Secondary Minerals and Constituents of the Marcellus Shale Formation

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This work identifies unknown crystals found encrusting the Marcellus Shale Formation at the Mapleton Quarry locality in Central Pennsylvania, over the course of a month. The outcrop has been exposed for sufficient time for there to be advanced chemical weathering, allowing for the presence of secondary minerals to form and changes in the composition of the surrounding water table and environment. The crystals found were examined under microscope and by an X Ray Defractometer and were positively identified as small clusters of gypsum, or CaSO$_4$·2H$_2$O. This gypsum was found in three different appearances, with the crystals being colored red-orange, yellow, ad white to colorless. All three types of segregated crystals were examined and the same conclusion was drawn, despite the possible impurities that iron may have gave to the colored gypsum. Visually, swallow tail twinning and monoclinic crystal forms were apparent in all three of the samples examined. Without the visual identification of the clear crystal group, identification would not have been possible, as the XRD pattern created was consistently terrible, in that no defined peaks could be produced.

*Keywords.*—Marcellus Shale; Gypsum; Precipitation; Crystal; Reduced Elements; X-Ray Diffraction

INTRODUCTION

The Marcellus Shale formation is a black shale with interbedded carbonate layers within the Hamilton Group, which was formed 375 million years ago during the Devonian period. This layer of sedimentary rock was deposited during changes in sea level, giving the formation alternating layers of shallow carbonates and deep sea shales (Faill, 1998, 428). The Acadian Orogeny, or mountain building event, created the Appalachian foreland basin (Faill, 1998, 429). This basin was then filled by sediments from the surrounding continental bodies, and depending on the depth, different rock layers were formed.

The Hamilton group was then deformed, giving the once flat lying rock strikes and dips across Western and Central Pennsylvania (Faill, 1998,
In the locality where the crystals were observed and sampled, the formation was uplifted into a near vertical position.

The carbon rich shale layers contain large amounts of pyrite (an iron sulfide) compared to the calcareous layers, which contain significant amounts of carbonates (Berner, 1970). In an anoxic environment, sulfur and iron are deposited in a reduced state, as the bacteria responsible for the transformation of oxidized iron to reduced iron is only found in anoxic environments (Berner, 1970). This environment that shales then form in allow for the formation of pyrite when the rock eventually lithifies under the weight of the sediment and water above (Berry, 1978).

The carbonate layers form in shallow seas, when the water is clear and the environmental conditions are right for marine organisms to thrive. The marine organisms produce calcium carbonate skeletons or shells, which are deposited during these ages when they die and eventually sink to the bottom of the sea. The alternating shale and limestone layers found in the Marcellus Formation are due to the rising and sinking sea levels, changing the depth of deposition, an in parallel changing the environment to the corresponding one.

Today, outcrops of the Marcellus Formation are exposed to an oxygen rich environment, allowing the pyrites to oxidize in the presence of oxygen and water. When the jointed rock produce cliff-like features as seen in the Mapleton Quarry, the Marcellus Formation is open to chemical and physical weathering processes.

The oxidations of sulphides, in this case pyrite, produces sulfuric acid and iron hydroxide. This reaction can be seen and written as follows (Martin, 2008):

\[
\text{FeS}_2(s) + 3.75\text{O}_2(aq) + 3.5(\text{H}_2\text{O})(l) \rightarrow \text{Fe(OH)}_3(s) + 2\text{H}_2\text{SO}_4(aq)
\]

This is what would occur if it was localized only to the pyritic rock, or shale layers. Because of the carbonate layers in the Marcellus Formation, calcium carbonate is introduced and further reactions can occur. In this case, gypsum can be formed as follows (Martin, 2008):

\[
\text{CaCO}_3(s) + 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}(s) + \text{CO}_2(aq)
\]

This is, of course, under the pretense that the calcium carbonate from the limestone is in solution and comes in contact with sulfuric acid in high enough concentrations where the gypsum would then precipitate out of solution. These circumstances may only occur where there is periodic, slow moving water across both the pyritic shale and calcareous limestone beds. Also, both the carbonate and sulfuric components need to interact in an aqueous environment, inferring that the dissolution of the carbonate from the calcium carbonate found within the limestone beds is occurring (Martin, 2008).

The Mapleton Quarry, located in Huntingdon County, Pennsylvania, has the Marcellus Formation exposed in an outcrop where water has been allowed to flow over it interrupted only by the rainy and dry seasons, as it has been abandoned for a number of years. Originally the quarry was used for the mining of quartz sand from the Ridgeley Formation. The mining project can be seen on maps dating back to 1962, so the quarry has been in existence for at least fifty plus years (Alexandria Quadrangle). This has given the surrounding environment ample time to weather the “fresh” outcrops created by the quarry to form gypsum and limonite/rust staining on and around the area.

At the base of the outcrop, the water and stream beds were colored orange and black, hinting at a high acidity environment that Pennsylvania has
struggled with due to ground disturbances (Orndorff, 2001). The iron hydroxide that has precipitated out of solution creates this staining on the outcrops jointing surface, and also at the stream bed/banks, in accordance to the previous chemical formulas listed above.

Determining the presence of the gypsum crystals will be a good way to show an in-the-field evaluation of the area. The presence of gypsum crystals such as in the outcrops observed infers the presence of a sulfuric water table and iron rich deposits, or the mobilization of iron from deposits.

### METHODS

Orange, yellow, and white/colorless crystals were observed on the surface of a Marcellus Shale Formation at a abandoned quarry in South Mapleton, Central Pennsylvania. Samples were taken at fifty meter intervals when applicable. These samples were found near heavy water flow areas on the outcrop. Along with the crystals, orange staining was present in abundance on the black and gray shales. Three samples of the crystals, one orange, one yellow, and one colorless/white were examined under microscope and with the X-Ray Diffractometer.

Samples were taken only a few days before the examination and testing to provide minimum error and decay. The encrusted crystals were then scraped off into 3 separate vials for storage, one containing orange crystals, another yellow, and a third being the white/colorless.

Crystals were also examined under microscope, and positively identified using identification tables in ID books. Separation of the crystals was done by hand under a binocular microscope using tweezers, a small pick, and a chopstick.

After grinding and physical preparation, packed mounts were made with samples that had enough powder for it, and smear mounts were done for the crystals that did not have sufficient material for a packed mount. Smear mounts were prepared using acetone to fix them to the slide.

The data was analyzed using the built in software that the XRD machine has, and hand to hand comparison with XRD scans logged into XRD mineral identification guides.

### RESULTS

The X-Ray Diffraction results were quite clear for the orange and yellow crystals, as seen in (Figure 1) and (Figure 2). For the white/colorless crystals, though, the scan readings came out quite muddy and unclear. The data was unusable in trying to identify those results as gypsum precipitates.

![Figure 1. This XRD scan shows the results for the orange gypsum crystals.](image1)

Under visual identification, all three samples were positively identified as gypsum as obvious swallow tail twinning and the softness of the crystals when handling and grinding. The
tabular form of the monoclinic crystals was also quite visible in the specimens. Visually, the colored crystals were harder to identify, but had cleaner results under XRD. The white/colorless crystals were easier to identify by hand, but under XRD they came out quite messy, as seen in (Figure 3).

Figure 3. This XRD scan shows the results for the clear gypsum crystals, with obvious muddled results.

These crystals must have formed within the last few years, as the outcrop has only been exposed to the oxidizing environment and the water table for the past 50-60 years, according to the data that has been collected. Gypsum, as a precipitant, is also soluble in water. Because of this, the life of gypsum crystals may not last the full 60 years that the outcrop has been around. It is possible that the crystals only take a short amount of time to grow, and then wash away easily during the rainy season or during high flow events. With the data that has been collected, there is no way to tell the growth period.

DISCUSSION

The crystals that I identified were in-fact gypsum precipitants from the mixture of sulfuric acid and aqueous solution carbonates found within the interbedded limestone layers and pyritic shale layers of the Marcellus Formation. This conclusion conforms well to other studies that have made the same observations, such as F. Martin and Orndorff. In these studies, they also concluded that gypsum has a significant presence within the oxidizing environment on the Marcellus Shale and other pyritic shale environments.

This study was done under small scale boundaries, and having more time to collect more data would have been beneficial towards the identification of the gypsum crystals and may have helped identify more minerals on the outcrops surface. The weather was a limiting factor also, for if there was less snow cover, more developed samples may have been found for additional observation.

Human error played a large role in collecting and verifying this data. With the clear crystals, crystals were hand picked under a binocular microscope and were ground up in very small quantities (twelve to twenty four grains). This may have been the cause of such a terrible XRD pattern being produced. In the future, larger amounts of crystal grains will be used for all of the samples, preferably with packed mounts. This will help stabilize some of the enormous amounts of static that were obtained. Specimen choice would be beneficial too.

To help this study, other samples from different localities but dealing with the same formations would have helped quantify the amount of precipitation, or maybe quantify the time it takes for the precipitates to occur by comparing the abundance of gypsum crystals, flow of the water table through the formations, and age of the outcrop (relatively). With this data, more thorough conclusion may be made possible.

REFERENCES


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US Geological Society. n.d.. Alexandria Quadrangle [Map]