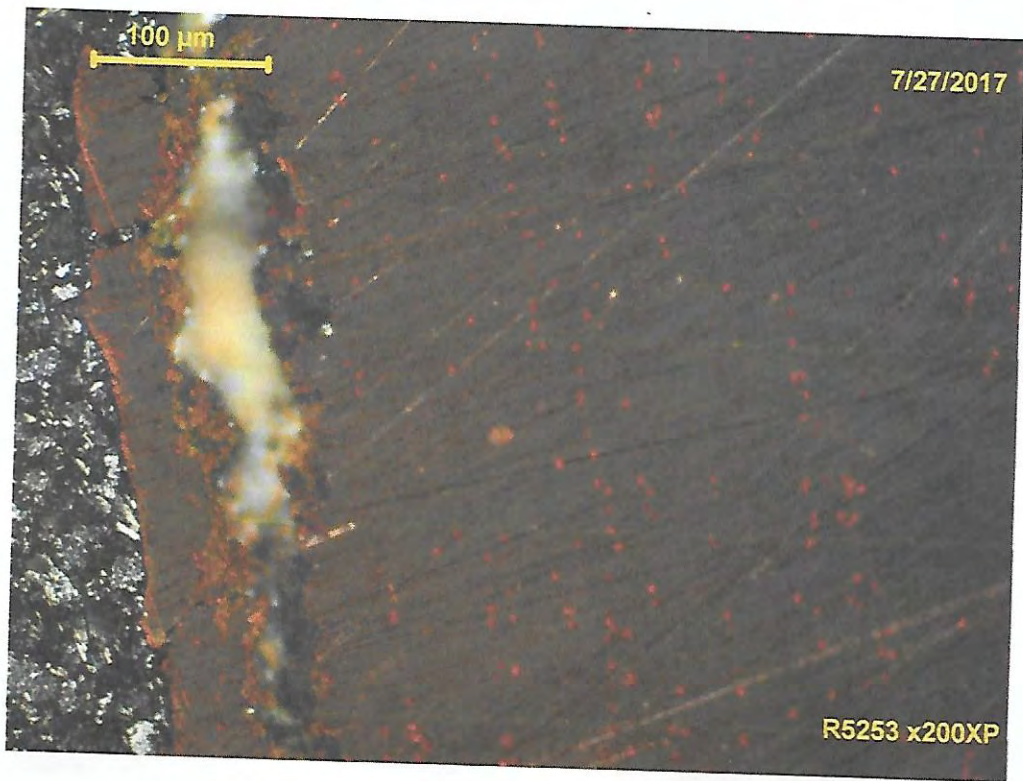


Fig. 2: #R5253, unetched, crossed polars

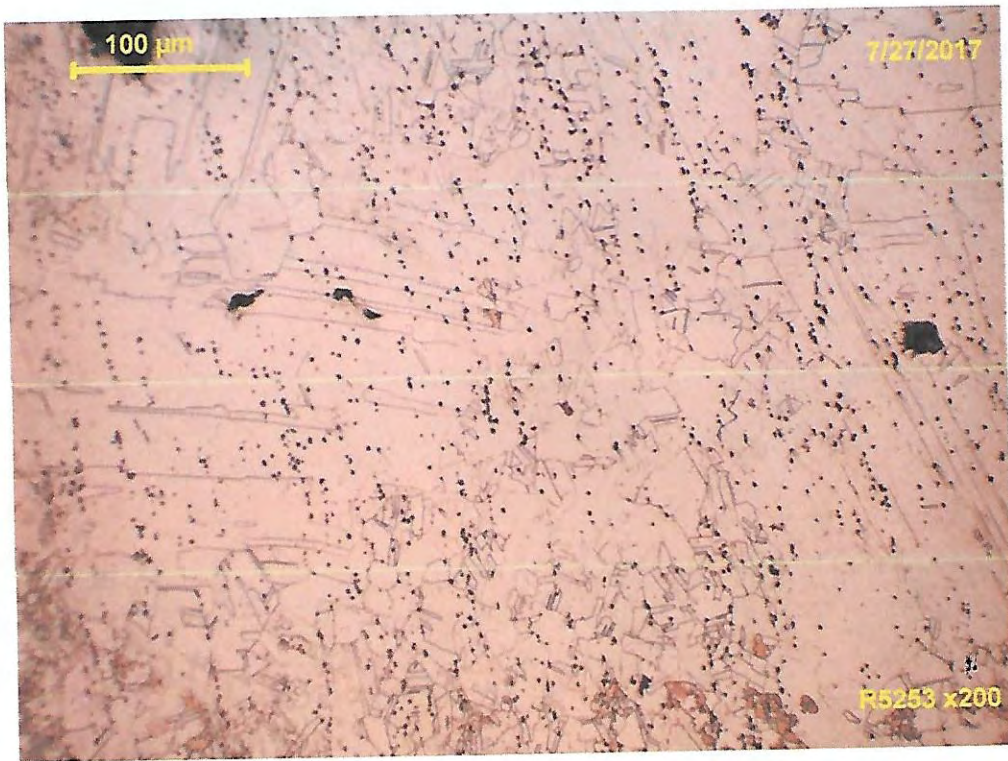


Fig. 3: #R5323, etched



Fig. 4: #R5324, unetched



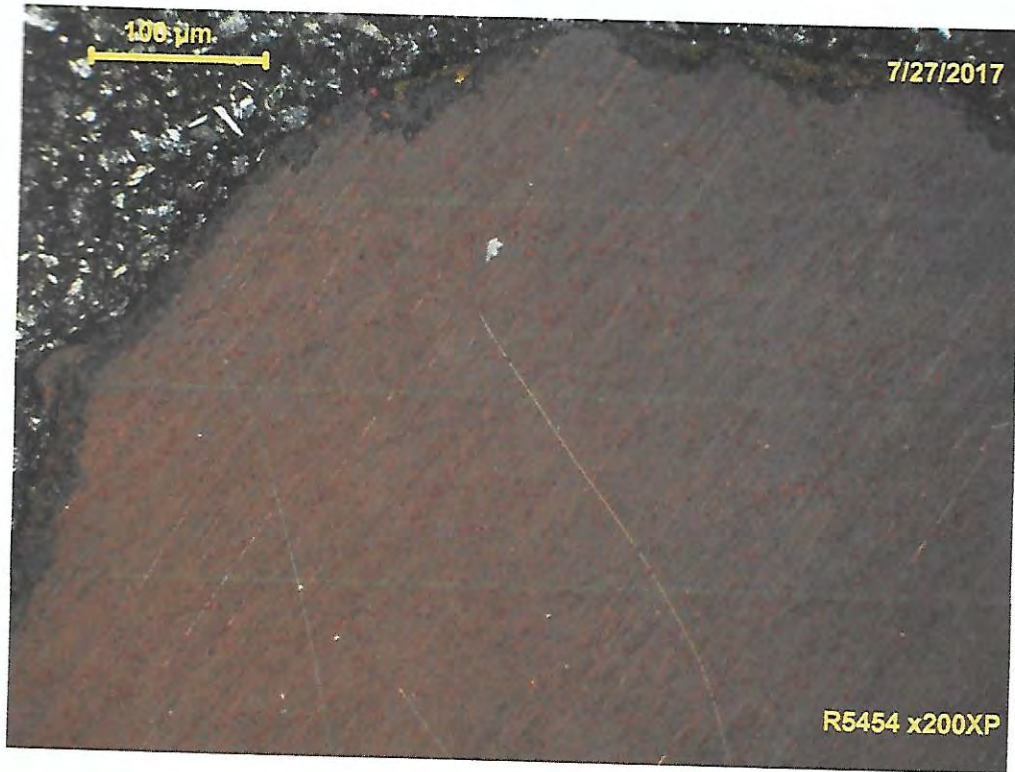


Fig. 5: #R5254, unetched, crossed polars

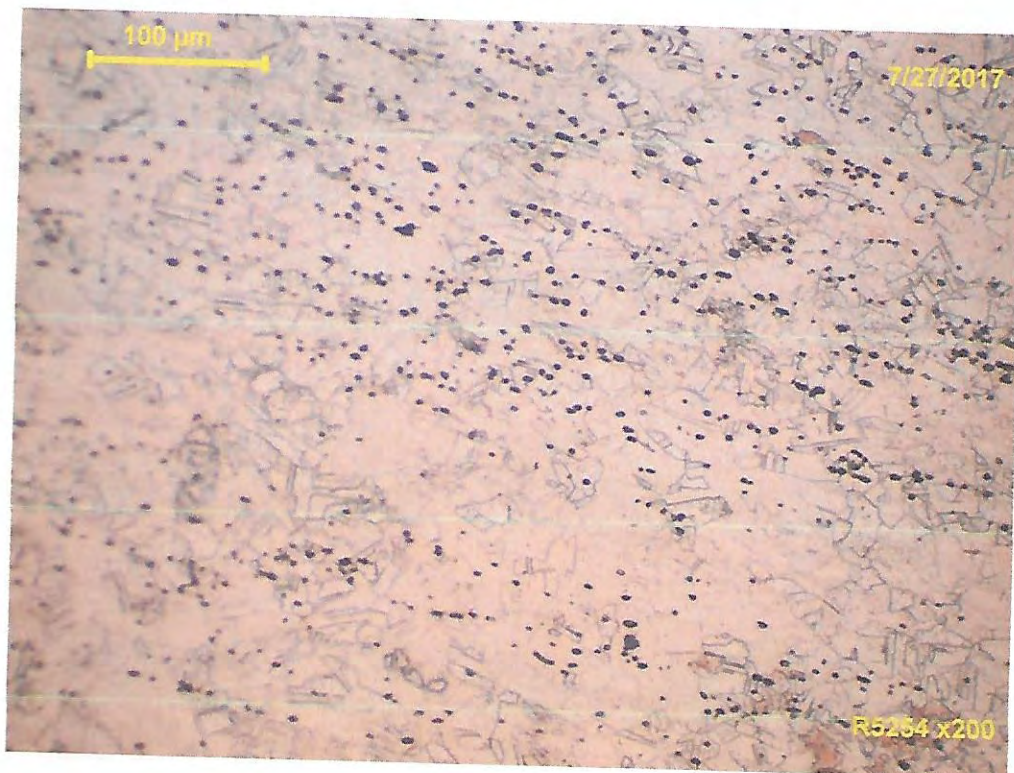


Fig. 6: #R5324, etched



Fig. 7: #R5255, unetched

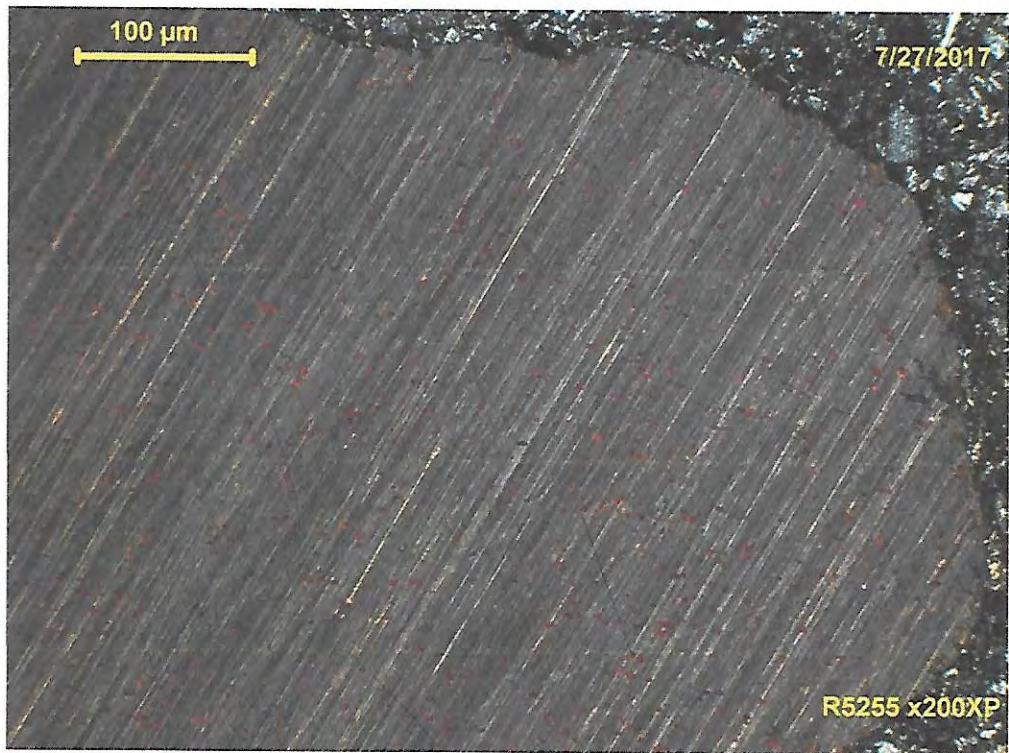


Fig. 8: #R5325, unetched, crossed polars

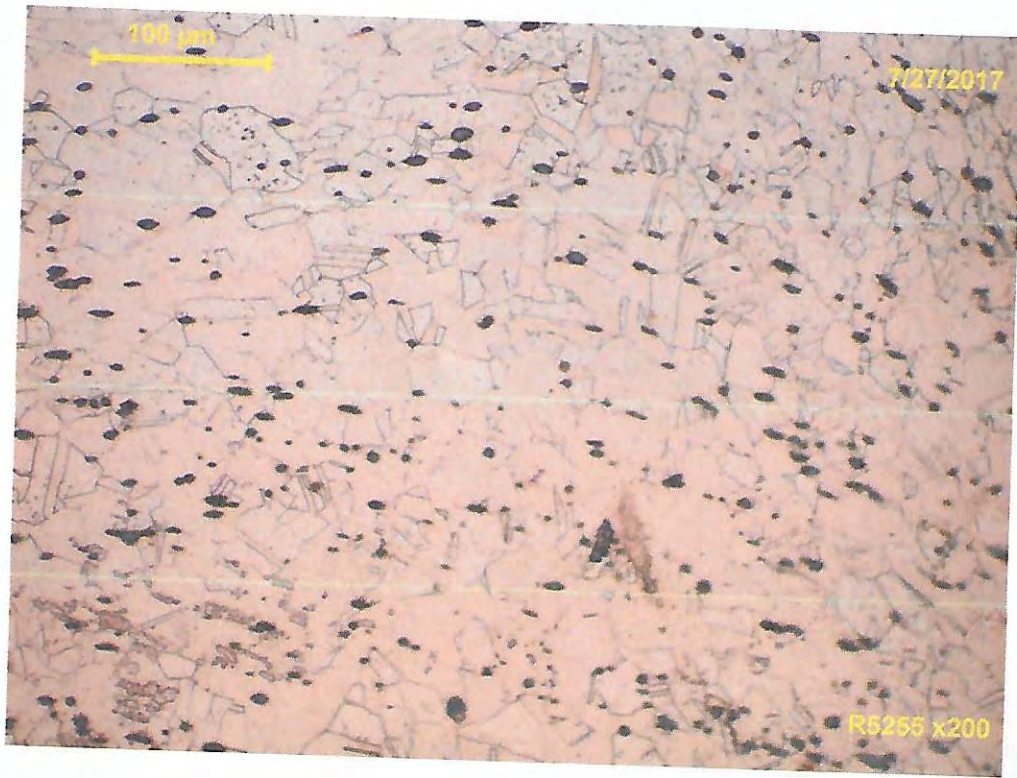


Fig. 9: #R5255, etched

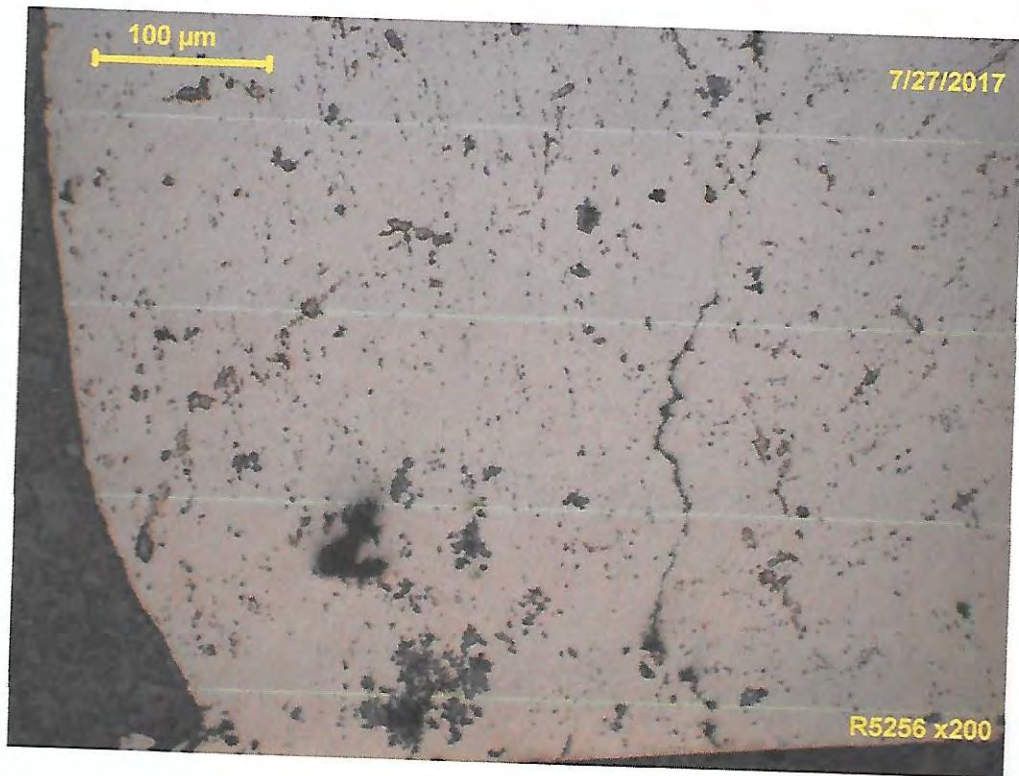


Fig. 10: #R5256, unetched

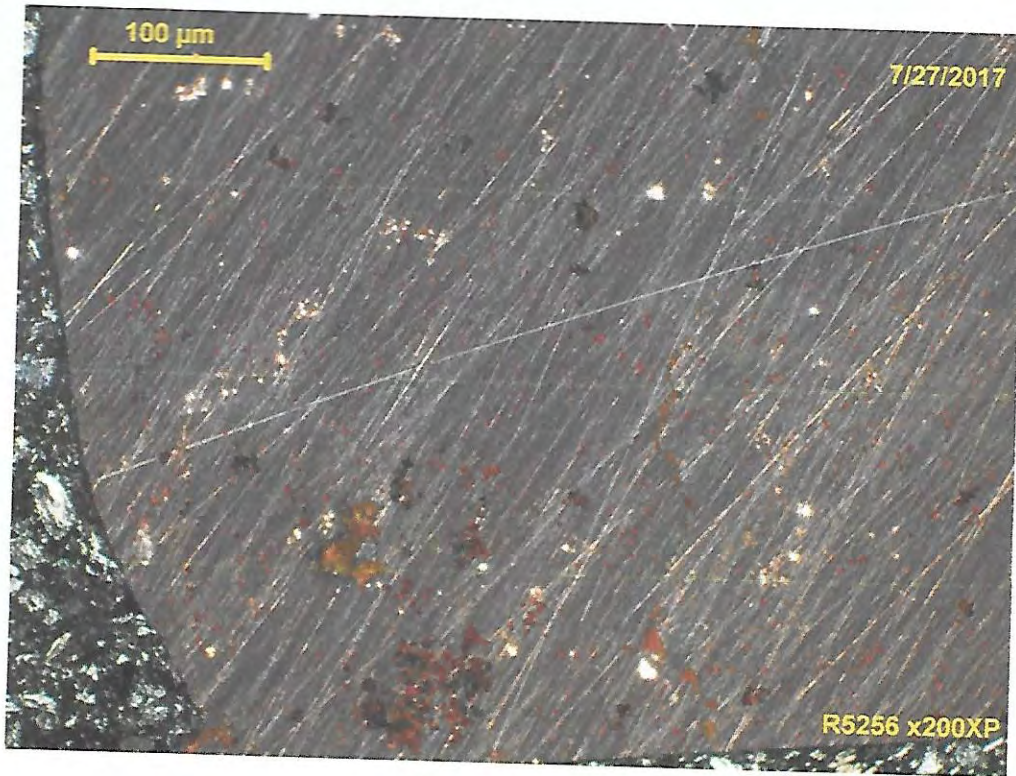


Fig. 11: #R5256, unetched, crossed polars

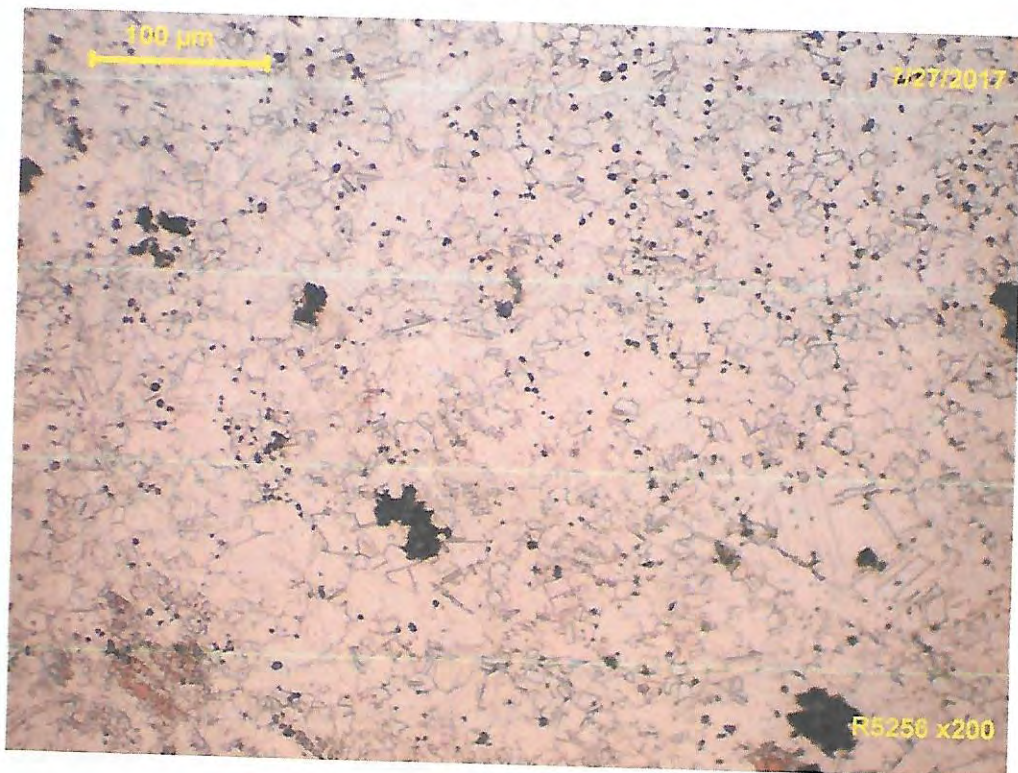


Fig. 12: #R5256, etched

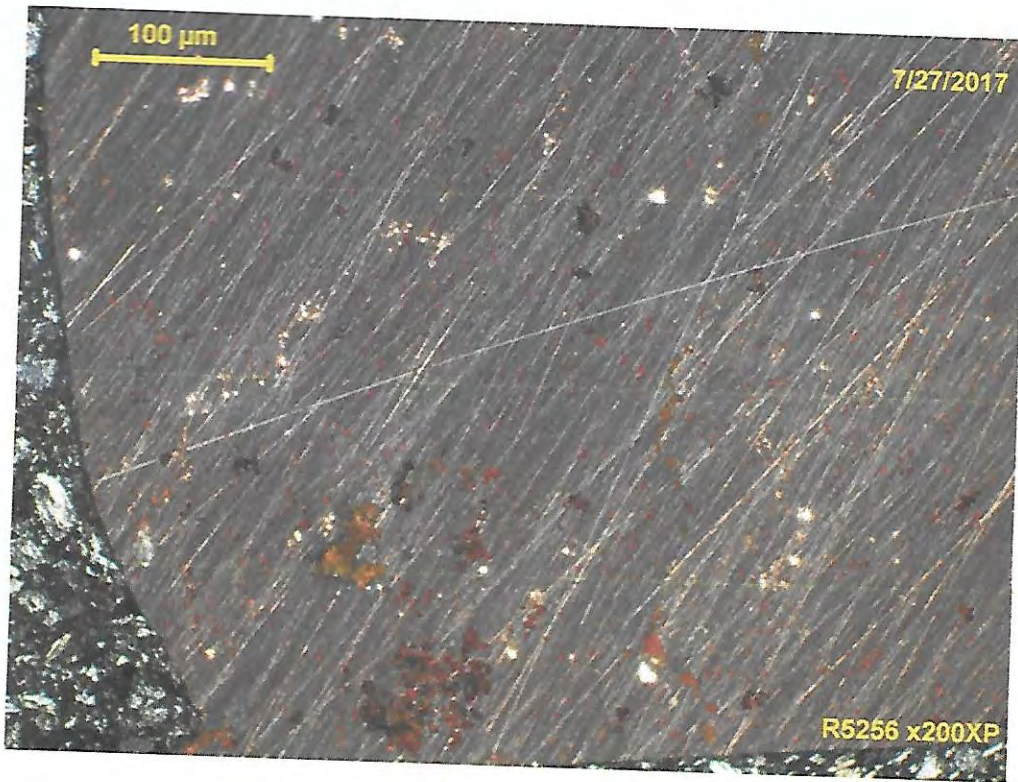


Fig. 11: #R5256, unetched, crossed polars

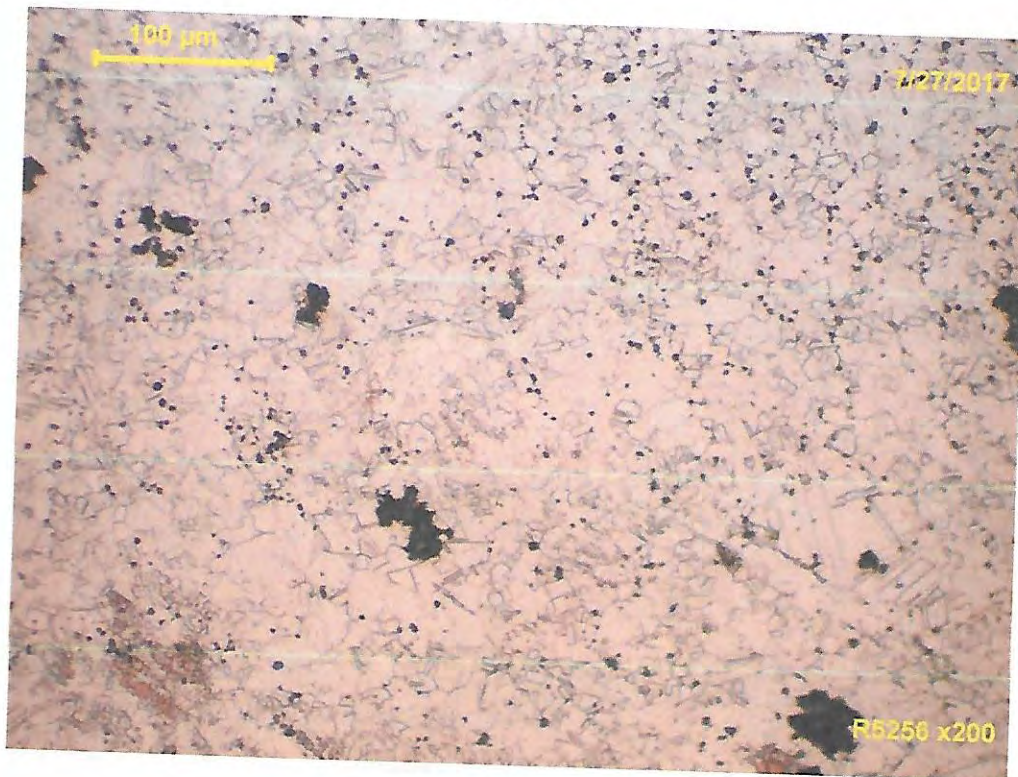


Fig. 12: #R5256, etched

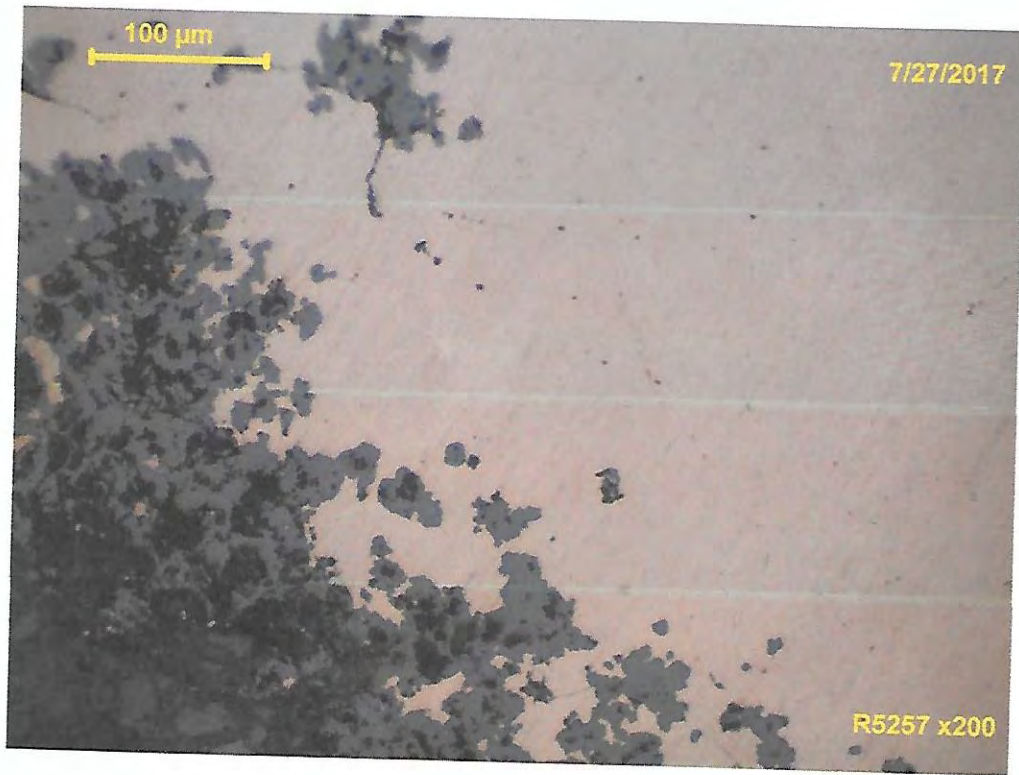


Fig. 13: #R5257, unetched

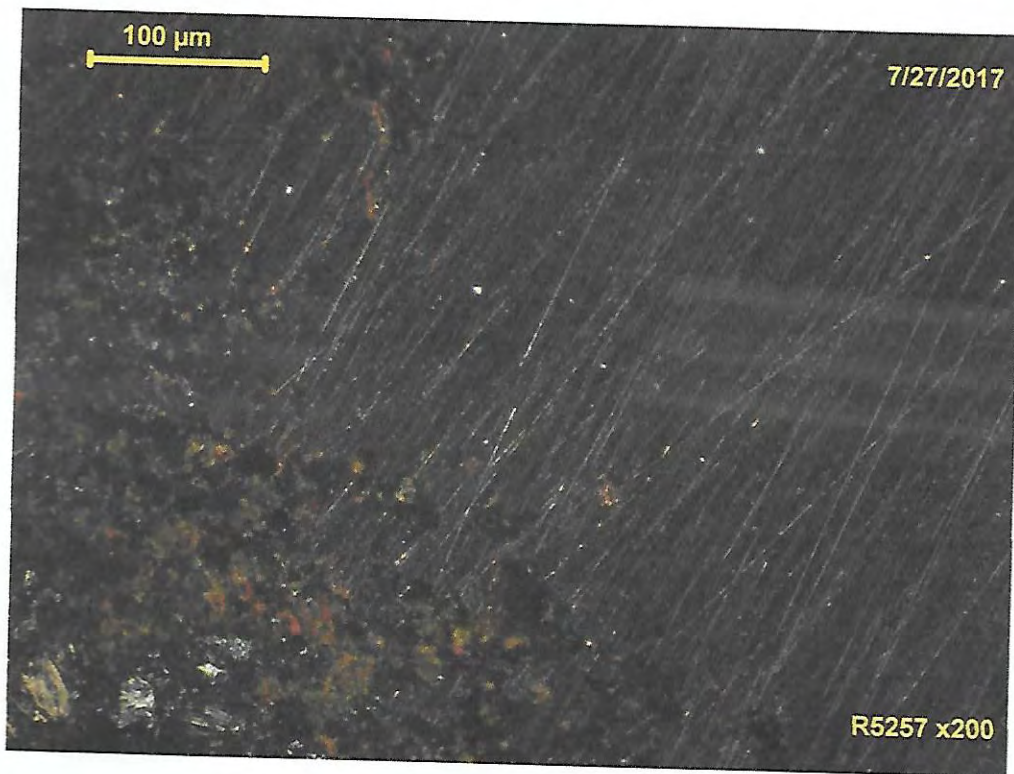


Fig. 14: #R5257, unetched, crossed polars

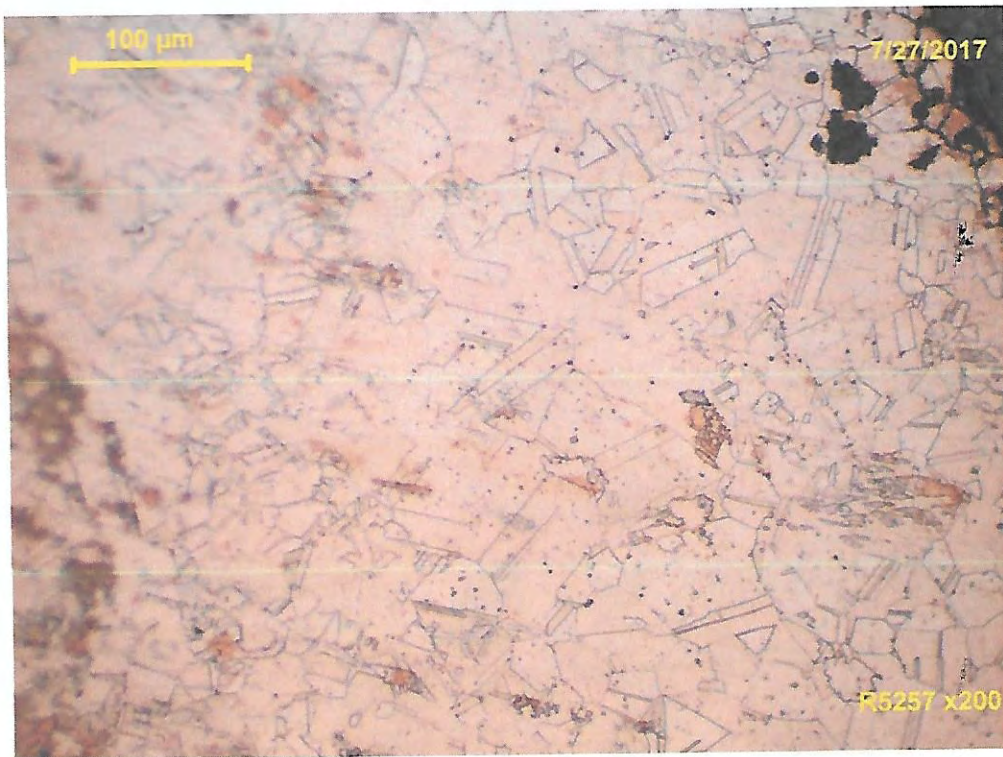


Fig. 15: #R5257, etched

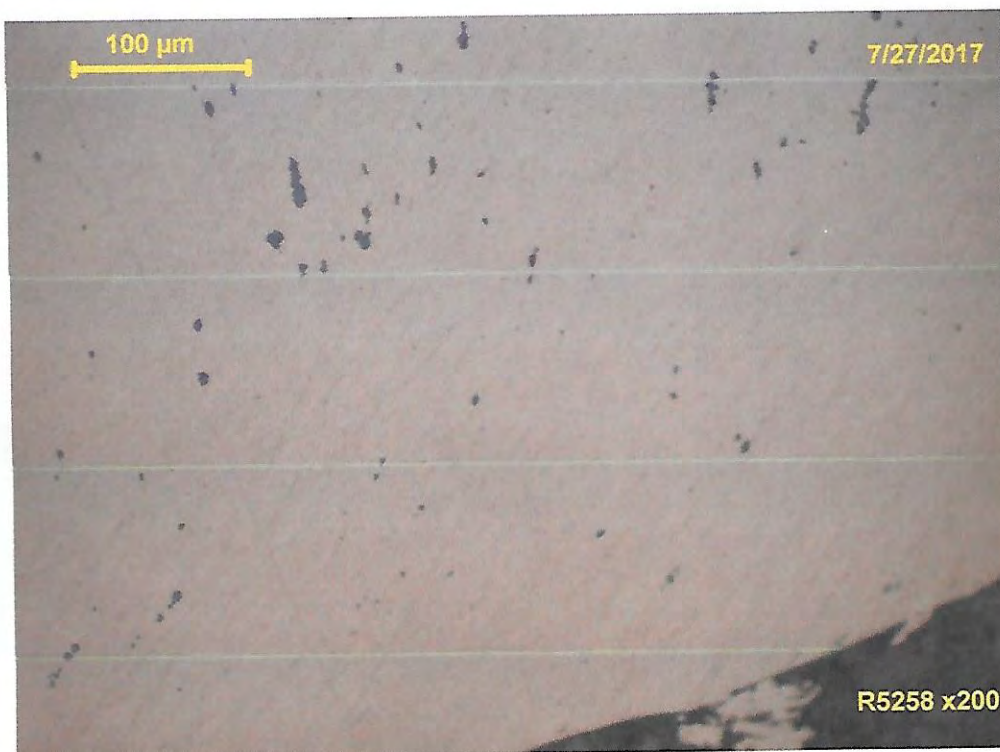


Fig. 17: #R5258, unetched

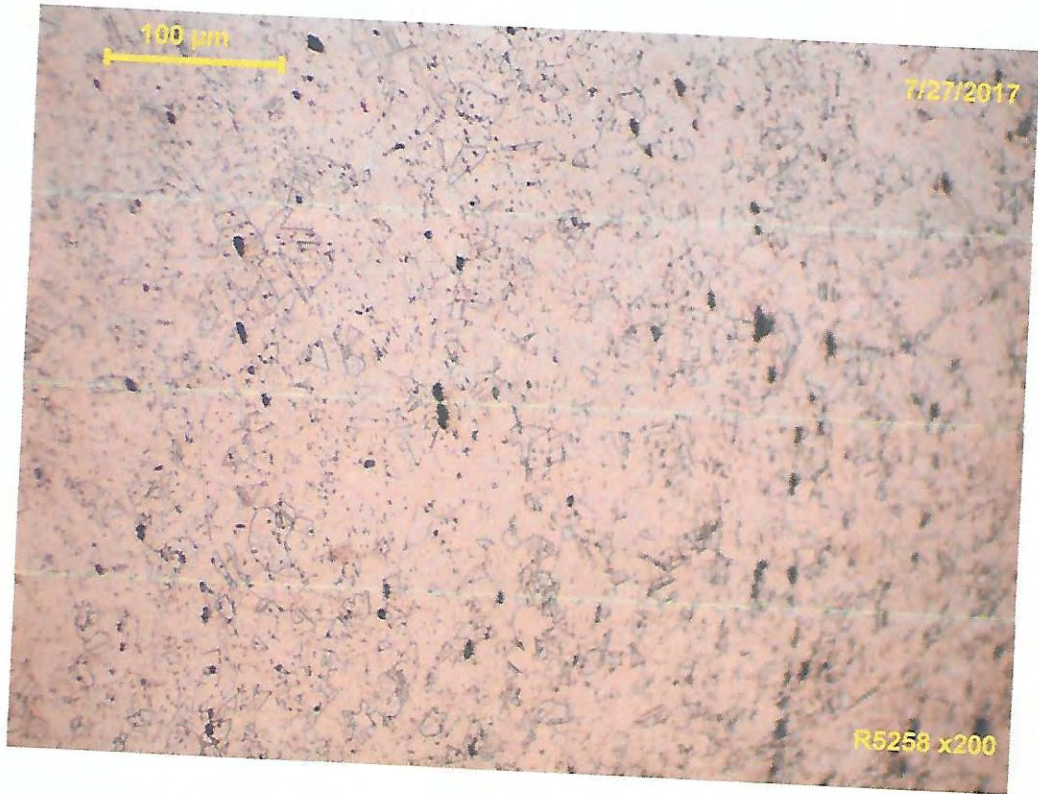


Fig. 17: #R5258, etched

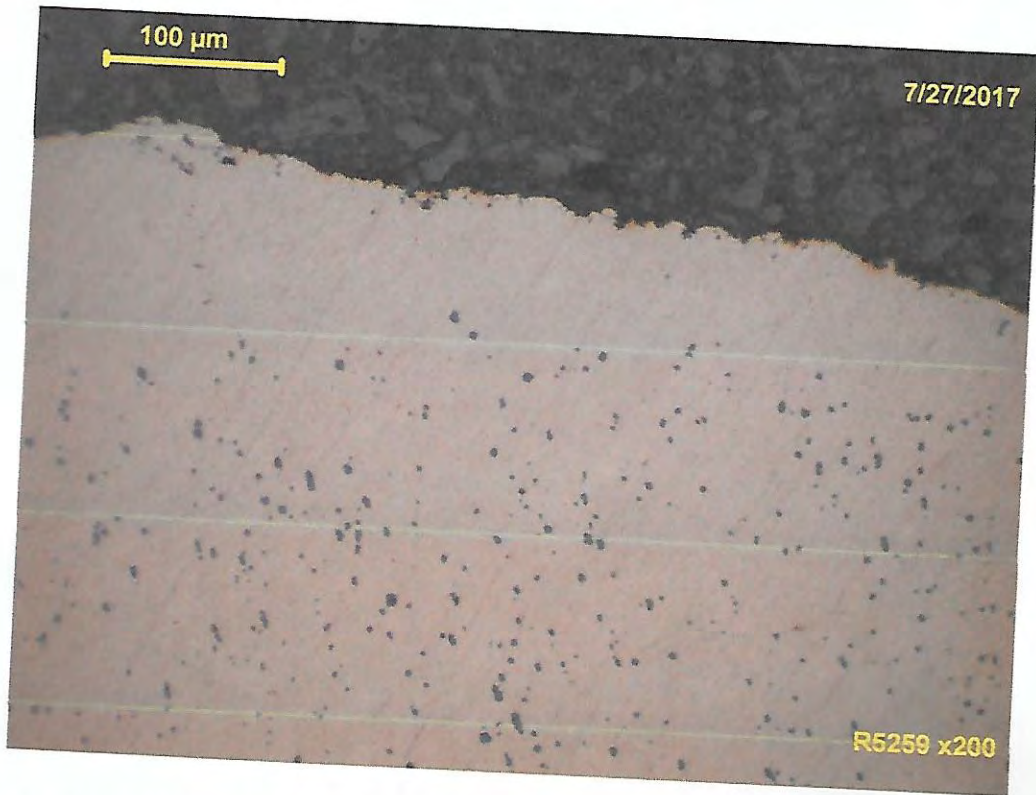


Fig. 18: #R5259, unetched



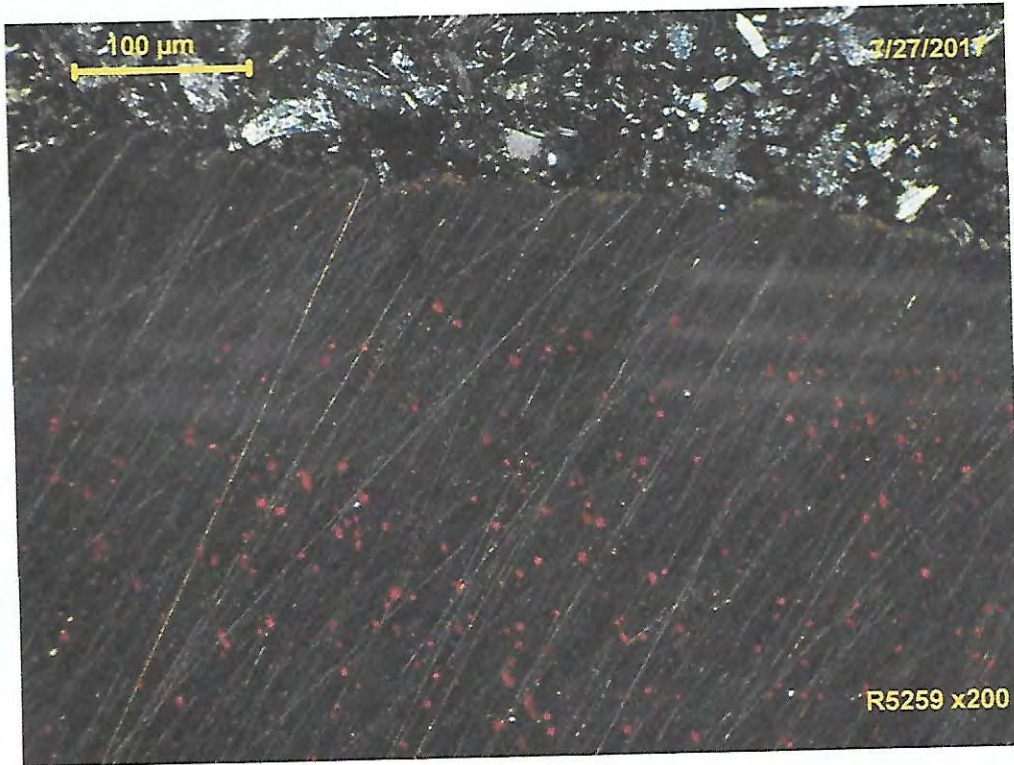


Fig. 19: #R5259, unetched, crossed polars



Fig. 20: #R5259, etched