SPECTRAL IDENTIFICATION OF PYRITE MUD WEATHERING PRODUCTS: A FIELD AND LABORATORY EVALUATION

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ABSTRACT:

Monitoring of mine waste on sulphide deposits through remote sensing hyperspectral data contributes to the prediction of potential surface water quality, quantitatively estimating acid drainage and metal contamination on a yearly basis. Based on previous Hymap mapping of salt efflorescence on mine wastes, various domains within the mine facilities (Iberian Pyrite Belt, Spain) selected because of their geomorphological setting were sampled to conduct a laboratory experiment. Samples from mine waste piles, pyrite mud tailings and river sediments were continuously exposed to the atmosphere during the summer, and spectral measurements were collected in the dark room on several days. The spectral response was monitored throughout the summer, when the pyrite oxidation process is active and the mineralogy on the surfaces changes continuously. The mineralogical identification capability of algorithms such as Spectral Angle Mapper, Binary Encoding and Spectral Feature Fitting based on archive spectral libraries is discussed. Trends of mineral growth differ spectrally over time according to the geological setting. Subtle mineralogical changes are described using the spectral response and their meaning as indicators of pyrite oxidation intensity on mine waste piles, pyrite mud tailings and river sediments. Therefore, sulphide mine waste weathering products may be used as small scale targets for a short-term record of climate variability, providing a useful tool to assess environmental geological indicators in semi-arid areas.

1. INTRODUCTION

Imaging Spectroscopy using spectral libraries has been developed as a reliable technique on mine waste enabling quick mineralogical analysis, which saves both time and cost - versus conventional sample collection and spatial interpretation of laboratory results through interpolation methods (Swayze et al 2000). Additionally, it permits the mineralogical diagnosis of ephemeral thin crusts concentrating heavy metals on inaccessible surfaces (Plumlee, 1999), providing an invaluable tool for environmental evaluation and information. Climate is the controlling factor on the growth and solution of salts from pyrite and other metallic sulphide in mine waste (Nordstrom and Alpers, 1999). Most of the previous work on mine waste mapping using hyperspectral data is focused on environmental evidence for predicting metal contamination concentration and acid drainage both in surface water and groundwater (Swayze et al 2000). Previous hyperspectral image processing using airborne Hymap data (Zabcic et al, 2005; Riaza et al, 2007) suggested that the mineralogical display of pyrite oxidation products could be an expression of seasonal and yearly changes on environmental moisture availability and evaporation rate. The spectral field and laboratory work that is described below intends to increase observations focusing on the same direction, monitoring spectral mineralogical changes on samples collected in the field at the beginning of the dry season throughout the summer.

Variations on the spectral identification of pyrite mud weathering products are suggested using archive spectral libraries related to the geological setting of the sample location. A geological and geomorphological influence on the spectral responses of surfaces on areas affected by pyrite oxidation is outlined.

2. METHOD

During the previous image processing of Hymap data (Riaza et al 2007), a clear spectral discrimination between oxidised areas and hydrated areas on pyrite mud weathering products could be established early in the image processing procedure. Therefore, three main test outcrops were selected for careful field and laboratory spectral monitoring: the accessible side of the pyrite mud tailings mass, the exposed inner wall of the pyrite mud dam, and a bar of river sediments close to the mine dumps (Figure 1).
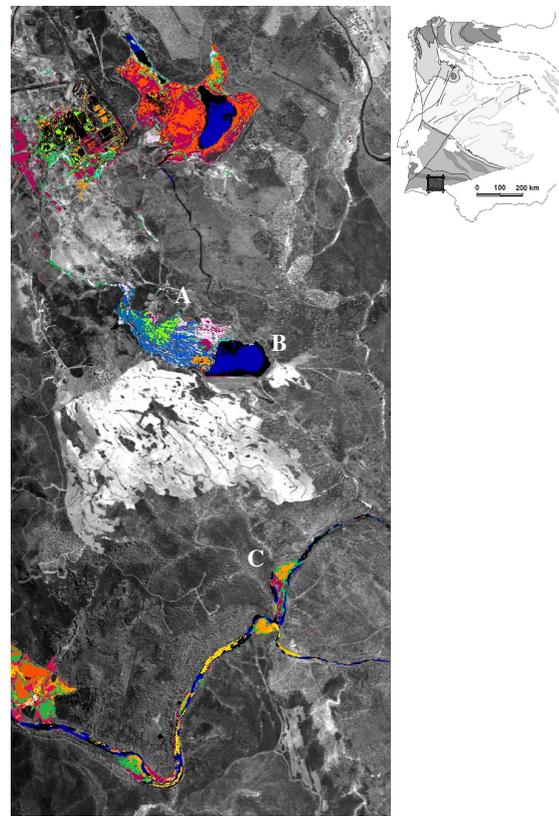
Figure 1. Area of study in the Iberian Hesperian Massif (Spain). Mine facilities of Sotiel (Huelva) mapped on Hymap data (Riaza et al, 2007). A, B, C, locations sampled.

Both field and laboratory spectra were taken with an ASD Fieldspec3 Spectrometer, operating between 400 and 2400 nm with a 1 nm spectral resolution.

A panel was used as a white reference at the beginning of every session.

Samples of mud crusts, coated boulders, and sand, were collected on river sediments, pyrite mud and mine dumps, and sealed in plastic bags or plastic boxes, to be used in the dark room for spectral measurements. Soil colour records were estimated using a Munsell Soil Colour Chart under a constant illumination source.

To monitor the seasonal mineralogical evolution of pyrite oxidation products during the dry season, the samples of boulders and gravels collected in early June were exposed to the atmosphere in uncovered plastic boxes in an open space unaffected by shadows during the day throughout the summer. Measurements were made in the dark room in July, August and the end of September, taking into account continuous dry periods and eventual short storms.

X ray diffraction analysis was performed after the sample collection in June, and subsequent analysis was made on selected samples throughout the summer accompanying spectral measurements.

The spectral libraries, both from field spectra measured in the early summer, and samples collected in the field in the early summer and measured later during the whole summer in the dark room, were spectrally analysed using as a reference the USGS spectral library developed for pyrite oxidation products (Crowley et al, 2003).

2. MINERALOGICAL IDENTIFICATION OF FIELD SPECTRA: THE GEOLOGICAL CONTROL

Most field and dark room spectra in the test sites are identified by the Spectral Analyst as schwertmannite as the first choice, goethite as the second, and ferrihydrite or jarosite as the third choice (Figures 2, 3 and 4), taking into account the final score using the three algorithms. The typical spectrum of any soil is close to the spectral response of schwertmannite, jarosite or ferrihydrite. Therefore, the spectral identification of such minerals in any soil, when using a selected spectral library of eighteen minerals typical of pyrite weathering should not be surprising. The real diagnostic features have to be extracted from this preliminary analysis, once the area and the geological background has been previously established.

Spectra with jarosite identified as first mineral constantly display a clear absorption at 0.439 µm, both in the field and dark room spectra (Figure 3). The influence of jarosite is also shown by 1.46 µm, 1.84 µm and 2.26 µm absorptions.

The pyrite mud spectra displays absorption features typical of the presence of gypsum in soils and also shows typically high overall reflectance, which is often identified by the Spectral Analyst as copiapite and melanterite (Figure 2). This typical gypsum bearing soil shape is also shown in part of the washed river bar pebbles coloured in white (Figure 4). The coupled absorption at 1.490 µm and 1.526 µm on the ascending slope between 1.300 and 1.700 µm, and the deep absorption at 1.943 µm are typical diagnostic features of the presence of gypsum in geologically favourable environments (Riaza et al, 2005).

The three algorithms used for mineral identification perform with varying degrees of success. Spectral Angle Mapper is the most influential algorithm and dominates the mineralogical identification. Binary encoding decides the dominant mineral identification in 10% of cases. Spectral Feature Fitting is highly inefficient at identifying minerals, and in many cases does not produce any score, particularly for the pyrite mud spectra.

Those main principles of observation frame the mineralogical interpretation in a

geological context. The need for a geologically qualified local spectral library in the area of study is obvious from the above considerations. The following spectral analysis will examine details in the spectral response of geologically mappable units with hyperspectral imagery through field and laboratory spectral measurements.

3.1. The pyrite mud tailings dam
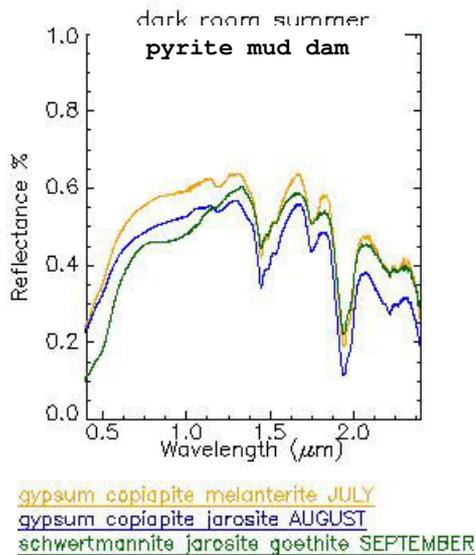
Figure 2. Spectra measured in the dark room during the summer on a white crust over pyrite mud (location A on figure 1).

Measurements taken in the dark room on the same samples in August and September (Figure 2) showed a progressive oxidation and loss of water, particularly in samples of dried mud foam and crusts with well-developed crystals. The change was emphasized from July to August. The typical absorptions for gypsum bearing samples within 1.4 µm and 1.7 µm were progressively smoothed

to a shape identified as schwertmannite in September. The dry mud in June was spectrally more stable throughout the summer.

3.2. The wall of the pyrite mud dam

Field spectra in June showed a clear identification of ferricopiapite-copiapite-jarosite with halotrichite on the pale yellow ribbon close to the water. In the dark room, spectra from those samples were identified as jarosite as the third choice, with schwertmannite and goethite as first and second choices.
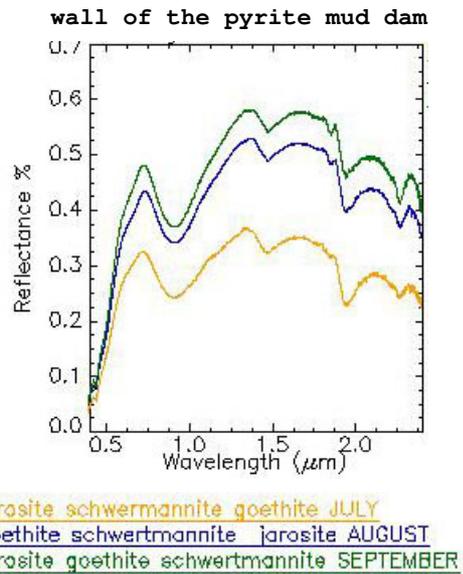
Figure 3. Spectra measured in the dark room during the summer in a sample collected closed to the water in the inner wall of the pyrite mud dam.

The mineralogical diagnosis did not change in the spectra measured in August in the dark room on samples from the lower pale yellow lower belt close to the water (Figure 3). Minor spectral features

typical of jarosite at 0.436 μm, 1.84 μm and 2.27 μm are present. A minor jarosite shoulder at 2.21 μm, appears in August and September, and the 2.27 μm absorption deepens. All those minor changes occurring in selected measurements indicate a slight progression of oxidation from the dominant schwertmannite-goethite shape.

3.3. The River Flow Path: a pebblebank at low water level

The mineralogical diagnosis of field spectra was quite varied, likely due to shade effects produced by pebbles of heterogeneous sizes.
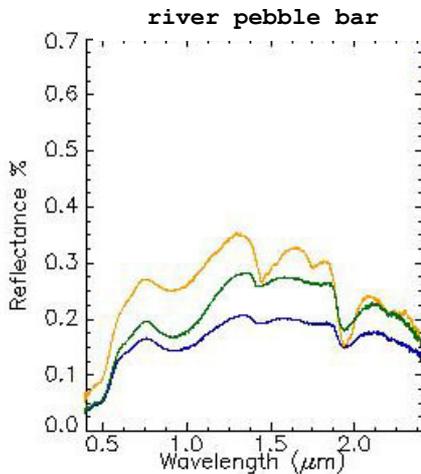
Figure 4. Spectra measured in the dark room during the summer on pebbles with white coatings on the river Odiel (location C in figure 1).

The reddish brown rim close to the water tended to be fibroferrite-ferricopiapite-copiapite if measuring coatings or sands.

In the reddish yellow dust, more oxidized assemblages like schwertmannite-ferrihydrite-goethite can be found, and the same diagnosis applies for the rest of the mud, regardless of the visible colour.

In the dark room, the only difference was a preference for jarosite as a third choice in the less oxidised samples rather than ferrihydrite (Figure 4). Through the summer, no changes in the diagnosis came from the spectra measured in the dark room. But slight changes in the absorptions typical of gypsum or copiapite which were not diagnosed as such, could be recognized in samples with jarosite as the third choice. The minimum at 1.44 μm (jarosite) in July shifts to 1.41 μm (gypsum) in August (Figure 4). This absorption weakened and rounded in September with increasing oxidation.

3. CONCLUSION

General trends in mineral oxidation sequences can be seen in the context of the selected outcrops in measurements made in the dark room on samples exposed to the atmosphere throughout the summer.

Laboratory monitoring of changes in the spectral behaviour of field samples exposed to the atmosphere throughout the summer point to small mineralogical changes showing increasing oxidation to be traced in the future. The spectral changes involved are subtle, but significant and meaningful.

Spectral Angle Mapper is the most influential algorithm and dominates the mineralogical identification when using the archive spectral library. Binary Encoding and Spectral Feature Fitting are inefficient for identifying minerals. The whole shape of the spectra must be taken into account for a meaningful mineralogical identification.

As a general trend, in originally hydrated phases, copiapite and ferricopiapite in the field and jarosite measured in the dark

room, shift towards more oxidized phases as schwertmannite, goethite and ferrihydrite throughout the summer.
The spectral features typical of jarosite are lost in favour of more rounded schwertmannite features as one of the increasing oxidation patterns. Shifts from 1.44 μm (jarosite) to 1.41 μm (gypsum) are often seen in river bar sediments.
Such small changes observed in the selected test outcrops need monitoring using airborne data over wider areas, often not accessible for direct observation, over the coming years.

ACKNOWLEDGEMENTS

REFERENCES

Crowley, J.K., Williams, D.E., Hammarstrom, J.M., Piatak, N., Chou, I-M. and Mars, J.C., 2003. Spectral reflectance properties (0.4–2.5 μm) of secondary Fe-oxide, Fe-hydroxide, and Fe-sulphate-hydrate minerals associated with sulphide-bearing mine wastes. *Geochemistry: Exploration, Environment, Analysis*, 3- 3, 219-228(10).

Nordstrom, D.K. and Alpers, C.N., 1999, Geochemistry of acid mine waters. *In* Plumlee G.S.and Logsdon M.J.: The Environmental Geochemistry of Mineral Deposits. Part A: Processes, Techniques, and Health Issues. *Reviews in Economic Geology,* 6A, 133-160.

Plumlee, G.S., 1999. The environmental geology of mineral deposits. Part A: Processes, Techniques, and Health Issues. *Reviews in Economic Geology,* 6A, 71-116.

Riaza, A., García-Meléndez, E., Suárez, M., and Müller, A., 2005. Mineral climate indicators on paleoflooded and emerged areas around lake marshes (Tablas de Daimiel, Spain) using Hyperspectral DAIS 7915 Spectrometer data, *International Journal of Remote Sensing*, 26-20, 4565-4582.

Riaza, A., Ong, C. and Müller, A., 2007. Pyrite mine wastes hyperspectral monitoring as a tool to detect Climate Change, *Proceedings 10th Intl. Symposium on Physical Measurements and Signatures in Remote Sensing*, ISPMSRS07, WG VII/1, March 12-14, 2007, Davos, Switzerland, pp. 228-233.

Swayze, G.A., Smith, K.S., Clark, R.N., Sutley, S.J., Pearson, R.M., Vance, J.S., Hageman, Ph.L., Briggs, P.H., Meier, A.L., Singleton, M.J., and Roth, S., 2000. Using imaging spectroscopy to map acidic mine waste. *Environmental Science and Technology,* 34, 47-54.

Zabcic, N., Ong, C., Müller, A., and Rivard, B., 2005, Mapping pH from airborne hyperspectral data at the Sotiel-Migollas mine; Calanas, Spain. *Proceedings 4th EARSeL Workshop on Imaging Spectroscopy*, 27th-29th April 2005, Warsaw, Poland), 467-472.