Smithsonian
Museum Conservation Institute

TECHNICAL STUDY REPORT
MCI 6043

Harriet F. (Rae) Beaubien

OBJECTS
Small samples (41) from 32 metal objects, excavated by Smithsonian Tropical Research Institute (STRI) archaeological staff – 31 from Cerro Juan Díaz and 1 from Abrigo Aclosa, in Panamá
Cerro Juan Díaz: M-2, 3, 4, 5, 6, 7, 9, 11, 13, 14, 15, 24, 27, 28-1, 28-2, 28-5, 35-1, 35-2, 35-3, 35-7, 42, 43, 54, 56, 59, 67, 68, 72, 73, 206, and CL-3-45 [MIT 5136]
Abrigo Aclosa: AA-01

CULTURAL AREA
Pre-Columbian, possibly Panamanian manufacture

MATERIALS/TECHNIQUES OF MANUFACTURE
Gold alloys, copper alloys and iron pyrite (iron sulfide)

REQUESTOR:
Smithsonian Tropical Research Institute (STRI), Panama City, Panamá
- Dr. Richard G. Cooke, STRI Archaeologist
  W tel: (507) 212-8747; cooker@si.edu

REQUEST
Information about alloy composition, as part of preliminary research on the origins and development of gold-working in Panamá

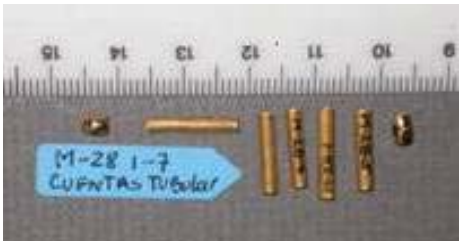
MCI STAFF/COLLABORATORS
- Harriet F. (Rae) Beaubien, Senior Conservator – project coordinator
- Roland H. Cunningham, Senior Conservator/Analyst – scanning electron microscopy (SEM), with energy dispersive X-ray analysis (EDS), for imaging and elemental information (semi-quantitative)
- R. Jeff Speakman, Head of Technical Studies; formerly MURR Scientist – laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), for elemental information (quantitative), at the University of Missouri-Columbia Reactor Research Center (MURR)
- Melvin J. Wachowiak, Senior Conservator – photomicrography
- Karla Muñoz Alcocer, Conservation contractor; formerly MCI Program Specialist – principal contact, sampling, photographs
- Aaron N. Shugar, MCI Research Associate – X-ray fluorescence spectroscopy (portable XRF), for elemental information (semi-quantitative)

REQUEST date/approval: 29 March 2006 / 24 April 2006
REPORT date: 5 October 2006 (revised 8 May 2007)

SUMMARY

Although numerous pre-Columbian gold artifacts have been found in Panama, most were long assumed to have been produced in Colombia and Ecuador, neighboring regions with ample archaeological evidence of metallurgy, including mining sites, manufacturing tools and finished products. However, iconographic studies, ethnohistoric records and, more recently, archaeological evidence of metallurgical activity suggest that Panama had developed its own gold-working tradition in pre-Columbian times.

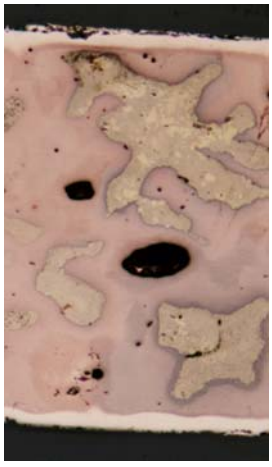
Reconstructing the origins and development of Panamanian gold-working requires a nuanced understanding of key technical aspects of the objects themselves, one of the most important of which is alloy composition. This study focused on a group of 39 metal artifacts, 38 of which were excavated at the site of Cerro Juan Díaz, an important village and funerary precinct in the Azuero Peninsula. The study group included 18 gold and gilded artifacts – one of the largest number found at a single site in Panama.



Tiny samples from 17 of the sampled metal objects were analyzed using scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDS) to identify major and minor elements present. The EDS data were useful in guiding a second round of analyses using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), carried out on 25 of the sampled metal objects. Quantitative information was collected on selected elements – gold, silver, copper, iron, manganese, nickel, zinc and osmium (the latter included as it has been found in gold of Ecuadoran and southern Colombian manufacture). Of these, only gold, silver, copper and iron were found.

The very good correlation between the findings from EDS and ICP techniques allowed the gold alloys to be provisionally sorted into the following general categories.

- *Gold (very high) with silver and copper* – 4 gold sheet fragments, 5 tubular beads and 1 ring. The sheet fragments were similar in composition, with silver>copper.
- *Gold and copper (both mid-range), varying silver* – 4 tubular beads, 1 ring, 1 half-disk and 1 flat figurine fragment.
- *Copper (very high) with gilding* – 2 copper alloy figurines (cast), with surface gilding traces.



Analyses of one additional sample highlighted the importance of selecting appropriate locations for sampling (e.g. from technologically informative and not overly corroded areas), and of examining not just surface composition but also the bulk composition – especially if lamination or surface depletion techniques are used, both well known from previous studies of pre-Columbian metal-working. X-ray fluorescence analysis (XRF) of the sample's outer surface indicated a copper-gold alloy, but a more complex picture emerged when the sample was mounted as a polished cross-section and analyzed by SEM-EDS. Gold-rich phases were detected in the "islands," surrounded by a copper-rich phase. Surface zones at the top and bottom of the sample displayed a different composition, with what appeared to be an extremely thin gold outermost layer.

Further technical investigation of gold artifacts from Panama is warranted. This should include detailed visual examination, non-invasive surface testing (such as with XRF analysis), and a thoughtful sampling strategy for a more in-depth analytical study.

OVERVIEW OF MCI ANALYSES

► In May 2006 at STRI, 38 objects excavated from the Panamanian sites of Cerro Juan Díaz (37) and Abrigo Aclosa (1) were examined, photographed and sampled by K. Muñoz Alcocer (May 2006). Of these, 31 objects were selected for sampling and either one or two tiny pieces were removed on May 16, for a total of 40 samples. Most were pieces taken from edges (at breaks where possible), some were powder (corrosion) samples, and some were taken from interior material, possibly not the metal itself. These samples were brought to MCI in May 2006. Another gold sample (CL-3-45), previously removed from another object excavated at CJD, was brought to MCI by Muñoz in June 2006. The comprehensive list of the objects, including thumb-nail photographs, is provided in *Appendix A*; data from all analytical procedures are also summarized (compiled by Muñoz and Beaubien).

► At MCI, SEM-EDS (scanning electron microscopy, coupled with energy-dispersive X-ray spectroscopy) was carried out by R. Cunningham (May-June 2006); 19 samples (27 spots) were analyzed from 17 objects. The chart in *Appendix A* includes the general quantitative ranking of elements, provided by Cunningham. His summary is included as *Appendix B***.**

► At MURR, LA-ICP-MS (laser ablation inducively coupled plasma spectroscopy-mass spectrometry) was carried out by R.J. Speakman (July 2006); 29 samples were analyzed from 25 objects. The chart in *Appendix A* includes data provided by Speakman. His full report is included in *Appendix C*: Robert J. Speakman, Laser Ablation ICP-MS Analysis of Cu and Au Alloys from Cerro Juan Díaz, Panama (report dated July 14, 2006).

► At MCI, XRF (X-ray fluorescence spectroscopy) was carried out by A. Shugar on both sides of the CL-3-45 sample (13 July 2006); three readings were taken on one side and two on the other. His data are included in *Appendix D*.

► At MCI, SEM-EDS was carried out by R. Cunningham (August 2006**)** on the CL-3-45 sample. A portion was mounted in cross-section; the matrix, bright phase "islands" and selected inclusions were analyzed by EDS and imaged in secondary and backscatter modes. Additional data were collected using two other SEM-EDS systems for comparison. Key components of the full report are included in *Appendix E*.

► At MCI, photomicrographs were taken of the CL-3-45 sample by M. Wachowiak, after it had been embedded and polished. These are included in *Appendix F*, along with Shugar's observations, notating several of the images of the mounted sample after etching.

PRELIMINARY OBSERVATIONS

Gold and gilded objects

EDS and XRF	1	**CJD** CL-3-45
ICP only	4	**CJD M** 27, 35(-3,-7), 206
Both EDS and ICP	13	**CJD M** 4, 5, 7, 11, 13, 14, 28(-1,-2), 35(-1, 2), 54, 67, **AA**-01
Sampled and not analyzed / probably gold	2	**CJD M** 6, 28(-5)
Not sampled / probably gold	7	**CJD M** 28 (-3, -4, -6, -7), 38 (-4,-5,-6)

The very good correlation between the findings from EDS and ICP techniques allowed the

gold/gilded samples to be further sorted into the following provisional categories, listed with source object type.

- *Gold (very high % by ICP), with silver and copper*
  4 gold sheet fragments [**CJD M** 4, 7, 13, 14], 5 tubular beads [**CJD M** 5, 11, 35(-3, -7), 67] and 1 ring [**CJD M** 27]. All 4 sheet fragments showed similar alloy compositions, with more silver compared to copper, suggesting the possibility of an alloy preference for production of this kind of item.
- *Gold and copper (both mid-range % by ICP), with varying amounts of silver*
  4 tubular beads [**CJD M** 28(-1, -2), 35(-1,-2)], 1 ring [**CJD M** 206], 1 half-disk [**AA**-01], and 1 flat figurine fragment [**CJD** CL-3-45], the latter on the basis of XRF only.
- *Copper (very high % by ICP) with gilding*
  2 copper alloy figurines with surface gilding traces [**CJD M** 54, 73], both formed by casting. No elements were detected by EDS that might have shed light on the gilding methods (such as mercury, for "fire gilding").

Several examples highlighted the importance of distinguishing surface composition and bulk composition. This is particularly the case when lamination, depletion gilding and other intentional surface alteration methods are among the technological possibilities; these are all well known from previous studies of pre-Columbian metal-working. Surface and bulk compositional differences might be readily apparent in the case of gilded copper alloy objects (as in the two examples in this study), but unfortunately no elements were detected by EDS that might have shed light on the particular gilding methods used (such as mercury, for fire gilding).

In the case of the CL-3-45 sample, X-ray fluorescence analysis (XRF) of its outer surfaces indicated a copper-gold-silver alloy, but a more complex picture emerged when the sample was mounted in cross-section (embedded, polished, and later etched), and analyzed by SEM-EDS. Gold-rich phases were detected in the "islands," surrounded by a copper-rich phase. Surface zones at the top and bottom of the sample, with what appeared to be an extremely thin gold outermost layer, were also visible. Although not analysed by EDS, the thin gold-rich layers on the outermost surfaces along with the zone of voids immediately below were interpreted by Shugar to be evidence of a traditional depletion gilding technique, in which a *tumbaga* alloy (gold-copper-silver) is acid-treated to dissolve away all but the gold components at the surface.

Further technical investigation of gold artifacts from Panama is clearly warranted. This should include detailed visual examination, non-invasive surface testing (such as with XRF analysis), and a thoughtful sampling strategy for a more in-depth analytical study. In addition to technological information, analysis of samples may provide information about provenience. In the current study, 8 elements were measured during ICP analyses – gold, silver, copper, iron, manganese, nickel, zinc and osmium. Osmium was included as an element of interest because it has been found in gold of Ecuadoran and southern Colombian manufacture, according to R. Cooke. While only gold, silver, copper and iron were found in this case, particular suites of elements may enable source distinctions to be made.

Copper alloy objects (excluding the 2 listed in the section above)

EDS only	0	
ICP only	3	**CJD M** 15, 42, 56
Both EDS and ICP	3	**CJD M** 9, 24, 68
Sampled and not analyzed / probably gold	3	**CJD M** 43, 59, 72
Not sampled / probably gold	0	

Four of the objects in this group are chisels or other tools [**CJD M** 24, 42, 56, 68], and two are

rings [**CJD M** 9, 15]. One item in each group produced inconsistent results; both were determined by appearance and by EDS to be copper, but analyzed by ICP as iron (chisel) or gold (ring). These conflicting results may have been a result of sampling.

Iron-rich objects

EDS only	1	**CJD M** 3
ICP only	1	**CJD M** 2
Both EDS and ICP	0	
Sampled and not analyzed / probably gold	0	
Not sampled / probably gold	0	

Both of these objects were beads, described as being made of the mineral pyrite (iron sulfide).

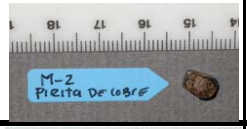
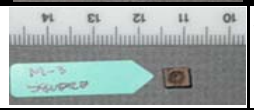
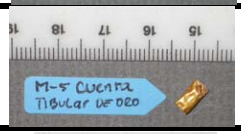
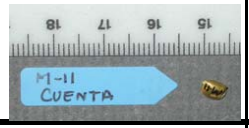
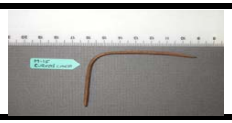
Reports and all supporting data are also archived at the Museum Conservation Institute, in Suitland, MD, under MCI 6043.

Proper credit must be given to MCI and to the scientist(s)/conservator(s) involved when referring to this work.

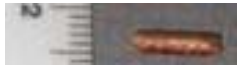
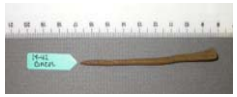
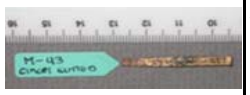
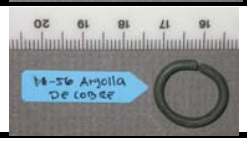
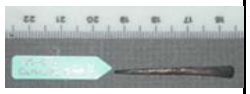
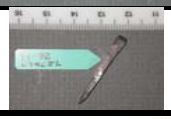
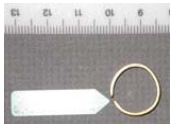
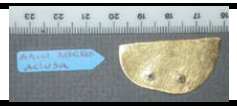
Inventory of Metal Objects from Panama

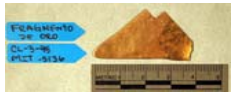
Karla Muñoz Alcocer and Harriet F. Beaubien

Panamá Gold Project

STRI Cat.No.	PROVENIENCE	OBJECT LABEL [Description] Condition Notes	MCI 6043 (May 2006) PHOTOS	MCI 6043 (May 2006) SAMPLES	MCI 6043 (July 2006) LA-ICP-MS %Au-Ag-Cu-Fe	MCI 6043 (May-June, Aug 2006) SEM-EDS
M-2	Cerro Juan Díaz	Pirita de cobre [Bead/pyrite (copper)] reddish (Cu alloy?)		**S01** small piece and powder from edge	0.0--0.0--0.0--**100.0**	
M-3	Cerro Juan Díaz	Cuenta de pirita cuadrado [Bead/pyrite, square] reddish (Cu alloy?)		**S01** two small pieces		Fe-Al
M-4	Cerro Juan Díaz	Oro laminado [Sheet (gold)] appears gold, uncorroded		**S01** one piece and powder from edge at end	**94.5**--3.9--1.3--0.3	Au-Si-Al-Fe (gold) Al-Fe-Ti-Au (corrosion)
				S02 small piece from edge at midpoint	**93.6**--4.0--1.9--0.5	
M-5	Cerro Juan Díaz	Cuenta tubular de oro [Bead, tubular (gold)] appears gold, uncorroded		**S01** piece from end	**85.7**--10.7--3.3--0.3	Au-Al
M-6	Cerro Juan Díaz	Alambre de metal [Wire (metal)] reddish/gold, uncorroded		**S01** piece from end		sample sent out before EDS
M-7	Cerro Juan Díaz	Lamina de oro [Sheet (gold)] appears gold, uncorroded		**S01** large piece and powder from edge	**88.9**--8.3--2.2--0.6	Au-Ag-Cu-Ti-Al
M-9	Cerro Juan Díaz	Sortija con piedra de concha (quizas colonial) [Ring, (possibly colonial)] green corroded, with frags		**S01** one of loose frags: large piece	**90.4**--5.9--3.5--0.3	Cu-Al-Fe-Zn-Pb-Ti (br/gr) Fe-Cu-Ti-Al (brown side) Cu-Fe-Zn-Pb-Al (green side)
M-11	Cerro Juan Díaz	Cuenta [Bead] appears gold, uncorroded		**S01** one large piece from edge	**88.0**--10.8--0.4--0.8	Au-Ag-Al-Cu
M-13	Cerro Juan Díaz	Gold sheathing {Sheet/wrapping] 2 fragments; appears gold, uncorroded		**S01** sm frag:from broken edge	**90.5**--6.9--2.3--0.4	Au-Al-Ti
				S02 lg frag: from broken edge	**93.3**--3.8--2.7--0.1	Au-Ag-Al-Cu-Fe-C-Fe-Ca
M-14	Cerro Juan Díaz	Gold sheathing/Envoltura [Sheet/wrapping] appears gold, uncorroded		**S01** large piece from broken edge	**90.4**--8.6--0.4--0.5	Au-Al-Ti
M-15	Cerro Juan Díaz	Curved Cincel [Chisel] reddish (strippd Cu alloy?)		**S01** from center curve	0.5--0.3--**99.1**--0.2	
				S02 from inside edge		

M-24	Cerro Juan Díaz	Cincel [Chisel] reddish (strippd Cu alloy?)		**S01** oxidized powder mid	0.0--0.0--7.4--**92.5**	Al-Cu-Fe-Ti (brown powder) Cu-Al-Co-Ti (red particles) Cu-Pb-Al-Fe (green particles)
M-27	Cerro Juan Díaz	Argolla nariguera [Ring, nose] appears gold, uncorroded		**S01** from open end	**93.4**--6.3--0.1--0.2	
M-28-1	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded		**S01** from end	50.6--4.7--44.5--0.3	Au-Cu-Ag-Ti
M-28-2	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded		**S01** from end	64.1--4.5--31.4--0.0	Au-Cu-Al-Ag
M-28-3	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded				
M-28-4	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded				
M-28-5	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded		**S01** from fold edge		
M-28-6	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded				
M-28-7	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded				
M-35-1	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] coppery-gold, uncorroded		**S01** from inside at end	57.7--0.9--41.4--0.0	Cu-Au-Ag-Fe-Ti Al-Fe-Au-Cu-Ti-Ag (corrosion)
M-35-2	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded		**S01** from inside at end	71.0--0.8--28.2--0.1	Cu-Au-Al-Fe-Th-Ag
M-35-3	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded		**S01** from fold edge at end	**87.2**--7.7--3.3--1.7	sample sent out before EDS
M-35-4	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded				
M-35-5	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded				

M-35-6	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded				
M-35-7	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] coppery-gold, uncorroded		**S01** from bend at end	**87.0**--7.4--4.3--1.4	
M-42	Cerro Juan Díaz	Cincel [Chisel] red-br (stripped Cu alloy?)		**S01** piece from midpoint	0.8--0.3--**98.8**--0.2	
				S02 powder near end		
M-43	Cerro Juan Díaz	Cincel gutteo [Chisel] coppery-gold, uncorroded		**S01** from "head" end		
M-54	Cerro Juan Díaz	Twin crocodrilos [Twin crocodiles] 2 fragments; reddish (stripped Cu alloy?)		**S01** sm frag: from back side	21.1--1.2--**77.6**--0.1	Cu-Au-Al-Ag-Fe
				S02 lg frag: from large head	4.6--0.0--0.0--**94.4**	sample sent out before EDS
M-56	Cerro Juan Díaz	Argolla de cobre [Ring (copper)] green corroded		**S01** from open end	7.4--0.7--**91.7**--0.2	
M-59	Cerro Juan Díaz	Cincel [Chisel] reddish (stripped Cu alloy?)		**S01** from end		
M-67	Cerro Juan Díaz	Cuenta tubular [Bead, tubular] appears gold, uncorroded		**S01** from center fold	**88.5**--8.7--2.0--0.8	Au-Ag-Cu-Al-Ti
				S02 lg piece from edge	**91.7**--6.0--1.5--0.8	Au-Ag-Cu-Fe
M-68	Cerro Juan Díaz	Unknown [Tool?] red/grn (part strippd Cu?)		**S01** lg piece and powder	0.2--0.0--**99.8**--0.0	Cu-Al-Pb-Fe Al-Cu-Fe
M-72	Cerro Juan Díaz	Cincel [Chisel] reddish (strippd Cu alloy?)		**S01** from end		
				S02 from edge at midpoint		
M-73	Cerro Juan Díaz	Twin animals dark brown substrate, gilded		**S01** from inside	3.3--0.4--**94.0**--2.2	sample sent out before EDS
				S02 from join area		sample sent out before EDS
M-206	Cerro Juan Díaz	Argolla anillo [Ring, finger (gold)] appears gold (silverish?)		**S01** from inside open end	77.6--5.0--17.3--0.1	sample sent out before EDS
				S02 from outside open end		sample sent out before EDS
AA-01	Abrigo Aclosa	[Disk half] appears gold, uncorroded		**S01** lg piece and powder from corner	62.9--2.1--34.8--0.2	Au-Cu-Ag-Al Au-Cu-Al-Ag
CL-3-45	Cerro Juan Díaz	Fragmento de oro		fragment from broken edge		Cu-Au-Ag bulk

MIT 5136		[Fragment, eagle ornament (gold)] appears gold, uncorroded				Au-Cu-Ag "islands" (2 spots) **XRF** Au-Cu-Ag (surfaces)
		TOTAL= 39 objects		**TOTAL= 32 objects** 41 samples	**TOTAL= 25 objects** 29 samples	**TOTAL= 18 objects** 20 samples / 30 spots

TOTAL/both = 16 objects

Scanning Electron Microscopy-Energy Dispersive X-ray Analysis (SEM-EDS)
Roland H. Cunningham

#	Designation	kV	W.D. mm	T/Sec.	Elements Found	Metals Present	Pb	Hg	As	Sb
1.	AA-01 S01 DISCO/TEST	25	39	120	Au > Cu > Ag Al > C > O > Si > N	Au > Cu > Ag > Al				
1a.	AA-01 S01 DISCO	25	39	120	Au > Cu > Al > Ag C > Si > O > Mg > N	Au > Cu > Al > Ag				
2.	M-4.01, 4.02 (gold)	25	39	120	Au > Si > Al O > Fe > C > N > Ca	Au > Si > Al > Fe (No Silver or Copper)				
2.a.	M-4.01, 4.02 (corrosion)	25	39	120	Si > Al > O > Fe > Ca K > Ti > Mg > P > Au > C	Al > Fe > Ti > Au (No Silver or Copper)				
3.	M -7. 01(gold)	25	39	120	Au > Ag > Cu > Ti C > Si > O > Al > N	Au > Ag > Cu > Ti >Al				
4.	M-9.S01 Brown/Green Sides	25	39	120	Cu > Si > O > Al > Fe > P > Ca > Zn K > Pb > Mg > Ti > C > Cl > S	Cu >Al > Fe > Zn > Pb > Ti (No Gold or Silver)	X			
4a.	M-9.S01 (Sortija) -Brown Side	25	39	120	P > Si > Mg > Fe > Cu > Ti > Cl > Ca > Al > O > K	Fe > Cu > Ti > Al (No Gold or Silver)				
4b.	M-9.S01 (Sortija) -Green Side	25	39	120	Cu > P > Ca > O > Fe > Si > Zn > Pb > K > Al > Cl > Mg	Cu >Fe > Zn > Pb >Al (No Gold or Silver)	X			
5.	M-35-1.S01- Cuenta tabular	25	39	120	Cu > Au Si > Al > O > Ag > Fe > C > Ca > Ti > Mg	Cu > Au > Ag > Fe > Ti				
5a.	M-35-1.S01- Cuenta tabular (Corrosion)	25	39	120	Si > Al > O > Fe > Au > Cu Ca > Ti > K > C > Ag > Mg	Al > Fe > Au > Cu > Ti > Ag				
6.	M-11.S01 - Cuenta	25	39	120	Au > Ag Si > O > N > C > Ca > Al > Cu	Au > Ag > Al > Cu				
7.	M.68.S01- Unknown Fragment	25	39	120	Cu > Al > O > Ca > C > Mg Pb > Si > P > Cl > Fe > S > K	Cu > Al > Pb > Fe (No Gold or Silver)	X			
7a.	M.68.S01- Unknown Fragment (re-run at 30 kV)	30	39	120	Al > Cu > Mg > Fe > O > C > Mn	Al > Cu > Fe (No Gold or Silver)				

#	Designation	kV	W.D .mm	T/Sec.	Elements Found	Metals Present	Pb	Hg	As	Sb
8.	M-24.S01. Cincel- Brown Powder	25	39	120	Si > O > Al > Cu > Ca > Fe P > Mg > C > K > Ti > Cl	Al > Cu > Fe > Ti (No Gold or Silver)				
8a.	M-24.S01. Cincel- Red particles	25	39	120	Cu > Cl > C > O > Al > Si > Co > K > Mg > Ti > Ca	Cu > Al > Co > Ti (No Gold or Silver)				
8b.	M-24.S01; Cincel- Green particles	25	39	120	Cu > Si Pb > C > Al > Ca > P > Mg > Fe	Cu > Pb > Al > Fe (No Gold or Silver)	X			
9.	M-54.S01 – Cocodrilos gamelos	25	39	120	Cu > Cl > O > C Au > Al > S > Si > Ca > Ag > Fe	Cu >Au > Al > Ag > Fe				
10.	M-13.S02 - Envoltura	25	39	120	Au Ag > Si > Al > O > Cu > N > C > Fe > Ca	Au > Ag > Al > Cu > Fe				
11.	M-54.S02 – Cocodrilos gamelos	25	39	120	SAMPLE SENT OUT BEFORE EDS ANALYSIS					
12.	M-13.S01 - Envoltura	25	39	120	Au Si > Al > O > C > N > Ti	Au > Al > Ti (No Copper or Silver)				
13.	M-14.S01- Envoltura	30	39	120	Au Ti > C > Si > N > Ag > Al > Fe	Au > Ti >Ag > Al > Fe (No Copper)				
14.	M-35-3.S01 – Cuenta Tabular	25	39	120	SAMPLE SENT OUT BEFORE EDS ANALYSIS					

#	Designation	kV	W.D .mm	T/Sec.	Elements Found	Metals Present	Pb	Hg	As	Sb
15.	M-73.S01 – Animales gamelos	25	39	120	SAMPLE SENT OUT BEFORE EDS ANALYSIS					
16.	M-206.S01 , M-206.S02 Argolla anillo	25	39	120	SAMPLE SENT OUT BEFORE EDS ANALYSIS					
17.	M-73.S02 – Animales gamelos	25	39	120	SAMPLE SENT OUT BEFORE EDS ANALYSIS					
18.	M-6.S01 – Alambre de metal	25	39	120	SAMPLE SENT OUT BEFORE EDS ANALYSIS					
19.	M-35-2.S01- Has Copper !	30	39	120	Cu > Au Si > Al > O > Fe > C > Th > Ag > Ca	Cu > Au > Al > Fe > Th > Ag				
20.	M-28-1.S01- Cuenta Tabular	20	39	120	Au > Cu Ag > N > C > Si > Ti	Au > Cu > Ag > Ti				
21.	M-5.S01- Cuenta Tubular de Oro	30	39	120	Au Al > C > N > Si > V > O > Ca	Au > Al > V (No Copper or Silver)				
22.	M-67.S02- One piece and powder	20	39	120	Au Al > Ag > Si > Cu > C > O > N > Fe > Mg > Ca	Au > Ag > Cu > Fe				
23.	M-28-2.S01- From the edge	20	39	120	Au > Cu Al > Ag > C > Si > V > N	Au > Cu > Al > Ag				
24.	M-67.S01 Cuenta Tabular	20	39	120	Au Ag > Cu > C > Al > Ti > N > Si	Au > Ag > Cu > Al > Ti				
25.	M-3.S01- Cuenta de pirita	20	39	120	Fe > S Si > O > Ca > Al > P > C > Mg > Na	Fe > Al Ferric Sulfide or Sulphate ?				

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)

Robert J. Speakman

Laser Ablation ICP-MS Analysis of Cu and Au Alloys from Cerro Juan Diaz, Panama

Report Prepared by:

Robert J. Speakman
Archaeometry Laboratory
University of Missouri
Research Reactor Center
Columbia, MO 65211

Samples Submitted by:

Dr. Paula DePriest & Ms. Karla Muñoz Alcocer
Smithsonian Institution,
Museum Conservation Institute
Museum Center Room D2002
4210 Silver Hill Road
Suitland MD 20746-2863

July 14, 2006

INTRODUCTION

Researchers at the Smithsonian Institution Museum Conservation Institute in collaboration with archaeologists at the Smithsonian Institution Tropical Research Institute are investigating the chemical compositions of Cu and Au alloys in archaeological materials excavated from Cerro Juan Diaz—a site located near Parita Bay on Panama's central Pacific coast. Excavations at Cerro Juan Diaz have been ongoing since 1992, and researchers anticipate that data obtained from this site can contribute to a better understanding of social and economic relationships in the region between 200 B.C. and 1600 A.D. To facilitate this study, small scrapings obtained from metal artifacts excavated at Cerro Juan Diaz were analyzed at the University of Missouri Research Reactor Center by laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS).

DESCRIPTION OF LASER ABLATION ICP-MS

In recent years, laser-ablation (LA) systems coupled to state-of-the-art inductively-coupled-plasma mass-spectrometers (ICP-MS) have gained increased popularity in archaeological science for chemical analyses of a variety of inorganic and organic matrices. In archaeology, LA-ICP-MS has facilitated research concerning provenance, trade, and technology through the analysis of metals, rocks, ceramics, pigments, and other archaeological materials (*1-10*). In addition, analyses of human teeth and bone by this technique have been used to make inferences regarding nativity (*11, 12*) and diet (*13*). LA-ICP-MS also has been used in attempts to identify chemical signatures in archaeological wood samples that might be useful for dating prehistoric volcanic eruptions (*14, 15*).

As an ICP-MS sample introduction technique, laser ablation provides a viable alternative for ICP-MS characterization studies that traditionally have required digestion of solid samples using a combination of heat and/or strong acids—a time consuming and unpleasant task. Laser ablation was first applied to ICP in the late 1970s (*16*), but it was not until the mid-1980s that a laser ablation system was coupled to an ICP mass spectrometer (*17*). The coupling of laser-ablation with ICP-MS has resulted in the development of extremely sensitive microprobes capable of determining most elements of the periodic table. LA-ICP-MS offers several advantages over other analytical methods, including high accuracy and precision, low detection limits, rapid analytical time, low cost per sample, high sample throughput, and minimal damage to the sample. The range of materials that can be characterized by LA-ICP-MS (rocks, ceramics, glasses, pigments, fauna and other organics) and types of analyses (bulk, surface, and microprobe) are unsurpassed by most other analytical techniques. The fact that in situ analyses can be conducted by LA-ICP-MS suggests less chance of contamination resulting from sample preparation in that the sample remains intact within its original matrix until the analysis. Although potential problems exist with data calibration, spectral

interferences, and fractionation, these problems can be ameliorated such that any negative impacts to the analysis are minimized. LA-ICP-MS has tremendous potential for providing chemical characterizations of archaeological materials, permitting questions regarding, prehistoric production, trade, interaction, and manufacturing technology to be addressed

The instrument used in the study reported here is a Thermo Elemental Axiom magnetic-sector inductively coupled plasma mass spectrometer coupled to a Merchantek Nd:YAG 213-nm wavelength laser ablation unit. The laser can be targeted on spots as small as 5 μm in diameter. The small spot size and the high sensitivity of magnetic-sector ICP-MS to a wide range of major, minor, and trace elements make LA-ICP-MS a very powerful microprobe. Moreover, laser ablation is virtually non-destructive to most samples considering that the ablated areas are often indistinguishable with the naked eye. Unlike instrumental neutron activation analysis (INAA), X-ray fluorescence (XRF), or ICP-MS of solutions which produces a bulk elemental characterization of the entire matrix, LA-ICP-MS provides a point specific characterization of the ablated area of the sample. Relatively homogeneous samples, such as obsidian and to a certain extent metals, cherts, paints, and glazes, are ideally suited for LA-ICP-MS given that spatial variation is minimal in these materials. ICP-MS can generate compositional data for 50–60 elements, whereas, other techniques typically generate compositional data for about 30 (or less) different elements. Some elements such as lead and phosphorus which cannot be measured by INAA but can be measured by LA-ICP-MS may prove important for separating materials into different compositional groups. For many elements LA-ICP-MS has lower detection limits than other instrumental techniques (e.g., Sr, Sb, Ba, and Zr).

In LA-ICP-MS, the sample is placed inside a sample holder or laser cell where ablation takes place. Ablation areas vary in size depending on the sample matrix, but the analyzed area is usually smaller than 500 X 500 μm and less than 30 μm deep. During analysis, the laser beam ablates (or vaporizes) the area of interest on the sample. The ablated material is transported from the laser cell using a 0.9–1.5 l/min. flow of argon and/or an argon/helium/nitrogen-mixed carrier gas through Tygon tubing and introduced into the ICP-MS torch, where argon gas plasma capable of sustaining electron temperatures between 8000 and 10,000 K is used to ionize the injected sample. The resulting ions pass though a two-stage interface (sample and skimmer cones) designed to enable the transition of the ions from atmospheric pressure to the vacuum chamber of the ICP-MS system. Once inside the mass spectrometer (in this case a high-resolution magnetic sector ICP-MS), the ions are accelerated by high voltage and pass through a series of ion optics, an electrostatic analyzer (ESA), and finally a magnet. By varying the strength of the magnet, the ions are separated according to mass/charge ratio and passed through a slit into the detector, which records only a small atomic mass range at a given time. By varying the magnet and flight-tube settings, the entire mass range can be scanned within a relatively short time.

LASER ABLATION ICP-MS SAMPLE PREPARATION

Laser ablation ICP-MS requires little sample preparation other than resizing the sample to fit inside the sample chamber which was not necessary for this study. For this analysis, metal fragments were mounted to a standard microscope slide using double-sided tape.

LASER ABLATION ICP-MS ANALYTIC PARAMETERS

Prior to data acquisition, the instrument is turned-on and permitted to warm-up for a minimum of one hour. Allowing the instrument to warm-up permits the internal components to reach their optimum operating temperature, greatly reducing instrument noise and drift. After an hour or so, a glass standard (NIST SRM 612, a glass wafer spiked with 60+ elements) was placed in the laser chamber and continuously ablated to produce a signal that permits the instrument settings to be adjusted so that sensitivity is maximized while noise is minimized. After tuning the instrument, data for a blank and four gold standards were generated. Following measurement of the standard data, the samples were placed in the laser cell and analyzed. Data for additional standards were collected midway through the analysis and at the conclusion of the analysis.

In order to compensate for the issues surrounding the determination of the best laser power settings, we tune the ICP-MS to maximize signal intensity then adjust the laser power settings to bring the signal up or down to a predetermined count rate depending on the sample matrix—usually 400,000–8,000 counts per second of indium on NIST SRM 612 using a 100-micron-diameter beam operating at 20 Hz, scanning along a line at a speed of 30 microns per second.

For the actual analysis of the metals, ablation parameters were identical for all unknowns and standards analyzed. The laser was operated using a 15-micron-wide beam, operating at 20 Hz, scanning along a line at a speed of 30 microns per second. The laser beam was permitted to pass over the ablation area twice prior to data acquisition to remove minimize the effects of surface contamination, to permit time for sample uptake, and to permit time for the argon gas plasma to stabilize after the introduction of the ablated material. Our experiments at MURR have demonstrated that pre-ablation permits the laser to couple better with the sample matrix. Each sample was analyzed three times each for Fe, Mn, Ni, Cu, Zn, Ag, Os, and Au; the resulting data from each analysis were averaged.

NORMALIZATION AND STANDARDIZATION OF DATA

A basic problem in LA-ICP-MS is that it is difficult to monitor the amount of material removed by the laser and transported to the ICP. Conditions such as hardness of

the material, position of the sample in the laser chamber, whether or not the surface of the artifact is flat, and other conditions clearly affect how much material reaches the ICP torch and thus the intensity of the signal monitored for the various atomic masses of interest. In addition, instrumental drift in the ICP-MS over several hours or days affects count rates.

The normalization approach used at MURR follows that suggested by Gratuze and others (*4, 6*). The basic assumption of the Gratuze approach is that the elements being measured represent essentially all of the major constituents contained within the analyzed material. Data generated from the analysis, expressed as counts per second, are then ratioed to an internal *standard* (in this case Au) to normalize for different count rates between samples and standards. Quantitative data are then obtained by comparing the normalized signal in the unknown samples to the normalized signals for the standard reference materials (BCR8079 and three in-house gold standards (18K, 14K, and 10K)). The resulting element concentrations are then normalized to 100%.

RESULTS

Although eight elements (Fe, Mn, Ni, Cu, Zn, Ag, Os, and Au) were measured in each of the archaeological samples Mn, Ni, Zn, and Os were consistently below detection limits. All samples were analyzed in a random order.

Tables 1 and 2 list the expected and measured concentrations determined for the four gold standards. Table 3 lists the concentrations measured for the 29 samples that were large enough to be analyzed. As expected, all of the samples have measurable concentration of Cu, Au, and Ag. Additionally, most of the samples contained minor quantities of Fe which may represent contamination from scarping the artifacts to obtain the sample. Three anomalous artifacts contained high concentrations of iron and should be disregarded from any interpretation of the data.

Although it was possible to analyze the specimens by LA-ICP-MS, long-term analyses of high-concentration metals by ICP-MS is, in general, not a good idea given that it can lead to high background levels in the instrument. Additionally, LA-ICP-MS is a microprobe technique, and as such, the analysis is focused on a relatively small area of the sample (in this case 15 microns). In at least two samples different metal phases (or inclusions) were observed in the ablation chamber (e.g., light colored and dark colored inclusions or phases). In general it would seem that future analyses would be best served by x-ray fluorescence which analyzes a larger area on a given surface. Despite potential problems with heterogeneity, several samples that had two aliquots (e.g., M-4, M-67) produced very comparable results indicating that heterogeneity may not be too big of an issue for some of the samples.

Table 1. Comparison of certified values (in bold) for BCR8079 and values obtained by LA-ICP-MS.

	Cu (%)	Au (%)	Ag (%)
BCR-8079	***(5)***	***15***	***80***
SRM8079-1	6.6	14.3	79.1
SRM8079-2	4.5	14.6	80.9
SRM8079-3	5.2	13.9	80.8
SRM8079-4	5.3	14.9	79.7
SRM8079-5	6.1	11.4	82.3
SRM8079-6	5.4	16.3	78.2
Mean	***5.5***	***14.2***	***80.1***
Std Dev	***0.7***	***1.6***	***1.5***

Table 2. Comparison of expected values (in bold) for 3 non certified gold standards (reported values measured by XRF and ICP) and values obtained by LA-ICP-MS.

	Fe (%)	Cu (%)	Zn (%)	Ag (%)	Au (%)
18K	***0.1***	***10.37***	***0.1***	***14.5***	***75.03***
18K	0.5	8.9	0.2	13.4	77.0
18K	0.1	10.1	0.1	15.4	74.2
14K	***0.1***	***28.64***	***5.74***	***7.26***	***58.39***
14K	0.1	25.5	6.1	5.6	62.7
14K	0.0	26.8	5.8	5.8	61.6
10K	***0.1***	***30.72***	***11.58***	***n/a***	***42.06***
10K	0.1	25.3	13.7	0.0	44.3
10K	0.0	27.2	14.2	0.0	42.9

Table 3. Descriptive information and values obtained from LA-ICP-MS analysis of the Cerro Juan Diaz metal objects.

Cat no.	Object Description	Fe (%)	Cu (%)	Ag (%)	Au (%)
AA-01.S01	Small Disk	0.2	34.8	2.1	62.9
M-04-01	laminated ore fragment	0.5	1.9	4.0	93.6
M-04-02	laminated ore fragment	0.3	1.3	3.9	94.5
M-05.S01	Cuenta Tabular de Oro	0.3	3.3	10.7	85.7
M-07.S01	Lamina de Oro	0.6	2.2	8.3	88.9
M-09.S01	Sortija, Quizas Colonial	0.3	3.5	5.9	90.4
M-11.S01	Cuenta	0.8	0.4	10.8	88.0
M-13.S01	Envoltura	0.4	2.3	6.9	90.5
M-13.S02	Envoltura	0.1	2.7	3.8	93.3
M-14.S01	Envoltura	0.5	0.4	8.6	90.4
M-15.S01	Cincel	0.2	99.1	0.3	0.5
M-206.S01	Argolla Anillo	0.1	17.3	5.0	77.6
M-27.S01	Argolla Nariguera	0.2	0.1	6.3	93.4
M-28-1.S01	Cuenta Tabular	0.3	44.5	4.7	50.6
M-28-2.S01	Cuenta Tabular	0.0	31.4	4.5	64.1
M-35-1.S01	Cuenta Tabular	0.0	41.4	0.9	57.7
M-35-2.S01	Cuenta Tabular	0.1	28.2	0.8	71.0
M-35-3.S01	Cuenta Tabular	1.7	3.3	7.7	87.2
M-35-7.S01	Cuenta Tabular	1.4	4.3	7.4	87.0
M-42.S01	Cincel	0.2	98.8	0.3	0.8
M-54.S01	Colgante Bicefalo Cocodrilos Gemelos	0.1	77.6	1.2	21.1
M-56.S01	Argolla de Cobre	0.2	91.7	0.7	7.4
M-67.S01	Cuenta Tabular	0.8	2.0	8.7	88.5
M-67.S02	Cuenta Tabular	0.8	1.5	6.0	91.7
M-68.S01	Unknown Fragment	0.0	99.8	0.0	0.2
M-73.S01	Animales Gemelos	2.2	94.0	0.4	3.3
Contaminated Samples?					
M-02.S01	Cuenta de Pirita	100.0	0.0	0.0	0.0
M-24.S01	Cincel	92.5	7.4	0.0	0.0
M-54.S02	Colgante Bicefalo Cocodrilos Gemelos	94.4	0.0	0.0	4.6

Acknowledgements: Purchase of the laser ablation system and ICP-MS was funded, in part, by a grant from the National Science Foundation (SBR-9977237). Operating support for the MURR Archaeometry lab is supported in part by a grant from the National Science Foundation (0405042).

REFERENCES

1. Devos, W.; Moor, C.; Lienemann, P., Determination of impurities in antique silver objects for authentication by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). *J. Anal. At. Spectrom.* **1999,** 14, (4), 621-626.
2. Devos, W.; Senn-Luder, M.; Moor, C.; Salter, C., Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for spatially resolved trace analysis of early-medieval archaeological iron finds. *Fresenius J. Anal. Chem.* **2000,** 366, (8), 873-880.
3. Kennett, D. J.; Neff, H.; Glascock, M. D.; Mason, A. Z., A geochemical revolution: Inductively coupled plasma-mass spectrometry. *The SAA Archaeological Record* **2001,** 1, (1), 22-36.
4. Neff, H., Analysis of Mesoamerican Plumbate pottery surfaces by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). *J. Archaeol. Sci.* **2003,** 30, (1), 21-35.
5. Pollard, A. M.; Heron, C., *Archaeological Chemistry*. Royal Society of Chemistry: Cambridge, 1996.
6. Gratuze, B., Obsidian characterization by laser ablation ICP-MS and its application to prehistoric trade in the Mediterranean and the Near East: Sources and distribution of obsidian within the Aegean and Anatolia. *J. Archaeol. Sci.* **1999,** 26, (8), 869-882.
7. Gratuze, B.; Blet-Lemarquand, M.; Barrandon, J. N., Mass spectrometry with laser sampling: a new tool to characterize archaeological materials. *J. Radioanal. Nucl. Chem.* **2001,** 247, (3), 645-656.
8. James, W. D.; Dahlin, E. S. C., D.L., Chemical compositional studies of archaeological artifacts: comparison of LA-ICP-MS to INAA measurements. *J. Radioanal. Nucl. Chem.* **2005,** 263, (3), 697-702.
9. Mallory-Greenough, L. M.; Greenough, J. D.; Dobosi, G.; Owen, J. V., Fingerprinting ancient Egyptian quarries: preliminary results using laser ablation microprobe -- inductively coupled plasma -- mass spectrometry. *Archaeometry* **1999,** 41, (2), 227-238.
10. Speakman, R. J.; Neff, H.; Glascock, M. D.; Higgins, B. J., Characterization of archaeological materials by laser ablation--inductively coupled plasma--mass spectrometry. In *Archaeological Chemistry: Materials, Methods, and Meaning*, Jakes, K. A., Ed. American Chemical Society: Washington, DC, 2002; Vol. No. 831, pp 48-63.
11. Cucina, A.; Neff, H.; Blos, V. T., Detecting provenience of African-origin individuals in the colonial cemetery of Campeche (Yucatan): a new approach using trace elements and LA-ICP-MS. In *Laser Ablation ICP-MS in Archaeological Research*,

Speakman, R. J.; Neff, H., Eds. University of New Mexico Press: Albuquerque, NM, 2005; pp 187-197.
12. Dolphin, A. E.; Goodman, A. H.; Amarasiriwardena, D., Variation in elemental intensitities among teeth and between pre- and postnatal regions of enamel. *Am. J. Phys. Anthropol.* **2005,** 127.
13. Song, R.-J. Ph.D. thesis, University of Massachusetts, Amherst, MA, 2004.
14. Pearson, C.; Manning, S. W.; Coleman, M.; Jarvis, K., Can tree-ring chemistry reveal absolute dates for past volcanic eruptions? *J. Archaeol. Sci.* **2005,** 32, (8), 1265.
15. Sheppard, P. R.; Ort, M.; Speakman, R. J.; Anderson, K.; Elson, M., Dendrochemical Analysis of Trees Affected by the Paricutin Eruption with Implications for Re-Analyzing the Sunset Crater Eruption. In *Geological Society of America Abstracts with Programs*, Salt Lake City, 2005; Vol. 37 (7), p 111.
16. Ambercrombie, F. N.; Silvester, M. D.; Murray, A. D.; Barringer, A. R., A New Multielement Technique for the Collection and Analysis of Airborne Particulates in Air Quality Surveys. In *Applications of Inductively Coupled Plasmas Emission Spectroscopy*, Barnes, R. M., Ed. Franklin Institute Press: Philadelphia, 1978; p 121–145.
17. Gray, A. L., Solid sample introduction by laser ablation for inductively coupled plasma source mass spectrometry. *Analyst* **1985,** 110, (5), 551-556.

X-ray Fluorescence Spectroscopy (XRF) of CL-3-45

Aaron N. Shugar

Date	Reading	Realtime (sec)	LiveTime (sec)	Mode	Cu	Ag	Pt	Au
13-Jul-06	Side1	90	73.73	Analytical	54.08	2.43	BDL	43.49
13-Jul-06	Side1	90	73.95	Analytical	54.16	2.56	BDL	43.27
13-Jul-06	Side 1	300	251.39	Analytical	54.94	2.93	BDL	42.13
13-Jul-06	Side 2	90	74.31	Analytical	48.52	3.75	BDL	47.74
13-Jul-06	Side 2	300	250.58	Analytical	50.23	3.52	BDL	46.25

Cu +/-	Ag +/-	Pt +/-	Au +/-
0.18	0.05		0.48
0.18	0.05		0.48
0.17	0.06		0.51
0.09	0.03		0.27
0.1	0.03		0.27

3	53.53	2.41	ND	43.05	98.99
4	54.06	2.56	ND	43.19	99.81
5	48.06	3.71	ND	47.29	99.06
9	49.54	3.47	ND	45.62	98.63
10	54.29	2.9	ND	41.63	98.82

Instrument specifications

Innov-X handheld ED-XRF (portable)

Features: miniature X-ray tube (10-40kV, 10-100μA), silver anode, silicon pin diode detector, with preset conditions and calibration curves

Modes: soil mode with light element analysis program (LEAP) settings, which optimize the instrument to look at elements lighter than Fe (K, Ca, Ti, Cr, Mn, Ba), using built-in X-ray tube beam settings

Scanning Electron Microscopy-Energy Dispersive X-ray Analysis (SEM-EDS) of CL-3-45 metallographic cross-section

Roland H. Cunningham

ANALYSIS

MCI # 6043

Object(s): Gold Fragment: CL-3-45. MIT-5136
Artist/Manufacturer: Unknown
Geog./Cult. Source: Panama

Material(s): Gold colored fragment, possible gold alloy or mixture.
Approximate overall dimensions: ca. 12 mm L x 25 mm x 1 mm thick.

Object Date: Unknown
Requestor: Republic of Panama

Date In: 8/01/06
Completed: 9/30/06

Requested Action: EDS Analysis, Secondary and Backscattered SEM imaging.

Procedure:

- A section of sample the sample approximately 3.1 mm wide x 6.0 mm deep x 1mm thick was removed using the Buehler Isomet low-speed saw and di-ionized water as a lubricant.
- After ultrasonic cleaning and drying in methanol, the sample was embedded in Buehler Epo-Thin low viscosity epoxy.
- After 12 hours curing time, the embedded sample was sectioned into two approximate halves with the Buehler Isomet low-speed saw . Di-ionized water was again used as a cutting fluid.
- After sectioning. One half of the embedded section was next ground and polished using the Buehler Minimet polishing system.
- Due to minor charging caused by the embedding plastic, the cross-section was carbon coated to increase conductivity under the electron beam. The coating was applied with an Edwards E306A Vacuum Coating Unit.

EDS Analysis:

The examination was broken down as follows:

Section A, SEM/EDS analyses and imaging of the sample's **matrix** material and estimated element weight percent for major elements detected.

Section B, SEM/EDS analyses and imaging of the sample's **bright phase** material and estimated element weight percent for major elements detected.

Section C, SEM/EDS analyses and imaging of (6) randomly picked **inclusions** embedded within the sample's matrix and estimated element weight percent for major elements detected. (see EDS spectra and Excel work sheets enclosed).

- All SEM/EDS data were collected at 25 kV for 120 seconds at a working distance of 39mm. The Magnification used was 5000X.
- A series of (10) EDS analyses were run on the cross-section's matrix material.
- A series of (10) EDS analyses were run on the cross-section's bright phase material.
- A series of (18) EDS analyses were run for (9) inclusions.

- The instrument used was a JEOL JXA-840A Scanning Electron Microscope (SEM) with a ThermoNORAN TN-5502 energy dispersive analytical attachment and, NORAN Vantage spectrum processing software. The system is also fitted with a low atomic number detector (Pioneer Premium detector with a Norvar window).

Photography:

- (18) SE and backscattered SEM image details were taken of the cross-sectioned sample.
- (9) SE and backscattered SEM image details were were taken of inclusions in the matrix.

Roland H. Cunningham
Sr. Paintings Conservator/Analytical Support Gp.
SCMRE

Bibliography

" The Forensic Examination of Paints & Pigments "
Crown, D.A. 1968: Charles C. Thomas, Pub.

" SEM: A Users Manual for Materials Science "
Gabriel, Barbara A. 1985: American Society for Metals

" Scanning Electron Microscopy & X-Ray Analysis "
J.I. Goldstein, D.E. Newbury, P. Echlin, D.C. Joy, et al .
N.Y.: 1992: 2nd Edition Plenum Press:

SECTION A

SEM/EDS Analysis and Imaging

Gold Cross-section

Matrix Material

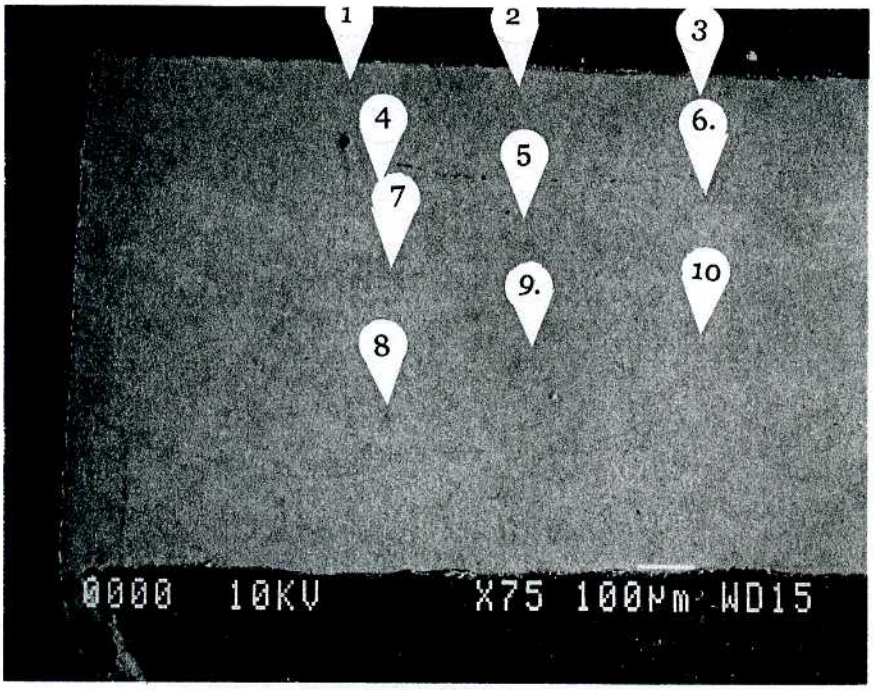
6043

EDS ANALYSIS

Cl-3-45 (MIT-5136)

Gold Cross-Section - Matrix Material

25kV Working Distance = 39mm 5000X



Gold Cross-Section

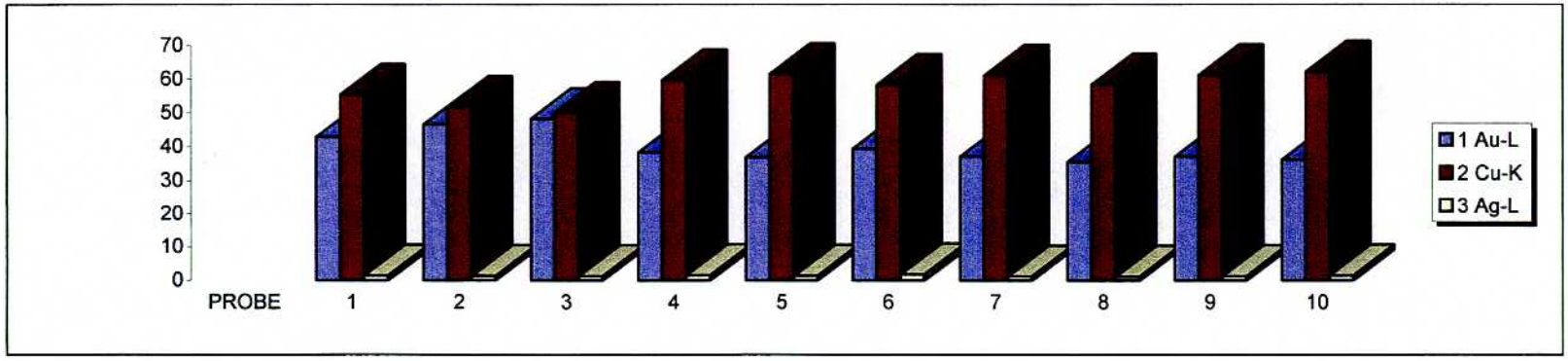
Cl-3-45 (MIT-5136)
Matrix Material (probes 1-10)

Work Sheet: Estimated Weight Percent/Element

Project: CI-3-45 (MIT-5136) (Matrix Material) **MCI #:** 6043 **kV:** 25 **W.D.:** 39 mm **Mag.:** 5000X

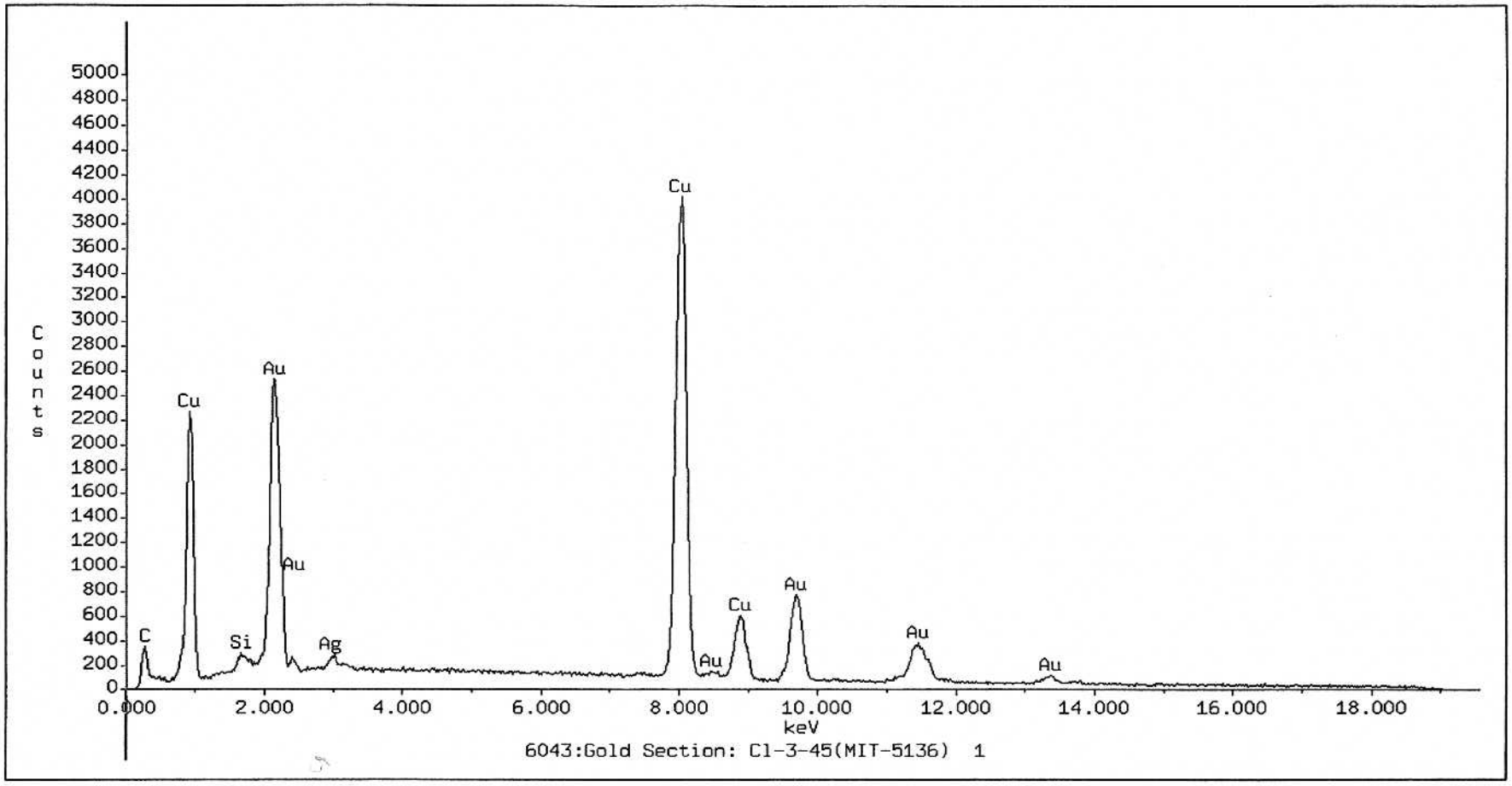
ELEMENT WEIGHT PERCENTAGES FOR ELEMENTS DETECTED

	1	2	3
	Au-L	**Cu-K**	**Ag-L**
PROBE			
1	42.87	55.49	1.46
2	46.58	51.91	1.29
3	48.27	50.14	1.27
4	38.31	59.74	1.59
5	36.92	61.58	1.42
6	39.35	58.35	1.88
7	37.11	61.11	1.25
8	35.47	58.4	1.22
9	36.98	61.18	1.31
10	36.14	62.21	1.44
	398	580.11	14.13



Estimated Element Wt/%

Thermo NORAN



6043:Gold Section: Cl-3-45(MIT-5136) 1

Accelerating Voltage: 25KeV Take Off Angle: 58.3506° Live Time: 120 seconds Dead Time: 34.098 seconds

Fri Jul 28 15:57:10 2006

6043:Gold Section: Cl-3-45(MIT-5136) 1

Refit _Si-K' _Si-K"
Filter Fit Method
Chi-sqd = 2.29 Livetime = 120.0 Sec.
Standardless Analysis

Element	Relative k-ratio	Error (1-Sigma)	Net Counts	Error (1-Sigma)
C -K	---	---	2744	+/- 67
Cu-L	---	---	24732	+/- 211
Si-K	0.00105	+/- 0.00017	551	+/- 87
Au-M	---	---	43863	+/- 446
Ag-L	0.01013	+/- 0.00135	2492	+/- 333
Cu-K	0.62396	+/- 0.00482	77230	+/- 596
Au-L	0.36486	+/- 0.00892	22087	+/- 540

Adjustment Factors	K	L	M
Z-Balance:	0.00000	0.00000	0.00000
Shell:	1.00000	1.00000	1.00000

PROZA Correction Acc.Volt.= 25 kV Take-off Angle=58.35 deg
Number of Iterations = 5

Element	k-ratio (calc.)	ZAF	Atom %	Element Wt %	Wt % Err. (1-Sigma)
Si-K	0.0010	1.837	0.61	0.19	+/- 0.03
Ag-L	0.0100	1.458	1.22	1.46	+/- 0.19
Cu-K	0.6158	0.901	78.59	55.49	+/- 0.43
Au-L	0.3601	1.190	19.59	42.87	+/- 1.05
Total			100.00	100.00	

Fri Jul 28 15:56:01 2006

6043:Gold Section: Cl-3-45(MIT-5136) 1

Livetime : 120.0 Sec.
Technique: Least Squares Fit

Elements Present:
C(6), Si(14), Cu(29), Au(79)
Possible Additional Elements:
Ag(47), Rb(37)

Energy (keV)	Intensity (counts)	Element Present	Element Possible
0.273	2499	C Ka	
0.937	21397	Cu La1	
1.683	668	Si Ka	
2.157	37491	Au Ma1	
2.443	925	Au Mg	
*2.999	1213		Ag La1
8.036	73278	Cu Ka1	
8.486	700	Au Ll	
8.897	9728	Cu Kb1	
9.697	13556	Au La1	
11.450	4200	Au Lb1	
*13.371	1266	Au Lg1	
			Rb Ka1

* Check peak labels manually, or acquire additional data for better statistics and re-run Automatic Ident.

SECTION B

SEM/EDS Analysis and Imaging

Gold Cross-section

Bright Phase Material

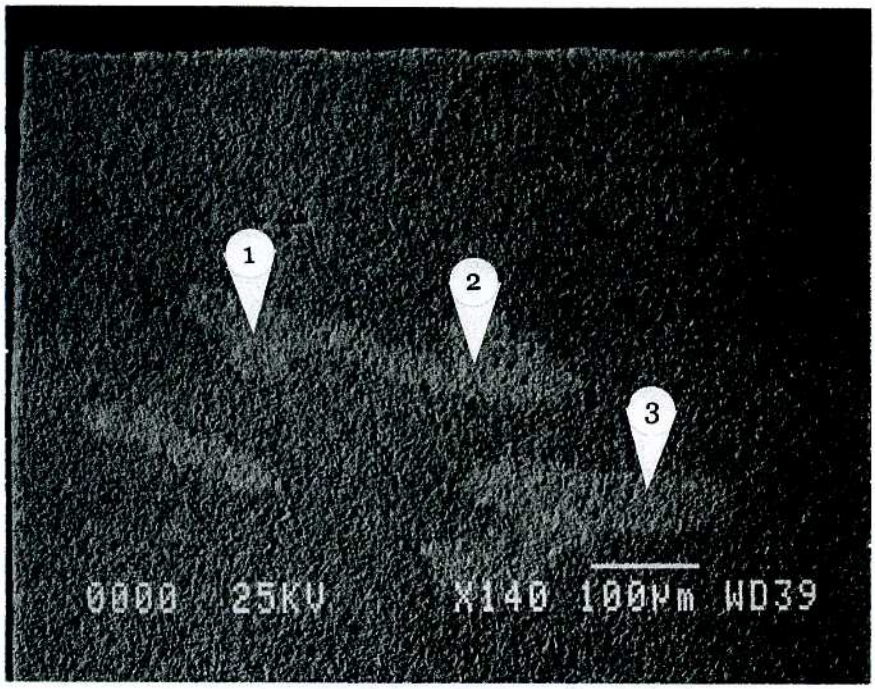
6043

EDS ANALYSIS

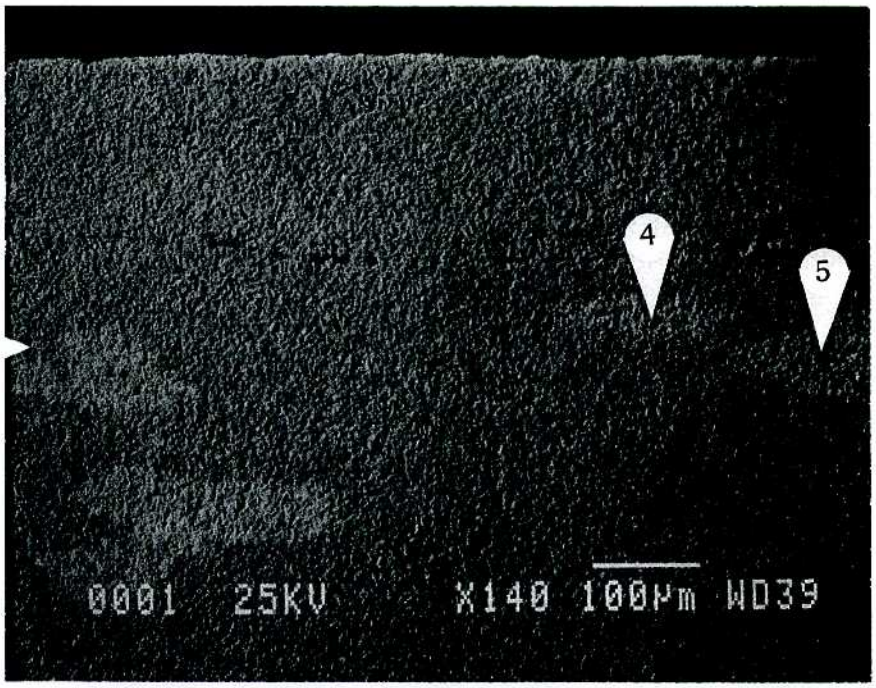
Cl-3-45 (MIT-5136)

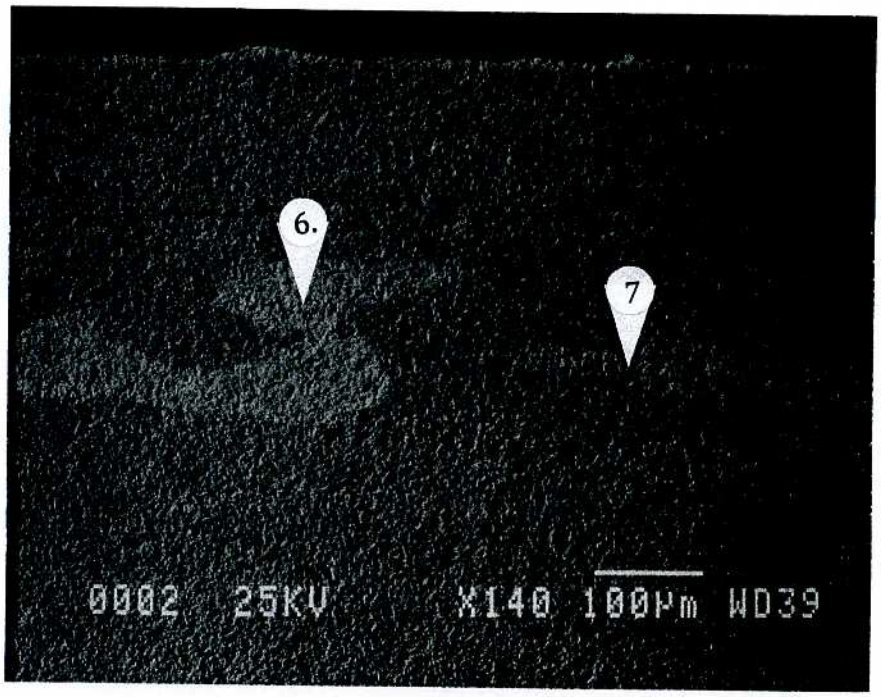
Gold Cross-Section - Bright Phase Material

25kV Working Distance = 39mm 5000X

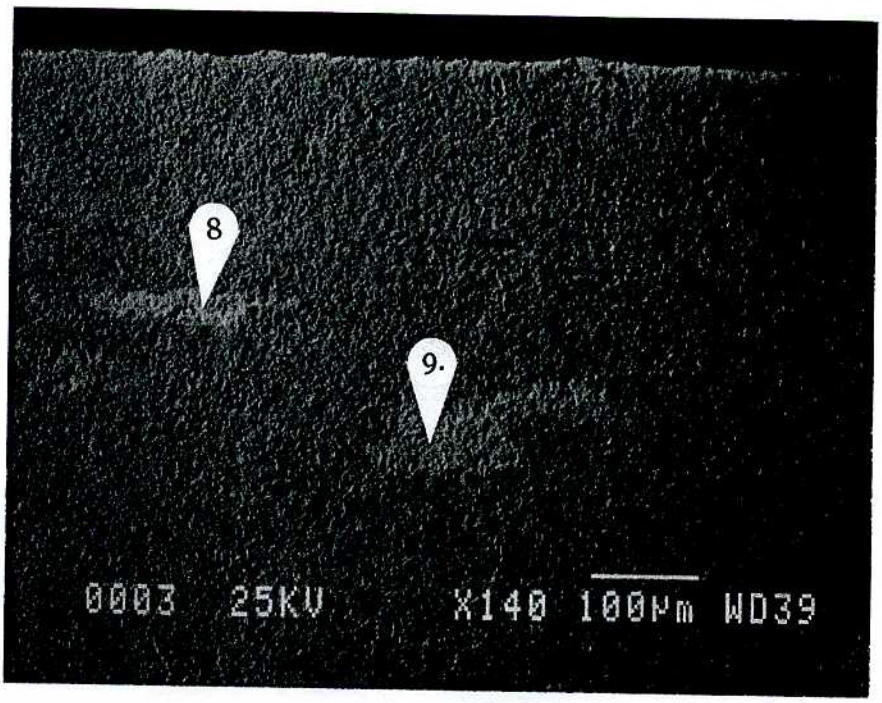


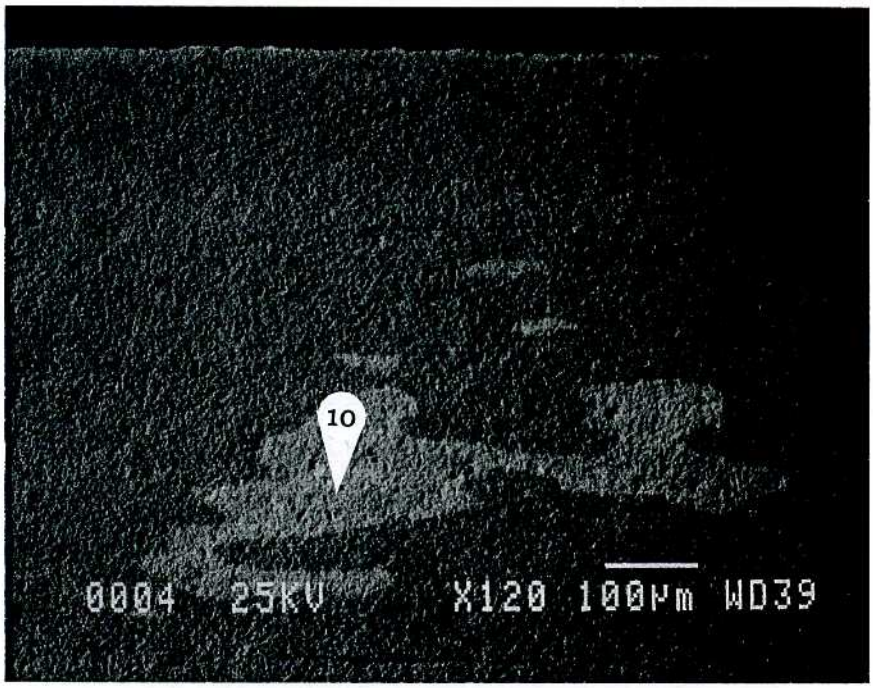
Gold Cross-Section
Backscatter Photo
Cl-3-45 (MIT-5136)
Bright Phase Material (probes 1-5)





Gold Cross-Section
Backscatter Photo
Cl-3-45 (MIT-5136)
Bright Phase Material (probes 6-9)





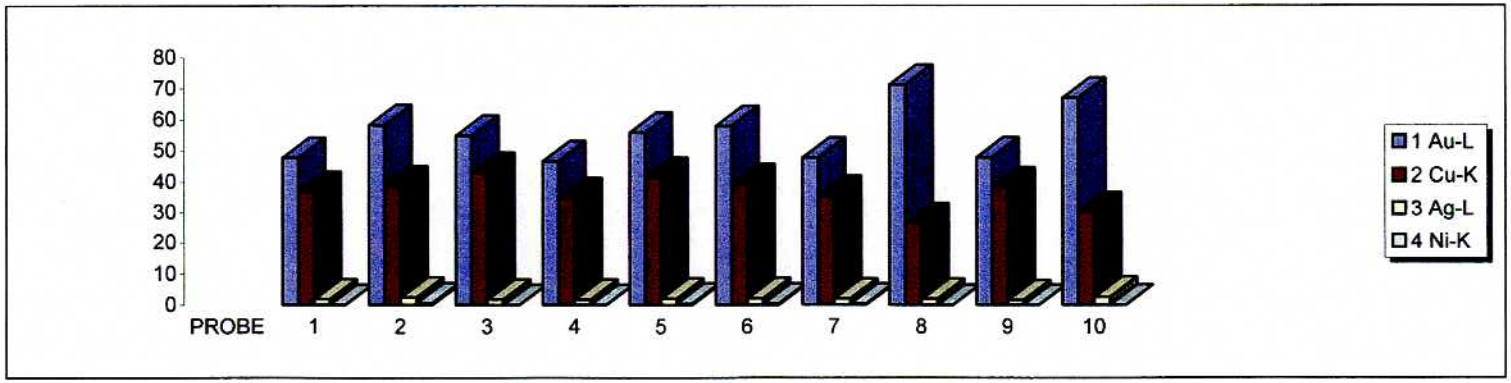
Gold Cross-Section
Backscatter Photo
Cl-3-45 (MIT-5136)
Bright Phase Material (probe 10)

Work Sheet: Estimated Weight Percent/Element

Project: **CI-3-45 (MIT-5136)** **MCI #:** **6043** **kV:** **25** **W.D.:** **39 mm** **Mag.:** **5000X**
(Bright Phase Material)

ELEMENT WEIGHT PERCENTAGES FOR ELEMENTS DETECTED

PROBE	1 Au-L	2 Cu-K	3 Ag-L	4 Ni-K
1	47.81	36.81	1.83	-
2	58.27	38.57	2.44	0.59
3	54.89	42.9	1.8	-
4	46.71	34.74	1.79	-
5	55.87	41.28	2.08	0.45
6	57.99	39.29	2.17	0.39
7	47.83	35.35	2.02	0.3
8	71.21	26.56	1.98	-
9	47.82	38.2	1.49	-
10	67	30.2	2.57	-
	555.4	363.9	20.17	1.73



Estimated Element Wt%

SECTION C

SEM/EDS Analysis and Imaging

Gold Cross-section

Random Inclusion Sites in Matrix Material

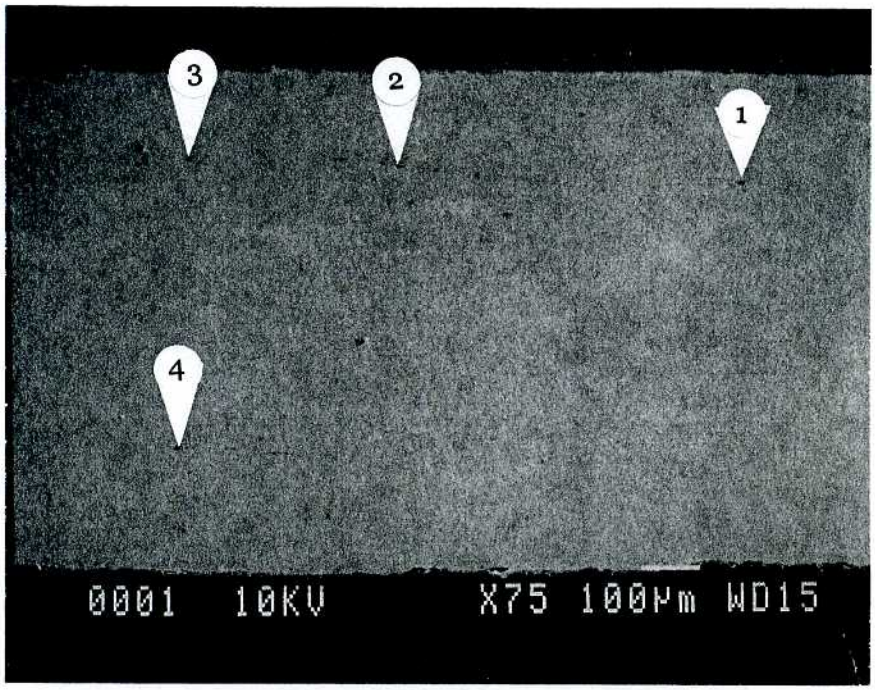
6043

EDS ANALYSIS

Cl-3-45 (MIT-5136)

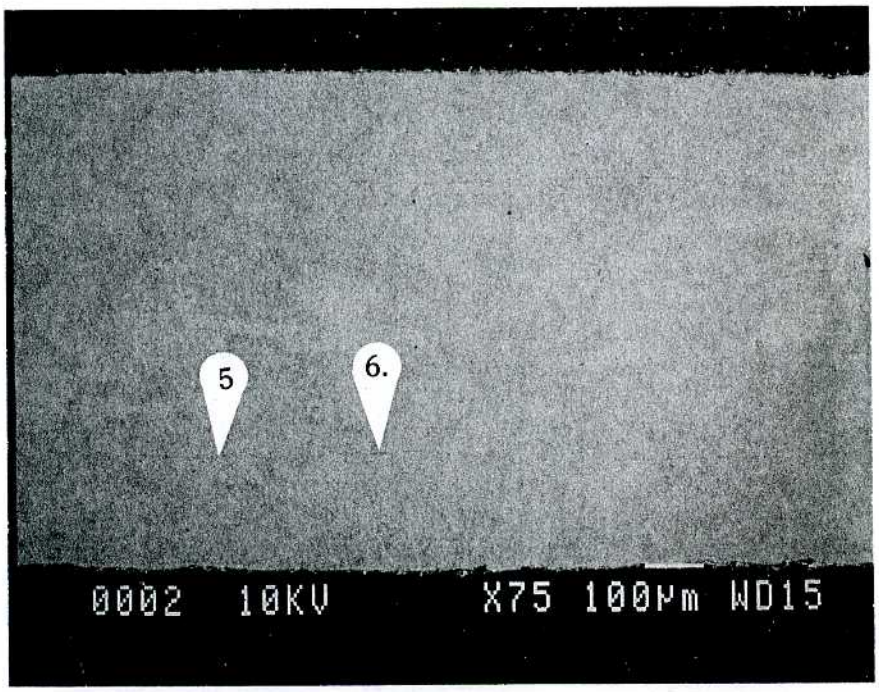
Gold Cross-Section - Inclusions (1a-1c)

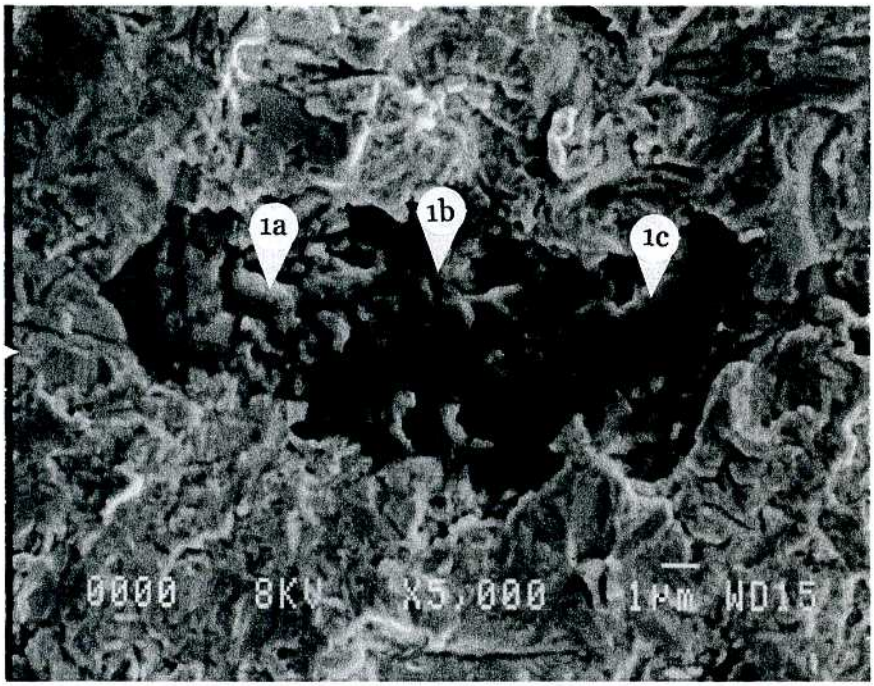
25kV Working Distance = 39mm 30,000-70,000 X



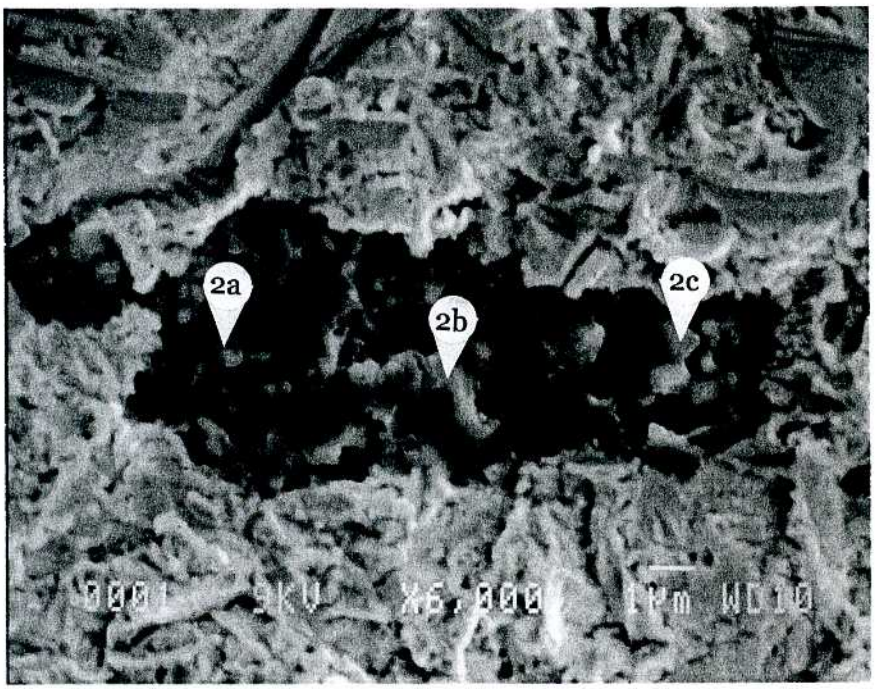
6043

Gold Cross-Section Cl-3-45 (MIT-5136)
2° images show locations of (6) inclusions selected for probing

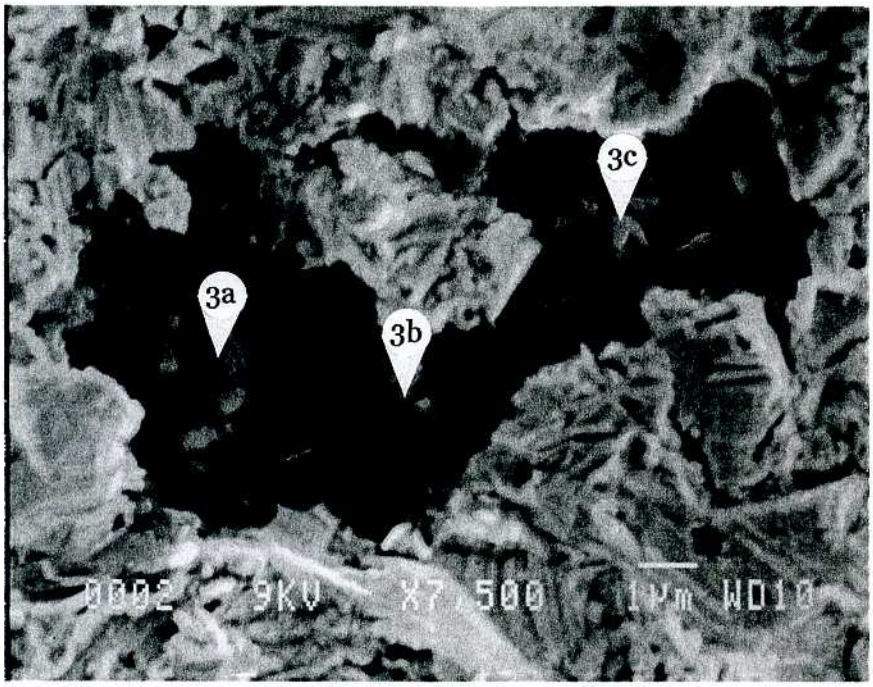




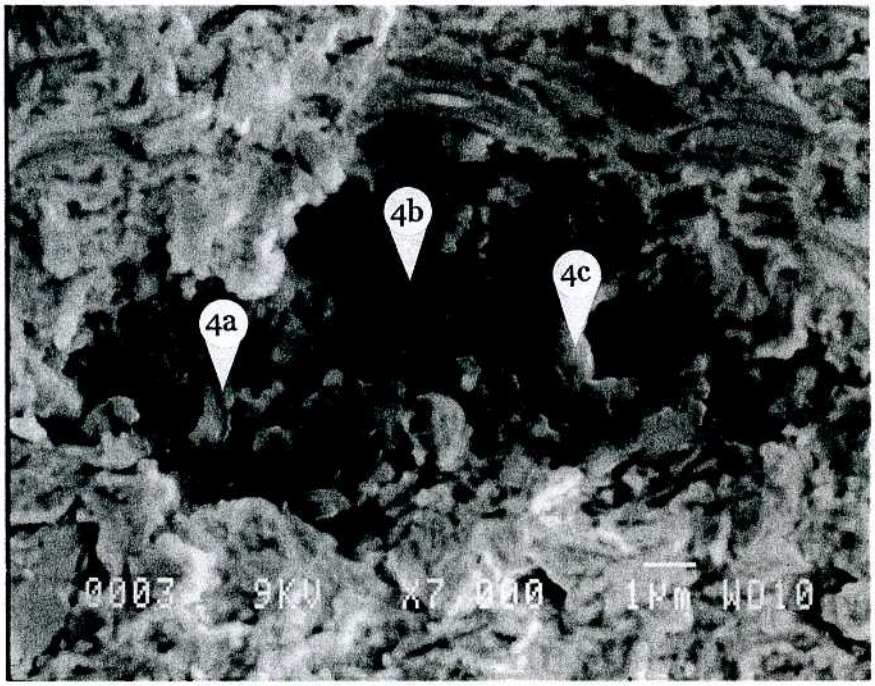
6043
Gold Cross-Section Cl-3-45 (MIT-5136)
2° image showing probe locations



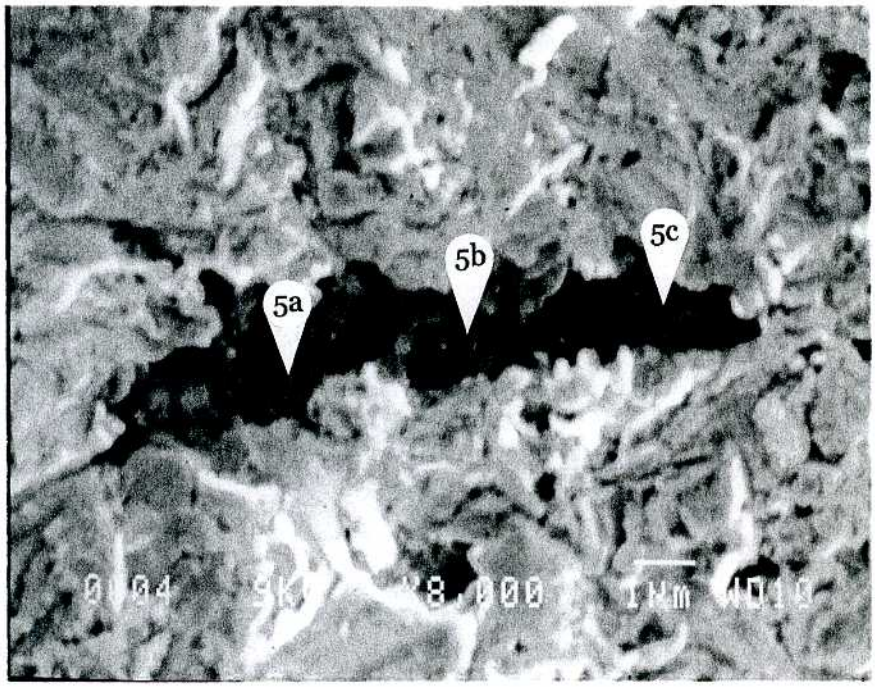
6043
Gold Cross-Section Cl-3-45 (MIT-5136)
2° image showing probe locations



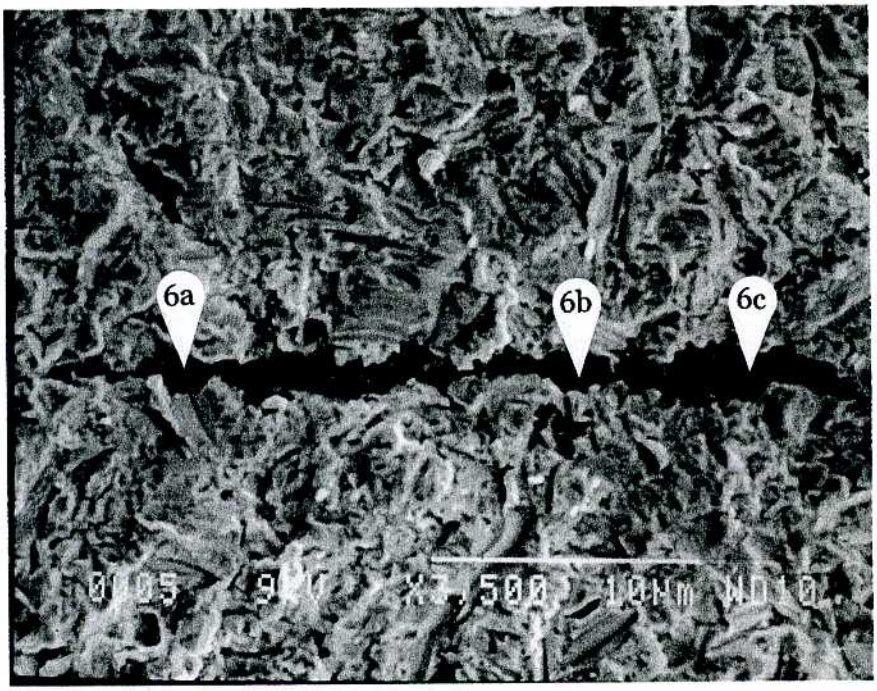
6043
Gold Cross-Section Cl-3-45 (MIT-5136)
2° image showing probe locations



6043
Gold Cross-Section Cl-3-45 (MIT-5136)
2° image showing probe locations



6043
Gold Cross-Section Cl-3-45 (MIT-5136)
2° image showing probe locations



6043
Gold Cross-Section Cl-3-45 (MIT-5136)
2° image showing probe locations

6043: Gold Section
Cl-3-45 (MIT 5136)

kV : 25
W.D.mm: 39
T/Sec.: 120 sec.
30,00-70,000X

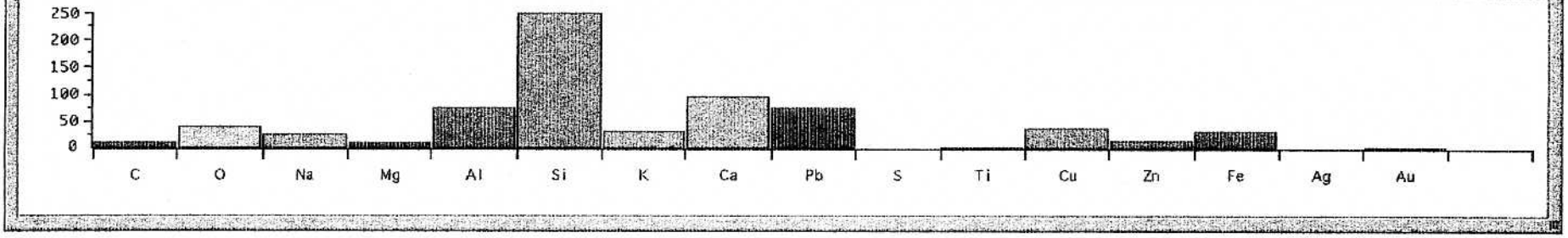
INCLUSIONS

	ELEMENT Wt. %														
Probe	**Na-K**	**Ag-L**	**Cl-K**	**Mg-K**	**Al-K**	**Si-K**	**K-K**	**Ca-K**	**Ti-K**	**Fe-K**	**Cu-K**	**Pb-L**	**Au-L**	**Zn-L**	**As-K**
1a	8.54	-	-	2.42	10.35	30.48	5.03	10.21	0.59	6.72	8.83	13.78	3.03	-	-
1b	9.08	-	-	1.69	11.01	29.74	5.26	11.81	0.54	5.95	7.70	14.74	2.48	-	-
1c	-	-	-	2.03	6.85	24.36	3.46	13.70	0.43	5.24	13.27	13.59	5.40	11.66	-
2a	-	1.16	-	-	8.71	18.41	0.99	3.17	-	3.82	41.94	7.58	14.21	-	-
2b	-	-	-	1.02	9.91	23.62	1.38	7.17	0.39	5.27	32.92	12.17	6.16	-	-
2c	-	-	-	1.17	8.68	23.59	0.65	9.65	-	4.66	36.13	4.81	10.65	-	-
3a	-	-		0.23	4.92	28.22	0.68	1.16	-	5.69	45.45	-	12.39	-	1.25
3b	-	-	1.43	0.40	2.90	14.94	0.39	2.17	-	3.99	60.58	3.84	9.37	-	-
3c				0.43	3.85	21.76	0.37	0.94	-	4.49	58.37	-	9.78	-	-
4a	7.17	-	-	-	20.28	32.14	9.57	5.61	-	1.81	12.12	7.30	4.00	-	-
4b	-	-	-	0.72	11.04	29.30	14.56	4.57	0.37	4.29	13.74	16.87	4.55	-	
4c	-	-	-	-	15.15	31.26	18.94	2.31	0.26	1.52	21.87	5.44	3.25	-	-
5a	-	0.43	0.49	1.36	6.23	10.86	-	3.44	-	2.94	51.04	4.79	18.41	-	-
5b	-	0.52	0.39	0.36	8.06	10.08	-	1.51	-	3.51	54.17	5.20	16.21	-	-
5c	-	-	-	1.56	6.76	12.14	-	3.41	0.26	3.43	54.08	-	18.38	-	-
6a	-	-	-	0.96	6.62	13.74	0.18	2.73	0.29	5.78	50.41	3.81	15.48	-	-
6b	-	1.52	-	0.29	3.75	7.57	-	1.60	-	1.65	53.75	4.43	25.44	-	-
6c		1.57	-	0.48	5.17	10.63	-	2.29	-	1.55	54.28	2.90	21.14	-	-

Work Sheet – Averaged Intensity (Counts)/Element
6043.1. Inclusions: Cl–3–45 (MIT–5136)
25 kV, 120 Secs. Working Distance = 39 mm 30,000 – 70, 000X

Probe	C	O	Na	Mg	Al	Si	K	Ca	Pb	S	Ti	Cu	Zn	Fe	Ag	Au	
1a	4263	15805	12131	5095	29004	92961	11989	27887	25123	-	884	10809	-	11955	-	482	
1b	4406	16681	14263	4012	32907	92983	12945	32742	27877	-	827	10183	-	10808	-	376	
1c	3608	9649	-	2206	14775	63041	8093	34390	23637	-	861	15820	14181	8873	-	1547	

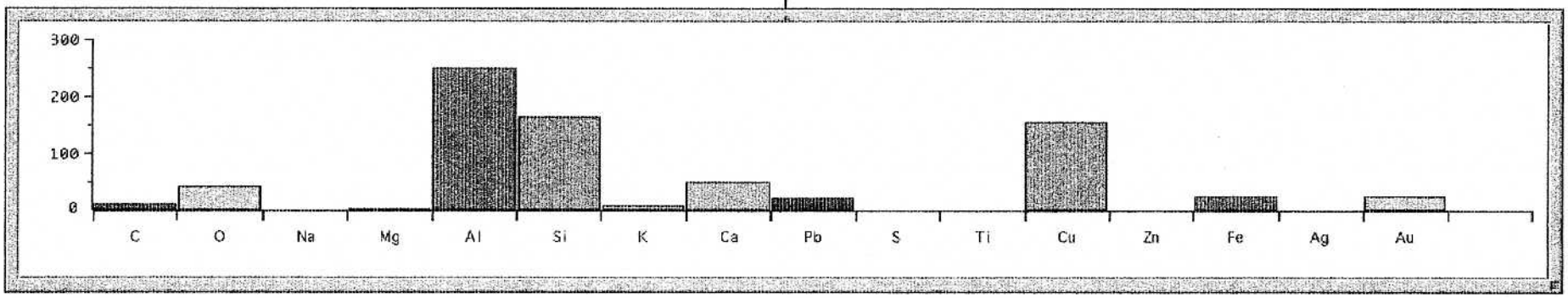
12277	42135	26394	11313	76686	248985	33027	95019	76637	0	2572	36812	14181	31636	0	2405	0	



Work Sheet – Averaged Intensity (Counts)/Element
6043.2. Inclusions: CI-3-45 (MIT-5136)
25 kV, 120 Secs. Working Distance = 39 mm 30,000 – 70,000X

Probe	C	O	Na	Mg	Al	Si	K	Ca	Pb	S	Ti	Cu	Zn	Fe	Ag	Au	
2a	4138	14377	-	-	21152	50841	2605	9204	2997	-	-	67189	-	7981	1202	16185	
2b	3845	14343	-	1867	210587	56447	3046	17097	17454	-	678	44512	-	9211	-	1375	
2c	3576	12631	-	2225	18368	55802	1379	23534	1282	-	-	43270	-	8279	-	6502	

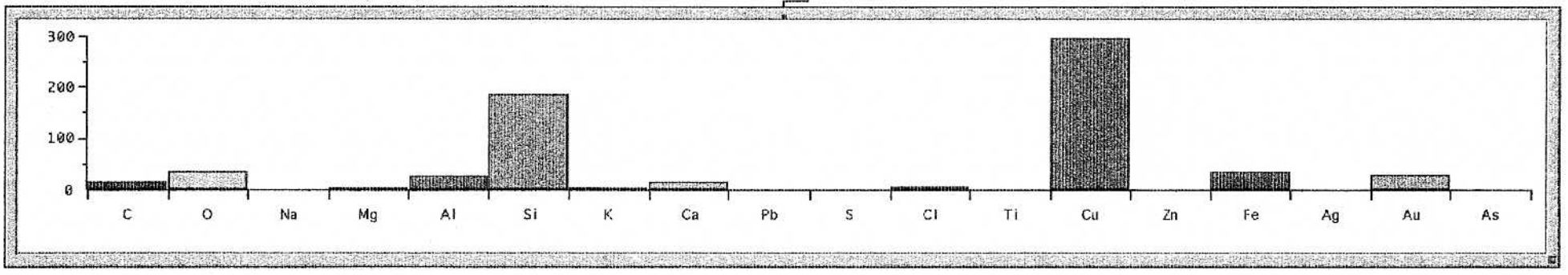
11559	41351	0	4092	250107	163090	7030	49835	21733	0	678	154971	0	25471	1202	24062	0	



Work Sheet – Averaged Intensity (Counts)/Element
6043.3. Inclusions: CI-3-45 (MIT-5136)
25 kV, 120 Secs. Working Distance = 39 mm 30,000 – 70,000X

Probe	C	O	Na	Mg	Al	Si	K	Ca	Pb	S	Cl	Ti	Cu	Zn	Fe	Ag	Au	As
3a	4578	14261	-	-	11089	76295	1416	3078	-	-	-	-	77233	-	12378	773	14898	1074
3b	4279	10309	-	1026	7348	47984	1124	8285	1363	-	5335	-	118451	-	11387	-	7232	-
3c	5848	10992	-	939	8690	61140	1097	3207	-	-	-	-	101075	-	11013	-	7134	-

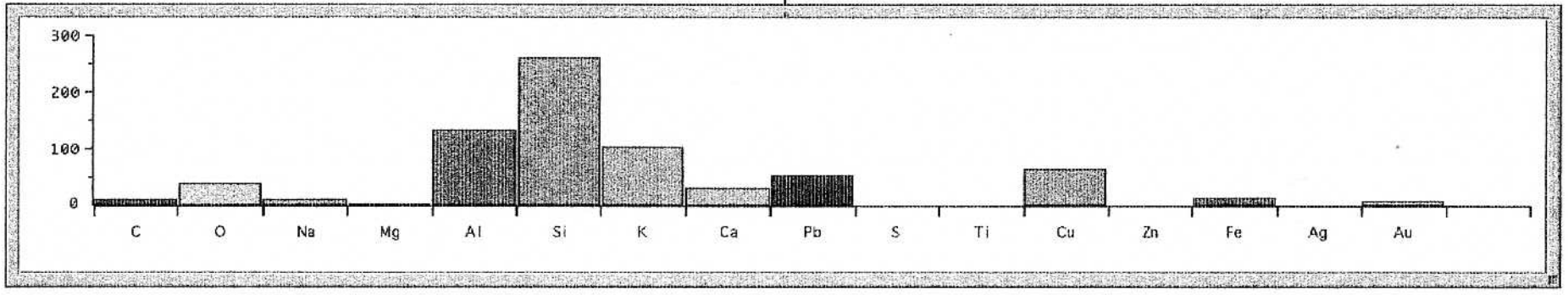
14705	35562	0	1965	27127	185419	3637	14570	1363	0	5335	0	296759	0	34778	773	29264	1074



Work Sheet – Averaged Intensity (Counts)/Element
6043.4. Inclusions: CI-3-45 (MIT-5136)
25 kV, 120 Secs. Working Distance = 39 mm 30,000 – 70, 000X

Probe	C	O	Na	Mg	Al	Si	K	Ca	Pb	S	Ti	Cu	Zn	Fe	Ag	Au	
4a	3597	14769	11261	-	61813	90173	22799	14336	12152	-	-	14680	-	2487	-	5350	
4b	4104	12931	-	1714	31865	90309	35337	11774	31100	-	689	19013	-	8156	-	1375	
4c	4183	10720	0	0	38502	80629	43412	5555	8599	-	428	28821	-	2373	-	710	

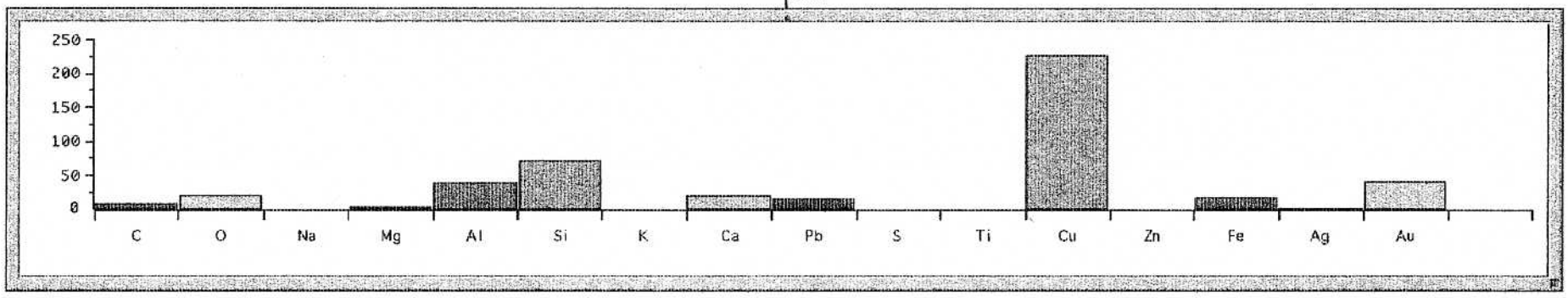
11884	38420	11261	1714	132180	261111	101548	31665	51851	0	1117	62514	0	13016	0	7435	0	



Work Sheet – Averaged Intensity (Counts)/Element
6043.5. Inclusions: Cl–3–45 (MIT–5136)
25 kV, 120 Secs. Working Distance = 39 mm 30,000 – 70, 000X

Probe	C	O	Na	Mg	Al	Si	K	Ca	Pb	S	Ti	Cu	Zn	Fe	Ag	Au	
5a	3533	9083	-	2968	15563	34478	-	12517	7511	-	-	98860	-	8148	631	19866	
5b	4015	10171	-	874	19001	29173	-	4529	9364	-	-	102477	-	8669	701	18986	
5c	809	2298	-	704	3793	8761	-	3104	-	-	183	25683	-	1638	-	3732	

8357	21552	0	4546	38357	72412	0	20150	16875	0	183	227020	0	18455	1332	42584	0	



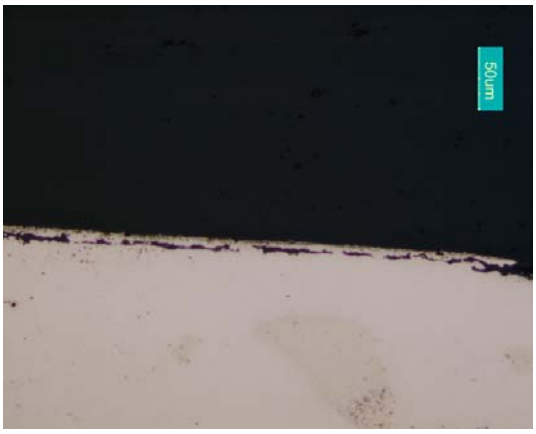
8/10/06

Photomicrography of CL-3-45 metallographic cross-section
Melvin J. Wachowiak

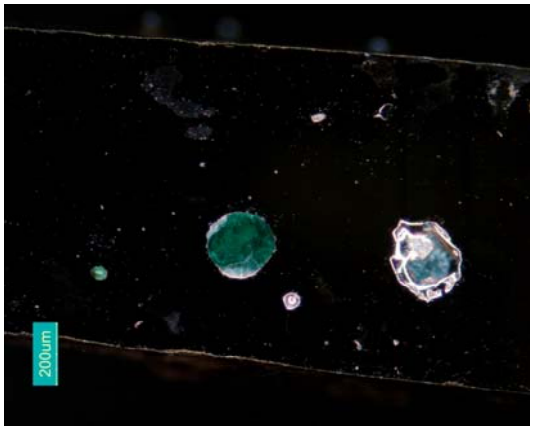
Commentary
Aaron N. Shugar

Photographs taken with a Leica DMLM
Magnification range: 50x-500x
Illumination: transmitted light, bright field and dark field

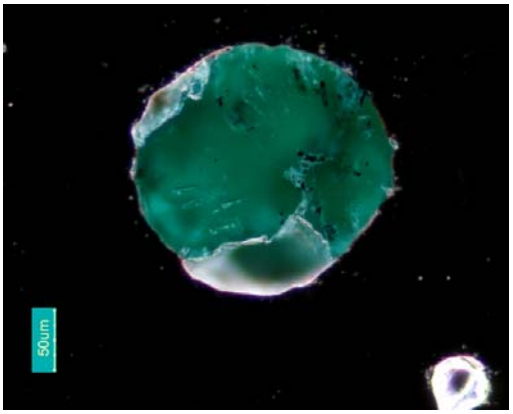
CL-3-45 cross-section (embedded and polished), bright field illumination: detail showing gold-rich and copper-rich phases and thin gold surface layer



CL-3-45 cross-section (embedded and polished), bright field illumination: detail showing zone of flattened voids just below gold surface layer

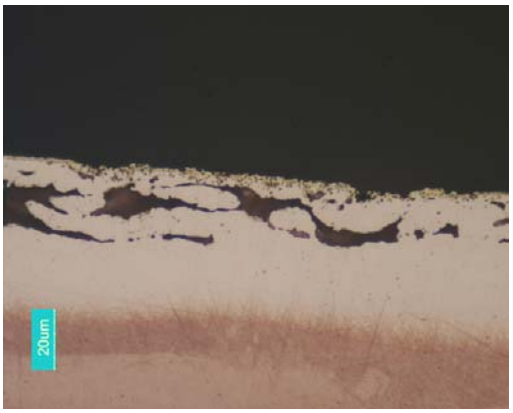


CL-3-45 cross-section (embedded and polished), dark field illumination: thin gold surface layers and inclusions are visible



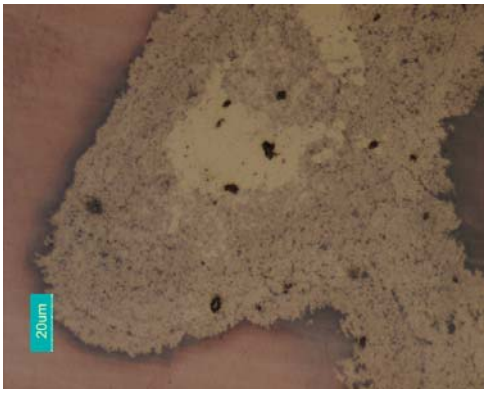
CL-3-45 cross-section (embedded and polished), dark field illumination: detail of inclusion

CL-3- cross-section (embedded, polished and etched): different alloy phases are visible, particularly in the zone adjacent to thin gold surface layers



CL-3-45 cross-section (embedded, polished and etched), bright field illumination: detail showing zone of flattened voids just beneath gold surface layer

CL-3-45 cross-section (embedded, polished and etched): detail of surface zone



CL-3-45 cross-section (embedded, polished and etched), bright field illumination: detail showing gold-rich and copper-rich phases