

# **Mapping Acid-Generating Minerals at the California Gulch Superfund Site in Leadville, Colorado using Imaging Spectroscopy**

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## **Introduction**

The Leadville mining district, located at an elevation of 3000 m in the Central Colorado Rockies, has been mined for gold, silver, lead and zinc for over 100 years. This activity has resulted in waste rock and tailings, rich in pyrite and other sulfides, being dispersed over a 30 km<sup>2</sup> area including the city of Leadville. Oxidation of these sulfides releases lead, arsenic, cadmium, silver, and zinc into snowmelt and thunderstorm runoff, which drains into the Arkansas River, a main source of water for Front Range urban centers and agricultural communities. The U.S. Environmental Protection Agency (EPA), U.S. Bureau of Reclamation (USBR), contractors, and responsible parties are remediating the mined areas to curtail further releases of heavy metals into various drainage tributaries of the Arkansas River. The USBRs' current work is directed toward characterizing and pinpointing localized sources of acid mine drainage and contamination from waste rock piles found throughout an area of 900 hectares.

## **Method**

The sulfide oxidation process is biologically driven along complex chemical pathways with feedback reactions that enhance the speed and magnitude of oxidation (Nordstrom, 1982). Release of heavy metals is facilitated by sulfide oxidation, since many of the sulfides contain the heavy metals (e.g. Pb, As, Cd, Ag, and Zn). The oxidation-weathering process produces low pH water in which the heavy metals dissolve as aqueous phases that are then transported by runoff into nearby streams. Secondary minerals such as jarosite, ferrihydrite, schwertmannite, goethite, and hematite are formed by sulfide oxidation or precipitation from metal-rich water. These secondary minerals are Fe-rich and usually hydroxyl-bearing, making it possible to identify them from their unique spectral signatures. As the pH of the stream water increases, from dilution with higher pH sources, the secondary minerals precipitate out as streambed coatings. Because the heavy metals can substitute for Fe, they are also precipitated from solution as constituents of secondary minerals or as contaminants adsorbed onto the surfaces of the secondary minerals (Smith and Macalady, 1991; Alpers et al., 1994). Subsequent pulses of low pH water may dissolve the secondary minerals and remobilize the heavy metals and transfer them downstream.

The sulfide mineral pyrite is a primary source of acid drainage. Because direct spectral detection of pyrite is hampered by its low reflectance level, its broad Fe-absorption,

and usual opaque coating of oxidation products, pyrite can only be detected when it is locally concentrated. However, our study shows that pyrite weathers first to copiapite, a mixed  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$ -sulfate, and then to jarosite, and eventually to hematite or goethite (Table 1), forming a sequence where the degree of oxidation and weathering is indicated by the species of secondary mineral that forms. Therefore, an indirect way to find oxidizing pyrite is to look for areas where the secondary minerals grade through the oxidation-weathering sequence (e.g. those areas with copiapite or jarosite surrounded by goethite or hematite). Quite fortuitously, the presence of heavy metals and low pH associated with the mine waste prevent the growth of vegetation over most waste piles leaving them exposed.

Table 1. Pyrite and Secondary Minerals

Pyrite	$\text{FeS}_2$ *
Copiapite	$\text{Fe}^{2+}\text{Fe}^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Jarosite	$(\text{Na},\text{K})\text{Fe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$
Goethite	$\alpha\text{-FeO}(\text{OH})$
Hematite	$\alpha\text{-Fe}_2\text{O}_3$

\* Formulas from Fleisher (1980)

The size of the Leadville mining district and presence of spectrally detectable secondary minerals from the pyrite oxidation-weathering process makes imaging spectroscopic analysis effective for locating those minerals related to the acid mine drainage sources. AVIRIS data was collected over Leadville on July 27, 1995 as part of the NASA SIR-C Data Integration Project (lead by F. Kruse). Data were calibrated from radiance to reflectance in two stages: 1) removal of solar flux, atmospheric absorption, and path radiance using the ATREM program (Gao et al., 1992), and 2) further corrections of the ATREM reflectance data using ground reflectance targets. One of the additional corrections was needed because ATREM overcorrected the AVIRIS scene's path radiance. We derived this correction by first extracting an average spectrum from the ATREM cube over fir trees in a shaded ravine, and then dividing this into a fir tree spectrum from our library. Next we used the low points in this spectral ratio to cubic spline a new curve which was then added back into the ATREM data cube to compensate for the overcorrection. Since the terrain around Leadville is heavily vegetated we used the Sugarloaf earthen-fill dam as our high reflectance ground calibration target. The dam surface consists of granite boulders and smaller fragments of metamorphic gneiss piled to form an irregular surface dipping uniformly away from the reservoir. Because of the heterogeneity of this site, a portable field spectrometer was used to record 300 reflectance spectra, each of a 0.4 meter diameter roving spot of the dam surface, relative to a spectralon standard. These spectra were averaged and then used to derive a multiplier which was applied to the ATREM cube to removed the remaining artifacts. Given the heterogenous composition of the dam's surface and the need to produce a correction relatively free of noise (to preserve the high S/N of the AVIRIS data), use of a portable field spectrometer was critical to producing the final AVIRIS reflectance calibration.

Calibrated AVIRIS reflectance data was spectroscopically mapped using the Tricorder

algorithm (Clark et al., 1995; Clark et al., in prep.). Tricorder is an expert system which is capable of simultaneously analyzing spectra of solids, liquids, and gases. It can preprocess data, then do an initial analysis, and from this decide on a number of alternate analysis paths. Tricorder's primary subroutine is a least-square shape-matching algorithm which compares spectra of unknown materials to hundreds of reference library spectra and picks the best spectral match. This subroutine uses thresholds on band depth, fit, and continuum slope to help constrain the spectral matching. The spectral library used to map AVIRIS Leadville data contains reference spectra of the individual secondary minerals and some mixtures of these, along with 160 spectra of other materials. Because the visible to 1.0- $\mu\text{m}$  spectral region is dominated by electronic absorptions due to transition metals, including Fe, and because the 2 to 2.5- $\mu\text{m}$  region is dominated by molecular vibrational absorptions, maps of the dominant materials in each spectral region were produced for the Leadville AVIRIS scene.

### **Results**

Examination of the electronic-absorption map shows the waste piles as having small zones of jarosite surrounded by jarosite-goethite zones, in turn surrounded by goethite and hematite zones. Field checks of these oxidation-weathering zones with a portable spectrometer and hand lens indicates that the jarosite zones are pyrite-rich. Coarse pyrite weathers more slowly than fine pyrite and enough had survived weathering that it was mapped in the Oregon Gulch tailings. At the Apache pile, concentrations of finer grained pyrite (used as a pigment to color beer bottles), had an oxidation coating of copiapite which was also identified and mapped. Reprocessed tailings in the Stray Horse Gulch waste piles mapped as hematite, providing a way to acrially separate these materials from the goethite-rich waste rock. Areas surrounding the site of an old smelter spectrally mapped as an amorphous Fe-hydroxide. Field investigation in these areas showed rocks coated with a grayish-coating of the condensed arsenic-rich effluent from the smelter smoke stacks.

Examination of the vibrational absorption map shows that the waste piles abruptly change composition from Na-montmorillonitic to kaolinite-sericitic alteration across a series of interconnected NW-trending graben faults. Since mineralization was hosted in limestones on both sides of the fault, the differences in alteration may be related to changes in the chemistry and temperature of the hydrothermal fluids or the composition of the waste rock. These spectrally observed compositional differences may, nevertheless, fingerprint waste rock piles as originating from specific mines or ore bodies. At present, no clear relationship can be drawn between the distribution of clays and the location of acid drainage point-sources.

### **Conclusions**

The mineral maps created from AVIRIS data are being used to guide USBR's investigation, characterization, and remediation efforts for the EPA at the California Gulch Superfund (NPL) Site. Based on the pattern of secondary oxidation-weathering minerals that form above pyrite-rich waste rock and tailings, a map of the electronic absorption spectral region can be used to locate potential sources of acid mine drainage. Those areas covered by jarosite and jarosite-goethite mine-waste are believed to have a high acid generating capacity and are surface point-sources for acid water and heavy metals. Areas covered by goethite and hematite can still contain heavy metals (adsorbed on or as components of the secondary minerals) but they will not be mobile in the absence of low pH water, normally found in the

jarosite-rich areas. It is possible that the minerals at the surface of the waste piles and tailings may not reflect the pile's composition at depth. Depending on the amount of precipitation and level of the groundwater table, unoxidized sulfides may be mantled by a layer of non-acid generating secondary minerals. In these cases, surficial mineral maps will not show the acid-generating capacity of the waste rock and tailings beneath the surface. In most instances, we believe that these oxidation rinds will prevent water from penetrating to the sulfides, and in effect, isolate them from the aqueous environment. As part of our ongoing investigation, we plan to correlate surface mineralogy with soil metal-concentration and pH information from drill cores and geoelectrical profiling, to better address this possibility.

Significant cost savings in investigation and remediation design have already been realized using AVIRIS data at this National Priority List Site.

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