

# DEHYDRATION AND OXIDATION OF PYRITE MUD AND POTENTIAL ACID MINE DRAINAGE USING HYPERSPECTRAL DAIS 7915 DATA (AZNALCÓLLAR, SPAIN)

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### ABSTRACT:

The observation of mine waste contamination from abandoned mines has increased during the last ten years using hyperspectral airborne data. Acid mine drainage is the natural result by water leaching of sulphide-bearing rocks and pyrite mine and ore processing plants. Oxidation of sulphides produces iron-bearing sulphate and other metals as secondary minerals. The solubility of secondary sulphates is selective according to water pH. Therefore, the presence of certain sulphate on waste surfaces or river sediment tailings traces the pH of the water at the time of precipitation. Mapping mineral mixtures at various stages of oxidation and dehydration on the pyrite mud in Aznalcóllar short after the spill in 1998 using hyperspectral airborne data has been achieved. The mineralogy of the outer crust of the pyrite mud in the mine dam 116 days after the spill, indicates a intermediate dehydrated stage.

## 1. INTRODUCTION

Pyrite mining on the Iberian Pyrite Belt (Spain) extends through history along 5000 years at least (Leblanc et al, 2000). Massive polymetallic sulphides have been exploited for historically changing industrial needs. On 25<sup>th</sup> April 1998, the walls of a pond of ore processing waste in Aznalcóllar broke, and the sludge spilled into the Agrio and Guadiamar river basin, spreading a layer of 7 cm average thickness of tailings over soils and sediments (López Pamo et al, 1999). The spread of mining tailings deposited a mat of pyrite mud (fine milled heavy metal-rich ore) over the main channel and floodplain of the river Agrio and Guadiamar with a thickness progressively decreasing downstream. The pyrite mud was deposited over the natural sediments without significant mobilisation of the latter and without relevant geomorphic changes (Gallart et al, 1999). Oxidation and solubilisation of the tailings increased with the distance from the spill. Therefore, removal of the upper 20 cm of the soil on the middle and lower areas of the river basin was encouraged on an early stage to prevent further contamination (Simon et al, 2002).

At the time of the spill, the tailings were saturated with water and afterwards began to dry progressively. As the tailings dried and aerated, sulphides oxidised to sulphates, the pH fell and the pollutants solubilized (Alastuey et al., 1999). The concentration of water-soluble  $\text{SO}_4^{2-}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in the tailings increased logarithmically with declining moisture (Simón et al, 1999). These solubilized elements, with evaporation, rose by capillary action to the surface, forming a white salty crust composed of Fe(II)-, Zn- and Mg-hydrated sulphates and high content in Cu, As, Cd and Sb (López-Pamo et al., 1999). Preliminary analysis and mineralogy of precipitates and efflorescent sulphate salt from various locations on the Pyrite Belt have been recently open to the public (Sánchez España et al, 2005). Hyperspectral mapping of the mine tailings of the Sotiel mine in the Iberian Pyrite Belt precedes this work (Zabcic et al, 2005).

During the summer, part of the sulphate crust was removed by wind, and pyrite cracks appeared. DAIS data were acquired on the 13<sup>th</sup> August 1998 over the Aznalcóllar mine facilities. The removal of tailings on the ground with heavy machinery which were afterwards returned to the mine open pit, ended on the 22<sup>nd</sup> July. On the 13<sup>th</sup> August, when the area was flown with DAIS hyperspectral Spectrometer, 116 days after the spill, part of the spilled tailings still remained on the ground close to the mine, where the mud had been thicker.

## 2. HYPERSPECTRAL STUDIES ON MINE WASTE TAILINGS

High spectral resolution on airborne and satellite spectrophotometers has enlarged the mapping capabilities of remote sensing data, developing widely with the use of AVIRIS data operating since 1988. Advances on data calibration and the development of algorithms able to extract information from a large number of spatial spectral data based on field spectra, encouraged applications on environmental issues. Early focus on mine tailings through the study of secondary minerals began concentrating initially on iron-bearing oxides and hydroxides (Farrand and Harsanyi, 1995). It expanded soon to related secondary minerals (Clark et al, 1998; Swayze et al, 1996; Levesque, 1997). Minerals generating acid environments attracted the attention of the scientific community because of their high mobility on the environment through solution on drainage water. The spectral behaviour of pyrite and sulphate derived by oxidation, and their solution properties was explored and patterns of precipitation established (Swayze et al, 1998; 2000). The development of spectral libraries from field sites has favoured the nearly automatic mapping of ephemeral mineral features related to acid mine drainage (Ong et al, 2002; Montero et al, 2002; Ong et al, 2003; Mars and Crowley, 2003; Sares et al, 2003). The contamination by the sludge spill in

Aznalcóllar (Spain) has been monitored with hyperspectral data on the middle and lower basin of the river Agrio-Guadiamar (Kemper and Sommer, 2003; García-Haro et al, 2005).

### 3. METHOD

#### 3.1 Dataset

DAIS 7915 Spectrophotometer data were collected over the mine facilities in Aznalcóllar on the 13<sup>th</sup> August 1998, 116 days after the spill (fig. 1). The spatial resolution of the flight is 5 m. Only data within 0.50-1.72  $\mu\text{m}$  wavelength range were considered for analysis, since the near infrared channels were noisy. Pre-processing was performed with routines developed at the German Space Establishment DLR (Oertel et al, 1995). Atmospheric correction followed established procedures (Richter, 1996) using a midlatitude summer profile.

Fieldwork was conducted several years after the spill. Samples were collected over the mine waste dumps on geomorphologically selected locations to simulate the chemical evolution of the mineral substances short after the spill. Laboratory spectral measurements on those samples were taken with a Perkin Elmer Lambda 9 Spectrophotometer provided with an integrating sphere, in the visible and near infrared wavelength range (0.4  $\mu\text{m}$ -2.4  $\mu\text{m}$ ) with a spectral resolution of 0.001  $\mu\text{m}$ . Samples both from loose material and crusts formed over the ground on mine dumps were measured to ascertain spectral differences related to dehydration, oxidation and subsequent compaction from solutions after rainy events. Selected samples of crusts and loose material from the mine dump were analysed by X-ray diffraction.

#### 3.2 Image processing

Masks for vegetation, water, ordinary soil, and pyrite mud were made with preliminary endmember selection using Minimum Noise Fraction Transforms, Pixel Purity Index and N-dimensional analysis (RSI, 2000). The area flooded by the spill showed dark signatures in the visible wavelength range, and could be easily isolated from ordinary soil. The area originally flooded by the spill was digitally analysed separately using the same procedure. The spectra from the resulting statistical populations were used as input endmembers on Spectral Angle Mapper. A map was compiled with SAM selected rules by their geological spatial pattern according to geomorphological criteria (fig. 2).

Hematite	$\text{Fe}_2\text{O}_3$
Goethite	$\text{FeO}(\text{OH})$
Ferrihydrite	$\text{Fe}^{3+}_2\text{O}_3 \cdot 0.5(\text{H}_2\text{O})$
Jarosite	$(\text{SO}_4)_2\text{KFe}_3(\text{OH})_6$
Alunite	$(\text{SO}_4)_2\text{KAl}_3(\text{OH})_6$
Gypsum	$\text{SO}_4\text{Ca} \cdot 2\text{H}_2\text{O}$
Epsomite	$\text{SO}_4\text{Mg} \cdot 7\text{H}_2\text{O}$
Schwertmannite	$\text{Fe}^{3+}_{16}\text{O}_{16}(\text{OH})_{12}(\text{SO}_4)_2$
Copiapite	$\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20(\text{H}_2\text{O})$

Table 1. Minerals product of oxidation and dehydration of sulphide sludge arranged according to hydration degree.

A number of individual mineral substances precipitated from pyrite acid water were identified on the public domain spectral

libraries, ranging from copiapite as the more hydrated substance, to hematite when dehydration and oxidation is completed (table 1). Thirty five existing spectra from sulphide oxidation products in public domain spectral libraries (Clark et al, 1993) were used as references with the Spectral Analyst (RSI, 2000) to get a comparative score of similarity for spectra from every map unit. Spectral Angle Mapper, Spectral Feature Fitting and Binary Encoding were taken into account on equal weights on the final similarity score. The dominant mineral was assigned to the map units (fig. 2, fig.3).

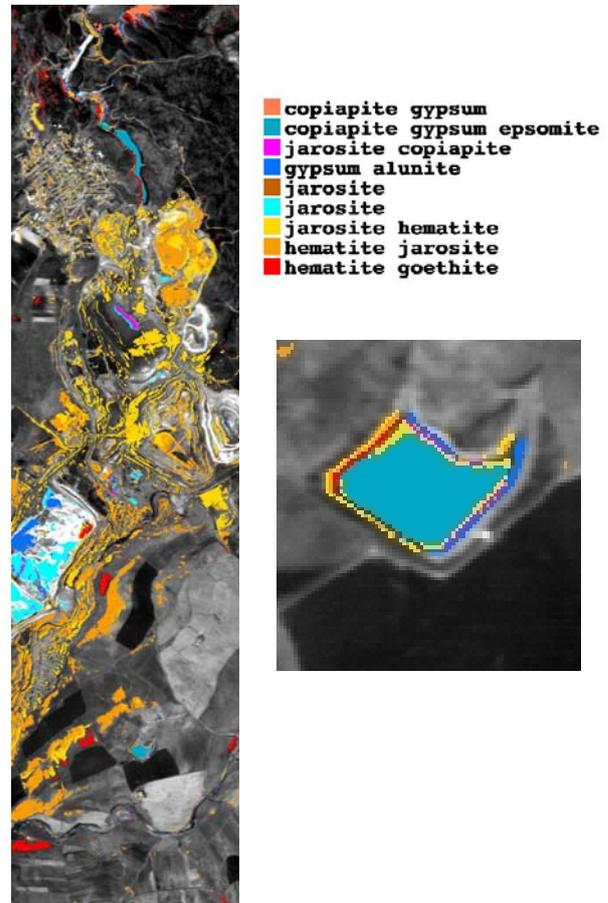
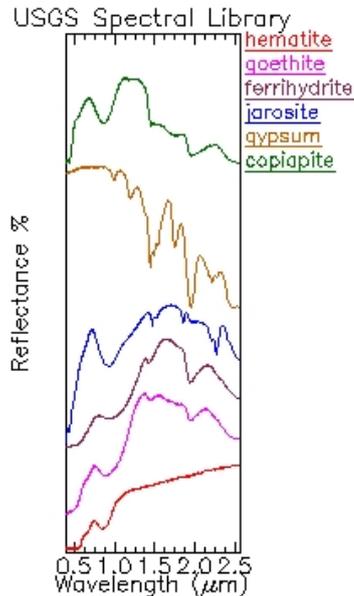


Figure 2: Map of oxidation and dehydration products from sulphides after the spill. Legend according to spectral analyst estimations from a spectral library of thirty-five existing spectra from sulphide oxidation products in public domain spectral libraries. Detail of pond.

#### 3.3 Laboratory spectra

Samples were collected on the mine dumps years after the pyrite spill on channel developments and slopes with varying mineralogical mixtures associated to their geomorphological position. Since the tailings were drying when the flight took place, poorly crystallized varieties of hydroxysulphates are expected. Gypsum precipitates at an early stage (Simon et al, 2002). Schwertmannite as poorly crystallized iron hydroxysulphate and jarosite when better crystallization occurs are mentioned on mineralogical studies on contaminated soils of the spill. Aluminium is precipitated as basic aluminum sulphate, presumably basaluminite (Simon et al, 2002).

On gullies on mine dumps, the high flat surfaces and slopes towards the bottom of the channel develop white saline efflorescences at human sight (fig. 4). After rainy periods, a crust is formed by intense evaporation of interstitial fluids flowing upwards by capillary action. The white crust consists of a combination of soluble iron, calcium and magnesium sulphate mainly, with accompanying metals variably hydrated (Simon et



al, 1999).

Figure 3: Spectra from the USGS spectral library related to oxidation and dehydration rates from sulphides. A spectral library of thirty five secondary acid drainage mineral spectra has been used. Spectra are

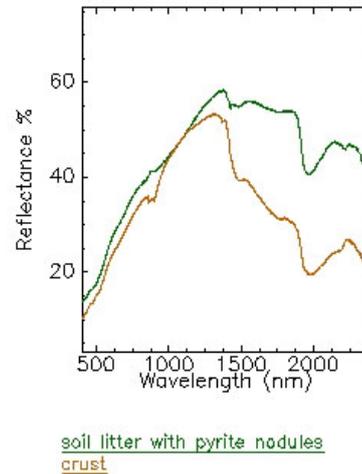


displaced vertically for clarity.

Figure 4: Geomorphologic pattern of oxidation and dehydration minerals from sulphides.

Laboratory spectra differ constantly from dust or litter over the ground to mud crusts developed by desiccation after a rainy event (fig. 4). Crusts, compared to regolith, show a general decrease in overall reflectance, emphasized between 1.3-2.4 µm

(fig. 4). The 2.2 clay µm absorptions from the soil spectra disappear, and iron absorptions are emphasized, with a minimum shifting to shorter wavelength ranges. On the spectra from crusts, a concave shape appears between 1.9-2.14 µm with a shoulder between 2.14 y 2.2 µm. Those general trends on the spectral behaviour from dusty soil and crusts are repeated regardless of the mineral composition of the crust. Such features are common to secondary minerals precipitated from solutions of sulphide minerals, both from natural sulphide-bearing outcrops, and from mine facilities and associated ore



processing plants.

Figure 5: Laboratory spectra of loose material and crust developed from it on the mine dump

The field sampling took place at an unusual yearlong dry period, therefore intensely hydrated mineral varieties are not expected on the surface of the mine dumps. The procedure used to assign mineralogical contents to the mapped units (fig.2,3) after image processing with the Spectral Analyst routine, was repeated for the laboratory spectra. Thirty-five existing spectra from sulphide oxidation products in public domain spectral libraries were used as references with the Spectral Analyst (RSI, 2000) to get a comparative score of similarity for laboratory spectra from field samples (fig. 6). In the same way as with the mapped units, Spectral Angle Mapper, Spectral Feature Fitting and Binary Encoding were taken into account on equal weights on the final similarity score for field crust samples.

Comparison with the selected sulphate and iron oxides and hydroxides spectral library through the Spectral Analyst (RSI, 2000) confirms field expectations and prior mineralogical studies (fig. 3). Spectra with dominant hematite, jarosite or alunite can be identified on well-developed crusts. On the contrary, areas covered by whitish or yellowish fine dust do not present any dominant mineral (fig. 4). Mineral amorphous phases with poor crystallinity precipitated by fast evaporation from colloids or solutions may be the reason for lack of identifiable spectral features on fine dusty samples.

The spectra of the units mapped after DAIS imagery display general trends related to the spectral features of minerals in spectral libraries (fig. 6). The units where copiapite, gypsum and epsomite are identified show a lower overall reflectance, increasing as jarosite and more dehydrated minerals are identified. A minimum at 0.84 µm shifting to 0.93 µm can also

be identified. A better atmospheric correction may be needed to identify minerals more accurately.

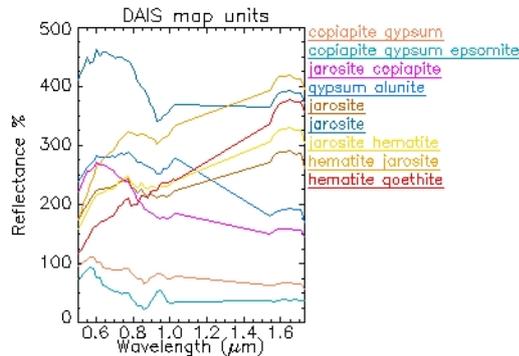


Figure 6: Spectra from DAIS images in the visible wavelength range for the mapped units after fig.2.

However, hyperspectral image processing is able to distinguish areas where various strongly hydrated phases existed (fig. 2) on the surface of the tailings dam in August 1998, likely absent when the field sampling took place.

#### 4. DISCUSSION

The minerals on the outer pyrite mud crust are ephemeral, and change rapidly as the mud dehydrates. The compiled map describes this process faithfully.

The hematitic and goethite dehydrated areas on the imagery correlate with slopes on the area flooded by the spill when overtopping and cutting across the channel banks over the river. They also occur on isolated zones on the tailings dam, and areas that were never covered by the pyrite mud. Mixtures of jarosite and hematite cover the open pit and adjacent areas, including the bottom of the channel cleaned from the pyrite mud spill. The areas where copiapite, gypsum and epsomite are indicated by the imagery are near ponds and water bodies, the most humid spaces.

According to the Spectral Analyst estimates, the broken tailings dam was covered at the time of the flight with a crust made out of mixtures of gypsum, jarosite and alunite, indicating a medium dehydrated state. Glimpses of copiapite occur on the bottom of rills flowing to the draining point, likely more humid in the recent past.

Therefore, there is a clear geomorphological spatial correlation between the mineral associations resulting from the Spectral Analyst, and the formerly analysed secondary minerals precipitating on the sulphate crusts short after the spill. Hyperspectral imagery is able to map various states of dehydration on pyrite mud. Since contaminating metals concentrate on the upper dry sulphate crust and because of their high solubility and mobility, a fast evaluation of potential contaminating mobilization can be done using hyperspectral imagery, even when using only the visible wavelength range.

#### 5. CONCLUSIONS

Hyperspectral data have been able to distinguish different degrees of oxidation and dehydration on pyrite mud on an abandoned mine facility. Mineral indicators of such stages are suggested using the spectral analysis techniques comparing with spectral libraries collected from foreign samples to the study site.

Following image processing, 116 days after the mud spill in Aznalcollar on April 1998, the broken tailings dam was covered by a mixtures of sulphate indicating a medium dehydrated state. Highly hydrated minerals are restricted to the bottom of rills flowing to the draining point of the dam.

Laboratory spectra on crusts collected on the site show spectral trends common to acid drainage minerals precipitated from sulphide solutions. Further work is needed with multitemporal imagery to qualify mineral mixtures and mineralogical processes on a spectral basis.

#### REFERENCES

- Alastuey, A., García-Sánchez, A., López, F., and Querol, X., 1999. Evolution of pyrite mud weathering and mobility of heavy metals in the Guadiamar valley after the Aznalcóllar spill, south-west Spain, *The Science of The Total Environment* 242 (1-3), pp 41-55.
- Clark, R. N., Swayze, G. A., Gallagher, A., King, T. V. V. and Calvin, W. M., 1993. The U.S. Geological Survey Digital Spectral Library: Version 1: 0.2 to 3.0 mm. *U.S. Geological Survey*, Open File Report 93-592.
- Clark, R.N., Vance, J.S., Livo, K. E., 1998. Mineral Mapping With Imaging Spectroscopy: The Ray Mine, Az, From: Mineral Mapping with Imaging Spectroscopy: the Ray Mine, AZ, Roger N. Clark, Sam Vance, Rob Green, *Summaries of the 7th Annual JPL Airborne Earth Science Workshop*, R.O. Green, Ed., JPL Publication 97-21. Jan 12-14, pp 67-75.
- Farrand, WH; Harsanyi, JC, 1995. Mineralogic Variations in Fluvial Sediments Contaminated by Mine Tailings as Determined From AVIRIS Data, Coeur d'Aldene River, Idaho, *AVIRIS Workshop*, pp 47-50, JPL Publication.
- Gallart, F., Benito, G., Martín-Vide, J.P., Benito, J., Prió, J. M., and Regüés, D., 1999. Fluvial geomorphology and hydrology in the dispersal and fate of pyrite mud particles released by the Aznalcóllar mine tailings spill, *The Science of The Total Environment*, 242 (1-3) , pp 13-26.
- García-Haro, F.J., Sommer, S. and Kemper, T., 2005., A new tool for variable multiple endmember spectral mixture analysis (VMESMA), *International Journal of Remote Sensing*, 26 (10), pp 2135-3162.
- Kemper, T. and Sommer, S., 2003, Mapping and monitoring of residual heavy metal contamination and acidification risk after the Aznalcóllar mining accident (Andalucía, Spain) using field and airborne hyperspectral data, *Proceedings 3<sup>rd</sup> EARSel Workshop on Imaging Spectroscopy*, Herrsching, Germany, 13-16<sup>th</sup> May 2003, pp 333-343.
- Leblanc, M., Morales, J.A., Borrego, J., and Elbaz-Poulichet, 2000. A 4500 years old mining pollution in Southwestern

- Spain: Long-Term concerns for modern mining, *Economic Geology* 95, pp 655-672.
- Lévesque, J., Szeredi, T., Staez, K., Singhroy, V., Bolton, D., 1997. Spectral Unmixing for Monitoring Mine Tailings Site Rehabilitation, Copper Cliff Mine, Sudbury, Ontario, *Twelfth International Conference and Workshops on Applied Geologic Remote Sensing*, Denver, Colorado, 17-19 November, pp 340-347
- López-Pamo, E., Baretino, D., Antón-Pacheco, C., Ortiz, G., Arránz, J.C., Gumiel, J.C., Martínez-Pledel, B., Aparicio, M. & Montouto, O. 1999. The extent of the Aznalcóllar pyritic sludge spill and its effects on soils. *The Science of the Total Environment*, 242, pp 57-88.
- John C. Mars and James K. Crowley, 2003. Mapping mine wastes and analyzing areas affected by selenium-rich water runoff in southeast Idaho using AVIRIS imagery and digital elevation data, *Remote Sensing of Environment*, 84 (3), pp 422-436.
- Irene Montero S. and George Brimhall, 2002. Multiplatform VIS/SWIR Hyperspectral Approach to the Study of Acid Mine Drainage from Abandoned Mines, *Denver Annual Meeting Geological society of America 2002*, pp 43507
- D. Oertel, F. Lehmann, S. H. Chang, 1995. A New 79 Channel Airborne Imaging Spectrometer: Its Functioning, Main Characteristics and Calibration, *ISPRS Workshop " From Pixels to Sequences "*, Zurich, March 22 -24.
- Cindy Ong and Thomas Cudahy, 2002. Deriving Quantitative Monitoring Data Related to Acid Drainage Using Multi-temporal Hyperspectral Data, *AVIRIS Workshop*, 5pp.
- Ong, C., Cudahy, T.J. and Swayze, G., 2003. Predicting Acid Drainage Related Physicochemical Measurements Using Hyperspectral Data, *Proc. 3<sup>rd</sup> EARSeL Workshop on Imaging Spectroscopy*, Herrsching, 13<sup>th</sup>-16<sup>th</sup> May 2003, pp 363-369.
- Richter, R., 1996, "Atmospheric Correction of DAIS Hyperspectral Image Data", *Computers & Geosciences*, 22 (7), pp 785-793.
- RSI, 2000. ENVI User's Guide, *Research Systems Inc. Publications*.
- Simón, M., Ortiz, I., García, I., Fernández, E., Fernández, J., Dorronsoro, C., and Aguilar, J., 1999. Pollution of soils by the toxic spill of a pyrite mine (Aznalcóllar, Spain), *The Science of the Total Environment*. 242, pp 105-115.
- Simón, M., Dorronsoro, C., I. Ortiz, I., Martín, F., and Aguilar J., 2002. Pollution of carbonate soils in a Mediterranean climate due to a tailings spill, *European Journal of Soils Science*, 52, pp 1-10.
- Sánchez España, J., López Pamo, E., Santofimia, E., Aduvire, O., Reyes, J., and Baretino, D., 2005. Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications, *Applied Geochemistry*, 20 (7), pp 1320-1356.
- Sares, A., Hauff, Ph. L., Peters, D. C., Coulter, D. W., Bird, D. A., Henderson, F. B., and Prosh, E. C., 2004. Characterizing Sources of Acid Rock Drainage and Resulting Water Quality Impacts Using Hyperspectral Remote Sensing – Examples from the Upper Arkansas River Basin, Colorado, *Proceedings Geospatial Conference 2004*, December 7<sup>th</sup>-9<sup>th</sup> 2004, Atlanta (GA, USA), pp 20.
- Swayze, G. A., K. S. Smith, et al., 2000. Using imaging spectroscopy to map acidic mine waste. *Environmental Science and Technology* 34, pp 47-54.
- Swayze, G.A; R.N. Clark; K.S. Smith; P.L. Hageman; S.J.; Sutley; R.M. Pearson; G.S. Rust; P.H. Briggs; A.L. Meier; M.J. Singleton; S. Roth, 1998. Using Imaging Spectroscopy To Cost-Effectively Locate Acid-Generating Minerals At Mine Sites: An Example From The California Gulch Superfund Site In Leadville, Colorado, *Airborne Visible/Infrared Imaging Spectrometer (AVIRIS): 1998 JPL Airborne Geoscience Workshop Proceedings*, 1998, pp 49-53.
- Swayze, G. A., R.N. Clark, R.M. Pearson and K.E. Livo, 1996. Mapping Acid-Generating Minerals at the California Gulch Superfund Site in Leadville, Colorado using Imaging Spectroscopy, In *Summaries of the Sixth annual JPL Airborne Earth Sciences Workshop*, R.O: Green (ed.), JPL Publication 96-4, March 4-8.
- Zabcic, N., Ong, C., Müller, A., 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), in press.

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