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2 **Characterization of waste rock associated with acid drainage at the**
 3 **Penn Mine, California, by ground-based visible to short-wave**
 4 **infrared reflectance spectroscopy assisted by digital mapping**

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12 **Abstract**

13 Prior to remediation at the abandoned Cu–Zn Penn Mine in the Foothills massive sulfide belt of the Sierra Nevada, CA, acid
 14 mine drainage (AMD) was created, in part, by the subaerial oxidation of sulfides exposed on several waste piles. To support
 15 remediation efforts, a mineralogical study of the waste piles was undertaken by acquiring reflectance spectra (measured in the
 16 visible to short-wave infrared range of light: 0.35–2.5 μm) using a portable, digitally integrated pen tablet PC mapping system
 17 with differential global positioning system and laser rangefinder support. Analysis of the spectral data made use of a continuum
 18 removal and band-shape comparison method, and of reference spectral libraries of end-member minerals and mineral mixtures.
 19 Identification of secondary Fe-bearing minerals focused on band matching in the region between 0.43 and 1.3 μm. Identification
 20 of sheet and other silicates was based on band-shape analysis in the region between 1.9 and 2.4 μm. Analysis of reflectance
 21 spectra of characterized rock samples from the mine helped in gauging the spectral response to particle size and mixtures. The
 22 resulting mineral maps delineated a pattern of accumulation of secondary Fe minerals, wherein centers of copiapite and jarosite
 23 formed at low pH (<3) that were surrounded successively by goethite and hematite, which mark progressive increases in pH.
 24 This pattern represents the evolution of acid solutions discharged from the pyritic waste piles and the subsequent accumulation
 25 of secondary precipitates by hydrolysis reactions. The results highlight the high capacity of the pyritic waste to release further
 26 acid mine drainage into the environment, as well as the effectiveness of the mapping method to detect subtle changes in surface
 27 mineralogy and to produce maps useful to agencies responsible for remediating the site.

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29 *Keywords:* Reflectance spectroscopy; Acid mine drainage; Jarosite; Goethite; Hematite; Fe sulfates

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31 1. Introduction

32 Abandoned mines are one of the most challenging
33 environmental problems faced by government, com-
34 munities and the mining industry worldwide. The
35 effects of historic mining activity in the western USA
36 are well illustrated in California, where water resour-
37 ces are threatened by the discharge of acid mine
38 drainage (AMD) from a plethora of abandoned mines
39 (California Department of Conservation, 2000). Inad-
40 equate characterization of AMD-generating mine
41 wastes is a major obstacle to remediation of their
42 sites. The abundance and variety of abandoned mines
43 is such that a complete inventory and assessment of
44 their environmental impact is far from complete,
45 which hinders the formulation of scientifically and
46 economically sound strategies for remediation.

47 The purpose of this paper is to present an
48 alternative and efficient way to characterize aban-
49 doned mines to assess their potential for AMD
50 discharge. The Penn Mine demonstrates the type of
51 limitations typically encountered in the remediation of
52 AMD-generating sites, such as difficult access to
53 relevant areas due to the steep topography of waste
54 piles, unstable and unknown mine workings, sparse
55 accurate historical records, and uncertainty regarding
56 the metal and sulfate load to adjacent water bodies.
57 Uncertainty regarding metal loads can arise from
58 difficulties in detecting and mapping minerals such as
59 water-soluble Fe sulfates and nanocrystalline Fe
60 phases. Detection of water-soluble sulfates depends
61 on the amount and timing of precipitation prior to
62 mapping. Mapping of water-soluble sulfates is critical
63 because some of these minerals incorporate consid-
64 erable amounts of heavy metals that can be quickly
65 released into water bodies after rainfall (Nordstrom
66 and Dagenhart, 1978; Jambor et al., 2000; Takagi and
67 Brimhall, 2001).

68 Fast and accurate mapping of the mineralogy of
69 waste piles circumvents many of these problems and
70 illustrates the need for efficient characterization
71 methods. Our approach is based on the mapping of
72 minerals that occur on the surface of waste-rock piles
73 and their surroundings, focusing on minerals that
74 serve as indicators of subaerial oxidation of pyrite and
75 the subsequent formation of AMD. In our mapping
76 methods, a digital mapping system is used in
77 combination with a portable reflectance spectrometer

that measures reflected solar light in the range 78
extending from visible to short-wave infrared. 79

80 Recent years have seen increased interest in the
81 use of remote spectral data to support the character-
82 ization and remediation of both operating and
83 abandoned mines (Ferrier, 1999; Swayze et al.,
84 2000; and references therein). At such sites, the
85 combination of geology, mining history and past
86 waste-disposal arrangements often result in geochem-
87 ical conditions that favor the occurrence of secondary
88 Fe minerals characteristic of AMD (Alpers et al.,
89 1994a). Minerals such as Fe-bearing sulfates, oxides
90 and oxyhydroxides have chemical and structural
91 properties that make them identifiable by reflectance
92 spectroscopy. Mineral maps based on reflectance
93 spectroscopy can then be used by interdisciplinary
94 teams (Dalton et al., 1998) to identify sources of
95 acidity, to estimate the possible metal load to water
96 bodies from soluble sulfate salts and to aid in the
97 evaluation of the site. The application of spectral data
98 to this problem has been shown to augment consid-
99 erably the efficiency of the remediation process,
100 saving valuable time and resources (Swayze et al.,
101 2000). At the Penn Mine, Fe mineral maps based on
102 reflectance spectroscopy illustrated the chemical
103 processes taking place in the unsaturated waste dumps
104 and the most active pyrite oxidation “hot spots”.
105 Additional potential applications of the mineral maps
106 include, but are not limited to, estimation of the
107 minimum volume of soluble Fe-sulfate salts present
108 in the waste piles, estimation of the minimum mass of
109 metals and sulfate likely to be released upon
110 dissolution of soluble Fe-sulfate salts and the priori-
111 zation of waste-rock piles for removal.

112 Chemical analysis-based assessment tools such as
113 acid–base accounting, net acid-production potential
114 and acid-neutralizing capacity have the advantage of
115 providing data regarding the potential reactions,
116 possible secondary minerals and the processes affect-
117 ing AMD. In comparison with ground-based reflec-
118 tance spectroscopy integrated into a digital mapping
119 system, such chemical methods have the marked
120 disadvantage of relying on discrete samples that may
121 fail to produce an encompassing view of the minesite,
122 the processes acting in it, and where and why critical
123 minerals accumulate.

124 Ground-based reflectance spectroscopy has been
125 used to aid atmospheric calibration (Kruse and Dwyer,

126 1995) of high-altitude remote-sensing data, to provide
 127 ground-truthing (Swayze et al., 2000) and as a tool for
 128 mineral identification of selected rock outcrops by
 129 limited SWIR spectrometers (Hauff et al., 2000). As
 130 the technology behind portable spectrometers
 131 improves, the combination of spectroscopy with
 132 efficient digital mapping allows workers to concen-
 133 trate on interpreting geochemical processes rather than
 134 simply mapping mineral occurrences. Other factors,
 135 such as availability of resources (i.e., time, atmos-
 136 pheric conditions and accessibility) highlight the need
 137 to make the spectral and spatial links in the field in
 138 order to adapt to unforeseen or changing field
 139 conditions, enabling the use of the evolving map
 140 patterns to delineate effectively the patterns that
 141 indicate AMD. The use of portable reflectance
 142 spectrometers combined with digital portable map-
 143 ping systems equipped with differential global posi-
 144 tioning system (DGPS) receivers and laser
 145 rangefinders facilitates the making of such links by
 146 assigning a precise location to each spectral measure-
 147 ment. Additional advantages of ground-based reflec-
 148 tance spectroscopy over high-altitude remote-sensing
 149 methods include improved reduction of noise intro-
 150 duced by atmospheric water (due to the short distance
 151 between the target and probe, and frequent optimiza-
 152 tion of the instrument with a white reflectance
 153 standard) and flexibility regarding coverage and time
 154 of acquisition.

155 2. Test area: Penn Mine, Calaveras County, CA

156 2.1. History of the Penn Mine

157 The Penn Mine is on the shore of Camanche
 158 Reservoir (Fig. 1), an East Bay Municipal Utility
 159 District (EBMUD) water reservoir on the Mokelumne
 160 River. Mining of Cu–Zn ore and associated smelting
 161 took place at the site from the 1860s to 1959, at which
 162 point the mine was abandoned (Clark and Lydon,
 163 1962). Reports of fish kills, surface runoff to
 164 Camanche Reservoir, elevated metal and SO₄ con-
 165 centrations, and low pH in groundwater in the vicinity
 166 of the mine (Hamlin and Alpers, 1996) prompted
 167 efforts for environmental remediation. During 1998–
 168 1999, the mine underwent environmental remediation
 169 under the direction of the EBMUD and the California

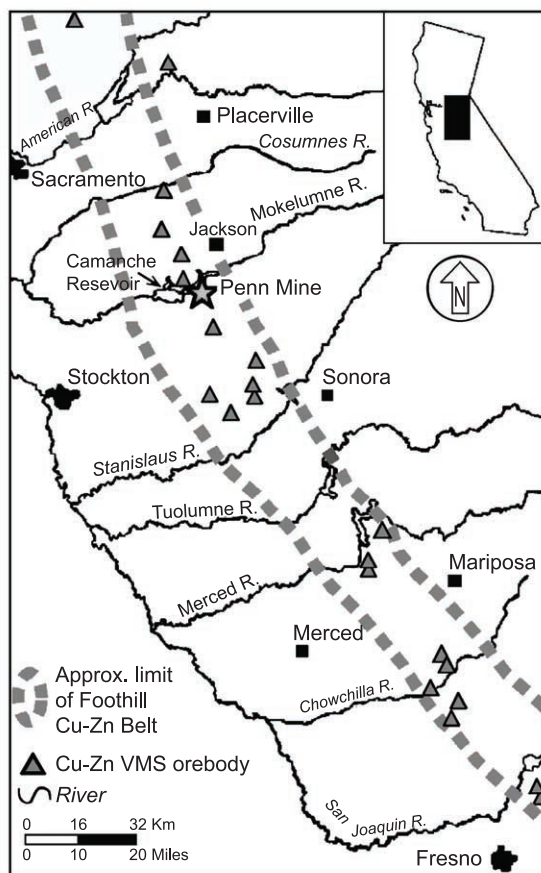


Fig. 1. Location of the Penn Minesite and other Cu–Zn VMS deposits within the Sierra Nevada Foothill Cu–Zn belt (after Heyl, 1944; Peterson, 1985).

Regional Water Quality Control Board-Central Valley 170
 Region. 171

2.2. Geological setting 172

173 Mining activity revolved around a volcanogenic
 174 massive sulfide (VMS) deposit within the 400-km-
 175 long Sierra Nevada Foothill Cu–Zn belt (Fig. 1),
 176 created in association with a sequence of submarine
 177 sedimentary and volcanic rocks within a Jurassic
 178 volcanic island arc (Peterson, 1985, 1988). This VMS
 179 deposit, classified as Sierran Kuroko by Singer
 180 (1992), was formed by hydrothermal activity in which
 181 heated sea water leached metals from existing rocks
 182 and formed stratiform lenses of fine-grained sulfides
 183 upon expulsion, as black smokers, into anoxic marine

184 environments (Singer, 1986). The orebodies and the
 185 felsic volcanic rocks that envelop them were subjected
 186 to low-grade metamorphism and deformation during
 187 accretion to the western edge of North America during
 188 the late Jurassic (Martin, 1988). Tertiary quartz
 189 gravels unconformably overlie parts of this sequence
 190 (Peterson, 1985).

191 Prior to remediation in 1998–1999 at the Penn
 192 Mine, there were 300,000 m³ of solid waste (Davy
 193 Environmental, 1993; Hamlin and Alpers, 1996),
 194 which included waste rock (low-grade ore and pyritic
 195 schist), metallurgical slag, mill tailings, disturbed
 196 bedrock and post-mining materials (infrastructure,
 197 mechanical aggregates and chemical precipitates).
 198 The waste was distributed in at least six waste-rock
 199 piles, three unlined water impoundments built with
 200 waste rock and earthen dams (Fig. 2). For this study,
 201 wastes were further classified as acid-producing or not

acid-producing according to their mineral makeup, 202
 their relative capability to oxidize and (or) produce 203
 acidity in subaerial conditions, and their abundance 204
 (Table 1). The pyritic quartz schist host-rock, low- 205
 grade massive sulfide ore, greenschist-grade metavol- 206
 canic rock and Tertiary quartz gravel made up most of 207
 the material in the waste-rock piles (Table 1). The 208
 pyritic schist consisted of quartz-muscovite schist 209
 with various degrees of chloritic, sericitic and silicic 210
 alteration. The massive sulfide orebodies contained 211
 fine-grained pyrite, sphalerite, chalcopyrite and wurt- 212
 zite, with minor bornite, tetrahedrite and galena, plus 213
 barite, calcite and gypsum as gangue minerals (Clark 214
 and Lydon, 1962). Low-grade ore consisted of quartz- 215
 muscovite schist with pyrite and sphalerite and 216
 variable chloritic and sericitic alteration. Greenschist 217
 in the waste piles consisted of chloriticized and 218
 metamorphosed basalts with abundant quartz and 219
 epidote. Prior to remediation, secondary minerals as 220
 fine ochreous powders coated many of the rocks in the 221
 waste piles and elsewhere on the property. In addition 222
 to the minerals listed in Table 1, minor occurrences of 223
 secondary fibroferrite $[\text{Fe}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}]$, schulen- 224
 bergite $[(\text{Cu},\text{Zn})_7(\text{SO}_4)_2(\text{OH})_{10} \cdot 3\text{H}_2\text{O}]$ and leonite 225
 $[\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}]$ were detected by powder X- 226
 ray diffraction in samples from the waste piles. 227
 Hamlin and Alpers (1995) reported occurrences of 228
 bornite, covellite, brochantite $[\text{Cu}(\text{SO}_4)(\text{OH})_6]$, halo- 229
 trichite-pickeringite $[(\text{Fe},\text{Mg})\text{Al}_2(\text{SO}_4) \cdot 22\text{H}_2\text{O}]$ and 230
 copiapite $[\text{Fe}^{2+}\text{Fe}^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}]$ on the 231
 waste piles. 232

2.3. AMD and secondary mineralization at the Penn Mine 233

234
 Sulfide minerals in the waste piles and in the mine 235
 workings were subjected to oxidation in the presence 236
 of atmospheric oxygen, microbial communities and 237
 aerated meteoric water (Ritchie, 1994). Measurement 238
 of how fast this process takes place in situ is 239
 complicated by the complex, biologically controlled 240
 oxidation pathway and by difficulties relating meas- 241
 ured rates to poorly understood physical parameters 242
 within a waste-rock pile (Nordstrom and Alpers, 243
 1999a). Nonetheless, a general estimate of the rate 244
 of pyrite oxidation can be obtained from the labo- 245
 ratory-measured rates of oxidation of pyritic material 246
 as measured by flux rates of oxygen depletion. In 247

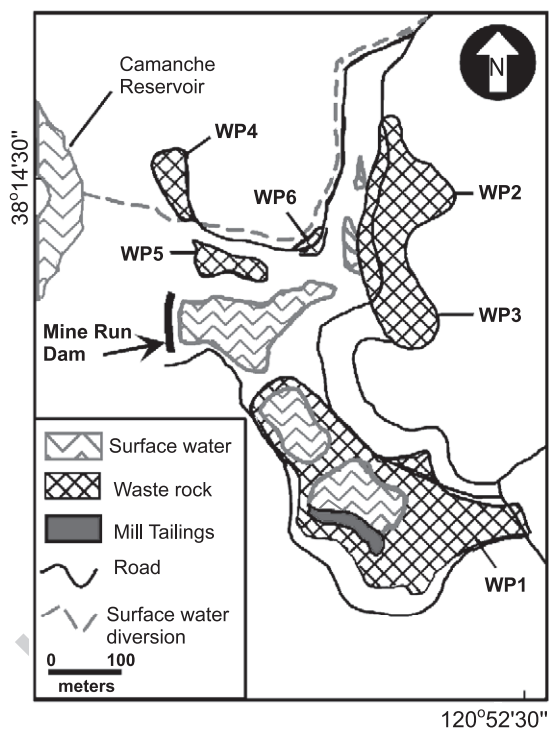


Fig. 2. Map of the distribution of waste material and the waste-water impoundments at the Penn Minesite (Davy Environmental, 1993). WP1 through WP6 are waste piles 1 through 6 according to scheme used by Davy Environmental (1993).

t1.1 Table 1
t1.2 Mineralogy of waste-rock piles at the Penn Mine as derived from XRD analysis of representative rock samples

Waste type	Rock type	Primary minerals									Secondary minerals						
		quartz	muscovite	kaolinite	illite	albite	chlorite	epidote	py, cp	sp, wz	barite	alunite	copiapite	jarosite	goethite	hematite	magnetite
Acid generating, natural	Pyritic muscovite-quartz schist																
	Massive sulfide																
Acid generating, mining products	Chemical precipitate																
	Mill tailings																
Non-acid generating, post-mining products	Chemical precipitate																
	Ferruginous mine waste																
Non-acid generating, natural	Greenstone																
	Disturbed Tertiary gravel																

t1.3 Py, cp: pyrite and chalcopyrite. Sp, wz: sphalerite and (or) wurtzite.

248 laboratory studies in which measurable oxygen was
249 depleted by reaction with pyritic material, oxidation
250 rates ranged from 0.03×10^{-8} to 60×10^{-8} mol m⁻¹
251 s⁻¹ (Nordstrom and Alpers, 1999a).

252 The biologically mediated oxidation process
253 released a low-pH solution, rich in Fe²⁺, Fe³⁺ and
254 SO₄, and known as AMD. Before remediation efforts
255 at the Penn Mine, AMD flowed through the unsatu-
256 rated waste piles and bedrock to unlined water
257 impoundments, reaching the groundwater and ulti-
258 mately the Camanche Reservoir (Alpers et al., 1994b,
259 1999). Aluminum, Cd, Cu, Fe and Zn released by
260 mineral dissolution have been detected in significant
261 amounts in acidic sulfate-rich surface water and
262 groundwater in the area (Hamlin and Alpers, 1996;
263 Alpers et al., 1999).

In waste piles, meteoric water is acidified by the
264 process of sulfide oxidation (mainly microbial oxida-
265 tion of pyrite) and is then partly neutralized by
266 hydrolysis reactions with aluminosilicates and other
267 minerals present in the waste piles as the solution
268 flows away from active oxidation points. This leads to
269 the accumulation of Fe sulfates, oxyhydroxides and
270 oxides in a spatial and temporal sequence that
271 represents the buffering of the acidic solution as it
272 moves away from its source (Swayze et al., 2000).
273 Copiapite and jarosite [KFe₃(SO₄)₂(OH)₆] form at pH
274 values <3, and accumulate near sources of acidity that
275 are also sources of heavy metals (Fig. 3; Bigham,
276 1994; Alpers et al., 1994a; Nordstrom and Alpers,
277 1999a). Goethite [α-FeOOH] forms at pH values
278 generally less than 6 from the dissolution of previous
279

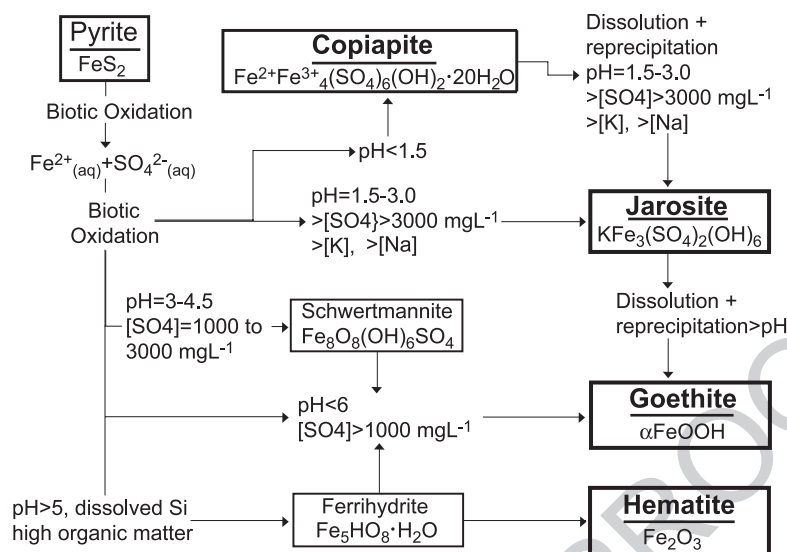


Fig. 3. Model of the accumulation of secondary Fe minerals in Fe sulfide-rich mine-waste environments according to pH values from field data. Modified from model by Bigham (1994), with additional data from Alpers et al. (1994a) and Nordstrom et al. (1978). Ranges of pH are approximate and are based on field observations of the aforementioned authors. Solid arrows represent possible paragenetic relationships of secondary Fe minerals to sulfide oxidation and to each other. Minerals in bold type were identified on waste-rock piles at the Penn Mine during the course of this study by reflectance spectroscopy.

280 minerals, including early-formed goethite and accu-
 281 mulates farther from contaminant sources (Bigham,
 282 1994). Hematite [Fe_2O_3] accumulates even farther
 283 from the sources of acidity after forming in a pH-
 284 dependent process that may involve the dehydration
 285 and transformation of earlier precipitates, such as
 286 those of goethite and ferrihydrite [nominally
 287 $\text{Fe}_5\text{HO}_8 \cdot \text{H}_2\text{O}$], with maximum production occurring
 288 at approximately pH 8 (Alpers et al., 1994a). The
 289 distribution of these secondary minerals about a
 290 source of acidity and active pyrite oxidation forms a
 291 spatial pattern in which copiapite and jarosite are
 292 relatively abundant near or at the source, and are
 293 surrounded by goethite and hematite (Swayze et al.,
 294 2000). A pattern of this type affords an opportunity to
 295 trace contaminant transport and to identify additional
 296 sources of contaminants. Numerous studies (Plumlee
 297 et al., 1999) have shown a negative correlation
 298 between pH and the concentration of toxic metals in
 299 water draining mines, thus highlighting the impor-
 300 tance of mapping low-pH zones.

301 Water-soluble sulfates, also known as efflorescent
 302 sulfate salts (Jambor et al., 2000), are among the most
 303 definite indicators of AMD (Nordstrom and Dagen-

304 hart, 1978). These sulfate salts are among the first
 305 products of sulfide oxidation and occur above the
 306 water table, closest to oxidizing pyrite, and in areas
 307 where the exposure of pyrite by erosion and the
 308 evaporation of AMD fluids create extremely low pH
 309 values (Jambor et al., 2000). Metals contained in the
 310 structure of these minerals (such as Fe, Cu, Zn, Pb, Al,
 311 Mn, Mg and K) can be readily released upon the rapid
 312 dissolution of sulfate salts during rainfall events or
 313 increased water flow (Nordstrom and Alpers, 1999b).
 314 The presence of efflorescent sulfate salts on surface
 315 waste piles depends on precipitation and evaporation
 316 rates (Jambor et al., 2000) that affect the pH and metal
 317 content of water in the waste-rock piles. Depending
 318 on when and where samples are collected, chemical
 319 analyses of water and rock samples can underestimate
 320 the extent of soluble sulfate salts. Visual identification
 321 of the salts is hampered by their small crystal size and
 322 by their similar appearance. Widely used methods
 323 such as high-altitude remote sensing commonly do
 324 not have the spatial resolution to identify small fields
 325 of soluble Fe-sulfate salts, and unless the methods are
 326 applied during different times of the year the season-
 327 ality of these salts is missed.

328 3. Instrumentation

329 The system (Fig. 4) used to map the mineral
 330 distribution of surface material at the Penn Mine
 331 incorporates a portable reflectance spectrometer that
 332 measures light in the visible to short-wave infrared
 333 (VNIR/SWIR) range, and a PC pen tablet digital
 334 mapping system supported by a differential GPS
 335 (DGPS) receiver and laser rangefinder equipped with
 336 internal digital inclinometer and magnetic compass.

337 3.1. Instrumentation: spectroscopy

338 Collection of field reflectance spectra at the Penn
 339 Mine, as well as reference spectra of selected
 340 mineral samples in controlled laboratory settings,
 341 was completed using a commercially available,
 342 battery-operated, portable reflectance spectrometer
 343 (Fig. 4A). Unlike contact field spectrometers, solar
 344 light in the VNIR/SWIR range that is reflected from
 345 a target is collected through the end of a fiber-optic
 346 cable probe held at a constant distance above the
 347 ground throughout the survey (Fig. 4A). Once
 348 collected by the probe, light is projected into a

349 diffraction grating, where it is separated by wave- 349
 length and reflected onto the unit's three detectors. 350
 From 0.35 to 1.05 μm , a silicon photodiode detector 351
 array of 512 channels yields a spectral resolution of 352
 0.003 μm . From 1.05 to 2.50 μm , two scanning 353
 InGaAs detectors have a resolution of 0.030 μm 354
 (Analytical Spectral Devices, 1999). Acquisition of 355
 spectra takes 100 ms per spectrum, after which 356
 manufacturer-provided software uses the response of 357
 the spectrometer to a Spectralon™ white reflectance 358
 standard to convert raw data to reflectance (Ana- 359
 lytical Spectral Devices, 1999; use of trade, product 360
 or firm names in this publication is for descriptive 361
 purposes only and does not imply endorsement by the 362
 U.S. government). Collection of the white reference 363
 standard must be done frequently during data collec- 364
 tion, during optimization of the spectrometer, and 365
 after dark-current correction, to maintain high signal- 366
 to-noise ratios and to compensate for changes in sun 367
 angle and for the temporal or spatial variability of 368
 atmospheric conditions, such as humidity. The size of 369
 a target area on the ground is approximately 30 cm^2 if 370
 the opening of the fiber-optic cable probe is held at 1 371
 m above the target. 372

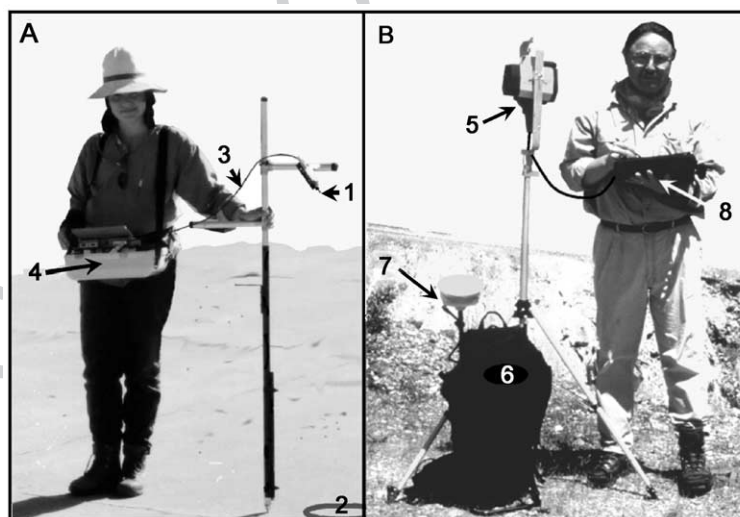


Fig. 4. I. Montero and G. Brimhall demonstrate the use of the digital mapping system. In A: (1) probe holder for the spectrometer's fiber-optic probe. Note that the staff on which the holder rests maintains the probe away from the operator at a constant height and angle above the ground. (2) Target on the ground; (3) fiber-optic cable for transmission of the light from the cable opening to the spectrometer; (4) portable, battery-operated spectrometer. In B, (5) laser rangefinder with internal digital inclinometer and magnetic compass; (6) portable DGPS receiver, which is inside the backpack; (7) DGPS antenna; (8) pen table portable PC computer.

373 3.2. Instrumentation: digital mapping

374 The digital mapping system (Fig. 4B) consists of a
375 battery-powered, pen tablet portable computer run-
376 ning a Windows®-based surveying-mapping program
377 called Geomapper® (Brimhall and Vanegas, 2001).
378 Location of survey points is supported by a DGPS
379 receiver and a reflectorless laser rangefinder, which
380 link to the PC pen tablet computer via serial ports. A
381 single DGPS receiver uses differential signal correc-
382 tion broadcast by the Omnistar satellite network,
383 which we have measured against known locations to
384 improve the GPS accuracy to approximately ± 1 m
385 horizontally. The location of spectral survey points is
386 determined by a laser rangefinder, which uses an
387 internal compass and inclinometer to compute a
388 vector from a base station (as determined by the
389 DGPS), to the target. The laser rangefinder uses a
390 laser beam with a 3 mrad divergence (Laser Atlanta,
391 2000) and an internal compass and inclinometer to
392 establish the location of a point away from the base
393 station. Measured independently of the DGPS receiver
394 errors, we determined the precision of the laser
395 rangefinder to be approximately 15.3 cm up to a
396 distance of 300 m.

397 4. Methods

398 4.1. Methods: site survey and sample collection

399 Among the several factors that influenced the
400 survey at the Penn Mine were the nature of the
401 surface materials, the topography of the site and the
402 risks associated with an abandoned minesite. Reme-
403 diation of the waste materials by several regional and
404 local agencies was to take place almost immediately
405 after the completion of the survey, thus limiting the
406 amount of time available. Furthermore, frequent
407 rainstorms resulting from the 1998 ‘El Niño’ event
408 proved to be the most limiting factor during the
409 spectral survey. All spectra reported in this work were
410 acquired after a 2-week dry period, during 2 low-
411 humidity days in late May 1998.

412 Accessible areas on five waste-rock piles were
413 mapped with spectral measurements regularly spaced
414 at 5-m intervals. Six remote measurements, spaced at
415 10-m intervals, were acquired on otherwise inacces-

sible steeper western slopes of WP2 and WP3 (Fig. 2) 416
from a distance of 5 m using a long-distance foreoptic 417
attachment that directed light within an 18° solid 418
angle to the spectrometer’s probe. The use of long- 419
distance foreoptic attachments has the advantage of 420
providing meaningful reflectance spectra from dist- 421
ances of up to 100 m, thus increasing the efficiency 422
of the method to map inaccessible areas of abandoned 423
mines. Areas of interest and sampling geometry were 424
defined on the basis of previous knowledge about the 425
site (Davy Environmental, 1993; Hamlin and Alpers, 426
1996) and on insight gained through visual inspection 427
of the field spectra during acquisition. The grid 428
spacing was selected on the basis of the size of the 429
area and available time. Control points were estab- 430
lished with DGPS along the length of waste piles and 431
were checked with a surveying tape. From control 432
points, a mapping operator used the laser rangefinder 433
to locate the position of a second moving spectrometer 434
operator. Care was taken to collect spectra over dry 435
material during the hours from 10 a.m. to 3 p.m., 436
when the sun was at less than 40° from its zenith, to 437
maintain a high signal-to-noise ratio. During survey- 438
ing, the probe of the spectrometer was held at a height 439
of approximate 1 m above the ground at 90° from 440
horizontal, with care to keep shadows or reflective 441
material away from the ground target. 442

Sixty spectral measurements were averaged for 443
each spectrum. Spectra acquisition and logging of 444
spectra location and identification number in the pen 445
computer required, on average, 1 min per spectrum. 446
This included time for spectral corrections (dark- 447
current correction, optimization of the spectrometers 448
and acquisition of a white reference) completed at a 449
rate of one every third spectrum. In total, two operators 450
acquired 513 field spectra over five waste piles 451
covering a total area of approximately 25,000 m² 452
and in <12 h (2 days) accurately surveyed field-spectra 453
locations and other features of the site. Twenty-four 454
samples of waste rock were collected and saved in 455
polypropylene bags as the survey progressed by 456
scraping the top 2–3 cm of surface material in areas 457
previously measured by the spectrometer. 458

459 4.2. Rock-sample analysis

Post-processing involved the conversion on the 460
field spectra to ASCII format and uploading of data to 461

462 a computer workstation for mineral identification.
 463 Location and logistic information regarding both the
 464 field spectra and other features were exported into a
 465 geographical information system (GIS) database of
 466 the Penn Mine. After surveying was completed, each
 467 waste-rock sample was carefully oriented, put into a
 468 dark box illuminated with two quartz-halogen lights,
 469 and its reflectance spectrum relative to that of a
 470 Spectralon® standard was measured with the same
 471 spectrometer used during fieldwork. The different
 472 materials observed in each waste-rock sample were
 473 then visually separated into subsamples (greenstone,
 474 pyritic schist or precipitate), ground with an agate
 475 mortar and pestle, and analyzed by powder X-ray
 476 diffraction (XRD) using a Cu X-ray source. The
 477 surfaces of 22 rock samples were analyzed separately
 478 by scratching the top 0.5–1 mm with a stainless steel
 479 tool and analyzing by XRD. The study of the top 1
 480 mm of each rock sample was crucial for under-
 481 standing the influence of substrate materials on the
 482 reflectance spectrum. Additional XRD study was
 483 conducted for 22 rock samples, for which 3 g portions
 484 were finely ground, suspended in distilled water and
 485 gravity-settled onto glass slides to improve detection
 486 of the sheet silicates (hereupon referred to as settling
 487 XRD). The XRD scans were obtained with a step of
 488 $0.01^\circ 2\theta$, at a scan rate of 2–3 s per step, depending
 489 on the need to minimize X-ray fluorescence from Fe-
 490 rich minerals. Identification of minerals from the
 491 XRD spectra was completed using commercial
 492 matching programs. Although care was taken to check
 493 for them, poorly crystallized nanophase Fe minerals
 494 such as ferrihydrite and schwertmannite were not
 495 identified in the samples analyzed. Hydrous Fe
 496 sulfates such as melanterite or rozenite were also not
 497 identified in the samples analyzed. Previous studies of
 498 the Penn Mine by Hamlin and Alpers (1995) also
 499 failed to detect melanterite or rozenite on the waste
 500 piles. Quartz, albite, muscovite, clinocllore, clinozoi-
 501 site and epidote were detected as the main primary
 502 silicates in the waste piles. Jarosite, goethite and
 503 hematite were the main secondary Fe minerals,
 504 occurring as coatings on larger rock fragments, as
 505 very fine loose grains and as aggregates over pyritic
 506 waste piles. Hematite was the only secondary Fe
 507 mineral in greenstone samples. Muscovite and chlorite
 508 were the most abundant sheet silicates, and even after
 509 settling XRD, illite was observed in only two samples

of waste-pile material. Kaolinite was detected in only 510
 two samples, and siderophyllite and glauconite each 511
 were detected in one greenstone sample. Pyrite, 512
 sphalerite, wurtzite and chalcopyrite were the only 513
 sulfides detected in low-grade ore and pyritic schist. 514
 Quartz and albite were the most abundant minerals in 515
 both pyritic schist and greenstones. The XRD study 516
 indicated that most of the finer particles consisted of 517
 secondary Fe minerals, and muscovite and chlorite. 518
 Fine-grained barite and alunite were found in mill 519
 tailings that were not spectrally surveyed. 520

4.3. Basis for spectral interpretation and mineral 521 identification 522

Field reflectance spectra of rocks measured over 523
 the VNIR/SWIR range represent the selective absorp- 524
 tion of sunlight by electrical and vibrational processes 525
 within a mineral's structure (Gaffey et al., 1993). The 526
 spectra can be used to resolve chemical composition 527
 and crystal structure, and to determine purity. 528

Electrical processes involving orbital electrons in 529
 transition metals give rise to broad absorption features 530
 that are observed from 0.40 to 1.3 μm (electrical 531
 region, Fig. 5A). Reflectance spectra of Fe minerals 532
 reflect single- and paired-electron transitions between 533
 energy levels in unfilled 3d orbitals and metal-ligand 534
 electron transfers (Sherman and Waite, 1985). The 535
 wavelength and intensity of absorption features in this 536
 region depend on the nature of the crystal field around 537
 the Fe atom and on the nature of the bonds around it 538
 because the nature of magnetic coupling between Fe^{3+} 539
 ions (as influenced by the crystal field) facilitates the 540
 transition of electrons between energy states (Sherman 541
 and Waite, 1985; Townsend, 1987; Rossman, 1976). 542
 Thus, in Fe^{3+} minerals, subtle differences in the shape 543
 and wavelength of the absorption features detectable 544
 after continuum removal reflect the crystal structure of 545
 the minerals and allow for their identification. 546
 Hematite possesses a structure of closely packed 547
 face-sharing FeO_6 octahedra (Burns, 1993), and the 548
 strong antiferromagnetic interactions among the Fe^{3+} 549
 ions affect the electron transitions and electric charge 550
 transfers to create a very strong absorption (delineated 551
 by low reflectance) at wavelengths shorter than 0.55 552
 μm (Rossman, 1996; Fig. 5A). A strong absorption 553
 caused by Fe^{3+} electron transition is characteristic at 554
 0.85–0.9 μm , with a concave downward inflection at 555

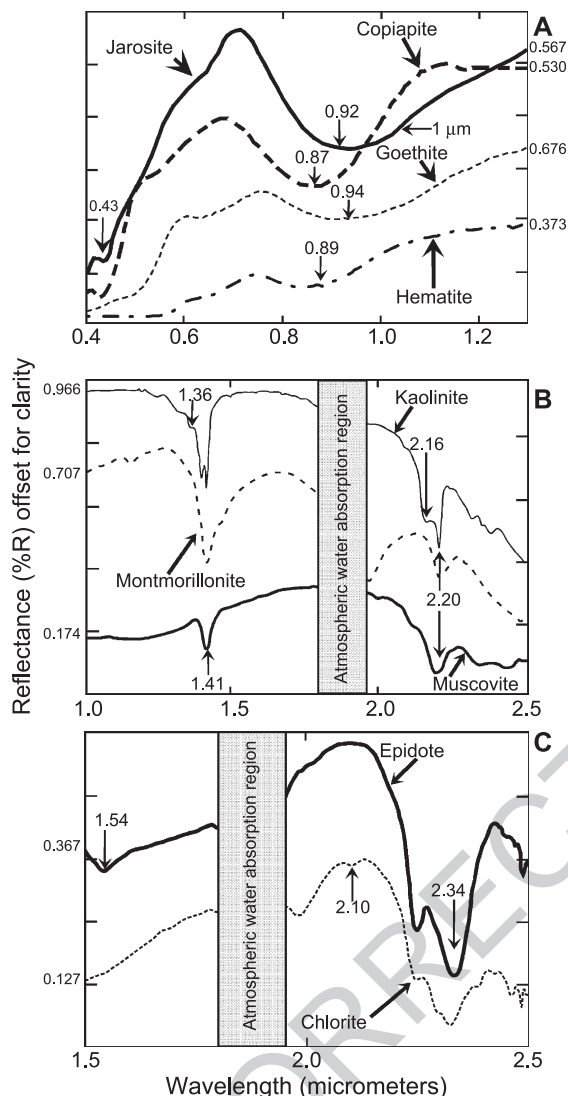


Fig. 5. Laboratory reflectance spectra of selected reference minerals. Spectra are vertically offset for clarity. Bold arrows identify mineral spectra. Light arrows indicate absorption features used in the identification of spectra, and the center of that feature (in μm) obtained by the continuum removal method of Clark et al. (1990a). (A) Secondary Fe minerals; horizontal arrow at 1.0- μm notes inflection point of jarosite. (B) Kaolinite, montmorillonite and muscovite. (C) Epidote and chlorite.

556 0.9–0.95 μm (Fig. 5A; Morris et al., 1985). The
 557 ferrihydrite structure has similarities to that of
 558 hematite except that some of the Fe sites are vacant
 559 and some oxygen sites are taken by H_2O and OH^-

(Murray, 1979). Electron and paired-electron transi- 560
 tions in Fe^{3+} cause a strong absorption centered at 561
 approximately 0.50 μm and a broad absorption at 562
 wavelengths greater than 0.95 μm , respectively 563
 (Bishop and Murad, 1995). Goethite has edge-sharing 564
 FeO_6 octahedra; paired and single Fe^{3+} electron 565
 transitions (Sherman et al., 1982) cause a strong 566
 absorption at 0.45 μm (edge at 0.55 μm) and a broad 567
 asymmetric absorption between 0.90 and 1.00 μm 568
 (Morris et al., 1985; Hunt et al., 1971). In schwert- 569
 mannite [$\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$], the presence of SO_4^{2-} 570
 bridges between some edge-sharing $\text{FeO}_3(\text{OH})_3$ octa- 571
 hedra creates two sites for Fe^{3+} (Bigham et al., 1990), 572
 which are reflected in a very broad asymmetric 573
 absorption feature at 0.9 μm and a strong absorption 574
 with a steep edge at wavelengths less than 0.5 μm 575
 (Bishop and Murad, 1995). Jarosite has edge-sharing 576
 FeO_6 octahedra bridged by hydroxyl and sulfate 577
 groups that form sheets separated by K^+ ions (Ross- 578
 man, 1976). Bridging of Fe by both OH^- and SO_4^{2-} 579
 gives rise to four electron and paired-electron transi- 580
 tions noted in the spectrum of well-crystallized 581
 jarosite (Fig. 5A; Morris et al., 1996). Spectral 582
 features diagnostic of jarosite include a narrow 583
 absorption feature near 0.43 μm and a broad feature 584
 near 0.92 μm . An inflection past 1.0 μm affects the 585
 symmetry of the broad absorption feature (Fig. 5A). In 586
 copiapite, Fe^{3+} octahedra are linked by corner-sharing 587
 OH^- and SO_4 molecules to form chains, and Fe^{2+} 588
 occupies the center of an isolated and weakly 589
 connected $\text{Fe}(\text{H}_2\text{O})_6$ octahedron at the origin of the 590
 unit cell (Fanfani et al., 1973). The strong magnetic 591
 interaction of ferric ions through the hydroxyl bridge 592
 gives rise to intense, narrow and symmetric absorption 593
 features at approximately 0.43 and 0.87 μm (Ross- 594
 man, 1975). Other Fe-bearing silicates (such as 595
 olivine, pyroxene and Fe-bearing smectites) that 596
 absorb in this range are not discussed because these 597
 minerals were not observed in this study and have not 598
 been reported to occur in rocks of the Penn Mine. 599

Combinations and overtones of fundamental vibra- 600
 tional modes of molecules such as H_2O , CO_3^{2-} and 601
 OH^- in mineral structures produce absorption features 602
 that can be observed most prominently in the vibra- 603
 tional region of the spectrum from 1.3 to 2.5 μm (Clark 604
 et al., 1990c). Kaolinite, muscovite and illite display 605
 combinations of an Al–OH bend overtone and a OH 606
 stretch (Fig. 5B; Clark et al., 1990c) that arise within 607

608 an edge-sharing Al(OH)₆ octahedral layer (gibbsite
609 layer) linked to sheets of SiO₄ tetrahedra (Klein and
610 Hurlbut, 1993). In kaolinite [Al₂Si₂O₅(OH)₄], the
611 gibbsite layer is linked via corner oxygens to one
612 sheet of SiO₄ tetrahedra (Klein and Hurlbut, 1993),
613 which affects the vibration of the Al–OH molecule to
614 create a double feature at 2.16 and 2.2 μm; OH
615 vibration stretch overtones create another doublet near
616 1.4 μm (Fig. 5B; Clark et al., 1990c). Muscovite
617 [KAl₂(AlSi₃O₁₀)(OH)₂] has two SiO₄ layers linked via
618 corner oxygens to the gibbsite layer, as well as some
619 Al substitution for Si in tetrahedral sheets, and has
620 characteristic narrow features at 1.4 (due to an over-
621 tone of an OH stretch), 2.2 and 2.34 μm (due to an Al–
622 OH bend vibration mode; Clark et al., 1990c).
623 Although illite [(K_{0.65}Al_{2.0}–Al_{0.65}Si_{3.35}O₁₀(OH)₂]²
624 departs from the composition of muscovite (Klein
625 and Hurlbut, 1993) both have similar features at 2.2,
626 2.34 (due to Al–OH bend mode) and near 1.4 μm (due
627 to an overtone of a OH stretch; Hunt, 1979; Gaffey et
628 al., 1993). Montmorillonite [(Na,Ca)_{0.3}(Al,Mg)₂
629 Si₄O₁₀(OH)₂·nH₂O] displays an Al–OH bend feature
630 near 2.2 μm (Fig. 5B), and overtones of OH vibrational
631 modes and combinations of H₂O vibrational modes
632 create a broad feature near 1.41 and 1.9 μm (Bishop et
633 al., 1994). Distinction among these minerals requires
634 high resolution and appropriate shape analysis because
635 differences in shape arise from structural differences
636 concerning the Al site (Hunt, 1979); careful analysis is
637 needed particularly for the smectite clays, wherein
638 substitution of cations such as Fe and Mg for
639 octahedral Al can alter the shape of the 2.2 μm
640 absorption and other features related to modes of the
641 H₂O molecule (Clark et al., 1990c; Bishop et al.,
642 1994). Iron-bearing silicates such as epidote
643 [Ca₂(Fe³⁺,Al)₃(SiO₄)₃(OH)] and chlorite (Fig. 5C)
644 can show electrical features (chlorite can show Fe
645 transitions near 0.4, 0.7, 0.9 and 1.0 μm), but were
646 most reliably identified on the basis of their vibrational
647 features. Chlorite [(Mg,Fe)₅Al(Si₃Al)O₁₀(OH)₈] dis-
648 plays a complex multiple band between 2.1 and 2.3 μm
649 that is interpreted to result from combined OH
650 stretching modes and Mg–OH bend modes (Hunt,
651 1979; King and Clark, 1989). Epidote shows a double
652 absorption near 2.3 μm, possibly resulting from Fe–
653 OH bend and OH stretching modes (Clark, 1999); an
654 additional feature at 1.54–1.55 μm arises from an OH
655 combination stretch mode as observed in clinozoisite

[Ca₂Al₃(SiO₄)₃(OH)] and epidote by Hunt et al. 656
(1973), and also in greenstones at the Penn Mine. 657
Quartz and most feldspars, including albite, lack 658
molecules that produce vibrational or electrical fea- 659
tures over the spectral range of interest, although they 660
can show H₂O-related features around 1.4 and 1.9 μm. 661
Other parameters, such as particle size, particle 662
orientation, particle shape, packing, porosity, type of 663
surface and viewing angle also affect the albedo and 664
the relative intensity of absorption features, or spectral 665
contrast, to an extent determined by the optical 666
properties of the material (Adams and Filice, 1967); 667
however, because the presence and position of 668
absorption features after continuum removal are 669
affected to a lesser extent, identification is possible 670
(Gaffey et al., 1993; Clark and Roush, 1984; Clark, 671
1999). The use of sets of continuum-removed absorp- 672
tion features, in addition to knowledge of the effects of 673
mixing and of variation of particle size in mixtures 674
(acquired from spectral analysis of well-known sam- 675
ples), helped reduce the uncertainty in assigning 676
spectral absorption features to the mineral occurrences. 677

678 Identification of minerals from field spectra was
679 carried out using the apparent continuum removal and
680 Band Shape Least-Squares algorithm developed by
681 Clark et al. (1990a,b). This algorithm identifies
682 minerals by matching the unknown spectrum to those
683 of reference minerals by removing from both an
684 apparent continuum (alternatively described as back-
685 ground reflectance) and using a modified least-squares
686 routine to compare their continuum-removed shapes
687 over a defined wavelength range. The result of the
688 comparison is a fit value. The fit value, if satisfactory
689 (i.e., above a threshold), is compared to fit values
690 obtained from comparison with several other mineral
691 reference spectra, and the best spectral match is
692 selected. Note that, in the context of this work, the
693 apparent continuum removal and algorithm of Clark et
694 al. (1990a) were used to identify the spectrally
695 dominant mineral in the field spectra by comparing
696 selected continuum-removed absorption bands to
697 those in a reference library of continuum-removed
698 spectra over the same spectral range. Unmixing and
699 correlation of spectral depth to mineral abundance
700 were not attempted because of the nature of intimate
701 mixtures of mineral grains on the surface of the waste
702 piles. Instead, a digital spectral library tailored to the
703 Penn Mine, which contained more than 100 reference

704 spectra of pure minerals, and more than 30 mechanical
705 binary mixtures of pure minerals and naturally occur-
706 ring mixtures, was used for the band-shape compar-
707 ison. The library data were acquired with the same
708 instrument that was used for fieldwork and also
709 incorporated spectra from the U.S. Geological Survey.
710 Reference minerals were obtained from the Mineral
711 Museum at the University of California-Berkeley, the
712 mineral collection of the Smithsonian Department of
713 Mineral Sciences and from the Penn Mine, and were
714 characterized by XRD, sieving and visual examina-
715 tion. One set of reference spectra was acquired using
716 solar light under atmospheric conditions and geometry
717 similar to those encountered during the spectral survey
718 of the Penn Mine, and a second set was acquired in a
719 dark box illuminated with two quartz-halogen lights. A
720 large reference library with many different types of
721 samples of various grain sizes, packing, degrees of
722 purity and extent of mixing, is crucial for the spectral
723 identification of minerals because of the effect of these
724 physical parameters on the spectra.

725 The study of laboratory spectra of characterized
726 rock samples and of reference minerals was completed
727 prior to the interpretation of field spectra. The analysis
728 of the reflectance spectra of the ‘standards’ provided
729 the wavelength ranges most diagnostic of each
730 mineral of interest for application of the apparent
731 continuum removal and algorithm. Identification of
732 secondary Fe minerals was focused on the comparison
733 between the field spectra and reference spectra in the
734 range from 0.75 to 1.3 μm . Identification of sheet
735 silicates and Mg–Fe-bearing silicates was done
736 mainly by identification of sets of absorption features
737 after continuum removal in the range from 1.9 to 2.4
738 μm . Despite jarosite having characteristic features in
739 the vibrational region, in natural mixtures with
740 muscovite or kaolinite the features of jarosite and
741 goethite were observed to be masked in the 1.9–2.4-
742 μm region by the more spectrally dominant features of
743 the sheet silicates. Many Fe minerals are weak
744 absorbers in the 1.3–2.2- μm region; if present as
745 submicrometer coatings on a substrate that is a strong
746 absorber in the 1.3–2.2- μm region, the spectra of the
747 substrate dominate (Sherman et al., 1982). This type
748 of association illustrates the difficulty in identifying
749 minerals from the spectra of geological materials,
750 many of which are intimate mixtures of fine-grained
751 to amorphous minerals. Reflectance spectra of mix-

tures are a nonlinear expression of the combined
spectra of the pure mineral end-members and their
abundances, in a way that reflects the accessibility of
light to each mineral grain, the complexity of
intergrain and intragrain light reflection and scatter-
ing, and the optical properties of each type of mineral
grain (Adams and Filice, 1967). In the study of
secondary minerals, variations in grain size that affect
the relative intensities of overlapping absorption
features must be considered because small secondary
minerals commonly coat larger particles and dominate
the reflectance spectra (Gaffey et al., 1993).

5. Results and discussion

5.1. Interpretation of reflectance spectra

Secondary Fe minerals in rock samples were
identified, using the apparent continuum removal and
band-shape least-squares algorithm, on the basis of the
diagnostic Fe^{3+} absorption in the electrical part of the
spectrum from 0.4 to 1.3 μm . Absorption edges and
peaks were not used in the identification process. The
secondary Fe minerals occur as fine-grained powdery
coatings or as a thin laminate on oxidized pyritic schist.
When powdery coatings of jarosite were identified by
XRD, confirmation by spectroscopy was unambigu-
ous. For jarosite coatings too thin to be detected by
XRD, the spectra displayed typical features of jarosite
at 0.43 and 0.92 μm after continuum removal (Fig. 6A).
Quartz-muscovite pyritic schist in which secondary Fe
minerals represented a minimal fraction on the surface
typically yielded high albedo and relatively flat
reflectance spectra with poorly defined features in the
electrical region (Fig. 6B). Samples of rock chips
consisting of various proportions of pyritic schist,
greenstone, gravel and ferruginous precipitate typically
contained a mixture of jarosite and goethite, with only
jarosite unambiguously detected by XRD. Analysis of
these complicated spectra (Fig. 6C) identified only the
most spectrally dominant phase in the mix, although
other nanophase Fe minerals may have been present.
As the identification method is geared to comparison
after continuum removal of absorption features, spectra
with extremely weak features were taken to represent
unidentifiable Fe minerals or poorly crystallized Fe
substances if no match was found. Identification of

796 poorly crystallized nanocrystalline (grain size <9 μm)
 797 Fe³⁺ minerals, which may be common as pigmentary
 798 agents in rocks in the waste piles, is difficult because of
 799 the lack of knowledge of their spectral features in
 800 natural mixtures, such as those containing well-crystal-

lized Fe minerals (Morris et al., 1993; Bishop et al., 801
 1998). Sulfides, the ultimate target of most acid- 802
 drainage remediation, generally can be readily identi- 803
 fied in the field through visual examination. Sulfides 804
 have very low reflectance and cannot be easily 805
 identified in reflectance spectra except where well 806
 exposed and in high concentration (Swayze et al., 807
 2000). 808

Identification of sheet silicates, Fe silicates, carbo- 809
 nates and non-Fe sulfates was conducted in the region 810
 from 1.9 to 2.4 μm by analysis of absorption features 811
 after continuum removal. Minerals containing Fe- 812
 Mg–OH, such as chlorite and epidote, which show 813
 very similar absorption features, can be distinguished 814
 by slight shape differences in the 2.3-μm feature. If 815
 both chlorite and epidote were present, the spectra of 816
 rock samples after continuum removal consistently 817
 showed multiple bands and shoulders between 2.25 818
 and 2.3 μm, plus narrow bands at 2.1 μm, attributable 819
 to OH in chlorite, and a band at 1.54 μm attributable to 820
 OH in epidote (Fig. 6C). Sheet silicates containing 821
 Al–OH were identified by band-shape analysis of the 822
 region between 2.2 and 2.34 μm. Rock samples 823
 containing muscovite yielded reflectance spectra with 824
 narrow features at approximately 2.2 and 2.34 μm. 825
 Narrow shoulderless features at 2.2 μm are character- 826
 istic of muscovite. Kaolinite was identified on the 827
 basis of the characteristic double-absorption feature in 828
 the 2.16–2.2-μm region (Fig. 6B). Slight symmetry 829
 differences in the 2.2-μm absorption feature attributed 830
 to muscovite indicated slightly different spectral 831
 behavior of the Al–OH bond in muscovite mapped as 832
 “muscovite 1” and “muscovite 2” in Fig. 7. 833
 Analysis of laboratory reflectance spectra of well- 834
 characterized rock samples and their corresponding 835
 field reflectance spectra served as a guide for the 836
 interpretation of field reflectance spectra and the 837
 application of the apparent continuum removal and 838
 band-shape least-squares algorithm. 839

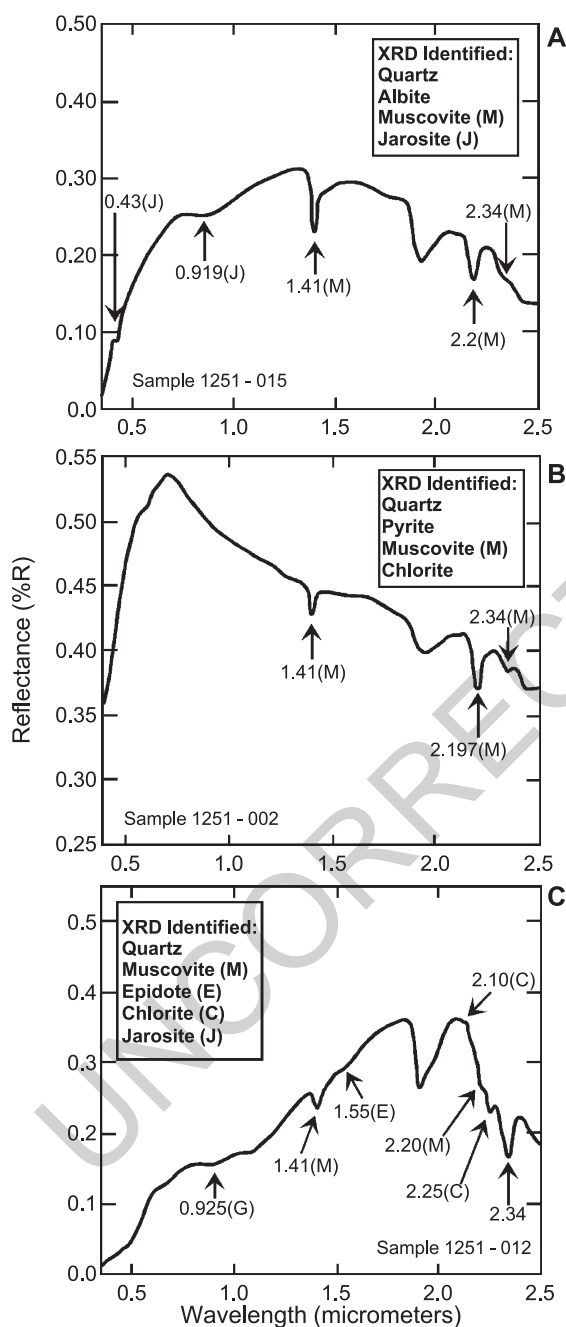


Fig. 6. Laboratory reflectance spectra of selected rock specimens collected at the Penn Minesite. The inserts list the minerals identified by XRD, with each accompanied by the letter used to identify its corresponding signature feature in the spectra. Arrows indicate spectral absorption features used to identify minerals from the laboratory spectra and the centers of those features after a continuum has been removed. (A) Oxidized muscovite-quartz schist. (B) Unoxidized pyritic muscovite-quartz schist. (C) Greenstone; G=goethite.

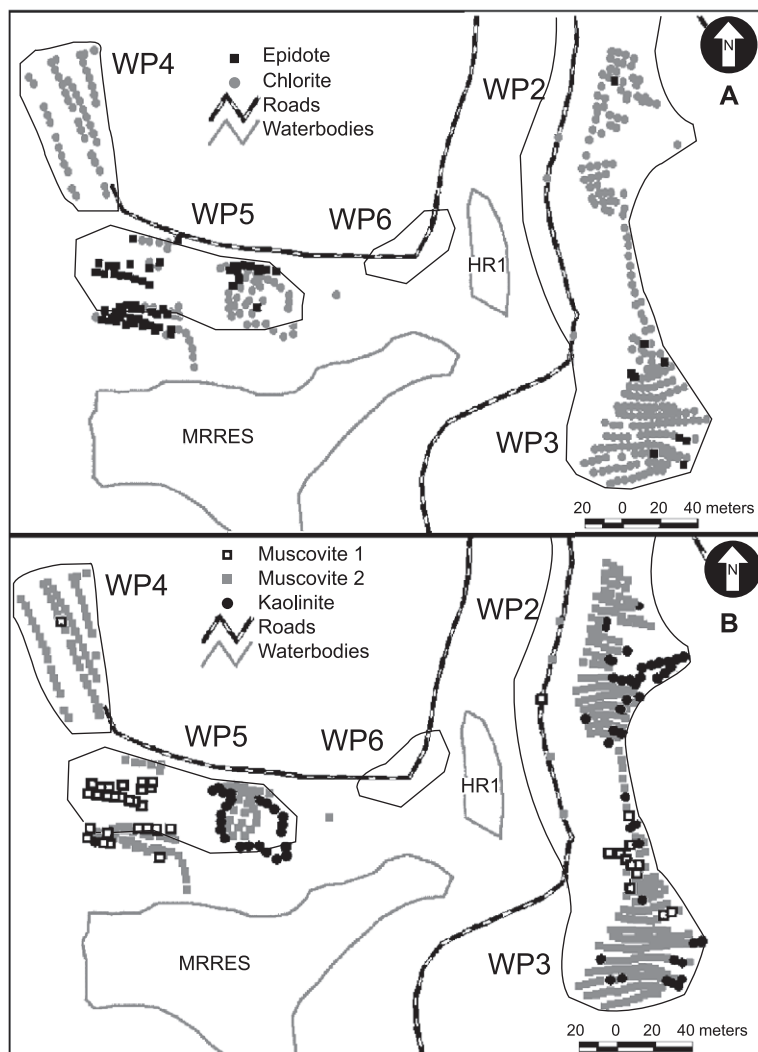


Fig. 7. Distribution of minerals on mining waste piles at the Penn Mine site as derived from reflectance spectra acquired over discrete localities. WP1 through WP6 are waste piles 1 through 6 (no spectra were acquired over WP6). HR1: Hinckley Run pond 1; MRRES: Mine Run reservoir. (A) Distribution of epidote and chlorite. (B) Distribution of muscovite and kaolinite.

840 5.2. Mineral zones discerned and environmental 841 implications

842 Interpretation of the field spectra was used to create
843 the mineral maps depicted in Figs. 7 and 8. These
844 maps identified at least one area of low potential
845 AMD generation, in a wide area of disturbed green-
846 stone bedrock. Greenstones at the Penn Mine are
847 sulfide-poor and do not present a high risk of AMD
848 generation. Areas were mapped as greenstone if the
849 field spectra showed the presence of epidote and

850 chlorite, the former of which occurred only in 850
851 unmineralized greenstone, whereas the latter is 851
852 present in both greenstone and in mineralized mine 852
853 waste. 853

854 Among the Al phyllosilicates, muscovite and 854
855 kaolinite were predominant in the waste-rock piles. 855
856 Reactions of muscovite with acidic solutions pro- 856
857 duced by sulfide oxidation can result in the 857
858 production of kaolinite and other clay minerals 858
859 and in the release of K necessary for jarosite 859
860 precipitation (Ritchie, 1994); detectable areas of 860

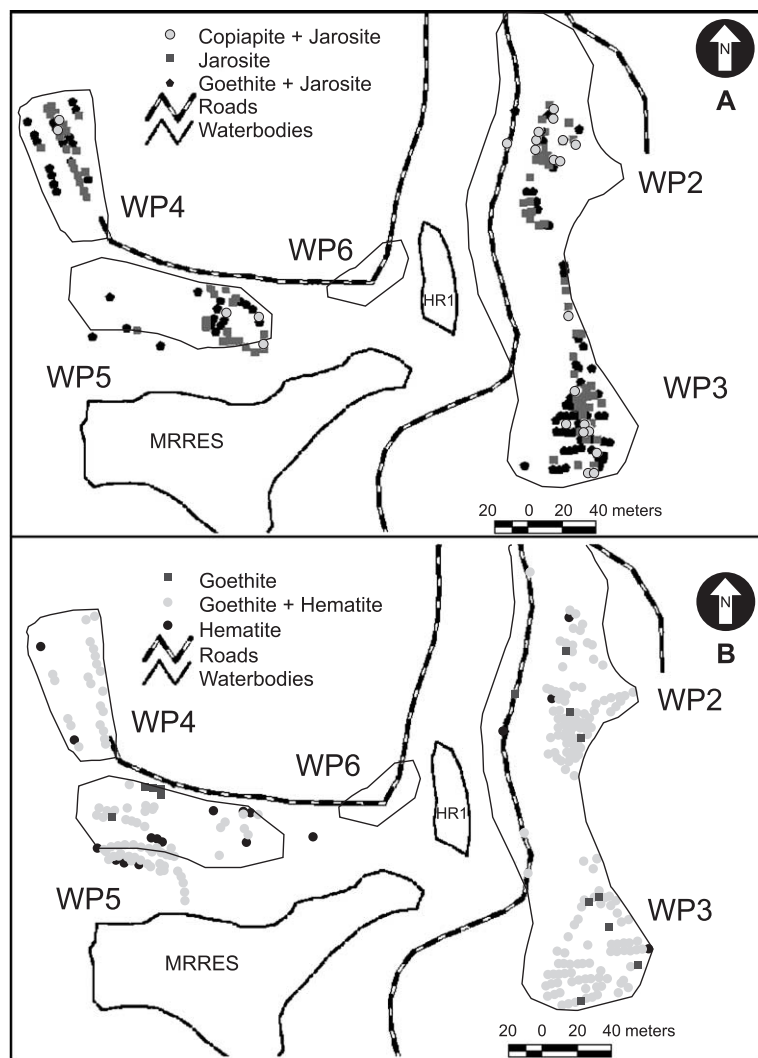


Fig. 8. Distribution of secondary Fe minerals at the Penn Mine. Sites are labeled as in Fig. 7 (no spectra were acquired over WP6). (A) Distribution of copiapite and jarosite, plus mixtures of jarosite and goethite, indicative of low-pH environments. (B) Distribution of goethite and hematite, indicative of higher pH environments.

861 kaolinite were expected where sulfide oxidation was
 862 thought to be intense enough to produce significant
 863 muscovite dissolution, but such areas were not
 864 detected. Kaolinite was mapped in waste pile 2
 865 and in the southeastern corner of waste pile 3, in
 866 areas known to have a thin soil cover and wherein
 867 kaolinite might have been the product of weathering
 868 of rock unrelated to AMD (Fig. 7B). Other kaolinite
 869 areas in waste piles 5, 2 and 3 might have been
 870 related either to muscovite dissolution or to hydro-

thermal alteration such as reported by Peterson 871
 (1985). 872

Fig. 8A and B indicate the four types of secondary 873
 Fe minerals mapped at the Penn Mine. Iron sulfates 874
 such as copiapite and jarosite that typically accumu- 875
 late in low-pH environments (pH 0.8–3.5; Nordstrom 876
 et al., 1978) that were caused by rapid erosion and 877
 oxidation of sulfides, as well as evaporation of ponded 878
 AMD, near the center and topographically higher 879
 areas of the waste-rock piles. Surrounding the 880

881 copiapite-jarosite centers are jarosite and mixtures of
882 jarosite+goethite, which suggest higher pH areas
883 where pore and surface water was less acidified by
884 the AMD process. Pure goethite was mapped around
885 jarosite, in areas typically near the outer limit of the
886 area surveyed, indicating even higher pH farther away
887 from oxidation centers. Rare occurrences of higher pH
888 minerals near low-pH ones are attributed to irregular
889 microtopography on the waste piles, which promoted
890 fast erosion of material in higher areas and the
891 ponding of surface waters at lower elevations. Given
892 the irregular surface on top of waste piles at the time
893 of the survey, the distribution of these minerals could
894 have been better resolved using a sampling interval
895 smaller than 5 m.

896 In terms of AMD generation, the accumulation of
897 copiapite and jarosite point to more acidic conditions
898 than elsewhere on the dump surface, and indicate the
899 source areas of AMD. The occurrence of low-pH
900 minerals indicates a relatively immature waste-rock
901 pile that had a high potential for AMD release. The
902 accumulation of copiapite 2 weeks after a series of
903 storms suggests that an even larger and more
904 significant buildup of soluble Fe sulfates likely
905 occurred and the end of each dry season. Given the
906 solubility of minerals such as copiapite, the contribu-
907 tion of metals and sulfate to Camanche Reservoir
908 from soluble sulfate salts was not insignificant. The
909 occurrence of copiapite in high and unsheltered areas
910 of the waste-rock piles, rather than in places sheltered
911 from the rain, leads the authors to believe that
912 copiapite observed during this study precipitated from
913 evaporating water during the 2-week dry period.

914 Goethite accumulation is distal to the active
915 oxidation centers, indicating an increase in the pH
916 of the aqueous effluents as they move away from the
917 unsaturated waste piles (Swayze et al., 2000).
918 Hematite is abundant only where the lithology is
919 dominated by greenstones, in areas with iron and steel
920 infrastructure waste, and in areas near non-acidic
921 standing water.

922 6. Applicability of method

923 Use of digital mapping methods at the Penn
924 Minesite has the advantages of mapping efficiency
925 and adaptability, which are crucial factors if the large

926 number of abandoned mines still to be characterized is
927 considered. During the survey, all information was
928 available to the mapping team immediately. Thus, the
929 survey could be modified quickly, control points
930 could be added or discontinued as needed, and
931 informed decisions could be made about how best to
932 use the limited time, as storms threatened to shorten
933 the field work period.

934 By using a field spectrometer close to the target
935 area on the ground, we believe noise introduced by
936 atmospheric water is minimized in comparison to
937 high-altitude remote-sensing platforms. Over most
938 areas at sea level, water molecules strongly absorb
939 light at about 1.4 and 1.9 μm , with other minor
940 regions of interference at 0.69, 0.76, 0.94 and 1.13
941 μm (Vane et al., 1993). During the survey of the Penn
942 Mine, light in the 1.4- μm region was not completely
943 absorbed by atmospheric water, and interference at
944 0.9 μm and other regions was minimal because of the
945 low humidity conditions, the short distance between
946 the target and probe, and frequent optimization of the
947 instrument with a white reflectance standard.
948 Reduced water-related noise in ground-based reflectance
949 spectroscopy provides a definite advantage over
950 high-altitude remote-sensing platforms, for which
951 data processing and noise reduction involve the use
952 of probabilistic models that have little to do with
953 actual atmospheric conditions on the day of data
954 acquisition.

955 The use of a non-contact reflectance spectrometer
956 facilitated the acquisition of reflectance spectra of the
957 inaccessible steep sides of waste piles by allowing
958 mineral identification of surfaces at a distance from
959 the instrument. The use of a non-contact spectrometer
960 also facilitated the future use of the ground-based data
961 for ground-truthing of high-altitude hyperspectral
962 data; the combination of airborne (or high altitude)
963 with detailed ground-based hyperspectral data is
964 commonly the optimal route for highly detailed
965 characterization of complex environments such as
966 abandoned mines.

967 Information in mineral maps (Figs. 7 and 8) that
968 describe the surface weathering and acid-producing
969 conditions at each waste pile are useful not only to
970 those interested in the mineralogy of AMD environ-
971 ments, but also to governmental or private agencies in
972 charge of remediating (or preventing) environmentally
973 problematic sites. Swayze et al. (2000) showed the

974 cost-effectiveness of obtaining hyperspectral remote-
 975 sensing data over the California Gulch Superfund site
 976 at Leadville, CO, as a guide to remediation efforts.
 977 Mineral maps such as Fig. 8A can also be useful to
 978 estimate the impact of the dissolution of soluble Fe
 979 sulfates to surface water bodies or stormwater
 980 management and treatment systems.

981 Mapping of mineral zones at the Penn Mine based
 982 on interpolation between survey points revealed an
 983 area of 1070 m² on the waste-rock piles that was
 984 overlain by a mixture of jarosite and copiapite. Using
 985 conservative assumptions that the Fe-sulfate minerals
 986 occur within the top 0.1 cm yields a Fe sulfate
 987 volume of 1070 cm³. If copiapite, of density 2.1 g
 988 cm⁻³ (Gaines et al., 1997), constituted as little as
 989 10% of this volume, an estimated mass of 2247 g of
 990 copiapite existed on the surface of the waste-rock
 991 piles. Dissolution by rain of those 2247 g of
 992 copiapite would result in a sudden release of
 993 approximately 1035 g of sulfate to surface water in
 994 addition to that contributed by other sources. Similar
 995 calculations can be carried out for metals present in
 996 the structure of Fe sulfates such as copiapite (Fe, Cu,
 997 Zn, Pb, Al, Mn, Mg and K) in order to estimate the
 998 mass of metals to surface water after dissolution. Use
 999 of mineral maps constructed from data acquired
 1000 before the start of the rain season could anticipate
 1001 and potentially help prevent bigger releases of sulfate
 1002 and metals.

10037. Conclusions

1004 The use of an integrated digital mapping system
 1005 proved to be an efficient way to map mine wastes
 1006 accurately and in detail at the relatively small,
 1007 abandoned Penn Mine. Most of the surface oxidation
 1008 and acid-production activity was focused in waste
 1009 piles 2, 3, 4 and the eastern part of pile 5, whereas
 1010 the western part of waste pile 6 has mostly
 1011 unmineralized greenstones and secondary minerals
 1012 that precipitate at a higher pH. Observations of this
 1013 type enable the translation of the mineral maps into
 1014 remediation-priority maps, in which the piles that
 1015 host high concentrations of low-pH minerals are
 1016 interpreted to have the most potential to release
 1017 AMD and thus could be scheduled for removal at an
 1018 optimal stage of the remediation. Mineral maps

1019 showing the distribution of soluble metal-bearing
 1020 sulfate salts are also useful in the design and
 1021 placement of stormwater diversions, berms and
 1022 neutralization basins.

1023 Results such as those derived in this study can be
 1024 used to aid both the interpretation and the
 1025 ground-truthing of remote-sensing data, thereby
 1026 enlarging the area that can be mapped and increasing
 1027 the accuracy of delineation of known and unidentified
 1028 AMD-generating sites. The advantages of using a
 1029 digital, portable mapping system in combination with
 1030 a portable spectrometer with DGPS and supporting
 1031 laser rangefinder were evident in light of the con-
 1032 strained working environment in which time was the
 1033 scarcest resource. Maps derived from the low-altitude,
 1034 low-atmospheric-noise, and closely sampled spectra
 1035 yielded abundant information regarding the distribu-
 1036 tion of AMD-related minerals on the surface of waste-
 1037 rock piles at the Penn Mine. The mineral maps offer a
 1038 detailed and complete view of the mineral distribution
 1039 on the surface of the waste-rock piles and surrounding
 1040 areas, thus offering a mine-wide view of the processes
 1041 at play in the generation of AMD.

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 1063 [PD]

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