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Recognizing acid lakes and groundwaters in the rock record

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Abstract

Permian red beds and evaporites in the midcontinent of the United States were formed and altered under the influence of extremely acidic (some with $\text{pH} < 1$) lake waters and groundwaters. Based upon geologic, geochemical, and biogeological data, as well as comparison of these Permian rocks with modern acid lake systems in Australia, we propose criteria for the recognition of the products of acid deposition and diagenesis elsewhere in the rock record. Diagnostic criteria for acidity include high bisulfate and aluminum in fluid inclusions. Other features of these Permian rocks, including possible acid minerals, acidophilic bacteria, red beds, and lack of carbonates, are considered possible, problematic, or ambiguous criteria for acidity. Regardless, recognition of this assemblage of features in other rocks may lead to the discovery of other ancient acid systems. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recent studies have identified significant areas of naturally occurring acid lakes and groundwaters. This important environment has largely gone unrecognized in ancient rocks, but may represent an important setting with paleoclimate implications. Recent studies have described the chemistry, hydrology, mineralogy, and microbiology of some modern acid systems, but the long-term products and processes of acid waters are not well known (e.g., Long and Lyons, 1992). It is essential that a set of criteria be developed for the recognition of acid systems of the geologic past.

Modern natural acid systems are not as well known as anthropogenic acid rain and acid mine waters. One such natural system is acid crater lakes with pHs around 0 caused by outgassing of volcanic H_2S (Delmelle and Bernard, 1994; Rowe, 1991). Another type of natural acid system owes its low pH waters ($\text{pH} < 4$) to sulfide and sulfate weathering in soils and sediments, resulting in acid groundwaters, acid lakes, and acid streams. Examples of this second type are regional acid lake systems in southern Australia (Fig. 1; McArthur et al., 1989, 1991; Long and Lyons, 1990, 1992; Long et al., 1992a,b; Alpers et al., 1992; Macumber, 1992; Benison et al., 2001). There, red-bed siliciclastic sediments host sulfuric acid saline lakes and groundwaters (pHs of 2–4) which precipitate alunite, jarosite, halite, gypsum, opaline silica, and possibly iron oxyhydroxides.

Although some possible acid paleosol features have been described in Tertiary rocks (Kraus, 1998), ancient

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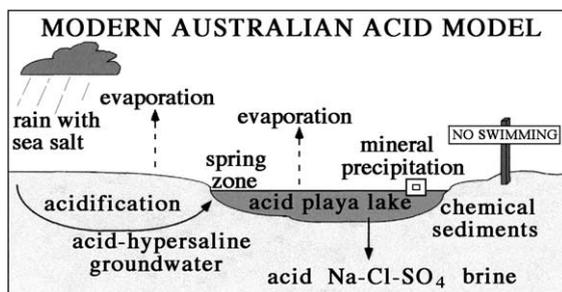


Fig. 1. Model depicting a modern natural acid lake and groundwater system in southern Australia. Acidification may occur in the groundwater by processes such as oxidation of pyrite, ferrollysis, and microbial reduction of iron oxyhydroxides. Modified from Long and Lyons (1992).

(pre-Tertiary) acid systems only recently have been identified (Benison et al., 1998). The objectives of this paper are twofold: (1) to report and describe ancient acid lake and groundwater systems that have been discovered in Permian evaporites and red beds of the US midcontinent region; and (2) to propose criteria for the recognition of acid water deposition and diagenesis in other ancient rocks.

Further investigation of ancient acid systems is warranted. Because modern acid systems form only in response to special geological, chemical, and clima-

tic conditions, their ancient counterparts may give us valuable information about the earth's past. Ancient acid systems may be important in terms of deciphering paleoweathering and paleoclimate trends, and their presence may have important implications for modeling the $p\text{CO}_2/\text{O}_2$ of earth's atmosphere. They may also have far-reaching implications for chemical evolution of groundwaters and red bed formation. The criteria described in this paper should serve only as a first step towards better recognition of ancient acid lake and groundwater settings.

2. Examples from the Permian

Permian red bed-hosted evaporites have a wide extent in North America, occupying much of the surface and subsurface of the midcontinent region (Fig. 2; Walker, 1967). Two such red bed and evaporite units, the Leonardian–Guadalupian Opeche Shale of North Dakota and age-equivalent Nippewalla Group of Kansas and Oklahoma, were the first ancient, extremely acid, sedimentary systems documented (Benison et al., 1998).

Both the Opeche Shale and the Nippewalla Group are composed of bedded halite and red siliciclastic

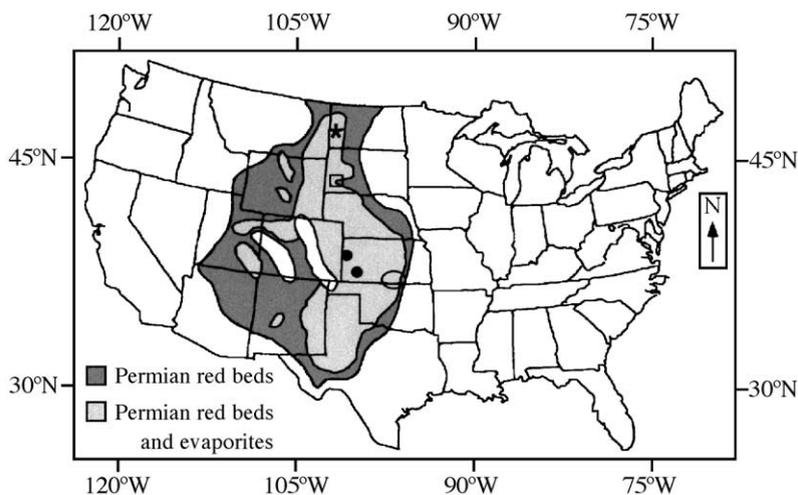


Fig. 2. Map of the USA showing distribution of Permian red beds and Permian red beds and evaporites. Star represents approximate locality of the Gulf-Romanyn 2-33-4B core of the Opeche Shale in western North Dakota. Open square marks area of field study of Opeche Shale in the Black Hills of southwestern South Dakota. Black dots give approximate locations for Nippewalla Group cores: the Atomic Energy Commission 5 core from western Kansas and the Anadarko-Davis 1 core from southwestern Kansas. Open circle marks area of field study of Nippewalla Group in southcentral Kansas and northcentral Oklahoma. Modified from Walker (1967).

mudstone, siltstone, and sandstone. The Nippewalla Group also contains bedded anhydrite and rare grey laminated siliciclastics. Three subsurface cores of the Opeche Shale and Nippewalla Group, as well as surface exposures and shallow cores of the Nippewalla Group, were examined (Fig. 2). Detailed sedimentologic study shows that these rocks were deposited in continental saline pan systems dominated by ephemeral saline lakes, saline mud flats, and dry mud flats (Benison and Goldstein, 2000, 2001).

Primary fluid inclusions are abundant and well preserved in both the Opeche and Nippewalla bedded halites, and are considered to be trapped remnants of Permian lake waters. Chevron and cumulate crystals (in bedded halite) contain alternating inclusion-rich and inclusion-poor growth bands. Most primary inclusions have cubic, negative crystal shapes and are between 5 and 30 μm . In the Opeche halite, many of the primary inclusions are two-phase, liquid–vapor inclusions that had been stretched during burial heating. At room temperature, most primary fluid inclusions in the Nippewalla halite are one-phase, all-liquid inclusions. Some inclusions contain crystals of anhydrite, polyhalite ($\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$), glauberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$), rare magnesite, or nahcolite (NaHCO_3), and at least two unidentified sulfate minerals that were trapped in fluid inclusions during halite growth. Anhydrite is also abundant as solid inclusions in bedded halite.

Displacive halite crystals, which grow from saline groundwaters in mud flats, are clear except for red mud and silt inclusions and large (at least 40–50 μm) isolated fluid inclusions. Because their isolation prevents the evaluation of relationships with other inclusions, these inclusions are ambiguous in origin (Goldstein and Reynolds, 1994). However, it is likely that they represent Permian groundwaters because modern displacive halites, grown in mud from saline groundwater, contain similar isolated fluid inclusions.

Petrographic and geochemical analyses identified mineralogical and geochemical features of the Nippewalla Group and the Opeche Shale (Benison and Goldstein, 2000, 2001). X-ray diffraction, laser Raman microspectroscopy (LRM), staining (Dickson, 1966), and bleaching confirmed mineralogy and presence of organic matter. LRM was also used to analyze the chemical composition of inclusion fluids. Fluid inclusions were analyzed nondestructively in-situ in un-

mounted pieces of halite using the model S-3000 Jobin–Yvon laser Raman microprobe. Alcohol-extracted fluid-inclusion leachates were analyzed using a Dionex 4000i ion chromatograph for the anions Cl, SO_4 , and Br and by a thermal Jerrel Ash polyscan 61E inductively coupled plasma-atomic emission spectrometer for the cations Na, K, Ca, Mg, Sr, Si, Al, and Fe. The PHRQPITZ geochemical model (Plummer et al., 1988) used geochemical and geological evidence to confirm pHs.

Strong evidence for extreme acidity was found in fluid inclusions from the Permian Opeche Shale and

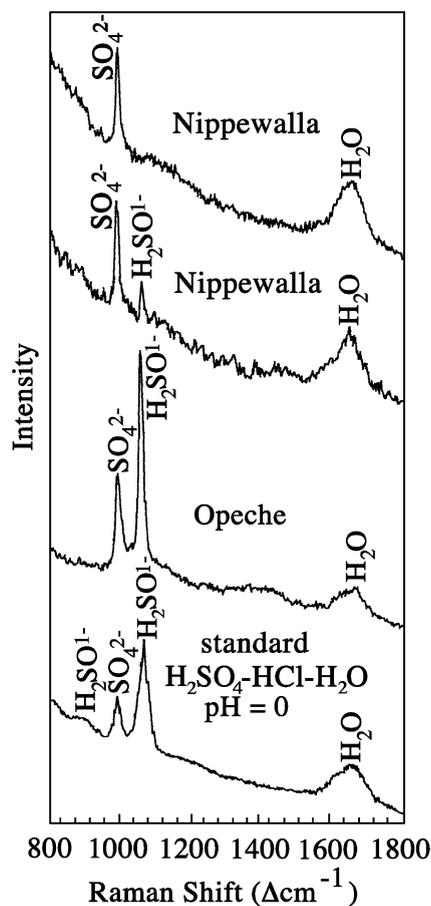


Fig. 3. Laser Raman spectra of H_2SO_4 – HCl – H_2O standard solution with $\text{pH}=0$, inclusion fluid from Opeche Shale bedded halite, and inclusion fluids from Nippewalla Group bedded halite. The HSO_4^- peak in all analyses from fluid inclusions in the Opeche Shale and in some analyses of fluid inclusions in the Nippewalla Group indicate that lake brines were extremely acidic, with pH s less than 1. Modified after Benison et al. (1998).

Nippewalla Group halites. LRM analyses of fluid inclusions detected HSO_4^- , an indication of pHs of less than approximately 1, according to comparisons with known solutions (Fig. 3; Benison et al., 1998). Fluid inclusion leachate analyses have shown high concentrations of Al (up to 2395 ppm), Fe (up to 344 ppm), and Si (up to 999 ppm), characteristic of modern acid waters (Benison, 1997).

3. Recognizing ancient acid–water sedimentary systems

The Permian examples and what is currently known about modern acid systems can be used to construct models for what is diagnostic and suggestive of ancient acid systems.

3.1. Diagnostic criteria

Strong geochemical evidence for extreme acidity was found in the form of LRM analyses and leachate analyses of fluid inclusions in halite from the Nippewalla Group and Opeche Shale. SO_4^{2-} is the dominant sulfur compound found in most natural waters. HSO_4^- is not a predominant sulfur species at pHs greater than 2 (Drever, 1988); it is only found in measurable quantities in extremely acidic, oxidizing waters (Langmuir, 1997). HSO_4^- is only detectable by LRM in solutions with pH less than 1 (Benison et al., 1998), and therefore, its identification in fluid inclusions should be considered diagnostic of extreme acidity.

Fluid inclusion leachates from the Permian examples contain high concentrations of Al, Fe, and Si, all found in modern natural acid waters. These elements are rarely found in high concentrations in natural waters. Although moderately high Fe and Si have been documented in rare alkaline saline waters, aluminum is particularly unique to extremely acid waters. Aluminum has only been detected in greater than trace quantities in waters with pHs less than approximately 3–4 (Nordstrom, 1982a; Drever, 1988; Soulsby and Reynolds, 1992; Delmelle and Bernard, 1994; Bigham et al., 1996; Langmuir, 1997). Furthermore, studies of modern acidic waters and associated neutral waters show that the concentrations of Al, Fe, and Si are generally inversely proportional to pH (Nordstrom

and Ball, 1986; Driscoll, 1989; Bigham et al., 1996; Langmuir, 1997; Singh et al., 1997).

Overall, fluid inclusion studies may be the best source of acidity data for ancient sedimentary systems. As primary fluid inclusions in chemical sedimentary rocks may preserve samples of ancient surface waters and groundwaters, they may be analyzed for HSO_4^- and Al as diagnostic indicators of acidity. Fluid inclusion data may provide the only truly diagnostic criteria for acid conditions in ancient lakes and groundwaters. Unfortunately, many ancient sedimentary acid deposits may lack suitable fluid inclusions.

3.2. Other criteria

Several distinctive features found in modern acid waters may or may not be preserved in ancient systems. Others may be characteristic, but nondiagnostic of acid systems. Such features of acid systems include possible remains of acidophilic microbes, “acid” minerals such as alunite and jarosite, presence of red beds, and absence or paucity of carbonates. Each could be considered as a possible criterion for acidity in ancient sedimentary rocks. However, each is problematic or ambiguous in some way.

3.2.1. Acidophilic microbes

There are unusual organic bodies found in the Opeche Shale halite. These “hairy blobs” (0.1–2 mm) are rare dark spherules with radiating acicular structures, or “hairs” (Fig. 4A and B). The spherule cores and “hairs” show the Raman spectral character of disordered graphite, characteristic of organic matter. The largest tend to be isolated, whereas the smaller ones tend to be clustered together in groups. Most are observed as solid inclusions along growth bands in chevron halite crystals, but some are trapped within primary fluid inclusions. All “hairy blobs” are exclusively associated with only the most acid fluid inclusions, those with pHs less than 0. SEM petrography shows that these “hairy blobs” appear to be clusters of tiny crystals coated with and closely associated with organic material (Benison and Phillips, 1999). Hollow, rod-like structures, 1–5 μm long, meniscus shapes between crystals, and micrometer-scale rounded bumps on crystal faces all suggest bacterial remains (Fig. 4C and D).

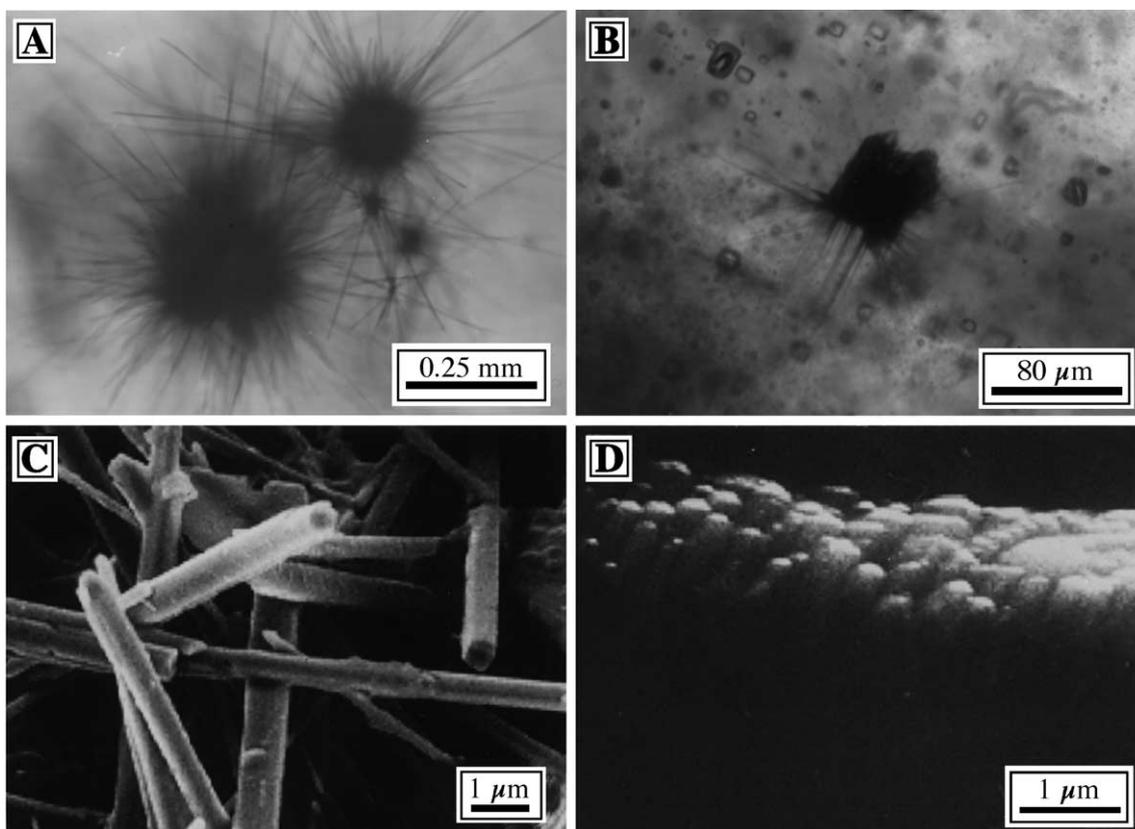


Fig. 4. Photomicrographs of “hairy blobs” composed of crystals and organic matter. (A) Transmitted light photomicrograph of clump of hairy blobs. (B) Transmitted light photomicrograph of a single hairy blob trapped in a primary fluid inclusion with “hairs” that have grown out of the fluid inclusion. Note close association with many smaller primary fluid inclusions. (C) SEM photomicrograph of core of a hairy blob showing rod-shaped, hollow structures (bright structure in center). (D) SEM photomicrograph of bumpy-textured organic matter coating the surface of a crystal in the core of a hairy blob. All hairy blobs are found exclusively in one bed of halite from the Permian Opeche Shale. This halite bed also hosts the only negative pH fluid inclusions found in this study.

Although the exact identity of these dark organic spherules remains undetermined, we can dismiss pollen, spores, diatoms, sponges, and forams based on appearance, and consider bacterial colonies as a possibility. We hypothesize that these are remains of bacterial colonies because they: (1) are carbon-based; (2) have structures within the same size range as modern bacteria; and (3) have the overall appearance consistent with a bacterial colony (Edwards and Benison, 1999).

New forms of microbial life have continued to be discovered as scientists investigate extreme environments. Ancient halotrophic bacteria preserved in halite from the Permian Salado Formation have recently been identified (Vreeland et al., 2000). Some microorganisms, including specialized forms of bacteria,

yeasts, fungi, and algae, tolerate and even thrive in modern acid waters (Langworthy, 1978; Nordstrom, 1982b). Bacteria are especially important contributors to the geochemistry of acid systems (Jorgensen, 1983; Nealson, 1983; Ehrlich, 1990). These acidophilic bacteria have been well documented in modern acid mine drainage, soils, lakes, streams, and bogs (Ivarson et al., 1982; Nordstrom, 1982b; Ross et al., 1982; Konhauser et al., 1993).

It is likely that acidophilic microorganisms lived in ancient acid lakes and acid groundwaters, and thus, if recognizable, should be considered criteria for the recognition of ancient acid systems. However, this type of criteria is problematic for two reasons: (1) preservation of acidophilic microorganisms is prob-

ably not particularly good in the rock record, and (2) identification of fossil microorganisms may be very difficult due to possible evolution and extinction of various forms over geologic time. Only identification to the genus and species level and matching to modern genus or species unique to acid environments will allow remains of ancient microorganisms to be used as unambiguous criteria for acid conditions.

3.2.2. Acid minerals

In the Nippewalla Group and Opeche Shale, sulfate accessory minerals are common as crystals within fluid inclusions, as solid inclusions in halite, and as displacive crystals in red beds. Although gypsum, anhydrite, polyhalite, and glauberite have been identified, unknown hydrated sulfate minerals have also been found with LRM. Petrographic and thermometric observations indicate that these crystals within fluid inclusions were trapped as the halite grew from lake waters, suggesting that the lake waters were saturated with respect to these sulfate minerals. Difficulty arises in attempts to identify some of these minerals because of their small size and because their Raman spectra may not be an exact match for any Raman spectra cataloged for a known mineral.

The high content of Al, Fe, and SO_4 in acid waters produces unique minerals in the systems $\text{Al}_2\text{O}_3\cdot\text{SO}_3\cdot\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3\cdot\text{SO}_4\cdot\text{H}_2\text{O}$. Two minerals closely associated with acid waters are alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) and jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$). Experimental work shows that a high H_2SO_4 concentration is needed for alunite and jarosite to be produced (Hemley et al., 1969), typically low pH environments. Other acid minerals in the alunite–jarosite family include, but are not limited to, natroalunite, alunogen, jurbanite, basaluminite, and rostitite (all in the system $\text{Al}_2\text{O}_3\cdot\text{SO}_4\cdot\text{H}_2\text{O}$) and natrojarosite, schwertmannite, halotrichite, melanterite, and copiapite (all in the system $\text{Fe}_2\text{O}_3\cdot\text{SO}_4\cdot\text{H}_2\text{O}$; Nordstrom, 1982a; Van Breemen, 1982; Bigham and Nordstrom, 2000).

Although these acid minerals are all found associated with acid waters, they are not found in all acid waters. For example, alunite and jarosite are the main acid minerals found in acidic Lake Tyrell in southeastern Australia (Long et al., 1992b), while some modern acid lake settings in Western Australia contain no acid minerals (Benison et al., 2001). Alternately, acid mine drainage at Iron Mountain Mine in California

is more diverse, enriched in the $\text{Fe}_2\text{O}_3\cdot\text{SO}_4\cdot\text{H}_2\text{O}$ minerals rhomboclase, voltaite, halotrichite, roemerite, and copiapite (Nordstrom, personal communication). These minerals also exist at different pH ranges. For instance, alunogen forms in waters with $\text{pHs} < 0$, whereas jarosite precipitates from waters with a pH of 2–4 and jurbanite forms in the pH range of 0–5 (Carson et al., 1982; Nordstrom, 1982a; Van Breemen, 1982).

Acid minerals may be problematic as criteria for acid water deposition and diagenesis in ancient sedimentary rocks. They may form in only very small quantities in acidic environments. They also seem to be metastable and thus, may not preserve well. Many acid minerals quickly disintegrate to a white or yellow, X-ray amorphous powder, appearing as “earthy” mottles in modern acid soils. Once formed in acid settings, acid minerals may undergo further reactions, breaking down into more stable forms of iron oxides (i.e., goethite or hematite; Bigham and Nordstrom, 2000), sulfates (i.e., gypsum or anhydrite; Van Breemen, 1982), and aluminosilicates (i.e., microcline or albite; Long and Lyons, 1992).

Furthermore, some acid minerals may form as weathering products of rocks rich in sulfides. If acid minerals are present in a specimen, the timing of formation of that mineral must be shown to be early and not confused with modern weathering.

Identification of acid minerals would be an excellent criterion for acid–water deposition and diagenesis. However, it is clear from the study of the Nippewalla Group and the Opeche Shale that relatively large crystals may be needed for their identification. In addition, the unstable nature of most acid minerals may mean that they are rarely preserved in ancient rocks.

3.2.3. Red beds

The red beds of the Nippewalla Group and Opeche Shale were deposited in nonmarine environments. Hematite grain coatings are interpreted as the result of very early (pre-lithification) diagenesis because they are postdated by early grey reduction spots and halite cement. The Permian red beds are quite similar to those in some modern acid lake and groundwater systems in Western Australia.

Iron reactions are important in modern acid waters. These reactions include: (1) oxidation of pyrite, (2) oxidation of ferrous iron to ferric iron, (3) ferric iron

reduction by pyrite, and (4) precipitation of ferric hydroxides. Iron oxyhydroxide minerals and dissolved iron are both important as contributors to and products of acid waters.

Red beds are not exclusive to acid deposition and diagenesis (Turner, 1980). However, because modern acid systems are hosted by red beds and because acidity is intimately associated with oxidized fluids, the presence of red beds should be expected in ancient acid systems, but should not be considered a diagnostic criterion.

3.2.4. *Absence/paucity of carbonates*

There is an unusual lack of carbonates in the Nippewalla Group and Opeche Shale. The only carbonate minerals identified in the Opeche Shale are rare magnesite and nahcolite crystals in a few fluid inclusions in halite. In the Nippewalla Group, calcite occurs rarely in a single stratigraphic interval as spherulitic calcretes in red mudstone and siltstone, but it is absent throughout the rest of the section. Siliciclastics (mainly quartz with some microcline, albite, and illite), evaporites (mostly halite and some anhydrite), and minor hematite make up the Nippewalla Group and Opeche Shale.

Carbonate minerals are typically associated with evaporites. Even in siliciclastic-rich, nonmarine evaporite deposits, magnesite and dolomite muds may be common (Casas, 1987). The only modern evaporative environments without any carbonate muds seem to be the southern Australian acid systems. The mineralogical composition in southern Australia is somewhat similar to that of the Nippewalla Group and Opeche Shale: quartz-rich siliciclastics with some feldspar and illite, halite, gypsum, and hematite.

Carbonates usually act as a buffer to any acids, keeping waters close to neutral or alkaline and paucity of carbonates may be a prerequisite for extremely low pH waters. Lack of or paucity of any carbonate minerals in lacustrine–paleosol–alluvial deposit should be considered a possible secondary criterion for an ancient acid system.

4. Conclusions

Geochemical and geological evidence has shown that the mid-Permian Nippewalla Group and Opeche

Shale were deposited and altered by acid lake and groundwaters with extremely low pHs of less than 1. These were acid systems that formed in red-bed paleosols and saline lakes and playas. Strong evidence for acidity in the Nippewalla Group and Opeche Shale is high HSO_4^- and Al in fluid inclusions in halite. Non-diagnostic supporting evidence for acidity includes possible acidophilic microbes, possible acid minerals, presence of red beds, and absence of carbonates. This paper represents the first systematic description of ancient acid lake and groundwater systems.

We propose the following as criteria for the recognition of ancient acid lakes and groundwaters: (1) high HSO_4^- in fluid inclusions in depositional and early diagenetic halite (or other evaporite mineral); (2) elevated concentrations of Al, as well as Fe and Si, in the same fluid inclusions; (3) identified remains of acidophilic bacteria or other acidophilic microbes; (4) acid minerals such as alunite or jarosite (or, more likely, the diagenetic products of acid minerals, such as gypsum or anhydrite); (5) presence of continental red beds; and (6) lack of carbonate minerals. Ancient red bed-hosted evaporite saline-pan and saline-lake deposits lacking carbonates should be considered prospects for ancient acid systems.

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