Sulfate Mineral Paragenesis in Pennsylvanian Rocks and The Occurrence of Slavikite in Nebraska

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SULFATE MINERAL PARAGENESIS IN PENNSYLVANIAN ROCKS AND THE OCCURRENCE OF SLAVIKITE IN NEBRASKA

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ABSTRACT—The acid weathering of pyrite-bearing Pennsylvanian clastic sedimentary rocks in southeastern Nebraska locally produces the secondary sulfate minerals alunogen, copiapite, epsomite, felsobanyaite/basaluminite, gypsum, halotrichite, jarosite, rozenite, and slavikite. Of these mineral occurrences, four are first-time discoveries in the state or the surrounding region. Slavikite (NaMg2Fe3(SO4)3(OH)6·33H2O), which has been reported only once before in North America and from a handful of sites in Europe and South America, was found in abundance at an outcrop at Brownville, NE. The pH values in 1:1 solutions of deionized water of the studied minerals, excluding epsomite, range from 1.94 to 4.82. Therefore, segregations of secondary minerals in themselves are significant microenvironmental reservoirs of acid that can be mobilized during precipitation events. Because of its role in liberating and concentrating ions such as Al³⁺, Fe²⁺, Fe³⁺, Mg²⁺, and SO₄²⁻, acid rock weathering should be considered in local to regional assessments of surface-water and groundwater chemistry. Observations also suggest that rock weathering by the growth of sulfate salts is a potential factor in local hillslope development, one that has not previously been considered in the study area.

Key Words: hydrated sulfate minerals, Nebraska, pyrite oxidation, slavikite

INTRODUCTION

The oxidation and acid weathering of naturally occurring metal sulfides, especially pyrite (FeS₂), play important roles in geochemical cycling, soil development, and the evolution of surface-water and groundwater chemistry (e.g., Van Breemen 1973, 1982; Jambor et al. 2000; Keith et al. 2001; Schippers 2004; Knoeller et al. 2004). Near-surface acid weathering of sulfide minerals, whether natural or anthropogenic (iron-ore and coal mines, tailings piles, etc.), assumes several different manifestations and produces a large variety of sulfate salts in the forms of surface efflorescences, crusts, and massive alteration zones (e.g., Bandy 1938; Michel and Van Everdingen 1987; Jakobsen...
The specific occurrences of these various mineral species depend on climatic or microclimatic conditions, time, pH, intensity of oxidation, and other factors (Jambor et al. 2000; Keith et al. 2001; Jerz and Rimstidt 2003; Buckby et al. 2003). Almost all of these minerals contain Fe$^{2+}$, Fe$^{3+}$, or a combination thereof, or Al. Some also incorporate K, Na, or Mg. As a general rule, salts produced by acid weathering are hydrated and highly soluble in water; most of them persist in large volumes only where climatic or microclimatic conditions limit or prohibit dissolution by rainfall or percolating meteoric waters (e.g., Bandy 1938; Jakobsen 1989; Jambor et al. 2000).

Until very recently (Joeckel et al. 2005), acid rock weathering in Nebraska had not been described. Moreover, the phenomenon has been described only sparingly from surrounding states in the American Midwest (e.g., Tien 1968; Cody and Biggs 1973; Blevins 1989; Davis and Webb 2002), although it should be a common phenomenon under existing geologic conditions. Our recent observations, detailed herein, as well as those of Joeckel et al. (2005), indicate that acid-weathering processes occur or have occurred at different temporal and spatial scales in many places in southeastern Nebraska and, by inference, in the surrounding region as well. At the largest scale of observation, there are regional oxidation fronts resulting from past and present meteoric weathering at the upper contacts of widespread, pyrite-bearing Cretaceous sediments such as the Dakota Formation, Carlile Shale, and Pierre Shale (see Condra and Reed 1959 for regional stratigraphy). Likewise, the widespread and conspicuous oxidation of Pliocene-Pleistocene (~2.5 Ma–600 ka) glacial tills in the eastern quarter of the state doubtless involves the weathering of finely disseminated pyrite derived from eroded sedimentary rocks to the north. At much smaller scales, there are extant microenvironments of acid weathering in quarries, natural outcrops, and road cuts in both Pennsylvanian and Cretaceous strata, some of which change on short-term timescales, depending on rainfall and atmospheric humidity (e.g., Joeckel et al. 2005). These microenvironments constitute a new realm of investigation in the study of regional mineralogy and mineral paragenesis.

The purposes of this paper are to describe some unique environments of pyrite oxidation, acid rock weathering, and new mineral formation in Nebraska, to document the occurrence of multiple mineral species never before described in the state or region (including slavikite, a rarely documented hydrated Mg-Fe hydroxide sulfate), and to comment on the larger significance of these phenomena.

**MATERIALS AND METHODS**

Mineral efflorescences and crusts from weathering rock surfaces were collected in April, July, and September from four sites (Fig. 1, Table 1) and were stored in sealed plastic bags at room temperature. Subsamples were processed and analyzed by x-ray diffraction (XRD) within a month after collection and within two hours after removal from storage bags. Prior to XRD analysis, these subsamples were hand-picked under a binocular microscope to remove host-rock debris and were powdered using a ceramic mortar; manual grinding was limited to less than 1 minute to minimize its peak-broadening effect on x-ray diffractograms. To obtain randomly oriented powder mounts, each of the hand-picked, ground subsamples was screened to minus 63 μm, and the oversize fraction was rejected. A Rigaku Mini-Flex™ X-ray diffractometer using CuKα radiation.
TABLE 1
LOCATION OF STUDY SITES IN NEBRASKA

<table>
<thead>
<tr>
<th>Study site</th>
<th>Legal description</th>
<th>Latitude/longitude</th>
<th>Stratigraphic unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NE 1/4 NE 1/4 NW 1/4 SE 1/4 Section 18, T. 5 N., R. 16 E.</td>
<td>40° 10' 34.0&quot;N 96° 35' 5.8&quot;W</td>
<td>Indian Cave Sandstone</td>
</tr>
<tr>
<td>2</td>
<td>S 1/4 NW 1/4 SW 1/4 Section 34, T. 3 N., R. 12 E.</td>
<td>40° 24' 2.5&quot;N 95° 39' 16.3&quot;W</td>
<td>White Cloud Sandstone (Scranton Formation)</td>
</tr>
<tr>
<td>3</td>
<td>NE 1/4 SE 1/4 SE 1/4 SW 1/4 Section 10, T. 8 N., R. 14 E.</td>
<td>40° 40' 8.5&quot;N 95° 49' 51.5&quot;W</td>
<td>Willard Formation</td>
</tr>
<tr>
<td>4</td>
<td>SW 1/4 NE 1/4 NW 1/4 NE 1/4 Section 23, T. 1 N., R. 12 E.</td>
<td>40° 2' 35.0&quot;N 96° 2' 9.7&quot;W</td>
<td>Nodaway Coal in Severy Shale</td>
</tr>
</tbody>
</table>

Notes: Refer to Condra and Reed (1959) and Fischbein (2005) for stratigraphy.

T = township and R = range

at 30 kV and 15 mA was employed for XRD analysis. Scans were made from 2° to 90° 2θ at a step time of 1° 2θ/minute. Mineral identification was facilitated by the search-match function in JADE™ release 7.1.2 software from Materials Data, Inc. (Livermore, CA), which uses the Powder Diffraction Files or PDFs (International Centre for Diffraction Data 2001) as references. Repeated onscreen qualitative comparisons of diffractograms and match lines were employed in addition to peak-matching software.

The pH values of 1:1 suspensions of powdered crusts in deionized water were measured with a Thermo Orion 550A™ pH meter and a combination pH electrode. Colors of mineral crusts and sediments were estimated using Munsell Soil Color Charts (Munsell Color 1998). Infrared spectroscopy was carried out with a Thermo Avatar 380™ Fourier transform infrared spectrometer; data were acquired with 16 scans/sample at a resolution of 4 cm⁻¹. Samples were made into pellets with CsI (instead of KBr) to allow any peaks between 225 and 4,000 cm⁻¹ to be seen. Scanning electron microscopy (SEM) was carried out with a Hitachi S-3000N™ electron microscope. An Oxford 7021™ EDX (energy-dispersion x-ray) analyzer was used to determine elemental spectra for selected samples.

RESULTS

Site Characteristics

Site 1 (Fig. 1; Table 1), at Brownville, NE, is the primary study site because surficial accumulations of secondary minerals are best developed and most prominent there, and because minerals never described before from Nebraska were found there at an early stage in our investigation. Sites 2, 3, and 4 (Fig. 1; Table 1) were investigated primarily for comparison with site 1. All the study sites are outcrops of Upper Pennsylvanian sandstones, tidal rhythmites (thinly interlaminated sandstone and shale deposited in estuaries or similar settings under tidal influence), shales, or coal (Table 1). At two of the sites, as at the sites described by Joeckel et al. (2005), efflorescences of different colors and mineralogical compositions are spatially segregated. This kind of segregation is not unusual in acid-weathering settings (e.g., Bayless and Olyphant 1993) and reflects the existence of localized physical and chemical controls on mineral precipitation.

Site 1 is an outcrop of sandstone-shale rhythmites at the steep base of a wooded bluff along the Missouri River, under a slight overhang. It is the only one of the four study sites where fresh, macroscopic pyrite can be observed on the outcrop face. Sandstones at the site are locally cemented by carbonate. Because the outcrop is east-facing, it is partly protected from westerly winds and, to some degree, from frontal weather systems associated with the most heavy rainfall in eastern Nebraska. The comparative persistence of surface salts at the site differs from that at fully exposed acid-weathering sites (e.g., Joeckel et al. 2005), at which surface salts are regularly dissolved by rainfall events and reprecipitate during intervals of dry weather. At site 1, surface efflorescences and crusts form in horizontally elongate, partly intergrown patches as much as 150 mm in width, on sandstone-shale rhythmites. Whitish and yellowish efflorescences originally form directly on the exposed surfaces of elongate, bedding-parallel pyrite nodules 20-100 mm in length. Pustulose ("popcorn-like") white (2.5Y 8/1) to pale yellow (2.5Y 8/2) crusts have formed atop shaler rhythmite intervals. These crusts are markedly "puffed" above the level of the outcrop face. Soft, powdery, white efflores-
Figure 2. (A) Northern part of exposure at site 1 (20 cm scale), showing (1) white crusts of halotrichite, (2) yellow copiapite or slavikite-dominated crusts, and (3) pile of sloughed rock debris weathered by salts, which seasonally contains halotrichite and epsomite efflorescences. (B) Weathering pyrite nodule at site 1. Such mineral efflorescences around pyrite nodules may be halotrichite or rozenite, depending on the season. (C) Yellow copiapite crusts at site 1.
ences also form episodically, mostly on and immediately around pyrite nodules and carbonate-cemented sandstone lenses, especially where the efflorescences are protected by small overhangs on the outcrop face. Subsequent analyses demonstrate that these efflorescences, although similar in color and appearance, consist of different minerals at different times of the year. Distinct, pale yellow (2.5Y 8/4) to yellow (2.5Y 7/6 and 8/6) crusts form in close proximity to the whitish crusts and efflorescences, but in many cases they form at separate stratigraphic intervals.

The weathering of bedrock by surficial salt growth is strongly evident at the site (Fig. 2), where spalled sheets of weathered material collect in a pile at the foot of the outcrop. The weathering of soft bedrock by the salt precipitation appears to be a self-reinforcing phenomenon in that the spalling of surficially weathered rock creates indentations that provide yet further protection for the subsequent growth of new sulfate-mineral crusts. In the driest weather periods during our study, the outcrop at site 1 was nearly dry, even though salts were present. Therefore, any discharge of porewater through the outcrop face at site 1 must be minimal, very diffuse, and episodic at best, rather than persistent. Atmospheric moisture appears to exert a larger influence on weathering at the site, making it differ from the acid-rock-weathering site in Nebraska described previously by Joeckel et al. (2005).

Site 2 (Fig. 1; Table 1) is an outcrop with a slight overhang, concealed by thick woods at the base of a south-facing hill. Site 3, an east-facing bluff on the Missouri River (Fig. 1; Table 1), is much more exposed to the elements than site 1. Rare surface salts, either pale yellow (2.5Y 8/2) to bright white or yellow (2.5Y 7/8 and 8/6), occur as moist efflorescences whose slightly pasty consistency is the result of their content of free water. These efflorescences appear on tidal rhythmites under very small overhangs produced by thin, resistant beds. Site 4 (Fig. 1; Table 1) is a south-facing, unprotected, weathered natural exposure along a stream bank, where soft nodules of pale yellow (2.5Y 8/4), earthy mineral material have formed within coal and an underlying shale. Strata at this site, although by no means intensely weathered, are nonetheless the most obviously weathered, in terms of oxidation features and rock character, of all four sites.

Minerology

Several minerals can be identified in the samples through XRD (Table 2). Felsöbányaité/basaluminite, copiapite, epsomite, gypsum, halotrichite, jarosite, rozenite, and slavikite (Tables 2 and 3) occur in crusts, efflorescences, and small nodules on and in weathering sedimentary rocks at the study sites. Felsöbányaité and basaluminite were first described occurrence from Nebraska by Pabian (1993) or by Joeckel et al. (2005).

Whitish cauliflower-like crusts from site 1 actually have a discernable horizontal microzonation consisting of a silky-appearing underlayer of long (2-7 mm), hairlike, radiating crystals, and an outer crust of shorter, bundled, subhorizontally oriented crystals tipped with subhedral masses of unknown alternation products (Fig. 3A-C). The underlayer of fine crystals in the crust has the distinctive morphology of halotrichite-group minerals (Fig. 3A-C), and the corresponding diffractogram (Fig. 4A) verifies that identification. The XRD patterns of halotrichite and pickeringite, another halotrichite-group mineral (Table 2), are difficult to distinguish, however, and the two minerals form a solid solution series with respect to Mg2+ (pickeringite) and Fe2+ (halotrichite). Intermediate compositions are indeed possible (Jambor et al. 2000), and EDX spectra (Fig. 3D) of samples from site 1 indicate that the halotrichite identified by XRD is in fact "magnesian" or is comparatively rich in Mg (cf. Brant and Foster 1959), but the Mg2+ content is too low for pickeringite. The outer

### Table 2

MINERAL SPECIES DISCUSSED IN DETAIL IN THIS PAPER

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alunogen*</td>
<td>Al2(SO4)3·17H2O</td>
</tr>
<tr>
<td>Copiapite*</td>
<td>(Fe,Mg)Fe4(SO4)6(OH)2·20H2O</td>
</tr>
<tr>
<td>Epsomite†</td>
<td>MgSO4·7H2O</td>
</tr>
<tr>
<td>Gypsum*</td>
<td>CaSO4·2H2O</td>
</tr>
<tr>
<td>Halotrichite*</td>
<td>FeAl2(SO4)4·22H2O</td>
</tr>
<tr>
<td>Jarosite*</td>
<td>KFe2(SO4)2(OH)6</td>
</tr>
<tr>
<td>Rozenite†</td>
<td>FeSO4·4H2O</td>
</tr>
<tr>
<td>Slavikite†</td>
<td>NaMg2Fe3(SO4)2(OH)6·33H2O</td>
</tr>
</tbody>
</table>

* Previously described from Nebraska by Pabian (1993) or by Joeckel et al. (2005).
† First described occurrence from Nebraska.
TABLE 3
CHARACTERISTICS OF SAMPLED EFFLORESCENCES AND CRUSTS

<table>
<thead>
<tr>
<th>Site</th>
<th>Sample</th>
<th>Color*</th>
<th>Mineralogy</th>
<th>Date collected</th>
<th>pH†</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ICSS white</td>
<td>2.5Y 8/1</td>
<td>Halotrichite</td>
<td>April 2006</td>
<td>3.07</td>
</tr>
<tr>
<td>1</td>
<td>ICSS yellow</td>
<td>2.5Y 7/6</td>
<td>Slavikite, copiapite</td>
<td>April 2006</td>
<td>3.60</td>
</tr>
<tr>
<td>1</td>
<td>ICSS 706-yellow1</td>
<td>2.5Y 8/4</td>
<td>Copiapite</td>
<td>July 2006</td>
<td>1.82</td>
</tr>
<tr>
<td>1</td>
<td>ICSS 706-white1</td>
<td>2.5Y 8/1</td>
<td>Rozenite, pyrite</td>
<td>July 2006</td>
<td>2.27</td>
</tr>
<tr>
<td>1</td>
<td>ICSS 706-white2</td>
<td>2.5Y 8/1</td>
<td>Halotrichite, pyrite</td>
<td>July 2006</td>
<td>1.90</td>
</tr>
<tr>
<td>1</td>
<td>ICSS 706-white4</td>
<td>2.5Y 8/1</td>
<td>Halotrichite</td>
<td>July 2006</td>
<td>2.65</td>
</tr>
<tr>
<td>1</td>
<td>ICSS 706-yellow2</td>
<td>2.5Y 7/6</td>
<td>Copiapite</td>
<td>July 2006</td>
<td>1.95</td>
</tr>
<tr>
<td>1</td>
<td>ICSS 706-yellow3</td>
<td>5Y 8/6</td>
<td>Copiapite</td>
<td>July 2006</td>
<td>1.94</td>
</tr>
<tr>
<td>1</td>
<td>ICSS 906-yellow1</td>
<td>2.5Y 7/6</td>
<td>Slavikite, alunogen</td>
<td>September 2006</td>
<td>2.55</td>
</tr>
<tr>
<td>1</td>
<td>ICSS 906-white1</td>
<td>~2.5Y 8/1</td>
<td>Episomite</td>
<td>September 2006</td>
<td>7.13</td>
</tr>
<tr>
<td>2</td>
<td>TRE-1</td>
<td>10YR 8/1</td>
<td>Halotrichite</td>
<td>July 2006</td>
<td>3.02</td>
</tr>
<tr>
<td>3</td>
<td>NCB-1</td>
<td>2.5Y 8/6</td>
<td>Copiapite</td>
<td>August 2006</td>
<td>2.12</td>
</tr>
<tr>
<td>3</td>
<td>NCB-2</td>
<td>2.5Y 7/2</td>
<td>Copiapite</td>
<td>August 2006</td>
<td>1.99</td>
</tr>
<tr>
<td>3</td>
<td>NCB-3</td>
<td>2.5Y 8/2</td>
<td>Halotrichite</td>
<td>August 2006</td>
<td>2.69</td>
</tr>
<tr>
<td>3</td>
<td>NCB-4</td>
<td>~2.5Y 8/1</td>
<td>Halotrichite</td>
<td>August 2006</td>
<td>2.20</td>
</tr>
<tr>
<td>4</td>
<td>FF-1</td>
<td>2.5Y 8/4</td>
<td>Jarosite</td>
<td>August 2006</td>
<td>4.82</td>
</tr>
</tbody>
</table>

† Values for pH represent 1:1 solutions in deionized water.

crust atop the fine-crustal underlayer appears similar to the bundled halotrichite crystals illustrated by Coskren and Lauf (2000) and also produces a diffractogram characteristic of halotrichite. The terminal subhedral masses on these crystal bundles, however, may consist of the minerals bilinite or römerite, hydrated iron sulfates that sometimes occur with halotrichite in pyrite-weathering environments. Halotrichite, bilinite, and römerite have overlapping XRD peaks (see International Centre for Diffraction Data 2001), and differentiating among them in a mixed sample by XRD is impossible.

Rozenite appeared in white efflorescences associated with weathering pyrite nodules exposed in the outcrop face in samples taken during July from site 1 (Fig. 4B). The diffractogram of rozenite is sufficiently different from other possible co-occurring hydrated sulfate salts that its identification is straightforward. Also at site 1, yellow slavikite-copiapite-alunogen crusts consistently form on the outcrop face, and yellow copiapite forms directly on or around weathering pyrite. Slavikite (Table 2) can be differentiated from copiapite through XRD analysis (Fig. 5). Slavikite yields, among others, intense X-ray reflections corresponding to approximate d values of 11.7, 10.1, 5.8, 4.2, 2.9, and 2.7 Å. Copiapite and magnesiocopiapite, in comparison, yield intense reflections corresponding to approximately 18-18.5 Å (Fig. 5A). Slavikite occurs as fine (4-20 μm) crystallites (Fig. 6A, B) similar to those shown in SEM photographs by Hammarstrom et al. (2003). EDX spectra confirm the presence of Mg in these crystallites (Fig. 7A).

Copiapite was the dominant mineral co-occurring with slavikite in April (Fig 5A) and July, whereas alunogen was more common in September (Fig. 5B). This pattern may reflect the concentration of Al3+ in evaporating porewaters in the late summer. Copiapite also grows directly on pyrite at site 1 (Fig. 6C).

Felsóbánaiite/basaluminite (Fig. 8A) occurs at site 1 as a 2-mm-thick seam of white, earthy material above a 3-mm-thick seam of coarsely crystalline gypsum under a deep overhang of fine, micaceous, pyritic sandstone. The overhang provides the best protection from the elements of any microenvironment at the site. Epsomite (Fig. 8B) was found in September at site 1 as a dry, powdery efflorescence at spots protected from rainfall by slight overhangs on the outcrop face. The mineral occurred alone around small lenses of calcite-cemented, pyrite-bearing sandstone and with halotrichite in the loose pile of sloughed rock at the base of the outcrop. Immediately south of the study site, epsomite was also found within loose, fluffy soil at the base of an outcrop that has been covered by a large corrugated-steel shelter to minimize mass wasting along the banks of the Missouri River.

At site 2, sparse, thin, white (10YR 8/1) surface crusts consist of halotrichite, although macroscopic halotrichite
crystals are not visible, as they are at site 1. Crusts at site 2 form directly on the outcrop face, but only in sheltered indentations. Halotrichite (whitish), again without macroscopic crystals, and copiapite (yellowish) appear in moist efflorescences at site 3 (Fig. 9), the latter mineral growing directly on pyrite in some cases. Pale yellow (2.5Y 8/4) nodules in coal and underlying shale at site 4 are jarosite (Fig. 6D).

**Acidity**

Excluding epsomite from site 1, which produces a nearly neutral pH, ground samples of the mineral efflorescences, crusts, and nodules all produce acidic pH values in 1:1 deionized-water solutions (Table 3). These acidic pH values range from 1.90 to 4.82, but almost all the values register at less than pH 2.70. As expected, jarosite produced the highest pH of all samples except those of epsomite (cf. Van Breemen 1973, 1982). Samples dominated by copiapite, or consisting of copiapite alone, produced the lowest pH values.

**DISCUSSION**

Felsöbányaita/basaluminite, epsomite, rozenite, and slavikite have never before been described from Nebraska. Slavikite, moreover, has been described from only one other locality in North America (Flohr et al. 1995; Lauf 1997; Coskren and Lauf 2000; Hammarstrom et al. 2003). Cody and Biggs (1973) found rozenite on Pennsylvanian sand-
Figure 4. (A) X-ray diffraction pattern of white halotrichite (hal) from site 1. (B) X-ray diffraction pattern of white halotrichite (hal) from site 1.

July 2006
pyrite (pyr)
Rosinite (roz)
ICSS706-white-1

April 2006
halotrichite (hal)
ICSS-1-white
Figure 5. (A) X-ray diffractogram of yellowish slavikite-dominated crust collected in April 2006 at site 1. (B) X-ray diffractogram of yellowish slavikite-dominated crust collected in September at site 1 (see Figs. 6A, B; 7).
Figure 6. (A) SEM of (1) slavikite and (2) probable copiapite crystallites in yellowish crust collected in April 2006 from site 1. (B) SEM image of slavikite crystallites collected in September 2006. (C) Copiapite crystallites (between arrows) growing on oxidizing pyrite at site 1. (D) Jarosite crystallites from a small nodule in shale below coal at site 4 (see Fig. 9C).

stones in north-central Iowa, more than 300 km northeast of the study area, and Kopsick (1978) produced rozenite by laboratory dehydration of melanterite in Kansas coal spoil, but she did not note its occurrence in the field. Tien (1968) found basaluminite in southeastern Kansas.

Halotrichite and jarosite were previously reported from Nebraska by Pabian (1993), Joeckel et al. (2005) described alunogen- and copiapite-bearing crusts resulting from the weathering of pyrite in the Cretaceous Dakota Formation in Jefferson County, NE.

Halotrichite is a common alteration product in pyritic rocks worldwide, and after jarosite, it may indeed be the most widespread mineral in acid-weathering environments in Nebraska. Halotrichite can form directly following the precipitation of rozenite (cf. Jerz et al. 2001) or as a result of the increase in Al:Fe ratios in host-rock porewater as outcrop-surface evaporation occurs (Jerz and Rimstidt 2003). Halotrichite occurs in the late stage of paragenesis at Iron Mountain, CA (Nordstrom and Alpers 1999), although its presence clearly does not represent the complete oxidation of Fe$^{2+}$ to Fe$^{3+}$, a process that typifies late-stage sulfate paragenesis as a whole (Jambor et al. 2000; Jerz and Rimstidt 2003). In some settings, halotrichite appears only in dry weather (Jerz and Rimstidt 2003) or it persists only in microenvironments that have some degree of protection from the elements, such as the outcrop at site 1. The halotrichite at site 1 has some degree of substitution of Mg$^{2+}$ for Fe$^{2+}$, which in this case is highly compatible with the co-occurrence of slavikite and epsomite, both of which contain Mg. Both pickeringite, the Mg end member of the solid-solution series with halotrichite, and Mg-rich halotrichite have previously been described from weathering pyrite-bearing Pennsylvanian sedimentary rocks in the midwestern United States (Brant and Foster 1959; Kerns 1967), and given the potentially widespread existence of Mg$^{2+}$-bearing calcite
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as a cement phase in sedimentary rocks, the occurrence of Mg-rich halotrichite and pickeringite is likely to be much more common than the published literature suggests.

Rozenite is typically considered to be an early-paragenetic species (cf. Jambor et al. 2000; Jerz et al. 2001; Jerz and Rimstidt 2003). Its presence directly atop pyrite nodules represents the initiation of a new cycle of weathering during midsummer at site 1. However, because ambient humidity controls the occurrence of rozenite at surface temperatures (Baltatzis et al. 1986; Young and Nancarrow 1988), rozenite is also likely to be the most stable hydrated Fe$^{2+}$ sulfate salt under hotter, lower-relative-humidity conditions (Ehlers and Stiles 1965; Chou et al. 2002; Hammarstrom et al. 2003). The appearance of rozenite is concluded to be a seasonal phenomenon at site 1.

Slavikite, persistently identified at site 1, is of particular interest because it has been described from a comparatively small number of sites in Europe (e.g., Meixner 1939; Van Tassel 1947; Makovicky and Stresko 1967; Paraffiniuk 1991), one in South America (Gordon 1941), and from one site, Alum Cave Bluff in Tennessee, in North America (Flohr et al. 1995; Lauf 1997; Coskren

Figure 7. (A) EDX spectrum of slavikite crystallites from site 1, showing the presence of Mg. (B) Infrared spectrum of slavikite-alunogen crust (slavikite dominant) collected in September 2006 from site 1. The presence of lattice water is indicated by absorption bands marked "W"; strong absorption at 1109 cm$^{-1}$ corresponds to SO$_4^{2-}$ ion.
Figure 8. (A) X-ray diffractogram of white, earthy material (felsobanyaite/basaluminite) associated with the gypsum seam on the underside of a deep overhang at site 1. Felsobanyaite and basaluminite are listed as separate minerals in various databases (e.g., International Centre for Diffraction Data 2001), but recent work suggests that they are one mineral. XRD peaks of felsobanyaite and basaluminite largely overlap (International Centre for Diffraction Data 2001), but distinct peaks assigned to felsobanyaite in powder diffraction files (PDF) are indicated; most peaks assigned to “basaluminite” also correspond to felsobanyaite. (B) X-ray diffractogram of white, powdery efflorescence around calcite cemented sandstone lenses, collected in September 2006 at site 1 (see Figs. 6A, B, 7).

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Figure 9. X-ray diffractograms of (A) halotrichite and (B) copiapite from site 3. (C) X-ray diffractogram of jarosite from site 4 (see Fig. 6D).
and Lauf 2000; Hammarstrom et al. 2003). The co-occurrence of slavikite and copiapite at site 1 (Fig. 5A) is not unexpected: the two minerals also co-occur at Alum Cave Bluff, along with halotrichite, melanterite, and rozenite (Flohr et al. 1995; Lauf 1997; Coskren and Lauf 2000; Hammarstrom et al. 2003). Slavikite and copiapite also co-occur at Mina Santa Elena, Argentina (Gordon 1941). Slavikite occurs with copiapite, halotrichite-group minerals, and fibroferrite on weathered pyritic schists at Wiesciszowice, Poland (Parafiniuk 1991), and a similar occurrence was described in Austria by Meixner (1939). EDAX spectra of slavikite crystallites from site 1 do not indicate the presence of sodium, which is included in the mineral’s ideal formula (e.g., Süss 1975), but the 1.80% Na indicated by the accepted chemical formula for the mineral may be below the detection limit. Sodium was reported to be absent in samples of slavikite analyzed by Coskren and Lauf (2000) and Gordon (1941); therefore, further study is probably needed to establish the range of chemical composition exhibited by the mineral. An infrared spectrum of the slavikite-alunogen crust collected in April 2006 (Figs. 5A, 7B) shows absorption bands for water (3,370.4 cm\(^{-1}\) and 1,658.8 cm\(^{-1}\)) and SO\(_4^{2-}\) (1,109 cm\(^{-1}\)) that are characteristic of sulfate minerals (Omori and Kerr 1963; Gadsen 1975).

Well-crystallized copiapite in samples from sites 1 and 3 indicates complete oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) (cf. Jerz and Rimstidt 2003). Copiapite-group minerals are among the most common minerals described from acid-weathering sites in pyritic materials, and they can be particularly persistent components in assemblages of hydrated sulfate salts (e.g., Zodrow 1980; Bayless and Olyphant 1993).

“Basaluminite” has been reported to occur in small quantities at several sites in the United States (e.g., Milton et al. 1955; Fröndel 1968; Tien 1968; Mitchell 1970; Gricius 1971). In Kansas, it was found in weathered coal-bearing clastic rocks (Tien 1968), an occurrence very similar to site 1. Moreover, the mineral frequently occurs with gypsum in weathered sediment and rocks (Fröndel 1968; Tien 1968; Mitchell 1970). Epsomite is known to occur with other hydrated sulfate minerals at both natural and anthropogenic acid-weathering sites (e.g., Van Tassel 1973; Coskren and Lauf 2000; Hammarstrom et al. 2003; Sánchez España et al. 2005).

The generation of salts and their role as an acid-storing phenomenon influences local environmental conditions. Pyrite weathering and the precipitation of sulfate salts must also contribute, at some level, to surface-water and groundwater quality by liberating, concentrating, and re-releasing ions such as Al\(^{3+}\), Fe\(^{2+}\), Fe\(^{3+}\), Mg\(^{2+}\), and SO\(_4^{2-}\). This potential linkage between rock weathering and water quality has largely been ignored in Nebraska. Observations at site 1 further suggest that the weathering of salts in pyrite-bearing, soft clastic sedimentary rocks can contribute to the geomorphic evolution of slopes. Together with physical weakening of porous sandstone by diffuse groundwater discharge, sulfate-salt weathering in the lower parts of sandstone outcrops like those around site 1 (Fig. 2) potentially contributes to the erosion of small alcoves, and ultimately, to the undermining of steep sandstone slopes. Considering the location of Indian Cave, a large and locally well-known sandstone shelter cave preserved in a state park by the same name near site 1, the possibility of past effects of salt weathering are intriguing.

**CONCLUSIONS**

Site 1 exhibits a broader variety and expression of sulfate minerals than the other sites because (1) it is comparatively well-protected from the elements, (2) magnesium is available in the local geochemical system, and (3) it is the only site at which fresh pyrite is regularly exposed to weathering by small-scale, salt-driven mass wasting of the outcrop face. It is speculated that localized carbonate cements in sandstones serve as the source for Mg\(^{2+}\) in halotrichite, slavikite, and epsomite, particularly because limestones are thin and rare in the local stratigraphic section, and they are absent at the site itself. Pyrite oxidation and acid weathering in such sandstones would solubilize Mg. Overall, however, copiapite and halotrichite appear to be the most common products of acid weathering on Pennsylvanian clastic rocks in the region, and indeed these minerals are common in the same kinds of settings elsewhere.

Bearing in mind the wide variety of possible minerals (e.g., Jambor et al. 2000) and the different paragenetic pathways that apply under changing environmental conditions (Jerz and Rimstidt 2003), it seems likely that additional minerals will be found in acid-weathering environments in Nebraska and surrounding areas. The results reported herein demonstrate mineralogical differences related to the availability of Mg, but further regional differentiation of acid-weathering sites may exist, depending on local microenvironmental conditions and the nature of host rocks. Conversely, although sulfate-salt precipitation in southeastern Nebraska is limited to small-scale environments, sulfate mineral assemblages resulting from acid weathering are direct indicators of the nature of local geochemical conditions, particularly the availability of constituent ions. Acid rock weathering, even
in an area where it has not been previously recognized, should be considered in local to regional assessments of surface-water and groundwater chemistry in southeastern Nebraska because of the long-term role of such weathering in liberating and concentrating ions such as \( \text{Al}^{3+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg}^{2+}, \text{and SO}_4^{2-} \), all of which can have a significant impact on water quality. The release of \( \text{Al}^{3+} \) into surface waters by the dissolution of surface salts produced during weathering has a potentially detrimental effect on aquatic organisms. The precipitation of sulfate salts can also cause engineering problems, particularly in road construction, and the potential of such effects in southeastern Nebraska should be reconsidered in the light of the results presented herein.

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