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Active hematite concretion formation in modern acid saline lake sediments, Lake Brown, Western Australia

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Abstract

Concretions can provide valuable records of diagenesis and fluid–sediment interactions, however, reconstruction of ancient concretion-forming conditions can be difficult. Observation of modern hematite concretion growth in a natural sedimentary setting provides a rare glimpse of conditions at the time of formation. Spheroidal hematite-cemented concretions are actively precipitating in shallow subsurface sediments at Lake Brown in Western Australia. Lake Brown is a hypersaline (total dissolved solids up to 23%) and acidic (pH ~ 4) ephemeral lake. The concretion host sediments were deposited between ~ 1 and 3 ka, based on dating of stratigraphically higher and lower beds. These age constraints indicate that the diagenetic concretions formed < 3 ka, and field observations suggest that some are currently forming. These modern concretions from Lake Brown provide an example of very early diagenetic formation in acid and saline conditions that may be analogous to past conditions on Mars. Previously, the hematite concretions in the Burns formation on Mars have been interpreted as late stage diagenetic products, requiring long geologic time scales and multiple fluid flow events to form. In contrast, the Lake Brown concretions support the possibility of similar syndepositional to very early diagenetic concretion precipitation on Mars.

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1. Introduction and background

1.1. The importance of hematite concretions

Concretions are common diagenetic products found in abundance throughout the sedimentary record. Despite their ubiquity, there is relatively limited understanding of the variability in conditions, processes, and time scales in which concretions can form. The discovery of hematite spherules interpreted to be concretions (Squyres et al., 2004) embedded in lithified dune and interdune sediments on Mars (Grotzinger et al., 2005) has brought a surge of attention to iron oxide concretion research, and continues to demonstrate the valuable records of diagenetic processes and fluid–sediment interactions that concretions contain. The presence of iron oxide concretions in sediments or sedimentary rocks suggests a history of intergranular fluid saturation and iron mobility that can be driven by changes in pH, redox conditions, and/or microbial activity. A better understanding of the range of conditions in which hematite concretions can form, will facilitate improved interpretations of diagenetic histories in ancient concretion-bearing terrestrial and Martian strata.

1.2. Regional acid saline lake conditions

Lake Brown is one of several hundred ephemeral saline lakes in southern Western Australia that occupy closed depressions within buried fluvial inset-valleys that are remnants of Jurassic (Clarke et al., 1996) to middle Eocene (deBroekert and Sandiford, 2005) incision of the Archean Yilgarn Craton (Fig. 1). The valleys
follow lithologic and structural contacts, leading to a wide variety of felsic and mafic basement rocks below and around the lakes that have been exposed to subaerial continental weathering conditions since as early as the Permian in some areas (Anand and Paine, 2002). Lake Brown specifically is underlain by Kellerberrin Batholith granite and gneiss (Muhling and Thom, 1979), although no basement outcrops were seen around the lake.

The acid saline lakes in Western Australia show diversity in geochemistry not typically observed in evaporative systems. They range in salinity up to 28% TDS (total dissolved solids), and have pHs that range from 1.5 to 10.5 (Benison et al., 2007). The lake and shallow ground waters are Na–Mg–Cl–SO₄ brines with variable yet locally high amounts of Ca, Br, Al, Fe, and Si (Bowen and Benison, 2006, in review). Our observations suggest that zones of low pH groundwater are formed from oxidation of diffusely distributed sulfide veins and lignites in the subsurface. The acid saline groundwater fluxes very slowly into the surface lake systems. Continued acidification in the lakes and shallow groundwater is promoted by localized ferrolysis, evapoconcentration, and microbial processes.

1.3. Western Australia acid saline playas as Mars analogs

The modern acid evaporite lakes in Western Australia have sedimentological, mineralogical, and diagenetic features that appear to be analogous to those observed in the lithified strata in the Meridiani Planum region of Mars (Benson and Bowen, 2006). Both systems include chemical sediments (gypsum) that were precipitated, reworked by eolian action, and deposited intrabasinally in shallow ephemeral saline and acidic surface waters. Both systems appear to have been altered by acid saline groundwater that precipitated intergranular minerals including jarosite and hematite, and early diagenetic products including displacive sulfate crystals and iron oxide concretions (Squyres et al., 2004). In addition to typical evaporite minerals (e.g., gypsum, halite), iron oxides, and iron-bearing sulfates (e.g., jarosite) commonly precipitate as evaporites directly from lake water and groundwaters within the acid saline lake sediments in Western Australia. Red coloration of the sediments from pervasive iron oxides is one of the most obvious and distinguishing features that sets apart the acidic lakes from the neutral to alkaline lakes in the region.

Here, we describe the geologic conditions in which the hematite concretions at Lake Brown are forming, and compare them to other hematite concretion examples. Evaluation of sedimentological and geochemical conditions of the modern Lake Brown concretions will help to constrain the processes involved in concretion formation, and identify conditions that may have been active in ancient concretion systems on Earth and on Mars.

2. Methods

Lake Brown is one of ~60 saline lakes investigated during three field excursions from 2001 until 2006 in southern Western Australia (Fig. 1; see Benison et al., 2007). The work at Lake Brown is a part of an ongoing overarching research project with the goals of characterizing the sedimentology (Benison et al., 2007), palynology (Story et al., 2006), geochemistry (Bowen and Benison, 2006; Bowen and Benison, in review), and microbiology (Hong, 2007; Mormile et al., 2007) of the lakes and associated environments at various temporal and spatial scales.

At Lake Brown, the field geochemistry (pH, salinity, temperature) of surface lake waters and shallow groundwaters (<1 m deep) were measured at numerous sites within and around the southern end of the lake (Figs. 1 and 2). Surface (n=7) and groundwater (n=12) samples from the Austral winter of 2005 and Austral summer of 2006 were analyzed in the laboratory for major and minor ions and elements (Table 1; Bowen and Benison, in review). Major inorganic ion species concentrations in the brines were measured with conductivity-suppressed ion chromatography (IC; Dionex DX-320 at Central Michigan University). Calibration was performed during analyses using sets of seven solutions of known concentrations

![Fig. 1. Locality maps of Lake Brown. (A) Landsat satellite image of southern Western Australia with dashed outline of the paleo-Yilgarn River Catchment. Lake Brown is one of hundreds of shallow ephemeral saline lakes that occupy topographically closed basins in the paleo-river channels within the Archean Yilgarn Craton region. Colored dots indicate location of lakes visited in the field as a part of larger-scale research in this area (see Benison et al., 2007). Blue = pH > 8, green = pH 6–8, yellow = pH 4–6, red = pH < 4. (B) Aerial image of Lake Brown (image credit: Google Earth™ mapping service). Location of detailed study area (shown in Fig. 2) marked with a star.](image-url)
Lake Brown surface water (LW) and groundwater (GW) geochemistry

Table 1

| Sample | pH avg | S.D. pH | TDS avg | S.D. TDS | Na avg | S.D. Na | Mg avg | S.D. Mg | K avg | S.D. K | Ca avg | S.D. Ca | Br avg | S.D. Br | Cl avg | S.D. Cl | SO4 avg | S.D. SO4 |
|--------|--------|---------|---------|----------|--------|---------|--------|---------|-------|-------|--------|---------|--------|-------|--------|---------|--------|---------|--------|
| GW-05  | 3.5    | 0.2     | 157     | 5        | 54,314 | 11,072 | 5514   | 1617    | 703   | 177   | 703    | 140     | 137   | 69    | 82,620 | 15,747 | 3274   | 654    |
| GW-06  | 3.4    | 0.4     | 152     | 48       | 53,357 | 17,310 | 5374   | 1796    | 685   | 217   | 672    | 198     | 136   | 63    | 81,899 | 26,516 | 3226   | 1042   |
| LW-05  | 4.3    | 0.1     | 193     | 38       | 69,805 | 18,603 | 1471   | 516     | 284   | 95    | 1063   | 301     | 61    | 21    | 100,679 | 21,036 | 2755   | 503    |
| LW-06  | 3.9    | 0.1     | 250     | 105,832  | 1842   | 317    | 1330   | 0       | 67,570 | 1645  |

Field-measured total dissolved solids in parts-per-thousand.
All ions and elements in ppm.

pH, TDS measured in field; Na, Mg, K, Ca, Br, Cl, and SO4 from IC; Si, Al, Fe from XRF; all others from ICP-OES.

These same powdered samples, and five other split whole concretions (samples from thin section preparation) were prepared from certified standards. Standard deviation for all species analyzed was <5% of the measured concentrations based on 2 replicates, and averaged only 1–2% for most species. Select semi-quantitative elemental concentrations were measured in the brines with standard analytical procedures using X-ray fluorescence (XRF; Bruker S4 Explorer at Central Michigan University) and inductively coupled plasma-optical emissions spectroscopy (ICP-OES at Activation Laboratories).

Sediments were excavated around Lake Brown at multiple sites for stratigraphic, sedimentological, geochemical, palynological, and geochronological analysis (see Benison et al., 2007), and during digging to access the groundwaters. It was during these excavations that the concretions were discovered. The stratigraphy of the sediments where concretions were found was documented in the field (Fig. 3). These sediments were cored with a PVC pipe for further documentation and sampling in the lab. Representative sediment samples from five localities around the lake, at a variety of depths, and covering the spectrum of typical sediment types observed at Lake Brown were sampled for geochemical analyses (Figs. 2–4). Seven sediment samples from the surface down to below the concretion-bearing bed, and four concretions with average size and morphology were analyzed for major oxides, SO4, and trace elements with IR and ICP-MS (at Activation Laboratories). Thin sections were made from five concretions, which were analyzed petrographically along with ~30 loose sediment samples.

The mineralogy of the concretions was investigated with powdered XRD and reflectance spectroscopy (Fig. 5). Self-supporting powder mounts were prepared by filling ~200 mg of gently crushed sample into an Al sample holder against paper to minimize preferred orientation. Diffraction patterns were obtained using a PANalytical X’Pert PRO MPD X-ray diffraction system (PANalytical Almelo, The Netherlands at Purdue University) equipped with a PW3050/60 0–2θ goniometer and a Co-target X-ray tube operated at 40 KeV and 35 mA. Incident beam optics consisted of an Fe beta filter, 0.04 radian Soller slit, a programmable divergence slit, and a beam mask set to illuminate a 10×10 mm sample area. A fixed, 1° anti-scatter slit was used at diffraction angles <12° 2θ. The diffracted beam optics consisted of a programmable diffracted beam anti-scatter slit, a 0.04 radian 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.

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analyzed with reflectance spectroscopy from in the visible to short-wave infrared range (0.35–2.5 μm).

Woody debris from organic-rich sedimentary beds above and below the concretion-bearing bed (Fig. 3) were analyzed by Accelerator Mass Spectrometry (AMS) to derive 14C ages (Arizona AMS Laboratory). The samples were pretreated with a standard acid–alkali–acid pretreatment and combusted to produce CO2. The CO2 was then reduced over iron to produce graphite, which was analyzed by AMS. The 14C ages were calibrated with CALIB 5.0 and no reservoir correction was applied.

3. Results

3.1. Lake Brown waters

Lake Brown is formally part of the Yilgarn River Catchment (Fig. 1) (Salama, 1994), but there are no modern perennial rivers on the Yilgarn Craton. It is currently an internally drained shallow depression. Lake water is shallow, typically on the order of 5 to 30 cm, and likely never deeper than ~1 m. Surface water at Lake Brown has been observed with a pH ranging from 3.9 during desiccation and evapoconcentration in the summer, to 4.5 during winter flooding (Fig. 2; Table 1). Salinity of the lake water ranged from 13 to 23% TDS. The pH of the groundwater that saturates the upper 0.5 m of sediment around the lake ranged from 3.1 to 3.7, with salinities from 15 to 16% TDS. Lake water conditions vary on diurnal, seasonal, and decadal scales, depending upon local and regional rainfall and drought events (Benison et al., 2007). Lake and ground waters at Lake Brown are Na–Cl–Mg–SO4-rich, with higher amounts of many minor and trace elements compared to most other natural waters (supplementary Table 3) (Bowen and Benison, 2006, in review). No bicarbonate was detected in any Lake Brown waters. Low pH is most likely due to sulfuric acid and smaller amounts of secondary hydrochloric and bromic acids (Bowen and Benison, 2006, in review). Iron concentration levels in the surface waters and shallow groundwaters range from ~0 to 300 ppm. These variations seem to be very localized and show no discernable spatial or temporal patterns.

3.2. Concretions in the field

Early diagenetic hematite concretions were discovered precipitating in situ at Lake Brown in subaqueous sediments about 30 cm below the lake bottom (Fig. 3). The zone of known concretion formation covered at least ~100 m², and may actually be much more extensive than that. The succession of
overlying sediments includes (from lake bottom downward) a halite crust, organic rich beds, and red mud and sand (Figs. 3 and 4). These beds are quite variable in thickness and laterally discontinuous.

The hematite concretions appeared to primarily envelop, yet slightly displace, the quartz and gypsum sand grains around them. The hematite concretions range in diameter from 2 mm up to 4 cm and can be divided into two populations. The majority of the concretions are hard, red, and/or dark yellow, while a second population is non-lithified, semi-soft, with a lighter colored, mottled, orange and gray color. The darker, more solidified concretions, are more spherical and have a narrower size range. The hard, dark red concretions range in size from 2.0 mm to 2.0 cm. The soft, lighter-colored concretions range in size from 5.0 mm to 4.0 cm. The concretions are spheroidal, but are not perfectly spherical. Measurements of the three primary axes from 84 hard, dark red concretions yield aspect ratios (longest/shortest dimension) that range from 1.0–2.0 with an average of 1.4. The aspect ratios of the soft, lighter-colored concretions range from 1.2–3.2 with an average of 1.7 (n=25).

The nearest neighbor distribution or volumetric density of the concretions was not measurable in the field since the sediments are in the subsurface and unlithified, and concretion distribution was disrupted with excavation. However, in general, 10 cm$^2$ of sediment yielded about 10–15 concretions, indicating a rough volumetric density of about 1 concretion/cm$^2$ of sediment.

Both concretion types, and other sediments sampled from below the shallow water table became significantly more cemented after collection due to rapid precipitation of minerals with evaporation of the acid saline pore waters. The lighter mottled concretions softened considerably when washed, suggesting that much of cement in these concretions is composed of halite and gypsum.

### 3.3. Age of concretions

The Lake Brown concretion-bearing sediments are underlain by an organic-rich layer containing woody debris with a radiocarbon age of 2913 (+/- 48) years BP (calibrated calendar age of 1260 to 1000 BCE). The concretions are within a bed that is younger than that. The concretion-bearing bed is overlain by another organic-rich layer containing debris with a radiocarbon age of 1410 (+/- 100) years BP (calibrated calendar age of 421 to 861 CE) (Fig. 3). These age constraints give a maximum age limit of less than $\sim$3000 years for the concretions themselves. Textural evidence, such as the softness of the concretions within the sediment, supports the relatively young age of the concretions. In this part of the lake, $\sim$25 cm of sediment is representative of deposition over $\sim$1400–2100 years.

### 3.4. Sedimentology of concretion bed

Depositional facies at Lake Brown (and the other acid salt lakes in the region) include lake, mudflat/sandflat, ephemeral channel, and dune facies (Benison et al., 2007). These same depositional facies are represented in the subsurface succession of sediments below Lake Brown (Fig. 3).

Subaqueous halite crusts occupy the lake floor much of the time. In June, 2005, the lake floor had a 5–6 cm thick halite bed composed of cumulate and chevron crystals dissolving from the

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**Fig. 5.** Mineralogy of Lake Brown concretions. X-ray diffraction patterns from 6 typical concretions (on left) and near-infrared reflectance spectroscopy absorption features for those same samples indicative of hematite and goethite. Data for individual samples offset for clarity.
top. Six months later, in January, 2006, we observed this truncated halite bed covered with a 1–2 mm hematite parting and then capped with a 5–6 cm bed of cumulate halite crystals that were actively precipitating (Fig. 4a–b). Although halite is the predominant mineral precipitating from the surface waters, a bed of vertically-oriented bottom-growth gypsum crystals in the subsurface (~ 50 cm deep) suggests that at times in the past, the lake waters were primarily precipitating gypsum. Additionally, the small, vegetated sand dunes surrounding the lake are composed of a combination of eolian quartz and reworked gypsum grains, indicating that in the past, the lake waters desiccated and exposed a gypsum flat that was eroded by wind. Our field observations of the sediments from 2005 to 2006 confirmed that both gypsum and halite are currently precipitating from groundwaters in the pores of the sediments below and surrounding the lake.

The concretions at Lake Brown are hosted by a ~ 10 cm thick coarse sand bed ~ 30 cm below the lake floor that underlies the surface lake facies, but not the adjacent sandflat, ephemeral channel, or dune facies. Quartz, gypsum, and rare quartzite grains comprise the white sand of the concretion host bed. Approximately 60% of the grains are quartz, 35% are gypsum, and 5% are quartzite. The quartz grains are clear, subangular to angular, 0.5 to 2.0 mm diameter grains with moderate to high sphericity. Some gypsum grains in the concretion bed are well-rounded, highly spherical, fine to medium sand-sized grains. Other gypsum grains are angular 1 to 9 mm diameter euhedral, tabular, and prismatic crystals. Twinned crystals are common. Some of the gypsum includes traces of hematite, trapped as inclusions within the crystals. The rare white quartzite grains are highly spherical, subrounded to subangular, and range in size from 2 to 4 mm.

Although sands are common in the acid saline lakes of southern Western Australia, white coarse sands such as these are not. Most sand in these environments are orange-red, due to hematite grain coatings on the grains. In contrast, only ~ 25% of the grains in this white sand bed have hematite coatings. This white sand bed is also among the coarsest we have observed in lakes on the Yilgarn Craton. All of the loose sediments from Lake Brown contained a significant clay-size fraction.

3.5. Concretion composition

The concretions are composed of three types of clastic grains: quartz, gypsum, and halite, and at least two generations of authigenic iron oxide (Fig. 6). Approximately 40% of the host sand grains within the concretions are composed of oolitic gypsum. We call these gypsum ooids due to their rounded, spherical shapes, their concentric internal structure, and their thin, concentric iron oxide grain coatings. Pure halite grains are less common, and are found as single halite cubes coated by orange hematite grains coatings (Fig. 6F). More commonly, halite is found at the center of some gypsum ooids, suggesting that these grains were originally halite ooids that have been partially replaced by gypsum. Some ooids contain both a gypsum and halite grain incorporated within orange iron oxide concentric coatings.

The first generation of hematite is orange and comprises the multiple thin (~ 10–50 μm) grain coatings on the oolitic gypsum and quartz grains (Fig. 6D–E). The second generation of hematite in the concretions is a red, massive, microcrystalline, isopachous, intergranular cement that forms the majority of the concretionary mass (Fig. 6A–B). All of the observed

![Fig. 6. Micrographs of Lake Brown hematite concretions. (A) Cross-sectional view of split concretion. (B) Mixed reworked evaporite and quartz grains cemented by hematite. (C) Oolitic gypsum grains cemented by hematite. (D) Quartz grain with secondary fluid inclusions coated by several generations of hematite. (E) Zoomed in on gypsum ooids that are coated by iron oxide. (F) Halite (lower cube) and gypsum (upper light grain) encased within hematite ooid. The lines within the halite cube are growth bands composed of primary fluid inclusions. (G) Individual hematite crystals within pore space where it appears that a cubic grain (halite?) has dissolved. (H) Hematite cement with “honeycomb” texture that could be indicative of microbial precipitation (e.g., Souza-Egipsy et al., 2006).](Image)
concretions have massive interior cement textures (Fig. 6A), rather than concentric shells or surface rinds that are commonly found in other hematite concretions (e.g., Chan et al., 2004). The concretions are generally not accretionary or layered, although they commonly contain individual grains that do have accretionary grain coatings of hematite. The clastic host grains show no signs of compaction within the concretions, indicating that at the time that the hematite cement precipitated, the sediment itself had a high porosity. Some of the iron oxide-coated evaporite grains within the concretions contain what appear to be primary fluid inclusions (Fig. 6F).

The authigenic component of the Lake Brown concretions is primarily composed of hematite. The concretions are 16 to 23 wt.% Fe₂O₃ (T) (Fig. 7, supplemental material Table 3), and XRD and reflectance spectroscopy confirm that the iron oxide phase is hematite, although some concretions (2 out of the 6 analyzed) contain a hematite-goethite mixture, with indication of Al substitution in the goethite (slightly lower goethite XRD peak with Al, Schalze, 1984) (Fig. 7). In comparison, some of the surrounding dark red sediments contain only 1 to 2% Fe₂O₃ (T). The major oxide analyses and XRD data show that the concretions and the host sediments also have a significant kaolinitic and clastic grain (quartz, gypsum) component (Figs. 5, 7). The concretions are enriched in some trace elements compared to the host matrix and surrounding sediments, including V, Cr, Ga, Zr, and As. In contrast, the concretions are depleted in elements such as Ba, Sr, Rb, La, and Ce (Fig. 7).

4. Discussion

4.1. Diagenetic concretions in acid saline sediments

One hypothesis for the presence of hematite concretions in the Lake Brown sediments is that they might have been depositional in origin, originating from either ferrigenous soils or anthropogenic surface covers and were washed into and buried within the lake sediments. Iron oxide nodules that are similar in appearance to the Lake Brown concretions are common within Western Australia soils, and are used as road gravel throughout the region (Fig. 8). However, there are several lines of evidence that support the interpretation that the hematite concretions found within the Lake Brown sediments formed in
from the Al- and Si-rich fluids (Table 1). The evaporite ooids however, additional clays may have precipitated diagenetically component was likely transported along with these sediments, wind and runoff during periods of flooding. A detrital kaolinite ing from the acid, saline, Fe-rich waters. The quartz and with accumulation of halite, gypsum, and iron oxide precipitat-
ing the evaporite nuclii around the lake bottom, creating the ooids filled enough to create conditions where wind could circulate the evaporite sand grains (Fig. 6). Preferential nucleation sites eolian processes. The massive concretionary hematite cement during subsequent flooding, evaporation, desiccation, and gypsum and quartz sand was buried by sediments deposited coated by hematite probably dissolved. Finally, the bed of soluble halite and gypsum interiors. However, newer halite not be expected with a depositional origin. Secondly, with the exception of iron oxide, the concretions contain the same grain type and composition as the host sediments. Third, concretions had a soft, somewhat gelatinous texture in the field, and had a range of textural maturities that suggest varying stages of development within concretion populations. And, finally (and most significantly), the radiocarbon ages of organic-rich beds above the concretion-bearing bed verify that the concretions pre-date a time when concretions or nodules would have been used as road gravel.

4.2. Paragenesis of host sand

Petrographic observations of the concretion interiors reveal several stages of depositional and diagenetic conditions that have existed at Lake Brown over the last ~3 ka. The evaporite composition of some of the host sand grains suggest that gypsum and halite beds were locally reworked intrabasinally by wind during periods of lake desiccation. Inclusions of hematite in some gypsum crystals show that these fluids were also iron-rich, likely suggesting acidic brine conditions. After eolian action eroded the evaporites into grains, the lake must have filled enough to create conditions where wind could circulate the evaporite nuclii around the lake bottom, creating the ooids with accumulation of halite, gypsum, and iron oxide precipitatin- from the acid, saline, Fe-rich waters. The quartz and quartzite grains were likely weathered from local Archean granite and transport into the lake basin with a combination of wind and runoff during periods of flooding. A detrital kaolinite component was likely transported along with these sediments, however, additional clays may have precipitated diagenetically from the Al- and Si-rich fluids (Table 1). The evaporite ooids did not dissolve with the input of dilute flood waters because the insoluble hematite grain coatings armored and protected the soluble halite and gypsum interiors. However, newer halite not coated by hematite probably dissolved. Finally, the bed of gypsum and quartz sand was buried by sediments deposited during subsequent flooding, evaporation, desiccation, and eolian processes. The massive concretionary hematite cement likely began to precipitate very soon after deposition, based on the lack of compaction and excellent preservation of soluble mineral phases.

4.3. Lake Brown concretion formation mechanisms

The conditions for concretion formation require: an iron source, mobilization and mass transfer of iron to the concretion growth sites, and a geochemical flux that drives precipitation in a medium that promotes the spheroidal geometry.

4.3.1. Fe source

We hypothesize that the iron that composes the hematite concretions was originally sourced from weathering of the underlying bedrock. Archean metamorphic and igneous rocks of the Yilgarn Craton have been subaerially exposed for much of the Cenozoic, and in some areas since as early as the Permian (Anand and Paine, 2002) leading to widespread deep weathering. Iron-rich ultisols are common throughout Australia (e.g., Little and Gilkes, 1982), and some areas in Western Australia contain ferrigenous pisolitic soils with abundant iron oxide nodules (e.g., Fig. 8). The iron that comprises the concretions at Lake Brown has likely undergone multiple episodes of dissolution and reprecipitation with periods of both vertical and lateral migration. There is abundant evidence of iron mobilization and recycling including extensive zones of bleaching and secondary ferrugenization within both basement and overlying sedimentary rocks in the region (e.g., Anand and Paine, 2002).

Most ancient redbeds are interpreted not to have been deposited as red sediment, but as acquiring their coloration over time with breakdown of ferro-magnesian mineral grains (Walker, 1967). In contrast, the red coloration in the sediments at Lake Brown and the other acid saline depositional environments in Western Australia, is acquired shortly after deposition due to the unusual acid saline geochemistry that facilitates syndepositional precipitation of iron oxide grain coatings and cements (Fig. 4). The concretion host bed is anomalous compared to surrounding clastic beds because it lacks iron oxide grain coatings, suggesting that the iron for the concretions may have been locally sourced from depletion of iron within this bed. Another possible geochemical pathway that may have been involved in providing iron to the Lake Brown concretions may have involved the breakdown of jarosite. While jarosite has not yet been identified in the sediments from Lake Brown, it has been identified in other acid saline lake sediments in the area (Benison and Bowen, 2006; Benison et al., 2007).

4.3.2. Fe mass transfer and precipitation

Whatever the source, the iron in the concretions was transported to the concretion growth sites as Fe$^{3+}$ by acidic groundwaters, or as Fe$^{2+}$ by reducing groundwaters. The abundance of red iron oxide grain coatings in the sediments suggests a fairly oxidized system. However, there are also substantial organic-rich horizons in the sediments that had a sulfuric odor suggesting bacterially-induced sulfur reduction. The concretion-bearing bed is the most permeable of all of the sediments within the upper half meter of the subsurface. This bed is bound by relatively impermeable clay-rich beds that separate the actively recharging and desiccating oxidizing surface waters from the deeper stagnant acid saline groundwaters. The pore fluids in the concretion bed are likely saturated with fluids that represent a mixing zone for these two water populations. Temporal and spatial gradients in pH and O$_2$ levels may drive diffusive mass transfer and reactions that could precipitate hematite. The observed pHs in the pore waters and surface waters fluctuate at around the boundary of iron solubility (Drever, 1988). Iron oxide precipitated in the pore space and partial replacement of some of the outer rims of the more reactive evaporite sand grains (Fig. 6). Preferential nucleation sites appear to be the oolitic grains already coated with iron oxide that
are regularly spaced throughout the sediment, which results in a regular concretion distribution. The periodic wetting and drying in this environment likely also enhanced leaching and concretionary precipitation of hydrated iron oxides.

While spatial and temporal gradients in the acid saline geochemistry are sufficient to produce the conditions needed for iron mobilization and precipitation via abiotic means, bacteria may also be important in mediating elemental cycling. Microbiological investigation of the acid saline waters and sediments have identified a diverse population of archaea and bacteria in what may have previously been assumed to be an inhospitable extreme conditions (Hong et al., 2006; Mormile et al., 2007). Petrographic observations of the concretion hematite show some honeycomb textures that are suggestive of microbially precipitated hematite cements (e.g., Souza-Egipsy et al., 2006) (Fig. 6H).

The overall spherical geometry of the concretions is consistent with the host sediment physical properties that are identified by Chan et al. (2004) as prerequisites for spherical concretion formation. In the Jurassic Navajo Sandstone in Utah, iron oxide concretions commonly form as diagenetic products at redox fronts (Chan et al., 2004; Beitler et al., 2005). These types of concretions tend to be spherical when the host medium is anisotropic and homogeneous, and take on unique shapes and patterns when preferential fluid flow pathways are present in the rocks. The Lake Brown sediments where the concretions are precipitating are anisotropic and generally homogeneous, and take on unique shapes and patterns when preferential fluid flow pathways are present in the rocks. The Lake Brown sediments where the concretions are precipitating are anisotropic and generally homogeneous, apparently promoting spherical concretion growth when saturated with the appropriate fluids. Additionally, the presence of chloride ions, which are abundant in these hypersaline fluids, has been identified to enhance precipitation of hematite with a spherical morphology (Kandori et al., 2000).

4.4. Comparisons with other terrestrial iron oxide concretions

4.4.1. Modern sedimentary Fe concretions

Other examples of environments with naturally forming modern hematite concretions include salt marsh, wetland, and ultisol soils (Harriss and Troup, 1970; Duan et al., 1996; Sundby et al., 1998; Pai et al., 2003; D’Amore et al., 2004). Growth of nodules and concretions in these settings is commonly related to microbial activity around specific favorable nuclii such as rhizomes or fecal pellets (e.g., Tyler and Buckney, 1980). Fe-rich concretions forming in some lacustrine settings seem to be somewhat analogous to seafloor Fe-and Mn-rich nodules forming at the sediment-water interface where metals are mobilized by the decomposition of organic matter (e.g., Halbach, 1986). In contrast, the Lake Brown concretions are forming in the subsurface within the sediment. In non-oceanic settings, iron-rich nodules commonly have accretionary annual growth bands that reflect wet–dry cycles that drive changes in redoximorphic conditions and mineral precipitation. In contrast, the Lake Brown concretions do not have accretionary growth bands, although some individual grains do (Fig. 6). Pedogenic iron nodules commonly occur in hydromorphic soils in humid temperate climates (Pai et al., 2003) and grow cyclically as iron is reduced and mobilized during times of saturated, waterlogged conditions, and precipitated with oxidation during dry times. Cyclic wet–dry intervals and redoximorphic cycling likely also play an important role in the growth of the Lake Brown concretions, however, these processes are complicated by the increased iron solubility due to the acidic conditions.

4.4.2. Ancient terrestrial Fe concretions

Many examples of terrestrial hematite concretions occur in lithified sedimentary rocks and formed millions of years prior to their exposure. Ancient examples provide good outcrop exposures that are similar to the ancient and weathering concretion-bearing outcrops on Mars (e.g., Chan et al., 2004). However, the subsurface geochemical and sedimentological conditions at the time of formation have to be inferred, based on authigenic minerals that may have undergone multiple episodes of diageneric over potentially millions of years. The effects of burial, multiple subsurface fluid flow events, structural overprints, erosion and exposure to surface weathering may complicate interpretations of host rock properties and conditions at the time of formation.

Some of the most extensively studied iron oxide concretions occur in the Jurassic Navajo Sandstone in southern Utah (Chan et al., 2004; Beitler et al., 2005; Chan et al., 2005, 2006). These concretions are commonly spherical, and form in buried lithified sandstone when iron-rich fluids encounter oxidizing conditions. While some of these concretions are formed of concentric rinds, it is common for them to contain solid hematite or goethite cement, similar to the form of the Lake Brown concretions. All of the Utah concretions are interpreted to be late-stage diagenetic products with iron sourced and mobilized from redbed bleaching from reducing fluids.

Hematite concretions have also been found associated with ancient acid saline sediments of the Permian Nippewalla Group (Benison, 2006). These concretions have not been observed in situ, but were discovered weathered out of evaporite-bearing redbeds. They are non-spherical and show no concentricity.

4.5. Comparison with Mars hematite concretions

The very successful Mars Exploration Rover (MER) mission has revealed not only an extensive sedimentary record of eolian and water-lain deposits on Mars, but also diagenetic features including hematite concretions, that suggest a history of subsurface fluid saturation (Squyres et al., 2004). The Mars hematite spherules occur within the bedded sedimentary rocks of the Burns formation (Grotzinger et al., 2005), are highly spherical, and average 4.2 mm in diameter (McLennan et al., 2005). Data on the composition of the Mars concretions is consistent with them being either 25–38 wt.% Fe₂O₃ (T) (Jolliff et al., 2007) with the remainder likely being host rock clastics, or up to 100% Fe₂O₃ with no siliciclastic component (Christensen et al., 2004). The Burns formation outcrops show sedimentological and mineralogical evidence of having been deposited in eolian dunes and interdune playas (Grotzinger et al., 2005). The sedimentary grains are composed of sulfates that were likely sourced from evaporite beds that were eroded by wind to create “dirty” (some siliciclastic component?) gypsum sand. The
presence of jarosite, diagenetic hematite concretions, and vugs of displacive crystal molds (Squyres et al., 2004) within these sedimentary rocks suggest that at some point the Mars sediments (or sedimentary rocks) were saturated with acidic and saline groundwaters.

Several possible Earth analogs and geologic scenarios have been proposed to help explain the genesis of the iron oxide spherules discovered in the Meridiani Planum region of Mars. While there are some proponents of a non-concretionary origin of the Mars spherules, constraints on the thermal infrared spectral characteristics of the Mars spherules suggest that they formed at low temperature, ruling out the possibility of formation as impact melt spherules or volcanic lapillii (Glotch et al., 2006). One argument for a non-concretionary origin of the Mars spherules has included the supposed lack of terrestrial analogs for understanding how the Mars concretions formed. Both systems also must have undergone localized transitions from depositional evaporite systems (to precipitate the initial sulfate), to erosional systems (to weather the evaporite into individual grains), back to depositional (to deposit the reworked grains in eolian and playa strata). At Lake Brown, we see this transition locally and intrabasinally, with seasonal lake desiccation, playa bed erosion, and eolian dune development along the shorelines and on berms between individual playas. While the scale of this depositional system Lake Brown alone is much more limited than the scale of the Mars sedimentary deposits, this lake is only one of hundreds to thousands of evaporite playas that cover the Yilgarn Craton. This type of patchy, yet regional evaporite playa network with a shallow acid saline groundwater system could potentially account for the scale of deposit that is present on Mars.

The assemblage of reworked evaporite and diagenetic minerals identified in the Meridiani outcrop have been interpreted to reflect non-equilibrium conditions with respect to a single fluid, therefore theoretically requiring long time periods and multiple geochemical fluid events to form (McLennan et al., 2005). However, in contrast, textural evidence within the Meridiani outcrops shows little alteration of primary bedding and grain textures, as would be expected from the extreme fluids that are deemed responsible for the concretion-forming diageneric within the highly reactive chemical grains. The excellent preservation of depositional textures suggests that the grains have not extensively recrystallized. The absence of extensive recrystallization supports the theory that the concretions are early- to medium-forming, precipitating from the same surface/shallow groundwater (water table) fluids that facilitated preservation of the eolian sediments. The evaporite lake surface conditions where the initial precipitation and erosion of the concretions at Lake Brown are presumable much younger than the Mars concretions, and with time, may self-organize into a more well-developed spherical shape and consistent size. Both acid saline depositional and diagenetic systems occur upon ancient (>3.5 Ga), highly weathered, tectonically stable cratons. This type of highly-weathered setting may be a prerequisite for natural (i.e., non-anthropogenic) development of acid evaporite systems with readily available iron for concretion formation. Both systems also have undergone localized transitions from depositional evaporite systems (to precipitate the initial sulfate), to erosional systems (to weather the evaporite into individual grains), back to depositional (to deposit the reworked grains in eolian and playa strata).

### Table 2

Comparisons between Mars concretion-bearing sedimentary rocks and Lake Brown, Western Australia

<table>
<thead>
<tr>
<th>Feature</th>
<th>Mars (Burns fm.) sed rocks</th>
<th>Lake Brown acid saline sed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depositional environment</td>
<td>Dune/interdune playa</td>
<td>Interdune playa</td>
</tr>
<tr>
<td>Pore fluid chemistry</td>
<td>Acid/saline</td>
<td>Acid/saline</td>
</tr>
<tr>
<td>Host sediment</td>
<td>Eolian reworked evaporites, basalt?</td>
<td>Eolian reworked evaporites, quartz, clay</td>
</tr>
<tr>
<td>Concretion cement mineralogy</td>
<td>Hematite</td>
<td>Hematite (+/− minor goethite)</td>
</tr>
<tr>
<td>Concretion diameter</td>
<td>Avg ~4 mm</td>
<td>2 mm–2 cm</td>
</tr>
<tr>
<td>Regional host lithology</td>
<td>Basalt</td>
<td>Granite, greenstone, basalt</td>
</tr>
</tbody>
</table>
impure Mars evaporites occurred, may have continued as the dune sediments were buried and syndepositional groundwaters saturated the pore space and precipitated concretions. These conditions are seen at Lake Brown today. While the concretions on Mars are surely diagenetic, with a relative timing that post-dates deposition of the eolian and interdune grains and formation of elongate displacive crystals (now seen as elongate vugs, e.g., Squyres et al., 2004), the absolute timing of concretion formation may have only been 10s to 1000s of years after deposition. The growth of very early hematite concretions within the reworked sub-playa evaporite sediments in Lake Brown illustrates the possibility of contemporaneous evaporite deposition, alteration, and concretion growth from syndepositional acid saline pore fluids. The possibility of syndepositional concretion precipitation in the dune and interdune playa sediments on Mars suggests that multiple or long periods of liquid fluid stability may not have been necessary to form the observed sedimentary record.

Mars concretions have been interpreted to form after deposition of the entire dune/interdune sequence because they are equally distributed across facies boundaries (McLennan et al., 2005). However, in ancient terrestrial concretion examples in dune and interdune facies, the facies boundaries are commonly related to preferential fluid flow pathways and differences in permeability and porosity (e.g., Beitler et al., 2005). Hydrologic differences, based on primary sediment textures and grain sizes, could alter the resulting distribution of secondary concretions. The absence of any differentiation in concretion distribution in the Burns formation indicates that these sediments maintained equal fluid flow properties. This consistency supports the theory that the concretions precipitated while the sediments were still saturated, un lithified, and non-compacted. Or, diagenetic processes within all of the primary sedimentary facies resulted in equal fluid-flow properties. Groundwaters in the Mars sediment are interpreted to have been stagnant and very slow moving (Squyres and Knoll, 2005), which is similar to the groundwater flow conditions at Lake Brown (Gray, 2001). As documented for Lake Brown, the concretions may have grown syndepositionally, as the stagnant acid saline water table rose consistently with accumulation and burial of sediments.

4.6. Trace element accumulation in concretions

Accumulation of trace metals may not typically be expected in a low temperature sedimentary system (Burt et al., 2007). However, when fluids involved in concretion growth are acidic or otherwise extreme in chemistry, high temperatures or geologically long time periods are not necessary to enrich the concretions in elements such as Al, Ti, Cr, and Ni (e.g., McLennan et al., 2005). Beitler et al. (2007) claim that sedimentary concretions should have a simplistic mineral composition that lacks enrichment of unusual trace elements such as Ni, which is reported to be enriched in the Meridiani spherules (Yen et al., 2005). Analyses of terrestrial hematite concretions, however, show enrichment of Ni and other trace elements in the Utah examples (Beitler et al., 2005) and the Lake Brown concretions (Fig. 7). Surface charge on naturally precipitated iron hydroxides varies with pH, resulting in specific pH conditions that would alter the capacity for adsorbing trace elements (Harriss and Troup, 1970). In the Utah case, Ni is believed to have adsorbed onto iron oxides at neutral pH. Lower pH would have a lower capacity for adsorbing trace elements, which could suggest zones of neutral water mixing with the acidic fluids to form the concretions at Lake Brown. In some systems, low hematite concretion growth rates could result in higher trace element concentrations (Harriss and Troup, 1970).

5. Conclusions

Early diagenetic hematite concretions appear to be actively precipitating in situ at Lake Brown within a subaqueous, mixed siliciclastic-evaporite bed, in pore space that is saturated with acid saline fluids. These concretions record a history of changing conditions in this environment that included the formation of evaporite ooids and multiple episodes of iron oxide precipitation in an acid saline system. The age of the concretions is constrained to $\sim 3$ ka by radiocarbon dating of organic-rich sediment layers above and below the concretion bed. This relatively young age suggests that deep burial, distinct groundwater flow events, or long geologic time was not needed to create conditions suitable for hematite concretion formation. The Lake Brown example provides the opportunity to observe modern conditions where iron oxide concretions are actively precipitating in a sedimentological setting that is potentially analogous to the past acid saline aqueous and eolian depositional system of the Burns formation on Mars.

The Lake Brown concretions provide a model for hematite concretions on Mars and illustrate the potential for very early, perhaps syndepositional, precipitation of spheroidal iron oxide concretions in reworked evaporite sediments saturated with acidic and saline fluids.

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Appendix A. Supplementary data


References


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