



Chemistry and mineralogy of four acid sulfate soils from Montana, North Dakota, and Wyoming
by Stephen Daniel Blodgett

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Land Rehabilitation

Montana State University

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Abstract:

Four acid sulfate soils from sites in Montana, North Dakota, and Wyoming were studied to determine chemical and physical properties, mineralogy, genesis, and long-term acid-production potential. Chemical characteristics were analyzed by atomic adsorption spectrophotometry (AAS), inductively-coupled plasma emission spectroscopy (ICP), and ion chromatography (IC). Standard methods of soil analysis were used for other properties. Optical techniques, including scanning electron microscopy/energy-dispersive analysis of x-rays (SEM/EDAX) and petrography, were used to identify soil mineralogy. Solubility experiments were performed on selected jarosite samples; results were analyzed with the computer program GEOCHEM.

Three soils are developing on Late Cretaceous Bearpaw or Pierre shale and one is developing on Early Cretaceous Mowry shale. Climate at all sites is continental, with an average of 25-40 cm/yr precipitation. All soils studied are in mid-slope positions.

Vegetative cover ranges from 10 to 70%, with site 2 having the least vegetation and site 3 having the most. All soils contain jarosite and iron oxides and are dominated by smectite clays.

Severe wind erosion is evident at site 1; site 2 has deep gullies from water erosion.

Soil pHs ranged from 3.6 to 5.1. Only site 2 had high levels of soluble salts, alkaline-earth cations, and heavy metals. Each soil contained montmorillonite, illite, and kaolinite clays and jarosite [KFe₃(SO₄)₂(OH)₆], goethite [FeOOH], gypsum [CaSO₄ 2H₂O], gibbsite [Al (OH)₃], and basaluminite [Al₄(SO₄)(OH)₁₀] mineralogy.

Weighted means for total liming rates determined from the sum of acid-base accounts and active (SMP buffer) acidity revealed that soils require from 15 to 56 mt CaCO₃/1000 mt soil to neutralize both current and potential soil acidity. Sulfur forms determined from two different particle sizes (-60 and -200 mesh) showed some statistically significant differences, but not enough to justify the added time and expense of grinding samples to smaller than 60 mesh. Results from solubility experiments indicated that each soil is oversaturated with respect to jarosite. Because of the insolubility of jarosite and semi-arid climate, these soils should produce additional acid very slowly over geologic time. Soils are well buffered due to high smectite clay contents and relatively insoluble iron and aluminum oxides and hydroxyoxides.

However, liming jarositic soils will cause hydrolysis of jarosite to goethite and continuing acid production that must be considered in reclamation.

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FROM MONTANA, NORTH DAKOTA, AND WYOMING

by

Stephen Daniel Blodgett

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Four acid sulfate soils from sites in Montana, North Dakota, and Wyoming were studied to determine chemical and physical properties, mineralogy, genesis, and long-term acid-production potential. Chemical characteristics were analyzed by atomic adsorption spectrophotometry (AAS), inductively-coupled plasma emission spectroscopy (ICP), and ion chromatography (IC). Standard methods of soil analysis were used for other properties. Optical techniques, including scanning electron microscopy/energy-dispersive analysis of x-rays (SEM/EDAX) and petrography, were used to identify soil mineralogy. Solubility experiments were performed on selected jarosite samples; results were analyzed with the computer program GEOCHEM.

Three soils are developing on Late Cretaceous Bearpaw or Pierre shale and one is developing on Early Cretaceous Mowry shale. Climate at all sites is continental, with an average of 25-40 cm/yr precipitation. All soils studied are in mid-slope positions. Vegetative cover ranges from 10 to 70%, with site 2 having the least vegetation and site 3 having the most. All soils contain jarosite and iron oxides and are dominated by smectite clays. Severe wind erosion is evident at site 1; site 2 has deep gullies from water erosion.

Soil pHs ranged from 3.6 to 5.1. Only site 2 had high levels of soluble salts, alkaline-earth cations, and heavy metals. Each soil contained montmorillonite, illite, and kaolinite clays and jarosite $[KFe_3(SO_4)_2(OH)_6]$, goethite $[FeOOH]$, gypsum $[CaSO_4 \cdot 2H_2O]$, gibbsite $[Al(OH)_3]$, and basaluminite $[Al_4(SO_4)(OH)_{10}]$ mineralogy. Weighted means for total liming rates determined from the sum of acid-base accounts and active (SMP buffer) acidity revealed that soils require from 15 to 56 mt $CaCO_3/1000$ mt soil to neutralize both current and potential soil acidity. Sulfur forms determined from two different particle sizes (-60 and -200 mesh) showed some statistically significant differences, but not enough to justify the added time and expense of grinding samples to smaller than 60 mesh. Results from solubility experiments indicated that each soil is oversaturated with respect to jarosite. Because of the insolubility of jarosite and semi-arid climate, these soils should produce additional acid very slowly over geologic time. Soils are well buffered due to high smectite clay contents and relatively insoluble iron and aluminum oxides and hydroxyoxides. However, liming jarositic soils will cause hydrolysis of jarosite to goethite and continuing acid production that must be considered in reclamation.

INTRODUCTION

Acid sulfate soils are characterized by pH values below 4 and mineralogies dominated by iron and aluminum hydroxy-sulfates, hydroxides, and oxides (van Breeman 1982). These soils are classified separately from conventional acid soils (e.g., certain forest soils) in recognition of their very low pH values and sulfate mineralogy inherited from oxidized sulfidic material (SCS staff 1987). Most of these soils are concentrated in tidal flats, estuaries, coastal plains, and swamps near the equator or in warm, moist environments (van Breeman 1982, Pons et al. 1982). However, recent research has identified acid sulfate soils in Texas (Carson et al. 1982) and in the semi-arid Northern Great Plains (Curtin and Mermut 1985, Bingham et al. 1984, Patterson and Arndt 1984, Opdahl et al. 1975).

Jarosite, a common mineral in acid sulfate soils, is frequently found in Cretaceous shales of Montana (Dr. R. B. Berg, pers. comm., 1988) and Wyoming (Dr. J. D. Love, pers. comm., 1988). In North Dakota, jarosite is sufficiently widespread to be used as a marker horizon for mapping the contact between the Pierre shale and Fox Hills sandstone (Feldman 1972, Daly 1984). Gypsum is commonly associated with jarosite in these shales.

Although acid sulfate soils developing on Cretaceous shales have been classified in Montana (e.g., Dilts, Julin, and Vaeda series in Veseth and Montagne 1980), little is known about the chemistry, mineralogy, and genesis of such soils in semi-arid environments.

Most of the research on acid sulfate soils has been done in the tropics (van Breeman and Harmsen 1975, Pons 1972). Researchers from the Northern Great Plains (Bingham et al. 1984, Patterson and Arndt 1984, Opdahl et al. 1975) and elsewhere (Pons 1972, Brinkman and Pons 1972, Rorison 1972) have noted the extreme infertility of acid sulfate soils. Consequently, detailed information on semi-arid acid sulfate soils is necessary to successfully reclaim these soils.

Objectives

Acid sulfate soils from two sites in Montana, one in North Dakota, and one in Wyoming were investigated to

1. identify the dominant minerals from each soil;
2. determine the factors causing acidity in each soil; and
3. predict long-term acid-production potential of each soil.

LITERATURE REVIEW

History

Acid sulfate soils have been recognized by agriculturists for centuries and have been the object of scientific study since the early 18th century (Pons 1972). Most of the original research on acid sulfate soils was performed in The Netherlands where the Dutch had become interested in the peculiar soils that developed in tidal flats reclaimed from the Zuidersea. In 1735, Linnaeus described two types of clay containing sulfuric acid while he was classifying rocks, minerals, and soils in Holland (in Pons 1972). Le Franc van Berkhey published a natural history of Holland in 1771 in which he distinguished two types of "cat clay", a term used to refer to sulfidic peats or muds long known to Dutch farmers (in Pons 1972). The term "cat" is from the Dutch vernacular of the 18th century and is connotative of harmful, evil, or mysterious qualities. Acid sulfate soils frequently appear to be fertile when they are drained, with high organic matter contents and close geographic association with productive soils. When Dutch farmers drained and plowed these "cat clays" the resulting soils proved to be remarkably infertile, and the farmers had been deceived by the original appearances. Elsewhere in northern Europe and throughout the world in coastal plains and deltas, mystery and evil are associated with vernacular names for these acidic soils (Pons 1972).

Genesis and Distribution of Acid Sulfate Soils

Acid sulfate soils develop when pyritic sediments in marshes, deltas, and alluvial and tidal flats are exposed to the atmosphere and pyrite is oxidized to ferrous sulfate, ferric oxide, jarosite, and sulfuric acid. These soils have pH values near 4 somewhere within the upper 50 cm of the soil profile and are usually poorly drained, highly pyritic, and contain mottles of jarosite and iron oxides (van Breeman 1982). Jarosite may persist in acid sulfate soils many years after reclamation (Verhoeven 1972).

Millions of hectares of acid sulfate soils and potential acid sulfate soils occur in recent coastal plains (van Breeman 1982). Although most of these soils are in tropical or moist environments, other acid sulfate soils have been described at coal and metal mines (Smith and Sobek 1978) and in semi-arid environments on the Great Plains (Patterson and Arndt 1984). Recent descriptions of soils with acid sulfate mineralogy from eastern Montana (Bingham et al. 1984), southwest North Dakota (Opdahl et al. 1975, Patterson and Arndt 1984), and Wyoming (unpublished SCS soil mapping of Weston County, Wyoming) indicate that acid sulfate soils occur in the semi-arid continental interior of the United States. These soils resemble traditional acid sulfate soils, with pH values ranging from 3 to 5, prominent stringers or mottles of jarosite, and iron- and aluminum-oxide mineralogy (Patterson and Arndt 1984). They differ from traditional acid sulfate soils in their weathering rates, moisture regimes, and lack of pyrite (SCS staff 1987).

Pyrite Formation

Sources and forms of iron and sulfur are two major factors in sedimentary sulfide fixation (Rickard 1972). Iron comprises approximately 5.1% of the lithosphere (Lindsay 1979). Sources of iron for sulfide fixation are primarily ferric oxides and oxyhydroxides. These compounds are supplied to the pyritization environment (in which either pyrite or marcasite may form, depending on physicochemical conditions) as solid-phase and amorphous components that are readily adsorbed on organic matter and fixed in inorganic matter by several exchange and adsorption mechanisms. Subsequent reactions with organic matter in sediments may release dissolved ferrous iron.

Sedimentary sulfide production occurs almost entirely through sulfate reduction by bacteria. Heterotrophic sulfate-reducing bacteria of the genera Desulfovibrio and Desulfotomaculum use sulfur-containing organic molecules (mainly amino acids and proteins) as energy sources (Rickard 1972). These bacteria are obligate anaerobes but otherwise they tolerate a wide range of physical and chemical conditions, with pHs from 5 to 9, Eh (redox potentials) from +80 to 400 mV (millivolts), temperatures from 0 to 70°C, and NaCl concentrations of 0 to 12% (Rickard 1972). Such broad tolerances explain the ubiquity of these bacteria in all anaerobic, sulfidic aqueous environments. Anaerobic sulfide-containing zones are commonly found beneath the surface in marine and fresh-water sediments, and in many soils.

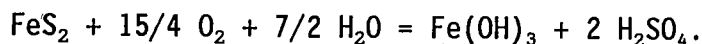
Pyrite Oxidation

Pyrite oxidation is a complex biogeochemical process that involves several redox reactions and microbial catalysis (Nordstrom 1982b). Because oxidized pyrite imparts acidity and secondary mineralogy to acid sulfate soils, understanding pyrite oxidation is crucial to interpreting such soils.

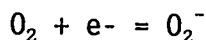
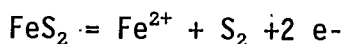
Aeration initially oxidizes pyrite in soils. Below a pH of 4, Thiobacillus ferrooxidans is the bacterium responsible for pyrite oxidation (Arkesteyn 1980). Non-biological processes (e.g., oxidation of Fe^{2+} to Fe^{3+} , exposure to O_2) initially reduce soil pH from 7 to 4; bacteria probably play a minor role in this initial pH decrease. Although several heterotrophic thiosulfate oxidizers (e.g., Thiobacillus thiooxidans and Thiobacillus thioparus) are found in soils with pH values from 4 to 7, Arkesteyn (1980) concluded that they do not accelerate pyrite oxidation in soils. However, Nordstrom (1982b) cited studies indicating that Thiobacilli may be involved in pH decreases from 7 to 4.

Pyrite is initially oxidized by atmospheric oxygen, with subsequent decreases in pH depending on the oxidation rate of sulfur to sulfate. Below a pH of 4.5, ferric iron becomes more soluble, begins to act as an oxidizing agent, and becomes the only important inorganic oxidizer of pyrite below a pH of 3. At pH values below 4, ferric iron and Thiobacilli are the primary pyrite oxidizers (Nordstrom 1982b, Ivarson et al. 1982).

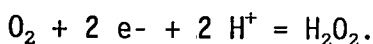
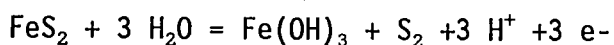
Nordstrom (1982b) summarized the overall stoichiometry of pyrite oxidation as follows:



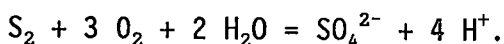
In acid media ($\text{pH} \leq 3$) the reactions are



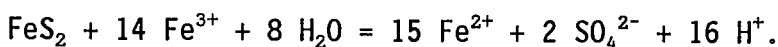
In slightly acid to basic media ($\text{pH} \geq 4$) the reactions are



The acid-generating phase is



The catalytic phase is



These reactions indicate that ferric iron, sulfate, and acidity are produced when pyrite is oxidized. Above a pH of 4, the inorganic rate-limiting steps are pH-dependent; below a pH of 3, oxidation rates are independent of pH changes. For pHs between 3 and 4, the rate-limiting steps may or may not be dependent on pH, according to the secondary minerals (iron hydroxy-sulfates, iron oxides and hydroxides, aluminum hydroxy-sulfates, and clays) present and the resulting solubility relationships (Nordstrom 1982b).

Pyrite reactivity is a function of particle size and surface area. Most sedimentary pyrite consists of aggregates of particles with diameters ranging from 0.1 to 1 μ (microns) (van Breeman 1972). Aggregate diameters range from 10 to 40 μ . These aggregates (framboids) exhibit the largest specific surface area (an average of

105 cm²/g for framboids of 30 μ diameter) of all the crystalline forms of pyrite (van Breeman 1972). Stumm and Morgan (1981) noted that increasing standard free energy, decreasing stability, and lattice defects also make pyrite more reactive as particle size decreases and surface area increases.

In some pyritic soils, oxidation does not proceed readily, and pyrite may persist for years, even though the soil is exposed to the atmosphere (Harmsen et al. 1954). Pyrite preservation in these soils probably results from larger particle size (10-100 μ diameter) and relatively high pH (van Breeman 1972).

The most important oxidant for pyrite is atmospheric oxygen (van Breeman 1972); however, at pHs from 1 to 4, microbial oxidation of Fe²⁺ to Fe³⁺ is much more efficient than oxidation by free oxygen. Near neutral pH, the rate of pyrite oxidation is slow. Optimum conditions for pyrite oxidation in soils are moisture content near field capacity, temperatures from 10 to 30°C, and soil flocculation sufficient for diffusion of O₂ through the soil profile (van Breeman 1972).

Iron Mineralogy and Chemistry

Several iron minerals, ranging from very insoluble iron hydroxides to very soluble hydrated iron sulfates, may form as a result of pyrite oxidation (Nordstrom 1982b, Schwertmann and Taylor 1977). The following relatively insoluble iron minerals are common in acid sulfate soils (van Breeman 1972):

Goethite FeOOH,

Hematite Fe₂O₃,

Potassium jarosite $KFe_3(SO_4)_2(OH)_6$,

Amorphous iron oxides and hydroxides.

Several highly soluble iron sulfate minerals can form in oxidizing pyritic material, but most of these minerals are removed by leaching in humid environments (van Breeman 1972).

Jarosite

Jarosite is classified in the hexagonal-ditrigonal (pyramidal) system and is characterized by a Mohs hardness of 2.5 to 3.5 and a specific gravity of 2.9 to 3.3 g/cm³. Jarosite is the most common product of pyrite oxidation and may form within weeks after pyritic material is exposed to the atmosphere (Bloomfield and Coulter 1973). A general formula for jarosite is $AB_3(SO_4)_2(OH)_6$, where

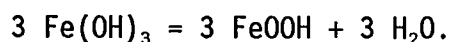
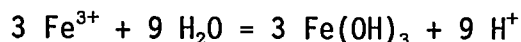
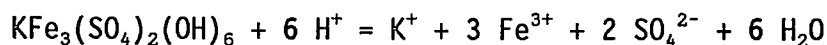
A= Univalent site containing K^+ , Na^+ , Pb^{2+} , NH_4^+ , or H_3O^+

B= Trivalent site containing Fe^{3+} or Al^{3+} (alunite).

In the univalent A site, substitution results in a continuous K^+ - Na^+ - H_3O^+ solid-solution series (Brophy and Sheridan 1965). Jarosite has been found as a pseudomorph after pyrite, indicating direct alteration of pyrite to jarosite. More commonly in soils, jarosite precipitates directly from solution at a pH of 4 if the activities of SO_4^{2-} , K^+ , and Fe^{2+} are adequate (van Breeman 1972). Brophy and Sheridan (1965) concluded that a strong preference exists for K^+ over Na^+ or H_3O^+ in the univalent position of the crystalline structure of jarosite. Only after K^+ is almost totally depleted will Na^+ be incorporated into the crystal structure. Hydronium jarosite is rare and persists only under low sodium conditions

(Brophy and Sheridan 1965). Aluminum (Al^{3+}) can substitute for Fe^{3+} in the trivalent B site to form the mineral alunite $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$. However, Brophy et al. (1962) performed experiments that indicate a strong preference for the uptake of Fe^{3+} over Al^{3+} into the jarosite structure.

Jarosite is stable under strongly oxidized (Eh= 0.5 to 1.2 volts) and acidic (pH= 2 to 4) conditions (van Breeman 1982, Lindsay 1979). Increasing pH will lead to hydrolysis of jarosite and the production of ferric oxide, SO_4^{2-} , and K^+ . Hydrolysis of jarosite may also lead to acid production through the following reactions, providing that the upper limit of Fe^{3+} activity is controlled by jarosite (van Breeman 1972):



Thus, 1 mole of jarosite may produce a net 3 moles of H^+ , with a final hydrolysis product of goethite or hematite. This reaction is believed to occur very slowly, but could result in significant acid production over geologic time (van Breeman 1972). The solubility product (K_{sp}) for jarosite has been reported by Lindsay (1979) and Vlek et al. (1974) as -98.5, indicating that jarosite is only sparingly soluble.

Jarosite Identification

Jarosite can be positively identified by x-ray diffraction, with diagnostic d-spacings producing peaks at 3.08 and 3.11 angstroms. Carson et al. (1982) report that jarosite gives a strong endothermic peak at

416°C in differential thermal analysis (DTA) and that scanning electron microscopy (SEM) can provide useful information in genesis and weathering studies of jarosite. Another useful tool for jarosite identification is energy-dispersive analysis of x-rays (EDAX), which can provide bulk-chemical analyses that can be used to suggest stoichiometry.

In the field, jarosite is characterized by yellow color with a common Munsell hue of 5 Y, values from 6 to 8, and chromas from 4 to 6 or more (Carson et al. 1982). In a soil from Thailand, van Breeman and Harmsen (1975) report jarosite with a Munsell color designation of 2.5 Y 8/4. Because jarosite is commonly found in association with goethite, hematite, and amorphous iron and aluminum oxides, colors of these mineral associations may range from pale yellow to brown, reddish-brown, or even gray (van Breeman and Harmsen 1975). Consequently, color alone is not sufficient to identify either jarosite or iron oxides.

Begheijn et al. (1978) describe methods for analyzing sulfur compounds in acid sulfate soils that can be used for semi-quantitative determinations of jarosite and other dominant sulfur fractions. Vlek et al. (1974) developed a modified EDTA method to determine the solubility product of various iron hydroxides and jarosite. Energy-dispersive analysis of x-rays can be used with a standard to provide reasonably accurate estimates of jarosite stoichiometry (Dr. Vernon Griffiths, pers. comm., 1988). However, because this technique cannot analyze elements below sodium in the periodic table, determinations of jarosite

stoichiometry by EDAX must be considered estimates. These estimates may be useful in suggesting a range of jarosite composition.

Aluminum Mineralogy and Chemistry

The role of aluminum in acid sulfate soils has been emphasized in the past three decades (Coleman and Thomas 1967, Frink 1972, McLean 1976). Aluminum is the most abundant metallic element in the earth's crust and is commonly found in soils as aluminosilicates, hydroxides, and hydroxyoxides (Hsu 1977). Several researchers in the 1940s discovered that "hydrogen clays" that impart acidity to soils rapidly decompose to form clays partially saturated with aluminum (Coleman and Thomas 1967). Aluminum can form a series of soluble monomers and polymers with the hydroxyl ion (Frink 1972, Bohn et al. 1985), but establishes few other stable complexes with ions usually present in soil solutions (Frink 1972).

Several insoluble aluminum hydroxy-sulfate minerals may occur in acid sulfate soils (Adams and Rawajfih 1977, Nordstrom 1982a). Whereas gibbsite $[Al(OH)_3]$ and kaolinite $[Al_2Si_2O_5(OH)_4]$ commonly regulate aluminum concentrations in natural waters and non-acid soils, the presence of sulfate can alter these solubilities under acid conditions (Nordstrom 1982a). Among the less soluble aluminum minerals likely to cause sulfate retention in acid soils are jurbanite $[Al(SO_4)(OH) \cdot 5H_2O]$, alunite $[KA_3(SO_4)_2(OH)_6]$, and basaluminite $[Al_4(SO_4)(OH)_{10} \cdot 5H_2O]$ (Nordstrom 1982a). Adams and Rawajfih (1977) provide strong evidence that one or more of these insoluble aluminum hydroxy-sulfate minerals controls sulfate retention in acid soils.

METHODS AND MATERIALS

Soil samples were collected from 3 pits at each of 4 sites. Site 1 is southwest of Glasgow in Valley County, Montana; site 2 is northwest of Forsyth in Rosebud County, Montana; site 3 is south of Marmarth in Bowman County, North Dakota; and site 4 is south of Newcastle in Weston County, Wyoming. See Figure 1 and Site Characterizations for exact locations.

Sample Collection and PreparationCollection

Three soil pits were dug at each site with a stainless steel sharpshooter shovel. Soil samples weighing from 0.5 to 1.5 kg were collected from 0 to 2 cm, 2 to 10 cm, 10 to 20 cm, 20 to 30 cm, 30 to 40 cm, and 40 to 50 cm depths. Samples were scooped into bags from soil-pit walls that had been scraped with a plastic trowel to prevent cross-contamination. In the field all samples were stored in coolers with ice until they were returned to the lab and stored in a freezer.

Vegetation samples were collected at each site. Plots were laid out adjacent to each soil pit, plants within each plot were identified, and total plant cover was estimated. Some plants were collected for later identification.

Preparation

After the samples were air dried, suspected jarosite and iron oxides were scraped off shale fragments from samples collected from 30 to 40 and 40 to 50 cm depths in each of 12 pits. These sub-samples were crushed by mortar and pestle for analysis in x-ray diffraction, scanning electron microscopy, energy-dispersive analysis of x-rays, and controlled dissolution solubility experiments. In addition, several shale plates from 30 to 40 and 40 to 50 cm depths in pits at extremely acid sites 2 and 4 were prepared as thin and polished sections. Remaining dried samples were flailed to -2 mm size by a small mechanical hammer mill. These samples were used for all other analyses.

Mineral Identification

Techniques used to identify soil and bedrock shale mineralogy include macroscopic hand-specimen analysis, XRD analysis of random powder mounts and oriented clay samples, transmitted- and reflected-light petrographic microscopy, SEM, and EDAX.

Macroscopic Identification

Some minerals like gypsum and jarosite are readily identified in hand specimens. Gypsum forms characteristic diamond-shaped crystals that are easily scratched by a fingernail (Hurlbut and Klein 1977). Jarosite precipitates as distinctive, pale to bright yellow, earthy masses and stringers in acid sulfate soils (van Breeman 1982). Although gypsum and jarosite were visually identified in many samples, other techniques were used for verification.

Iron oxides like goethite and hematite exhibit distinctive yellow, brown, or reddish-brown cutans or mottles in many acid sulfate soils (van Breeman and Harmsen 1975). These weathering products were identified in the field, but additional techniques were used for verification.

X-ray Diffraction

In x-ray diffraction analysis, crystalline minerals produce characteristic peaks in accordance with their d-spacings (Brown 1961). Some minerals not easily identified by optical techniques (e.g., basaluminite) yield diagnostic peaks in XRD analysis. Clay minerals are identified in XRD analysis by preparing oriented slides that take advantage of the horizontal stacking of tetrahedral and octahedral sheets in layer silicates (Grim 1968). The technique of Taskey and Harward (1979) was used to prepare clay slides and interpret XRD results. Samples containing suspected jarosite, gypsum, and iron oxides were crushed by mortar and pestle and affixed to glass slides as random powder mounts for XRD analysis.

Many iron and aluminum oxides and hydroxides are amorphous and are not amenable to diagnosis by XRD (Hsu 1977, Jackson 1965). Amorphous oxides and hydroxides are usually intimately mixed with crystalline minerals in soils (Hsu 1977). Because of this association, identifying and quantifying amorphous materials is difficult. Diagnostic d-spacings for all minerals identified were taken from Johnson and Vand (1968).

Microscopy

Transmitted-light. Transmitted-light petrographic microscopy is widely used to identify non-opaque minerals (Larsen and Berman 1934). Thin sections were prepared from shale samples (30 to 40 and 40 to 50 cm depths) from sites 2 and 4. Three thin sections from each site were examined.

Reflected-light. Six polished sections were prepared, three each from sites 2 and 4. Reflected-light microscopy is used to identify opaque minerals (Short 1940, Ramdohr 1969). Pyrite is an opaque mineral that exhibits several optical properties making it amenable to identification by ore microscopy. However, framboidal pyrite is frequently too small ($< 2 \mu$ diameter) to permit optical identification (Ramdohr 1969). Rubey (1929) mentioned visible pyrite in the Mowry shale, but he gives no details. Davis (1963) noted that pyrite is uncommon in the Mowry, although jarosite is frequently found in the Mowry above the water table.

SEM/EDAX. Scanning electron microscopy was used for examining the micromorphology of soil minerals to better understand weathering processes and mineral associations (Kittrick 1965). Eight samples of suspected jarosite and iron oxides from sites 2 and 4 were crushed and mounted in colloidal graphite atop aluminum disks. Two disks from each site were sputter-coated with carbon; these disks were used for chemical analysis by EDAX. The remaining four disks were sputter-coated with gold, a technique that generally provides better resolution for SEM photography. Each sample was scanned by the electron beam, and the mineralogy of specific particles was verified by EDAX before photographs

were taken. An auxiliary feature of the scanning electron microscope used in this study is the EDAX equipment. This apparatus and its accompanying software allow the user to quickly identify elemental compositions of objects under the focus of the electron beam. For example, accurate distinctions can be made between clays (aluminosilicates), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), jarosite [$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$], goethite (FeOOH), and pyrite (FeS_2). In this study, samples were scanned until particles of suspected jarosite, gypsum, or iron oxides were located. Particle mineralogy was then verified by EDAX. Particles or crystals exhibiting representative morphologies were identified, then photomicrographs were taken at scales that most effectively portrayed these morphologies.

Graphs of EDAX spectra were created for representative particles or crystals; these graphs provide evidence of specific particle mineralogy. In addition, some particles were analyzed by EDAX for bulk chemical composition. These analyses are close approximations of actual chemical composition for a specific particle (Dr. Vernon Griffiths, pers. comm., 1988). Several bulk-chemical analyses were generated by EDAX to suggest a range of composition for jarosite particles (i.e., the relative percentages of potassium, iron, and sulfur).

Chemical and Physical Analyses

Standard techniques for analyzing soil pH, particle-size distribution, electrical conductivity, cations and anions, cation exchange capacity, exchangeable acidity, water-holding capacity, and organic carbon are referenced in Table 1. The following section

discusses specific techniques and equipment used. Many analyses follow the exact procedures outlined by references in Table 1; where these procedures have been modified, changes and reasons are discussed.

Cations and Anions

Saturated paste extracts were obtained from all samples by weighing 150 g of each -2 mm sample into a beaker, saturating with double distilled, de-ionized water, and allowing the paste to sit overnight. Samples were then placed in Buchner funnels and suctioned through number 2 Whatman filters into beakers. This extract was collected and forced through syringes containing 0.2 μ filters to remove solids, particularly aluminosilicates. Two ten-milliliter aliquots were made from each extract. One aliquot was analyzed by atomic adsorption spectrophotometry (AAS) for soluble copper, iron, manganese, nickel, and zinc. Matrices of the other aliquots were stabilized (to prevent microbial growth) for ion chromatography (IC) and inductively-coupled plasma emission spectroscopy (ICP) analysis by adding 0.1 ml of 2 M HCl. The latter samples were analyzed for soluble SO_4^{2-} , and NO_3^- on the ion chromatograph and for Ca, Mg, Na, K, Al, Si, and S on the ICP.

Sulfur Forms and Acid-Base Accounting

Fifty grams of each -2 mm sample were analyzed for sulfur forms (CH2M Hill 1987,). To compare the effects of particle size on sulfur results, each sample was split and ground to -60 and -200 mesh. Samples were then analyzed in a Fisher sulfur analyzer.

Table 1. Soil physical and chemical parameters and references.

Parameter	Reference
Particle-size distribution (hydrometer method)	Day 1965
pH (saturated paste extract)	McLean 1982
Electrical conductivity (" " ")	Rhoades 1982b
Sodium adsorption ratio (" " ")	Richards 1969
Cation exchange capacity (NH ₄ OAc)	Rhoades 1982a
Exchangeable acidity (BaCl ₂ -TEA pH= 8.2)	Thomas 1982
Active acidity (SMP buffer test)	McLean 1982
Organic carbon	Snyder and Trofymow 1985
1/3 and 15-bar moisture	Peters 1965

Organic sulfur was determined by subtracting the sum of hot-water rinse-sulfur, HCl-rinse sulfur, and HNO₃-rinse sulfur from total sulfur. Pyritic (reduced) sulfur was obtained from the nitric acid rinse. Hot-water-rinse sulfur represented soluble sulfate-sulfur, and insoluble sulfate-sulfur was determined from the HCl rinse. Potential acidity was determined from the following equation (CH2M Hill 1987):

$$\text{Potential Acidity} = 31.25(\text{HNO}_3\text{-S} + \text{Organic-S}) + 23.44(\text{HCl-S}).$$

Potential acidity was subtracted from neutralization potential to give the acid-base account (ABA), which is expressed as (±) metric tons of CaCO₃ required to neutralize 1000 metric tons of soil. Further explanation of the ABA is given in Results under Sulfur Forms.

Solubility Experiments

Soil pits at site 4 contained jarosite that most closely resembles classic field descriptions (Bandy 1938, van Breeman and Harmsen 1975, Nordstrom 1982b). Here, jarosite formed earthy masses on shale fragments and was readily collected and prepared for analysis. Two solubility experiments were performed to obtain ion activity products for jarosite from this site. In the first experiment, 0.5 g of jarosite from samples collected from 30 to 40 and 40 to 50 cm depths was added to 100 ml of 0.01 M NaCl solution in eight polypropylene bottles. These samples were mechanically shaken for one month and the resulting solutions were forced through 0.2 μ filters; pH values were then measured in each solution.

In a second controlled dissolution experiment, 0.1 g of jarosite was added to 200 ml of 0.01 M NaCl solution in eight beakers. Solution pH was controlled by a pH-stat (laboratory equipment that maintains a constant pH by dropwise addition of either acid or base) at 4 (for 4 samples) and 4.5 (for the remaining 4 samples). A solution of 0.1 M HCl was added dropwise by the pH-stat to maintain desired pH. Each sample was stirred mechanically and the resulting solution was collected and filtered when no more acid was being added by the pH-stat (i.e., conditions near equilibrium were achieved). Eight solutions from each experiment were analyzed on the ion chromatograph for total SO_4^{2-} and by ICP for total K and Fe. These results were entered into the computer program GEOCHEM (Sposito and Mattigod 1979, Parker et al. 1987) and the predicted activities were used to calculate an ion activity product (IAP) for jarosite. Results from GEOCHEM were plotted

against theoretical jarosite solubility conditions (Figures 17 and 18) to determine the properties of jarosite at site 4.

Slaking Tests

Weathered shales (Cr horizons) and samples from A horizons were assessed for potential slaking and dissolution (Moriwaki 1979). Shale fragments and aggregates from all depths were immersed in beakers of tap water at room temperature and checked daily for dissolution, disaggregation, and other slaking behavior.

SITE CHARACTERIZATIONS

Four sites chosen for soil sampling are described in the following section. For each site, the following attributes have been considered:

1. Physiography
2. Geologic history
3. Climate
4. Parent material
5. Vegetation.

These traits correspond to the five factors that contribute to soil genesis (Jenny 1941). Climatological data are given in Table 2. Detailed field descriptions and classifications for each soil are included in Appendix A. Field notes follow the format established by the Soil Conservation Service staff (1975) for soils mapping. Classifications adhere to the most recent soil taxonomy for soils in the United States (SCS staff 1987).

Site 1

This site is in Valley County, Montana, in NW 1/4 SE 1/4 sec. 36, T. 28 N., R. 36 E., approximately 30 km west-southwest of Glasgow and 1 km southeast of an abandoned bentonite processing plant at the terminus of a Burlington Northern railroad spur (Figures 1 and 2). Bentonite was mined in this area until the 1970s, and hundreds of shallow, mined-out pits provide evidence of past mining.

The area is characterized by gently rolling hills that are dissected by intermittent streams. Major drainages are the North Fork of Little Beaver Creek and the South Fork of Brazil Creek. Several small dammed stock ponds have been created in drainages and depressions in the vicinity. Elevations range from 670 to 760 m.

Table 2. Climatological data for Glasgow (site 1) and Forsyth, Montana (site 2), Bowman County, North Dakota (site 3), and Newcastle, Wyoming (site 4) (National Oceanographic and Atmospheric Administration 1982).

Parameter	Site 1	Site 2	Site 3	Site 4
Mean annual temperature (°C)	5.4	7.5	7.2	8.0
Mean annual precipitation (cm)	28	26	35	37
Mean max. temperature 30-yr period (°C)	11.8	16	16.5	15
Mean min. temperature 30-yr period (°C)	-1.1	-0.5	1.2	2.0
Mean max. precip. 30-yr period (cm)	40	42	53	50
Mean min. precip. 30-yr period (cm)	16	14	20	23
Mean annual wind speed 30-yr period (km/hr)	15	10	10	12
Climate type	Continental	Continental	Continental	Continental



Figure 1. Location map for study sites in Valley Co., MT (1), Rosebud Co., MT (2), Bowman Co., ND (3), and Weston Co., WY (4).

Soils in the study area have developed on Bearpaw shale, a marine deposit from shallow continental seas covering western North America during the Late Cretaceous about 65 million years ago (Kauffman 1977, Berg 1969). The region was covered by the Laurentide ice sheet during continental glaciation in the Pleistocene Epoch approximately 10,000 years ago (Alden 1932, Colton et al. 1961, Fullerton and Colton 1986). Glaciation is believed to have occurred in two stages. The first stage covered Valley County as far south as the Missouri River valley; the second stage was less extensive, reaching only as far south as the Milk

