Authigenic phyllosilicates in modern acid saline lake sediments and implications for Mars

Stacy Story,[1] Brenda Beitler Bowen,[1] Kathleen Counter Benison,[2] and Darrell G. Schulze[3]

[1] Aluminum- and Fe/Mg-phyllosilicates are considered important geochemical indicators in terrestrial and Martian sedimentary systems. Traditionally, Al-phyllosilicates are characterized as forming and remaining stable under conditions of low to moderate pH, while Fe/Mg-phyllosilicates are considered representative of only dilute and moderate to high pH conditions. However, we have observed Al- and Fe/Mg-phyllosilicates in acid saline lake sediments in Western Australia. Phyllosilicate formation mechanisms in these lake systems include direct precipitation from lake waters, early diagenetic precipitation from shallow groundwaters, and deposition/alteration of detrital grains. X-ray diffraction analysis of silt- and clay-size sediments from two acid saline lakes in Western Australia indicates the presence of several complex mineral assemblages with extreme spatial heterogeneity that reflects the complex geochemistry of these lakes. These assemblages include unique combinations of authigenic and/or detrital phyllosilicates (e.g., kaolinite, smectite, and palygorskite-sepiolite), sulfates (e.g., alunite, jarosite, and gypsum), Fe-oxides (e.g., hematite and goethite), and other silicates (e.g., mullite and heulandite-clinoptilolite). Observations of Fe/Mg-phyllosilicates found in acid saline sediments in southern Western Australia suggest their degradation under conditions of low pH (2.5–5.4) is slowed by the high salinity (5–25%) of the lake and shallow groundwaters. The occurrence of both Al- and Fe/Mg-phyllosilicates in these acid saline lake sediments suggests that environmental interpretations based on the occurrence of phyllosilicates require additional consideration of their spatial distribution and association with other minerals. Moreover, the similarity between the diverse mineral assemblages in these terrestrial acid saline systems and those on Mars indicates similar conditions may have existed on Mars.

1. Introduction

[2] Ephemeral salt lakes with extreme acidity are common in the semiarid landscape of southern Western Australia (WA) [e.g., *Benison et al.*, 2007]. The lakes and associated groundwaters in this region have unusual and complex brine geochemistries [*Mann*, 1983; *McArthur et al.*, 1991; *Gray*, 2001; *Bowen and Benison*, 2009], which affect the mineralogy of the associated sediments. Other natural, modern environments with the combination of extremely low pH and high salinity are rare on Earth [e.g., *Risacher et al.*, 2002]; but remnants of these types of environments have been identified in ancient sedimentary records in the Permian of the mid-U.S. [*Benison et al.*, 1998; *Benison and Goldstein*, 2002] and in the Meridiani Planum, Mawrth Valles and Nili Fossae regions of Mars [*Squyres et al.*, 2004; *Clark et al.*, 2005; *Grotzinger et al.*, 2005; *Bishop et al.*, 2008; *Wray et al.*, 2009b]. The complex chemistry of lake waters and groundwaters in southern WA allows the mobilization and evaporative concentration of uncommon elements as well as the subsequent precipitation of some minerals not commonly associated with evaporite sedimentary systems. As a result, these acid saline systems host unique mineral assemblages that record important fingerprints of the extreme fluids that exist there. Detailed study of the sedimentary mineralogy in acid saline lakes can expand our understanding of mineral formation and stability for the mineral groups observed, and will allow for better identification of these types of systems in the geologic record.

[3] Phyllosilicates, including clay minerals (e.g., Fe/Mg- and Al-smectites, kaolin group minerals), have been detected on Mars and have recently been interpreted as evidence of weathering by significant reservoirs of waters of moderate

[1] Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, Indiana, USA.
[2] Department of Geology, Central Michigan University, Mt. Pleasant, Michigan, USA.
[3] Department of Agronomy, Purdue University, West Lafayette, Indiana, USA.

to high pH and high water activity [*Bibring et al.*, 2005; *Newsom*, 2005; *Poulet et al.*, 2005; *Catling*, 2007; *Chevrier et al.*, 2007; *Michalski and Noe Dobrea*, 2007; *Mustard et al.*, 2008; *McKeown et al.*, 2009]. However, the additional identification of acid sulfate minerals (e.g., jarosite and alunite) [*Swayze et al.*, 2008], acid-tolerant kaolin group minerals [*Bishop et al.*, 2008; *Ehlmann et al.*, 2009], and possible chlorides [*Osterloo et al.*, 2008] suggests that the water in some regions of Mars may have been quite acidic [*Squyres et al.*, 2004; *Squyres and Knoll*, 2005] and saline, resulting in significant leaching of the host rock [*Bishop et al.*, 2008]. The identification of these minerals has also been used to infer at least two temporally separate geochemical (e.g., phyllosian and theiikian) and climatic eras on Mars [*Bibring et al.*, 2006; *Chevrier et al.*, 2007].

[4] Although theoretical thermodynamics indicate that the majority of phyllosilicate formation is favored by moderate to alkaline pH conditions [e.g., *Velde*, 1995], kaolinite has been shown to precipitate at low pH [*Fialips et al.*, 2000]. In addition to the uncertainty regarding phyllosilicate stability in low pH systems, the behavior of phyllosilicates in high ionic strength solutions is not well understood. The Western Australia acid saline field area provides a natural laboratory to investigate the occurrence of a range of minerals, including Al- and Fe/Mg-phyllosilicates that form and/or persist under extreme ranges of pH and salinity. Our observations reveal that some of the more acid-susceptible phyllosilicates (e.g., Fe/Mg-smectites) are able to persist in sediments saturated with high ionic strength, acid saline lake and groundwaters in WA. Here we investigate the type, abundance, and distribution of the silt- and clay-size minerals from two contrasting acid saline lake systems in southern Western Australia.

2. Geologic Setting

[5] Lake Aerodrome (32.210°S, 121.761°E) and the Twin Lakes (33.054°S, 121.675°E) are two of many ephemeral acid saline lakes that occur in southern WA [*Benison et al.*, 2007; *Bowen and Benison*, 2009]. Both lakes are located on the Archean Yilgarn Craton, a region of variable and intensely weathered igneous and metamorphic rocks [*Anand and Paine*, 2002]. The regional bedrock surrounding both of these lakes is composed of a combination of granite, gneiss, intermediate and mafic schists, and/or quartzites that have been exposed to an increasingly arid climate since Permian glaciations [*Anand*, 2001]. The craton has been incised by extensive paleochannel systems (up to 250 m deep, 3 km wide, and many km long) that were likely created by high-energy fluvial systems during the Jurassic [*Clarke et al.*, 1996] to middle Eocene [*de Broekert and Sandiford*, 2005]. These deeply incised paleodrainages suggest a wet, tropical/semitropical climate was prevalent at the time. Following incision, these valleys were filled with fluvial, estuarine, marine, and lacustrine sediments, which include sands, lignite, kaolinite- and smectite-rich sediments, and ferruginous gravel lenses [*Lawrance*, 2001; *Anand and Paine*, 2002; *Cornelius et al.*, 2008]. Lake Aerodrome now occupies a shallow remnant basin within the Lefroy paleoriver drainage [*van de Graaff et al.*, 1977] while the Twin Lakes lie

just outside of the paleoriver channel and are hosted instead by Archean bedrock. In several areas on the Yilgarn, supergene Au mineralization crosscuts paleochannel sediments, suggesting that flow of high ionic strength ore fluids postdates the formation and sedimentary fill of the paleochannels [*Lawrance*, 2001].

[6] The surface sedimentary facies at both lakes include lake, mud/sandflats, channels, and dunes as described in detail by *Benison et al.* [2007]. The waters and sediments in and around these acid saline lakes are strongly influenced by flooding (yet maximum depths are on the order of meters), evapoconcentration, desiccation, and eolian transport [*Benison et al.*, 2007; *Bowen et al.*, 2008]. Halite and gypsum precipitate in all of the acid saline lakes in WA, although some lakes are dominated by one of these minerals over the other. The water table in nearby salt lake environments has been observed to fluctuate seasonally between 0 and 10 m depth [*Lawrance*, 2001]. The lakes are fed by a combination of this regionally acidic and saline shallow groundwater and meteoric waters that fall directly onto the lakes and are transported into the lakes from occasional sheet flood runoff [*Bowen and Benison*, 2009]. The source of the acidity in the Yilgarn region is thought to be dominantly a product of sulfide oxidation and ferrolysis [*Gray*, 2001; *Bowen and Benison*, 2009].

[7] Lake Aerodrome is located on the southeastern edge of the Lake Cowan basin near Norseman, WA (Figure 1). The lake contains a dominantly gypsum precipitating acid brine (Figure 2, lake water pH 2.7–3.7, TDS 6–15%; shallow groundwater pH 2.5–3.7, TDS 6–24%) and is surrounded by gypsum- and quartz-rich mud/sandflats and dunes [*Benison et al.*, 2007; *Bowen and Benison*, 2009]. There are no outcrops at Lake Aerodrome, but mafic schists have been observed 3–6 km away on the western and northern edges of the Lake Cowan basin (32.210°S, 121.741°E). The Twin Lakes (Twin Lake West and Twin Lake East) are located approximately 95 km south of Lake Aerodrome and are in fact a single lake divided by the Coolgardie-Esperance Highway (Figure 1). In contrast to Lake Aerodrome, the Twin Lakes host dominantly halite precipitating acid brines (Figure 2, lake water pH 2.7–3.9, TDS 11–22%; groundwater pH 2.4–5.4, TDS 5–24%) and are sitting directly on Archean basement rocks that include granite, gneiss, intermediate and mafic schists, and quartzite [*Benison et al.*, 2007; *Bowen and Benison*, 2009]. All of these rock types outcrop in and around the Twin Lakes, many in direct contact with lake water. These basement rocks are sparsely overlain by modern patches of Quaternary quartz sand and gravel and ferruginous sandstones.

[8] Preliminary mineralogical investigations have identified the presence of a rare sedimentary mineral assemblage, including halite, gypsum, iron oxides, kaolinite, jarosite and alunite [*Benison and Bowen*, 2006; *Benison et al.*, 2007; *Bowen et al.*, 2008]. However, further work was needed to carefully identify and further distinguish between authigenic and detrital minerals and interpret the significance of their spatial distribution. Characterizing these unique assemblages and understanding how they form and/or persist in modern acid saline systems is necessary in order to recognize similar deposits preserved in the rock record and infer
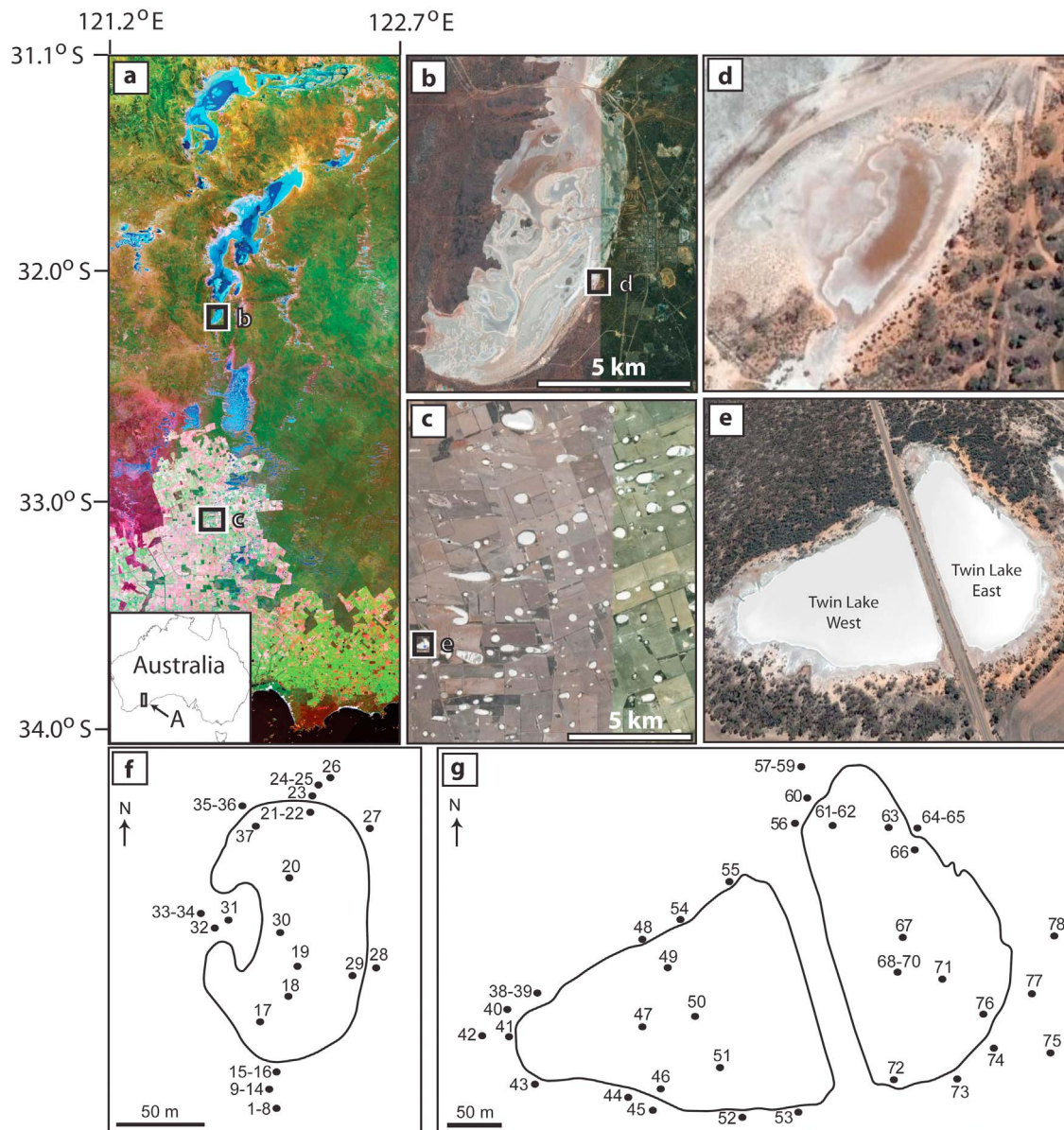
Figure 1. Regional map of field area. (a) False-color Landsat 7 ETM+ satellite image of Western Australia lake systems with boxes indicating the locations of (b) Lake Aerodrome and the (c) Twin Lakes. (d) Lake Aerodrome (32.210°S, 121.761°E), along the eastern edge of the southern portion of the Lake Cowan basin (location marked in Figure 1b). (e) The Twin Lakes (33.054°S, 121.675°E), separated by the Coolgardie Esperance Highway (location marked in Figure 1c). (f) Sample locations at Lake Aerodrome. (g) Sample locations at the Twin Lakes. Note that these lake names are given by us, as they are not named on any maps or signs that we have observed.

the chemical and physical conditions of the environment in which they formed.

3. Methods

3.1. Field Work

[9] Sediment samples for this study were collected from Lake Aerodrome and the Twin Lakes in July 2001, June 2005, January 2006, and January 2008. Measurements taken at each lake included pH, salinity, temperature, and depths of lake and groundwaters, with careful attention paid to both spatial and temporal distribution [Benison et al., 2007; Bowen and Benison, 2009]. In addition, sedimentary facies were mapped and sediment and water colors, sedimentary textures, sedimentary structures, and organic remains were noted. Physical and chemical processes occurring at and near the lakes were also observed. Surface and shallow subsurface sediments, as well as waters, were collected from both lake and adjacent mudflat and sandflat facies and were returned to our laboratories. Shallow subsurface observa-
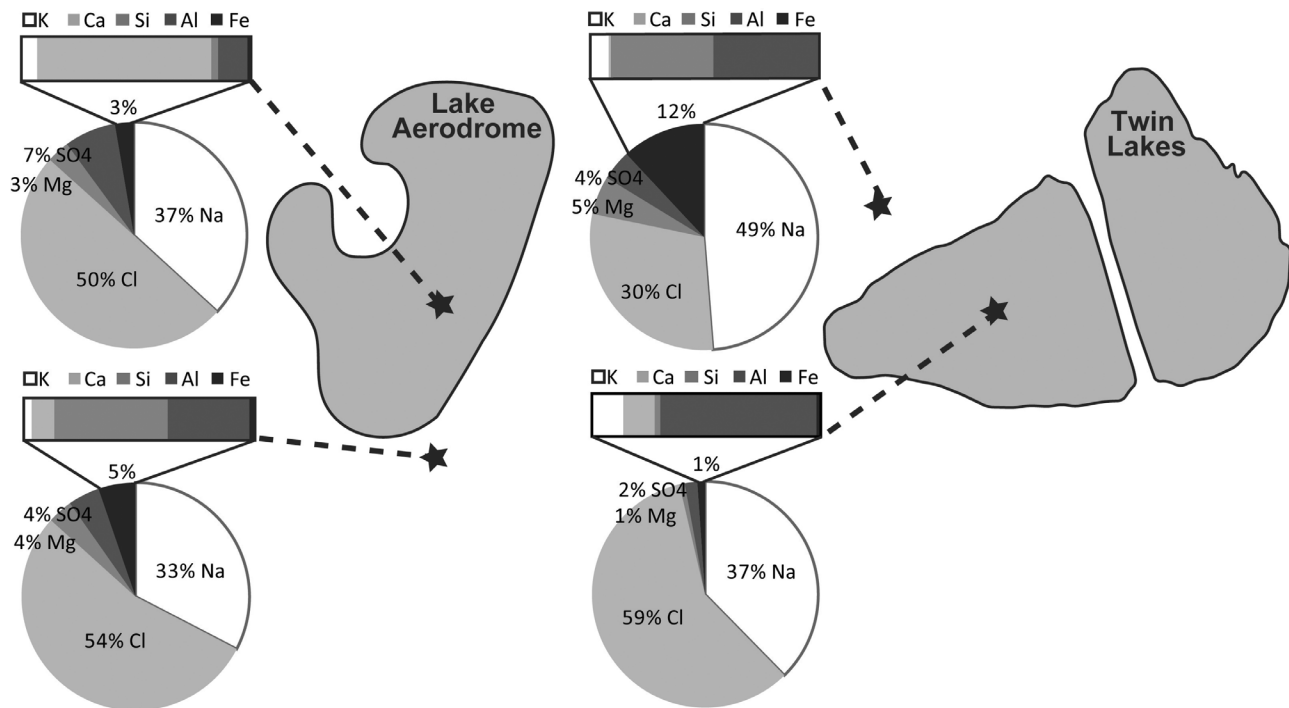
Figure 2. Representative cation and anion compositions in acid brine lake water and groundwater at Lake Aerodrome and Twin Lakes. (data after *Bowen and Benison* [2009]). All samples were collected in 2005 when the lakes were flooded.

tions (≤2 m) and sampling was done by trenching with a shovel and by taking shallow cores with PVC pipe segments. In total, this study focuses on 41 sediment samples from the Twin Lakes and 31 sediment samples from Lake Aerodrome (Figure 3). Upon collection in the field, the samples were stored in individual airtight, zip-top plastic bags or plastic containers and remained in storage until prepped for analysis.

3.2. Desalinization and Mohr Titrations

[10] While the traditional and common soluble salt minerals, such as halite and gypsum, in these WA systems are important environmental archives for both biological and geochemical conditions [*Benison et al.*, 2008; *Jagniecki and Benison*, 2010], the focus of this study is on the phyllosilicates. The majority of the salts are halite and gypsum, but bassanite ($2CaSO_4 \cdot H_2O$) and anhydrite ($CaSO_4$) have also been identified. Because the significant soluble salt component present in these sediments can interfere with the signal obtained during X-ray diffraction (XRD) analysis, the most-soluble salts were removed prior to mineralogical analysis. This allowed for quantification of the amount of salt that the samples originally contained. The sediment samples were split into two portions: a control (unwashed) and a whole sample from which the salts were removed and quantified by Mohr titration [*Doughty*, 1924; *Sheen and Kahler*, 1938; *Skoog et al.*, 1996]. Prior to XRD analysis, the whole samples from the Twin Lakes were desalinized and divided into three size fractions: >62 μm (sand), 2–62 μm (silt) and <2 μm (clay-size). The >62 μm fraction was wet-sieved from the whole sample using a #230 sieve. These sediments were then washed with DI water, allowed to air-dry

on filter paper, mounted with double sided tape on petrographic slides and photographed. The <2 μm fraction was then isolated from the remaining ≤62 μm fraction by following the sieve and beaker separation method [*Jackson*, 2005]. The whole samples from Lake Aerodrome were desalinized and divided by wet sieving into two size fractions: >62 μm (sand) and ≤62 μm (silt/clay-size). Select wash-water samples were also analyzed with ion chromatography to assess the accuracy of the Mohr titration calculations and to determine if other soluble salts, in addition to Cl-salts, were being removed with this procedure.

3.3. Laser Grain Size Analysis

[11] Half a gram of the desalinized <2 μm fractions of six samples from the Twin Lakes and 0.5 g of the ≤62 μm fractions of five samples from Lake Aerodrome were added to a 2.5 g/L concentration sodium metaphosphate solution (deflocculant) and placed in 50 mL conical vials. The samples were shaken at hourly intervals for 48 h. Each sample was later sonicated for 60 s and split using a standard sample splitter. Sample splits were analyzed using a Malvern Instruments Hydro2000MU laser grain size analyzer and data was collected using Malvern Instruments Mastersizer 2000 software. For consistency, all grain size parameters were set to measure particles ranging from 0.01 μm to 100 μm and to sort them into 50 bins. The grain size analyzer was calibrated using a deionized water blank, which provided a measurement of the background noise that was automatically subtracted from each sample measurement. Obscuration values were maintained within the suggested range and each sample was analyzed four times. These four measurements were averaged to provide the final data presented here.

Figure 3. Field photos of (a–f) Lake Aerodrome and (g–l) Twin Lakes sediment examples. (a) Shallow (~30 cm) pit dug into laminated sandflats near samples #15–16. (b) Hematite bearing sediment and iron-rich groundwater near site #34. (c) "Toothpaste" textured halloysite clay from ~30 cm below the sediment surface from within the lake, near sample #29. (d) Sandflat to mudflat transition. (e) Mottled clay-rich sediment near sample #32. (f) Bottom-growth gypsum crystals from the sediment-water interface near sample #18. (g–i) Iron oxide-rich mottling in sandflat and mudflat sediments around the lake. (j) Outcrops along the southern shore that have undergone extreme diagenesis and are cemented with iron oxides and clays similar to the lake sediments. (k) Jarosite and alunite rich sediment from within the lake near sample site #46. (l) Example of bedded halite from the lake water-sediment interface composed of accumulated halite rafts as well as chevron bottom growth halite crystals, and displacive halite crystals within the siliciclastic sediment below the halite bed. This example was collected near sample site #49.

3.4. XRD Analysis

[12] The 2–62 μm fractions (Twin Lakes) and $\leq$62 μm fractions (Lake Aerodrome) were analyzed for bulk mineralogical composition using pressed powder XRD. Self-supporting powder mounts were prepared by filling ~200 mg of gently crushed sample into an aluminum sample holder against paper to minimize preferred orientation. Diffraction patterns were obtained using a PANalytical X'Pert PRO MPD
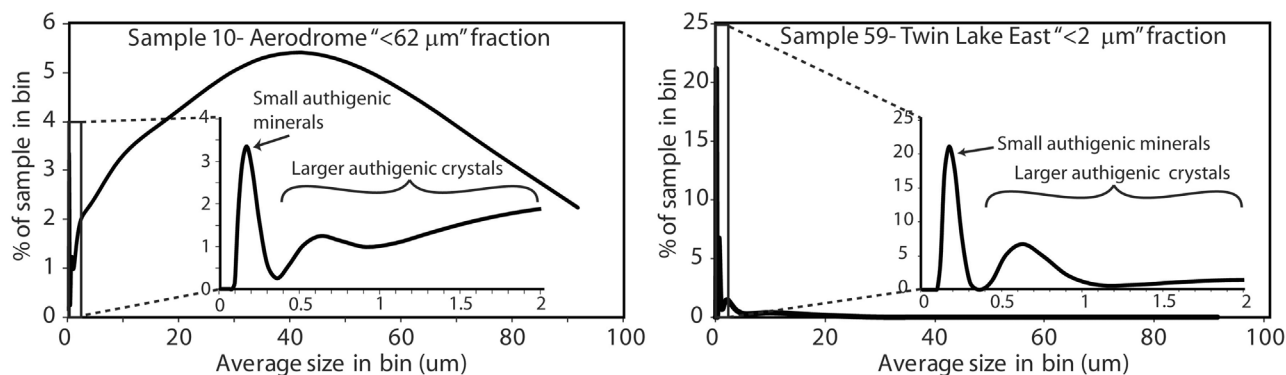
Figure 4. Grain size analysis examples from (left) Lake Aerodrome and the (right) Twin Lakes (soluble minerals removed). Sample #10 from Lake Aerodrome, sieved to separate the less than 62 μm fraction. Inset shows bimodal size distribution for sizes less than 2 μm. Sample #59 from the Twin Lakes, sieved and gravity settled to separate the less than 2 μm fraction. Note bimodal distribution for sizes less than 2 μm. Separation in "clay" size population is interpreted as being a smaller authigenic component and a larger detrital component.

X-ray diffraction system (PANalytical, Almelo, The Netherlands) at Purdue University equipped with a PW3050/60 $\theta-\theta$ goniometer and a Co-target X-ray tube operated at 40 KeV and 35 mA. Incident beam optics consisted of a Fe beta filter, 0.04 rad Soller slit, a programmable divergence slit, and a beam mask set to illuminate a 10×10 mm sample area. A fixed, 1° antiscatter slit was used at diffraction angles <12° 2θ. The diffracted beam optics consisted of a programmable diffracted beam antiscatter slit, a 0.04 rad Soller slit, and a PW3015/20 X'Celerator detector configured for an active length of 2.12° 2θ. Samples were scanned from 2 to 80° 2θ at 0.03° steps. The data were analyzed with the X'Pert High Score Plus software package (PANalytical, Almelo, The Netherlands) and were converted to a fixed 1° divergence slit prior to phase analysis and plotting.

[13] The <2 μm fraction (Twin Lakes) was separated from the sieved ≤62 μm fraction using Stoke's Law for gravity settling [*Jackson*, 2005] and analyzed for bulk mineralogical composition using standard methods of sample preparation for the XRD of oriented clays (<2 μm) mounted on corundum disks [*Amonette*, 2002]. Two subsamples were prepared for each <2 μm sample, one Mg^{2+}/glycerol-saturated and one K$^+$-saturated. Basally oriented subsamples were prepared on porous corundum disks and air-dried overnight. After equilibration, diffraction patterns were collected using the same PANalytical X'Pert PRO MPD X-ray diffraction system. The K$^+$-saturated samples were reanalyzed after heating them stepwise for an hour each at 100°, 300° and 550°C to collapse expandable clay minerals and aid in identifying interstratified clay minerals [*Amonette*, 2002].

[14] Following mineral identification, the mineralogical composition of each sample was quantified (+/− 1%) using the X'Pert High Score Plus software package (PANalytical, Almelo, The Netherlands). The quantitative data from each size fraction were then subjected to average linkage cluster analysis (minimum variance, squared Euclidean distance) using MultiVariate Statistical Package (MVSP 3.1) [*Kovach*, 2002] in order to characterize mineralogical similarities within each fraction.

3.5. SEM Analysis

[15] Select samples from the Twin Lakes <2 μm fraction (#43, 50, 53 and 54) were imaged using an FEI NOVA nanoSEM located in the Life Science Microscopy Facility at Purdue University. This machine uses an Everhart-Thornley secondary electron detector. Imaging parameters were set to probe current = 5 kV, spot size = 3 and working distance = 4.47 mm. These images were used to observe the mineral assemblages within these samples at micron-scale to nano-scale and characterize the authigenic minerals present within the <2 μm fraction.

4. Sediment Characterization

4.1. Desalinization and Mohr Titrations

[16] Chloride concentrations from the Mohr titrations show that prior to removing the salts, the whole (unwashed) sediment samples from the Twin Lakes contain up to 17.4 wt% chloride salts, and those from Lake Aerodrome contain up to 7.7 wt% chloride salt. Sediment samples collected from within the lake facies at the Twin Lakes typically have more than ~2.9 wt% salts. Similarly, those collected from within the lake facies at Lake Aerodrome typically have more than ~1.3 wt% salts. Preliminary IC data from the soak waters collected from 17 of the Twin Lakes samples agreed with the Mohr titration data (R^2 = 96), and showed that in addition to chloride salts, soluble sulfate (≤8,000 ppm) and nitrate (≤325 ppm) salts were also removed from the sediments. Sediment samples collected from the mud/sandflat and dune facies at both lakes tend to have less salt content than those collected from within the lake facies, especially with depth below the surface.

4.2. Laser Grain Size Analysis

[17] All but one of the samples from either of the two lakes (Twin Lakes #70) shows a bimodal distribution of grains that fall below 2 μm (clay-size) (Figure 4). The divide between these two populations occurs at approximately 0.4 μm. The first population is present in all of the samples and consistently peaks around 0.2 μm, and the
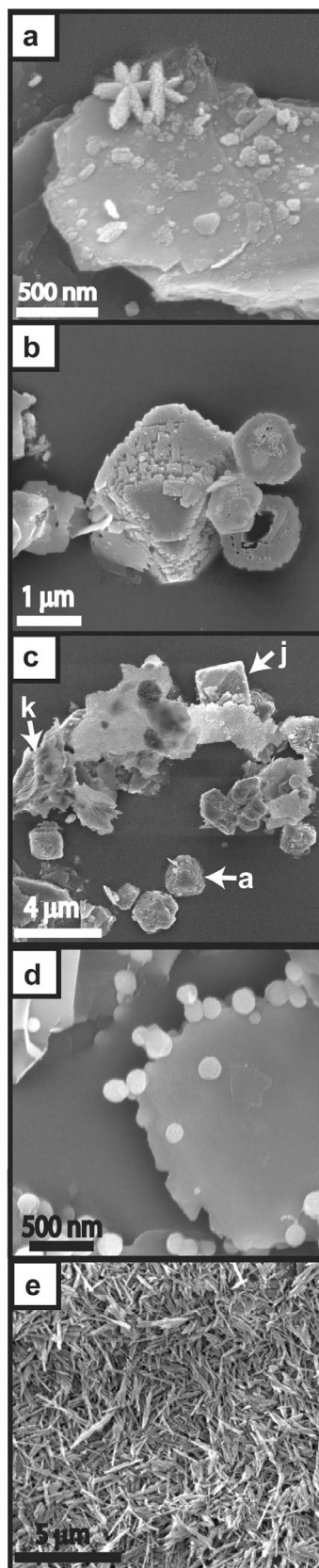
second population peaks around 0.6 μm. While the 0.2 μm population will be dominated by fine-grained authigenic minerals [*Tabor and Montañez*, 2005], the 0.6 μm population likely contains a combination of larger and/or flocculated authigenic crystals (e.g., kaolinite) and a lesser amount of the smallest detrital particles. Efforts were made to isolate the 0.2 μm fraction by centrifugation, but collection and identification of the minerals in this size fraction was impossible due to the small amount of sediment available (<50 g).

[18] In the Lake Aerodrome samples, the <2 μm population makes up an average of 35% (by number) of the ≤62 μm fraction (15% is <0.2 μm), and the detrital silt/sand population makes up the remaining 65%. However, in the Twin Lakes samples, the <2 μm population makes up an average of ~75% of the "<2 μm" fraction that was analyzed (~47% is <0.2 μm). The remaining ~25% is composed of particles ranging in size from 2 to 100 μm. This is because Stoke's Law for gravity settling applies strictly to spherical particles rather than to platy clay particles; therefore, the maximum diameter of "2 μm" clay particles may be significantly larger than 2 μm [*Moore and Reynolds*, 1997].

4.3. SEM Analysis

[19] Of the samples imaged using SEM, Twin Lakes midlake sample #50, exhibits the greatest mineral heterogeneity (Figure 5), which includes micron-scale to nanoscale euhedral bladed gypsum crystals on larger kaolinite flakes and micron-scale subhedral alunite and euhedral jarosite crystals. The Twin Lakes sample #43 is less diverse, but contains nanometer-scale silica spheres clinging to the edges of larger, micron-scale kaolinite flakes. The Twin Lakes sample #54 is the most homogenous of those imaged, and contains tubular structures characteristic of halloysite. As was suggested by the laser grain size analysis, SEM analysis confirms the presence of two size populations within the <2 μm fraction and the subeuhedral to euhedral nature of many of these micron-scale crystals confirms the dominance of authigenic grains in the <2 μm fraction.

4.4. Sediment Composition

[20] The composition of the acid saline sediments in these lakes reflects the importance of physical processes such as surficial weathering and eolian transport, as well as the chemical processes unique to the low pH and high salinity. While the water chemistry does vary with temporal changes (e.g., flooding, evapoconcentration, and desiccation) [*Bowen and Benison*, 2009], these changes are intimately intertwined and any one stage is relatively short-lived on a geologic time scale. As a result, the minerals forming and/or persisting in these environments reflect a combination of temporal conditions.

Figure 5. SEM images of Twin Lake sediments. Sample #50, midlake in Twin Lake West: (a) authigenic gypsum crystals on kaolinite; (b) subhedral alunite crystal; and (c) mixed mineralogy including euhedral jarosite crystal (j), kaolinite (k), and subhedral alunite crystal (a). (d) Silica spheres on kaolinite (sample #43). (e) halloysite tubules (sample #54). Mineral identification is based upon crystal morphology and XRD.

[21] After removing the soluble salt component, the silt- and/or clay-size fractions from both lakes contain the following minerals (Table 1 and Table S1): micas (e.g., Fe-muscovite, $K_2(Al, Fe)_4[Si_6Al_2O_{20}](OH, F)_4$), kaolinite ($Al_2Si_2O_5(OH)_4$), alunite ($KAl_3(SO_4)_2(OH)_6$), jarosite ($KFe_3(SO_4)_2(OH)_6$), gypsum ($Ca(SO_4) \cdot 2H_2O$), rozenite ($Fe^{2+}(SO_4) \cdot 4H_2O$), marcasite ($FeS_2$), hematite ($Fe^{3+}_2O_3$), goethite ($Fe^{3+}O(OH)$), gibbsite ($Al(OH)_3$), quartz ($SiO_2$), K-feldspar ($K[AlSi_3O_8]$), Na/Ca-feldspar ($Na[AlSi_3O_8]$-$Ca[Al_2Si_2O_8]$), and amphibole (e.g., riebeckite, $Na_2(Fe^{2+}_3, Fe^{3+}_2)Si_8O_{22}(OH)_2$).[1] In addition to these, the Lake Aerodrome ≤ 62 μm fraction contains varied amounts of chlorite-smectite (variable composition, possibly interstratified), dickite ($Al_2Si_2O_5(OH)_4$), amesite ($Mg_2Al(Si, Al)O_5(OH)_4$), and calcite ($CaCO_3$). The Twin Lakes sediment samples (2–62 μm and/or <2 μm fractions) also contain halloysite ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$), smectite (variable composition), palygorskite-sepiolite (($Mg,Al)_5(Si,Al)_8O_{22}(OH)_2 \cdot 8H_2O$)-($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$), hydrobasaluminite ($Al_4(SO_4)(OH)_{10} \cdot 12-36H_2O$), anatase ($TiO_2$), silica spheres ($SiO_2$), mullite ($3Al_2O_3 \cdot 2SiO_2$) and heulandite-clinoptilolite (($Ca, Na)_{2-3}(Al_3(Al,Si)_2Si_{13}O_{36} \cdot 12H_2O$)). Halloysite was indicated by the peak pattern and confirmed by SEM, but was quantified via XRD as pure kaolinite. The silica spheres were identified using SEM, but were quantified via XRD as quartz.

4.5. Spatial Distribution

[22] The sediments in both lakes exhibit extreme spatial heterogeneity from macroscales to nanoscales. Eolian dunes around Lake Aerodrome and erosion scarps on the lake margins of the Twin Lakes provide diverse and highly localized clastic sediment input. It is difficult to separate background concentrations of ions released during long-term physical weathering of the surrounding Archean bedrock/saprolite/laterite from high ion concentrations related to evapoconcentration of the acid lake and groundwaters. However, the abundance of clay minerals and mottling within the lake and mud/sandflat sediments suggests minimal groundwater movement (e.g., low permeability [*Easterbrook*, 1999]). This agrees with the observed cycles of repeated wetting drying of groundwater saturated sediments [*Benison et al.*, 2007] and with reports of very low regional groundwater flow rates (centimeters per thousand years) (D. Grey, personal communication, 2008). As a result, the high concentrations of dissolved ions in the lake and shallow groundwaters are locally sourced from chemical weathering of the basement rocks and semistabilized eolian dunes adjacent to the lakes and are not quickly removed from the system.

4.5.1. Lake Aerodrome <62 μm Fraction

[23] At Lake Aerodrome, the most commonly encountered mineral assemblage (i.e., with the highest number of samples) is LA1 (Figure 6), which includes six samples from mud/sandflats, three samples from inside the lake and one sample from the eastern dunes (Figure 7a). These samples come from depths ranging from 0 to 20 cm and tend to be brown, quartz-rich sediments (average 57%) with possible organic matter. Given the distribution of these samples, Assemblage LA1 likely represents a combination of outwash sands and the overall mud/sandflat composition.

[24] The second most common mineral assemblage at Lake Aerodrome is LA2, which includes seven samples from mud/sandflats and two samples from inside the lake. The mud/sandflat samples were collected from within the farthest landward and topographically highest dunes at the southern end of the lake (from depths of 0–18 cm). On average, the samples in this assemblage tend to be brown/black sediments and are composed of nearly equal amounts of quartz (average 36%) and muscovite (average 36%). Due to the quartz- and muscovite-rich nature of these samples, Assemblage LA2 likely reflects the influence eolian input from the mafic schists exposed in the larger Lake Cowan basin has on the quartz dunes surrounding Lake Aerodrome.

[25] The third most common mineral assemblage is LA3, which includes two samples from mud/sandflats and three samples from inside the lake. The mud/sandflat samples were collected from the surface (western edge) and at 35 cm (eastern edge), while the lake samples were all collected from depths ≤ 10 cm. They contain nearly equal parts gypsum (average 22%), alunite (average 20%) and quartz (average 18%). The abundance of alunite in this assemblage suggests prolonged acidity in this location, which agrees with the field observations. The combination of nearly equal gypsum and quartz in this assemblage suggests input from the quartz/muscovite-dominated sands coming in from the Lake Cowan basin and indicates an additional source of gypsum sand – likely formed from Lake Aerodrome itself during periods of desiccation.

[26] The fourth and least common mineral assemblage is LA4, which includes four samples from mud/sandflats and one sample from inside the northern edge of the lake. The mud/sandflat samples were collected from ≤ 10 cm, and the lake sample was collected from the subaqueous gypsum crust. These samples are primarily gypsum-rich (average 78%). As a result, Assemblage LA4, likely reflects the composition of the gypsum-dominated eolian dune sediments that are found on northwestern edges of the lake.

[27] Calcite is the only carbonate mineral identified at either lake and was present in only three samples from Lake Aerodrome ($\leq 2\%$ each). All three came from a depth of 4 to 10 cm. Because calcite is quite soluble at the low pH values observed at Lake Aerodrome (lake water pH: 2.7–3.7, groundwater pH: 2.5–3.7), the calcite crystals are unlikely to have formed in situ, unless they formed by recent evaporation of the pore water and have not yet been exposed to the acidic groundwater. It is also possible that they were transported into the region by wind or water, buried and are actively breaking down in the subsurface.

4.5.2. Twin Lakes 2–62 μm Fraction

[28] At the Twin Lakes, the most commonly encountered mineral assemblage in the silt fraction (i.e., with the highest number of samples) is TS1 (Figure 6), which includes four samples from Twin Lake West (two from mud/sandflats, two from inside the lake) and fifteen samples from Twin Lake East (eight from mud/sandflats, seven from inside the lake) (Figure 7b). The sediments in this assemblage vary in color and texture and were collected from depths ranging from the surface to 40 cm, but tend to be associated with outcrops of the regional gneiss/schist/quartzite bedrock and the surrounding outwash surfaces. They contain significantly more muscovite (average 34%) than any other assemblage and also have a considerable amount of quartz

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Table 1. Minerals Identified in the Lake Aerodrome (<62 μm) and Twin Lake (2–62 μm and <2 μm) Sediments

Mineral	Common Soil/Sedimentary Environment	Lake, Fraction			Authigenic?
		Aerodrome (<62 μm)	Twins (2–62 μm)	Twins (<2 μm)	
Phyllosilicates					
Micas: e.g., Fe-muscovite $K_2(Al,Fe)_4[Si_6Al_2O_{20}](OH, F)_4$	Present in all weathering profiles; commonly weathered from igneous or metamorphosed intermediate to acid igneous parent rocks; may form pedogenically in arid climates [*Thompson and Ukrainczyk*, 2002].	X	X	X	Possibly
Kaolinite $Al_2Si_2O_5(OH)_4$	Typically forms via weathering of feldspars, muscovite and other Al-rich silicates in acid rocks, may be transported under appropriate nonalkaline conditions and deposited in nonmarine environments, authigenic precipitation occurs at shallow depths and low temperatures in mud rocks, clastic sediments and coals [*White and Dixon*, 2002].	X	X	X	Yes
Dickite $Al_2Si_2O_5(OH)_4$	Forms in environments similar to kaolinite [*White and Dixon*, 2002].	X			Yes
Halloysite $Al_2Si_2O_5(OH)_4*2H_2O$	Tends to occur at elongated tubes [*White and Dixon*, 2002] and is common in young soils, especially those derived from volcanic ash [*Dixon and McKee*, 1974; *Dixon*, 1989]. Also occurs as an intermediate in lateritic weathering [*Salter and Murray*, 1993].			X	Yes
Smectite variable composition	May be sourced from parent materials, may form from weathering of other micas or may precipitate authigenically in soil environments with high Si and Mg activity, basic pH and poor drainage [*Reid-Soukup and Ulrey*, 2002; *Jackson*, 1965; *Kittrick*, 1971a, 1971b; *Weaver et al.*, 1971].	X		X	Possibly
Chlorite variable composition	Found in many rocks and soils, but generally is not abundant. In surface sediments, can be detrital or pedogenic, but detrital chlorites are unstable in acidic weathering environments [*Kohut and Warren*, 2002].	X		X	Possibly
Palygorskite-Sepiolite (($Mg,Al)_5(Si,Al)_8O_{22}(OH)_2*8H_2O$)- ($Mg_4Si_6O_{15}(OH)_2*6H_2O$)	Rich in Si and Mg and relatively unstable, except in environments where evapotranspiration greatly exceeds precipitation and any extra moisture comes from saline shallow groundwater/surface water [*Singer*, 2002]. Palygorskite occurs in marine, lacustrine, and soil environments [*Jones and Galan*, 1988], while sepiolite occurs in similar environments but is less abundant in soil [*Singer*, 2002].		X		Not likely
Amesite $Mg_2Al(Si,Al)O_5(OH)_4$	Occurs in metamorphic rocks with high Al [*Deer et al.*, 1992].	X			Not likely
Sulfates					
Alunite $KAl_3(SO_4)_2(OH)_6$	Occurs in sulfuric horizons of active acid sulfate soils [*Fanning et al.*, 2002], and is associated with fumaroles and hydothermal alteration zones in K-rich igneous rocks [*Perkins*, 2002].	X	X	X	Yes
Jarosite $KFe_3(SO_4)_2(OH)_6$	Common in sulfuric horizons of active acid sulfate soils [*Fanning et al.*, 2002], and occurs as a secondary mineral in some iron ores [*Perkins*, 2002].	X	X	X	Yes

Table 1. (continued)

Mineral	Common Soil/Sedimentary Environment	Lake, Fraction			Authigenic?
		Aerodrome (<62 μm)	Twins (2–62 μm)	Twins (<2 μm)	
Gypsum Ca(SO$_4$)*2H$_2$O	Most common sulfate mineral, forms in evaporite deposits and may be associated with other bedded evaporites. Also occurs interlayered with limestones and shales or as a secondary deposit in fractures, as a gangue mineral or alteration product in some ore deposits [Perkins, 2002].	X	X	X	Yes
Rozenite Fe^{2+}(SO$_4$)*4H$_2$O	Most common ferrous sulfate mineral at intermediate humidity [Fanning et al., 2002].	X		X	Yes
Hydrobasaluminite Al$_4$(SO$_4$)(OH)$_{10}$*12–36H$_2$O	Dehydrates to basaluminite, which is associated with allophane, gypsum and aragonite [Palache et al., 1951].		X	X	Yes
Sulfides					
Marcasite FeS$_2$	Low-temperature mineral, occurs in lead/zinc-bearing sulfide veins or as a replacement mineral in limestones or shale [Perkins, 2002].	X	X		Not likely
Oxides					
Hematite Fe$^{3+}_2$O$_3$	Common in aerobic soils in tropical, subtropical, arid and semiarid climates; abundant at higher temperatures with less organic matter [Bigham et al., 2002].	X	X	X	Yes
Goethite Fe^{3+}O(OH)	Present in all weathering profiles; abundant in cool, wet climates and with increased organic matter [Bigham et al., 2002].	X	X	X	Yes
Anatase TiO$_2$	Common in highly weathered soils and sediments as a weathering product of other Ti-bearing silicates; also forms authigenically [Fitzpatrick and Chittleborough, 2002].		X	X	Possibly
Hydroxides					
Gibbsite Al(OH)$_3$	Common in highly weathered, tropical and subtropical ancient landscapes, saprolites and young soils forming in rapidly weathering volcanic ash [Huang et al., 2002].	X	X	X	Yes
Carbonates					
Calcite CaCO$_3$	Common in alkaline soils; forms coatings, nodules, cemented layers and silt- and clay-sized particles [Doner and Grossl, 2002].	X			Possibly
Other Silicates					
Quartz SiO$_2$	Second most abundant mineral, common in residual and transported components [Monger and Kelly, 2002].	X	X	X	Possibly

Table 1. (continued)

Mineral	Common Soil/Sedimentary Environment	Lake, Fraction			Authigenic?
		Aerodrome (<62 μm)	Twins (2–62 μm)	Twins (<2 μm)	
K-feldspar K[AlSi$_3$O$_8$]	Essential components of acid igneous rocks (e.g., granite) and are common in acid and intermediate gneisses; also form authigenically as a result of weathering [Deer et al., 1992].	X	X	X	Possibly
Na/Ca-feldspar Na[AlSi$_3$O$_8$]–Ca[Al$_2$Si$_2$O$_8$]	Most common rock-forming mineral, common in igneous, metamorphic and sedimentary rocks; also form authigenically as a result of weathering [Deer et al., 1992].	X	X	X	Possibly
Riebeckite Na$_2$(Fe^{2+}$_3$,Fe^{3+}$_2$)Si$_8$O$_{22}$(OH)$_2$	Occurs in some granites and low-grade schists, but is common in the Iron Formations of Western Australia as a precursor to crocidolite [Deer et al., 1992].	X	X		Not likely
Mullite 3Al$_2$O$_3$*2SiO$_2$	Typically forms in pelitic xenoliths in basic igneous rocks; Fe-mullite has been described as forming during thermal metamorphosis of lateritic kaolinite [Deer et al., 1992].			X	Yes
Heulandite-Clinoptilolite (Ca,Na)$_{2–3}$(Al$_3$(Al,Si)$_2$)Si$_{13}$O$_{36}$*12H$_2$O	Occur in cavities of mafic igneous rocks; also commonly derived from volcanic or other silica-rich parent materials [Boettinger and Ming, 2002].		X		Not likely

(average 23%), likely as a result of their proximity to the bedrock outcrops. Given the distribution of these samples, Assemblage TS1 likely represents the detrital composition of the mud/sandflat sediments, especially those in direct contact with the bedrock.

[29] The second most common mineral assemblage in the Twin Lakes silt fraction is TS2, which includes eight samples from Twin Lake West (six from mud/sandflats, two from inside the lake) and two samples from inside Twin Lake East. These samples were collected from depths less than 10 cm, including one sample of the highly weathered, white sandstone bedrock (underlying an ironstone ledge) along the southwestern edge of the lake. These samples are kaolinite-rich (average 70%), but also contain a significant amount of heulandite-clinoptilolite (8%). Like Fe/Mg-phyllosilicates, most zeolites are unstable at the pH values measured at these lakes, but their stability may be enhanced by the high Si/Al ratios and high salinities of these acid saline lake and groundwaters [Boettinger and Ming, 2002]. Given the proximity to the highly weathered, white sandstone bedrock and high abundance of kaolinite, Assemblage TS2 likely reflects the composition of this highly weathered rock and the surface processes that wash it into the lake. Interestingly, this outcrop was not noted at Twin Lake East, but the inclusion of two Twin Lake East lake samples in this assemblage suggests that the bedrock may actually be in contact with the lake water near the middle of the lake.

[30] The third most common mineral assemblage in the Twin Lakes silt fraction is TS3, which includes four samples from Twin Lake West (three from mud/sandflats and one from inside the lake) and two samples from inside Twin Lake East. The sediments in this assemblage tend to be yellowish in color and were all collected from the surface. Like Assemblage TS2, they are also kaolinite-rich (average 42%) but contain the highest amount of jarosite (average 9%) and alunite (average 7%), which suggests that these samples represent the most acidic conditions at these lakes.

[31] The fourth and least common mineral assemblage in the Twin Lakes silt fraction is TS4, which includes two mud/sandflat samples from Twin Lake West and three mud/sandflat samples from Twin Lake East. These samples were primarily collected from the mud/sandflat surface and tend to be reddish in color. They are quartz-rich (average 43%) and also contain nearly equal amounts of kaolinite (average 18%), Ca-feldspar (average 15%), and K-feldspar (average 13%). These samples have the highest amount of quartz and feldspars and are likely in direct contact with the granitic bedrock. It is possible that like the samples in TS2, these samples reflect the highly weathered nature of the bedrock and the restricted lateral transport of weathered materials.

4.5.3. Twin Lakes <2 μm Fraction

[32] The most commonly encountered mineral assemblage in the clay fraction (i.e., with the highest number of samples) is TC1 (Figure 6), which includes seven samples from Twin Lake West (three from mud/sandflats and four from inside the lake) and thirteen samples from Twin Lake East (seven from mud/sandflats and six from inside the lake) (Figure 7c). The sediments in this assemblage vary in color and texture, were collected from depths ranging from the surface to 30 cm, and tend to be associated with outwash surfaces. They have the second highest amount of kaolinite (average 68%). Given the broad distribution of these sam-
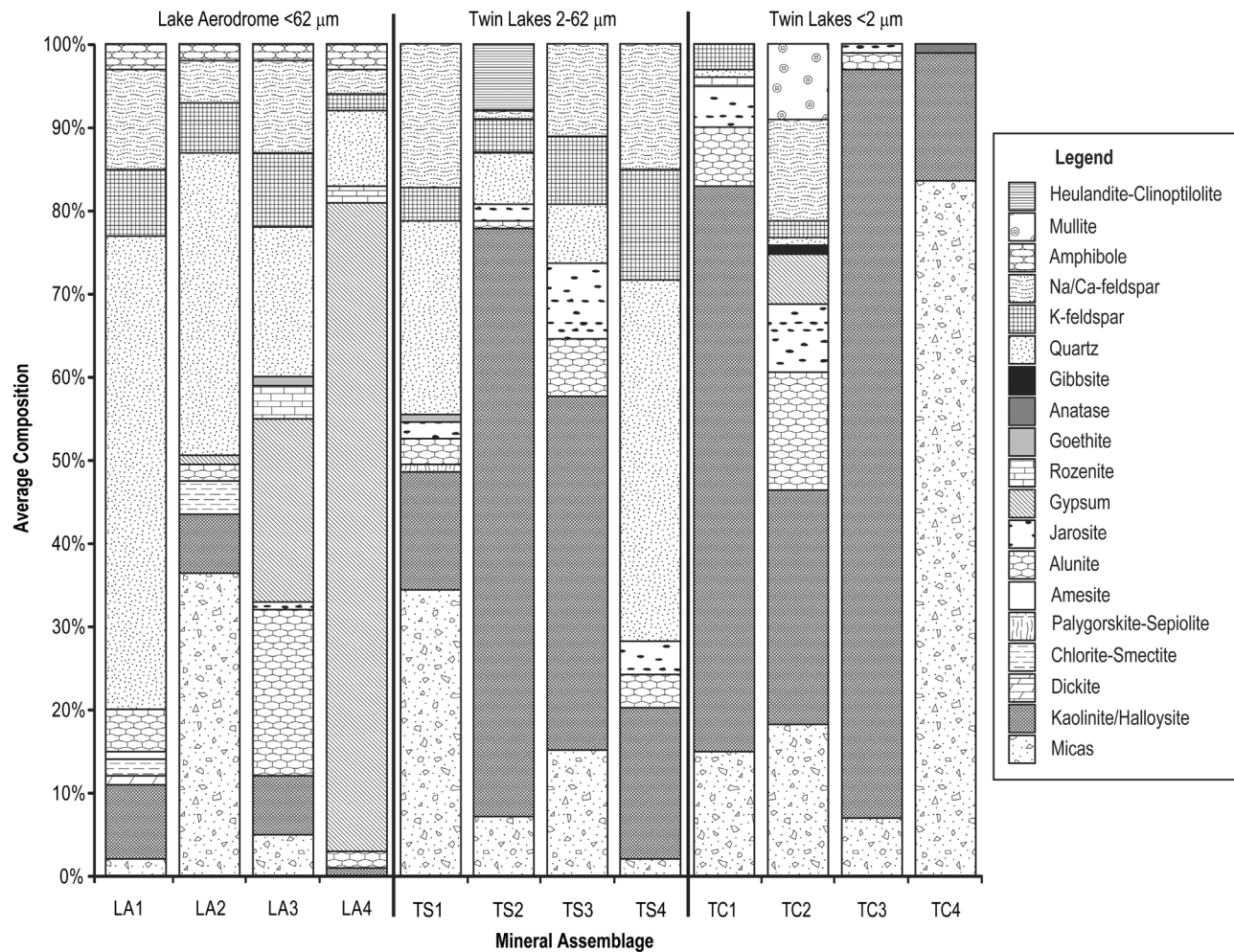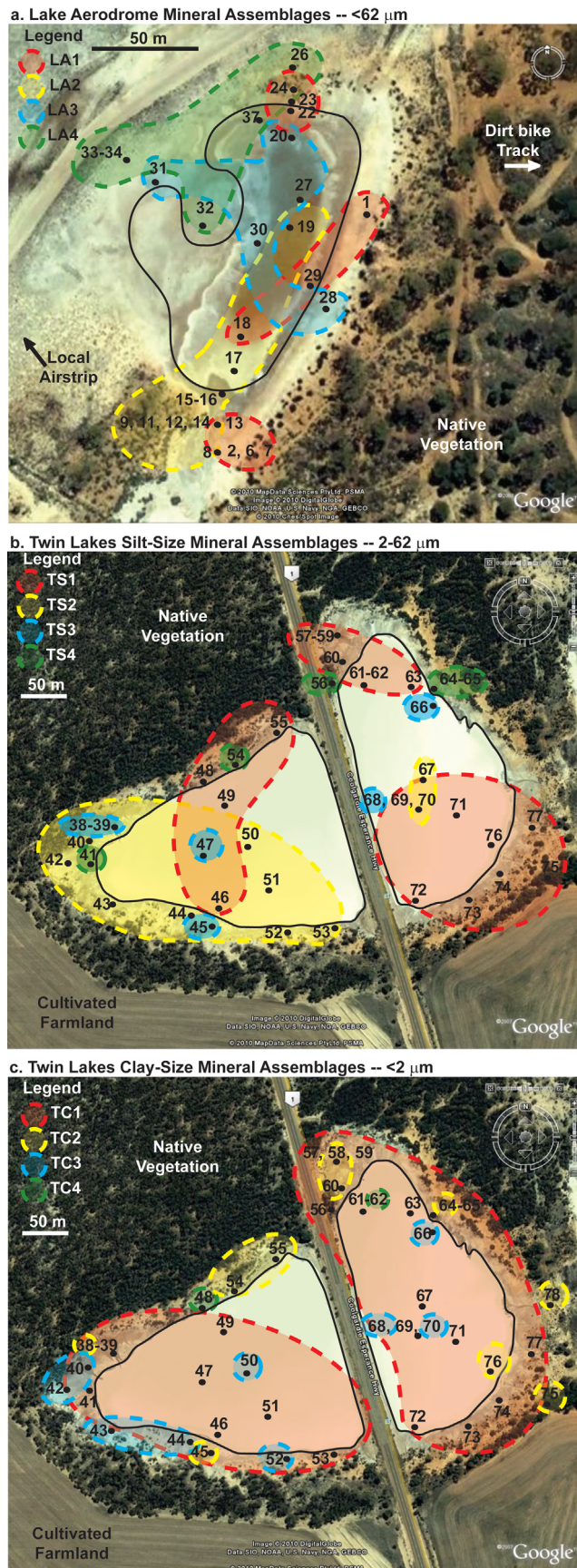
Figure 6. Average compositions of mineral assemblages present at (left) Lake Aerodrome (<62 μm), (middle) Twin Lakes (2–62 μm), and (right) Twin Lakes (<2 μm). Halloysite was identified in sample #54 (TS4/TC2). Nanometer-scale silica spheres were identified in sample #43 (TS2/TC3). Trace minerals (not shown) are those with an average abundance in each assemblage of ≤1% and include the following: smectite (TC1 and TC4), alunite (TC4), jarosite (LA2), gypsum (LA1, TS4, and TC1), hydrobasaluminite (TC1 and TC2), marcasite (LA1, LA2, and TS1), hematite (LA1, LA2, and TS3), goethite (LA1, TC1, TC2, and TC2), anatase (TS1, TS2, TS4, TC1, and TC2), gibbsite (LA1, LA2, TS1, and TC1), calcite (LA1 and LA2), and amphibole (TS3 and TS4).

ples, Assemblage TC1 likely reflects the background clay composition of the mud/sandflats surrounding these lakes.

[33] The second most common mineral assemblage in the Twin Lakes clay fraction is TC2, which includes four mud/sandflat samples from Twin Lake West and six samples from Twin Lake East (five from mud/sandflats and one from inside the lake). The sediments in this assemblage also vary in color and texture, were collected from depths ranging from the surface to 40 cm, and tend to be associated with outcrops of the regional gneiss/schist/quartzite bedrock. They are also dominantly kaolinite/halloysite (average 28%). In fact, one sample, collected from the northern mud/sandflat at Twin Lake West, was from a depth of 25 cm and had a white, "toothpaste" texture (~42% kaolinite, ~41% muscovite). In addition, this assemblage also contains the highest amounts of alunite (average 14%), Ca-feldspar (average 12%), mullite (average 9%), and jarosite (average 8%).

Like Assemblage TS3, the high amount of alunite and jarosite in this assemblage, suggests that these samples represent the most acidic conditions at these lakes. The high amount of Ca-feldspar in these samples likely reflects the abundance of feldspar pebbles on the outwash fan. The significant amount of mullite in this assemblage comes from two samples that are located on the eastern edge of Twin Lake East (#75 and 78), near the trees and several meters landward of the lake edge. This mineral is indicative of past thermal metamorphism due to fire [*Deer et al.*, 1992] and is consistent with the fire-prone nature of the vegetation.

[34] The third most common mineral assemblage in the Twin Lakes clay fraction is TC3, which includes six samples from Twin Lake West (five from the mud/sandflats and one from inside the lake) and three samples from inside Twin Lake East. Like Assemblage TS2, this assemblage includes a sample from the white, highly weathered sand-

stone that outcrops along the southwestern mud/sandflat (#43, with nanometer-scale silica spheres). These samples are nearly pure kaolinite (average 90%). Assemblage TC3 likely reflects the composition and depositional contribution from the highly weathered sandstone outcrop on the southwestern edge of Twin Lake West and suggests additional outcrop contacts just below the surface of Twin Lake East.

[35] The fourth and least common mineral assemblage in the Twin Lakes clay fraction is TC4, which includes one mud/sandflat sample from Twin Lake West and one from inside Twin Lake East. These samples were collected from similar depths (10–15 cm) and are composed primarily of muscovite (average 83%). Presumably, this assemblage weathered directly from partially exposed mafic/gneiss rocks near the shoreline.

4.6. Phyllosilicate Formation Mechanisms

[36] When analyzed with respect to their grain size and spatial distribution, the mineral assemblages described here suggest that when the bedrock is exposed and in considerable contact with the surface water, the mineralogy of the silt fraction will reflect the composition of the bedrock, while the clay-sized fraction will provide a better estimation of the subsequent lake and shallow groundwater chemistry. Aluminum-phyllosilicates, such as kaolinite and Fe-muscovite, are the dominant authigenic phyllosilicates in these acid saline settings, and they form in several ways: (1) direct precipitation from acid lake waters to result in clay beds at lake bottoms, (2) direct precipitation from shallow acid groundwaters to make early diagenetic cements, and (3) alteration (or weathering) of feldspars and amphiboles to make replacement rinds. These Al-phyllosilicates are not found concentrated in the ephemeral channels or sheet flood deposits, as might be expected if they were dominantly detrital in origin. Instead, most are found in contact with acid the brines and are intimately associated with other minerals forming in situ, such as gypsum, halite, hematite, goethite, jarosite, and alunite. This suggests that water chemistry, rather than physical transport into the lakes, is the primary controlling factor for much of the phyllosilicate formation. The mineral assemblages described here illustrate the importance of fluid composition over pH in determining mineral stability.

[37] Authigenic precipitation of Al-phyllosilicates either from acid saline lake waters or groundwaters is not uncommon in Western Australia [e.g., *McArthur et al.*, 1991], and in fact the low pH of the acid saline lake systems may actually improve the crystallinity of kaolinite in these deposits [*Fialips et al.*, 2000]. Mineral stability in any environment is principally affected by Eh, pH, temperature, and cation availability. For example, even acid-tolerant Al-phyllosilicates, such as kaolinite, are generally more stable at neutral pH

Figure 7. Locations of sediment sample collection sites and mineral groups identified in (a) Lake Aerodrome (<62 μm), (b) Twin Lakes (2–62 μm), and (c) Twin Lakes (<2 μm). The black lake outline is the approximate location of the boundary between lake and mud/sandflat facies during a flooding stage in 2005. Sample locations and mineral assemblages correspond to detailed mineralogy in Figure 6. Google Earth imagery ©Google Inc. Used with permission.

than they are at pH extremes (low and high pH). However, as pH fluctuates to one extreme or the other, the solubilities of dissolved Al^{3+} and Si^{4+} increase [*Burley et al.*, 1985], which increases their concentration in solution and can counter mineral instability due to low or high pH conditions. In the acid saline lakes of WA, the felsic bedrock has been extensively leached, but continues to supply ample Al^{3+} and Si^{4+} ions into the system, especially when in contact with the acid saline lake or groundwaters. Once these ions have entered the system, they may fluctuate with cycles of flooding (e.g., mineral dissolution), evaporation, and desiccation (e.g., mineral precipitation), but will only be completely removed from the system by physical transport.

[38] Unlike Al-phyllosilicates, Fe/Mg-phyllosilicates (e.g., saponite) tend to be much less stable under acidic pH conditions (half-life <1 year) [*Huertas et al.*, 2001; *Ehlmann et al.*, 2008], but are present in moderate amounts (~2–16% in #9, 11–13, 15–19) in the ≤62 μm fraction of the Lake Aerodrome sediments and in smaller amounts (~1% in #39 and 48) in the clay-size fraction of the Twin Lake West sediments. In addition to pH, Fe/Mg-phyllosilicate precipitation and stability is controlled by the concentration of dissolved Mg^{2+} [*Harder*, 1972; *Weaver et al.*, 1971]. While these clays are less likely to be authigenic in this acid saline environment, it is possible that they are being transported into the lake water by surface flow and their subsequent degradation is slowed by the high ionic strength of the lake ([Mg^{2+}]: 1631–5415 mg/L) [*Bowen and Benison*, 2009] and groundwaters ([Mg^{2+}]: 1843–9425 mg/L) [*Bowen and Benison*, 2009]. Unlike kaolinite, smectite tends to be the major phyllosilicate in alkaline soil environments, but has been documented as the major mineral in acid soils, such as in West Africa and East Texas [*White and Dixon*, 2002], and will precipitate from poorly drained aqueous solutions provided they contain high enough concentrations of the elemental constituents of smectite [*Borchardt*, 1989; *Reid-Soukup and Ulrey*, 2002].

[39] Regardless of their authigenic or detrital origin, Al- and Fe/Mg-phyllosilicates are both exposed to the same conditions once they have entered the lake or groundwaters. As a result, understanding how these minerals interact with the surrounding fluid at an atomic level will provide an explanation as to how these minerals are able to coexist. At the atomic level, there are two types of charges on the surface of all phyllosilicates. The edge charge is variable and is balanced by H^+ or OH^- ions in the surrounding fluid. In an acidic aqueous environment, the excess H^+ ions will attach primarily to the negative edge charges on the phyllosilicates, which results in a net positive edge charge. The now positive edges are attracted to the remaining negative layer charges and the clay-size particles will begin to flocculate. Unlike the edge charge, the layer charge is permanent, and arises due to cation substitution within the tetrahedral (e.g., Al^{3+} for Si^{4+}) and octahedral (e.g., Mg^{2+} for Al^{3+}) sheets, which can be balanced by the presence of interlayer cations, such as Na^+ and Ca^{2+}. If the solution has a high concentration of divalent and trivalent cations (e.g., Mg^{2+}, Ca^{2+}, Fe^{2+}, Al^{3+}, Fe^{3+}), like those at Lake Aerodrome and the Twin Lakes [*Bowen and Benison*, 2009], these will be attracted to the negative surface charge on the phyllosilicate particles and fewer cations will be needed to balance the charge. As a result, the layer of cations on the clay surface

will be thinner, the authigenic particles will flocculate due to Van der Waals forces much more quickly, and the detrital grains will degrade much more slowly than in a less-saline acid solution [*Moore and Reynolds*, 1997].

[40] Phyllosilicates precipitating directly from the acid lake waters form beds of clay minerals along the lake bottom. An example is the thick, but laterally discontinuous kaolinite/halloysite bed located in the mud/sandflat on the northwestern edge of Twin Lake West. Phyllosilicates precipitating directly from shallow acid saline groundwater form patchy cements between reworked gypsum and quartz grains in otherwise loose clastic sand. These early intergranular cements are found in sediments directly beneath the lakes and just centimeters below the surface of mud/sandflats immediately adjacent to the lakes. Most common are the Al-phyllosilicate cements (e.g., kaolinite), which are associated with early hematite, jarosite, and alunite cements and hematite concretions [*Benison and Bowen*, 2006; *Bowen et al.*, 2008].

[41] Detrital phyllosilicates occur in these acid saline lake environments as a result of weathering. Examples include the presence of detrital muscovite, chlorite-smectite, palygorskite-sepiolite, and amesite, especially in sample sites near Archean outcrops. In this type of sedimentary environment, detrital muscovite (and other micas) can serve as an indicator of lithologic discontinuities [*Thompson and Ukrainczyk*, 2002]. At Lake Aerodrome, the abundance of muscovite consistently increases with depth, which is the expected trend in an environment where the sediments are derived from homogeneous parent materials. In contrast, the abundance of muscovite at the Twin Lakes does not follow this trend, suggesting more lithological variation, which is in fact the case. Chlorite-smectite cements form when hydroxides precipitate in the interlayer region of 2:1 phyllosilicates [*Kohut and Warren*, 2002]. In acid environments with low organic matter, oxidizing conditions and frequent cycles of wetting and drying, this interlayer hydroxide is most likely hydroxyl Al [*Rich*, 1968; *Kohut and Warren*, 2002], but may also include Si [*Matsue and Wada*, 1989; *Kohut and Warren*, 2002]. In Australia, Mg-rich palygorskite-sepiolite cements may precipitate directly from low pH solutions with high enough concentrations of Mg^{2+} and Si^{4+} or by alteration of smectite and micas [*Singer and Norrish*, 1974; *Singer*, 2002]. High levels of Mg and Si are primarily attained in sediments affected by rising groundwater under conditions of strong and continuous evaporation [*Singer*, 2002], the occurrence of which has been documented in and around these acid saline lakes [*Benison et al.*, 2007]. While it is possible that palygorskite-sepiolite is precipitating authigenically, it tends to be unstable in acidic conditions and will weather back to smectite [*Singer*, 2002]. Amesite is a common metamorphic alteration product of Mg silicates in ultrabasic igneous rocks but weathers quickly in the soil environment. The amesite present at Lake Aerodrome was likely transported from the mafic schists on the western and northern edges of Lake Cowan.

4.7. Implications for Phyllosilicates on Mars

[42] Minerals common to both Mars and these Western Australian acid saline lakes include Fe/Mg-smectites, kaolinite, halloysite, chlorite, muscovite, gypsum, alunite, jarosite, hematite and goethite [*Murchie et al.*, 2009; *Ehlmann*,

2010]. Martian phyllosilicates have been categorized into three main types: deep, layered and fluvial/lacustrine sedimentary [*Ehlmann*, 2010]. Deep phyllosilicates are found in the oldest (Noachian) and often stratigraphically lowest exposed, altered crust on Mars (e.g., Nili Fossae fracture system) [*Ehlmann*, 2010]. This crust is composed of basaltic material that has been partially altered to Fe/Mg-smectite, with lesser amounts of low-grade metamorphic minerals, such as analcime, illite and prehnite in the craters [*Ehlmann*, 2010]. In addition to Fe/Mg-smectite, Mg/Fe-carbonates have also been identified at Nili Fossae and in the Columbia Hills of Gusev crater [*Morris et al.*, 2010]. Together these minerals suggest that there was once neutral to alkaline liquid water in these locations [e.g., *Velde*, 1995]. Layered phyllosilicates are found in aerially extensive deposits at Mawrth Vallis and the Nili Fossae. In these locations, Al-phyllosilicates (e.g., kaolinite or halloysite) unconformably overlie Fe/Mg-smectites [*Ehlmann*, 2010]. In some instances, the Al-phyllosilicate layer also contains a separate layer of kaolinite above a layer of montmorillonite and opaline silica, which is separated from the Fe/Mg-smectites by a ferrous component [*Bishop et al.*, 2008; *Mustard et al.*, 2008; *Wray et al.*, 2008; *McKeown et al.*, 2009]. It has been hypothesized that top-down leaching (i.e., laterization) of the original smectite-rich rock has removed Fe, Mg and Ca cations from the surface, leaving behind a kaolinite-rich upper unit [*Wray et al.*, 2008; *Ehlmann et al.*, 2009; *McKeown et al.*, 2009]. In fact, the recent discovery of kaolinite, montmorillonite and Fe/Mg-smectites in Stokes crater in the Northern Plains of Mars, suggests that the formation of a weathered kaolinite-rich surface was a global phenomenon [*Carter et al.*, 2010]. Similarly, significant leaching of the saprolite surface in WA has removed most of the weatherable minerals, leaving behind thick deposits of authigenic kaolinite, goethite, and hematite and residual quartz grains [*Anand and Paine*, 2002]. A second hypothesis for the formation of the Martian layered phyllosilicates suggests that the Al-phyllosilicate layer is a younger sedimentary or altered pyroclastic deposit [*Michalski and Noe Dobrea*, 2007; *Wray et al.*, 2008; *McKeown et al.*, 2009]. Fluvial/lacustrine sedimentary phyllosilicates are found primarily within craters and record a variety of geochemical conditions [*Ehlmann*, 2010]. The Fe/Mg-smectites and Mg-carbonate bearing sediments found in Jezero crater suggest that it once hosted neutral to alkaline waters, while the alunite and Al-phyllosilicate bearing sediments found in Cross Crater, a closed basin in Terra Sirenum, suggest that it once hosted much more acid waters [*Swayze et al.*, 2008; *Ehlmann*, 2010]. Like Cross Crater, Columbus crater (29°S, 166°W), also located in Terra Sirenum, is host to a complex assemblage of minerals that includes widespread gypsum, Mg-sulfate, and kaolinite, as well as less extensive Fe/Mg-smectite and jarosite [*Wray et al.*, 2009a], and has been compared to the acid saline lake deposits of WA [*Baldridge et al.*, 2009; *Wray et al.*, 2009b].

[43] Despite differences in the composition of the major host rocks (mafic on Mars versus felsic in WA) and some alteration minerals, many of the geochemical, sedimentological, and mineralogical features seen in these modern acid saline lake systems are similar to features that have been observed in the sedimentary rock record on Mars, and suggest that similar acid saline lakes and groundwaters may

have once been present on the surface of Mars [*Benison and LaClair*, 2003; *Benison and Bowen*, 2006; *Baldridge et al.*, 2009; *Wray et al.*, 2009b]. For example, a sedimentary deposit in the Meridiani region contains jarosite, calcium sulfate evaporites, and Fe-oxides suggesting either that the pH of Martian waters in this region has not exceeded a value greater than 4, was saline, and was oxidizing [*Clark et al.*, 2005], or that significant acid weathering took place inside a large-scale ice deposit [*Niles and Michalski*, 2009]. The complexity of the observed mineral assemblages and the variability over small lateral distances in Australia, despite extensive regional leaching, suggests that similar heterogeneity may be expected on Mars. The presence of both sulfates and phyllosilicates on Mars has been interpreted by some as having required two temporally separate geochemical and climatic eras on Mars [*Chevrier et al.*, 2007]; however, interbedded sulfates and phyllosilicates have been found in Endeavor crater [*Wray et al.*, 2009b]. This discovery combined with the fact that sulfates and phyllosilicate are currently forming together in the acid saline lake of Western Australia suggests that two temporally separate geochemical eras are not necessary to explain the Martian deposits [*Baldridge et al.*, 2009]. While Lake Aerodrome and the Twin Lakes have similar depositional environments, there are significant differences in their mineralogy and similar variations between crater lakes on Mars may be expected.

5. Conclusions

[44] Mineralogical characterization of silt- and clay-size acid saline lake sediments reveals the presence of complex and spatially heterogeneous mineral assemblages that include phyllosilicates, sulfates, Fe-oxides and other silicates. Our observations show that in addition to known acid-tolerant minerals, phyllosilicates that are typically not considered stable in acid settings are in fact persisting in the acid saline lake sediments in southern Western Australia. The mineralogical heterogeneity present at and among these terrestrial acid saline lakes suggests that similar variety may be preserved in Martian deposits. The similarity between the diverse mineral assemblages in these terrestrial acid saline systems and those on Mars indicates similar conditions may have existed on Mars. We suggest that spatial patterns in abundance and associations with other minerals are needed to interpret conditions of phyllosilicate formation on both Earth and Mars.

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K. C. Benison, Department of Geology, Central Michigan University, 314 Brooks Hall, Mt. Pleasant, MI 48859, USA. (benis1kc@cmich.edu)

B. B. Bowen and S. Story, Department of Earth and Atmospheric Sciences, Purdue University, 550 Stadium Mall Dr., West Lafayette, IN 47907, USA. (bbowen@purdue.edu; sstory@purdue.edu)

D. G. Schulze, Department of Agronomy, Purdue University, 915 W. State St., West Lafayette, IN 47907, USA. (dschulze@purdue.edu)