Preliminary Progress Report

Mineralogy and Geochemistry of Well Cuttings

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Introduction

This is a preliminary report with analytical results in support of a possible application for "Beneficial Use Determination" for well cuttings. Well cuttings from the Matejka well in Chemung County and outcrops in the Devonian of central New York State have been analyzed using X-Ray Fluorescence, X-Ray Diffraction and Scanning Electron Microscopy in order to determine major and trace element composition, and mineral composition. The program Rock Jock is used and X-Ray Diffraction to assess mineral composition and quantitative mineral abundance. This data allows assessment of sulfur-bearing minerals such as pyrite. XRF data for mobile metals including lead, copper, and zinc, in addition a well cuttings leachate experiment will test for dissolved chemical components. The results will support the next phase of work toward Beneficial Use Determination status according to the NYSDEC.

Materials

The samples analyzed include well cuttings from the Matejka Well located in Erin, NY (see Table 1). Additional samples collected in the field from New York include units in the Devonian sequence of central New York: Solsville Bridgewater West, Esopus Route 20 Cherry Valley, Cherry Valley Upper Union Springs, Chittenango Mower Road, Bridgewater Shale, and Basal Chittenango Cherry Valley (see Table 2). Also included are a sample of the Marcellus shale, and a sample of the Tully formation both from a Penssylvanian well.

Methods

Analyses of bulk chemistry were conducted using a Philips PW 2404 x-ray fluorescence spectrometer. Well cuttings or rock chips were powdered and dried and the powder divided for firing to determine loss on ignition and for disc-making. Glass discs were made by processing powdered and weighed samples mixed with lithium tetraborate in a Fluxy. Trace element analysis required that samples be weighed and combined with copolywax and pressed into pellets.

Mineralogy of the samples was determined using JEOL JSM-6360LV Scanning Electron Microscope, which required that well cuttings be molded in epoxy chips. A Philips X'Pert x-ray system was used to derive diffractograms of powdered samples with an internal zincite standard. The USGS software package "RockJock" was then used to analyze XRD spectra and determine the weight percent mineral abundances in samples.

Results

Table 1 and 2 characterize samples based on stratigraphic unit and lithology.

Matejka Well Sample Name	Stratigraphic Unit	Lithology
Matejka 1550-1560	Genesee Formation	Shale, silty shale
Matejka 1590-1600	Genesee Formation	Shale, silty shale
Matejka 1630-1640	Genesee Formation	Shale, silty shale
Matejka 1740-1750	Genesee Formation	Shale, silty shale
Matejka 1800-1810	Genesee Formation	Shale, silty shale
Matejka 1850-1860	Genesee Formation	Shale, silty shale
Matejka 1900-1910	Genesee Formation	Shale, silty shale
Matejka 1950-1960	Genesee Formation	Shale, silty shale
Matejka 2130-2140	Geneseo Shale	Dark silty shale
Matejka 2140-2150	Tully Formation	Calcareous shale/mudstone
Matejka 2280-2290	Hamilton Group	Silty shale
Matejka 2380-2390	Hamilton Group	Silty shale
Matejka 2440-2450	Hamilton Group	Silty shale
Matejka 2500-2510	Hamilton Group	Silty shale
Matejka 2620-2630	Hamilton Group	Silty shale
Matejka 2680-2690	Hamilton Group	Silty shale
Matejka 2760-2770	Hamilton Group	Silty shale
Matejka 2800-2810	Hamilton Group	Silty shale
Matejka 2900-2910	Hamilton Group	Silty shale
Matejka 2990-3000	Hamilton Group	Silty shale

Table 1. Stratigraphic unit and lithology of Matejka Well samples.

Field Samples Sample Name	Stratigraphic Unit	Lithology
Tully TVD	Tully Formation	Calcareous siltstone
Upper Marcellus TVD	Marcellus	Gray shale
Bridgewater Shale	Bridgewater	Gray silty shale
Solsville Bridgwater West	Solsville member	Fine sandstone
Chittenango Mower Rd	Chittenango	Gray silty shale
Esopus Cherry Valley	Cherry Valley	Gray siliceous shale
Basal Chittenango	Chittenango Mbr	Black Shale
Upper Union Springs	Union Springs	Black Shale

Table 2. Stratigraphic unit and lithology of field samples.

Figures 1 though 6 represent trace and major element analyses conducted using x-ray fluorescence. These results are compared to the North American Shale Composite (NASC) which is a standard for shale compositions as determined by Gromet et al 1984.

The purpose of these visuals is to show the extent of compositional differences (if any) in our samples from those of a standard shale. In particular we are interested in the levels of potentially mobile and deleterious metals such as, strontium, zinc, copper, and lead; these may pose difficulties in obtaining a Beneficial Use Determination. As is apparent from these figures, the samples in question do not significantly differ from the standard composition. Moreover, the results support our expectations of mineralogical/elemental composition. For example, the Solsville sample was predicted to contain a high proportion of quartz (SiO2) relative to the others based on field description.

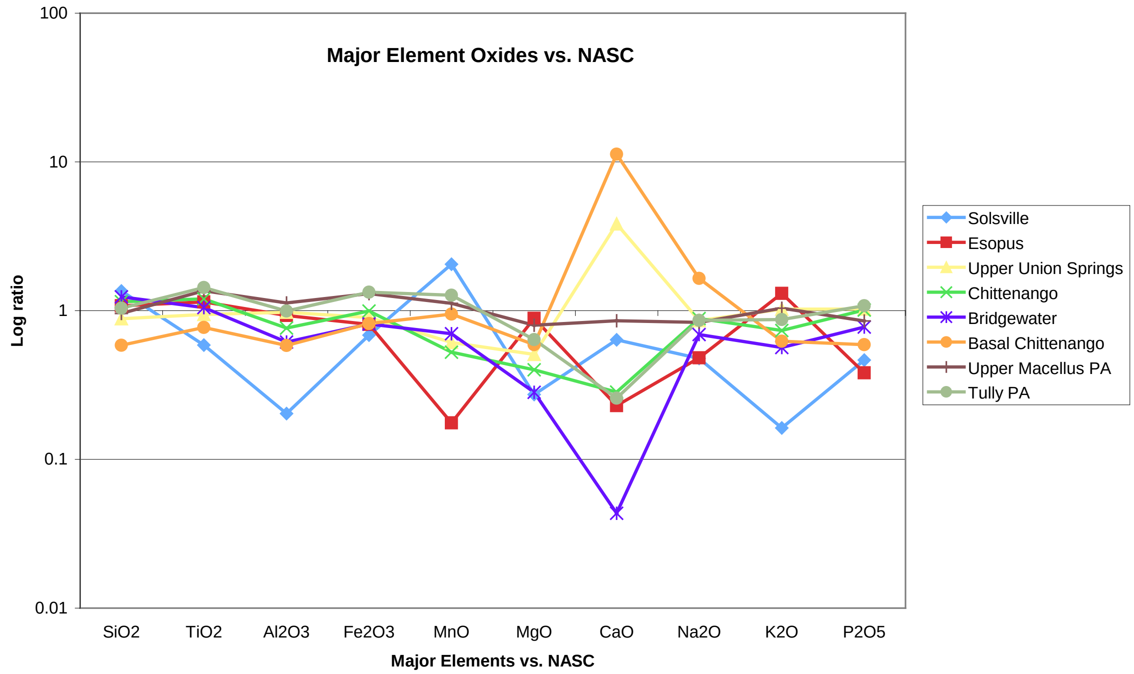

Figure 1. Major element oxides in field samples compared to NASC.

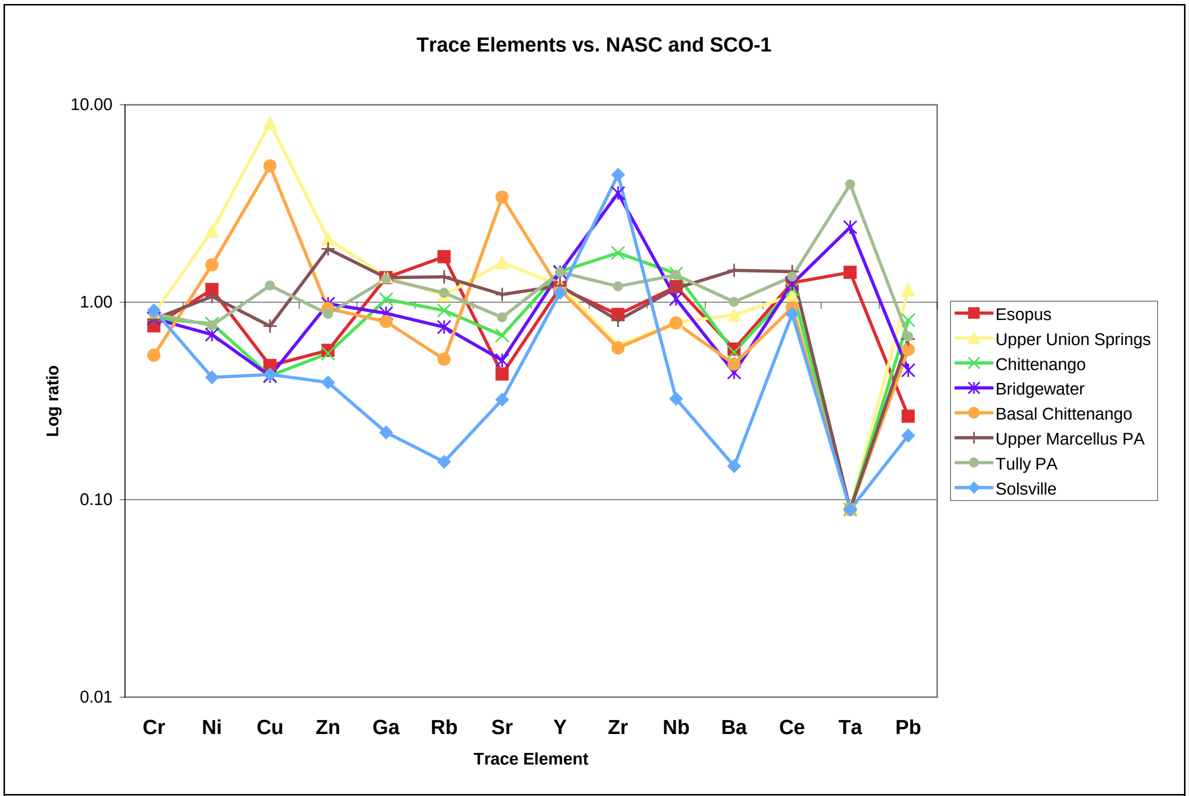

Figure 2. Trace elements in field samples compared to NASC.

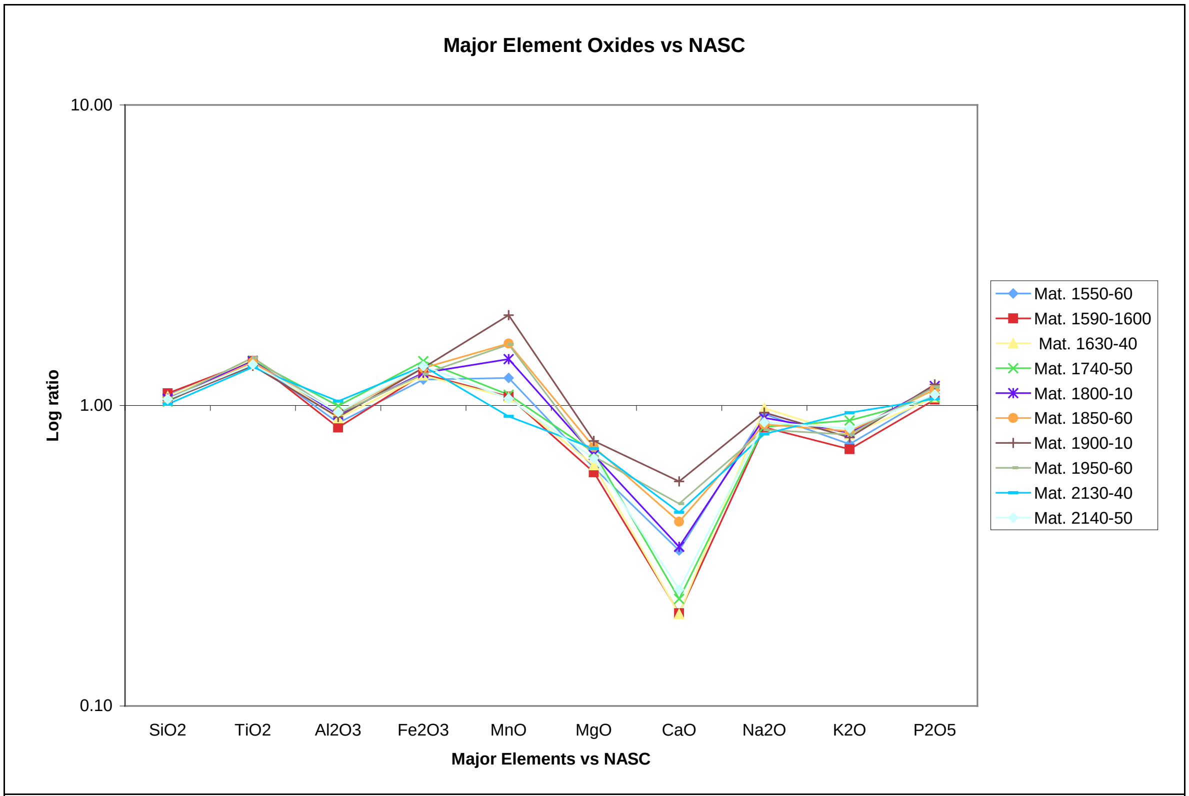

Figure 3. Major element oxides in Matejka Well samples compared to NASC.

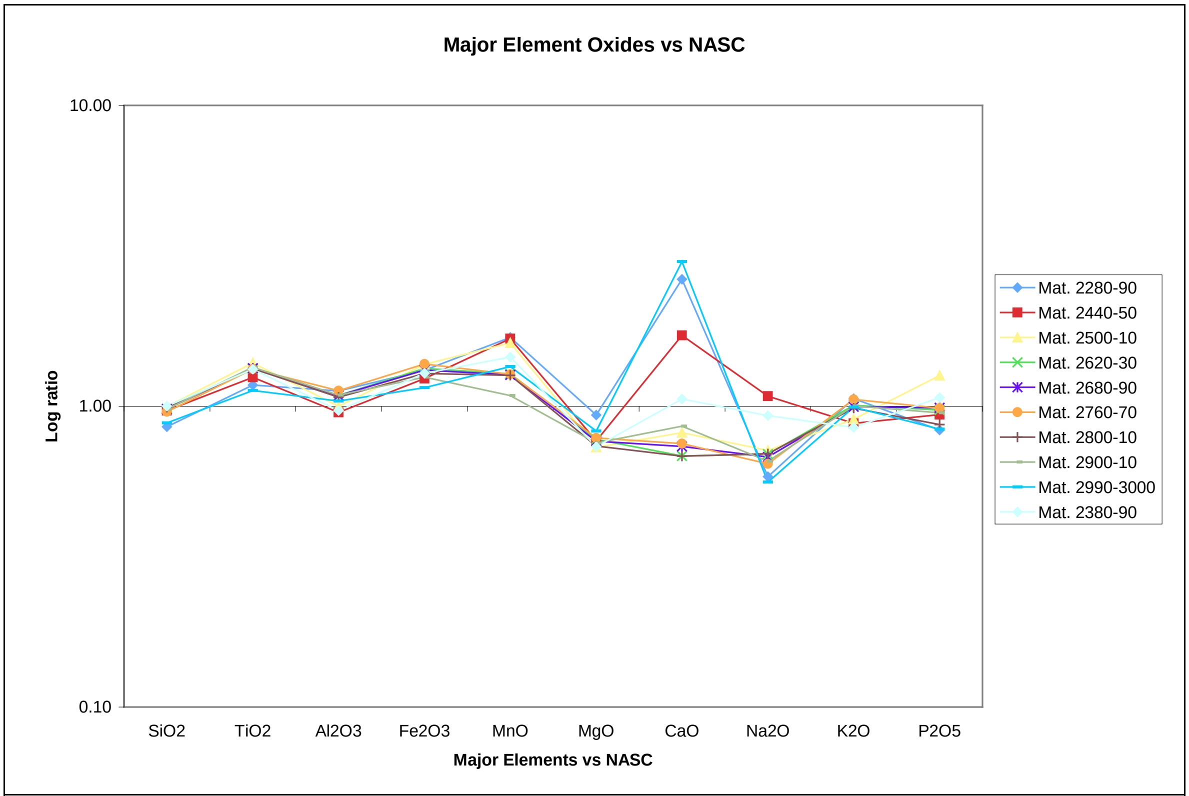

Figure 4. Major element oxides in Matejka Well samples compared to NASC (cont.).

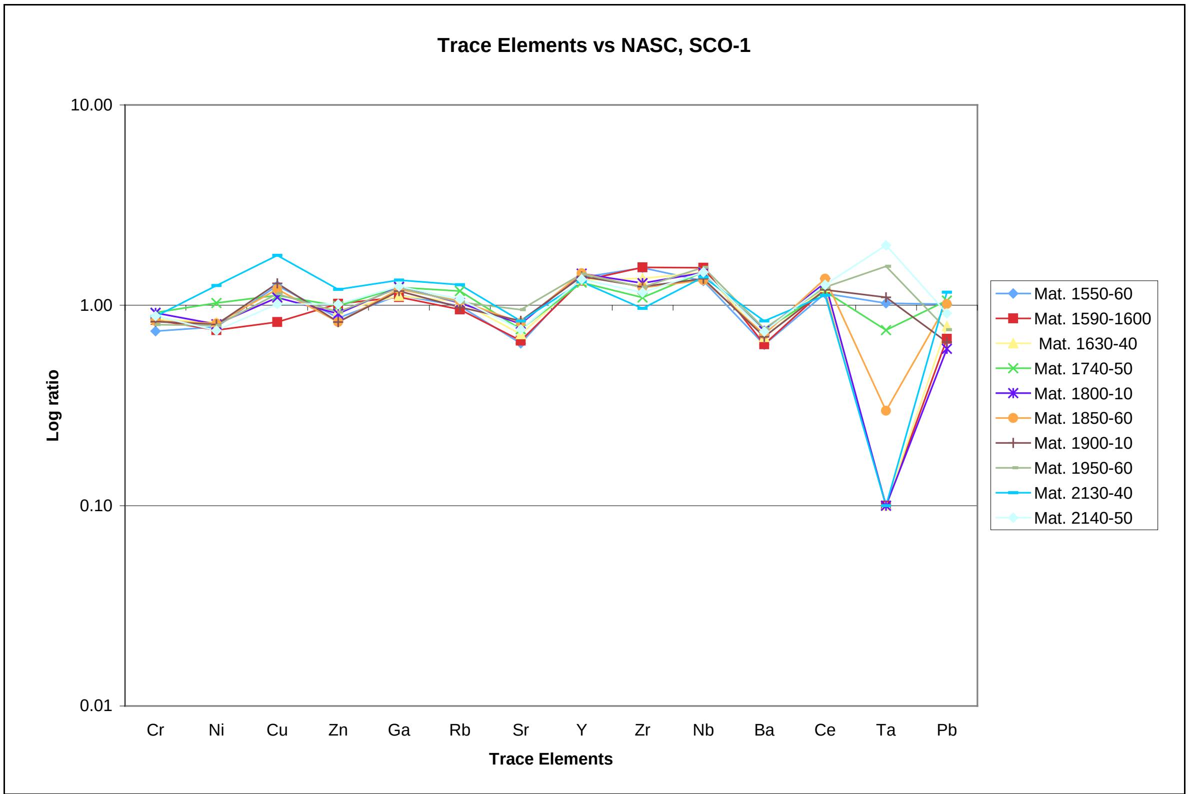

Figure 5. Trace elements in Matejka Well samples compared to NASC.

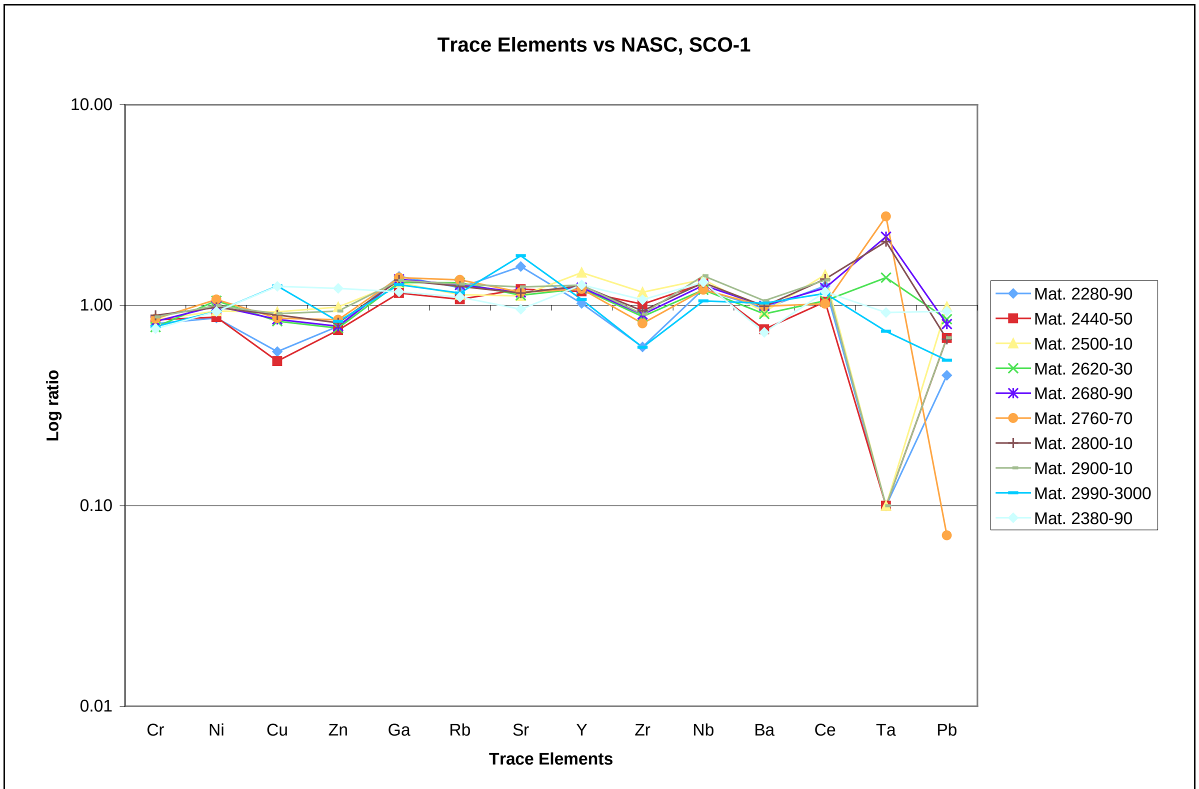

Figure 6. Trace elements in Matejka Well samples compared to NASC.

Tables 3 through 10 show the normalized oxide and trace element composition of the Matejka well and field samples.

Oxide	Mat. 1550-60	Mat. 1590-1600	Mat. 1630-40	Mat. 1740-50	Mat. 1800-10	Mat. 1850-60
SiO2 (%)	1.08	1.10	1.07	1.03	1.05	1.04
TiO2 (%)	1.41	1.41	1.41	1.41	1.41	1.39
Al2O3 (%)	0.87	0.84	0.91	1.00	0.93	0.95
Fe2O3 (%)	1.22	1.27	1.26	1.40	1.28	1.33
MnO (%)	1.23	1.07	1.06	1.09	1.43	1.61
MgO (%)	0.62	0.60	0.63	0.70	0.68	0.73
CaO (%)	0.33	0.20	0.20	0.23	0.34	0.41
Na2O (%)	0.94	0.85	0.98	0.85	0.91	0.87
K2O (%)	0.74	0.71	0.80	0.89	0.81	0.82
P2O5 (%)	1.09	1.05	1.06	1.06	1.16	1.13

Table 3. Normalized oxide percentages in Matejka well samples.

Mat. 1900-10	Mat. 1950-60	Mat. 2130-40	Mat. 2140-50	Mat. 2280-90	Mat. 2380-90	Mat. 2440-50
1.04	1.05	1.01	1.05	0.85	1.00	0.97
1.36	1.44	1.34	1.37	1.18	1.33	1.25
0.92	0.94	1.03	0.95	1.12	0.97	0.95
1.34	1.27	1.35	1.35	1.32	1.29	1.24
2.00	1.59	0.92	1.05	1.69	1.46	1.68
0.76	0.68	0.72	0.67	0.93	0.73	0.77
0.56	0.47	0.44	0.24	2.64	1.06	1.72
0.95	0.83	0.80	0.88	0.58	0.93	1.08
0.78	0.80	0.95	0.84	1.06	0.85	0.88
1.17	1.15	1.05	1.09	0.83	1.07	0.94

Table 4. Normalized oxide percentages in Matejka well samples.

Mat. 2500-10	Mat. 2620-30	Mat. 2680-90	Mat. 2760-70	Mat. 2800-10	Mat. 2900-10	Mat. 2990-3000
1.00	0.98	0.98	0.96	0.99	0.98	0.88
1.39	1.33	1.34	1.33	1.33	1.35	1.13
1.00	1.09	1.08	1.13	1.07	1.09	1.04
1.38	1.33	1.32	1.38	1.28	1.25	1.15
1.62	1.28	1.27	1.28	1.27	1.08	1.35
0.73	0.78	0.77	0.78	0.74	0.75	0.83
0.82	0.68	0.74	0.75	0.68	0.86	3.03
0.71	0.69	0.68	0.64	0.70	0.66	0.56
0.91	1.01	1.00	1.05	0.98	1.00	0.99
1.27	0.97	0.99	0.99	0.87	0.95	0.84

Table 5. Normalized oxide percentages in Matejka well samples.

Element	Mat. 1550-60	Mat. 1590-1600	Mat. 1630-40	Mat. 1740-50	Mat. 1800-10	Mat. 1850-60
Cr	0.74	0.84	0.85	0.92	0.92	0.83
Ni	0.78	0.75	0.82	1.03	0.81	0.81
Cu	1.25	0.83	1.08	1.12	1.09	1.20
Zn	0.86	1.02	0.94	0.99	0.91	0.83
Ga	1.12	1.10	1.11	1.23	1.24	1.20
Rb	0.99	0.95	1.04	1.18	1.03	1.05
Sr	0.65	0.67	0.72	0.76	0.81	0.82
Y	1.38	1.33	1.34	1.30	1.44	1.45
Zr	1.54	1.55	1.36	1.09	1.29	1.23
Nb	1.32	1.54	1.46	1.47	1.46	1.34
Ba	0.64	0.64	0.69	0.75	0.74	0.72
Ce	1.15	1.20	1.23	1.17	1.30	1.36
Ta	1.02	0.10	0.10	0.75	0.10	0.30
Pb	1.01	0.68	0.79	1.06	0.61	1.02

Table 6. Normalized trace element abundance in Matejka well samples.

Mat. 1900-10	Mat. 1950-60	Mat. 2130-40	Mat. 2140-50	Mat. 2280-90	Mat. 2380-90	Mat. 2440-50
0.83	0.80	0.88	0.89	0.81	0.89	0.85
0.80	0.79	1.25	0.75	0.86	0.75	0.87
1.29	1.14	1.78	1.02	0.59	1.02	0.53
0.82	0.92	1.20	1.01	0.79	1.01	0.75
1.18	1.22	1.34	1.24	1.39	1.24	1.15
0.98	1.04	1.27	1.07	1.22	1.07	1.07
0.84	0.95	0.84	0.76	1.56	0.76	1.20
1.39	1.43	1.31	1.35	1.02	1.35	1.17
1.24	1.23	0.96	1.16	0.62	1.16	1.01
1.36	1.55	1.38	1.46	1.20	1.46	1.28
0.70	0.76	0.84	0.74	0.96	0.74	0.76
1.19	1.23	1.12	1.26	1.25	1.26	1.04
1.10	1.57	0.10	1.99	0.10	1.99	0.10
0.66	0.75	1.16	0.91	0.45	0.91	0.69

Table 7. Normalized trace element abundance in Matejka well samples.

Mat. 2500-10	Mat. 2620-30	Mat. 2680-90	Mat. 2760-70	Mat. 2800-10	Mat. 2900-10	Mat. 2990-3000
0.85	0.78	0.83	0.86	0.89	0.87	0.78
0.94	1.05	0.99	1.07	0.98	1.00	0.93
0.93	0.83	0.85	0.86	0.90	0.91	1.25
0.98	0.77	0.79	0.85	0.82	0.94	0.83
1.30	1.30	1.35	1.37	1.34	1.33	1.27
1.13	1.30	1.26	1.34	1.24	1.27	1.15
1.11	1.12	1.16	1.16	1.15	1.23	1.77
1.46	1.21	1.23	1.20	1.25	1.26	1.07
1.16	0.88	0.90	0.81	0.94	0.90	0.62
1.34	1.19	1.26	1.19	1.29	1.40	1.05
0.93	0.91	0.99	0.99	0.99	1.05	1.02
1.42	1.05	1.22	1.02	1.35	1.33	1.15
0.10	1.37	2.20	2.77	2.08	0.10	0.74
0.99	0.85	0.81	0.07	0.68	0.69	0.53

Table 8. Normalized trace element abundance in Matejka well samples.

Oxide	S'ville Bridge-water West	Esopus Rt. 20 Cherry Valley	Cherry Valley Upper Union Spring	Chitten-ango Mower Rd.	Bridge-water Shale	Basal Chitten-ango Cherry Valley	Upper Marcell-us TVD	Tully TVD
SiO2 (%)	1.36	1.08	0.88	1.15	1.24	0.59	0.96	1.04
TiO2 (%)	0.59	1.15	0.94	1.20	1.05	0.77	1.36	1.43
Al2O3 (%)	0.20	0.93	0.97	0.76	0.61	0.58	1.13	0.99
Fe2O3 (%)	0.68	0.81	0.90	0.99	0.81	0.82	1.30	1.33
MnO (%)	2.05	0.18	0.61	0.53	0.70	0.95	1.12	1.27

MgO (%)	0.27	0.89	0.51	0.40	0.28	0.59	0.80	0.64
CaO (%)	0.64	0.23	3.83	0.28	0.04	11.27	0.85	0.26
Na2O (%)	0.48	0.48	0.86	0.88	0.69	1.64	0.83	0.86
K2O (%)	0.16	1.30	1.02	0.74	0.57	0.62	1.04	0.87
P2O5 (%)	0.47	0.38	1.02	1.01	0.77	0.59	0.85	1.08

Table 9. Normalized oxide percentages in field samples.

Element	S'ville Bridge-water West	Esopus Rt. 20 Cherry Valley	Cherry Valley Upper Union Spring	Chitten-ango Mower Rd.	Bridge-water Shale	Basal Chitten-ango Cherry Valley	Upper Marcell-us TVD	Tully TVD
Cr	0.91	0.76	0.88	0.83	0.83	0.54	0.82	0.87
Ni	0.42	1.16	2.29	0.78	0.69	1.55	1.07	0.76
Cu	0.43	0.48	8.09	0.42	0.42	4.90	0.76	1.22
Zn	0.39	0.57	2.09	0.55	0.98	0.93	1.86	0.87
Ga	0.22	1.33	1.35	1.03	0.88	0.80	1.33	1.31
Rb	0.16	1.70	1.09	0.91	0.75	0.51	1.35	1.12
Sr	0.32	0.43	1.59	0.68	0.51	3.40	1.10	0.84
Y	1.12	1.18	1.22	1.43	1.42	1.16	1.21	1.42
Zr	4.43	0.87	0.61	1.78	3.57	0.59	0.81	1.20
Nb	0.32	1.20	0.79	1.40	1.04	0.78	1.18	1.37
Ba	0.15	0.58	0.86	0.56	0.44	0.49	1.45	1.00
Ce	0.87	1.26	1.09	1.16	1.24	0.94	1.43	1.35
Ta	0.09	1.42	0.09	0.09	2.40	0.09	0.09	3.95
Pb	0.21	0.26	1.16	0.81	0.45	0.58	0.65	0.67

Table 10. Trace abundance in field samples.

Figures 7 and 8 are SEM images taken at high magnification so as to identify mineral grains. We have labeled pyrite which is visually identifiable given its characteristic brightness and habit. As a sulfide pyrite is one of the minerals of special concern.

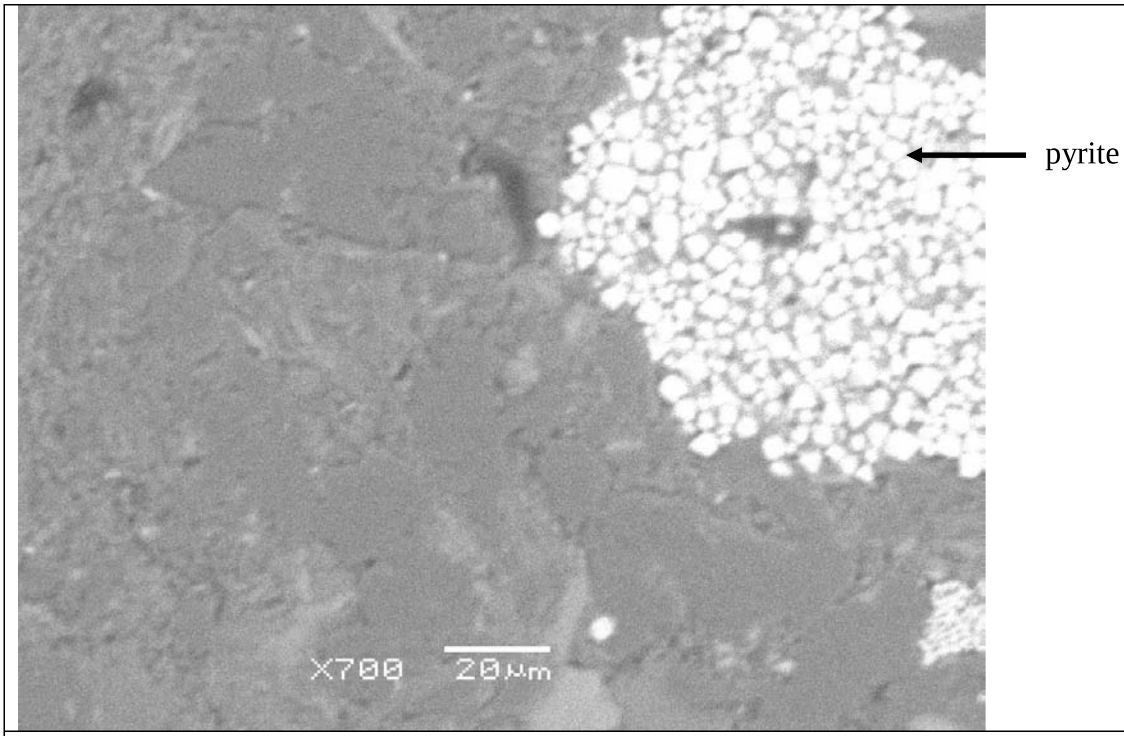

Figure 7. SEM photograph of Tully TVD sample magnified x700.

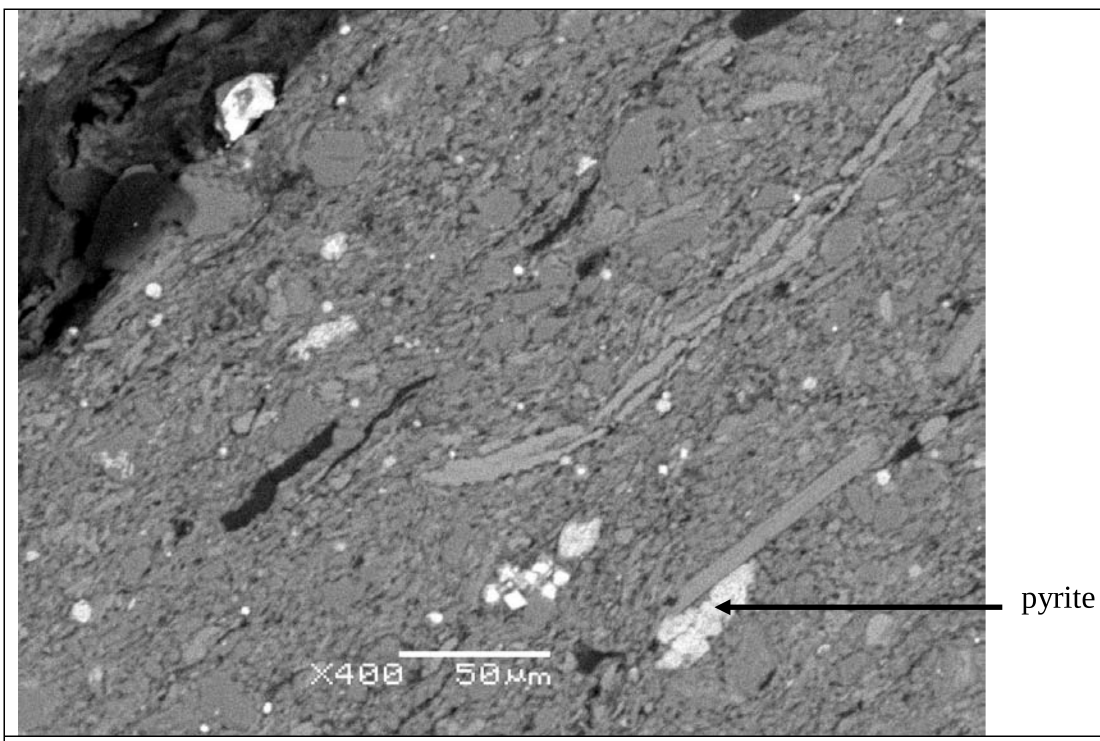

Figure 8. SEM photograph of Solsville Bridgewater West sample magnified x400.

Figures 9 though 23 present results of analyses conducted using x-ray diffraction and software analysis. Pie charts also illustrate relative abundance. For each sample, the measured vs. calculated x-ray diffractograms are shown. Well-matched patterns are indicative of accurate analytical results. In general, the relatively minor percentages of pyrite (generally 1% or less in most samples analyzed to date), and presence of calcite in samples with pyrite suggest that acidification due to pyrite oxidation would not be a concern should these cuttings be exposed to surface conditions. The results of our leachate experiments will provide much better information regarding acidification and potential mobility of metals.

Minerals	Normalized Percent
Quartz	53
Illite & Muscovite	32
Chlorite	8
Feldspar	6
Calcite	0
Pyrite	1

Figure 9. Mineral weight percent of Matejka 1630-40 produced by Rock Jock software.

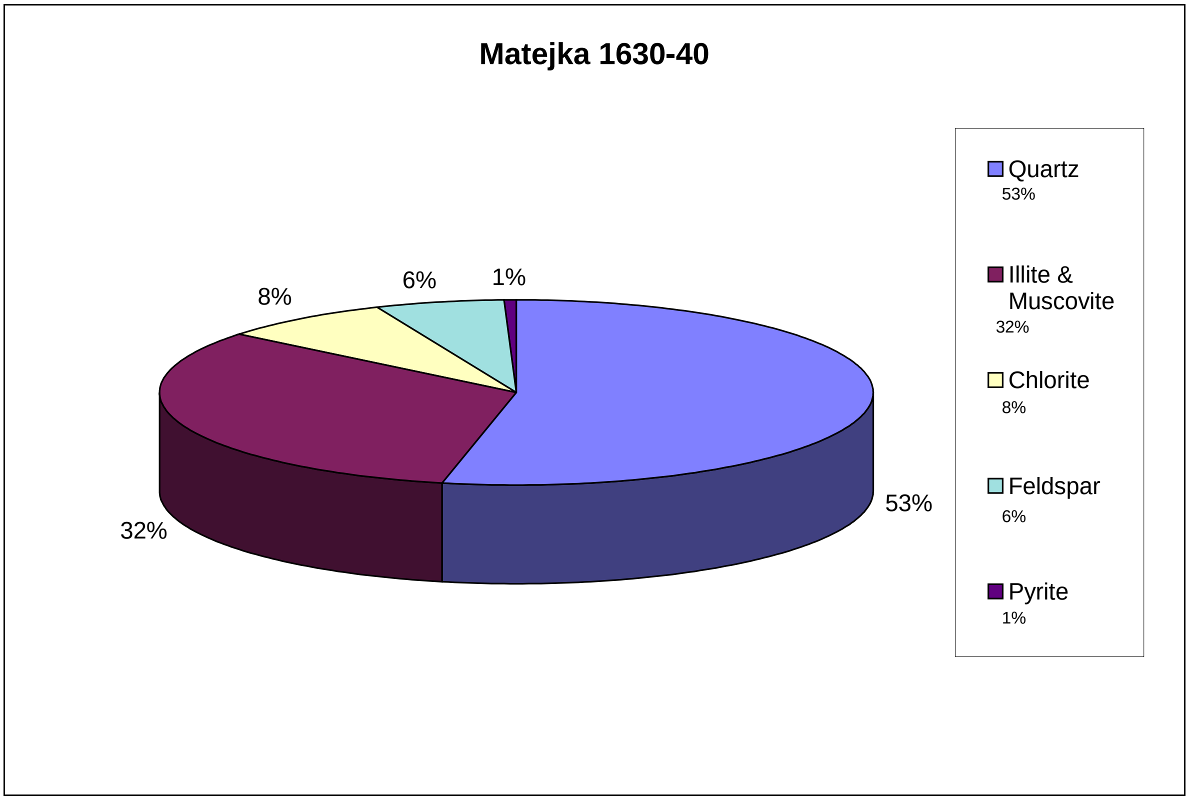

Figure 10. Pie chart displaying mineral weight percent based on Rock Jock analysis of Matejka 1630-40 XRD data.

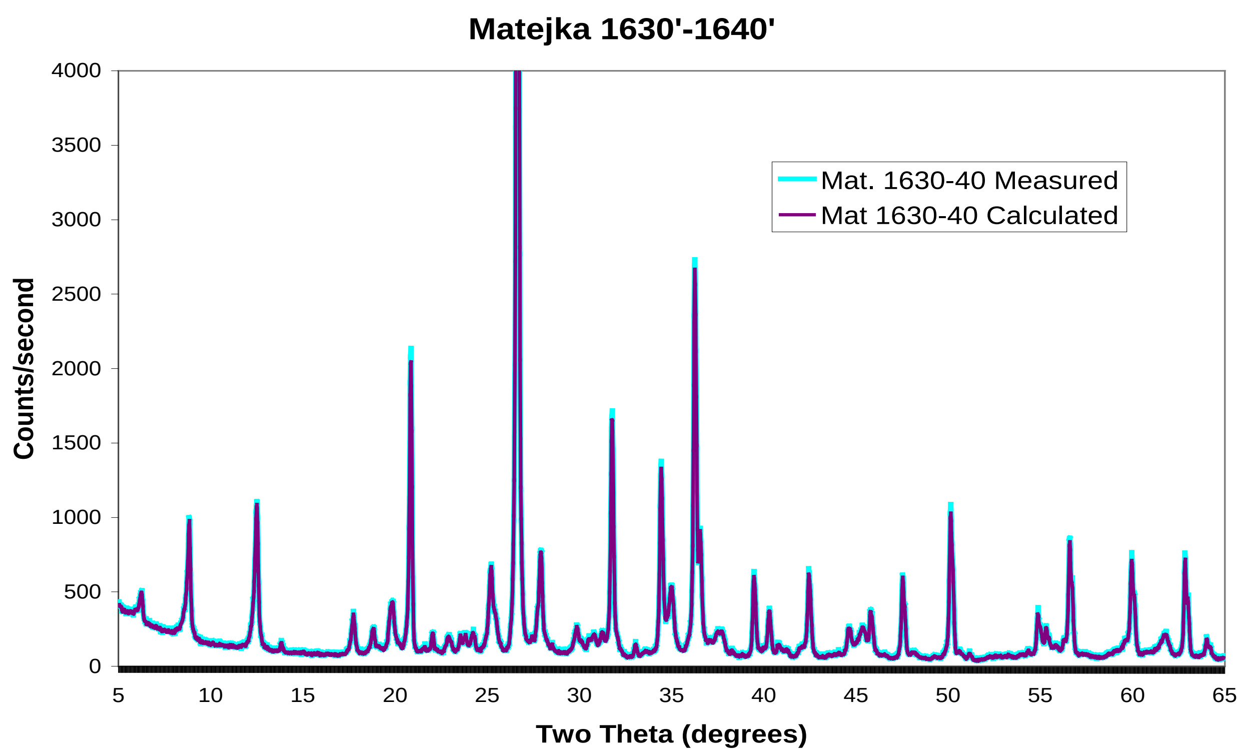

Figure 11. Measured XRD spectra for Matejka 1630-40 compared to calculated Rock Jock spectra.

Minerals	Normalized percent
Quartz	48
Illite & Muscovite	32
Chlorite	12
Feldspar	7

Figure 12. Mineral weight percents of Matejka 1800-10 produced by Rock Jock software.

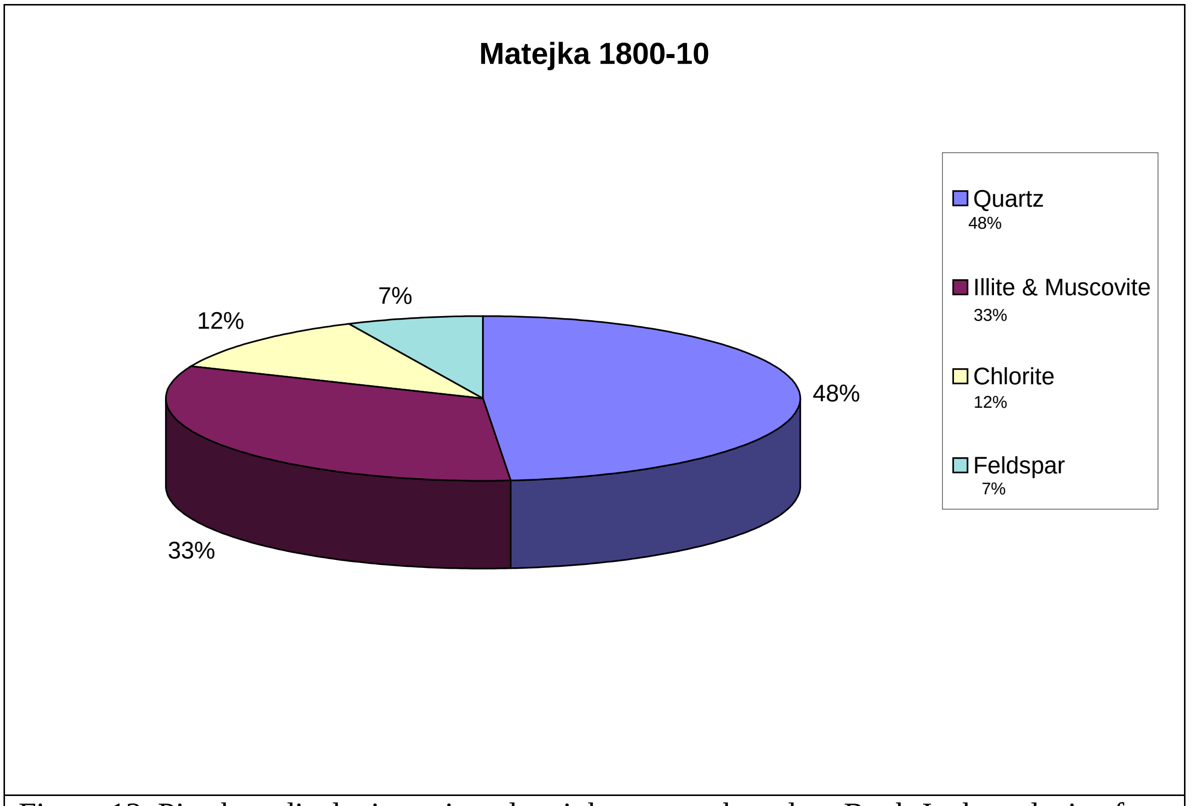

Figure 13. Pie chart displaying mineral weight percent based on Rock Jock analysis of Matejka 1800-10 XRD data.

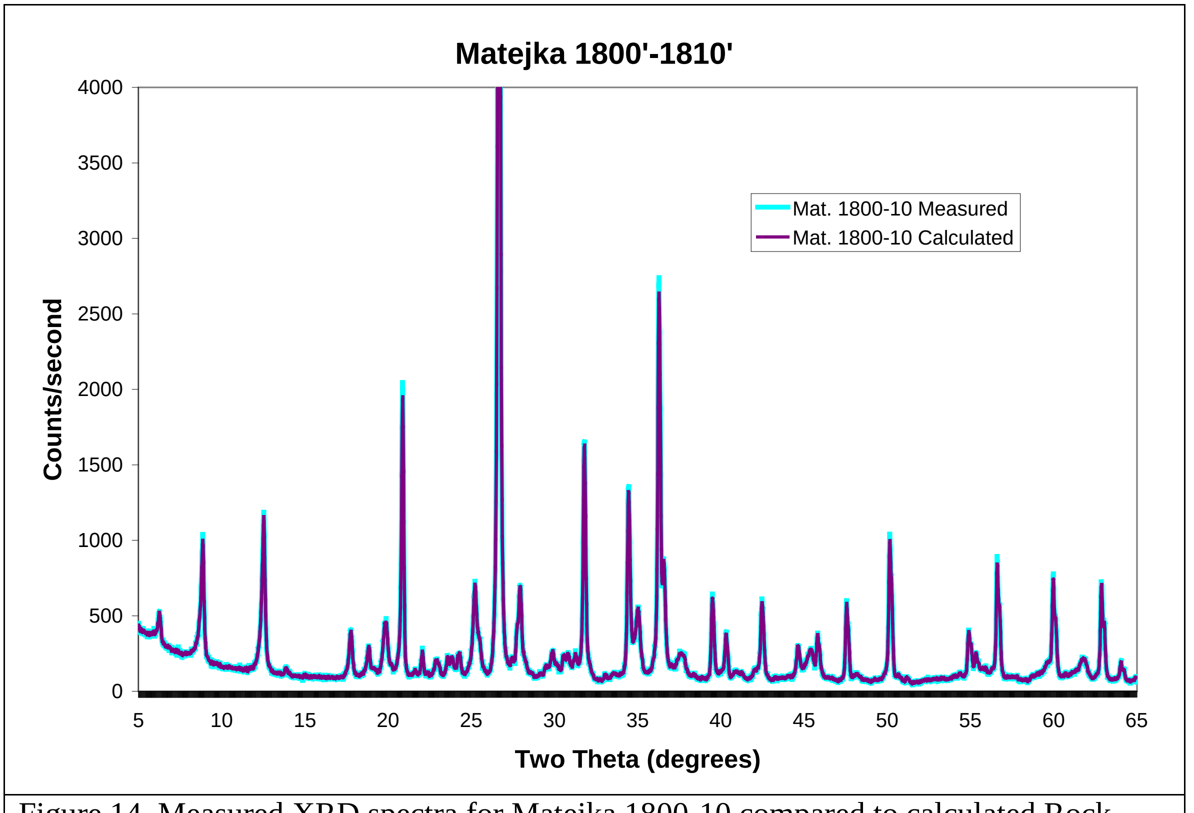

Figure 14. Measured XRD spectra for Matejka 1800-10 compared to calculated Rock Jock spectra.

Minerals	Normalized percent
Quartz	41
Illite & Muscovite	37
Chlorite	13
Feldspar	5
Calcite	2
Pyrite	1

Figure 15. Mineral weight percent of Matejka 2500-10 produced by Rock Jock software.

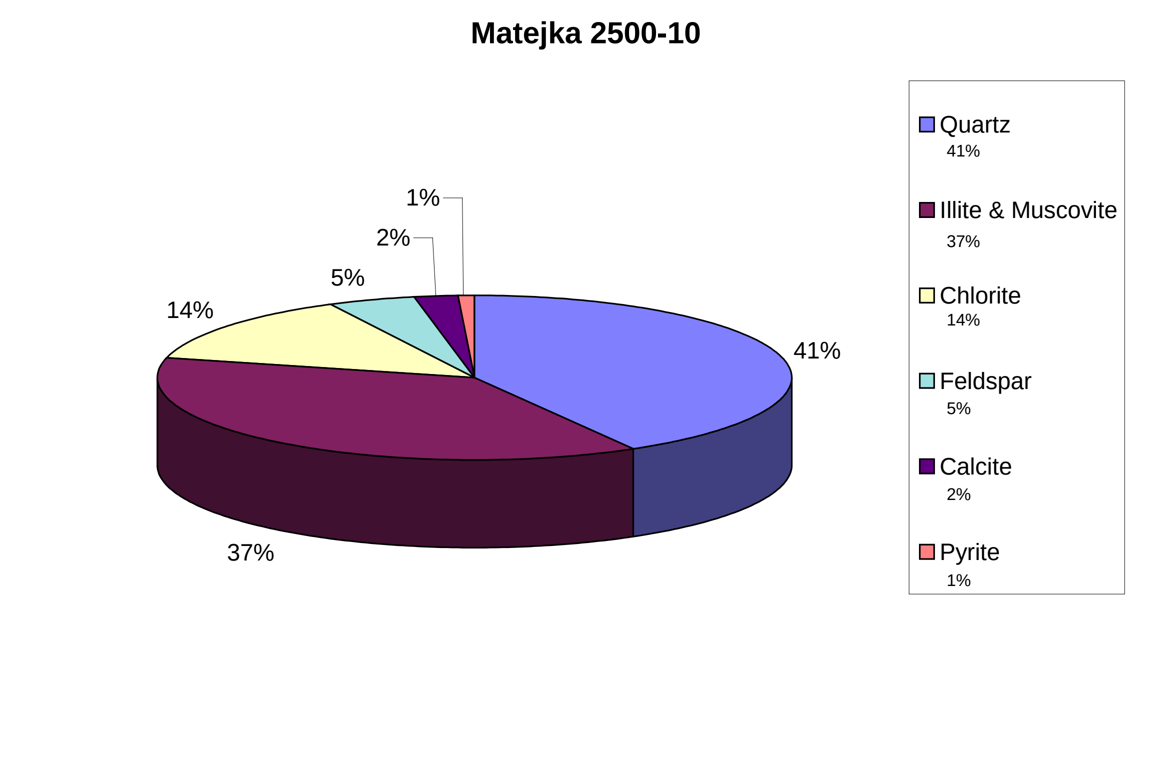

Figure 16. Pie chart displaying mineral weight percent based on Rock Jock analysis of Matejka 2500-10 XRD data.

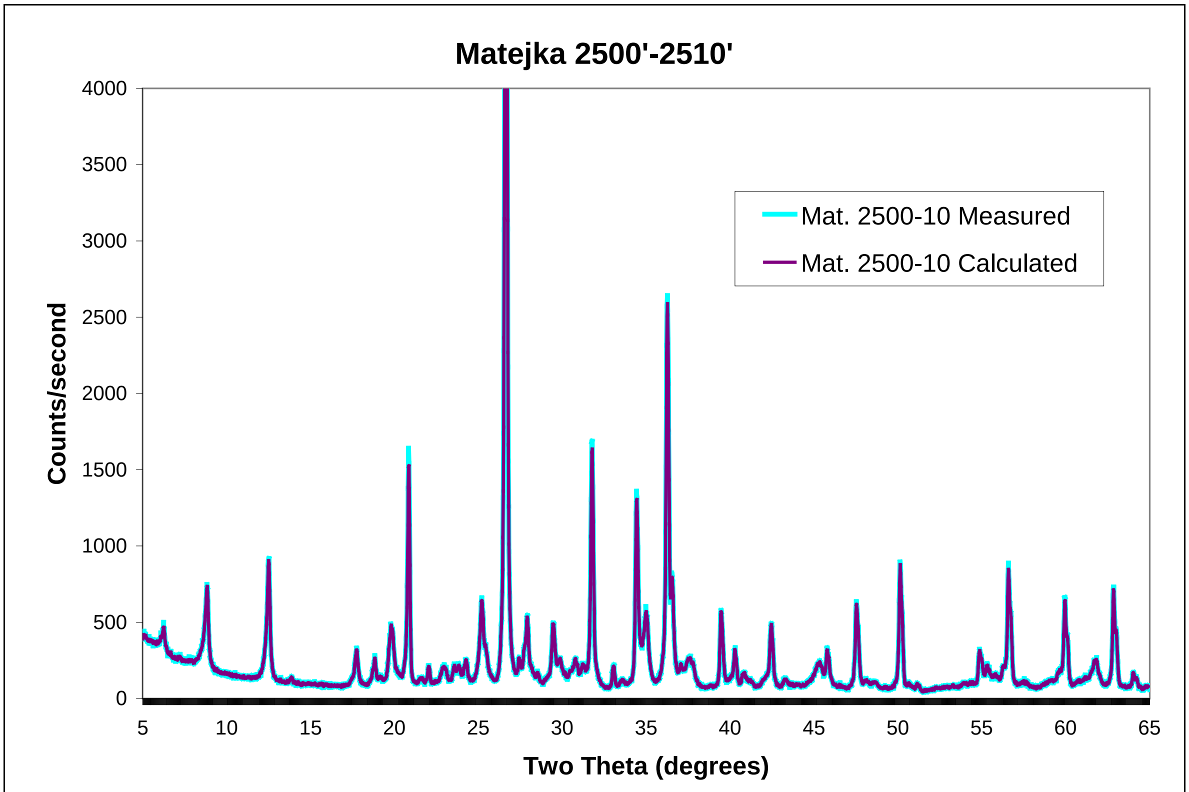

Figure 17. Measured XRD spectra for Matejka 2500-10 compared to calculated Rock Jock spectra.

Minerals	Normalized Percent
Quartz	93
Illite & Muscovite	3
Feldspar	3

Figure 18. Mineral weight percent of Solsville Bridgewater West produced by Rock Jock software.

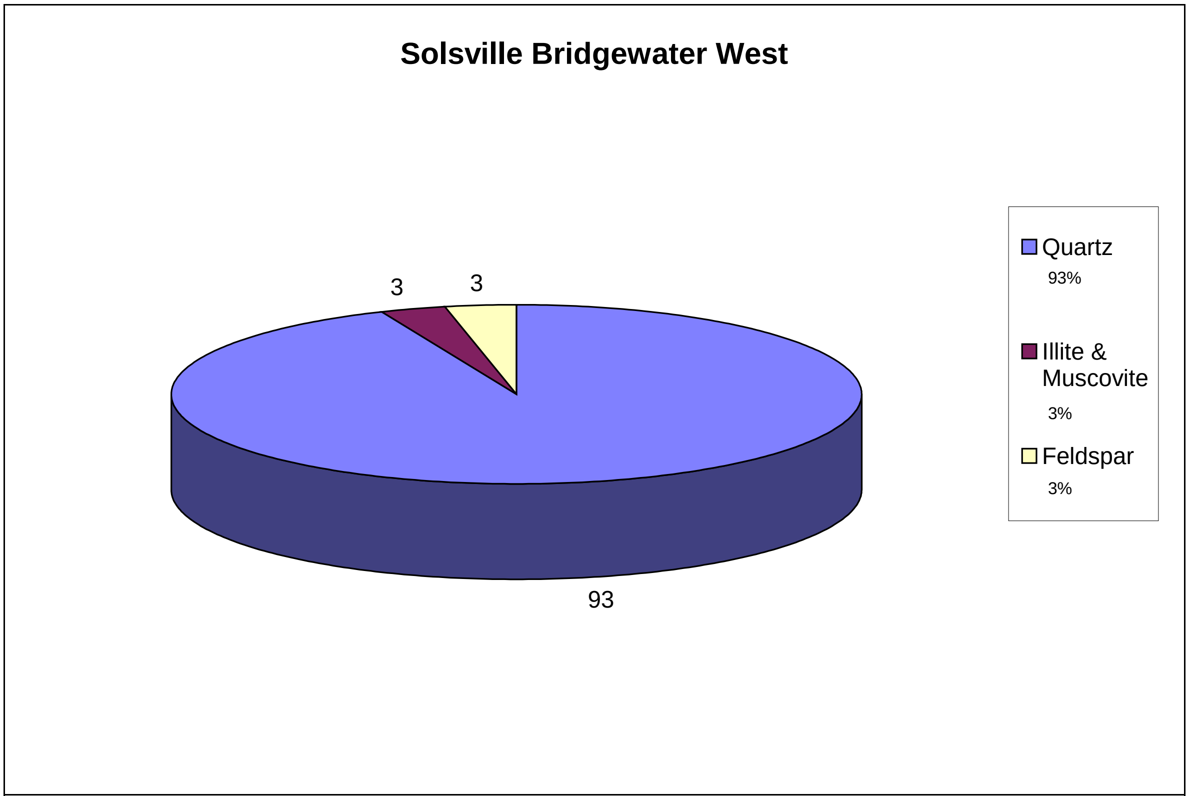

Figure 19. Pie chart displaying mineral weight percent based on Rock Jock analysis of Solsville Bridgewater West data.

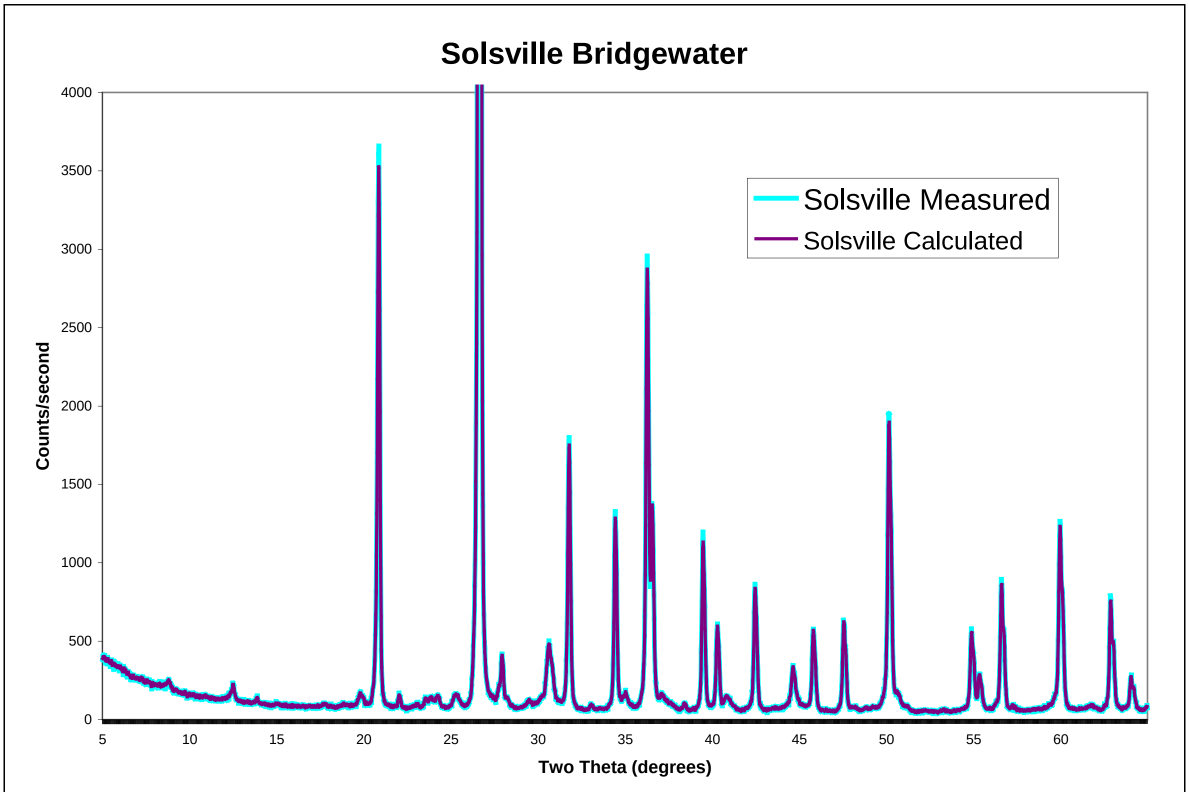

Figure 20. Measured XRD spectra for Solsville Bridgewater compared to calculated Rock Jock spectra.

Minerals	Normalized Percent
Quartz	25
Illite & Muscovite	45
Chlorite	5
Feldspar	3
Calcite	21
Pyrite	1

Figure 21. Mineral weight percent of Upper Union Springs produced by Rock Jock software.

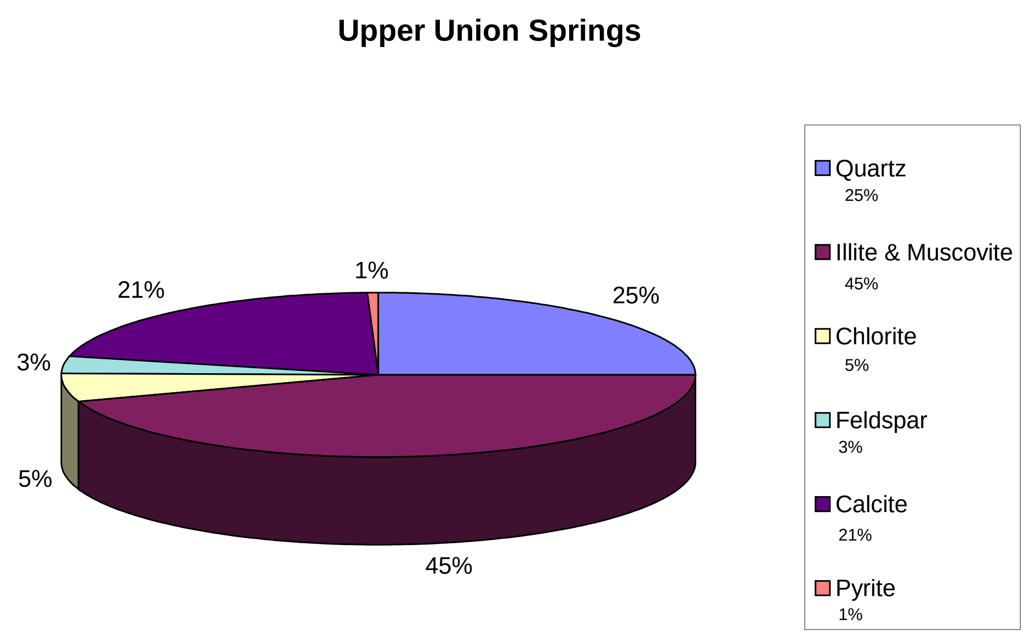

Figure 22. Pie chart displaying mineral weight percent based on Rock Jock analysis of Upper Union Springs data.

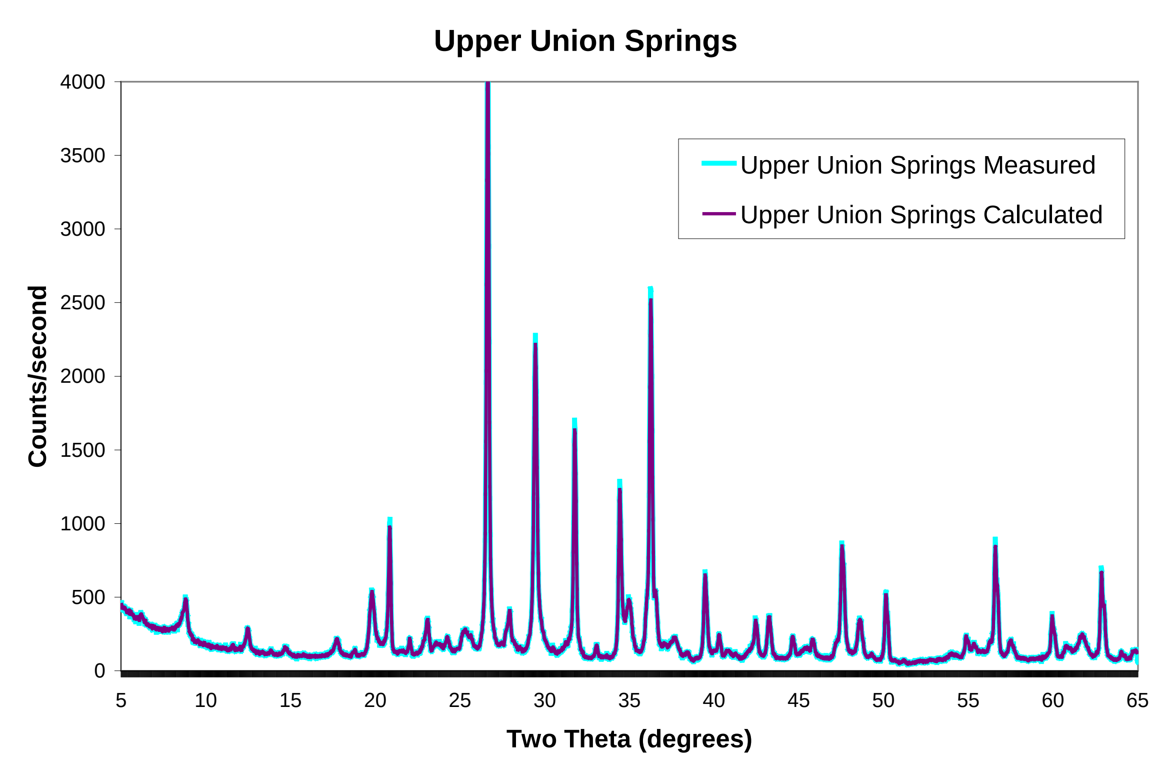

Figure 23. Measured XRD spectra for Upper Union Springs compared to calculated Rock Jock spectra.