

Sulfate-mineral crusts from pyrite weathering and acid rock drainage in the Dakota Formation and Graneros Shale, Jefferson County, Nebraska

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Abstract

Pyrite weathering in the uppermost Dakota Formation and lower Graneros Shale (Cretaceous) near Fairbury, Nebraska, produces acid materials and soils (typically pH<6), acid rock drainage (pH<2.5), and surface crusts of gypsum and the hydrated Fe³⁺ and Al-sulfate minerals copiapite, alunogen, metahohmannite, coquimbite, paracoquimbite, and meta-alunogen. The Fe and Al minerals produced by acid-sulfate weathering are relatively rare (heretofore undocumented from Nebraska), and form in quantity only during episodes of dry weather lasting up to several weeks. The maturation of mineral crusts on the Dakota Formation involves the dehydration of hydrous Fe³⁺ and Al minerals. Precursor Fe²⁺ sulfates, as found in many other cases of pyrite weathering, were not observed in surface crusts during the study period. Surficial mineral crusts on the Graneros Shale consist only of gypsum with included clay minerals and quartz derived from the underlying shale. The processes described herein are noteworthy in a regional geochemical and hydrogeological context, and also by virtue of their apparent dependency on weather conditions.

The acid-sulfate weathering sites described herein seem to be relatively unique in the surrounding region. Nonetheless, the study of these sites suggests that there are potentially widespread effects of natural acid-sulfate weathering associated with the Dakota Formation and other pyritiferous Cretaceous strata in the region, and that the localized effects of anthropogenically induced acid-sulfate weathering in roadcuts, quarries, and other excavations can present engineering problems. Acid-sulfate weathering is likely to have influenced the development of regional groundwater chemistry during the Quaternary and may create adverse engineering and environmental conditions, such as the retardation of vegetation cover, encouragement of subsoil gypsum growth, acceleration of shale slaking, and possibly even the corrosion of roadbed materials.

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1. Introduction

Pyrite oxidation and its role in forming acid-sulfate soils and acidic waters are widely known from many of the world's coastal plains (e.g., Van Breemen, 1982 and references therein). Fewer studies (e.g., Ivarson, 1973; Poelman, 1973; Carson et al., 1982; Carson and Dixon, 1983; Curtin and Mermut, 1985; Mermut and Arshad, 1987; Ross et al., 1988; Wagner et al., 1982) have documented near-surface pyrite oxidation far inland from marine shorelines. In North America, published reports of inland acid-sulfate weathering describe either sub-regional soils on Cretaceous marine shales (Curtin and Mermut, 1985), or more geographically localized coal and metal-sulfide mines (e.g., Dixon et al., 1982; Keith et al., 1999). The view of pyrite weathering in the near-surface environment seems to be limited both by this apparent geography of phenomena and by the venues of published research. Soil-science literature has emphasized the pedological occurrence of jarosite and acid-sulfate soil formation, in its strictest sense (e.g., Bryant, 1981; Carson and Dixon, 1983; Curtin and Mermut, 1985). Many other minerals, however, can form after pyrite oxidation under a range of geochemical conditions

and by a variety of physical, biological, and chemical processes (Van Breemen, 1973; Nordstrom, 1982; Dixon et al., 1982; Keith et al., 1999; Jambor et al., 2000). An improved understanding of pyrite weathering and its consequences may benefit from an identification of the array of secondary sulfate minerals and documentation of conditions and processes of their formation in a variety of geological and geographic settings.

There has been little investigation of pyrite weathering in the midcontinental United States despite the widespread distribution of multiple pyrite-bearing shale units, as well as shale-derived glacial tills. The widespread Dakota Formation, which contains abundant pyrite in mudrocks and sandstones, is part of one of the most extensive aquifer systems in North America and underlies about 94% of Nebraska. Many natural and anthropogenically exposed outcrops of the Dakota Formation show extensive oxidation of pyrite, as well as of siderite [FeCO_3], locally to depths of several meters. On the basis of geomorphology and geochronology (e.g., Boellstorff, 1978), we surmise that much of this oxidation occurred just below the land surface during the Late Cenozoic, and well after the onset of continental glaciation in the Late Pliocene.

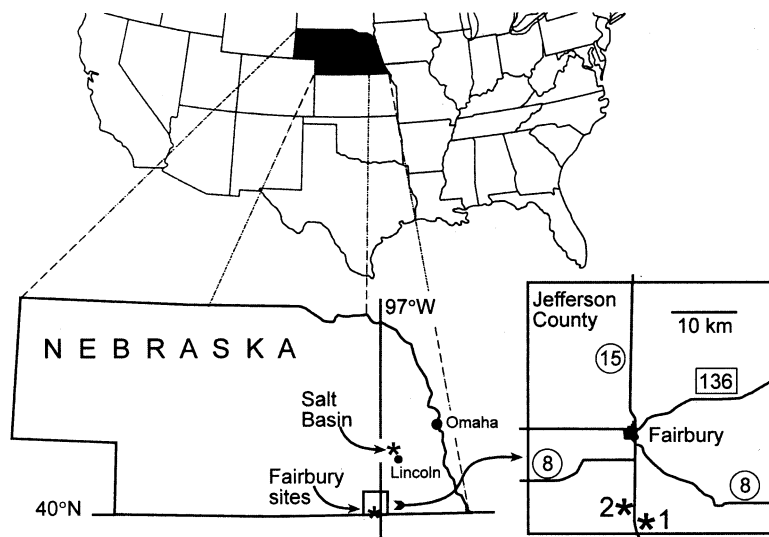


Fig. 1. Maps showing location of study area. Site 1 (main study site) is a road cut on the east side of Highway 15 (W1/2 SW1/4 SW1/4 SE1/4 of section 26, T1N R2E, Jefferson County, Nebraska), where thick crusts of Fe- and Al-sulfate minerals occur on acid-weathering Dakota Formation; site 2 is a road cut on the west side of Highway 15 (W1/2 NE1/4 NE1/4 SE1/4 SW1/4 of section 23, T1N R2E), where mineral precipitates formed in sandy sediment infilling a ditch below an outcrop of Dakota Formation sandstones. Salt Basin in Lancaster County is the site of halite and thenardite precipitation associated indirectly with water movement through the Dakota Formation.

The Dakota aquifer is chemically diverse, and includes large volumes of saline waters, some of which discharge at the land surface to produce salt crusts under alkaline conditions at Salt Basin, near Lincoln, Nebraska (Fig. 1). Acidic conditions produced by the weathering of Dakota Formation rocks, however, have not previously been studied in Nebraska, or, to our knowledge, in adjacent states. The objectives of this study are to: (1) describe two regionally noteworthy occurrences of pyrite oxidation and acid rock-drainage in uppermost Dakota Formation (Cretaceous) strata exposed in highway excavations south of Fairbury, Jefferson County, Nebraska (Fig. 1); (2) analyze surface crusts of authigenic sulfate minerals that form with this pyrite oxidation; (3) compare the Jefferson County sites to similar occurrences described in published literature; and (4) interpret these occurrences and speculate on their broader geological, environmental, and engineering implications.

2. Analytical techniques

2.1. Chemistry and mineralogy

Colors of mineral crusts and sediments were estimated using Munsell Soil Color Charts (Munsell Color, 1998) and Munsell Color Charts for Plant Tissues (Munsell Color, 1977). Measurements of ground- and surface-water pH, temperature, conductivity, and oxygen reduction potential (ORP) were made with an Oakton® pH/Con 10 Meter and with an Oakton® Acron Series pH meter and an attached ORP electrode. The pH, conductivity, and ORP (converted to Eh) of drainage water at the site were measured in place. Measurements of soil (including slightly weathered shale material) pH were made on 1:1 mixtures of soil-distilled water at time intervals of 30, 60, 1440, and 2880 min. Mineral crusts were ground manually for 1–3 min in an agate mortar and pestle and were stored in moisture-proof vials.

Minerals were then characterized by X-ray diffraction (XRD) of randomly oriented powder mounts in a Scintag PAD5® diffractometer with a graphite monochromator and double Soller slits, using CuK α radiation at 30 kV and 40 mA. Mineral identification

was facilitated by the search-match function in DMS 2000® version 3.18 software; diffraction peak positions were calculated automatically using the split Pearson peak-fit calculation (Howard and Preston, 1989).

Infrared (IR) analysis was done with an Avatar 360 ESP® single-beam spectrometer manufactured by Nicolet Instruments. Sample splits for IR were prepared by grinding with dry KBr, followed by compression into transparent pellets; the spectra were acquired in single-beam transmission mode. The instrument background was acquired on a blank pellet, and the final spectra were normalized to this background to allow spectral presentation as percent transmittance following the fast Fourier transform of the acquired interferogram. For quantification, these data were converted to absorbance units prior to measurement of peak areas using the peak-integration utilities in the Nicolet Omnic® software (Nicolet Instruments, 1999).

Thermogravimetry (TG) and derivative thermogravimetry (DTG) were done with a TA Instruments TG 51® thermogravimetric analyzer (TGA) at the National Soil Survey Center in Lincoln, Nebraska. Sample splits analyzed by TG were stored for 24 h prior to analysis at 55% relative humidity (over MgCl₂). Thermogravimetry was run from room temperature to 900 °C, ramping at 20 °C min⁻¹. A Hitachi S-3000N scanning electron microscope (SEM) was used to examine and image Pt–Pd coated samples of mineral crusts shortly after their collection in the field.

2.2. Microbiology

Samples of shale-water suspension were removed from the main study site (site 1) and stored in plastic containers in a refrigerator at 4 °C. These samples were used to inoculate Fe-oxidizing media, which were incubated either in stationary tubes or on a rotary shaker at room temperature. Two culture media were used: the Fe-oxidizing medium of Atlas (1995) and the modified 9K medium of Silverman and Lungren (1959). Samples of cultures using the Atlas (1995) medium were prepared for denaturing gradient gel electrophoresis (DGGE) by centrifuging a broth culture and removing most of the supernatant, then resuspending and combining the pellets in a

sterile, 50-mL Falcon tube. Samples were packed on wet ice packs and were sent to Microbial Insights, (Rockford, TN, USA) by overnight mail. DNA was extracted from the microbial population, 16S rDNA fragments were amplified by polymerase chain reaction, and the resulting product was separated

using DGGE. DGGE allows a direct visualization of the genetic diversity of the microbial populations, and the number of electrophoretic bands should be proportional to the number of species in the population (Muyzer and de Waal, 1994). Appropriate standards were used to verify all procedures.

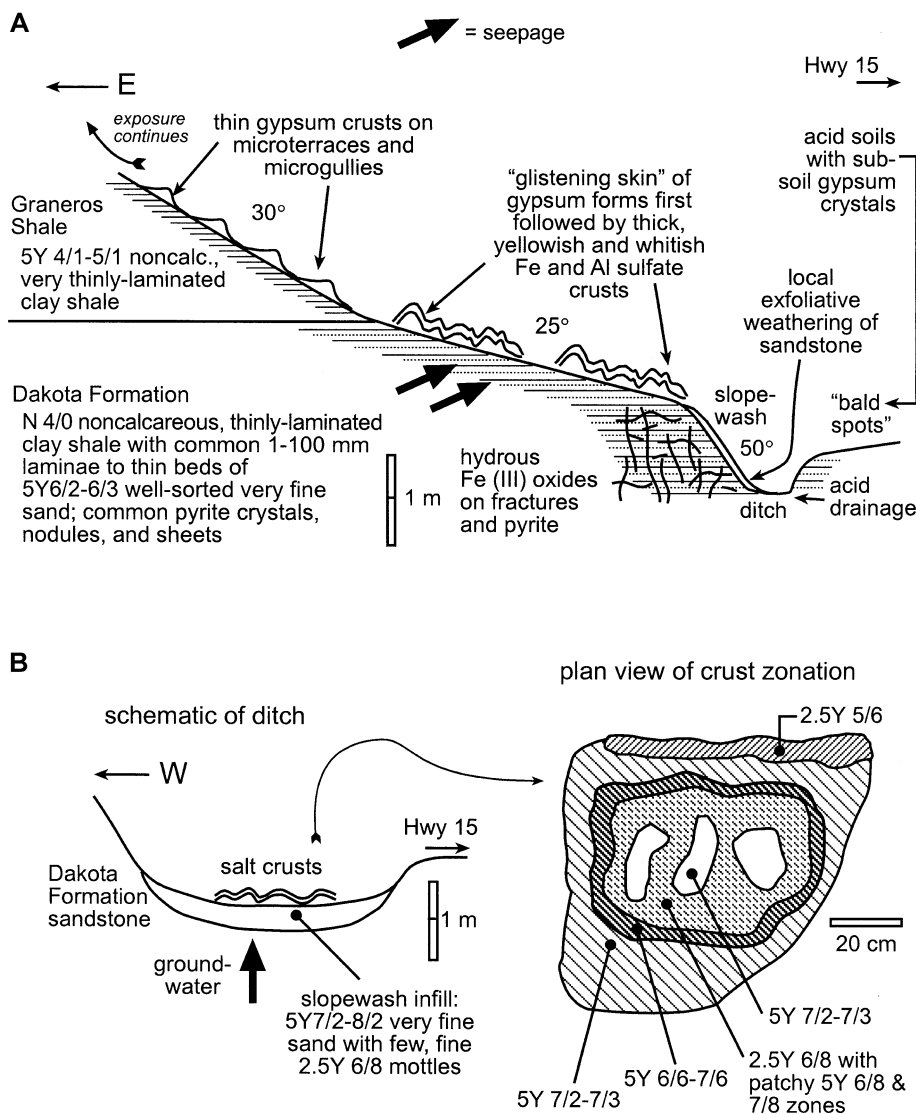


Fig. 2. (A) Stratigraphic section and slope profile through uppermost Dakota Formation and lowermost Graneros Shale at site 1 (see Fig. 1); Greenhorn Limestone (not shown) overlies Graneros Shale upsection several meters. Regional thickness of Dakota Formation exceeds 100 m. "Bald spots" are low-pH patches along the highway right-of-way that lack vegetation; typically, fine (≤ 2 mm) gypsum crystals have crystallized in subsoil cracks beneath these spots. (B) Schematic cross-section of road ditch at site 2, and plan view of salt-crust color zonation, which appears to be due to the presence of sulfate minerals together with hydrous Fe oxides.

3. Geological setting

The Dakota Formation, which is characterized by a complex pattern of fluvial, estuarine, and near-shore marine sedimentary facies (Brenner et al., 2000), contains pyrite at many stratigraphic layers. The uppermost Dakota Formation can be particularly pyrite-rich, containing an estimated 2% macroscopic pyrite at site 1 in the form of discoidal nodules (as much as 15 cm in diameter), irregular crystalline masses (as much as 20 cm in length), and discontinuous sheets 1–3 mm thick, along bedding planes. Microscopic pyrite generally makes up $\leq 1\%$ of total rock volume in both the uppermost Dakota Formation and the Graneros Shale (Hattin, 1965). Because of their thinness and problems encountered in identifying the contact between them, Graneros Shale and overlying Greenhorn Limestone formations have been mapped as one interval in Nebraska. Furthermore, the Graneros Shale is now known to pinch out eastward across northeastern Nebraska and into Iowa (Hattin, 1965; Brenner et al., 2000), demonstrating that part of the lower Greenhorn Limestone was previously correlated erroneously as the Graneros Shale. The

strata called Graneros Shale in this study, however, are correctly correlated because they lie below the well-known “X” bentonite, a prominent stratigraphic marker (Hattin, 1965).

At site 1 (Fig. 2A), the uppermost Dakota Formation consists of interbedded very fine sand and shale, a small-scale stratigraphic pattern that causes large vertical variations in hydraulic characteristics through only a few centimeters. The sand beds are almost always moister than the shales. Throughout the period of study, regardless of the weekly to monthly pattern of rainfall, both sand and shale beds were never dry except for a thin zone a few millimeters below the land surface. Thus, shallow groundwaters apparently are being discharged upward or laterally through the Dakota Formation in the study area. Impressive crusts of efflorescent sulfate salts episodically “bloom” on the uppermost Dakota Formation at site 1. Crusts forming simultaneously on the overlying Graneros Shale contain only gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] as an authigenic mineral and are much less impressive.

Groundwater chemistry in the Dakota Aquifer varies considerably over distances of kilometers to

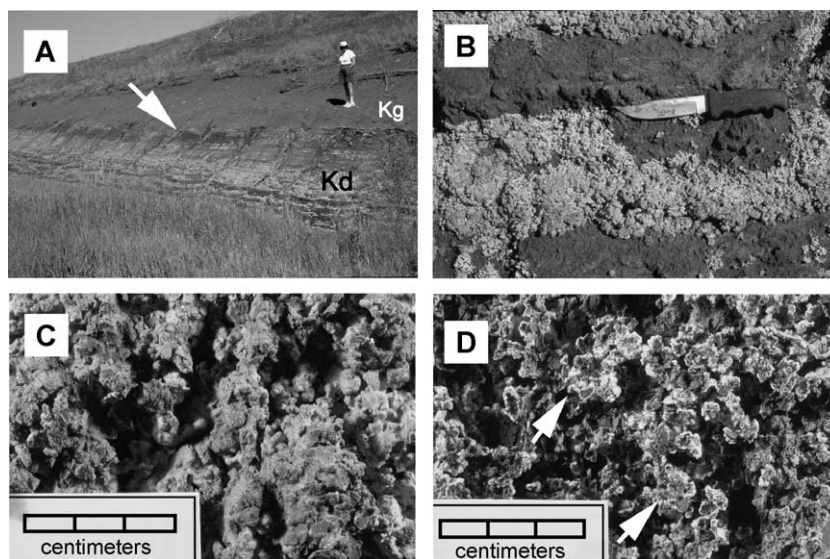


Fig. 3. (A) Main study site (site 1), showing uppermost Dakota Formation (Kd), where thick crusts of hydrated sulfate minerals (patchy, light-colored areas on Dakota Formation outcrop) formed at surface, and Graneros Shale (Kg); contact between units is indicated by arrow; B.J. Ang Clement is 1.7 m tall. (B) Close-up view of crusts of hydrated sulfate minerals forming preferentially on shale beds in uppermost Dakota Formation, September 2000; knife is 25 cm long. (C) Upper surface of mature, desiccated crust from site 1, showing irregular, folded upper surface consisting of fine gypsum crystals and shale chips. (D) Underside of same sample, showing crusty plates (arrows) of yellowish sulfate minerals, which began as moist, pasty “fungoid” masses.

tens of kilometers (Gosselin et al., 2001), and some of this variability is probably related to water–rock interaction within the formation itself. Sulfate, which could be derived at least in part from pyrite oxidation, is a significant contributor to the total dissolved solids in the Dakota Formation aquifer (Gosselin et al., 2001). The Salt Basin, approximately 100 km north-east of the Jefferson County study sites (Fig. 1), has surficial halite [NaCl] and thenardite [Na₂SO₄] precipitates. This occurrence is also associated with migrating groundwaters from the Dakota Formation, except under alkaline conditions.

The overlying Graneros Shale at site 1 differs from the uppermost Dakota Formation in its color, higher degree of fissility, and lateral uniformity of shale facies. The Graneros Shale has little macroscopic pyrite, but its dark, organic-rich shales contain very fine (<1 mm) pyrite crystals. On the basis of regional patterns in groundwater use and well design, it is inferred that the Graneros Shale consistently has a lower hydraulic conductivity than the generally coarser-grained Dakota Formation (Figs. 2A and 3A). The Graneros Shale functions as a confining unit over the Dakota Formation in the region (Veatch, 1969).

At site 1, completely unoxidized, partly weathered (i.e., masses of hydrous Fe oxides around a remnant pyritic core), to completely weathered pyrite are visible in both the Dakota Formation and the Graneros Shale. Widespread weathering of pyrite probably was not initiated until after a major re-engineering of the roadcut in the early 1970s, which followed a massive slope failure at the site. Nonetheless, natural outcrops nearby strongly suggest that localized pyrite oxidation along deep fractures began at site 1 long before human disturbance. Acidic conditions produced by pyrite weathering occur at site 1 (Fig. 4). Almost all of the exposed Dakota Formation and much of the Graneros Shale have remained unvegetated (Fig. 3A) since the last major slope grading at site 1 in 1982, but the upper part of the Graneros Shale and almost all of the overlying Greenhorn Limestone are now covered with sod and cottonwood saplings.

A different crust morphology was observed at site 2, a roadcut through upper Dakota Formation sandstones (a stratigraphic level several meters below the base of the Graneros Shale) about 2 km north of site 1 (Figs. 1, 2B and 5). Sulfate

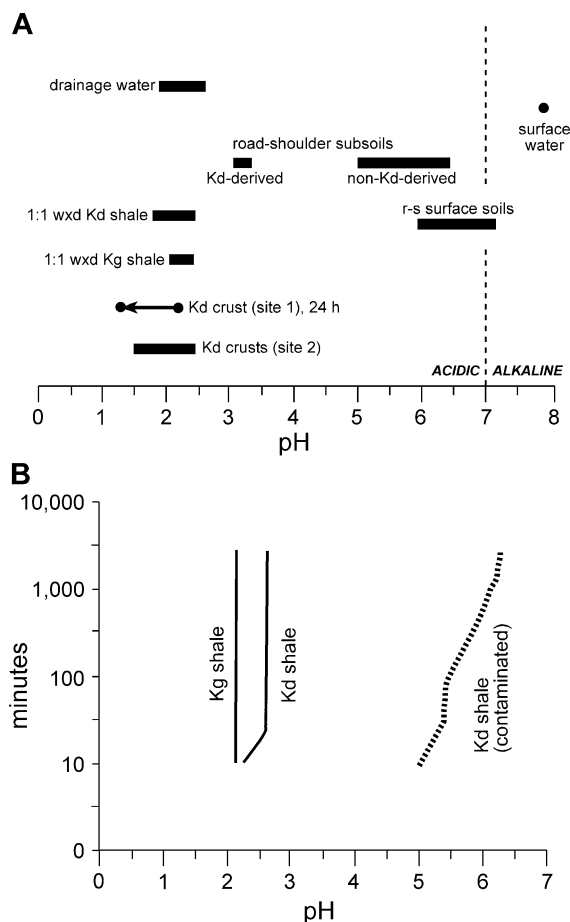


Fig. 4. (A) Regime of pH of pyrite weathering and surrounding environments at site 1. Samples of shale from uppermost Dakota Formation (Kd) and lower Graneros Shale (Kg) have strongly acid pH values, as do drainage waters, whereas the nearest standing surface water to the site, in a small natural drainage to the west, is slightly alkaline. "Road-shoulder" (r-s) refers to soils alongside highway at site 1, which are developed both on in-place Dakota Formation materials (Kd-derived) and in transported soil material (non-Kd-derived); surface portions of such soils are not strongly acid, but subsoils are if developed on in-place Dakota Formation or Greenhorn Limestone. Pulverized sulfate-mineral crusts from the Dakota Formation (Kd crusts [site 1], 24 h) develop very low pH after 24 h in 1:1 aqueous solution. Crusts from site 2 (Kd crusts [site 2]) range into slightly higher pH (up to 2.5) in solution. (B) Typical evolution of pH in samples of ground, slightly weathered Dakota Formation (wdx Kd shale) and weathered Graneros Shale (wdx Kg shale) in a 1:1 mixture with distilled water, and pH change in a Dakota Formation shale sample (from drainage ditch at site 1) contaminated with Greenhorn Limestone eroded from upslope, which progressively neutralized sample pH.

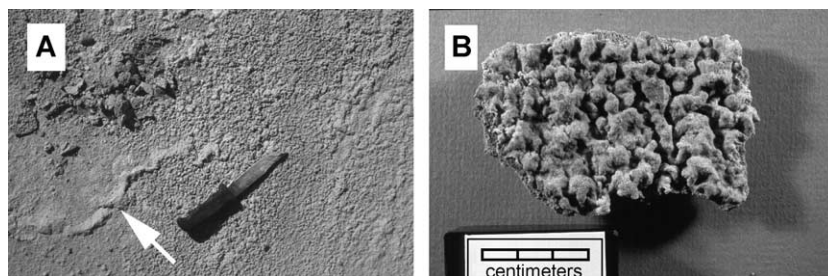


Fig. 5. (A) Crusts of alunogen- and copiapite-cemented sand formed at site 2 during the exceptionally dry late summer of 2000. Note buckling of crust by desiccation (arrow); knife is 25 cm long. (B) Close-up of irregular surface of yellowish cemented sand crust from site 2.

crusts at site 2 formed in very fine, sandy slopewash (eroded Dakota Formation sediments) that accumulated in a broad ditch (Fig. 2B), and did not occur directly atop weathered rock as at site 1, or around weathered masses of pyrite. The crusts at site 2 consist of redeposited sediment cemented by authigenic minerals. This occurrence is in contrast to site 1, where crusts consist almost entirely of authigenic minerals. Crusts at site 2 were observed only once, for a period of less than 2 weeks in September 2000. Their appearance followed a prolonged episode of exceptionally dry weather (Fig. 6).

At site 2, macroscopic pyrite is absent at the surface, but hydrous Fe oxides are common in concretions, cements, and surficial stains in the Dakota Formation. Our observations of multiple exposures of Dakota Formation in Jefferson County demonstrate that there is a continuum from: (1) unoxidized pyritic features (nodules, burrow linings, sheets along bedding planes) in exposures below the level of Late Cenozoic oxidation, to (2) partly oxidized pyritic features, to (3) hydrous Fe-oxide features that appear to have had pyrite precursors. Site 2 seems to be near the local interface between completely and partly oxidized levels within the Dakota Formation.

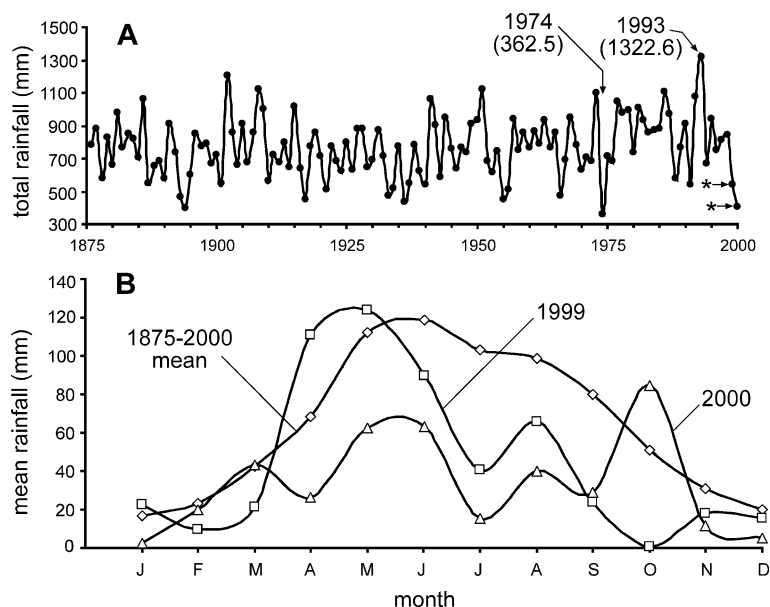


Fig. 6. Rainfall at Fairbury, Nebraska, emphasizing dry conditions throughout much of 1999 and 2000, when crusts were discovered at site 1. (A) Annual record, 1875–2000. (B) monthly records, 1875–2000, mean values for 1875–2000 compared with 1999–2000 data.

4. Results

4.1. Mineralogy of crusts

The first authigenic mineral precipitates to form at site 1 after a rainfall event are moist, pasty, bright yellow “fungoid” masses for which four of the six highest intensity XRD peaks match those for copiapite or, possibly, ferricopiapite (Fig. 7; Table 1). In addition, alunogen can be distinguished in the same diffractogram by its characteristic peak at about 13.5° 2θ ($d \sim 0.65$ nm); this peak, however, is roughly one-twentieth the intensity of that of the most intense copiapite peak on the diffractogram (Fig. 7).

Diffractograms of mature, desiccated Dakota Formation crusts from site 1 (Fig. 8B–D), however, indicate the presence of multiple sulfate minerals. Copiapite is still relatively easily distinguished in these diffractograms (Fig. 8B–D), but other peaks not assignable to either copiapite or alunogen are prominent. Samples KD1, KD2, and KD3 (Fig. 8B–D) all show peaks at about 10.6° 2θ ($d \sim 0.83$ nm), which matches closely with the primary peak for coquimbite (“cq”) at 10.7° 2θ ($d = 0.826$ nm). Sample KD2 (Fig. 8C) has peaks at 12.29° 2θ ($d = 0.7196$ nm), 20.75° 2θ ($d = 0.4278$ nm), 22.73° 2θ ($d = 0.3909$ nm), and 27.21° 2θ ($d = 0.3275$ nm), all of which match major peaks of metahohmannite (“m”). Hohmannite (Table 1) may have originally been present in this sample, because

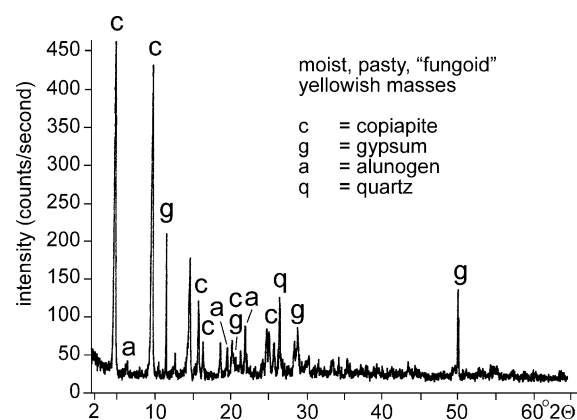


Fig. 7. Diffractogram of “fungoid” clump of moist, pasty, yellowish sulfate material from microgully in uppermost Dakota Formation at site 1 (collected in September 2000). c=copiapite (possibly ferricopiapite) with 2θ values at 4.8° ($d \sim 1.8$ nm), 9.8° ($d \sim 0.90$), 14.7° ($d \sim 0.60$), 15.9° ($d \sim 0.56$); a=alunogen, g=gypsum, q=quartz.

Table 1

Ideal formulas for sulfate minerals mentioned in the text

Aluminocopiapite	$(\text{Al}_{2/3-1/3})\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$
Bassanite	$2\text{CaSO}_4 \cdot \text{H}_2\text{O}$
Copiapite	$\text{Fe}^{2+}\text{Fe}_3^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Coquimbite	$\text{Fe}_2^{3+}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$
Ferricopiapite	$(\text{Fe}_{2/3-1/3}^{3+})\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Halotrichite ^a	$\text{Fe}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
Hohmannite	$\text{Fe}_2^{3+}(\text{SO}_4)_2\text{O} \cdot 8\text{H}_2\text{O}$
Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$
Melanterite ^a	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Meta-alunogen	$\text{Al}_4(\text{SO}_4)_6 \cdot 27\text{H}_2\text{O}$
Metahohmannite	$\text{Fe}_2^{3+}(\text{SO}_4)_2(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ (?)
Rozenite	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
Szomolnokite	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
Tamarugite	$\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
Thenardite	Na_2SO_4

Formulas are from Mandarino and Back (2004), except for metahohmannite (Scordari et al., 2004).

^a Previously described from Nebraska by Pabian (1993).

metahohmannite is produced by its dehydration (Gaines et al., 1997). It is likely that peaks at about 10.3° 2θ ($d \sim 0.86$ nm) and 32.3° 2θ ($d \sim 0.27$ nm) in sample KD3 (Fig. 8D) are paracoquimbite, which ideally has reflections at 9.95° 2θ ($d \sim 0.8880$ nm) and 32.40° 2θ ($d \sim 2.761$ nm). It is possible that meta-alunogen may be represented in the two samples (Fig. 8C,D) of mature, desiccated crust; the potential presence of meta-alunogen is credible considering that it, like metahohmannite, forms as a dehydration product (in this case, of alunogen). Gypsum makes up the Graneros Formation crusts (Fig. 8A, “g”). Iron- and Al-bearing minerals were not detected in these crusts.

Infrared spectra of the mineral crusts from site 1 (Fig. 9) supply ancillary data for mineral characterization. The most obvious difference among the spectra of the crusts is the broad region of absorption bands in the region ~ 2950 – 3500 cm^{-1} in the Dakota Formation crust samples (Fig. 9: KD1, KD2, and KD3), versus the narrow peak at 3400 cm^{-1} in the Graneros Shale crust (Fig. 9: KG1). The spectrum for sample KG1 is similar in the latter respect to the spectra of gypsum presented by Omori and Kerr (1963), which show relatively narrow, well-defined absorption bands in the region of 3300 – 3400 cm^{-1} . The spectra of Dakota Formation crust samples, however, are similar to those of more highly hydrated

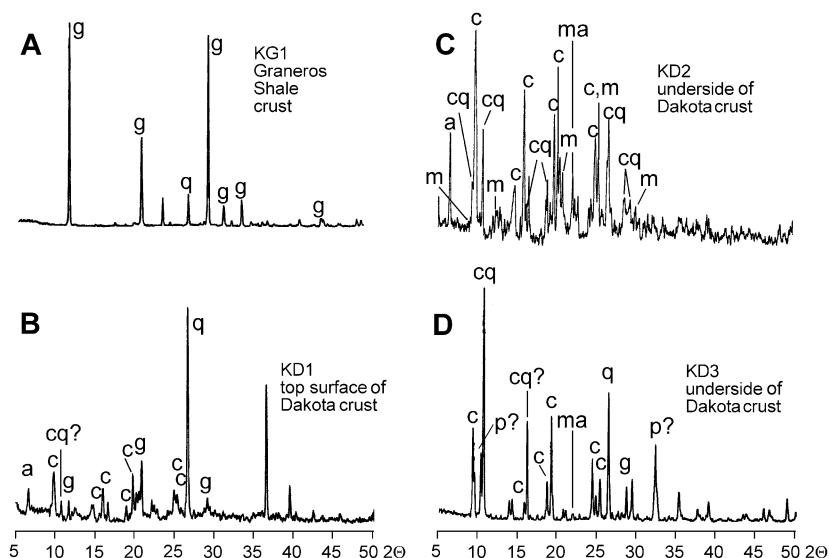


Fig. 8. Diffractograms of samples of mature mineral crusts (i.e., those collected after prolonged dry weather in November 1999) produced by weathering at site 1: a=alunogen, c=copiapite (possibly ferricopiapite), cq or cq?=coquimbite or probable coquimbite, g=gypsum, m=metahohmannite, ma=meta-alunogen, q=quartz, p?=probable 'paracoquimbite'. (A) Sample KG1, a thin gypsum crust from surface of lower Graneros Shale. (B) Sample KD1, the top surface (thin, grayish layer) of a thick, mature crust formed on uppermost Dakota Formation. (C, D) Samples KD2 and KD3, underside (yellowish and whitish sulfates) from the same crust.

Fe, Cu, Mg, or Al sulfates, including halotrichite, melanterite, coquimbite, and alunogen (Omori and Kerr, 1963), as well as to the spectrum of the hydroxyl-bearing mineral copiapite (Omori and Kerr, 1963). In the spectra for these diverse minerals provided by Omori and Kerr (1963), there are typically two prominent absorption bands in the region of 2950–3500 cm^{-1} . Although Omori and Kerr (1963) is a comprehensive publication of infrared spectra of sulfate minerals, it should be noted that some of the XRD data presented by these authors were later judged to be faulty (Erd et al., 1965).

Thermogravimetry (TG) of the samples of site 1 crust also assists in the identification of the minerals. According to Karathanasis and Harris (1994), TG has been employed less widely to characterize sulfates (except for gypsum and bassanite) than several other mineral groups. All of the Dakota Formation mineral crusts analyzed by TG lost much more overall mass (Fig. 10: KD1–KD3; 42–69% loss) with heating than did the gypsum crust from the Graneros Shale (Fig. 10: KG1; 22.5% loss), indicating the completion of a series of chemical reactions with increasing temperature. The maximum 69% total mass loss in Dakota Formation crust samples is analogous to the 69.8%

mass loss with the heating of synthetic $(?)\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ determined by Todor (1976).

DTG curves (Fig. 10) help resolve the multiple, overlapping reactions in TG curves. All of the Dakota Formation samples (KD1–KD3) have multiple peaks on their DTG curves in the approximate range of 40–160 $^{\circ}\text{C}$ that indicate progressive dehydration (cf. Todor, 1976). The samples also have DTG peaks roughly in the range of 250–360 $^{\circ}\text{C}$ that probably represent additional water loss. Todor (1976) obtained thermal analyses of synthetic hydrated ferrous sulfate that was produced by dissolving Fe_2O_3 in sulfuric acid. He also noted that the boiling point of H_2SO_4 was 338 $^{\circ}\text{C}$, and loosely related that reaction to a DTG peak for the synthetic hydrated Fe^{2+} sulfate at about 340 $^{\circ}\text{C}$ (Todor, 1976). A thermal analysis of synthetic $(?)\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ showed DTG peaks in the 200–240 $^{\circ}\text{C}$ range and at 790 $^{\circ}\text{C}$ (Todor, 1976). Todor's thermal analysis of synthetic $(?)\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ indicated DTG peaks at 140 $^{\circ}\text{C}$ and 330 $^{\circ}\text{C}$ due to dehydration, and a desulfuration peak at about 875 $^{\circ}\text{C}$. The TG curve for alunogen (Bayliss, 1964) is "stepped", with the loss of 14 water molecules at about 150 $^{\circ}\text{C}$, followed by the loss of two more at 330 $^{\circ}\text{C}$. In the Dakota Formation samples, other DTG

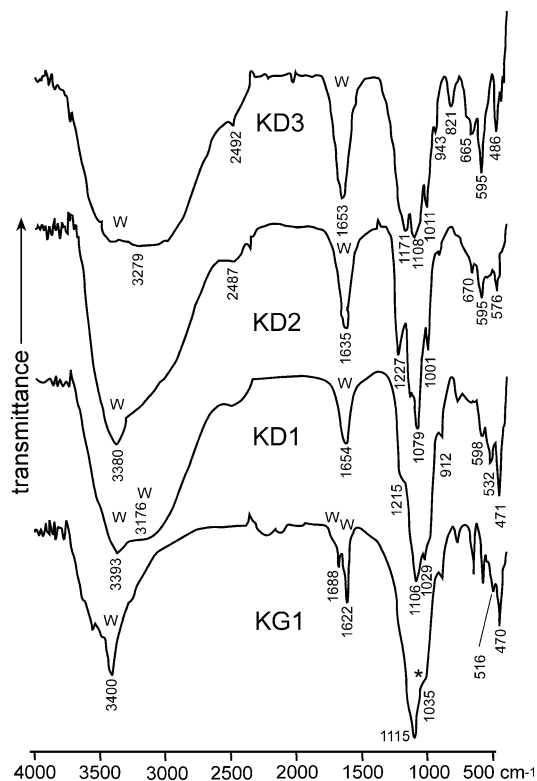


Fig. 9. Infrared spectroscopy of splits from the same samples represented by diffractograms in Fig. 8. Broad region of absorption bands at 2950–3500 cm^{-1} in Dakota Formation crust samples (KD1, KD2, and KD3) is compatible with high state of hydration of minerals such as copiapite.

peaks in the range of 600–750 °C (Fig. 10) probably represent the complete breakdown of the original minerals, presumably producing both Al and Fe oxides, and culminating in desulfuration at the high end of this temperature range (cf. Bayliss, 1964; Zodrow et al., 1979; Todor, 1976).

In terms of authigenic minerals, Graneros Shale crusts at site 1 contain only gypsum, although clay minerals and quartz from the underlying shale are included within the crusts (KG-1 in Figs. 8–10). XRD analysis indicated that crusts at site 2 are cemented by alunogen and copiapite; the latter mineral, and small amounts of hydrous Fe oxides (not detectable by XRD) are partly responsible for the concentric zonation of color (Fig. 2B) observed at the site.

The mature Dakota Formation crusts from site 1 consist of smooth areas (basal growth zones of crystals) and of masses of plate-like crystals, each

10–100 μm (Fig. 11A,B). Finely detailed, fan-shaped splays of gypsum crystals are observable on the underside of gypsum crusts on the Graneros Shale (Fig. 11C).

4.2. Description of crusts

4.2.1. Dakota Formation crusts

The sloping (25°) surface of the Dakota outcrop at site 1 is covered discontinuously by a layer, 3–5 mm thick, of fine chips of shale (Figs. 2A and 3A). This layer is more continuous over parts of the ditch where material washed downslope is deposited and where weak cementation by mineral precipitates commonly anchors weathered materials in place (Fig. 2A). In situ

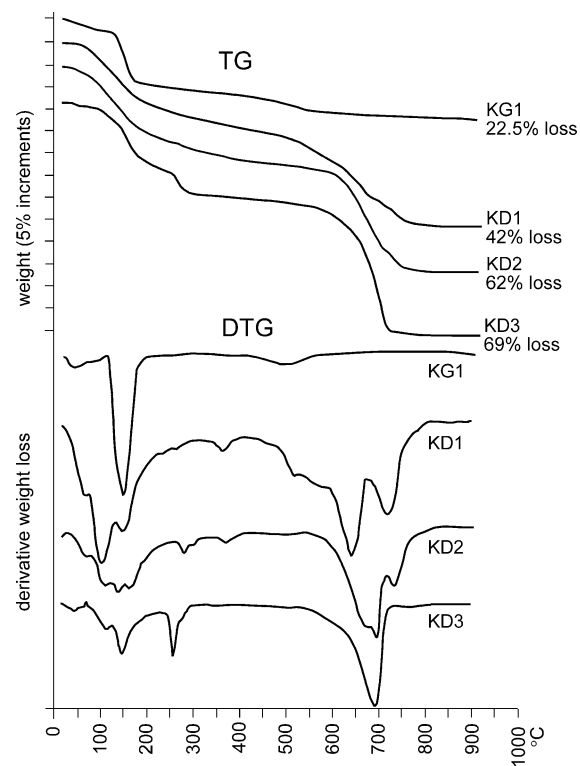


Fig. 10. Thermogravimetry (TG) and differential thermogravimetry (DTG) of powdered crust samples. Dakota Formation mineral crusts KD1 to KD3 lost much more overall mass (42–69% loss) with heating than did crust from Graneros Shale (KG1; 22.5% loss). Dakota Formation samples have multiple peaks on their DTG curves at 40–160 and 250–360 °C, probably representing loss of waters of hydration; DTG peaks in the range 600–750 °C probably represent completion of the breakdown, presumably producing oxides of Al and Fe, and evolving SO_3 .

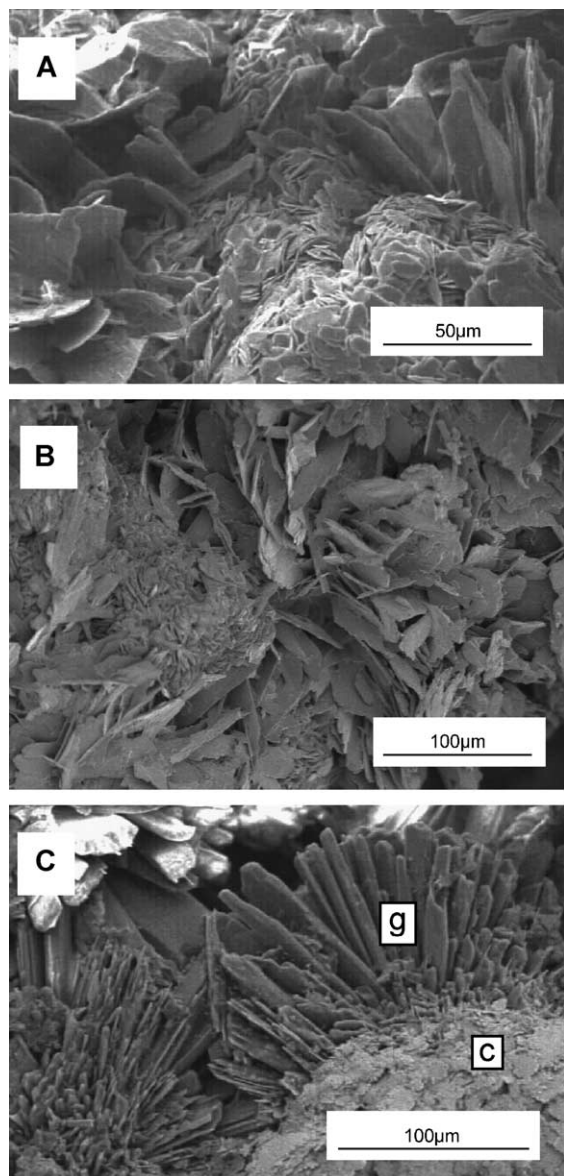


Fig. 11. SEM images of mineral crusts from site 1. (A, B) Two size populations of plate-like crystals, possibly representing a transition from copiapite to coquimbite, in crust from atop uppermost Dakota Formation. (C) Fan-shaped splays of gypsum crystals (g) from underside of crust atop Graneros Shale; note clay platelets (c) in shale fragment incorporated within crust. Gypsum crystals on upper surface of crust are rounded (possibly by partial dissolution by light rain or dew) and lack well-defined forms.

shale beneath the outcrop surface is highly fractured; fracture faces are stained dark reddish brown (5YR 3/3), yellowish red (5YR 4/6), strong brown (7.5YR 5/

6), yellowish brown (10YR 5/6), and pale yellow (5Y 8/4) by hydrous Fe^{3+} oxides, and possibly jarosite, produced by the oxidation of pyrite. A yellowish brown flocculate of hydrous Fe oxides and clay minerals appears in the drainage ditch below the outcrop after major precipitation events in the summer. The pH of the drainage waters is 1.27–1.65 and the Eh is 685–789 mV; specific conductance is typically $2.6\text{--}10.4\ \mu\text{S cm}^{-1}$. The margins of standing pools of hydrous Fe-oxide-bearing summertime drainage waters usually have a faint greenish precipitate floating at the water's surface. Sufficient amounts of this precipitate could not be collected for analysis, but we speculate that may be “green rust” or mixed Fe^{2+} – Fe^{3+} hydroxide (e.g., Schwertmann and Fechter, 1994; Cuttler et al., 1990) forming at the interface between acid, oxidizing water and the surrounding pyritic shale.

In early-to-mid-November 1999, near the end of a 5-month dry period in which only 149 mm of precipitation fell at Fairbury (11.2 mm during October and November: Fig. 6), a 1–3 cm crust of yellowish and whitish mineral had formed over $\sim 80\text{ m}^2$ at site 1. This crust formed atop the weathered shale chips on the outcrop, and was not directly associated with individual pyrite nodules or stringers. Rather, it covered large areas continuously. Thick crusts were also observed during dry periods in mid-June 2000 (after no rain fell at Fairbury during a period exceeding 2 weeks), and in mid-to-late September 2000 (after only 15 mm of rain in 42 days). Although the crusts were very prominent during the period from the fall of 1999 to the fall of 2000, no similar crust had been observed in many previous visits to the site at irregular intervals over 15 years, although the crusts may indeed have formed unobserved during dry periods. Abundant hydrous Fe-oxide coatings directly associated with pyrite, however, had always been noted at the site. The observation of thick sulfate crusts during two successive dry periods in the late summer–fall suggests a direct relationship between crust formation, infrequent rainfall, and decreasing atmospheric humidity. Rainfall records from the city of Fairbury indicate that 1999 (543.3 mm) and 2000 (403.6 mm) were the 15th and 3rd driest years between 1875 and 2000 (Fig. 6).

Thick, desiccated (“mature”) mineral crusts from atop the Dakota Formation at site 1 have a character-

istic morphology consisting of: (1) a nearly continuous, thin (1–2 mm), gray to light gray (5Y 6/1–7/1) upper layer over (2) a continuous, much thicker lower layer of yellowish (5Y hue) sulfates with minor, interstitial white material (Fig. 3C,D). The top surface of the upper layer has many fine desiccation cracks, and includes a discontinuous layer of shale chips cemented by lathlike crystals (1 mm long) and clusters of crystals of gypsum, as well as very finely granular, subhedral crystals (possibly alunogen). The upper layer is upwarped slightly, partly separating it from the underlying yellowish sulfate, which has grown underneath it. In effect, the upper layer is locally “microfolded” by upwarping, and even some small-scale recumbent folds are present (Fig. 3C). Locally, the thin upper layer is absent, causing the yellowish sulfate layer to be exposed at the crust’s surface; such exposure shows smooth, rounded masses of yellowish sulfate with a pronounced vitreous appearance and few or no masses of fine, euhedral crystals. In such cases, the yellowish sulfate may have been partially dissolved or eroded by the condensation of atmospheric moisture (precipitation would have dissolved the crusts completely).

The layer dominated by yellowish sulfate consists of two or more levels of irregular, horizontally oriented, slightly convex-upward plates (2–10 mm in diameter) or irregular masses of sulfate with botryoidal, cauliflower-like upper surfaces (Fig. 3D). The surfaces of plates or masses of yellowish sulfate have tracts of minute euhedral crystals embedded in smoother-appearing sulfate that is not macroscopically crystalline. These smooth areas are basal zones from which crystals have grown inward into the masses of sulfate, rather than outward, in which case crystals would be clearly visible. Closer examination of fractured faces in masses of yellowish sulfate reveals small (<1 mm in diameter), roughly circular zones of well-crystallized, brilliant, yellowish copiapite surrounded by much less strongly crystalline yellowish sulfate minerals with a subvitreous to earthy luster.

On the basis of serial visits to site 1, the following sequence of crust development is proposed (Fig. 12). The original manifestation of crusts on the Dakota Formation is a <1 -mm-thick, slightly sticky, dark brown to dark grayish brown (10YR 2/2–3/2), glistening skin (very thin, weak crust) of gypsum that

develops several days after a precipitation event in summer or early fall. This gypsum skin may persist between precipitation events, considering the lower solubility of gypsum relative to the other sulfate minerals in mature crusts. From a distance, the sheen on the skin is sufficient to give the impression of wetness, and although the weathered shale underneath is moist, the sheen itself results from the orientation of microscopic gypsum crystal faces.

The gypsum skin and adhering shale chips within and underneath it are gradually pushed upward from the outcrop surface by the gradual growth of yellowish and whitish Fe- and Al-sulfate minerals underneath. Sulfates of Fe and Al first appear as separate, yellowish (5Y 8/8), “fungoid” masses (rounded, botryoidal, convex-upward bodies about 4–20 mm in diameter, with slight basal concavities) in microgullies, fractures, and small recesses about 10–14 days after a precipitation event. These “fungoid” masses are dominated by copiapite and remain moist and pasty in consistency for several days into a dry period.

Eventually, “fungoid” masses grow together and steadily desiccate into intergrown crusty plates of brighter yellow (approximately 5Y 8/4–8/6) sulfate, which are pushed away from the outcrop surface as fresh sulfate material forms underneath them. Voids between crusty plates develop additional cauliflower-like masses of yellowish sulfate that bind the crust together. After 4–6 weeks of dry weather, the final result of these processes is a mature thick, brittle, porous crust that is cohesive enough to be pried off the outcrop in irregular sheets as big as 20×25 cm. Despite the formation of such widespread mature, desiccated crusts over a period of weeks, however, moist, pasty, copiapite-dominated, “fungoid” sulfate masses can persist deep in microgullies, under protected overhangs, and on the underside of maturing crusts. Desiccated “mature” crusts form preferentially over shale layers within the Dakota Formation, whereas the intervening thin sand beds may be covered only by a persistent very dark brown to dark grayish brown glistening skin of gypsum until crusts from adjacent shale layers have coalesced over the outcrop face. XRD analyses confirm that this transition in crust morphology corresponds with dehydration, in that “mature” crusts also contain other, less hydrated minerals in addition to copiapite and alunogen (Table 1).

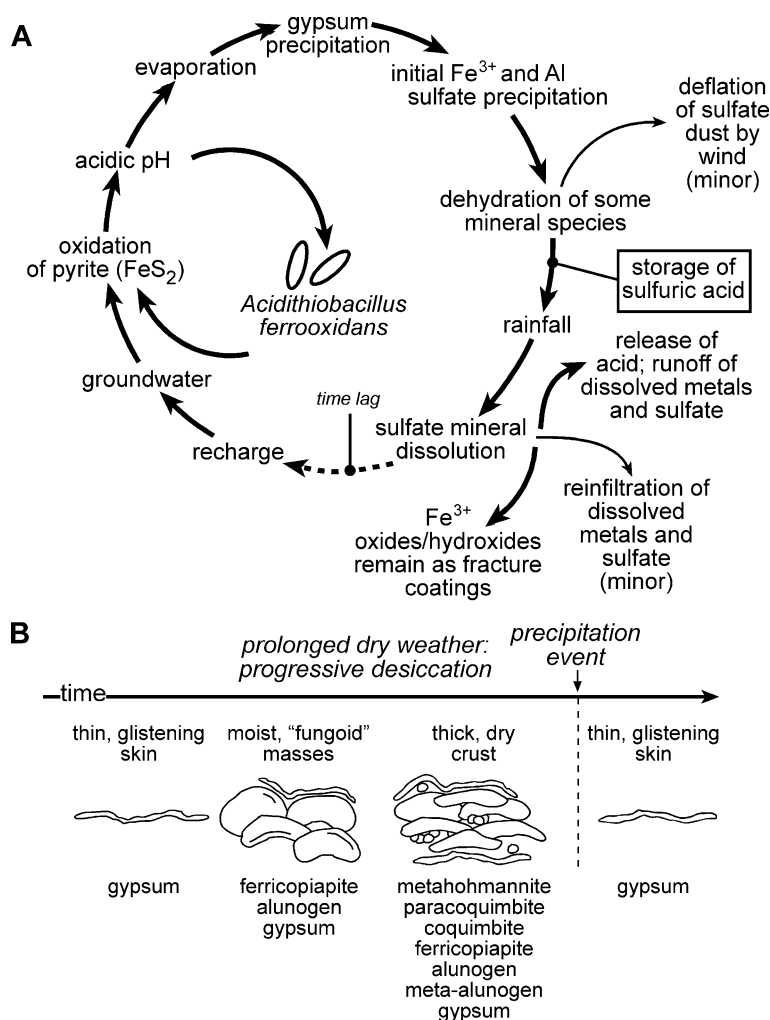


Fig. 12. (A) Pyrite weathering and related processes at site 1. On the basis of direct observation, runoff of dissolved sulfate is likely to dominate over re-infiltration of sulfate-rich waters. Deflation of sulfate-mineral dust by wind was observed in September 2000, although its effects are not likely to be volumetrically significant. Precipitation of hydrous Fe^{3+} oxide along fractures within the outcrop probably occurs simultaneously with pyrite oxidation and as a phenomenon separate from the dissolution of Fe^{3+} sulfates in mineral crusts at outcrop surfaces. (B) Perceived cycle of crust development at site 1. Glistening gypsum "skin" is a persistent feature on the surface of uppermost Dakota Formation outcrop, even shortly after rainfall. Several days of dry weather are required for development of moist, "pasty" masses of sulfate (copiapite and alunogen), and then weeks for subsequent maturation of crusts, which produces coquimbite, probable 'paracoquimbite', metahohmannite, and possibly meta-alunogen, the last two of which are presumed to form by dehydration of precursor mineral species (hohmannite and alunogen, respectively).

At site 2, thin (2–4 mm) crusts of gray to yellowish, weakly cemented sand (eroded from adjacent Dakota Formation sandstones) with a characteristically "pustulose" morphology (rounded surface irregularities 4–20 mm in diameter; Fig. 5) appeared for a short time in September 2000. This

crust had antiformally buckled and "blistered" 1–1.5 cm above the soil surface at regular intervals; some of the "microantiforms" on the crust surface exceeded 40 cm in length (Fig. 5B). Within the expanse of lighter-colored salt crust at this second locality were large (5–200 cm in diameter), irregular patches consisting of

roughly concentric zones of color ranging from pale yellow to light olive brown (Fig. 2B). Sparse, whitish (approximately 5Y 8/1) efflorescences (gypsum?) were present at the margins of this ditch. Within the crust were many, fine, smooth-walled vesicles, presumably similar to those found in association with salt crusts in other settings (e.g., Joeckel and Ang Clement, 1999). All of these characteristics suggest a process of mineral precipitation by surface evaporation accompanying the capillary rise of water (cf. Joeckel and Ang Clement, 1999) from the Dakota Formation through a thin mantle of unconsolidated granular material. Such a process differs from crust formation directly atop weathering Dakota bedrock at site 1.

Samples of Dakota Formation shale from site 1, collected when crusts were absent, developed extensive surface efflorescences of yellowish and whitish sulfate minerals within 48 h of exposure to the air in the laboratory at 22–27 °C. When these samples encountered diurnal summertime fluctuations in ambient humidity resulting from the cyclic operation of a climate-control system over a period of 2 weeks, the shale samples disintegrated almost completely. Furthermore, filter paper on which these specimens were sitting developed stains indicating the wicking of expelled moisture away from the specimens. Thus, the partly weathered Dakota Formation shale can undergo further decomposition under the influence of changing atmospheric humidity and without the addition of liquid water. In comparison, oven-dried, fresh specimens of the same shale slaked completely in deionized water, but within 30–60 min.

4.2.2. Graneros Shale crusts

Because of its more uniform lithological character, the Graneros Shale weathers into a thicker and more laterally continuous layer of fine shale chips than does the Dakota Formation. Moreover, the surface of the weathered Graneros Shale is also typically dry (to a depth of 5 mm or more), as opposed to the uppermost Dakota Formation below it, which remains moist year-round due to the presence of sand interbeds that have relatively higher hydraulic conductivity. Bare surfaces on the lower part of the Graneros outcrop exhibit prominent microterraces, about 2–6 cm wide and 1–5 cm high, which are cut by microgullies 2–20 cm deep. These

microterraces are most prominent after rainfall events, but they are probably formed by a combination of slopewash and soil creep. Microgully walls and microterrace “risers”, but not the entire outcrop face of the Graneros Shale, develop a thin (1–2 mm), white (5Y 8/1) and dark gray (5Y 4/1) gypsum crust in dry weather, particularly when the crusts on the Dakota Formation are prominent. The Graneros Shale crust has a rough upper surface and a smoother underside that is studded with included shale chips.

4.3. Water and soil pH

The pH of the weathered shale and mineral crusts on both the Dakota Formation and the Graneros Shale is strongly acidic, generally less than pH 2.5 (Fig. 4). Samples of weathered shale from the Dakota Formation at the outcrop ranged in pH from 1.8 to 2.4 (except for a sample contaminated with Greenhorn Limestone, which eventually evolved a pH of 6.3: Fig. 4), and their pH values did not change significantly after 30 min in distilled water (Fig. 4). Likewise, the samples of Graneros Shale are acidic (pH 2.1–2.4) and have stable pH values after 30 min (Fig. 4). Along the highway shoulder, subsoil material derived from either of the geological units is also acidic, although the probably imported topsoils may not be (Fig. 4). In the laboratory, samples of the yellowish sulfate material in thick Dakota Formation crusts from site 1 dissolve quickly in distilled water at room temperature and produce a distinctly yellowish to brownish, acidic solution (pH 1.3–2.2) containing only a small amount of remnant, very dark grayish brown (10YR 2/2) particulate matter. The pH of such solutions decreases over time, indicating minimal buffering capacity, probably due to the hydrolysis of Fe^{3+} and Al^{3+} . However, the surrounding soils and geological materials (particularly the Greenhorn Limestone) readily neutralize the acidity of both the weathering products and the drainage waters. Furthermore, acidity from such point sources as single outcrops likely would be diluted with increasing magnitude of precipitation and runoff. No stream or lake waters in the immediate vicinity of the study sites have pH values below 7. Cemented sand crusts from site 2 also produced acidic pH values, ranging from 1.5 to 2.5 (Fig. 4).

4.4. Microbiology

Media were inoculated with moist weathered shale samples taken from site 1. After 10–15 days, Fe oxidation was indicated by color changes in inoculated media relative to uninoculated media. The inside walls of test tubes containing inoculated media became coated with reddish brown hydrous Fe-oxide precipitates, whereas inoculated broth in shaker flasks became turbid and turned light brown. In both types of media, cultured media exhibited accelerated oxidation of Fe relative to uncultured media. Furthermore, a neutral-pH medium showed no growth when inoculated with either raw samples or previously cultured organisms. These preliminary results indicated that Fe-oxidizing, acidophilic microbes dominated.

Observations of culture samples with an optical microscope indicated Gram-negative aerobic microbes, and a tentative visual count of 3.5×10^9 cells/g of soil. Two bands were eventually obtained by DGGE, one showing phylogenetic similarity to *Acidithiobacillus ferrooxidans* (similarity index=0.747) and the other showing strong similarity to *Flavobacterium* sp. or *Cytophaga* sp. (similarity index=0.875). *A. ferrooxidans* has frequently been implicated in rapid pyrite oxidation (Nordstrom, 1982; Van Breemen, 1982; Nordstrom and Southam, 1997), and therefore a microbial role in the oxidation of pyrite at the study sites was anticipated. The significance of the co-occurring bacteria *Flavobacterium* or *Cytophaga* of the Order Cytophagales (Stanier, 1947; Mitchell et al., 1969; Oyaizu and Komagata, 1981), however, is uncertain. Cytophagales are obligate aerobes that exhibit gliding motility, can adapt to low nutrient levels (Höfle, 1982, 1983), and probably subsist by degrading biomacromolecules, such as cellulose. They exist in a wide variety of natural environments.

5. Discussion and interpretation

5.1. Comparison of pyrite weathering and mineral transformations

Pyrite weathering can occur rapidly if liquid water and oxygen are readily available in the near-surface

environment. For example, Bryant (1981) detected a major decrease in soil pH (6.3 to 2.3) and a simultaneous precipitation of appreciable amounts of jarosite at the soil surface in greenhouse studies of fresh, pyritic lignite overburden subjected to only a few months of wetting and drying. Similarly, Van Breemen (1982) stated that decreases in soil pH from 7 to 4 can occur within a month if pyritic material is well-exposed to the atmosphere (as at site 1), although the rate of pyrite oxidation is limited by the rate of oxygen diffusion into wet soils. Therefore, the conspicuousness of weathering products at site 1, although impressive, is not unexpected given that as much as 2% of the uppermost Dakota Formation consists of pyrite.

There are distinguishing features of the weathering environments described herein. First, soluble sulfate minerals are present in surface crusts, but relatively insoluble jarosite, so typical in many acid-sulfate soils, is absent. Second, Fe^{2+} sulfates such as rozenite [$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$], szomolnokite [$\text{FeSO}_4 \cdot \text{H}_2\text{O}$], and melanterite [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$], which have been identified in several other cases of pyrite weathering (e.g., Van Breemen, 1973; Zodrow and McCandlish, 1978; Nordstrom, 1982; Wagner et al., 1982; Young and Nancarrow, 1988; Jambor et al., 2000), were not observed in the crusts during our study. The absence of these minerals indicates relative undersaturation of drainage waters with respect to Fe^{2+} during the formation of the Dakota Formation crusts. Direct formation of aluminocopiapite from pyrite was proposed by Zodrow et al. (1979), and a similar phenomenon may apply to the formation of the copiapite described in this study. Third, the pH of the Dakota Formation weathering regime is lower than those recorded in many acid-sulfate soil profiles, although not strictly unfavorable to the precipitation of jarosite, which also depends on the activities and concentrations of its constituent ions. Lower pH values in pyritic weathering profiles are generally interpreted to be the result of the initial, very active stages of pyrite oxidation (e.g., Van Breemen, 1973; Carson et al., 1982; Charoenchamratcheep et al., 1987). Fourth, the formation of new minerals at the main Fairbury study site is limited to times of favorable weather conditions.

The soluble Fe-sulfate minerals identified in Dakota Formation crusts appear in quantity only in

dry regions, such as northern Chile and North Greenland, where sulfide minerals have undergone oxidation and where the products of that weathering are not regularly removed by meteoric dissolution (e.g., Bandy, 1938; Jakobsen, 1989). Wagner et al. (1982) and Van Breemen (1973) described the ephemeral nature of soluble sulfates in acid-sulfate soils of humid regions and the connection with the early stages of pyrite oxidation. Similarly, Youngson (1995) and Keith et al. (1999) described rainfall-dependent, seasonal formation of soluble sulfate-mineral crusts in New Zealand and California. Zodrow et al. (1979) proposed a cyclic sulfate-mineral paragenesis in the Sydney Coalfield (Nova Scotia, Canada) that is linked directly to seasonal changes in rainfall, temperature, and atmospheric humidity. Later work by Zodrow (1980) found that copiapite-group minerals were “the most resistant to seasonal changes” in weather, whereas other hydrated sulfate minerals only appeared in the summer. Nordstrom (1982) implied that copiapite formed by the oxidation of rozenite and szomolnokite, following their formation by the dehydration of melanterite. Similarly, Zodrow et al. (1979) proposed aluminocopiapite formation from melanterite through a rhomboclase or fibroferrite precursor, although it was also proposed that aluminocopiapite would form directly from pyrite in some cases.

The Al sulfates at site 1 are similar in their origins and their responses to ambient humidity-weather and dissolution. Martin et al. (1999) identified alunogen and meta-alunogen, as well as halotrichite, melanterite, tamarugite [$\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$], and other minerals, in efflorescences near geothermal vents at Te Kopia, New Zealand, where the pH of the water is as low as 2–3. Formation of alunogen was attributed to the breakdown of kaolinite by acid waters, and it was also noted that the mineralogical composition of efflorescences was dependent on the amount of local rainfall. At Te Kopia, however, halotrichite, melanterite, and tamarugite are present only during dry periods, whereas alunogen and meta-alunogen are more resistant to dissolution even though they are readily dissolved by excess moisture. In general, however, the occurrence of Al sulfates and associated minerals described by Martin et al. (1999) resembles the mineralogy and setting of site 1, at which the dissolution of clay minerals may be a source of Al.

Although the Graneros Shale contains pyrite and produced an acid solution in the laboratory, only gypsum has formed in the mineral crusts. Parts of the Graneros Shale are strongly calcareous, in contrast to the Dakota Formation. Calcium is released from Graneros Shale and from the Greenhorn Limestone as they weather. Thus, gypsum is likely to form preferentially to any other sulfate mineral.

5.2. Implications for hydrogeology and engineering geology

At site 1, the formation of widespread sulfate crusts above a layer of weathered shale indicates transportation of dissolved ions in diffusely discharging soil water and shallow groundwater, followed by evaporation at the land surface over periods of several days to weeks. Microbial pyrite oxidation is probably taking place at some depth, and not merely at the land surface.

The pyrite weathering described here may have only a transient effect on the pH of local surface water and regional groundwater because of the neutralizing capacity of other soils and unaffected waters, yet its hydrogeochemical significance may be greater than these observations indicate by themselves. The dissolved sulfate produced by the dissolution of pyrite, or liberated by the dissolution of surface crusts of sulfate minerals, may be a primary source of that ion in groundwaters. This hypothesis is made more credible by the first author's observation of persistent oxidized zones a meter or more thick in the weathered zones of Cretaceous pyritic shales and sandstones (Dakota Formation, Carlile Shale, Pierre Shale) at many localities in Nebraska and adjacent states. There are obvious precedents elsewhere for a linkage between the weathering of pyritic shale and the groundwater chemistry (including salinity levels) at a local to regional scale (e.g., Mermut and Arshad, 1987).

The Jefferson County sulfate crusts contrast strongly with those of more widespread and well-documented soil-surface crusts of thenardite and halite associated with groundwater discharge from the Dakota Formation in the Salt Basin (Fig. 1), about 100 km northeast near Lincoln, Nebraska (Joeckel and Ang Clement, 1999). Variability in water chemistry in the Dakota Formation aquifer is probably the product

of the difference in local flow systems, as well as possible input of solutes from the dissolution of distant evaporites in other geological units (Gosselin et al., 2001).

Weathering processes at work at site 1 may have general implications in engineering geology. A road failure and landslide at the site in the early 1970s was the product of the site's overall hydrology and stratigraphy, but weathering geochemistry may have been a contributing factor. The growth of sulfate minerals at the outcrop surface definitely accelerates physical weathering by the expansion of the shale mass. Alunogen, for example, has been shown to make a slight contribution to rock weathering during wetting and drying cycles, although alum salts have stronger effects (Williams and Robinson, 1998).

The laboratory observation of rapid and thorough disintegration of Dakota Formation shales from site 1 under atmospheric humidity and in slaking tests with deionized water imply potential engineering problems. Long-term maintenance of slopes and the control of erosion at site 1 or similar sites might be problematic, particularly under the constraint that extremely low soil-pH places on any potential seeding of the slopes. Other observations raise similar concerns. Broken fragments of asphalt from an earlier (pre-1982) highway roadbed at site 1 are heavily encrusted with yellowish sulfates and appear to have undergone appreciable external weathering. Also, gypsum produced by the liberation of SO_4^{2-} after pyrite weathering is growing readily in cracks in shallow (<30 cm) subsoil materials immediately adjacent to the current highway. Site 2 also illustrates that dissolved ions produced by weathering, particularly SO_4^{2-} , can be wicked upward on road shoulders and under road beds. This phenomenon should be considered as a potential threat to the stability of the road grade, or to any concrete structures in the area, by virtue of its potentially destructive expansion properties.

6. Summary and conclusions

The suite of efflorescent sulfate minerals found at the Fairbury sites is the result of a series of processes (Fig. 12A). Shallow groundwater discharge by evaporation and recharge by precipitation are the driving

forces. Observations of crusts over large areas at site 1 indicate that most pyrite oxidation probably occurs below the land surface (perhaps millimeters to tens of centimeters). The oxidation seems to be catalyzed by *A. ferrooxidans*. Acid rock-drainage waters are produced, and dissolved Fe^{3+} and SO_4^{2-} in shallow groundwater are transferred to the land surface by evaporation. The Al is probably produced by weathering of clay minerals in an acidic environment and likewise is transported to the land surface. Calcium is also moving upward to the land surface, and is derived from the dissolution of calcite in the overlying Graneros Shale and Greenhorn Limestone. Episodic surficial precipitation, dissolution, and removal of a restricted suite of soluble, hydrated Fe^{3+} - and Al-sulfate minerals, some of which are formed by the progressive dehydration of precursor sulfates (Fig. 12B), follow during dry weather, especially during droughts. Gypsum precipitates first, followed by more highly hydrated Fe and Al sulfates, and then by less highly hydrated sulfates produced by gradual dehydration (Fig. 12B). For precipitation of Fe- and Al-sulfate minerals to reach its full expression, dry weather must last at least a month. As long as dry weather continues, Fe- and Al-sulfate crusts act as a surface store of acid, which is mobilized with the next rainfall event (Fig. 12A). Direct observations indicate that runoff after rapid and complete dissolution of crusts during rainfall events is the major out-of-system flux of ions, whereas hydrous Fe oxides persist (Fig. 12A). A small amount of deflation of sulfate particles was also observed at site 1.

During intervals of persistent rainfall, the formation of sulfate minerals is suppressed at both sites. The main expression of pyrite weathering in such times at site 1 is the occurrence of hydrous Fe-oxide coatings on fractures and other weathered rock surfaces. Presumably, Fe^{2+} oxidation by *A. ferrooxidans* and hydrolysis dominate during non-drought conditions at site 1 (cf. Nordstrom, 1982).

The occurrence of crusts at site 2 also indicates that dissolved Fe^{3+} , Al^{3+} , and SO_4^{2-} are carried by shallow groundwater slowly discharging from the Dakota Formation, through surficial sediment, and then evaporating. Dissolved constituents at site 2 are being moved farther from their source than at site 1. Site 2 illustrates how local to regional Dakota Formation pyrite oxidation might affect shallow aquifer systems

by the transportation of ions through the Dakota Formation across geological contacts (cf. Veatch, 1969). This scenario is similar to the leakage of Dakota Formation groundwaters through Late Quaternary alluvium in the Salt Basin of Lancaster County, Nebraska, which also produces salt crusts.

Differences in the nature of rock weathering and local to regional groundwater chemistry are reflected in the composition of mineral crusts and efflorescences associated directly or indirectly with the Dakota Formation. The Jefferson County sites and the Salt Basin in Lancaster County (Joeckel and Ang Clement, 1999) together illustrate the range of hydrogeochemistry associated with the Dakota Formation. Significantly, both occurrences involve transfers of sulfate. More comprehensive studies of pyrite weathering, potential acid rock drainage, and interactions between rock and groundwater–surface water in the Dakota Formation will improve the understanding of its hydrogeochemistry and potential as an aquifer. Furthermore, we surmise from our limited study that it is advisable from environmental and engineering standpoints to investigate potential occurrences of human-accelerated acid rock drainage in roadcuts and other excavations through pyrite-bearing shales throughout midcontinental North America.

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