

## **MINERALOGICAL ABUNDANCES AS DETERMINED BY X-RAY DIFFRACTION IN SELECT SAMPLES OF THE UPPER FLORIDA AQUIFER**

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### **EXECUTIVE SUMMARY**

Analysis of 53 bulk powders derived from various rocks of the Upper Floridan Aquifer reveal calcite, dolomite/ankerite, quartz, apatite, and smectite to be the dominant minerals, with the clay and apatite phases only noted in bulk samples from the Hawthorn Group. In general, bulk mineralogies agree well with mineral determinations made independently in thin section.

Clay and fine-silt sized insoluble residues concentrated by the dissolution of carbonate phases were recovered and analyzed in 51 of the 53 samples. Quartz, potassium feldspar, smectite, mixed layer clays dominated by smectite, and organic matter are the dominant insoluble phases. Less common are pyrite, apatite, illite, palygorskite, and kaolinite. Rarely observed are calcic and sodic plagioclases, sepiolite (a clay mineral), barite (a possible drilling contaminant), and celestite.

The quartz is present in all Hawthorn and Suwannee samples, but rare in the Ocala and even rarer in Avon Park samples. Apatite was noted in the insoluble residues of 75% of the Hawthorn samples, no Suwannee samples, 1 Ocala sample, and no Avon Park samples. Potassium feldspar, sodic plagioclase, and calcic plagioclase were all observed in the Hawthorn, sometimes with 2 or more of these phases present in the same samples. This suggests that much, if not all, of the Hawthorn feldspars and plagioclases are detrital. In contrast, potassium feldspar was observed in 22 of 37 non-Hawthorn samples and a sodic plagioclase was detected in only one non-Hawthorn sample. This suggests that most, and perhaps all, of the potassium feldspars are authigenic in the non-Hawthorn units.

Pyrite was definitely detected in the XRD analyses of only 10 of 52 insoluble residues (~20%), yet it was observed in 64% of all thin sections. Even where it was detected, it was but a trace constituent as evidenced by very low intensity peak heights. Its apparent absence in so many samples in which it is known to be present maybe due to oxidation of pyrite during dissolution of the carbonate phases or by large amounts of other insoluble residues diluting the relative abundance of the pyrite below its detection limit.

Based on the color of the insoluble residues, organic matter is probably a constituent of at least 30 of the samples. Ten samples that yielded ample residue also exhibited either no crystalline phases or just minimal traces of clays or other minerals. Residues from 5 of these samples were tested for organic matter with hydrogen peroxide and indeed, all residues were digested within a week, indicating that organic matter was the only insoluble phase present.

Clay minerals are very abundant, abundant, or moderately abundant in 24 of 51 samples, present in small or trace amounts in 19 samples, and absent in 8 samples. In the Hawthorn, clay minerals are more likely to be moderately abundant to very abundant (11 of 15 samples), whereas clay minerals in the Avon Park are more likely to be absent or just trace components (16 of 20

samples). In Suwannee and Ocala samples, clay mineral abundance shows no pattern.

Smectite is the most common clay mineral, occurring in 36 of the 43 samples that contained clays, but there is no pattern to its distribution. In 11 samples the smectite occurs by itself; in 25 samples it is the dominant component of mixed layer clays. The mixed layer clays also contain illite (23 samples), kaolinite (12 samples), palygorskite (3 samples) and sepiolite (7 samples). None of the later three clay minerals occur as the sole clay in any sample. The palygorskite and sepiolite are more likely to be in Hawthorn rocks (50% or more of their occurrences), whereas kaolinite is more likely to be in Avon Park rocks (58% of the kaolinite occurrences). Illite occurs independently of smectite in 8 samples, 4 of which are from the Hawthorn. It is the sole clay in only 2 of those 8 samples; it is associated with palygorskite or sepiolite in the other 6 samples.

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## INTRODUCTION

Fifty-three samples from 16 cores were provided for mineralogical analyses. The 53 samples are a subset of materials being evaluated by the Florida Geological Survey for the presence and geologic framework of arsenic-bearing minerals in potential injection zones of an aquifer storage and recovery system. The material presented herein does not directly address whether arsenic-bearing minerals are present, but does provide background information useful in deciphering the mineralogical context for any samples subsequently found to contain such minerals.

What follows is: (1) a description of the analytical methods and then (2) a summary of the minerals detected by X-ray diffraction of bulk-rock and insoluble residue fractions. All references to depth are relative to feet below land surface (bls).

## METHODS

### **Whole-Rock Bulk Mineralogy**

Quantitative estimates of mineral abundance were determined on 53 bulk rock samples using powder x-ray diffraction. Most samples were provided as ground powders. Those that were not were first crushed and then partially ground by hand for ~ 10 minutes in a mortar and pestle until all material was fine silt or less in size. Thereafter, 0.333 g of zinc oxide was added to 3.00 g of each sample and the resultant mixture was further ground in a McCrone micronizing mill for 5 minutes with methanol as the lubricating agent (Bish and Reynolds, 1989, p. 77). After air-drying, a side-packed powder mount of the now finely ground bulk sample and zinc oxide mixture was prepared. The x-ray diffraction scan was run on a Scintag PADV from 5° to 65° 2 $\theta$  at 0.1° per minute with Cu-radiation.

Peak positions on the resultant diffractograms, peak intensity relative to the zinc oxide spike, and mineral abundances (in weight percent) were determined using the numerical code *RockJock5* (Eberl, 2003, <ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/RockJock>). Based on the peaks observed and petrographic observations, *RockJock5* was instructed to calculate abundances for a stoichiometric calcite, an Mg-bearing calcite, stoichiometric dolomite, a ferroan dolomite (ankerite), quartz, apatite, pyrite, goethite, hematite, and smectite. Addition of any other phase reduced the quality of the calculated pattern fit.

Analyses with known mixtures of just calcite and quartz indicated an analytical uncertainty of  $\pm 5.4$  weight percent (wt %) for major constituents (i.e., at contents of ~10% to 90% of the sample), with calcite typically overestimated and quartz underestimated. *RockJock* typically calculated 0.1 to 0.9 weight % for all other phases even though none were present. This suggests calculated values of  $\leq 0.9$  wt % for any mineral in an Upper Floridan Aquifer (UFA) sample is merely noise. Values  $\geq 1.0$  wt % in a UFA sample may indicate a phase is present (i.e., 1.0 wt % is the minimum detection limit), but the absolute percentage should not be considered accurate unless the value is  $>5$  wt %.

*RockJock* also calculates a residual of “unfit” data for the entire pattern, with lower residuals reflecting a better fit. For the know calcite-quartz mixtures, residuals ranged from 0.134 (75% quartz, 25% calcite) to 0.180 (25% quartz, 75% calcite). These residuals suggest that the quantitative calculations are poorest as the amount of calcite increases, and that a residual of 0.20 or less for a UFA pattern would be a very good fit. Slightly larger residuals should be expected, in part due to the fact that the standard XRD patterns in *RockJock* are typically for stoichiometric phases, yet the natural calcite, dolomite, and apatite in the UFA samples are undoubtedly non-stoichiometric phases. That is, they each exhibit various cation and anion substitutions (a fact especially true for sedimentary apatite). Thus, XRD patterns of stoichiometric standards may not perfectly match the non-stoichiometric phase actually present in the UFA samples.

### **Insoluble Residue (“fines”) Mineralogy**

The mineralogy of the fine silt- and clay-sized components of the insoluble mineral fraction was also assessed. Powdered whole-rock subsamples (0.5 to 35 gm depending on amount of material provided; mean =  $15.1 \pm 6.7$  gm) were placed in 200 ml of Morgan’s solution (1M

sodium acetate and 10% glacial acetic acid at pH 4.5) in order to dissolve the carbonate phases without impacting clay phases (Rabenhorst and Wilding, 1984). Dissolution was aided by the shaking of the samples on a shaker table and heating at 60°C for 48 hours for limestones and 96 hours for dolomite-bearing samples. After dissolution of the carbonates was complete, each sample was centrifuge (3000 rpm for 12 minutes) and the Morgan's solution poured off. Samples were then rinsed in distilled water, centrifuged again, and the solution poured off again.

The resultant insoluble residues could include sand to clay sized material. To concentrate just the finest sized material, the insoluble residues were flushed with distilled water into 8-cm tall, 50-ml bottles. Sodium pyrophosphate (2.8 ml) was added as a dispersant to prevent flocculation of clays and the bottles were vigorously shaken by hand. They were then allowed to sit for 30 minutes. Based on Stokes' Law, all grains coarser than 23  $\mu\text{m}$  (i.e., upper medium silt and greater) should have settled to the bottom of the bottles. The water and finer grains still in suspension were then removed with an automatic pipette and placed in a new 250 ml jar. A spherical, 15  $\mu\text{m}$ -wide pyrite grain is the hydraulic equivalent of a spherical, 24  $\mu\text{m}$ -wide quartz grain, thus the concentrated fines should include clay- to very fine silt-sized framboidal pyrite, if pyrite is present.

An aliquot of the concentrated fine silt- and clay-sized insoluble residues were then rinsed with deionized water and vacuum filtered onto 0.45  $\mu\text{m}$  millipore filters. The damp concentrated residue was then lightly pressed onto glass slides for X-ray diffraction analysis (5° to 65° 2 $\theta$  at 2° per minute with Cu-radiation on the Scintag PADV unit). Automated background removal, peak finder, and search-match routines were applied with the Scintag DSMNT program (Diffraction Management System Software v. 1.37). When necessary, peaks were also identified manually, and all identified peaks were used to determine the presence/absence of mineral phases. Peaks associated with quartz, dolomite, and calcite (small fractions of the later two may have survived dissolution) were identified first, and then any remaining peaks were analyzed for their affinity. Generally, a minimum of 4 peak matches (including the two most intense diffractions) was used to confirm that a non-clay mineral was present in at least trace amounts. In most cases, 5 or more peaks actually supported each mineralogical determination.

If any clay minerals were indicated in the initial XRD analysis of the insoluble residue slide (i.e., any sharp or broad peaks at d-spacings > 6Å), then the slide was exposed overnight to an atmosphere of ethylene glycol to enlarge expandable clay layers and then x-rayed a second time (2° to 20° 2 $\theta$  at 2° per minute) to discriminate expandable smectitic clays. The samples were then heated to 350°C and x-rayed a third time (2° to 20° 2 $\theta$  at 2° per minute), and then heated to 550°C and x-rayed a fourth time (2° to 20° 2 $\theta$  at 2° per minute). The successive heating permits distinction of the various clay minerals from each other (Table 1).

## RESULTS

### **Whole-Rock Bulk Mineralogy**

Quantitative results for all 53 bulk-rock samples analyzed from the UFA are shown in Table 2. Examples of the bulk mineral XRD scans are illustrated in Figures 1 through 5, which

Table 1. – Simplified flow chart for the distinction of clay minerals by X-ray diffraction and various treatment methods (from Starkey et al., 1984, their Plate 1).

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- A peak at a d-spacing of  $\sim 17\text{\AA}$  after glycolation means **smectite**. With heating, that peak collapses to  $\sim 10\text{\AA}$  and additional heating takes it closer to  $10\text{\AA}$ .
  - A peak at a d-spacing of  $\sim 14$  to  $14.3\text{\AA}$  after glycolation means **chlorite or vermiculite**. With heating, chlorite stays at  $14$  to  $14.3\text{\AA}$ , but vermiculite collapses to  $\sim 10\text{\AA}$ .
  - A peak at a d-spacing of  $12.1$  to  $12.8\text{\AA}$  after glycolation means **sepiolite**. With heating, it disappears (partially at  $350^\circ\text{C}$ , completely at  $550^\circ\text{C}$ ).
  - A peak at a d-spacing of  $\sim 10.3$  to  $10.5\text{\AA}$  and one at  $6.4\text{\AA}$  after glycolation means **palygorskite**. With heating, both disappear (partially at  $350^\circ\text{C}$ , completely at  $550^\circ\text{C}$ ).
  - A peak at a d-spacing of  $\sim 10\text{\AA}$  after glycolation that does not change with heating means **illite**.
  - A peak at a d-spacing of  $7.2\text{\AA}$  after glycolation that does not change at  $350^\circ\text{C}$  but disappears after heating to  $550^\circ\text{C}$  means **kaolinite**.

illustrate the diffraction peaks associated with calcite, dolomite, quartz, and clay minerals in a limestone (>95% calcite), dolostone (>95% dolomite), dolomitic limestone, quartz-bearing limestone, and a quartz-bearing dolomitic claystone.

As indicated by the petrographic analyses, calcite, dolomite (non-ferroan, ferroan, or ankerite), and quartz dominate the 53 samples, with apatite being a common secondary mineral in many Hawthorn rocks. Pyrite, though observed in thin sections of many of the samples, is too minor a constituent to be detected in any of the bulk rock samples. A Na-smectite (syn. montmorillinite) is the only clay detected in the bulk mineral analyses, and then only in four Hawthorn samples. No kaolinite, illite, or chlorite was detected in any bulk sample.

There are nine samples in which the bulk XRD mineralogy did not agree perfectly with the previously determined thin-section observations (Table 3). In all nine cases, the discrepancies relate to the relative proportions of the major minerals (quartz, dolomite, and calcite). That is, in six of the nine cases, small amounts of quartz and/or dolomite are present in either thin section or bulk mineralogical result, but not the other. In the other three cases, the samples were called sandstone based on the thin section whereas the XRD subsamples were a sandy claystone, quartz-rich dolostone, and a quartz-rich limestone. Presumably all these differences result from the fact that each XRD sample was derived from a larger amount of material than the smaller thin-section sample. That is, although the thin section and mineralogical sample are from the same interval in the core, they are not derived from the exact same aliquot of rock.

## Appendix 15.

**TABLE 2 - Mineral abundances based on quantitative X-ray diffraction analyses of bulk rock powders (values in weight %). Asterisks indicate that the stratigraphic interpretation differs from that of other determinations in this report due to differences in the indicator used.**

Core	footage (ft)	Stratigraphic Unit	XRD Lithology	% Calcite	% Dolomite	% Quartz	% Apatite <sup>1</sup>	% Pyrite <sup>2</sup>	% Hematite	% Goethite	% Smectite	Peak Fit Residual
W-16329	724-725	Hawthorn	Quartz-bearing, phosphatic, dolostone	7.0	53.1	29.0	6.2	0.2	1.0	3.6	0.0	0.188
W-17001	616-617	Hawthorn	Quartz-bearing, dolomitic claystone	3.0	7.6	5.9	9.2	0.5	0.1	1.2	72.4	0.210
W-17001	704-706	Ocala	Limestone	98.4	0.4	0.3	0.0	0.2	0.1	0.4	0.0	0.252
W-17001	810-811.5	Ocala	Limestone	98.0	0.9	0.3	0.0	0.2	0.2	0.3	0.0	0.22
W-17986	1015-1016	Hawthorn	Phosphatic, quartz-bearing limestone	75.3	1.4	14.3	5.1	0.2	0.7	3.0	0.0	0.326
W-17986	1022-1023	Hawthorn	Limestone	95.1	0.8	2.3	0.6	0.3	0.0	0.9	0.0	0.202
W-17986	1043-1044	Hawthorn	Quartz-bearing limestone	90.8	1.3	6.9	0.1	0.0	0.3	0.6	0.0	0.243
W-17986	1046-1048	Hawthorn	Phosphatic, quartz-bearing dolostone	7.8	44.6	38.8	4.0	0.4	1.7	2.7	0.0	0.198
W-17986	1049-1050	Hawthorn	Phosphatic, quartz-bearing dolostone	9.0	46.1	35.7	4.1	0.9	1.6	2.8	0.0	0.229
W-17986	1133-1134	Avon Park	Limestone	97.9	0.5	0.6	0.0	0.1	0.0	0.8	0.0	0.345
W-17986	1155-1156	Avon Park	Limestone	97.2	0.4	1.0	0.0	0.2	0.0	1.2	0.0	0.275
W-17986	1170-1171	Avon Park	Dolomitic limestone	84.1	14.2	0.5	0.0	0.2	0.6	0.5	0.0	0.231
W-18253	874-875	Suwannee	Quartz-bearing dolomitic limestone	90.8	4.4	3.3	0.3	0.1	0.4	0.6	0.0	0.300
W-18253	881-882	Suwannee	Dolomitic limestone	94	3.2	1.5	0.1	0.1	0.1	1.0	0.0	0.275
W-18253	1005-1006	Ocala	Limestone	97	1.3	0.3	0.0	0.6	0.0	0.7	0.0	0.226
W-18253	1304-1305	Avon Park	Dolomitic limestone	85	13.7	0.2	0.2	0.2	0.3	0.4	0.0	0.197
W-18253	1314-1315	Avon Park	Limestone	96.7	1.3	0.5	0.3	0.2	0.2	0.7	0.0	0.257
W-18255	580-585	Ocala	Limestone	97.6	0.3	0.5	0.4	0.3	0.3	0.4	0.0	0.209
W-18255	686-687	Ocala	Dolomitic limestone	72.8	26.4	0.3	0.0	0.0	0.3	0.3	0.0	0.259
W-18255	690-691	Ocala	Dolomitic limestone	75.1	24.0	0.3	0.0	0.1	0.3	0.3	0.0	0.276
W-18255	800-830	Ocala & Avon Park***	Limestones & dolostones	87.5	10.7	0.3	0.0	0.3	0.1	1.2	0.0	0.256
W-18256	802-803	Ocala	Quartz-bearing, dolomitic limestone	83.7	7.1	8.0	0.1	0.2	0.2	0.7	0.0	0.245
W-18463	643-643.5	Hawthorn	Argillaceous, dolomitic limestone	58.8	8.6	2.6	2.1	0.1	0.3	0.9	26.6	0.235
W-18463	932-933	Avon Park	Dolomitic limestone	82.7	16.3	0.1	0.0	0.0	0.3	0.7	0.0	0.245
W-18463	1058-1059	Avon Park	Limestone	98.3	0.3	0.3	0.0	0.1	0.1	0.9	0.0	0.219
W-18464	556-567	Hawthorn	Quartz-bearing, phosphatic limestone	89.7	1.5	3.6	3.8	0.2	0.5	0.7	0.0	0.251
W-18464	759-760	Hawthorn	Quartz-bearing limestone	66.8	0.5	31.1	0.3	0.0	0.5	0.7	0.0	0.190
W18464	905-906	Suwannee	Limestone	96.7	0.4	1.6	0.0	0.2	0.2	0.7	0.0	0.187

## Appendix 15.

TABLE 2 Continued

W18594	545-547	Hawthorn	Quartz-bearing, phosphatic dolostone	4.3	72.5	5.8	5.0	0.0	0.6	0.0	11.9	0.167
W-18594	709-710	Hawthorn	Quartz-bearing limestone	64.7	0.5	33.6	0.2	0.2	0.1	0.8	0.0	0.188
W-18594	782-783	Hawthorn	Quartz-bearing limestone	81.4	0.9	15.4	0.6	0.3	0.0	1.5	0.0	0.193
W-18594	849-850	Suwannee	Limestone	96.3	0.5	2.5	0.0	0.1	0.1	0.5	0.0	0.220
W-18594	1000-1001	Ocala	Dolostone	2.6	95.6	0.1	1.2	0.0	0.5	0.0	0.0	0.200
W18706	1144-1159	Avon Park***	Limestone	98.3	0.6	0.3	0.0	0.2	0.4	0.3	0.0	0.325
W18706	1251-1266	Avon Park***	Limestone	97.1	0.5	0.5	0.2	0.0	1.6	0.2	0.0	0.282
W-18714	1126-1136	Avon Park***	Limestone	98.5	0.3	0.5	0.0	0.2	0.1	0.5	0.0	0.281
W-18714	1225-1233	Avon Park***	Limestone	98.4	0.5	0.5	0.0	0.1	0.0	0.4	0.0	0.305
W-18715	963-974	Hawthorn	Limestone	95.3	0.6	2.1	0.8	0.2	0.4	0.6	0.0	0.287
W-18715	1090-1100	Avon Park***	Limestone	98.2	0.3	0.9	0.0	0.0	0.1	0.5	0.0	0.242
W-18720	838-839	Ocala	Dolomitic limestone	90.9	7.6	0.3	0.0	0.0	0.4	0.8	0.0	0.289
W-18720	1028-1029	Avon Park***	Dolomitic limestone	87.5	10.1	0.5	0.0	0.0	0.4	1.6	0.0	0.290
W-18720	1194-1195	Avon Park***	Limestone	96.6	0.9	0.6	0.9	0.0	0.0	0.9	0.0	0.332
W-18720	1330-1331	Avon Park	Limestone	95.4	1.2	0.6	0.7	0.3	0.6	1.2	0.0	0.282
W-18725	410-420	Avon Park	Quartz-bearing, dolomitic limestone	69.2	8.7	20.5	0.3	0.1	0.5	0.7	0.0	0.208
W-18725	620-630	Avon Park	Limestone	96.7	0.8	0.9	0.0	0.3	0.2	1.1	0.0	0.253
W-18725	915-920	Avon Park	Limestone	96.8	0.6	0.4	0.8	0.4	0.1	0.8	0.0	0.222
W-18726	637-638	Hawthorn	Quartz-bearing, dolomitic claystone	3.0	7.7	5.9	9.2	0.5	0.1	1.2	72.4	0.221
W18726	861-862	Ocala	Limestone	97.9	0.5	0.5	0.0	0.2	0.1	0.7	0.0	0.328
W-18726	863-864	Ocala	Dolostone	3.5	96.4	0.0	0.1	0.0	0.0	0.0	0.0	0.209
W-18726	1201-1202	Avon Park	Dolostone	1.9	97.4	0.0	0.4	0.0	0.2	0.0	0.0	0.201
W-18728	797-798	Hawthorn	Quartz-bearing, phosphatic, dolomitic limestone	58.3	13.5	13.5	9.9	0.8	1.7	2.3	0.0	0.256
W-18728	944-945	Ocala	Limestone	98.3	1.1	0.4	0.0	0.1	0.4	0.8	0.0	0.297
W-18728	1289-1290	Avon Park	Dolomitic limestone	70.6	28.9	0.0	0.0	0.1	0.4	0.0	0.0	0.204

1 - detection limit for APATITE (detrital phosphate) is consider to be relatively high as "apatite" only approximates sedimentary Ca-phosphate

2 - PYRITE may be present in trace amounts, but still not be detectable in bulk rock XRD analysis

Appendix 15.

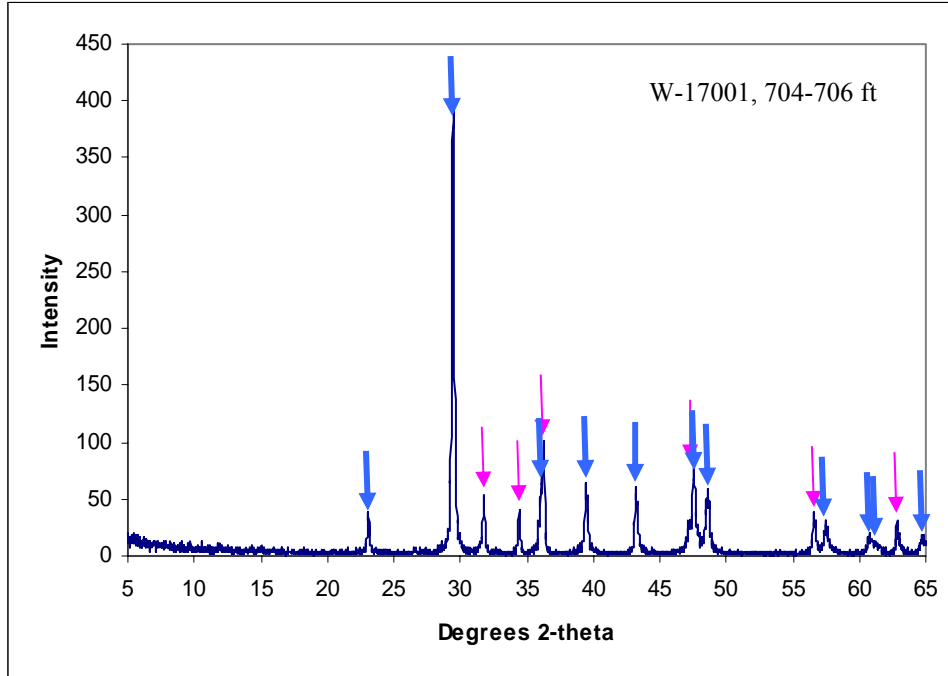


Figure 1. Example of a limestone's X-ray diffractogram. The only phases detectable are calcite (blue arrows) and the zinc-oxide standard (pink arrows) added for the *RockJock* analysis.

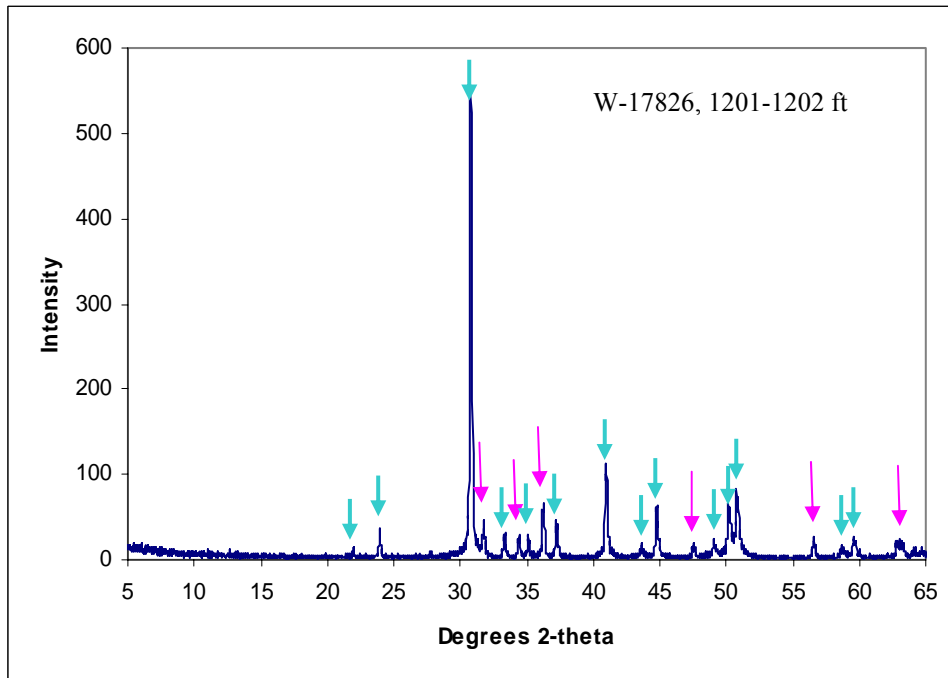


Figure 2. Example of a dolostone's X-ray diffractogram. The phases detectable are dolomite (blue-green arrows) and the zinc-oxide standard (pink arrows) added for the *RockJock* analysis.



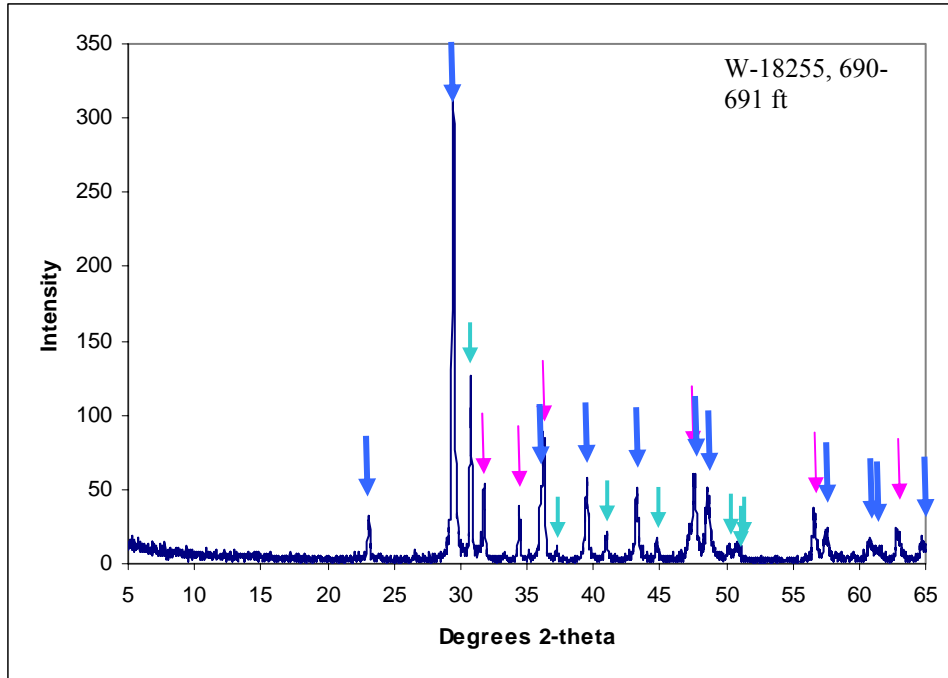


Figure 3. Example of a dolomitic limestone's X-ray diffractogram. The sample is 75% calcite (blue arrows) and ~25% dolomite (blue-green arrows). Some minor dolomite peaks visible in Figure 2, where dolomite is 100% of the sample, are not detectable in this mixed mineralogy. Pink arrows are zinc oxide peaks, a phase added for the *RockJock* analysis.

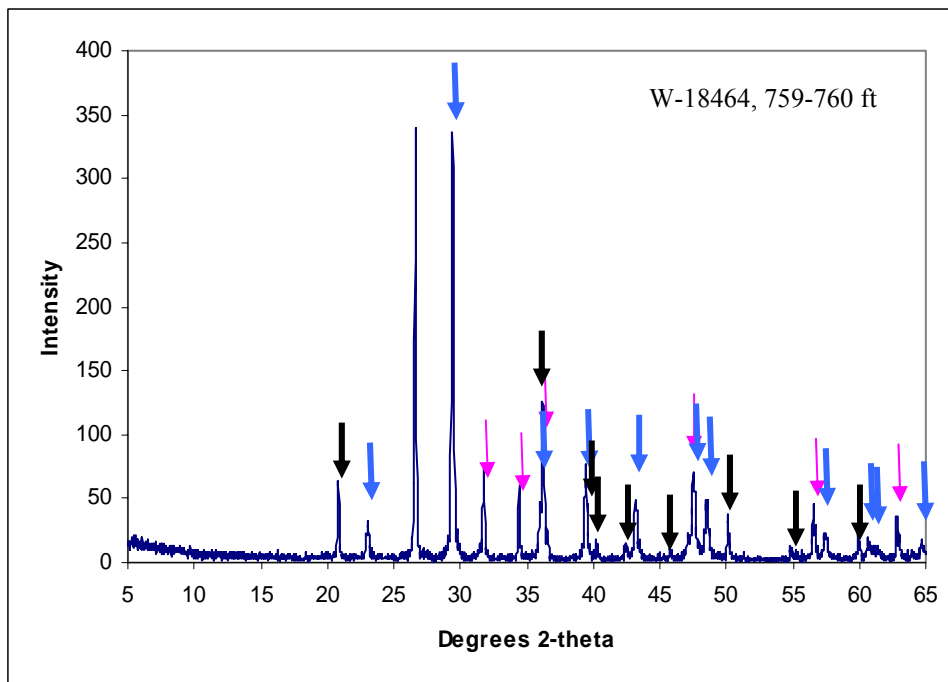


Figure 4. Example of a quartz-bearing limestone's X-ray diffractogram. The sample is 67% calcite (blue arrows) and ~32% quartz (black arrows). Pink arrows are zinc oxide peaks, a phase added for the *RockJock* analysis.

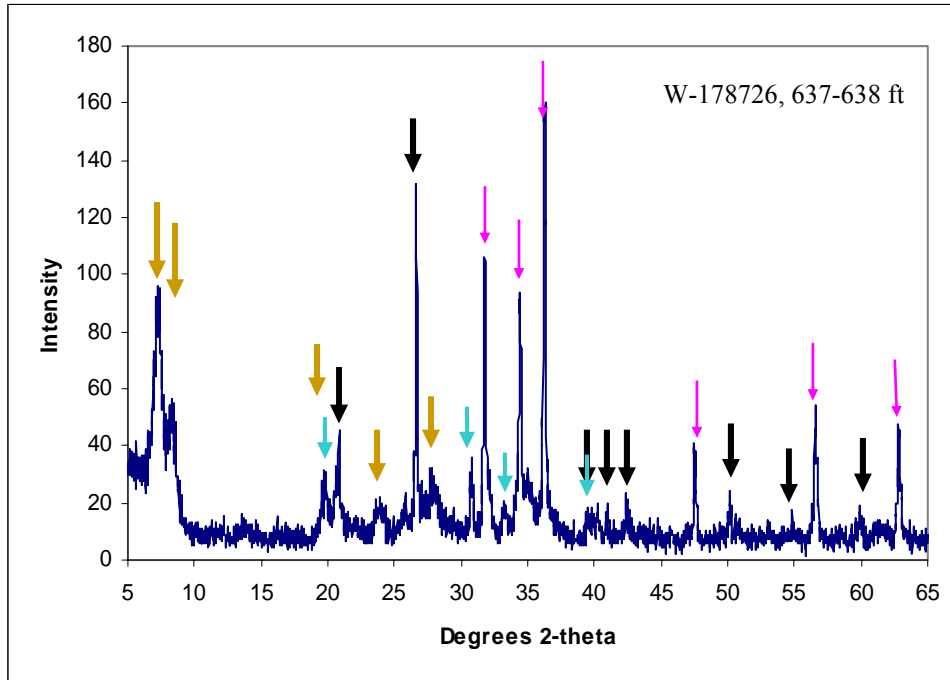


Figure 5. Example of a quartz-bearing, dolomitic claystone's X-ray diffractogram. The sample is 72% clay, which was modeled as a smectite (brown arrows) by RockJock. Quartz is indicated by the black arrows and dolomite by the blue-green arrows. Pink arrows are zinc oxide peaks, a phase added for the *RockJock* analysis.

Table 3 – Samples in which the XRD analysis did not completely agree with thin-section estimated mineralogy. The two analyses are run on different aliquots of material from the sample interval, thus variability is not an unreasonable outcome.

<u>Sample</u>	<u>XRD Mineralogy</u>	<u>Thin Section Mineralogy</u>
W-17001, 616-617	quartz-bearing, phosphatic, dolomitic claystone	phosphatic, dolomitic sandstone
W-17896, 1046-1048	phosphatic, quartz-bearing dolostones	phosphatic, dolomitic sandstone
W-17896, 1170-1171	dolomitic limestone	limestone
W-18253, 874-875	quartz-bearing dolomitic limestone	quartz-bearing limestone
W-18253, 1314-1315	limestone	dolomitic limestone
W-18463, 932-933	dolomitic limestone	limestone
W-18594, 849-850	limestone	quartz-bearing limestone
W-18725, 410-420	quartz-bearing, dolomitic limestone	limestone
W-18728, 797-798	quartz-bearing, phosphatic, dolomitic limestone	limy, phosphatic, dolomitic sandstone

### **Insoluble Residue (“fines”) Mineralogy**

Two of 53 samples generated no insoluble residues. For one sample (W-18594, 782-783 ft) this was probably due to insufficient amount of material; in the other case (W-18255, 686-687 ft) there was some yield but not enough to concentrate for analysis. The other 51 samples generated sufficient insoluble residues for analysis, and the results are summarized in Table 4. Quartz, potassium feldspar, smectite, mixed-layer clays dominated by smectite, and organic matter are the dominant insoluble phases. Less common are pyrite, apatite, palygorskite, kaolinite, illite, and calcic and sodic plagioclases. Rarely observed are sepiolite (a clay mineral), barite, and celestite. Details of the nature and distribution of these phases is given below, with representative XRD traces shown in Figures 6 through 13.

#### Non-clay phases

The most common non-clay phase observed was quartz (Fig. 6). Quartz is present in all Hawthorn samples, all Suwannee samples, 4 of 12 Ocala samples, and 2 of 20 Avon Park samples. All samples that exhibited 1.5% or more of quartz in their bulk mineralogy (Table 2) showed quartz in their insoluble fractions. However, only 4 samples (W-18255, 580-585 ft; W-18594, 1000-1001 ft; W-18720, 1194-1195 ft; and W-18728, 944-945 ft) that had less than 1.5% quartz indicated in their bulk mineralogy actually revealed quartz in their insoluble fractions. This indicates that quartz was a minor or trace component in those 4 samples and absent in all others that did not have quartz at 1.5% or more of the bulk mineralogy.

Feldspars are also present in many samples and the mineralogies of the best-fit match to the peaks observed are given in Table 4. Feldspars form a solid-solution series between their component end-members. Various cations substitute for each in the crystal structures of these minerals and that produces slightly different  $2\theta$  positions for the reflection peaks. Perfect matches to the predicted peaks of feldspar minerals are only achieved if the sample has the same composition as known standards. Thus, although specific feldspar phases are listed in Table 4, those results are discussed in more general terms as potassium feldspar (orthoclase, microcline, adularia, sanidine), sodic plagioclases (albite, anorthoclase), or calcic plagioclases (anorthite).

Potassium feldspar, sodic plagioclase, and calcic plagioclase were all observed in the Hawthorn, sometimes with 2 or more of these phases present in the same sample (Fig. 7). This suggests that much, if not all, of the Hawthorn feldspars and plagioclases are detrital. In contrast, potassium feldspar (Fig. 8) was observed in 22 of 37 non-Hawthorn samples (1 Suwannee, 9 Ocala, and 12 Avon Park samples), and a sodic plagioclase (albite) was detected in one other Avon Park sample. No other sodic or calcic plagioclases were noted in non-Hawthorn samples. This suggests that most, and perhaps all, of the potassium and sodic feldspars are authigenic in the non-Hawthorn units.

Apatite (Fig. 6) was noted in the insoluble residues of 12 of 15 Hawthorn samples, no Suwannee samples, one Ocala sample, and no Avon Park samples. The peak analyses indicate that fluorapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ] and carbonate hydroxyl apatite [ $(\text{Ca}_{10}(\text{PO}_4)_5(\text{CO}_3)(\text{OH})\text{F})$ ] are both present in the Hawthorn. The presence of apatite in the one Ocala sample (W-18255, 580-585 ft) may mean its formation assignment is incorrect.

Appendix 15.

**TABLE 4 - Mineralogical contents of the insoluble residue fractions. Asterisks indicate that the stratigraphic interpretation differs from that of other determinations in this report due to differences in the indicator used.**

Core	footage (ft)	Stratigraphic Unit***	Bulk XRD Lithology	Color of the dry insoluble residue	Estimated Clay Abundance	Clay Type(s)	Non-clay mineral Insoluble Minerals	Pyrite Present?
W-16329	724-725	Hawthorn	Quartz-bearing, phosphatic, dolostone	gray	abundant clay	smectite, sepiolite	quartz, apatite, trace of orthoclase	YES
W-17001	616-617	Hawthorn	Quartz-bearing, dolomitic claystone	gray	moderate amounts of clay	smectite	quartz, apatite, trace of microcline	no
W-17001	704-706	Ocala	Limestone	light brown	small amounts of clay	smectite	sanidine, illite	maybe trace
W-17001	810-811.5	Ocala	Limestone	light brown	small amounts of clay	smectite-illite	sanidine, orthoclase	trace
W-17986	1015-1016	Hawthorn	Phosphatic, quartz-bearing limestone	tan	trace amounts of clay	smectite-illite	quartz, flourapatite, maybe anorthite	no
W-17986	1022-1023	Hawthorn	Limestone	light brown	small amounts of clay	smectite	barite, quartz, maybe anorthite	no
W-17986	1043-1044	Hawthorn	Quartz-bearing limestone	tan	moderate amounts of clay	smectite-illite, kaolinite	quartz, orthoclase, maybe a Na-feldspar	no
W-17986	1046-1048	Hawthorn	Phosphatic, quartz-bearing dolostone	light gray	abundant clay	smectite-illite, kaolinite	quartz, anorthite, trace of apatite	trace
W-17986	1049-1050	Hawthorn	Phosphatic, quartz-bearing dolostone	light gray	abundant clay	smectite-illite, palygorskite	quartz, albite, anorthoclase, maybe anorthite, trace of apatite	YES
W-17986	1133-1134	Avon Park	Limestone	dark brown	trace amounts of clay	smectite, kaolinite	none	no
W-17986	1155-1156	Avon Park	Limestone	dark cream	trace amounts of clay	smectite-illite, kaolinite	none	no
W-17986	1170-1171	Avon Park	Dolomitic limestone	light brown	-----	-----	orthoclase	no
W-18253	874-875	Suwannee	Quartz-bearing dolomitic limestone	dark brown	small amounts of clay	smectite-illite, perhaps chlorite	lots of quartz, orthoclase	no
W-18253	881-882	Suwannee	Dolomitic limestone	brown	moderate amounts of clay	smectite	quartz	no
W-18253	1005-1006	Ocala	Limestone	brown	very abundant clay	smectite	disordered sanidine	no
W-18253	1304-1305	Avon Park	Dolomitic limestone	dark cream	-----	-----	nothing	no
W-18253	1314-1315	Avon Park	Limestone	light brown	trace amounts of clay	smectite	orthoclase	no
W-18255	580-585	Ocala	Limestone	light gray	moderate amounts of clay	smectite-illite, kaolinite	quartz, kaolinite, trace of apatite	trace

Appendix 15.

TABLE 4 Continued

W-18255	686-687	Ocala	Dolomitic limestone	no yield	no yield	no yeild		no yield	-----
W-18255	690-691	Ocala	Dolomitic limestone	light brown	trace amounts of clay	illite		sanidine	no
W-18255	800-830	Ocala & Avon Park***	Limestones & dolostones	tan	moderate amounts of clay	smectite-illite, sepiolite		barite, trace of orthoclase	YES
W-18256	802-803	Ocala	Quartz-bearing, dolomitic limestone	brown	small amounts of clay	smectite-illite		quartz, sanidine	YES
W-18463	643-643.5	Hawthorn	Argillaceous, dolomitic limestone	tan	very abundant clay	illite & sepiolite (not mixed-layers), some palygorskite?	quartz, trace of apatite, trace of orthoclase, and two distinct peaks that best match jordanite (Pb <sub>14</sub> As <sub>6</sub> S <sub>23</sub> )		no
W-18463	932-933	Avon Park	Dolomitic limestone	dark brown	moderate amounts of clay	smectite-illite, kaolinite		orthoclase, sanidine	YES
W-18463	1058-1059	Avon Park	Limestone	light brown	-----	-----		orthoclase, sanidine, microcline	YES
W-18464	556-567	Hawthorn	Quartz-bearing, phosphatic limestone	tan	-----	-----		quartz, apatite, maybe albite	YES
W-18464	759-760	Hawthorn	Quartz-bearing limestone	cream	moderate amounts of clay	smectite		quartz, maybe orthoclase	no
W18464	905-906	Suwannee	Limestone	light brown	abundant clay	smectite		quartz	no
W18594	545-547	Hawthorn	Quartz-bearing, phosphatic dolostone	light gray	very abundant clay	illite, palygorskite		quartz, apatite, trace of albite	no
W-18594	709-710	Hawthorn	Quartz-bearing limestone	pink	abundant clay	smectite, possibly sepiolite		quartz, trace of apatite, maybe orthoclase	no
W-18594	782-783	Hawthorn	Quartz-bearing limestone	no yield	no yield	no yield		no yeild	no yield
W-18594	849-850	Suwannee	Limestone	dark gray	moderate amounts of clay	smectite		quartz	no
W-18594	1000-1001	Ocala	Dolostone	dark brown	very abundant clay	illite, palygorskite		quartz, sanidine	no
W18706	1144-1159	Avon Park***	Limestone	dark brown	-----	-----		none	no
W18706	1251-1266	Avon Park***	Limestone	dark brown	trace amounts of clay	smectite-illite, kaolinite		none	no

Appendix 15.

TABLE 4 Continued

W-18714	1126-1136	Avon Park***	Limestone	dark brown	trace amounts of clay	illite, sepiolite, kaolinite	maybe microcline	no
W-18714	1225-1233	Avon Park***	Limestone	brown	trace amounts of clay	smectite-illite, kaolinite	none	no
W-18715	963-974	Hawthorn	Limestone	gray	small amounts of clay	smectite-illite, kaolinite	apatite, quartz	no
W-18715	1090-1100	Avon Park***	Limestone	light brown	trace amounts of clay	illite, sepiolite	trace of albite	no
W-18720	838-839	Ocala	Dolomitic limestone	brown	small amounts of clay	smectite-illite	sanidine	maybe
W-18720	1028-1029	Avon Park***	Dolomitic limestone	dark cream	-----	-----	sanidine	trace
W-18720	1194-1195	Avon Park***	Limestone	brown	small amounts of clay	smectite-illite	orthoclase, trace of quartz	no
W-18720	1330-1331	Avon Park	Limestone	dark brown	trace amounts of clay	smectite	celestite	no
W-18725	410-420	Avon Park	Quartz-bearing, dolomitic limestone	brown	-----	-----	lots of quartz, trace of sanidine	no
W-18725	620-630	Avon Park	Limestone	brown	abundant clay	smectite-illite, kaolinite	orthoclase	YES
W-18725	915-920	Avon Park	Limestone	dark brown	abundant clay	smectite-illite	trace of orthoclase or sanidine	no
W-18726	637-638	Hawthorn	Quartz-bearing, dolomitic claystone	light greenish gray	very abundant clay	illite, sepiolite	orthoclase, anorthite, adularia	YES
W-18726	861-862	Ocala	Limestone	dark brown	abundant clay	smectite-illite	orthoclase or sanidine	no
W-18726	863-864	Ocala	Dolostone	cream	abundant clay	smectite-illite	orthoclase	maybe trace
W-18726	1201-1202	Avon Park	Dolostone	brown	trace amounts of clay	smectite-illite	sanidine	no
W-18728	797-798	Hawthorn	Quartz-bearing, phosphatic, dolomitic limestone	light greenish gray	abundant clay	illite	apatite, quartz	no
W-18728	944-945	Ocala	Limestone	dark brown	moderate amounts of clay	smectite-illite, kaolinite	trace of quartz	no
W-18728	1289-1290	Avon Park	Dolomitic limestone	dark brown	trace amounts of clay	smectite-illite	trace of orthoclase	YES

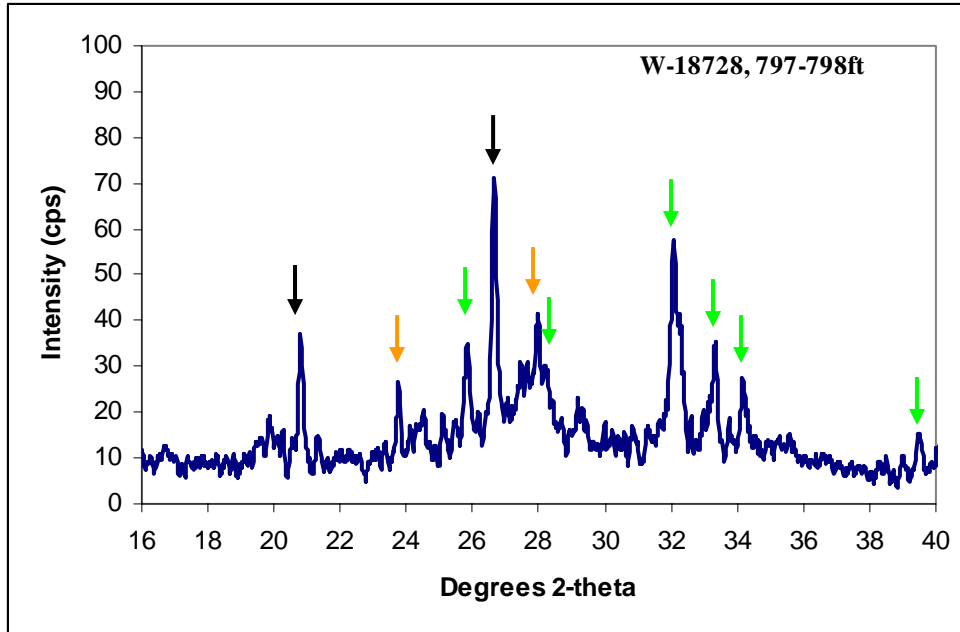


Figure 6. Portion of an XRD scan showing the presence of quartz (black arrows), apatite (green arrows) and the higher angle peaks of an illite (brown arrows). Sample is a quartz-bearing, phosphatic, dolomitic limestone from the Hawthorn Group.

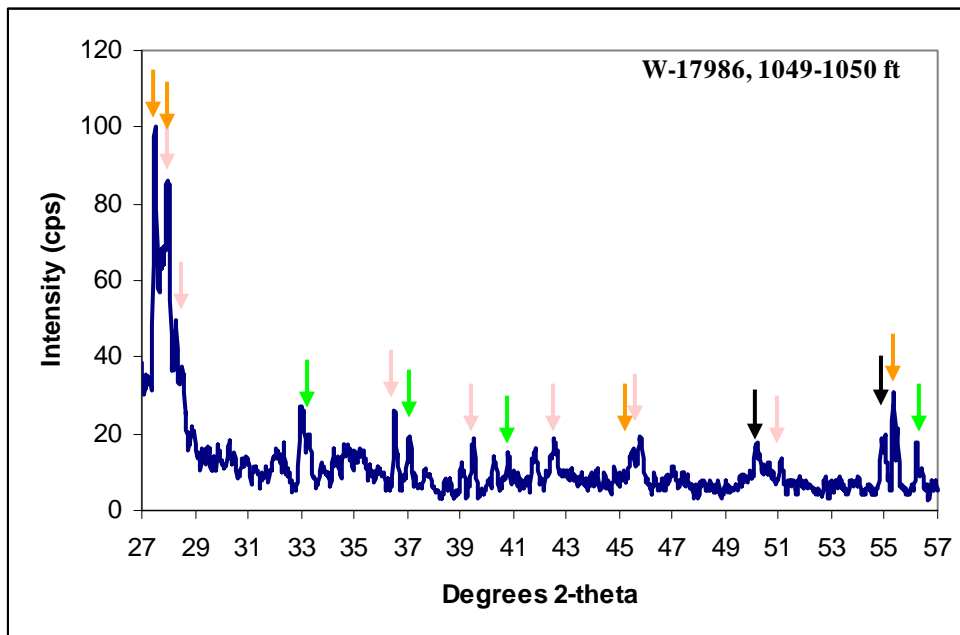


Figure 7. Portion of an XRD scan of the insoluble residues showing the four main peaks of pyrite (bright green). This example had the highest intensity pyrite peaks. Also present are a sodic plagioclase (albite, dull pink arrows), a calcic plagioclase (anorthite, orange arrows) and minor peaks of quartz (black arrows).

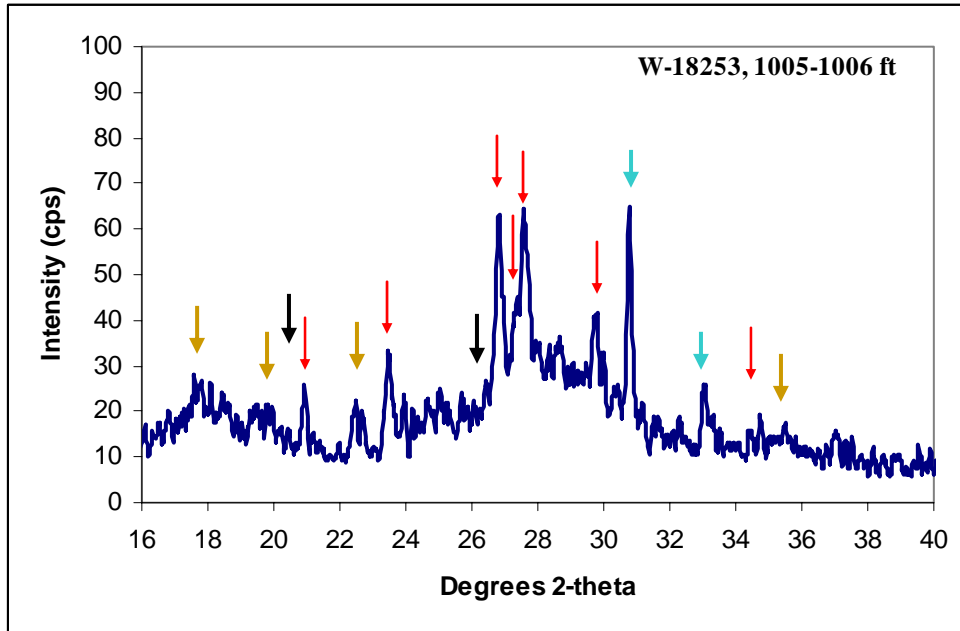


Figure 8. Portion of an XRD scan of the insoluble residue of an Ocala limestone. Brown arrows are minor peaks of smectite. Blue-green arrows denote ankerite (indicating not all carbonate was dissolved from the sample). Black arrows are where the major peaks of quartz would appear if quartz were present. Red arrows are the peaks of potassium feldspar (sanidine), which is the dominant non-clay phase.

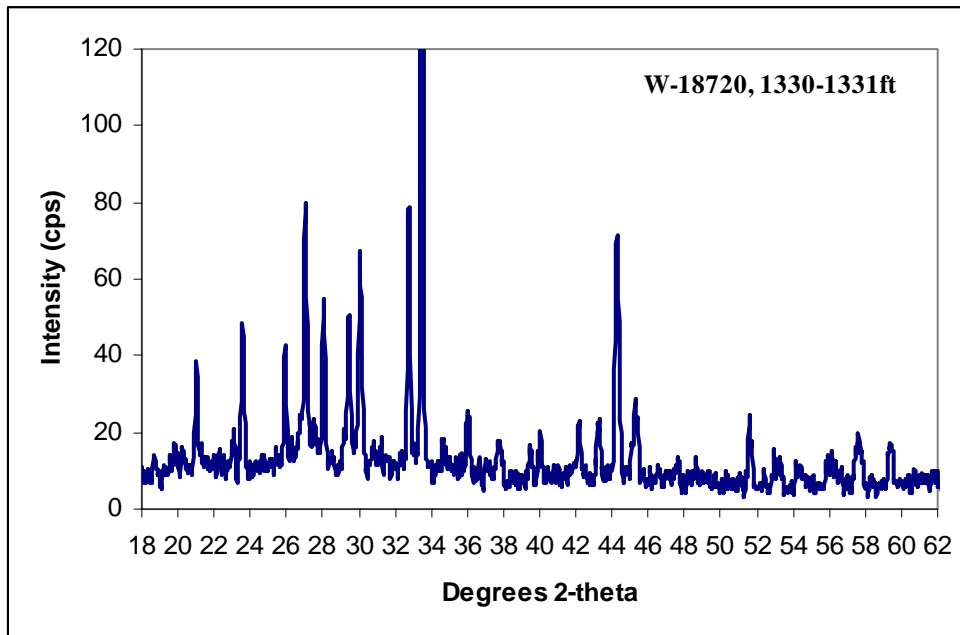


Figure 9. Portion of an XRD scan in which every peak is due to celestite. Sample is an Avon Park limestone.



709-710 ft and W-18715, 963-974 ft) that had less than 2% apatite in the bulk mineralogy actually revealed apatite in their insoluble fractions. This means apatite is a minor or trace component in those 2 samples and absent in all 40 other samples that did not have apatite at 2% or more of the bulk mineralogy.

Pyrite (Fig. 7) was definitely detected in the XRD analyses of only 10 of 52 insoluble residues (~20%), yet it was observed in 64% of all thin sections. Even where it was detected, it was but a trace constituent as evidence by very low intensity peak heights. Its absence in so many samples in which it is known to be present can be explained in two ways. First, many samples contained a large amount of insoluble residues, particularly those samples with abundant quartz, clay, or organic matter. The pyrite may simply have been too small a constituent to be detected by XRD analyses in those rocks even with the carbonates removed. Second, oxidation of pyrite is certainly possible given that the samples were subjected to acidic, oxygenated waters at 60°C. This may have removed significant portions of the pyrite present. Indeed, after dissolving the carbonate minerals, most of the Morgan's solutions had an orange tint to them as they were poured off, suggesting the presence of colloidal oxidized iron. Whether that was in the samples originally or generated during reaction with the Morgan's solution is unknown.

Celestite ( $\text{SrSO}_4$ ) was observed in one Avon Park sample (W-1872, 1330-1331 ft; Fig. 9). Celestite typically forms during closed system alteration of originally aragonite-rich sediments to calcite, particularly if that alteration occurs in marine pore waters. Another source of celestite would be as a trace phase in anhydrite-rich sediments.

Barite ( $\text{BaSO}_4$ ) was observed in two samples, W-18255, 800-830 ft (Fig. 10) and W-17896, 1022-1023 ft. The former sample was derived from well cuttings, the latter from a core. Drilling mud was used in the recovery of both samples. As barite is a common additive to drilling mud, it is possibly a contaminant in the two samples in which it was found. Bentonite, a smectitic clay, is typically the main component of drilling mud. Thus the smectite in the two samples with bentonite might also be a contaminant, particularly in the W-18255 sample that exhibited only trace amounts of clay.

Organic matter (OM), if present in a rock, is insoluble and concentrated with the mineral phases. It should darken the color of the insoluble residues, and indeed 30 of the residues exhibited a brown or dark brown color (others were pink, cream, tan, or gray). Ten of the samples that yielded ample residue either showed no crystalline phases (Fig. 11) in the XRD analyses (W-18253, 1304-1305 ft and W-18706, 1144-1159 ft), or exhibited just minimal traces (Fig. 12) of clays or other minerals (W-17986, 1133-134 ft, 1155-1156 ft, and 1170-1171 ft; W-18253, 1314-1315 ft; W-18706, 1251-1266 ft; W-18714, 1225-1233 ft; W-18715, 1090-1100 ft; and W-18720, 1028-1029 ft). In these 10 samples, OM is interpreted to be the dominant insoluble residue. To test this interpretation, 15 ml aliquots of the residue from 5 of these samples (W-17986, 1133-134 ft; W-18253, 1304-1305 ft and 1314-1315 ft; W-18706, 1144-1159 ft and 1251-1266 ft) were mixed with 15 ml of 30% hydrogen peroxide and reacted at 60°C for 5 days. Initially the wet residues in these five samples had brown to orange-brown colors, and there was material that readily floated in the solutions. After 5 days, all residue and color disappeared in all 5 reaction vessels, indicating the residues were organic matter.

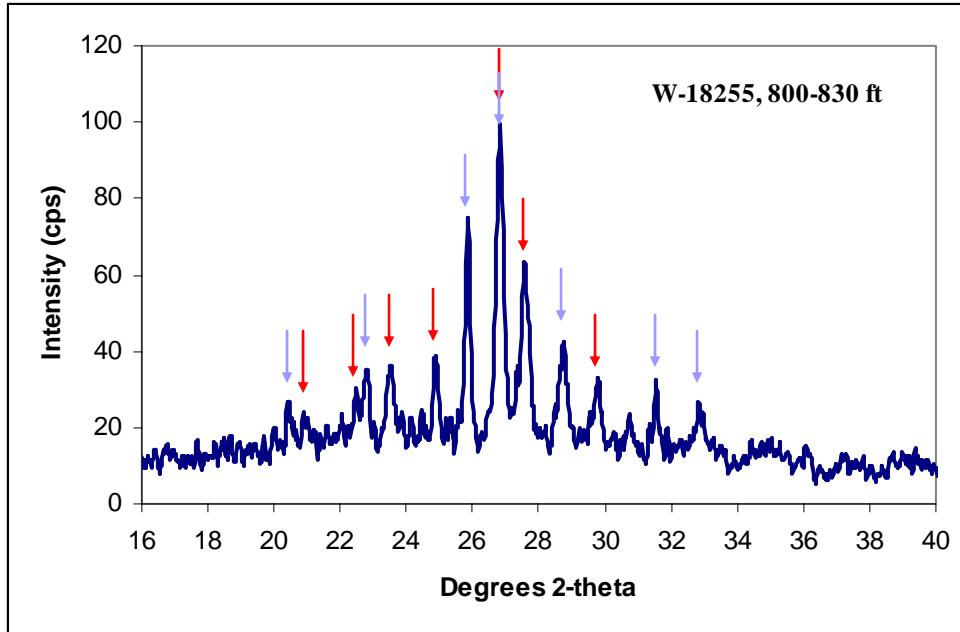


Figure 10. Portion of an XRD scan containing barite (light purple) and potassium feldspar (orthoclase, red arrows).

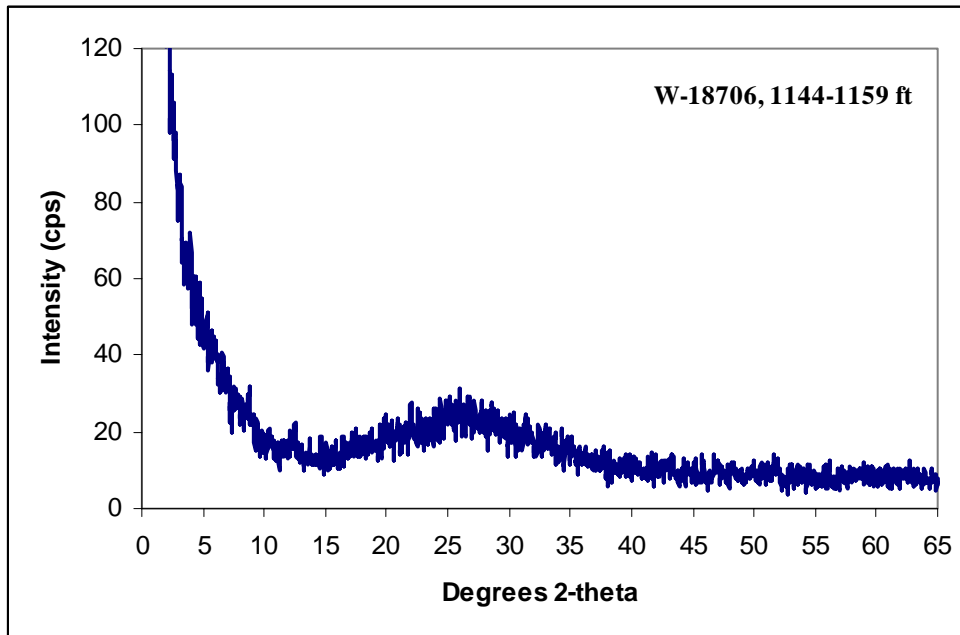


Figure 11. XRD scan that exhibits no peaks, and hence the insoluble residue contains no crystalline phases. The high background intensity from 2° to 10° is due to x-ray scattering at low angles.

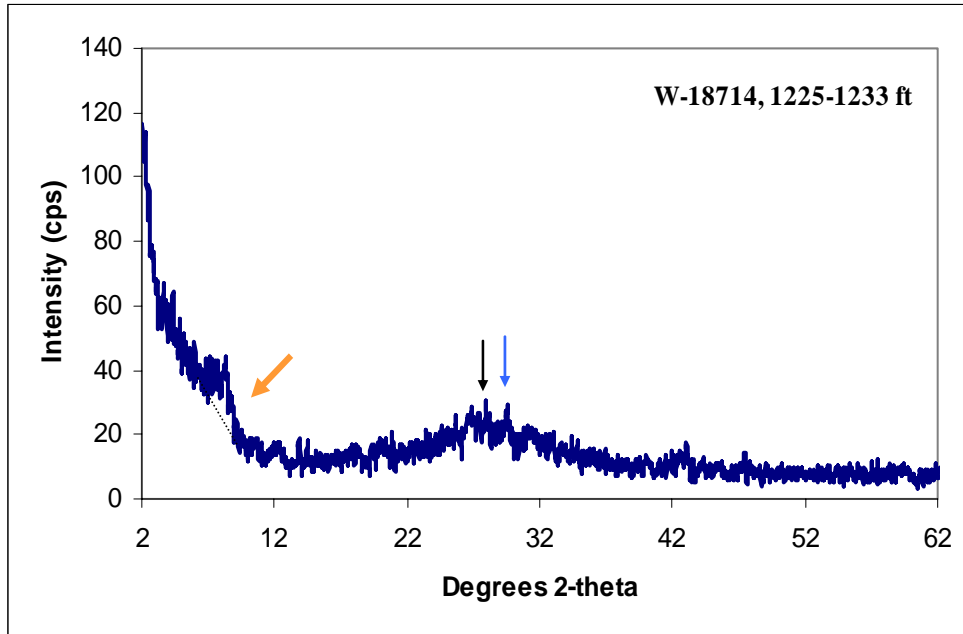


Figure 12. XRD scan that exhibits just minimal peaks. Blue arrow is possibly the highest intensity peak of calcite and the black arrow is possibly the highest intensity peak of quartz. Brown arrow points to a definite increase above background (dashed line) at low reflection angles. This is a trace amount of clay mineral. Glycolation and heating revealed the clay to be a mixed-layer smectite-illite.

### Clay Minerals

Clay minerals were not only identified, but their relative abundance was estimated (Table 4) based on the sharpness and height of the reflections between  $10\text{\AA}$  and  $14\text{\AA}$ . If there was a clear peak with intensity 5 times or more above background, then clays are termed “very abundant” (Fig. 13). If there was a clear peak but intensity was 3 to 5 times background, then clays are described as “abundant”. If a clear peak at intensities 2.5 to 3 times background, then clays are present in “moderate amounts” (Fig. 13). If just a “bump” was present on the diffractogram, meaning intensity was 2 to 2.5 times greater than background but there was no clear peak over that  $4\text{\AA}$  range, then clays are termed to be present in “small amounts” (Fig. 13). If just a small rise in intensity was present, (i.e., intensity was less than 2 times background, which also produces no clear peak between  $10\text{\AA}$  and  $14\text{\AA}$ ), then the clays are described as present in trace amounts (Fig. 12).

When both smectite and illite are present, it is reported as a mixed-layer smectite-illite (Fig. 13), however, in most samples smectite is probably far more abundant than the illite as evidenced by relative peak heights after glycolation. Kaolinite, when present, always occurs in small amounts as evidenced by the low intensity (1.5 to 2.5 times background) of its major peak at  $7.2\text{\AA}$  (Fig. 13). It never occurs alone, suggesting it may only be present in mixed-layer clays (most likely with smectite). The abundance of palygorskite, which occurs in just three samples, is hard to judge as its main peak overlaps with all mixed-layer clays. However, based on abundance of its secondary peak at  $6.4\text{\AA}$ , it is usually just a minor to trace constituent amongst the clay phases. Sepiolite, which occurs in seven samples ranges from being very abundant in some Hawthorn rocks (e.g., W-18463, 643-643.5 ft; Fig. 13) to a trace component in mixed-layer clays.

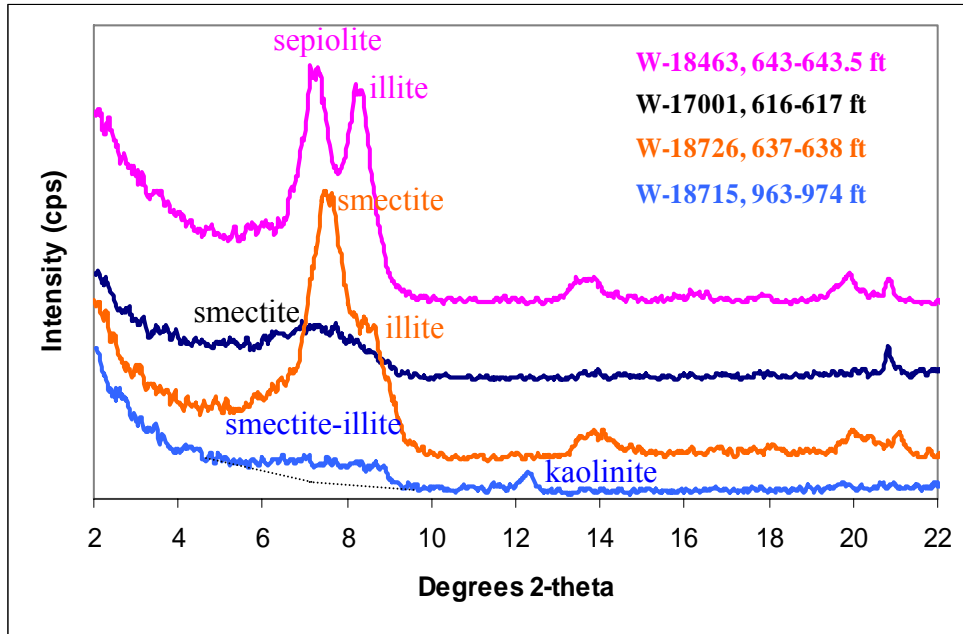


Figure 13. XRD scans illustrating the peak characteristics of untreated clay minerals. The purple and orange scans have “very abundant” clays, the black scan has a moderate amount of clays, and the blue scan has a small amount of clays. The peaks are labeled according to the clay minerals they represent, as determined by successive glycolation and heat treatments.

Clay minerals are very abundant, abundant, or moderately abundant in 24 of 51 samples (Table 5), present in small or trace amounts in 19 samples, and absent in just 8 samples. In Hawthorn samples, clay minerals were more likely to be very abundant, abundant, or moderately abundant (11 of 15 samples), whereas clay minerals in Avon Park samples are more likely to be absent or just trace components (16 of 20 samples). In Suwannee and Ocala samples, clay mineral abundance shows no pattern

Smectite (syn. montmorillinite) is the most common clay mineral, occurring in 36 of the 43 samples that contained clays. There is no pattern to its distribution. In 11 samples the smectite occurs by itself. In 25 samples it is the dominant component of mixed-layer clays.

In addition to smectite, the mixed layer clays mostly contain illite (23 samples). Other minerals that may occur in the mixed layer phases include kaolinite (12 samples), palygorskite (3 samples) and sepiolite (7 samples). None of the later three clay minerals occur as the sole clay in any sample. The palygorskite is more likely to be in Hawthorn rocks (two of its three occurrences), whereas kaolinite is more likely to be in Avon Park rocks (58% of the kaolinite occurrences). Sepiolite is also most likely to be in Hawthorn samples (four of seven occurrences).

Illite occurs independently of smectite in 8 samples, 4 of which are from the Hawthorn. It is the sole clay in only 2 of those 8 samples. It is associated with palygorskite in two of the other 6 samples, and with sepiolite in four of the other six samples.

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