Effects of Iron, Nickel, and Nutrient Supply on Pyrite Crystal Formation in Marsh Sediments

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With the guidance and support of

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Abstract

Pyrite (FeS₂) forms commonly in salt marsh sediments and acts as a crucial control on the amount of sulfur in its various forms (SO₄²⁻, H₂S, etc.) that remains in the environment. A better understanding of the mechanisms behind pyrite formation is critical in comprehending global patterns in sulfur cycling, both now and in the past. In this experiment, I extracted sediment cores from five different marsh locations to analyze for iron and sulfur, the two components of the pyrite mineral. Cores from one marsh site, Little Sippewissett Marsh, were oxidized and then incubated in different seawater-based treatments to determine the primary influences on pyrite crystal formation in marsh sediments. By testing for iron and sulfur and imaging these sediments with a scanning electron microscope (SEM), I was able to come to a number of conclusions about pyrite. Elevated nitrate levels may inhibit pyrite formation in sediments as nitrate can act as an oxidant on pyrite. Fresher waters may reduce pyrite precipitation as there are fewer ions, specifically sulfate, in solution to promote pyrite accumulation. In the incubated cores, increased ferrous iron (Fe²⁺) input to the sediment had a much more positive effect on pyrite precipitation than the input of ferric iron (Fe³⁺) due to the different pyrite formation pathways between these two types of iron. Four primary crystal forms appeared across the samples, but I found no nickel-pyrite as this reaction requires a hydrothermal environment. This experiment shows that the formation of the mineral pyrite depends on certain environmental factors such as type of available nutrients, type of available iron, and amount of organic material; my experiment also emphasizes the variety of pyrite crystal shapes found in marsh sediments.

Key words and phrases
Pyrite, pyrite crystallization, marshes, marsh sediments, iron, sulfur, sulfate, hydrogen sulfide, crystal shapes, nickel-pyrite, nutrients.

**Introduction**

Pyrite functions as an important control on global sulfur cycling as 60 million tons of sulfur is buried each year as pyrite in sediments (Rickard 2015). Sulfur in the form of sulfate is an extremely important element in the environment, both beneficial and harmful. Sulfate is an essential electron acceptor for sulfate reducing bacteria, which convert sulfate to hydrogen sulfide as a source of energy. Hydrogen sulfide can become toxic for wildlife and humans in high enough concentrations, and an overabundance of sulfate can cause an ecosystem shift to bacterial sulfate reducers. Sulfur is equally important for plants as it represents a fundamental part of plant proteins; plants take up sulfur from the soil in the form of sulfate. Sulfate is even a component of acid rain, which can cause irreparable harm to the environment if left unchecked. The formation and subsequent burial of pyrite in sediments modulates the concentration of sulfate and hydrogen sulfide in the environment. This allows microorganisms and plants to remain in healthy competition, hydrogen sulfide concentrations to stay low, and acid rain frequency to decrease.

Much of the pyrite buried in marsh sediments is found in the form of pyrite framboids, small raspberry-like clusters of individual pyrite crystals aggregated together under the influence of their surface electrical charges (Rickard 2015). Other individual dodecahedral, octahedral, and even cubic crystals are common, but a large percentage of the total pyrite buried accumulates in a spherical framboidal form. These pyrite framboids can require anywhere from three hours to three years to form, but the average formation time hovers around five days (Rickard 2019).
Pyrite, and specifically pyritic framboids, can even act as indicators of paleo conditions in aquatic systems. Studies have shown that the size of pyrite framboids can suggest whether they formed in a euxinic or oxic-dysoxic environment. Total organic matter and even gas content from thermochemical sulfate reduction can be estimated from data gleaned from pyrite framboids (Liu et al. 2019). Therefore, understanding how and why pyrite forms today can inform us about past climatic conditions on Earth.

While the formation and burial of pyrite in the ocean remains a very slow process (Figure 1a), pyrite precipitation in marsh sediments seems to be much more rapid. Many experts have proposed that pyrite precipitates quickly from the direct reaction between ferrous iron \((\text{Fe}^{2+})\) and polysulfides (like \(\text{S}_3^{2-}\)) (Giblin et al. 1988). The iron in solution is a product of direct deposition of iron compounds, and the polysulfides develop from the bacterial sulfate reduction product hydrogen sulfide (Figure 1b). This rapid precipitation allows for pyrite formation to be experimentally measured on short time scales.

**Methods**

I recovered sediment cores from five separate locations that include:

- 15 cores from Little Sippewissett Marsh
- 2 cores from fertilized plots at Great Sippewissett Marsh
- 2 cores from unfertilized plots at Great Sippewissett Marsh
- 2 cores from a Plum Island, MA marsh near a sewage treatment plant
- 2 cores from a pristine marsh at Plum Island, MA
All of these cylindrical cores were over 7 cm long with diameters of 4.75 cm. I collected them by hammering a plastic core tube into the ground, extracting it, and transferring the sediment into a thinner storage tube.

The eight total cores from Great Sippewissett and Plum Island were returned to the lab for analysis. There, they were cut and separated into an upper sediment layer (0 to 5 cm in depth) and a lower sediment layer (5 to a maximum of 13 cm in depth). I cut off a small, representative subsample (5 cm in depth) from at least one core from every site/treatment to use for imaging on the scanning electron microscope (SEM). I pipetted 10-15 ml of ethyl alcohol onto each of the subsamples and left them to dry for 2-3 days before they were taken to the SEM. The rest of the cores were then left to dry in a drying oven for a few days. Once dry, a representative portion of each sample was ground to a fine powder using a coffee grinder, placed in a plastic bag, and labelled.

Three of the fifteen cores obtained from Little Sippewissett were immediately harvested as initial measurements. They underwent the same separation, drying, and grinding process mentioned above. I let the remaining cores sit for two days suspended by ring clamps over bottles into which they could drain. Then, the oxidation process began. I used a solution of nine parts deionized water to one part seawater to flush the cores. In total, the cores were flushed five times with 100 ml of solution each time for a total solution input of 500 ml. For the first three flushings, the solution was poured onto the top of the core and allowed to flow through, past the mesh holding the bottom of the cores in place. For the final two flushings, the tubes were capped, and the cores were allowed to sit in the deionized water – seawater solution for two hours. I kept this liquid after every flushing and tested its pH to ensure that the effluent water had a lower pH compared to the solution poured onto the cores. A more acidic effluent meant that the solution
should be oxidizing the core. After an oxidation period of ten days, I poured 100 ml of only seawater through each core to prepare them for the incubation period. I then took the effluent liquid from the oxidation process, filtered it, and diluted .8 ml of the filtered solution to 100 ml with deionized water. Suzanne Thomas then analyzed this solution for sulfate (SO$_4^{2-}$) and chloride (Cl$^-$) ion concentrations using the Dionex DX-120 Ion Chromatograph. From this data I could calculate the amount of sulfate drained out of the cores by subtracted the expected sulfate concentrations (using a sulfate to chloride ratio of 0.0517) from Suzanne’s measured sulfate concentrations.

I harvested three of the oxidized cores to be dried, ground, analyzed for iron and sulfur, and imaged on the SEM leaving nine cores remaining for treatment. Four treatments were chosen:

- 3 cores were incubated in pure seawater
- 2 cores were incubated in a seawater solution spiked with ferric citrate, Fe(C$_6$H$_5$O$_7$)
- 2 cores were incubated in a seawater solution spiked with ferrous sulfate, FeSO$_4$
- 2 cores were incubated in the same ferrous sulfate solution with added nickel chloride, NiCl$_2$

In marsh sediments, despite a very large range the average iron content is around 5 mg of iron per g of sediment; most of this iron is in the form of pyrite. Factoring in the density of peat yields 1 mg of iron per cubic centimeter. I calculated the individual volume of each core so that incubation solutions could be created to approximate this iron content. In other words, I created the three solutions spiked with iron to simulate around 1 mg of iron added for every cubic centimeter of sediment. For the last treatment with elevated nickel, I added enough nickel to the solution to create a 1:1 nickel to iron mass ratio, as their respective molecular weights are fairly
similar. Once I made all the solutions for the cores, I poured enough solution into the top of the capped core tube to just barely cover the top of the sediment. I ensured that these cores were always covered with solution throughout the experiment so that the system remained anaerobic.

The nine treatment cores incubated for thirteen days; afterwards they were broken down in the same manner as all the others for imaging and iron and sulfur analysis. For the top 5 cm of every core, I used a version of the Forstner and Salomons method for total trace metal analysis. I weighed out ~0.100 g of dry, ground core sediment into a 50 ml centrifuge tube for each core. Then I added 5 ml of concentrated HNO$_3$, heated the tubes in a water bath at 60°C for two hours, let them cool, and added metal grade concentrated HCl. After that I filtered the solution through a Whatman filter into a volumetric flask and diluted the solution to 100 ml with deionized water. In theory, this treatment should liberate all the iron in its various forms (iron oxides, iron bound to clays, FeS, FeS$_2$, etc.) from the sediment to provide the total iron content. I used a similar method to obtain the concentration of all non-pyritic forms of iron. Again, I weighed out ~0.100 g of dry, ground core sediment into a 50 ml centrifuge tube for each core to which I added 10 ml of 6N HCl. After letting the solution extract the iron from the sediment, I filtered the solutions through a Whatman filter into a volumetric flask and diluted to 100 ml with deionized water. Finally, all the cores from both treatments were ready for iron analysis. I ran these solutions on the Atomic Absorption Spectrophotometer to obtain a concentration of iron in solution. From this, I could calculate the milligrams of pyritic iron per gram of sediment.

For the sulfur analysis, Sam Kelsey and I took .2 grams of ground sediment from both the upper 5 cm and lower 5 cm of each sediment core and burned every sample using the LECO S635 Sulfur Analyzer. This process provided a mass percent of sulfur contained in the sediment.
Further preparation of the samples bound for the SEM was required. I took the subsamples dried with ethyl alcohol, cut off a millimeter size slice and pasted it to a metal stub. I then coated the sample on each of these stubs with either platinum or carbon. I used platinum for the first batch but then converted to carbon as the data seemed better. The thickness of each coating was about 20 nm. Finally, I was able to image the samples using the scanning electron microscope. I verified that all the crystals I identified were pyrite using the Energy Dispersive Spectroscopy (EDS) capability of the SEM. This tool allows an image to be analyzed pixel by pixel to determine where specific elements (iron, sulfur, and nickel) are more abundant.

**Results**

*Iron and sulfur in sediment*

The fertilized plots at Great Sippewissett Marsh had the highest amount of pyritic iron in the sediment layer, totaling just over 9.3 milligrams of pyritic iron per gram of sediment. All of the other untreated sites possessed a mg/g ratio under 4, with the Plum Island marsh near the wastewater treatment plant being the lowest at just over 1.2 mg/g (Figure 2). For the treated cores, the Little Sippewissett initial cores (analyzed right from the field) and the Little Sippewissett post oxidation cores (analyzed after the oxidation process) had about the same mg/g ratio around 3.5. Among the four treatments the ferrous sulfate one possessed the most pyritic iron followed by the nickel-iron, ferric citrate, and seawater treatments in that order (Figure 3).

Great Sippewissett fertilized plots again possessed the most overall sulfur, with a mass percent of over 3.6. This result is corroborated by Lamborg et al. who found a sulfur mass percent of these high fertilized (HF) plots at Great Sippewissett to be around 3.92, a figure that closely matches mine (Lamborg et al. 2019). The Plum Island marsh near the treatment plant was
lowest in sulfur percent as well, followed by the sediments from Little Sippewissett, the Plum Island pristine marsh, and the Great Sippewissett unfertilized plots in that order (Figure 4). Mass percent sulfur for the Little Sippewissett treated cores were much more homogeneous, ranging from 0.9% to just under 1.5% (Figure 5).

The total iron in each of the sediment cores in units of milligrams of total iron to gram of sediment varied from 2.8 mg/g at the Great Sippewissett unfertilized plots to over 22 mg/g at the Plum Island marsh near the wastewater treatment plant (Figure 6). I also found the ratio of pyritic iron to total iron for each of the sites/treatments, which also had great variation. Some sites had a ratio of over 0.55, but others had a ratio as low as 0.06 (Figure 7).

The three different forms of sulfur in the sediments was broken down into three categories: pyritic sulfur, sulfur from organic material, and the remaining sulfur. This remaining sulfur constituted the majority of the total sulfur for all of the cores, with pyritic sulfur accounting for the second largest amount and organic sulfur making up only a fraction of the total (Figure 8).

The amount of sulfur oxidized out of the cores during the oxidation process corresponds to the difference between the measured and expected sulfate concentrations of the oxidation process effluent. These concentrations are captured in Figure 9. These values vary tremendously from highly positive to negative concentrations. These negative values indicate sulfate was taken up by the cores from the oxidizing solutions.

**SEM/EDS images**

Using the scanning electron microscope, I was able to image two main individual pyrite crystal shapes: dodecahedrons (Figures 11 and 12) and octahedrons (Figure 13). Moreover, two
different types of pyrite framboids were visualized, a “loose” framboid (Figures 14 and 15) and a “packed” framboid (Figure 16). I ensured these crystals were actually pyrite crystals using the Energy Dispersive Spectroscopy function. All of the images that were checked using this capability possessed the requisite iron and sulfur content to be pyrite crystals. No nickel was taken up during the crystal formation process, but more background nickel in the sediment could be perceived in the nickel-iron treatments.

**Discussion**

*Iron and sulfur in sediment*

The high fertilization plots at Great Sippewissett Marsh have the highest amount of both pyritic iron and sulfur for a number of possible reasons. The intense fertilization allows for the proliferation of grasses and other organic material for which sulfur is a critical element. The sediments at the Great Sippewissett fertilized plots did have the highest percent carbon after all (Figure 10). Therefore, it follows that the more organic material is present, the more sulfur will be found. However, these plots also have the highest raw amount of pyritic iron and the largest ratio of pyritic iron to total iron, so there must be significant pyrite in these sediments (Figures 2 and 7). This is probably a result of the high reducing conditions in these fertilized plots which allows for a reduced form of sulfur to proliferate and the additional input of iron from the fertilizer itself. Some have even postulated that pyrite prefers to form around vascular plant tissue (Giblin et al. 1988), which would promote pyrite precipitation at the organic-rich high fertilization plots. That is probably of lesser importance in this context. Additionally, an organic nitrogen fertilizer is used these plots which does not act as a pyrite oxidant the same way as other forms of nitrogen like nitrate do.
The Plum Island marsh near the wastewater treatment plant has the least amount of pyritic iron and the smallest mass percent sulfur due to the fresher water and the input of nitrate to the sediment (Figures 2 and 4). This nitrate acts as an oxidant which oxidizes out all the sulfur from the sediment to sulfate in the water and converts pyritic iron to other forms of iron. This is not to say that there is no iron in the Plum Island “sewer” cores; these cores actually have the most total iron among all of the treatments and sites at over 22 mg total iron/g of sediment (Figure 6). Iron is simply present as iron oxides brought about by the influx of nitrate to the marsh system. The amount of oxidized iron dwarfs the amount of pyritic iron as seen in Figure 7. The Plum Island marsh near the wastewater treatment facility has by far the lowest pyritic iron to total iron ratio of all the sites and treatments.

Proportionally, the sediment cores from the Great Sippewissett unfertilized plots and the Plum Island pristine marsh do not match up between the bulk pyritic iron and the percent sulfur in the sediment. In comparison to the other sites, these two locations have much lower amounts of pyritic iron (Figure 3) when you consider their fairly high sulfur percentages (Figure 5). Figure 8 further emphasizes this point by displaying how pyritic sulfur represents a comparatively small portion of the total sulfur at these two sites. This indicates that alternate forms of sulfur, the “remaining” sulfur, are very prevalent in these sediments. Sulfur could be present in high concentrations in two main forms in these regions: FeS or elemental sulfur.

The same is true for two of the Little Sippewissett treated cores, the seawater treatment and the ferric citrate treatment. They both possess proportionally higher sulfur mass percentages compared to the bulk pyritic iron values (Figures 5 and 3). This again suggests that alternate forms of sulfur, like FeS and elemental sulfur, proliferate. Ferric citrate in particular tends to
form alternate sulfur compounds before they eventually convert to pyrite, which could explain why other forms of sulfur are more concentrated in these treated cores.

Among the four different treatments, the ferrous sulfate treatment proved to be the most effective at producing pyrite. The ferrous iron (Fe$^{2+}$) ion is the ideal form of iron for the direct precipitation of pyrite due to the elemental charge. This means that it is easier for pyrite to form when there is ample ferrous iron available, as there was in the ferrous sulfate treatment. The nickel-iron treated cores contained the second highest amount of pyritic iron again due to the prevalence of ferrous iron in the treatment. Next was the ferric citrate treated cores. Ferric iron (Fe$^{3+}$) often forms alternate iron compounds like iron oxides before converting to pyrite, so it may take longer for pyrite to accumulate in these treated cores. This could have resulted in a lower amount of pyritic iron with the limited treatment time available in the experiment. Of course, the seawater treated cores contained the least amount of pyritic iron because there was no additional iron added to these cores, just seawater (Figure 3).

Unfortunately, the post oxidation cores from Little Sippewissett closely match the initial cores taken from Little Sippewissett. Ideally, these post oxidation cores would be much lower than the initials as sulfur was oxidized out to sulfate and pyritic iron was converted to iron oxides during the oxidation period. This is not the case. The post oxidation cores are only slightly lower than the initials in terms of both pyritic iron and percent sulfur; they were actually higher than all of the treated cores in both categories as well (Figures 3 and 5). In a perfect world, the post oxidation cores would have been much lower in terms of sulfur and pyritic iron compared to the four treatments. There were a couple reasons why this was not the case. First was time. In the context of the experiment, ten days was not enough time to fully oxidize the cores. Figure 9 underscores this reality as it displays how sulfate concentrations from the effluent of the
oxidation process varies widely between cores. Some of the concentrations remain high while others are negative indicating sulfur was added to the core, not oxidized out of the core. Cores four, seven, and nine were the cores used for post oxidation analysis, all of which have oxidation effluent that had “negative” or minimally positive drained sulfate values. The pyrite in these cores did not oxidize out. Another possible reason for the oxidation results could be that cores four, seven, and nine possessed high total and pyritic iron levels from the start compared with the other cores. I may have oxidized much of the pyrite out, but the cores simply started at a much higher level than the others, so this oxidation does not appear in the results.

Sulfur from organic sources accounts for only a small portion of the total sulfur in the marsh sediments (Figure 8). Using the percent carbon value and a C:S weight ratio of 100, I was able to calculate the amount of sulfur in the sediment from organic sources. For all the sites, this value hovered around one micromole per gram of sediment, a sliver of the overall sulfur content of the soil. Pyritic sulfur represented a much larger portion of the bulk sulfur in the sediment, but not as large as we expected. For all the cores, pyritic sulfur makes up less than half, sometimes much less than half, of the total sulfur. Most of the sulfur in the sediments falls into the “remaining sulfur” category which corresponds to alternate forms of sulfur like elemental sulfur and FeS. We were anticipating pyritic sulfur to constitute a larger percentage of the total sulfur. Our methods could explain this discrepancy. During the strong acid treatments, the samples were allowed to sit for possibly longer than they should have. This may have dissolved some pyrite that would have otherwise appeared when the samples were run on the Atomic Absorption Spectrophotometer, creating an underestimate of pyrite. Furthermore, alternate forms of sulfur simply may have been more abundant than we previously expected.
I found four main pyrite crystal formations while imaging the sediment samples with the scanning electron microscope:

- Individual dodecahedral crystals (Figures 11 and 12)
- Individual octahedral crystals (Figure 13)
- “ Loose” framboidal pyritic aggregates (Figures 14 and 15)
- “Packed” framboidal pyritic aggregates (Figures 14 and 16)

The two types of individual crystals found in the samples are dodecahedrons and octahedrons. The octahedral crystals are very obvious as the diamond-shaped crystals in the sediment. Conversely, the dodecahedral crystals are more difficult to discern because while it is apparent that these crystals have many sides, all twelve sides of the crystals are not clear. However, the crystals are noticeably not cubic or octahedral, which means that they must be the dodecahedral shape common for pyrite (King 2019). I confirmed that these octahedral and dodecahedral crystals were actually pyrite using the Energy Dispersive Spectroscopy function of the SEM. As shown in Figures 18a-e, the locations of individual octahedral and dodecahedral pyrite crystals align with areas where the image is abundant in both iron and sulfur, the two elements in pyrite. The sulfur signal is much brighter because there is twice as much sulfur in pyrite as there is iron. With these pseudo-heat maps, it remains clear that these individual crystals are indeed pyrite.

Pyrite is also commonly found in spherical aggregates of individual crystals, two types of which I came across in my imaging. The “loose” framboid of pyrite made up of individual dodecahedral pyrite crystals (Figures 14 and 15) aggregated together loosely contrasts greatly with the “packed” framboid made up of cubic crystals drawn together very tightly (Figures 14 and 16). As mentioned previously, pyrite framboids can require anywhere from three hours to
three years to form, but they average around five days. These two types of framboids probably represent different stages of framboidal development. It is still remarkable how different they appear in terms of how tightly packed they are and their individual crystal habits. Again, the EDS function showed these framboids to be abundant in both iron and sulfur, the components of pyrite (Figures 17a-e).

While iron and sulfur are the two components of pyrite, they are not the most common elements found in the overall sediment. The spectral emission chart (Figure 18f) for one of the EDS images unsurprisingly displays that silicon and oxygen are the most abundant elements in the image of the sediment sample. Quartz and feldspars, the two most common rock building minerals in these sediments, are the reason for the prevalence of both silicon and oxygen, as they both are primarily composed of these two elements.

None of the pyrite crystals from the nickel-iron treatments contain significant nickel according to the EDS analysis. It seems as though hydrothermal activity is required to form nickel-pyrite, as nickel does not appear to serve as a viable iron substitute under salt marsh temperature and pressure conditions. I did find more background nickel in the nickel-iron treated sediments, but none of that nickel had been used in the pyrite crystal formation. It remains spread throughout the sediment sample (Figures 19a and 19b).

**Acknowledgements**

I would like to thank my mentor Anne Giblin for her constant excitement for and support of this project. This project also would not have been possible without the help of Louie Kerr, who trained me on the SEM and EDS, Sam Kelsey, who showed me how to analyze my sulfur samples, and Suzanne Thomas, who was kind enough to run my sulfate samples. Finally, I would
like to thank Rich McHorney for keeping me sane through this entire semester and the teaching assistants, Emily, Nick and Rachel, for being unbelievable TAs and even better friends.

References


Figure 1. Two models of pyrite formation: (a) typical subtidal sediment. Pyrite forms by
the slow conversion of iron monosulfides and elemental sulfur (see Berner 1984). (b) Model
proposed for marsh sediments. Pyrite forms rapidly by the direct precipitation of iron and
polysulfides. A substantial portion of the pyrite may be reoxidized to iron oxide minerals
supplying the iron required for new pyrite formation (see Howarth and Teal 1979; Giblin
and Howarth 1984).

Figure 1: Models for pyrite formation in both slow tidal reactions (a) and fast marsh reactions (b)
Figure 2: Pyritic iron (mg pyritic iron per g sediment) content of untreated cores
Pyritic Iron in Little Sippewissett Cores

Figure 3: Pyritic iron (mg pyritic iron per g sediment) content of Little Sippewissett treated cores
Figure 4: Sulfur mass percent of untreated sediment cores
Figure 5: Sulfur mass percent of Little Sippewissett treated sediment cores

Figure 5: Sulfur mass percent of Little Sippewissett treated sediment cores
Figure 6: Total iron (mg total iron per g sediment) in sediment cores
Figure 7: Ratio of pyritic iron to total iron in sediment cores
**Figure 8: Different forms of sulfur contained in the untreated sediment cores**
Figure 9: Sulfur drained from the treated Little Sippewissett sediment cores as sulfate
Figure 10: Percent carbon in the untreated sediment cores (NOTE: * for Little Sippewissett indicates an estimate, this value was not actually measured)
Figure 11: SEM image from a Plum Island pristine marsh sample displaying numerous dodecahedral crystals
Figure 12: A zoomed-in SEM image of the same sediment sample as Figure 11
Figure 13: An SEM image of octahedral pyrite crystals from a nickel-iron treated Little Sippewissett sample.
Figure 14: SEM image of two types of pyrite frambooids from a ferrous sulfate treated Little Sippewissett sample
Figure 15: Zoomed-in SEM image of "loose" pyrite framboids from the same sample as Figure 14
Figure 16: Zoomed-in SEM image of a "packed" pyrite framboid from the same sample as Figure 14
Figure 17a: EDS electron image of the frambooids from the same sample as Figure 14
Figure 17b: EDS map for iron showing iron (red) is most abundant where the pyrite frambooids are found
Figure 17c: EDS map for sulfur showing sulfur (yellow) is most abundant where the framboids are found.
Figure 17d: EDS map for nickel showing little to no nickel (green) in the sediment sample
Figure 17e: An overlain EDS map image showing iron (red), sulfur (yellow), and nickel (green) abundance in the same framboid image
Figure 18a: An EDS electron image of a ferrous sulfate treated Little Sippewissett sample
Figure 18b: An EDS map for iron showing iron (red) is most abundant where frambooids and individual pyrite crystals are found.
Figure 18c: An EDS map for sulfur showing sulfur (yellow) is most abundant where framboids and individual pyrite crystals are found.
Figure 18d: An EDS map for nickel showing minimal to no nickel (green)
Figure 18e: An overlain EDS map image showing iron (red), sulfur (yellow), and nickel (green) abundance in the same image
Figure 18f: A sum spectral emission chart displaying the abundance of all elements contained in the EDS image with weight percentages.
Figure 19a: An EDS electron image of a nickel-iron treated Little Sippewissett sample
Figure 19b: An EDS map for nickel showing more background nickel (green) than other treatments