Analysis of corrosion phenomena on the *Marchinbar* coins

Dr Ian D MacLeod

Western Australian Maritime Museum

Fremantle WA 6160

11th May 2016

Background
A series of historic copper alloy coins had been found on Marchinbar Island, Northern Territory, and had come into the collection of the Powerhouse Museum in Ultimo (now rebadged back to the original Museum of Applied Arts and Sciences) with little known history other than the location in which they were found. Conservation staff requested assistance from the author to help characterise the coins owing to the inherent interest in their nature and origins. The original plan of having the SEM and EDS examination conducted via a Skype call failed so the ability to write critical comment is limited and is based on the report of Dr Daryl Wesley and the electronic images of the SEM screen and the associated analytical data.

Given that there were no treatment records for the coins some precautionary steps were taken to ensure that any adventitious materials were gently removed before the coins were placed in the environmental chamber of the SEM at the Australian National University (ANU) in Canberra. They were rinsed in a bath of absolute ethanol and then dried in an oven at 60°C before being stored in a low humidity case to remove any organic copper corrosion products that may have arisen on the surface from many years in storage cabinets. This preparation was carried out so that it did not remove any of the interesting corrosion products that pertained to the burial or recovery microenvironment. Examination of the coins was undertaken using the JEOL6000 SEM/EDS desktop machine at the Department of Archaeology and Natural History at the ANU. Instrumental problems limited the analysis to one day for the five coins.

The coins
The Dutch coins were a 1690 copper Doit of the Verenigde Oostindische Companie (VOC) Gelderland Mint (N21359-1) and a 1784 Zeeland minted Doit (N21359-3). The early East Africa coins were all Falus coins which came from the Kilwa Sultanate - N21359-5 was from the period of Sulaiman ibn al-Hasan (c. AD 1294-1308) while N21359-7 related to the sultan Ali ibn al-Hasan (c. AD 1480-1482) and the final coin N21359-9 was from the period of the sultan Al Hasan ibn Sulaiman (c. AD 1482-1493). All imagery and EDS results taken for each coin are listed in the tables and on a USB storage device in named folders for each coin which was provided by Dr Wesley.

Doit Coinage
The Marchinbar Island coins did not appear to have very much encrusted or build-up of corrosion materials, as evidenced by the optical images. The 1690 coin (21359-1) surface had suffered severe corrosion with many signs of deep pitting corrosion and a corrosion matrix that was consistent with the dominant decay products being cuprite (Cu_2O), copper (II) hydroxychlorides of the form $Cu_2(OH)_3Cl$, consistent with corrosion in proximity to the marine environment. Consistent with the morphology of the surface deposits there are some halite (NaCl) crystals. Although there was no supportive X-ray diffraction data it is consistent with the EDS spectra that there are also lumps of copper carbonates mixed in with a generally poorly defined crystalline matrix (spot 4 on area 1). A more detailed examination of area 2 (see optical micrograph in file) showed up a generally planar surface with significant amounts of pitting around the grains of the metallographic structure with major intergranular corrosion which has resulted in an essentially fractured surface which is predisposed to attracting dust and thus moisture condensation leading to exacerbation of the underlying corrosion problems. The back-scattered image shows that the general surface is composed of copper and that the intergranular areas (light coloured) are a mixture of CuCl and oxidative and hydrolysis reactions resulting in the $Cu_2(OH)_3Cl$ deposits around the grains.

Conclusion: 1690 Doit
The 1690 coin is a highly corroded and surface modified copper coin which has suffered much from intergranular corrosion which has weakened the surface layers. The presence of halite crystals on the surface attests to the depositional microenvironment being close to the sea. Preventive care of the coin should have it placed in a low relative humidity microenvironment of approximately 30-40 % to minimise future corrosion if the original corrosion products are to be retained for historical purposes and for future research on the mobilisation of trace impurities in the copper through this form of corrosion mechanism.

The more modern, 18th century, Doit (N21359-3) was the 1784 Zeeland minted coin has reasonably fine crystalline structure which is consistent with either annealing after the coin blank was formed or with some hot working after formation before the blanks were cut from the sheet, though this is a less likely scenario. Typical grain sizes were estimated to be in the range of 8-18μm. The light phase is the secondary copper (II) hydroxychloride, $Cu_2(OH)_3Cl$, which was readily seen in comparison with the darker phase of cuprite which was the primary corrosion product. The gouge across the surface is consistent with major physical impact such as the grinding of hard rocks or a metal excavation tool across the surface. There is clear evidence of brushing with a series of random scratches consistent with using a stiff brush to remove archaeological debris. It is apparent that the gouge was historic as detailed examination of the surface shows that deep inside the double "v" of the scratch there are localised pitting points with primary copper (I) chloride and the oxidative hydrolysis products of the typical blue-green copper (II) hydroxyl chloride. The highest magnification used showed up the equiaxed nature of the grains of the copper crystals. In amongst the corrosion matrix and materials entrained with the corrosion products there was some silica which again is consistent with long term exposure to a marine environment.

Conclusion: 1784 Doit

The copper Doit coin is in a significantly deteriorated condition with little to no evidence of any previous conservation intervention as the corrosion matrixes have all the characteristics of an archaeological deposit. As with the case of the 1690 Doit it is recommended that the coin is stored at a relative humidity less than 30-40 % to keep the surface in a stable condition to facilitate more detailed examination of the trace amounts of impurities that have reported to the intergranular corrosion areas.

Kilwa coins: General Observations

The three Kilwa coins all had what appears to be a manufacturing split associated with the leaded bronze alloys. They all had white to greenish-white corrosion deposits in the splits and on areas on the surfaces of the coins. Comments by Dr Wesley attested to the challenges of being able to determine what surface details were definitely associated with the archaeological context in which they were recovered, for there appears to be scant information extant pertaining to the precise chain of evidence from the time of recovery until the time in which they appeared at the Museum of Applied Arts and Sciences in Sydney.

The oldest coin (213549-5) from the period 1294-1308 had titanium, silicon, aluminium, carbon, oxygen and copper in the cracks and on the surface. It is reasonable to assume that the titanium was associated with "beach sands" such as ilmenite $FeTiO_3$. The aluminium and silicon are associated with clay like minerals of aluminium silicates with carbon, oxygen and copper being connected with the aerial oxidation of the primary copper corrosion product of cuprite (Cu_2O) to secondary copper (II) hydroxycarbonates, such as $Cu_2(OH)_2CO_3$. Spot analysis on area 4 gave the primary alloying elements of copper and tin along with moderate amounts of silver and lead, both of which are typically associated with sulphide deposits of copper such as chalcocite Cu_2S and covellite CuS, mixed in with galena PbS and the Ag_2S argentite or acanthite. The presence of these trace metals is typical of old bronze coinage. Area 6 just gave copper and oxygen which is consistent with the major surface corrosion product of cuprite. The first area looked at with x400 magnification showed up the presence of multiple phases, with the aluminium likely to be associated with clay-like minerals. This area is dominated by tin corrosion products with the notable absence of chloride which is consistent with corrosion in a land site rather than being in a marine environment. The second spot analysis showed up phases consistent with hydroxycarbonates of copper which had formed along the intergranular cracks in the metal structure in response to secondary oxidation of the initial cuprite patina, as a result of moisture being trapped in the cracks and bringing with it higher concentrations of dissolved carbon dioxide, hence the formation of copper (II) carbonates. On the alternate side (B) there was evidence of a higher amount of lead associated with the copper corrosion products along with the aforementioned clay-like minerals associated with aluminium and magnesium. It is likely that side B was uppermost in the archaeological context since there is preferential corrosion of the copper rich α-phase in which significant amounts of lead were dissolved or had reported to the corroded grain boundaries. Side A with its much higher concentration of tin corrosion products is typical of a downward facing surface of the coin where there is a lower supply of oxygen so the corrosion mechanism favours selective corrosion of the $\alpha+\delta$ dendritic phase.

Conclusion: Kilwa coin 21359-5

This coin has well defined differences in the corrosion products found on sides A and B which relate to different microenvironments in terms of access to areas of higher or lower dissolved oxygen content in the moist soils containing the coins. It is very likely that specific sampling of the different mineral phases present will provide a unique insight into the burial environment from which the coin came. The copper ores associate with the production of the bronze coin have come from a sulphide deposit rather from an oxidized ore body associated with copper ores in Cyprus and other related locations.

The second Kilwa coin (213549-7) came from the period of 1480-1482 and the presence of phosphorus amongst the detected elements was most unusual and indicates that it was recovered from a terrestrial rather than a marine site where the concentration of phosphates in seawater is very low, certainly too low to have a high enough concentration to precipitate a mineral phase. Under x4000 magnification it is clear that the surface is covered with a complex matrix of corrosion products which included copper, calcium, sulphur, carbon and oxygen. The presence of such a milieu of phases is consistent with some significant changes occurring during the depositional time of the coin in its archaeological context and so sampling of the phases to characterise the minerals that are present, using x-ray diffraction, is an essential step in unravelling the corrosion history of the object. Under the x40 secondary electron image of the coin it is seen that the micromorphology of the corrosion products is a reflection of the underlying structure of the coin. One of the corrosion masses was formed like a mesa which is likely to be a specific mixed copper carbonate phosphate. Like the other 13th century coin, the presence of lead in spot 17 in association with copper and tin is likely a reflection of corrosion of the dendritic phase under low oxygen conditions. The areas of spot analysis numbered 18 and 19 reflected copper, aluminium and oxygen which are indicative of clay like minerals and cuprite as a corrosion product. The morphology of the underside of the coin (B) has pustular growths of copper (I) oxide along with adventitious alumina so it is likely that side B was uppermost in the deposit that entrained the coin. The semi-quantitative SEM-EDS analyses do not readily transform into discrete empirical formulae associated with well-established corrosion products on bronze objects recovered from a terrestrial site.

Conclusion: Kilwa coin 21349-7

The coin has a very complex corrosion matrix and it should also be further investigated by X-ray diffraction as the presence of measureable amounts of phosphorus is very unusual in a bronze coin matrix. Given the solubility of phosphate minerals it is most likely that this coin was also recovered originally from a land site and that the source of the phosphorus may relate to bird guano. The absence of chloride ions strongly supports the supposition that corrosion was dominated by dissolved oxygen with the bronze coin being buried in a soil that contained the normal range of clay minerals (alumino-silicates). The difference in the composition of the surfaces also indicates which zone was uppermost and which was buried deeper in the depositional microenvironment.

The third bronze Kilwa coin was no 213549-7 and it came from the late 15th century. Like the previous coin it was unusual to find phosphorus amongst the corrosion products and so this has the same implications regarding the burial environment but the presence of chloride ions (spot 28) in the one instance does not indicate a marine corrosion environment but rather it could reflect windborne salts being mobilised many kilometres inland by prevailing winds. From the report by Dr Wesley it appears that only one side (A) of the coin was examined but in the wide crack on the coin it was clear that there is an abundant collection of corrosion matrices from which it should be possible to choose samples that are suitable for X-ray diffraction analyses. The deep fissure is filled with corrosion products and the adjacent area has lost some sections of surface decay products but there is sufficient material to enable relevant samples to be taken. Spot analysis no 28 showed up the presence of chloride ions with copper and there is evidence of the secondary growth of $Cu_2(OH)_3Cl$ on top of the primary CuCl complex corrosion mound. There is very little sign of tin corrosion but some lead has been mobilised and so it indicates that the corrosion mechanism has been dominated by the kinetically controlled corrosion of the α-copper rich phase which has protected the inherently more reactive α+δ eutectoid from oxidation. There does not appear to be any entrained clay like minerals in contrast to the previous coinage so the burial environment of the coins can be reasonably assumed to be different.

Conclusion: Kilwa coin 21359-9

The coin examination was limited to one side so it is not possible to determine which side was uppermost in the burial environment. The absence of tin decay products is a clear indication that there was selective attack on the copper-rich α-phase, which is kinetically more readily attacked in a richer oxygenated environment. The absence of entrained clay minerals indicates that the burial environments of the two 15th century bronze coins were different. The presence of measurable amounts of phosphorus indicates that the site may have been very close to some bird guano deposits.

Summary

Additional detailed surface analysis of the coins is essential if the true nature of the burial microenvironments of each coin is to be ascertained. Samples of the corrosion products from both sides of each coin should be taken for X-ray diffraction analysis as this is the only definitive way in which to discern the nature of the burial environments. The corrosion on the two Doits is commonly observed on high quality copper materials exposed to a marine environment and they are inherently at risk for uncontrolled corrosion and decay if stored in poor damp conditions. It is preferable that all the coins in the Marchinbar collection are stored a relative humidity around 30-40 % or placed in Intercept® bags to avoid access to oxygen and moisture.

The Kilwa coins from East Africa have corroded in a manner that is consistent with an archaeological deposit that is not close to the shore line but one that is somewhat inland and near the presence of birds, which are the most likely source of the phosphate minerals found in amongst the corrosion matrices retained in the cracked surface of the leaded tin bronze coins. For the coins no 5 and 7 there was clear evidence from the SEM and EDS analysis as to which side had been uppermost in the archaeological deposit and so additional SEM and XRD analysis is required on surface B of the number 9 coin to ensure that the corrosion processes can be appropriately determined. Because cast bronzes are very sensitive to the amount of dissolved oxygen present in the moist microenvironment in which they are buried the corrosion products can vary quite significantly from one side of the coin to the other. The upper most surfaces have kinetically controlled oxidation of the α-phase (Cu-rich) while the lower surfaces have thermodynamically controlled corrosion of the (α+δ) eutectoid phase which gives a much higher proportion of tin corrosion products. The α-phase corrosion products are dominated by copper minerals with some lead minerals which result from inter-dendritic corrosion or simultaneous release from lead microdroplets dispersed through the α-phase.

Care should be taken with the interpretation placed on the SEM semi-quantitative analyses as they are only a guide to the amount of each element present and do not reflect the mineral phases nor their overall distribution across the complex and often convoluted surfaces of the coins. In the absence of destructive methods such as mounting the sectioned coins and conducting detailed metallurgical examination the only way forward to assist with the interpretation of the corrosion processes associated with the decay of the five coins is for a detailed XRD mapping of the matrixes on the upward and downward sides of each coin.

Appendix I: Report by Dr Wesley of the Australian National University in Canberra.
Analyses of the five coins found on Marchinbar Island from the MAAS collection, Ultimo NSW.

1. N21359-1 Coin, Netherlands, Dutch East India Co., Doit, copper alloy, Gelderland Mint, 1690

Table 1 List of SEM Images and EDS Sheets for N21359-1 Doit 1690

#	Image/File Name	Analysis (SEM or EDS)	Mag (x)	Notes
1	Coin 1 Side A Area 2 240X	SEM	240	Flat surface of copper with white corrosion crystallisation in crevices
2	Coin 1 Side A Area 1 4K	SEM	4400	Poor quality image. Shows white crystalline structures within eroded copper surfaces
3	Coin 1 Side A Area 1 22x	SEM	22	A general area showing a depression occurring from significant loss of the metal from corrosion. Created a 'crater' shaped area. White corrosion material adhering in the cracks around the depression. At the top of the image there is an area 1mm in length of the original smooth surface of the coin.
4	Coin 1 Side A Area 2 4K Doit	SEM	4000x	A high magnification image of the white crystallised grain shaped material (rounded to sub-rounded and angular) occurring in the cracks and crevices of the coin. Most of these grains less than 2 µm.
5	Coin 1 Side A Area 2 22x	SEM	22	Showing the differential corrosion on the surface of the coin. Areas to the left showing original surface with majority of area in this image corroded to some depth.
6	Coin 1 Side A Area 2 10K	SEM	10000	Attempt to capture a very high magnification image of the eroded coin surface. Showing some of the white material adhering to the copper. Was interesting that the corroded copper surfaces appear concave and very smooth.
7	Side A (1)	SEM	4000	Poor image on day machine not working properly.
8	Side A (2)	SEM	4000	Attempt to get a clear image when sorting out machine. Has shown quite nicely the way the corrosion has shaped the surface of the copper metal. Evidence of the corrosive material still present. Shows concavity effect on the copper.
9	Side A Area 2 Spot 1 BSA	EDS	240	Spot (007) analysis of an area of the original coin surface. Mass: Cu 100%.
10	Side A Area 2 Spot 2	EDS	240	Spot (006) analysis of an area of the original coin surface. Mass: Cu 100%.
11	Side A Area 1 Area Analysis	EDS	4000	An attempt to see what an EDS area analysis would tell us by analysing the entire area in the frame. Returned Mass: Cu 100% with the trace elements in the graph. Not particularly informative
12	Side A Area 1 Spot 1	EDS	4000	The 'crater' feature shown in #1. Mass: Elements C (Carbon) 11.53%; O (oxygen – oxides?) 32.37%; Cu (Copper) 56.1%.
13	Side A Area 1 Spot 2	EDS	4000	The 'crater' feature shown in #1. Mass: Elements Cu (Copper) 100%. Trace elements in the graph.
14	Side A Area 1 Spot 3	EDS	4000	The 'crater' feature shown in #1. Mass: Elements O (oxygen – oxides?) 32.83%; Fe (iron) 22.06%; Cu (Copper) 45.11%.
15	Side A Area 1 Spot 4	EDS	4000	The 'crater' feature shown in #1. Mass: Elements C (Carbon) 11.33%; Cu (Copper) 88.67%.

3. N21359-3 Coin, Netherlands, Dutch East India Co., Doit, copper alloy, Zeeland Mint, 1784

There is a green-white coloured corrosion material on approximately <5% of the coins surface.

Table 2 List of SEM Images and EDS Sheets for N21359-3 Doit 1784

#	Image/File Name	Analysis (SEM or EDS)	Mag (x)	Notes
1	Coin 3 Side A Gouge 20X	SEM	20	A 'gouge' like feature on the surface of the coin approximately 6mm in length by 0.25mm in width. Scratches can be seen in the top left corner of the image. These scratches are found across the whole surface of the coin and generally consist as these 2 to 3 parallel scratch marks averaging 1 to 2mm in length. The gouge appears at first to not have any of the white corrosion prominent on the coin surface top left half of image. However several white areas can be seen.
2	Coin 3 Side A Gouge 40X	SEM	40	At this magnification the gouge has a distinct raised line parallel running along the gouge giving a 'vv' shape. Either side of the gouge is a narrow flattened surface.
3	Coin 3 Side A Gouge 110x	SEM	110	Higher magnification to look at nature of gouge and its base. Noted white corrosion material in the base of the gouge. Surfaces either side of gouge very corroded.

#	Image/File Name	Analysis (SEM or EDS)	Mag (x)	Notes
4	Coin 3 Side A Gouge 400X	SEM	400	Higher magnification of gouge bottom. Shows well defined parallel scratches on the top side of the gouge. Interesting that the scratches on the bottom right surface are multi-directional. White corrosion material in the base of the gouge showing the corroding loss of metal around the white material.
5	Coin 3 Side A Gouge 500X	SEM	500	Higher magnification of gouge bottom to show white corrosion material in the base of the gouge showing the corroding loss of metal around the white material. The metal folding may indicate the direction of the force that created the gouge went from bottom left to top right
6	Coin 3 Side A Area 1 220x	SEM	220	Illustrating typical distribution of the patterning of the corrosion materials within the cracks and depressions of the coin surface.
7	Coin 3 Side A Area 1 22x	SEM	22	Image to illustrate typical scratches and wear found on this coin.
8	Side A Gouge Spot 1	EDS	500	Quantitative analysis of Spot 1 (top area of corrosion material) Mass: O (oxygen) 14.28%; Si (Silicon) 24.16%; Cl (Chlorine) 4.85%; Cu (copper) 56.71%.
9	Coin 3 Side A Gouge Spot 2	EDS	500	Unable to get EDS to capture date on the bottom area of corrosion material as seen in Analysis 8
10	Coin 3 Side A Gouge Spot 3	EDS	400	Moved to lower section of gouge to analyse another corrosion material area on the bottom. Mass returned result of Cu (Copper) 100%.
11	Coin 3 Side A Area 1 Spot 1	EDS	4000	Analysis of the base of corroded area where there was metal loss. Cu 100%.
12	Coin 3 Side A Area 1 Spot 2	EDS	4000	Corrosion material next to Spot 1. Chlorine (7.7%) and Copper 92.3%.
13	Coin 3 Side A Area 1 Spot 3	EDS	4000	Corrosion material that appears as an angular structure. Mass: Oxygen 16.24%; Chlorine 17.47%; Copper 66.29%.
14	Coin 3 Side A Area 1 Spot 4	EDS	4000	Corrosion material that appears as an angular to sub rounded structure. Mass: Oxygen 29.17%; Chlorine 16.02%; Copper 54.81%.
15	Coin 3 Side A Area 1 Spot 5	EDS	220	Examined an area filled with corrosion material amongst corroded surfaces. Mass: Oxygen 26.06%; Chlorine 15.57%; Copper 58.37%.
16	Coin 3 Side A Area 1 Spot 6	EDS	220	Examined non corroded area of coins surface. Mass: Copper 100%.

<u>5. N21359-5 Coin, Kilwa Sultanate (East Africa), Falus, copper alloy, Sulaiman ibn al-Hasan (c. AD 1294-1308)</u>

Side A analysis concentrated on the top of crack area at 4K magnification and the material in crack. A total of 4 EDS analysis points were made in the crack area on and off the ‘white’ accumulation and on the surface of coin. Side B Area 1 to right of split area of green and white substance on edge of coin. Sample 3 spots in this area. Could not get SEM to focus @ 4K.

Table 2 List of SEM Images and EDS Sheets for N21359-5 Kilwa AD1294-1308

#	**Image/File Name**	**Analysis (SEM or EDS)**	**Mag (x)**	**Notes**
1	Coin 5 Side A Area 1 Analysis 40X	SEM	40	A general image of the ‘manufacturing split’ typical of Kilwa coins noted by numismatic specialists. This area was a focal area for investigation. Illustrates the amount of corrosion deposits in the split and on left side of image.
2	Coin 5 Side A Area 1 Analysis 2 400X	SEM	400	Magnification of the split. SEM machine developed vibration during this time we could not fix. The image does illustrate depth of the split on the left hand side of the image.
3	Coin 5 Side A Area 1 Crack	SEM	4000	A crack at the bottom end of the split
4	Coin 5 Side A Area 1 Crack	SEM	20	Illustrating the deposition of corrosion materials and the retreating eroding edge of the coin
5	Coin 5 Side B Area 1 4K Poor image	SEM	4000	Attempt at gaining image at high magnification of the corrosion material on the edge of the coin illustrated in image 4. Corrosion material appears angular to sub-angular deposits

#	Image/File Name	Analysis (SEM or EDS)	Mag (x)	Notes
6	Coin 5 Side A Area 1 Analysis 1 Spot 1	EDS	400	Spot on the corroded mass. Mass: Carbon 1.91%; Oxygen 45.88%; Aluminium 4.41%; Silicon 4.35%; Titanium 4.57%; Copper 34.65%; Tin 7.24%.
7	Coin 5 Side A Area 1 Analysis 1 Spot 2	EDS	400	Spot analysis to the side of the corroded mass but on an area of significant weathering/corrosion in the split. Mass: Carbon 0.54%; Oxygen 31.63%; Phosphorous 0.92%; Sulphur 0.56%; Chlorine 0.53%; Copper 33.39; Silver 12.68%; Tin 7.35%; Lead 12.40%
8	Coin 5 Side A Area 1 Analysis 1 Spot 2	EDS	4000	Selected a spot in the depth of the split. Returned mass Oxygen 30.18%; Copper 69.82%
9	Coin 5 Side A Area 1 Analysis 2 Spot 1	EDS	4000	High magnification in the split area of an area that appears to be corrosion mass. Mass: Carbon 1.05%; Oxygen 19.8%; Aluminium 0.74%; Sulphur 0.82%; Chlorine 2.06%; Copper 69.83%; Tin 3.42%
10	Coin 5 Side A Area 1 Analysis 2 Spot 2	EDS	4000	Spot analysis to the side of the metal but on an area of significant weathering/corrosion in the split. Mass: Carbon 0.68%; Oxygen 8.74%; Chlorine 0.64%; Copper 88036%; Tin 1.57%
11	Coin 5 Side B Area 1 Spot 1	EDS	4000	Spot analysis on corrosion near the edge of the coin as shown in Images # 4 and 5 of Side B. Mass: Carbon 0.29%; Oxygen 31.93%; Aluminium 8.87%; Phosphorous 8.20%; Chlorine 0.45%; Potassium 0.55%; Calcium 0.32%; Copper 40.78%; Lead 9.61%
12	Coin 5 Side B Area 1 Spot 2	EDS	4000	Spot analysis on corroded area near the edge of the coin as shown in Images # 4 and 5 of Side B. Mass: Oxygen 12.96%; Magnesium 2.11%; Aluminium 26.72%; Phosphorous 1.16%; Copper 40.74%; Lead 16.30%
13	Coin 5 Side B Area 1 Spot 3	EDS	4000	Selected 3rd spot to replicate results on corroded area near the edge of the coin as shown in Images # 4 and 5 of Side B. Mass: Carbon 0.28%; Oxygen 6.48%; Magnesium 1.99%; Aluminium 22.05%; Phosphorous 0.41%; Copper 62.73%; Lead 6.07%

Side A

N21359-5
07/12/2015

Side B

N21359-5
07/12/2015

7. N21359-7 Coin, Kilwa Sultanate (East Africa), Falus, copper alloy, 'Ali ibn al-Hasan (c. AD 1480-1482)

Table List of SEM Images and EDS Sheets for N21359-7 Kilwa AD 1480-1482

#	**Image/File Name**	**Analysis (SEM or EDS)**	**Mag (x)**	**Notes**
1	Coin 7 Side A Area 1 Split 75mag	SEM	75	Manufacturing split on this Kilwa coin with significant corrosion material accumulation in the split. Either side of the split illustrates the nature of the corrosion loss effect on the surface of the coin.
2	Coin 7 Side A Area 1 4K	SEM	4000	Image to illustrate the nature of the corrosion mass in the split, very angular crystallisation.
3	Coin 7 Side A Area 2 40mag	SEM	40	Area illustrating corrosion material accumulation around the raised script on the lower part of the coin away from the split.
4	Coin 7 Side A Area 2 4K	SEM	4000	Poor image – too much vibration
5	Coin 7 Side B Area 1 4K	SEM	4000	Poor image – attempt to obtain image on other side of corrosion in the manufacturing split.
6	Coin 7 Side A Area 1 Split Spot 1	EDS	4000	Investigating the manufacturing split area of the coin where there is build-up of corrosion material. Mass: Carbon 1.01%; Oxygen 40.32%; Aluminium 4.26%; Silicon 1.95%; Phosphorous 13.8%; Sulphur 1.19%; Chlorine 2.07%; Calcium 3.07%; Copper 32.23%
7	Coin 7 Side A Area 1 Spot 2	EDS	4000	Investigating the manufacturing split area of the coin where there is build-up of corrosion material. Mass: Carbon 1.18%; Oxygen 58.67%; Aluminium 8.89%; Silicon 12.65%; Phosphorous 12.65%; Chlorine 0.74%; Potassium 0.65%; Calcium 1.38%; Copper 9.38%
8	Coin 7 Side A Area 1 Spot 3	EDS	4000	Area in the split. Mass: Oxygen 14.50%; Aluminium 8.89%; Silicon 12.65%; Potassium 5.23%; Calcium 2.06%; Copper 78.12%
9	Coin 7 Side A Area 2 Spot 1	EDS	4000	Area away from the split between the raised writing. Mass Carbon 0.99%; Oxygen 63.41%; Phosphorus 3.65%; Copper 31.95%
10	Coin 7 Side A Area 2 Spot 2	EDS	4000	Area away from the split between the raised writing. Mass: Carbon 1.12%; Oxygen 48.98%; Aluminium 0.93%; Silicon 0.6%; Phosphorous 9.95%; Chlorine 0.97%; Calcium 0.76%; Copper 36.69%
11	Coin 7 Side A Area 2 Spot 3 4K	EDS	4000	Off the obvious corrosion build-up material. Mass: Carbon 1.41%; Oxygen 47.02%; Phosphorous 11.10%; Chlorine 0.93%; Calcium 0.76%; Copper 38.78%
12	Coin 7 Side A Area 3 Surface Spot 1	EDS	4000	Area off the corrosion next to Area 2. Mass: Carbon 0.56%; Oxygen 13.02%; Aluminium 0.76%; Sulphur 0.52; Chlorine 4.85%; Copper 67.88%; Lead 12.42%
13	Coin 7 Side B Area 1 Spot 1 Split	EDS	4000	Area in the Side B Split. (Image poor – vibrations) Mass Oxygen 40.42%; Aluminium 23.54%; Copper 36.04%
14	Coin 7 Side B Area 1 Spot 2 Split	EDS	4000	Area in the Side B Split. (Image poor – vibrations) Mass Oxygen 37.58%; Aluminium 25.4%; Copper 37.03%

<u>9. N21359-9 Coin, Kilwa Sultanate (East Africa), Falus, copper alloy, Al Hasan ibn Sulaiman (c. AD 1482-1493).</u>

Appeared to be the most damaged of the Kilwa coins.

Table List of SEM Images and EDS Sheets for N21359-9 Kilwa AD1482-1493

#	Image/File Name	Analysis (SEM or EDS)	Mag (x)	Notes
1	Coin 9 Side A Area 1 Split 100x	SEM	100	Image of the corroded material in the manufacturing split. Also illustrating the nature of the corrosion on the surface of the coin either side of the split.
2	Coin 9 Side A Area 1 Split 4K	SEM	4000	Image at high magnification of the nature of the corrosion material in the manufacturing split. Machine vibration poor image however still able to see angular to sub-rounded nature of the corrosion mass.
3	Coin 9 Side A Area 2 40x	SEM	40	Nature of the steeply eroded edge of the coin
4	Coin 9 Side A Area 3 4K	SEM	4000	Attempt to capture the nature of the surface of the coin towards the centre. Vibrations in machine poor image.
5	Coin 9 Side A Area 1 Split Spot 1	EDS	4000	Investigating the split. Inspecting particular particle. Mass Aluminium 100% - machine not working properly at this point. Reset moved to Area 2
6	Coin 9 Side A Area 2 Spot 1	EDS	4000	Investigated corroded edge of the coin. Very angular topography. Mass: Carbon 0.51%; Oxygen 57.78%; Phosphorous 9.95%; Copper 32.49%; Lead 7.71%
7	Coin 9 Side A Area 2 Spot 2	EDS	4000	Investigated corroded edge of the coin. Spot taken just to the right off the angular feature of Spot 1. Mass: Oxygen 36.65%; Aluminium 1.34%; Silicon 1.17%; Phosphorous 16.69%; Calcium 1.12%; Copper 25.93%; Lead 17.68%
8	Coin 9 Side A Area 3 Spot 1	EDS	4000	Attempt to investigate a crack in the coin. Mass: Oxygen 3.38%; Copper 96.62%
9	Coin 9 Side A Area 3 Spot 2	EDS	4000	Attempt to investigate a crack in the coin. Shifted spot sample to the left on corrosion material. Carbon 0.77%; Oxygen 8.90%; Chlorine 0.9%; Copper 86.95%; Tin 2.48%.

Side A

N21359-9
07/12/2015