



**Diffuse Reflectance Infrared Spectra of the Meade Peak
Phosphatic Shale Member of the Permian Phosphoria
Formation, Caribou County, Idaho**

By Robert J. Horton

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Introduction

The U.S. Geological Survey (USGS) has studied the Permian Phosphoria Formation in southeastern Idaho and the Western U.S. Phosphate Field throughout much of the twentieth century. In response to a request by the U.S. Bureau of Land Management (BLM), a new series of resource and geoenvironmental studies was initiated by the USGS in 1998. These studies involved many scientific disciplines within the USGS and consist of: (1) integrated, multidisciplinary research directed toward resource and reserve estimations of phosphate in selected 7.5-minute quadrangles; (2) elemental residence, mineralogical, and petrochemical characteristics; (3) mobilization and reaction pathways, transport, and disposition of potentially toxic trace elements associated with the occurrence, development, and use of phosphate rock; (4) geophysical signatures; and (5) improving the understanding of depositional origin.

This report presents the diffuse reflectance infrared Fourier transform (DRIFT) spectra for samples of phosphatic shale collected from the Enoch Valley mine located in the Caribou County, Idaho. These measurements were made to characterize the infrared spectral signatures of different rock types within the more-weathered and less-weathered sections of the Meade Peak phosphatic shale member of the Phosphoria Formation. These sections are described in detail by Tysdal and others (1999).

Infrared (IR) spectra were collected on a Nicolet Magna-IR 760 Fourier transform infrared spectrometer (FTIR) equipped with a liquid nitrogen cooled mercury cadmium telluride (MCTA) detector, a KBr beam splitter, and a Barnes Analytical/Spectra-Tech diffuse reflectance accessory. Diffuse reflectance spectra were collected in two overlapping regions of the infrared spectrum, including the near-IR region from 10,000 to 2,000 cm^{-1} and the mid-IR region from 5,000 to 500 cm^{-1} . For the near-IR region a white-light source was used; and for the mid-IR region, an IR glow-bar source was used. The data were

collected with a nominal resolution of 2 cm^{-1} ; typically 200 interferograms were co-added to produce each spectrum.

Ten samples, five from the more-weathered section A, and five from the less-weathered section B, were measured. Samples were selected to represent the upper and lower ore zones and the different waste zones (fig. 1). The bulk mineralogy of the samples, as determined by XRD analysis, are given in table 1 (from Knudsen and Gunter, in press). The measured samples were splits of samples prepared for mineralogical (Knudsen and others, 2000) and chemical (Herring and others, 1999 and 2001) analysis. The samples were measured as received. They had been air dried and ground to >100 mesh ($<0.15\text{mm}$). No additional preparation was performed.

Results

The DRIFT spectra for each sample are given in figures 2 through 11. The position of absorption bands observed in the spectra can be used to identify minerals present in the samples. The given spectra were corrected for atmospheric water and CO_2 absorptions by using a silvered mirror background reflectance spectra as a reference. Band positions and intensities at band minimums, were obtained using the Nicolet peak analysis software (OMNIC, 1999). No additional spectral processing was performed. On the figures the band position of major absorption features are labeled in wave numbers (cm^{-1}). Minor absorption features are not labeled on the figures but are given in Appendix 1.

Absorption band intensities are given as percent reflectance, relative to the background reference spectra. When collecting the background spectrum off the mirror, the aperture of the Magna-IR 760 spectrometer typically is closed to a minimum setting. Many of the phosphatic shale samples are black, with very low spectral reflectance. To measure the spectra of these dark samples, the spectrometer's aperture was opened to a maximum setting to compensate for the

samples' low reflectance. Due to the wide-open aperture, some of the measured sample reflectance may exceed the background reflectance, resulting in a percent reflectance calculation greater than 100 percent for some parts of the measured spectra.

Ore Zone Samples

Samples wpsa006c and wpsb008c are from the lower ore zone of sections A and B, whereas samples wpsb131c and wpsb133c are from the upper ore zone of section B. These samples primarily consist of apatite, ranging from 75 to 88 percent. These ore zone samples have very similar spectral signatures (fig. 12), regardless of the section (A or B) or ore zone (lower or upper). A characteristic absorption band at 966 cm^{-1} is a fundamental apatite vibrational band (Ross, 1974).

Sample wpsb038c is a carbonate-rich sample from the lower ore zone of the less-weathered section B. The wpsb038c spectrum (fig. 8) is significantly different than other spectra due to the high percentage of calcite. Characteristic calcite absorption bands (White, 1974) are observed at 880, 1,099, $1,409\text{ cm}^{-1}$. Other high intensity bands observed at 2,163, 2,336, 2,525, 2,628, 2,898 and $3,022\text{ cm}^{-1}$ are not seen in the noncarbonate sample spectra and, therefore, probably represent overtone and combination bands of calcite fundamental absorption features.

Waste Zone Samples

Samples wpsa085c, wpsa087c, wpsa131c, and wpsb095c are from the middle waste zone. The spectra of these middle waste samples are somewhat similar (fig. 13); however, the spectrum of sample wpsb095c varies due to the relatively high carbonate content. These middle waste samples also contain buddingtonite, an ammonium feldspar, in percentages ranging from ~16 to 53 percent. Figure 14 shows the characteristic absorption band at $\sim 4,717\text{ cm}^{-1}$

produced by the NH^{4+} ion within the buddingtonite crystal structure (Clark and others, 1993).

Sample wpsa156c is from the upper waste zone of the more-weathered section A. The wpsa156c spectrum (fig. 6) is similar to the middle waste spectral signatures; however, it lacks the $4,717 \text{ cm}^{-1}$ buddingtonite absorption feature. The $4,527 \text{ cm}^{-1}$ band is a combination band (OH stretch + OH bend) produced by clay minerals.

Equivalent Interval Samples

Several samples were collected from essentially the same interval, but from different sections. Samples wpsa006c and wpsb008c come from the lower ore zone of the more-weathered and less-weathered sections, respectively. These ore zone samples do have very similar spectra as shown fig. 15. The weathering, which differentiates the two sections has not produced significant differences in the spectral character of these lower ore zone samples. However, subtle differences are present in the higher frequency part of the spectra, particularly in the $3,000$ to $5,000 \text{ cm}^{-1}$ region. Absorption band position data given in Appendix 1 indicate a $4,526 \text{ cm}^{-1}$ clay band in the more-weathered wpsa006c spectra but not in the less-weathered wpsb008c spectra.

Samples wpsa131c and wpsb131c are from much higher in the section. Although these samples are from the same interval, they are located in different units. Sample wpsa131c is from the middle waste unit, whereas sample wpsb131c is from the D bed of the upper ore zone (Tysdal and others, 1999). These samples have significantly different mineral compositions (table 1) producing markedly different spectral signatures (fig. 16).

Summary

DRIFT spectra were collected to characterize the infrared spectral signatures of different rock types within the more-weathered and less-weathered

sections of the Meade Peak Phosphatic Shale member of the Phosphoria Formation. The ore-bearing samples have characteristic spectral signatures produced by the high concentration of apatite in the ore zones. No significant differences were observed in the spectra of ore samples from the upper and lower ore zone samples. Minor spectral differences were observed between ore samples from the more- and less-weathered sections, caused by the presence of clay minerals in the more-weathered section. Samples from the different waste zones have significantly different spectral signatures. The spectral signature of carbonate-bearing waste is distinguished easily from that of noncarbonate bearing waste by the presence of characteristic calcite absorption bands. Waste containing buddingtonite is characterized by an absorption band at $\sim 4,717 \text{ cm}^{-1}$.

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Table 1. Sample mineralogy as determined by XRD analysis (From Knudsen and Gunter, in press).

Sample	Apatite	Quartz	Muscovite	Illite	Albite	Orthoclase	Buddingtonite	Kaolinite	Dolomite	Calcite
wpsa006c	85	6.3	6	0.1	0.1	0.1	0	1.3	0	0
wpsa085c	3.4	40	13	0.1	7.9	8	23.5	3.4	0	0
wpsa087c	10.7	5.9	34	0.1	0.4	3	53	2.4	1.5	0
wpsa131c	0.5	39	5	0.1	23	15	16.2	0.1	0.2	0
wpsa156c	9.2	53	10	0	5.1	9.1	0.4	6.6	0	0
wpsb008c	88	7.3	2	0.1	0.1	0.1	0.8	0	0	0
wpsb038c	4.4	10.1	0.1	0.1	3.4	1.9	1	0	0	79
wpsb095c	10.9	40.3	9.7	0.1	10.3	4.3	17	1.3	0.4	8.7
wpsb131c	75	8.1	15	2	0.1	0.1	0.1	0	0	0.1
wpsb133c	83	8.8	6	0.1	0.1	0.1	1.7	0	0.4	0.1

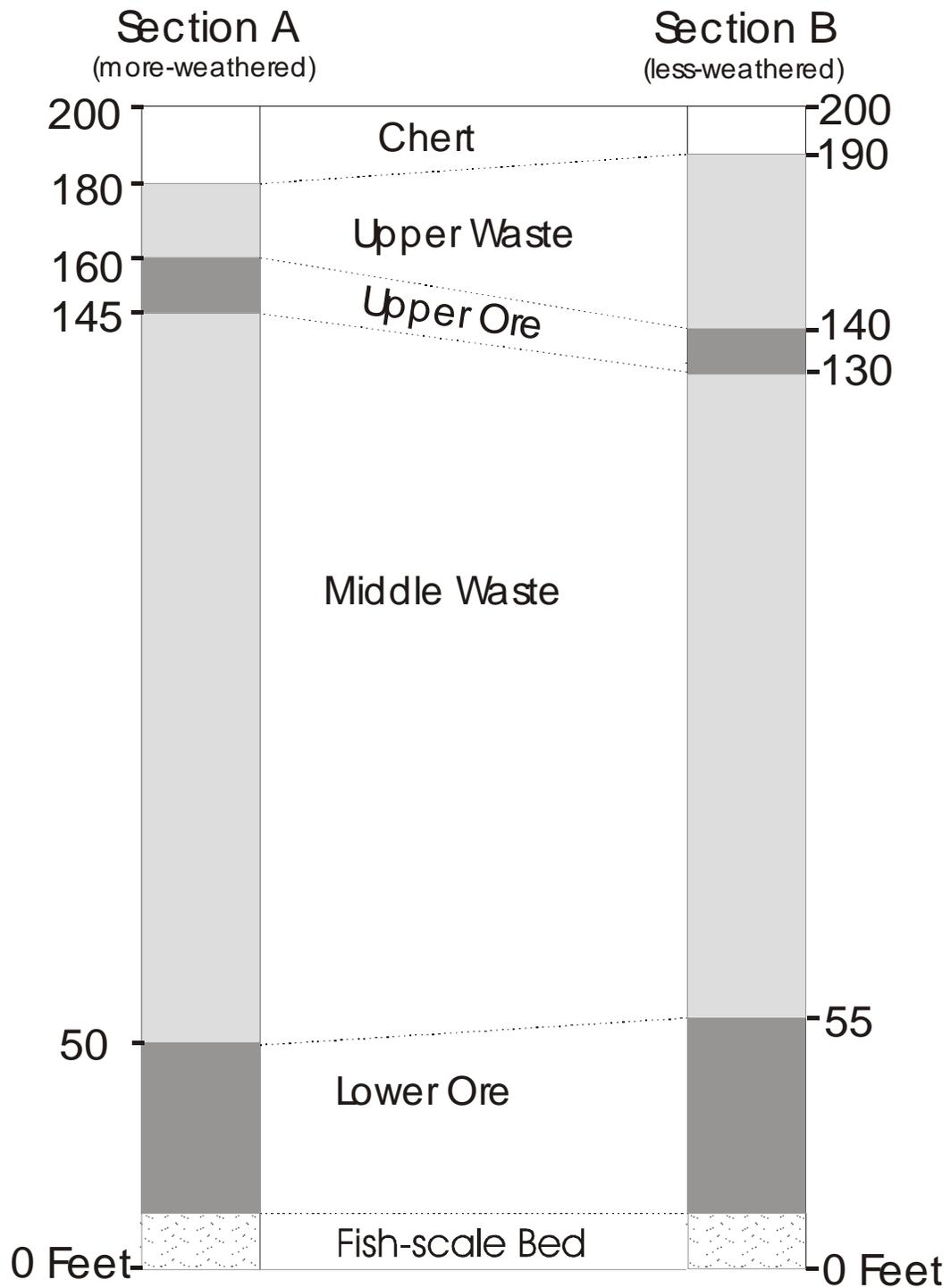


Figure 1. Simplified stratigraphic sections A and B of the Mead Peak phosphatic shale member of the Phosphoria Formation. Numbers are in feet, using the base of the Fish-scale bed as a datum. Modified from Herring and others (2001). Note the figure is not to scale.

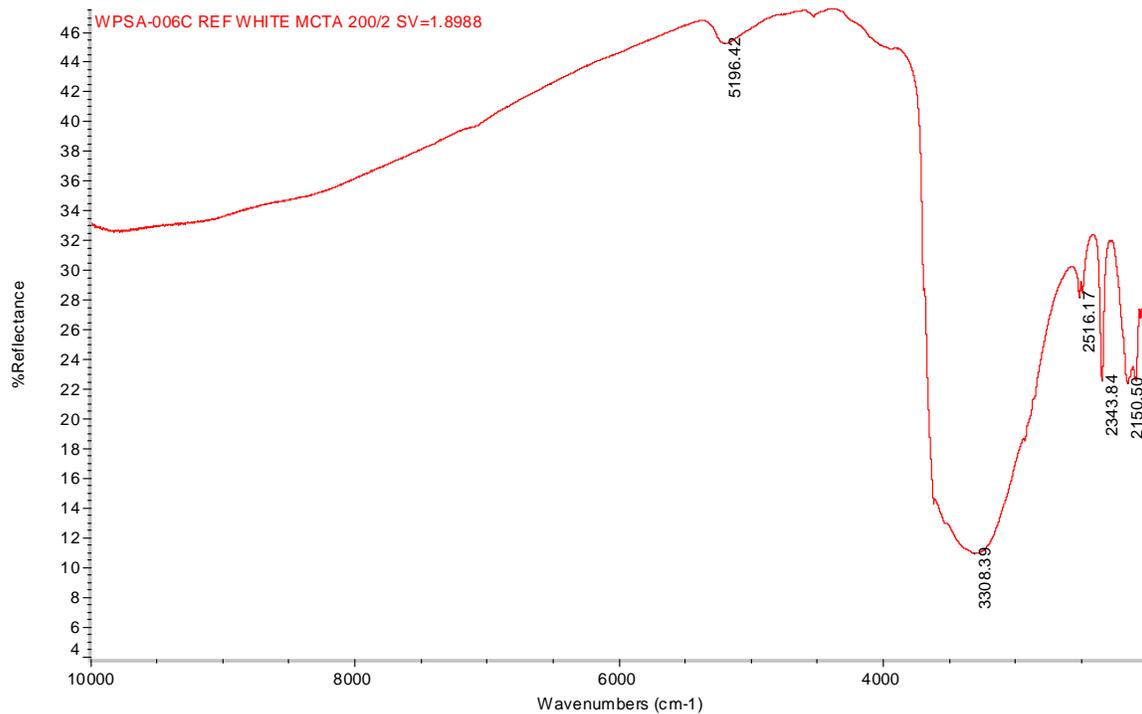
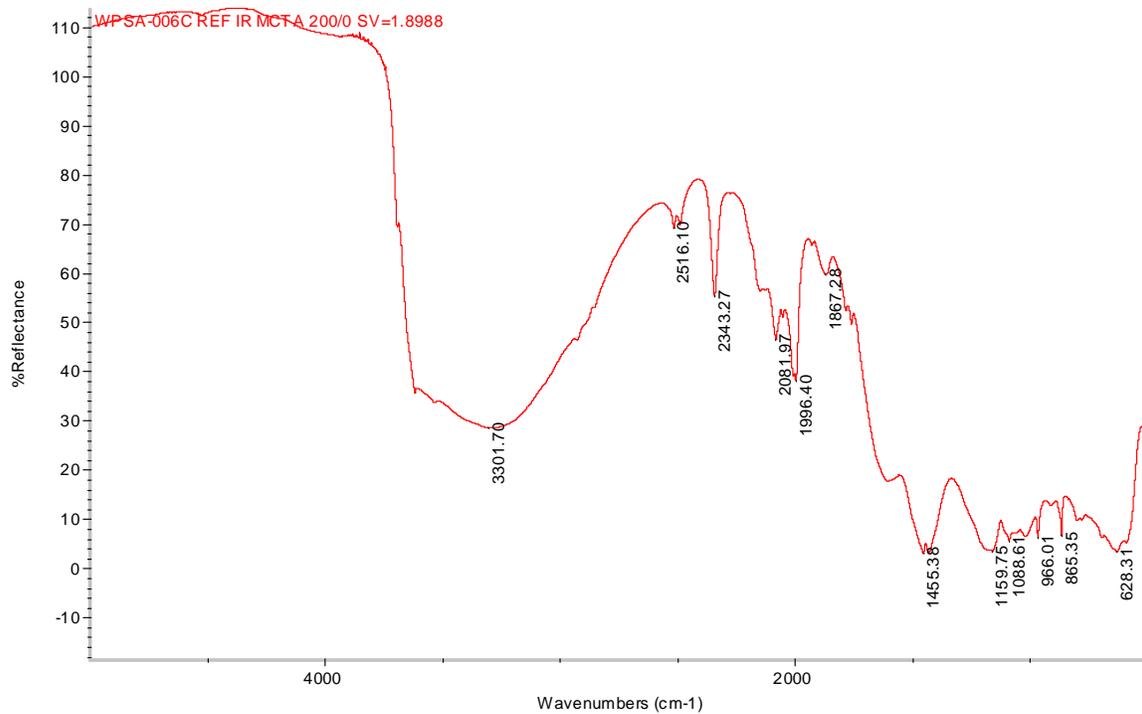


Figure 2. Mid-IR (top) and near-IR (bottom) spectra of sample wpsa006c from the lower ore zone of the more-weathered section A.

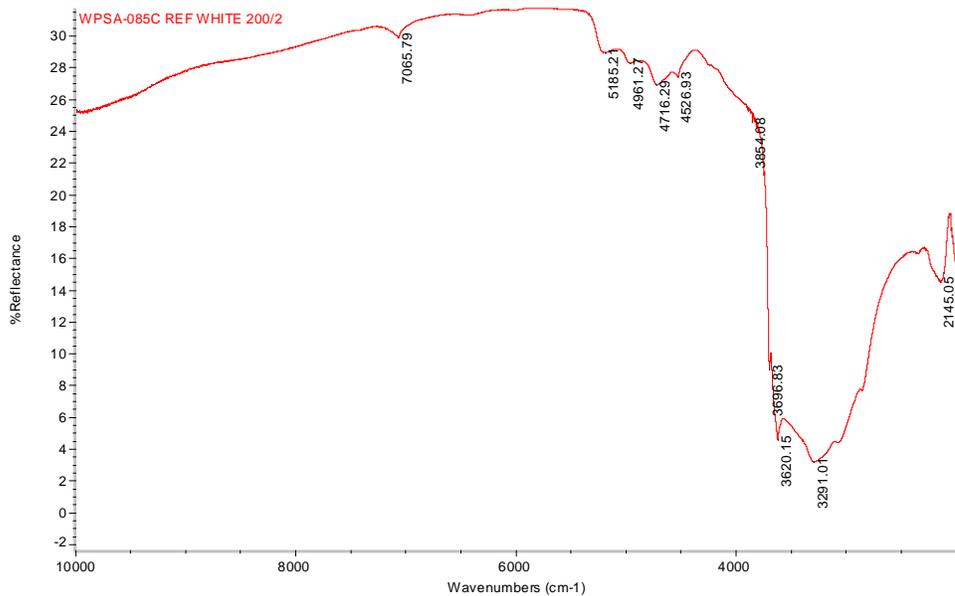
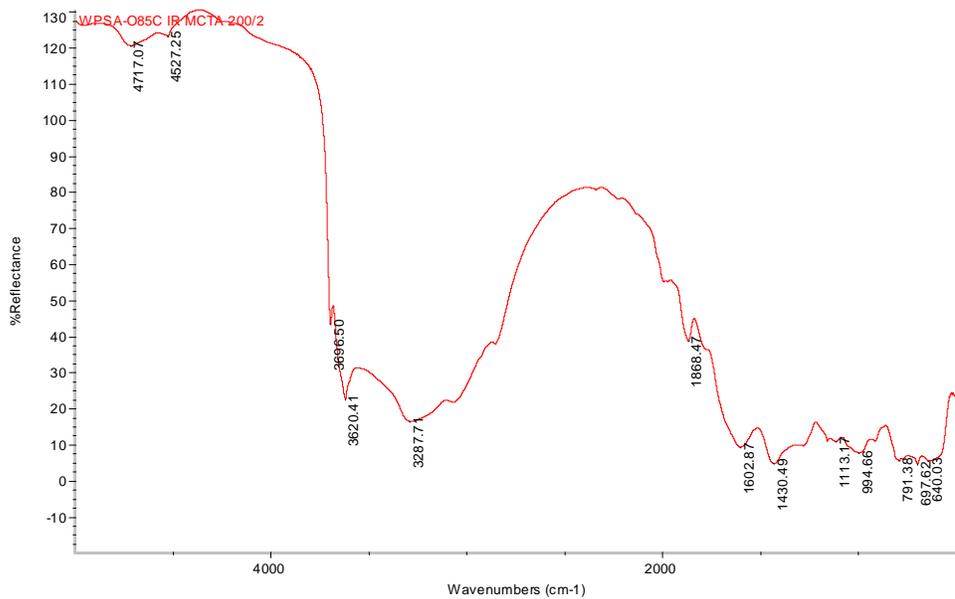


Figure 3. Mid-IR (top) and near-IR (bottom) spectra of sample wpsa085c from the middle waste zone of the more-weathered section A.

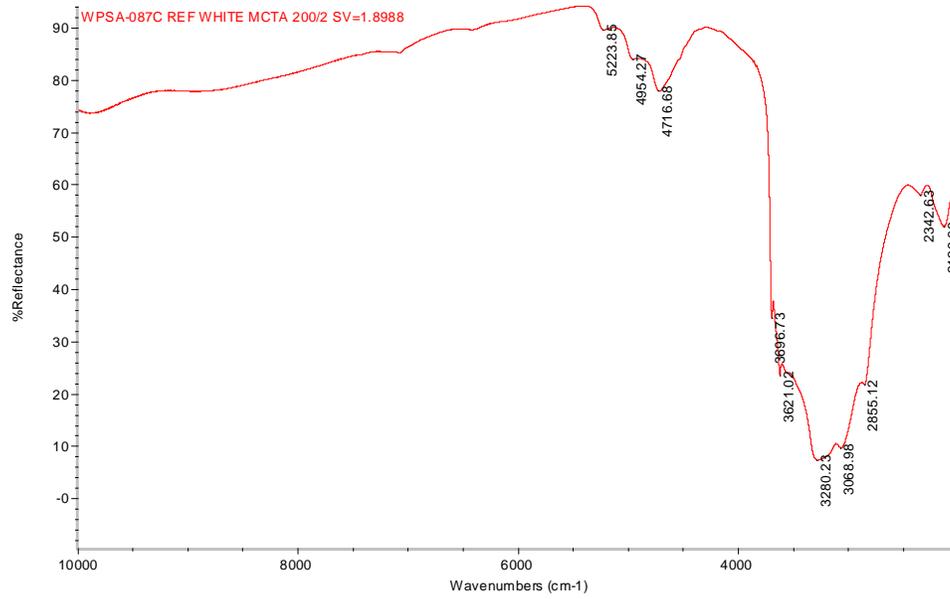
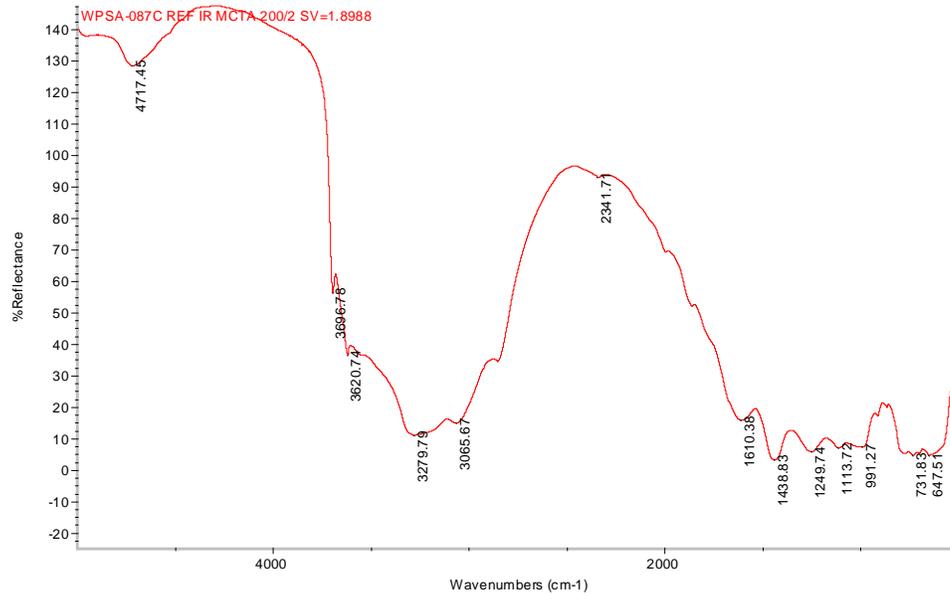


Figure 4. Mid-IR (top) and near-IR (bottom) spectra of sample wpsa087c from the middle waste zone of the more-weathered section A.

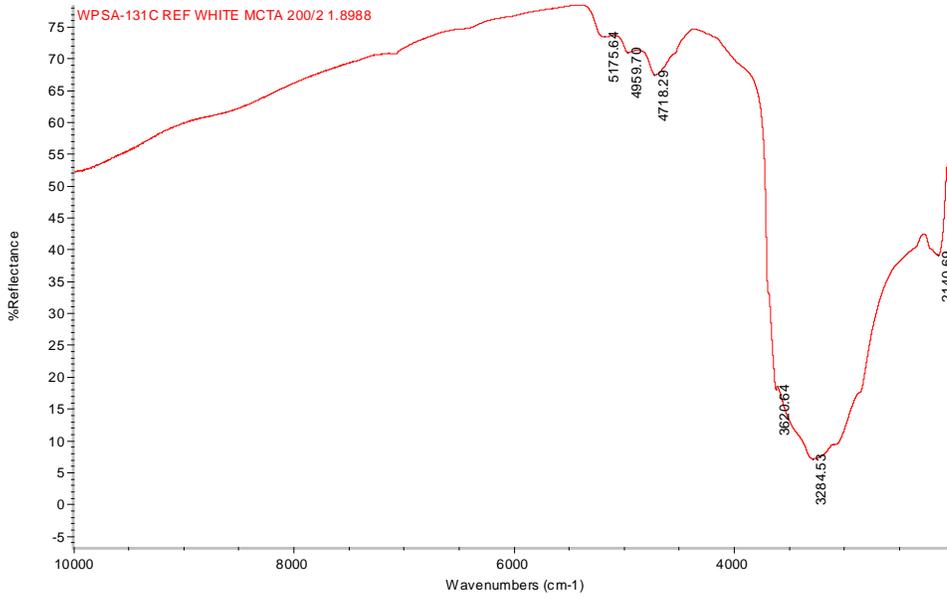
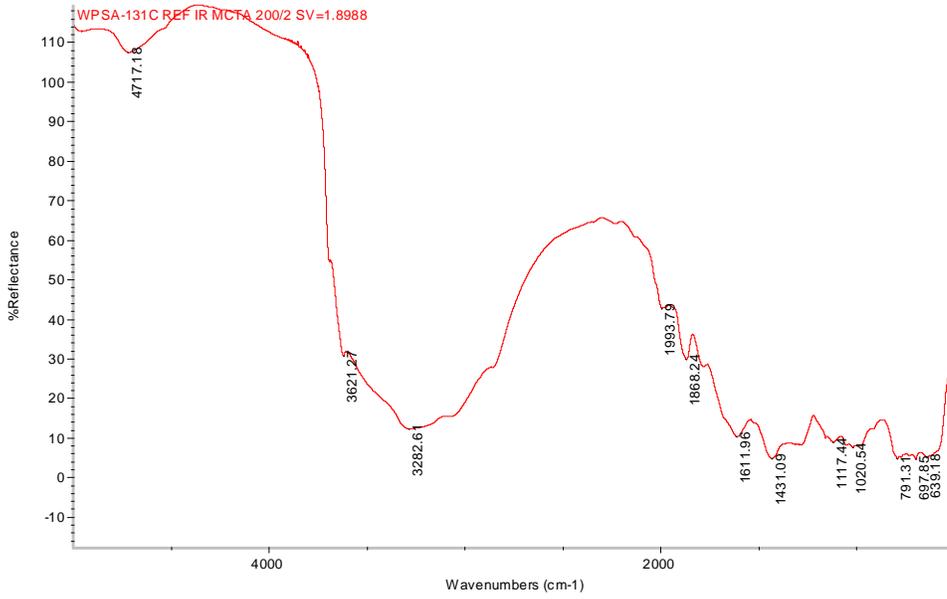


Figure 5. Mid-IR (top) and near-IR (bottom) spectra of sample wpsa131c from the middle waste zone of the more-weathered section A.

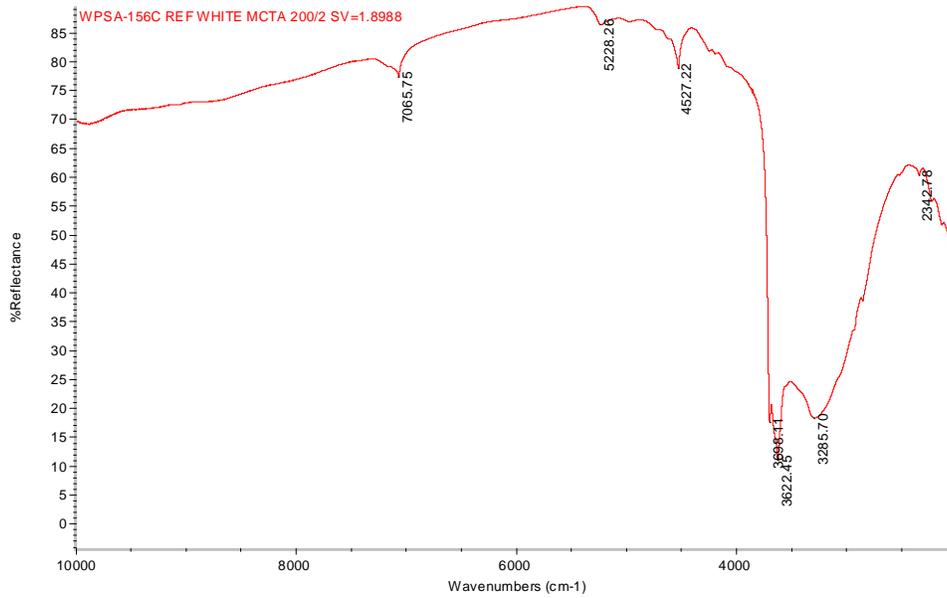
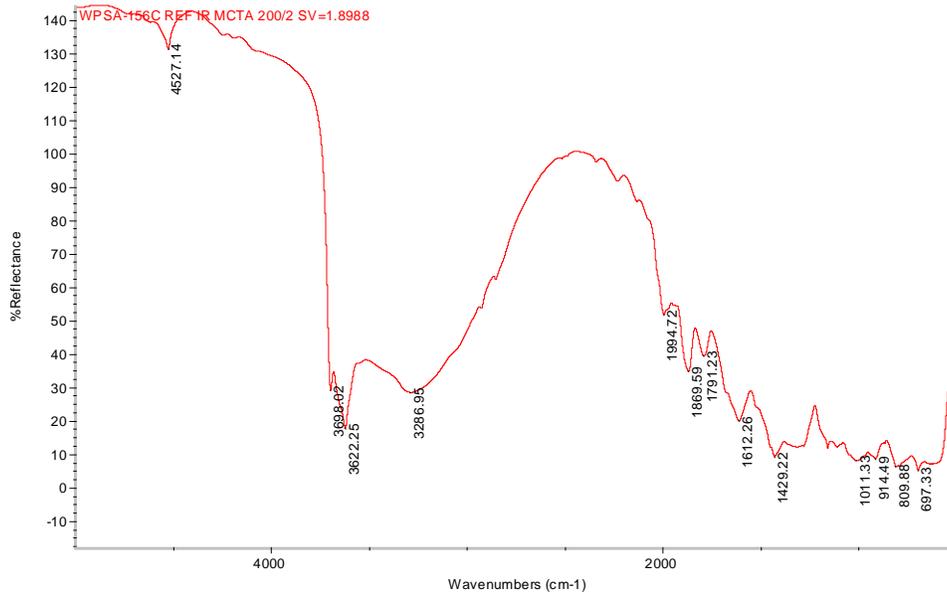


Figure 6. Mid-IR (top) and near-IR (bottom) spectra of sample wpsa156c from the upper waste zone of the more-weathered section A.

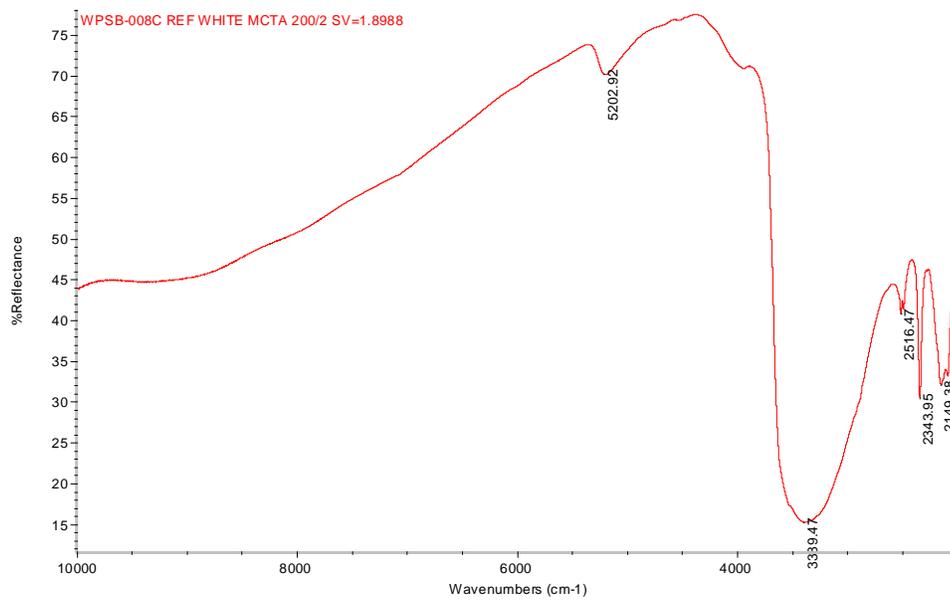
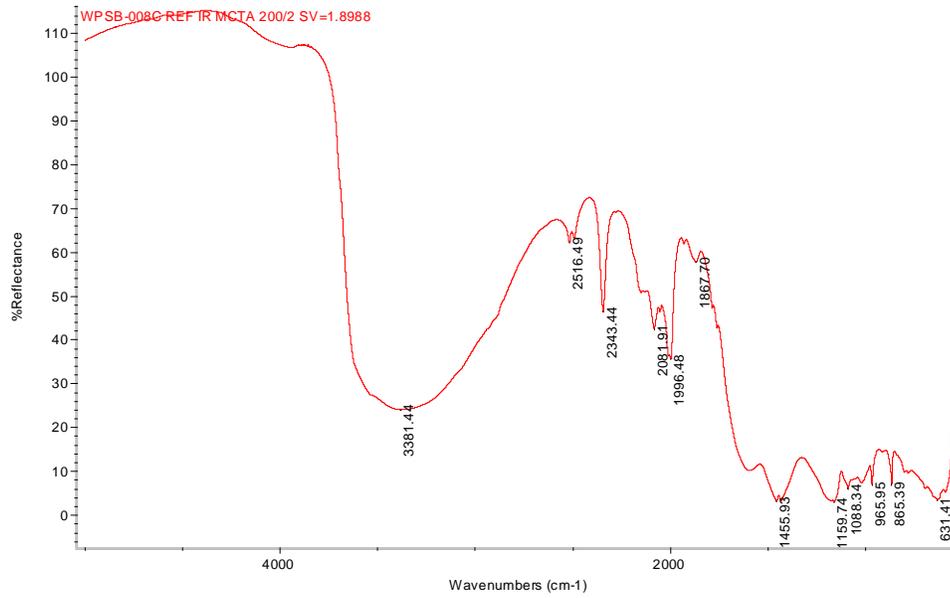


Figure 7. Mid-IR (top) and near-IR (bottom) spectra of sample wpsb008c from the lower ore zone of the less-weathered section B.

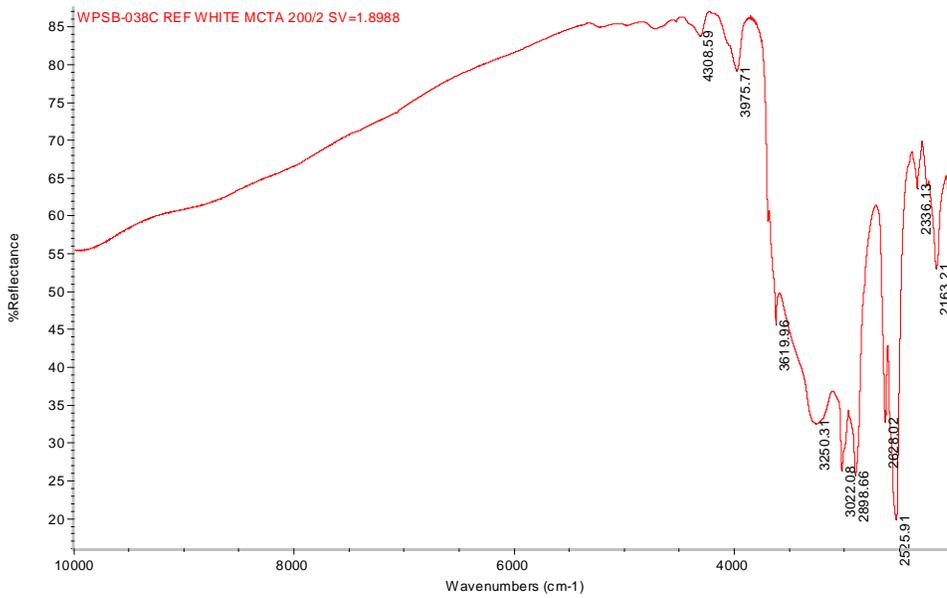
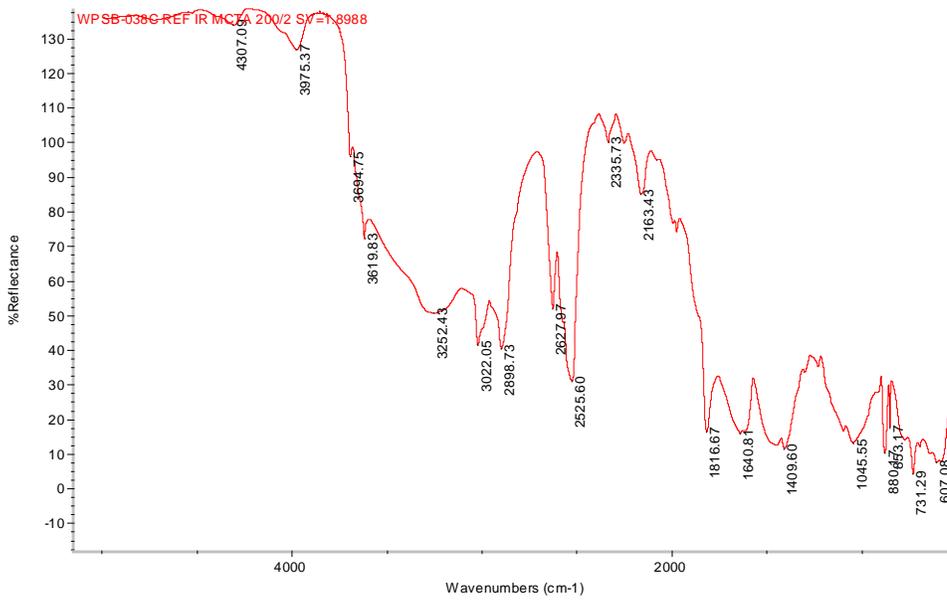


Figure 8. Mid-IR (top) and near-IR (bottom) spectra of carbonate-rich sample wpsb038c from the lower ore zone of the less-weathered section B.

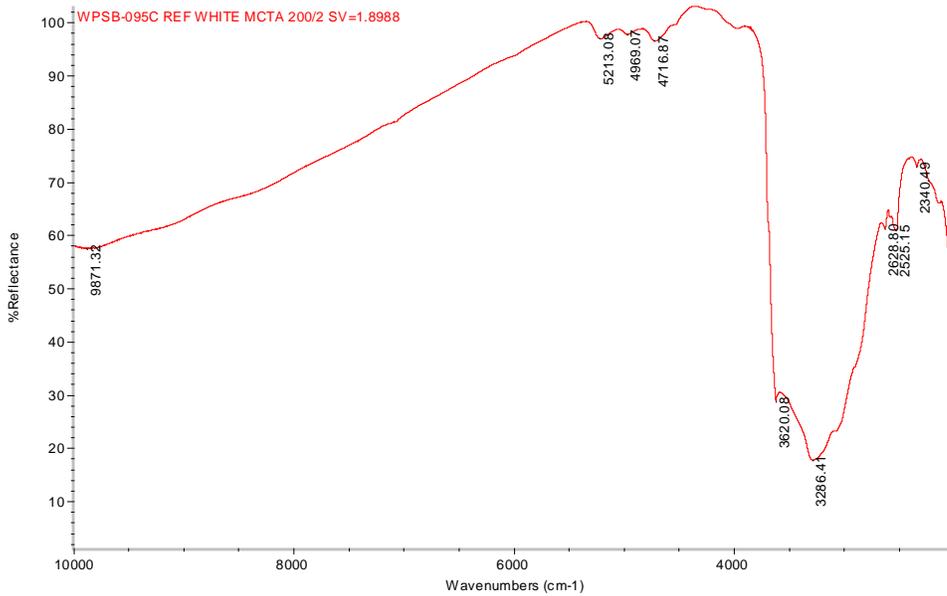
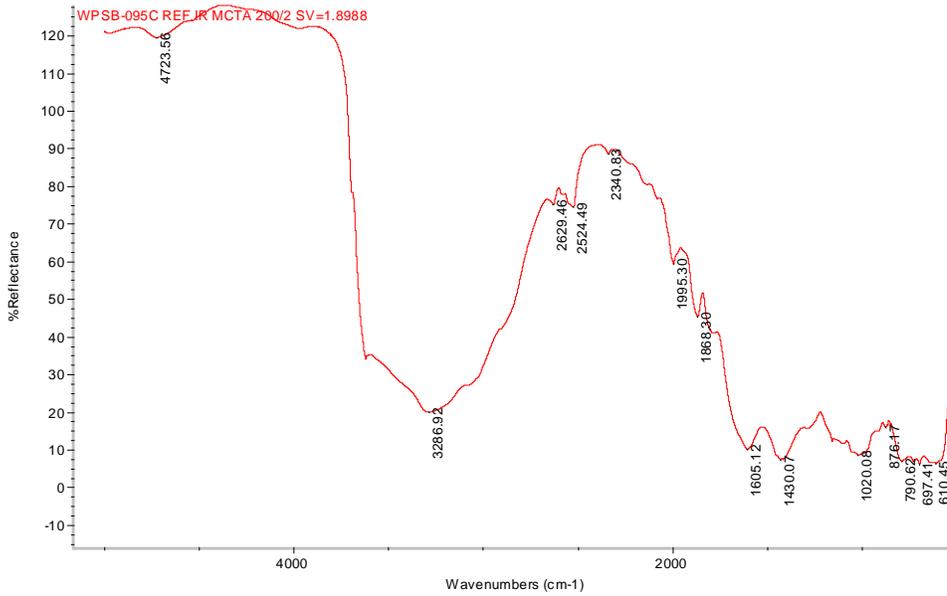


Figure 9. Mid-IR (top) and near-IR (bottom) spectra of sample wpsb095c from the middle waste zone of the less-weathered section B.

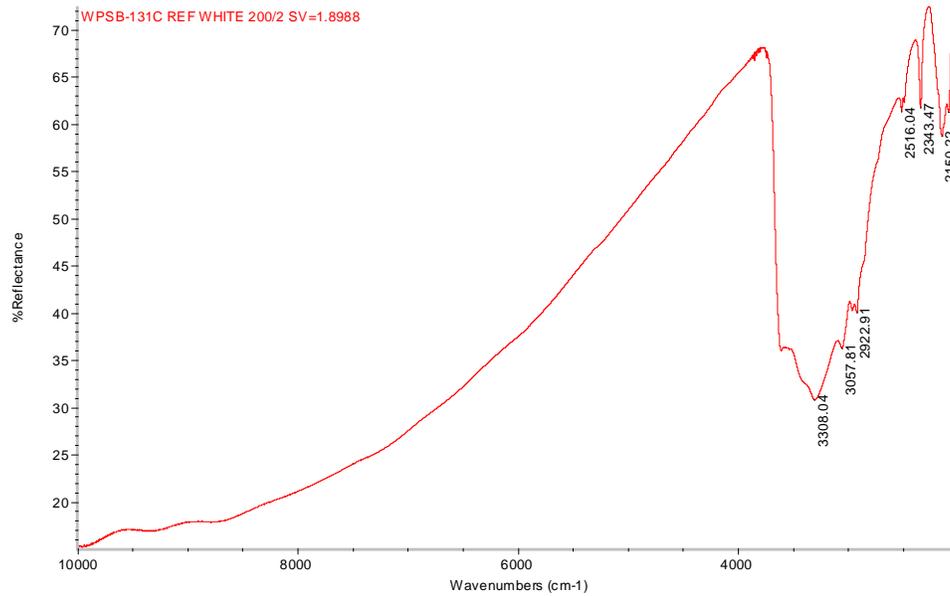
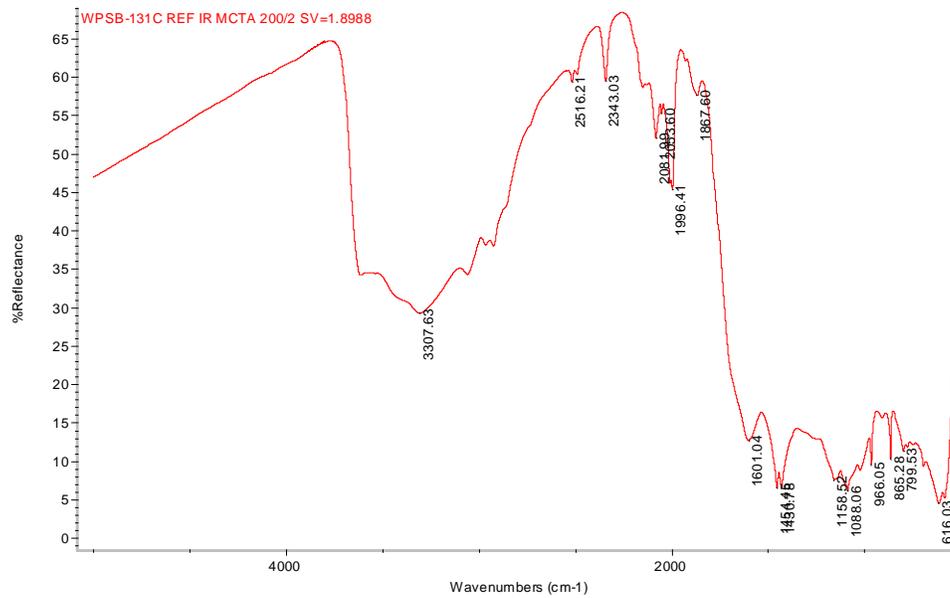


Figure 10. Mid-IR (top) and near-IR (bottom) spectra of sample wpsb131c from the upper ore zone of the less-weathered section B.

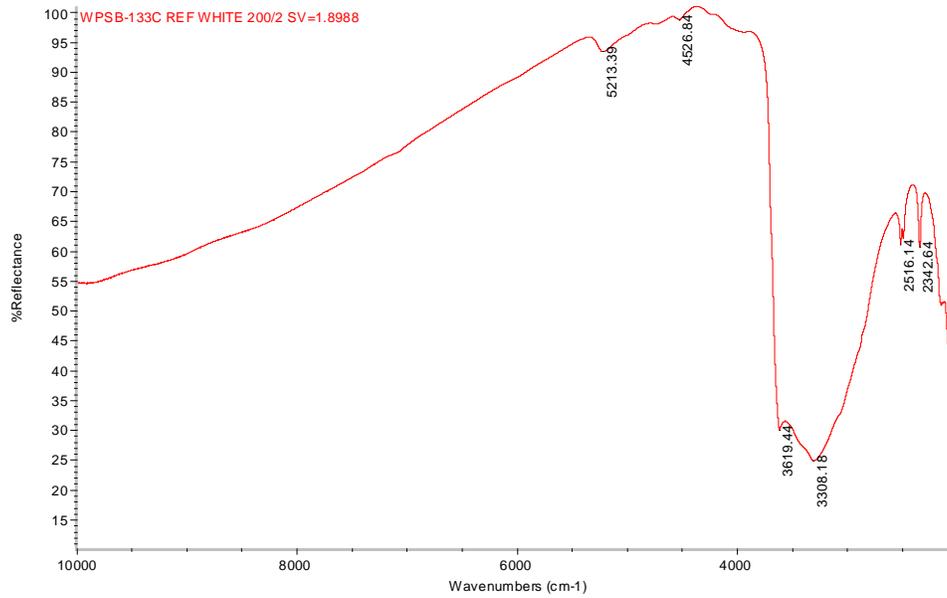
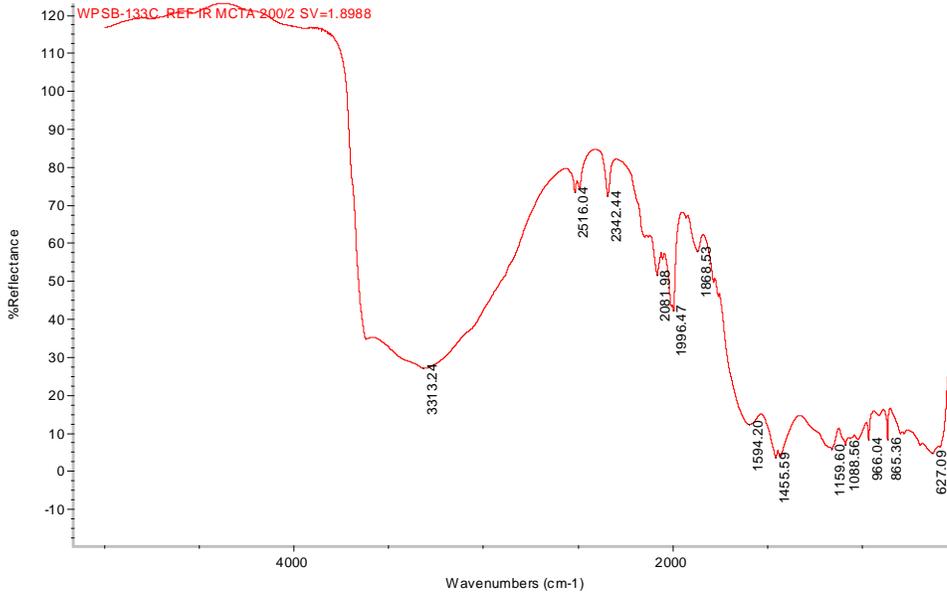


Figure 11. Mid-IR (top) and near-IR (bottom) spectra of sample wpsb133c from the upper ore zone of the less-weathered section B.

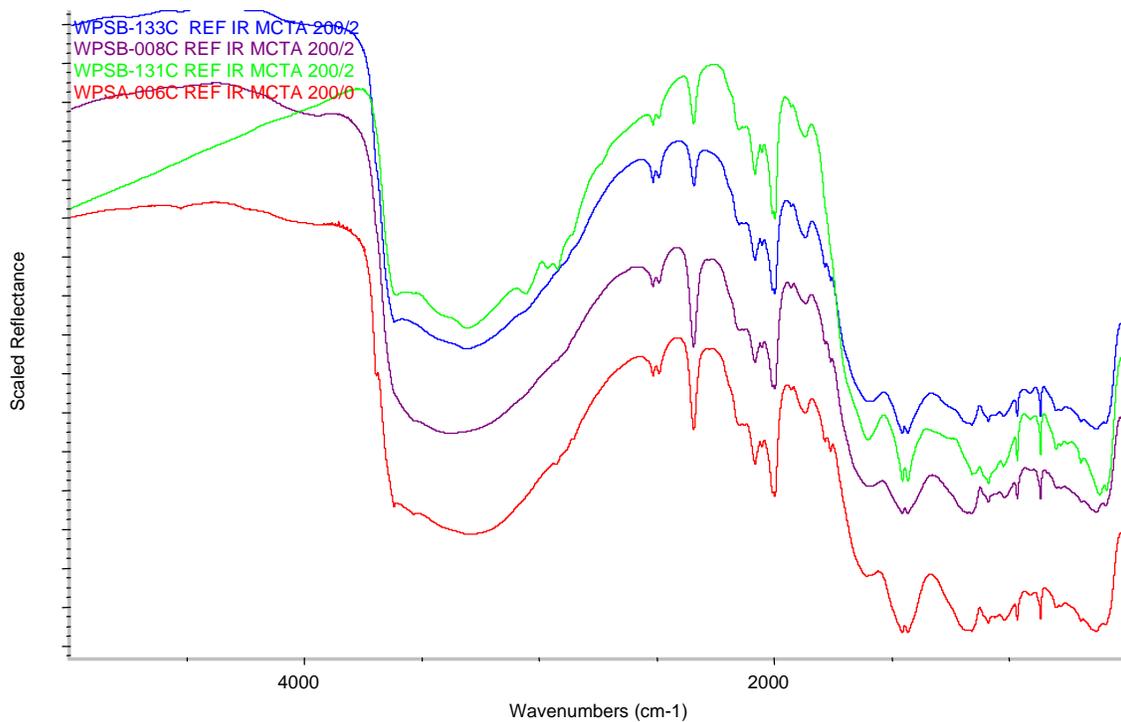


Figure 12. Stacked mid-IR spectra of ore samples. These samples are 75 to 88 percent apatite, resulting in similar spectral signatures.

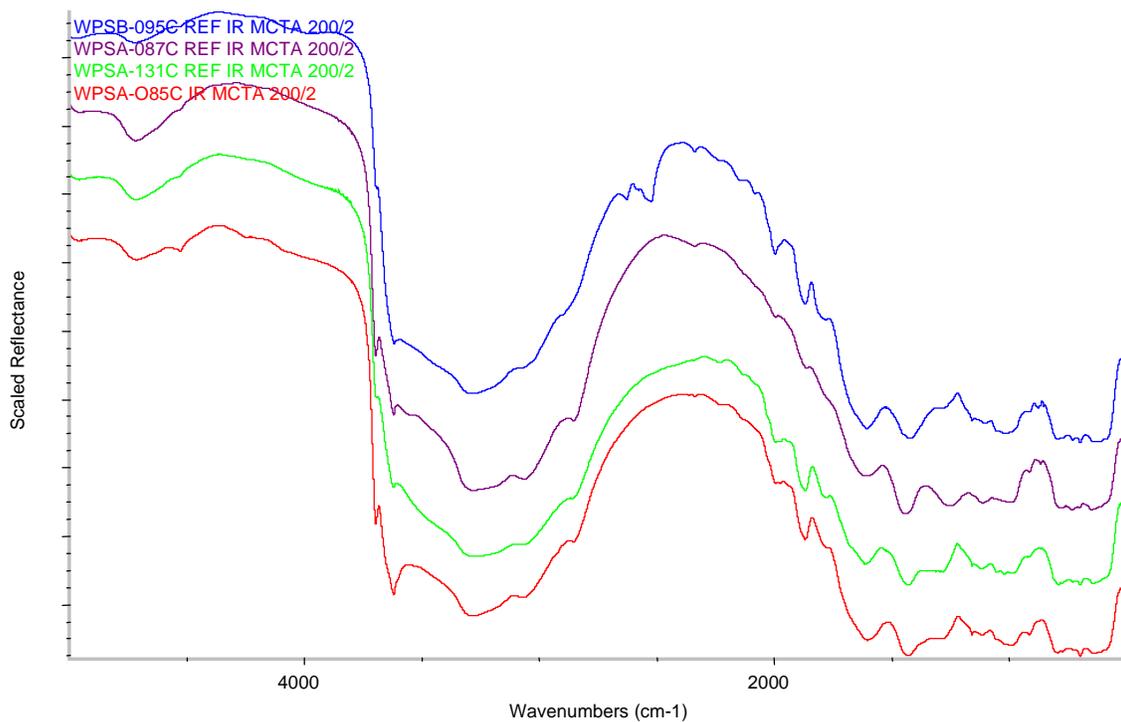


Figure 13. Stacked mid-IR spectra of middle waste samples.

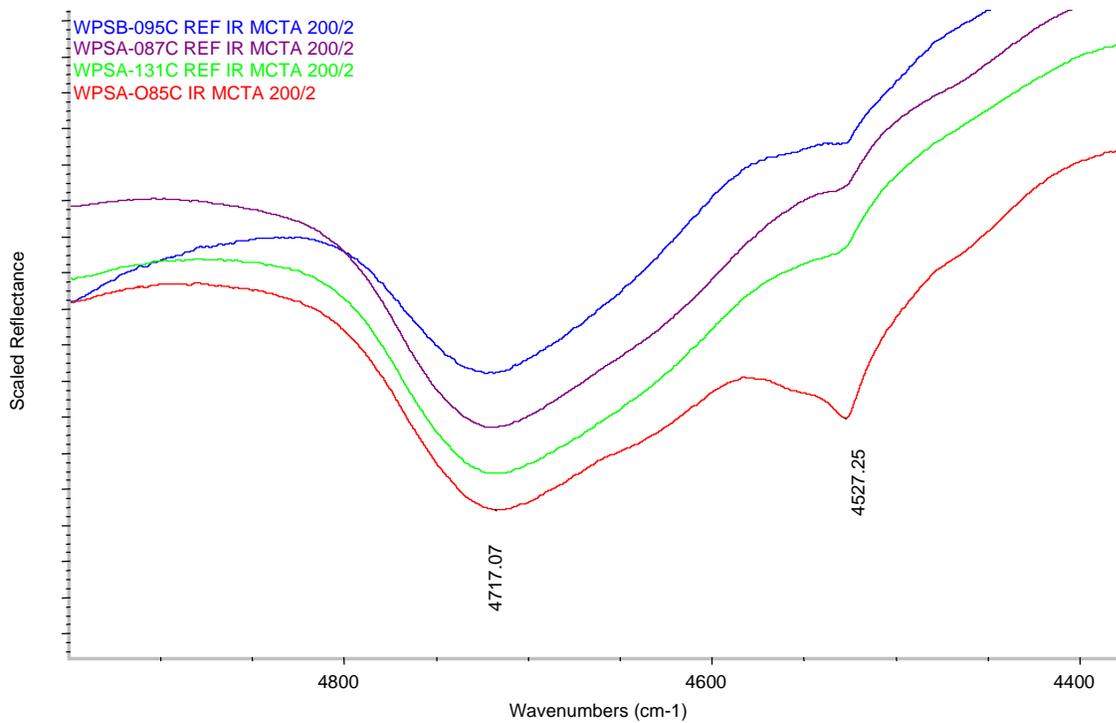


Figure 14. Stacked mid-IR spectra of middle waste samples showing the 4717cm^{-1} absorption band produced by the NH_4^+ ion within the buddingtonite structure. The 4527 cm^{-1} feature is a clay band.

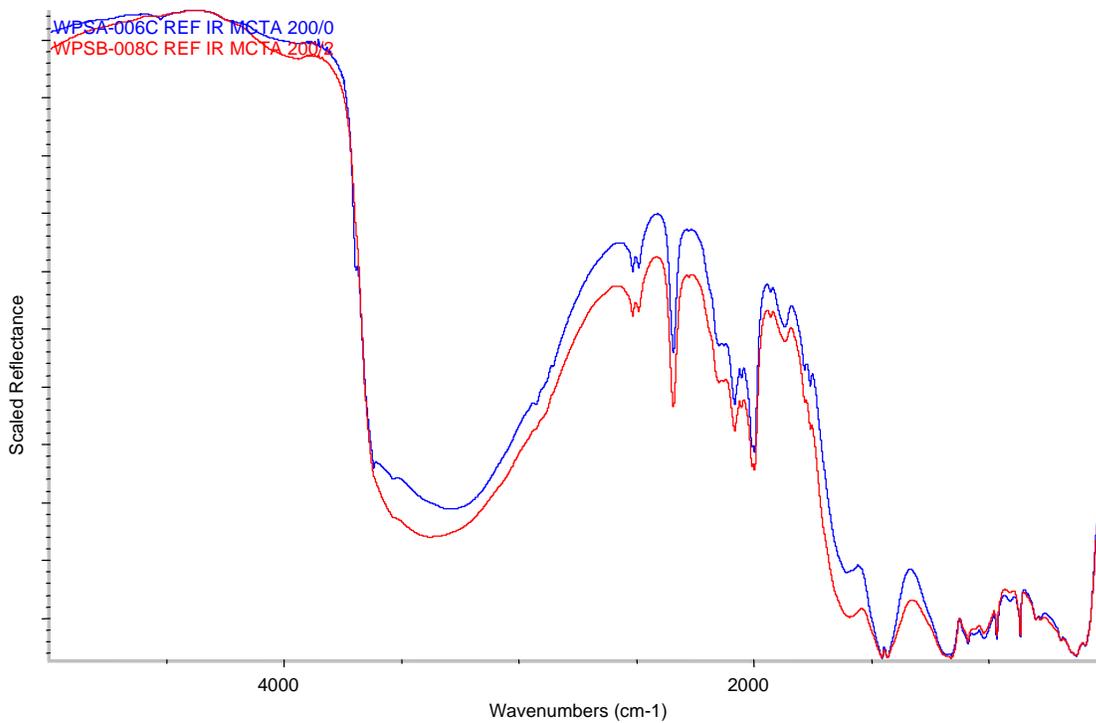


Figure 15. Mid-IR spectra of samples wpsa006c and wpsb008c from the lower ore zone. These samples were collected from essentially the same interval, but from the different sections.

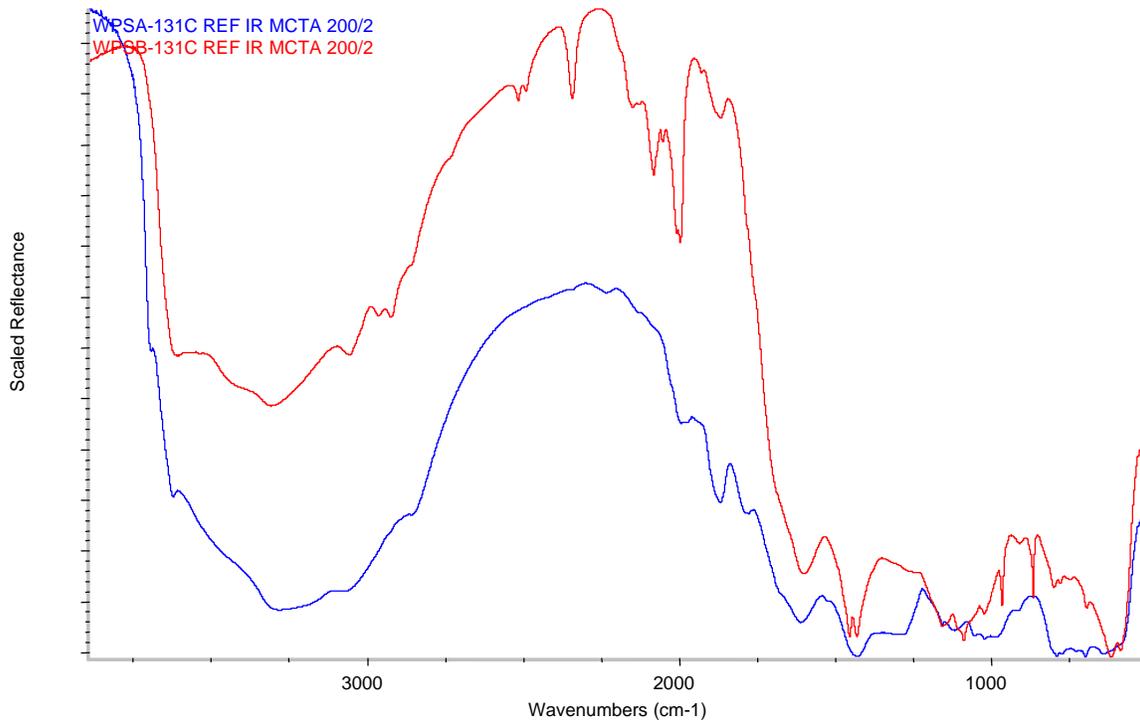


Figure 16. Mid-IR spectra of samples wpsa131c and wpsb131c. These samples were collected from essentially the same interval, but from the different sections. The different spectral signatures indicate these samples have significantly different mineralogy.

APPENDIX 1

DRIFT absorption band positions (cm^{-1}) and intensities (% reflectance), at band minimums, obtained by using the Nicolet peak analysis software (OMNIC, 1999). Absorption band intensities are given as percent reflectance relative to a background reference spectra. Many of the phosphatic shale samples have very low diffuse reflectance. To measure the spectra of these dark samples, the spectrometer's aperture was opened to a maximum setting to compensate for the samples low reflectance. Due to the large aperture setting, the measured sample reflectance may exceed the background reflectance resulting in a greater than 100 percent intensity calculation.

WPSA-006C

Region:	5000-500	Region:	10000-2000
Position:	Intensity:	Position:	Intensity:
628.31	3.143	2054.74	26.674
799.52	9.338	2085.33	22.42
865.35	6.283	2150.5	22.278
911.34	12.475	2343.84	22.485
966.01	5.988	2490.73	28.382
1021.63	6.104	2516.17	28.058
1088.61	5.296	3308.39	10.811
1159.75	3.12	3619.62	14.135
1430.98	2.8	4526.48	46.975
1455.38	2.754	5196.42	45.183
1605.32	17.429	9762.08	32.465
1760.35	49.403		
1785.43	52.017		
1867.28	59.493		
1929.49	65.392		
1996.4	37.886		
2053.69	50.714		
2081.97	46.215		
2343.27	55.062		
2490.77	69.638		
2516.1	68.897		
3301.7	28.258		
3619.62	35.314		
3694.21	69.071		
3858.95	107.643		

WPSA-O85C

Region:	5000-500	Region:	10000-2000
Position:	Intensity:	Position:	Intensity:
522.47	23.651	2145.05	14.422
640.03	5.095	3291.01	3.096
697.62	4.279	3620.15	4.474
791.38	5.236	3696.83	8.947
913.94	10.618	3854.08	24.502
994.66	7.373	4716.29	26.841
1113.17	10.453	7065.79	29.79
1158.84	10.484		
1430.49	4.389		
1602.87	8.985		
1868.47	38.509		
1973	54.875		
2341.78	80.378		
2854.45	37.515		
3069.6	21.46		
3287.71	16.041		
3620.41	22.263		
3696.5	43.08		
4527.25	122.918		
4717.07	120.374		
4964.12	126.069		

WPSA-087C

Region:	5000-500	Region:	10000-2000
Position:	Intensity:	Position:	Intensity:
647.51	4.168	2041.7	52.861
731.83	4.108	2129.69	51.717
774.48	4.692	2342.63	57.745
865.38	19.447	2855.12	21.501
913.85	16.836	3068.98	9.378
991.27	6.848	3280.23	7.073
1113.72	6.518	3621.02	23.24
1249.74	5.456	3696.73	34.274
1438.83	2.822	3856.41	83.143
1610.38	15.5	4716.68	77.675
1861.38	51.735	5223.85	89.438
1994.25	68.835	7068.01	84.98
2341.71	92.673	8934.74	77.594
2854.83	34.148	9896.17	73.415
3065.67	14.5		

WPSA-087C continued

Region:	5000-500
Position:	Intensity:
3279.79	10.702
3620.74	36.041
3696.78	55.938
4717.45	128.193

WPSA-131C

Region:	5000-500	Region:	10000-2000
Position:	Intensity:	Position:	Intensity:
639.18	4.773	2140.69	38.908
697.85	4.312	3284.53	6.862
791.31	4.421	3620.64	17.816
1020.54	7.199	4718.29	67.239
1117.44	8.602	4959.7	70.818
1158.61	9.467	5175.64	73.258
1431.09	4.366		
1611.96	9.907		
1778.72	27.691		
1868.24	29.581		
1993.79	42.416		
2236.91	63.807		
3282.61	11.958		
3621.27	30.369		
3693.5	54.221		
3857.13	109.117		
4717.18	107.282		
4958.94	112.61		

WPSA-156C

Region:	5000-500	Region:	10000-2000
Position:	Intensity:	Position:	Intensity:
632.35	6.644	2133.17	51.467
697.33	4.709	2222.51	55.637
809.88	5.841	2342.78	60.101
914.49	8.203	2854.07	38.3
1011.33	7.791	3285.7	18.037
1111.79	11.795	3622.45	10.75
1159.09	11.531	3698.11	17.327
1314.85	11.58	3856.38	74.7
1429.22	8.924	4527.22	78.628
1612.26	19.626	4974.82	86.762
1791.23	39.08	5228.26	86.194

WPSA-156C continued

Region:	5000-500	Region:	10000-2000
Position:	Intensity:	Position:	Intensity:
1869.59	34.547	7065.75	77.127
1994.72	51.43	9879.49	68.956
2133.67	85.354		
2235.13	91.541		
2341.83	97.137		
2853.81	61.92		
3286.95	28.124		
3622.25	17.303		
3698.02	28.812		
4527.14	130.89		

WPSB-008C

Region:	5000-500	Region:	10000-2000
Position:	Intensity:	Position:	Intensity:
590.52	4.895	2009.36	31.796
631.41	3.155	2052.06	40.208
778.79	9.259	2090.97	33.009
865.39	6.625	2149.38	31.946
965.95	6.661	2343.95	30.305
1020.75	7.005	2491.43	41.218
1088.34	5.66	2516.47	40.675
1159.74	2.712	3389.47	15.035
1431.73	2.817	3937.16	70.745
1455.93	2.784	5202.92	70.032
1593.76	9.847	9414.98	44.523
1760.03	42.356		
1784.87	46.991		
1867.7	57.52		
1929.41	61.646		
1996.48	35.281		
2053.68	46.048		
2081.91	42.11		
2148.51	50.484		
2343.44	46.158		
2491.14	62.797		
2516.49	61.883		
3381.44	23.708		
3937.98	106.452		

WPSB-038C

Region:	5000-500	Region:	10000-2000
Position:	Intensity:	Position:	Intensity:
607.08	7.227	2163.21	52.913
696.51	11.637	2336.13	63.403
731.29	3.817	2525.91	19.644
853.17	17.23	2628.02	32.557
880.17	10.01	2898.66	25.451
1045.55	12.815	3022.08	26.125
1099.14	16.062	3250.31	32.339
1230.84	34.815	3619.96	45.466
1409.6	11.118	3694.4	59.147
1453.4	12.208	3975.71	79.028
1640.81	15.584	4308.59	83.626
1816.67	16.088	4723.92	84.638
1975.04	73.845		
2163.43	84.817		
2251.86	99.504		
2335.73	99.75		
2525.6	30.634		
2627.97	51.612		
2898.73	40.111		
3022.05	41.17		
3252.43	50.372		
3619.83	72.005		
3694.75	95.745		
3975.37	126.524		
4307.09	133.786		
4724.53	135.224		

WPSB-095C

Region:	5000-500	Region:	10000-2000
Position:	Intensity:	Position:	Intensity:
610.45	6.042	2340.49	72.671
697.41	5.727	2525.15	60.684
730.1	6.487	2628.8	61.034
790.62	6.611	3286.41	17.458
876.17	15.611	3620.08	28.575
1020.08	8.258	3975.41	98.777
1099.62	11.35	4716.87	96.37
1158.86	11.832	4969.07	97.621
1430.07	7.029	5213.08	96.833
1605.12	9.813	9871.32	57.248
1868.3	45.039		

WPSB-095C continued

Region:	5000-500
Position:	Intensity:
1995.3	59.098
2340.83	88.348
2524.49	74.204
2629.46	74.803
3286.92	19.626
3619.71	33.757
3969.7	121.723
4723.56	119.319

WPSB-131C

Region:	5000-500	Region:	10000-2000
Position:	Intensity:	Position:	Intensity:
616.03	4.368	2051.55	67.252
799.53	11.159	2090.27	61.183
865.28	10.083	2150.22	58.632
966.05	9.363	2343.47	61.635
1088.06	5.962	2516.04	61.225
1158.52	7.314	2922.91	39.935
1430.78	6.376	3057.81	36.114
1454.45	6.339	3308.04	30.707
1601.04	12.53		
1867.6	57.518		
1996.41	45.216		
2053.6	55.195		
2081.99	51.934		
2343.03	59.452		
2516.21	59.272		
2923.29	37.855		
3058.14	34.18		
3307.63	29.108		

WPSB-133C

Region:	5000-500	Region:	10000-2000
Position:	Intensity:	Position:	Intensity:
627.09	4.316	2050.93	43.53
779.58	9.429	2082.49	43.274
865.36	7.813	2148.73	50.744
913	14.246	2342.64	60.494
966.04	7.852	2491.35	61.878

WPSB-133C continued

Region:	5000-500
Position:	Intensity:
1023.38	7.896
1088.56	6.504
1159.6	5.301
1431.78	3.312
1455.59	3.226
1594.2	11.944
1785.27	49.362
1868.53	57.505
1996.47	41.981
2053.57	55.537
2081.98	51.2
2342.44	72.057
2491.24	74.157
2516.04	73.071
3313.24	26.757

Region:	10000-2000
Position:	Intensity:
2516.14	60.907
3308.18	24.677
3619.44	29.801
4526.84	98.643
5213.39	93.263