

*Quantitative
Rietveld XRD
Mineralogy of
Copper and
Molybdenum Ore
Products*

Doug Allen

April 24, 2012

Safety Share – Watch the Ground – Even in the Parking Lot



Our Targets
Reduce Cost, Minimize Risk, Optimize Metallurgy



- **Profitable Cu Recovery**
- **Longevity of Lower Grade Resources**
- **Getting Maximum Value & Mine Life Out of Existing Resources & Core Assets.**



Mineralogy – The Driver for Ore Control & Processing

Concentrators

Comminution
Ore Hardness
Liberation/Locking
Reagent Use/Consumption
Selectivity
Middlings
Thickener Problems
Optimal Recovery
Slimes Generation

Heap/Stockpile Leaching

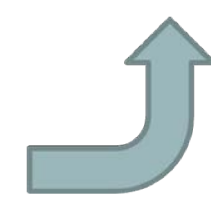
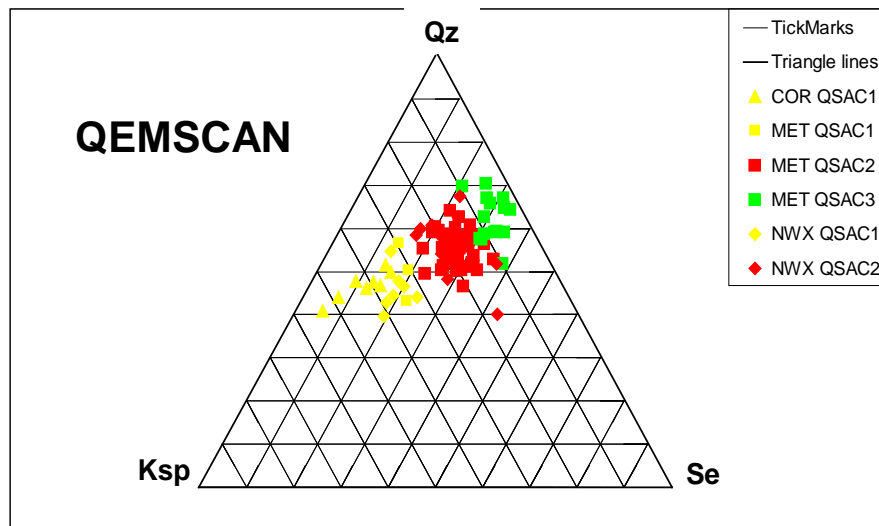
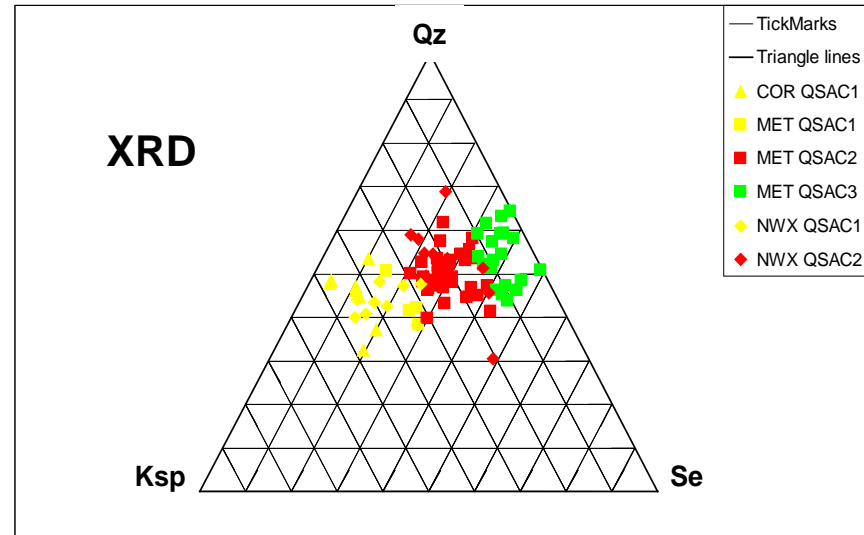
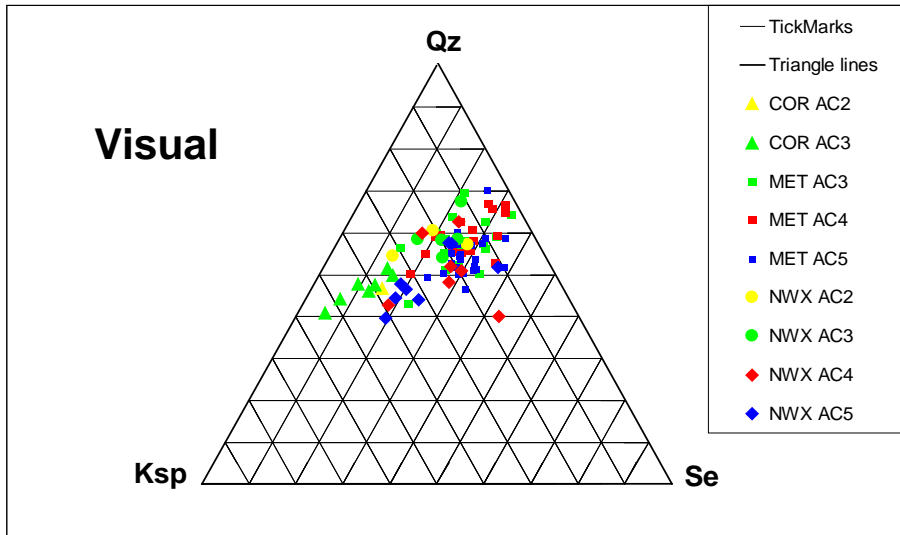
Crushing Response
Throughput
Agglomerate Quality
Moisture Addition
Liquid & Air Permeability
Cu Extraction
Salt Precipitation
Pyrite Content
PLS Impurities
Acid Consumption

Mineralogical Parameters Affect All Of The Process Parameters

Ore Control & Process Optimization Require New Tools

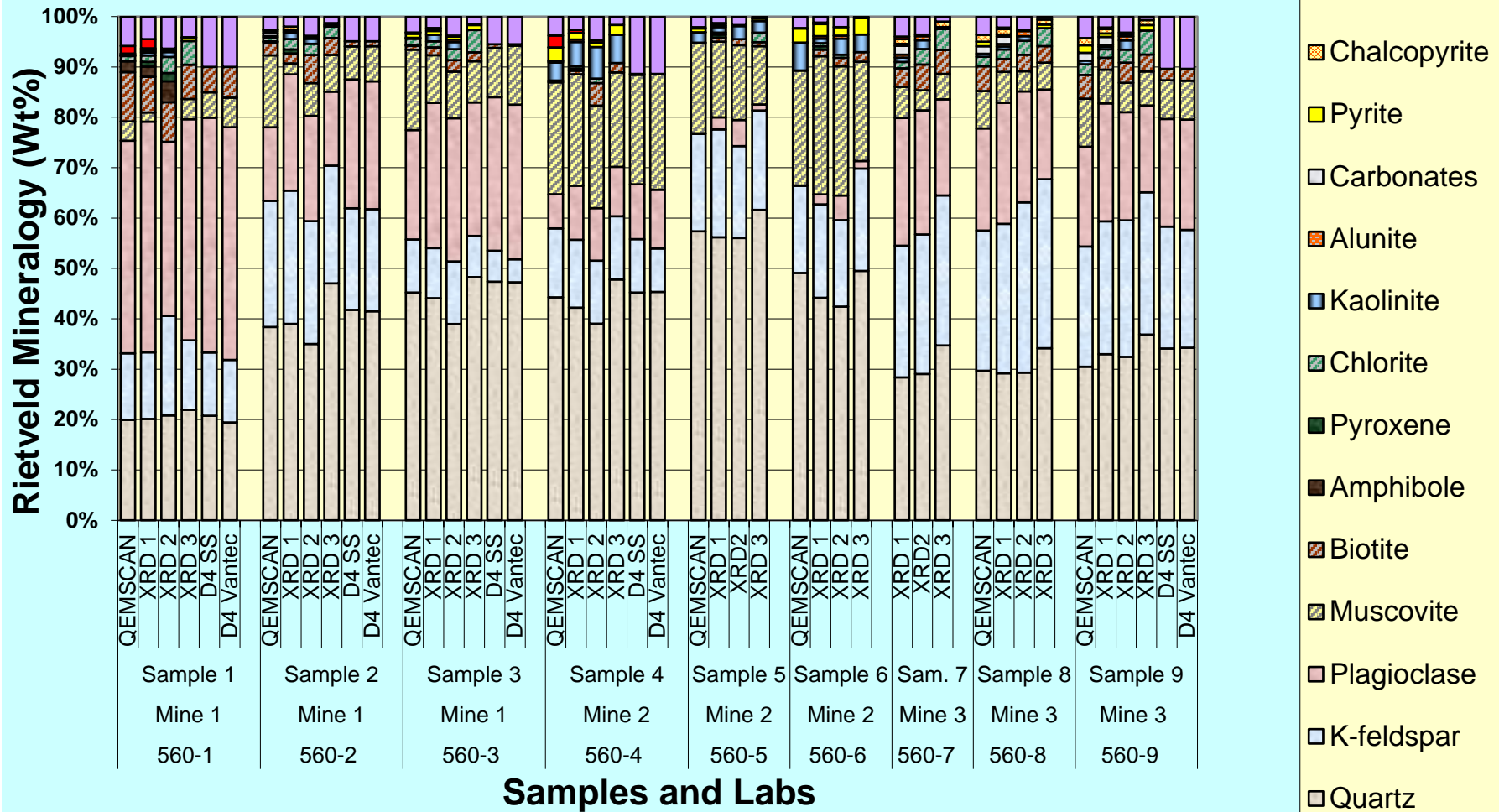


Ore Type Coding Comparison



Graphical Presentation of Data

Rietveld Round Robin Results



Freeport-McMoRan Technology Center XRD History



Year	Developments	Instru- ments	Miner- alogist	Tech- nician	XRD /Yr	NIR /Yr
2000	Occasional XRD by microscopists. Old orphaned Philips	1	0.2	0	~100	
2002	Rietveld by contract for NIR models. 1st Bruker D4	1	1	0	~100	
2003	Began in-house support of NIR Models	1	1	1	~1K	
2004	Began micronizing	1	1	2	~2K	
2005	Changed to Co Radiation. Phased out contract lab.	2	2	3	~3K	
2006	Earliest in-house automated Rietveld	2	2		~4K	
2007	Design of Automated AXN Lab	4	2		7K	
2008	Construction of AXN Lab	4	2	5	14K	
2009	Began AXN Operations	7	5	9	17K	100K
2010	Automated import of Results to Excel or LIMS	7	6	9	24K	110K
2011	Fully implemented automated Rietveld.	7	7.5	12	28K	168K
2012	Implemented chemistry reconciliation macro	7	7	13	36K	185K

XRD-NIR Design Capacity



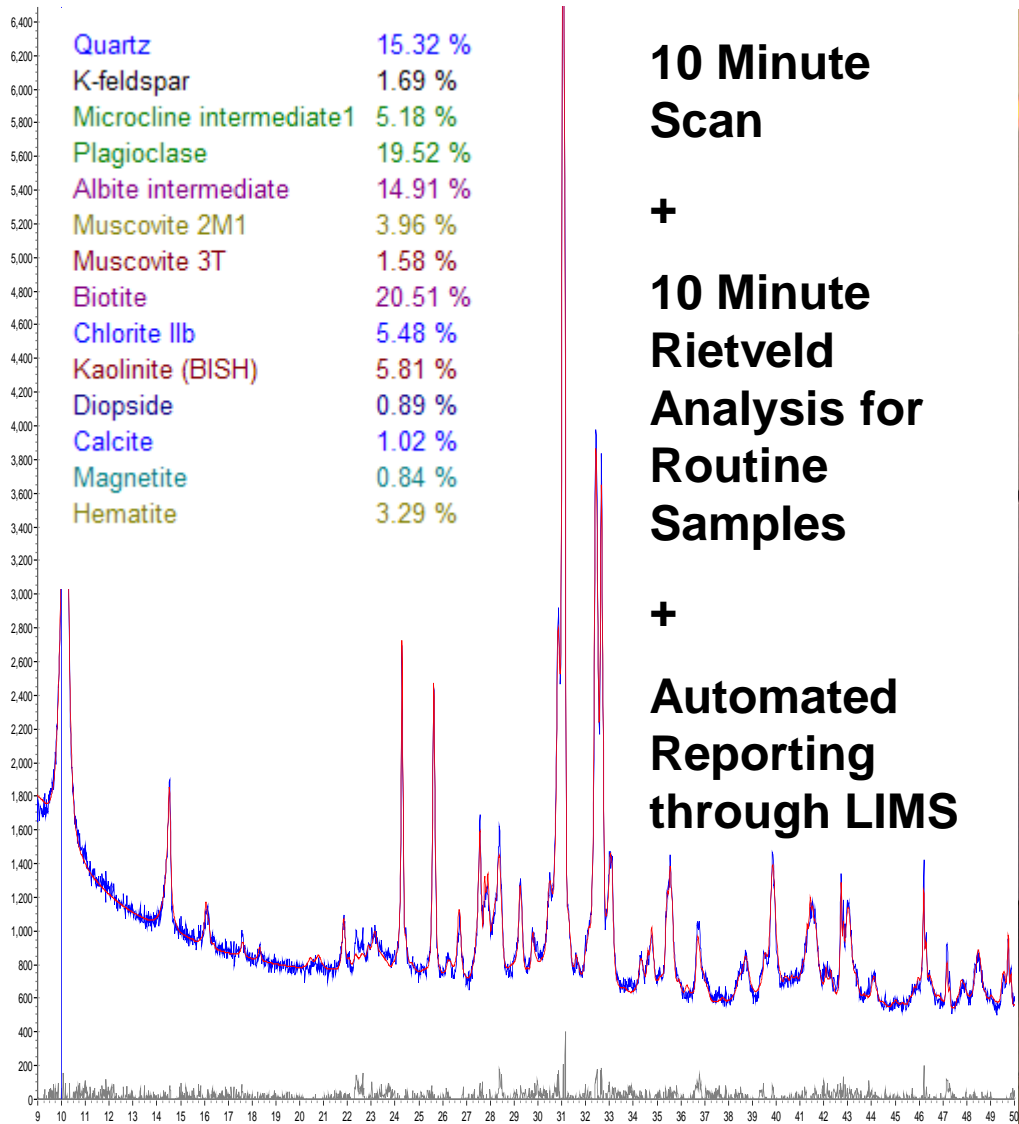
- **500 Samples/Day + 50 QC Samples – XRD**
- **700 Samples/Day + 50 QC Samples – NIR**

- **Turnaround 24-36 Hours**

- **24 hour/day operation**

- **Automatic Transfer of Blast Hole Splits From Central Analytical Services Center (CASC)**

XRD Analysis



10 Minute Scan

+

10 Minute Rietveld Analysis for Routine Samples

+

Automated Reporting through LIMS



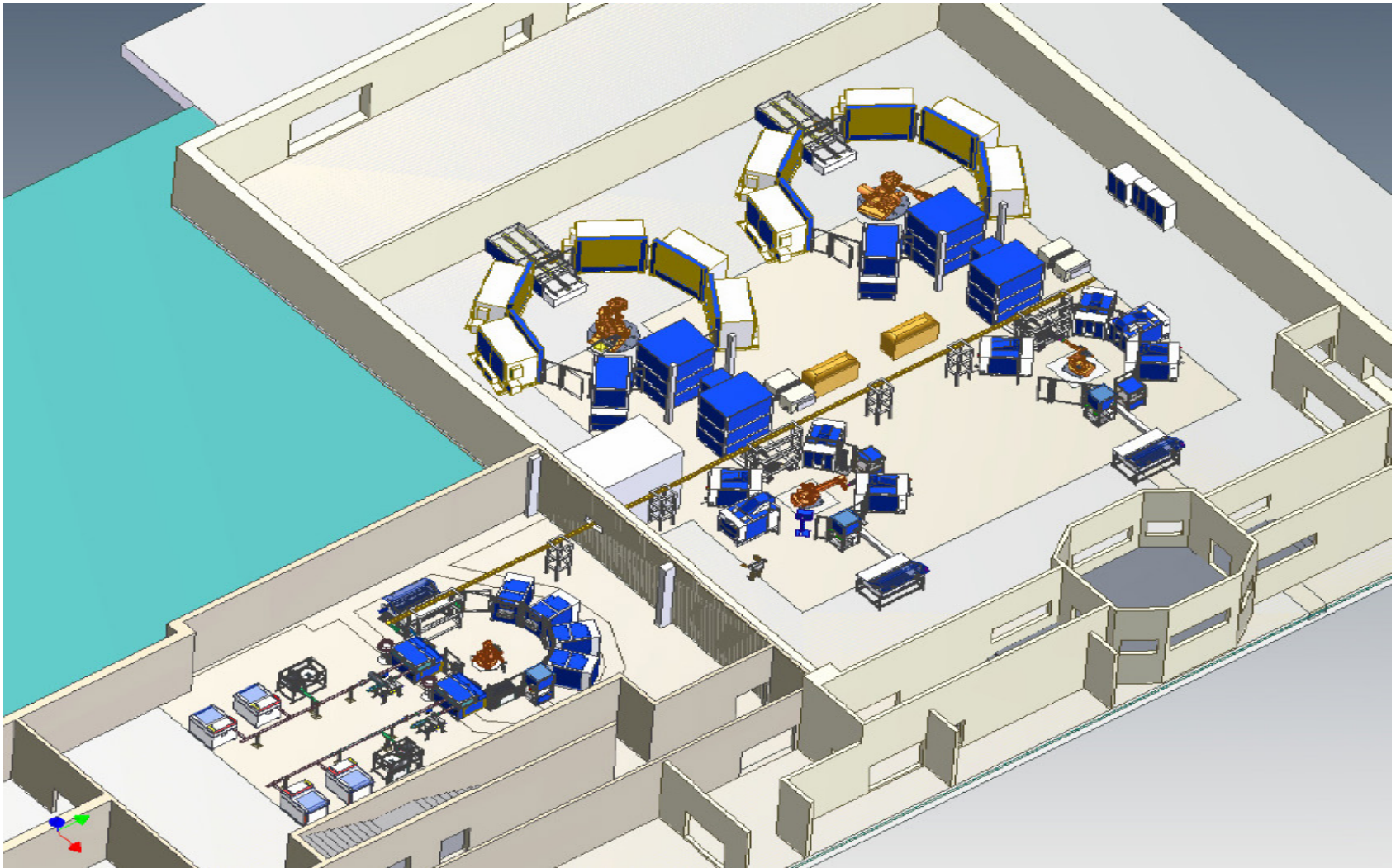
Near Infrared (NIR) at AXN Lab

- High Performance
- Extremely Fast Scanning Time
30 seconds
- Very User Friendly
- Analyzes for Clay and Alteration Minerals
- Excellent tool for Resource Control
- **Calibration Model Must be Constructed for Each Ore Body – 300 to 500 XRD Refinements**
- Non-destructive Testing
- NIR eliminates the need for the hazardous reagents and time consuming analysis



Auto XRD-NIR (AXN) Lab Safford

High Throughput-Low Cost Mineralogical Ore Profiling



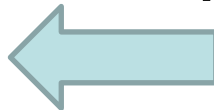
Auto XRD-NIR Lab Safford

High Throughput-Low Cost Mineralogical Ore Profiling

Modern “Bucking” Room



**Automatic XRD and NIR
Data Capture**



XRD-NIR Instrument Room



Prepmaster Control Software

Sample registration

Show samples

Messages

Define Worksheet

RAS numbers

Processed Samples

Playback

Sample Counters

RUN HOLD

Sample Counters

Daily Counters	Line 1
XRD	21
NIR	54
Total	55

Reset Daily Cou

Total Counters	Line 1
XRD	21
NIR	54
Total	55

Reset Total Cou

Both Lines	Daily
XRD	44
NIR	100
Total	102

...	Type	Location	Message	Infotext
1	Message	HPM 90	M04 Machine in operation	
2	Message	HP-PD6 #1	M04 Machine is ready for operation	
3	Message	NIR Automation #1	M03 Machine ready for operation	
4	Message	Transport XRD/NIR #1	M03 Machine ready for operation	
5	Message	Transport XRD/NIR #2	M03 Machine ready for operation	
6	Message	NIR Automation #2	M03 Machine ready for operation	
7	Message	HP-PD6 #2	M02 Machine is in operation	
8	Message	XRD #3	S01 No measurement active (on line,idle)	

7/22/2009 10:25:15 AM

HERZOG

Login

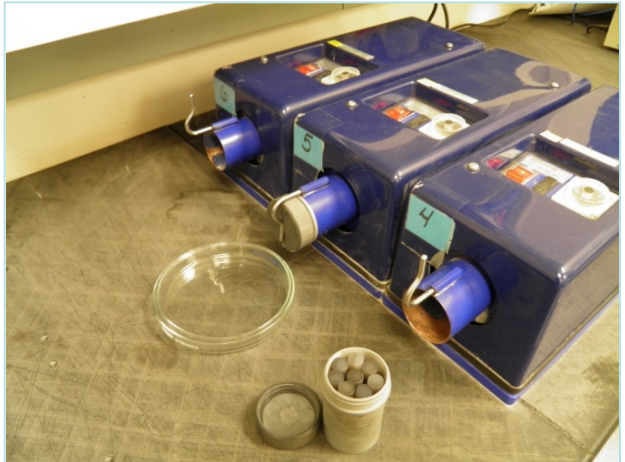
Exit

Shutdown

Show system tray

7/22/2009 10:25 List: 20 Window: 20

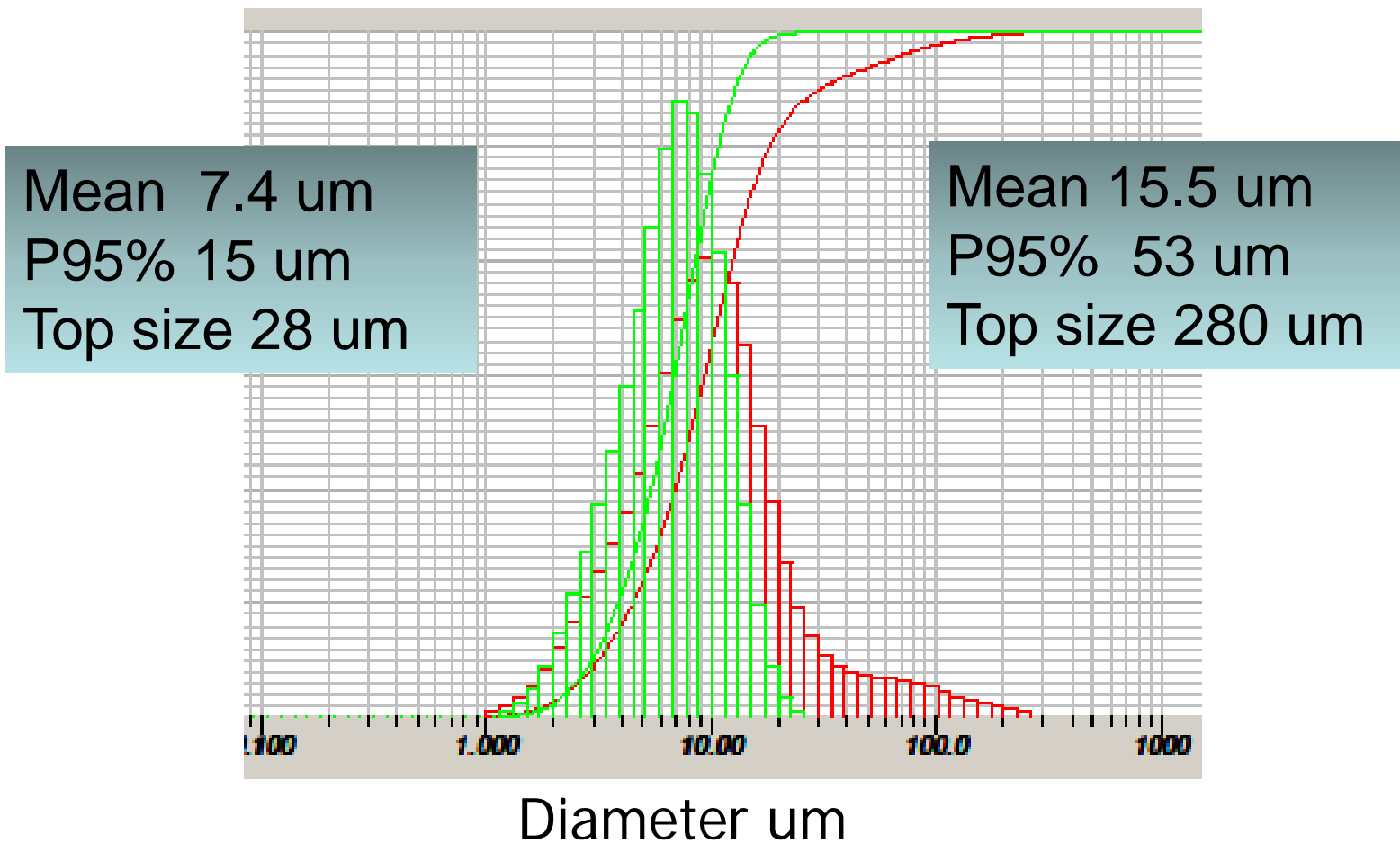
Micronizing Lab – Not Automated



Typical Particle Size



Wet Micronize vs Auto Dry Grind



Press Requirements



Developing an automated press designed for XRD (not XRF) was the key to the automated circuit.

Back-Loading Against Frosted Surface

No Binder

Low Pressure

Minimize Preferred Orientation

Press Development



Manual Prototype



Herzog Automation



AXN QA/QC Overview



- **NIST Corundum standard analyzed daily on each XRD
EVA peak position and area plotted on control chart**
- **Mylar Standard analyzed daily on NIR**
- **AXN Ore Standard (Granite) analyzed daily on each XRD
Synthetic standard being developed for XRD
Topas Rietveld refinement results for charting**
- **Site Specific Ore Standards analyzed daily on NIR**
- **Minimum of 5 % of samples are duplicated**
- **Blank (Glass) samples prepared daily to check for contamination**
- **Pulverizing mills checked daily to ensure proper particle size is produced**

NIST 1976 Mounted in Bruker Ring

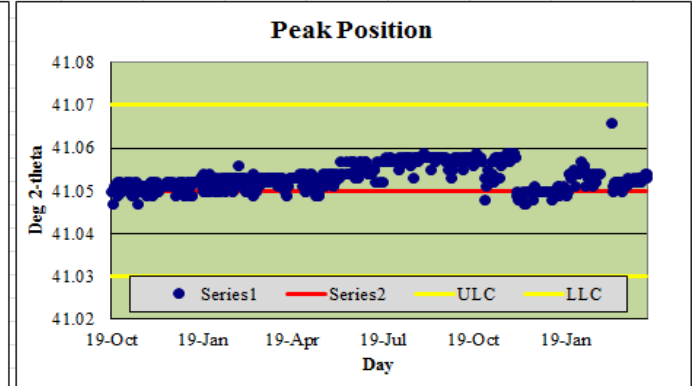
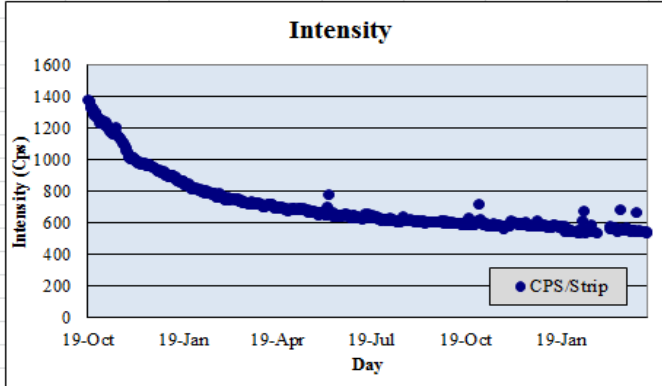
XRD # 4 Oct 2011 to Apr 2013

XRD 4 Control Charts

Tube installed: 10/18/2011
 Nominal net height: 1058
 Intensity average this week: 549
 Tube strength(percent of initial): 51.85%
 Average peak position this week: 41.053
 End of Week PM counter: 7849

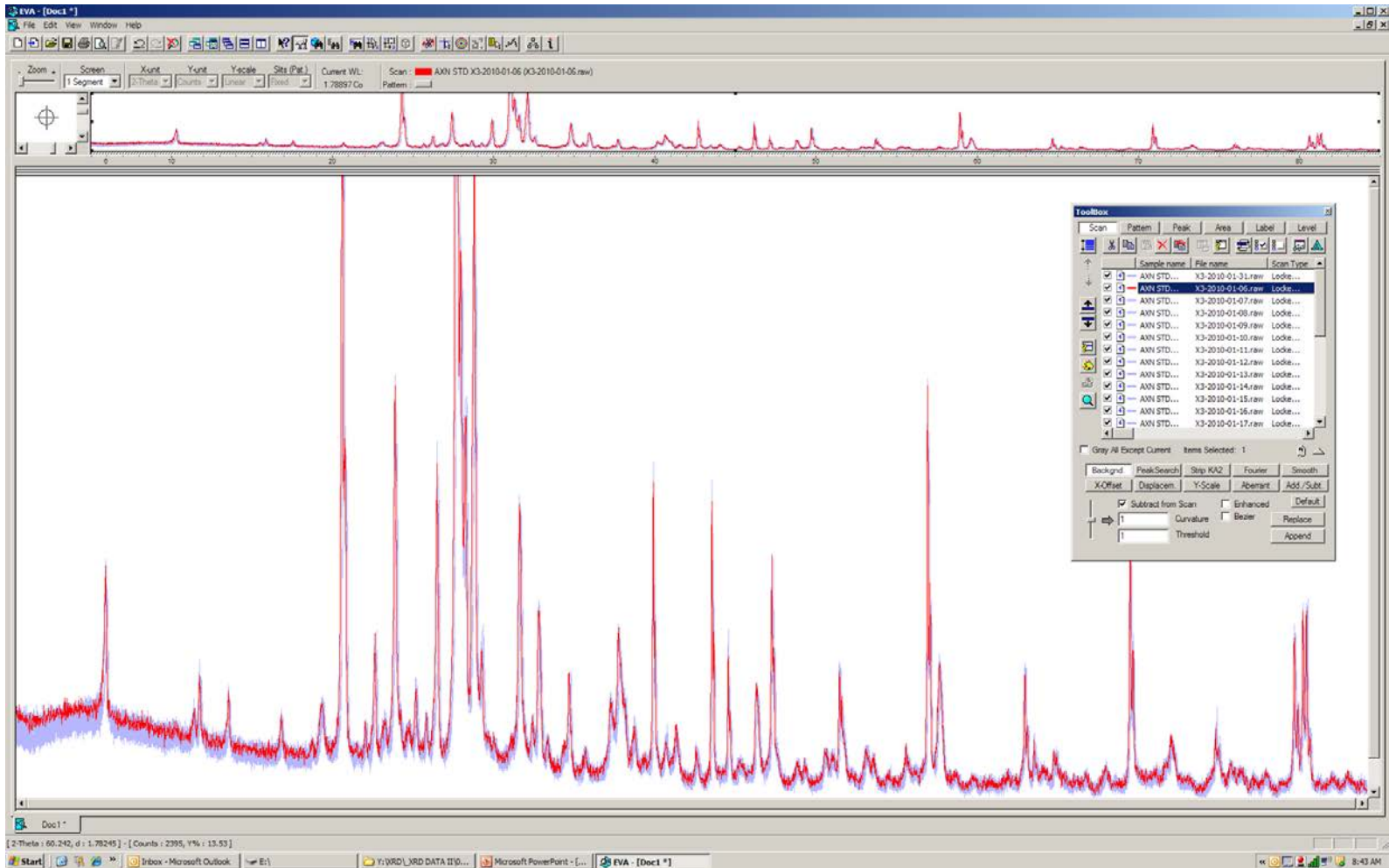
Comments:

No Data 4/6, 7



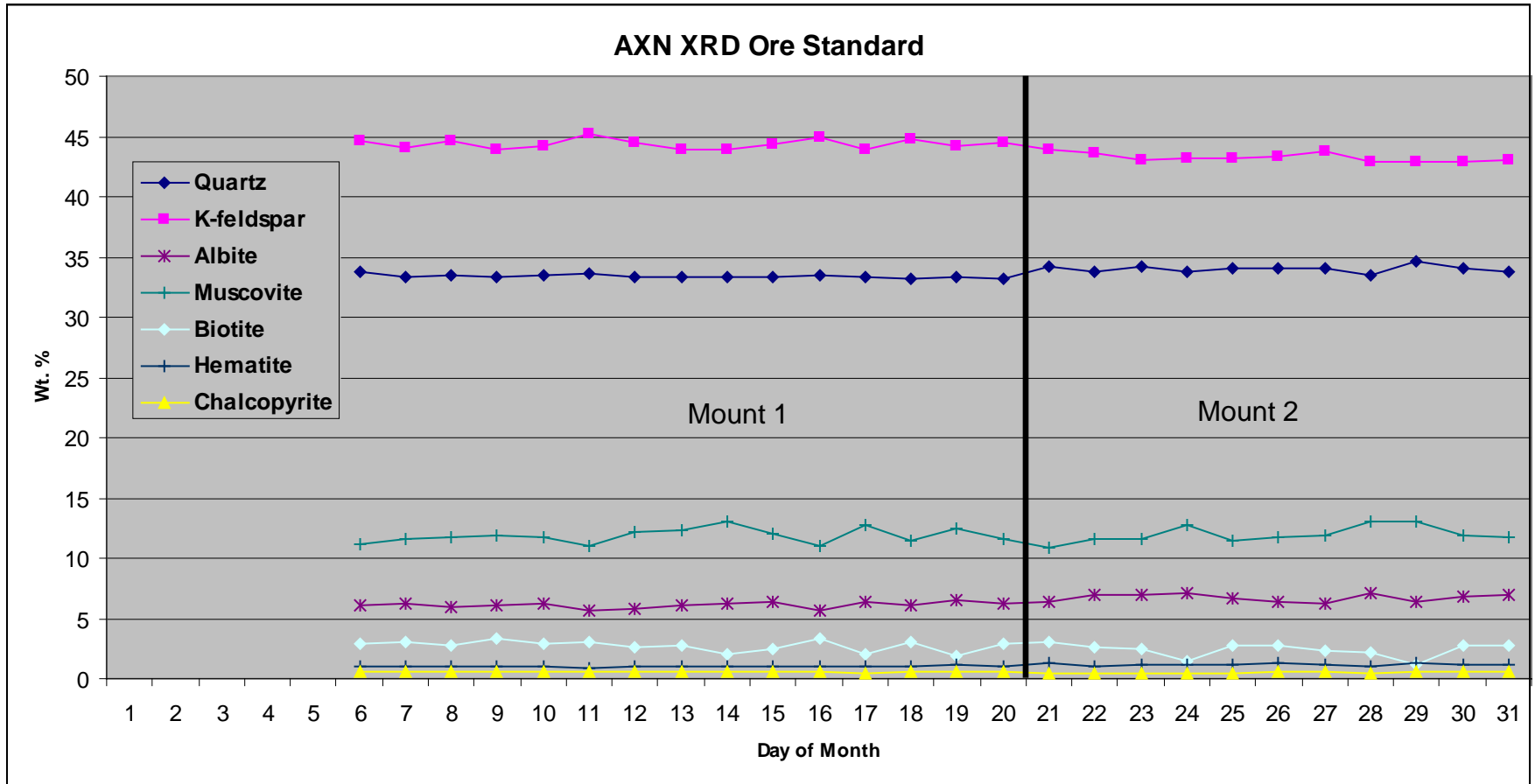
		NIST 1976			Targeted Peak		
Creation Date/Time	Obs. Max (peak position)	Net Height (intensit)	FWHM (peak wid)	Position	ULC	LLC	
3/20/2013 5:58	41.052	564	0.064	41.05	41.07	41.03	
3/21/2013 5:55	41.051	567	0.064	41.05	41.07	41.03	
3/22/2013 6:00	41.052	574	0.064	41.05	41.07	41.03	
3/23/2013 5:38	41.053	567	0.063	41.05	41.07	41.03	
3/24/2013 5:54	41.052	557	0.064	41.05	41.07	41.03	
3/25/2013 5:50	41.052	560	0.064	41.05	41.07	41.03	
3/26/2013 6:02	41.052	550	0.066	41.05	41.07	41.03	
3/27/2013 6:17	41.052	561	0.065	41.05	41.07	41.03	
3/28/2013 5:58	41.052	557	0.065	41.05	41.07	41.03	
3/29/2013 6:25	41.053	557	0.064	41.05	41.07	41.03	
3/30/2013 5:59	41.052	557	0.065	41.05	41.07	41.03	
3/31/2013 5:57	41.052	555	0.064	41.05	41.07	41.03	
4/1/2013 8:36	41.053	669	0.065	41.05	41.07	41.03	
4/2/2013 5:47	41.053	554	0.066	41.05	41.07	41.03	
4/3/2013 5:47	41.053	557	0.064	41.05	41.07	41.03	
4/4/2013 5:48	41.053	549	0.066	41.05	41.07	41.03	
4/5/2013 6:16	41.052	555	0.064	41.05	41.07	41.03	
4/8/2013 13:10	41.053	550	0.065	41.05	41.07	41.03	
4/9/2013 6:03	41.054	550	0.065	41.05	41.07	41.03	
4/10/2013 5:48	41.054	547	0.065	41.05	41.07	41.03	
4/11/2013 6:42	41.053	542	0.065	41.05	41.07	41.03	

AXN XRD Granite Ore Standard XRD # 3 – January 2010



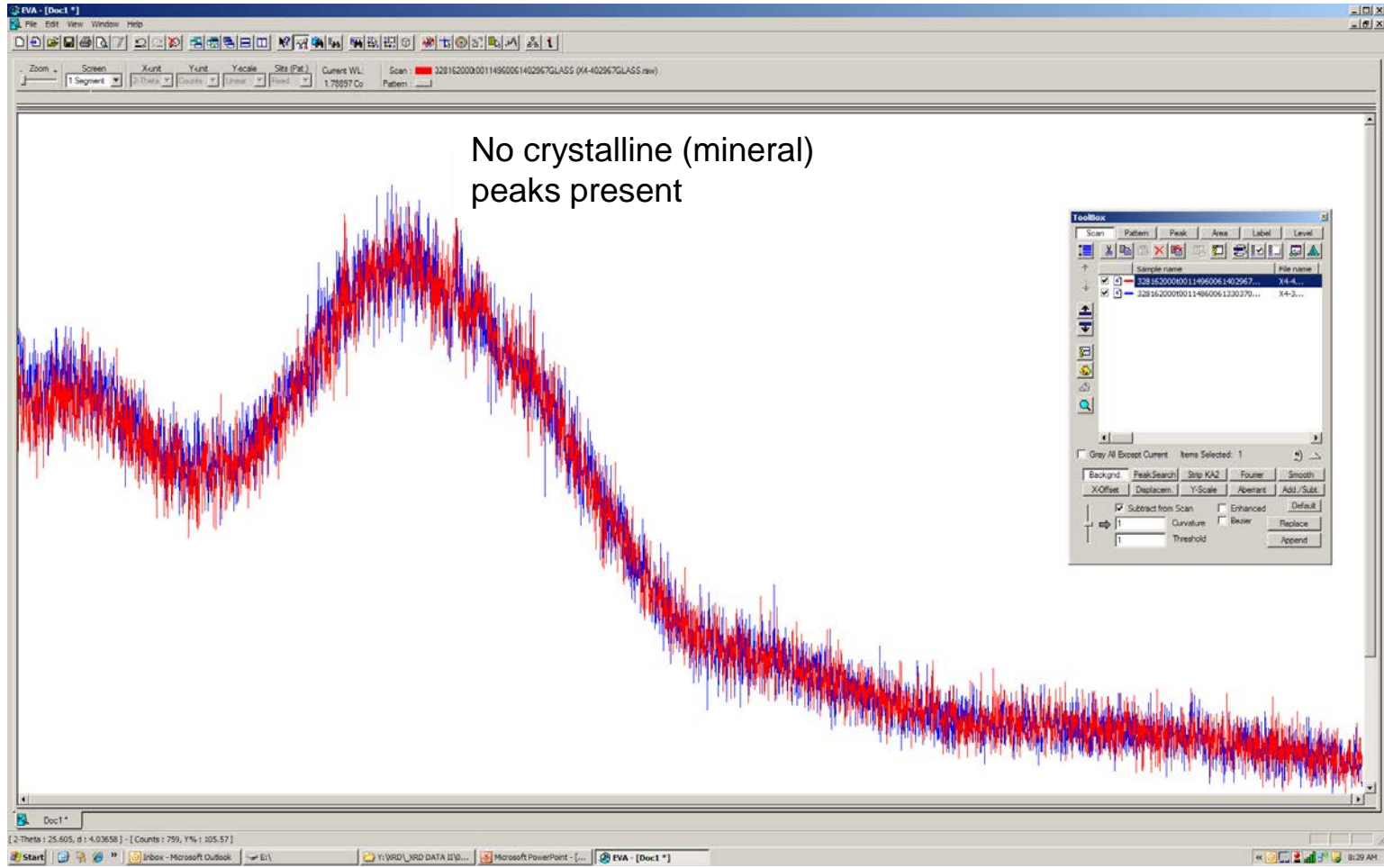
Sample analyzed daily on each XRD

AXN XRD Ore Standard XRD # 3 – January 2010



- Sample scanned every day on each individual XRD machines
- Mount replaced approximately every two weeks

AXN Glass Sample



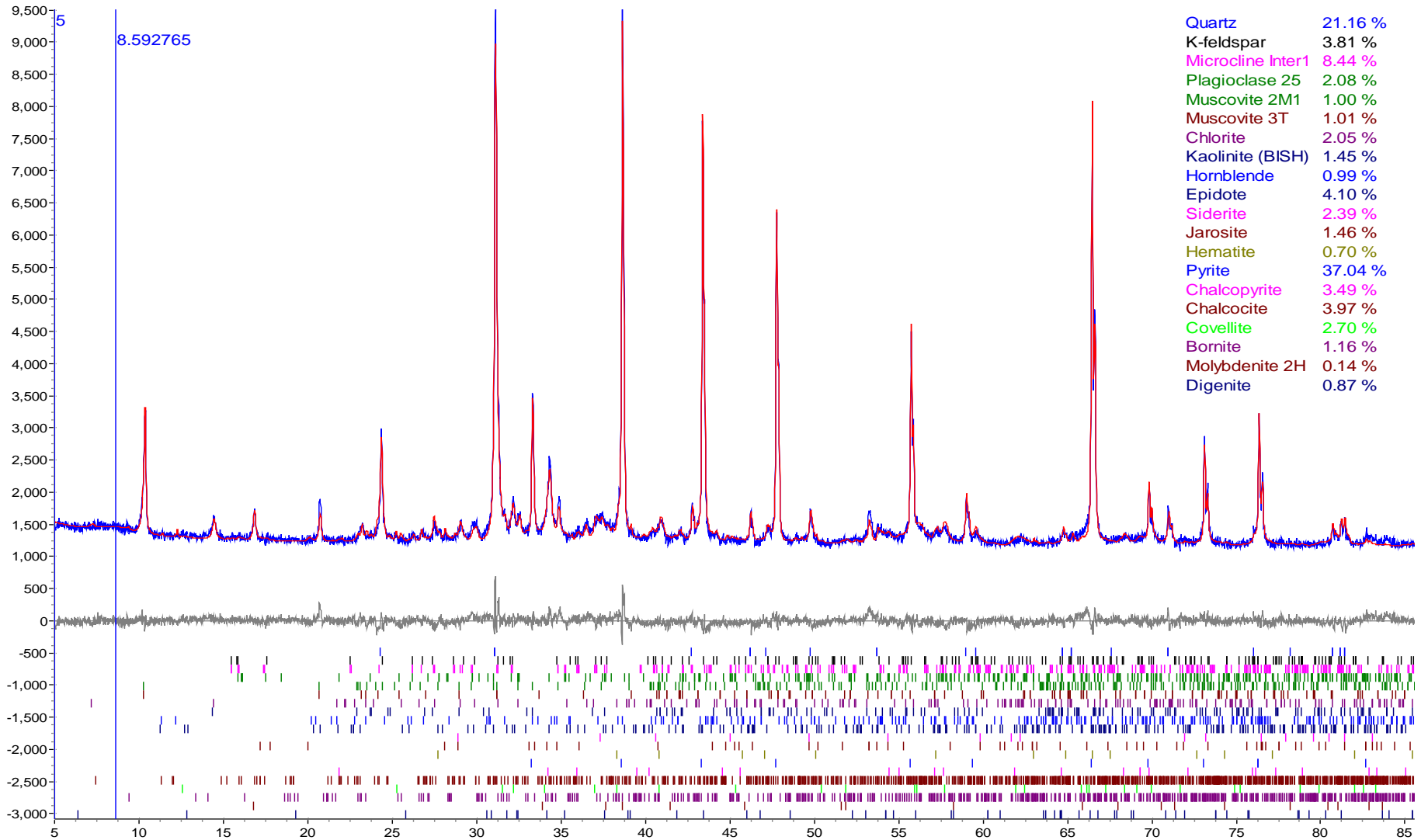
Scanned daily to check for contamination from the XRD mills

Bulk of Freeport-McMoRan XRD

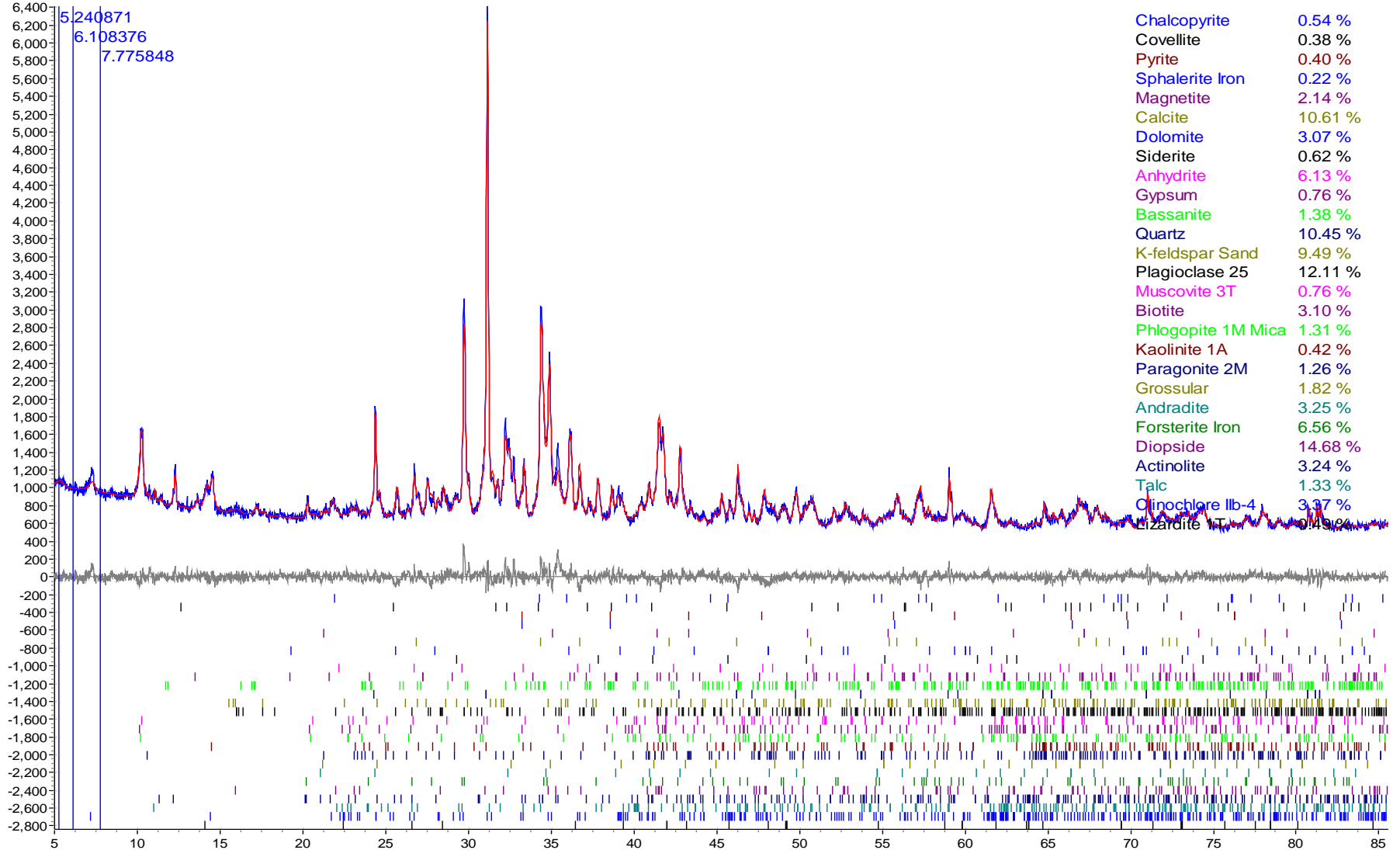


- Most Freeport-McMoRan samples are not complete unknowns.
 - Blasthole Samples.
 - Mill Feeds, Concentrates, Tailings.
 - Exploration Drill Core or Cuttings.
 - Leach Pile Feed & Residue Samples.
- We have a good idea of the minerals that are present in each project.
- Most large projects have very similar samples with variations in Wt%.
- Some sample types, however, are very complex.

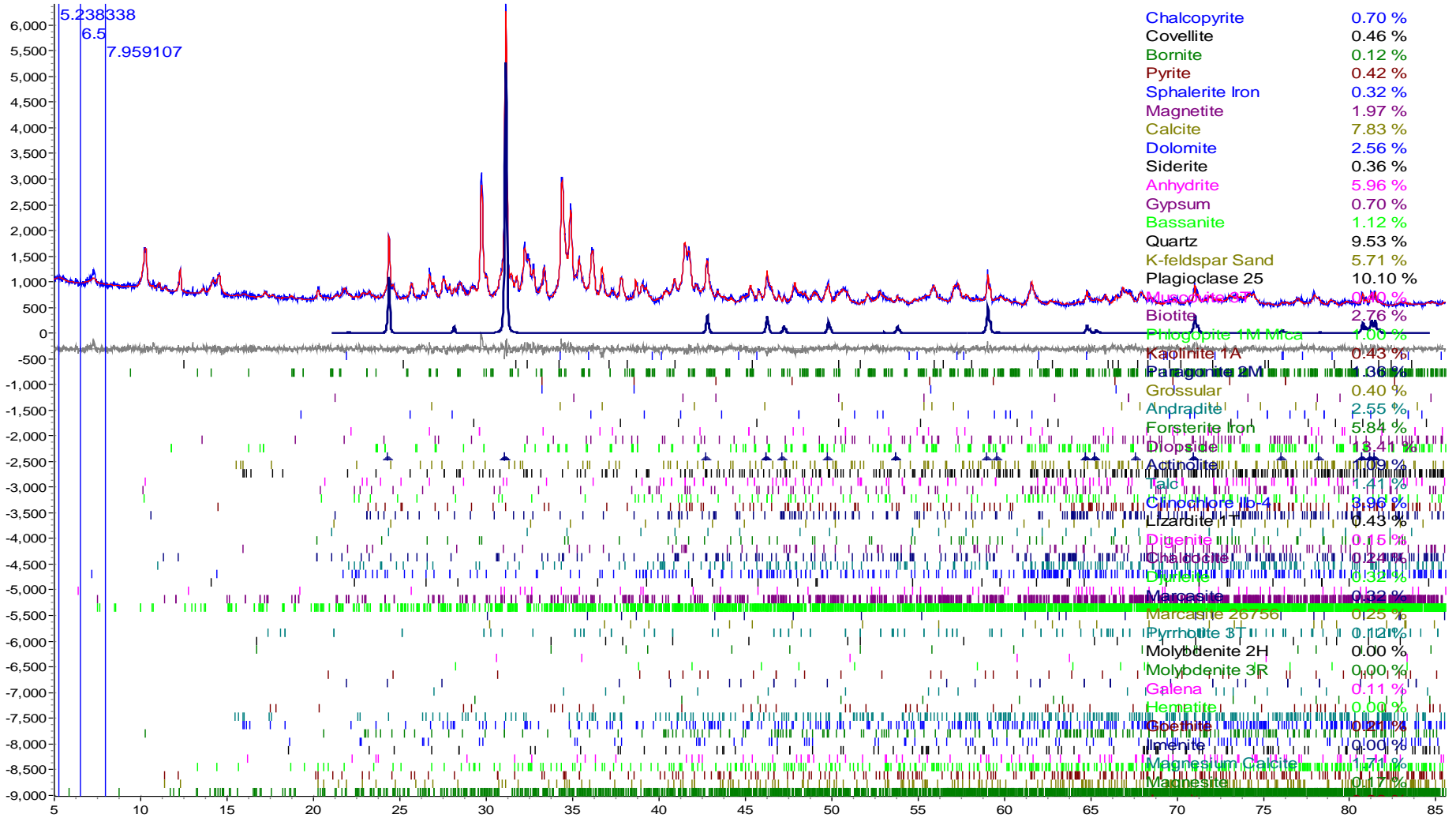
Typical Sample Copper Rougher Concentrate



A More Complex Mill Feed Composite



Full List of Minerals Pushes Topas Limits But It Still Converges



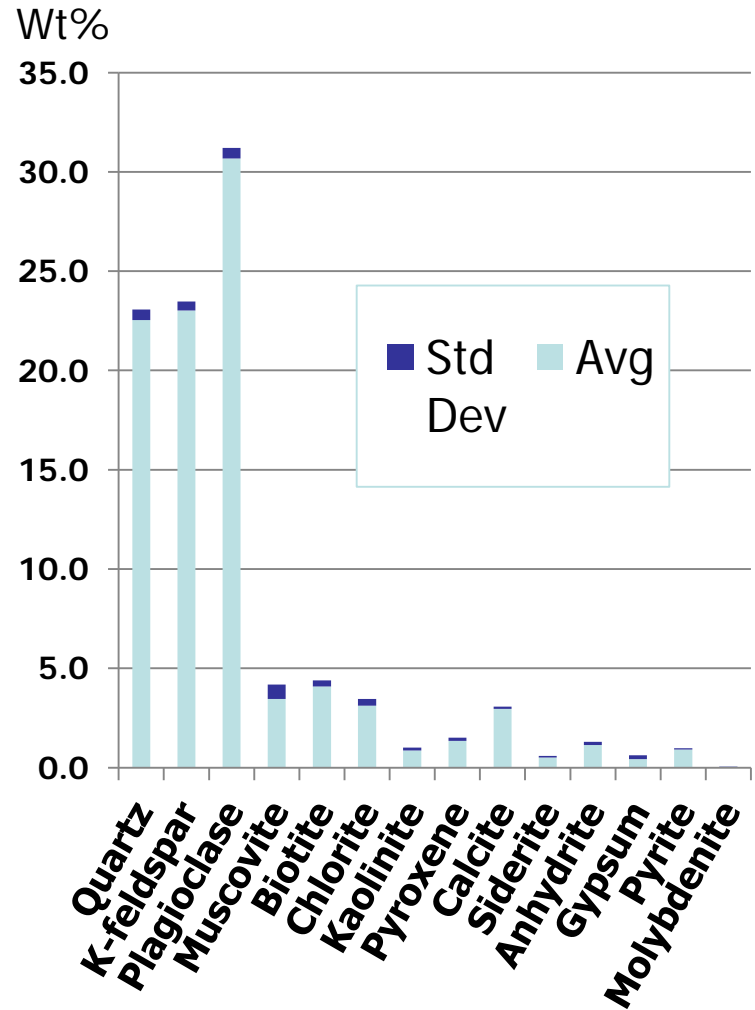
42 of 53 phases displayed

Typical Variability

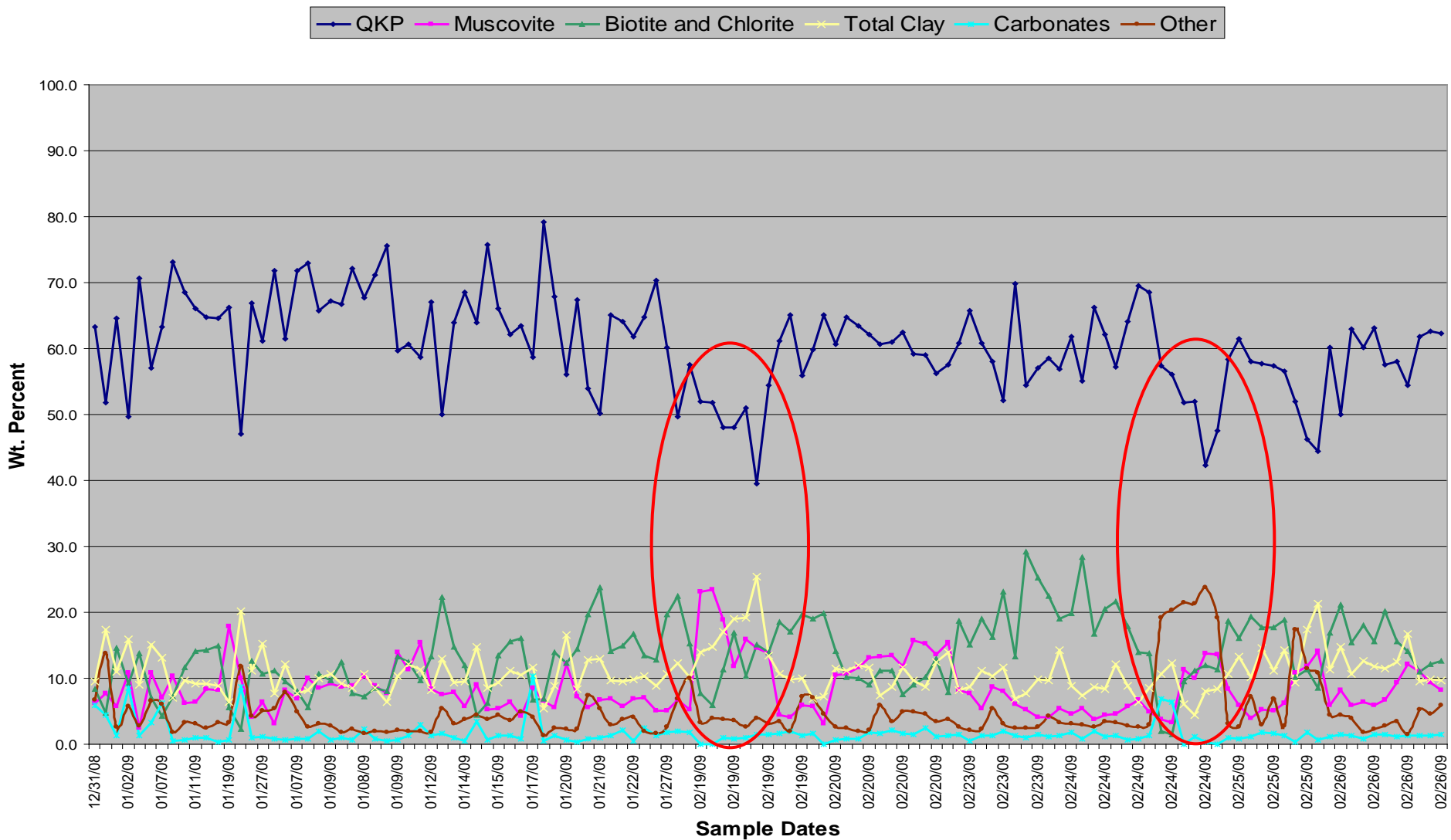
Mill Feed Composites

- Aug 2009 through April 2010.
- Two shift composites/day.
- Variability measured on 29 pairs of duplicates.

Mineral	Std	
	Avg	Dev
Quartz	22.5	0.53
K-feldspar	23.0	0.46
Plagioclase	30.7	0.52
Muscovite	3.5	0.72
Biotite	4.1	0.31
Chlorite	3.1	0.33
Kaolinite	0.9	0.15
Pyroxene	1.3	0.17
Calcite	3.0	0.11
Siderite	0.5	0.08
Anhydrite	1.1	0.16
Gypsum	0.4	0.19
Pyrite	0.9	0.08
Molybdenite	0.04	0.015

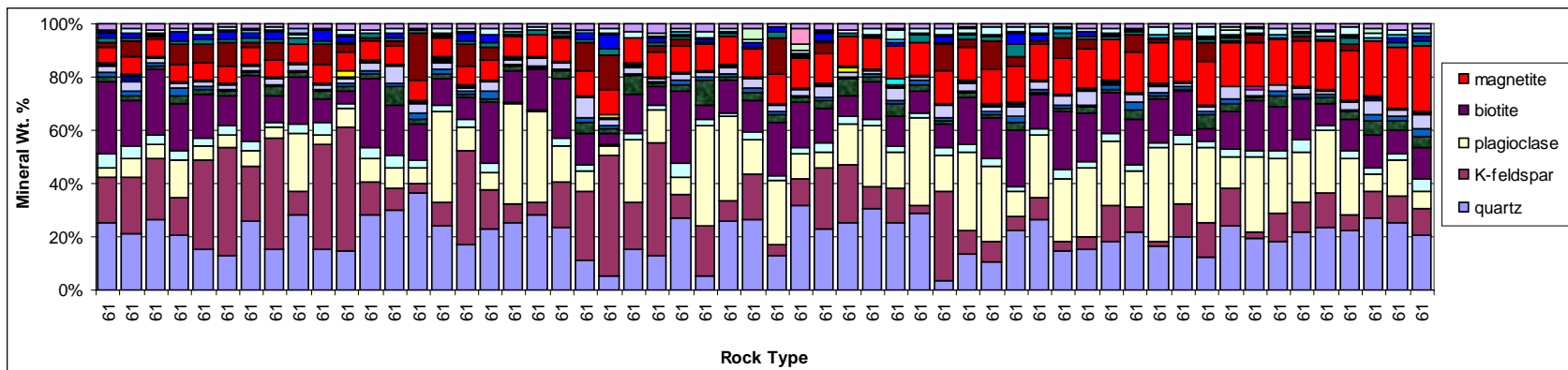
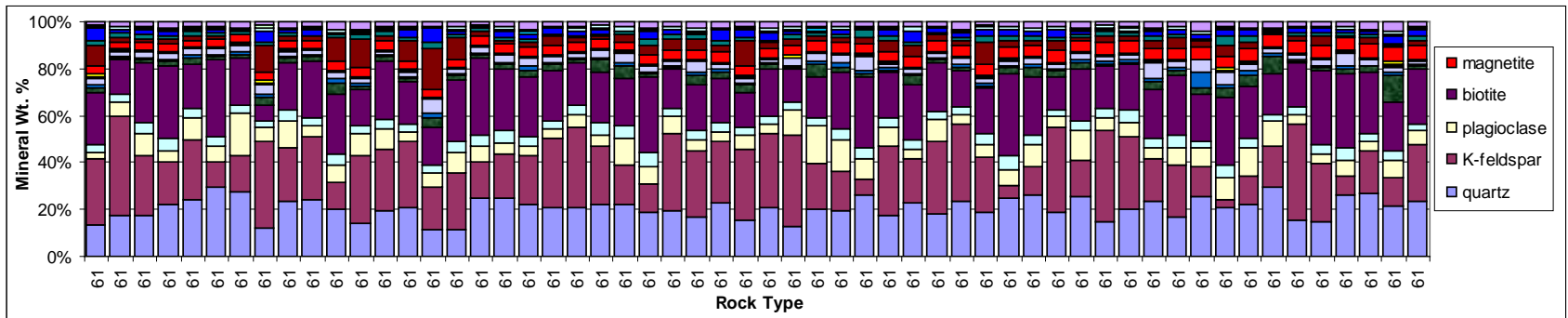
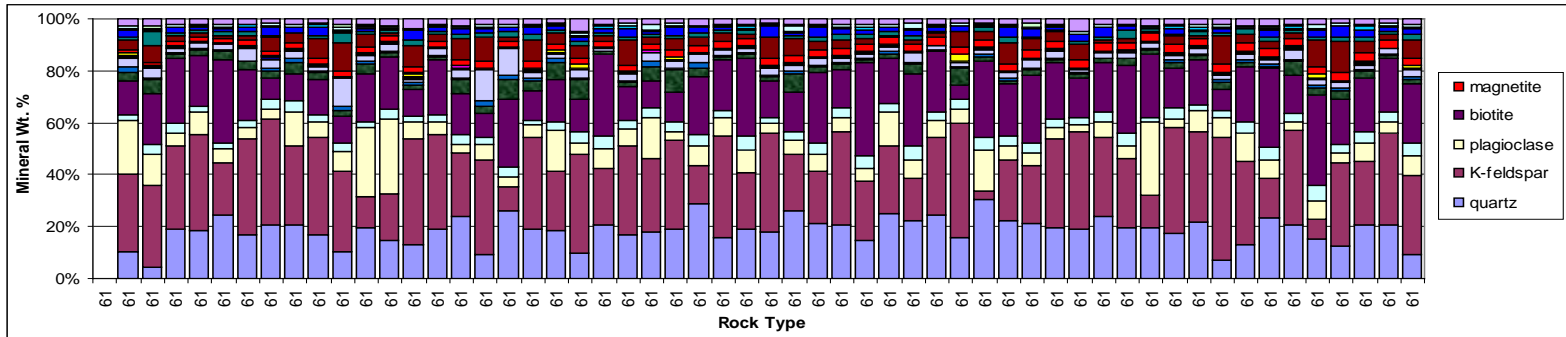


One Month Daily Blast Hole Analysis

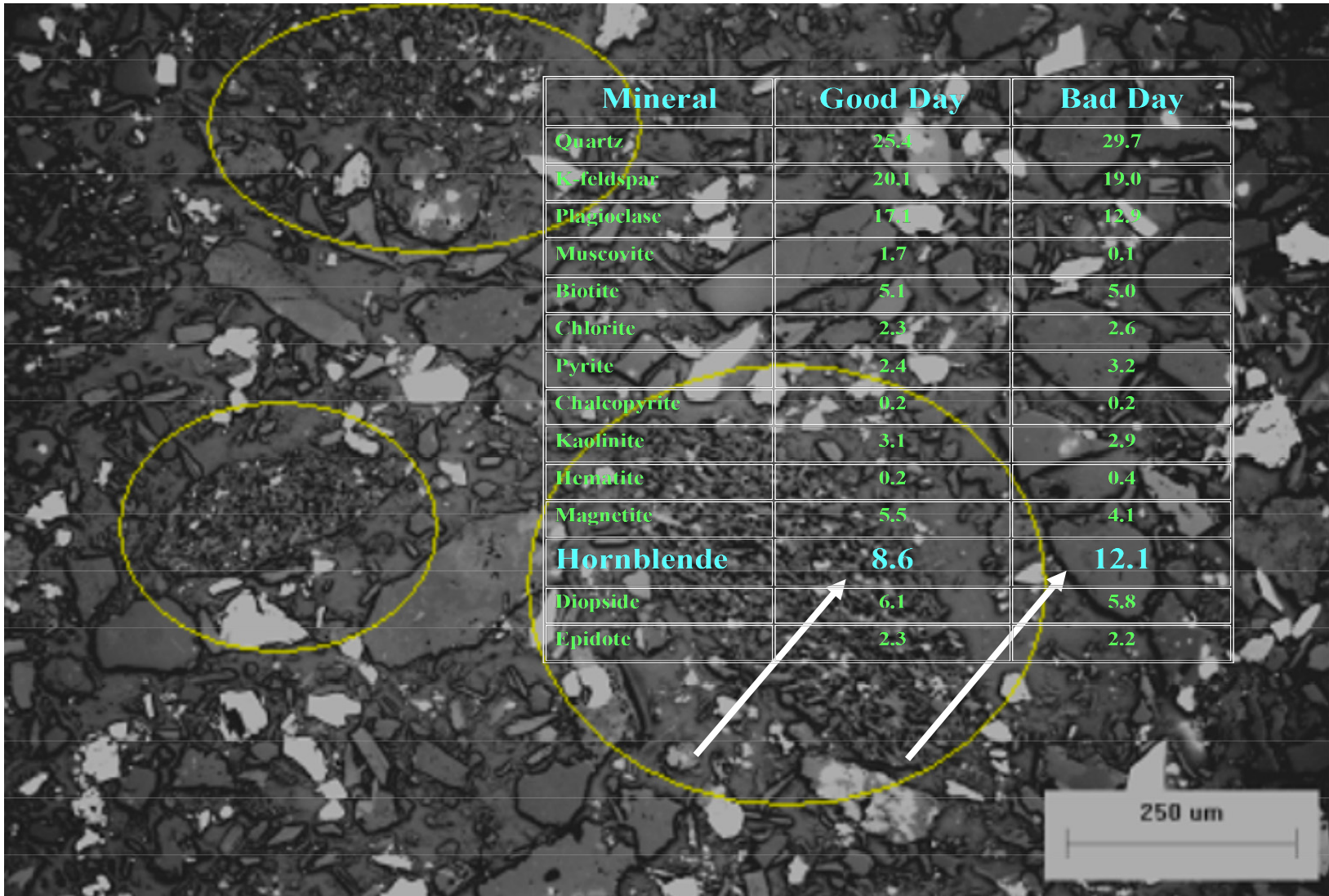


XRD Mineralogy of Ore Logged as Type 61

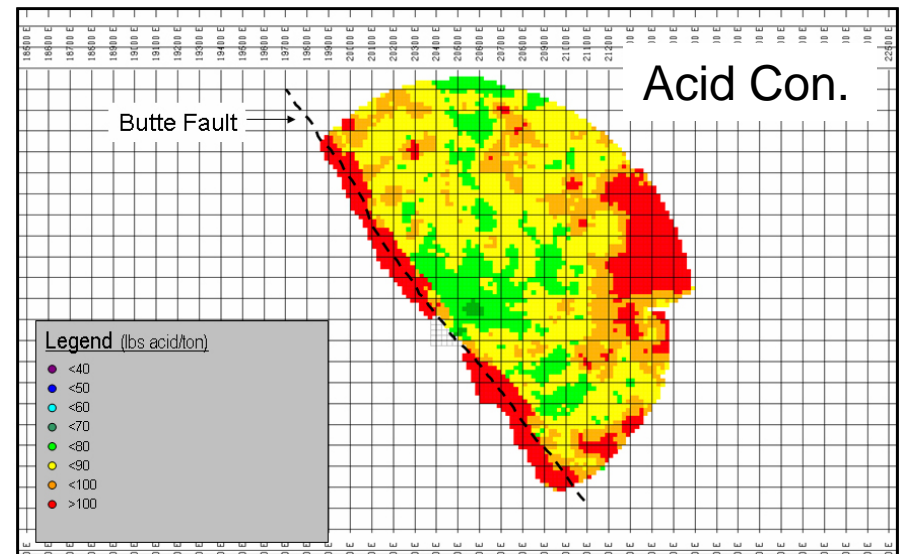
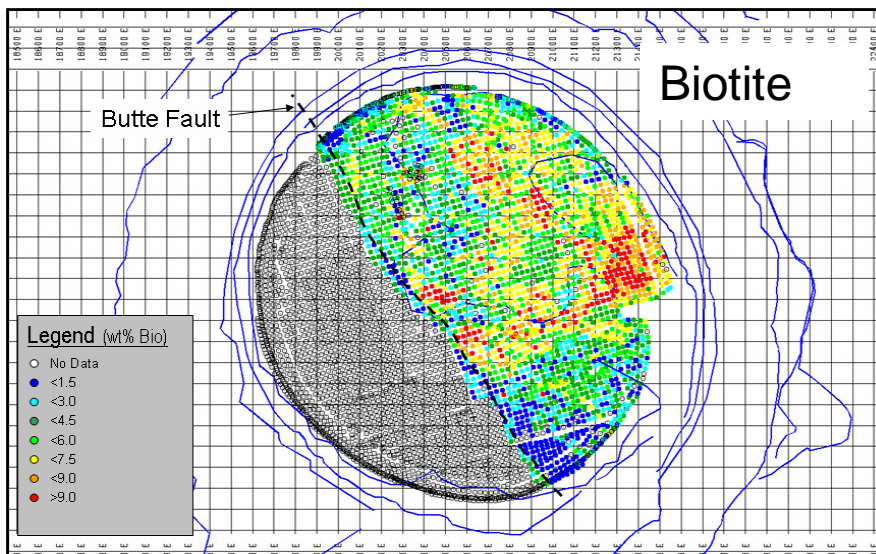
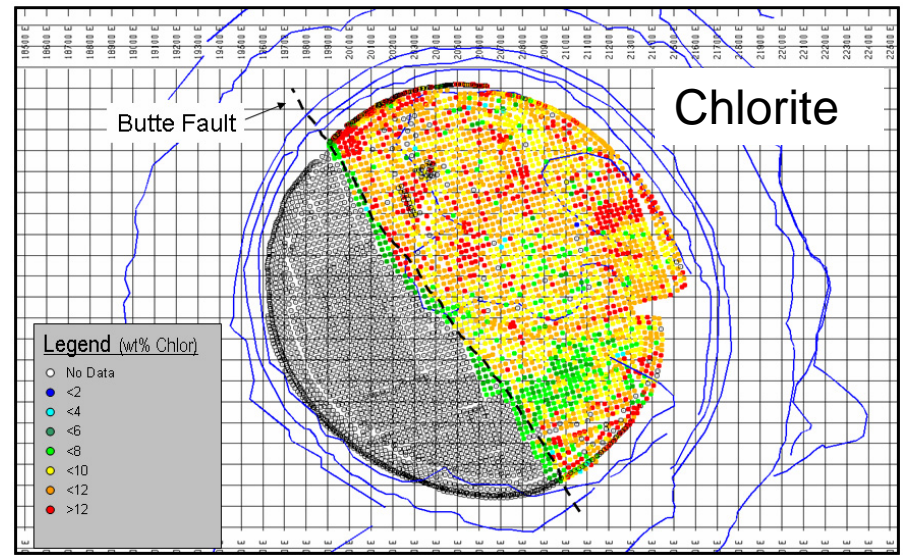
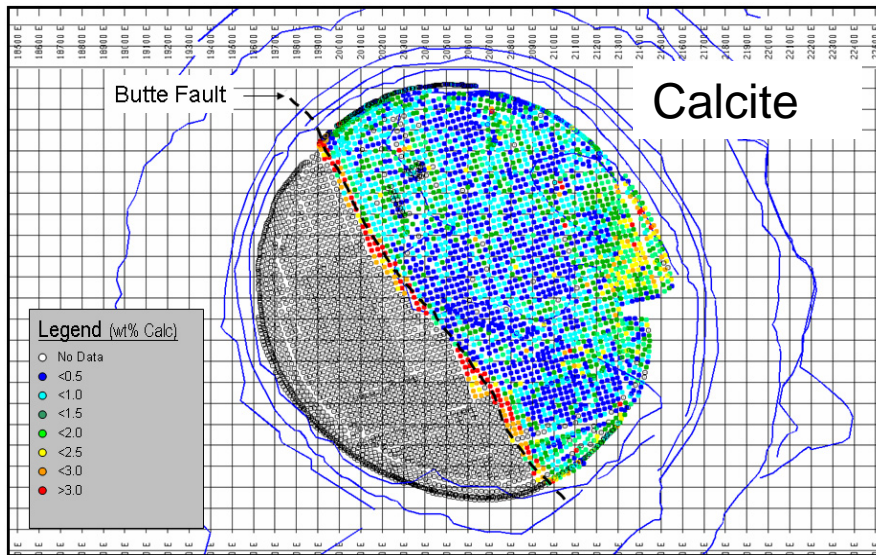
Typically 75% of Mill Feed



Tailing Thickener Product High Settling/Rake Breakdown



3750 Bench NIR Blasthole Data



Recent Developments

- **Automated Refinement in Batch Mode**
- **Refinement Reconciliation with Chemical Assay**
- **Automated Results Import into LIMS/Business Objects**

Batch Rietveld Automation



We rejected TOPAS BBQ Option

- Refinements are run automatically and reported
- It has no facility to check refinements visually and rerun
- Has been successful in cement industry

Developed an in-house automated refinement program

- Visual Basic macros in MS Excel
- Runs repeated samples using the same start file in batch mode
- Results are (.pro) files that can be opened in Graphical User Interface (GUI)
- Mineralogists or expert techs can rapidly open each (.pro) file in the GUI for a final check and/or make any adjustments needed.

Batch Rietveld Automation

Topas Auto Refinement Program

Load Inp & Pro files

Selected .inp file:

Selected .pro file: Clear X

Detection Limits

Mineral Name	Det. Limit (wt%)

----- Snip -----

Restore all colors.
 Keep obs & calc line colors.
 Show Topas refinement window.

Load profiles and Start.

Browse to directory with saved (.inp) file exported from start.pro file.

Filename are copied into macro.

Optional detection limits can be set.

Plotting options for output (.pro) file.

Controls whether "DOS" window is visible.

Opens startfile directory (or browse); Select and open any number of (.raw) files; Creates (.inp) file for each (.raw) file; runs tc.exe for each, turns off phases <DL, reruns from start conditions; converts (.out) file to (.pro) file for use in GUI

Chemical Assay Reconciliation



Screenshot of chemistry setup page

	A	B	C	D	E	F	G	H	I
7	C	Calcite, Mg	0.1200	Strong XRD overlap with chalcopyrite					
8	C	Calcite, Mg-Calcite	0.1200						
9	C	Magnesium Calcite	0.1200						
10	C	Cerussite	0.0449						
11	C	Dolomite	0.1303						
12	C	Magnesite	0.1425						
13	C	Malachite	0.0543						
14	C	Pyroaurite	0.0182						
15	C	Rhodochrosite	0.1045						
16	C	Sidente	0.1037						
17	C	Smithsonite	0.0958						
18	Cu	Antlerite	0.5375						
19	Cu	Azurite	0.5532						
20	Cu	Bonattite	0.2975						
21	Cu	Bornite	0.6332						
22	Cu	Bornite F23	0.6332						
23	Cu	Brochantite	0.5621						
24	Cu	Carrollite	0.2052						
25	Cu	Chalcanthite	0.2546						
26	Cu	Chalcocite	0.7986						
27	Cu	Chalcocyanite	0.3982						
28	Cu	Chalcopyrite	0.3463	Strong XRD overlap with calcite					
29	Cu	Copper	1.0000						
30	Cu	Cerussite	0.0449						

↓

AssayVsXRD Results0 Assay Results External Assay Sample List **Chemistry Calc Configuration** Lims Mineral List Prod Lims Mineral List PTC L

Chemical Assay Reconciliation

Screenshot of XRD – Assay Comparison Page

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	Relimport	Calc	SC	C			Cu		Pb		Zn		Mo		
2			XRD	Assay	XRD	Sample	XRD	Assay	XRD	Assay	XRD	Assay	XRD	Assay	
49	3274-0043	0.95	0.30	0.37	2.57	2.96	0.33	0.34	0.00	0.01	0.00	0.02	0.00	ULTIVALUE	
50	3274-0044	1.45	0.32	0.34	2.68	2.72	6.48	7.41	0.00	0.21	0.32	0.31	0.02	0.04	
51	3274-0045	2.81	0.55	0.55	4.59	4.40	2.67	3.24	0.00	0.10	0.17	0.18	0.00	0.02	
52	3274-0046	3.54	0.56	0.61	4.72	4.88	0.65	0.80	0.00	0.03	0.00	0.07	0.00	0.01	
53	3274-0047	3.15	0.55	0.59	4.65	4.72	0.21	0.23	0.00	0.01	0.00	0.03	0.00	0.01	
54	3274-0048	0.78	0.28	0.32	2.34	2.56	0.00	ULTIVALUE	0.00	0.00	0.00	<0.0 %	0.00	DES MS	
55	3274-0049	0.99	0.33	0.35	2.71	2.80	0.34	0.32	0.00	0.01	0.00	0.02	0.00	DES 0 MS	
56	3274-0050	1.90	0.26	0.34	2.26	2.72	7.32	8.51	0.00	0.24	0.37	0.38	0.03	0.04	
57	3274-0051	2.87	0.55	0.53	4.57	4.24	2.14	2.52	0.00	0.07	0.20	0.15	0.00	0.02	
58	3274-0052	3.31	0.56	0.57	4.70	4.56	0.49	0.50	0.00	0.02	0.00	0.04	0.00	0.01	
59	3274-0053	3.58	0.47	0.58	3.90	4.64	0.15	0.19	0.00	0.01	0.00	0.02	0.00	0.01	
60	3274-0054	0.74	0.30	0.33	2.62	2.64	0.00	ULTIVALUE	0.00	0.00	0.00	<0.0 %	0.00	ULTIVALUE	
61	3274-0055	1.03	0.33	0.36	2.79	2.88	0.26	0.34	0.00	0.01	0.00	0.02	0.00	ULTIVALUE	
62	3274-0056	1.69	0.36	0.37	2.95	2.96	6.58	7.31	0.00	0.20	0.36	0.32	0.09	0.05	
63	3274-0057	2.82	0.51	0.54	4.26	4.32	1.75	2.16	0.00	0.07	0.00	0.14	0.00	0.02	
64	3274-0058	3.29	0.46	0.59	3.87	4.72	0.44	0.49	0.00	0.02	0.00	0.06	0.00	0.01	
65	3274-0059	3.52	0.46	0.57	3.82	4.56	0.17	0.16	0.00	0.01	0.00	0.03	0.00	0.01	
66	3274-0060	0.80	0.27	0.33	2.25	2.64	0.00	ULTIVALUE	0.00	0.00	0.00	<0.0 %	0.00	ULTIVALUE	
67	3274-0061	0.95	0.29	0.34	2.44	2.72	0.35	0.35	0.00	0.01	0.00	0.02	0.00	ULTIVALUE	
68	3274-0062	1.43	0.36	0.36	3.01	2.88	7.23	7.92	0.00	0.24	0.62	0.46	0.00	0.04	

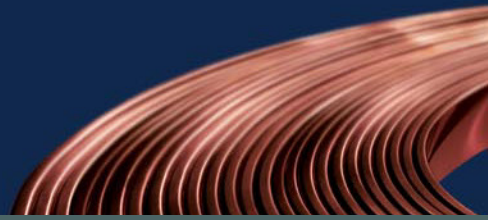
AssayVsXRD Results0 Assay Results External Assay Sample List Chemistry Calc Configuration Lims Mineral List Prod Lims Mineral List P

Ready

Continuing Issues

- **Automated Micronizing**
- **Eliminating Preferred Orientation**
- **Modeling Highly Variable Disordered Clays
(including Chrysocolla)**

Thank You



Questions or Suggestions?