A Classification and Mineralogical Description of Ferricrete Samples in the New World Mining District of Montana

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Introduction

The New World Mining District is located in southwestern Montana, about two and one half miles from the border of Yellowstone National Park. This study centers on several of the creeks in this district-- principally "Daisy" creek, which flows into the Stillwater River The headwaters of Daisy creek are fed by a historic open pit mine, which is one of the many historic sites in the area. This past mining activity plus the naturally acidic, pyrite-rich source rock have created an acid rock drainage problem in the valley. The cause of this acidity is sulfuric acid, which is generated by the dissolution of pyrite. This reaction also produces Fe^{2+} iron in solution, which later reprecipitates as an iron oxide in the stream beds. This iron oxide forms "ferricrete" which is an iron cemented conglomerate.

The aim of this project is threefold: 1) to characterize the different types of ferricrete based on the appearance and environment of their formation, 2) to collect laboratory data to try and discover the types of iron minerals present in the samples, and 3) to determine the ions present in the water samples collected from nearby stream channels. Further study could show if the external features of the ferricrete reflect the different internal types of iron oxides, and if this mineral composition agrees with the ions in the water. In addition, if a correlation between the types of ferricretes and water pH could be established, this would provide a means of establishing historical pH levels. If the time of deposition was known, this would give a means of measuring the change in water quality since the advent of mining.

Field Methods

The field work included descriptions of the ferricrete, and water sampling. The first step was to correctly identify the ferricrete, which could be challenging due to the similarity between severely altered bedrock and ferricrete. Since there is very little written about the formation of ferricrete by acid rock drainage, no detailed descriptions of the physical appearance of it could be found in the literature. Therefore, after becoming aquatinted with the ferricrete found in the valley, a classification scheme was developed. The classification was based on differences in the physical appearance, apparent age, and areas of formation of the ferricretes. Samples representative of the various types of ferricretes were collected in Daisy creek, as well as a few samples from adjacent drainages. A nearby creek whose channel intersected a limestone bed was also sampled in order to evaluate the impact of carbonates on pH and hence on iron deposition. It would have been beneficial to sample a drainage of similar aspect which had not been affected by mining, however, all of the surrounding valleys of the same aspect which contained the same stratigraphic sections had also been mined.

Water sampling methods included measurements of pH, dissolved oxygen, temperature, and conductivity. Wherever possible, water samples were taken at the locations of different types of ferricretes, as well as in zones of mixing or other notable changes such as water color. Sample bottles of water were collected and acidified with nitric acid for later laboratory testing.

Laboratory Analysis of Hand Samples

Several different techniques were used to identify the different types of iron oxides found in the samples, including magnetic susceptibility, x-ray diffraction, thin section analysis and scanning electron microscopy. The iron cement could not be separated from the clasts by acid dissolution without altering the iron speciation, and an attempt at magnetic separation was unsuccessful. As a result, the clasts and the iron cement remained together for these tests.

Water Sample Analysis

The water samples were analyzed using Induced Plasma Coupling (ICP). The samples were tested for a range of elements, including Mn, Fe, Co, Ni, Cu, Zn, As, Se Sr, Ag, Cd, Sn, Sb, Ba, La, Hg, Pb, Th, and U. Several samples which were not acidified in the field due to a lack of sufficient acid supplies, were acidified in the lab in hopes that any material which had absorbed onto the sides of the container would go back into solution.

Field Classification

The results of the hand sample analysis show that there are several different "types" of ferricrete. These divisions were based on the environment in which the sample is found, the color (using the Munsell color classification scheme), the relative abundance of clasts, relative hardness and cohesiveness.

The first type of ferricrete distinguished is the "Y-type" ferricrete. This ferricrete is mottled dark red to purple to grey in color, with fewer and smaller-sized clasts than other samples. The color may be indicative of Mn oxides, such as pyrolucite, or vericolored iron minerals such as ferrihydrite. The ferricrete is found on the hillsides beneath the pit mine, but not in the stream channels. It weathers in a distinctive manner, forming small, desiccated chips of iron oxide which form a pedagenic surface atop the parent material. The results of the laboratory analysis of this sample will be discussed below.

The next type of ferricrete distinguished is the "Q-type" ferricrete. This is a clast rich, stream bed conglomerate, cemented by bright orange iron oxides of perhaps limonite and goethite, and clay. This type of ferricrete forms in the gullies which have been eroded beneath the pit.

At one location in Daisy Creek, and in several sites in nearby Miller Creek, older, lichen covered, ferricrete layers were discovered. This "B-type" ferricrete formed shelves of orange, clast rich ferricrete are as much as fifteen feet above the present stream bed. The layers in Miller creek are very resistant, and provide an erosional cap for the underlying material.

Laboratory Results

One of the main objectives of the laboratory work was to identify which iron minerals were present in the ferricrete. Understanding the internal chemical structure could help account for the different external appearances of different types of ferricretes. Distinct mineral species would also indicate different ages, compositions, and environments of formation. For instance, ferrihydrite ($Fe_5HO_8 * 4H_2O$) transforms spontaneously to goethite (FeO(OH)), but the rate is quite slow, and is dependent upon pH (Schwertmann and Fitzpatrick, 1992). Likewise, the presence of the mineral jarosite ($(Na,K) Fe_3 (OH)6(SO_4)_2$) is an indicator of the environment of formation, as it is formed under the most acid (pH<3.5) conditions (Bigham, Schwertmann, and Carlson, 1992).

Unfortunately, identification of specific Fe minerals species has proved to be quite a challenge. According to Skinner and Fitzpatrick (1992), ". . . these materials are difficult, indeed arduous, to identify as they are not well crystallized with exceedingly fine grain size, typical of low temperature, low solubility, precipitates." In addition, established Eh-pH diagrams which are valid for equilibrium conditions cannot be reliably used in a natural water system, since the natural water system is not in equilibrium (Drever, 88). Yet another source of confusion stems from the enormous importance of bacterial catalysts on the precipitation of iron and the oxidation of pyrite. According to Nordstrom, "To interpret these [oxidation-reduction] reactions in natural aquatic systems requires the addition knowledge of microbial ecology, hydrology, and geology. It is not surprising that important aspects of this process are not clearly understood and many question remain unresolved, " (Nordstrom, 1982).

Thus, trying to correlate the XRD, SEM and thin section analysis has produced interesting, if inconclusive, results. Some of the iron minerals which could be present include: goethite, hematite, siderite, ferrihydrite, "MDM" (mine drainage mineral), jarosite, lepidocrocite, feroxyhyte, akaganeite, vivianite, melanterite, rozentie, szomolnokite, copiapite (Nordstrom, 1982; Schwertmann and Fitzpatrick, 1992; Bigham, Schwertmann and Carlson, 1992).

The XRD analysis produced a variety of d-spacings, but a majority of the samples produced peaks at either 3.09 A or 3.38A (see attached graphs). The primary peak of 3.09, which is found in the "Y-type" ferricrete samples agrees with that of jarosite (3.08 A), however; the secondary and tertiary peaks do not. The primary peak of 3.38 is produced by both the "Q-type" and "B-type" samples, but does not agree with the peak of any of the known iron minerals.

The SEM was used in order to determine if any elements unique to certain iron oxides--such as the Na or K in jarosite (Na, K) $Fe_3(OH)_6(SO_4)_2$--could help identify the minerals in the samples. One sample of "Y-type" ferricrete showed significant amounts of Al, Fe, and Si. Because of its general abundance, the Si can be disregarded, but the abundance of Al can most likely be attributed to clays (see attached graphs). Another sample of "Y-type" ferricrete had peaks corresponding to Al, Fe, S, Si, P and K, which could mean the sample contained vivianite ($Fe_2(PO_4))_2$ *$8H_2O$). The third sample, a "Q-type" ferricrete, contained significant amounts of Fe and S, but no Al. This absence of aluminum could relate to the physical differences between the samples.

The thin sections provided information about the layered nature of the iron precipitation around clasts, although they did not give any mineralogical clues due to the poor crystalinity of the iron precipitate.

In an attempt to determine the rate of formation of the ferricrete, a wood sample which was overlain by 3' 10" of ferricrete was radiocarbon dated. The calibrated age of the sample was 1651 AD, +/- 50 years. However, the 95% certainty envelope on the date would run from 1529 to the present. This still provides useful information, since this means 3' 10" of ferricrete formed in a maximum of 465 years, and probably significantly less.

Water Samples

The ICP analysis showed elevated amounts of Fe, S, Mg, Al, Ca and in some cases Cu in proximity to the mining pit. The amounts of sulfur (which form the sulfuric acid) and hence the amount of iron should have been directly related to pH; however, when iron and sulfur content are plotted against pH, they do not show a linear relationship. The discrepancies in this data could have been caused by a failure to re-calibrate the pH meter.

Conclusions

The ferricrete samples collected from the Daisy creek area can be classified based on several criteria. "Y", "Q", and "B" types of ferricrete are differentiated based on their physical characteristics, and environments of formation. Although XRD and SEM data indicates the types of minerals found in these samples are often distinct from each other, a consistent correlation between XRD peaks, SEM results, and ferricrete type has not yet been established. Likewise, while the water sample results support a high rate of ferricrete formation in metal-rich waters, the mineralogy of the rock samples does not necessarily coincide with the ions present in the water. The relatively young date obtained from the wood sample supports other data which indicates that the ferricrete forms quite quickly. Further study of this unique situation could provide answers to these questions, and would contribute to the understanding of past and present acid mine drainage.

References:

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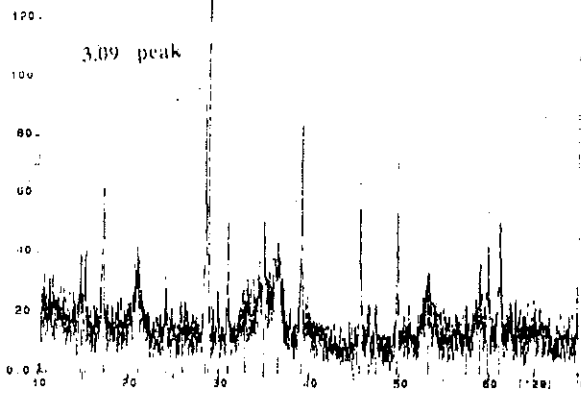
Sample #70: Limonite and Goethite rich ferricrete sample from the Daisy Creek Drainage
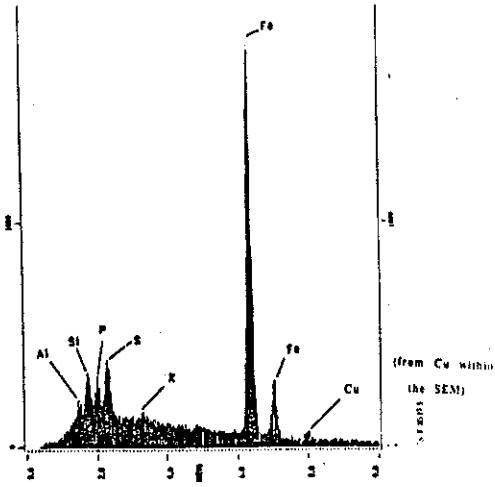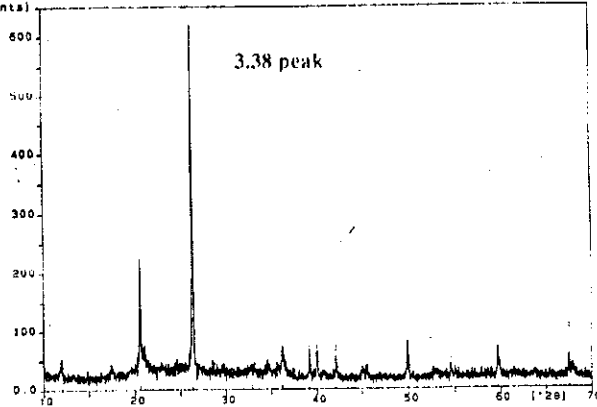
3.09 peak

"Y-type" ferricrete sample from Daisy Creek

3.09 peak

"Q-type" ferricrete sample from Daisy Creek

Sample #72: Q-type, organic-rich ferricrete from the Daisy Creek Drainage

3.38 peak
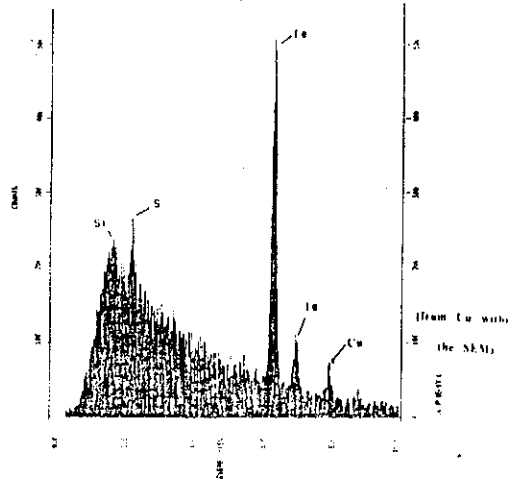
"B-type" ferricrete sample from Miller Creek