

Detailed Geochemical Investigation of the Mineralogic Associations of Arsenic and  
Antimony Within the Avon Park Formation, Central Florida: Implications for Aquifer

Storage and Recovery

by

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**DETAILED GEOCHEMICAL INVESTIGATION OF THE MINERALOGIC  
ASSOCIATIONS OF ARSENIC AND ANTIMONY WITHIN THE AVON PARK  
FORMATION, CENTRAL FLORIDA: IMPLICATIONS FOR AQUIFER  
STORAGE AND RECOVERY**

**Angela C. Dippold**

**ABSTRACT**

The mineralogic associations of arsenic (As) and antimony (Sb) were investigated for the Avon Park Formation (APF) in central Florida to determine its viability for aquifer storage and recovery (ASR). Rock samples were taken from fourteen different cores and samples were taken according to core length, interval samples, and based on areas suspected to contain high levels of arsenic and antimony, such as molds, dissolution fractures, pyrite, clays, and organic matter, targeted samples. Permeable samples were also taken from high permeability zones. In total 373 samples were described in hand specimen and analyzed for bulk rock chemistry. Inductively coupled plasma optical emission spectrometry and hydride generation atomic fluorescence spectrometry were used to determine Fe, Al, Si, Mg, Ca, S, P, Mn, Sr, Mo, As, and Sb in bulk samples, while electron-probe microanalysis was used to analyze Sb, As, Fe, S, Zn, Ca, Mo in

discrete minerals.

The mineralogic and geochemical investigation showed: (1) bulk As and Sb concentrations within the APF are low; (2) As values range from  $< 0.1$  to 30.8 mg/kg and Sb from  $< 0.1$  to 6.76 mg/kg; (3) average values are 2.24 mg/kg As and 0.28 mg/kg Sb; (4) pyrite is present as framboids, hollow framboid rings, “honeycomb” pseudo-framboids, small irregularly shaped pieces with topography, and euhedral crystals; it is typically associated with oxidized organic laminations, fractures, and molds; (5) the framboid rings may have been precipitated by a bacteria making them biogenic; (6) euhedral pyrites contain significantly less As than other morphologies while irregular pyrites have the most; (7) individual pyrites range from  $< 0.1$  to 5820 mg/kg As while Sb ranges from  $< 0.1$  to 2470 mg/kg; (8) the samples from zones of high permeability have lower As and Sb averages than those of the other samples: 1.02 mg/kg As and 0.15 mg/kg Sb versus 1.32 mg/kg As and 0.19 mg/kg Sb for interval and 3.16 mg/kg As and 0.37 mg/kg Sb for targeted samples; (9) As is found mainly in pyrite but is possibly from organic matter and clay; (10) overall As concentrations and correlations may be low but individual cores and zones have high values; (11) the APF has appropriately permeable zones for ASR; (12) the success of ASR in the APF formation depends on the degree of geochemical alterations, presence of competing anions and simple organic ligands, and the amount of trace metals sorbed to surfaces versus coprecipitated.

## CHAPTER ONE

### INTRODUCTION

It is important to understand all potential sources of arsenic and antimony within an aquifer matrix to limit the release of these metals into Floridan aquifers. The Avon Park Formation (APF) is currently being assessed for potential sources of arsenic (As) and antimony (Sb) to determine its viability for aquifer storage and recovery (ASR). The known mineralogical associations of As and Sb are critical to this determination.

Aquifer storage and recovery is an important topic in Floridan hydrogeology. It involves the injection of treated water into an aquifer during periods of low water consumption and high availability. Aquifers for injection are selected based on their native water quality and hydrogeologic parameters. Water is later recovered via the same well when demand increases, typically during dry seasons. An ideal ASR aquifer is brackish, anoxic, and confined with sufficient permeable zones to support efficient recovery of injected water. Geochemical and hydrologic characteristics determine the efficiency for recovered water. Ideally the injected water has a relatively low mixing ratio with native water to prevent altering native water chemistry and thereby increase the recovery efficiency of the injected water.

There are currently 80 ASR facilities in Florida, 34 are in testing or operation while the rest are proposed or pending construction (FLDEP, 2008). In addition 333

ASR wells are proposed for the Comprehensive Everglades Restoration Project (CERP) (Arthur et al., 2007). The CERP and other ASR projects cannot move forward until the issue of metal mobilization is resolved. The ASR method is beneficial because evaporation or surface runoff rates are low and limited land and equipment are required potentially making it less expensive than surficial storage. Large volumes of water can be stored for seasonal, long term, or emergency use. This is beneficial for areas with climates of wet and dry months and high evaporation rates. It is therefore necessary to solve the trace metal mobilization issue to insure adequate sources of drinking water.

### 1.1 Problem Statement

The Florida Department of Environmental Protection's (FLDEP) Underground Injection Control (UIC) program regulates injections into the subsurface to protect underground sources of drinking water (USDW). Injected material should not degrade the water quality of the native groundwater or surrounding aquifers. According to the FLDEP and US Environmental Protection Agency (EPA) regulations, injected water must meet Florida's drinking water standards. Therefore, water must be treated before injection, which greatly increases its dissolved oxygen content (FLDEP, 2008). Native groundwater, specifically within a confined aquifer, is oxygen depleted, reducing (Jones and Pichler, 2007). During ASR processes native and injected waters inevitably mix. Thus injecting treated surface water into a confined aquifer alters the geochemical properties of both waters that in turn affect mineral stability.

There are currently 190 ASR wells in Florida in various stages of construction or production. Of these 15 ASR wells are not in compliance with federal drinking water regulations due to the mobilization of trace metals such as As, molybdenum (Mo), Sb,

and uranium (U) (Arthur et al., 2007; Llewellyn, 2008). Of the 15, 7 have exceeded As concentrations of greater than 50.0 µg/L at least once (Llewellyn, 2008). The EPA drinking water standard for As is 10 µg/L and for Sb is 6.0 µg/L (EPA, 2006). This lead to hesitate permitting of ASR wells from the FLDEP, and thus made it more difficult for companies to obtain state and federal funding for ASR facilities. Thus this potentially viable source of water storage for Florida cannot be used on a large scale until further research can reveal that the mobilization of metals can be prevented or limited.

The stability of pyrite is a critical geochemical parameter that is altered causing the mobilization of As and potentially Sb (Jones and Pichler, 2007). Pyrite naturally exists throughout Florida and is the most common sulfide mineral in surficial environments (Rickard and Luther, 2007). It is stable under reducing aquifer conditions. The introduction of oxygenated water causes conditions where pyrite becomes unstable (Figure 1). Arsenic and antimony behave similar chemically and have a high affinity for sulfide species like pyrite. Arsenic chemically behaves similarly to sulfur (S) resulting in the substitution of As for S (Figure 2). Research is limited and conflicting on the geochemical behavior of Sb but it is thought to be similar to As since high concentrations of naturally occurring Sb are associated with As rich sulfide ores (Filella et al., 2002a, b). Thus it is also likely to substitute for S. Antimony III ( $\text{Sb}^{3+}$ ) compounds are soluble in alkaline sulfide waters. Its behavior in the natural environment with S can be seen in Figure 3.

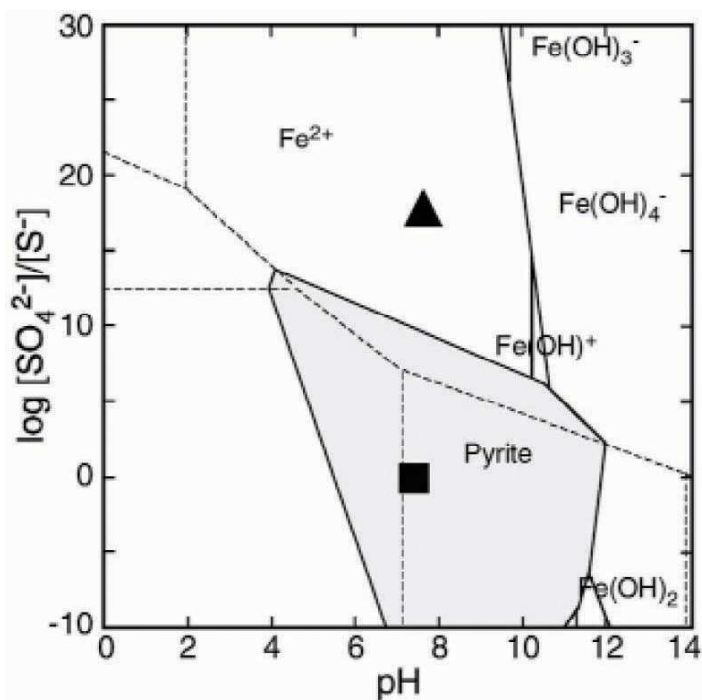


Figure 1. Diagram from Jones and Pichler (2007) showing how the stability of pyrite is altered when a mixing ratio of  $1 \times 10^{15}$  for injected to native water occurs. The square represents the native aquifer water and the triangle is for the mixed water.

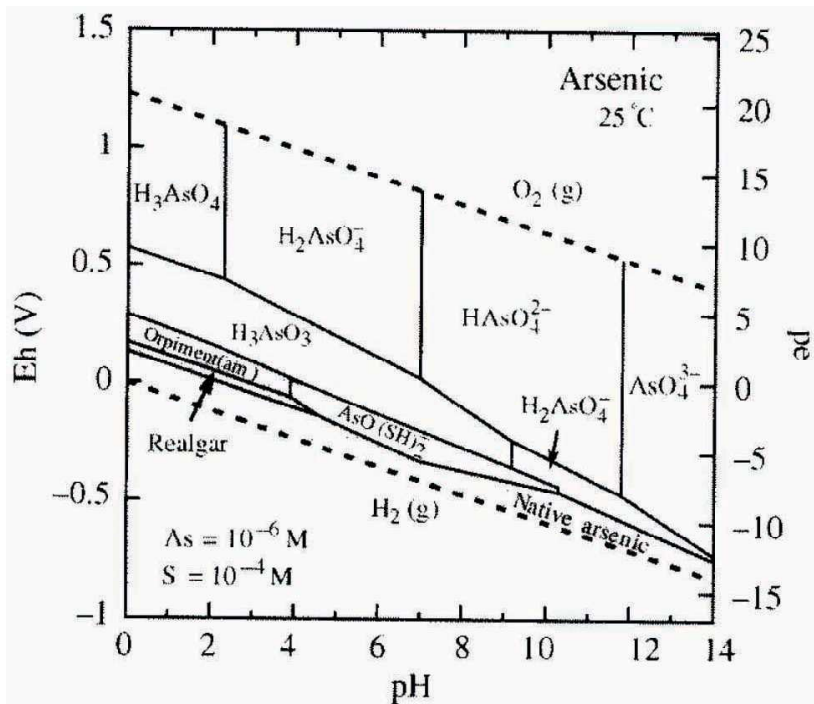


Figure 2. This figure shows the stability of arsenic in the presence sulfur at 25°C and 1 bar of pressure. The dashed lines define the stability field of water. (Plant et al., 2004).

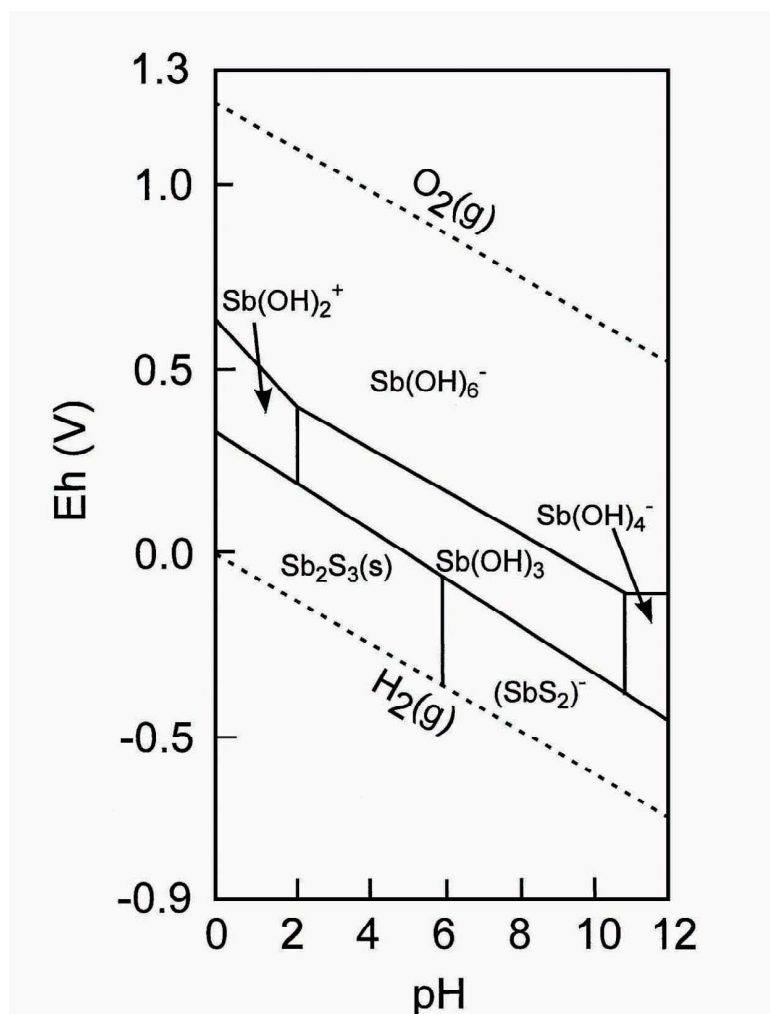


Figure 3. Diagram of antimony stability in a Sb-S-H<sub>2</sub>O system with dissolved Sb ( $10^{-8}$  mol/L ) and dissolved S ( $10^{-3}$  mol/L) (Filella et al., 2002b).

The average crustal abundance of As is 1.5 mg/kg and 2.6 mg/kg in limestones while the average crustal abundance for Sb is 0.7 mg/kg and 0.2 mg/kg in carbonates (Baur and Onishi, 1969; Filella et al., 2002a; Smedley and Kinniburgh, 2002). Their concentrations in sulfide minerals may vary greatly even within individual grains. All of these chemical characteristics indicate a detailed investigation of the mineralogic associations of As and Sb within the Avon Park to determine its viability for ASR is necessary. Past studies Lazareva and Pichler (2007) and Price and Pichler (2006)

attributed the main source of As to pyrite in the Suwannee Limestone and Hawthorn Group within the Southwest Florida Water Management District (SWFWMD). This study was conducted in the southern two thirds of the SWFWMD from Hillsborough to Charlotte County (Figure 4). This is the first study to target permeable zones and examine Sb in bulk rock and individual pyrites.

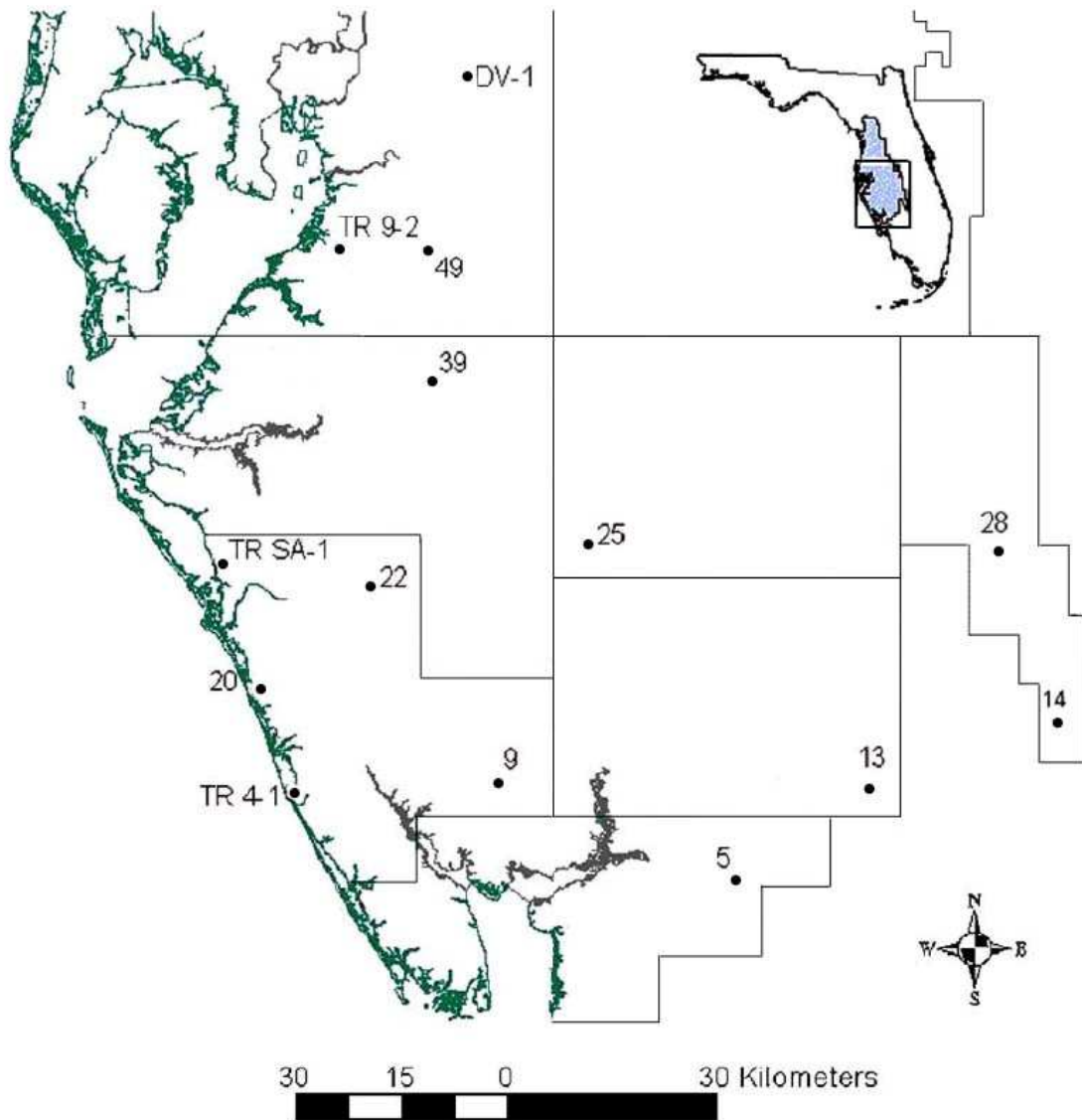


Figure 4. The study area covers the southern two-thirds of the Southwest Florida Water Management District. The numbered dots represent the location of the ROMP wells cores were obtained from.

## 1.2 Research Plan

Various geochemical and petrographic analyses were conducted on samples from fourteen different cores, DV-1, ROMP 22, ROMP 20, TRSA-1, TR4-1, TR9-2, ROMP 5, ROMP 9, ROMP 13, ROMP 14, ROMP 25, ROMP 28, ROMP 39, and ROMP 49, to determine the abundance and mineralogic associations of As and Sb in the Avon Park Formation (Table 1). These cores are part of the SWFWMD's Regional Observation Monitoring Well Program (ROMP) and were used in similar studies by Lazareva and Pichler (2007) and Price and Pichler (2006) investigating the Hawthorn Group and Suwannee Limestone located stratigraphically above the Avon Park Formation. A comparative analysis between the three units was conducted. Cores were analyzed under a petrographic microscope. The general lithology was described along with porosity and any interesting features that may potentially contain As or Sb. These features include but are not limited to molds, dissolution fractures, pyrite, clay, and organic matter. Lithologic descriptions were compared with descriptions of the same core by David Budd, a carbonate petrologist (2001,2002). Several samples were chosen for further analysis by scanning electron microscopy (SEM) based on the descriptions.

A representative sample from each of the core samples was selected for chemical analysis. An inductively coupled plasma – optical emission spectrometer (ICP-OES) was used to analyze for: aluminum (Al), calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), phosphorus (P), silica (Si), strontium (Sr), and sulfur (S). The samples were analyzed for arsenic (As) and antimony (Sb) using hydride generation-atomic fluorescence spectrometry (HG-AFS). A variety of samples with high and low bulk arsenic concentrations containing targeted features were made into thin

sections and analyzed with a petrographic microscope to determine the presence and mineral associations of pyrite. The pyrites were then analyzed with an electron microprobe (EPMA) for As, molybdenum (Mo), Sb, and zinc (Zn).

Table 1. Length of cores and physical characteristics for ROMP wells sampled within the Avon Park Formation. A ? indicates that the formation extends beyond the depth drilled.

| ROMP<br>Number | ROMP<br>Name        | USGS<br>Well<br>ID | County       | Surface<br>Elevation<br>(ft-bsl) | APF<br>Depth<br>Range<br>(ft) | Total<br>well<br>depth<br>(ft) | Core<br>Length of<br>APF (ft) | Sampling<br>interval<br>(ft) |
|----------------|---------------------|--------------------|--------------|----------------------------------|-------------------------------|--------------------------------|-------------------------------|------------------------------|
| TR SA-1        | Payne<br>Terminal   | 17452              | Sarasota     | 8                                | 1009-?                        | 1210                           | 201                           | 10                           |
| TR 4-1         | Casperson<br>Beach  | 17488              | Sarasota     | 10                               | 1070-<br>1174                 | 1174                           | 104                           | 10                           |
| TR 9-2         | Apollo<br>Beach     | 16618              | Hillsborough | 13                               | 697-?                         | 872.5                          | 175.5                         | 25                           |
| DV-1           | Dover<br>Elementary | 16576              | Hillsborough | 112                              | 521-?                         | 839                            | 318                           | 20                           |
| 5              | Cecil Webb          | 16913              | Charlotte    | 40                               | 1080.4-?                      | 1304                           | 223                           | 25                           |
| 9              | North Port          | 17056              | Sarasota     | 25                               | 1040- ?                       | 1175                           | 135                           | 10                           |
| 13             | Tippen Bay          | 17392              | Desoto       | 60                               | 1054-?                        | 1544                           | 490                           | 40                           |
| 14             | Hicoria             | 17001              | Highlands    | 145                              | 1019-?                        | 1277                           | 258                           | 30                           |
| 20             | Osprey              | 17087              | Sarasota     | 15                               | 1208-?                        | 1439                           | 231                           | 15                           |
| 22             | Utopia              | 16783              | Sarasota     | 35                               | 941-?                         | 1813                           | 872                           | 20                           |
| 25             | Lily                | 17608              | Hardee       | 85                               | 976-1790                      | 1911                           | 72                            | 10                           |
| 28             | Kuhlman             | 17000              | Highlands    | 82                               | 860-?                         | 2112                           | 1252                          | 50                           |
| 39             | Oak Knoll           | 16740              | Manatee      | 129                              | 990.4-?                       | 1694                           | 990-1013;<br>1680-1694        | 5                            |
| 49             | Balm Park           | 16456              | Hillsborough | 146                              | 825-1575                      | 1575                           | 74.5                          | 10                           |

## CHAPTER TWO

### GEOLOGY AND HYDROGEOLOGY

#### 2.1 Regional Geology

The Avon Park Formation (APF), is of middle Eocene age and is comprised of the Lake City Limestone overlain by the Avon Park Limestone defined by (Applin and Applin, 1944). Miller (1986) suggested combining the two units based on lithologic characteristics; the units have since been referred to as the Avon Park Formation (Figure 5). The APF is comprised of interbedded limestone and dolomite and deeper beds of continuous dolomite that increase in evaporites towards the base. The APF was formed as a peritidal platform comprised of cyclic shallow-open-marine to tidal-flat carbonates with some “salt marsh and swamp deposits of peat and carbonaceous material” deposited on the Florida platform (Gilboy, 1985). The peat deposits are indicative of a shallow, warm, lagoonal setting surrounded by the broad carbonate bank consisting of the entire Florida peninsula (Chen, 1965).

The lower portion of the APF was dolomitized in the Eocene by normal to hypersaline seawater (Cander, 1994). The base is described as a thick brown to dark brown fine crystalline dolomite unit comprised of a gypsiferous wackestone-mudstone (Chen, 1965; Cander, 1994). It is notably muddier and lower in porosity compared to the underlying Oldsmar Formation. It is also particularly muddier in the upper portion, containing mudstones, pelleted muds, and algal laminated mudstones, than the overlying

Ocala Limestone (Cander, 1991). In some regions it is unconformably overlain by the Ocala Limestone, Late Eocene, and in all regions underlain unconformably by the Oldsmar formation, early Eocene (Cander, 1994; Randazzo and Douglas, 1997). The erosion that has removed the Ocala Limestone in certain areas caused the APF to be overlain by "undifferentiated post Miocene sediments" (Scott, 1989).

The limestone is fine to coarse grained, cream to brown, recrystallized fossiliferous packstone with variable amounts of organic-rich, peat, laminations and numerous seagrass fossil beds near the top of the formation (Tihansky, 2005). There are also zones of grainstone, wackestone, and mudstone (Scott, 1989). It has minor intergranular calcite cement with primary porosity (Cander, 1994). The limestone may also be "interbedded with dark brown to tan very-fine to coarse-grained, vuggy fossiliferous dolostones and has typically experienced some form of dolomitization (Arthur et al., 2009). The dolomite is hard, light to dark brown sucrosic in texture and highly fractured.

Moving deeper in the APF, interstitial void spaces are filled with evaporites. The evaporites occur in the dolomite as interstitial gypsum and anhydrite and are interbedded in the lower two thirds of the formation increasing with depth resulting in reduced porosity (Tihansky, 2005). Arthur et al. (2009) identified chert, pyrite, gypsum, and quartz as accessory minerals. The lower portion is almost completely dolomitized (Tihansky, 2005). The undolomitized limestone is found in the upper 100 meters where it is interbedded with dolomitized packstone, wackestone, and mudstone (Cander, 1991).

| System     | Series                     | Gulf Coast |  | Alabama |                           | Florida   |                           | Georgia |                                                      | South Carolina |                                         |
|------------|----------------------------|------------|--|---------|---------------------------|-----------|---------------------------|---------|------------------------------------------------------|----------------|-----------------------------------------|
|            |                            |            |  | West    | East                      | Panhandle | Peninsula                 |         |                                                      |                |                                         |
| Quaternary | Holocene                   |            |  |         | Undifferentiated Deposits |           | Undifferentiated Deposits |         | Undifferentiated Deposits                            |                | Undifferentiated Deposits               |
|            | Pleistocene                |            |  |         |                           |           |                           |         |                                                      |                |                                         |
| Tertiary   | Post-Miocene rocks         |            |  |         | Wisconsin to Nebraskan    |           | Terrace deposits          |         | Undifferentiated terrace and shallow marine deposits |                | Terrace deposits                        |
|            |                            |            |  |         |                           |           |                           |         | Colonsauchoe Formation and equivalents               |                | Waccamaw Formation                      |
|            | Pliocene                   |            |  |         | Fuluyan                   |           | Citronelle Formation      |         | Bone Valley Formation                                |                | Chertown Formation                      |
|            | Rocks of Miocene age       |            |  |         | Clovelian                 |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         | Duckizkian                |           |                           |         |                                                      |                |                                         |
|            | Rocks of Miocene age       |            |  |         | Napoleonvillian           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         | Anahuacian                |           |                           |         |                                                      |                |                                         |
|            | Rocks of Oligocene age     |            |  |         |                           |           | Undifferentiated Deposits |         | Alum Bluff Group                                     |                | Undifferentiated upper Miocene deposits |
|            |                            |            |  |         |                           |           |                           |         | Hawthorn Formation                                   |                | Hawthorn Formation                      |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
| Tertiary   | Rocks of late Eocene age   |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
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|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            | Rocks of middle Eocene age |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
| Tertiary   | Rocks of early Eocene age  |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
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|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
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|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            | Rocks of Paleocene age     |            |  |         |                           |           |                           |         |                                                      |                |                                         |
|            |                            |            |  |         |                           |           |                           |         |                                                      |                |                                         |

Figure 5. Lithostratigraphic units of Florida defined by Miller (1986).

## 2.2 Local Geology

Within the study area, the Southwest Florida Water Management District (SWFWMD), the APF has thick interbedded fossiliferous limestone and dolomite consisting of rocks ranging from wackestone to grainstone along with thin layers of peloidal and carbonaceous mudstones and wackestones (Randazzo, 1980). Various sedimentary features associated with modern tidal-flat environments were also recognized (Randazzo, 1980). Similar to the general APF description, the lower segment of the formation in this region has experienced more dolomitization, extensive enough to destroy or distort the rock's original microfabric, than overlying strata (Randazzo, 1980). The middle portion of the formation has interbedded units representing the most distinctive cyclical depositional patterns associated with subtidal beds. Abundant lenses of peat and carbonaceous plant remains are also present. The uppermost portion of the formation exhibits "wide vertical and lateral variations" (Randazzo, 1980). Unlike the APF in other Florida regions, the upper portion in some areas of the SWFWMD has experienced extensive dolomitization.

The base of the APF formation varies from 305 to 732 m below mean sea level and thickness ranges from 305 to 488 m (Miller, 1986). Limestone is limited to the first 20 meters and the rest of the formation has experienced some form of dolomitization (Cander 1991). There are several laminations of carbonaceous material representing possible marine grasses from 280-290 meters. Budd and Vacher (2004) interpreted the "plane and crinkly laminations" within the limestones as tidal deposits. The dolomite was described as vuggy, hard, and sugary at 305 meters. It then changes to "dark brown, non-porous, dense, hard, and sparkling in crystallinity" at 312 meters (Cander, 1991).

Massive dark brown crystalline dolomite was encountered at 312 meters and extends to 327 meters where the core ended (Cander, 1991). Dissolution channels and centimeter-sized vugs were noted in hand samples suggesting conduit-type permeability instead of the interparticle porosity noted regionally (Cander, 1991).

### 2.3 Floridan Aquifer System

The Floridan Aquifer System (FAS) is comprised of thick carbonaceous units that comprise all or part of the Paleocene to Early Miocene Series covering an area of 259,000 km<sup>2</sup> from southern South Carolina, through southeastern Georgia and part of southern Alabama to the entire state of Florida (Budd and Vacher, 2004; Scott, 1992). It is confined in areas where it is overlain by the intermediate aquifer system or intermediate confining unit. In other areas these layers are absent, and it is overlain by only the surficial aquifer (Scott, 1992). It is thus divided into the Upper Floridan Aquifer (UFA), Intermediate Aquifer System and Lower Floridan Aquifer (LFA) based on the hydrologic properties of the present lithologic units. The top of the aquifer is defined by the loss of substantial siliclastic segments and the presence of a vertically continuous carbonate segment. Most of the time this corresponds with the top of the Suwannee Limestone or Ocala Group (Scott, 1992). The base in peninsular Florida is defined by the presence of regionally extensive anhydrite beds, which are an indication of the top of the Cedar Keys Formation. In the panhandle of Florida the fine-grained siliciclastic rocks of the Middle Eocene Series form the base (Scott, 1992).

The FAS thickness ranges from less than 30 meters in the western panhandle to more than 1067 meters in southwestern peninsular Florida (Miller, 1986). Permeability varies widely depending on the depositional environment and structural elements and is

greatly dependent upon diagenesis and dissolution. Budd and Vacher (2004) measured  $<10^{-14.4} - 10^{-11.1} \text{ m}^2$  for matrix permeability within the confined aquifer regions and a much higher secondary permeability. Average overall matrix porosity can span from 30-35% in cores and geophysical logs while individual core samples can be 10-50% (Budd and Vacher, 2004) .

The FAS underlies the entire study area where it acts as a significant source of potable water. The top of the FAS is fairly flat in the northern two-thirds of the study area and dips to the south in the southern portion. In the far north portion of the study area it is more than 427 meters thick and thins to the south to about 180 meters at the northern third of the study area where it thickens moving south to more than 730 meters (Scott, 1992). Regional groundwater flow is towards the coasts. The primary section of the FAS consists of the Avon Park and Oldsmar Formations (Scott, 1992).

## 2.4 Hydrogeology

The APF plays an integral part in the FAS. The upper portions of the Avon Park along with the Ocala Limestone are the most permeable formations within the FAS (Randazzo and Douglas, 1997). High transmissivity values of the Tertiary carbonates have been attributed to secondary porosity and permeability caused by fracturing and dissolution processes during the Quaternary period (Gilboy, 1985; Stringfield, 1966). The Upper Floridan aquifer is comprised of the Suwannee and Ocala Limestones and the APF (Randazzo and Douglas, 1997). The upper portion of the APF comprises the lower part of the UFA system. Its lower segment, along with the Oldsmar Formation and the upper segment of the Cedar Keys Formation, makes up part of the LFA (Randazzo and Douglas, 1997). In some areas the APF's lower dolomitized portion containing sulfate

and evaporite rich segments produces degraded water quality classifying it as part of the middle-confining unit (Tihansky, 2005; Gilboy, 1985).

Within the study area, the FAS is confined with the exception of the northern third of the study area where it acts as a surficial aquifer (Ryder, 1985). Transmissivity values range from 4600 m<sup>2</sup>/day to 23,000 m<sup>2</sup>/day depending on the aquifer and confining unit thicknesses (Randazzo and Douglas, 1997). Miller (1986) attributed the majority of the porosity in Avon Park limestones to primary interparticle porosity. Cander (1991) described the porosity in APF dolomite as “well connected, interparticle or intercrystalline.” The average porosity of Avon Park limestone is approximately 25% while the dolomite varies from 15% to 20% (Cander, 1991). Arthur et al. (2009) found total porosity for the APF within the study area to average around 31.7% ranging from 22.3% to 42.0%. Limestone permeability averages 10<sup>-13.0</sup> m<sup>2</sup> with grainstones being the most permeable at 10<sup>-12.4</sup> m<sup>2</sup> while dolostones average 10<sup>-13.8</sup> m<sup>2</sup> with sucrosic dolostones having the highest permeability of 10<sup>-12.0</sup> m<sup>2</sup> (Budd and Vacher, 2004). Grainstone permeability decreases with depth due to “compaction-related burial diagenesis” (Budd, 2001; Budd, 2002).

## 2.5 Possible Sources of Arsenic and Antimony in the Avon Park Formation

### 2.5.1 Arsenic

Since the APF is part of the UFA, it is referred to as an aquifer in the following section. With the exception of mineral deposits, groundwater is thought to contain the highest values of naturally occurring arsenic. Arsenic (As) in groundwater is commonly found in young aquifers with slow groundwater flow typically due to low flat-lying topography. Localized areas of sulfide oxidation are also sources (Smedley and

Kinniburgh, 2002). These factors describe the APF so the presence of As is highly likely there. Within an aquifer, the critical chemical reactions that determine the separation of arsenic into liquid and solid form occur at the “particle-water interface” (Stumm, 1992). Arsenic species are stored in the aquifer matrix through adsorption and precipitation reactions controlled by redox conditions and saturation levels and released by desorption and dissolution reactions. Redox reactions may store or release As species depending on the chemical behavior of the reactants and products involved, specifically competing anions (Welch et al., 2000). Compared to other oxyanion-forming elements like antimony (Sb) and heavy metalloids, As is rather sensitive to changes in redox conditions at the pH range of groundwaters (pH 6.5-8.5) in reducing and oxidizing environments (Smedley and Kinniburgh, 2002).

The conditions for the formation of As minerals are quite specific, which is why Smedley and Kinniburgh (2005) consider them rare in low temperature depositional environments. Instead As is commonly incorporated into oxyanions such as sulfates, phosphates, and carbonates through adsorption and coprecipitation (Welch et al., 1988; Welch et al., 2000). The amount of As that can later be desorbed from the minerals depends on pH changes and competition for adsorption sites with inorganic ( $\text{OH}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ) and simple organic ligands (Foster, 2003; Appelo et al., 2002; Jain and Loeppert, 2000; Meng, 2002). If the As is coprecipitated, its release will depend on the bulk mineral’s solubility since the majority of the As is not on the surface but contained within the mineral structure (Foster, 2003; Smedley and Kinniburgh, 2002). One of the keys to As mobilization is thus how much is sorbed to a mineral surface and how much is incorporated into its crystalline structure.

Arsenic's mobility is unique because it can occur in reducing and oxidizing conditions. Once in solution, As will occur as an oxyanion of arsenite ( $\text{As}^{3+}$ ) or arsenate ( $\text{As}^{5+}$ ) (Smedley and Kinniburgh, 2002). Arsenite is stable under reducing conditions and lower pH while the arsenate is stable in oxidizing conditions at higher pH values (Figure 6). Since As has a unique ability to exist in different conditions and adsorb to different minerals, it is found at low (non-toxic) concentrations in most natural waters (Smedley and Kinniburgh, 2002).

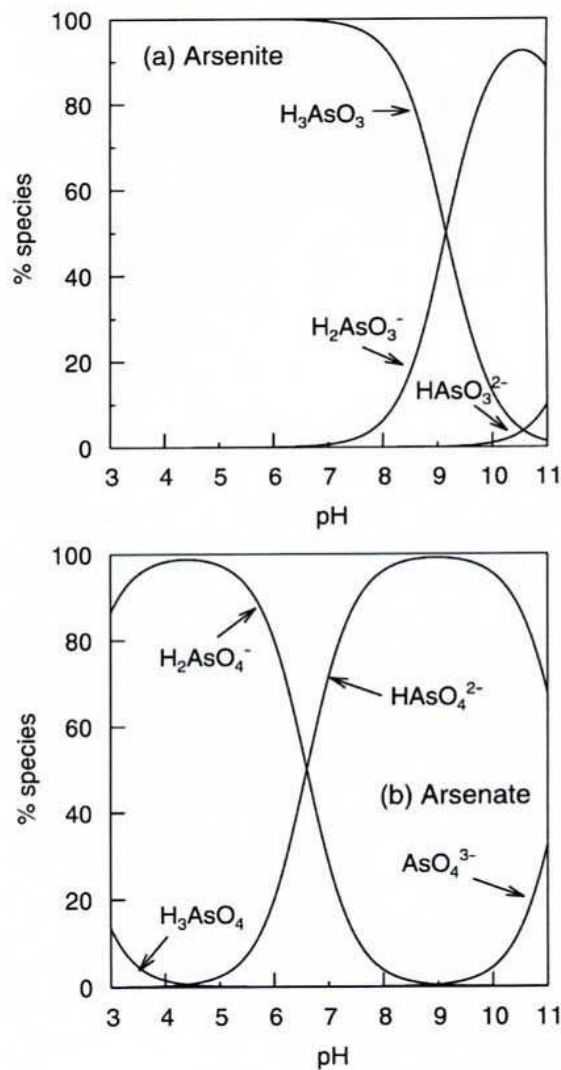


Figure 6. Speciation of arsenite (a) and arsenate (b). (Smedley and Kinniburgh, 2002).

#### 2.5.1.a Sulfide Minerals such as Pyrite

Sulfide minerals are capable of releasing and storing As within an aquifer (Welch et al., 2000). These minerals, specifically pyrite and arsenopyrite, are also considered the predominant source of As in aquifers (Foster, 2003; Nickson et al., 2000; Peters et al., 1999; Smedley and Kinniburgh, 2002). Sulfide minerals are capable of As concentrations of more than  $10^5$  mg/kg (Dudas, 1984; Fleet and Mumin, 1997). The primary release of As into the aquifer via sulfide minerals occurs when they are oxidized by the introduction of oxygen or other gases in the drawdown cone surrounding a well or along fractures during pumping or natural drawdown events (Arthur et al., 2001; Arthur et al., 2005; Mirecki, 2004; Stuyfzand, 1998). Arsenic is a chalcophile element and is therefore attracted to sulfur. The largest concentrations of As are found in sulfide minerals, and pyrite is the most abundant sulfide mineral (Smedley and Kinniburgh, 2002). A sample may have a low bulk concentration of As but individual pyrites or framboidal clusters of pyrite have been found to contain up to 11,200 mg/kg of arsenic (Price and Pichler 2006). Studies by Lazareva and Pichler (2007) and Price and Pichler (2006) determined pyrite to be the predominant source of As in the Hawthorn Group and Suwannee Limestone within the SWFWMD.

Rickard and Luther (2007) have estimated that about 5 million tons of pyrite is formed annually in marine environments. The APF was formed in a shallow oceanic setting and has also accumulated authigenic pyrite during diagenesis. Pyrite is considered a primary sink for sedimentary sulfur (Brassell et al., 1986; Kohnen et al., 1989; Vairavamurthy et al., 1995a). The chalcophile nature of As causes it to incorporate naturally into the mineral structure of pyrite by substituting for sulfur (S). When the

stability of pyrite is altered in aerobic conditions, it oxidizes to hydrous ferric [iron] oxides releasing sulfate, acid ( $H^+$ ), and trace elements such as As (Smedley and Kinniburgh, 2002).

#### 2.5.1.b Organic Matter and Clays

The major form of organic matter present in the APF is algal laminations. As previously stated simple organic ligands compete with As for adsorption sites. The presence of these ligands can therefore prevent the adsorption of As keeping it in solution. Decomposing organic matter forms localized strongly reducing environments. These intense reducing conditions are favorable to pyrite formation (Haque et al., 2007; Kohnen et al., 1989). Organic matter is therefore capable of locally concentrating pyrite, a significant source of As.

Layered aluminosilicates, clays, have a net negative charge on their basal planes limiting the adsorption of the negatively charged As oxyanions. The oxyanions are able to bond to the edges of the aluminosilicates where amphoteric aluminum octahedra exist (Christensen et al., 1989; Foster, 2003; Hamdy and Gissel-Nielsen, 1977). The small clay grains create a large surface area where As can adsorb. The similarity of the  $Al^{3+}$  atom to  $Fe^{3+}$  causes the oxides and hydroxides of aluminum (Al) to behave similarly to those of hydrous ferric oxides toward arsenic (Waychunas, 1991). Studies have found that the arsenic bound to these clay minerals is easily released compared to hydrous aluminum oxides or hydrous ferric oxides (Christensen et al., 1989; Hamdy and Gissel-Nielsen, 1977).

#### 2.5.1.c Hydrous Ferric Oxides (HFO)

Hydrous ferric oxides  $\text{FeO}(\text{OH})\cdot\text{H}_2\text{O}$  are referred to in the field as limonite but are comprised of cryptocrystalline goethite or lepidocrocite that have been hydrated due to rapid changes in redox or pH conditions (Cornell and Schwertmann, 2003; Schwertmann and Cornell, 2000; Deer et al., 1962). They are fine grained or colloidal with a large surface area for adsorption. Welch et al. (2000) states that hydrous ferric [iron] oxides are the most common source of pervasive As concentrations exceeding  $10\text{ }\mu\text{g/L}$  because they are capable of releasing As when they react with organic carbon or within alkaline aquifer environments. Multiple studies have discovered the affinity of As with [iron oxides] hydrous ferric oxides (HFO) because As<sup>3+</sup> substitutes for Fe<sup>3+</sup> (Appelo et al., 2002; Bowell, 1994; Jain and Loeppert, 2000; Manning et al., 1998). The As is either sorbed to the hydrous ferric [iron] oxide or coprecipitated with the crystalline structure where the As<sup>3+</sup> substitutes for Fe<sup>3+</sup>. The greatest amounts of As (up to  $7.6 \times 10^4\text{ mg/kg}$ ) associated with HFO's were found when they formed as an oxidation product of a primary Fe sulfide mineral, such as pyrite, and then coat these minerals (Pichler et al., 1999).

#### 2.5.2 Antimony

As was previously stated, there has been limited research on the geochemical behavior of antimony (Sb). Natural waters have less than  $1\text{ }\mu\text{g/L}$  Sb unless there is an anthropogenic cause, sulfide ores, or geothermal waters (Filella et al., 2002a). None of these conditions exist for the APF so the presence of high Sb concentrations is unlikely; however, there are significant sources of S. Antimony is a chalcophile element.

Antimony III ( $\text{Sb}^{3+}$ ) compounds are soluble in alkaline sulfide waters. The behavior of

Sb in the natural environment with S can be seen in Figure 3. The  $\text{Sb}^{3+}$  exists as  $\text{SbO}^+$  in acidic conditions and  $\text{Sb}(\text{OH})_4^-$  or is hydrated as  $\text{SbO}_2^-$  in basic conditions (Schuhmann, 1924). The hydrolysis of  $\text{Sb}^{5+}$  has not been well studied and is thought to be immobile in oxidizing conditions (Lefebvre and Maria, 1963; Brookins, 1986; Brookins, 1988). The  $\text{Sb}^{3+}$  is common in reducing conditions, and  $\text{Sb}^{5+}$  is found in oxidizing environments, although appreciable amounts of each species are found in both environments (Filella et al., 2002a). However, thermodynamic calculations do not favor this. The  $\text{Sb}^{5+}$  is also different from  $\text{As}^{5+}$  because it is theorized to be octahedrally coordinated with oxygen instead of tetrahedrally (Pauling, 1933). The  $\text{Sb}^{3+}$  forms neutral species  $[\text{Sb}(\text{OH})_3]$  and  $\text{Sb}^{5+}$  negative species  $[\text{Sb}(\text{OH})_6^-]$  in solutions within the pH range of natural waters (Filella et al., 2002b). Antimony tends to form insoluble minerals which is why studies of it in the natural environment are limited.

#### 2.5.2.a Sulfide Minerals such as Pyrite

Antimony (III) is capable of forming antimonites rendering it soluble in alkaline sulfide solutions (Filella et al., 2002b). In S rich conditions within anoxic environments, Sb forms a soluble  $\text{SbS}_2^{2-}$ . It can also be found in trace amounts in pyrite (Arthur et al., 2007). The abundance of S in the APF may allow for the formation of species containing the anion  $\text{H}_2\text{SbO}_3^-$ , antimonites.

#### 2.5.2.b Organic Matter and Clays

Studies involving the adsorption of Sb to natural organic material are particularly limited. One study by Pilarski et al. (1995) found that adsorption of  $\text{Sb}^{3+}$  either did not change or decreased when pH was changed from 3.1 to 5.4. The adsorption of  $\text{Sb}^{5+}$  was

found to not occur above 10  $\mu\text{mol/L}$  (Pilarski et al., 1995). Studies examining Sb adsorption by natural organic material within a pH range of 7 to 11 indicate a weak but stable  $\text{Sb}^{5+}$  humate (Bowen et al., 1979). Literature about the adsorption of Sb to clays was not found.

#### 2.5.2.c Hydrous Ferric Oxides (HFO)

Antimony can be removed from solution by adsorption onto manganese and hydrous ferric [iron] oxides (Andreae and Froelich, 1984; Cutter et al., 1991; Spencer et al., 1972; Takayanagi and Cossa, 1997). The  $\text{Sb}^{5+}$  is adsorbed to hematite in acidic conditions (pH 2.5-4.7) and adsorption steadily decreases as pH increases. Small amounts of hematite are sometimes incorporated into HFO's (Deer et al., 1962). Ions adsorbed in a pH range of 2-5 were not desorbed with an increase in pH after 5 days (Ambe et al., 1986). According to Filella et al. (2002) the majority of Sb is bound to immobile compounds in soil and sediment. It may still be possible for ASR operations to cause the release of Sb adsorbed to certain hydrous ferric oxides.

## CHAPTER THREE

### METHODS

#### 3.1 Sampling

Lithologic logs for 20 wells were examined to determine the length of core available for the Avon Park Formation (APF). After examination, 14 wells from within the Southwest Florida Water Management District (SWFWD) were selected for sampling. The length of core available determined the interval at which each core was sampled. Cores over 500 ft long were sampled at 40-50 ft intervals while shorter cores were sampled every 10 to 30 ft. The goal was to have about 10 samples that represent interval (I) samples to provide an unbiased general chemistry for each core. Targeted (T) samples were also taken to determine a potential source of trace metals and permeable (P) samples were taken because these are areas where aquifer storage and recovery (ASR) operations will potentially be conducted. The samples from the fourteen cores, DV-1, ROMP 22, ROMP 20, TRSA-1, TR4-1, TR9-2, ROMP 5, ROMP 9, ROMP 13, ROMP 14, ROMP 25, ROMP 28, ROMP 39, and ROMP 49, were obtained from the Florida Geologic Survey in Tallahassee.

Upon return to the University of South Florida (USF), the cores were examined under a SZ-PT Olympus stereomicroscope with a Fostec<sup>R</sup> 150 watt tungsten halogen light source. The general lithology was described along with porosity and any interesting features that may potentially contain arsenic (As) or antimony (Sb). These features

include but are not limited to molds, dissolution fractures, pyrite, clay, and organic matter and represent T samples. The molds and fractures are places where oxidized waters can flow, altering the geochemical conditions and potentially releasing As or Sb sorbed in or on pyrite, clay, or organic matter. High permeability and higher porosity zones were also examined and recorded as P samples (Table 2). Lithologic descriptions were compared with those conducted on the same core by David Budd (2001, 2002). In total there were 373 samples; 163 interval samples and 209 target, 26 of which were specifically selected from high permeability zones. There were also 35 samples from I and T areas that were within permeable zones. This data was included with the original 26 permeable samples in the P group.

Table 2. Zones of porosity and permeability for the Avon Park listed by SWFWMD. Colors were used to more easily distinguish between the different levels of porosity.

| ROMP Number | ROMP Name        | USGS Well ID | Depth of Porosity zones (ft)                                                                                                                                               | Zones of Permeability                                                                                       |
|-------------|------------------|--------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|
| TR SA-1     | Payne Terminal   | 17452        | 25% 1015.1-1016.2 40% 1010.1-1010.6                                                                                                                                        | None listed                                                                                                 |
| TR 4-1      | Casperson Beach  | 17488        | 25% 1087-1090 30% 1069.4-1072; 1077-1087 35% 1090-1093.5; 1096.2-1098 1102-1109.5                                                                                          | 1090-1093.5; 1096.2-1098; 1102-1109.5 possibly high                                                         |
| TR 9-2      | Apollo Beach     | 16618        | Not measured                                                                                                                                                               | 713.7-726; 794.2-795.6; 868-869.5; 945-953; 1000-1090                                                       |
| DV-1        | Dover Elementary | 16576        | 15% 760-762.8; 824-832 20% 736-737; 759-760; 762.8-763.3; 832-834 25% 557-563; 601-604.5; 608-614; 620-629 30% 604.5-608; 638-653 35% 527-555; 658-573; 580-590; 719-719.6 | 527-555; 557-563; 580-590; 604.5-608; 620-629; 638-653; 719-719.6; 736-737; 759-763.3; 824-834              |
| 5           | Cecil Webb       | 16913        | 10% 1360-1407; 1467-1527; 1537-1580 15% 1086-1095.1; 1437-1467                                                                                                             | 1086-1095.1; 1360-1407; 1437-1527; 1537-1580                                                                |
| 9           | North Port       | 17056        | 20% 1066-1089.7; 1155-1158.3; 1164.7-1173.5 25% 1041-1053; 1054.8-1066; 1092.3-1101                                                                                        | 1041-1053.3; 1054.8-1089.7; 1092.3-1101; 1155-1158.3; 1164.7-1173.5 possibly high intergranular moldic      |
| 13          | Tippen Bay       | 17392        | 22% 1077.5-1081; 1091-1092.5; 1295-1304.1; 1312-1315.2; 1512-1514.3 25% 1132.5-1143.5                                                                                      | None listed                                                                                                 |
| 14          | Hicoria          | 17001        | 10% 1019-1024; 15% 1024-1042; 1049-1066; 1187.5-1188; 1219.4-1223; 1232.8-1235; 1248.5-1249; 1254-1259; 1260.5-1279 20% 1218-1219.4; 1225-1228; 1259-1260.5                | 1019-1042; 1049-1066; 1187.5-1188; 1218-1223; 1225-1228; 1232.8-1235; 1248.5-1249; 1254-1279; possibly high |
| 20          | Osprey           | 17087        | 25% 1254-1255 30% 1431-1439                                                                                                                                                | 1431-1439; 1450-1480 possibly high                                                                          |

| Table 2 Continued. |           |              |                                                                                                                                                                                                                                                               |                                                                                                                                                          |
|--------------------|-----------|--------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|
| ROMP Number        | ROMP Name | USGS Well ID | Depth of Porosity zones (ft)                                                                                                                                                                                                                                  | Zones of Permeability                                                                                                                                    |
| 22                 | Utopia    | 16783        | Not measured                                                                                                                                                                                                                                                  | 1030.9-1056.3; 1064-1114.2; 1280-1380; 1403-1445; 1495-1535; 1650-1670; 1705-1709; 1716-1724 possibly high                                               |
| 25                 | Lily      | 17608        | 25% 981.4-988 26% 1042.5-1048 30% 988-992; 1218-1228 35% 1228-1344                                                                                                                                                                                            | 1218-1228; 1228-1421 possibly high                                                                                                                       |
| 28                 | Kuhlman   | 17000        | 25% 1125.5-1127.5; 1225.5-1299.1; 1264.5-1269.5 30% 864-872; 891-896; 1289-1295; 1299.5-1304.5; 1785-1805; 1905.5-1906; 1919-1920; 1970-1980; 1990-2000; 2010-2015 40% 1908-1910                                                                              | 2010-2015 possibly high                                                                                                                                  |
| 39                 | Oak Knoll | 16740        | 15% 990.4-991.8; 1025-1035; 1045-1055; 1115-1125; 1185-1195; 1222.7-1302; 1383-1390; 1490-1500; 1530-1550; 1570-1580 20% 1008.5-1013.5; 1085-1110; 1135-1145; 1460-1470; 1590-1600 25% 1035-1045; 1065-1075 30% 1060-1065; 1125-1135; 1580-1590 35% 1110-1115 | 990.4-991.8; 1008.5-1013.5; 1025-1055; 1060-1075; 1085-1145; 1185-1195; 1222.7-1302; 1383-1390; 1460-1470; 1490-1500; 1530-1550; 1570-1600 possibly high |
| 49                 | Balm Park | 16456        | Low or not measured                                                                                                                                                                                                                                           | 901-904, 909-910, 925-930; 1063-1065, 1085-1105, 1120-1135 possibly high                                                                                 |

### 3.2 Analytical Preparations

A representative sample from each of the core samples was selected for chemical analysis. All of the samples were powdered by hand with an agate mortar and pestle that was cleaned with pure quartz sand and rinsed with distilled water between samples to prevent cross contamination. An electronic scale was used to weigh out  $0.5 \pm .005$  grams of powdered sample into vials for digestion. Duplicate samples were randomly selected for approximately 10% of the samples and had a reproducibility of  $\geq 95\%$  on the ICP-OES and  $\geq 90\%$  on the HG-AFS. Aqua regia (10 mL), a 3:1 mixture of HCl and HNO<sub>3</sub> was used to digest the samples. For each digestion batch, 54 samples, 2 internal standards (homogenous local limestone), 1 external standard (JLS-1), 2 spiked samples, and a blank were included for quality control. The internal and external standards were unable to be used for quality control because the As concentrations in them were below

our lowest standard. Blanks however did not contain detectable concentrations of As or Sb. The spiked samples were selected from each batch and spiked with 25 mg/kg As before digestion returning results with less than 11% error. The total number of samples analyzed was 469.

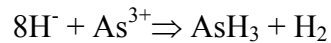
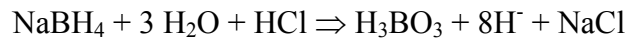
The samples were capped with a ribbed plastic watch glass to prevent the escape of arsine gas and placed on a hot block for 30 minutes at 80°C. The glasses were then removed and the condensation rinsed from each lid with DI. Once cooled the digestates were diluted to 50 mL with DI water and allowed to settle for at least 24 hours before being passed through a 2.0 µm Teflon filter to remove undigested material.

### 3.3 Chemical Analyses

Two mL of the filtered samples were diluted with 8 mL of DI water into 15 mL conical tubes in preparation for analysis with an auto-sampler on the Perkin Elmer Optima 2000 DV inductively coupled plasma – optical emission spectrometer (ICP-OES) at USF calibrated for Al, Si, Fe, Mg, Ca, P, Sr, S, Mo, and Mn. Detection limits are as follows in µg/L: 0.9 Al, 4.0 Si, 0.2 Fe, 0.1 Mg, 0.02 Ca, 30 P, 0.06 Sr, 30.0 S, 2.0 Mo, and 0.03 Mn. The digested acid blanks were either zero or below detection limits for all analytes.

The samples were then prepared for As and Sb totals analyses using hydride generation-atomic fluorescence spectrometry (HG-AFS) on a PSA 10.055 Millennium Excalibur instrument at USF with detection limits of 5.0 -10.0 ng/L. A calibrated pipette was used to add 10 mL of digested sample to a new Teflon vial. Trace metal grade HCl (15 mL) was then added along with DI water to ~ 40 mL to prevent a reaction between the HCl and 1 mL of KI that was then added to reduce all of the arsenic to As<sup>+3</sup>. Each

aliquot was completed to 50 mL with DI water, and then capped and inverted a few times to mix the solution. A reductant of sodium tetraborohydride ( $\text{NaBH}_4$ ) was used to form an arsenic hydride ( $\text{AsH}_3$ ) gas. The following reactions occur between the sodium borohydride, hydrochloric acid, and sample:



Argon gas is used as a carrier for the arsenic hydride and excess hydrogen. It brings them into the reaction vessel with a diffusion flame where they become atomized and detected via atomic fluorescence spectrometry. The calibration curves for all AFS analyses had a  $R^2$  value of .995 or greater. None of the digested acid blanks contained detectable levels of As or Sb. The prepared aliquots were measured within 24 hours of preparation.

### 3.4 Mineralogic Analyses

Samples containing pyrite and other visible targeted features were selected for detailed inspection on a Hitachi 3500 scanning electron microscope (SEM) with energy dispersive spectrometry (EDS) at the USF's St. Petersburg campus. Thin sections were made with blue dye impregnation by Texas Petrographic Services Inc. from a variety of samples with high and low bulk As and Sb concentrations and targeted features. The 31 thin sections were analyzed with a Nikon Eclipse LV100 POL petrographic microscope to determine the presence and mineral associations of pyrite. The individual pyrites were then analyzed at the USGS headquarters in Reston, Virginia for As, Mo, Ca, Zn, Fe, S, and Sb with a JEOL JXA-8900R five spectrometer, fully automated electron microprobe (EPMA) with wavelength-dispersive X-ray spectrometry (WDS). Celestine was also examined for the previously listed elements along with Sr and Ba. Elemental maps were

produced to show the concentrations of Sr, S, Fe, As, Ca, Mg, K, Si, and Al within and around pyrites. The operating conditions consisted of using an accelerating voltage of 20.0 keV, 30 nA probe current, counting times on peaks of 20 to 60 seconds, and a focused spot size of 1  $\mu\text{m}$  for sulfides and a 10  $\mu\text{m}$  defocused for celestine.

Reflected light microscopy, back-scattered electron imaging, and energy dispersive spectroscopy (EDS) were used to determine analytical points. Reference materials consisted of natural and synthetic sulfide, sulfate, silicate, and oxide. Calcium was analyzed as an excitation-volume monitor during sulfide analysis as some samples were small, irregular, and thin. The analyses were corrected for electron beam and matrix effects, and instrumental drift and dead time using a Phi-Rho-Z algorithm supplied with the JEOL WDS electron microprobe (Armstrong, 1995). Relative accuracy of the analyses, based upon comparison between measured and published compositions of standard reference materials, is ~1-2 % for concentrations >1 wt. % and ~5-10% for concentrations <1 wt.%. Analyzed elements and oxides and their detection limits (wt.%) at 3 sigma (background) are as follows: Sb (0.02), As (0.05), Fe (0.03), S (0.03), Zn (0.07), Mo (0.08), FeO (0.05), SrO (0.09), MnO (0.04), BaO (0.04), CaO (0.04), As<sub>2</sub>O<sub>5</sub> (0.09), MgO (0.03), SO<sub>4</sub> (0.08).

## CHAPTER FOUR

### RESULTS

#### 4.1 Lithology and Hydrogeology

##### 4.1.1 Stereo and Petrographic Microscopy

After the petrographic examination of samples it was discovered that the Avon Park Formation (APF) within the study area contains pure limestones in the upper portion that with depth become increasingly dolomitized and interbedded with dolomite. Complete lithologic descriptions for each sample are listed in Appendix 1. Lithologically the limestones are secondary spar ranging from mudstone to packstone. The packstones typically consist of peloidal limestone with high porosity. Significant amounts of organic laminations are found throughout the limestone along with molds and casts of small mollusks, foraminifera, and echinoderms (Figure 7). Dolomite occurs as either highly sucrosic or semi to non-sucrosic with increasing depth. The sucrosic dolomites contain pure recrystallized sucrosic calcite crystals inside the molds. With increasing depth, gypsum is incorporated into the molds and grain spaces of the dolomite. An evaporite zone exists in Romp 39 at about 1680 feet. Small celestine crystals are found in the dolomites and some partially dolomitized limestones. Porosity is granular, moldic, or not visible. Pyrite is found in small peppered clusters on the limestones, with organic laminations, and in dolomite molds with trace HFOs (Figure 8). These HFO's may be due to exposure to moist air while in storage.

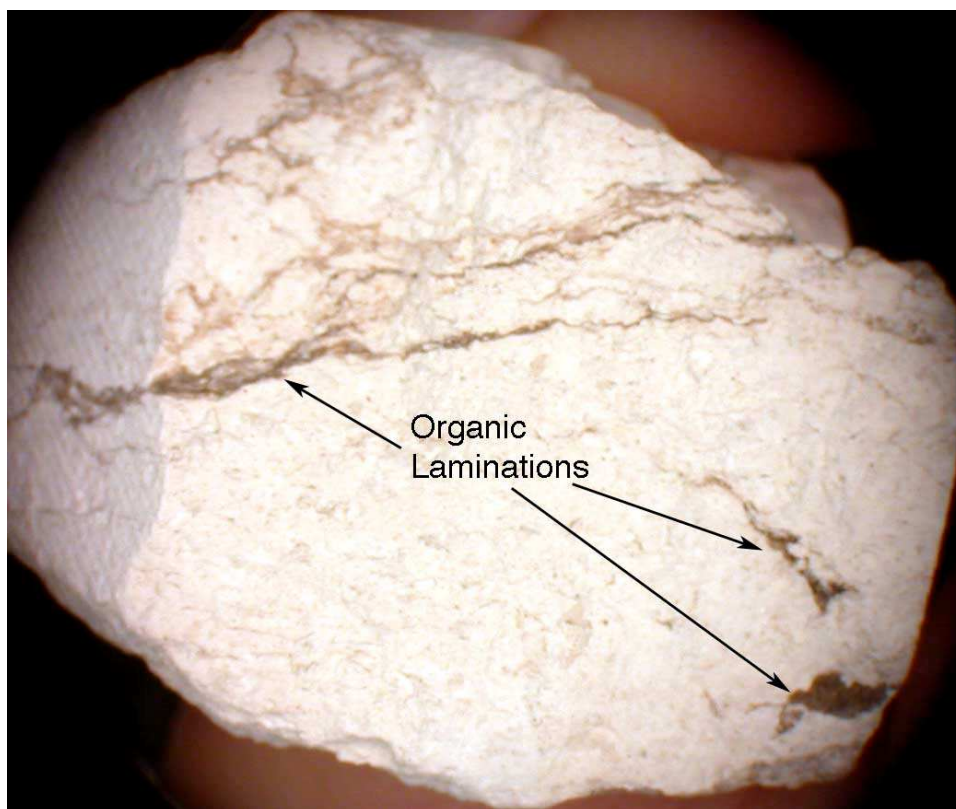


Figure 7. Sample DV-1 630 with organic laminations.

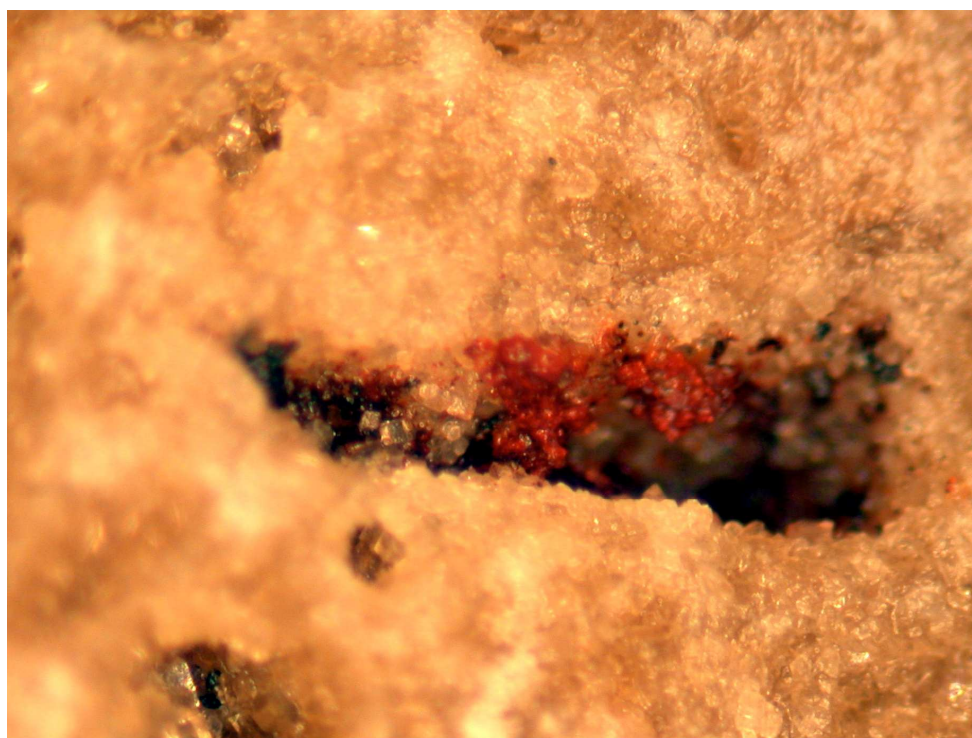


Figure 8. Sample TR4-1 1079 with pyrite and HFO in a sucrosic dolomite mold.

Examination of thin sections under a polarizing microscope revealed the presence of pyrites, gypsum, celestine, calcite, and dolomite. The matrix is fine grained and the limestones have significant biogenic molds and casts (Figures 9-10).

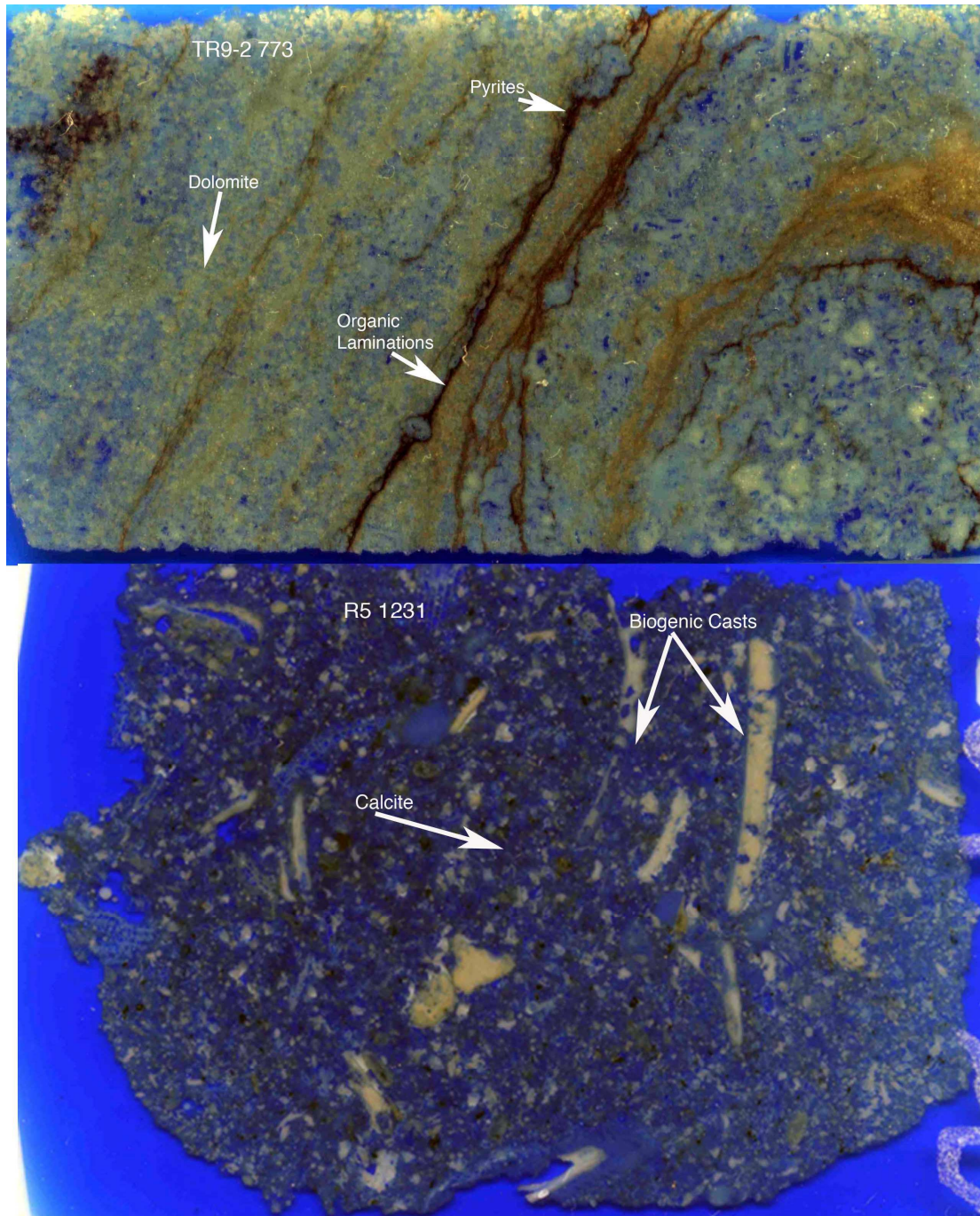


Figure 9. Thin section images from TR9-2 773 and R5 1231 revealing the various minerals and lithologic characteristics found.

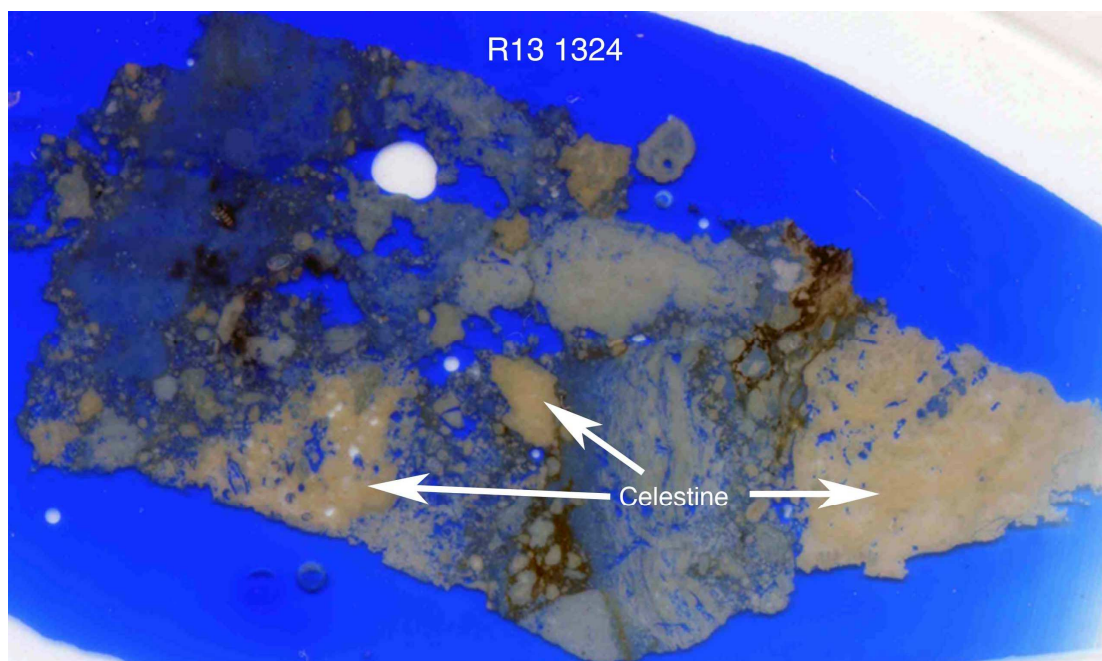


Figure 10. Thin section from R13 1324 showing a large amount of celestine.

#### 4.1.2 Scanning Electron Microscopy (SEM)

During the lithologic examination samples containing pyrite, HFOs, organic laminations, or unidentifiable minerals were selected for analysis using a SEM with EDS capabilities in back-scattered electron (BSE) mode for the presence of arsenic (As) and antimony (Sb) bearing minerals. The porous and uneven nature of the samples made it difficult to obtain proper EDS readings. Thin sections were made of the samples to obtain better EDS readings and identify unknown minerals or confirm the presence of various minerals along with their morphology. The sensitivity of the EDS was too low to detect the presence of As or Sb. Calcite exists as fine micrite, casts, and recrystallized spar within mold or grain spaces. Dolomite is either fine grained or rhombic (sucrosic). Small celestine ( $\text{SrSO}_4$ ) grains are scattered throughout some of the samples. The presence of euhedral, framboidal, biogenic, honeycomb, irregular, and other pyrites was noted (Figure 11). The pyrites are located in the matrix, biogenic molds or casts, or

within fine grained oxidized organic laminations. They sometimes occur in clusters or as individual grains. Their nature and presence are ubiquitous throughout all the samples. Several samples contain hydrous ferric oxides on their exterior within molds and are associated with pyrite.

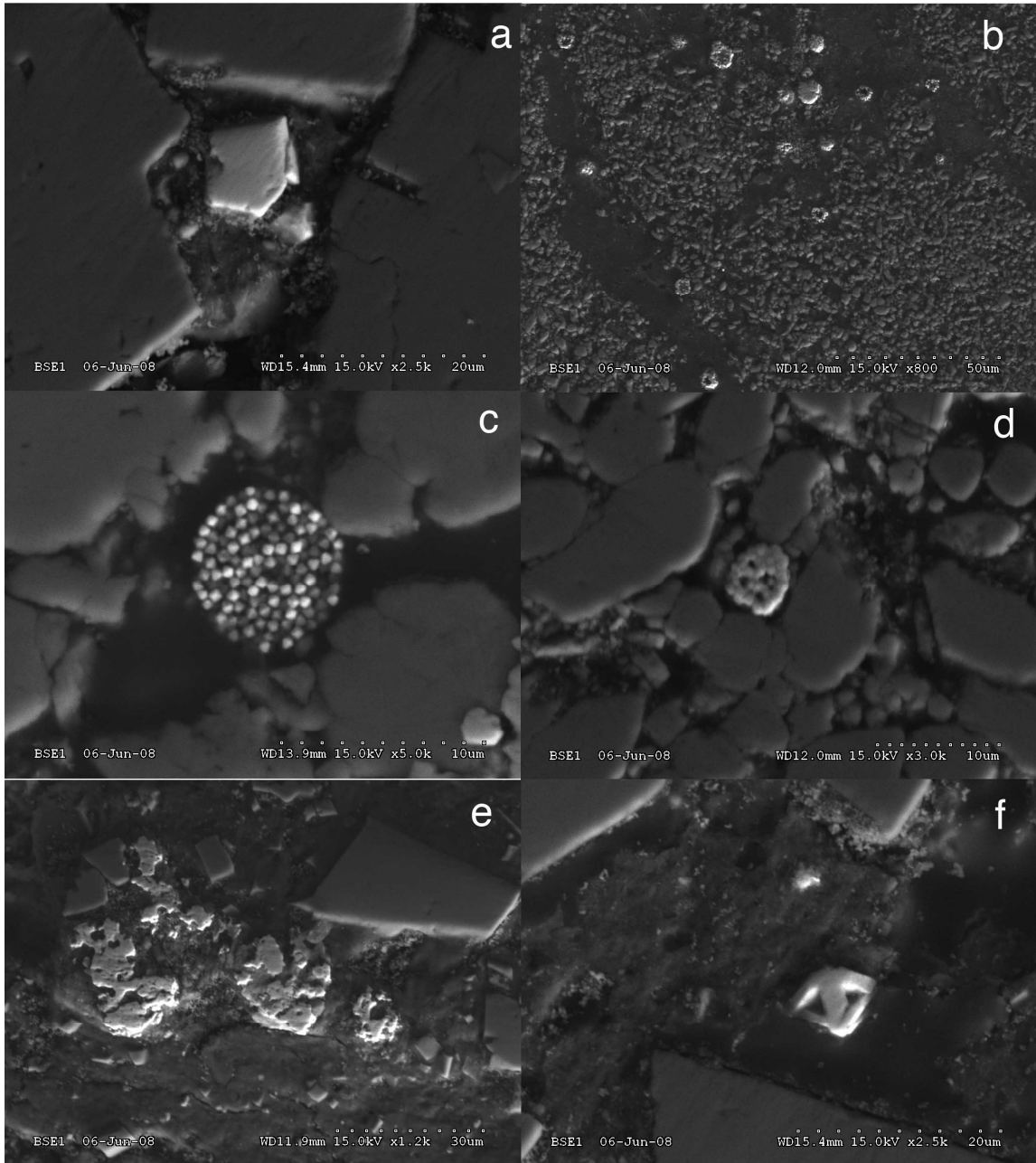


Figure 11. BSE images of the various pyrite morphologies. (a) euhedral; (b) biogenic; (c) framboid; (d) honeycomb; (e) irregular; (f) other.

#### 4.1.3 Hydrogeology

Different studies have described high permeability zones within the Avon Park Formation (APF) and consider it to be one of three most productive units within the Floridan Aquifer System (FAS) (Miller, 1986; Ryder, 1985; Wolansky et al., 1980). The highly permeable “Boulder Zone” facies, that is discontinuously found throughout peninsular Florida, was reported in the APF in Charlotte County, the southern most part of the Southwest Florida water Management District (SWFWMD) (Maliva et al., 2001). The southern two-thirds of SWFWMD contain fractured well-indurated dolostones with large dissolution channels. This high permeability zone is about 30.5m below the top of the APF in the central part of SWFWMD and about 122 m below the APF top in the southern part of SWFWMD (Wolansky et al., 1980). The lithologic examinations revealed that there are indeed sufficiently permeable regions within the APF to support aquifer storage and recovery (ASR). The zones defined with high permeability and porosity by the lithologic logs are confirmed in this study. Regions with high porosity and permeability are the most appropriate for ASR (Table 2). These zones were typically found in the sucrosic dolomites. The presence of various sulfur bearing minerals such as pyrite, celestine, and pore infilling gypsum along with organic layers create problems for conducting ASR in the Avon Park.

#### 4.2 Bulk Analysis

Arsenic and antimony values were analyzed via HG-AFS for 367 samples. The As values range from < 0.01 mg/kg to 30.8 mg/kg with a 2.24 mg/kg mean ( $\mu$ ) and a standard deviation ( $\sigma$ ) of 4.19 mg/kg. The Sb values are < 0.01 mg/kg to 6.76 mg/kg

with a ( $\mu$ ) of 0.28 mg/kg and a ( $\sigma$ ) of .644 mg/kg. The statistical breakdown of the bulk analysis can be seen in Table 3. The means are slightly elevated due to the targeted samples; the permeable and interval samples have low means. The As interval samples range from < 0.01 mg/kg to 21.4 mg/kg with a  $\mu$  of 1.32 mg/kg and a  $\sigma$  of 2.46 while Sb was < 0.01 mg/kg to 4.83 mg/kg with a  $\mu$  of 0.185 mg/kg and a  $\sigma$  of 0.473 mg/kg. The As permeable samples range from < 0.01 mg/kg to 5.04 mg/kg with a  $\mu$  of 1.02 mg/kg and a  $\sigma$  of 1.16 mg/kg, and Sb is < 0.01 mg/kg to 1.68 mg/kg with a  $\mu$  of 0.145 mg/kg and a  $\sigma$  of 0.263 mg/kg. The As targeted samples have a range of .05 mg/kg to 30.8 mg/kg with a  $\mu$  of 3.16 mg/kg and a  $\sigma$  of 5.31 mg/kg, and Sb is < 0.01 mg/kg to 6.76 mg/kg with a  $\mu$  of 0.365 mg/kg and a  $\sigma$  of 0.779 mg/kg.

Bulk elemental analysis conducted on the ICP-OES for calcium (Ca), magnesium (Mg), aluminum (Al), sulfur (S), silica (Si), manganese (Mn), phosphorus (P), iron (Fe), strontium (Sr), and molybdenum (Mo) confirmed lithologic observations and provided new information (Table 4). Calcium is the most abundant element and only decreases when Mg is elevated, which occurs in the dolomites. The dolomites and calcites identified in hand samples matched the chemical data. Aluminum and Si are present in small quantities but increase in the fine-grained “muddy” samples confirming clay in the samples. Manganese is only found in trace amounts and P is also limited. There is a significant presence of S relative to Fe indicating that there is more S in the samples than can be attributed to just pyrite. Strontium levels are also elevated compared to the average for carbonates.

Table 3. The totals for As and Sb from HG-AFS analysis within individual ROMP cores.

| ROMP ID       | As (mg/kg) |      |      |          | Sb (mg/kg) |      |      |          |
|---------------|------------|------|------|----------|------------|------|------|----------|
|               | $\mu$      | Min  | Max  | $\sigma$ | $\mu$      | Min  | Max  | $\sigma$ |
| <i>DV-1</i>   | 1.68       | 0.00 | 7.45 | 1.88     | 0.13       | 0.00 | 1.02 | 0.211    |
| <i>R13</i>    | 2.67       | 0.06 | 22.9 | 4.73     | 0.39       | 0.00 | 2.54 | 0.568    |
| <i>R14</i>    | 0.84       | 0.04 | 4.21 | 0.87     | 0.09       | 0.00 | 0.48 | 0.109    |
| <i>R20</i>    | 3.37       | 0.05 | 27.5 | 5.75     | 0.52       | 0.00 | 4.83 | 1.12     |
| <i>R22</i>    | 3.05       | 0.07 | 18.4 | 4.95     | 0.37       | 0.00 | 2.66 | 0.649    |
| <i>R25</i>    | 3.05       | 0.04 | 30.8 | 7.00     | 0.25       | 0.00 | 1.12 | 0.335    |
| <i>R28</i>    | 3.49       | 0.00 | 20.5 | 5.60     | 0.41       | 0.00 | 3.75 | 0.786    |
| <i>R39</i>    | 3.34       | 0.00 | 30.4 | 7.41     | 0.63       | 0.00 | 6.76 | 1.63     |
| <i>R49</i>    | 0.66       | 0.00 | 3.11 | 0.74     | 0.08       | 0.00 | 0.43 | 0.115    |
| <i>R5</i>     | 3.16       | 0.24 | 20.7 | 4.80     | 0.20       | 0.02 | 0.66 | 0.157    |
| <i>R9</i>     | 1.47       | 0.32 | 7.67 | 1.54     | 0.11       | 0.00 | 0.41 | 0.083    |
| <i>TR4-1</i>  | 1.30       | 0.44 | 2.15 | 0.52     | 0.12       | 0.03 | 0.25 | 0.052    |
| <i>TR9-2</i>  | 1.35       | 0.00 | 11.0 | 2.28     | 0.27       | 0.00 | 2.10 | 0.541    |
| <i>TRSA-1</i> | 1.36       | 0.03 | 5.04 | 1.36     | 0.19       | 0.00 | 1.68 | 0.32     |

Table 4. Averages from the ICP-OES analysis by core with the standard deviation, average, maximum, and minimum.

| ROMP ID       | Ca (g/kg) |     |     |          | Mg (g/kg) |      |      |          | Al (mg/kg) |      |       |          |
|---------------|-----------|-----|-----|----------|-----------|------|------|----------|------------|------|-------|----------|
|               | $\mu$     | Min | Max | $\sigma$ | $\mu$     | Min  | Max  | $\sigma$ | $\mu$      | Min  | Max   | $\sigma$ |
| <i>DV-1</i>   | 294       | 204 | 382 | 71.6     | 52.8      | 4.47 | 120  | 52.7     | 133        | 0.0  | 1588  | 308      |
| <i>R13</i>    | 335       | 147 | 388 | 52.9     | 8.75      | 2.28 | 44.1 | 7.94     | 67.3       | 0.0  | 740   | 139      |
| <i>R14</i>    | 333       | 230 | 391 | 32.1     | 16.0      | 3.03 | 108  | 24.1     | 123        | 0.0  | 1700  | 339      |
| <i>R20</i>    | 346       | 211 | 421 | 40.1     | 12.4      | 3.48 | 108  | 24.8     | 64.8       | 0.0  | 661   | 138      |
| <i>R22</i>    | 306       | 197 | 436 | 64.7     | 36.7      | 4.12 | 111  | 38.6     | 183        | 0.0  | 1712  | 330      |
| <i>R25</i>    | 312       | 142 | 402 | 63.2     | 29.3      | 4.98 | 97.6 | 30.7     | 207        | 0.0  | 3045  | 692      |
| <i>R28</i>    | 330       | 222 | 378 | 41.6     | 18.0      | 2.99 | 102  | 30.0     | 144        | 0.0  | 1015  | 275      |
| <i>R39</i>    | 224       | 174 | 353 | 49.1     | 85.3      | 4.15 | 110  | 40.3     | 81.8       | 0.0  | 426   | 128      |
| <i>R49</i>    | 217       | 206 | 228 | 6.4      | 109       | 103  | 116  | 3.19     | 97.6       | 0.0  | 517   | 108      |
| <i>R5</i>     | 285       | 74  | 370 | 94.9     | 35.8      | 3.86 | 108  | 41.3     | 1393       | 0.0  | 15248 | 3510     |
| <i>R9</i>     | 220       | 172 | 305 | 22.9     | 103       | 57.1 | 113  | 15.6     | 284        | 0.0  | 1044  | 237      |
| <i>TR4-1</i>  | 216       | 207 | 222 | 4.6      | 109       | 103  | 113  | 2.51     | 263        | 97.7 | 584   | 110      |
| <i>TR9-2</i>  | 250       | 207 | 357 | 48.4     | 84.4      | 4.82 | 113  | 35.5     | 31.7       | 0.0  | 162   | 40       |
| <i>TRSA-1</i> | 310       | 213 | 418 | 52.9     | 45.0      | 3.84 | 113  | 38.9     | 100        | 0.0  | 567   | 148      |

Table 4 Continued.

| <i>ROMP ID</i> | S (mg/kg) |      |        |          |  | S corrected (mg/kg) |      |        |          |  | pyrite S (mg/kg) |      |      |          |
|----------------|-----------|------|--------|----------|--|---------------------|------|--------|----------|--|------------------|------|------|----------|
|                | $\mu$     | Min  | Max    | $\sigma$ |  | $\mu$               | Min  | Max    | $\sigma$ |  | $\mu$            | Min  | Max  | $\sigma$ |
| <i>DV-1</i>    | 1134      | 556  | 2076   | 362      |  | 1109                | 518  | 2076   | 363      |  | 174              | 16.2 | 1283 | 238      |
| <i>R13</i>     | 3553      | 748  | 17066  | 4945     |  | 2529                | 227  | 11229  | 2994     |  | 221              | 16.9 | 911  | 213      |
| <i>R14</i>     | 1189      | 577  | 2439   | 405      |  | 1112                | 558  | 2241   | 372      |  | 235              | 29.5 | 1439 | 314      |
| <i>R20</i>     | 1494      | 520  | 2454   | 513      |  | 1436                | 520  | 2297   | 458      |  | 244              | 30.6 | 803  | 202      |
| <i>R22</i>     | 2549      | 506  | 17294  | 3290     |  | 2060                | 506  | 11582  | 2101     |  | 495              | 40.6 | 2691 | 710      |
| <i>R25</i>     | 1427      | 539  | 7483   | 1519     |  | 1394                | 517  | 7238   | 1467     |  | 507              | 40.9 | 5588 | 1248     |
| <i>R28</i>     | 1557      | 626  | 5421   | 1048     |  | 1479                | 607  | 5194   | 1022     |  | 535              | 43.6 | 2585 | 719      |
| <i>R39</i>     | 20833     | 692  | 155147 | 42097    |  | 20724               | 692  | 154525 | 41992    |  | 258              | 70.2 | 1312 | 353      |
| <i>R49</i>     | 1005      | 586  | 1563   | 280      |  | 986                 | 586  | 1550   | 288      |  | 166              | 51.2 | 425  | 109      |
| <i>R5</i>      | 1129      | 282  | 7456   | 1433     |  | 1064                | 272  | 6936   | 1334     |  | 693              | 37.0 | 6793 | 1407     |
| <i>R9</i>      | 1545      | 543  | 6509   | 1189     |  | 1503                | 509  | 6403   | 1155     |  | 712              | 95.8 | 4079 | 784      |
| <i>TR4-1</i>   | 1399      | 1003 | 2219   | 315      |  | 1399                | 1003 | 2219   | 314      |  | 656              | 266  | 1174 | 241      |
| <i>TR9-2</i>   | 821       | 438  | 1473   | 202      |  | 820                 | 438  | 1470   | 201      |  | 136              | 37.7 | 410  | 87       |
| <i>TRSA-1</i>  | 1284      | 670  | 2536   | 471      |  | 1257                | 670  | 2444   | 446      |  | 239              | 49.1 | 1327 | 271      |

Table 4 Continued.

| <i>ROMP ID</i> | Si (mg/kg) |       |      |          |  | Mn (mg/kg) |      |      |          |  | P (mg/kg) |      |      |          |
|----------------|------------|-------|------|----------|--|------------|------|------|----------|--|-----------|------|------|----------|
|                | $\mu$      | Min   | Max  | $\sigma$ |  | $\mu$      | Min  | Max  | $\sigma$ |  | $\mu$     | Min  | Max  | $\sigma$ |
| <i>DV-1</i>    | 307        | 28.7  | 1620 | 361      |  | 14.3       | 4.68 | 48.9 | 9.4      |  | 108       | 49.4 | 181  | 51.5     |
| <i>R13</i>     | 253        | 26.5  | 1359 | 270      |  | 0.55       | 0.00 | 8.43 | 2.00     |  | 52.1      | 19.8 | 124  | 29.1     |
| <i>R14</i>     | 331        | 15.6  | 2063 | 440      |  | 1.21       | 0.00 | 19.6 | 4.1      |  | 63.3      | 15.0 | 162  | 38.5     |
| <i>R20</i>     | 215        | 13.8  | 853  | 197      |  | 0.17       | 0.00 | 3.13 | 0.71     |  | 46.7      | 19.3 | 189  | 40.0     |
| <i>R22</i>     | 410        | 33.5  | 1595 | 415      |  | 2.16       | 0.00 | 25.0 | 5.9      |  | 97.1      | 25.5 | 206  | 58.8     |
| <i>R25</i>     | 337        | 62.0  | 2097 | 464      |  | 3.99       | 0.00 | 23.9 | 7.3      |  | 98.4      | 29.8 | 208  | 55.9     |
| <i>R28</i>     | 233        | 21.5  | 779  | 220      |  | 4.65       | 0.00 | 34.0 | 9.0      |  | 91.4      | 31.0 | 431  | 88.1     |
| <i>R39</i>     | 218        | 6.9   | 574  | 155      |  | 1.47       | 0.00 | 5.75 | 1.83     |  | 145       | 22.3 | 195  | 59.6     |
| <i>R49</i>     | 345        | 129.7 | 680  | 157      |  | 20.0       | 0.52 | 37.8 | 10.7     |  | 193       | 170  | 243  | 18.7     |
| <i>R5</i>      | 643        | 39.4  | 2791 | 788      |  | 2.26       | 0.00 | 11.6 | 3.4      |  | 528       | 75.5 | 2712 | 819.0    |
| <i>R9</i>      | 678        | 110.9 | 1370 | 330      |  | 13.9       | 3.39 | 29.1 | 7.9      |  | 257       | 140  | 338  | 55.5     |
| <i>TR4-1</i>   | 697        | 377.0 | 1169 | 216      |  | 15.8       | 9.24 | 27.3 | 6.4      |  | 280       | 225  | 334  | 28.7     |
| <i>TR9-2</i>   | 180        | 32.8  | 414  | 92       |  | 3.62       | 0.00 | 24.3 | 6.0      |  | 144       | 32.6 | 219  | 40.6     |
| <i>TRSA-1</i>  | 332        | 54.4  | 1356 | 319      |  | 1.98       | 0.00 | 19.4 | 4.3      |  | 114       | 32.0 | 240  | 61.1     |

Table 4 Continued.

| <i>ROMP ID</i> | Fe (mg/kg) |       |      |          |  | Sr (mg/kg) |     |       |          |  | Mo (mg/kg) |      |      |          |
|----------------|------------|-------|------|----------|--|------------|-----|-------|----------|--|------------|------|------|----------|
|                | $\mu$      | Min   | Max  | $\sigma$ |  | $\mu$      | Min | Max   | $\sigma$ |  | $\mu$      | Min  | Max  | $\sigma$ |
| <i>DV-1</i>    | 151        | 14.1  | 117  | 207      |  | 346        | 119 | 648   | 148      |  | 8.12       | 0.00 | 38.5 | 8.92     |
| <i>R13</i>     | 194        | 14.7  | 793  | 186      |  | 3132       | 400 | 16090 | 5428     |  | 136        | 1.03 | 3800 | 649      |
| <i>R14</i>     | 205        | 25.7  | 1253 | 273      |  | 544        | 369 | 1117  | 171      |  | 6.64       | 0.00 | 16.9 | 4.71     |
| <i>R20</i>     | 213        | 26.6  | 699  | 176      |  | 493        | 290 | 2057  | 335      |  | 35.8       | 2.38 | 329  | 60.4     |
| <i>R22</i>     | 431        | 35.3  | 2343 | 618      |  | 1641       | 194 | 15799 | 3518     |  | 26.6       | 1.50 | 271  | 49.2     |
| <i>R25</i>     | 442        | 35.7  | 4866 | 1087     |  | 396        | 251 | 810   | 116      |  | 12.7       | 1.50 | 47.5 | 13.9     |
| <i>R28</i>     | 466        | 37.9  | 2251 | 626      |  | 543        | 390 | 939   | 122      |  | 17.1       | 0.00 | 118  | 26.0     |
| <i>R39</i>     | 248        | 11.6  | 1399 | 391      |  | 514        | 149 | 2838  | 721      |  | 25.5       | 0.00 | 179  | 47.3     |
| <i>R49</i>     | 145        | 44.6  | 370  | 94.9     |  | 253        | 189 | 610   | 100      |  | 5.73       | 0.00 | 22.5 | 7.1      |
| <i>R5</i>      | 735        | 32.0  | 6369 | 1433     |  | 462        | 203 | 1496  | 252      |  | 5.80       | 0.00 | 19.2 | 5.57     |
| <i>R9</i>      | 620        | 83.4  | 3552 | 682      |  | 320        | 178 | 1142  | 261      |  | 2.37       | 0.00 | 18.6 | 5.07     |
| <i>TR4-1</i>   | 571        | 231.4 | 1022 | 210      |  | 191        | 168 | 216   | 15.0     |  | 0.48       | 0.00 | 3.5  | 0.919    |
| <i>TR9-2</i>   | 119        | 32.9  | 357  | 76       |  | 234        | 169 | 360   | 53.0     |  | 13.1       | 2.00 | 152  | 27.5     |
| <i>TRSA-1</i>  | 208        | 42.7  | 1156 | 236      |  | 376        | 198 | 781   | 145      |  | 12.7       | 0.00 | 36.2 | 11.4     |

#### 4.3 Arsenic and Antimony with Depth

Arsenic and Sb concentrations were plotted vs. depth to see if specific zones had higher concentrations of trace metals. This revealed nothing of significance other than most areas with high As also contain high Sb (Figures 12 and 13). These are both spatially scattered throughout the study area and not confined to certain depths. The correlations between arsenic and antimony were generally significant and are discussed in section 5.4.

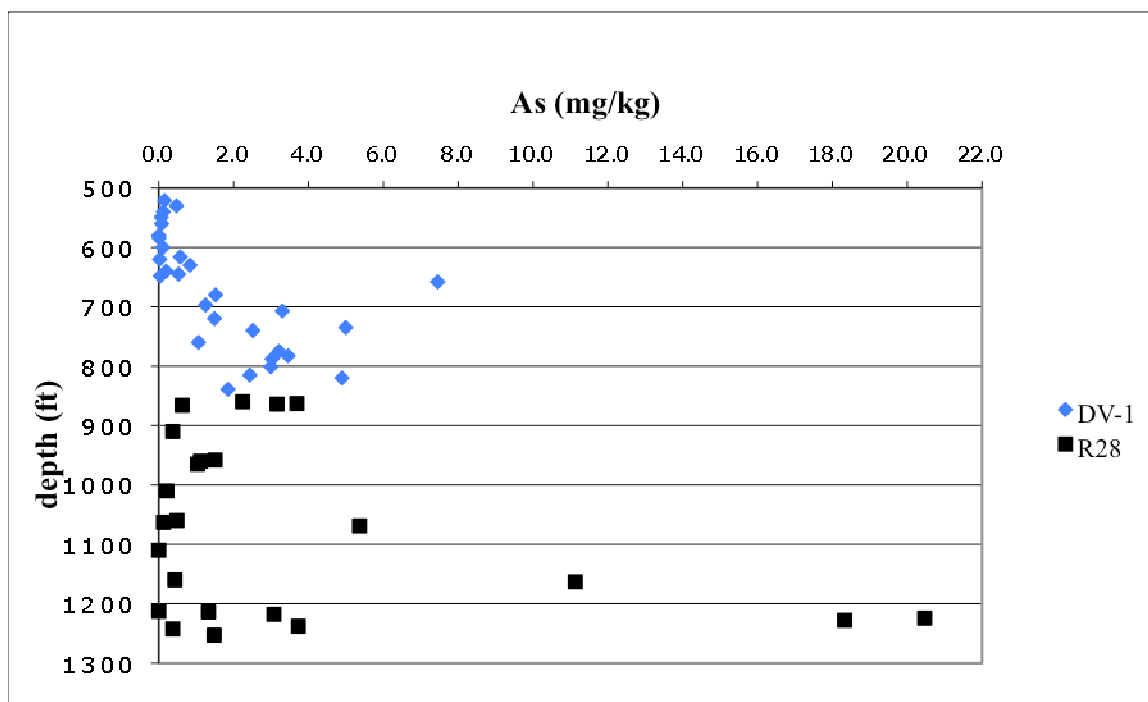


Figure 12. Plot of As with depth from cores DV-1 (grey) and R28 (black). High concentration zones are from T samples but are not confined to a depth spatially over the study area.

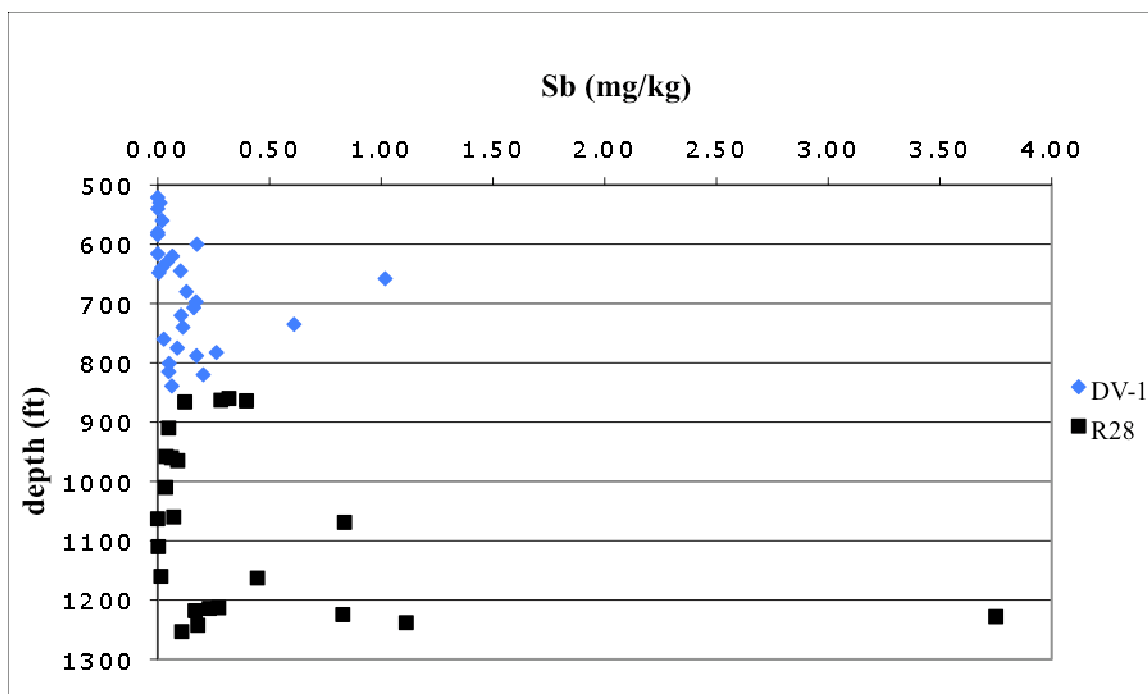


Figure 13. Plot of Sb with depth for cores DV-1 and R28. Again concentrated zones are apparent and occur at the same depths as the arsenic in the T samples.

#### 4.4 Electron Microprobe Analysis (EPMA)

##### 4.4.1 Pyrite

Lithologic descriptions of hand samples and bulk As and Sb data were used to select 31 samples to be made into thin sections. Most of these samples were from the T category and contained pyrite, clay, and or organic laminations. The bulk As and Sb values range from 0.01 to 30.8 mg/kg As with a  $\mu$  of 10.3 mg/kg and 0.0 to 4.8 mg/kg Sb with a  $\mu$  of 1.14 mg/kg. The petrographic and EPMA notes along with the As and Sb data can be seen in Appendix 5. From the initial 31 thin sections, 30 were analyzed with the microprobe. A total of 301 individual pyrites were analyzed for Fe, S, Ca, Sb, As, Zn, and Mo.

Some of the results could only be used for qualitative analysis since the element totals were below 95%. This typically occurred when the pyrites were either too thin or too small to obtain quantitative measurements. The quantitative measurements represent 228 pyrites with As and Sb values ranging from 0.0 to 5820 mg/kg and 0.0 to 2470 mg/kg respectively (Table 5). The average value for As is 945 mg/kg; the other trace metals have rather low averages. The elemental analysis results for the 301 pyrites are listed in Appendix 6 according to qualitative and quantitative values.

Table 5. Quantitative results from the EPMA analysis in mg/kg.

|                    | Sb    | Fe     | S      | Zn     | Ca    | As    | Mo    |
|--------------------|-------|--------|--------|--------|-------|-------|-------|
| Minimum            | 0.00  | 415400 | 472300 | 0.00   | 700.0 | 0.00  | 0.00  |
| Maximum            | 2470  | 480300 | 552700 | 1070   | 43700 | 5820  | 4340  |
| Mean               | 34.87 | 456073 | 514496 | 173.25 | 12179 | 945.4 | 97.15 |
| Standard Deviation | 175.6 | 14264  | 17228  | 205.8  | 7556  | 1026  | 516.4 |

#### 4.4.1.a Morphology

The pyrite morphology was examined to determine if there was a relationship between morphology and trace elements. The morphology is related to the environment of formation and diagenic processes. The pyrites were separated into six different classes (Figure 11). The biogenic class represents the pyrites that are almost framboids but have holes in the center. They look as if they had been precipitated around something such as bacteria. The irregular category consists of pyrites that do not have a distinctive morphology. They look similar to framboids but are elongate or wispy and weathered. The highest As average is found in this morphology but they represent only 6% of samples (Table 6). The euhedral pyrites are the most abundant morphology (44%) but have the second lowest average of As. The framboid category consists of about 17% of the samples even though samples in other studies by Lazareva and Pichler (2007) and Price and Pichler (2006) had abundant framboids. The honeycomb category appears to be incipient framboids. They have holes resembling a honeycomb. The other category consists of samples that did not have their morphology recorded.

Table 6. The mean values from the elemental analysis for the various pyrite morphologies. All values are in mg/kg.

| Class     | % of samples | Sb    | Fe     | S      | Zn     | Ca      | As      | Mo     |
|-----------|--------------|-------|--------|--------|--------|---------|---------|--------|
| Biogenic  | 4%           | 23.33 | 454511 | 512400 | 148.89 | 16285.6 | 212.22  | 0.00   |
| Irregular | 6%           | 5.83  | 448033 | 502917 | 143.33 | 13607.5 | 1570.83 | 23.33  |
| Euhedral  | 44%          | 9.89  | 461235 | 520787 | 174.35 | 10426.6 | 756.85  | 0.00   |
| Framboid  | 17%          | 36.11 | 457050 | 514669 | 138.33 | 12164.2 | 870.28  | 20.28  |
| Honeycomb | 23%          | 29.18 | 448920 | 506939 | 195.31 | 14383.1 | 963.47  | 210.00 |
| Other     | 6%           | 13.33 | 459717 | 511258 | 89.17  | 12515.0 | 1130.83 | 343.33 |

#### 4.4.1.b Maps

An elemental map was made on sample R22 1185 because it contains abundant celestine. Minerals present are celestine, dolomite, framboidal pyrites, and a carbonate rich clay matrix (Figure 14). The As values are rather low and represented in green. Antimony was below detection limits and therefore not mapped. Arsenic is scattered throughout the dolomite and matrix (Figure 15). It appears to be concentrated in the celestine and some of the framboidal pyrites. The elevated levels of As in the celestine may simply be the result of the high atomic weight of the celestine mineral, 167.7 g/mol compared to As, 74.9 g/mol. This effect is also seen when looking at the maps of Sr and S. The high atomic weight of Sr (87.62 g/mol) compared to S (32.07 g/mol) makes it difficult for the detector to measure S in the celestine. The analysis of the celestine was unable to detect As, so it is likely that there is an interference with the Sr causing the celestine to appear to have elevated As.

Two different maps were made from sample R28 1224.5 because it contains abundant pyrite. The first map has calcite grains and some trace feldspar pieces (Figure 16). The irregular pyrites infill different sections of a large calcite grain. It looks like this was once an organism that has experienced calcite replacement. The matrix is a high magnesium calcite. Arsenic can clearly be seen in the pyrites and scattered throughout the rest of the sample (Figure 17). The second image taken from R28 1224.5 consists of calcite grains, in a high magnesium calcite matrix, with some large framboidal pyrites (Figure 18). A couple siliclastic grains exists along with a couple calcite grains enriched with Sr. Once again the As is elevated in the pyrites and scattered throughout the rest of the minerals (Figure 19).

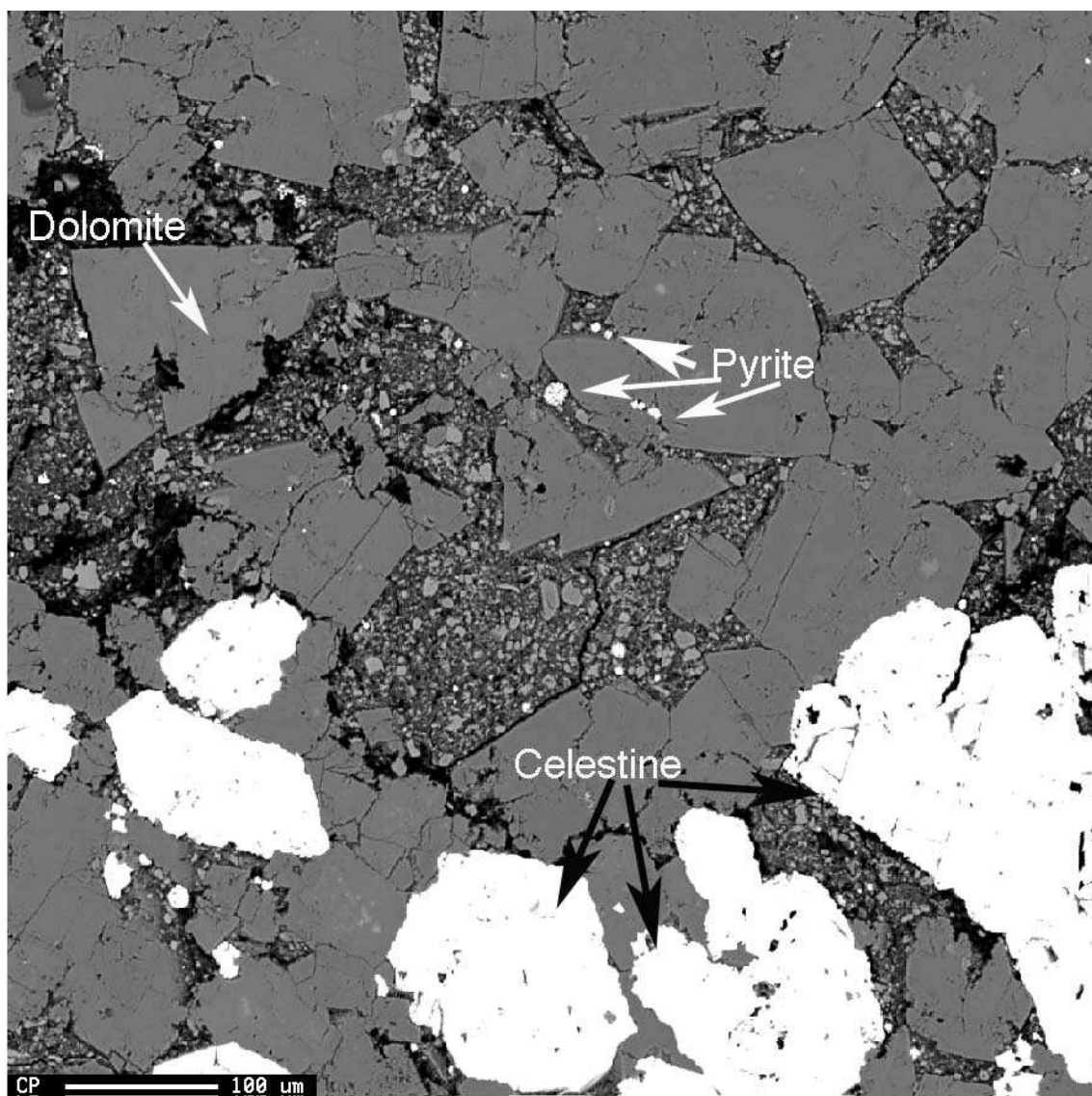


Figure 14. BSE image of sample R22 1185. There are small framboids scattered throughout the matrix material. The large grey grains are dolomite and the large white grains at the bottom of the image are celestine.

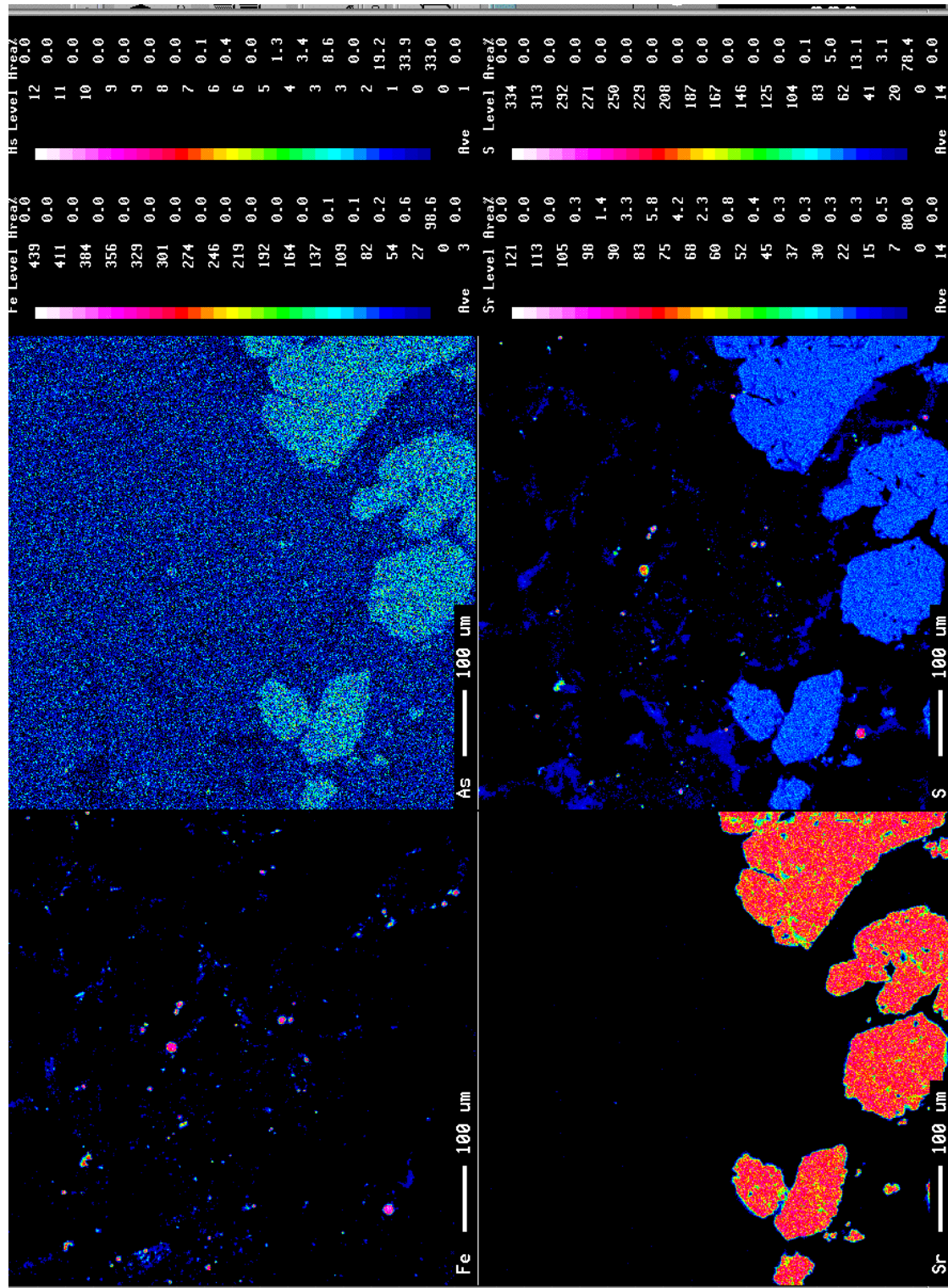


Figure 15. EPMA map of As, Fe, S, and Sr in Sample R22 1185.

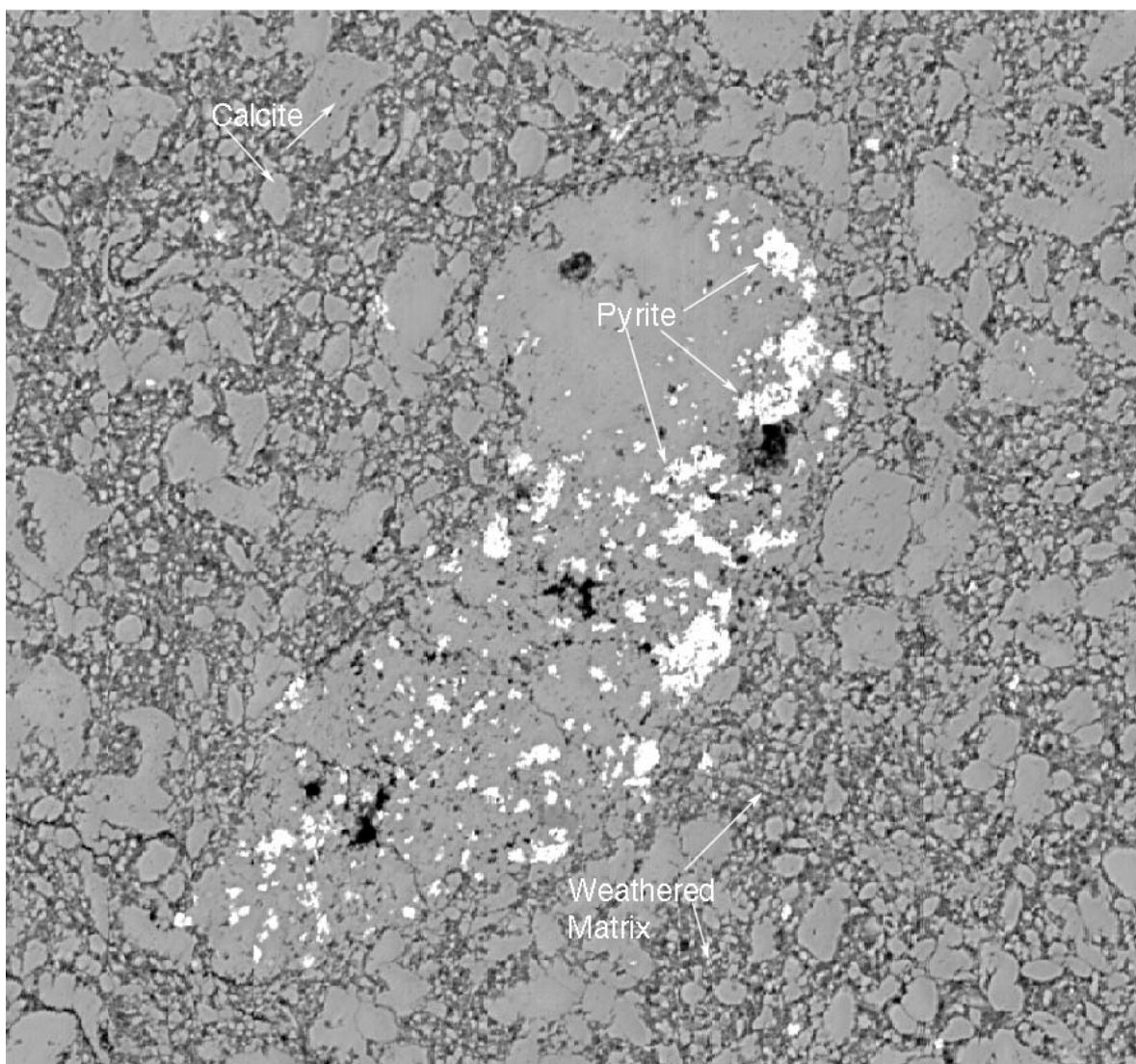


Figure 16. BSE image from sample R28 1224.5. The white areas are pyrite, the visible grey grains are calcite, and the fine-grained areas are weathered carbonate matrix.

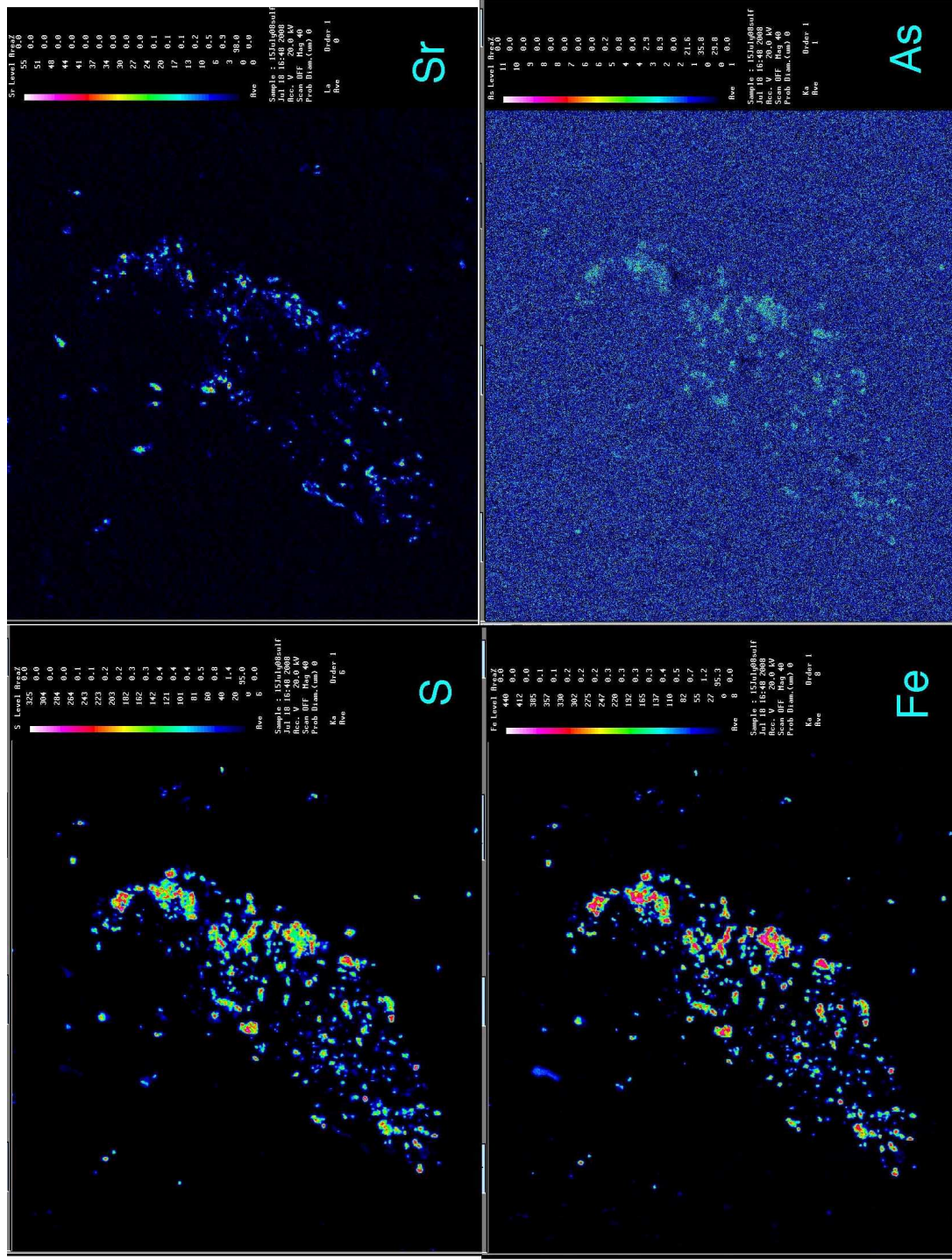


Figure 17. EPMA map of As, Fe, S, and Sr in sample R28 1224.5.

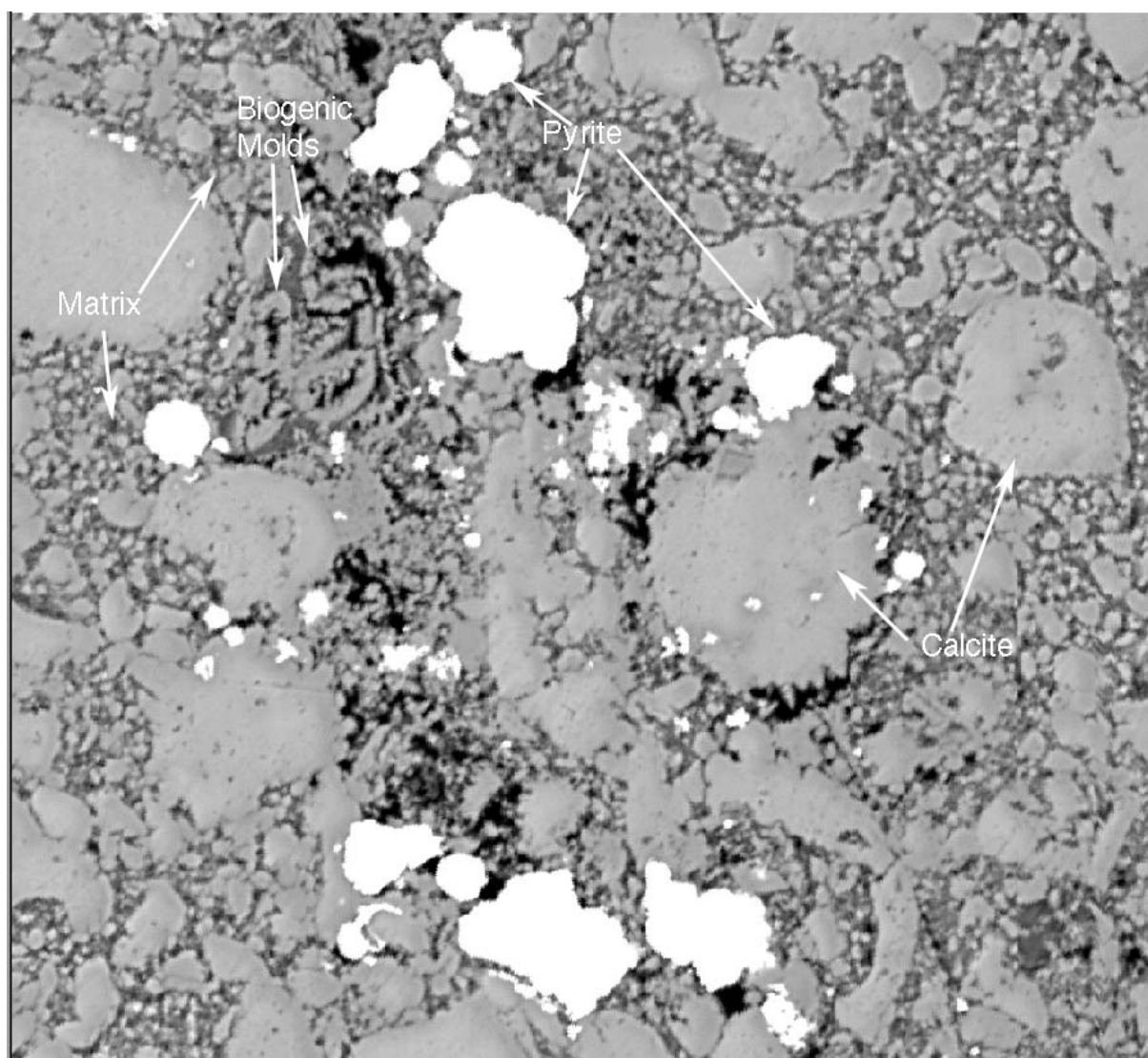
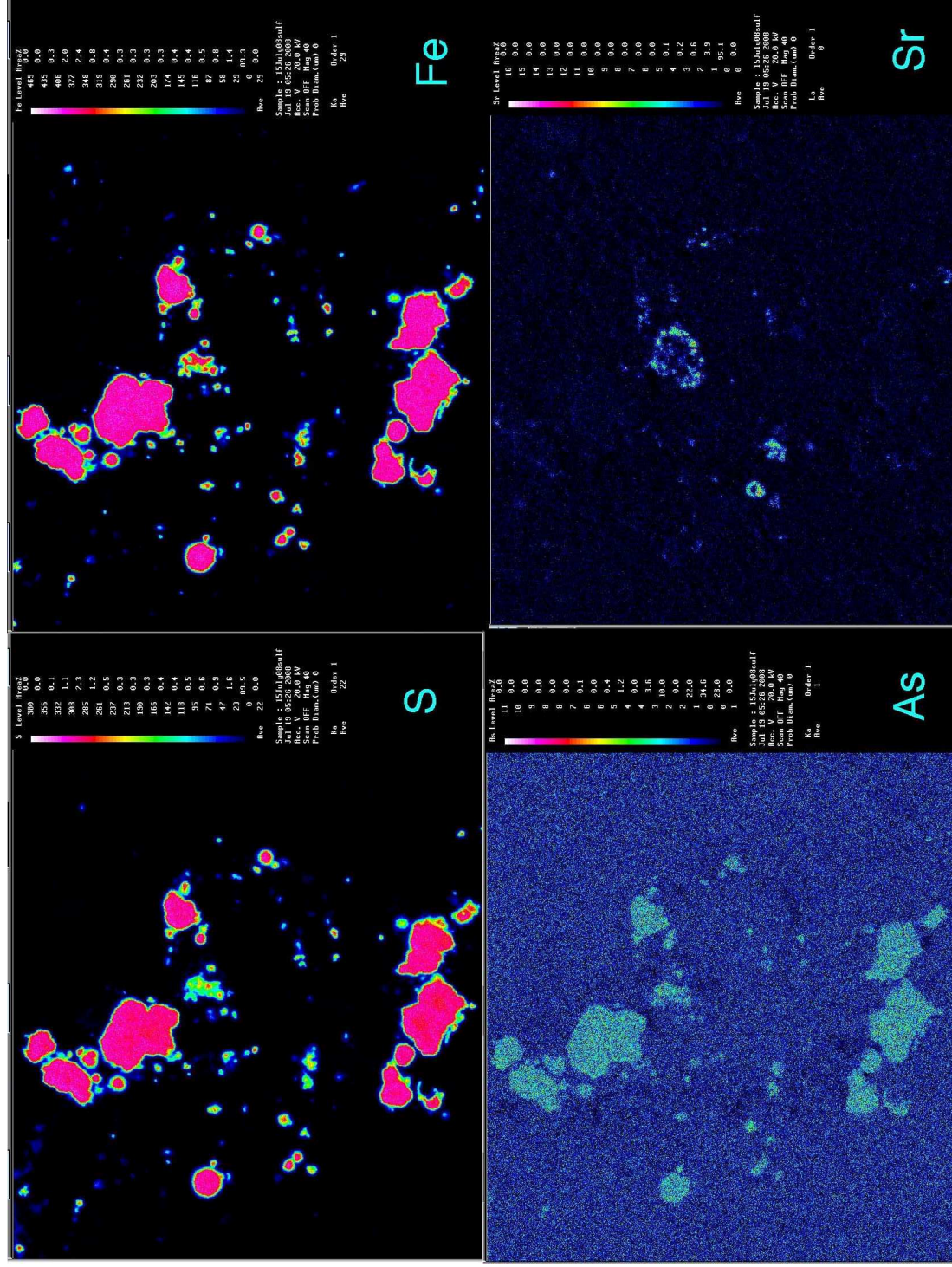


Figure 18. BSE image from sample R28 1224.5b. The white areas are pyrite, light gray is calcite, and the matrix consists of weathered high magnesium calcite.



#### 4.4.2 Comparisons with the Hawthorn Group and Suwannee Limestone

The APF has a significantly smaller range of As values and overall lower average than the those found in the Suwannee and Hawthorn (Table 7). This may be due to the fact that more pyrites were analyzed in the APF samples, and the analysis was not conducted on just the samples with the highest As values as in the Suwannee and Hawthorn. The use of some low bulk As samples lowered the overall average of the APF. However several of the thin sections were from samples with the highest As values. The highest value found in the APF was about half the highest As values in the Suwannee and 0.66 of the highest Hawthorn value.

Table 7. A comparison of the mean, minimum, and maximum values of As between the three geologic units. All values are in mg/kg. <sup>+</sup>(Price and Pichler, 2005); <sup>\*</sup>(Lazareva and Pichler, 2007).

| As                                 | Mean | Max   | Min |
|------------------------------------|------|-------|-----|
| Suwannee <sup>+</sup><br>(n = 25)  | 2300 | 11200 | 100 |
| Hawthorn <sup>*</sup><br>(n = 126) | 1272 | 8260  | <1  |
| Avon Park<br>(n = 228)             | 945  | 5820  | <1  |

#### 4.4.3 Celestine

The low correlations between As and Fe and S along with the somewhat low values of As in pyrites suggests it is likely present in other minerals. Elemental mapping suggests that some As may be found in celestine grains. Ten celestine crystals from sample R22 1185 were analyzed for Sr, Ba, Ca, S, Fe, As, Mg, Mn (Appendix 7). Each celestine crystal had three analytical points for a total of 30 analyses. The Fe, As, Mg, and Mn were all below detection limits. The average, minimum, and maximum values

for Sr, Ba, Ca, and S are listed in Table 8. The celestine crystals typically have barium rich centers.

Table 8. The statistical results from the analysis of 10 different celestine crystals from sample R22 1185. Each crystal was large enough to have 3 different analytical points of measurement.

|      | Sr     | Ba    | Ca   | S      |
|------|--------|-------|------|--------|
| Mean | 570989 | 3658  | 1396 | 428060 |
| Min  | 547866 | 430   | 270  | 415700 |
| Max  | 588357 | 18200 | 6110 | 437100 |

## CHAPTER FIVE

### DISCUSSION

#### 5.1 Statistical Analysis

A statistical program, JMP 7.0 was used to examine whether the data are normally distributed and determine their statistical significance. Histograms and normal quantile plots were used to test for normality. The histograms offer a visual check to determine normality. An actual test is performed with the normal quantile plot function. If the points plot in a straight line or within the dashed lines, the data are considered normal. The formula used for this calculation is  $\Phi^{-1}(r_i/N + 1)$  (Sall and Lehman, 1996). The  $r_i$  is the rank of the observation being analyzed,  $N$  is the number of observations, and  $\Phi^{-1}$  is the function that produces the normal quantile for a probability with the argument  $(r_i/N + 1)$ .

Since the majority of the data are nonparametric, the Van der Waerden test must be used to test for statistical significance. This test can be applied to both parametric and nonparametric data. The Van der Waerden test determines whether the distribution of  $k$  populations is equal. It is a type of analysis of variance (ANOVA) test for determining the significance of independent variables in nonparametric multi-factor models (Conover, 1999). The results from a one-way ANOVA using the Kruskal-Wallis test are converted to normal scores and the Van der Waerden test is then applied. The test is defined as the following:

Let  $n_i$  ( $i = 1, 2, \dots, k$ ) represent the sample sizes for each of the  $k$  groups of data.

Let  $N$  be the sample size for all groups. Let  $X_{ij}$  represent the  $i^{th}$  value in the  $j^{th}$  group where the normal scores are calculated by  $A_{ij} = \phi^{-1}(R(X_{ij})/N + 1)$ . The  $R(X_{ij})$  is the rank of observation while the  $X_{ij}$  and  $\phi$  denote the normal quantile function.

The average and variance of the normal scores are then calculated. Finally the Van der Waerden test can be applied:

$H_0$ : All of the  $k$  population distribution functions are identical

$H_a$ : At least one of the populations tends to yield larger observations than at least one of the other populations

$$T_1 = \frac{1}{s^2} \sum_{i=1}^k n_i \bar{A}_i^2 \quad (\text{Conover, 1999})$$

This test was applied to the bulk data in a fit Y by X analysis in JMP with the analyte as the Y and the sample type as the X. It was also done for the EPMA analysis with the analyte as the Y and the morphology as the X. A Kruskal-Wallis and ANOVA test were also computed to see how the tests compared. If the data are considered statistically significant, the ANOVA tests returns a probability greater than F value close to zero while the Kruskal-Wallis and Van der Waerden calculate a probability greater than chi square value close to zero.

#### 5.1.1 Bulk Statistical Analyses

None of the bulk data analytes are parametric data. The histogram and quantile plot for arsenic (As) can be seen in Figure 20. The Van der Waerden test concludes that all the bulk data and sample type categories are statistically significant (Appendix 2).

The green outlines are calculated with the ANOVA analysis. The farther apart they are

vertically from each category, the more significant the categories. The permeable (P) samples sometimes were similar to the interval (I) samples because several of the samples included in the P group also fell in the I group. This however did not affect the statistical significance of the data.

**As**

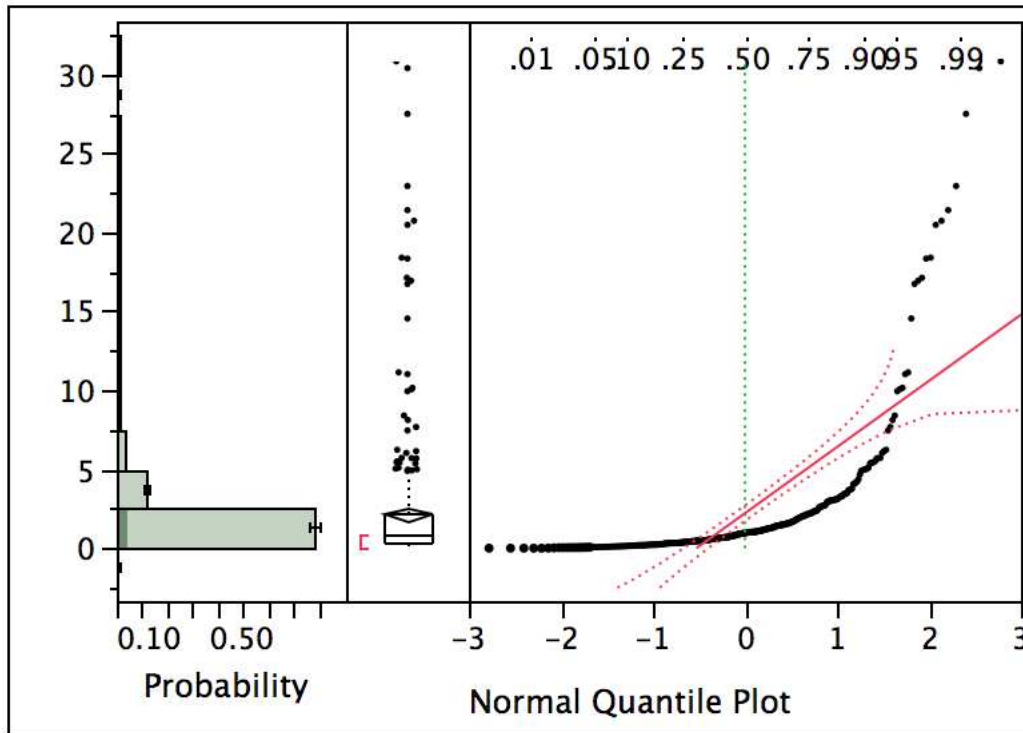


Figure 20. Histogram and normal quantile plot information produced in JMP Statistics 7.0. The non-bell shaped histogram and the nonlinear points outside the red dashed line indicate that the data is nonparametric. The middle image is an outlier box plot. The box represents the interquartile range. Samples plotted individually above the box are past 1.5 interquartile ranges from the quartiles and are considered outliers.

### 5.1.2 EPMA Statistical Analyses

The sulfur (S), iron (Fe), and calcium (Ca) data from the EPMA analysis are normally distributed according to the normal quantile plots while the As, antimony (Sb), molybdenum (Mo), and zinc (Zn) are not (Appendix 2). The Van der Waerden test indicates that the morphological categories and the various analytes are statistically

significant (Appendix 2). The difference between the morphological categories can be seen in Appendix 2 with Fe where the green boxes all plot differently than the rest with the exception of the N/A category.

## 5.2 Bulk Element Corrective Calculations

There is more sulfur (S) in the samples than can be attributed to just pyrite and this would interfere with correlations between iron and sulfur for pyrite. The S data were corrected for the presence of celestine in the samples since it is the only other S-bearing mineral found in abundance, with the exception of gypsum in the deeper cores. Another potential mineral could be strontionite. Strontium (Sr) typically substitutes for calcium (Ca) in calcite and dolomite. Once there is more than 50% Sr versus Ca it becomes strontionite. Only a couple strontionite grains were found in the samples so the Sr instead formed celestine in the abundant sulfur environment. Floridan calcites typically have about 400 mg/kg Sr (Budd, 2008). The percent of calcite for each sample was calculated assuming that a pure calcite contains 400,000 mg/kg Ca. This percent was then multiplied by 400 to determine the mg/kg amount of Sr in the calcite. This amount was subtracted from the total Sr to determine the Sr available to form celestine. Strontium and S were converted to moles and all the Sr was used to form celestine with S. The S used to form celestine was subtracted from the total leaving the rest of the S to form pyrite or other minerals. The correlations were corrected with this adjusted sulfur value and are all presented as simply S to represent the corrected value unless otherwise noted.

Petrographic, SEM, and EPMA analysis did not reveal the presence of any iron (Fe) bearing minerals other than pyrite and trace HFOs. All iron present could then be assumed to form pyrite with sulfur because if Fe and S are present in reducing sediments

they will preferentially form pyrite. A molar comparison between Fe and S was conducted. Pyrite was “made” using all the Fe within each sample using a molar ratio of 2 Fe to 1 S. Some samples still had a significant amount of sulfur left indicating that other sulfur bearing minerals are abundant. Petrographic analysis confirmed the presence of gypsum and celestine.

### 5.3 Correlations

Correlations between Fe and S were made on the corrected data for celestine but were rather low (.2488) unless samples containing visible gypsum were removed (.7026) (Figure 21). Six samples from R13 and two from R22 with significantly high S values compared to Fe and visible celestine and gypsum were removed to obtain this correlation. These eight samples can be seen in the upper left hand corner of Figure 21. This reveals that pyrite is not abundant in these samples. It also shows the interfering effect sulfate minerals have on this correlation. These eight samples were included in the rest of the correlations since pyrite is not the only source of As and Sb. Plotting the samples looking at Fe vs. S along with the pyrite line reveals that there are other sources of S besides pyrite. All 367 samples with the exception of 5 plot above the pyrite line indicating an excess of S relative to Fe (Figure 21). The intercept of the Fe vs. S line confirms that there are other S bearing minerals besides celestine. The interference of other sulfur containing minerals leaves Fe as the best candidate to look at the relationship between pyrite and As and Sb. However, the correlations between Fe and As are still low (Figure 22). The majority of the correlations are statistically significant with directional p values close to zero (Table 9a). Since pyrite was the only iron containing mineral seen in abundance it indicates that there are other sources of As.

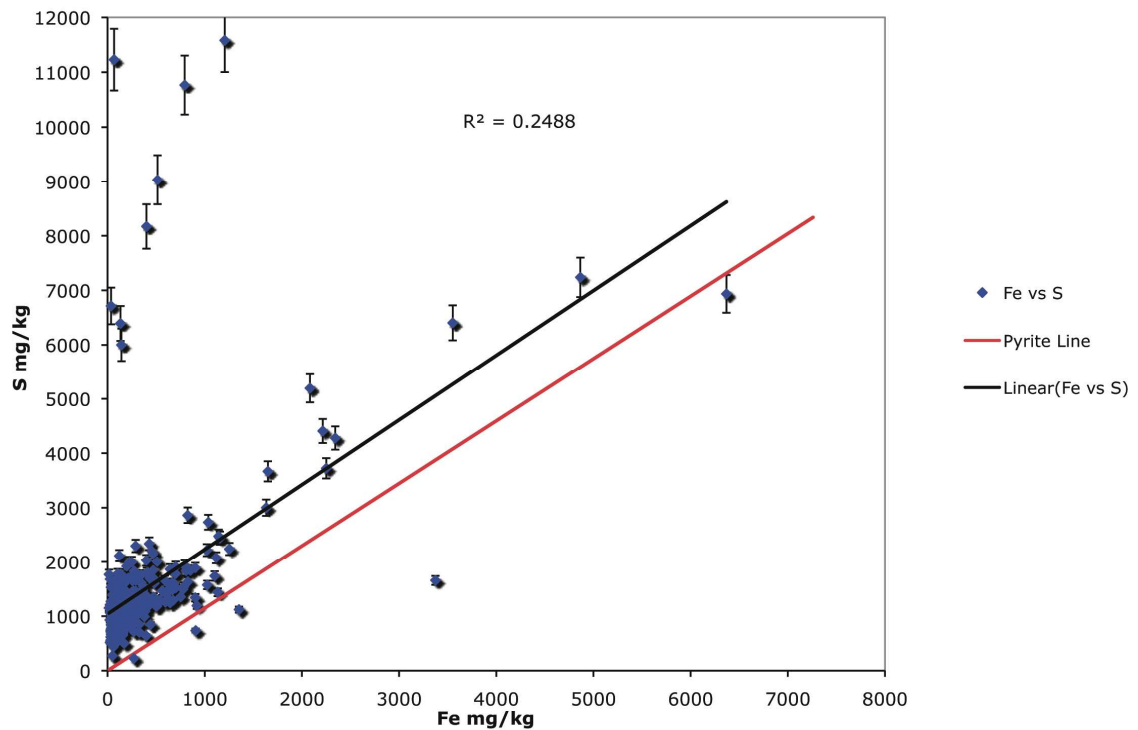


Figure 21. Plot of Fe vs. S with a low correlation value. S was corrected for the presence of celestine. The majority of the samples plot above the pyrite line. Ignoring the samples in the upper left corner gives a correlation of .7026.

Distinct groups can also be delineated and examined within the various correlation plots. There are several samples that plot along the bottom in Figure 22 with high As but low Fe indicating that their source is not from an Fe source. If these are removed, there is a much higher correlation between As and Fe. The samples that are high in As but not Fe have large amounts of organic laminations or clay. The correlations with S and As (.2646) are somewhat similar to the Fe correlations (Figure 23). It is evident that there is an excess of sulfur since the trendline originates at 1000 mg/kg. The samples with high amounts of S and low As contain gypsum or anhydrite. There is a distinct trend of increasing S and As located below the trendline (Figure 23). These are samples with large amounts of pyrite but no organic matter or clays.

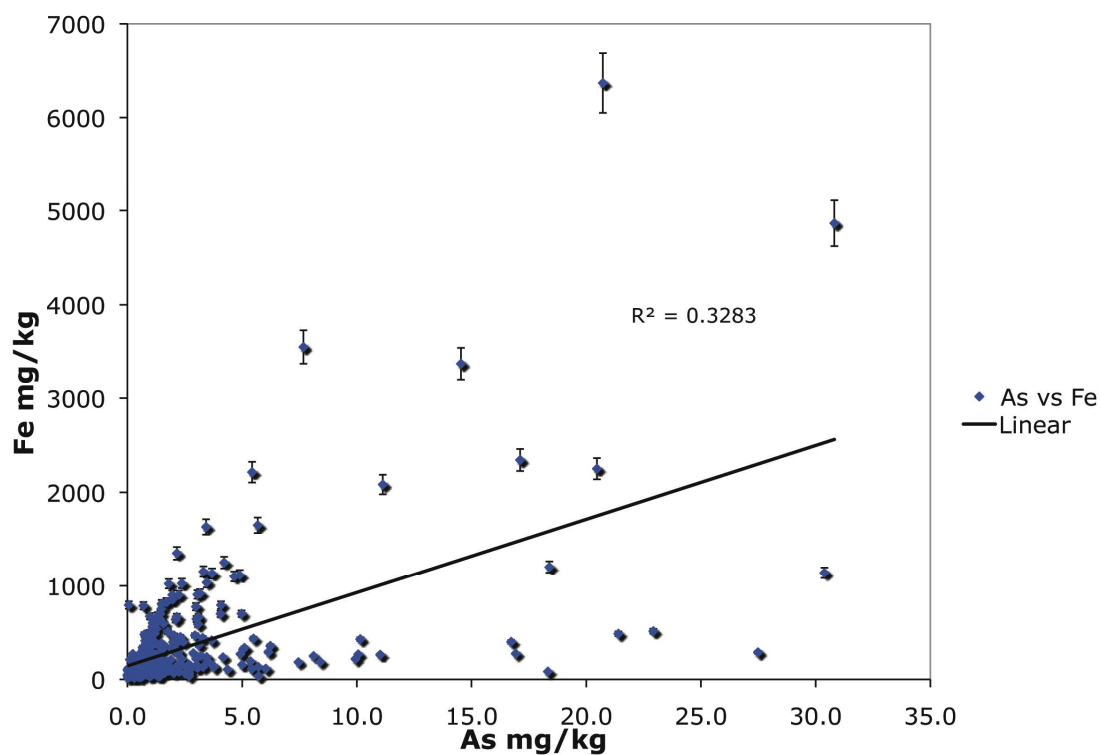


Figure 22. Plot of As vs. Fe for all samples.

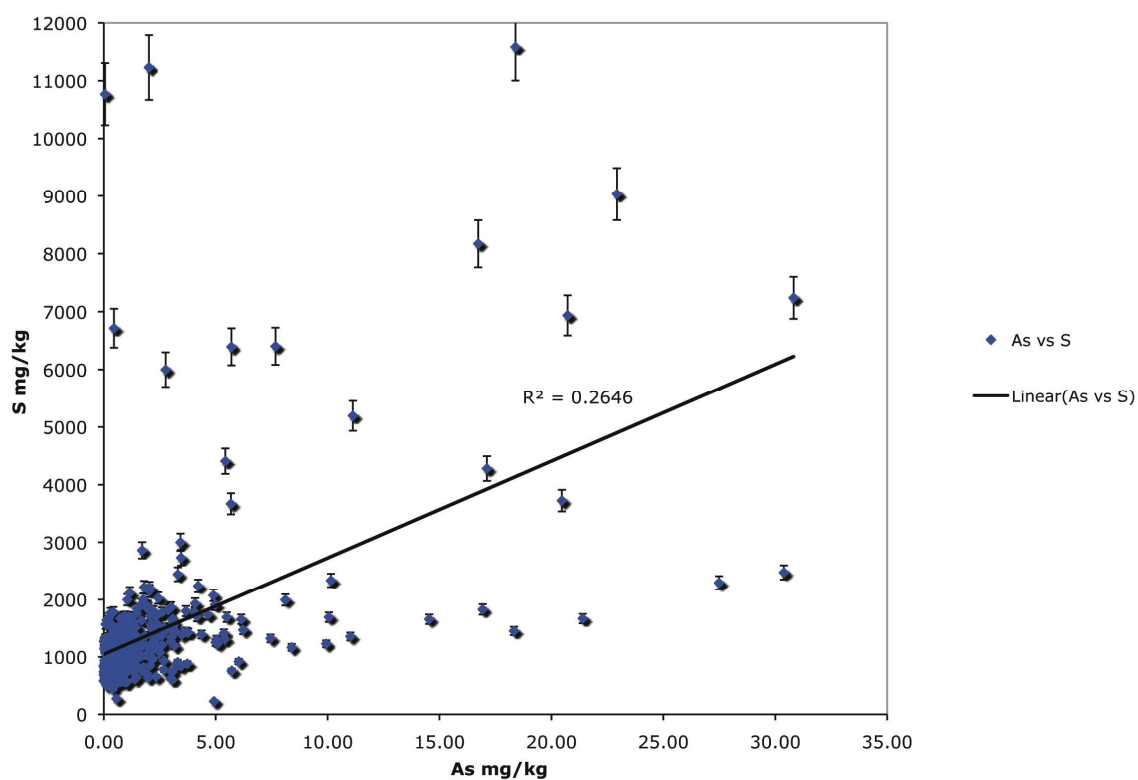


Figure 23. Plot of As vs. S. Sulfur was corrected for the presence of celestine.

Table 9a. The various correlation values calculated for Fe, S, As, and Mo. The directional probability is also listed as the p value.

| Sample Type  | Fe vs. S      | p value          | As vs. Fe     | p value          | As vs. S      | p value          | p value          | As vs. Mo      | p value          | S vs. Mo       | p value          |
|--------------|---------------|------------------|---------------|------------------|---------------|------------------|------------------|----------------|------------------|----------------|------------------|
| Interval     | 0.2521        | 0.0007           | 0.2649        | 0.0004           | 0.2418        | 0.0011           | 0.0004           | 0.8393*        | <.0001           | .1925*         | 0.0077           |
| Permeable    | 0.3596        | 0.0020           | 0.4165        | 0.0004           | 0.2691        | 0.0172           | 0.0002           | 0.3217         | 0.0054           | 0.1034         | 0.2119           |
| Targeted     | 0.2363        | 0.0007           | 0.3241        | <.0001           | 0.3062        | <.0001           | <.0001           | 0.5680         | <.0001           | 0.2125         | 0.002            |
| <b>Total</b> | <b>0.2488</b> | <b>&lt;.0001</b> | <b>0.3283</b> | <b>&lt;.0001</b> | <b>0.2646</b> | <b>&lt;.0001</b> | <b>&lt;.0001</b> | <b>0.6087*</b> | <b>&lt;.0001</b> | <b>0.2305*</b> | <b>&lt;.0001</b> |

\* value not including an outlier

Looking at the correlations between different sample types, there are similar trends with As vs. Fe and S for the interval (I) and targeted (T) samples (Table 9a) (Figures 22-25). The interval group has some samples with low Fe but high As (Figure 24). These again are the samples with organic laminations. The same can be seen in the targeted group (Figure 25). As expected there are more targeted samples with organics than the interval group since the organic samples were specifically targeted. There is also a distinct group in the interval samples that have increasing Fe but relatively unchanged As (Figure 24). Most of these samples interestingly contain hydrous ferric oxides with pyrite. It is possible that the As they once contained was released during core recovery and or storage leaving only the oxidized pyrites behind. The best correlation is with the Fe and As in the permeable samples while the S was a bit lower. The permeable As vs. Fe is not shown but there is a distinct group with high Fe and As and another with low Fe but high As. These samples are those with organics.

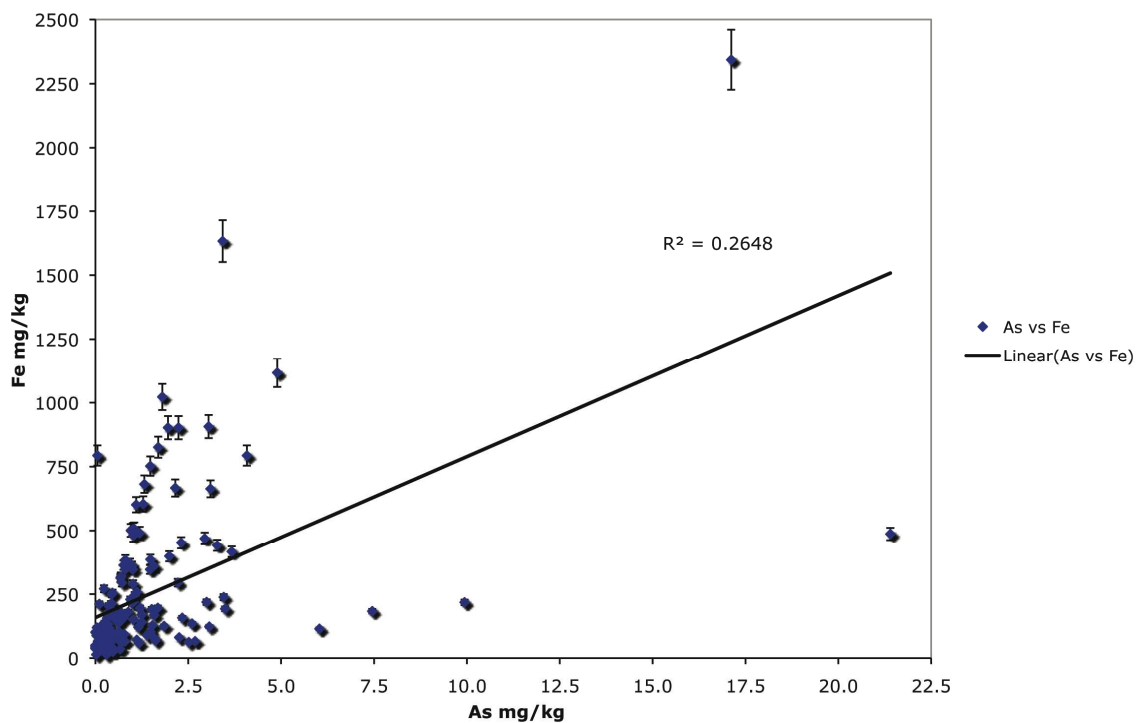


Figure 24. Correlation plot of As vs. Fe for all samples from the Interval group.

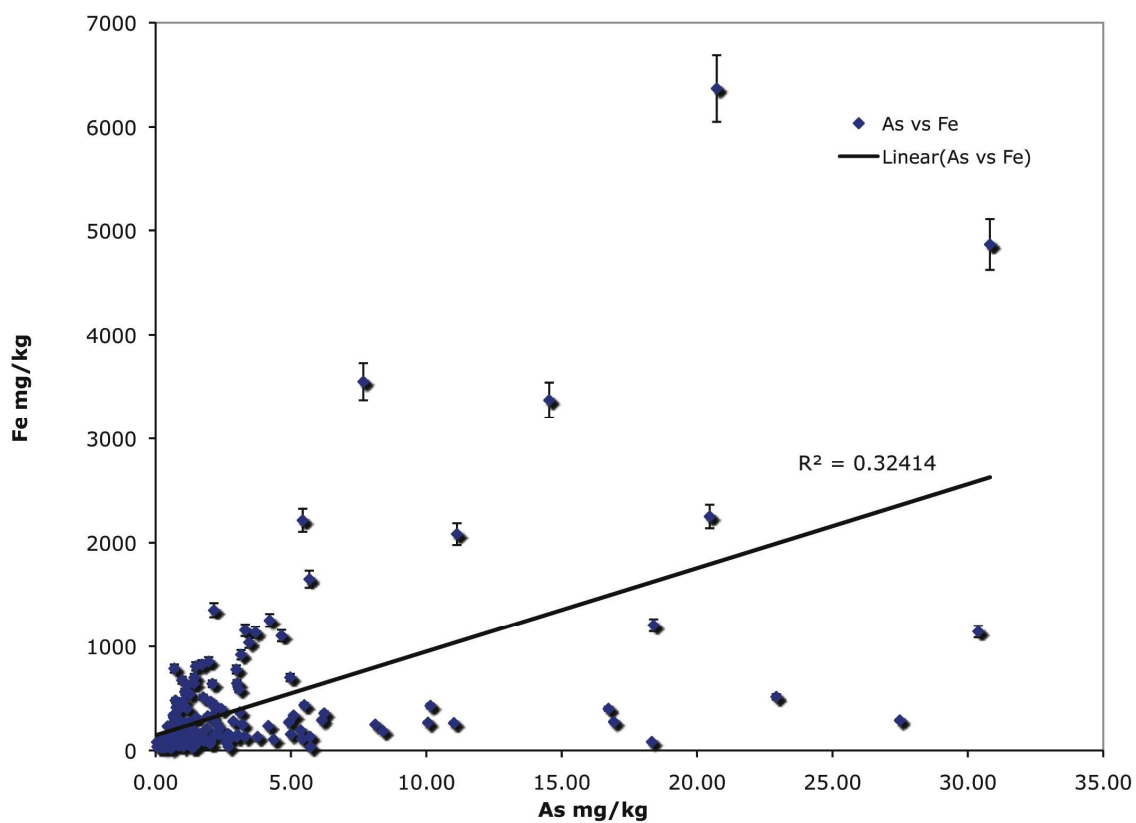


Figure 25. Correlation plot of As vs. Fe for all samples from the Targeted group.

Correlations were also conducted with pyrite S that was calculated from the corrected bulk S values. The values of Fe and S were converted to moles. Pyrite was made with 1 mole of Fe for every 2 moles of S and the values converted back to mg/kg. It was assumed that all the Fe present would form pyrite. The amount of S required to make pyrite was determined with this calculation along with the percent of pyrite, celestine, and remaining S in the sample. All correlation values involving S with Fe or As increase when pyrite S is used (Appendix 3). According to the correlations however, S containing minerals cannot account for the entirety of As (Appendix 3).

The correlations between Sb and S and Fe are insignificant with all correlations falling below .08 (Table 9b). The directional p values also confirm this. Some of the best correlations exist between Sb and As with a value of .6143 (Table 9b) (Figure 26). This is interesting because according to the correlations, As is associated with pyrite while Sb is not. It is likely that they exist together but not in the same minerals or they exist in a mineral that does not contain Fe and S. The correlations between the different sample types are about the same.

Table 9b. The various correlation values calculated for Sb, Fe, S, pyrite S, As, and Mo. The directional p value is also listed confirming or rejecting statistical significance.

| Sample Type  | Sb vs. Fe    | p value       | Sb vs. S     | p value       | Sb vs. As    | p value          | Sb vs. Mo    | p value          |
|--------------|--------------|---------------|--------------|---------------|--------------|------------------|--------------|------------------|
| Interval     | 0.016        | 0.4209        | 0.002        | 0.49          | 0.583        | <.0001           | .547*        | <.0001           |
| Permeable    | 0.025        | 0.4235        | 0.024        | 0.4266        | 0.599        | <.0001           | 0.498        | <.0001           |
| Targeted     | 0.012        | 0.4361        | 0.088        | 0.1187        | 0.625        | <.0001           | 0.668        | <.0001           |
| <b>Total</b> | <b>0.017</b> | <b>0.3727</b> | <b>0.066</b> | <b>0.1036</b> | <b>0.614</b> | <b>&lt;.0001</b> | <b>0.63*</b> | <b>&lt;.0001</b> |

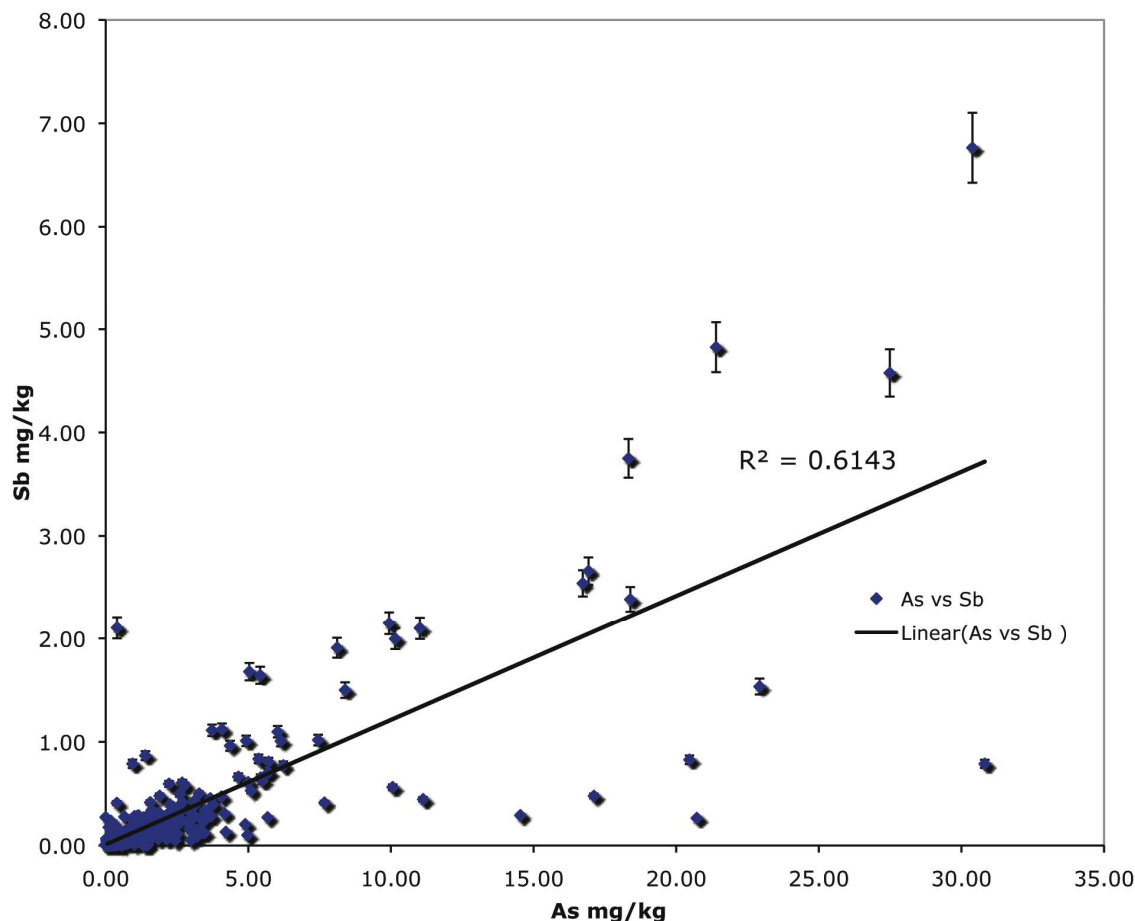


Figure 26. Correlation plot of Sb vs. As for all samples.

Correlations were conducted for various other elements (Appendix 4). Not all correlations are low; individual cores have better correlations (Table 10). There are five cores with correlation values between Fe and S above 0.87 while four have values below 0.5. The correlations between Fe and S corrected for celestine do not significantly change. The four cores, (R25, R39, R5, and R9) have good correlations for Fe vs. S and As vs. Fe and S. Core R9 even has good correlations of Sb with Fe and S. There are 7 cores with correlations above .6 for As vs. Mo and 6 for Sb vs. Mo. The grain type (dolomite or calcite) and size (micrite, sucrosic, packstone) were examined but do not reveal strong trends with the correlation values.

Table 10. A wide range of correlations categorized by cores for various elements. A general lithologic description for each core is also listed. The values in parentheses represent the correlation after an outlier sample was removed.

| ROMP ID | Fe vs. S | Fe Vs S corrected        | As vs. Fe                   | As vs. S                    | Sb vs. Fe                  | Sb vs. S                   | Sb vs. As | As vs. Mo | Sb vs. Mo | Core Description                                                                                                                                               |
|---------|----------|--------------------------|-----------------------------|-----------------------------|----------------------------|----------------------------|-----------|-----------|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| DV-1    | 0.4341   | 0.4651                   | 0.2917<br>(.3424)           | 0.2453                      | 0.0327                     | 0.0415                     | 0.6762    | 0.4169    | 0.4006    | Secondary spar; mudstone to packstone and sucrosic dolomite with gypsum; rest is non sucrosic dolomite                                                         |
| R13     | -0.0586  | 0.1898                   | 0.126                       | 0.2659                      | 0.0672                     | 0.1479                     | 0.716     | .0152*    | .5341*    | Micrite to grainstone with celestine and calcite                                                                                                               |
| R14     | 0.5633   | 0.5618                   | 0.6021                      | 0.5404                      | 0.0084                     | 0.0216                     | 0.202     | 0.1664    | 0.271     | Recrystallized from micrite to grainstone                                                                                                                      |
| R20     | 0.6186   | 0.4575                   | 0.1335                      | 0.2114                      | 0.0851                     | 0.1312                     | 0.9184    | 0.8711    | 0.758     | Spar micrite to wackestone with gypsum<br>Secondary spar ranging from micrite to wackestone with small area of sucrosic dolomite and partial sucrosic dolomite |
| R22     | 0.7174   | 0.88<br>0.9703<br>(.594) | 0.3502<br>0.9355<br>(.1085) | 0.3986<br>0.9066<br>(.0848) | 0.0623<br>.2161<br>(.2996) | 0.2558                     | 0.7088    | 0.7672    | 0.6041    | Recrystallized micrite to grainstone                                                                                                                           |
| R25     | 0.9712   |                          |                             |                             |                            | 0.2226                     | 0.3256    | 0.263     | 0.6201    | Recrystallized micrite to packstone with peloidal grains                                                                                                       |
| R28     | 0.6964   | 0.6986                   | 0.3931                      | 0.4197                      | 0.001<br>0.4448<br>(.1819) | 0.0131<br>.0308<br>(.1275) | 0.5354    | 0.7157    | 0.8201    | Mostly sucrosic to semisucrosic dolomite                                                                                                                       |
| R39     | 0.8871   | 0.8945                   | 0.5551                      | 0.8916                      | 0.2321                     | 0.3056                     | 0.9832    | 0.9329    | 0.8588    | Non to sucrosic dolomite                                                                                                                                       |
| R49     | 0.5237   | 0.541<br>0.8779          | 0.3749                      | 0.4442                      | 0.2321                     | 0.3056                     | 0.903     | 0.6327    | 0.6599    | Micrite to packstone                                                                                                                                           |
| R5      | 0.8705   | (.622)<br>0.9731         | 0.9338                      | 0.7737                      | 0.0612                     | 0.0695                     | 0.1233    | 0.0245    | 0.4653    | Semi sucrosic to sucrosic in molds dolomite                                                                                                                    |
| R9      | 0.9633   | (.8145)                  | 0.9183                      | 0.9215                      | 0.7395                     | 0.6856                     | 0.8186    | 0.6014    | 0.319     | Mostly sucrosic dolomite                                                                                                                                       |
| TR4-1   | 0.8874   | 0.8873                   | 0.7241                      | 0.5929                      | 0.2659                     | 0.1755                     | 0.6529    | 0.3278    | 0.1389    | Dolomite with interbedded wack/packstone and sucrosic dolomite                                                                                                 |
| TR9-2   | 0.4166   | 0.4077                   | 0.2839                      | 0.5064                      | 0.0521                     | 0.0672                     | 0.485     | 0.9173    | 0.4985    | sucrosic dolomite with secondary spar wacke/packstone and partially dolomitized with gypsum                                                                    |
| TRSA-1  | 0.4716   | 0.4846                   | 0.3374                      | 0.1593                      | 0.0141                     | 0.0109                     | 0.4615    | 0.4022    | 0.3769    |                                                                                                                                                                |

### 5.3.1 Comparisons with Hawthorn and Suwannee

The correlations of Fe vs. S in the APF are quite poor compared with those from the Hawthorn and Suwannee (Table 11). The Suwannee has the best correlations with As vs. Fe and S. The APF only has better correlations than the Hawthorn in the targeted samples with As vs. Fe and S.

Table 11. Comparison of correlations between the Avon Park, Suwannee Limestone, and Hawthorn Group.

| Fe vs S   | Avon Park | Suwannee | Hawthorn |
|-----------|-----------|----------|----------|
| Total     | 0.2488    | 0.6712   | 0.87     |
| Interval  | 0.2521    | N/A      | 0.69     |
| Targeted  | 0.2363    | N/A      | 0.95     |
| Permeable | 0.3596    | N/A      | N/A      |
| As vs S   |           |          |          |
| Total     | 0.2646    | 0.5307   | 0.40     |
| Interval  | 0.2418    | N/A      | 0.26     |
| Targeted  | 0.3062    | N/A      | 0.13     |
| Permeable | 0.2691    | N/A      | N/A      |
| As vs Fe  |           |          |          |
| Total     | 0.3283    | 0.5773   | 0.35     |
| Interval  | 0.2649    | N/A      | 0.32     |
| Targeted  | 0.3241    | N/A      | 0.17     |
| Permeable | 0.4165    | N/A      | N/A      |

## 5.4 Arsenic and Antimony Abundance

### 5.4.1 Bulk

A review of the analysis of the internal and external standards used in this study reveals the heterogeneous nature of powdered limestones. Even though these samples were finely powdered and mixed to ensure homogeneity, it was difficult to obtain repeatable values for As and Sb. The external standard (JLS-1) should have 0.145 mg/kg As and 0.0166 mg/kg Sb. Even with careful sample preparation, it is difficult to obtain

repeatable results with such low values (Table 12 a). This same problem can be seen within duplicate samples. Some of the results below 0.50 mg/kg and above 10.0 mg/kg As did not replicate as well supporting the heterogenic nature of the samples (Table 12 b). Another analytical method such as ICP-MS could be used to better determine whether the inconsistencies were due to analytical methods or sample heterogeneity.

Table 12a. External standard (JLS-1) results for As and Sb. The notes were recorded from the As analysis. The difficulty of measuring small amounts of As and Sb in a homogenous limestone is evident.

| <b>JLS-1<br/>Standard</b> | <b>As mg/kg</b> | <b>Notes</b>         | <b>Sb mg/kg</b> |
|---------------------------|-----------------|----------------------|-----------------|
| EXT STD 1                 | 0.0614          |                      | 0.0223          |
| EXT STD 2                 | 0.0995          | after 1.19 ppb       | 0.0075          |
| EXT STD 3                 | 0.0388          | after 1.2 ppb        | 0.0000          |
| EXT STD 4                 | 0.1636          | after 3.67 ppb       | 0.0214          |
| EXT STD 5                 | 0.5285          | after spike 8.3 ppb  | 0.0050          |
| EXT STD 6                 | 0.0000          | after spike 5.9 ppb  | 0.0000          |
| EXT STD 7                 | 0.0058          | after blank          | 0.0059          |
| EXT STD 8                 | 0.0000          | after spike 8.17 ppb | 0.0129          |
| EXT STD 9                 | 0.0000          |                      | 0.0166          |

Table 12 b. Some of the duplicate results for As. These are some of the samples with results below 0.50 mg/kg or above 10.0 mg/kg.

| <b>Sample</b> | <b>As mg/kg</b> | <b>Sample</b> | <b>As mg/kg</b> |
|---------------|-----------------|---------------|-----------------|
| DV-1 560A     | 0.000           | R25 981A      | 30.817          |
| DV-1 560B     | 0.077           | R25 981B      | 28.718          |
| DV-1 600A     | 0.109           | R28 1063A     | 0.124           |
| DV-1 600B     | 0.007           | R28 1063B     | 0.022           |
| R13 1161A     | 0.333           | R39 1001A     | 30.385          |
| R13 1161B     | 0.197           | R39 1001B     | 28.002          |
| R13 1481A     | 0.605           | R39 1010.5A   | 0.471           |
| R13 1481B     | 1.601           | R39 1010.5B   | 0.577           |
| R14 1109A     | 0.225           | R39 1690A     | 0.153           |
| R14 1109B     | 0.347           | R39 1690B     | 0.000           |
| R22 1165A     | 0.298           | R49 875A      | 0.111           |
| R22 1165B     | 0.334           | R49 875B      | 0.195           |
| R22 1180A     | 17.117          | TR9-2 741A    | 2.183           |
| R22 1180B     | 14.646          | TR9-2 741B    | 1.640           |

The bulk chemical data for As and Sb indicate that certain cores and thus areas within the study area have higher As and Sb values (Figure 27). There are six cores with As averages above 3.0 mg/kg while none of the cores have significant averages for Sb. These cores are concentrated toward the southern part of the study area, excluding a section in the southern-most area. There are also zones within individual cores that have higher levels of As. These zones are typically small, not extending more than 3 meters and more often localized to 1 or 2 meters. The average for R39 is elevated but only three localized samples were high (30.3, 8.3, and 7.9 mg/kg) while the rest of the samples were below 1.9 mg/kg.

The bulk chemical data indicate that As is not confined to certain depths or lithologies. Even though the As appears to be concentrated in one region of the study area, all the cores except two (R49 and TR4-1) have samples containing at least 7.0 mg/kg. The two lower value cores are near others with high values. Arsenic appears to be ubiquitous and not spatially constrained within the APF. A similar study conducted in the Hawthorn Group found a trend of decreasing As with depth and associated it with decreasing siliclastic content (Lazareva and Pichler, 2007). Some APF samples with elevated silica (Si) have higher As values while others do not. The three cores with a higher average of siliclastic material are not the same six with the high As averages (Figure 28). It is interesting to note that these three are at the southernmost part of the study area where the formation dips to the south.

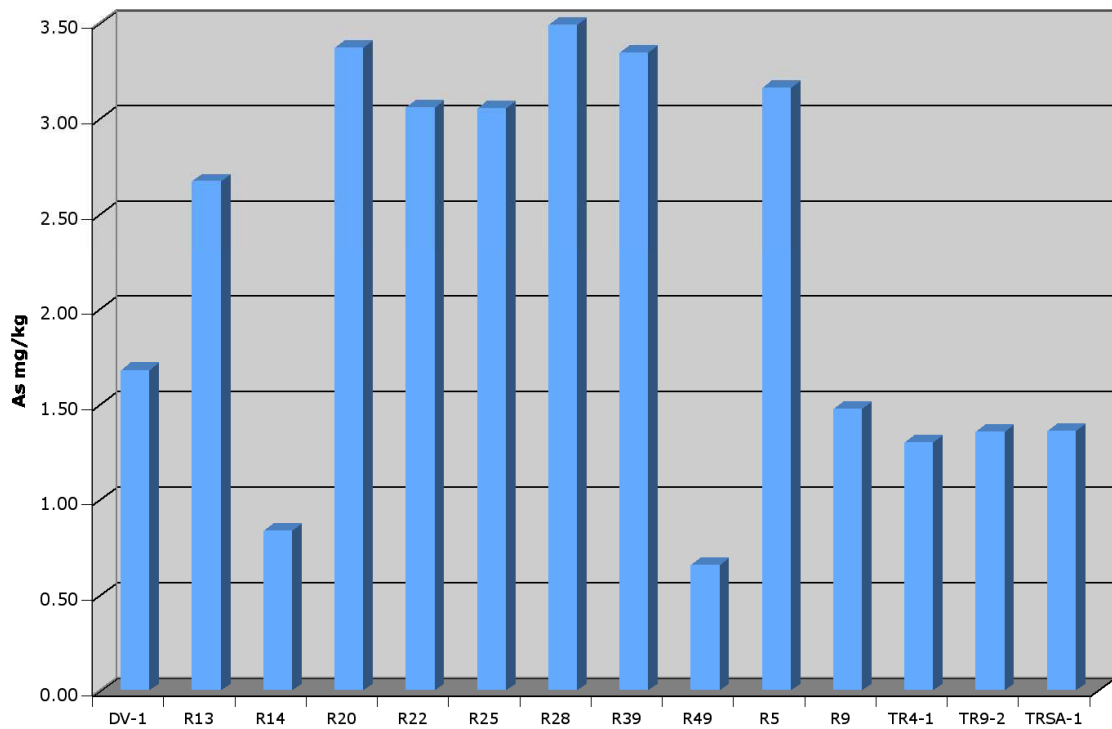
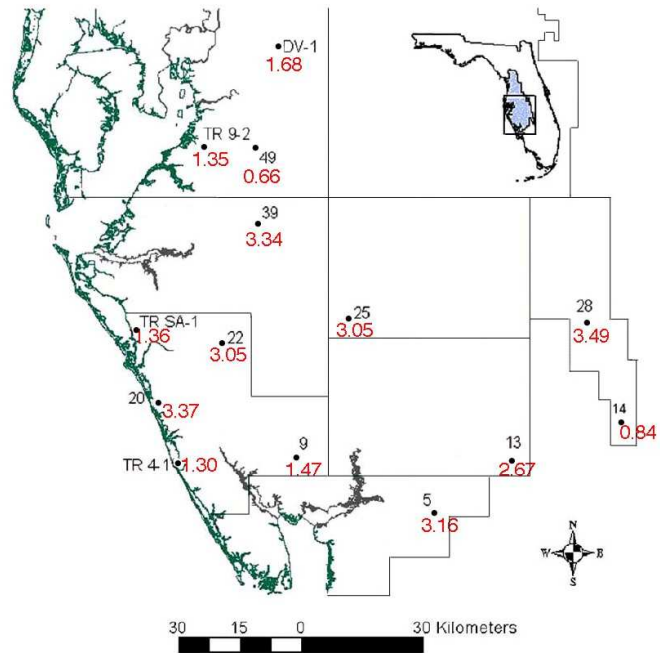


Figure 27. Distribution of average As concentrations (mg/kg) by core within the study area. Black numbers represent the Romp well ID while red are the As values.

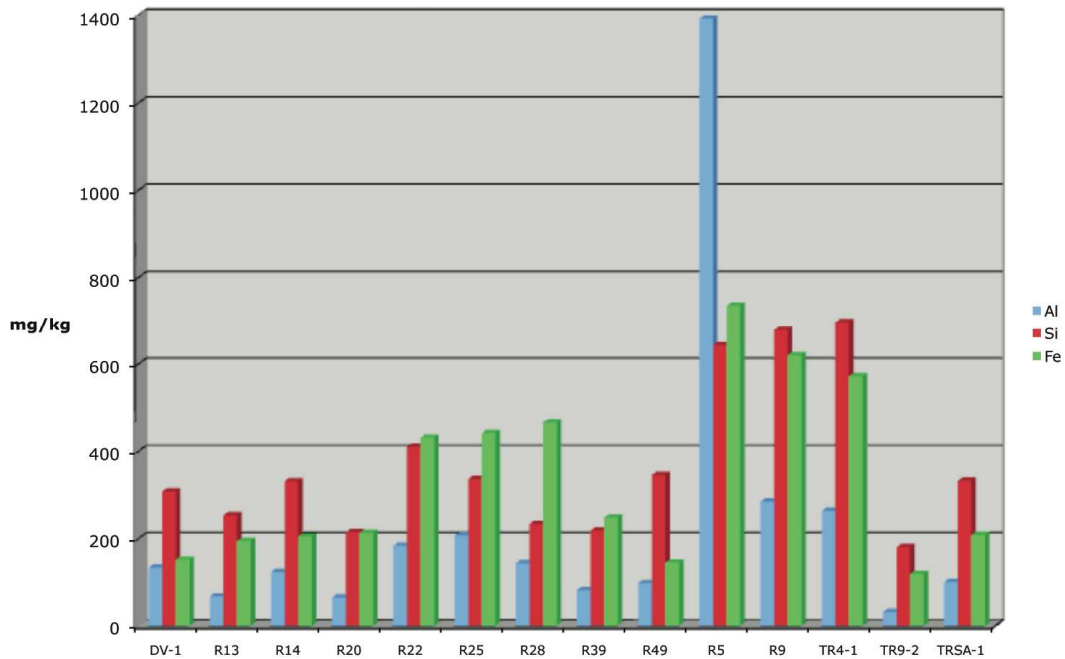


Figure 28. Average values for selected elements by core in the APF. The three cores with the highest siliclastic content are located in the southern most part of the study area.

### 5.5 Sources of Arsenic and Antimony

The depositional environment of the APF is conducive for concentrating trace metals such as As and Sb. The oxyanions of As accumulate in evaporitic environments by reacting with carbonate, chloride and sulfate salts (Goldstein et al., 2007). This is why redox-sensitive elements such as As are used to examine paleoenvironments. These elements are typically associated with anoxic to subanoxic environments formed in evaporite environments (Bordoloi et al., 2006; McKay et al., 2007; Orberger et al., 2007; Tribovillard et al., 2004). Unlike the Hawthorn Group and Suwannee limestone, siliclastic sediments are limited in the APF due to the presence of the Suwannee Channel in north Florida. It is also possible that there were no large streams present during the Eocene to transport clastic sediments (Chen, 1965). The later Suwannee had sand lenses and siliclastics (Arthur et al., 2009)

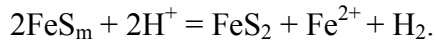
### 5.5.1 Pyrite

Pyrite as a source of As has been well established in various studies (Arthur et al., 2007; Huerta-Diaz and Morse, 1992; Kolker and Nordstrom, ; Lazareva and Pichler, 2007; Mirecki, 2006; Price and Pichler, 2006; Schreiber et al., 2000; Smedley and Kinniburgh, 2002). It is not surprising that As is incorporated into this sulfide because arsenopyrite (FeAsS) is the common ore mineral for As. Furthermore, in sulfur-rich anaerobic conditions, like the APF, arsenic is coprecipitated with secondary sulfide minerals (Moore et al., 1988). Sulfur is released during diagenesis of sulfur-rich organisms and is then reduced to H<sub>2</sub>S. The reduced sulfide is then incorporated into metal sulfides or organics (Staudt and Schoonen, 1995).

This study also confirms pyrite as a source of As but not Sb (Figure 29). However, pyrite does not account for all the As. The R<sup>2</sup> value for correlations between As and Fe and As and S were simply not large enough to account for most of the variability in As (Figures 22 – 25). Pyrite is formed from metastable minerals such as mackinawite (FeS<sub>m</sub>) or greigite (Fe<sub>3</sub>S<sub>4</sub>) or it is spontaneously nucleated in kinetically limiting supersaturated solutions. As a result local heterogeneities in sedimentary and aqueous environments determine whether or not pyrite will form (Rickard and Luther, 2007). This explains the ubiquitous presence of pyrite in the APF. The type of pyrite formation may also affect which trace elements are incorporated into its structure, explaining why some pyrites contain undetectable amounts of As while others have up to 5820 mg/kg.

It is also important to note that trace metals that are incorporated into pyrite precursor minerals are not necessarily incorporated into the pyrite. This is not a

continuous solution process. A precursor mineral such as  $\text{FeS}_m$ , common to near shore marine environments, dissolves releasing trace elements into solution (Wilkin and Barnes, 1996). Pyrite then forms according to the following reaction:



When systems with limited Fe are encountered, such as the APF, the concentration of Fe (II) controls the rate of reaction. It is therefore likely that the bulk As concentrations for the APF may increase or decrease significantly depending on the samples and number of samples taken. The heterogeneous presence of pyrite makes it difficult to obtain an accurate account of bulk pyrite and the trace metals associated with it. The only way to obtain reasonably accurate results is to sample randomly and in conjunction with targeted locations and increase the sample size. This study has used random and targeted sampling methods and a statistically significant number of samples. Increasing the number of samples can only improve the accuracy of the results but this must be balanced with the added time needed to sample, analyze, and interpret the extra data.

#### 5.5.1.a Morphology

A relationship between pyrite morphology and trace metal content could not be definitively established but emphasizes the role of diagenesis. The irregular and honeycomb categories of pyrites likely consist of diagenetically altered framboids. A study by Kalliokoski and Cathles (1969) found that framboids are often altered during diagenesis, causing them to lose some or all of their crystal morphology. Since the irregular category has the highest As concentrations, it may be that the As was incorporated during a diagenetic process. The formation of framboids themselves is not completely understood but is thought to be the result of diagenetic processes. Euhedral

pyrites are typically precipitated from solution and either grow or shrink during diagenesis (Rickard et al., 1995). This may help support the idea that trace metals are incorporated during diagenetic alteration of framboids. The previous studies conducted in the Hawthorn and Suwannee found framboids to be the dominant morphology (Lazareva and Pichler, 2007; Price and Pichler, 2006). The large amount of euhedral pyrites compared to framboids in the APF may explain why the APF overall has less As than the Hawthorn Group and Suwannee Limestone.

The six different morphologic classes were examined to see if they occurred in a particular lithology, with certain minerals, or features such as molds or fractures (Table 13). It appears that the euhedral pyrites may be associated with clays. Samples from R22 944, R22 954, R5 1082, R13 1324, R25 981, and R14 1248 all have mostly euhedral pyrites and contain significant amounts of clay. However R20 1364 and TRSA-1 1138.5 have mostly euhedral pyrites but are mostly pure limestone or partially dolomitized limestone, TRSA-1. Samples containing biogenic pyrites contained organic laminations but there were samples with organic laminations and no biogenic pyrites. Samples R13 1483 and TRSA-1 1080 contained mostly framboids and had organic laminations but sample R28 1224.5 has mostly framboids that were found in fractures. The irregular pyrites were not the dominant type in any of the samples making it difficult to associate them with anything. They are most likely the result of some type of weathering. The other category has only sample TR9-1 765 with more than 1 other type pyrite. An association can therefore not be made with this category. The honeycomb pyrites also seem to have an association with organic laminations. They were dominant in samples that contained abundant oxidized organic laminations.

Table 13. The morphologic pyrite categories broken down by core along with the pertinent lithological information for the core.

| Core  | Depth     | Sample Type | Biogenic | Euhedral | Framboid | Irregular | Other | Honey-comb | Total | Lithologic notes                                                                            |
|-------|-----------|-------------|----------|----------|----------|-----------|-------|------------|-------|---------------------------------------------------------------------------------------------|
| DV1   | 707       | T           |          | 2        |          |           | 1     |            | 3     | trace detrital, dolomite, pyrite in molds, gypsum and FeOH mixed                            |
| DV1   | 775       | T           |          | 1        |          | 2         |       | 1          | 4     | dolomite, pyrite scattered and in fractures                                                 |
| DV1   | 820       | I           |          | 4        | 1        |           |       | 7          | 12    | gypsum and K-spar, dolomite with oxidized pyrites                                           |
| TR9-2 | 765       | T           |          | 5        |          | 1         | 4     | 1          | 11    | half sucrosic dolo with micrite and oxidized lamms, solid dolo rest, pyrite in grain spaces |
| TR9-2 | 773       | T           |          | 1        | 1        |           |       |            | 2     | oxidized organic lamms, pyrite in laminations, dolo grains and fractures                    |
| R22   | 1004-1007 | T           | 1        | 3        | 3        |           |       | 4          | 11    | recrystal limestone with partial dolo grains                                                |
| R22   | 1022      | T           | 2        | 3        | 1        |           |       | 7          | 13    | organic laminations, pyrite in fractures and laminations                                    |
| R22   | 1185      | T           |          |          | 1        |           |       |            | 1     | celestine and feldspar                                                                      |
| R22   | 944       | T           |          | 9        |          | 2         |       | 1          | 12    | clays in limestone pyrite in crystals and grain spaces, irregular in dolomite               |
| R22   | 954       | T           |          | 7        |          |           | 1     |            | 8     | clays in limestone                                                                          |
| R5    | 1082      | T           |          | 16       |          |           |       |            | 16    | clay, pyrites along fractures and clusters                                                  |
| R5    | 1107      | T           |          | 1        |          | 2         | 1     | 1          | 5     | detrital phosphate, apatite with pyrite, siliclastic clay                                   |
| R5    | 1231      | I           |          | 1        | 2        |           |       | 3          | 6     | recrystal wacke pyrite with calcite and in molds, some celestine                            |
| R28   | 1163      | T           |          | 2        |          |           |       | 4          | 6     | organic lamms and clay, pyrite in fractures and molds                                       |
| R28   | 1224.5    | T           |          |          | 4        |           |       | 1          | 5     | framb on cracks and fractures, partial dolo wackestone                                      |
| R28   | 1228      | T           | 3        | 2        | 1        |           |       |            | 6     | recrystal wackestone, oxidized organic lamms, gypsum, pyrite in lamination and matrix       |
| R14   | 1248      | T           |          | 6        | 2        | 2         | 1     | 1          | 12    | wackestone, some clay, biogenic casts, pyrites inside casts                                 |
| R20   | 1233      | T           | 4        |          |          |           |       | 3          | 7     | organic laminations                                                                         |
| R20   | 1333      | T           |          | 1        |          |           |       |            | 1     | gypsum, limestone                                                                           |

| Table 13 Continued. |        |   |           |           |           |           |           |           |            |                                                                                        |
|---------------------|--------|---|-----------|-----------|-----------|-----------|-----------|-----------|------------|----------------------------------------------------------------------------------------|
| R20                 | 1335   | T |           |           |           |           |           |           | 8          | organics along fractures, looks like bioturbated layers                                |
| R20                 | 1340   | T |           |           |           | 1         |           |           | 1          | gypsum, fine limestone, some oxidized organic lamms                                    |
| R20                 | 1364   | T |           |           | 7         | 2         | 1         | 1         | 13         | organics in limestone biogenic casts, pyrite throughout, irregular honeycomb           |
| R13                 | 1324   | T |           |           | 5         |           |           |           | 5          | wackestone some clay, biogenic casts, Sr, gypsum and celestine in clay                 |
| R13                 | 1395   | T |           |           |           | 1         |           |           | 1          | celestine, micrite matrix, grainstone inclusions in micrite                            |
| R13                 | 1483   | T |           |           |           | 8         |           |           | 8          | a lot of organic laminations limestone                                                 |
| TRSA-1              | 1080   | T |           |           |           | 6         |           |           | 11         | organics in dolomite, biogenic casts                                                   |
| TRSA-1              | 1138.5 | T |           |           | 6         |           | 2         | 1         | 9          | recrystal packestone with partial dolo, lots of biogenic casts                         |
| TR4-1               | 1171   | T |           |           | 2         |           | 1         |           | 3          | dolomite, pyrites in molds with HFO, euhebral in dolo grains, pyrites in molds, gypsum |
| R25                 | 981    | T |           |           | 8         | 2         |           |           | 10         | clay, dolomite, pyrite in grain space, matrix, dolomite                                |
| <b>Totals</b>       |        |   | <b>10</b> | <b>92</b> | <b>36</b> | <b>13</b> | <b>10</b> | <b>49</b> | <b>210</b> |                                                                                        |

### 5.5.2 Organic Matter and Clays

Dissolved and total organic carbon was not examined for this study. The fact that other minerals and sources examined cannot account for all the As and Sb indicate that organic matter (OM) may be a likely source. Iron minerals and reactive OM actively compete for reduced S species to form either pyrite or S enriched OM (Vairavamurthy et al., 1995b). The limited Fe in carbonate platforms results in S enriched OM. Even after accounting for S associated with pyrite and celestine, most samples still contained excess S. An abundance of other S containing minerals was not observed in lithologic, petrographic, or EMPA analysis. Gypsum and anhydrite are the only other minerals observed in some of the deeper samples. It is therefore likely that the excess S exists as organic S. The algal laminations throughout the formation are probably the source of organics and thus organic S.

Sulfur itself is unique because it can act as a redox agent, or react with and incorporate itself into organic matter (Goldstein and Aizenshtat, 1994; Williamson and Rimstidt, 1992). These chemical properties enable it to undertake multiple stepwise redox reaction forming various sulfur species. It is possible that through these many reactions, trace elements like As, are incorporated into the organic matter.

A review by Plant et al. (2004) on As concluded that S rich anaerobic environments (APF) are conducive for the coprecipitation of As with clay. The sorbed As is sensitive to changes in the surface area and charge of the clay. Thus the diagenetic changes occurring to the clay will affect whether the As remains sorbed. The siliclastic and therefore clay content of the APF increases in the southern part of the study area (Figure 28). Correlations between siliclastic related elements such as Al, Si, and Mn

with As and Sb are poor (Appendix 4). Certain individual samples did have high Si content with corresponding high As. It is likely that arsenic is associated with some clay minerals but not enough to quantify as a significant source of As.

#### 5.5.3 Celestine

Samples high in celestine and other sulfate ( $\text{SO}_4^{2-}$ ) minerals were most likely deposited in oxic environments because this S (+VI) species is the only dominant species in oxic conditions (Domenico and Schwartz, 1990). Metal ion concentrations may be high in these sulfate rich solutions because there are limited solubility restraints to remove solids from solution. The amount of celestine in the samples was calculated from the corrected S value. The difference between total S and the corrected S was the amount of S that could theoretically form celestine. A correlation matrix for the S associated with celestine along with Sr was produced to see if there were any relationships between celestine and As and Sb (Figure 29). There are no significant relationships. The EPMA analysis confirms this because no trace metals were found above detection limits (Appendix 7).

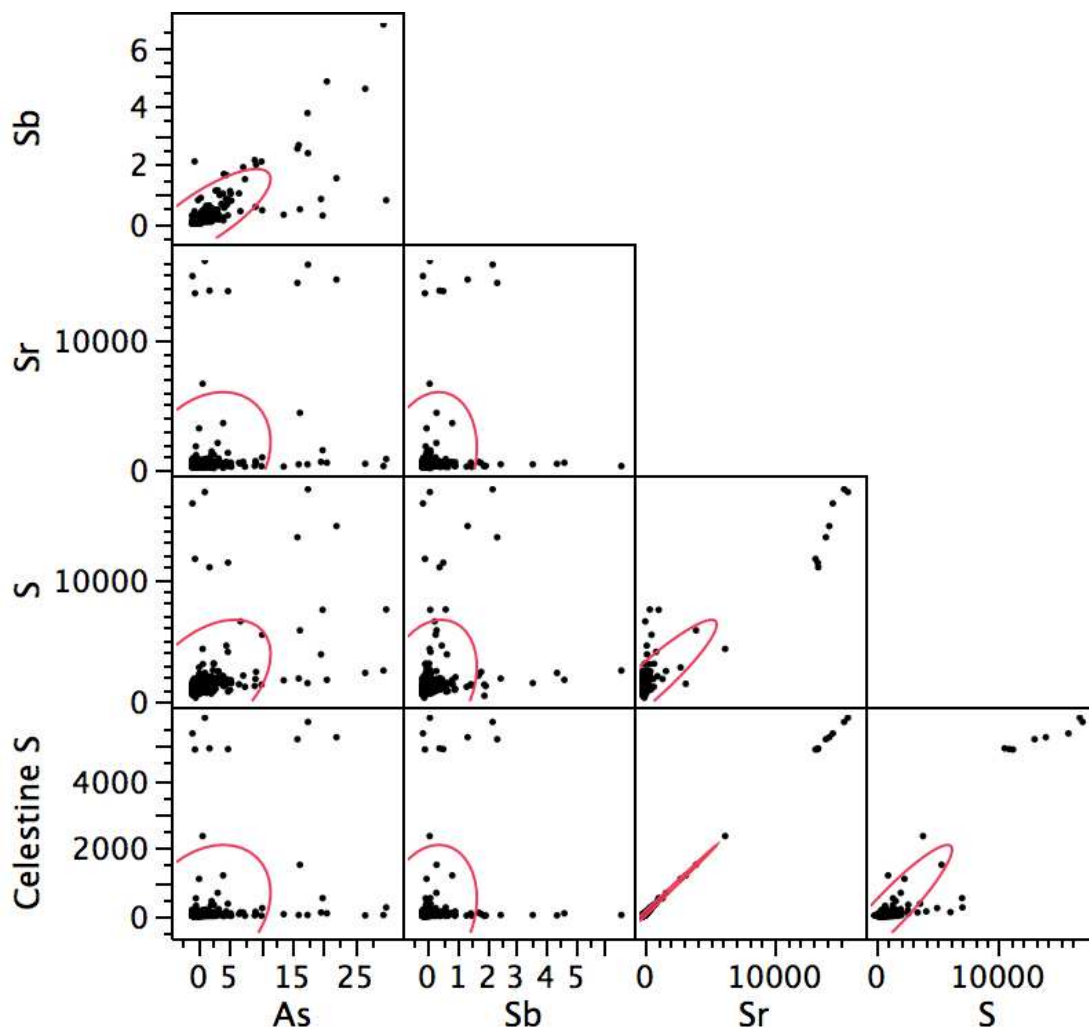


Figure 29. Correlation matrix with density ellipses for As, Sb, Sr, total S, and S associated with celestine. A cluster of high celestine S can be seen. The rest of the samples are low and do not correlate with either As or Sb.

#### 5.5.4 Hydrous Ferric Oxides (HFO)

Various studies have distinguished hydrous ferric [iron] oxides as scavengers of As for their ability to adsorb and or coprecipitate with As (Goldberg, 1986; Inskeep et al., 2002; Pichler et al., 2001). A review by Plant et al. (2004) on As describes how pH controls adsorption of As species to HFO. At low pH and concentrations the arsenate species is strongly adsorbed to HFO and begins to desorb past a pH of 9 due to an

increasing electrostatic repulsion between the arsenate and negatively charged HFO surface (Plant et al., 2004). The predominate arsenite species ( $\text{As}(\text{OH})_3$ ) is neutral in a pH range of 4-9. It remains sorbed over a broad pH range and is considered somewhat pH independent. This study was not able to find many hydrous ferric oxides. Some were seen in the lithologic examination of hand samples. They are found in the sucrosic dolomite molds with pyrite (Figure 8). The HFO were not seen in thin section or EPMA analysis. It is likely that they were not formed in the subsurface but during storage. The samples become wet during the drilling process and core excavation. Once at the surface the wet pyrites were oxidized and formed HFO. This is important for ASR, because it shows what happens to the pyrite once it is oxidized. The ASR operations could potentially form HFO in oxidizing conditions that concentrate trace metals. When the aquifer returns to reducing conditions, the metals can be released.

## 5.6 Quantified Role of Pyrite

Calculations were performed to quantify the role of pyrite in concentrating As. The bulk and EPMA measurements for Sb are negligible, and the correlations with pyrite are poor. The bulk and EPMA data for As is significant along with some of the correlations with pyrite so this was the only element examined. The amount of pyrite in a sample was calculated from the bulk iron data. The only mineral found in lithologic and EPMA analysis containing iron, with the exception of trace HFOs, was pyrite. The HFOs are likely secondarily derived from pyrite during core removal and storage. All Fe was assumed to be associated with pyrite. From that using a molar ratio of 1 Fe for every 2 moles of S, the amount of S associated with pyrite was calculated (Table 14). The percent of pyrite in 1 kg of sample was then calculated. This percentage along with the

EPMA data was used to calculate the amount of As in a sample. Table 14 lists the number of pyrites that were analyzed along with an average value for the thin section calculated from the mg/kg value of each analyzed pyrite. The calculated values were then compared with the bulk data from the HG-AFS analysis for As.

Table 14. The amount of S associated with pyrite ( $S_{\text{pyrite}}$ ) was calculated from bulk Fe data. These along with EPMA data were used to calculate the amount of As contributed by pyrites. The number of analyzed pyrites is listed along with the quantitative number used to calculate the arsenic.

| Sample            | Fe<br>(mg/kg) | $S_{\text{pyrite}}$<br>(mg/kg) | FeS <sub>2</sub><br>(mg/kg) | (%)<br>FeS <sub>2</sub> | #<br>pyrites | quant<br># | As<br>(mg/kg)<br>thin<br>section | Calculated<br>As (mg/kg) | Bulk<br>As<br>(mg/kg) |
|-------------------|---------------|--------------------------------|-----------------------------|-------------------------|--------------|------------|----------------------------------|--------------------------|-----------------------|
| DV-1 658          | 183.4         | 210.6                          | 394.0                       | 0.00039                 | 4            | 1          | 4420                             | 1.74                     | 7.45                  |
| DV-1 707          | 133.1         | 152.8                          | 285.9                       | 0.00029                 | 8            | 4          | 1420                             | 0.406                    | 3.3                   |
| DV-1 775          | 250.1         | 287.2                          | 537.3                       | 0.00054                 | 9            | 4          | 1562.5                           | 0.840                    | 3.2                   |
| DV-1 820          | 1116.9        | 1282.7                         | 2399.6                      | 0.00240                 | 16           | 13         | 1126                             | 2.70                     | 4.9                   |
| R13 1324          | 270.4         | 227.0                          | 497.4                       | 0.00050                 | 6            | 5          | 448                              | 0.223                    | 4.9                   |
| R13 1395          | 400.5         | 459.9                          | 860.3                       | 0.00086                 | 1            | 1          | 0                                | 0.000                    | 16.7                  |
| R13 1483          | 514.2         | 590.5                          | 1104.7                      | 0.00110                 | 10           | 8          | 627.5                            | 0.693                    | 22.9                  |
| R14 1248          | 233.7         | 268.4                          | 502.2                       | 0.00050                 | 14           | 12         | 779.2                            | 0.391                    | 0.53                  |
| R20 1233          | 248.7         | 285.6                          | 534.3                       | 0.00053                 | 9            | 7          | 247.1                            | 0.132                    | 8.1                   |
| R20 1333          | 288.5         | 331.4                          | 619.9                       | 0.00062                 | 9            | 5          | 1498                             | 0.929                    | 27.5                  |
| R20 1335          | 267.1         | 306.7                          | 573.9                       | 0.00057                 | 14           | 8          | 987.5                            | 0.567                    | 10.0                  |
| R20 1340          | 487.1         | 559.3                          | 1046.4                      | 0.00105                 | 5            | 2          | 1885                             | 1.97                     | 21.4                  |
| R20 1364          | 456.9         | 524.7                          | 981.6                       | 0.00098                 | 16           | 13         | 492.3                            | 0.483                    | 2.0                   |
| R22 1004-<br>1007 | 274.4         | 315.1                          | 589.5                       | 0.00059                 | 13           | 11         | 845.5                            | 0.498                    | 16.9                  |
| R22 1022          | 428.8         | 492.4                          | 921.2                       | 0.00092                 | 15           | 15         | 659.3                            | 0.607                    | 10.1                  |
| R22 1185          | 1205.2        | 1384.1                         | 2589.3                      | 0.00259                 | 9            | 2          | 875                              | 2.27                     | 18.4                  |
| R22 944           | 2214.1        | 2542.7                         | 4756.9                      | 0.00476                 | 13           | 12         | 493.3                            | 2.35                     | 5.43                  |
| R22 954           | 823.9         | 946.1                          | 1770.0                      | 0.00177                 | 10           | 8          | 163.8                            | 0.290                    | 1.7                   |
| R25 981           | 4865.6        | 5587.6                         | 10453.2                     | 0.01045                 | 10           | 10         | 218                              | 2.28                     | 30.8                  |
| R28 1163          | 2082.6        | 2391.7                         | 4474.3                      | 0.00447                 | 13           | 7          | 1537                             | 6.88                     | 11.1                  |
| R28 1224.5        | 2250.7        | 2584.7                         | 4835.4                      | 0.00484                 | 15           | 9          | 2548                             | 12.32                    | 20.5                  |
| R28 1228          | 83.2          | 95.5                           | 178.7                       | 0.00018                 | 7            | 6          | 168                              | 0.030                    | 18.3                  |
| R5 1082           | 6368.5        | 6792.7                         | 13161.2                     | 0.01316                 | 16           | 16         | 2314                             | 30.5                     | 20.7                  |
| R5 1107           | 3374.1        | 1657.0                         | 5031.1                      | 0.00503                 | 6            | 5          | 3568                             | 18.0                     | 14.5                  |
| R5 1231           | 157.5         | 180.9                          | 338.4                       | 0.00034                 | 8            | 6          | 685                              | 0.232                    | 2.34                  |
| TR4-1 1171        | 639.3         | 734.2                          | 1373.6                      | 0.00137                 | 8            | 3          | 833.3                            | 1.14                     | 2.1                   |
| TR9-2 765         | 32.9          | 37.7                           | 70.6                        | 0.00007                 | 17           | 11         | 421.8                            | 0.030                    | 1.32                  |
| TR9-2 773         | 263.2         | 302.3                          | 565.5                       | 0.00057                 | 8            | 4          | 517.5                            | 0.293                    | 11.0                  |
| TRSA-1<br>1080    | 254.8         | 292.6                          | 547.3                       | 0.00055                 | 11           | 11         | 310                              | 0.170                    | 0.46                  |
| TRSA-1<br>1138.5  | 42.7          | 49.1                           | 91.8                        | 0.00009                 | 11           | 9          | 445.6                            | 0.041                    | 0.22                  |

Most of the calculated values of As are much lower than the measured values with the exception of two samples that have lower values than the calculated ones. There are some that are close to the measured values and confirm pyrite as the dominant source of pyrite (Figure 30). Only two samples were overestimated and were both from R5 within 8 meters of each other. A sufficient number of pyrites were analyzed in these samples so it may be just an error involved with calculating As. It can also indicate the heterogeneous nature of the pyrites within one sample. The digested bulk sample may have had less pyrite than the thin section sample. A plot of the calculated vs. measured values can be seen in Figure 30. The values that lie below the line of equal concentration indicate that the As was calculated above the measured value. Samples plotting above the equal concentration line indicate the underestimation of the calculated pyrite. All the samples that were significantly under calculated with the exception of R25 98, which has large amounts of clay, contain organic laminations. This shows that the organic layers are also a likely source of As along with clay for certain samples.

If the samples with high amounts of clay and organic laminations are eliminated, the correlation between the calculated and measured arsenic has a  $R^2$  value of .7586 (Figure 30). It can be said that the samples outside the circled area have pyrite as their main source of As. There are several samples that resulted in relatively correct calculations. This indicates that a sufficient number of pyrites were analyzed and other As sources such as organics and clay are limited. This quantification indicates that in some areas pyrite plays a role as an As source while in others, organics and clays are more important.

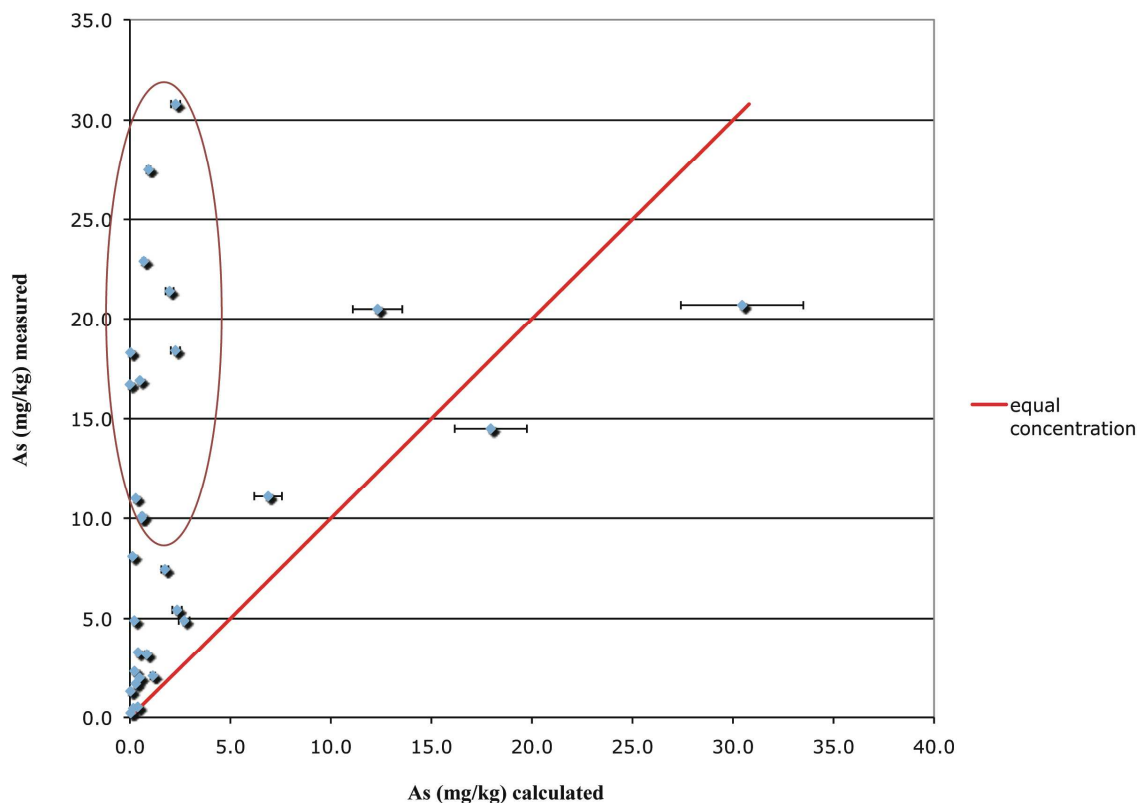


Figure 30. A correlation between calculated and measured arsenic values. The circled points significantly underestimated the measured value indicating that pyrite is not the main source of arsenic. If these are ignored there is an  $R^2$  value of .7586. 10% error bars are shown.

### 5.7 Mobilization of Arsenic during Aquifer Storage and Recovery (ASR)

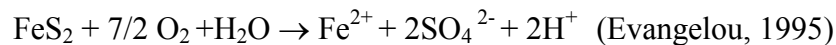
Smedley and Kinniburgh (2002) reviewed the literature on As distribution and found that aquifers throughout the U.S. have As concentrations ranging from  $<1 - 2,600 \mu\text{g/L}$  but a study by Focazio et al. (1999) found that only 7.6% of groundwater used for public supply exceeded the EPA standard of  $10 \mu\text{g/L}$  and 64% had  $< 1 \mu\text{g/L}$ . A literature review of the previous studies along with many others and this study prove that the release of trace metals such as As is dependent upon pH, redox conditions, and competing anion species. Once As is adsorbed, it is subject to desorption when geochemical conditions are altered. Altered conditions include pH changes that cause

phase dissolution and competitive desorption that occurs when high concentrations of inorganic ligands such as  $\text{OH}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  and simple organic ligands are present (Foster, 2003; Appelo et al., 2002; Jain and Loeppert, 2000; Meng, 2002). The speciation of the As, or ratio of arsenite to arsenate, changes variably in the presence of redox-active solids, specifically organic carbon, the activity of microorganisms, and the availability of oxygen. If  $\text{Fe}^{3+}$  and sulfate reduction are occurring, arsenite species dominate (Smedley et al., 2001; Smedley et al., 2003). Even if the specific geochemical environment of an area is known, it is still difficult to predict the As concentration that a particular well may return. Smedley and Kinniburgh's 2002 review found that As is spatially highly variable in groundwater and may be high in one well and relatively low in a neighboring one.

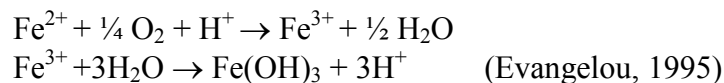
It is more important to determine the solubility of the bulk mineral when determining the availability of coprecipitated arsenic because the majority of As is found within the mineral interior as opposed to the surface (Foster, 2003). Since As may be coprecipitated with clays and secondary sulfide minerals, it is important to determine whether ASR operations will alter the bulk solubility of these minerals. It is also important to examine the effects of the competing ligands in the APF because environments rich in bicarbonate and sulfate limit the re-adsorption of arsenic after desorption as explained in a review by Smedley and Kinniburgh (2002). The bicarbonate and sulfate compete with As species for adsorption sites once the environment has returned to reducing. This increases problems for ASR in Florida's sulfur rich carbonate aquifers. Once the As is mobilized, it will take longer for the As to re-adsorb to the aquifer matrix and it is likely some will remain in solution.

Even though there is competition for sorption sites, minerals like HFOs will preferentially adsorb arsenic ( $\text{H}_2\text{AsO}_4^-$ ) from solution in oxidizing environments with a pH less than 6.9 (Nordstrom and Archer, 2003). This adsorption is increased with the presence of the cations  $\text{Fe}^{2+}$  and  $\text{Ca}^{2+}$  (Appelo et al., 2002). The APF has limited HFOs so it is unlikely that they can scavenge enough As to prevent ASR operations from recovering high As. Even if there were significant HFOs, arsenate is preferentially adsorbed over arsenite in neutral to acidic oxidizing conditions (Plant et al., 2004). This preference becomes more dominant at low As concentrations. There would have to be an unrealistic amount of HFOs present to prevent the recovery of the more toxic arsenite.

The bulk solubility of pyrite should be determined for the aquifer selected for ASR. Pyrite exposed at the surface to water and  $\text{O}_2$  reacts forming  $\text{H}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{Fe}^{2+}$ :



It is reasonable to think the same reaction occurs in an aquifer when oxygenated water is introduced during ASR operations. If the pyrite is completely dissolved, all the trace metals are released into solution. In addition the  $\text{Fe}^{2+}$  released can go on to react with more oxygen forming  $\text{Fe}^{3+}$ . This is then hydrolyzed to form iron hydroxide and protons increasing the acidity of recovered water:



Even though the bulk As concentrations of the APF are low, the potential for arsenic release above the 10  $\mu\text{g/L}$  limit is possible. Young aquifers with relatively average As concentrations ranging from 1.0 - 20 mg/kg are capable of producing groundwaters with up to several mg/L As (Edmunds et al., 1989; Smedley and Kinniburgh, 2002). Thus the release of As within the APF may come from oxidative

dissolution of minerals like pyrite, clays, and OM along with reductive desorption of these same materials.

## CHAPTER SIX

### CONCLUSIONS

This detailed mineralogic and geochemical investigation has concluded the following:

- (1.) The bulk arsenic (As) and As within individual pyrite is lower than that found in the Suwannee Limestone and Hawthorn Group.
- (2.) The bulk values of arsenic ( $>0.1 - 30.8$  mg/kg) and antimony (Sb) ( $>0.1 - 6.76$  mg/kg) were highly variable from sample to sample and core to core.
- (3.) Pyrite is abundant in the Avon Park Formation (APF) and occurs as euhedral grains and framboids with minor amounts of biogenic and honeycomb pyrites.
- (4.) Arsenic was the only trace element detected by EPMA with an average concentration (945 mg/kg) and a maximum of 5820 mg/kg.
- (5.) The irregular and other morphological categories of pyrite contained the highest average concentrations ( $\mu\text{g/kg}$ ) of arsenic, while the honeycomb, framboid, and biogenic categories had the highest average concentrations of antimony.
- (6.) Arsenic is conclusively found in pyrite but can also be found in organic matter and clay and adsorbed or incorporated into HFOs formed from the oxidation of pyrite while the source of antimony is uncertain because it is found in such low concentrations.
- (7.) Arsenic is incorporated into framboidal pyrite during diagenesis but antimony is not found in significant amounts in any pyrite.
- (8.) The overall correlations and concentrations of As with Fe and S may be low, but individual cores and samples may have high As values.
- (9.) The core examination and literature prove the APF has sufficient permeable zones for ASR operations.
- (10.) Aquifer Storage and Recovery (ASR) operations have the potential to release trace metals such as As and Sb depending on how the geochemical parameters

are altered by injection, the presence of competing anions such as  $\text{OH}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  and simple organic ligands, and how much is sorbed to a material versus coprecipitated and incorporated into a material.

- (11.) From the current data the best areas to further investigate for potential ASR use are in the vicinity of R14 and R49.

A study is needed to determine the stability of pyrite within the APF and the affects of “normal” ASR conditions on arsenic sorbed to OM and clay to conclusively determine the viability of the APF for ASR.

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## APPENDICES

## APPENDIX 1

Lithologic logs of ROMP cores.

| Well         | Depth | Porosity                 | Description                                                                                                                                                            | Notes                                    |
|--------------|-------|--------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------|
| 16456<br>R49 | 824.5 | sm granular              | very sm sucrosic dolo w pepper and some areas of conc pepper. Possibly in sm molds. Trace HFO pieces                                                                   | pepper, molds, trace HFO                 |
| 16456<br>R49 | 835   | granular                 | sucrosic lt brown dolo w large silver dollar olds and some sm molds. Most are filled in w secondary dolo but one is hollow w HFO. Pyrite scattered in grain spaces     | mold w HFO, pyrite in grain space        |
| 16456<br>R49 | 838   | granular and some moldic | sucrosic dolo w lots of lrg and sm molds. Some lrg molds infilled w lrg sucrosic dolo. Pyrite and HFO in molds                                                         | pyrite, HFO in molds                     |
| 16456<br>R49 | 843   |                          | semisucrosic lt br dolo w lots sm molds and some large ones. Good amt of molds lines w orange-HFO and some molds w pyrite and some scattered pieces of possible pyrite | molds w HFO and others pyrite; scattered |
| 16456<br>R49 | 845   |                          | semisucrosic dolo w sm molds and trace pyrite and HFO                                                                                                                  | trace pyrite and HFO                     |
| 16456<br>R49 | 847   | limited granular         | semisucrosic dolo w pieces of HFO and pyrite that likely infilled previous molds                                                                                       | HFO, pyrite - form casts                 |
| 16456<br>R49 | 853   |                          | semisucrosic dolo lt br w lots of sm molds. Scattered areas w darker grey grains-possibly pyrite                                                                       | pyrite scattered on grains?              |
| 16456<br>R49 | 855   | sucrosic                 | sucrosic darker dolo w some sm and med molds. Pieces of pyrite or possibly HFO                                                                                         | pieces of pyrite and HFO?                |
| 16456<br>R49 | 857   | granular and mold        | sucrosic dolo w lots of sm molds some of the cubes are a light amber color-possible oxidation? Trace black pieces-pyrite?                                              | trace pieces pyrite?                     |
| 16456<br>R49 | 858   |                          | semisucrosic dolo but some areas more sucrosic scattered pepper or pieces. More sucrosic part has patch of lots dk pepper-pyrite?                                      | patch dk pepper-pyrite?                  |
| 16456<br>R49 | 859   | fractures                | fractured semisucrosic dolo w lots of sm molds. Fractures are lined w HFO and some pyrite. Scattered darker spots-pyrite?                                              | fractures w HFO and pyrite; scattered    |
| 16456<br>R49 | 865   | granular                 | semisucrosic lt br dolo w some small molds, one half is more sucrosic than the other, trace possible pyrite in molds                                                   | trace possible in molds                  |
| 16456<br>R49 | 868   | granular moldic          | sucrosic dolo w lrg and sm molds, pepper and some larger pieces scattered around, trace HFO                                                                            | pepper, trace HFO                        |
| 16456<br>R49 | 874   | granular                 | lt tan sucrosic dolo w some small molds, trace possible pieces of pyrite and possible trace in molds                                                                   | possible trace pepper ;molds             |
| 16456<br>R49 | 875   | granular moldic          | orangish br sucrosic dolo w lots sm molds, lots of pieces/clumps of pyrite scattered around and some HFO                                                               | pyrite pieces scattered some HFO         |

| Appendix 1 Continued. |       |                                             |                                                                                                                                                                                                                                                            |                                          |
|-----------------------|-------|---------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------|
| 16456<br>R49          | 878.5 | limited granular,<br>fractures, sm<br>molds | yellow br sucrosic dolo w some areas,<br>semi sucrosic. Some areas w pepper<br>clumps and couple areas w pyrite and<br>HFO-possibly from fractures, some sm<br>molds                                                                                       | pepper clumps,<br>HFO from<br>fractures? |
| 16456<br>R49          | 882   |                                             | somewhat sucrosic dolo w some fractures                                                                                                                                                                                                                    |                                          |
| 16456<br>R49          | 885   | limited granular                            | lt br semisucrosic dolo, sm area w more<br>sucrosic and lots of sm molds. Sm molds<br>scattered throughout. Trace pieces of HFO<br>or possible pyrite                                                                                                      | trace HFO and<br>possible pyrite         |
| 16456<br>R49          | 885.5 | sm granular                                 | somewhat sucrosic dolo w varying grains<br>sizes, a few dissolution lateral fractures,<br>some trace oxidized areas w pieces of<br>HFO                                                                                                                     | oxidized areas w<br>HFO                  |
| 16456<br>R49          | 887.5 | tiny granular in<br>one layer               | dolo w laminations of dk and oxidized-<br>HFO                                                                                                                                                                                                              | lamns oxidized-<br>HFO                   |
| 16456<br>R49          | 892   | SEM-molds w<br>HFO                          | semisucrosic dolo w sm lateral fractures<br>that are lined w oxidized surface and some<br>black pieces-HFO; some sm molds, some<br>old molds w HFO?                                                                                                        | HFO on<br>fractures? And<br>molds        |
| 16456<br>R49          | 894   | limited granular                            | lt br dolo w some pepper and lamns of<br>dker dolo, gradually becomes more<br>sucrosic, some lamns seem to be oxidized<br>and w possible pyrite. Scattered pieces of<br>pyrite                                                                             | ox lamns w<br>pyrite? Scattered          |
| 16456<br>R49          | 895   |                                             | br dolo w pepper and some sort lamns of<br>pyrite and or HFOs. Some bits/areas w<br>oxidized stains                                                                                                                                                        | pepper, lamns<br>with pyrite or<br>HFO   |
| 16456<br>R49          | 897.5 |                                             | extremely fine white dolo w fracture and<br>pepper and then 2 dk lamns w sucrosic<br>orangish dolo on top                                                                                                                                                  | pepper w fracture                        |
| 16456<br>R49          | 898   |                                             | dolo w laminations of dker br/amber dolo<br>more crystal like and rest is nonsucrosic,<br>lrg pure layer-white nonsucrosic, then<br>more lamns. One lamn looks like pyrite<br>and HFO then somewhat oxidized more<br>sucrosic dolo w molds infilled w dolo | pyrite and HFO<br>in lamn?               |
| 16456<br>R49          | 899.5 |                                             | semi sucrosic lt br dolo w scattered areas<br>w pepper or clusters of pyrite and other<br>areas w tiny short veins/lamns of iron<br>stains and some pieces of HFO                                                                                          | pepper, clusters,<br>ox-lamns w HFO      |
|                       |       |                                             |                                                                                                                                                                                                                                                            |                                          |
| 16576/<br>DV1         | 521   | granular/<br>fractures                      | recrystal packstone - pure lime- med<br>calcite grains; some quartz (very sm);<br>larger trace organic; long narrow molds<br>filled w calcite; sample crumbles in fine<br>bits-soft; very pure                                                             |                                          |
| 16576/<br>DV1         | 530   | granular lrg                                | secondary spar- micrite/wackestone; very<br>light (non dense); sm casts, some calcite in<br>molds; gypsum infills some spaces and<br>molds-miliolidae, forams, echinoids,<br>bivalves, gastropods; trace pyrite; 2 orange<br>veins                         | trace                                    |

| Appendix 1 Continued. |     |                            |                                                                                                                                                                                                                                                                                                             |                          |
|-----------------------|-----|----------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|
| 16576/<br>DV1         | 540 | granular                   | grainstone with lots of casts-miliolidae, forams, echinoids, bivalves and peloidal grains. Red/brown organic piece on sand dollar                                                                                                                                                                           |                          |
| 16576/<br>DV1         | 549 | lots granular              | grainstone with lots of peloidal grains and casts of miliolidae, forams, echinoids, bivalves                                                                                                                                                                                                                |                          |
| 16576/<br>DV1         | 560 | granular                   | grainstone with some peloidal grains, miliolidae, forams, echinoids, bivalves casts, trace pieces/spots of brown grey-organic?                                                                                                                                                                              |                          |
| 16576/<br>DV1         | 580 | granular                   | cream recrystal grainstone with small casts and some large ones with yellow secondary calcite-miliolidae, forams, echinoids, bivalves                                                                                                                                                                       |                          |
| 16576/<br>DV1         | 584 | lots granular              | cream/tan peloidal grainstone. Lots of casts and some peloids miliolidae, forams, echinoids, bivalves, cross bedding                                                                                                                                                                                        |                          |
| 16576/<br>DV1         | 600 | lots granular              | grainstone with some peloidal grains, micrite casts of mollusks and peloids.miliolidae, forams, bivalves Some larger molds with yellow brown calcite. Cross bedding                                                                                                                                         |                          |
| 16576/<br>DV1         | 616 | granular, moldic           | recrystal - sucrosic reworked; lots of lrg molds miliolidae, forams, bivalves; trace org splotches w possible frambs; some intergranular spaces(veins)- dk br/bl mineral w shiny faces (pyrite); others have sugary calcite/dolo w shiny tiny flecks                                                        | intergran spaces;<br>org |
| 16576/<br>DV1         | 620 |                            | cream recrystal wackestone with trace organics and some small casts-miliolidae, forams, intraclasts                                                                                                                                                                                                         |                          |
| 16576/<br>DV1         | 630 | granular tiny, some moldic | recrystal wackestone-floatstone; calcite grains;miliolidae, forams, echinoids, bivalves thick org laminations (splotches); bioturbation, some tiny quartz flecks; trace org red/br flecks; trace black flecks- one blob w possible frambs and other thick lamination w shiny faces; lrg calcite filled mold | org; flecks              |
| 16576/<br>DV1         | 640 | lots granular, some moldic | granular grainstone with lots of peloidal grains and some casts- milioladae, forams. Piece of dk grey with orange oxidized ring stain around it                                                                                                                                                             | one piece                |
| 16576/<br>DV1         | 645 | granular/<br>fractures     | recrystal limestone bordering /packstone (float/rudstone); irregular microbial lamns-org splotchy laminations-tidal flat; very soft/crumbly; some foram molds; one black piece w rainbow cleavage                                                                                                           |                          |
| 16576/<br>DV1         | 648 | lots granular              | grainstone with some small localized areas with a matrix, peloidal and short cylindrical grains, miliolidae forams, cross bedding                                                                                                                                                                           |                          |

|                       |       |                              |                                                                                                                                                                                                                                                                     |                  |
|-----------------------|-------|------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|
| Appendix 1 Continued. |       |                              |                                                                                                                                                                                                                                                                     |                  |
| 16576/<br>DV1         | 658   | granular                     | recrystal limestone- mudstone mostly; lots of org lamns (splotchy red/br) w lots of tiny shimmery flecks (pyrite/quartz); some bits of quartz; tiny peppered areas, cross bedding intraclasts, miliolidae, forams                                                   | organic; pepper  |
| 16576/<br>DV1         | 680   | some moldic                  | recrystal cream wackestone with lots small scattered grey calcite- some as casts. Some miliolidae, foram, large echinoid molds with secondary calcite, trace oxidized piece                                                                                         | with calcite?    |
| 16576/<br>DV1         | 697   | granular lots                | "br sugar" dolo w some white micrite inclusions(gypsum); trace dark crystals; ranges bw opaque white/tan crystals to oxidized brown ones-occur in blobs. Echinoids                                                                                                  | dolomite         |
| 16576/<br>DV1         | 707   | granular in dolo             | changes from dolo-sm crystals to very fine grained dk grey w br laminations into lighter grey w laminations (splotchy organic) and dk black tiny inclusions; one vert lamination w possible framb; fine grains do not effervesce - have lots of quartz..all quartz? | dolo and organic |
| 16576/<br>DV1         | 720   | limited moldic               | tan and clear dolo wackestone with sucrosic grains in the molds, some oxidized fractures and lamns-tidal flat, oval ring on outer core (dk grey)                                                                                                                    | fractures?       |
| 16576/<br>DV1         | 735   | granular<br>lots/large       | dolomite- some sucrosic (lrg) other parts are dull w gypsum infill. Oxidized veins in one piece, exposed surface oxidized- look like splotchy organic that was dolo; dolo ranges from dk br to very light; cyclic layers of color changes-tidal flat                |                  |
| 16576/<br>DV1         | 740   | fractures, mold              | splotchy dolo with darker bands, scattered clear crystals, organic (oxidized) lamns. Fractures, molds with sucrosic grains. Bioturbated                                                                                                                             | bands in dolo?   |
| 16576/<br>DV1         | 760   | moldic                       | brown/tan dolo grainstone with lots of large and sm molds. Some molds have sucrosic grains in them                                                                                                                                                                  |                  |
| 16576/<br>DV1         | 775   | no visible                   | non sucrosic dolo ranging from opaque yellow/clear to br. Fine powdery micrite in molds; lots of lrg pepper. Mud cracks intraclasts                                                                                                                                 | pepper           |
| 16576/<br>DV1         | 782.5 |                              | tan dolo with some apparently sealed fractures and trace black organic pieces and some non continuous organic lamns. Bioturbated                                                                                                                                    |                  |
| 16576/<br>DV1         | 788   | granular lrg but<br>not many | dolomite w gypsum inclusions; some areas of sm sucrosic dolo; lots of tiny sparkly flecks (calcite); some sm oval pieces of greenish br grain; bioturbated, fractures                                                                                               |                  |

| Appendix 1 Continued. |     |                        |                                                                                                                                                                                                                                                  |                                            |
|-----------------------|-----|------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|
| 16576/<br>DV1         | 801 | granular               | fine grained sucrosic dolo w more micrite matrix; some lrg pores; appears to be anhydrite in some areas (bluish); lots of organic laminations-tidal flat; dark splotches; tiny gold shimmer in pores and molds (pyrite?); some non sucrosic dolo | molds and pores                            |
| 16576/<br>DV1         | 815 | no visible             | non sucrosic dolo- ranges from light br to thick dk br to light again; thin layer of micrite; lots of tiny crystals-intraclasts; bw one dark and light there is black layer-organic splotches and dolo                                           | org dolo                                   |
| 16576/<br>DV1         | 820 | moldic                 | tan/grey splotchy dolo with some small sucrosic clear grains, oxidized organic areas. One extensive very red and orange other molds have lots oxidized orange red in them and others dk grey-rubble: possible cave breccia                       | molds                                      |
| 16576/<br>DV1         | 839 | granular some          | dolomite- some tiny sucrosic, most has very dull shine or is very tightly packed; some areas of gypsum. Grains range from cream to orangish br; trace quartz; exposed surface very br and other black (looks organic)                            |                                            |
| 16618<br>TR9-2        | 697 | granular/ moldic       | yellow tan sucrosic dolo w scattered amber crystals                                                                                                                                                                                              | amber crystals?                            |
| 16618<br>TR9-2        | 699 | granular/ moldic       | light yellow tan sucrosic dolo w lots sm and some lrg molds. Scattered pepper. Mold has grayish sheen in one area.                                                                                                                               | pepper                                     |
| 16618<br>TR9-2        | 701 | molds and granular     | semi sucrosic dolo lt br w lots of molds. One mold has oxidized surface some scattered black/amber crystals or areas                                                                                                                             | oxidized mold and scattered amber crystals |
| 16618<br>TR9-2        | 712 | granular               | packstone of sucrosic yellow, clear, tan calcite w some black pepper                                                                                                                                                                             | pepper?                                    |
| 16618<br>TR9-2        | 713 | lots mold and granular | yellow/br sucrosic dolo w lots of molds some large areas of grey black                                                                                                                                                                           | grey black areas                           |
| 16618<br>TR9-2        | 721 | lots granular          | recrystal packstone w orgs and molds. Pellated grains. Area w lots of pepper splatter                                                                                                                                                            | pepper                                     |
| 16618<br>TR9-2        | 725 | lots granular          | recrystal pelated packstone w lots of casts and some molds                                                                                                                                                                                       |                                            |
| 16618<br>TR9-2        | 727 |                        | wackestone w yellow calcite and some calcite is br or black. Scattered quartz                                                                                                                                                                    |                                            |
| 16618<br>TR9-2        | 728 | granular               | wackestone w yellow calcite and some areas of black/grey calcite. Some pepper                                                                                                                                                                    | pepper?                                    |
| 16618<br>TR9-2        | 736 |                        | wackestone w bands of yellow calcite. Porous only where molds are infilled. some pepper. Mold of shell w pellated material. Lots sm cubic calcite                                                                                                | pepper?                                    |
| 16618<br>TR9-2        | 737 | sm fracture            | packstone w micrite inclusions in molds. Some lrg casts, quite a few grey/black crystals. Fracture. Yellow br calcite                                                                                                                            | gr/black grains?                           |

| Appendix 1 Continued. |     |                                 |                                                                                                                                                                                                                                                                                            |                          |
|-----------------------|-----|---------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|
| 16618<br>TR9-2        | 741 |                                 | distinct changes b/w wacke and packstone w calcite crystals. Some are large and other are laminations of smaller crystals. Bottom has orange/yellow lrg grains-sharp contacts. Some crystals are grey black and scattered but not in bottom layers of br calcite with trace amber crystals | w calcite?               |
| 16618<br>TR9-2        | 742 |                                 | recrystal wackestone w yellow/white calcite and scattered gr/bl crystals. Molds-silver dollar w yellow calcite. Some mollusk casts                                                                                                                                                         | gr/bl crystals           |
| 16618<br>TR9-2        | 753 | moldic                          | yellow br dolo w oxidized br algal laminations                                                                                                                                                                                                                                             | oxidized laminations?    |
| 16618<br>TR9-2        | 756 | moldic                          | light tan semi sucrosic dolo with some oxidized areas                                                                                                                                                                                                                                      |                          |
| 16618<br>TR9-2        | 757 | moldic                          | dolo w discontinuous laminations. Some oxidized                                                                                                                                                                                                                                            | oxidized laminations     |
| 16618<br>TR9-2        | 759 |                                 | pack/wackestone w yellow and white calcite grains. Lots of laminations that almost look burnt and camo-black and dk reddish/orange br                                                                                                                                                      | w organic laminations?   |
| 16618<br>TR9-2        | 765 | lots granular in sucrosic       | half sucrosic br/orange dolo w micrite laminations and oxidized br/bl laminations and other half is sold dk br/orange dolo. Gre/yellow dolo piece w black ring around it                                                                                                                   | oxidized with dolo       |
| 16618<br>TR9-2        | 772 |                                 | gradational -upper has dk br/orange and black laminations. A band of quartz and then changes b/w blobs or bands of dense sucrosic calcite pack to wackestone areas that are somewhat pelated                                                                                               |                          |
| 16618<br>TR9-2        | 773 |                                 | pack/wackestone w oxidized algal laminations-br/black. Calcite areas have some amber crystals. Some calcite is yellow or white. some areas pack and other more micrite                                                                                                                     | amber crystals w calcite |
| 16618<br>TR9-2        | 782 | granular/ moldic                | recrystal packstone w lots of molds and some casts. Lots of oxidized algal laminations                                                                                                                                                                                                     | algal lamns?             |
| 16618<br>TR9-2        | 787 | lots sm granular                | yellow br sucrosic dolo w trace br/black amber crystals                                                                                                                                                                                                                                    | trace-amber crystals?    |
| 16618<br>TR9-2        | 802 | sm granular                     | pack/wackestone w yellow/white calcite and some peloids. Trace black gr grains                                                                                                                                                                                                             |                          |
| 16618<br>TR9-2        | 804 | sucrosic areas-granular\ moldic | semi sucrosic dolo w some molds. Trace pieces of br oxidized (amber color)                                                                                                                                                                                                                 |                          |
| 16618<br>TR9-2        | 814 | lots granular                   | sucrosic yellow/br dolo w fractures and large molds-oxidized br pieces in a mold. Scattered amber crystals                                                                                                                                                                                 | HFO? In mold             |
| 16618<br>TR9-2        | 817 | granular                        | medium dark brown sucrosic dolo w some micrite and calcite inclusions                                                                                                                                                                                                                      |                          |
| 16618<br>TR9-2        | 832 | granular tight                  | brown sucrosic dolo w some sm areas w micrite and calcite. Some small grains are stained orangish. Piece of oxidized black                                                                                                                                                                 | trace HFO?               |

| Appendix 1 Continued. |        |                                 |                                                                                                                                                                                                |                                    |
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| 16618<br>TR9-2        | 835    | moldic                          | dk br dolo w varying lighter areas. Trace amber crystals and areas. Lots sm calcite cubes                                                                                                      | trace amber crystals               |
| 16618<br>TR9-2        | 845    |                                 | br dolo with one sucrosic end. Dk grey/br laminations. Lots of small calcite cubes scattered. Some oxidized lamns w lots of pepper                                                             | oxidized lamns w pepper            |
| 16618<br>TR9-2        | 847    | sm mold and granular            | dk tan/br sucrosic dolo and some areas of lighter dolo                                                                                                                                         |                                    |
| 16618<br>TR9-2        | 848    | areas w molds and tiny granular | dk oxidized br dolo. Some areas sucrosic and others not. Possible algal laminations                                                                                                            | oxidized dolo and algal lamns?     |
| 16618<br>TR9-2        | 862    | lots granular                   | light br sucrosic dolo w some micrite                                                                                                                                                          |                                    |
| 16618<br>TR9-2        | 877    | sm granular                     | yellow br dolo-tightly packed sm grains. Sucrosic zones w molds w more sucrosic larger grains surrounding molds. Trace bl/gr grains                                                            |                                    |
|                       |        |                                 |                                                                                                                                                                                                |                                    |
| 16740<br>R39          | 991    | lots moldic, granular           | tan dolo with lots of molds, areas around and in molds are sucrosic cubes, white other blobs are semisucrosic/platy                                                                            |                                    |
| 16740<br>R39          | 992    | fractures, granular             | semisucrosic tan dolo with fractures. Scattered pieces of dk grey- pyrite? And also some amber grains                                                                                          | scattered pepper?                  |
| 16740<br>R39          | 995    | fractures, moldic               | banded sucrosic dolo- yellow to tan. Cubic crystals, moldic spaces with lots of cubic crystals. Grain space is very limited. Darker bands contain algal lamns- fractures run along             | with fractures and algal lamns?    |
| 16740<br>R39          | 996.5  | some moldic, granular           | semisucrosic yellow/tan dolo with small molds                                                                                                                                                  |                                    |
| 16740<br>R39          | 1001   | tiny granular, fractures        | semisucrosic tan dolo with lots of fractures. Band with splotchy oxidized dark burnt organics                                                                                                  |                                    |
| 16740<br>R39          | 1003   | fractures                       | semisucrosic tan dolo with fractures, black slippery bits on outside of core. Some areas with lots of tiny HFO and pyrite. Scattered dark areas in grains                                      | peppered with HFO, in dolo grains? |
| 16740<br>R39          | 1005   | fractures                       | cream wackestone with partially dolo semisucrosic grains. Lots of lamns of oxidized organic grades into a more crystalline dolo with fractures filled with sucrosic crystals and organic lamns |                                    |
| 16740<br>R39          | 1005.5 | moldic, granular                | semisucrosic tan dolo with fractures and bands and lamns of dark organic                                                                                                                       |                                    |
| 16740<br>R39          | 1006.5 |                                 | semisucrosic tan dolo with bands of darker dolo. Some grains are a dark grey. Some molds with cubic crystals                                                                                   | with dolo?                         |
| 16740<br>R39          | 1010.5 | good amt granular               | packstone with lots of small molds and casts. Trace pieces of organic and possible pyrite                                                                                                      | trace pieces?                      |

| Appendix 1 Continued. |         |                          |                                                                                                                                                                                                                                                                                                     |                                 |
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| 16740<br>R39          | 1011.5  | moldic, lots<br>granular | cream/tan packstone with peloidal and branching grains. Some areas have recemented pore spaces, outside of core has lots of black pepper - contamination?                                                                                                                                           |                                 |
| 16740<br>R39          | 1680    |                          | massive deposit of opaque white with vitreous pearly anhydrite crystals and also darker grey ones. Veins of an organic tan type material                                                                                                                                                            |                                 |
| 16740<br>R39          | 1685.5  | tiny granular            | cream micrite with lots of small pieces of pyrite and very small HFO. Thin lamns of splotchy organic                                                                                                                                                                                                | pieces in micrite with HFO      |
| 16740<br>R39          | 1687.5  | moldic, fractures        | heavily compacted and cemented tan micrite. Lots of small molds, most concentrated in a band. Molds have HFO and pyrites in them. Fractures filled with anhydrite. Large clasts of bluish gray anhydrite                                                                                            | in molds with HFO               |
| 16740<br>R39          | 1689    |                          | heavily compacted recrystal limestone with lots of bits and pieces of organics, pyrites, tiny lamns of organic. Thick lamn of dk burnt organic with tiny "mud cracks"                                                                                                                               |                                 |
| 16740<br>R39          | 1690    | moldic                   | packstone with lots of molds leaving a branching matrix. Most molds filled with anhydrite. Large band of large anhydrite. Layer of less molds with more infilled matrix. Small molds                                                                                                                |                                 |
| 16740<br>R39          | 1694    | fractures                | micrite with lots of fractures. Gypsum-glassy fibrous is in some fractures and areas. Organic and pyrite bits are scattered throughout                                                                                                                                                              | scattered with organic          |
|                       |         |                          |                                                                                                                                                                                                                                                                                                     |                                 |
| 16783/<br>R22         | 941-942 | granular sm              | tan wackestone w fine white casts in molds, mostly very fine grains of calcite and quartz; some dolo laminations (w pyrite?) some crystals in molds are black. Bioturbated                                                                                                                          | with dolo laminations and molds |
| 16783/<br>R22         | 944     | fractures/<br>granular   | wackestone w fossils; 2ndary calcite w quartz; molds and fractures; one chunk of dark/br/bl w possible pyrite                                                                                                                                                                                       | possible                        |
| 16783/<br>R22         | 954     | granular                 | very fine recrystallized wackestone with large echinoid molds, some filled with cast of lighter limestone; black flecks some oxidized in clay layer; 1 pc has distinct change bw porous limestone and a tan more dolomitized mud; calcite replacement in molds, possible dolomite, mold with pyrite | yes                             |
| 16783/<br>R22         | 960     | lots granular            | secondary calcite forms lots of casts. Wacke/packstone -storm deposits? Trace grey calcite, calcite grains make up rest and then some mudstone                                                                                                                                                      |                                 |
| 16783/<br>R22         | 964     | granular tiny            | chalky tan/white limestone; very fine grained packstone; seems compressed-everything oriented in one direction; few grains visible; lots of black flecks. Bioturbated. Echinoids                                                                                                                    | lots flecks?                    |

| Appendix 1 Continued. |               |                             |                                                                                                                                                                                                                                                                                   |                    |
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| 16783/<br>R22         | 978           | granular tiny               | chalky white recrystal limestone; some visible intraclasts; cross bedding. some molds filled w calcite and possible pyrite; scattered black flecks (organic/pyrite?); some oxidized areas                                                                                         | molds and pepper   |
| 16783/<br>R22         | 982           | granular tiny/<br>fractures | tan very fine recrystal limestone mud; some tiny calcite in fractures; scarce spotted oxidized particles                                                                                                                                                                          |                    |
| 16783/<br>R22         | 989           | granular tiny               | fine grained recrystal wackestone lots of molds; no visible grains except in molds; some quartz; possible pyrite in a mold; lithoclasts. lots of reddish br laminations (organic)                                                                                                 | trace in mold      |
| 16783/<br>R22         | 994           | granular                    | limestone with lots of the splotchy organic (grey, br, black) lamns some have dark rings with a browner inside and trace sparkly (quartz/pyrite?) sm molds; one piece has orange/br coating (oxidized?) w/ possible pyrite; some sm quartz. Tidal flat                            | likely             |
| 16783/<br>R22         | 999           | granular                    | limestone w fine matrix and lots of tanish euhedral dolo crystals; some dark black and brown laminations (organic); sm quartz frags; some pepper. Tidal flat                                                                                                                      |                    |
| 16783/<br>R22         | 1001          | granular/fractures          | pure white recrystal limestone matrix w calcite that has filled veins and molds, some dolomitized; lots of quartz; lots of molds and fractures; piece with more pure limestone w dolo calcite that forms laminations. Tidal flat                                                  | possible pepper    |
| 16783/<br>R22         | 1004-<br>1007 | granular /moldic            | chalky white recrystal limestone w very fine matrix; some tiny quartz; fine dark br/bl laminations (organic splotches); another piece has grains partially dolomitized (pack/wackestone) with some fine limest inclusions; some pepper; laminations of fine limestone. tidal flat | pepper             |
| 16783/<br>R22         | 1017          | granular sm                 | light tan limestone; very fine band of calcite grains; some dark grey; possible pyrite rhombs and oxidized areas bioturbated                                                                                                                                                      | possible rhombs    |
| 16783/<br>R22         | 1020          |                             | cream wackestone with yellow and grey calcite casts and grains, some molds and casts                                                                                                                                                                                              |                    |
| 16783/<br>R22         | 1022          | granular                    | white limestone; fine grained w groupings of calcite that are opaque, some have dark ring and br/gr inside; some br and black on calcite (organic?) possible pyrite; lots of dark organic laminations-tidal flat                                                                  | with organic       |
| 16783/<br>R22         | 1040          | lots granular               | cream recrystal packstone with some casts with calcite, rest are calcite grains, trace casts have grey assoc with them                                                                                                                                                            |                    |
| 16783/<br>R22         | 1045          | granular                    | chalky white recrystal limestone w fine matrix; few calcite grains; some quartz; some sm pores and molds; scattered dark grains/flecks (pyrite?)                                                                                                                                  | grains and flecks? |

| Appendix 1 Continued. |        |                        |                                                                                                                                                                                                                                |                    |
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| 16783/<br>R22         | 1061   | granular /moldic       | chalky white limestone; large pores and empty spaces where shell frags were, some shell frags and echinoids; calcite in lrg molds; sm quartz; trace br in molds (organic) - very fine reworked layer                           |                    |
| 16783/<br>R22         | 1075   | granular               | relatively pure recrystal packstone, some sm molds w black or red material; some calcite in molds-miliolidae, forams, echinoids                                                                                                | molds?             |
| 16783/<br>R22         | 1080   | granular               | grainstone w molds-miliolidae, forams, echinoids filled w calcite; reworked secondary limestone; molds w calcite and br/bl organic; black flecks                                                                               |                    |
| 16783/<br>R22         | 1101.5 | granular, moldic       | recrystal (half packstone w lots of casts and molds, other is wackestone with molds) more porosity with packstone, oxidized red/orange in a linear pattern-areas of water flow? Trace grey calcite as casts-miliolidae, forams |                    |
| 16783/<br>R22         | 1120   | granular               | part is peloidal grainstone with some grey/blue lithoclasts Rest has very large mudstone with molds and infilled with grains. Some oxidized areas                                                                              |                    |
| 16783/<br>R22         | 1124   | granular               | looks like a breccia but has pure fine grained limestone inclusions w mostly dark orange/br dolo crystals-mud cracks; dark rings around some veins and molds; some glassy quartz in veins; possible pyrite-tidal flat          | possible           |
| 16783/<br>R22         | 1139   | granular sm            | tan limestone matrix with yellowish dolo crystals (packstone); some quartz                                                                                                                                                     |                    |
| 16783/<br>R22         | 1146.5 | granular               | tannish to light br sucrosic dolo; sig amt of pores/voids bound by less porous; lrg amt of quartz-some in molds; sm inclusions of micrite; dk bl/br grains scattered pyrite?                                                   | scattered          |
| 16783/<br>R22         | 1159   | moldic                 | tan dolomite w clear calcite crystals in molds, lamns of organic intertidal                                                                                                                                                    |                    |
| 16783/<br>R22         | 1165   | granular in dark bands | tan to creamy limestone w dolo laminations/bands of light brown; some limited quartz and oxidized organic pieces?; laminations of organic; some molds with darker br/bl organic                                                | molds and organic? |
| 16783/<br>R22         | 1170   | granular               | partially dolo limestone- lithoclasts limestone; lots of grain supported yellow/br dolomite crystals; tiny glassy quartz; likely pyrite w/in dolomite                                                                          | likely             |
| 16783/<br>R22         | 1174   | granular               | chalky white recrystal limestone, fine grained w lots of scattered yellow br dolo crystals -wackestone; possible pyrite on dolo; distinct boundaries bw limestone and dolo layers; sm quartz                                   | with dolo          |
| 16783/<br>R22         | 1180   | granular/fractures     | tan limestone w clay layer containing 2ndary calcite-collapse fill; sm fractures; pyrite-black framboids                                                                                                                       | framb?             |

| Appendix 1 Continued. |      |                    |                                                                                                                                                                                                                                                                                                                    |              |
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| 16783/<br>R22         | 1185 | granular           | mostly tan sucrosic dolo crystals w fine grained limestone lithoclasts and matrix; a lot of rather lrg anhydrite crystals (diamond like); reworked grains; lrg fine grained bands w thin dark ones; calcite; dark minerals (Mg?); spotted dark organic circles-collapse fill/breccia                               | high Sr      |
| 16783/<br>R22         | 1189 | lots granular      | dk br sucrosic dolo w fractures and pore spaces; some calcite; some limestone inclusions; lots of br and black flecks (pyrite?); lots of little anhydrite. Collapse fill-breccia                                                                                                                                   | flecks?      |
| 16783/<br>R22         | 1195 | granular/fractures | half is light br dolo w limestone inclusions and other is dark fr-more clumped grains of dolomite-collapse fill breccia; another piece is very dark dolo; all sucrosic; dark has voids and fractures bw grains; molds have oxidized organic; some sm black in lighter portion (pyrite?) and some oxidized surfaces |              |
| 16783/<br>R22         | 1200 | large moldic       | dark brown oxidized dolo with small clear calcite crystals scattered. Collapse fill-breccia Molds are usually large and some infilled with smaller grains. Organic lamns                                                                                                                                           |              |
| 16783/<br>R22         | 1282 | granular           | crystalline calcite cement w tiny quartz, lots of molds filled w chalky limestone or orangish almost sandy texture (spar?); peloidal grains; some shell frags, lots of clumps have sparry coating; black lamination                                                                                                | possible     |
|                       |      |                    |                                                                                                                                                                                                                                                                                                                    |              |
| 16913<br>R5           | 1081 |                    | cubic calcite w micrite, wackestone small fractures, siliclastic areas-grey, trace pyrite                                                                                                                                                                                                                          | trace        |
| 16913<br>R5           | 1082 | vugs               | dk br muddy material w micrite areas and dk black pieces-camo looking. Sharp contact                                                                                                                                                                                                                               |              |
| 16913<br>R5           | 1086 |                    | quartz with cubic calcite crystals, trace micrite, scattered pepper, grey smoky quartz wavy throughout. Sharp contact                                                                                                                                                                                              | pepper       |
| 16913<br>R5           | 1086 | lots granular      | recrystal wackestone with calcite and trace pepper                                                                                                                                                                                                                                                                 | trace pepper |
| 16913<br>R5           | 1098 |                    | quartz and calcite with micrite wacke/packstone with pepper, pyrite pieces-br/orange bl. lithoclasts                                                                                                                                                                                                               | pepper       |
| 16913<br>R5           | 1106 |                    | quartz w fine white micrite (no effervescence) pepper and oxidized black/br/bronze pieces (strands)-pyritized sea grass                                                                                                                                                                                            |              |
| 16913<br>R5           | 1107 |                    | quartz mudstone w gold shimmer and dk bands w bronze mineral. Reddish dolo matrix                                                                                                                                                                                                                                  |              |
| 16913<br>R5           | 1128 | granular           | recrystal packstone w some pepper                                                                                                                                                                                                                                                                                  | pepper?      |
| 16913<br>R5           | 1131 | some granular      | recrystal packstone some pepper                                                                                                                                                                                                                                                                                    | pepper?      |

| Appendix 1 Continued. |      |               |                                                                                                                                                                                                              |                          |
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| 16913<br>R5           | 1156 | sm granular   | recrystal packstone w casts and molds, some pepper and quartz                                                                                                                                                | pepper?                  |
| 16913<br>R5           | 1172 | lots granular | recrystal wackestone, creamy white, shell frags, casts and molds-miliolidae, forams, echinoids, trace pepper, one mold w dk br calcite and gold shimmer-vugs filled with overlying facies. Pref cementation. | pepper                   |
| 16913<br>R5           | 1181 | sm granular   | recrystal wackestone w grey muddy coatings (clay?) very fine-poor recovery                                                                                                                                   |                          |
| 16913<br>R5           | 1199 |               | recrystal packstone, tiny calcite cubes, calcite molds, trace tiny pepper. bioturbated                                                                                                                       | pepper?                  |
| 16913<br>R5           | 1203 |               | recrystal limestone, micrite w some pepper and possible pyrite, sm quartz/calcite, black in some cracks, lamination of tan organic with dk br speckles on it. Bioturbated                                    | pepper and cracks        |
| 16913<br>R5           | 1206 | sm granular   | fine recrystal limestone w pepper. Bioturbated                                                                                                                                                               | pepper?                  |
| 16913<br>R5           | 1228 | sm granular   | recrystal/packstone with calcite casts-miliolidae, forams, echinoids, bivalves, quartz, grey smokey quartz? Pepper                                                                                           | pepper?                  |
| 16913<br>R5           | 1231 | low           | recrystal wackestone w large oval molds (miliolidae, forams, echinoids, bivalves and calcite, good amt of pepper and large pepper- siliclastic material in mold                                              | pepper? - siliclastic    |
| 16913<br>R5           | 1256 |               | recrystal wackestone w orgs, lots of pepper, sm quartz or calcite, some reddish/br pieces (HFO?). Bioturbated. Miliolidae, forams, bivalves                                                                  |                          |
| 16913<br>R5           | 1259 | sm granular   | packstone of yellow calcite and lots sm sucrosic, pepper and black pieces. Bioturbated. Miliolidae, forams, bivalves                                                                                         | pepper/pieces?           |
| 16913<br>R5           | 1260 |               | yellow calcite and quartz, micrite infill, lots pepper Miliolidae, forams, bivalves                                                                                                                          | pepper?                  |
| 16913<br>R5           | 1274 | no visible    | packstone w calcite and lots of black/grey mineral, some quartz. Bioturbated. Miliolidae, forams, bivalves                                                                                                   |                          |
| 16913<br>R5           | 1281 | sm granular   | recrystal limestone w some sm casts and molds-Miliolidae, forams, bivalves, micrite, good amt pepper-some black-siliclastic and other br-pyrite? Bioturbation. Scattered phosphate                           | pepper? With siliclastic |
| 16913<br>R5           | 1304 | granular      | recrystal limestone w lots calcite and pepper, black in sm molds, casts and grayish black in some areas, some shell frags. Bioturbation scattered phosphate. Miliolidae, forams                              | pepper and molds         |
| 17000<br>R28          | 860  |               | recrystal wackestone w small scattered dk grey molds, circular and elongate. Trace are oxidized red.                                                                                                         |                          |
| 17000<br>R28          | 863  | moldic        | tan wackestone with yellow/tan calcite filling molds of various orgs and lots of dk grey calcite filling molds, some possible pyrite                                                                         | possible pyrite          |

| Appendix 1 Continued. |      |                       |                                                                                                                                                                                                                    |                                                |
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| 17000<br>R28          | 864  | granular, fracture    | wackestone cream with lots of casts-peloidal and sand dollars, possible chert nodule, one end has lots of grey/blue calcite                                                                                        |                                                |
| 17000<br>R28          | 866  | granular              | packstone fossiliferous with peloids and mollusks and some sand dollars                                                                                                                                            |                                                |
| 17000<br>R28          | 910  | granular              | cream recrystal micrite-XRD shows pure calcite with some peloidal fossil grains, some other fossil molds with calcite, trace organic flecks                                                                        |                                                |
| 17000<br>R28          | 958  | limited moldic        | light tan dolo grainstone w small clear calcite crystals scattered throughout. Trace spots of possible HFO or pyrite. Molds filled w crystalline dolo. Laminations-tidal flat                                      | trace pepper of HFO and pyrite possible        |
| 17000<br>R28          | 960  | limited tiny granular | recrystal cream wackestone with bands and lamns of yellowish calcite? Tidal flat                                                                                                                                   |                                                |
| 17000<br>R28          | 965  | limited granular      | white recrystal packstone w lots of calcite forming molds, peloidal, mollusk, sand dollar, trace impurity flecks, couple algal lamns                                                                               |                                                |
| 17000<br>R28          | 1010 | granular              | cream recrystal wackestone w scattered fossil molds-miliolidae, forams, echinoids. Bioturbated                                                                                                                     |                                                |
| 17000<br>R28          | 1060 | granular              | recrystal cream wackestone w molds, trace dk grey slivers some yellow/br oxidized lamns-green algae. Echinoids                                                                                                     | dk grey slivers?                               |
| 17000<br>R28          | 1063 | granular              | packstone w lots of peloidal grains and sand dollar fossils. Some large casts of mudstone-very pure. Tidal flat                                                                                                    |                                                |
| 17000<br>R28          | 1069 |                       | cream/white recrystal limestone with thin mm brown/orange lamns of organic and trace pepper flecks-upper intertidal to lower supratidal                                                                            | trace pepper flecks with organic lamns         |
| 17000<br>R28          | 1110 | lots granular         | cream grainstone with peloidal well sorted grains, large fracture running through. Miliolidae                                                                                                                      |                                                |
| 17000<br>R28          | 1160 |                       | recrystal cream mud/wackestone, thick layers of heavily oxidized brown with limestone inclusions. Some algal lamns-burnt looking-tidal flat                                                                        |                                                |
| 17000<br>R28          | 1163 |                       | cream mudstone inclusions surrounded by a matrix of tan/grey mudstone with lots of organic mixed in. organic lamns. Black pieces of organic. Bioturbated. Tidal flat                                               |                                                |
| 17000<br>R28          | 1213 | granular, moldic      | looks like a breccia with matrix of an iron stained color, lithoclasts are large and small tan and cream wackestone w calcite grains. Some molds and pore spaces have oxidized organic and possible HFO and pyrite | possible HFO and pyrite in mold and pore space |
| 17000<br>R28          | 1214 | some moldic           | recrystal limestone cream bands; rest is brownish oxidized lamns some very dk, fine sucrosic grains-mudstone intraclasts                                                                                           |                                                |

| Appendix 1 Continued. |        |                  |                                                                                                                                                                                                                                         |                               |
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| 17000<br>R28          | 1218   | some granular    | grey/tan recrystal wackestone with molds-forams, grey flecks/pepper, some organic lamns and areas. Pieces of oxidized brown scattered-tidal flat                                                                                        | pepper and ox pieces          |
| 17000<br>R28          | 1224.5 |                  | partially dolo recrystal cream wackestone with lots of grey blue molds. bioturbated                                                                                                                                                     |                               |
| 17000<br>R28          | 1228   | moldic, granular | recrystal tan wackestone w some peloidal grains. Lots of oxidized algal lamns-tidal flat. Miliolidae, forams, bivalves, indurated                                                                                                       |                               |
| 17000<br>R28          | 1238   | granular, moldic | looks like breccia w oxidized brown matrix clasts are cream limestone. Matrix is calcite but is yellow and br and oxidized. Some are dk grey-pyrite?                                                                                    | pyrite with oxidized calcite? |
| 17000<br>R28          | 1242.5 |                  | tan dolo wackestone matrix with flecks of organics and tan calcite lithoclasts and some grey flecks. Algal lamns-thin and oxidized. Grades into a partially dolo w lots of clear crystal cubes and heavily oxidized organics-supratidal |                               |
| 17000<br>R28          | 1253   | moldic           | recrystal cream wackestone w molds of grey blue calcite and some areas with orangish stain- organics? Peppered areas, miliolidae, echinoid                                                                                              | pepper areas, orange stain    |
|                       |        |                  |                                                                                                                                                                                                                                         |                               |
| 17001<br>R14          | 1019   | some moldic      | chalky micrite w some calcite and lots casts-sm lots of slivers of possibly organic                                                                                                                                                     |                               |
| 17001<br>R14          | 1031   | granular         | packstone of yellow calcite that has replaced orgs-form casts, some clear calcite                                                                                                                                                       |                               |
| 17001<br>R14          | 1045   | granular moldic  | high porosity, pelleted zone w lots of molds and casts and clear calcite rhombs and cubes, capped by a micrite w lots of scattered pepper, some quartz                                                                                  | lots pepper in micrite        |
| 17001<br>R14          | 1049   | tiny granular    | pure white recrystal chalky micrite                                                                                                                                                                                                     |                               |
| 17001<br>R14          | 1077   |                  | recrystal wacke w tiny yellow calcite grains, molds filled w grey/blue calcite, some oxidized orange pieces, trace pepper, scattered clear mineral                                                                                      | trace pepper                  |
| 17001<br>R14          | 1079   | granular         | wackestone w some bands w more micrite and others w more yellow calcite, lots of clear calcite, trace grey/blue calcite, some zones more porous, trace organic bits and possible trace pyrite                                           | trace possible                |
| 17001<br>R14          | 1083   | granular         | pelleted micrite grains and some yellow calcite mixed in (partially dolo) also lots of clear calcite                                                                                                                                    |                               |
| 17001<br>R14          | 1109   | granular mold    | recrystal micrite w trace organic specks, some tiny clear calcite/quartz                                                                                                                                                                |                               |
| 17001<br>R14          | 1117   |                  | grainy micrite w bands of diff colors of micrite- grey and tan br w pepper scattered throughout but more prevalent w bands                                                                                                              | pepper and w bands            |

| Appendix 1 Continued. |      |                           |                                                                                                                                                                                                                                     |                                  |
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| 17001<br>R14          | 1121 | granular moldic           | packstone w lots of molds and casts, lrg molds filled w yellow calcite, trace pepper in some areas and grain spaces                                                                                                                 | trace pepper                     |
| 17001<br>R14          | 1139 |                           | micrite w bands of dk tan (calcite?) containing lots of pepper (pyrite) rest of micrite has trace pepper and organic pieces                                                                                                         |                                  |
| 17001<br>R14          | 1140 |                           | recrystal wacke w micrite casts and lrg oval molds w yellow and white calcite, some lined w grey, some quartz and anhydrite                                                                                                         |                                  |
| 17001<br>R14          | 1167 | lots granular             | pelleted grainstone w 2 large molds filled w yellow calcite, trace pepper                                                                                                                                                           | trace pepper                     |
| 17001<br>R14          | 1169 | granular                  | recemented grains w casts-sm, packstone grain spaces infilled w smaller grains, some areas slightly oxidized                                                                                                                        |                                  |
| 17001<br>R14          | 1186 | granular sm               | recrystal wacke w some yellow calcite grains and sm perfect calcite grains, layer of oxidized organic lamns some sm pepper-pyrite?                                                                                                  | pepper in organic lamns          |
| 17001<br>R14          | 1192 | mold and sm granular      | sucrosic partially dolo pack/grainstone w some molds and casts, tiny grains, fracture zone                                                                                                                                          |                                  |
| 17001<br>R14          | 1199 |                           | wackestone w calcite grains, some molds have br organic in them, scattered blue/grey calcite and noncontinuous lamns of yellow calcite, some large casts (oval) some scattered organic and clear crystals                           |                                  |
| 17001<br>R14          | 1226 | granular lots             | lots of pelleted grains w some branching solid calcite and some lrg solid molds                                                                                                                                                     |                                  |
| 17001<br>R14          | 1229 | granular                  | recrystal wackestone w casts and some tiny calcite and quartz some pepper and oxidized pieces, some organic areas,                                                                                                                  | pepper and oxidized?             |
| 17001<br>R14          | 1233 | granular                  | partially dolo packstone w lots yellow calcite and micrite inclusions, lots of glassy cubic calcite, some oxidized organic lamns, pieces possible pyrite                                                                            | pieces                           |
| 17001<br>R14          | 1246 |                           | micrite w changing bands of color, goes from cream to more tan, some lamns of grey/dk grey-clay, lots peppered organic and possibly pyrite                                                                                          | possible pepper w organic        |
| 17001<br>R14          | 1248 | limited granular, burrows | recrystal wacke w 2 zones of high granular porosity w tanish calcite and pepper and some sm casts and molds. Rest is micrite w grey/bl calcite, lrg mold w grey calcite and possible pyrite, perfect rainbow calcite in molds/pores | mold w calcite?                  |
| 17001<br>R14          | 1259 | lots granular             | grainstone w peloids w micrite and rest are yellow/tan calcite pellets                                                                                                                                                              |                                  |
| 17001<br>R14          | 1260 | lots granular             | grainstone w white casts and rests of grains are pelleted                                                                                                                                                                           |                                  |
| 17001<br>R14          | 1269 | lots granular             | pelleted grainstone w lots porosity, trace pepper-pyrite but some surfaces stained orange w lots of pepper and what looks like HFO                                                                                                  | pepper on surface in pores w HFO |

| Appendix 1 Continued. |      |                          |                                                                                                                                                                                  |                                                             |
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| 17001<br>R14          | 1277 | sm granular              | micrite w scattered organic bits, some pelleted grains, casts and molds                                                                                                          |                                                             |
| 17056<br>R9           | 1041 | moldic                   | lt br dolo w lots of small molds, pyrite is trace in molds, zone of amber br on dolo                                                                                             | trace in molds                                              |
| 17056<br>R9           | 1049 | moldic and lots granular | sucrosic dolo w lots of lrg molds giving very high permeability and porosity. Molds filled w clear sucrosic cubes, pyrite and HFO                                                | pyrite in molds w calcite and HFO                           |
| 17056<br>R9           | 1052 | tiny granular            | sm sucrosic dolo w some sm molds, pyrite is peppered throughout and in short concentrated lamns and in molds. Some molds with HFO and pyrite. 1 large blob w lots pyrite and HFO | pepper, lamns, molds, w HFO                                 |
| 17056<br>R9           | 1056 | moldic                   | semisucrosic br dolo w lots of med molds, some w pyrite-usually smaller ones and good amt of these w HFO                                                                         | molds w pyrite and HFO                                      |
| 17056<br>R9           | 1058 | lots granular and moldic | sm sucrosic dolo w lots of molds for high permeability and porosity, some molds w pyrite, half of dolo is a lighter color and has orange oxidized tint-HFO                       | in molds, oxidized dolo with HFO                            |
| 17056<br>R9           | 1071 | granular                 | br sucrosic dolo w some sm molds. Pyrite is in short wavy lamns and scattered and in mold, trace HFO                                                                             | pyrite in short lamns, pepper, mold, trace Hfo              |
| 17056<br>R9           | 1074 | moldic                   | lt br dolomite-sucrosic in molds, lots of sm molds-pyrite in molds w cubic dolo, trace HFO in molds and one piece                                                                | in molds w clear crystals and some HFO                      |
| 17056<br>R9           | 1084 | granular                 | sucrosic lt br dolo w lots sm molds. Some molds w cubic crystals and pyrite. Some pepper, some HFOs w pyrite and trace pieces HFO                                                | pyrite in molds w cubic crystals, pepper, some HFO w pyrite |
| 17056<br>R9           | 1086 | some moldic              | semisucrosic lt br dolo w lots of sm and some big molds. Trace molds have pyrite but all have cubic dolo                                                                         | some molds w cubic dolo                                     |
| 17056<br>R9           | 1098 | gran                     | sm sucrosic dolo w some sm molds, lamns are somewhat oxidized br on dolo grains, peppered pyrite throughout and pyrite in molds, trace oxidized pieces                           | pepper and molds, oxidized areas?                           |
| 17056<br>R9           | 1101 | granular                 | very sucrosic lt br dolo w shallow sm molds throughout. Most molds filled w pyrite and trace HFO, lots of clear sucrosic cubes                                                   | in molds w HFO                                              |
| 17056<br>R9           | 1116 |                          | very fine sucrosic dolo grains- powdery w pepper and trace HFO pieces                                                                                                            | pepper and trace HFO                                        |
| 17056<br>R9           | 1117 | granular moldic          | sucrosic dolo w sm molds w clear dolo, pyrite is peppered and in molds. Lrg areas of oxidized burnt orange w larger pyrites                                                      | pepper, molds, oxidized areas                               |
| 17056<br>R9           | 1120 | granular                 | semi sucrosic dolo w sm molds, lrg cast of shell. Pyrite in molds w cubic dolo and some w lots of HFO. Pyrite and oxidized on shell cast                                         | molds w cubic dolo and HFO, on shell cast w oxidized        |

| Appendix 1 Continued. |               |                        |                                                                                                                                                                                                                                                                                                              |                                                        |
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| 17056<br>R9           | 1124          | tiny granular          | very fine sucrosic dolo w bits of peppered pyrite scattered throughout and some HFOs- 1lrg piece, gradational color changes-kind of camo                                                                                                                                                                     | pepper and HFO                                         |
| 17056<br>R9           | 1131          | granular               | sm sucrosic lt br dolo w sm molds throughout. Pepper pyrite throughout and in molds w cubic clear dolo and some HFO                                                                                                                                                                                          | pepper, molds w clear calc and HFO                     |
| 17056<br>R9           | 1145          | tiny granular          | tiny sucrosic dolo w some larger crystals scattered throughout. Darker bands of dolo in one section. Pyrite and peppered throughout and some conc. Some HFOs conc on large pyrites and what seem to be preexisting molds                                                                                     | pepper and conc, HFO on lrg pyrites and casts in molds |
| 17056<br>R9           | 1147          | limited                | most just lt br dolo w sm molds throughout. Pepper pyrite throughout and in molds w cubic clear dolo and some HFOs                                                                                                                                                                                           | pepper and molds w clear dolo and HFO                  |
| 17056<br>R9           | 1157          | lots mold and granular | lrg sucrosic dolo w molds, trace HFO and pyrite-pyrite is concentrated in a couple molds                                                                                                                                                                                                                     | molds w HFO                                            |
| 17056<br>R9           | 1160          | moldic and granular    | dolo w lots of lrg oval and sm molds filled w secondary spar and micrite, some calcite is reddish br or grey. Fracture in dolo, granular porosity in molds                                                                                                                                                   |                                                        |
| 17056<br>R9           | 1161          | granular and moldic    | light tan sucrosic dolo w finer tiny grains. Some sm molds and a lrg oval one, some grains are grey or dk                                                                                                                                                                                                    |                                                        |
| 17056<br>R9           | 1173          | granular and moldic    | repeating intervals of fine grained br sucrosic dolo w peppered pyrite and layers w lots of lrg oval molds and smaller molds w recrystal calcite grains-lrg and micrite, some grains dk grey. Trace HFO and some molds w pyrite                                                                              |                                                        |
| 17056<br>R9           | 1174-<br>1175 |                        | lrg dolo crystals w lots of lrg oval casts filled w a white crystallized micrite, some dolo crystals are grayish                                                                                                                                                                                             |                                                        |
|                       |               |                        |                                                                                                                                                                                                                                                                                                              |                                                        |
| 17087<br>R20          | 1208          |                        | wackestone with small grains of yellow and grey calcite. Some lamns of larger yellow and grey grains and some are vertical-path of water flow. Band of more concentrated grains at top with some organic lamns- bioturbated tidal flat. Miliolidae, forams, bivalves                                         |                                                        |
| 17087<br>R20          | 1215          | granular               | dull light gray limestone w fine matrix but mostly grain supported packstone w fine laminations of organic and sm pores; molds-miliolidae, forams, bivalves filled with limestone; mold w br/bl and possible frambis; veins w calcite and dark material; some spots w lots of br/bl and pyrite? bioturbated. | possible in molds and vein                             |
| 17087<br>R20          | 1222.5        |                        | very fine grained white chalky recrystal limestone; trace yellow dolo grains ; some black flecks(pyrite) and red/br organic and in tiny short laminations                                                                                                                                                    | flecks                                                 |

| Appendix 1 Continued. |        |                    |                                                                                                                                                                                                                                                                                                                                     |                                 |
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| 17087<br>R20          | 1229   |                    | very fine grained limestone w tiny laminations of red/br; lighter band on piece and darker ones on others; exposed laminations show dk grey organic material w some oxidized areas and possible frambes present; trace tiny quartz; couple yl/br dolo grains w possible frambes. tidal flat. miliolidae, forams, bivalves           | frambes-org& dolo               |
| 17087<br>R20          | 1233   | granular sm        | chalky white recrystal limestone w lots of grey laminations of organic and iron stained material- tidal flat storm deposits; sm br spots-pyrite on calcite?; some calcite crystals in molds- miliolidae, forams                                                                                                                     | w calcite?                      |
| 17087<br>R20          | 1237   |                    | fine grained matrix -packstone; molds; trace quartz; trace molds have some black in them (pyrite) miliolidae, forams, echinoids, bivalves                                                                                                                                                                                           | molds                           |
| 17087<br>R20          | 1243   | granular fractures | partially dolo limestone w lots of fractures; lots of br/gr/bl ppt on areas where fractures are or were -grey silica w pyrite?; lots of casts filled with yellow/br recrystal lime; some dolo grains; appears to be frambes-dolo w br/bl things; some molds are filled w pure micrite miliolidae, forams, echinoids                 | fractures; frambes              |
| 17088<br>R20          | 1253   | granular           | packstone with secondary calcite forming the grains and casts, trace grey calcite. Miliolidae, forams, echinoids                                                                                                                                                                                                                    | with calcite?                   |
| 17087<br>R20          | 1259   | granular tiny      | fine recrystal limestone w some dolo grains; some gray grains; few molds w calcite and quartz; one has yellow/br mineral; trace red br - shaped flecks again. Miliolidae, forams, echinoids                                                                                                                                         |                                 |
| 17087<br>R20          | 1268   |                    | grey recrystal limestone w lots casts of small shells; scarce pyrite in some molds?; some calcite and reddish br organic in molds; quartz; black piece-sparkly (pyrite?) bioturbated. Miliolidae, forams, echinoids. Indurated                                                                                                      | mold? Black piece               |
| 17087<br>R20          | 1269   | granular tiny      | very fine grained recrystal limestone matrix w tiny grains and lots of molds molds have red/br organic; some larger dolo grains (yl/br) w quartz; area w grey/br splotches - possible silica pyrite; trace tiny quartz. Bioturbated, miliolidae, forams, echinoids. indurated                                                       | silica                          |
| 17088<br>R20          | 1283.5 |                    | recrystal cream micrite with some sm grey grains. Trace casts with yellow secondary calcite. Miliolidae, forams, echinoids, bivalves. Indurated                                                                                                                                                                                     | with calcite?                   |
| 17087<br>R20          | 1285   | granular           | recrystal limestone w lots of molds and casts of shells and actual shells; some calcite(yellow/white); part partially dolo with recrystal calcite in molds. laminations with pyrite; lrg mold filled w calcite and limestone and iridescent quartz; possible pyrite with calcite Miliolidae, forams, echinoids, bivalves. Indurated | calcite in mold, lamn of pyrite |

| Appendix 1 Continued. |      |                          |                                                                                                                                                                                                                                                                                                                                          |                      |
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| 17087<br>R20          | 1300 | granular                 | recrystal limestone w lots of shell molds and casts and fossils; trace pyrite in pores; calcite in molds Miliolidae, forams, echinoids, bivalves. Indurated                                                                                                                                                                              | pores                |
| 17087<br>R20          | 1307 | granular/moldic          | recrystal limestone w fine matrix; fine br/reddish laminations (organic) other flecks; trace tiny quartz; layer of gr/bl organic; some grey/blue calcite grains; some br black splotches (organic) w possible framb Miliolidae, forams, echinoids, bivalves. Indurated                                                                   | organic              |
| 17087<br>R20          | 1309 | granular fractures       | recrystal limestone w oxidized zones in fractures; some dark (organic/clay?) in some of the zones; sm pores; some molds and casts; calcite present Miliolidae, forams, echinoids, bivalves. Indurated                                                                                                                                    | fractures/organic?   |
| 17087<br>R20          | 1315 | granular tiny            | recrystal limestone w fine matrix and 2ndary calcite crystals; molds; seems to be lots of tiny crystals w calcite- quartz or calcite or framb?; trace br on some grains; one piece w layers of tanish (dolo- lrg yellow grains) and white limestone-lots of red/br flecks in tan part Miliolidae, forams, echinoids, bivalves. Indurated | possible             |
| 17087<br>R20          | 1324 | granular sm              | recrystal fine limestone; some calcite rinds; veins and diff areas have the splotches of br/gr/bl -organic; reddish br along fracture zones; molds filled w yllw/br calcite w possible framb tidal flat. Miliolidae                                                                                                                      | calcite molds; framb |
| 17087<br>R20          | 1329 |                          | fine grained matrix w partial dolo-mottled calcite grains throughout; flecks of black-organic; area w laminations-break and get the br grey/bl splotches -organic. Bioturbated. Miliolidae                                                                                                                                               |                      |
| 17087<br>R20          | 1333 | fractures                | looks like breccia (intraclast) w large casts filled w fine limestone and some pelloids filled w drusy calcite; matrix is yellw/br; some areas have dk br spots/pieces or lines; br bl splotches usually surround/move around casts-molds pure white micrite; dk also along old fractures; black flecks-trace                            | pepper and org       |
| 17087<br>R20          | 1335 | granular tiny; fractures | fine grained matrix laminated limestone-mud cracks; some lams are dolo-ylw/br; others are splotchy organic; organic seem to move along pre-exist fractures                                                                                                                                                                               | org fractures        |
| 17087<br>R20          | 1340 | granular tiny; fractures | fine grained recrystal limestone w laminations again; splotchy red/br lamins (organic); some molds (miliolidae) have bl/reddish/br                                                                                                                                                                                                       | molds organic        |
| 17087<br>R20          | 1345 | granular tiny            | very fine recrystal limestone w what appears to be lots of dk bl/br flecks of pyrite; distinct change in color bw cream to grey; some molds (miliolidae) lighter color is less recrystal. lithoclasts                                                                                                                                    | pepper               |

| Appendix 1 Continued. |      |                             |                                                                                                                                                                                                                                                                                                                                                                                     |                 |
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| 17087<br>R20          | 1348 | granular sm                 | fine recrystal limestone w lots of yellow br splotches that seem to go along old fractures; trace isolated dk br areas w what appears to be framb. Lithoclasts. Karst sed fill ill fractures. Miliolidae, echinoids, bivalves                                                                                                                                                       | framb? Organic  |
| 17087<br>R20          | 1356 | granular fractures          | limestone w lots of fracture and molds infilled w mostly dark material (dolo?) some br; some oxidized spots on surface; molds of shells                                                                                                                                                                                                                                             |                 |
| 17087<br>R20          | 1358 | granular tiny               | recrystal limestone-some molds but grains are pretty sm (wacke/pack); tiny quartz throughout; sm molds-miliolidae, echinoids, bivalves have black (pyrite?); trace organic flecks. bioturbated                                                                                                                                                                                      | molds           |
| 17087<br>R20          | 1364 | tiny moldic pores/granular  | recrystal limestone-micrite matrix but "grains" don't seem to be actual grains-wacke/packstone; splotchy (mostly br) organic; laminations-lots of black flecks throughout entire sample (pyrite); some tiny quartz; distinct facies change bw packstone yellow calcite grains (dolo) to finer grained packstone fractures. tidal flat                                               | pepper          |
| 17087<br>R20          | 1372 | granular tiny dis fractures | recrystal lime-mudstone w sm molds and trace black in tiny moldic (pyrite); trace light red/br organic on molds; some yellow calcite filled molds; some tiny dissolution fractures (most filled in)-rotated ceiling rocks with sed infill                                                                                                                                           | molds           |
| 17087<br>R20          | 1376 | granular dis fractures      | recrystal packstone; some peloidal grains; fracture laminations of organic w possible pyrite; trace quartz; lots of pepper pyrite; distinct change bw finer whiter lime and grayish one but pyrite is uniform. Lots of large lithoclasts-lag. Top of breccia                                                                                                                        | pepper/ organic |
| 17087<br>R20          | 1381 | granular sm                 | recrystal lime that looks like breccia again; pure micrite lithoclasts larger molds filled w yellow calcite and some tiny quartz; some sm splotchy organic; trace peloids and bluish grains (anhydrite?); almost a packstone-lrge recrystal inclusions w finer yllwish grains as matrix; piece w "veins" bands of micrite w lots of pepper; org laminations and splotches (smaller) | micrite         |
| 17087<br>R20          | 1384 | granular sm                 | looks like breccia w large micrite lithoclasts; fossiliferous molds -peloids/mollusks; infiltrated cave matrix wackestone in areas w/o incl; lots of splotchy orgs; some molds filled w bluish calcite (anhydrite?); some black flecks (pyrite) in micrite incl                                                                                                                     | micrite         |
| 17087<br>R20          | 1388 | none                        | breccia again but harder; recrystal lime; lithoclasts and intraclasts much smaller-packstone; grains are rather lrg and appear to be molds filled w calcite (yellow) and bluish (anhydrite?); doesn't effervesce as much-may be somewhat dolo; lots of organic splotches make up matrix bw calcite molds; abundant quartz; all grains lrg; some areas w recrystal lime              |                 |

| Appendix 1 Continued. |      |                        |                                                                                                                                                                                                                                                     |                  |
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| 17087<br>R20          | 1390 | granular tiny          | breccia w recrystal limestone -packstone lithoclasts. Lots of molds filled w bluish calcite (anhydrite) or clear slight yellow calcite; rest is somewhat dolo w fine quartz and org splotches (br) w some black                                     |                  |
| 17087<br>R20          | 1403 |                        | tan recrystal wackestone with small grains and casts, a vertical vein of yellow br calcite fractured                                                                                                                                                |                  |
| 17087<br>R20          | 1418 |                        | wackestone/micrite with very fine micrite and rest small grey grains lots of intraclasts (lag)- some are casts, veins of dark yellow calcite and in some molds. Some casts and molds, some veins have clear crystals. Some orange organic splotches | with calcite?    |
| 17087<br>R20          | 1433 | granular, moldic       | clast supported breccia with mud matrix splotchy dolo with colors of tan, dk brown, and oxidized lithoclasts, sucrosic grains are clear, orange, and yellow. Organic layers and pieces- some burnt                                                  |                  |
| 17087<br>R20          | 1435 | large moldic, granular | dark splotchy dolo ranging from tan to dk brown and grey lithoclasts. Abundant sucrosic grains of clear, tan, yellow and orange, lots organic-burnt                                                                                                 |                  |
|                       |      |                        |                                                                                                                                                                                                                                                     |                  |
| 17392<br>R13          | 1081 |                        | recrystal micrite w lots of large oval echinoid molds filled w calcite (some grey) and anhydrite trace pepper and oxidized br bits, trace sm quartz?                                                                                                | pepper?          |
| 17392<br>R13          | 1086 |                        | alternating layers of grainstone w micrite in oval molds and recrystal wackestone w casts and echinoid molds w micrite and calcite, calcite in lrg oval molds is gray, scattered pepper and trace tiny quartz?                                      | pepper?          |
| 17392<br>R13          | 1090 |                        | micrite w tiny grains and mold lined w grey calcite, next band is almost a grainstone w tiny grains and lots of molds and sm organic lamn, rest is a wacke w tiny grains and molds, calcite in molds is yellow and clear crystals, trace pepper     | pepper?          |
| 17392<br>R13          | 1121 |                        | recrystal bioturbated packstone w lots of casts of orgs, trace quartz and anhydrite, trace tiny pepper-lower/middle tidal flat                                                                                                                      | pepper?          |
| 17392<br>R13          | 1127 |                        | tiny sucrosic wackestone w lots of blu/gr calcite in molds, other molds have br organic-echinoid bryozoan, some oxidized orange molds, scattered pepper, some molds possibly pyrite, some anhydrite in molds                                        | molds pepper?    |
| 17392<br>R13          | 1128 |                        | recrystal wackestone w yellow calcite and some grey, lots molds-echinoid, bryozoan, filled w micrite or calcite, some sm quartz, some areas are packstone lamns of grainstone calcite and algal, trace pepper and oxidized pieces                   | pepper oxidized? |

| Appendix 1 Continued. |        |               |                                                                                                                                                                                                                               |                |
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| 17392<br>R13          | 1137   | lots granular | grainstone w casts, branching coralline structure                                                                                                                                                                             |                |
| 17392<br>R13          | 1159.4 |               | chalky micrite w some areas of red/br organic? And little lamns of organic w possible pyrite, some yellow calcite. Tidal flat                                                                                                 | organic veins? |
| 17392<br>R13          | 1161   | sm granular   | recrystal packstone w lots of molds echinoids and casts, scattered sm blue calcite. Anhydrite?-some large is a replacement. Trace sm org br pieces                                                                            |                |
| 17392<br>R13          | 1167   |               | chalky micrite w lots of organic lamns, some are orange br and others dk br and black, trace quartz and sm anhydrite.                                                                                                         |                |
| 17392<br>R13          | 1201   | sm granular   | recrystal wacke w tiny sucrosic micrite, some molds, lots of tiny casts, some areas are yellowed or browned, trace pepper, some molds w black in them, trace tiny quartz? Cross bedding                                       | pepper molds?  |
| 17392<br>R13          | 1209   | tiny granular | recrystal wacke w casts some molds, laminations of orange br organic and some of yellow br calcite, organic in molds and possible pyrite, gypsum trace tiny quartz, distinct area of yellow calcite                           | molds?         |
| 17392<br>R13          | 1241   | moldic        | wackestone w inclusions and lamns of yellow br calcite, also organic oxidized lamns and pieces w possible pyrite, some molds and casts, some calcite is white and cubic.                                                      | lamns?         |
| 17392<br>R13          | 1247   | granular mold | wackestone w moldic and some granular porosity, some casts, organic lamns, quartz scattered and perfect calcite in some molds, pyrite possible, scattered br oxidized pieces w laminated areas-tidal flat                     | lamns?         |
| 17392<br>R13          | 1277   | tiny granular | recrystal wackestone w granular micrite and lots of algal lamns and organic pieces. Pepper throughout. Lots of molds and casts, some blue/grey (intraclasts) calcite and tiny anhydrite, larger anhydrite? W lamns-tidal flat | pepper         |
| 17392<br>R13          | 1281   |               | recrystal wackestone w lots of casts that are micrite (pure white) calcite is either yellow or grey blue-lots, trace pepper, some black pieces-organic? Piece of orange/red                                                   | pepper?        |
| 17392<br>R13          | 1285   | granular      | recrystal wackestone casts and some molds, trace br organic pieces, some algal lamns w anhydrite?, possible pyrite w oxidized organic areas (HFO?)orange and an area w lots of pepper                                         | pepper HFO     |
| 17392<br>R13          | 1308   | granular      | alternating layers of grey/blue calcite and tan w lots of casts-forams and lots of algal lamns, some anhydrite?, rest is branching coral highly porous grainstone w some interbedded areas infilled w micrite. Bioturbated    |                |

| Appendix 1 Continued. |      |                             |                                                                                                                                                                                                                                                                                               |                     |
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| 17392<br>R13          | 1313 | granular mold               | recrystal packstone w lots of casts, bands of solid low porosity- bioturbated, scattered pepper, some blue calcite intraclasts, anhydrite throughout?                                                                                                                                         |                     |
| 17392<br>R13          | 1321 | tiny granular               | packstone w lots of casts and some molds, cast w calcite and cubic calcite crystals, yellow br calcite lithoclasts; some organic veins, other larger anhydrite?                                                                                                                               | pepper?             |
| 17392<br>R13          | 1323 | tiny granular               | recrystal micrite w scattered tiny br/bl pepper and some orange oxidized areas, big piece of very dk br/bl organic w possible pyrite. Lithoclasts                                                                                                                                             | pepper and organic? |
| 17392<br>R13          | 1324 | granular                    | recrystal wacke w some pelleted grains, casts w yellow calcite, lithoclasts anhydrite scattered, small clear cubic crystals, trace gr/blue calcite, some high porosity areas w pepper and pelated grains, 2 fracture areas: one w organic and other dk grey and greenish br chert             | pepper?             |
| 17392<br>R13          | 1354 | granular                    | recrystal only pure white micrite as casts, rest are grains (grainstone) lots of casts, intraclasts, lots of sm areas w blue calcite and some black and lrg mold of blue calcite, trace sm quartz-collapse breccia fill                                                                       |                     |
| 17392<br>R13          | 1361 |                             | crystalline micrite w lots of organic layers and lamns, layers have grey calcite and quartz and anhydrite crystals, some br speckled on areas and one organic seems almost burnt-broke on this face, some gran porosity in layer w/o organic, lots of pyrite w organic. collapse breccia fill | w organic           |
| 17392<br>R13          | 1393 |                             | micrite inclusions in algal organic-br/bl w lots of anhydrite Some crystals are smoky grey. Tidal flat                                                                                                                                                                                        |                     |
| 17392<br>R13          | 1395 |                             | looks like breccia, lrg inclusions of grainstone surrounded by br and black organic w lots of tiny anhydrite Lamns of dk grey calcite w organic. Tidal flat                                                                                                                                   |                     |
| 17392<br>R13          | 1401 | tiny granular               | recrystal wackestone w lots of sm molds and casts, lots of scattered blue grey calcite in molds, trace pepper, tiny quartz? And trace molds w oxidized br                                                                                                                                     | pepper?             |
| 17392<br>R13          | 1441 | moldic                      | recrystal semisucrosic grainy calcite intraclasts w moldic pores, trace pepper on outsides, trace anhydrite?                                                                                                                                                                                  |                     |
| 17392<br>R13          | 1444 | granular, fracture, burrows | grades from a porous packstone w pelated grains and burrows to a wackestone w fewer casts and very limited porosity, lamns are yellowed calcite somewhat oxidized, some anhydrite? Tidal flat                                                                                                 |                     |
| 17392<br>R13          | 1481 | molds granular              | recrystal wackestone w lots of casts and sm molds-miliolidae, forams, some grey calcite, some lrg molds w anhydrite? Pepper all over and concentrated in lamns (oxidized) tidal flat                                                                                                          | pepper lamns?       |

| Appendix 1 Continued. |      |                      |                                                                                                                                                                                                                              |                       |
|-----------------------|------|----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| 17392<br>R13          | 1483 | tiny granular        | tiny sucrosic grains of limestone w lots of oxidized lamns (algal) and pieces of organic, lamns have lots of big clear crystals (anhydrite) tidal flat. Miliolidae, forams                                                   |                       |
| 17392<br>R13          | 1485 | some molds           | micrite w lots of layers of organic w pyrite and large glassy anhydrite crystals tidal flat                                                                                                                                  |                       |
| 17392<br>R13          | 1514 | some granular        | packstone of white calcite grains w oxidized organic lamns that seem to have moved along fractures w possible pyrite and yellow calcite and quartz. tidal flat miliolidae, forams                                            | fractures?            |
| 17392<br>R13          | 1520 | granular mold        | grainstone w lots of casts and molds- miliolidae, forams; w sucrosic micrite, some trace organic pieces, some grey calcite in molds, pelltated casts, trace pepper                                                           | pepper?               |
|                       |      |                      |                                                                                                                                                                                                                              |                       |
| 17452/<br>TRSA-<br>1  | 1010 | lrg moldic, granular | brown dolo w large sand dollar molds, some infilled w sucrosic grains and or yellow calcite                                                                                                                                  |                       |
| 17452/<br>TRSA-<br>1  | 1015 | moldic, granular     | light tan dolo grainstone with molds, clear crystal cubes scattered about. Very dense band of dolo with large sand dollar molds, some filled with yellow partially dolo calcite                                              |                       |
| 17452/<br>TRSA-<br>1  | 1020 | granular lots        | sucrosic br dolo w some sm micrite inclusions; lots of sm quartz; some larger calcite crystals; peppered dk splotches- possible organic that has been dolo or pyrite; lrg mold on top sm golden framb                        |                       |
| 17452/<br>TRSA-<br>1  | 1027 | no visible           | recrystal limestone-wackestone; white/cream; visible grains are partially dolo; vein filled w calcite and micrite; tiny quartz; peppered black and also larger pepper of grey-silica pyrite?                                 | mold; dolo; organic   |
| 17452/<br>TRSA-<br>1  | 1030 | granular tiny        | recrystal packstone- very reworked; micrite (sugary) matrix w calcite of assorted sizes and shapes; some look partially dolo - yellow sugary; trace tiny quartz; some molds; trace tiny black in some pore spaces, echinoids | silica pyrite; pepper |
| 17452/<br>TRSA-<br>1  | 1037 | no visible           | packstone- sm grains w micrite; some lrg fossil molds filled w micrite and others calcite; tiny quartz sprinkled throughout; scattered black- various sizes and shapes w possible framb                                      | pores                 |
| 17452/<br>TRSA-<br>1  | 1040 |                      | pack/wackestone with small grains of yellow, tan, and grey calcite with pure micrite casts and some large sand dollar molds with secondary yellow calcite                                                                    |                       |
| 17452/<br>TRSA-<br>1  | 1050 |                      | packstone with very small calcite grains and trace dk grey/black. Abrupt lamn of larger br and dk grey calcite grains and larger yellow and br calcite grains above this layer(intraclasts)                                  | with calcite?         |

| Appendix 1 Continued. |      |                                      |                                                                                                                                                                                                                                                                                                                      |                                 |
|-----------------------|------|--------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------|
| 17452/<br>TRSA-<br>1  | 1059 | granular bw<br>calcite and<br>matrix | recrystal limestone- again framework of<br>yellow partially dolo calcite w micrite<br>matrix; some calcite almost br; lots of lrg<br>pepper on surface - not on fresh surface;<br>micrite forms some almost continuous<br>lateral bands. Rapid non-scale fabric<br>changes-tidal flat                                |                                 |
| 17452/<br>TRSA-<br>1  | 1062 | granular and<br>moldic               | fine sucrosic dolo- few micrite inclusions;<br>exposed surfaces have some pyrite and in<br>the matrix; med rainbow quartz                                                                                                                                                                                            | pepper and<br>calcite           |
| 17452/<br>TRSA-<br>1  | 1069 | granular                             | matrix is micrite w yellow partial dolo<br>calcite making framework again; org<br>laminations; med-sm rainbow quartz;<br>possible pyrite trace; lrg powdery micrite<br>inclusions are recrystallized w fine powder<br>matrix                                                                                         | trace                           |
| 17452/<br>TRSA-<br>1  | 1070 | granular good<br>amt                 | recrystal limestone w fine matrix -<br>packstone; lots of molds and casts; trace<br>quartz; some dk br reddish bl organic? In<br>molds; pyrite seems to be in depression<br>areas                                                                                                                                    | pepper                          |
| 17452/<br>TRSA-<br>1  | 1072 | granular some                        | recrystal limestone- white recrystal w<br>yellow cream matrix- packstone; mollusk<br>molds have yellow br cast w gold<br>glimmer; two lateral lenses of whiter<br>limestone; vert vein of dolo grains in<br>micrite- more porosity; sprinkled dolo<br>grains in rest; trace tiny quartz and<br>possible black pyrite | in depressions                  |
| 17452/<br>TRSA-<br>1  | 1080 | no visible                           | partially dolo-packstone/wackestone-<br>calcite grains are sm dolo, fine matrix-<br>powdery; short organic lamns; scattered<br>rainbow quartz; lots dolo grains have<br>black on them (pyrite) w possible framb<br>and in organic areas; some molds,<br>bioturbation                                                 | molds; pepper                   |
| 17452/<br>TRSA-<br>1  | 1083 |                                      | partial dolo packstone w micrite<br>inclusions/matrix; sm dolo grains- yellow<br>dk br; organic spots and lamns; whiter<br>areas are ones that have molds in whitish<br>blue; sparkly tiny quartz throughout                                                                                                         |                                 |
| 17452/<br>TRSA-<br>1  | 1089 | granular                             | recrystal limestone w no visible<br>calcite/dolo grains; sm org scattered<br>throughout in little molds- lots;<br>laminations of greyer looking recrystal<br>lime- doesn't look that diff under<br>microscope though, rapid mm scale fabric<br>changes-tidal flat deposits                                           | dolo and organic;<br>some molds |
| 17452/<br>TRSA-<br>1  | 1091 | granular sm                          | recrystal wackestone- very fine and pure<br>white w some molds w a lamn of<br>grey/dirtier that has lots of organic on sm<br>molds and pyrite scattered; another lamn<br>w org and pyrite bu not as dirty                                                                                                            | organic                         |
| 17452/<br>TRSA-<br>1  | 1094 | granular                             | sucrosic dolo- some is oxidized rust br<br>while rest is typical br sugar; powdery<br>matrix is even same color but in some<br>places is white; lots of organic splotches<br>and lamns-tidal flat                                                                                                                    |                                 |

| Appendix 1 Continued. |               |                                    |                                                                                                                                                                                                                              |                       |
|-----------------------|---------------|------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| 17452/<br>TRSA-<br>1  | 1099          | granular some                      | partially dolo- sm grains w micrite matrix; extensive lamins of org and also lenses-tidal flat; some molds; some lrg inclusions of muddier less dolo limestone; other lrg inclusions w recrystal limestone and lots of molds | organic; molds        |
| 17452/<br>TRSA-<br>1  | 1100          | granular; lrg fracture and sm ones | recrystal limestone; pure white framework w sm partial dolo grains and sm organic areas and some laminations-tidal flat; other pieces look more like partial dolo grains( packstone)                                         |                       |
| 17452/<br>TRSA-<br>1  | 1110          | granular                           | recrystal limestone- more yellow calcite w white framework; lots of molds-echinoids; very pure powdery layer; calcite vein; trace organic flecks; one exposed top has lots of pepper                                         |                       |
| 17452/<br>TRSA-<br>1  | 1120-<br>1121 | granular                           | relatively pure recrystal grainstone small sucrosic calcite along w a micrite matrix; lots of molds-echinoids; trace pepper on some exposed areas; and another piece has lots of black and br org pepper                     | pepper and organic    |
| 17452/<br>TRSA-<br>1  | 1132          | intergranular                      | recrystal grainstone- some grains are partially dolo; lots of molds-echinoids and casts; scattered partial dolo grains; trace organic spots; trace tiny quartz; trace pepper                                                 | pepper/ orgs          |
| 17452/<br>TRSA-<br>1  | 1138.5        | granular; dissolution fractures    | recrystal packstone- calcite is partially dolo w fine micrite matrix; some sm org spots w apparent framb and pepper; area w vein of lrg partially dolo sucrosic yll calcite w lots of pyrite on it                           | trace pepper          |
| 17452/<br>TRSA-<br>1  | 1142          | no visible                         | fine calcite(clear/yllw) crystals - sucrosic packstone w fine micrite matrix/ some white inclusions; miliolidae; bioturbation; pieces of splotchy organic; trace calcite has dark bl/br on them (pyrite)                     | calcite/dolo; organic |
| 17452/<br>TRSA-<br>1  | 1149          | granular                           | recrystal grainstone; lots of molds-miliolidae foram, echinoids, gastropods and casts; peppered pyrite; splotchy organic layer w some rainbow quartz                                                                         | trace w calcite       |
| 17452/<br>TRSA-<br>1  | 1160          | granular/ diss fractures           | recrystal limestone-no visible grains except casts; lots molds and casts-miliolidae, forams, echinoids; sucrosic like grains; some molds w organic; peppered w lots of pyrite? Some calcite casts are somewhat greenish      | pepper lots           |
| 17452/<br>TRSA-<br>1  | 1168          | granular                           | recrystal siltstone- sucrosic- sm grains; lots of sm organic pieces; also a good amt of pepper; tiny quartz w some calcite casts; 2 org spots are bright green? Miliolidae                                                   | pepper                |
| 17452/<br>TRSA-<br>1  | 1172          | granular sm                        | partially dolo- yellow br; wackestone; white micrite matrix; lots of extensive laminations of splotchy organic-tidal flat; good size rainbow quartz scattered; some peppered pyrite                                          |                       |
|                       |               |                                    |                                                                                                                                                                                                                              |                       |

| Appendix 1 Continued. |      |                              |                                                                                                                                                                                |                                           |
|-----------------------|------|------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------|
| 17488<br>TR4-1        | 1071 | lots granular and moldic     | lt br sucrosic dolo w lots of molds, pepper scattered and concentrated in smaller molds w clear crystals, some trace sm HFO w pyrites                                          | in sm molds w clear calcite and trace HFO |
| 17488<br>TR4-1        | 1077 | lots granular and moldic     | lt br and clear sucrosic dolo w pyrite scattered throughout(pepper) and in molds. Zone of no molds w short lamns of pyrite, lots of clear sucrosic crystals                    | pepper, molds, lamns of pyrite            |
| 17488<br>TR4-1        | 1079 | lots granular and moldic     | br sucrosic dolo w lots of platy molds filled w white sucrosic dolo, scattered pepper and molds w pyrite, one w lots of orange (HFO) on pyrite                                 | molds w calcite and HFO                   |
| 17488<br>TR4-1        | 1083 | lots granular and mold       | br sucrosic dolo w lots of clear dolo crystals forming in molds w pyrite on them, pyrite is found in and around random molds                                                   | molds w calcite and pyrite                |
| 17488<br>TR4-1        | 1086 | lots granular and mold       | br sucrosic dolo w lots of clear dolo crystals forming in molds w pyrite on them, pyrite is found in and around random molds                                                   |                                           |
| 17488<br>TR4-1        | 1093 | lots mold and granular       | br sucrosic dolo w lots of clear sucrosic crystals in molds. Some molds are white-dissolving, random molds filled w pyrite and around, one mold has red piece                  | molds w calcite                           |
| 17488<br>TR4-1        | 1095 | lots mold and granular       | lt br sucrosic dolo w clear calcite cubes, lots of moldic space, trace pepper                                                                                                  | trace pepper                              |
| 17488<br>TR4-1        | 1104 | gran and moldic              | sucrosic dolo w platy forms of molds, trace scattered pepper and some areas seem to be oxidized                                                                                | trace pepper                              |
| 17488<br>TR4-1        | 1107 | lots moldic and granular     | lt br sucrosic dolo w clear calcite cubes, lots of moldic space, lots molds w lots pyrite in them and scattered around molds                                                   | lots in molds                             |
| 17488<br>TR4-1        | 1117 | lots granular and mold       | br sucrosic dolo w lots of clear sucrosic crystals in molds, some molds are white inside w crystals. Random molds filled w pyrite and around. One has green and red blob in it | w white crystals in molds                 |
| 17488<br>TR4-1        | 1120 | granular                     | sucrosic dolo w sm molds, pyrite is scattered throughout along w HFO, some molds w pyrite but mostly scattered                                                                 | pepper and HFO, some molds                |
| 17488<br>TR4-1        | 1131 | moldic and lots granular     | sucrosic dolo w lots of sm molds, only trace concentrated clusters of pyrite/HFO                                                                                               | trace conc clusters of pyrite and HFO     |
| 17488<br>TR4-1        | 1137 | granular and sm moldic       | sucrosic dolo w some sm molds scattered pyrite is peppered and in some molds, possible trace HFO                                                                               | pepper and molds, trace HFO               |
| 17488<br>TR4-1        | 1143 | granular                     | semi sucrosic dolo w some sm molds, random molds w pyrite, trace pepper                                                                                                        | molds and pepper                          |
| 17488<br>TR4-1        | 1155 | sm molds, fracture, granular | sucrosic dolo, some areas only semisucrosic w some fractures and dk lamns, scattered sm molds, molds contain pyrite and clear crystals, some scattered pepper                  | pepper and in molds w clear crystals      |

| Appendix 1 Continued. |      |                             |                                                                                                                                                                                           |                             |
|-----------------------|------|-----------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|
| 17488<br>TR4-1        | 1167 | granular fracture           | tight grainstone of sucrosic lt dolo w pepper, pyrite scattered throughout, fractures-one recemented, some short lamns of pyrite                                                          | lamns and scattered         |
| 17488<br>TR4-1        | 1168 | granular                    | sucrosic dolo, no molds, pyrite speckled and concentrated in random larger clusters, HFO w some clusters                                                                                  | pepper and clumps and HFO   |
| 17488<br>TR4-1        | 1171 | granular and some moldic    | sucrosic dolo w scattered pepper. Most only has some sm molds with pepper but area with large molds; one has orange on crystals and other lined w pyrite. Some HFO in molds w pyrite      | molds HFO                   |
| 17488<br>TR4-1        | 1174 | granular, moldic, fractures | sucrosic dolo w large fractures and lots of molds, pyrite (lrg) peppered along edge of fractures, some molds filled w pyrite, oxidized zones and areas, old fracture seems to be oxidized | pepper and fractures, molds |
|                       |      |                             |                                                                                                                                                                                           |                             |
| 17608<br>R25          | 976  |                             | packstone w br calcite and lots sm cl calcite, yllw/br micrite, molds filled w micrite, tiny rust colored piece (HFO), some scattered black/gr pieces                                     |                             |
| 17608<br>R25          | 981  |                             | clay dk br/grey with lots of quartz and calcite, rest is harder calcite grains                                                                                                            |                             |
| 17608<br>R25          | 984  |                             | half is br carb mud w lots of lrg oval molds w calcite and other is all calcite crystals and orgs(shells)                                                                                 |                             |
| 17608<br>R25          | 986  | lots in some areas          | recrystal packstone w areas of high porosity and molds and other densely packed non porous layers, molds and casts w calcite                                                              |                             |
| 17608<br>R25          | 990  | lots granular               | recrystal packstone w large molds infilled w diff calcite-clear, yellow,white,br, silver dollar cast                                                                                      |                             |
| 17608<br>R25          | 996  |                             | recrystal wacke/packstone w calcite and quartz, some calcite is yellow in molds, trace black/grey pieces w pepper in them                                                                 | scattered pieces w pepper   |
| 17608<br>R25          | 997  |                             | recrystal wackestone with yellow and bluish clear calcite in molds, other grayish blue opaque calcite and spots, some quartz                                                              |                             |
| 17608<br>R25          | 998  | granular                    | recrystal limestone w lots lrg molds w yellow calcite, some grey/blue pieces                                                                                                              |                             |
| 17608<br>R25          | 1006 | sm granular                 | recrystal wackestone w casts of mollusks and other sm orgs, trace pepper, some sm calcite cubes                                                                                           | pepper                      |
| 17608<br>R25          | 1011 |                             | micrite w some sm calcite crystals and oval molds, trace pepper, pipe dope possible                                                                                                       |                             |
| 17608<br>R25          | 1016 | limited                     | wackestone w br/bl trace pepper and bluish grey spots, some sm calcite                                                                                                                    | pepper                      |
| 17608<br>R25          | 1020 |                             | recrystal wacke/micrite w orange br laminations containing pepper w some small calcite cubes                                                                                              | oxidized laminations        |
| 17608<br>R25          | 1026 |                             | chalky wackestone w calcite and quartz, trace black minerals                                                                                                                              |                             |

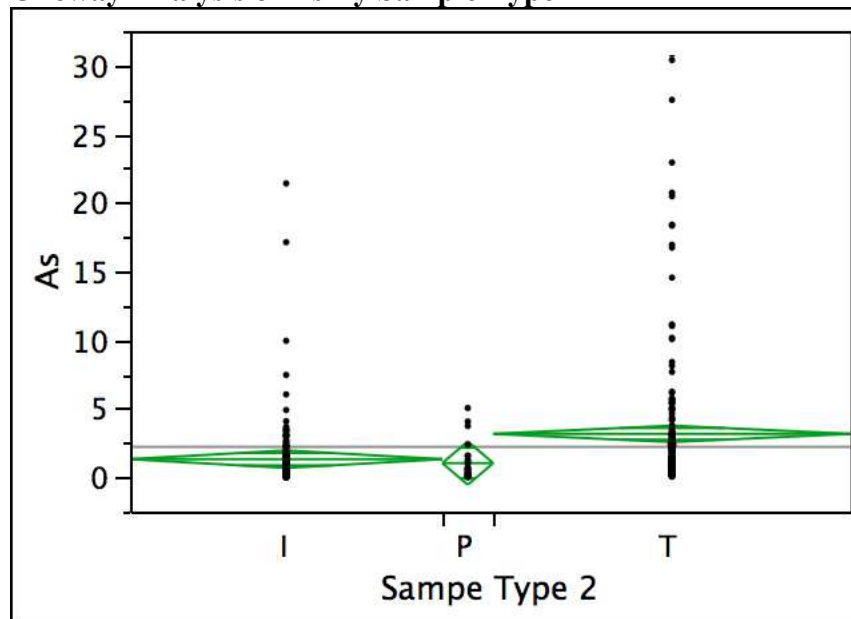
| Appendix 1 Continued. |      |                    |                                                                                                    |                               |
|-----------------------|------|--------------------|----------------------------------------------------------------------------------------------------|-------------------------------|
| 17608<br>R25          | 1028 |                    | yellow br calcite w micrite inclusions and some sm quartz, micrite replaces shells as casts        |                               |
| 17608<br>R25          | 1033 | granular and molds | calcite and quartz w lots of rust stained algal laminations and rust in some molds                 | HFO?                          |
| 17608<br>R25          | 1036 |                    | fine recrystal limestone w calcite cubes, some oxidized surfaces on calcite and trace black pieces | trace and oxidized on calcite |
| 17608<br>R25          | 1041 | sm granular        | recrystal wackestone w laminations of oxidized br calcite                                          |                               |
| 17608<br>R25          | 1046 | lots granular      | recrystal packstone w some peloids                                                                 |                               |
| 17608<br>R25          | 1048 | lots granular      | recrystal grainstone branching structure and pelleted                                              |                               |

## APPENDIX 2

Statistical plots:

An example of the output data for the Van der Waerden test using JMP. The Prob > ChiSq value is almost zero indicating the statistical significance of the data. This value agrees with the Kruskal-Wallis and ANOVA tests.

### Oneway Analysis of As By Sample Type



### Oneway ANOVA Analysis of Variance

| Source       | DF  | Sum of Squares | Mean Square | F Ratio | Prob > F |
|--------------|-----|----------------|-------------|---------|----------|
| Sampe Type 2 | 2   | 327.5492       | 163.775     | 9.7699  | <.0001   |
| Error        | 364 | 6101.7829      | 16.763      |         |          |
| C. Total     | 366 | 6429.3321      |             |         |          |

### Means for Oneway ANOVA

| Level | Number | Mean    | Std Error | Lower 95% | Upper 95% |
|-------|--------|---------|-----------|-----------|-----------|
| I     | 159    | 1.31602 | 0.32470   | 0.678     | 1.9545    |
| P     | 26     | 1.02754 | 0.80295   | -0.551    | 2.6066    |
| T     | 182    | 3.15962 | 0.30349   | 2.563     | 3.7564    |

Std Error uses a pooled estimate of error variance

### Van der Waerden Test (Normal Quantiles)

#### 1-way Test, ChiSquare Approximation

| ChiSquare | DF | Prob>ChiSq |
|-----------|----|------------|
| 39.2544   | 2  | <.0001     |

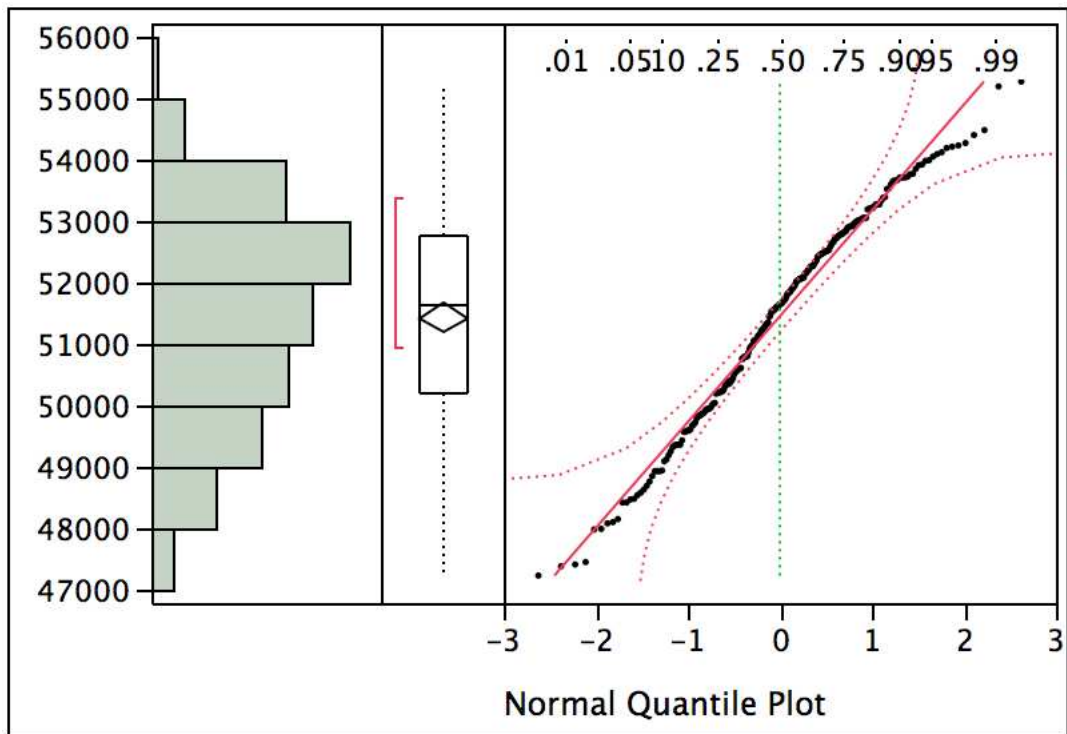
### Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

#### 1-way Test, ChiSquare Approximation

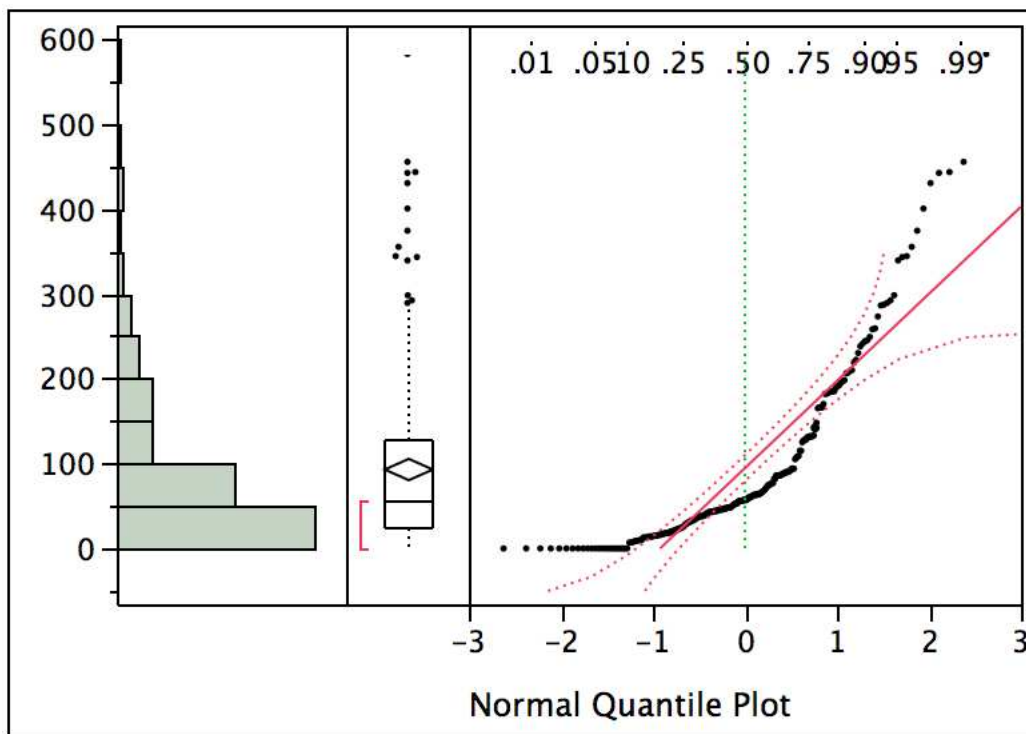
| ChiSquare | DF | Prob>ChiSq |
|-----------|----|------------|
| 35.1278   | 2  | <.0001     |

The histogram, outlier, and normal quantile plots for S and As. The S is normally distributed while the As is not.

**S**

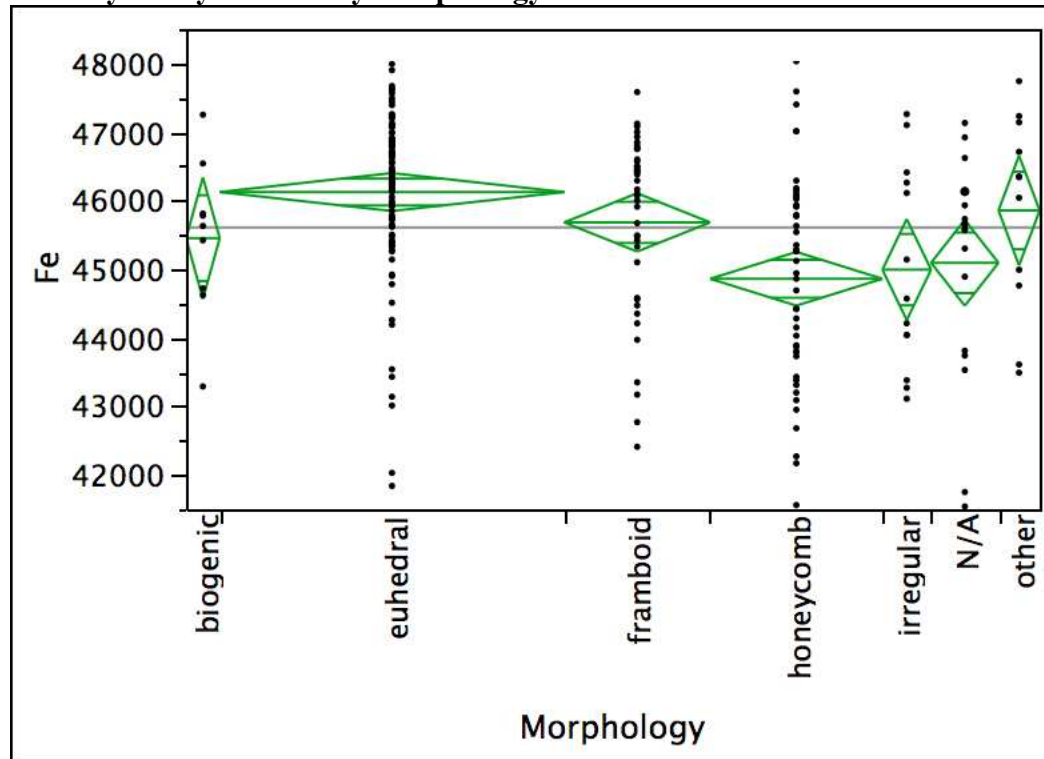


**As**



The results from the one-way ANOVA, Kruskal-Wallis and Van der Waerden tests for Fe. The morphological categories and Fe data are statistically significant.

#### Oneway Analysis of Fe By Morphology



#### Oneway ANOVA Analysis of Variance

| Source     | DF  | Sum of Squares | Mean Square | F Ratio | Prob > F |
|------------|-----|----------------|-------------|---------|----------|
| Morphology | 6   | 61069384       | 10178231    | 5.6124  | <.0001   |
| Error      | 221 | 400786530      | 1813513.7   |         |          |
| C. Total   | 227 | 461855914      |             |         |          |

#### Means for Oneway ANOVA

| Level     | Number | Mean    | Std Error | Lower 95% | Upper 95% |
|-----------|--------|---------|-----------|-----------|-----------|
| biogenic  | 9      | 45451.1 | 448.89    | 44566     | 46336     |
| euhedral  | 92     | 46123.5 | 140.40    | 45847     | 46400     |
| framoid   | 39     | 45681.3 | 215.64    | 45256     | 46106     |
| honeycomb | 46     | 44859.1 | 198.56    | 44468     | 45250     |
| irregular | 13     | 44992.3 | 373.50    | 44256     | 45728     |
| N/A       | 18     | 45091.7 | 317.41    | 44466     | 45717     |
| other     | 11     | 45854.5 | 406.04    | 45054     | 46655     |

#### Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

##### 1-way Test, ChiSquare Approximation

| ChiSquare | DF | Prob>ChiSq |
|-----------|----|------------|
| 31.7175   | 6  | <.0001     |

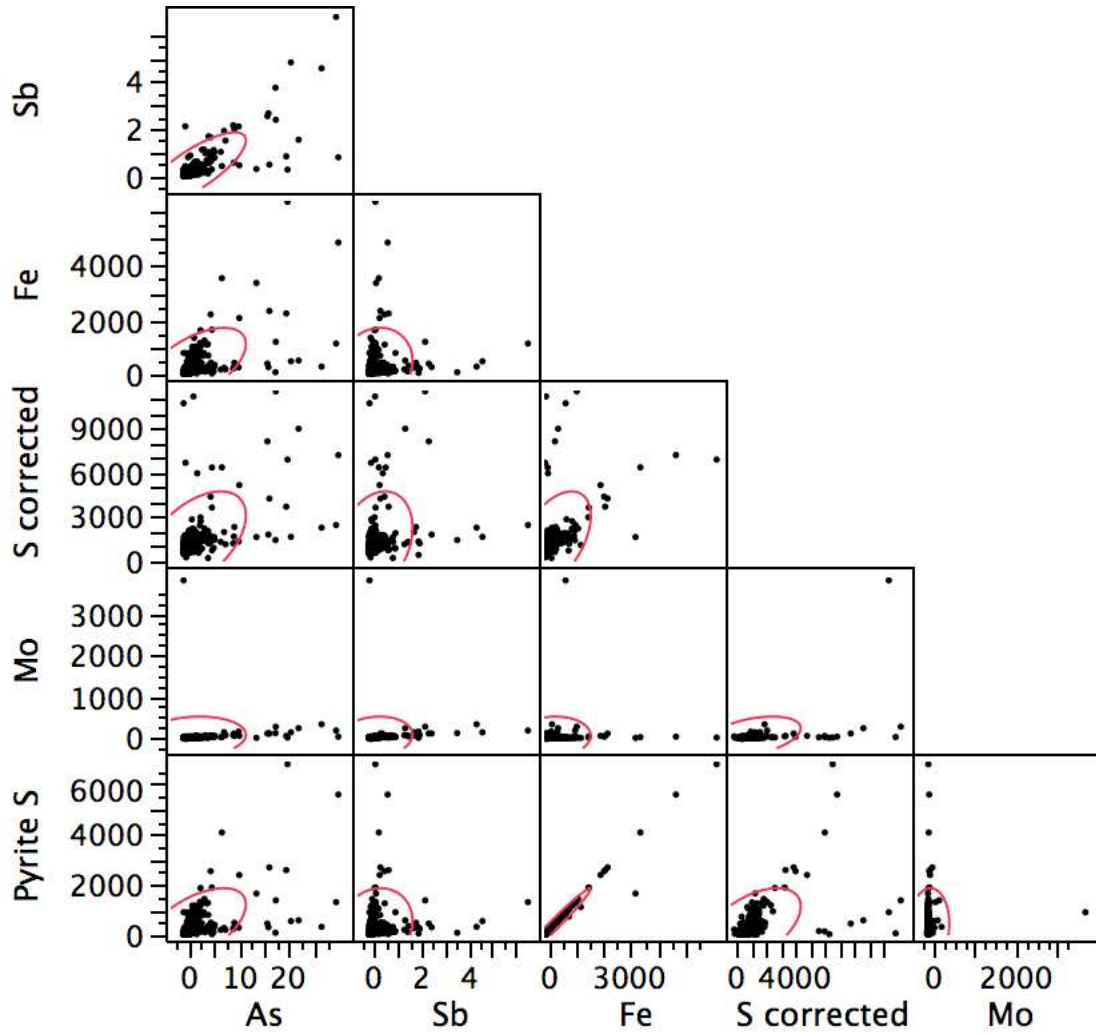
##### Van der Waerden Test (Normal Quantiles)

##### 1-way Test, ChiSquare Approximation

| ChiSquare | DF | Prob>ChiSq |
|-----------|----|------------|
| 28.3941   | 6  | <.0001     |

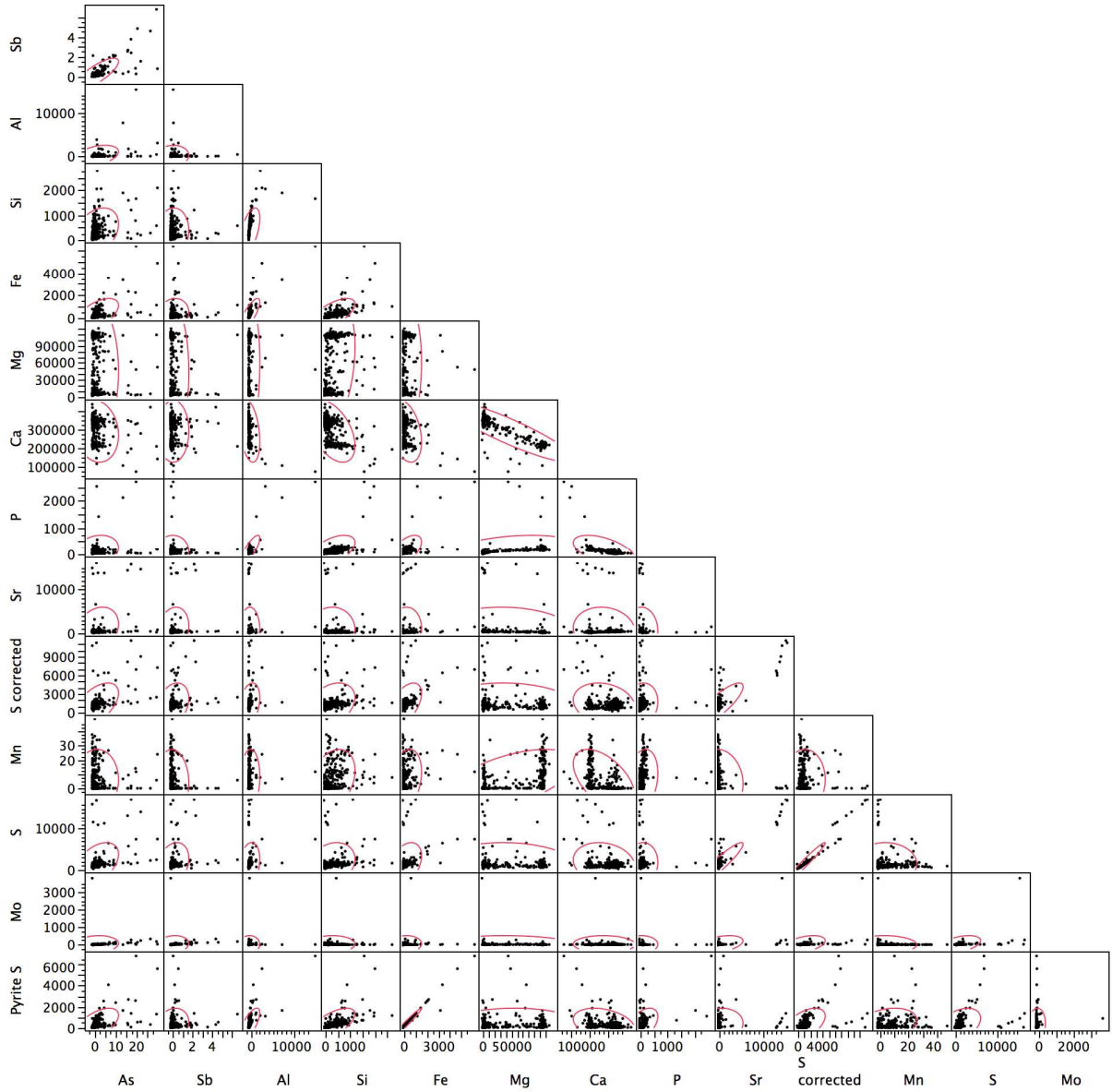
### APPENDIX 3

Correlation matrix associated with Table 9a.



## APPENDIX 4

Correlation matrix for all elements analyzed. Density ellipses are shown in red. The relationship between Mo and As and Sb is obscured by a high Mo sample.



## APPENDIX 5

Analytical, physical, lithologic, and EPMA notes for the 31 thin sections.

| FLDEP/<br>ROMP<br>ID | Depth<br>(ft) | Sample<br>Type | Reason for<br>selection                                          | As<br>mg/kg | Sb<br>mg/kg | Petrographic notes                                                                                                                                            | EPMA notes                                                                                                                                                                                                                       |
|----------------------|---------------|----------------|------------------------------------------------------------------|-------------|-------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 16576/<br>DV1        | 658           | T              | organics,<br>pyrite with<br>dolomite                             | 7.45        | 1.1         | bioclasts, oxidized<br>areas, small quartz,<br>dolomite, pyrite in grain<br>spaces and inside<br>bioclasts                                                    | many organisms                                                                                                                                                                                                                   |
| 16576/<br>DV1        | 707           | T              | WDS<br>lamination                                                | 3.3         | 0.16        | a lot of small pyrite<br>framoids and others<br>scattered throughout and<br>concentrated in darker<br>layers                                                  | dolomite but small<br>scattered pure calcite<br>within (replacement?)<br>some barite crystals,<br>some trace detrital- rutile<br>and Al, Si, Mg clusters of<br>biogenic wispy pyrite in<br>molds, gypsum and<br>FeOH globs mixed |
| 16576/<br>DV1        | 775           | T              | pyrite in<br>dolomite                                            | 3.2         | 0.088       | framoids scattered<br>throughout                                                                                                                              | altered framoids, solid<br>grains- possibly<br>framoids that were<br>altered or never formed,<br>scattered and in fractures-<br>concentrated, some are<br>wispy altered, many<br>horseshoe shaped orgs<br>that have dissolved    |
| 16576/<br>DV1        | 820           | I              | oxidized<br>fracture and<br>mold                                 | 4.9         | 0.2         | dolomite with framoid<br>clusters and rhombs<br>scattered about,<br>bioclasts, some<br>clustered and octahedral<br>pyrites, FeOH with<br>pyrite               | some K-spar in molds,<br>euhedral clusters<br>scattered about, little bit<br>of gypsum in molds, also<br>almost framoids- holey<br>bumpy, some pyrite with<br>K-spar                                                             |
| 16618/<br>TR9-2      | 765           | T              | dolomite<br>with pyrite,<br>organic<br>laminations,<br>fractures | 1.32        | 0.002       | very small pyrites<br>throughout                                                                                                                              | calcite replacement<br>within the dolomite,<br>pyrite in grain spaces,<br>some framoids and<br>holey pyrites, also solid<br>euhedral crystals                                                                                    |
| 16618/<br>TR9-2      | 773           | T              | fractures<br>with organic<br>laminations                         | 11          | 2.1         | frambs and oxidized<br>laminations, some<br>rhombs; laminations are<br>very oxidized, frambs in<br>matrix and within holes<br>in grains                       | dolomite with secondary<br>calcite, framoids and<br>honeycomb in<br>laminations and fractures,<br>pyrite inside dolomite<br>grains also                                                                                          |
| 16783/<br>R22        | 1004-<br>1007 | T              | organic<br>layer, pyrite<br>laminations                          | 16.9        | 2.66        | framoids in organic<br>layers, some rhombs<br>spread out, a lot of<br>bioclasts and small<br>quartz, a lot of<br>framoids in clay                             | many organisms,<br>framoids grown together<br>with holes and lumpy-<br>biogenic, a lot<br>honeycomb and rings                                                                                                                    |
| 16783/<br>R22        | 1022          | T              | organic<br>laminations                                           | 10.1        | 2           | octahedral and<br>framoids, some hollow<br>in middle, one side has a<br>lot, other framoids in<br>organic laminations,<br>laminations with pyrite<br>and FeOH | euhedral and oxidized<br>holey pyrites made by<br>bacteria, rings of pyrite-<br>not framoids, pyrite in<br>fractures and laminations,<br>honeycomb structures,<br>many scattered in<br>fractures and laminations                 |

Appendix 5 Continued.

|               |        |   |                                                              |      |       |                                                                                                                                                                                                  |                                                                                                                                                                                                                                                                                    |
|---------------|--------|---|--------------------------------------------------------------|------|-------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 16783/<br>R22 | 1185   | T | pyrite in calcite and organic layers                         | 18.4 | 2.4   | a lot of organic matrix with calcite grains, a lot of framboid clusters in matrix, larger with dolomite grains, small dissolution holes or in matrix- also very small rhombs                     | a lot of large Celestine (SrSO <sub>4</sub> ) large fractured dolomite grains, small sulfides throughout, secondary calcite, Kspar grains                                                                                                                                          |
| 16783/<br>R22 | 944    | T | organic with pyrite, pyrite between clay layers and in molds | 5.43 | 0.665 | pyrite between layers and in molds, organic piece with pyrite, calcite grains angular with fine matrix, rhombic pyrite framboids less common within matrix and calcite, edges oxidized fractures | dolomite crystals with some small calcite, pyrite in crystals and in grain spaces, euhedral pyrites also some wispy holey ones in dolomite                                                                                                                                         |
| 16783/<br>R22 | 954    | T | pyrite in clay mold                                          | 1.7  | 0.095 | very fine grained with bioclasts and small framboids scattered, other half bioclasts and less pyrite, pyrite in clay and mold                                                                    | secondary calcite in biogenic molds, euhedral crystals, scattered euhedral and beaten up holey pyrites, very tiny                                                                                                                                                                  |
| 16913/<br>R5  | 1082   | T | muddy dolomite                                               | 20.7 | 0.26  | large areas of pyrite, no structure visible, some spherical framboids but individual very small                                                                                                  | loaded with rhombs, pyrites along fractures, many pyrite clusters, small ilmenites                                                                                                                                                                                                 |
| 16913/<br>R5  | 1107   | T | grey layers, pyrite                                          | 14.5 | 0.29  | too thick- calcite with one pyrite area                                                                                                                                                          | trace zircon, monazite-pieces of detrital phosphate, phosphate-small scattered and circular probably a source of high As, weathered ilmenites, some apatite has pyrite growing in it, small amount with ilmenite and pyrite growing on the side, dolomite rhombs with Si Mg matrix |
| 16913/<br>R5  | 1231   | I | blue/grey calcite ?                                          | 2.34 | 0.164 | a lot of molds with sparry calcite infill, fine matrix, rhombs, some casts filled with pyrite                                                                                                    | many shell casts and molds, pyrite with calcite as organisms and in molds with dolomite rhombs containing bits of calcite, dolomite rhombs and sparry calcite, trace ilmenites, trace SrSO <sub>4</sub> replacement                                                                |
| 17000/<br>R28 | 1163   | T | organic laminations                                          | 11.1 | 0.45  | oxidized large inclusions with pyrite, pyrite in oxidized layers, fine micrite with some larger calcite and bioclasts, oxidized laminations, pyrite throughout framboids and euhedral            | a lot of biogenic pyrite, fused honeycomb framboids and weird shapes in cracks and molds                                                                                                                                                                                           |
| 17000/<br>R28 | 1224.5 | T | blue and grey calcite?                                       | 20.5 | 0.83  | large cluster of pyrite striations visible also within certain grains, concentrated and spread out in matrix, matrix inclusions have high pyrite concentrations                                  | pyrite everywhere! Pyrite in secondary calcite and isolated, large framboids clumped together, many along cracks and fractures                                                                                                                                                     |

Appendix 5 continued.

|               |      |   |                                                       |      |       |                                                                                                                                           |                                                                                                                                                                                                                                                                                                                                                      |
|---------------|------|---|-------------------------------------------------------|------|-------|-------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 17000/<br>R28 | 1228 | T | organic laminations, porosity                         | 18.3 | 3.75  | mineral clear in nonreflective light outlined with pyrite and sparkly in reflective-very small amounts                                    | very fine wispy pyrites with small reworked matrix. Some pyrites with holes in middle- grew around stuff, piece of barite, FeO, SrCO <sub>3</sub> ; some gypsum in solid matrix, pyrites in laminations and debris                                                                                                                                   |
| 17001/<br>R14 | 1248 | T | blue calcite? Pyrite with calcite?                    | 0.53 | 0.013 | pyrites-small rhombs scattered and within casts, very small framboids form clusters, bioclasts, scattered areas with a lot of clusters    | some organisms, trace chalcopryite, pyrites inside holes of organisms                                                                                                                                                                                                                                                                                |
| 17001/<br>R14 | 1259 | I | porosity                                              | 0.1  | 0.01  | a lot of biogenic clasts, edges of grains have very tiny pyrites- line edges-not many, a lot of small quartz                              | N/A                                                                                                                                                                                                                                                                                                                                                  |
| 17087/<br>R20 | 1233 | T | organic laminations with pyrite, pyrite with dolomite | 8.1  | 1.9   | a lot of tiny quartz, very fine matrix, some rhombic pyrite, oxidized layers, a lot of oxidized layers with FeOH and pyrite               | bacteria like pyrite-honeycomb and rings, organisms in matrix, oxidized organics with C, S, Ca, secondary spar in grains, in cracks and laminations, matrix doesn't have visible grains                                                                                                                                                              |
| 17087/<br>R20 | 1333 | T | reworked organics and pyrite                          | 27.5 | 4.6   | a lot of tiny pyrites and oxidized scattered throughout, organics visible with pyrite in them, FeOH, few framboids, rest has no structure | calcium grains and some gypsum, balls of gypsum with calcite grains on top (frags), gypsum balls hold calcite together, euhedral pyrite and some pyrite with calcite, rings of pyrite, organisms throughout                                                                                                                                          |
| 17087/<br>R20 | 1335 | T | pyrite with organic laminations and dolomite          | 10   | 0.56  | brown organic laminations, pyrite framboids scattered, bioclasts, secondary spar                                                          | many organisms and small micrite grains, pyrites are biogenic honeycomb type, layers look like bioturbation                                                                                                                                                                                                                                          |
| 17087/<br>R20 | 1340 | T | pyrite with organic laminations                       | 21.4 | 4.8   | only visible grains are biogenic, rest is muddy, orange oxidized laminations, small framboids in the oxidized layers                      | a lot of gypsum                                                                                                                                                                                                                                                                                                                                      |
| 17087/<br>R20 | 1364 | T | pyrite in organic layer                               | 2    | 0.2   | a lot of bioclasts, oxidized pyrites line insides of casts, ooids-peloidal grains                                                         | many calcite organisms, pyrites scattered throughout, mostly irregular framboids holey                                                                                                                                                                                                                                                               |
| 17392/<br>R13 | 1324 | T | pyrite in fracture                                    | 4.9  | 1     | a lot of bioclasts, small pyrites line mold spaces (not many) lamination with a lot                                                       | many organisms and some dolomite rhombs, a lot of Sr bearing stuff throughout, reworked grains, SrS- comes in and incorporates along cracks of orgs (SrSCa) or grains in holes of old orgs (pure Sr S) mix of gypsum and Sr sulfate worked into muddy matrix areas also pyrite, grains of high Sr Carbonate- Strontionite, limited pyrite mostly SrS |

| Appendix 5 continued. |        |   |                                                            |       |       |                                                                                                                                            |                                                                                                                                                                                                           |
|-----------------------|--------|---|------------------------------------------------------------|-------|-------|--------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 17392/<br>R13         | 1395   | T | reworked<br>organic<br>laminations                         | 16.7  | 2.5   | very fine matrix with<br>some calcite grains-<br>irregular, spread out<br>rhombic and framboids,<br>organic laminations<br>with pyrite     | a lot of celestine all the<br>large lighter areas,<br>celestine is rhombic and<br>matrix is micrite                                                                                                       |
| 17392/<br>R13         | 1483   | T | blue calcite?<br>and organic<br>laminations<br>with pyrite | 22.9  | 1.5   | large quartz organic<br>layers, rhombic and<br>framboids in the organic<br>layers, vein with lots<br>calcite?                              | many large grains of<br>celestine and barite, many<br>small framboids in<br>laminations, small CaS,<br>lots of framboids                                                                                  |
| 17452/<br>TRSA-<br>1  | 1080   | T | pyrite in<br>calcite                                       | 0.459 | 0.038 | quartz, calcite,<br>dolomite, feldspar?,<br>scattered rhombic<br>pyrite, oxidized areas<br>with pyrite                                     | many peloids and<br>organisms                                                                                                                                                                             |
| 17452/<br>TRSA-<br>1  | 1138.5 | T | pyrite in<br>molds and<br>calcite                          | 0.22  | 0.02  | pyrite-very small<br>surrounds grains and<br>within fractures, within-<br>very small peloids,<br>veins, or areas with a lot<br>of pyrite-  | many organisms- calcite<br>replacement and dolomite<br>rhombs, trace euhedral<br>pyrite                                                                                                                   |
| 17488/<br>TR4-1       | 1171   | T | pyrite in<br>molds                                         | 2.1   | 0.188 | a lot of pyrite<br>surrounding molds and<br>in grain spaces, may be<br>tiny framboids but<br>mostly not                                    | euhedral crystals in<br>between dolomite grains<br>and lots of areas where<br>molds infilled with pyrite<br>crystals, gypsum in some<br>areas around mold holes<br>and with pyrite                        |
| 17608/<br>R25         | 981    | T | clay with<br>pyrite                                        | 30.8  | 0.79  | some octahedra, a lot of<br>quartz and feldspar,<br>pyrites in matrix and<br>many little clusters on<br>edge of grains, rhombs<br>and FeOH | dolomite grains with<br>micrite, euhedral pyrite in<br>grain spaces and matrix<br>everywhere and in<br>dolomite, grown crystals<br>not organic, matrix fill is<br>Ca, Al, Si, Mg with a<br>little S and K |

## APPENDIX 6

EPMA results for all 301 pyrites expressed in weight percent. Totals below 95% were considered qualitative instead of quantitative. Values of 0 were below detection limits.

| Sample ID       | Sb   | Fe    | S     | Zn   | Ca   | As   | Mo   | Total |
|-----------------|------|-------|-------|------|------|------|------|-------|
| TR92.765.12     | 0.00 | 0.01  | 0.05  | 0.00 | 2.78 | 0.11 | 0.03 | 2.98  |
| DV1.707.8       | 0.00 | 32.67 | 35.98 | 0.00 | 7.51 | 0.52 | 0.37 | 77.05 |
| TR4-1_1171.7    | 0.02 | 48.08 | 31.62 | 0.02 | 0.43 | 0.19 | 0.00 | 80.35 |
| DV-1_658.3      | 0.44 | 34.62 | 35.53 | 0.00 | 9.73 | 0.94 | 0.00 | 81.26 |
| R22_944.1       | 0.01 | 36.19 | 40.06 | 0.00 | 5.90 | 0.09 | 0.00 | 82.25 |
| R22_954.3       | 0.01 | 39.77 | 39.06 | 0.03 | 3.65 | 0.20 | 0.00 | 82.72 |
| DV-1_658.1      | 0.24 | 41.44 | 36.73 | 0.01 | 4.39 | 0.78 | 0.00 | 83.59 |
| R28_1163.11     | 0.00 | 42.17 | 40.02 | 0.04 | 1.89 | 0.33 | 0.00 | 84.45 |
| R20_1333.6      | 0.14 | 38.69 | 36.66 | 0.01 | 7.67 | 1.43 | 0.46 | 85.06 |
| TR4-1_1171.8    | 0.01 | 42.24 | 41.77 | 0.05 | 1.02 | 0.20 | 0.00 | 85.29 |
| R22_1185.7      | 0.02 | 44.51 | 40.29 | 0.03 | 0.84 | 0.07 | 0.19 | 85.94 |
| TR92.765.8      | 0.00 | 37.95 | 42.38 | 0.00 | 5.62 | 0.23 | 0.00 | 86.18 |
| R22_954.8       | 0.02 | 46.08 | 38.47 | 0.04 | 1.65 | 0.15 | 0.07 | 86.47 |
| TR92.765.3      | 0.00 | 39.24 | 41.74 | 0.00 | 5.51 | 0.03 | 0.00 | 86.52 |
| R20_1335.8      | 0.12 | 43.85 | 40.54 | 0.01 | 1.71 | 0.60 | 0.10 | 86.93 |
| R14.1248.10     | 0.00 | 39.53 | 43.92 | 0.00 | 3.42 | 0.07 | 0.00 | 86.94 |
| R28_1163.12     | 0.00 | 44.75 | 40.67 | 0.04 | 1.30 | 0.37 | 0.18 | 87.31 |
| R5.1231.2       | 0.00 | 41.01 | 44.73 | 0.00 | 1.56 | 0.04 | 0.00 | 87.34 |
| R28_1163.3      | 0.03 | 43.59 | 41.52 | 0.03 | 1.58 | 0.63 | 0.02 | 87.40 |
| R28_1163.7      | 0.00 | 44.03 | 42.96 | 0.03 | 0.90 | 0.28 | 0.00 | 88.20 |
| R22_1185.1      | 0.01 | 44.76 | 41.63 | 0.01 | 1.63 | 0.09 | 0.20 | 88.33 |
| R20_1233.3      | 0.09 | 42.15 | 41.39 | 0.05 | 3.95 | 0.90 | 0.00 | 88.53 |
| R20_1335.12     | 0.02 | 43.37 | 42.94 | 0.03 | 2.27 | 0.17 | 0.00 | 88.80 |
| R20_1335.9      | 0.02 | 38.75 | 48.19 | 0.02 | 1.73 | 0.35 | 0.38 | 89.45 |
| R28_1228.2      | 0.01 | 37.99 | 43.00 | 0.04 | 8.37 | 0.10 | 0.00 | 89.51 |
| R28_1163.4      | 0.03 | 42.33 | 45.33 | 0.65 | 0.81 | 0.52 | 0.00 | 89.66 |
| DV1.775.4       | 0.00 | 40.62 | 45.81 | 0.02 | 3.03 | 0.30 | 0.14 | 89.92 |
| R20.1364.12     | 0.00 | 42.08 | 44.63 | 0.00 | 3.56 | 0.11 | 0.00 | 90.38 |
| DV1.775.7       | 0.00 | 43.47 | 44.69 | 0.00 | 2.32 | 0.04 | 0.00 | 90.52 |
| TR92.765.16     | 0.00 | 47.33 | 40.91 | 0.00 | 1.32 | 0.21 | 0.76 | 90.53 |
| R20_1340.3      | 0.02 | 40.46 | 46.82 | 0.04 | 3.14 | 0.22 | 0.00 | 90.69 |
| TRSA_1.1138.5.5 | 0.00 | 41.55 | 43.93 | 0.00 | 5.35 | 0.04 | 0.00 | 90.87 |
| TR92.765.11     | 0.00 | 42.95 | 44.94 | 0.00 | 2.95 | 0.03 | 0.00 | 90.87 |
| R20_1333.4      | 0.00 | 40.20 | 47.00 | 0.01 | 4.06 | 0.10 | 0.00 | 91.37 |
| R28_1224.12     | 0.00 | 44.09 | 43.84 | 0.04 | 2.17 | 0.40 | 0.84 | 91.38 |
| R20_1233.8      | 0.02 | 41.60 | 45.32 | 0.00 | 4.43 | 0.07 | 0.00 | 91.44 |
| DV1.820.1       | 0.00 | 44.12 | 45.36 | 0.03 | 1.82 | 0.17 | 0.00 | 91.50 |
| R20_1340.4      | 0.02 | 41.21 | 46.68 | 0.04 | 3.23 | 0.33 | 0.00 | 91.51 |
| TR92.765.2      | 0.00 | 45.27 | 44.81 | 0.00 | 1.34 | 0.10 | 0.00 | 91.52 |
| R5.1231.6       | 0.00 | 42.53 | 45.49 | 0.00 | 3.45 | 0.22 | 0.02 | 91.70 |
| R20_1335.11     | 0.03 | 41.56 | 47.98 | 0.01 | 1.76 | 0.24 | 0.19 | 91.77 |

|                       |      |       |       |      |      |      |      |       |
|-----------------------|------|-------|-------|------|------|------|------|-------|
| Appendix 6 continued. |      |       |       |      |      |      |      |       |
| R28_1163.6            | 0.01 | 41.19 | 49.82 | 0.02 | 0.64 | 0.12 | 0.00 | 91.81 |
| TRSA_1.1138.5.9       | 0.00 | 44.00 | 45.48 | 0.00 | 2.39 | 0.03 | 0.00 | 91.90 |
| DV1.707.4             | 0.00 | 42.80 | 45.99 | 0.03 | 2.36 | 0.28 | 0.46 | 91.92 |
| R20.1364.4            | 0.00 | 46.14 | 44.34 | 0.00 | 1.28 | 0.07 | 0.12 | 91.95 |
| R22_1004-1007.1       | 0.01 | 43.39 | 45.55 | 0.03 | 3.11 | 0.23 | 0.00 | 92.31 |
| R20_1335.1            | 0.01 | 44.46 | 45.64 | 0.04 | 1.84 | 0.26 | 0.18 | 92.42 |
| TR9-2_773.1           | 0.01 | 40.63 | 49.24 | 0.03 | 2.31 | 0.21 | 0.00 | 92.43 |
| R20_1335.10           | 0.00 | 42.61 | 46.40 | 0.02 | 3.39 | 0.03 | 0.00 | 92.45 |
| DV1.775.2             | 0.00 | 41.89 | 48.30 | 0.03 | 1.92 | 0.36 | 0.01 | 92.51 |
| R14.1248.8            | 0.00 | 44.48 | 46.68 | 0.01 | 1.24 | 0.11 | 0.00 | 92.51 |
| R22_1022.5            | 0.00 | 42.03 | 49.83 | 0.00 | 0.75 | 0.00 | 0.00 | 92.61 |
| R28_1224.13           | 0.02 | 43.13 | 45.85 | 0.01 | 3.09 | 0.60 | 0.23 | 92.93 |
| R13_1483.6            | 0.02 | 42.86 | 46.32 | 0.02 | 3.59 | 0.22 | 0.00 | 93.03 |
| R22_1185.9            | 0.09 | 40.16 | 51.50 | 0.02 | 0.52 | 0.38 | 0.54 | 93.20 |
| TRSA-1_1080.5         | 0.00 | 42.17 | 48.08 | 0.04 | 2.97 | 0.02 | 0.00 | 93.28 |
| R22_954.5             | 0.00 | 41.84 | 48.48 | 0.11 | 2.96 | 0.00 | 0.00 | 93.39 |
| TR9-2_773.4           | 0.00 | 42.41 | 49.59 | 0.02 | 1.41 | 0.08 | 0.00 | 93.51 |
| DV1.820.16            | 0.00 | 46.73 | 45.67 | 0.06 | 0.95 | 0.17 | 0.00 | 93.58 |
| DV1.775.6             | 0.00 | 41.85 | 49.22 | 0.09 | 2.25 | 0.17 | 0.00 | 93.58 |
| R22_1185.8            | 0.00 | 45.47 | 47.42 | 0.02 | 0.63 | 0.08 | 0.07 | 93.68 |
| DV1.707.6             | 0.00 | 43.61 | 48.10 | 0.04 | 1.09 | 0.44 | 0.41 | 93.70 |
| R20.1364.7            | 0.00 | 45.33 | 46.69 | 0.00 | 1.50 | 0.10 | 0.10 | 93.72 |
| R22_1022.10           | 0.00 | 42.68 | 49.61 | 0.04 | 1.39 | 0.04 | 0.00 | 93.76 |
| R28_1163.5            | 0.02 | 43.09 | 49.25 | 0.01 | 0.70 | 0.27 | 0.43 | 93.78 |
| DV1.707.7             | 0.00 | 45.13 | 46.86 | 0.00 | 1.54 | 0.28 | 0.00 | 93.81 |
| R5.1107.4             | 0.00 | 44.98 | 48.27 | 0.00 | 0.22 | 0.40 | 0.00 | 93.87 |
| R22_944.9             | 0.00 | 43.11 | 49.69 | 0.00 | 0.89 | 0.20 | 0.00 | 93.89 |
| TR4-1_1171.4          | 0.01 | 46.78 | 46.54 | 0.02 | 0.45 | 0.21 | 0.00 | 94.01 |
| TR9-2_773.2           | 0.00 | 42.07 | 50.10 | 0.03 | 1.77 | 0.10 | 0.00 | 94.06 |
| R20_1333.2            | 0.06 | 41.54 | 49.79 | 0.04 | 1.67 | 0.58 | 0.39 | 94.08 |
| R20_1233.2            | 0.00 | 43.29 | 48.42 | 0.04 | 2.34 | 0.00 | 0.00 | 94.09 |
| R20.1364.13           | 0.00 | 43.49 | 48.76 | 0.00 | 1.84 | 0.05 | 0.00 | 94.14 |
| DV-1_658.2            | 0.42 | 41.60 | 46.93 | 0.02 | 4.33 | 0.86 | 0.00 | 94.16 |
| R13.1324.6            | 0.00 | 43.00 | 45.50 | 0.06 | 5.73 | 0.03 | 0.00 | 94.32 |
| TR4-1_1171.3          | 0.02 | 45.58 | 47.66 | 0.02 | 0.96 | 0.18 | 0.00 | 94.42 |
| R20.1364.6            | 0.00 | 43.97 | 48.63 | 0.00 | 1.68 | 0.13 | 0.01 | 94.42 |
| DV1.775.8             | 0.00 | 45.23 | 48.03 | 0.07 | 1.12 | 0.03 | 0.00 | 94.48 |
| R5.1107.6             | 0.00 | 44.04 | 49.88 | 0.02 | 0.36 | 0.29 | 0.00 | 94.59 |
| TR9-2_773.5           | 0.00 | 42.38 | 50.94 | 0.03 | 1.27 | 0.07 | 0.00 | 94.69 |
| DV1.820.6             | 0.00 | 44.42 | 48.42 | 0.00 | 1.80 | 0.06 | 0.00 | 94.70 |
| R22_1022.11           | 0.00 | 43.79 | 49.12 | 0.03 | 1.76 | 0.04 | 0.00 | 94.74 |
| R20_1333.5            | 0.00 | 43.81 | 48.85 | 0.02 | 2.00 | 0.09 | 0.00 | 94.77 |
| TR4-1_1171.5          | 0.01 | 47.35 | 47.12 | 0.03 | 0.20 | 0.15 | 0.00 | 94.86 |
| TR9-2_773.3           | 0.00 | 45.05 | 47.98 | 0.02 | 1.87 | 0.05 | 0.00 | 94.97 |
| R5.1107.2             | 0.00 | 42.95 | 48.54 | 0.00 | 3.12 | 0.40 | 0.00 | 95.01 |
| R22_954.7             | 0.02 | 46.04 | 47.99 | 0.02 | 0.91 | 0.07 | 0.00 | 95.04 |

|                       |      |       |       |      |      |      |      |       |
|-----------------------|------|-------|-------|------|------|------|------|-------|
| Appendix 6 continued. |      |       |       |      |      |      |      |       |
| R20_1335.5            | 0.01 | 42.27 | 49.72 | 0.02 | 2.71 | 0.18 | 0.14 | 95.06 |
| R14.1248.11           | 0.00 | 43.27 | 50.23 | 0.02 | 1.58 | 0.06 | 0.00 | 95.16 |
| DV1.820.7             | 0.00 | 46.27 | 47.85 | 0.04 | 0.92 | 0.09 | 0.00 | 95.17 |
| R20_1335.2            | 0.01 | 44.15 | 49.57 | 0.02 | 1.41 | 0.09 | 0.00 | 95.25 |
| DV1.707.2             | 0.00 | 43.54 | 48.93 | 0.00 | 2.86 | 0.02 | 0.00 | 95.35 |
| R20_1233.7            | 0.02 | 43.87 | 47.23 | 0.02 | 4.18 | 0.09 | 0.00 | 95.41 |
| R20_1340.5            | 0.03 | 44.21 | 49.43 | 0.03 | 1.49 | 0.29 | 0.01 | 95.49 |
| R5.1231.1             | 0.00 | 45.93 | 47.38 | 0.00 | 2.07 | 0.08 | 0.06 | 95.51 |
| DV1.775.5             | 0.00 | 42.77 | 50.79 | 0.03 | 1.78 | 0.19 | 0.00 | 95.56 |
| R20_1335.6            | 0.00 | 43.80 | 49.35 | 0.02 | 2.40 | 0.03 | 0.00 | 95.59 |
| R14.1248.9            | 0.00 | 43.14 | 50.51 | 0.00 | 1.84 | 0.13 | 0.00 | 95.62 |
| R20_1233.5            | 0.00 | 44.86 | 49.19 | 0.04 | 1.63 | 0.05 | 0.00 | 95.77 |
| R28_1163.8            | 0.00 | 44.28 | 50.76 | 0.02 | 0.48 | 0.26 | 0.00 | 95.80 |
| R20_1333.9            | 0.00 | 43.43 | 49.57 | 0.05 | 2.79 | 0.01 | 0.00 | 95.85 |
| TRSA_1.1138.5.2       | 0.00 | 44.21 | 48.58 | 0.00 | 3.06 | 0.03 | 0.00 | 95.88 |
| R5.1231.8             | 0.00 | 45.67 | 49.36 | 0.00 | 0.75 | 0.13 | 0.00 | 95.91 |
| R20_1333.1            | 0.00 | 43.74 | 49.87 | 0.00 | 2.31 | 0.05 | 0.00 | 95.97 |
| R28_1163.9            | 0.00 | 44.03 | 51.32 | 0.01 | 0.46 | 0.18 | 0.00 | 96.00 |
| R20_1233.1            | 0.00 | 45.81 | 48.69 | 0.03 | 1.49 | 0.01 | 0.00 | 96.03 |
| TR92.765.10           | 0.00 | 45.27 | 49.09 | 0.01 | 1.59 | 0.07 | 0.00 | 96.03 |
| R20_1335.4            | 0.00 | 43.31 | 50.23 | 0.04 | 2.37 | 0.09 | 0.01 | 96.04 |
| R13.1324.5            | 0.00 | 44.26 | 47.41 | 0.00 | 4.37 | 0.07 | 0.00 | 96.11 |
| DV1.775.3             | 0.00 | 44.04 | 50.35 | 0.00 | 1.62 | 0.23 | 0.00 | 96.24 |
| R13_1483.3            | 0.01 | 43.17 | 49.83 | 0.01 | 3.21 | 0.03 | 0.00 | 96.26 |
| R22_1004-1007.7       | 0.01 | 43.20 | 51.29 | 0.01 | 1.56 | 0.13 | 0.09 | 96.28 |
| R22_1022.1            | 0.00 | 43.89 | 51.24 | 0.03 | 1.06 | 0.11 | 0.00 | 96.32 |
| R22_1022.6            | 0.00 | 41.75 | 53.05 | 0.01 | 1.18 | 0.20 | 0.18 | 96.36 |
| DV1.775.1             | 0.00 | 43.38 | 51.66 | 0.05 | 1.08 | 0.17 | 0.03 | 96.37 |
| TRSA_1.1138.5.6       | 0.00 | 44.90 | 47.45 | 0.00 | 3.99 | 0.03 | 0.00 | 96.37 |
| TR9-2_773.7           | 0.00 | 45.59 | 49.36 | 0.02 | 1.38 | 0.08 | 0.00 | 96.43 |
| R5.1107.3             | 0.00 | 45.50 | 50.21 | 0.00 | 0.52 | 0.21 | 0.00 | 96.44 |
| R22_1022.14           | 0.00 | 46.15 | 48.94 | 0.03 | 1.16 | 0.09 | 0.07 | 96.45 |
| R20_1335.14           | 0.00 | 58.75 | 36.43 | 0.00 | 1.26 | 0.02 | 0.00 | 96.46 |
| DV1.820.3             | 0.00 | 45.42 | 49.95 | 0.02 | 1.00 | 0.09 | 0.00 | 96.48 |
| TRSA_1.1138.5.4       | 0.00 | 45.14 | 48.15 | 0.00 | 3.16 | 0.06 | 0.00 | 96.51 |
| R20.1364.11           | 0.00 | 45.77 | 49.67 | 0.00 | 1.01 | 0.07 | 0.00 | 96.52 |
| R22_1004-1007.11      | 0.01 | 46.45 | 48.93 | 0.03 | 1.05 | 0.05 | 0.00 | 96.52 |
| R25_981.4             | 0.00 | 45.42 | 50.25 | 0.01 | 0.91 | 0.00 | 0.00 | 96.59 |
| DV1.820.15            | 0.00 | 46.28 | 49.36 | 0.01 | 0.83 | 0.13 | 0.00 | 96.60 |
| R22_1004-1007.6       | 0.02 | 43.01 | 49.97 | 0.04 | 3.40 | 0.17 | 0.00 | 96.60 |
| R13_1483.9            | 0.00 | 44.35 | 50.55 | 0.00 | 1.60 | 0.11 | 0.00 | 96.61 |
| R13_1483.8            | 0.00 | 44.58 | 50.04 | 0.00 | 2.04 | 0.01 | 0.00 | 96.67 |
| R14.1248.12           | 0.00 | 45.49 | 50.01 | 0.05 | 1.07 | 0.06 | 0.00 | 96.69 |
| R20.1364.14           | 0.00 | 44.19 | 49.92 | 0.02 | 2.56 | 0.04 | 0.00 | 96.73 |
| TRSA-1_1080.7         | 0.01 | 43.38 | 51.13 | 0.07 | 2.10 | 0.11 | 0.00 | 96.80 |
| R28_1163.13           | 0.00 | 45.66 | 50.30 | 0.04 | 0.73 | 0.13 | 0.00 | 96.86 |

|                       |      |       |       |      |      |      |      |       |
|-----------------------|------|-------|-------|------|------|------|------|-------|
| Appendix 6 continued. |      |       |       |      |      |      |      |       |
| R14.1248.6            | 0.00 | 44.56 | 51.06 | 0.05 | 1.12 | 0.09 | 0.00 | 96.88 |
| R20_1233.9            | 0.01 | 44.72 | 49.94 | 0.00 | 2.22 | 0.02 | 0.00 | 96.91 |
| R22_1004-1007.10      | 0.00 | 43.35 | 51.94 | 0.01 | 1.41 | 0.17 | 0.05 | 96.93 |
| R20_1335.7            | 0.00 | 43.73 | 51.44 | 0.02 | 1.67 | 0.08 | 0.00 | 96.94 |
| R5_1082.5             | 0.01 | 44.78 | 51.70 | 0.01 | 0.10 | 0.36 | 0.00 | 96.96 |
| DV1.820.10            | 0.00 | 45.12 | 50.55 | 0.00 | 1.19 | 0.13 | 0.00 | 96.99 |
| R22_1004-1007.3       | 0.00 | 46.20 | 50.21 | 0.03 | 0.47 | 0.09 | 0.00 | 97.00 |
| TRSA_1.1138.5.7       | 0.00 | 45.92 | 48.47 | 0.00 | 2.65 | 0.06 | 0.00 | 97.10 |
| R28_1163.10           | 0.01 | 44.94 | 51.54 | 0.02 | 0.49 | 0.13 | 0.00 | 97.14 |
| R20_1335.13           | 0.00 | 44.69 | 51.46 | 0.00 | 1.01 | 0.04 | 0.00 | 97.20 |
| R14.1248.3            | 0.00 | 45.38 | 50.35 | 0.08 | 1.24 | 0.17 | 0.00 | 97.22 |
| R22_1022.15           | 0.00 | 45.33 | 50.76 | 0.00 | 1.19 | 0.01 | 0.00 | 97.29 |
| R22_1004-1007.12      | 0.01 | 44.42 | 51.07 | 0.03 | 1.71 | 0.13 | 0.00 | 97.37 |
| R5_1082.7             | 0.00 | 46.32 | 50.80 | 0.01 | 0.11 | 0.19 | 0.00 | 97.43 |
| DV-1_658.4            | 0.25 | 44.89 | 50.59 | 0.00 | 1.26 | 0.44 | 0.00 | 97.43 |
| R5_1082.6             | 0.01 | 45.34 | 51.60 | 0.02 | 0.12 | 0.34 | 0.00 | 97.43 |
| R5_1082.4             | 0.00 | 45.14 | 51.56 | 0.05 | 0.39 | 0.30 | 0.00 | 97.44 |
| R5.1231.4             | 0.00 | 45.65 | 50.19 | 0.00 | 1.60 | 0.01 | 0.00 | 97.45 |
| R22_944.12            | 0.00 | 46.26 | 50.21 | 0.00 | 0.92 | 0.07 | 0.00 | 97.46 |
| DV1.820.4             | 0.00 | 45.85 | 50.60 | 0.00 | 0.97 | 0.05 | 0.00 | 97.47 |
| R5.1231.3             | 0.00 | 46.49 | 49.59 | 0.00 | 1.34 | 0.06 | 0.00 | 97.48 |
| R22_944.5             | 0.00 | 44.92 | 51.65 | 0.02 | 0.90 | 0.04 | 0.00 | 97.53 |
| DV1.820.13            | 0.00 | 46.13 | 50.37 | 0.04 | 0.87 | 0.14 | 0.00 | 97.55 |
| R5_1082.16            | 0.00 | 45.62 | 51.64 | 0.02 | 0.10 | 0.19 | 0.00 | 97.56 |
| R14.1248.2            | 0.00 | 45.33 | 50.58 | 0.00 | 1.61 | 0.06 | 0.00 | 97.58 |
| R14.1248.7            | 0.00 | 44.57 | 51.54 | 0.08 | 1.28 | 0.11 | 0.00 | 97.58 |
| DV1.820.5             | 0.00 | 46.06 | 50.92 | 0.00 | 0.55 | 0.06 | 0.00 | 97.59 |
| R22_1022.8            | 0.02 | 43.53 | 52.66 | 0.05 | 1.18 | 0.19 | 0.00 | 97.62 |
| R22_1004-1007.13      | 0.01 | 46.54 | 49.32 | 0.03 | 1.68 | 0.05 | 0.00 | 97.62 |
| R5_1082.11            | 0.00 | 45.26 | 52.02 | 0.04 | 0.14 | 0.25 | 0.00 | 97.71 |
| TRSA-1_1080.1         | 0.00 | 44.47 | 52.21 | 0.06 | 0.93 | 0.06 | 0.00 | 97.73 |
| R22_1022.2            | 0.00 | 46.10 | 50.03 | 0.01 | 1.59 | 0.03 | 0.00 | 97.77 |
| TR9-2_773.8           | 0.00 | 45.93 | 50.39 | 0.01 | 1.41 | 0.04 | 0.00 | 97.77 |
| R20_1335.3            | 0.00 | 45.91 | 50.79 | 0.01 | 1.16 | 0.05 | 0.00 | 97.92 |
| R22_1004-1007.4       | 0.00 | 43.43 | 53.21 | 0.03 | 1.21 | 0.07 | 0.00 | 97.95 |
| R14.1248.5            | 0.00 | 45.54 | 50.97 | 0.04 | 1.36 | 0.06 | 0.00 | 97.96 |
| R20.1364.10           | 0.00 | 46.11 | 50.39 | 0.00 | 1.46 | 0.03 | 0.00 | 97.99 |
| DV1.820.14            | 0.00 | 45.48 | 51.52 | 0.06 | 0.70 | 0.24 | 0.00 | 98.00 |
| R22_1022.4            | 0.00 | 44.76 | 52.04 | 0.02 | 1.18 | 0.02 | 0.00 | 98.02 |
| R5_1082.8             | 0.01 | 46.91 | 50.80 | 0.02 | 0.11 | 0.18 | 0.00 | 98.03 |
| TR92.765.1            | 0.00 | 48.03 | 48.93 | 0.00 | 1.02 | 0.04 | 0.03 | 98.05 |
| R22_1022.13           | 0.00 | 45.92 | 51.23 | 0.03 | 0.93 | 0.05 | 0.00 | 98.16 |
| R22_1004-1007.9       | 0.01 | 47.12 | 49.94 | 0.04 | 1.03 | 0.04 | 0.00 | 98.18 |
| R13_1483.2            | 0.01 | 45.91 | 50.61 | 0.01 | 1.67 | 0.04 | 0.00 | 98.25 |
| R28_1224.7            | 0.03 | 46.42 | 50.86 | 0.01 | 0.60 | 0.37 | 0.00 | 98.29 |
| TR4-1_1171.2          | 0.01 | 46.41 | 51.21 | 0.00 | 0.47 | 0.21 | 0.00 | 98.30 |

| Appendix 6 continued. |      |       |       |      |      |      |      |       |
|-----------------------|------|-------|-------|------|------|------|------|-------|
| DV1.820.2             | 0.00 | 45.26 | 51.89 | 0.03 | 0.96 | 0.17 | 0.00 | 98.31 |
| DV1.820.12            | 0.00 | 46.29 | 51.14 | 0.02 | 0.77 | 0.13 | 0.00 | 98.35 |
| R5_1082.14            | 0.00 | 45.99 | 52.03 | 0.04 | 0.10 | 0.22 | 0.00 | 98.38 |
| DV1.707.1             | 0.00 | 45.73 | 51.33 | 0.02 | 1.27 | 0.09 | 0.00 | 98.43 |
| R5_1082.10            | 0.01 | 45.73 | 52.27 | 0.02 | 0.20 | 0.25 | 0.00 | 98.47 |
| R22_1022.3            | 0.00 | 44.51 | 52.26 | 0.01 | 1.65 | 0.05 | 0.00 | 98.48 |
| R28_1224.5            | 0.02 | 45.30 | 52.08 | 0.02 | 0.74 | 0.34 | 0.00 | 98.49 |
| R5_1082.1             | 0.01 | 45.38 | 52.76 | 0.03 | 0.10 | 0.29 | 0.00 | 98.57 |
| R22_944.3             | 0.00 | 45.78 | 51.85 | 0.01 | 0.94 | 0.02 | 0.00 | 98.59 |
| R22_944.13            | 0.00 | 45.27 | 52.34 | 0.01 | 0.98 | 0.05 | 0.00 | 98.65 |
| R20.1364.5            | 0.00 | 45.10 | 51.15 | 0.00 | 2.35 | 0.07 | 0.00 | 98.67 |
| R28_1224.10           | 0.00 | 46.15 | 51.81 | 0.00 | 0.51 | 0.21 | 0.00 | 98.67 |
| R5.1107.1             | 0.00 | 44.99 | 51.05 | 0.00 | 2.18 | 0.46 | 0.00 | 98.68 |
| R28_1224.14           | 0.01 | 45.35 | 52.15 | 0.01 | 0.99 | 0.24 | 0.00 | 98.76 |
| TRSA_1.1138.5.10      | 0.00 | 46.48 | 49.85 | 0.00 | 2.41 | 0.04 | 0.00 | 98.78 |
| TR92.765.7            | 0.00 | 46.34 | 50.98 | 0.00 | 1.45 | 0.01 | 0.00 | 98.78 |
| R28_1224.11           | 0.02 | 46.00 | 52.06 | 0.01 | 0.36 | 0.34 | 0.00 | 98.79 |
| R22_1185.3            | 0.00 | 45.48 | 52.49 | 0.00 | 0.78 | 0.09 | 0.00 | 98.84 |
| TRSA_1.1138.5.8       | 0.00 | 46.43 | 50.45 | 0.00 | 1.97 | 0.06 | 0.00 | 98.91 |
| R22_1185.6            | 0.00 | 46.92 | 51.35 | 0.02 | 0.55 | 0.09 | 0.00 | 98.92 |
| R28_1224.15           | 0.02 | 45.57 | 52.65 | 0.04 | 0.35 | 0.26 | 0.05 | 98.94 |
| R22_1022.12           | 0.01 | 46.26 | 51.72 | 0.01 | 0.93 | 0.03 | 0.00 | 98.96 |
| R14.1248.4            | 0.00 | 45.96 | 51.77 | 0.00 | 1.19 | 0.05 | 0.00 | 98.97 |
| R28_1228.5            | 0.00 | 45.63 | 51.61 | 0.00 | 1.83 | 0.00 | 0.00 | 99.07 |
| R5.1231.7             | 0.00 | 46.60 | 51.08 | 0.00 | 1.35 | 0.08 | 0.00 | 99.11 |
| R13.1324.1            | 0.00 | 46.28 | 51.83 | 0.02 | 0.96 | 0.05 | 0.00 | 99.15 |
| R13.1324.2            | 0.00 | 46.35 | 51.84 | 0.01 | 0.96 | 0.02 | 0.00 | 99.19 |
| TRSA_1.1138.5.11      | 0.00 | 46.71 | 50.41 | 0.00 | 2.02 | 0.05 | 0.00 | 99.19 |
| DV1.820.8             | 0.00 | 47.40 | 50.95 | 0.00 | 0.85 | 0.09 | 0.00 | 99.28 |
| R25_981.3             | 0.00 | 46.85 | 51.90 | 0.01 | 0.54 | 0.02 | 0.00 | 99.32 |
| R5_1082.13            | 0.00 | 46.24 | 52.81 | 0.01 | 0.07 | 0.20 | 0.00 | 99.33 |
| R5_1082.3             | 0.00 | 45.72 | 53.21 | 0.03 | 0.17 | 0.21 | 0.00 | 99.34 |
| R25_981.5             | 0.00 | 46.16 | 52.36 | 0.02 | 0.75 | 0.09 | 0.00 | 99.37 |
| R22_1185.5            | 0.00 | 45.85 | 51.73 | 0.04 | 1.71 | 0.05 | 0.00 | 99.38 |
| R22_1022.9            | 0.01 | 45.28 | 52.98 | 0.02 | 1.04 | 0.06 | 0.00 | 99.38 |
| R5_1082.12            | 0.00 | 45.75 | 53.38 | 0.01 | 0.07 | 0.18 | 0.00 | 99.40 |
| R20_1233.6            | 0.01 | 46.18 | 51.67 | 0.02 | 1.53 | 0.00 | 0.00 | 99.40 |
| TR92.765.13           | 0.00 | 46.62 | 51.93 | 0.08 | 0.88 | 0.05 | 0.00 | 99.56 |
| R5.1107.5             | 0.00 | 47.10 | 51.61 | 0.00 | 0.45 | 0.43 | 0.00 | 99.59 |
| R14.1248.13           | 0.00 | 46.44 | 52.20 | 0.00 | 1.02 | 0.02 | 0.00 | 99.68 |
| R28_1163.2            | 0.00 | 46.78 | 52.14 | 0.00 | 0.72 | 0.05 | 0.00 | 99.69 |
| R20.1364.15           | 0.00 | 45.62 | 52.17 | 0.05 | 1.83 | 0.06 | 0.00 | 99.72 |
| R28_1228.3            | 0.00 | 44.62 | 53.01 | 0.00 | 2.08 | 0.03 | 0.00 | 99.74 |
| R28_1224.8            | 0.00 | 46.43 | 52.53 | 0.00 | 0.75 | 0.05 | 0.00 | 99.76 |
| R13_1395.1            | 0.00 | 46.29 | 52.31 | 0.00 | 1.18 | 0.00 | 0.00 | 99.78 |
| TR92.765.6            | 0.00 | 46.35 | 52.43 | 0.00 | 0.93 | 0.09 | 0.00 | 99.81 |

|                       |      |       |       |      |      |      |      |        |
|-----------------------|------|-------|-------|------|------|------|------|--------|
| Appendix 6 continued. |      |       |       |      |      |      |      |        |
| R14.1248.1            | 0.00 | 46.38 | 52.06 | 0.00 | 1.31 | 0.08 | 0.00 | 99.83  |
| R20.1364.8            | 0.00 | 47.59 | 51.26 | 0.00 | 0.96 | 0.03 | 0.00 | 99.84  |
| DV1.820.11            | 0.00 | 47.01 | 52.25 | 0.00 | 0.54 | 0.06 | 0.00 | 99.86  |
| R28_1224.9            | 0.00 | 46.07 | 52.79 | 0.01 | 0.83 | 0.19 | 0.00 | 99.89  |
| R20_1233.4            | 0.00 | 45.78 | 53.02 | 0.04 | 1.11 | 0.01 | 0.00 | 99.95  |
| R13_1483.1            | 0.00 | 46.76 | 52.08 | 0.00 | 1.03 | 0.12 | 0.00 | 99.99  |
| DV1.707.3             | 0.00 | 45.49 | 53.12 | 0.00 | 1.28 | 0.10 | 0.00 | 99.99  |
| R28_1224.6            | 0.03 | 45.66 | 53.72 | 0.05 | 0.26 | 0.29 | 0.05 | 100.05 |
| R5_1082.9             | 0.00 | 46.13 | 53.60 | 0.01 | 0.10 | 0.22 | 0.00 | 100.06 |
| R28_1228.4            | 0.01 | 46.10 | 52.45 | 0.02 | 1.49 | 0.02 | 0.00 | 100.08 |
| R13_1483.10           | 0.01 | 47.08 | 51.57 | 0.00 | 1.36 | 0.09 | 0.00 | 100.11 |
| R22_944.11            | 0.00 | 46.82 | 52.52 | 0.00 | 0.75 | 0.06 | 0.00 | 100.15 |
| R5_1082.2             | 0.00 | 46.67 | 53.02 | 0.01 | 0.26 | 0.19 | 0.00 | 100.15 |
| R13_1483.4            | 0.01 | 46.38 | 52.27 | 0.00 | 1.54 | 0.01 | 0.00 | 100.21 |
| R13.1324.3            | 0.00 | 46.85 | 52.61 | 0.00 | 0.70 | 0.06 | 0.00 | 100.22 |
| R25_981.2             | 0.00 | 46.56 | 53.05 | 0.04 | 0.54 | 0.06 | 0.00 | 100.25 |
| R20.1364.9            | 0.00 | 46.71 | 52.51 | 0.00 | 1.01 | 0.02 | 0.00 | 100.25 |
| TR92.765.9            | 0.00 | 47.39 | 52.07 | 0.00 | 0.80 | 0.00 | 0.00 | 100.26 |
| R22_944.8             | 0.00 | 45.92 | 53.53 | 0.00 | 0.82 | 0.00 | 0.00 | 100.27 |
| R20_1333.8            | 0.00 | 46.62 | 52.46 | 0.06 | 1.20 | 0.01 | 0.00 | 100.35 |
| R22_1004-1007.5       | 0.00 | 46.05 | 53.19 | 0.00 | 1.13 | 0.00 | 0.00 | 100.37 |
| R28_1163.1            | 0.00 | 47.07 | 52.58 | 0.06 | 0.63 | 0.06 | 0.00 | 100.39 |
| TRSA_1.1138.5.3       | 0.00 | 46.90 | 51.98 | 0.00 | 1.55 | 0.01 | 0.00 | 100.44 |
| R20.1364.16           | 0.00 | 46.89 | 52.42 | 0.00 | 1.07 | 0.08 | 0.00 | 100.45 |
| R22_944.6             | 0.00 | 46.87 | 52.96 | 0.01 | 0.66 | 0.03 | 0.00 | 100.53 |
| TR92.765.17           | 0.00 | 47.08 | 52.71 | 0.02 | 0.71 | 0.04 | 0.00 | 100.57 |
| DV1.775.9             | 0.00 | 46.99 | 52.79 | 0.00 | 0.77 | 0.04 | 0.00 | 100.59 |
| R22_1022.7            | 0.00 | 45.42 | 54.23 | 0.01 | 0.87 | 0.07 | 0.00 | 100.60 |
| R25_981.1             | 0.00 | 47.22 | 52.90 | 0.03 | 0.46 | 0.00 | 0.00 | 100.61 |
| R22_1004-1007.8       | 0.00 | 46.02 | 53.33 | 0.03 | 1.22 | 0.04 | 0.00 | 100.64 |
| TRSA-1_1080.6         | 0.00 | 45.63 | 53.05 | 0.06 | 1.93 | 0.00 | 0.00 | 100.67 |
| R13_1483.5            | 0.00 | 46.50 | 52.73 | 0.01 | 1.35 | 0.09 | 0.00 | 100.67 |
| DV1.820.9             | 0.00 | 46.57 | 53.27 | 0.00 | 0.75 | 0.12 | 0.00 | 100.70 |
| TRSA-1_1080.9         | 0.00 | 46.85 | 53.00 | 0.03 | 0.82 | 0.02 | 0.00 | 100.71 |
| TR92.765.15           | 0.00 | 47.26 | 52.47 | 0.00 | 0.99 | 0.00 | 0.00 | 100.72 |
| R5.1231.5             | 0.00 | 46.93 | 52.48 | 0.01 | 1.43 | 0.06 | 0.00 | 100.91 |
| R20.1364.1            | 0.00 | 46.13 | 53.24 | 0.01 | 1.50 | 0.04 | 0.00 | 100.92 |
| R25_981.8             | 0.01 | 47.44 | 52.84 | 0.02 | 0.63 | 0.00 | 0.00 | 100.93 |
| R22_944.2             | 0.00 | 46.23 | 53.92 | 0.02 | 0.78 | 0.03 | 0.00 | 100.99 |
| R22_944.10            | 0.00 | 46.79 | 53.52 | 0.00 | 0.67 | 0.02 | 0.00 | 100.99 |
| TR92.765.4            | 0.00 | 47.23 | 52.89 | 0.00 | 0.84 | 0.06 | 0.00 | 101.02 |
| TRSA-1_1080.11        | 0.00 | 47.58 | 52.51 | 0.00 | 0.89 | 0.05 | 0.00 | 101.02 |
| TRSA-1_1080.3         | 0.00 | 46.80 | 53.20 | 0.04 | 1.09 | 0.00 | 0.00 | 101.13 |
| TR9-2_773.6           | 0.01 | 46.72 | 53.27 | 0.01 | 1.13 | 0.01 | 0.00 | 101.15 |
| R28_1228.7            | 0.00 | 46.68 | 53.85 | 0.00 | 0.62 | 0.02 | 0.00 | 101.16 |
| R13.1324.4            | 0.00 | 47.99 | 51.73 | 0.00 | 1.42 | 0.02 | 0.00 | 101.16 |

| Appendix 6 continued. |      |       |       |      |      |      |      |        |
|-----------------------|------|-------|-------|------|------|------|------|--------|
| R5_1082.15            | 0.00 | 47.56 | 53.39 | 0.02 | 0.07 | 0.15 | 0.00 | 101.19 |
| R20.1364.2            | 0.00 | 46.80 | 52.92 | 0.00 | 1.48 | 0.02 | 0.00 | 101.22 |
| R25_981.10            | 0.00 | 47.09 | 53.71 | 0.02 | 0.37 | 0.04 | 0.00 | 101.23 |
| R28_1228.6            | 0.00 | 47.25 | 52.92 | 0.00 | 1.04 | 0.02 | 0.00 | 101.23 |
| R22_944.7             | 0.00 | 46.65 | 53.71 | 0.03 | 0.81 | 0.04 | 0.00 | 101.23 |
| TRSA-1_1080.8         | 0.00 | 45.79 | 53.98 | 0.04 | 1.38 | 0.04 | 0.00 | 101.23 |
| TR4-1_1171.1          | 0.00 | 47.49 | 52.83 | 0.02 | 0.87 | 0.04 | 0.00 | 101.25 |
| TR92.765.14           | 0.00 | 47.67 | 52.77 | 0.00 | 0.77 | 0.05 | 0.00 | 101.26 |
| TR92.765.5            | 0.00 | 47.74 | 52.72 | 0.03 | 0.74 | 0.05 | 0.00 | 101.27 |
| R22_944.4             | 0.00 | 46.16 | 54.21 | 0.02 | 0.88 | 0.04 | 0.00 | 101.31 |
| TRSA_1.1138.5.1       | 0.00 | 47.26 | 52.91 | 0.00 | 1.16 | 0.06 | 0.00 | 101.39 |
| R20.1364.3            | 0.00 | 46.70 | 53.27 | 0.08 | 1.35 | 0.02 | 0.00 | 101.42 |
| R22_954.1             | 0.00 | 46.16 | 54.27 | 0.01 | 1.08 | 0.00 | 0.00 | 101.52 |
| R14.1248.14           | 0.00 | 47.14 | 53.67 | 0.00 | 0.86 | 0.06 | 0.00 | 101.72 |
| DV1.707.5             | 0.00 | 46.99 | 53.91 | 0.00 | 0.86 | 0.02 | 0.00 | 101.78 |
| TRSA-1_1080.10        | 0.00 | 47.01 | 53.99 | 0.04 | 0.79 | 0.00 | 0.00 | 101.83 |
| TR4-1_1171.6          | 0.00 | 47.23 | 53.76 | 0.00 | 0.87 | 0.00 | 0.00 | 101.86 |
| TRSA-1_1080.4         | 0.00 | 47.00 | 53.77 | 0.02 | 1.10 | 0.00 | 0.00 | 101.89 |
| R22_954.4             | 0.00 | 47.10 | 53.71 | 0.00 | 1.17 | 0.00 | 0.00 | 101.98 |
| R22_954.6             | 0.00 | 46.69 | 54.09 | 0.01 | 1.24 | 0.01 | 0.00 | 102.04 |
| R22_954.10            | 0.00 | 46.55 | 54.48 | 0.00 | 1.01 | 0.00 | 0.00 | 102.04 |
| R25_981.9             | 0.00 | 47.13 | 54.19 | 0.10 | 0.66 | 0.00 | 0.00 | 102.08 |
| R22_954.2             | 0.00 | 47.23 | 53.66 | 0.01 | 1.14 | 0.04 | 0.00 | 102.08 |
| R28_1228.1            | 0.00 | 47.20 | 54.12 | 0.00 | 0.84 | 0.02 | 0.00 | 102.19 |
| R25_981.7             | 0.00 | 47.90 | 54.05 | 0.02 | 0.43 | 0.00 | 0.00 | 102.40 |
| R25_981.6             | 0.00 | 47.63 | 54.40 | 0.03 | 0.53 | 0.01 | 0.00 | 102.60 |
| TRSA-1_1080.2         | 0.00 | 46.75 | 55.19 | 0.02 | 0.88 | 0.05 | 0.00 | 102.88 |
| R20_1340.2            | 0.00 | 47.13 | 53.65 | 0.06 | 2.62 | 0.09 | 0.00 | 103.55 |
| R22_954.9             | 0.00 | 47.61 | 55.27 | 0.08 | 0.98 | 0.02 | 0.00 | 103.95 |

## APPENDIX 7

The EPMA results for 10 different celestine minerals in sample R22 1185. Each grain had three analytical points.

| Sample       | Sr (mg/kg) | Ba (mg/kg) | Ca (mg/kg) | S (mg/kg) |
|--------------|------------|------------|------------|-----------|
| R22_1185.C.1 | 55816.2    | 208        | 184        | 43050     |
| R22_1185.C.2 | 56232      | 257        | 110        | 42840     |
| R22_1185.C.3 | 55242      | 462        | 111        | 42890     |
| R22_1185.C.1 | 56588.4    | 43         | 139        | 42920     |
| R22_1185.C.2 | 57528.9    | 0          | 78         | 43500     |
| R22_1185.C.3 | 57370.5    | 0          | 92         | 43400     |
| R22_1185.C.1 | 57222      |            | 212        | 42810     |
| R22_1185.C.2 | 57360.6    | 577        | 65         | 43390     |
| R22_1185.C.3 | 57004.2    | 60         | 84         | 43500     |
| R22_1185.C.1 | 56835.9    | 273        | 198        | 42790     |
| R22_1185.C.2 | 57350.7    | 81         | 153        | 42980     |
| R22_1185.C.3 | 58518.9    | 0          | 107        | 42430     |
| R22_1185.C.1 | 57410.1    | 709        | 112        | 43710     |
| R22_1185.C.2 | 57390.3    | 86         | 105        | 41920     |
| R22_1185.C.3 | 57915      | 228        | 84         | 41950     |
| R22_1185.C.1 | 57410.1    | 199        | 130        | 41570     |
| R22_1185.C.2 | 57875.4    | 431        | 86         | 42800     |
| R22_1185.C.3 | 57459.6    | 609        | 139        | 42720     |
| R22_1185.C.1 | 58271.4    | 200        | 102        | 43420     |
| R22_1185.C.2 | 58835.7    | 414        | 36         | 42490     |
| R22_1185.C.3 | 58004.1    | 88         | 153        | 43130     |
| R22_1185.C.1 | 57113.1    | 74         | 611        | 43010     |
| R22_1185.C.2 | 57033.9    | 0          | 257        | 42320     |
| R22_1185.C.3 | 56746.8    | 0          | 343        | 42390     |
| R22_1185.C.1 | 57489.3    | 664        | 126        | 42340     |
| R22_1185.C.2 | 57637.8    | 491        | 27         | 42690     |
| R22_1185.C.3 | 54786.6    | 1820       | 49         | 42600     |
| R22_1185.C.1 | 55935      | 0          | 96         | 43090     |
| R22_1185.C.2 | 56014.2    | 74         | 74         | 43140     |
| R22_1185.C.3 | 56568.6    | 0          | 124        | 42390     |